An Investigation of Ion-selective Membranes by Impedance Techniques

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ABSTRACT

A number of ion-selective electrode membranes have been investigated using a.c. impedance measurements. Membranes containing the antibiotic valinomycin have been studied in both liquid and PVC matrix form, and dibenzo-18-crown-6, 2,2,2-cryptand, and a new ionophore, COD-I were investigated in PVC membranes. The effects of incorporating various levels of tetraphenylborate into the membranes were also investigated.

For both liquid and PVC membranes, measurements were made using a four-electrode system, allowing the impedance of the membrane alone to be determined, without contributions from the cell and current-carrying electrodes, and potentiometric data were also obtained for all membranes to establish the degree of cation selectivity, and the extent of anion exclusion. A computer-controlled measuring system, and associated software was developed, to allow repeated, and accurate measurement of the impedance over long time periods.

The rate of exchange between the membrane and aqueous solutions was determined for the primary ion, potassium, and the major interferent, sodium, and relative mobilities of species within the membrane were calculated. The impedance behaviour of PVC membranes was also studied prior to contact with aqueous solutions, and measurements were made on the individual membrane components.

On the basis of these measurements the mechanism of cation selectivity for valinomycin-containing membrane is deduced. For liquid membranes a simple exclusion mechanism appears to operate, whilst for PVC matrix membranes a more complicated mechanism is apparent, in which all types of ion can gain access to the membrane, but the ionophore controls the overall concentration of the cationic species. For the crown and cryptand, which show poorer selectivities, the ion-exchange at the membrane/solution interface appears to be hindered, whilst the COD-I shows more similarity with valinomycin.

For both liquid and PVC matrix membranes, the presence of negative sites within the membrane was found to be necessary for effective anion exclusion.

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Chapter 1

Introduction

1.1 Ion-Selective Electrodes

Since the 1960s, when a wide variety of new types of electrode became available which were selectively responsive to certain ions, ion-selective electrodes (ISEs) have become common tools in analytical chemistry and a great deal of work is currently being undertaken to investigate various aspects of their design, response, and mechanism of operation. This is particularly true of electrodes based on neutral complexing agents.

The work presented here is an investigation of neutral-carrier based electrodes using ac impedance measurements in an attempt to gain further insight into these factors.

1.1.1 Introduction

Ion selective electrodes are electrochemical devices by which the activity, and therefore the concentration, of a given chemical species in solution (generally an aqueous solution), can be determined by reference to a standard solution of the species of known activity. They comprise, in general, a membrane separating the sample solution (containing the species in question at an unknown concentration) and a reference solution of known concentration, although in practice the concentration of an unknown solution is obtained by comparison with a series of standards, rather than by direct comparison with the reference solution.

In the past electrodes have been classified in a number of ways by different workers, including the physical state of the membrane, and its supposed mechanism of operation. Originally, the classification was generally based on the physical state of the active part of the electrode,

i.e. glass, liquid membrane or solid state (1.1). This type of classification is no longer strictly applicable as many electroactive materials can now be incorporated into a variety of electrodes in different forms, and in some cases, the physical state of the membrane itself is open to argument (e.g. some workers refer to electrodes consisting of macrocyclic polyethers dispersed in a PVC matrix as a liquid membrane electrode, but others would hold that the PVC matrix cannot be treated as a liquid phase, and must be considered as a solid state membrane). Perhaps the most practical classification is one based on the active material and its properties alone, and on this basis the following divisions are suggested:

a. Glass electrodes: Selective to cations, they generally consist of lithia or aluminosilicate, or special multi-component glasses.

b. Solid State Electrodes: These are based on crystalline substances. e.g. single crystals of halides, pressed pellets of polycrystalline materials, sintered or cast materials, or suspensions of precipitates in polymeric matrices.

c. Ion-Exchanger Electrodes: These electrodes consist of ionic or ionogenic species (e.g. acids, bases or salts) dispersed in an organic liquid which is immiscible with water.

d. Neutral Carrier Electrodes: These electrodes incorporate an uncharged complexing agent, which will selectively bind a particular ion or group of ions. The membrane may be formed as a liquid film (supported or unsupported) or as a doped polymer membrane.

e. Enzyme electrodes: Recently electrodes have been developed which are based on the action of an enzyme on a substrate, which produces a species which can be detected by a device in one of

the above categories.

f. Gas sensors: Some gas sensors can be classed as ISEs, where a potential response is generated indirectly as in e. above.

g. ISFETS: Ion-Selective Field Effect Transistors: The gate region of a metal oxide semiconductor field-effect transistor (MOSFET) is coated with an ion sensitive membrane (usually in the form of a polymer matrix), which then affects the current through the device, unlike ISEs which show a potentiometric rather than an amperometric response.

The work carried out for this thesis has involved a number of neutral-carrier electrodes both in polymer matrix form, and as liquid membranes with the active material dissolved in an organic solvent.

A number of different cell configurations have been devised and used since the first ion-selective electrodes were fabricated early in the century, and electrodes are now available which are sensitive to a wide variety of chemical species. Thousands of papers are published each year reporting new developments in ion-selective electrode technology and new electroactive materials, and it would be impossible to produce a fully comprehensive review of the current state of the art here. A number of books have been published covering a wide range of different aspects and applications of ion-selective electrodes (1.1-1.15), along with several excellent reviews of current literature (1.16-1.24). A brief review of the history and development of ion-selective electrodes is given below, with particular reference to neutral-carrier ISEs.

1.1.2 A Brief History and Perspective

The first ion-selective electrode to be discovered was the glass electrode, first reported by Cremer in 1906 (1.25) and later studied by Haber and Klemensiewicz (1.26), which was sensitive to the concentration of H^+ ions in aqueous solutions. The mechanism by which this electrode operates was not at first appreciated, and little progress was made in the field of ion-selective electrodes until the development of new glasses sensitive to a variety of cations including Na^+, K^+, Ag^+, NH_4^+, Tl^+, Li^+, and Cs^+ by Eisenman and co-workers in the late 1950s and early 1960s (1.2,1.27,1.28).

Tendeloo (1.30) unsuccessfully tried to formulate the first non-glass ion-selective membranes in 1936 using naturally occurring fluorite, finally achieving a calcium sensitive membrane in the late 1950s as a result of work with paraffin wax membranes incorporating calcium salts (1.31,1.32), but the response of the membranes produced was not good (1.33). In 1966, Frant and Ross (1.34) published details of a fluoride-selective electrode based on a single crystal of lanthanum fluoride, but it was not until the following year that the first commercially viable sensor based on a non-glass membrane was produced (1.35). This device was sensitive to calcium and was based on a calcium salt dissolved in di-n-octylphenylphosphonate. These electrodes were followed by similar sensors for other cations and for anions, based both on dissolved salts and solid crystals (1.33,1.36,1.37), and absorbed onto conducting substrates (1.38).

Work with neutral carriers commenced with the discovery in 1955 of valinomycin (1.39), a cyclic depsipeptide antibiotic which has the ability to selectively complex potassium ions.

Earlier attempts to produce a potassium selective electrode based on potassium tetraphenylborate (1.40), and later efforts using potassium tetrakis (p-chlorophenylborate) (1.41) were not highly successful. The potassium complexation capability of valinomycin was first noted in work with lipid bilayer membranes where drastic changes in potassium permeability were found when the antibiotic was added to the membrane (1.42). This early work led to the production in 1969 of the first ISE based on valinomycin (1.43), which proved to have excellent selectivity for potassium ions in the presence of sodium, and has yet to be improved upon.

Other depsipeptides have also been investigated as electroactive materials, particularly the enniatins (1.44). Apart from these species, several other groups of compounds have been found to exhibit metal-ion transport in biological systems or selective complexation of metal ions in extraction studies. The most widely studied of these are the peptides gramicidin (1.45) and alamethicin (1.46), the macrotetralides of the homologous nactin series (1.47-1.49), and a series of carboxylic acid ionophores including nigericin (1.50,1.50a), monensin (1.50), grisorixin, X-206 (1.46), X-537A and A23187 (1.51). The latter group differs from all the others in that they form neutral complexes with metal ions, i.e. they act as charged complexing agents.

Difficulties of extraction and purification of many of these substances have prompted attempts to produce synthetic compounds which will exhibit similar ion-binding properties. The first such compounds synthesised were a series of cyclic polyethers, the so-called crowns, produced by Pederson (1.52,1.53), and, since the initial synthesis, all members of the homologous serie from 12-Crown-4 to 30-Crown-10 have been synthesised, along with

a whole range of derivatives (1.55), including several attempts to bind the polyether ring to a polymer chain backbone (1.56).

The ion-binding properties of these compounds have been investigated by a number of methods, but although providing useful information on the structure-selectivity relationship, few show high selectivities (comparable to valinomycin) when incorporated into ISEs (1.57), although improved results have been achieved with bis-(crown) ethers (1.58,1.59).

Another series of ligands showing promise as electroactive materials are the bridged polyamine cryptands (1.60-1.62), and other ligands reported include a carboxylic acid polymer (1.63), various cyclic peptides (1.64), a large number of acyclic compounds produced by Simon et al (1.65), poly-(glycol)s (1.66,1.67), and a novel series of compounds based on THF subunits (1.68).

A full discussion of several of these compounds, which exhibit potassium selectivity, is given in Chapter 3, including a consideration of the structural aspects of ion-complexation.

1.2 The ac Impedance Technique

1.2.1 Introduction

The use of ac impedance measurements in electrochemistry was pioneered by Sluyters (1.69,1.70), since when it has become established as a useful tool for the investigation of electrochemical systems. The great advantage of impedance measurements over other techniques commonly used in electrochemistry is that high quality results can be achieved using signals of very low amplitude which only cause very small perturbations to the system under study. Thus the system remains

in the equilibrium state for the particular experimental conditions in use, and the results obtained can reliably be related to these conditions. The impedance technique also allows high precision data to be obtained, as the response to a given signal under a fixed set of conditions will be invariant with time (notwithstanding the effects of irreversible chemical or physical changes) and therefore signals can be averaged over a long time period. Another advantage of this method is that the magnitude of the perturbing signal is sufficiently small for the response of the system to be described in terms of linearised equations describing the current-potential relationships. Thus, detailed knowledge of the i-E response curve is not required at currents and potentials far from the equilibrium position.

In the following section, the theory of electrochemical impedance measurements is covered along with the interpretation of the results, and their relation to the actual chemistry of the system under study.

1.2.2 Theory

A purely sinusoidal voltage can be represented mathematically by the expression

$$e = E \sin(\omega t) \qquad 1.1$$

where ω is the angular frequency ($\omega=2\pi f$ where f is the conventional frequency). It is customary when discussing ac circuits to picture the voltage as a rotating vector (or phasor), of length E, and frequency of rotation ω. This is represented diagrammatically in Fig 1.1. The variation of the voltage with time can be seen by a projection of the vector on to a set of axes with time as the abscissa and voltage as the ordinate

Fig 1.1 Rotating vector (phasor) diagram for an alternating voltage.

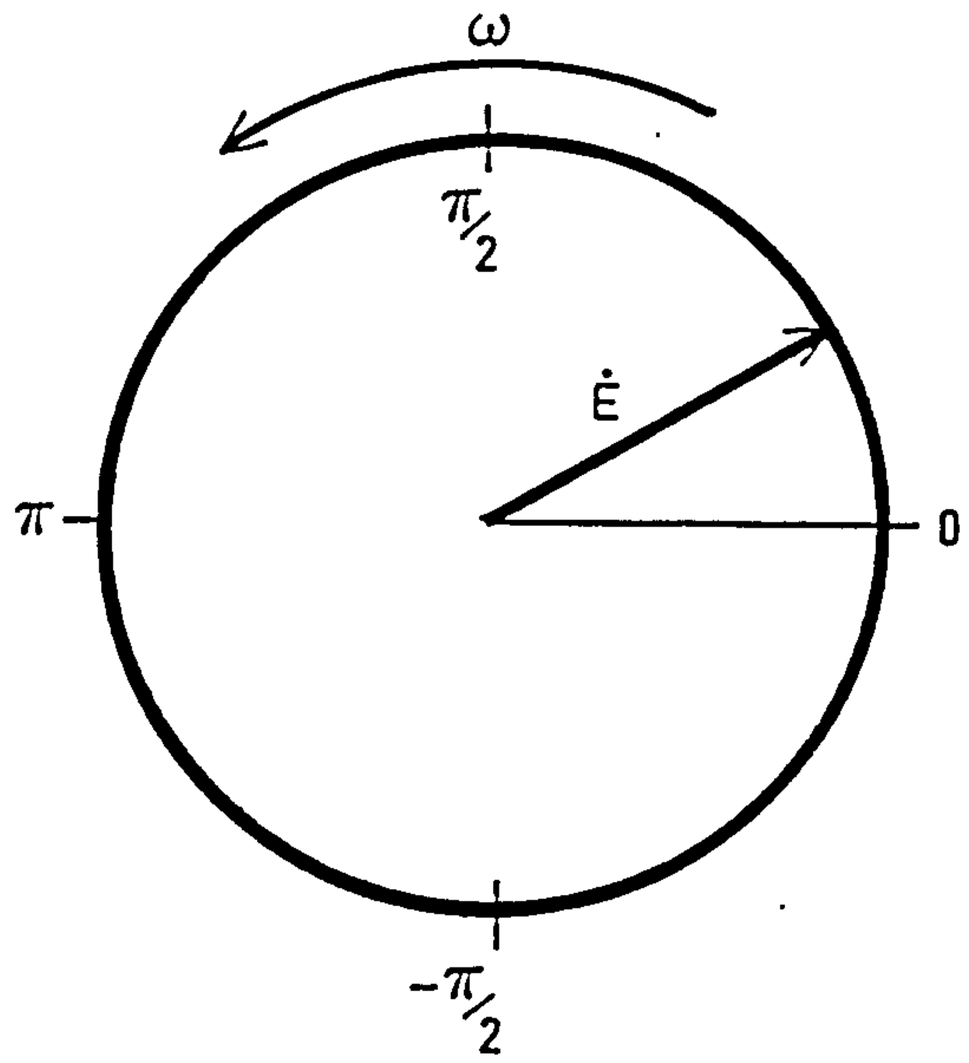
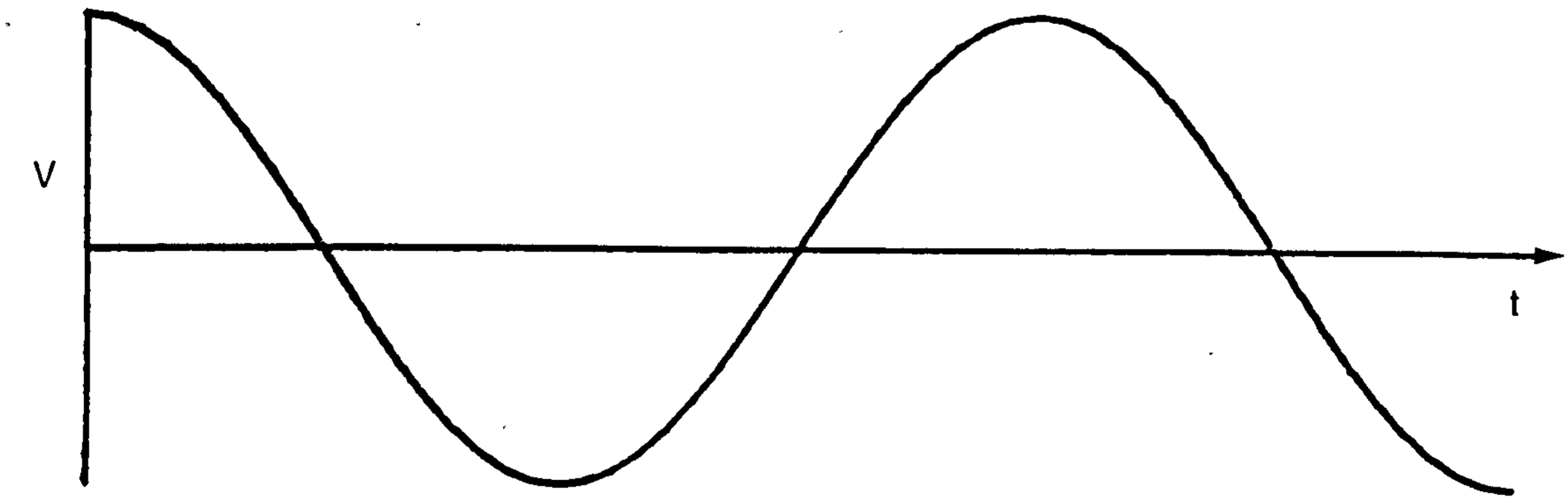


Fig 1.2 Projection of a rotating voltage vector on to co-ordinate axes (abscissa=time, ordinate=voltage).



(Fig 1.2). The application of a voltage to an electrochemical system gives rise to a sinusoidal current in the cell under test. This current can also be represented as a phasor, with the same rotational frequency as the applied voltage and both phasors can be shown on the same diagram as they both have the same rotational frequency. Generally the current will be out of phase with the voltage by a certain amount and this is represented by the phase angle (φ) between the two phasors. The voltage is usually taken as the reference point and φ is expressed with respect to the voltage phasor.

The current can thus be expressed as

$$i = I \sin(\omega t + \varphi) \qquad 1.2$$

As the phase angle is invariant with time for a voltage of a given frequency, it is customary to refer to and represent the two quantities i and e as vectors on non-rotating axes (Fig 1.3).

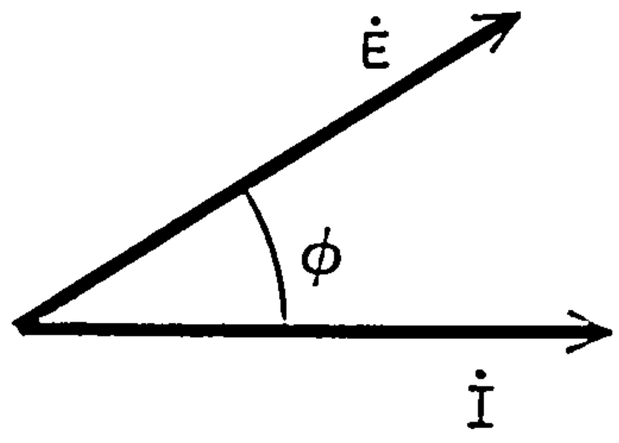


Fig 1.3 Voltage and current vectors on non-rotating axes.

If the voltage is applied across a pure resistor, Ohms' law applies and the current is therefore given by

$$i = \frac{E}{R} \sin(\omega t) \qquad 1.3$$

or, using phasor notation

$$\dot{I} = \frac{\dot{E}}{R} \qquad 1.4$$

The phase angle between the two vectors is zero and therefore the vector diagram is as shown in Fig 1.4.

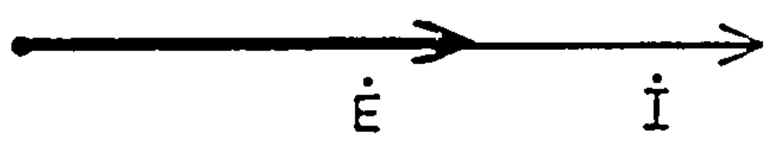


Fig 1.4 Voltage and current vectors with zero phase angle.

The current in an electrical circuit can be expressed as the rate of movement of charge through the circuit, ie

$$i = C \frac{de}{dt} \qquad 1.5$$

If a sinusoidal voltage is applied across a pure capacitor, it follows from equations 1.1 and 1.5 that

$$i = C\,\omega E\cos(\omega t) \qquad 1.6$$

or

$$i = \frac{E}{\mathcal{X}} \sin(\omega t + \pi/2) \qquad 1.7$$

where $\mathcal{X}$ is the capacitive reactance,

$$\mathcal{X} = 1/\omega C \qquad 1.8$$

In this case, the current leads the voltage by $\pi/2$ degrees. The vector diagram for this situation is shown in Fig 1.5. It is conventional to use complex notation as the vector diagram now represents a plane, thus components along the abscissa are 'real' and those along the ordinate are 'imaginary' and are multiplied by j ($j = \sqrt{-1}$). Thus, from equation 1.7, it can be seen that

$$E = \frac{i\mathcal{X}}{\sin(\omega t + \pi/2)} \qquad 1.9$$

or in phasor notation,

$$\dot{E} = -j\mathcal{X}\dot{I} \qquad 1.10$$

It can be seen from eqns 1.4 and 1.10 that $\mathcal{X}$ is expressed in Ohm and from eqn 1.8 that the magnitude of $\mathcal{X}$ decreases with increasing frequency.

When the sinusoidal voltage is applied across a series combination of a resistor and a capacitor, the total voltage drop

Fig 1.5 Vector diagram with current leading voltage by $\pi/2$ degrees.

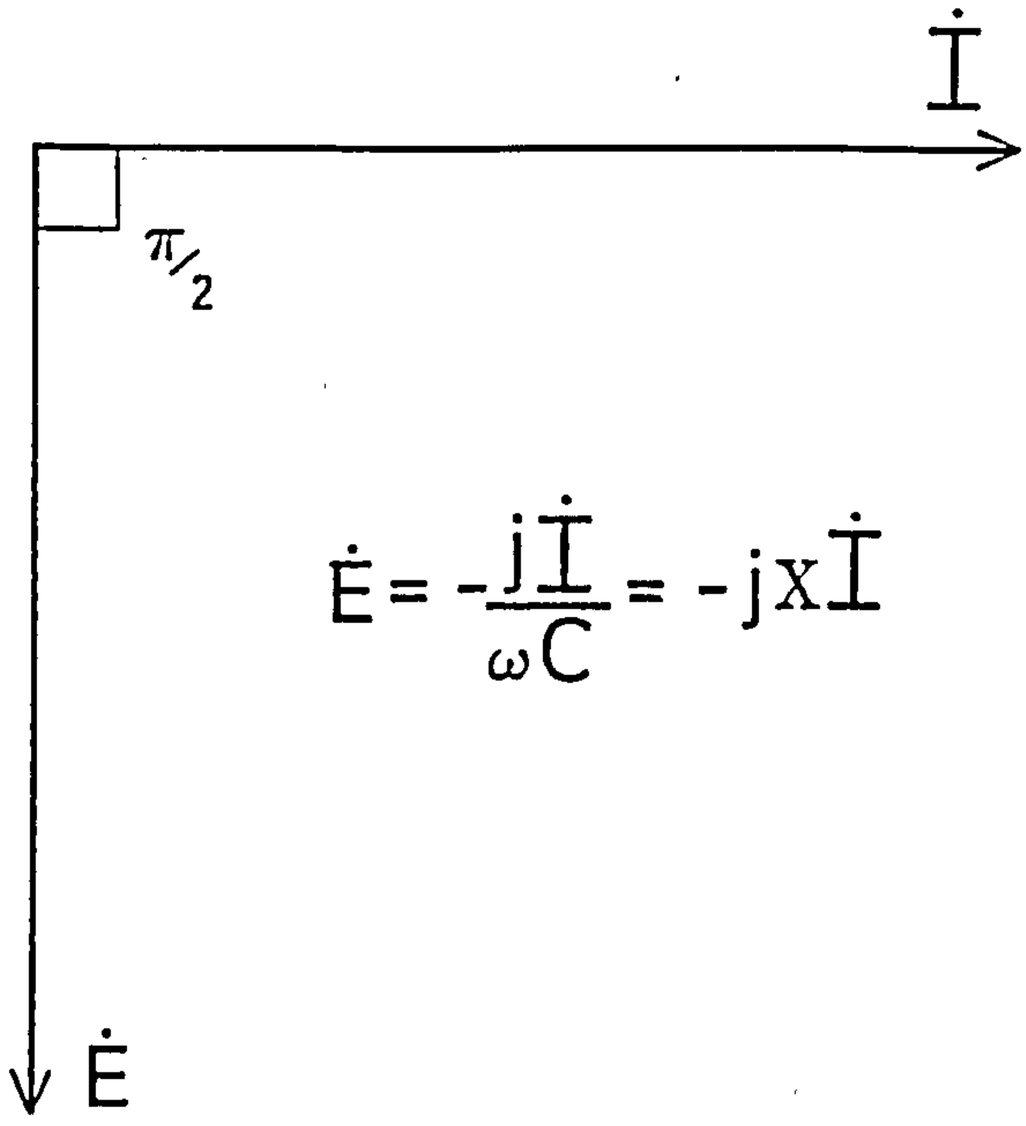
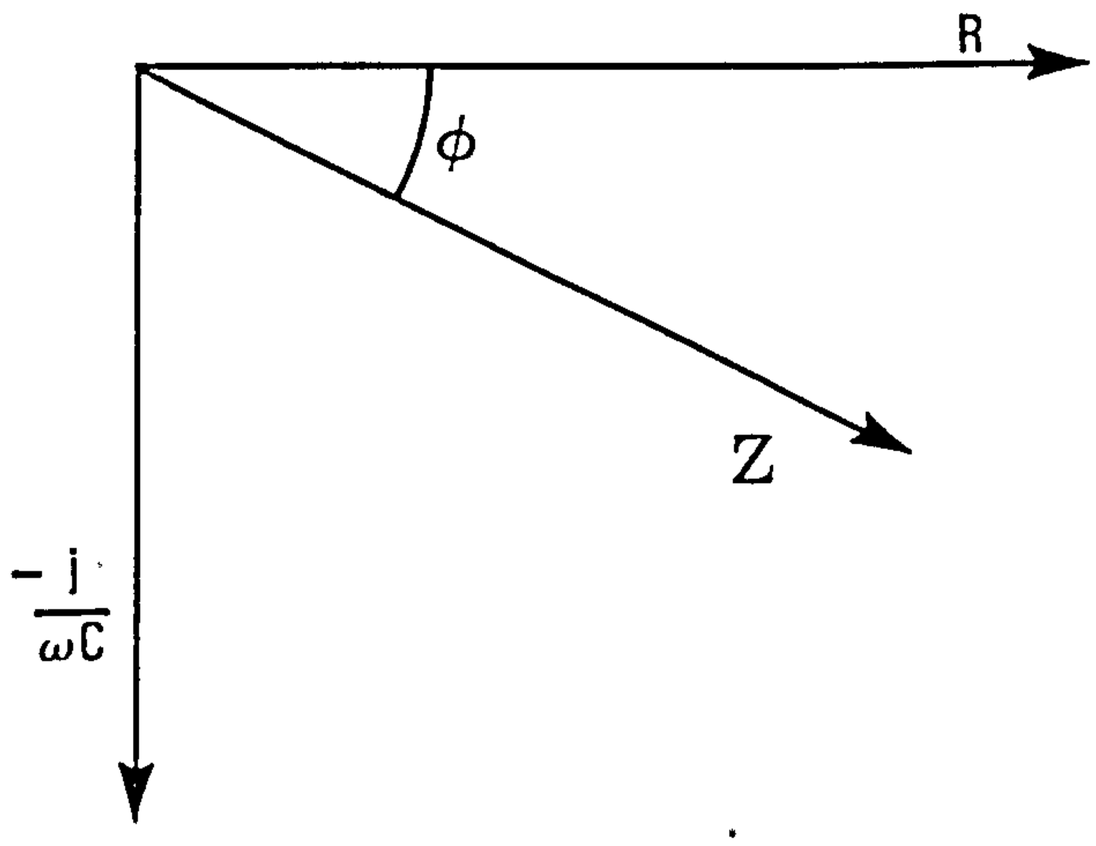


Fig 1.6 Vector diagram showing the relationship between Z, R and j/wC.



across the cell must be equal to the sum of the voltage drops across the individual components. Therefore, using phasor notation,

$$\dot{E} = \dot{E}_r + \dot{E}_c \qquad 1.11$$

$$= \dot{I}R + \dot{I}(-j\mathcal{X}) \qquad 1.12$$

$$= \dot{I}(R - j\mathcal{X}) \qquad 1.13$$

or $$\dot{E} = \dot{I}Z \qquad 1.14$$

where Z is the impedance, which links the voltage and current vectors and

$$Z = R - j\mathcal{X} \qquad 1.15$$

This is shown diagramatically in Fig 1.6.

For a parallel combination of resistor and capacitor, the impedance can be calculated as follows.

The voltage drop across the whole network is given by equation 1.3, but by Kirchhoff's Laws,

$$I_{tot} = I_r + I_c \qquad 1.16$$

From equation 1.14 the current through the resistor (I_r) and capacitor (I_c) are given by E/Z_r and E/Z_c respectively. Thus

$$I_{tot} = \frac{E}{Z_r} + \frac{E}{Z_c} \qquad 1.17$$

$$= E\,(1/Z_r + 1/Z_c) \qquad 1.18$$

As Z = E/I, it follows that

$$Z = (1/Z_r + 1/Z_c)^{-1} \qquad 1.19$$

$$= \frac{Z_r Z_c}{Z_r + Z_c} \qquad 1.20$$

Substituting for Z_r and Z_c from eqn. 1.15, we have

$$Z = \frac{R}{1 + j\omega CR} \qquad 1.21$$

$$= (1/R + j\omega C)^{-1} \qquad 1.22$$

The above theoretical treatment and equations relate to the impedance of a system at a single frequency. If the frequency of the applied voltage is varied, then the measured impedance will

be affected according to the circuit components as described by equations 1.15-1.22 above. From eqn 1.15 it can be seen that the impedance of a pure resistor is invariant with frequency and so if the impedance is measured at a variety of frequencies, and the measured value is plotted in the complex plane, the resulting vector diagram is a single point lying on the real axis (Fig 1.7a). Equation 1.15 also shows that the impedance of a pure capacitor decreases with frequency so the complex plane plot for a capacitor appears as a series of points lying on the imaginary axis. Due to the inverse relationship between the impedance and the frequency of the applied signal, the data points lie increasingly further from the origin as the frequency of the measuring signal decreases (Fig 1.7b).

Eqn 1.15 shows that the impedance of a series combination of a capacitor and a resistor is merely the linear combination of the two components Zr and Zc, so that the total ımpedance will vary with frequency, but the complex plane plot will look similar to that for a pure capacitance. The resistive component merely introduces a displacement along the real axis corresponding to the value of the series resistor (Fig 1.8a).

If a parallel combination of a resistor and capacitor are encountered, then the total impedance is not a simple combination of the two component impedances. It can be shown that eqn 1.22 corresponds to the equation for a circle, and so the impedance of such a combination is represented by a locus of points in the complex plane, with diameter equivalent to the magnitude of the resistive component of the parallel network (Fig 1.8b). The impedance behaviour of multiple combinations of these basic circuit elements can be treated as a linear combination of the separate parallel or series networks as shown in Fig 1.9,

Fig 1.7a Complex plane impedance plot for a pure resistor.

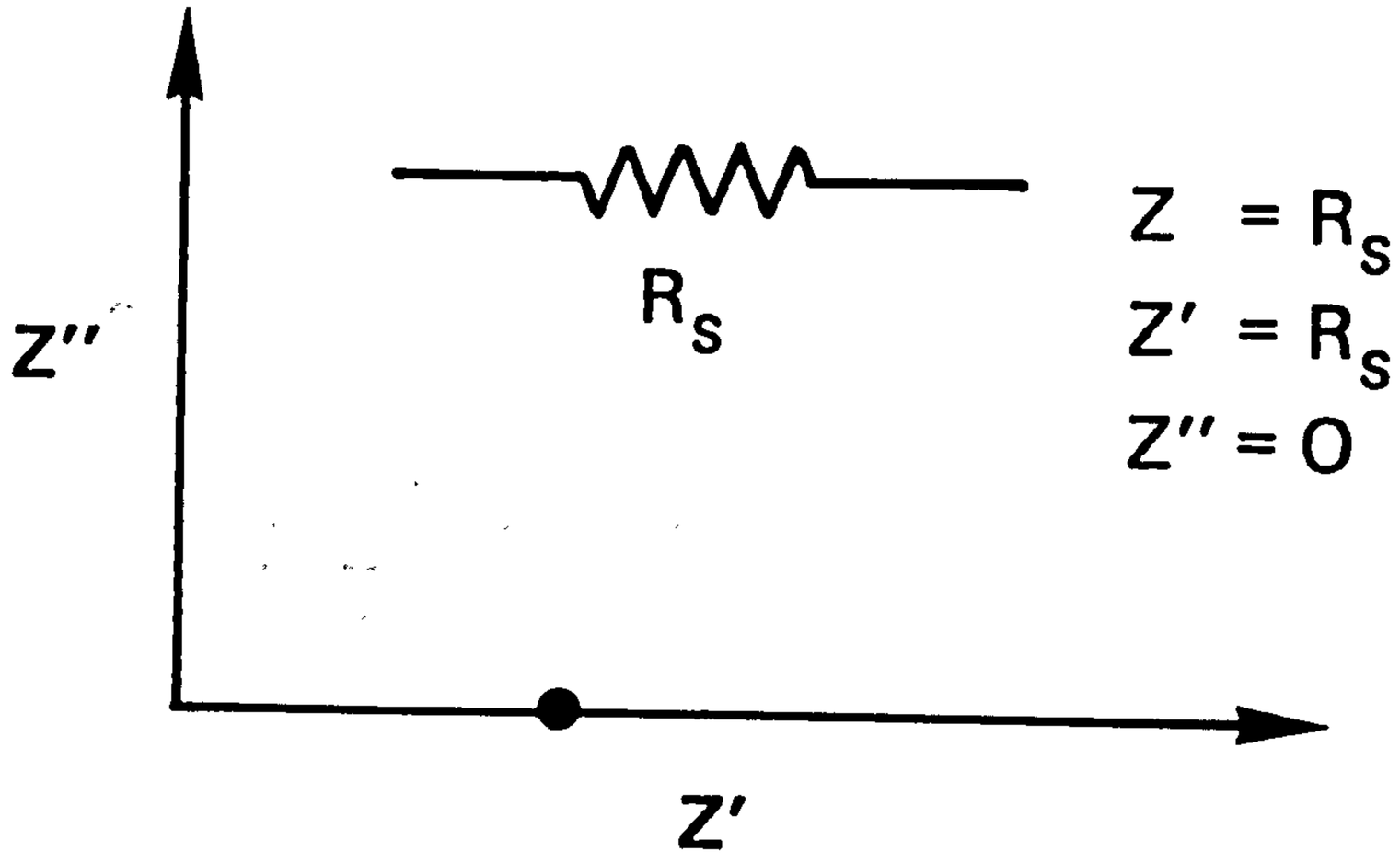


Fig 1.7b Complex plane impedance plot for a pure capacitor.

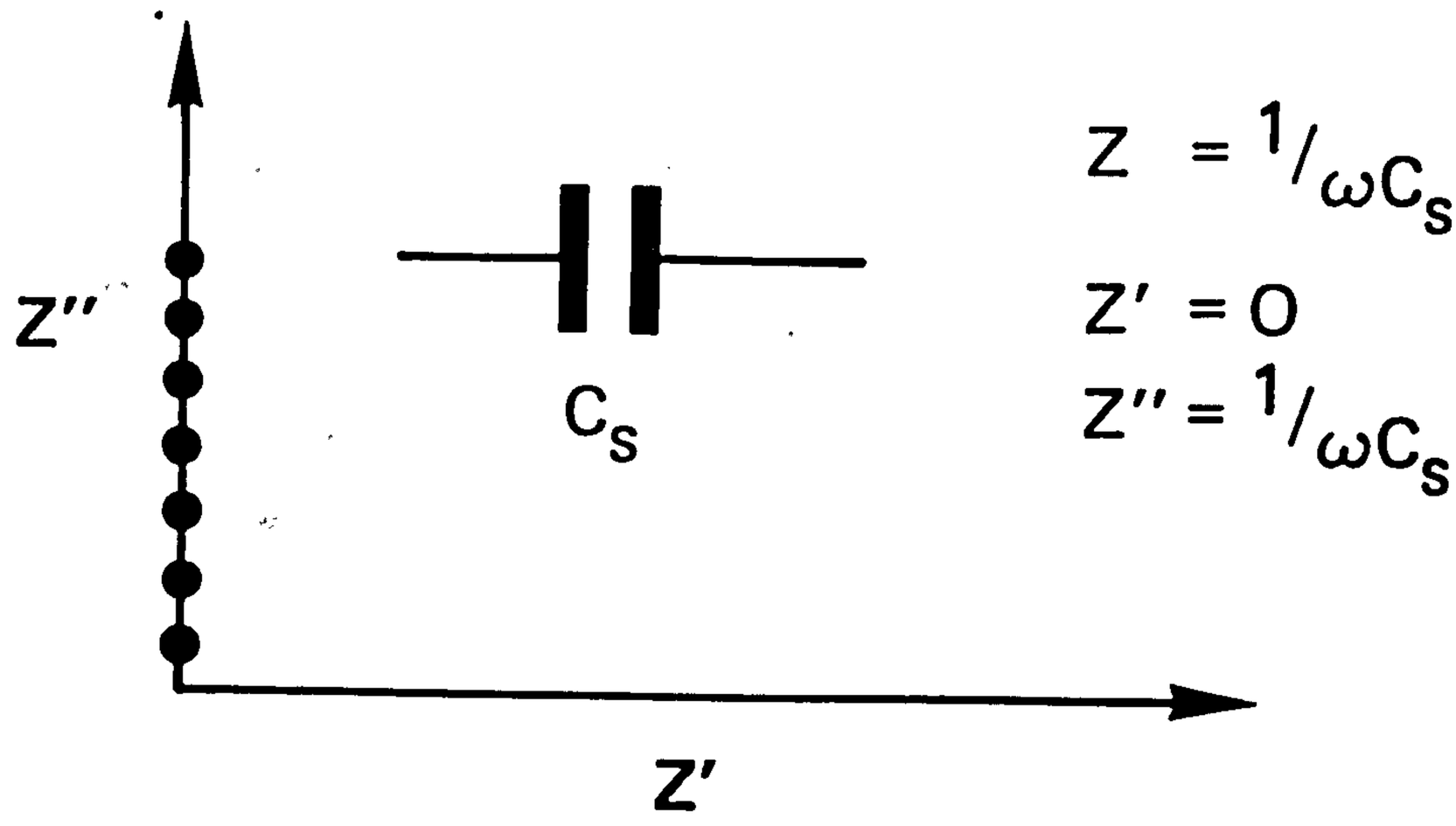


Fig 1.8a Complex plane impedance plot for a series combination of a resistor and a capacitor.

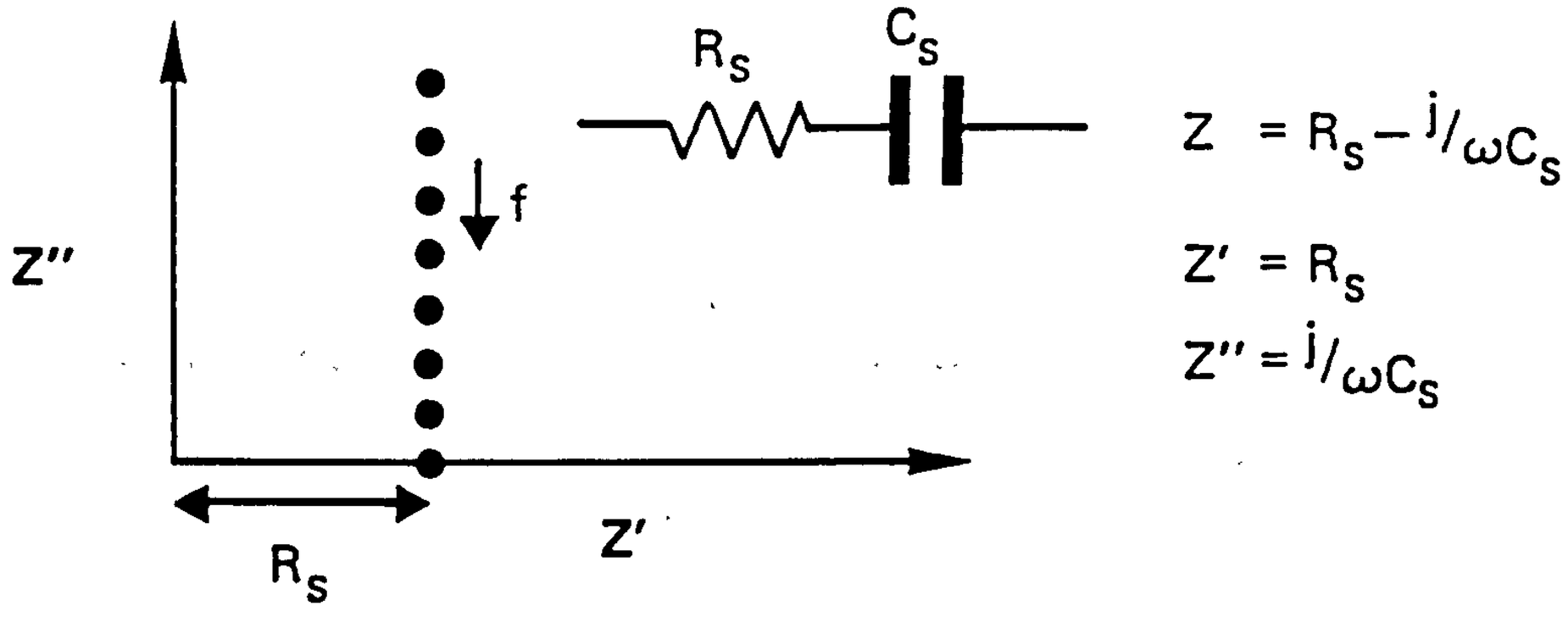


Fig 1.8b Complex plane impedance plot for a parallel combination of a resistor and a capacitor.

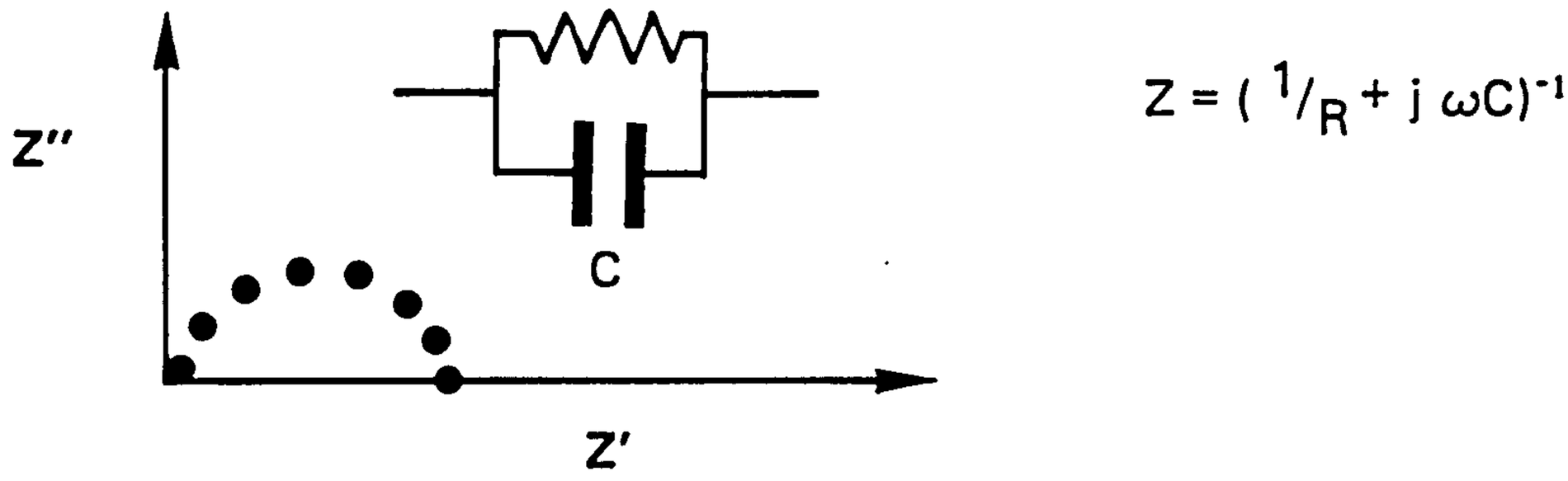
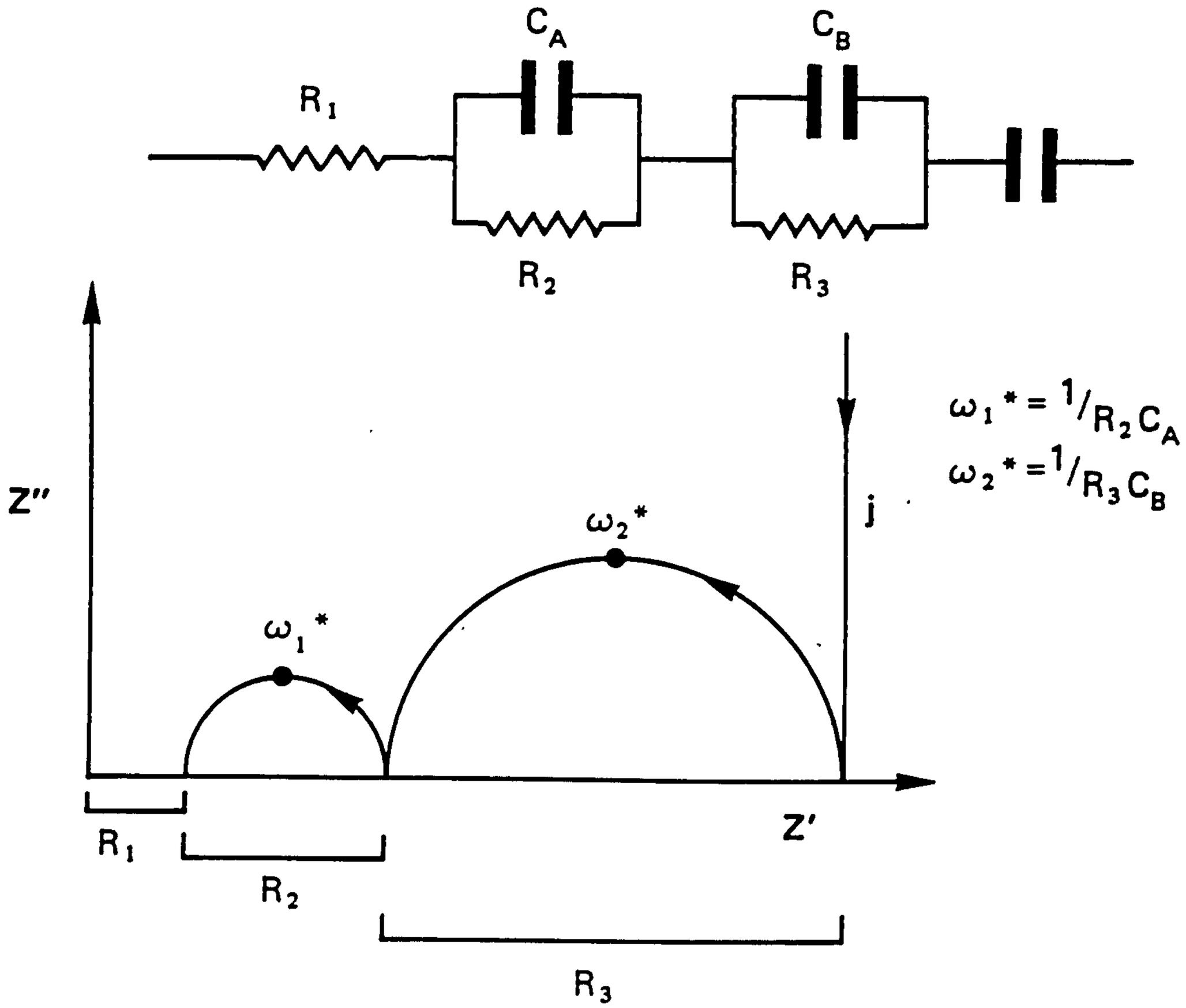


Fig 1.9 Complex plane impedance plot for a multiple combination of series and parallel networks (with equivalent circuit).



allowing the values of the individual components to be determined from the complex plane plot.

1.2.2.1 Series and Parallel Components

Given any series RC circuit, it is possible to calculate the values for R and C which would be required to construct a parallel RC circuit having the same frequency response. For a series circuit of Rs and Cs, the total impedance, Z is given by

$$\frac{1}{Z} = \frac{\omega C}{\omega RC - j} \qquad 1.23$$

$$= \frac{\omega C(\omega RC + j)}{(\omega RC)^2 + 1} \qquad 1.24$$

and for the equivalent parallel network, Z is given by

$$\frac{1}{Z} = \frac{1}{R_p} + j\omega C \qquad 1.25$$

setting $M = (\omega RC)^2$, we have for the series case,

$$\frac{1}{Z} = \frac{M}{R(M + 1)} + \frac{j\omega C}{(M + 1)} \qquad 1.26$$

Equating the real and imaginary components in the two situations, we find the following.

$$Rp = \frac{Rs}{M(M + 1)} \qquad 1.27$$

$$\text{and} \quad Cp = \frac{C}{(M + 1)} \qquad 1.28$$

1.2.3 Equivalent Circuits

In a general sense an electrochemical cell will act simply as an impedance to a small sinusoidal excitation, and so it is reasonable to be able to represent its electrical behaviour by an equivalent circuit of resistors and capacitors that pass current with the same amplitude and phase as the real cell under the same excitation.

When using ac impedance measurements on electrochemical cells it is customary to use this approach to construct an equivalent circuit of basic electrical components which, if it were connected to the measuring system, would produce impedance data similar to the data obtained for the real system under test. An attempt is then made to assign the various equivalent circuit components (resistances, capacitances and inductances) to parts of the electrochemical system under investigation. This process is usually carried out by visual inspection of the complex plane plot although computation of the circuit components by curve fitting procedures has been carried out (1.70a-1.70e).

To construct the equivalent circuit, pure resistances can be measured directly from the real axis of the plot, and pure capacitance can likewise be calculated from the values of the imaginary components with the use of equation 1.15. For semicircles in the complex plane, the resistive component of the parallel network can be measured directly from the diameter of the semicircle on the real axis and the capacitive component can be obtained using the expression

$$\omega^{*} = 1/CR$$

where ω^{*} is the rotational frequency ($2\pi f$) at which the maximum point of the semicircle occurs.

1.2.4 Instrumentation

The simplest experimental set-up for measuring the impedance of a cell involves the use of an ac bridge. The cell under test is connected in one arm of the bridge (Fig 1.10a) and the resistive and capacitive components are balanced against standard components in the other arm. At the balance point, the measured

Fig 1.10a Basic ac bridge circuit.

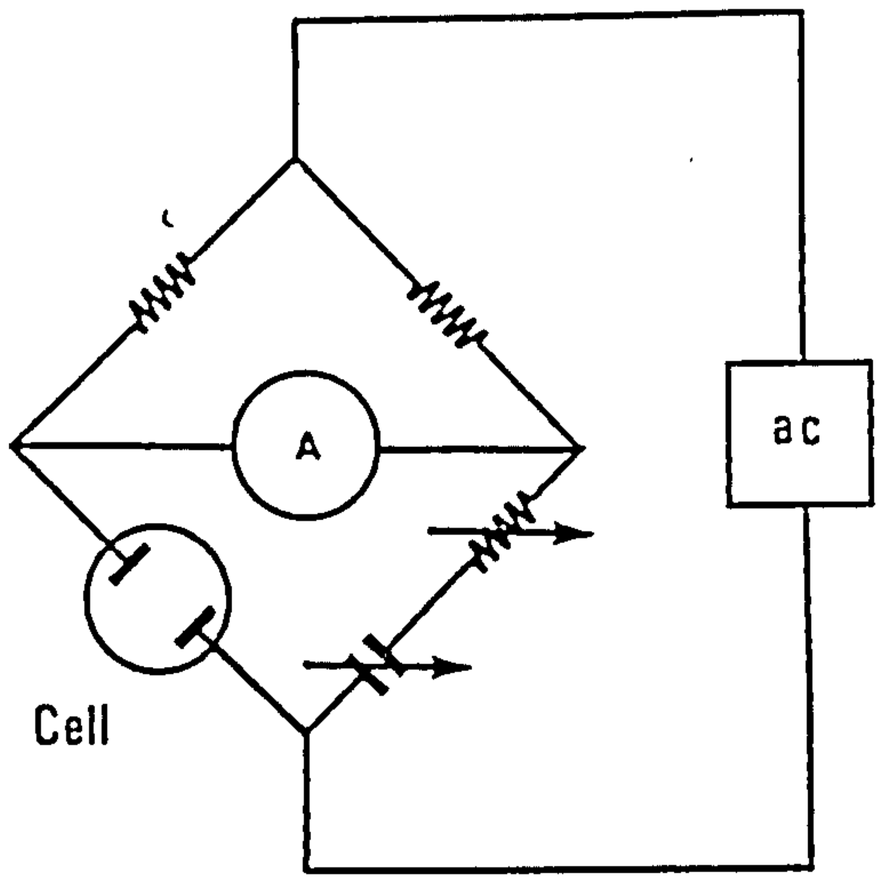
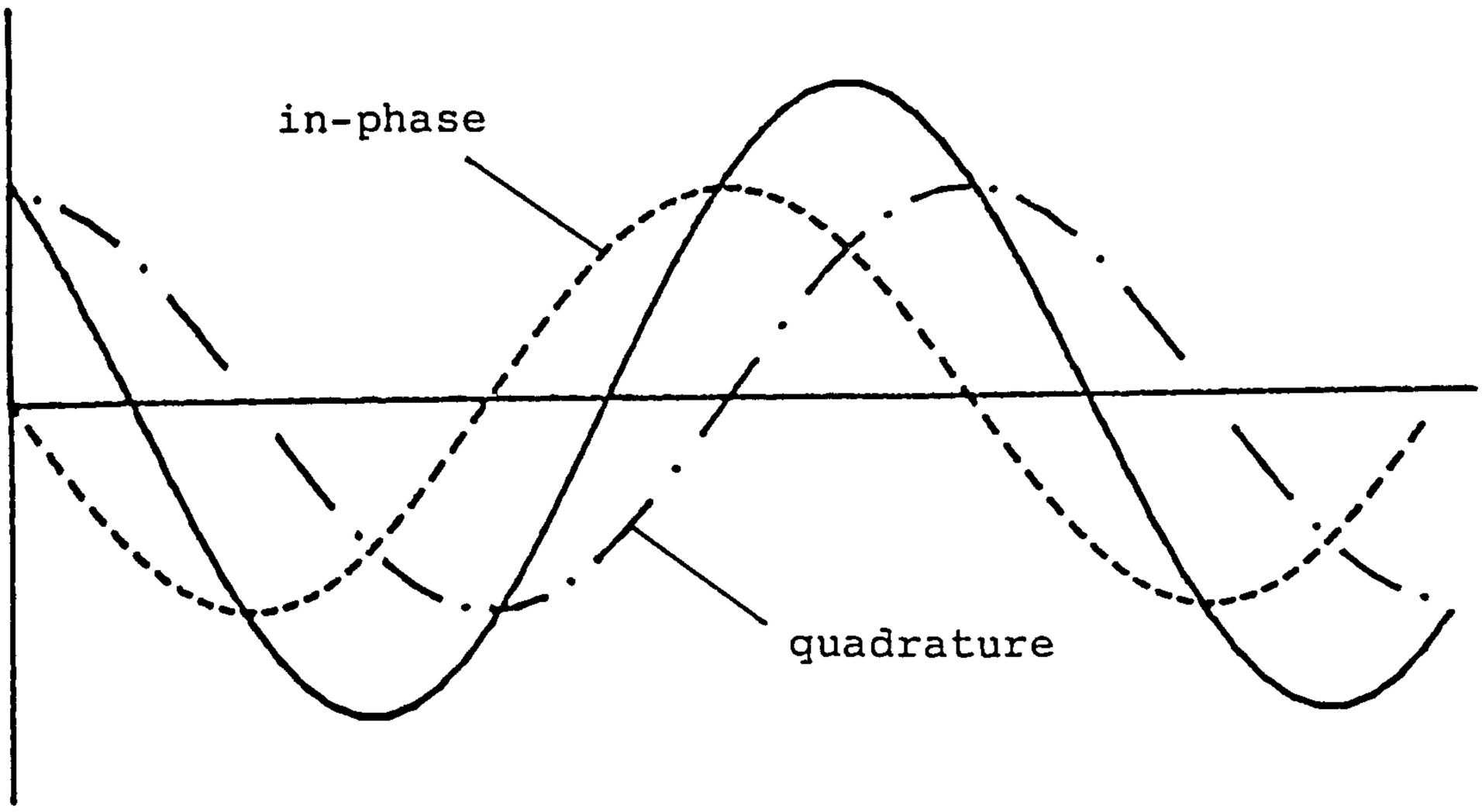


Fig 1.10b Diagram showing the combination of in-phase and out-of-phase (quadrature) components of the current signal.



components of the impedance are the series resistance and capacitance, R_s and C_s, from which the equivalent parallel components R_p and C_p can be obtained using equations 1.27 and 1.28. The real and imaginary components of the impedance can then be obtained ($Z'=R_p$, $Z''=1/\omega C_p$). Although good quality data can be obtained using such a set-up, measuring an impedance spectrum over a wide range of frequencies is extremely time consuming, as a signal generator must be manually adjusted and a balance point obtained for each measurement. In addition, the range of frequencies which can be investigated with such an arrangement is limited to the region of 30kHz to 100Hz, without the aid of sophisticated detection systems.

A more efficient method of measuring the impedance of a sample cell is to use a phase-sensitive detector. Such a device gives a dc output related to the amplitude and phase of the sinusoidal input. Applying phase shifts it is possible to determine the real and imaginary components of the impedance. The total current signal can be divided into an in-phase and out-of-phase (quadrature) component which can be separately determined to find the current response (Fig 1.10b). Although it is possible to carry out this procedure manually, in modern instrumentation all data are processed as collected to give real and imaginary impedance components, and a large range of frequencies can be covered in a relatively short time. Such an automated system also allows averaging of signals over a period of time leading to increased accuracy of data. The Solartron 1170 series of frequency response analysers (see Chapter 2) are essentially phase-sensitive detectors, which offer these facilities.

With all such measurements, the time required to collect the

data can be a limiting factor, even with sophisticated computer-controlled apparatus such as described in Chapter 2. To collect sufficient data for the impedance to be calculated it is necessary for the applied signal to complete a full cycle. This means that as progressively lower frequencies are employed, the time for a single measurement even without averaging, can become prohibitively long. With an applied signal of 10 mHz, the Solarton 1170 series analysers require a measurement time of at least 200 s to measure the impedance at a single frequency, with no integration over a series of repeated measurements. Approximately two days are required to complete a full scan from 1 MHz to 7 mHz with averaging of each measurement (at each frequency) over ten cycles, and collect a single spectrum. In view of this, some workers have made attempts to speed up further the measurement process, using Fourier and Laplace transforms to evaluate a whole spectrum from a single measurement. These systems are at present not commercially available and can still require long periods of signal averaging (1.71,1.72).

1.2.5 I.S.E. Membranes: Expected Equivalent Circuits

The simplest equivalent circuit, which one might expect for an ion-selective membrane in contact with aqueous solutions on both sides is shown in Fig. 1.11a. The circuit consists of two solution resistances R_s, in series with a parallel network representing the membrane. The resistive component of this network R_b is the bulk resistance of the membrane arising from the transport of charge carriers through the membrane phase, disregarding interfacial processes or blocking at the membrane-solution interfaces. The capacitive component of the

Fig 1.11a Equivalent circuit for a simple membrane model (two solution resistances in series with a single parallel network).

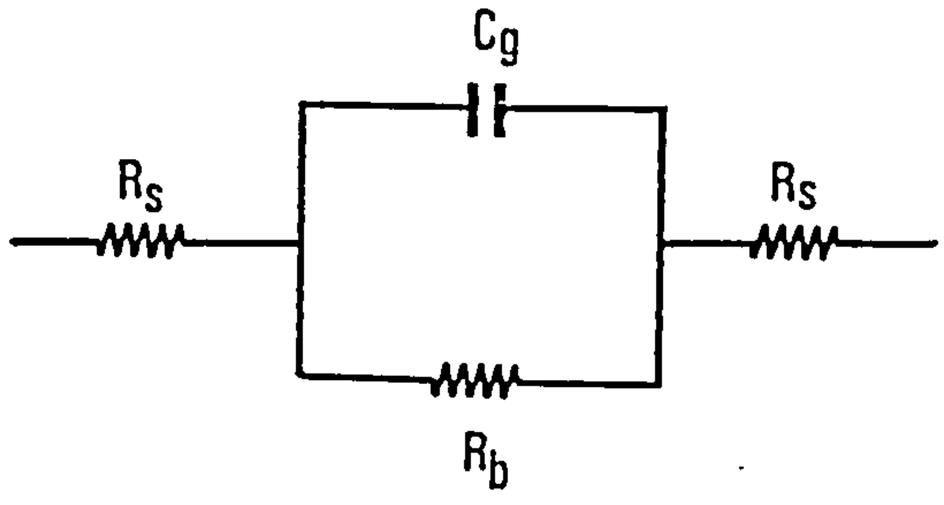
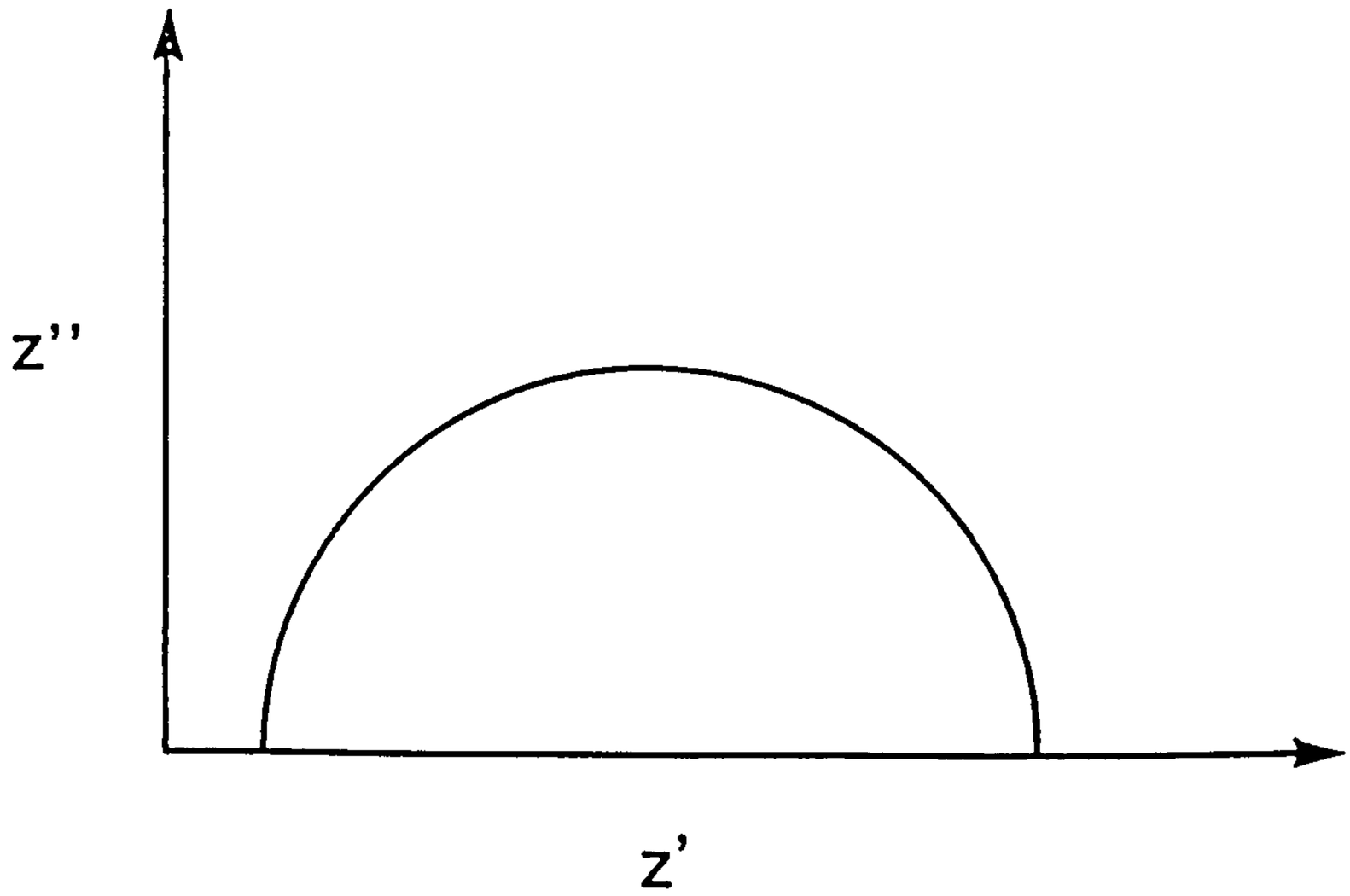


Fig 1.11b Complex plane plot for Fig 1.11a



network C_g, is the geometric capacitance inherent in the membrane resulting from the space charge regions at the membrane surfaces. The complex plane impedance plot which would result from this equivalent circuit is given in Fig 1.11b. If all interfacial processes were fast and unhindered, the above circuit would represent an ion-selective membrane in contact with solution of the primary ion. It is likely, however, that these processes will be less facile and will affect the membrane impedance, giving rise to other features in the complex plane.

Considering a simple ion transfer from the aqueous phase to the organic phase, it is probable that an energy barrier must be overcome to move an ion across the interface, similar to the Butler-Volmer activation overpotential of classical electrochemistry. This barrier would manifest itself as a charge-transfer resistance in series with the bulk membrane network. In parallel with this resistance there would also be a capacitance due to the diffuse electrical double layer existing at each interface, forming a second parallel network which would then give rise to a second semicircle in the complex plane (Fig 1.12).

The question of whether or not both of these features could be expected to be visible in the impedance plot depends largely on the magnitude of the various equivalent circuit components. It is generally true that such features can be separately distinguished when the time constants for the two networks are more than two orders of magnitude apart. Fig. 1.13 shows theoretical complex plane plots calculated using the expressions

$$Z' = \frac{R}{1 + \omega^2 R^2 C^2} \qquad 1.30$$

Fig 1.12a: Alternative equivalent circuit for a simple membrane model including slow interfacial processes.

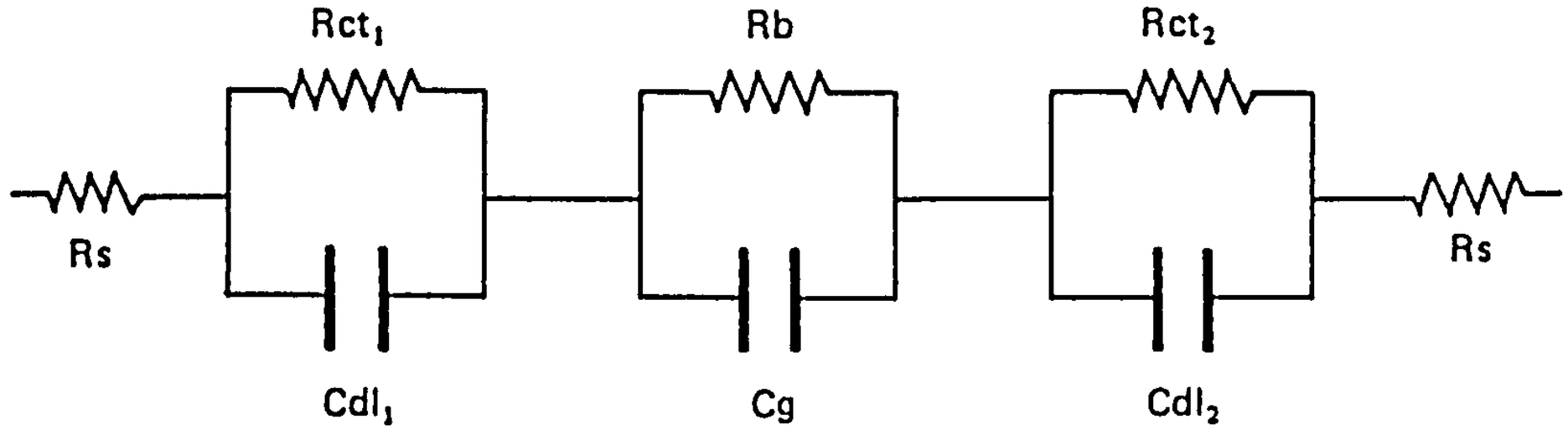


Fig 1.12b Complex plane plot for Fig 1.12a

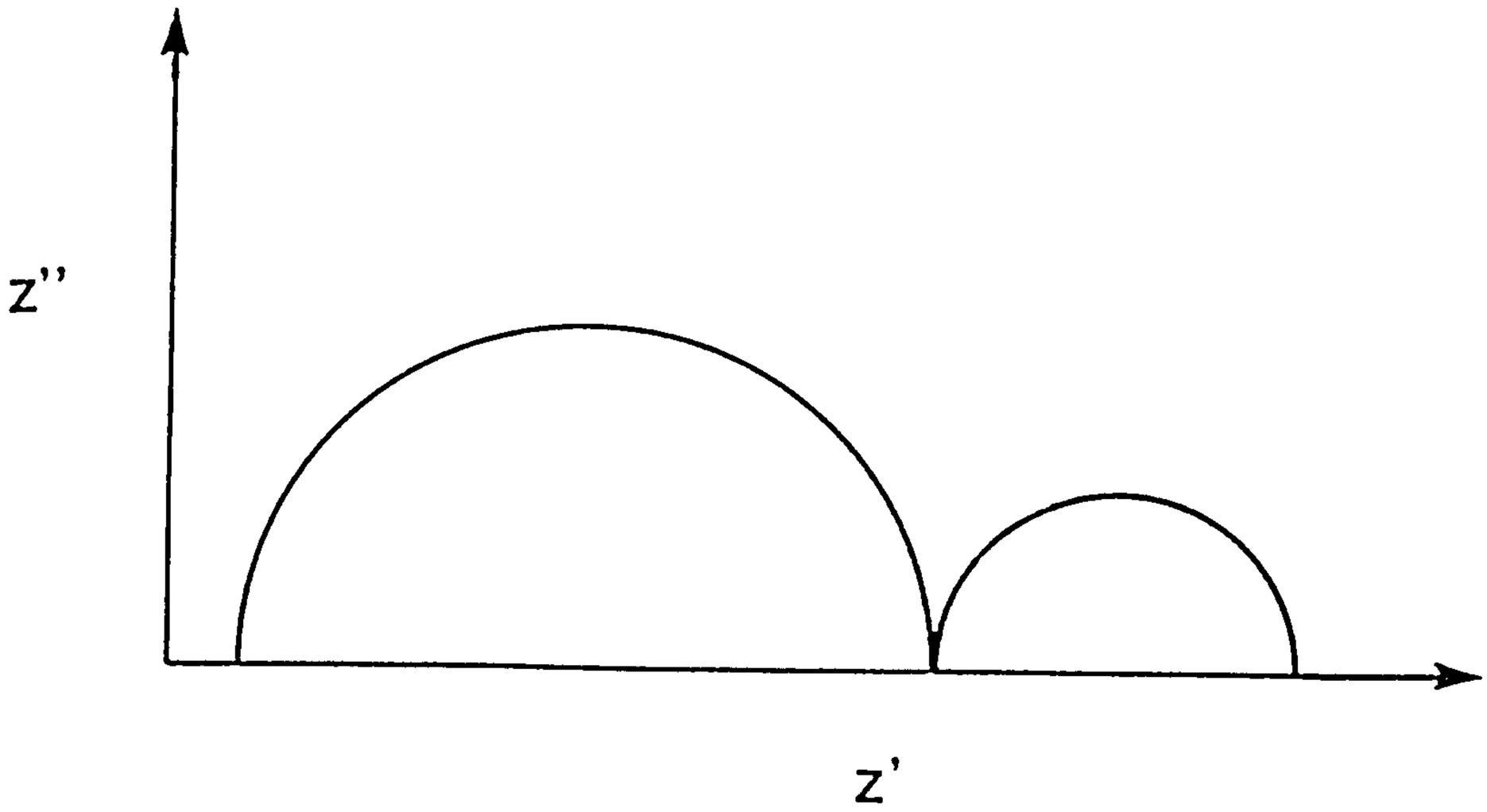
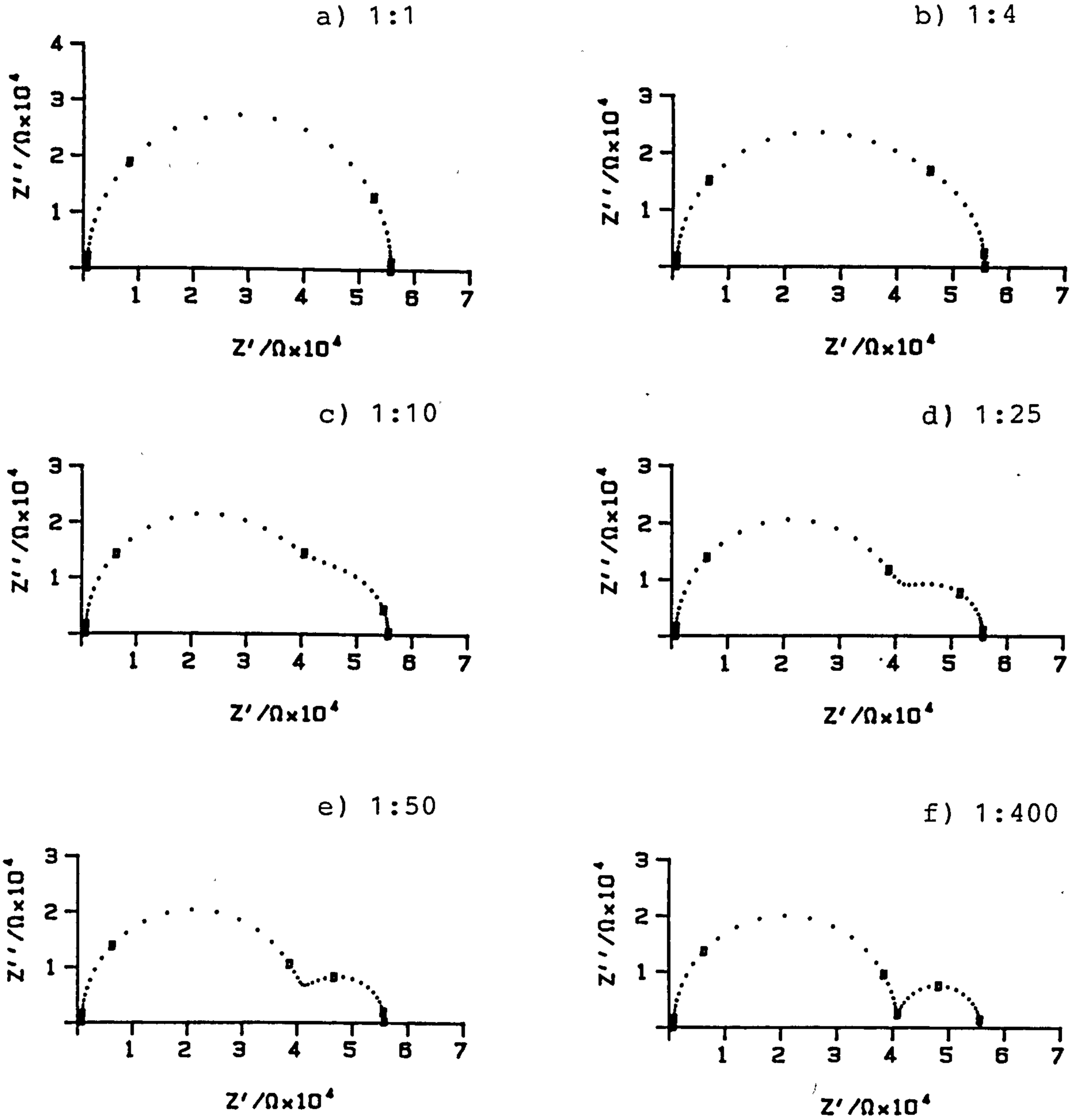


Fig 1.13 Theoretical plots showing the convolution of separate semicircles with various ratios of time constants.



and

$$Z'' = \frac{-\omega R^2 C}{1 + \omega^2 R^2 C^2} \qquad 1.31$$

for the equivalent circuit with various ratios of the two time constants.

Simulated data were calculated using the program Simplot on the Apple microcomputer, which produces a dummy data file for plotting with Analysis 1 and Analysis 2. (A listing of Simplot is given in Appendix A along with the main data control system programs).

It is also possible that the impedance of the ion-selective membrane system could include a Warburg impedance Z_W. This arises generally from the presence of a diffusion, or mass transfer controlled process occurring in the system under study. In this case the equivalent circuit becomes as in Fig 1.14a, where the real and imaginary components are given by;

$$Z' = R_s + \frac{R_{ct} + s\omega^{-1/2}}{(C_{dl} s\omega^{1/2} + 1)^2 + \omega^2 C_{dl}^2 (R_{ct} + s\omega^{-1/2})^2} \qquad 1.32$$

$$Z'' = \frac{C_{dl}(R_{ct} + s\omega^{-1/2})^2 + s\omega^{-1/2}(\omega^{-1/2} C_{dl} s + 1)}{(C_{dl}\, s\omega^{1/2} + 1)^2 + \omega^2 C_{dl}^2 (R_{ct} + s\omega^{-1/2})^2} \qquad 1.33$$

(The derivation of these expressions is given in Appendix B)

For an ion-selective electrode, a Warburg impedance would represent the diffusion of charge carriers or complexes within the system becoming a controlling process. This can be viewed (1.73) as a resistive component Z_W and a capacitive component C_W, where Z_W arises from the addition at one interface and loss at the other of charge carriers in each half cycle of the measuring

Fig 1.14a: Equivalent circuit for a membrane system containing a Warburg impedance and slow interfacial processes.

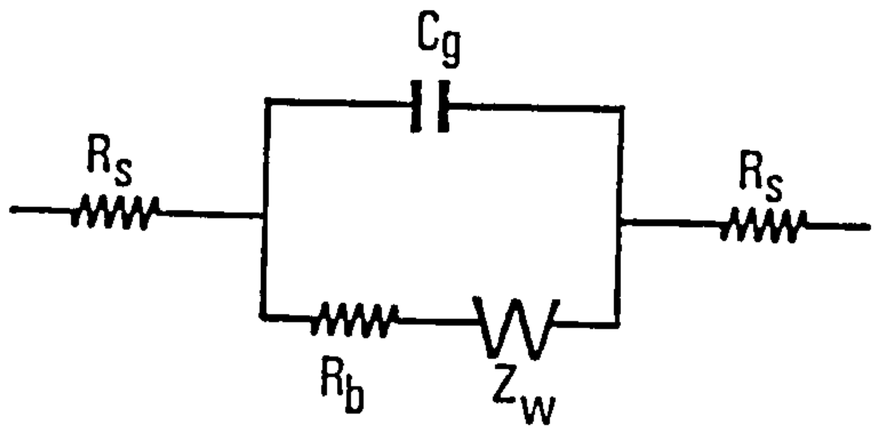
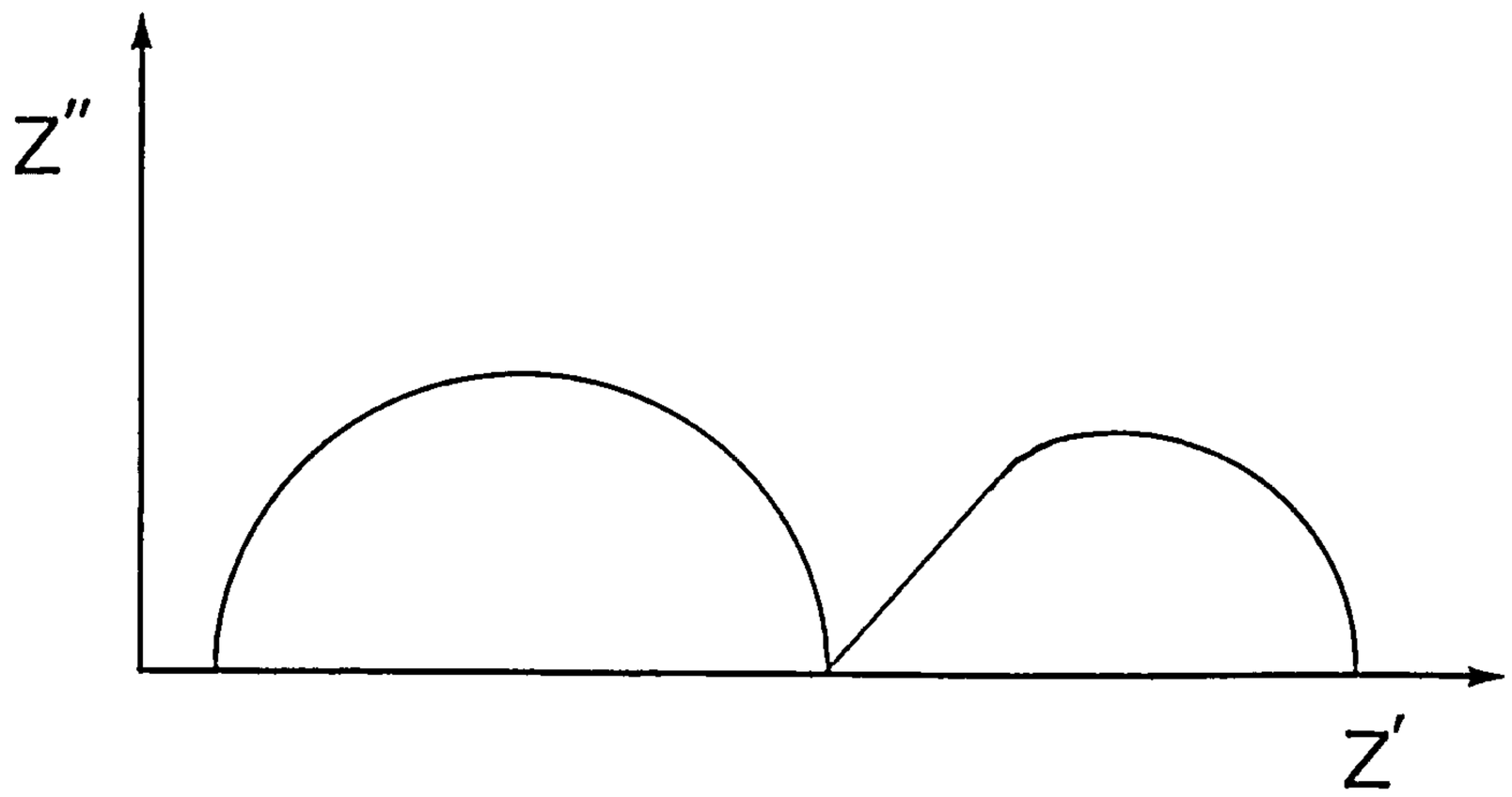


Fig 1.14b: Complex plane plot for the equivalent circuit shown in Fig 1.14a.



signal, and C_w is a pseudo-capacitance due to charge separation from ions moving at different velocities. If this were the case, then the complex plane plot for the system would appear as in Fig 1.14b.

It is apparent that several factors will affect the impedance of the ion-selective electrode system, both on a microscopic and a molecular level. Viewing the system as a simple model as above requires that the membrane itself is chemically homogeneous, and also that it is physically smooth and planar. The effect of surface roughness or discontinuities would be to create a series of parallel R_{ct} and C_{dl} networks, probably exacerbated by a chemically non-uniform surface. These multiple networks would be manifested in the impedance plot as a convoluted series of semicircles, all having very similar time constants. This type of feature has been reported elsewhere and is generally treated as a single, large semicircle with its centre below the real axis (Fig 1.15). If pure capacitive behaviour is present, surface roughness is also manifested by deviations from the vertical of the low-frequency capacitive feature in the complex plane plot (1.74).

More obvious possibilities for the factors affecting the impedance concern the nature, number, and mobility of the charge carrying species. R_{ct}, and ultimately R_b, will be affected by the rate of transfer of charge carriers from and to the membrane phase, and R_b will depend also on the mobility of the charge carriers within the membrane, the magnitude of their charge, and the rate at which carriers are generated or lost from sites within the membrane, ion pairs, and complexes. C_g and C_{dl} will depend largely on the location and type of space charges, and charges adsorbed on to the membrane surface.

Fig 1.15a: Equivalent circuit representation of multiple RC parallel networks in series (as may occur with a membrane with surface roughening).

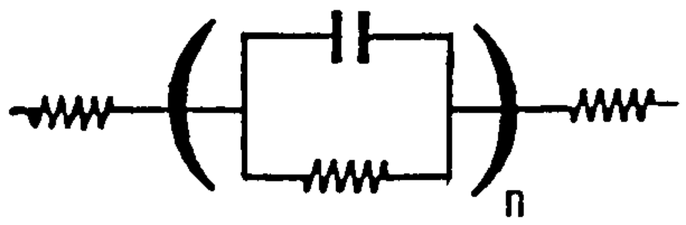
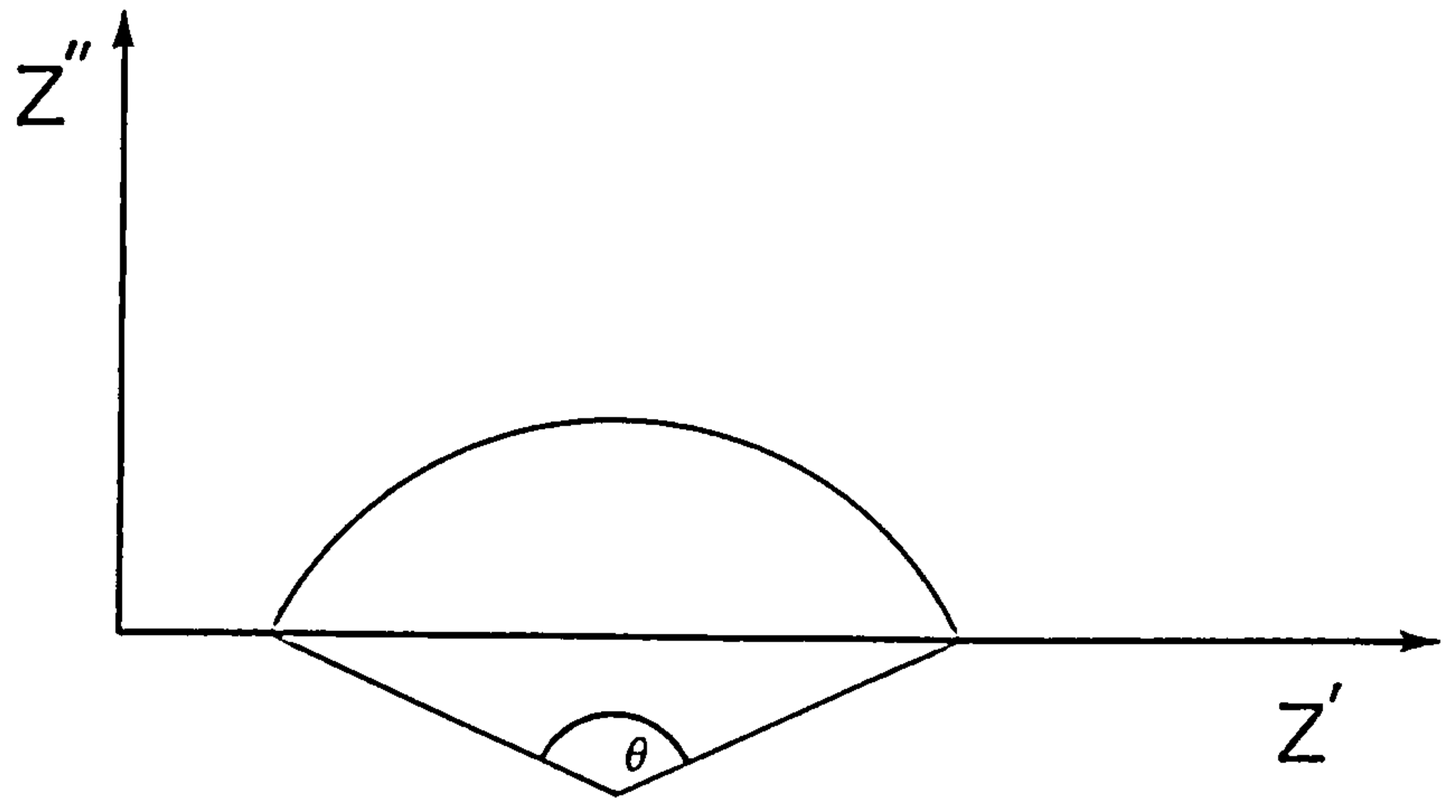


Fig 1.15b: Complex plane plot for the equivalent circuit shown in Fig 1.15a.



1.2.6 Impedance Measurements Applied to ISEs: Previous Work

Several workers have attempted or proposed (1.75,1.76) impedance measurements on ion-selective electrodes in the past, and the theoretical treatment of the problem has received some attention. Until recently, however, the lack of sophisticated equipment for impedance measurement has meant that the data collected have been generally of a poor quality and only initial, qualitative conclusions about the electrodes under study could be drawn. A review of the literature is given below, divided according to the type of electrode studied and presented chronologically within each sub-heading.

1.2.6a Theoretical

Early work by MacDonald (1.77) on the theory of polarisation of electrochemical systems under the influence of ac signals, preceded the first work on the impedance of glass membranes by Buck (1.78), who calculated equivalent circuits and theoretical values for the shape and magnitude of the membrane impedance using theoretical expressions for the current-potential-time characteristics of the membrane.

Macdonald's work included considerations of the effects of ac signal on electrolytes and was followed by treatments specific to membrane with mobile sites by Sandblom et al. (1.79), who predicted an equivalent circuit for such a membrane, consisting of a parallel RC network in series with a resistor (similar to that discussed above). De Levie et al (1.80) derived an expression for the admittance of a membrane permeable to only one type of ion, using the Poisson-Nernst-Planck equations and

predicted an equivalent circuit similar to that of Sandblom but with the additional feature of a Warburg impedance. This work was extended to carrier-mediated ion-transport, by De Levie (1.81).

Brumleve and Buck (1.82) produced numerical solutions to the Nernst-Planck and Poisson equations by utilising computers and produced theoretical concentration profiles and impedance loci for a variety of membrane types, and Macdonald (1.83) published a highly detailed treatment for two-electrode systems consisting of;

electrode/membrane/electrode

Specific results applicable to glass membranes were derived by Buck (1.55) from the Laplace transform of the potential-current relationship.

Sandblom et al. (1.79) carried out theoretical work on the expected impedance of a mobile-site membrane, using a very simplified model, and using an HCl solution as a model membrane. The resistance of this model membrane was calculated from experimentally-determined diffusion coefficients, and this was then used to calculate the solution impedance using the applied voltage function. The results of this early work predicted, in general, a membrane whose equivalent circuit could be represented by a capacitor and resistor in parallel,in series with a second resistance.

The extent to which these theories and predictions agree with experimental data is discussed below and in later chapters.

1.2.6b <u>General</u>

The first experimental data for the impedance of an

ion-selective membrane were obtained by Brand and Rechnitz in 1969 (1.84), using a manually operated system which could only cover the limited range of 20Hz to 20kHz. The data obtained were of low quality, although it was possible to obtain an approximate value for the bulk resistance of the whole electrode assembly. It was necessary in this work to use a peak to peak voltage of 1V, which is sufficiently large for polarisation of the system to have occurred. Measurements were made on commercial electrodes for Cl^-, Ca^+, Cu^{2+} and water hardness.

1.2.6c Glass Electrodes

Initial measurements by Buck and Krull on glass pH electrodes (1.85) were extended to lower frequencies by Sandifer and Buck (1.86). It was found that the complex plane impedance plot showed two semicircles, representing an equivalent circuit of two parallel RC networks in series. This was interpreted as a bulk resistance and geometric capacitance giving rise to the higher frequency semicircle, and interfacial processes giving rise to lower frequency feature.

Brand and Rechnitz (1.87) also investigated the impedance of surface films on glass electrodes, although experimental data were still hampered by a lack of sophisticated measuring systems.

Brand and Rechnitz (1.88) also made impedance measurements on pH electrodes, sodium glass electrodes and monovalent cation electrodes, finding similar results to those of Buck, although disagreeing to some extent (1.87) on the nature of the equivalent circuit, but still accepting the presence of two features representing the bulk phase and the surface layer.

1.2.6d Silver Halide Electrodes

Buck et al. (1.89) made measurements on silver chloride crystals with various types of contacts, and found that no charge transfer semicircle was present in the complex plane impedance plot, implying that the interfacial kinetics under normal circumstances were very fast, and unlike the glass electrodes, no surface film or hydrated layer existed. Rhodes and Buck extended this work to silver/silver chloride layers deposited electrochemically on to silver electrodes (1.90). Rhodes and Buck also made measurements on silver bromide finding results similar to those found for the silver chloride electrode (1.91).

1.2.6e Fluoride Electrodes

Mertens et al. (1.92,1.93) made impedance measurements on several different lanthanum fluoride F^- electrodes and again found a two component impedance plot similar to those described above.

1.2.6f Precipitate-Based Electrodes

The only impedance work carried out on a precipitate based system was by Rhodes and Buck (1.94) on silver sulphide electrodes, in the form of a rotating disk electrode. Complicated results were obtained which could not easily be resolved into an equivalent circuit. Effects due to dissolution of the silver sulphide and to grain boundaries in the pressed-pellet electrodes were present.

1.2.6g Liquid Membrane (Ion-Exchanger) Electrodes

Mathis and Buck (1.95,1.96) carried out a number of impedance measurements on liquid ion-exchange membranes based on tricaprylmethylammonium nitrate (Aliquat nitrate) in solution in nitrobenzene. The membrane was created by supporting the solution between polymer support films to achieve thick membranes. Various support media were investigated, and it was found that the impedance spectrum of the system depended on the type of polymer support used, although the impedance plot remained as a two-semicircle plot. Dielectric constants, conductivities and capacitances were calculated and were found to be close to theoretically predicted values.

1.2.6h Neutral Carrier Electrodes

Initial measurements by Handyside (1.97) outlined the basic features of the impedance spectrum of the Orion series 92 liquid membrane potassium electrode. Ahmad-Bitar et al (1.98,1.99) have also made two-electrode measurements on PVC membranes using a rudimentary system giving data over a very limited frequency range, which did not allow the conclusive determination of the bulk membrane resistance or any other equivalent circuit parameters.

1.2.7 Summary and Thesis Objectives

Of the many different ion-selective electrodes produced commercially, potassium electrodes are one of the most important and widely used, although debate still continues as to the

precise mechanism of operation of the neutral carrier electrodes, and a synthetic alternative has yet to be found which exhibits the same degree of selectivity for potassium as does valinomycin.

The ac impedance technique has been used with some success to characterise the behaviour of solid state electrodes, and in the present study neutral-carrier electrodes are investigated in a similar way.

A review of the literature relating to mechanistic aspects of ion-selective electrodes and the application of ac impedance techniques to such systems is given earlier in this chapter, and an introduction to the theory of ac impedance measurements is also included. The impedance measuring system itself is described in detail in Chapter 2, with details of the purpose-written software required for its control. Chapter 2 also includes an introduction to ISE methodology, along with full experimental details, and a discussion of the various aspects of cell design required for the work.

Chapter 3 contains a review of contemporary theory of the mechanism of operation of neutral carrier electrodes, considering the question of electroneutrality within the membrane, and giving a theoretical background and introduction to the material presented in the following chapters. The membrane is considered from the point of view of the exclusion of anions, a necessary requirement for the membrane potential to be described by the Donnan potential which relates the potential to the external solution compositions.

The main objective of the work was to characterise fully the impedance behaviour of membranes containing neutral carrier for both liquid and polymer matrix membranes, to provide a sound basis for further, less general studies. In addition to the general

investigation, several more detailed questions are addressed, concerning the nature of the charge-carrying species and the mechanism of anion exclusion in both types of membrane. The impedance measurements also permit the role of the various membrane components to be investigated by way of a systematic variation of the membrane composition.

Measurements on model liquid membrane electrodes are reported and discussed in Chapter 4, including details of attempts to improve the response of the nitrobenzene-based liquid membrane by improving its selectivity for cations over anions. On the basis of the results obtained, a simple explanation of the operation of the electrodes is suggested.

In most current neutral carrier electrodes, the ionophore is incorporated into a PVC matrix, and Chapter 5 concerns the nature of the matrix used, considering its electrical and physical properties through impedance measurements on dry membranes, which have had no contact with aqueous solutions, and also by electron microscopy.

In Chapter 6 results of impedance and potential measurements are presented for a variety of PVC membranes. The behaviour of the basic PVC matrix in contact with aqueous solutions of alkali metal salts is investigated, both with and without the presence of valinomycin. The addition to the membrane of salts of large anions has been reported to improve the anion exclusion properties of neutral-carrier electrodes, and various membranes containing potassium and sodium tetraphenylborates, both with and without the presence of valinomycin were included in the study.

Potential measurements are also discussed in Chapter 6 as a measure of cation transport number and a mechanism is suggested on the basis of both these measurements and the ac impedance data

to explain the cation-selectivity of PVC membranes containing valinomycin.

In Chapter 7, a comparison is made between valinomycin and several synthetic ionophores including a novel sulphur-containing, crown-type ligand known as COD-I, and Chapter 8 contains a final summary and discussion.

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Chapter 2

Experimental

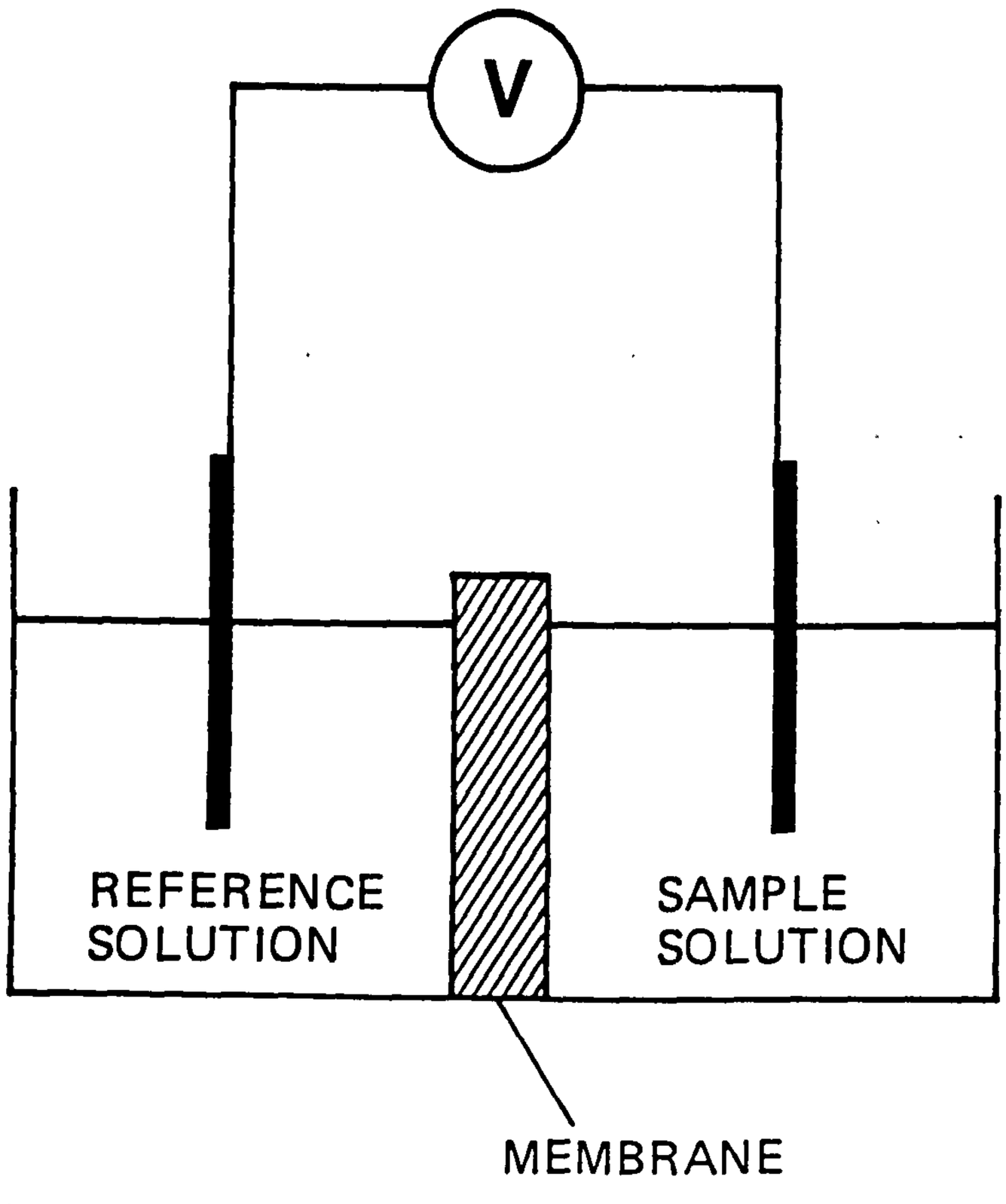
2.1 Introduction

The experimental details described in this chapter concern the methods of fabrication of the ion-selective electrodes used in this work, and the techniques used to make potentiometric and impedance measurements on them. Details of membrane calibration and selectivity determination are given, and a description of the impedance measuring system and software is also included. A discussion of the theoretical aspects of the impedance technique is given in Chapter 1, and the theory of membrane potentials for neutral carrier-based ion selective electrodes is discussed in Chapter 3.

2.2 Considerations In Cell Design

The essence of any functional ion-selective electrode is a sensitive membrane containing the electroactive material separating a sample solution and a reference solution. In the case of potassium selective electrodes, the reference solution is normally 0.1 mol dm^{-3} KCl. A reference electrode in contact with each solution allows the potential difference across the membrane to be determined (Fig 2.1). Normally the reference electrode, reference solution and membrane are contained within the same housing. For the purpose of potentiometric measurements, the actual geometry and proportions of the cell are largely irrelevant as long as the electrode gives a stable response (notwithstanding the requirements of different reference electrode designs). For impedance measurements the requirements are however more rigorous as the geometry of the cell used can have a marked effect on the measured cell impedance. This is

Fig 2.1: Basic schematic diagram of an ion-selective electrode



only to be expected when it is considered that the total impedance is a combination of the different component capacitances and resistances occurring in the cell, all of which have a certain dependence on geometric factors. It is therefore desirable to obtain as simple a cell geometry as possible, cells which are cylindrically symmetrical being the ideal. Details of cells used in this work are given below.

2.3 Ion-Selective Electrode Membranes

A variety of different types of neutral carrier ion-selective electrodes have been reported and used in working environments including liquid membranes, PVC-matrix membranes and coated wire electrodes (2.1-2.5). In the present work, the first two types of electrode were studied.

2.3.1 Liquid Membrane Electrodes

The first neutral carrier based ion-selective electrodes were of the liquid membrane type (2.6), where the active material is dissolved in an organic solvent which is immiscible with water, to give the membrane solution. The membrane may be formed by supporting a portion of the solution in a U-tube, glass capillary or similar apparatus. A more robust membrane can be formed by absorbing the solution into a porous support medium - a technique which has successfully been employed in the Orion series 92 'dip-type' electrode. The cellulose acetate filters manufactured by the Millipore Corporation (Bedford, Mass., USA) are available with a variety of pore sizes and make ideal membrane support media which can be cut to size with a sharpened cork borer

(internal diameter 3mm). Handyside (2.7) found the Millipore EGWP filter (pore size 0.2 μm) to be a suitable support and this type of filter was used for all liquid membranes used in the present work.

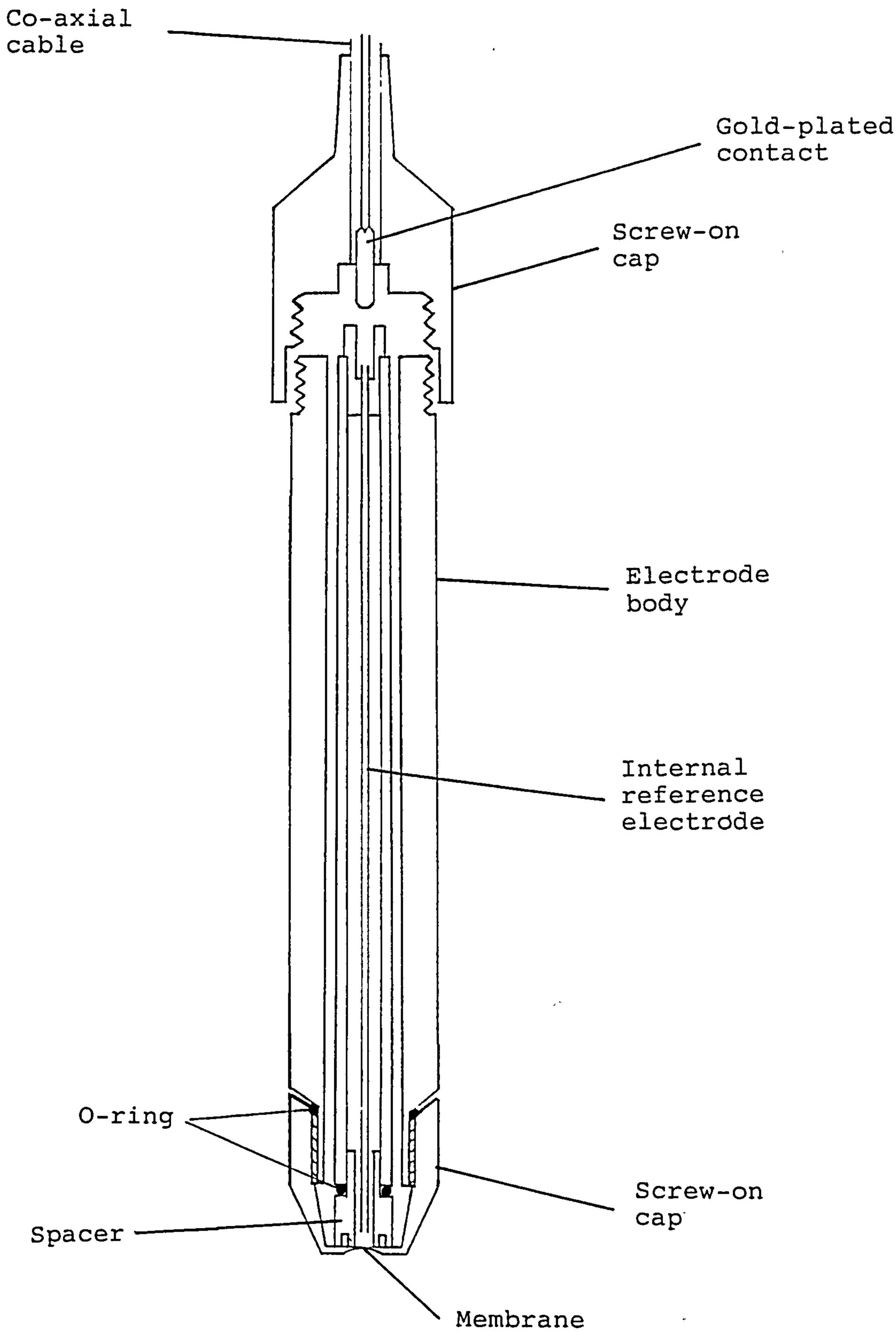
The liquid membrane has been superceded to a large extent in neutral carrier based electrodes by the PVC membrane first reported by Shatkay (2.8), and perfected by Thomas (2.9), but the former still offer advantages over the latter in certain situations for research purposes. The main advantage of the liquid membrane system is its simplicity in terms of chemical composition. The purity of the solvent can easily be established by standard analytical techniques, and assuming a pure sample of the active material is used, the membrane composition is well defined. Thus the liquid membrane provides a 'clean' system for theoretical consideration.

2.3.2 Liquid Membrane Preparation and Cell Design

The liquid membranes used in this work consisted of either Valinomycin dissolved in 2,3-dimethylnitrobenzene (2,3-DMNB) at various concentrations, or of pure 2,3-DMNB. Solutions were shaken on an orbital shaker for a minimum of 24 hours to ensure complete dissolution of the valinomycin.

The 'classical' cell used for work on liquid membrane electrodes is the Orion Series 92 electrode body shown schematically in Fig 2.2. This electrode largely fulfils the geometrical requirements of cell design for impedance work outlined above, being approximately symmetrical about the membrane. It was felt that any minor improvements in geometry which could be achieved by designing a new cell would not offset

Fig 2.2: The Orion 'Series 92' dip-type electrode



the difficulties in creating a design which would still provide a reservoir of the membrane solution constantly in contact with the membrane. A slight modification was made to the Orion body to achieve a greater membrane surface area, by making a new screw-cap with a larger opening and a new spacer.

The electrode body is machined from a robust and chemically resistant fluorocarbon, with a screw on cap and spacer of the same material. The original 'O' rings supplied were made of silicone rubber, but it was found that these perished after prolonged contact with the 2,3-dimethylnitrobenzene solvent, and so they were replaced by Viton 'O' rings (George Angus Ltd, Wallsend, UK) which are specifically designed for use with such solvents.

The internal reference electrode consists of a chloridised hollow silver tube, forming a silver/silver chloride electrode, mounted on a fluorocarbon plug. This then locates in the central bore of the electrode body forming an air-tight seal at the top. Electrical contact with the internal reference electrode is achieved by a gold-plated pin housed in the screw-on top which connects to a screened coaxial cable. The main electrode body houses the membrane support which is held in place by a spacer and the lower screw-on cap. The membrane support is supplied from a reservoir which continuously replaces any solution lost from the membrane during its lifetime.

The electrode is assembled as follows. First the 'O' rings are located on the spacer and the main body. The body is then inverted and the spacer is fitted over the end of the internal reference electrode. The membrane support must then be carefully located in the centre of the spacer using plastic tweezers. Due to the build up of static electricity, the cellulose acetate

filter tends not to stay in position on the spacer during electrode assembly but this can be cured by dropping a small amount of the membrane solution on to the filter once it is in position, and then carefully tightening the screw cap down over it. Incorrect positioning of the filter, or over-tightening of the cap, causes cracks in the support resulting in leakage of the internal reference or membrane solutions producing an unstable electrode response and so this must be avoided.

Once the membrane support is firmly in place, the reservoir can be filled with the membrane solution using a syringe inserted into one of the side holes in the electrode body. The amount of solution used has no effect on the operation of the membrane, it merely determines the lifetime of the electrode. A working electrode can be produced with a single drop of membrane solution. The electrode is then left for a minimum of half an hour for the solution to permeate fully the filter support, after which it can be checked for leaks by gently pressing a piece of lens tissue over the end of the electrode body. If there is no trace of any membrane solution on the tissue then it is unlikely that excessive leakage is occuring, which would cause an unstable potential response. The internal reference solution can then be added by injecting it down the centre of the reference electrode. The presence of air bubbles in the internal reference system is avoided by repeatedly flushing the cavity with the reference solution (a bleed hole is drilled into the side of the electrode body for this purpose).

Once assembled, the electrode can be stored dry or in a standard low-concentration solution of the primary ion. In normal operation, the electrode would be conditioned in a solution of the primary ion for several minutes after assembly,

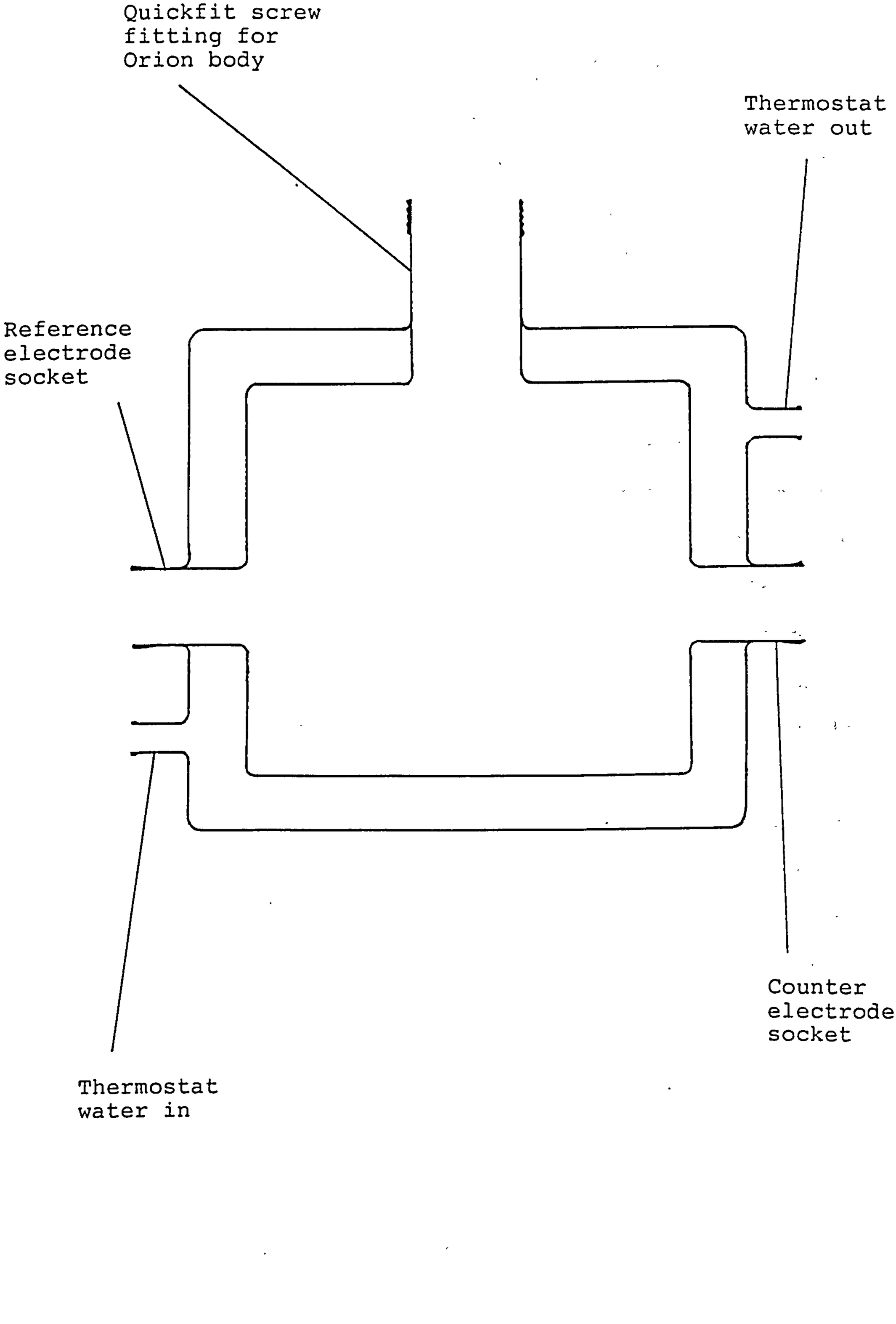
prior to use, but, for impedance measurements where the time dependent nature of the frequency response was being investigated, the electrode was loaded directly into the measuring system. The calibration and selectivity data were then collected after all impedance measurements were completed. Sample electrodes from each batch of membrane solution were fabricated and tested prior to carrying out any impedance work to ensure that the solutions would produce good, working, ion-selective electrodes.

All parts of the electrode body were cleaned prior to the fabrication of each new electrode by immersion in acetone for twenty-four hours.

The electrode as described above is normally used as a dip type electrode which is simply immersed in the sample solution with a separate reference electrode, and this configuration was used for two-electrode impedance measurements on the liquid membranes. The electrode body was housed in a glass cell (Fig 2.3), fitted with a water jacket through which water was circulated by a peristaltic pump from a thermostatically controlled water bath. The glass cell has a Quickfit B24 glass screw connector with a rubber seal through which the electrode body was mounted into the cell, giving a good airtight seal. The counter electrode consists of a circular silver /silver chloride electrode mounted in a B24 glass stopper which is inserted into the side of the cell by a ground glass socket. The electrode was constructed so that the circular part was concentric with the central axis of the Orion electrode body.

Calibration and selectivity measurements were carried out by suspending the Orion body in a beaker containing the sample solution, with a standard saturated calomel reference electrode

Fig 2.3: Glass cell for measurements using the Orion 'Series 92' electrode body



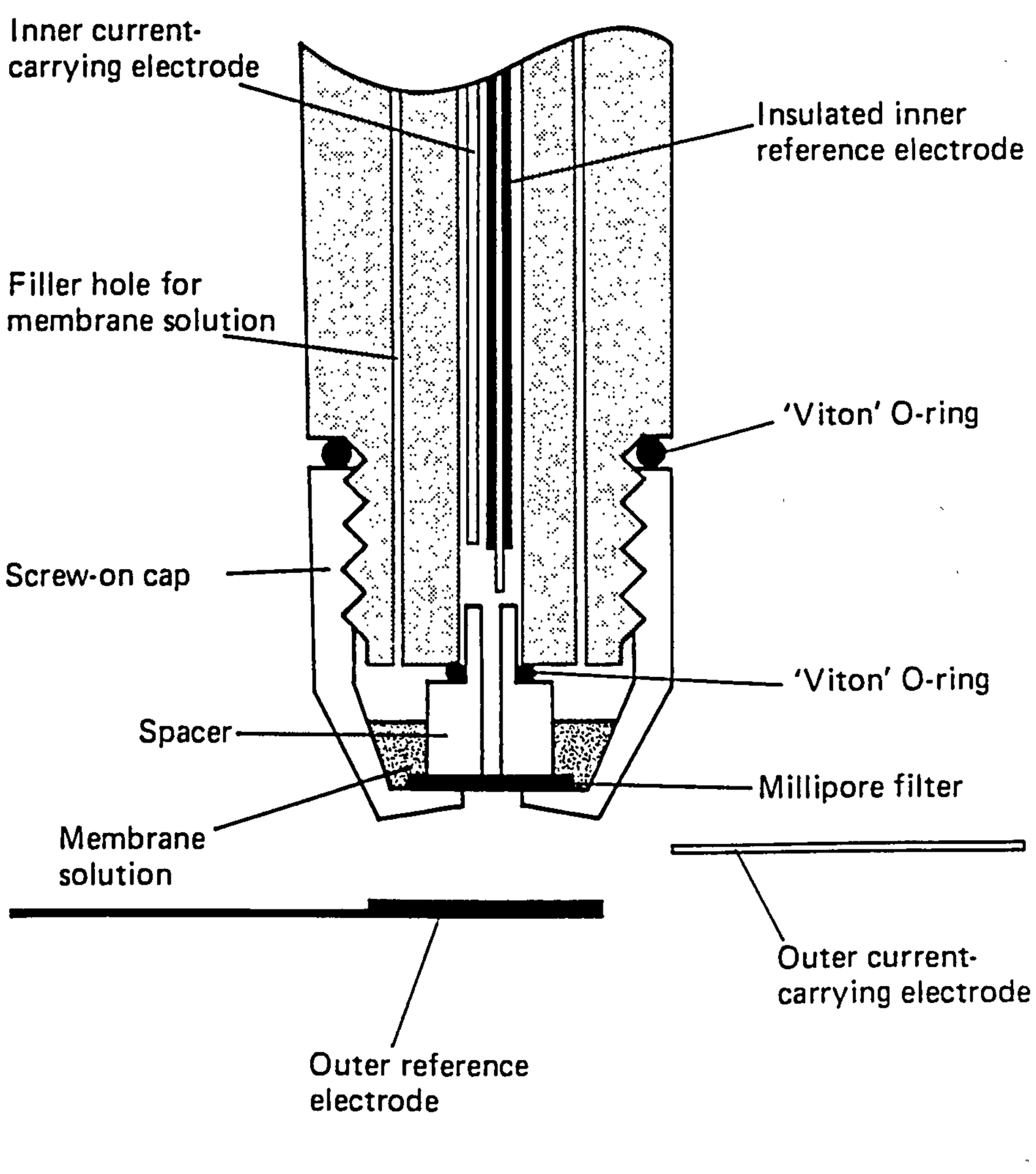
fitted with a salt bridge of 3.5 mol dm^{-3} tetramethylammonium chloride. The solutions were magnetically stirred (500 rpm) with the stirrer electrically and thermally isolated from the sample beaker. Care was taken that the magnetic follower did not come into contact with either the ISE or the reference electrode.

In order to make impedance measurements in a four electrode configuration, two more electrodes were necessary, giving two internal and two external electrodes (Fig 2.4). This was achieved by fitting a PVC sheath around a second Orion silver/silver chloride tube electrode which could then be inserted down the central bore of the electrode body, next to the original internal electrode. Contact between these two internal electrodes was prevented by inserting the unsheathed tube only to a depth where its' tip was above the level of the sheathing on the other electrode. The sheathed tube was used as the reference electrode and the unsheathed one as the current-carrying electrode. The two tubes were supported and held apart by clamp stands at the top of the body. Evaporation of the internal reference solution was prevented by fitting the two tubes through a rubber cap which fitted over the end of the Orion body. Electrical connections were then made directly on to the tubes by clean crocodile clips. The second external electrode was obtained by inserting another silver/silver chloride electrode through a second socket in the glass cell; this became the current-carrying electrode, with the original external electrode as the reference.

2.3.3 PVC-Matrix Membrane Electrodes

The liquid membrane has largely been superceded in the

Fig 2.4: Modified 'Series 92' electrode body, allowing four-electrode measurements



fabrication of neutral carrier ion-selective electrodes by the PVC-matrix membrane, in which the active material is suspended in a chemically inert support matrix. The PVC membrane affords much greater mechanical strength and ease of electrode assembly than does the liquid membrane, and PVC membranes can easily be incorporated on to ion-selective field effect transistors (ISFETs). Unfortunately, the chemical composition of the PVC membrane is much less well defined than that of the liquid membrane, due largely to the presence of various additives incorporated in the PVC during manufacture (see Chapter 5). Nonetheless, these electrodes perform extremely well as ISEs.

2.3.4 Cell Design

In potentiometric studies, the PVC membrane is usually mounted on a B7 glass socket into which a silver/silver chloride electrode can be fitted to give a complete ion-selective electrode assembly (Fig 2.5) which can be used in a similar way to the Orion series 92 electrode. It was felt that in the case of the PVC membrane electrodes, where no reservoir of membrane solution is required, an improved cell geometry could be achieved, particularly with a view to four-electrode measurements. A new cell was designed which fulfilled these requirements, and which would allow both two- and four-electrode measurements on the PVC membranes (Fig 2.6). The cell body is machined out of a rod of polytetrafluoroethylene (PTFE) as are the electrode plugs. The two halves of the cell are clamped together by way of a spring loaded 'top hat' arrangement which maintains constant and even pressure on the membrane and gives a water-tight seal. The electrode plugs consist of solid silver

Fig 2.5: B7 Glass electrode assembly for PVC membranes

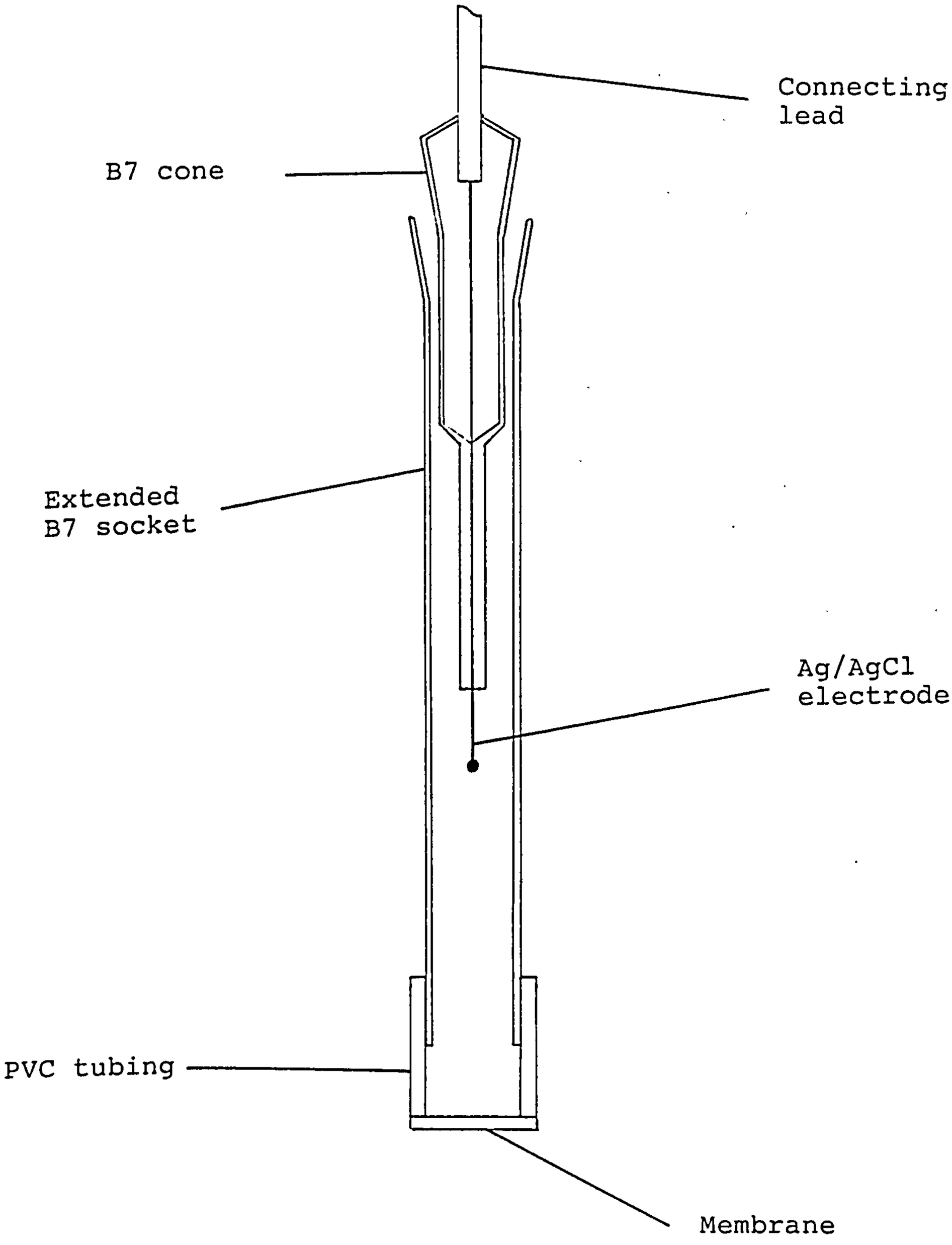
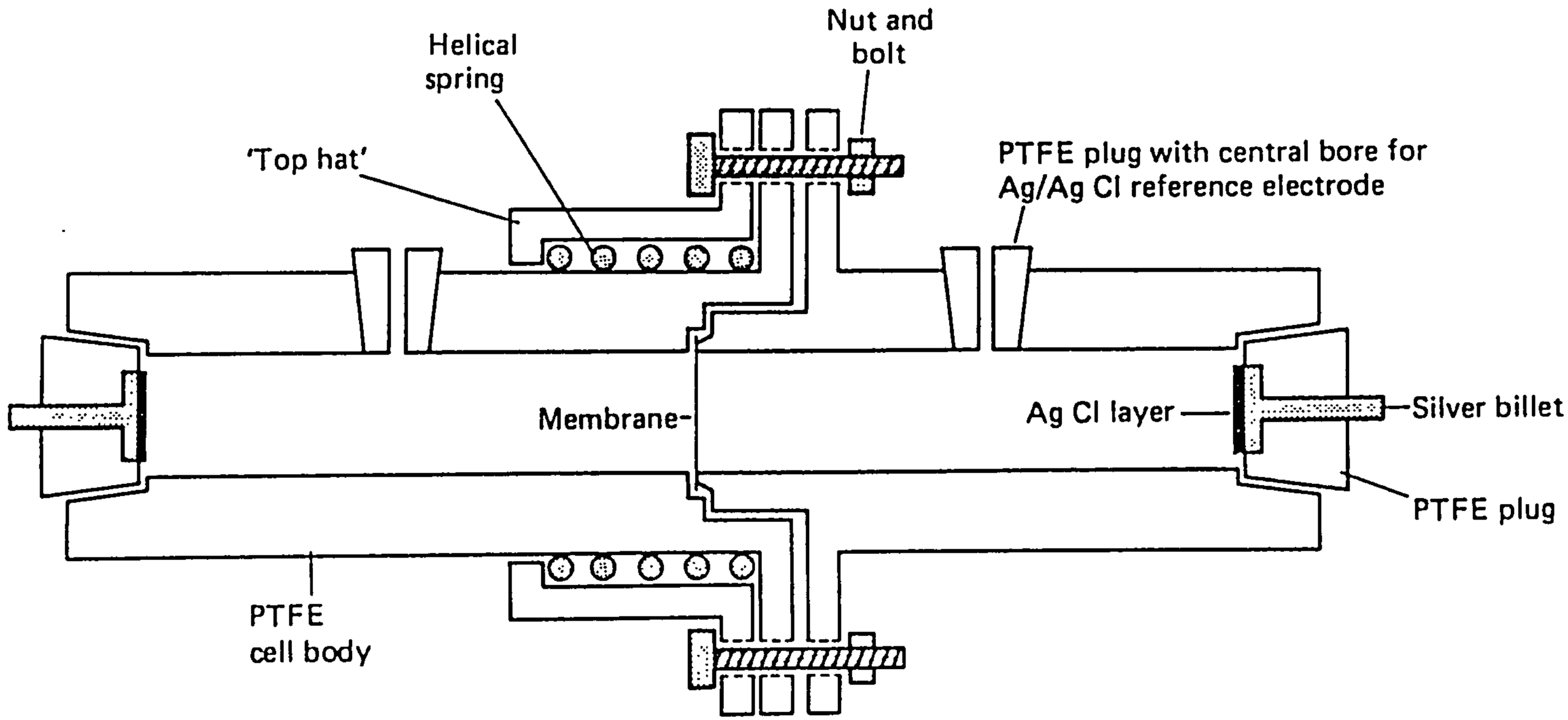


Fig 2.6: PTFE cell for impedance studies on PVC membranes



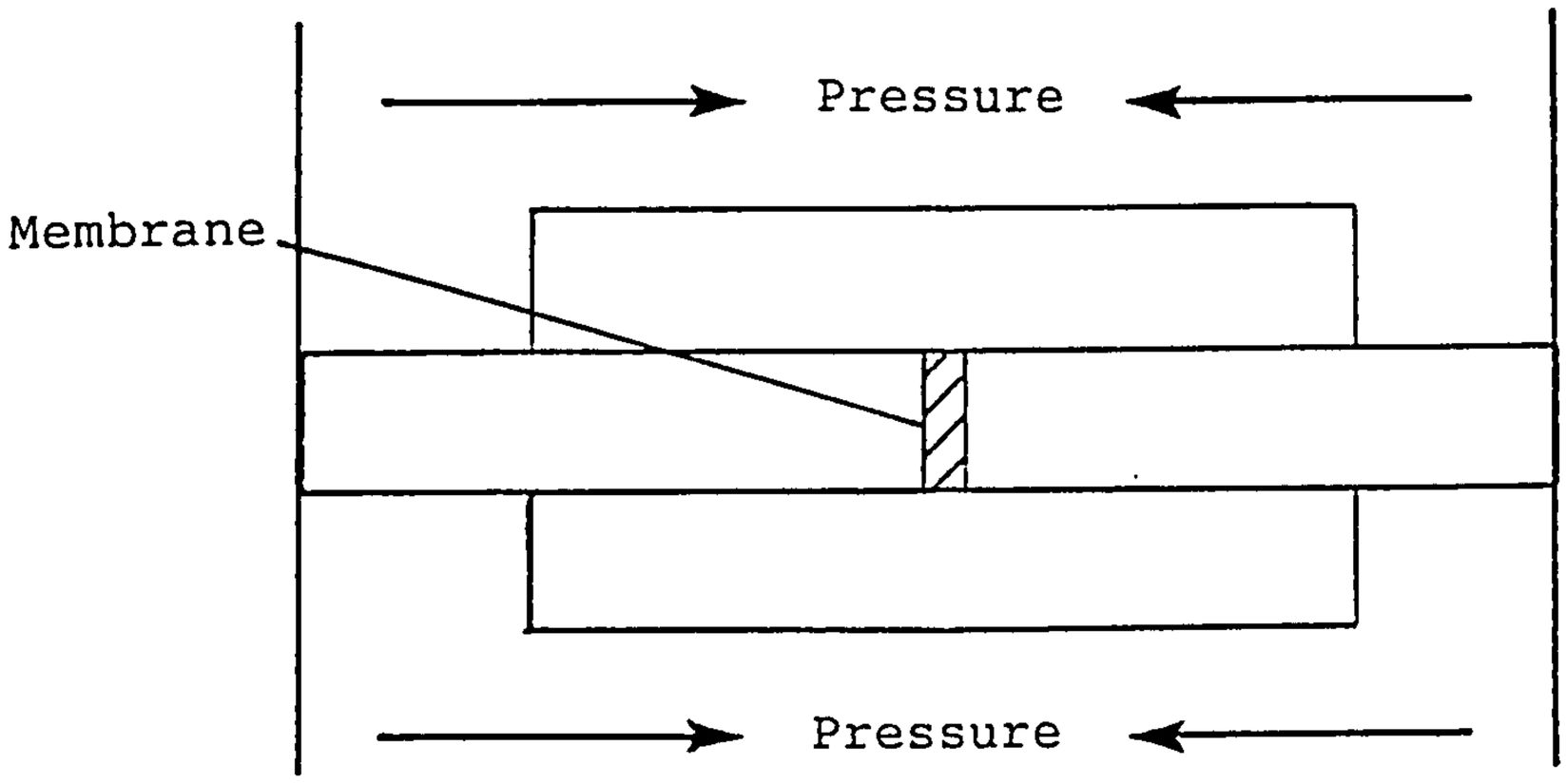
ingots, chloridised on their exposed faces, set into PTFE plugs which locate into holes in the cell body.

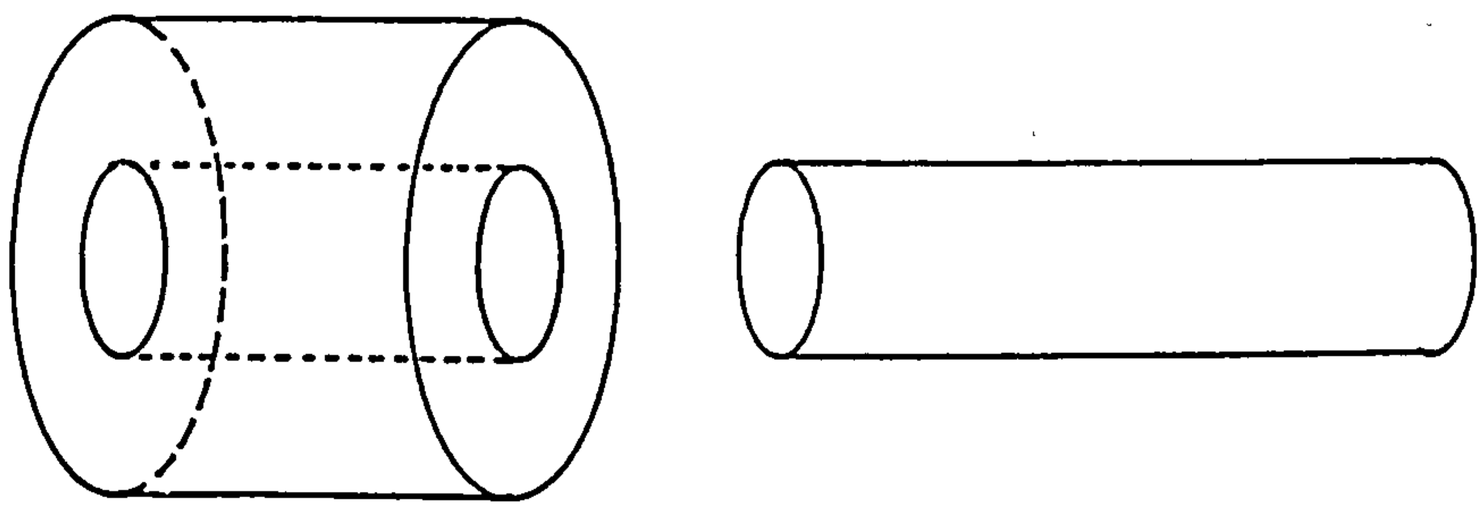
It was also necessary to carry out impedance measurements on certain membranes before contact with aqueous solutions. To allow such measurements to be made, direct contact was made on both sides of the membrane with solid stainless steel electrodes. The membrane was compressed between the two cylindrical steel electrodes which were housed in a non-conducting polycarbonate cylinder. In this way, good contact between the membrane and the electrodes could be ensured by applying pressure to the assembly by a hydraulic press. A statimeter gauge was also included to measure the pressure applied to the membrane, and the whole assembly was situated in a glove box with a dry atmosphere (<2ppm water). The apparatus is shown schematically in Fig 2.7a.

2.3.5 PVC Membrane Preparation

The PVC membranes for this work were of the form first investigated by Thomas et al. (2.9,2.10). The membranes comprise PVC (supplied as a powder), a plasticiser, and the electroactive material in the ratio 33:66:1 (approx.). Some membranes also incorporated potassium, sodium or caesium salts of the tetraphenylborate anion (TPB^-) in very low concentrations as used by Band (2.11). A variety of plasticisers have been used in PVC membrane ion-selective electrodes, although no conclusive evidence has been produced to suggest that any particular one is preferable to any other (2.12-2.14). Recently Arami (2.12) has found evidence to suggest that different plasticisers behave differently on contact with water but this does not appear to affect the operation of the electrode membrane. The majority of

Fig 2.7a: Cell for dry membrane impedance work

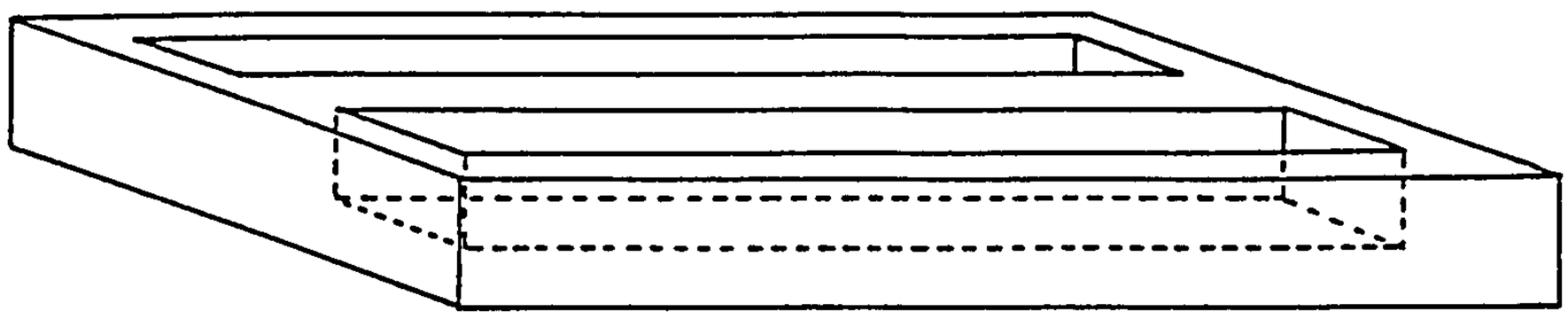




Insulating support (polycarbonate)

Stainless steel electrode

Fig 2.7b: Diagram of PTFE mould for casting PVC membranes



plasticisers used for ion-selective PVC membranes are either esters or diesters of dibasic acids in the homologous series from ethanedioic to decanedioic acid, or esters of phthalic acid. Handyside (2.7) found bis-(2-ethylhexyl) sebacate to be a satisfactory choice and this was used throughout the present work.

The membrane components were dissolved in tetrahydrofuran (THF) and complete dissolution was ensured by shaking for a minimum of 24 hours on an orbital shaker after which the solution was transferred to a PTFE mould (Fig 2.7b) placed on a flat surface in a dust free location. The mould was then covered with a weighted pad of filter papers to allow slow evaporation of the solvent over several days. Once the solvent had completely evaporated, the membrane was carefully removed from the mould with a pair of plastic forceps. The films produced had a uniform thickness of approximately 0.1 mm. Circular cuttings with a diameter of 1.5 cm were taken from the master membrane using a specially constructed stainless steel cutter similar to a cork borer. These could then be loaded into the cell by carefully positioning the film over the central bore on one half of the cell using plastic forceps, followed by clamping the two halves of the cell together. The cell was then ready for filling with the relevant aqueous solutions.

Moulds were cleaned between castings by washing with THF followed by immersion for twenty-four hours in acetone.

2.4 General Details

All glassware used in this work was cleaned by immersion in chromic acid for a mimimum of one hour followed by repeated

rinsing with copious quantities of triply distilled water and drying in a clean oven.

All electrical connections were regularly checked for good contact and plugs and sockets were cleaned with emery cloth. All leads were checked for low resistance and continuity of screening.

All impedance measurements were carried out at thermostatted temperatures. For the liquid membranes, temperature control was by means of a water jacket incorporated into the glass cell (see above) giving an accuracy of $\pm$0.5 degrees centigrade. The PTFE cell used for the PVC membranes has no such means of control and so the whole cell was housed in a polystyrene box, which was then partially immersed in a thermostatted water bath. Cell temperature was then monitored by using a thermocouple taped to the cell body. It was found that this arrangement allowed control of the cell temperature to an accuracy of $\pm$0.5 degrees centigrade.

2.4.1 Chemicals

Valinomycin was obtained from the Sigma Chemical Company (Poole, Dorset, UK) and was used as supplied. Crown compounds and the 2,2,2 cryptand were supplied by Dr J.C.Lockhart (Inorganic Chemistry Dept., Newcastle University).

All solutions were made up using AnalaR grade chemicals with maximum impurity levels of alkali metals of 0.005%. Solutions were made up using volumetric glassware.

2,3-dimethyl nitrobenezene obtained from Koch-Light Ltd (Haverhill, Suffolk, UK). The purity of the 2,3-DMNB was verified by nmr and IR spectroscopy.

The THF used in this work was UV spectroscopy grade, with no added stabilisers (Fluka (Fluorochem), Glossop, Derbyshire, UK).

PVC was supplied by BDH (Poole, Dorset, UK) with a molecular weight of 100000. No purification of the PVC was attempted. The bis-(2-ethylhexyl) sebacate (dioctyl sebacate) plasticiser was obtained from Sigma. Ultraviolet and infra-red spectroscopy, and gas-liquid chromatography (glc) showed the sample obtained to be pure.

Sodium tetraphenylborate was obtained from BDH. Potassium and caesium tetraphenylborates were obtained by precipitation from a saturated aqueous solution of sodium tetraphenylborate by addition of a solution of the corresponding chloride at a concentration of 0.1 mol dm^{-3}. The samples thus obtained were washed ten times in either potassium or caesium chloride solutions (0.1 mol dm^{-3}) followed by washing in triply distilled water. The samples were then dried in a desiccator.

2.4.2 Reference and Counter Electrodes

Silver/silver chloride electrodes (other than those supplied for use with the Orion series 92 electrode body) were chloridised by anodising in a 0.1 mol dm^{-3} KCl solution at a current of 0.1 mA cm^2 for two hours using a platinum counter electrode.

2.5 Instrumentation

Any current drawn from the ion-selective electrode produces a non-equilibrium condition invalidating the Nernst relationship (section 2.7). Drawing current from the electrode assembly also polarises the silver/silver chloride electrodes and the membrane,

making measurements meaningless. It is therefore essential to operate the electrodes under conditions of zero current drain. This means that a potential measuring device with a very high input impedance is required to measure correctly the potential response of the ISE. To this end a high input impedance buffer amplifier was constructed, enabling measurement of the cell potential with a standard laboratory digital voltmeter (DVM) (Farnell Electronics, Wetherby, Yorks., UK). The circuit of the buffer amplifier is shown in Fig 2.8. It consists of an operational amplifier utilising a field effect transistor (RS Electronics, London, UK), connected in a non-inverting configuration as a unity gain voltage follower. In this configuration the amplifier produces an output voltage equal to the input voltage. Due to the high input impedance of approximately 10^{12} Ohm, practically no current is drawn on the input circuit, whilst the output current is of the order of several milliamps - sufficient to drive a DVM. The performance of the amplifier was regularly checked using a standard voltage source (Time Electronics, Tonbridge, Kent, UK).

2.6 The ac Impedance Measuring System

The heart of the ac impedance system is the Solartron 1174 frequency response analyser (FRA) (Solartron Electronics Group, Farnborough, UK) which actually measures the impedance of the cell under test. Data collection from the FRA, and subsequent processing, can be achieved in a number of ways, with or without the aid of a computer, although the use of a computer affords much greater flexibility, speed of data acquisition, and accuracy in timing, and allows the monitoring of the impedance of a system

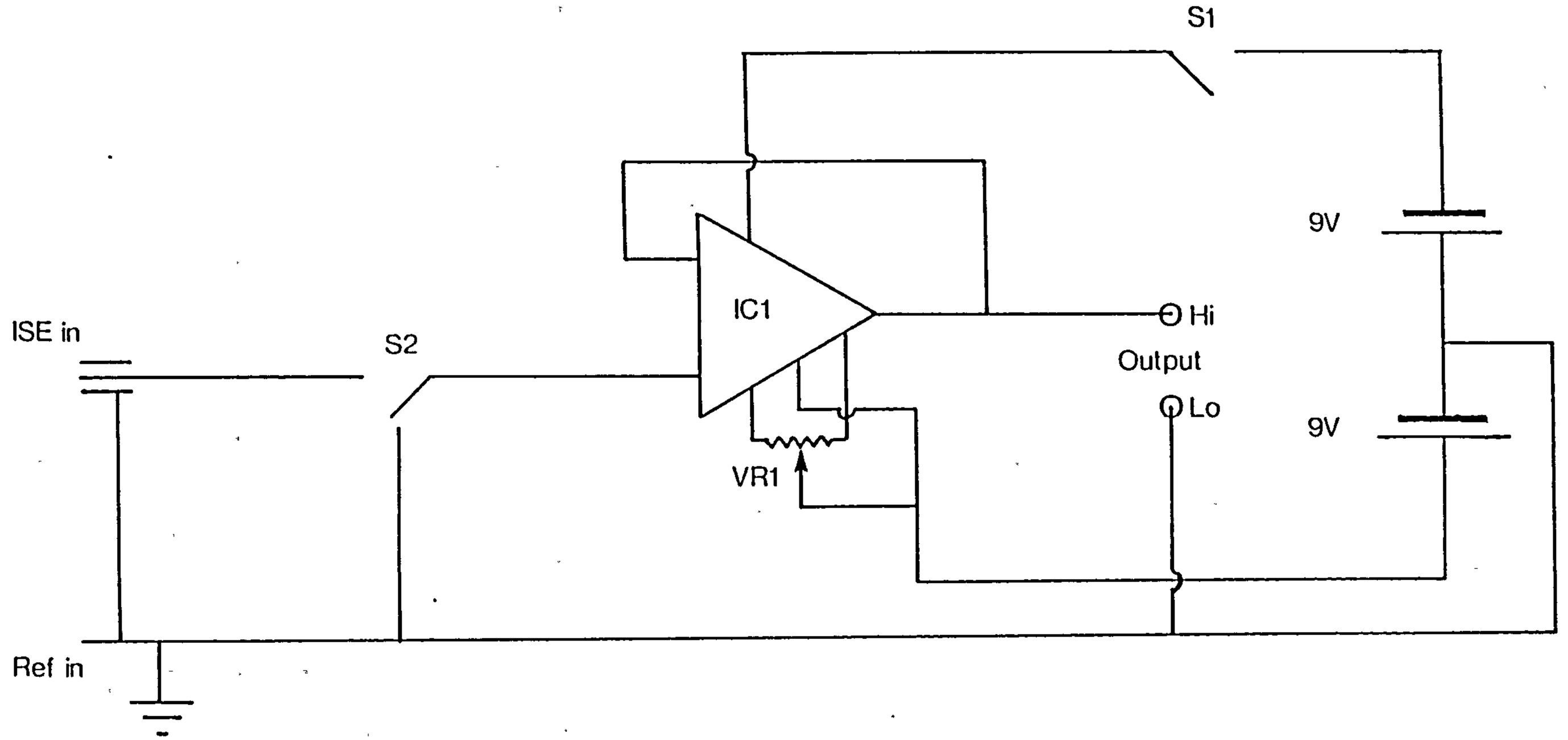


Fig 2.8: Circuit diagram for a buffer amplifier for measuring potential differences accross ion-selective electrode assemblies

continuously over a period of days.

The system originally employed in these laboratories for ac impedance measurements comprised the FRA driving a paper tape punch via a Solartron data transfer unit (DTU), and a Bryans A3 xy plotter (giving real-time plotting of the data) via a Solartron digital to analogue converter. All impedance runs were carried out by manual operation of the FRA with each data point being dumped on to punched tape as it was collected. Data processing was possible by feeding the punched tape through a tape reader connected to a North-Star Horizon computer. The computer allowed high quality plots of data to be drawn on a Hewlett-Packard graphics plotter, and numeric data listings could be obtained via an Anadex dot-matrix printer. The system allowed basic impedance plots to be obtained, but was time consuming to operate and did not allow continuous monitoring of the impedance for time-dependent effects.

The system based on the North-Star Horizon computer was replaced after the first year of this project by a much more flexible integrated impedance system using software specially written for the system (which is described below and in appendix A). This new impedance measuring system is still based around the Solartron 1174 FRA, but is now fully under the control of an Apple II microcomputer. A Solartron 1186 electrochemical interface (ECI) is also connected to the FRA allowing measurements to be made under potentiostatic or galvanostatic conditions. In addition to controlling the FRA the computer also drives the graphics plotter and an Epson dot-matrix printer. A detailed description of the system software is given in Appendix A.

2.6.1 The Frequency Response Analyser

The FRA combines a programmable signal generator and a phase sensitive detector, allowing the impedance of a system to be measured over a range of frequencies both quickly and accurately. The impedance data can be output from the FRA either in the form of polar co-ordinates, or x,y data pairs, representing points in the complex plane (see Chapter 1). It is customary in impedance work on electrochemical systems to represent data as complex plane plots using real and imaginary axes, and this convention was followed throughout the present work.

The Solartron FRA has an operating frequency range of 9.999×10^{5} Hz down to 10^{-4} Hz with a maximum of 99 measurements per decade change in frequency. These specifications give a sufficiently wide frequency range for most practical electrochemical systems to be studied. In the present work, all membranes investigated were found to have impedance spectra which could be fully determined within this range.

The impedance which the FRA actually measures is the total impedance between the X and Y input sockets on the front panel, ie. all connections and leads used to connect the cell under test to the FRA will make a contribution to the measured impedance and it is therefore of the utmost importance to minimise all such unwanted contributions. This is best done by keeping all leads to the absolute minimum length required, ensuring that leads do not twist together or form loops, and using clean connections with large contact area. In addition to these precautions, screened oscilloscope probes were used to connect the FRA to the comparison resistor box. The probes were

trimmed to balance their capacitive components and were replaced if good characteristics could not be obtained.

The FRA has been fitted with a Solartron 1183-C IEEE-488 interface so that full two-way communication with the Apple computer can be carried out, enabling complete program control of all aspects of its operation.

2.6.2 The Electrochemical Interface

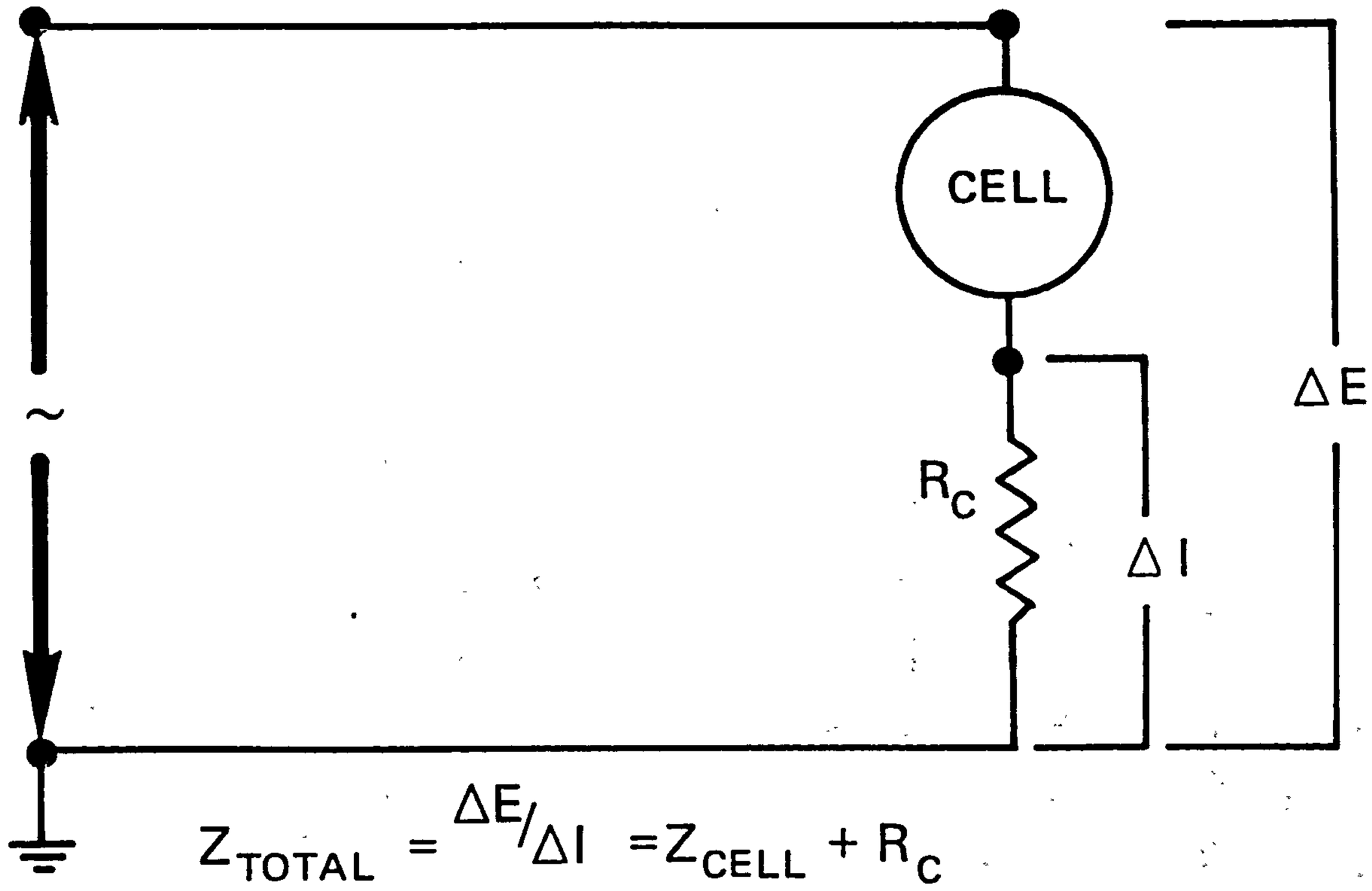
The Solartron 1186 Electrochemical Interface (ECI) is essentialy a potentiostat which can be coupled directly to the FRA, allowing impedance measurements to be made using three or four-electrode cells, rather than the more usual two-electrode cell. The ECI can also be operated in a galvanostatic mode, but this facility was not utilised in the work reported here.

Prior to the present study, basic impedance measurements had been made on some neutral carrier ion-selective electrodes, but only in a two-electrode configuration (Fig 2.9 and also see Chapter 1). The problem in such a situation is that the impedance measured includes the impedances of the two reference electrodes, the bathing solutions, and the leads from the cell to the current measuring resistor box. Connecting the FRA via the ECI with two reference electrodes and two current-carrying electrodes allows the impedance of the membrane alone to be determined.

2.6.3 The North-Star Horizon Microcomputer

The Horizon microcomputer (North-Star, UK) is based on an IEEE S100 bus system. The S100 is a one hundred wire bus, each

Fig 2.9: Diagram showing the connection of the FRA to the cell, and the calculation of the cell impedance



wire having a specific function (data lines, control lines, power supply etc.). This system allows a variety of circuit boards to be connected on to the bus, depending on users needs, giving great flexibility. The Horizon computer uses a 4MHz Zilog Z80 microprocessor as its CPU, which is housed on a circuit board along with various peripheral chips. In addition to the processor board, there are several other boards connected on the bus as detailed below :-

i. Two RAM boards giving a total of 48K of memory.

ii. Two boards giving a total of four serial I/O ports.

iii. A disk drive controller board controlling two Shuggart single-sided, double-density, 180K disk drives.

iv. An IEEE-488 interface board.

v. A board giving two parallel I/O ports

vi. A power supply board

The computer does not have a built-in keyboard or display screen and therefore must be used in conjunction with a visual display unit (vdu) which contains the keyboard, screen and all the necessary hardware and software to decode and encode the keyboard signals and operate the screen. The vdu used was an ADDS Consul 980, giving a twenty-four line display with eighty characters per line and rudimentary graphics facilities.

2.6.4 The Apple II Microcomputer

The computer used to control the upgraded impedance measurement system is an Apple II Europlus (the standard model sold in Europe prior to the launch of the Apple IIe in 1983). This computer is based around a 6502 microprocessor and is supplied with a total of 64 kilobytes (64k) of memory. Of this

memory, 16k is allocated to ROM and the remaining 48k to RAM. The ROM chips include the BASIC language interpreter and the system monitor.

Of the 48k of RAM available to the user, several areas are, out of necessity, allocated to various facilities as shown in the memory map (Fig 2.10). The main blocks which are thus lost to the user are as follows :-

$0000-$0800 System pointers, processor registers & stack, keyboard buffer and general system workspace.

$4000-$6000 Memory-mapped high resolution graphics.

$9600-$C000 Disk operating system.

The result of this memory allocation is that if high resolution graphics are required, the user is limited to approximately 14k of high level language program space, situated between $0800 and the bottom of HGR2 (the high resolution graphics page) at $4000. As a result of this limited amount of program space, and also from considerations of program speed, it was convenient to write certain parts of the software in machine code, which can be stored above the memory space allocated to variable storage. For some routines, it was a matter of necessity to use machine code in order to access parts of the machine operating system effectively. A full description of the programs comprising the IDCS is given in Appendix A.

The computer has twin 140k, single-sided, single-density, $5^{1/4"}$ disk drives, and is used with a monochrome monitor screen, giving a 24 line display with 40 characters per line.

2.6.5 The IEEE-488 Interface

Both the Apple and the Horizon computers were fitted with an

Fig 2.10: Apple II Memory Map

		Hex	Decimal
	Monitor ROM 2k (&800)	FFFF	65,335
		F7FF	63,487
	AppleSoft Basic Rom 10k (&27FF)		
ROM		D000	53,248
	I/O Space & memory for accessory cards i.e. IEEE-488 & Printer Interfaces		
		C000	49,152
	Disk Operating System (DOS) 10.5k (&2A00)		
		9600	38,400
	String Storage (Builds Down)		
		HIMEM	
	Array Variables & String Pointers (Build Up)		
	Simple Variables & String Pointers (Build Up)		
		6000	24,576
		(LOMEM)	
	High-resolutions graphics Page 2 Graphics only; 280x192 pixels 8k (&2000)		
		4000	16,384
	High-resolutions graphics Page 1 280x192 pixels & 4 lines of text free for program storage if HGR2 used 8k (&2000)		
		2000	8192
	Program storage space (excluding Hi-res graphics page 1) 6K (&1400)		
		0C00/	3,072/
		0800	2048

System Stack, Data, Pointers etc.
Keyboard Buffer, Monitor Vectors
Text pages 1 & 2, Free space
(127 Bytes) For user Machine code)

IEEE-488 interface board. On the Horizon, this interface was used solely to drive the graphics plotter, this being the only method available to obtain hard copy plots of impedance data. With the Apple computer, an IEEE-488 interface (California Computer Systems, Sunnyvale, Calif., USA) is used to drive the graphics plotter and, with the addition of the 1183-C interface to the FRA, to control the FRA as described above. A duplicate system has also been set up using similar hardware, but with an Apple IEEE-488 interface (Apple part £031-0197-B) driving a Solartron 1172 FRA.

2.6.6 The Epson Dot-Matrix Printer

Hard copy printed output can be obtained from the Apple using an Epson MX82III F/T dot-matrix printer. The printer has a serial impact, nine wire, bi-directional print head with a continuous print speed of 80 cps (characters per second). Characters are made from a 9x9 matrix, and a full 96-character ASCII character set, with descenders, is available in eight international formats. Bit-image reproduction of memory-mapped graphics is available with true 1:1 scaling from screen to printer, with a typical time of 1.5 minutes for dumping of an impedance plot on to paper from the Apple computer. The use of this facility allows easy and rapid access to hard copy of impedance plots without the need to use the graphics plotter.

2.6.7 The Graphics Plotter

High quality graphical output is available via a Hewlett-Packard HP 7225A digital graphics plotter. The 7225A

has a plotting area of 210 x 297mm with a resolution of 11400 x 8900 plotter units, giving addressable pen movements of as little as 0.032 mm. A full ASCII character set is resident in ROM for use in labelling etc., and full control over character size, scaling and orientation is available. A total of thirty-eight different plotter control instructions are available, including user-defined character facilities. Plotting speeds of up to three characters per second can be achieved, giving a typical plotting time for an impedance plot of approximately one minute. The plotter is connected to the computer via the IEE-488 interface, where it functions both as a listener, receiving plotting instructions, and a talker, sending error codes and allowing digitisation of graphics material from the plotter platen.

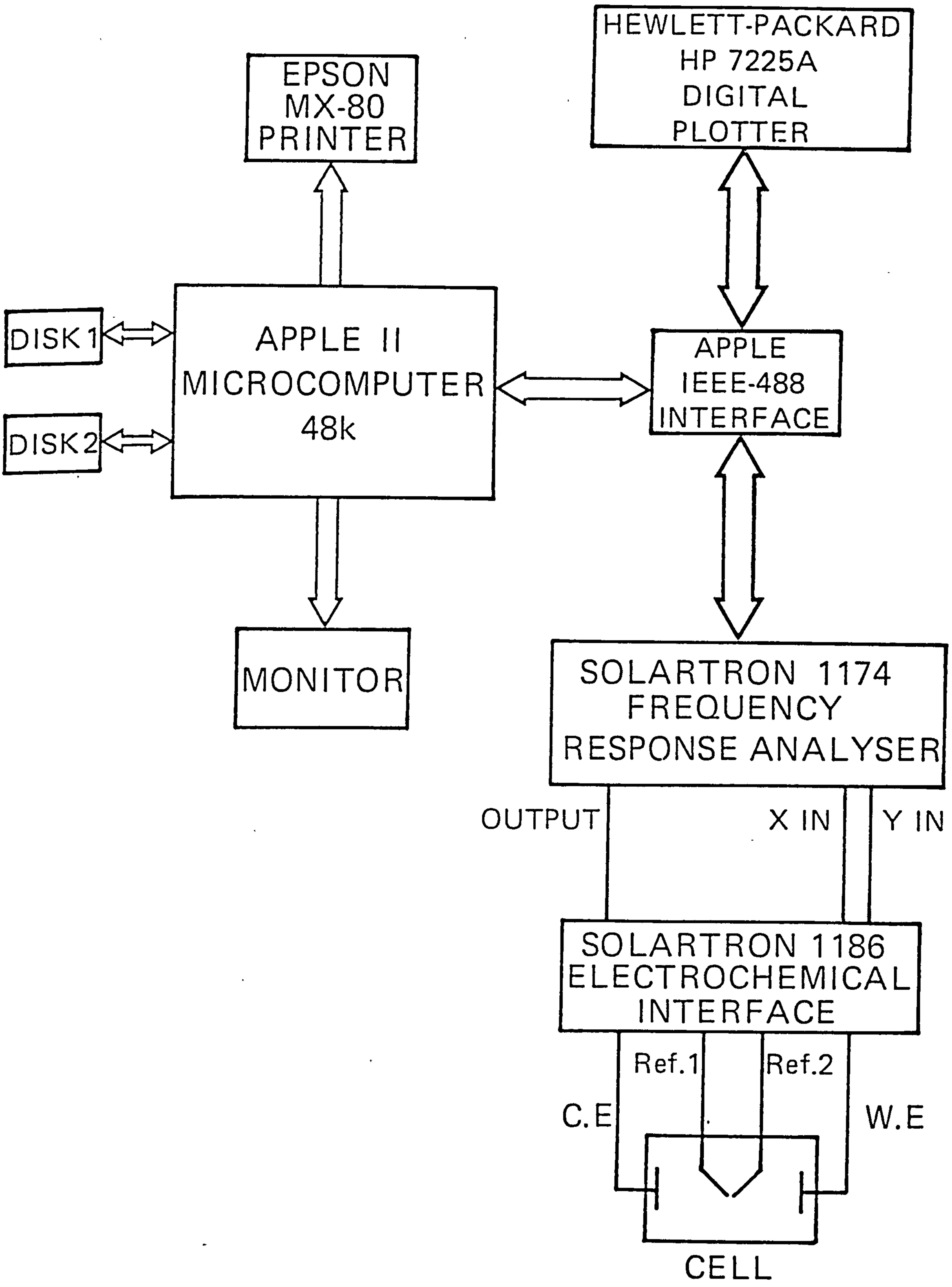
2.6.8 System Software - The Impedance Data Control System (C)

A block diagram of the impedance measuring system is shown in figure 2.11. The diagram shows the main data transfer routes and connections between the various devices comprising the impedance measurement system.

2.6.8.1 Program Requirements

There were several requirements that had to be considered when writing the software for control of the impedance measuring system. The main objective was to develop a system which would be as flexible as possible so that future projects and users could be accommodated without needing to rewrite the whole package. Also, as the system consists of several pieces of

Fig 2.11: Block diagram of the impedance measurement system



hardware by different manufacturers, it was likely that replacement of individual pieces of equipment would occur in the future. To minimise the effects of such changes, and to allow future users the facility to expand the system if required, it was decided to develop a package of program modules, each one controlling a different aspect of the system and being as self-contained as possible. The intention was that, if a single piece of the hardware were replaced, the relevant program module for controlling that part of the system could be re-written, or modified, and the rest of the software could continue to be used, unaltered.

Another requirement was that inexperienced users could operate the system with a minimum of assistance. To accomodate this, all the system programs were written on a menu-driven basis so that the operator is always confronted with options for action, and the system automatically loads and runs on powering-up the computer.

2.6.8.2 General Program Details

The Impedance Data Control System (IDCS) as a whole comprises six programs as detailed below. The IDCS allows all front panel settings of the FRA to be set, and all data to be collected and saved via the computer. Impedance data can be further analysed and output in numerical or graphical form to a dot-matrix printer, and in graphical form to a graphics plotter.

During data collection, the FRA is set into the local mode except when data is actually being transferred to or from the computer. This allows all generator controls to be altered via the front panel during a run. Data can be displayed on the

monitor screen as it is collected, either in numeric form, or in graphical form as a real-time plot. Switching between these display modes can be carried out at any point during the run, via the T (text) and G (graphics) keys on the keyboard. The keyboard is constantly monitored during the run for key presses.

The impedance data is stored in the computer memory in a three element, five hundred-point array. This allows for an impedance spectrum covering ten decades of frequency, with fifty points per decade, more than sufficient for any practical system likely to be studied. All data collected are automatically saved on floppy disk at the end of the run so that no loss of data due to operator error can occur. In the event of a disk being full so that no more data can be saved, the operator is prompted to load a new disk, and the data saving process is repeated, so that no data is lost. Data are saved in the form of a binary image of the area in memory where the data array resides. This maximises disk storage capacity and speeds up the process of saving or loading a file considerably. Each data file has a corresponding description file which is saved along with it, containing all details of the run. These details include all settings used on the FRA and all experimental details entered by the operator.

The IDCS incorporates a multiple run facility whereby a particular run, once programmed, can be repeated several times, with a user-specified time delay between successive runs. This also allows the collection of data at a single frequency over a period of time, in order to follow the time dependence of the impedance of a sample at a fixed frequency. With these single-frequency runs, a choice of three real-time displays is available; Z' vs time, Z'' vs time, or double-layer capacitance

(DLC) vs time. The double layer capacitance is calculated from the imaginary component of the impedance, using the assumption that at high frequencies, the following relationship holds:-

$$Z'' = \frac{1}{2fCA} \qquad 2.1$$

where f is the frequency of the measuring signal, C is the double-layer capacitance, and A is the surface area of the electrode (or membrane). This assumption is only valid at frequencies above 1kHz, and so use of this facility at lower frequencies would yield unreliable data. The type of display chosen for the real-time plot does not affect the collection or storage of the data - both real and imaginary components are entered into the data array along with the frequency for each measurement, irrespective of which is actually displayed on screen.

The IDCS does not use the normal Apple CATALOG command when a listing of a disk directory is required during a programme run. Instead, a machine-code routine is used which differs considerably from the CATALOG command in that only locked binary files (i.e. impedance data files) are shown, and the files are displayed on the monitor screen in blocks of fifteen, numbered sequentially. The desired file can then be selected by entering its number, in contrast to the Apple CATALOG routine which displays all files, in a continuous listing, with no facilities for file selection, and filenames must be entered in full, giving more scope for errors.

All the IDCS programs are run on a menu-driven basis and offer a list of options for action which guide the operator through a logical sequence of operations from setting up the FRA and collecting data, through to detailed data analysis. The system as a whole comprises six BASIC programs and one block of

machine code as follows:-

START-UP	(BASIC)
DCOLLECT	(BASIC)
ANALYSIS 1	(BASIC)
ANALYSIS 2	(BASIC)
HPPLOTTER	(BASIC)
BSHAPE	(Machine Code)

Detailed descriptions of each program are given in Appendix A.

2.7 Electrode Calibration And Selectivity Coefficient Determination

All electrodes used in this work were assessed for correct functioning as ion-selective electrodes. From each batch of liquid membrane solution, or each PVC master membrane, electrodes were fabricated and tested prior to making any impedance measurements. Potential responses were also measured for all electrodes on which impedance measurements were made, and, in situations where the time dependence of the cell impedance was being investigated, the electrode assessment was carried out after all impedance measurements were completed.

2.7.1 Electrode Calibration

The utility of ion-selective electrodes as analytical devices is based entirely on the potential difference which arises across the membrane, due to the difference in activity of certain ions on either side of it. The various theories of how the membrane potential actually arises are discussed in Chapter 3.

The cell potential is the sum of all the potential differences arising throughout the electrode cell. In addition

to the membrane potential (E_m) these include junction potentials (E_j), reference electrode potentials, and all potentials arising from connections in the measuring circuit. Assuming that the symmetrical arrangement of the measuring circuit causes all the latter contributions to cancel out, and that the reference electrode maintains a constant potential (E_r), the overall cell potential can be represented by the following equation:-

$$E_{cell} = E_r + E_j + E_m \qquad 2.2$$

The junction potential contribution is caused by the difference in ionic mobilities in the sample solution and the salt bridge solution of the reference electrode. It cannot be separately determined, and must therefore be included in the value for E_m, which may as a result produce a non-Nernstian response. In the case of the liquid membrane electrodes E_j is generally not zero, but careful cell design can minimise its contribution to the measured potential.

For the PVC membranes, potential difference measurements were carried out in the PTFE cell described in section 2.3.5 which contains no liquid junction, with the result that E_j becomes zero and the only variable component of the cell potential is the membrane potential, E_m.

E_m can be related to the two solution concentrations via a modified form of the Nernst equation, which for an electrode selective for a univalent ion, i, is generally written as:-

$$E_m = \frac{RT}{F} \ln \frac{a_i''}{a_i'} \qquad 2.3$$

where a_i'' and a_i' refer to the activities of the primary ion in the sample and reference solutions respectively, R is the gas constant, T the absolute temperature, and F is the Faraday

constant. The calculation of membrane potentials is discussed fully in Chapter 3.

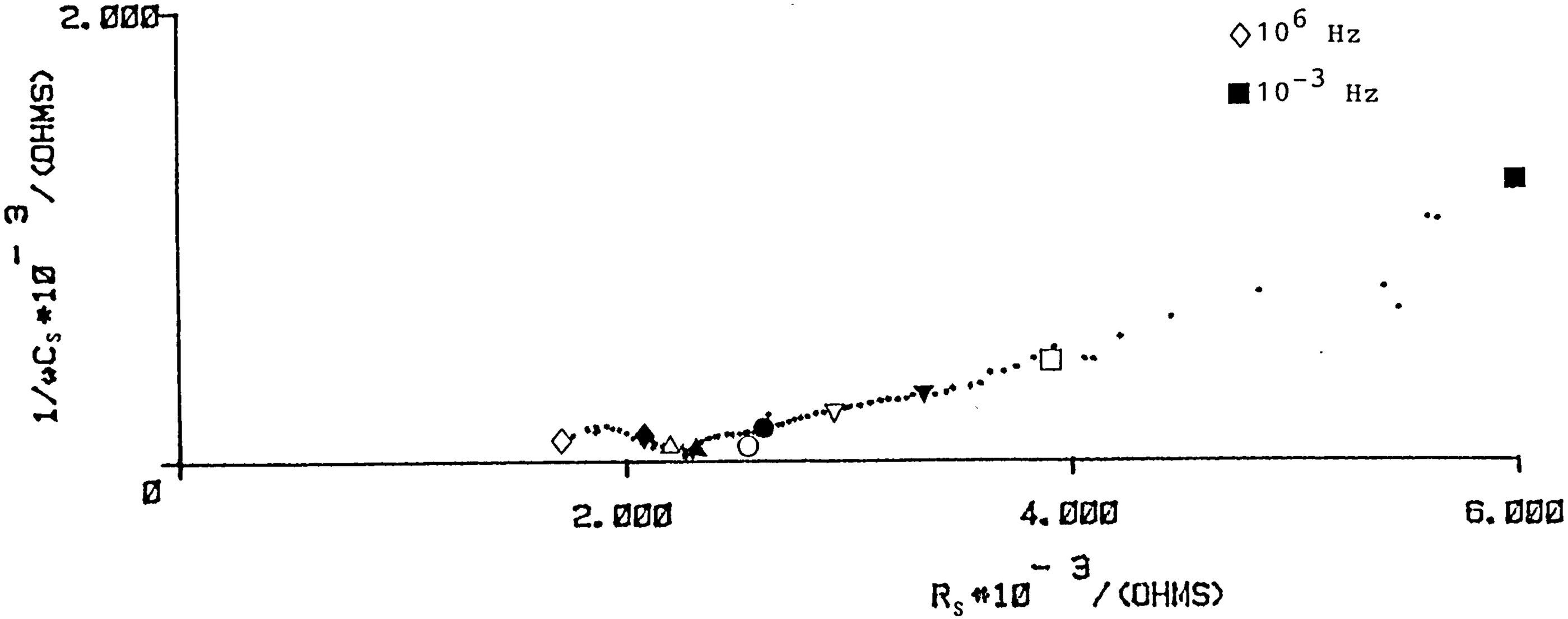
If the activity of the primary ion is held constant in the reference solution, the change in cell potential in response to a change in activity of ion i in the sample solution is Nernstian. The equation for the cell potential then becomes linear. ie:-

$$E_{cell} = E_0 + s \log(a_i'') \qquad 2.4$$

where E_0 is the standard potential of the cell (given by the y axis intercept), and the gradient, s, is the Nernst Factor (RT/F)ln10, which is equal to 59.18 mV at 298K for an electrode selective for a univalent ion.

An electrode which is placed in a series of sample solutions of decreasing primary ion activity, should therefore give a linear plot of potential against the log of solution concentration. In practice this is not the case, as the activity of the primary ion is not equivalent to the solution concentration except at low concentrations (less than 0.001 mol dm^{-3}) and any real electrode has a limited working range. It is therefore customary to construct a calibration curve for an electrode by measuring the potential developed when it is placed in a series of solutions as described above. It is usually considered that six different concentrations (normally 10^{-1} mol dm^{-3} down to 10^{-6} mol dm^{-3}) are sufficient to determine the calibration curve and this number of solutions was employed for all calibration and selectivity measurements reported here.

Fig 2.13: Two-electrode impedance spectrum obtained for the Orion body (KCl solutions).



2.7.2 Selectivity Coefficient Determination

It is, of course, in solutions containing other ions in addition to the primary ion that ion-selective electrodes are normally used. Ideally, the electrode would still respond only to the primary ion under such conditions, as if the interferent ions were not present in the solution. In reality, however, the ideal behaviour described by equation 2.4 is not achieved. The membrane is normally not only sensitive to the primary ion, but to several others as well, and it is desirable to have a measure of the effect that a given interferent ion will have on the cell potential.

The first quantification of the interferent effect was made by Nikolskii (2.15) when considering the sodium error in glass pH electrodes. This approach was based on the existence of an equilibrium of the form,

$$i^{z+}(glass) + j^{z+}(aq) \rightleftharpoons i^{z+}(glass) + j^{z+}(aq) \qquad 2.5$$

with equilibrium constant Kij. An extension of the modified Nernst equation can then be constructed, ie:-

$$E = E^{O} + \frac{RT}{z_i F} \ln\left[a_i + \sum_{j=i} K_{ij}\, a_j\right] \qquad 2.6$$

where the subscripts i and j refer to the primary ion and the interferent ion respectively, z denotes the charge on a given ion and k_{ij} is the selectivity coefficient for the electrode for the two named ions. This was extended by Eisenman (2.16) to accomodate the diffusion potential in the membrane, giving an equation of the form shown overleaf.

$$E = E^{O} + \frac{RT}{z_i F} \ln \left[a_i z_i + \sum_{j=i} K_{ij}^{Pot} a_j z_i / z_j \right] \qquad 2.7$$

The k_{ij} term in this case is the potentiometric selectivity coefficient which incorporates the relative mobilities of the two species (the primary ion i, and interferent ion j) i.e.

$$K_{ij}^{Pot} = \frac{u_j}{u_i} K_{ij} \qquad 2.8$$

This semi-empirical expression for the membrane potential, generally known as the Nikolskii-Eisenman equation, adequately describes the response of most ISEs in practical situations and the factor K_{ij} gives a measure of the effect that a given interferent will have on a given electrode. The smaller the value of K_{ij}, the smaller the contribution of the interferent ion to the membrane potential. Often in the literature, reciprocal values for K_{ij} (i.e. K_{ji}) are quoted, so that a value of K_{ij} of 10^{-3} becomes a K_{ji} value of 1000, although the meaning is still that the electrode is one thousand times more sensitive to ion i than to j. It is also often the case that selectivity coefficients are quoted as selectivity constants. This is not strictly correct as the value of K_{ij} depends on a variety of factors including interferent ion concentration, active material concentration in the membrane and, particularly, the method of determination used. For this reason, it is recommended by IUPAC (2.17) that the term selectivity coefficient is used and that the method of determination and all relevant experimental details be included with the value of K_{ij} quoted. A number of different methods are available to determine the value of K_{ij} and these are briefly outlined below.

2.7.2a Separate Solution Methods

Two calibration curves are plotted, one using solutions containing only the primary ion i, and the other using solutions containing only the interferent ion j. Equation 2.7 becomes

$$E_1 = E_o + s \log a_i \qquad 2.9$$

when no j is present in the solutions, and

$$E_2 = E_o + s \log K_{ij}\, a_j \qquad 2.10$$

when no i is present (where $s=2.303RT/zF$). If $a_i = a_j$ then the selectivity coefficient is given by

$$\log K_{ij} = \frac{E_2 - E_1}{s} \qquad 2.11$$

Alternatively, when $E_2 = E_1$ it can be seen that

$$K_{ij} = a_i/a_j \qquad 2.12$$

Separate solution methods have been used extensively in the past but are not recommended for two reasons. It is arguable that measurements made in separate solutions do not reflect the situation which exists when an electrode is in a mixed solution containing several ions. As a result of this, it is suggested that any values of K_{ij} obtained are therefore inapplicable to any normal situation where measurements are made on samples containing both ions. It is also the case that widely differing values are obtained depending on which of the above conditions is used to calculate K_{ij}, and at which concentrations the equivalence points, where $E_1=E_2$, are taken.

2.7.2b Mixed Solution Methods

As the name suggests, mixed solution methods involve measurements with both primary and interferent ions together in the same solutions and several workers have utilised these

methods in different forms.

There are essentially two approaches to the analysis of data obtained by the mixed solution method. Fig 2.12 shows a typical selectivity plot for an ion selective electrode. From this it can be seen that as the activity of the primary ion is reduced the interferent ion begins to affect the potential response and at a given primary ion activity the interferent completely controls the potential. The two linear portions of the curve can be extrapolated to a point where they intercept. This provides an arbitary reference point from which the selectivity constant can be calculated using equation 2.6, as a_j can be taken as the constant background interferent concentration.

An alternative method, which can be adopted, is to take the point where the difference between the experimentally determined curve and the extrapolated line is 18/z mV. This gives the activity of the primary ion required for equation 2.6 and a_j can be taken as before.

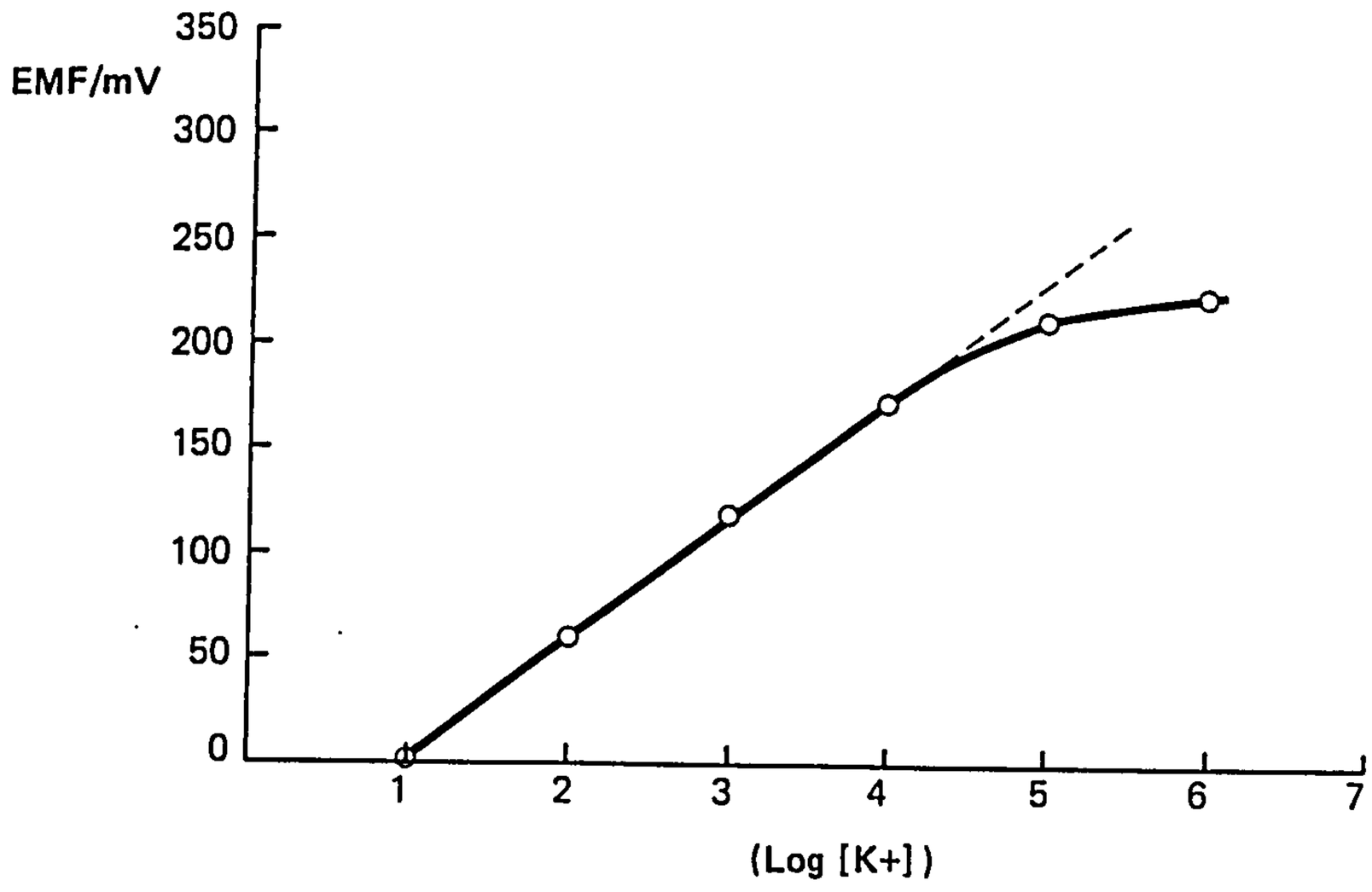
The problem can be approached in the opposite way i.e. the primary ion concentration can be held constant and the level of interferent ion varied.

An entirely different approach has been suggested (2.18). An initial potential is measured in a solution containing only the primary ion, when for an electrode sensitive to univalent ions the following equation holds,

$$E_1 = E_o - 2.303 \frac{RT}{F} \log a_i \qquad 2.13$$

Measured quantities of the interferent are introduced to the solution, the potential being noted after each addition. These potentials can then be related to the new primary ion activity by equation 2.14.

Fig 2.12: Typical mixed ion response curve for a valinomycin-based ISE



$$E_2 = E_o - 2.303 \frac{RT}{F} \log (a'_i + K_{ij} a'_j) \qquad 2.14$$

Combination of these two equations gives

$$K_{ij} a'_j = a_i 10^{\left[\frac{E_1 - E_2}{(RT/F)\ln 10}\right]} - a'_i \qquad 2.15$$

which is evidently linear, if the interferent activity is plotted against the righthand side of the expression, with a slope of K_{ij}.

All selectivity coefficients quoted in this thesis were obtained using the method of constant interferent activity and extrapolation of the linear portions of the curve to their intercept.

2.8 Factors Affecting Impedance Measurements

In addition to the effects of cell geometry discussed in section 2.2, and any chemical changes which may occur, a number of factors can affect the measured impedance of a sample (2.19). Depending on the materials used, and the chemical composition of the cell contents, a small change in temperature can have a significant effect on the measured impedance. For this reason, it is always advisable to maintain the sample cell at a constant temperature. All measurements carried out in the present study were made at constant temperature as described earlier.

The cell itself will have an impedance existing in parallel with the impedance of the electrochemical system contained within the cell. Although this cell impedance will generally be very high, it cannot always be ignored, and care must be taken to use materials which will minimise the effects of this unwanted contribution.

The input impedance of the measuring system, particularly capacitance and resistance in connecting leads, can give rise to artefacts in the complex plane, which can be minimised by using coaxial screened leads where possible, keeping all leads as short as is practicable, and balancing the impedance of the FRA probes.

The current measuring resistor can itself give rise to errors, as it may not be a pure resistor. Every effort was made to use current measuring resistors of near zero capacitance or inductance, measuring the impedance of all the resistors used on a separate ac bridge. It is also necessary to ensure that all connections and soldered joints are clean and well made to minimise further capacitive or resistive interference. Ideally the value of the current measuring resistor should be identical to the resistance of the cell under test. It is impractical to achieve this for every frequency measured and so resistance boxes are used with a series of resistors covering the range of the cell resistance so that the CMR is of similar magnitude. If too low a current measuring resistor is employed, the accuracy of the measurement becomes very poor whilst too high a resistor can lead to the appearance of pseudo-inductive loops in the complex plane, particularly at high frequencies.

Measurements were made on the cells used for both the liquid and the PVC membranes with no membrane present, so that the resistance of the cell assembly and the silver/silver chloride electrodes alone was measured. Fig 2.13 shows a typical spectrum obtained for the Orion body in a two-electrode configuration. The complex plane plot is closely similar to those obtained by Buck for silver/silver halide electrodes (section 1.2.6d) and can be interpreted as a resistive offset

representing the solution resistances within the cell, in series with the Ag/AgCl impedance. The magnitude and form of the impedance makes it desirable to exclude the contribution of the silver/silver chloride electrodes from the measured impedance. It would be possible to measure the impedance of the empty cell and to subtract this mathematically from any data obtained from a cell containing a complete membrane, and this approach has been adopted in the past, both in this laboratory and elsewhere. This approach is not entirely satisfactory, however, as there is no guarantee that the empty cell impedance will duplicate exactly the impedance of the cell components when a membrane is present. An alternative approach is to use a four-electrode cell configuration, which utilises two current-carrying electrodes, and two reference electrodes, one of each situated on both sides of the membrane. The membrane impedance can then be measured by way of the reference electrodes, thus avoiding contributions from other parts of the cell, and minimising the solution resistances measured. This approach requires more sophisticated electronics, but at the end of the first year of the project, a four-electrode potentiostat, the Solartron 1186 ECI, became available, designed specifically for connection to, and use with, the Solartron 1170 series frequency response analysers. It was originally hoped to use the 1186 coupled to the 1174 for all impedance measurements, however, it was found that the 1186 introduces a phase lag into the system at high frequencies, which manifests itself as an inductive loop in the complex plane when the data are plotted. For this reason, it was necessary to use the 1174 coupled directly to the sample cell at high frequencies and the 1186/1174 combination could only be used at low frequencies. This is an acceptable

situation, as it can be seen from Fig 2.13 that the Ag/AgCl electrode impedance only becomes significant at frequencies below about 1Hz. Table 2.1 gives the frequencies for various dummy cells, at which the error introduced by the 1186 falls below given tolerance levels.

In some situations, the solution resistance as it appears in the impedance spectrum, seems to be of the order of megohms, whilst in reality, it can be measured with no membrane present to be in the region of 700 ohms, as above. This apparent discrepancy is due to the choice of comparison resistor used. A small resistor should be used to measure the value of the high-frequency limit, where Z becomes purely resistive. With some membranes, however, as a result of the value of the time constant for the high-frequency process, the maximum frequency of the measuring system is not sufficient to reach this limit, and the imaginary component of the impedance is sufficiently large to require a larger comparison resistor. The use of a larger resistor results in a loss of accuracy in the data as discussed in Chapter 1.

In practice, it is customary to measure the high frequency part of the spectrum initially with as low a comparison resistance as possible to verify that the solution resistance is as expected. For subsequent runs, a larger comparison resistor is used so that it is not necessary to change over to a higher resistor when the impedance at lower frequencies is measured.

Table 2:1 Measurement Accuracy: The 1174 and 1174/1186 Systems Compared

Resistance	Tolerance	1174 Alone	1174/1186
1 MOhm	20%	3.971 kHz	1.254 kHz
	10%	1.989 kHz	629.8 Hz
	1%	198.9 Hz	79.28 Hz
	Zero error	< 1.0 Hz	6.298 Hz
100 kOhm	20%	39.71 kHz	1.254 kHz
	10%	19.89 kHz	629.8 Hz
	1%	998.0 Hz	79.28 Hz
	Zero error	125.4 Hz	6.298 Hz
10 kOhm	20%	397.1 kHz	15.78 kHz
	10%	198.9 kHz	6.298 Hz
	1%	25.04 kHz	-
	Zero error	125.4 Hz	998 Hz

Above the frequencies shown, the error in measurement exceeds the given tolerance level.

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Chapter 3

Mechanistic Aspects of Neutral-Carrier Ion-Selective Electrodes

3.1 Introduction

There are two main aspects of the operation of ion-selective electrodes which must be encompassed by any theory or model describing them; these are:-

a) The origin of the selectivity of the electrode with respect to ions of one sort over other species of the same charge.

b) The mechanism by which ions of the opposite charge are excluded from the membrane.

Many of those investigating the subject from both theoretical and experimental points of view have studied biological membranes (3.1,3.2), and have considered the effect of neutral carriers such as valinomycin on lipid bilayer, and natural cell membranes (3.3-3.14). Much of the work has produced conflicting results and theories, possibly due to the fact that such a wide variety of experimental procedures have been used, and that it is not necessarily valid to apply the conclusions from one type of experiment, with one type of membrane, to the results from another.

This chapter contains a summary of the contemporary models and theoretical treatments of the membrane potential for neutral carrier-based ion-selective electrode membranes. Also included is a discussion of the structural factors involved in the functioning of the carrier molecule in such a membrane.

3.2 Structural Aspects of Neutral Carrier Electrodes

In neutral carrier electrodes, the basis of the selectivity of the membrane can clearly be illustrated, by way of extraction studies and measurement of formation constants, to be dependent on the structure of the carrier molecule (the ionophore) itself, although the relationship is not always a simple one. A large amount of effort has been directed at considering these various structural and kinetic factors (3.15-3.33) and, to explain the marked differences in formation constants exhibited by these compounds for one type of ion compared to another, it is necessary to consider the molecular interactions of the compound concerned.

3.2.1 Ionophore/Ion Interactions

A wide range of factors controls the interactions between the host molecule and the ion to which it is bound, the basic principle being that of the host molecule providing a cavity into which the complexed ion can fit (although so-called sandwich type complexes are known for some ionophores (3.34)). On these grounds, the selectivity can be considered in terms of the extent to which the cavity is exclusive to one particular ion, although this may not depend on ion size alone.

Other factors which will affect the complexation process include the following:-

i. Flexibility: The flexibility of the host molecule will determine the ease with which the molecule can adopt a new conformation to accommodate the ion. Certain species, such as valinomycin, or the cryptates, present a truly three-dimensional

cavity, whereas molecules such as 18-C-6 (1,4,7,10,13,16 -hexaoxacyclooctadecane) and its derivatives can only provide what is essentially, a two-dimensional location in the centre of a ring, which involves less conformational distortion and rearrangement. This will in turn affect the activation energy for the complexation process and also the stability of the complex formed. Hydrogen bonding or other bridging processes, can enhance the stability of the complex, but may affect the flexibility and ease of complexation.

ii. Lipophilicity/Hydrophobicity: The polarity of the internal and external parts of the host molecule will affect the operation of the molecule in an ISE. It is desirable to have a molecule with a sufficiently polar interior to bind the ion, and a sufficiently apolar exterior to make the complex soluble in the non-aqueous membrane phase. It has been suggested (3.35) that the ideal ligand will have between five and eight co-ordinating sites in the interior co-ordination sphere to achieve optimum co-ordination of a metal ion.

iii. Kinetics: For an ionophore to be useful as the electroactive species in an ISE, it is desirable to have kinetics such that both complexation and decomplexation are rapid, if an effective ion-transport mechanism is to operate. This will depend largely on i. and ii. above.

iv. Ion Charge: The charge density of the ion will affect the complex as this will control the strength of the ion-ionophore coordination, and also the hydration of the ion.

v. Hydration effects: It has been noted (3.20) that the specific ionic effects in chemistry and biology do not follow simple orders or series such as the Hoffmeister series (a measure of the lipophilicity of a given ion relative to others), the

series of hydrated radii for the ions, or the bare ion radii. As long ago as 1919, Bungenburg de Jong (3.37) proposed a factor to explain these effects in terms of the polarisability of the ion, and in 1932 Jenny (3.37,3.38) suggested that the fact that sequences occurred with selectivity preferences other than those mentioned above, could be explained on the grounds of the ease with which an ion was hydrated. It was proposed that the more hydrated an ion was in solution, the more easily the dehydration process necessary for complexation would affect it. Neither series, though, had any ion other than Li or Cs as the most preferred, which is manifestly not the case in biology and ISE work. Eisenman (3.20) has proposed a different set of sequences, based on energetic considerations of the balance between hydration and binding by a receptor site, which allow for the sequences found in real systems.

The coordination process itself will also be affected by the extent of hydration of the ion, as this must involve a stepwise removal of the hydration sphere, and Morf (3.39-3.41) and Guggenheim (3.42) have suggested a theory to explain the selectivities in terms of the effects of the free energy of the dehydration process.

vi. Counter-Ion Effects: It has been reported that for some cyclic polyether ligands, the nature of the counter ion markedly affects the stability of complexes formed with metal ions (3.43).

3.2.2 Neutral Carrier Structures

The characterisation of the structure of many neutral carriers and their complexes has been carried out using x-ray crystallography on the solid form, and by a variety of techniques

on the liquid (solution) forms (3.44-3.48).

In the uncomplexed state, certain species can have a number of different conformations, the particular conformation adopted depending on the dielectric constant and the polarity of the medium in which the ionophore is dispersed (3.49,3.50). Valinomycin (Fig 3.1) has three separately identifiable structures in the uncomplexed form (3.51,,3.51a,3.51b). The 'A' form of valinomycin adopted in apolar solvents (CCl_4, $CHCl_3$) has six internal hydrogen bonds as shown in Fig 3.2a, giving a cage-like structure, with a regular crown-like configuration possessing a threefold axis of symmery. In solvents of higher polarity (ethanol, dimethylformamide), the molecule adopts a second configuration, the 'B' form, which has three internal H-bonds, giving a propeller-like structure (Fig 3.2b). In fact two 'B' forms have been identified, one with H-bonds formed by the D-Val residues (the B-I form), and one with H-bonds formed by the L-Val residues (the B-II form), with a rapid equilibrium occurring between the two forms. In polar solvents (methanol, dimethylsulphoxide), the molecule exists as an open, flexible ring structure (the C form) with no internal hydrogen bonds and a high degree of flexibility, with H-bonding to solvent molecules. The relationship between these three structures is shown schematically in Fig 3.3.

The potassium complex of valinomycin has been shown to have a cage-like conformation similar to that adopted in apolar solvents (Fig 3.4)(3.52,3.53) with the potassium ion occupying the cavity within the centre of the molecule. In contrast, the structure of the sodium complex as determined by crystallography shows that the sodium ion actually sits above the valinomycin cage in a much less stable conformation, and is coordinated to a water molecule

Fig 3.1: Schematic diagram of the structure of the valinomycin molecule

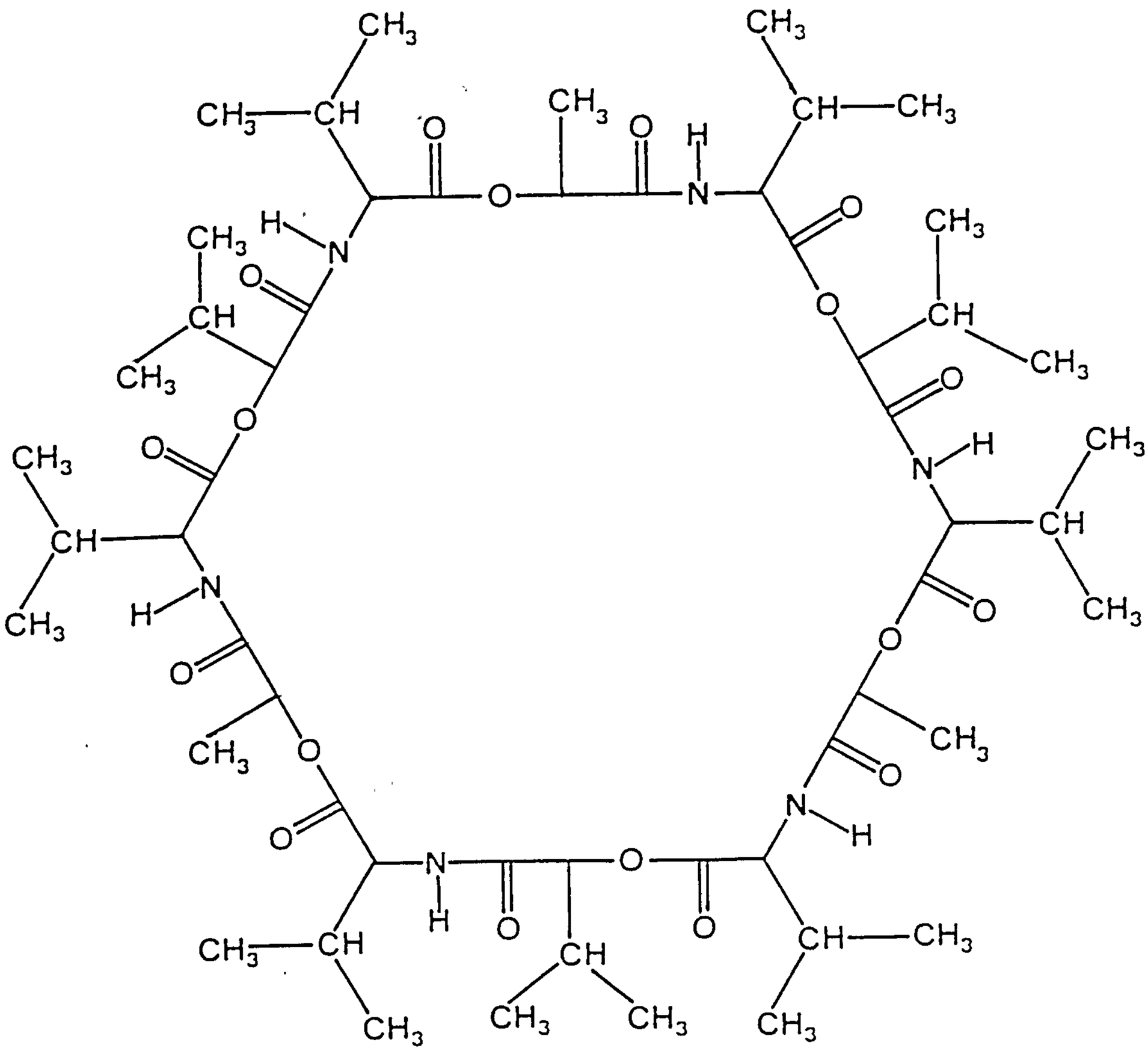


Fig 3.2a: The 'A' Form of the uncomplexed valinomycin molecule

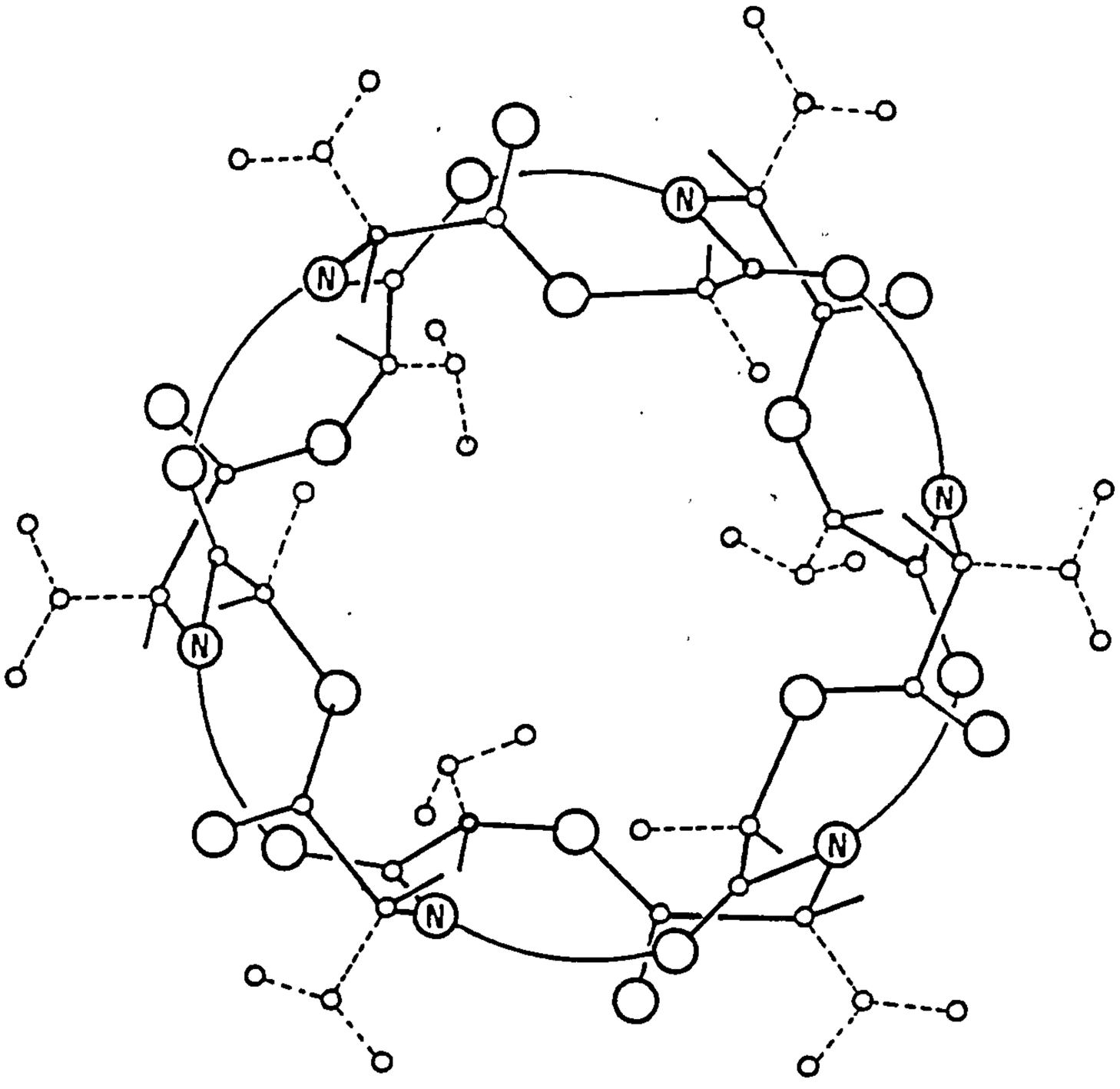


Fig 3.2b: The 'B' Form of the uncomplexed valinomycin molecule

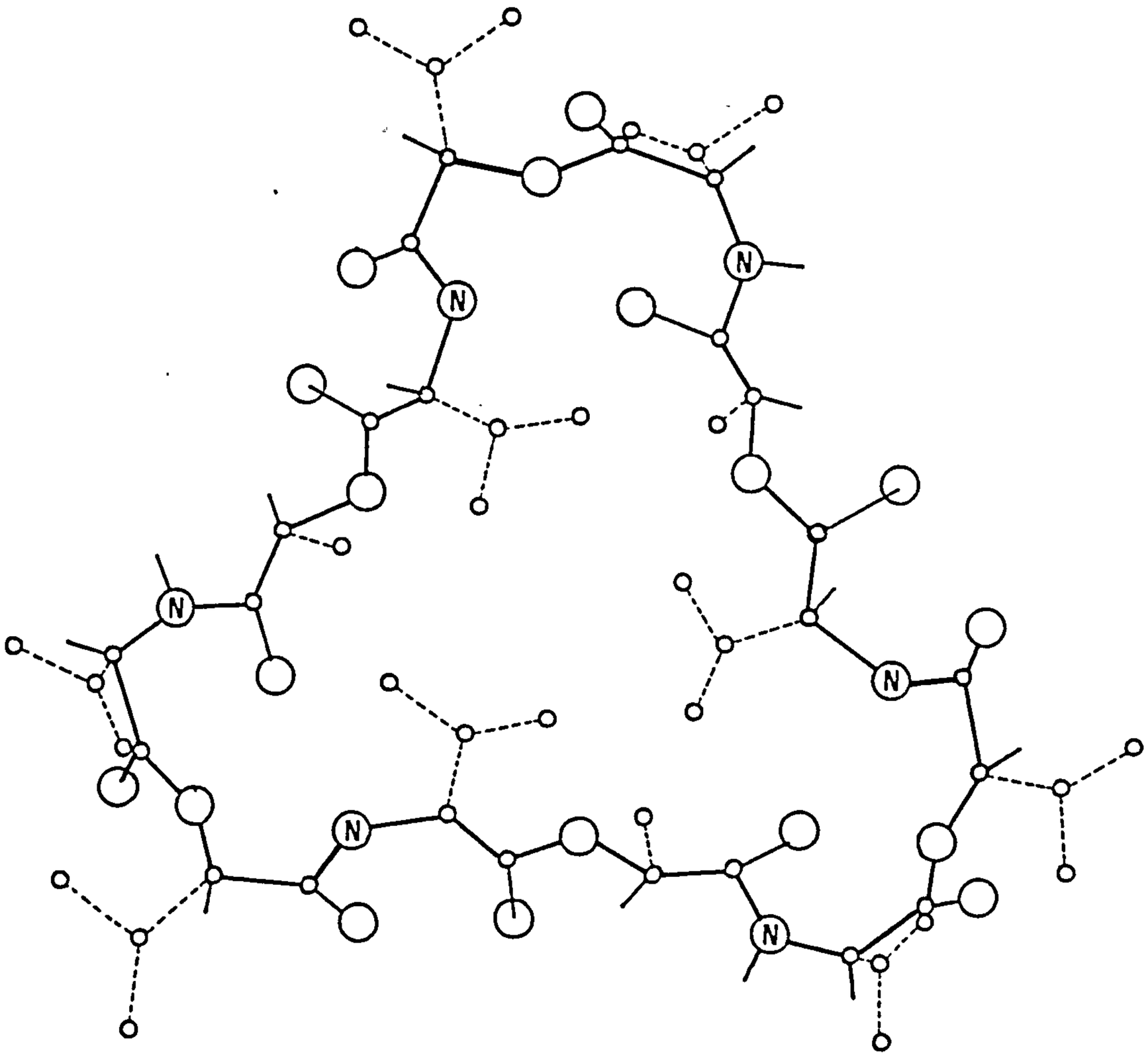


Fig 3.3: Diagram showing the equilibrium between the different forms of valinomycin

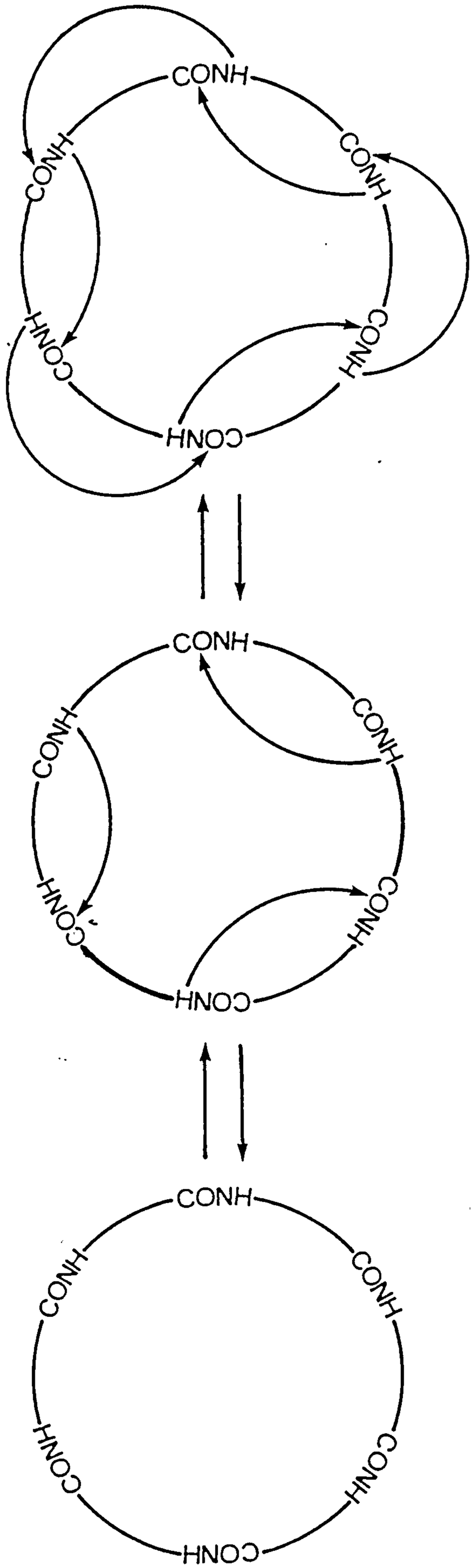
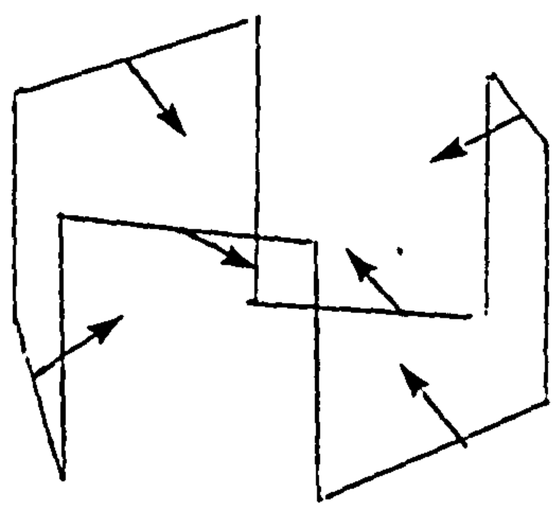
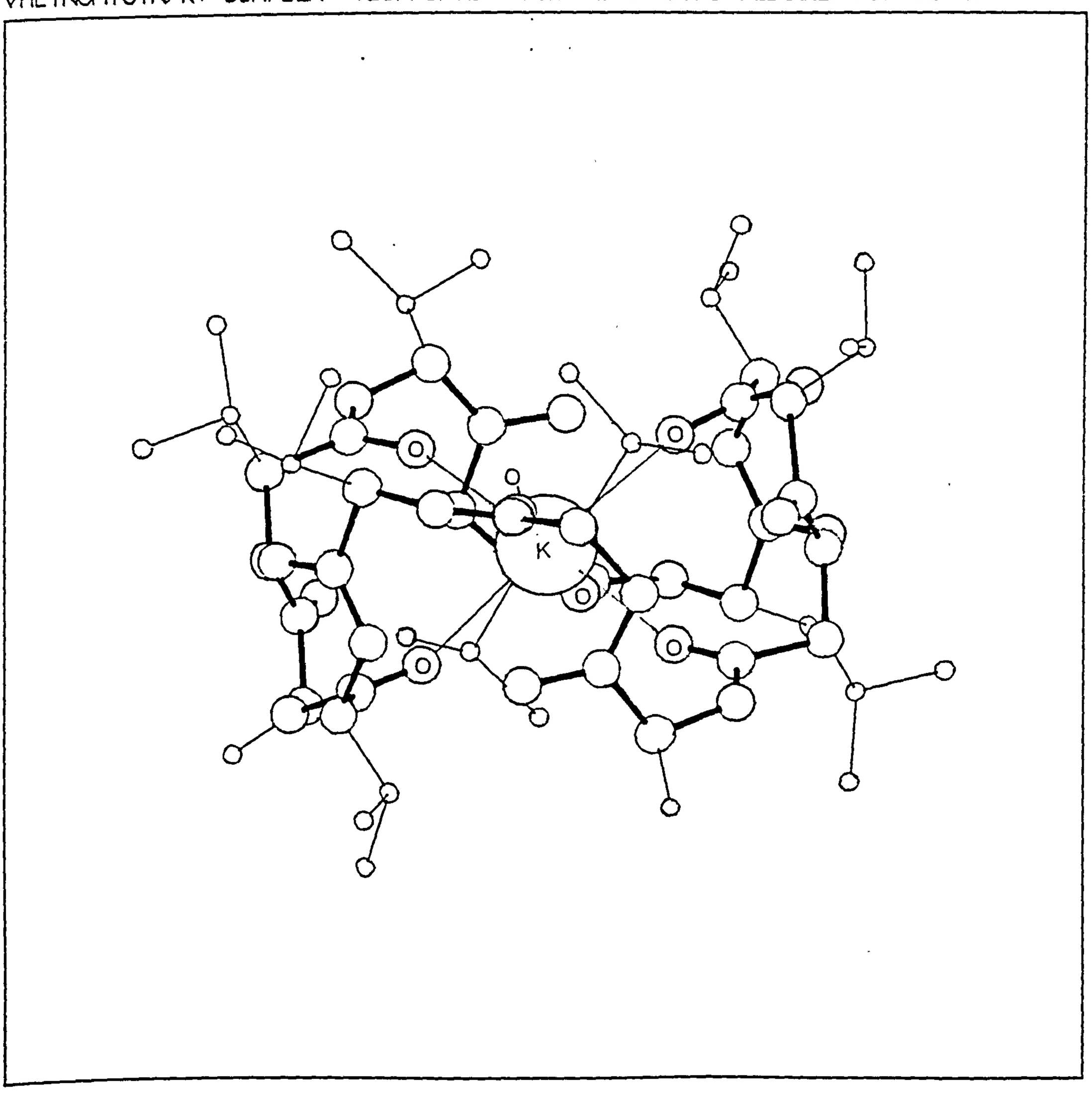


Fig 3.4: The structure of the K+/valinomycin complex





which occupies a more central position in the cavity (Fig 3.5)(3.54). Thus the difference between the structures of the complex with the primary ion and the main interferent reflects the difference in selectivity of the valinomycin electrode.

The significance of this structural information in explaining the ionophoric properties of valinomycin is apparent. The molecule can adopt a series of stable structures, allowing progressive encapsulation of a potassium ion from an aqueous solution, giving a complex which is energetically favourable in apolar media.

The synthetic ionophores show a marked difference in their structural properties. The smaller crowns are both less flexible and offer poorer encapsulation of the target ion. Figs 3.6a and 3.6b show the structure of uncomplexed dibenzo-18-C-6 and its potassium complex, as determined by x-ray diffraction. From these plots it can be seen that there is relatively little difference between the two structures and the crown cannot envelop the ion giving the hydrophobic exterior/hydrophilic interior of the valinomycin complex. The second point of note here is that the cavity of the ionophore is essentially a two-dimensional hole, which is easily accessible to any ion small enough to occupy the site. Any such ion would be expected to form a complex, although one particular ion will obviously provide the optimum energetics by way of its size and charge density. This is upheld in practice, with stable complexes being formed for all the smaller alkali metal ions, and with little difference in stability between the different complexes. Similar results are obtained for the other 18-C-6 derivatives. Larger crowns offer much greater flexibilty, and more effective encapsulation of the ion, but lack the stability of the

Fig 3.5: The structure of the Na+/valinomycin complex

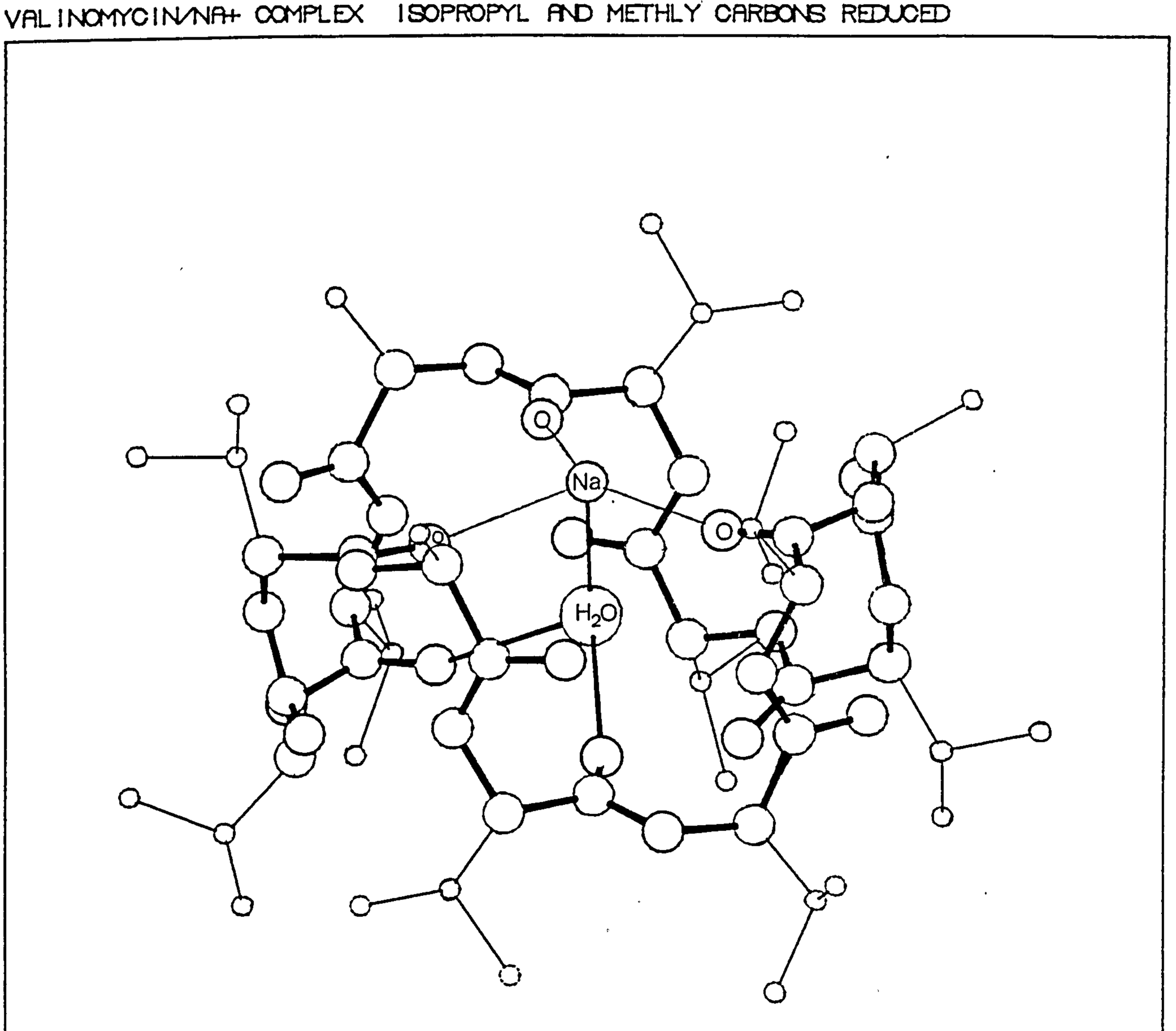


Fig 3.6a: The structure and conformation of uncomplexed dibenzo-18-Crown-6

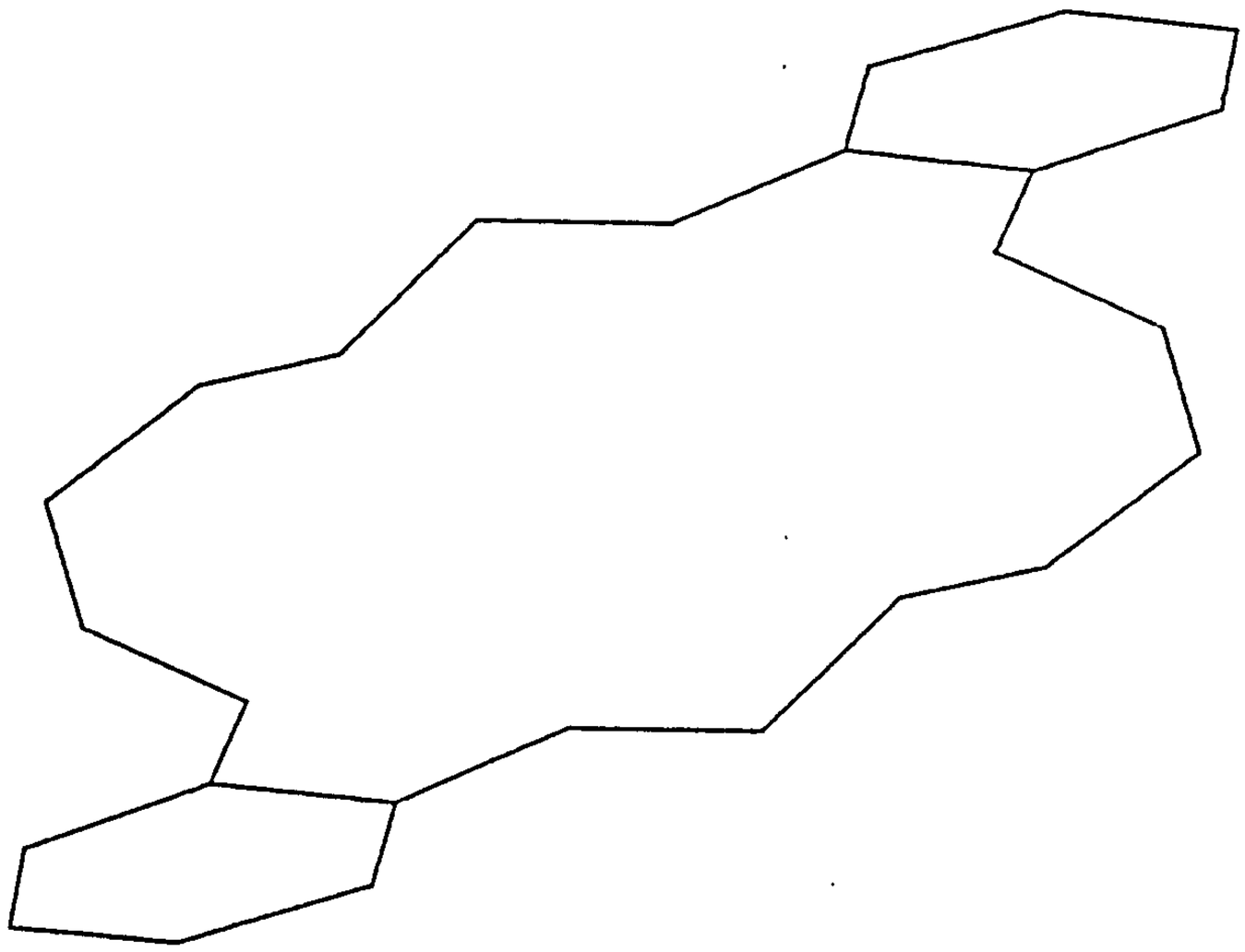
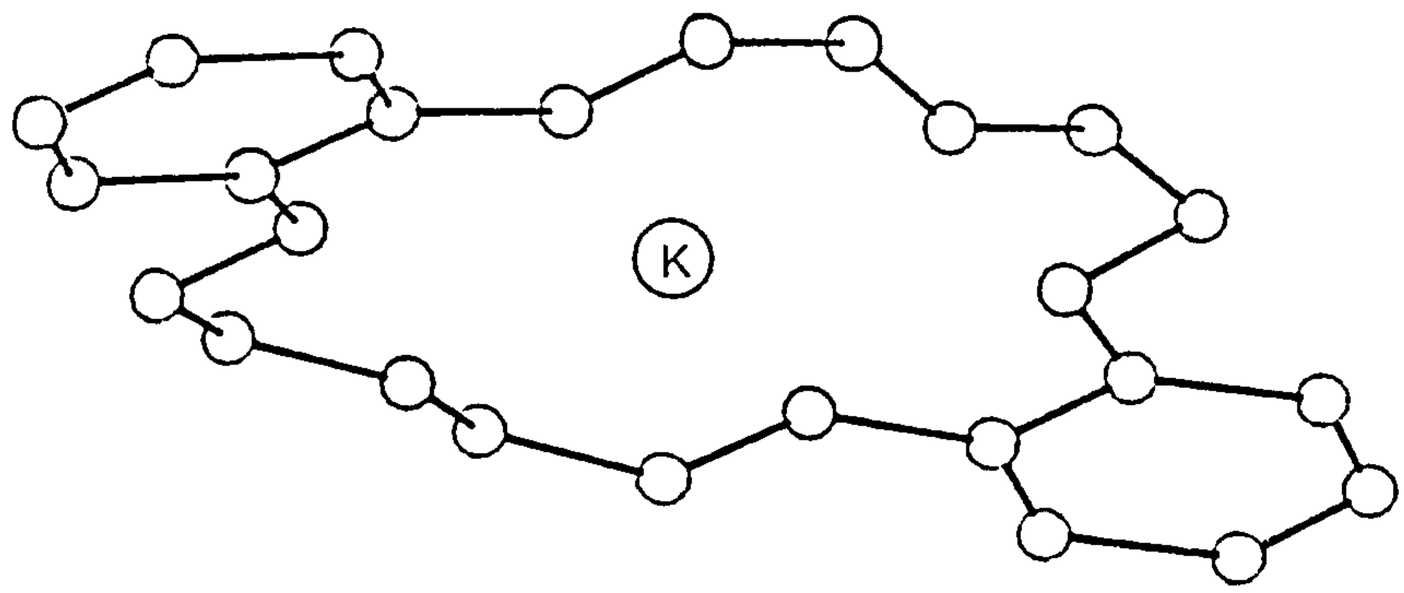


Fig 3.6b: The structure of the potassium complex of dibenzo-18-Crown-6



valinomycin molecule afforded by internal hydrogen bonding.

The group of molecules known as the cryptands (Fig 3.7) give a true three-dimensional cavity where a greater degree of encapsulation and stability is available, but are also not entirely satisfactory as the lack of flexibility of the molecule results in very slow decomplexation kinetics.

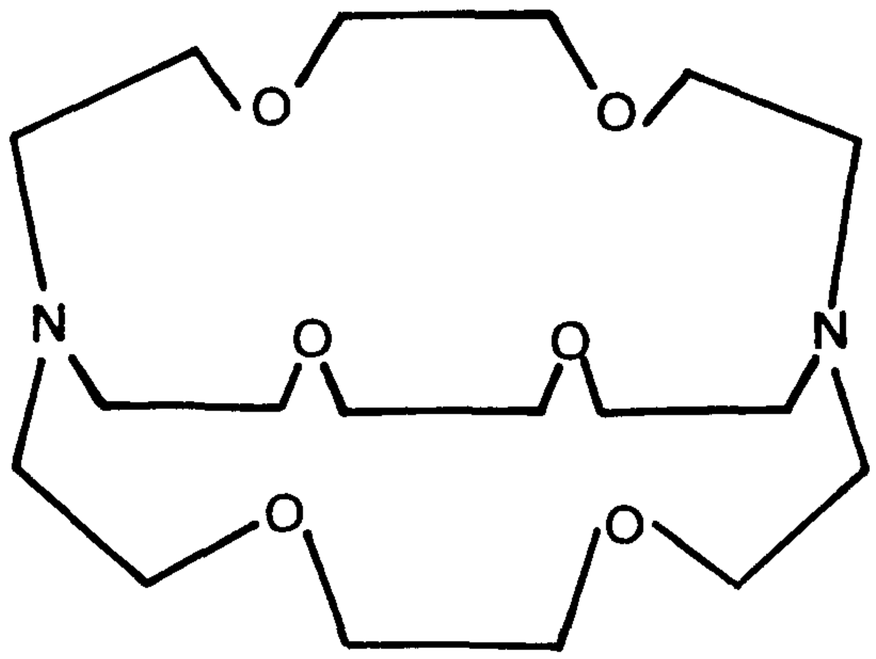
Many of these materials have been assessed in terms of their relative extraction coefficients with various ions and yet when incorporated into ISE membranes, their early promise is not fulfilled. This highlights the fact that extraction studies alone do not necessarily yield sufficient information for the assessment of new ionophores.

When considering these factors, it is also important to consider that the structural and kinetic information obtained under specific experimental conditions may not be applicable to a different situation. The extent to which structural information, and kinetic data obtained from extraction studies and nmr work in liquid solvents can be extrapolated to cover supported liquid and PVC membranes is not clear. It is likely that the two present very different environments to the ion and ionophore, and that the kinetics involved and the structure adopted, in these situations may be quite different to those found in the idealised experimental conditions. The mobility of the neutral molecule and its charged complex, must also be dependent on the medium in which it is situated.

3.3 The Membrane Potential

The theoretical treatment of the development of the membrane potential is a complex area, as it must necessarily account for

Fig 3.7: Schematic representation of the 2,2,2-cryptand molecule



a number of possible effects. In a completely comprehensive treatment, these will include permeation of both cations and anions, and transport of cations, anions, complexes and uncomplexed carrier molecules. It is not possible here to review and comment on, in detail, all the different theoretical solutions which have been produced to date, but a general expression for the membrane potential is derived, and theoretical treatments relating to neutral carrier electrodes are discussed.

When any two aqueous solutions containing ionic species at different activities are separated by a barrier through which some of the ions may pass, equilibration of the electrochemical potential of the system results in an electrical potential difference being set up between the two solutions. This potential difference can be considered to comprise two boundary potentials for the barrier/solution interface at each side of the barrier, and a diffusion potential arising out of the differing ionic mobilities of the species within the barrier. These are outlined from a theoretical viewpoint below.

3.3.1 The Phase Boundary (Donnan) Potential

Given any system involving an interface between two immiscible phases which contain ions of non-zero mobility, a potential will develop across the interface due to the uneven distribution of charged species between the two phases. In the ideal situation of equal distribution between the phases, no potential would develop, but in real systems this situation is seldom encountered. The difference in distribution of the charged species is manifested in the electrochemical potentials

of the species in the two phases, which consist of the chemical potential with an additional term to account for the charge on the ions, i.e:-

$$\bar{\mu}_i = \mu_i + z_i F\phi \qquad 3.1$$

The standard expression for the chemical potential μ_i, for species i, is

$$\mu_i = \mu_i^o + RT \ln a_i \qquad 3.2$$

Combining this with equation 3.1, gives,

$$\bar{\mu}_i = \mu_i^o + RT \ln a_i + z_i F\phi \qquad 3.3$$

Given a system comprising a membrane separating two solutions differing only in the activity of species i and its counterion, then we can assume that at equilibrium, the electrochemical potentials on either side of the interfaces will be equal, and that

$$\mu_i^o(aq) + RT \ln a_i' + z_i F\phi' = \mu_i^o(m) + RT \ln a_i(O) + z_i F\phi(O) \qquad 3.4$$

for the interface at distance x=0 through the membrane,

and

$$\mu_i^o(aq) + RT \ln a_i'' + z_i F\phi'' = \mu_i^o(m) + RT \ln a_i(d) + z_i F\phi(d) \qquad 3.5$$

for the other interface, at x=d.

It is evident that the standard chemical potentials $\mu_i^o(m)$ and $\mu_i^o(aq)$ will be the same for each interface, assuming that the standard potentials do not vary within the membrane, and from this consideration, a new parameter, k_i, the distribution coefficient, can be defined as shown in eqn 3.6.

$$k_i = \exp\left[\frac{-(\mu_i^{o}(m) - \mu_i^{o}(aq))}{RT}\right] \qquad 3.6$$

From this, the expressions for the interfacial potentials become,

$$\phi(0) = \phi' + \frac{RT}{Z_i F} \ln\left[\frac{k_i a_i'}{a_i(0)}\right] \qquad 3.7$$

and

$$\phi(d) = \phi'' + \frac{RT}{Z_i F} \ln\left[\frac{k_i a_i''}{a_i(d)}\right] \qquad 3.8$$

Similar expressions can be obtained from the standard Butler-Volmer expression relating to reaction rates at electrode surfaces, i.e.

$$J_i = \overrightarrow{k_i} a_i' \exp\left[\frac{-\alpha z_i F(\phi(0)-\phi')}{RT}\right] - \overleftarrow{k_i} a_i(0) \exp\left[\frac{(1-\alpha) z_i F(\phi(0)-\phi')}{RT}\right] \qquad 3.9a$$

for the interface at x=0, and

$$J_i = \overleftarrow{k_i} a_i(d) \exp\left[\frac{(1-\alpha) z_i F(\phi(d)-\phi'')}{RT}\right] - \overrightarrow{k_i} a_i'' \exp\left[\frac{-\alpha z_i F(\phi(d)-\phi'')}{RT}\right] \qquad 3.9b$$

for the interface at x=d, where J_i is the total flux density for species i, $\overrightarrow{k_i}$ and $\overleftarrow{k_i}$ are the forward and backward rate constants for the transfer reaction and α is the transfer coefficient.

At equilibrium, J_i becomes zero and therefore,

$$a_i(0) = k_i a_i' \exp\left[\frac{-z_i F}{RT}(\phi(0) - \phi')\right] \qquad 3.10a$$

and

$$a_i(d) = k_i a_i'' \exp\left[\frac{-z_i F}{RT}(\phi(d) - \phi'')\right] \qquad 3.10b$$

The distribution coefficient is now described in kinetic rather than thermodynamic terms, where

$$k_i = \frac{\overline{k_i}}{\overline{k_i}} \qquad 3.11$$

The total interfacial potential, E_b, is given by ($\varphi' - \varphi''$) and from equations 3.7 and 3.8, the following can be obtained,

$$E_b = \frac{RT}{z_i F} \ln\left[\frac{k_i a_i'}{a_i(O)}\right] - \frac{RT}{z_i F} \ln\left[\frac{k_i a_i''}{a_i(d)}\right] \qquad 3.12$$

$$= \frac{RT}{z_i F} \ln\left[\frac{a_i'\ a_i(d)}{a_i''\, a_i(O)}\right] \qquad 3.13$$

3.3.2 The Diffusion Potential

The diffusion potential can be derived by solution of the classical Nernst-Planck equation based on Ficks' diffusion law.

The general form of the equation is

$$\overrightarrow{J_i} = c_i \overrightarrow{v_i} \qquad 3.14$$

where $\overrightarrow{J_i}$ represents the flux density within the membrane phase, c_i the concentration, and $\overrightarrow{v_i}$ the flow velocity for species i.

Restricting the treatment to the flow of ions in the direction at right-angles to the membrane surface (i.e. directly through the membrane), J_i is given by equation 3.15

$$J_i = -u_i c_i \frac{d\bar{\mu}}{dx} \qquad (0 < x < d) \qquad 3.15$$

Using equation 3.3 to describe the electrochemical potential of the species i, gives

$$J_i = -RT\ u_i c_i \frac{d\ln a_i}{dx} - z_i F\ c_i u_i \frac{d\phi}{dx} \qquad 3.16$$

from which it can be seen that the controlling factors in the diffusion potential are the potential gradient ($d\varphi/dx$) and the

gradient of the activity of species i.

Taking j, the electrical current density at equilibrium to be

$$j = 0 = F\Sigma z_i J_i \qquad 3.17$$

a general expression for the diffusion potential can be deduced,

i.e.

$$F\sum z_i \left[-u_i c_i RT \frac{d\ln a_i}{dx} - z_i c_i u_i F \frac{d\phi}{dx}\right] = 0 \qquad 3.18$$

and so

$$-z_i u_i c_i \; RT \; \frac{d\ln a_i}{dx} = z_i^2 c_i u_i F \; \frac{d\phi}{dx} \qquad 3.19$$

and

$$E_d = \int_0^d \frac{d\phi}{dx}\, dx = \frac{-RT}{F}\int_0^d \frac{\Sigma\, z_i u_i c_i (d\ln a_i/dx)}{\Sigma z_i^2 c_i u_i}\, dx \qquad 3.20$$

which holds for all species permeating the membrane.

If the electrical transference number is defined as

$$t_i = \frac{z_i^2 u_i c_i}{\Sigma z_i^2 u_i c_i} \qquad 3.21$$

then equation 3.20 becomes

$$E_d = -\frac{RT}{F}\int_0^d \Sigma \frac{t_i}{z_i}\, d\ln a_i \qquad 3.22$$

as given by Guggenheim (3.42). This expression requires a detailed knowledge of concentration (and therefore activity) profiles within the membrane and these can only be assumed. Various workers have provided solutions for the Nernst-Planck equation in this way, by the use of different restrictions and assumptions, with various activity profiles and boundary conditions.

The general form of the solution for the integral equation

(eqn 3.22), as derived by Nernst is as follows,

$$E_d = \left[\frac{u_m}{z_m u_m + z_x u_x}\right]\frac{RT}{F}\ln\frac{\Sigma a_m(O)}{\Sigma a_m(d)} - \left[\frac{u_x}{z_m u_m + z_x u_x}\right]\frac{RT}{F}\ln\frac{\Sigma a_x(O)}{\Sigma a_x(d)} \qquad 3.23$$

where m=cation and x=anion. If $u_x = 0$ and $u_m = 1$, equation 3.23 reduces to

$$E_d = -\frac{RT}{F}\ln\left[\frac{a_m(O)}{a_m(d)}\right] \qquad 3.24$$

which will hold true in an ideally cation-selective electrode. In reality permeation of the membrane by other species will occur, resulting in a relationship which is still logarithmically linear, but with a sub-Nernstian gradient.

3.3.3 The Total Membrane Potential - Anion Exclusion

The total membrane potential will evidently be the algebraic sum of the diffusion potential and the Donnan potential, and as a result it is not possible to evaluate these two terms separately. In the case of an ideally selective membrane, combination of equations 3.13 and 3.24 gives;

$$E_m = \frac{RT}{z_i F}\ln\left[\frac{a_i(O)}{a_i(d)}\right] + \frac{RT}{z_i F}\ln\left[\frac{a_i'}{a_i''}\,\frac{a_i(d)}{a_i(O)}\right] \qquad 3.25$$

which reduces to

$$E_m = \frac{RT}{z_i F}\ln\left[\frac{a_i'}{a_i''}\right] \qquad 3.26$$

and relates the external solution concentrations to the membrane potential. Evidently, the form of the expression obtained relies on the solutions for E_d and E_b which are used.

The solutions derived should adequately describe the potential-activity relationship for an ISE if they are to be of

any practical use. Generally this relationship is of the form of a flattened hyperbola, with a region of linear cation response at low concentrations which reaches a maximum and finally the response reverses at higher salt activities.

A large number of solutions have been obtained for the Nernst-Planck equations, in the form outlined above, from the original work of Nernst (3.55), Planck (3.56) and others (3.57-3.59).

Goldman (3.60) utilised the assumption that a linear profile exists for the electrical potential and that all solutions behave ideally. This treatment holds well for very thin membranes such as lipid bilayers and biological membranes and uses a convenient permeability factor P_i, as a measure of the degree of ion transport. Teorell (3.61,3.62) and Meyer and Sievers (3.63) produced solutions for membranes with several classes of permeating species by excluding the space charge regions and assuming an electroneutral membrane.

Ciani and Eisenman (3.64,3.65) derived solutions for ideal membranes with several permeating species, which were extended to cover the effects of neutral carriers on lipid bilayers by Eisenman, Ciani et al (3.66-3.70). De Levie (3.71) further examined the implications of the Ciani-Eisenman-Szabo (CES) theory, which is essentially a segmented potential model as outlined above. The CES theory suggests that phospholipid membranes behave so that the boundary to ion permeation is the internal hydrocarbon-like section. i.e. a simple organic solvent phase made into a membrane of the same thickness as a phospholipid membrane would behave in the same way. This theory uses the Poisson-Boltzmann equation to describe the equilibrium potential profile, which comprises two interfacial

and interior potential contributions. The ionic fluxes are described by the Nernst-Planck equations of motion. The theory does not require the presence of fixed charges within the membrane and requires that ions of only one charge are present within the membrane. Essentially the ionophore just solubilises the cation in the membrane phase. The potential maximum occurs in this model due to cation-carrier complex concentration becoming decreased as a result of ion-pairing, rather than the total consumption of the carrier species.

Alternatives to the above models were derived by Lauger and Stark (3.71a-3.71c). Their model was again constructed for phospholipid bilayer membranes, the main difference between this and the CES theory being that the diffusion/migration barrier of the former is replaced by an activation energy barrier and an Eyring-jump type mechanism controlling forward and backward transport rates.

Neutral carrier membranes used in ISEs are thicker than the Debye length, and cannot therefore be considered thin in the present context, and so overall electroneutrality within the bulk membrane phase (excluding the interfacial capacitive space-charging regions) must be maintained, and the assumptions regarding the potential profiles within the membrane no longer hold.

Schlogl (3.72,3.73) produced the first treatment applicable to the latter type of membranes, allowing for any number of permeating ions as well as the presence of fixed ionic sites within the membrane.

The CES model was extended by Boles and Buck (3.74) to incorporate transport of uncomplexed anions and cations, cation-carrier complexes and the formation of neutral

cation-carrier-anion complexes. Three extreme cases of the model were identified, i.e. (i) the classical CES situation, where only cation permeation and transport occurs, (ii) the situation of high anion permeability where the membrane is electroneutral, (iii) and an exclusive-anion permeability case. For all three cases, predicted response curves are found to be in agreement with experimental results. A further extension of the theory is included incorporating the idea suggested by Kedem (3.75,3.76), that anion exclusion is aided by the presence of fixed negative sites within liquid membranes, bound chemically to the support material. Earlier work on cellulose acetate and nitrate membranes showed that negative sites in these membranes give rise to perm-selectivity in the absence of any carrier agent (3.77-3.79). The Boles and Buck model assumes exclusion of the anions due to space charging at low salt concentrations and that the maximum, and reversal, in the response occurs when the membrane is electroneutral. Complete consumption of carriers is not presumed to occur due to the low formation constants for ion-carrier complexing and ion-pairing. This theory has several faults, these being that large deviations from electroneutrality are still required in the membrane bulk, and that a fundamental consequence of the model is that a typical ISE membrane would be expected to have a resistance of approximately 10^{17}Ohm, well in excess of the resistances reported here and elsewhere (10^{6}Ohm). The fact that the theory of Boles and Buck fails to predict the membrane resistance correctly (although allowing for the presence of negative sites), in conjunction with the very high concentration of cations required within the membrane, appears to disprove the CES-Boles-Buck approach to the anion exclusion problem.

In view of the apparent failure of these models to describe adequately all the characteristics of thick membranes, several alternative theories have been proposed based on the assumption that anions, present within the membrane, are either fixed, or of very low mobility, compared to the cation/carrier complexes, and that anions from the aqueous solutions are therefore excluded by electrostatic repulsion, with the membrane acting purely as an ion-exchanger. The anions in the membrane do not become involved in the expression for the membrane potential due to their low or zero mobility.

Morf and co-workers (3.80-3.82) have suggested that the membrane contains anions which are immobilised within the membrane due to poor water solubility. Wuhrmann (3.83,3.84) proposes a slightly different situation whereby the membrane extracts anions from the aqueous phase, which then have a low mobility within the membrane, and this idea has been supported elsewhere (3.85).

Simon et al (3.86), have carried out electrodiffusion experiments on stacked PVC membranes, to determine the carrier, cation and anion concentration profiles in the membrane. The results support the suggestion that carriers traverse the membrane (and as a result must also diffuse back across the membrane to replenish the supply). The work also showed that although anions were entering the membrane from the aqueous solutions, the quantity doing so was very much smaller (a factor of approximately 85) than the quantity of cations doing so. The only possible explanations for this are the large deviations from electroneutrality suggested by Boles and Buck, or that there are other anionic species within the membrane providing the balancing charge.

Morf suggests that the fact that there is an uneven distribution of chloride ions though the membrane stack rules out the possibility of fixed sites within the membrane. Also, it is suggested that the level of sites present is far in excess of what could reasonably be expected from impurities. The source of the negative sites is suggested as being OH^- ions which form conglomerates within the membrane, reducing their mobility, corresponding to the idea of anions of low mobility entering the membrane from the solution. This theory requires an equilibrium of the form,

$$K^+aq + Val_m + H_2O_m \rightleftharpoons KVal_m + OH^-_m + H^+aq \quad 3.27$$

The point where the experimental work supporting this theory can be most criticised, is that large voltages (up to 70 V) were applied to the membrane stack to polarise it. Whether results obtained under these conditions can be said to mimic those found in a zero current, steady state situation, is not resolved.

Morf (3.87) has extended this idea of mobile negative charged sites by dissolving large lipophilic anions into the membrane phase, providing trapped ion-exchange sites within the membrane. Replacement of possibly extracted anions by permanently membrane-soluble anions, such as tetraphenylborate, improved the cation response at low salt activities, but did not prevent maximum formation and the diminished high activity response. It should be noted, though, that experiments with unsupported organic solvent membranes with no added carrier have shown that such membranes will produce a potential response over a limited concentration range (3.88), even though no fixed sites are possible, and so the fixed site theory may not be universally applicable.

On the basis of electrodiffusion measurements, Luch et al. (3.89) favour the view that fixed sites are inherent in PVC membranes and suggest a concentration of fixed sites of 5.0 $x10^{5}$ mol dm^{-3} with a spacing between sites of approximately 3.0 $x10^{-8}m$.

Recently Stover and Buck (3.90-3.92) and Seto et al, (3.93) have extended the Teorell, Meyer and Sievers model to cover thick membranes and the model correctly predicts a maximum in the response. A model has also been produced by the same authors for membranes with mobile negative sites.

It is important here to distinguish between results from supported liquid membranes, and those from PVC matrix membranes. In supported membranes, the filter support is usually of the Millipore type, i.e. cellulose acetate or nitrate. Cellulose nitrate filters are well known for their ability to act as ion-exchangers (3.94), and cellulose acetate membranes are also known to behave as ion-exchangers in solutions of low salt concentration (<0.01 mol dm^{-3}). The acetate filters can undergo hydrolysis and oxidation (3.95) with the result that protons are lost to the aqueous solutions and negative sites remain in the membrane giving rise to the ion exchange properties. It is also possible that impurities arising as a result of the manufacturing process will provide further negative sites.

PVC membranes, as would be expected, have a completely different chemistry, and the structure of the membrane is markedly different from the Millipore filter type of membrane. As discussed in Chapter 4, in the supported liquid membrane the liquid effectively forms a separate bulk phase in the membrane pores. In the PVC membranes, however, the membrane presents a

single homogeneous phase which is porous at a molecular level. The manufacture of PVC is quite different from that of cellulose acetate and nitrate polymers, and in plasticised PVC there is an even greater scope for creation of negative sites from the PVC itself, and from impurities and the plasticiser. On this basis it is not unreasonable to assume that the process of anion exclusion, whilst possibly relying on negative sites in both cases, arises out of different processes.

In the light of this body of work supporting the concept of sites which are fixed or are of low mobility within the membrane, it follows that permeation of the membrane by anions which are soluble and therefore mobile in the membrane phase will disrupt the ion-selective behaviour of the membrane. This has been proven to be the case on many occasions (3.74, 3.80-3.82, 3.96, 3.97).

The uptake of such ions will result in a large increase in the mobility of anions within the membrane and decrease in the concentration of free carriers at the membrane/solution interface due to the formation of cation-complex/lipophilic-anion pairs. This consumption of carriers results in a maximum in the response followed by reversal into an anion response.

3.3.4 Cation Selectivity

The above discussion provides a summary of the history of the theory of membrane potentials and the state of current thinking on the subject. These theories apply to ideal neutral-carrier membranes which are solely responsive to the cationic primary ion species at low salt activities.

Unfortunately real electrodes only obey these equations over a limited concentration range, and they are also found in practice to be responsive to other species than the primary ion. These interferent species all contribute to the membrane potential to a greater or lesser extent, and subsequently to the apparent primary ion activity as measured. The extent to which they affect the electrode response is found to vary enormously from one type of electrode to another and it is therefore desirable to have a measure of the extent to which a given ion will affect a given electrode. In practice, empirical, or semi-empirical treatments are required such as the Nikolskii-Eisenman equation discussed in Chapter 2.

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Chapter 4

Liquid Membranes

4.1 Introduction

Liquid-membrane ion-selective electrodes were the first type of neutral-carrier electrodes to become commercially available, and although now superceded in many commercial applications, the liquid membrane system provides a useful environment in which to study the mechanism of operation of the electrode membranes, as it is chemically well defined, and full control of the membrane composition can be exercised. Using this system therefore, it should be possible to obtain meaningful data concerning the action of the membrane as an ion selective barrier.

Early work by Simon and others on sensors based on macrotetralide antibiotics (4.1-4.4) led to the first functional valinomycin-based electrode, reported by Pioda et al (4.5), which incorporated a liquid membrane. Stefanac and Simon had investigated electrodes comprising a series of monactin homologues (4.2a) and a variety of electrode designs, and found that, for liquid membranes, the support which gave the most satisfactory results was a sintered glass disk, although Millipore filters, nylon mesh, and polyethylene sheet were also found to be quite effective. These electrodes produced calibration slopes close to the theoretical value of 29mV per decade for divalent ions. Pioda also tested monactin and nonactin as membrane components but found selectivities of 100 and 120 respectively for K^+ over Na^+ whereas the selectivity of the valinomycin electrode reflected the large difference in

formation constants found for the potassium and sodium complexes, and a value of 4000 was reported for the selectivity coefficient for potassium over sodium. (The presence of 0.1 mol dm^{-3} NaCl was found to only reduce the linear range of the response to 3.5 decades from 4.2 with the valinomycin membrane). Also, the slopes of the calibration plots obtained for nonactin and monactin, were found to be 54.5 and 53.0 mV/decade respectively, compared to 58.3 $\pm$1 mV/decade for valinomycin.

The electrode used by Pioda utilised a membrane solution consisting of the active material dissolved in diphenyl ether (4.5), which was given physical support by a porous filter. A similar, but more simple design was patented by Ross in 1967 (4.6), which formed the basis of the first commercially available valinomycin based electrode, the Orion series 92 (Orion-92-29) electrode which became available in 1969-1970. This electrode was tested extensively by Lal and Christian (4.7) who found slopes of approximately 52 millivolts per decade over the range 10^{-4} - 10^{-1} mol dm^{-3} KCl with no interferent ion present. Slight anion responses were.found for a variety of common anions (halides, NO_3^-, ClO_4^-, SCN^-, OH^-, HCO_3^-), but the electrode as a whole gave excellent results. This electrode body has been widely used in work on ISEs and is probably the most successful cell design for liquid membrane electrodes to date in that a variety of membrane support materials can be used with any desired membrane solution. The Orion body was used for all studies on liquid membranes reported here. Details of the Orion electrode construction, and of some modifications carried out are given in Chapter 2.

The object of this study was to determine the basis of the selectivity of the valinomycin electrode, and its anion exclusion properties.

4.2 Experimental Procedure

Several types of membrane were investigated in this study, using membranes consisting of 2,3-DMNB alone and also with various concentrations of valinomycin. Electrodes were constructed and tested using alternative support materials to the untreated Millipore filter, and an attempt was made to fabricate liquid membrane electrodes using the PTFE cell constructed for use with the PVC membranes, and with a modified cap and spacer for the Orion electrode body (Fig 4.0).

With the PTFE cell, it was found to be impossible to obtain a working electrode, despite attempts to use alternative support materials, and supports with different pore sizes. To construct the electrode, the support was soaked in the membrane solution for 24 hours prior to assembly, to ensure full permeation of the 2,3-DMNB, but even so, the potentiometric response of the cell was poor, and a stable potential could not be obtained. The normal interpretation of this would be that leakage of the membrane was occurring, allowing direct contact of the two aqueous solutions at some point. The cell impedance also showed a very low bulk membrane resistance, supporting this idea.

The main differences between the PTFE cell and the Orion body are that the former has no membrane solution reservoir, and that the membrane area exposed to the aqueous solutions is much larger. It seems that either one of these, or the combination of the two is sufficient to disrupt the operation of the membrane, although it is possible that the membrane surface area is the more important of the two, in view of the fact that the Orion body can be operated as a functional ISE with no solution reservoir present.

Fig 4.0a: Standard Orion Series 92 electrode cap.

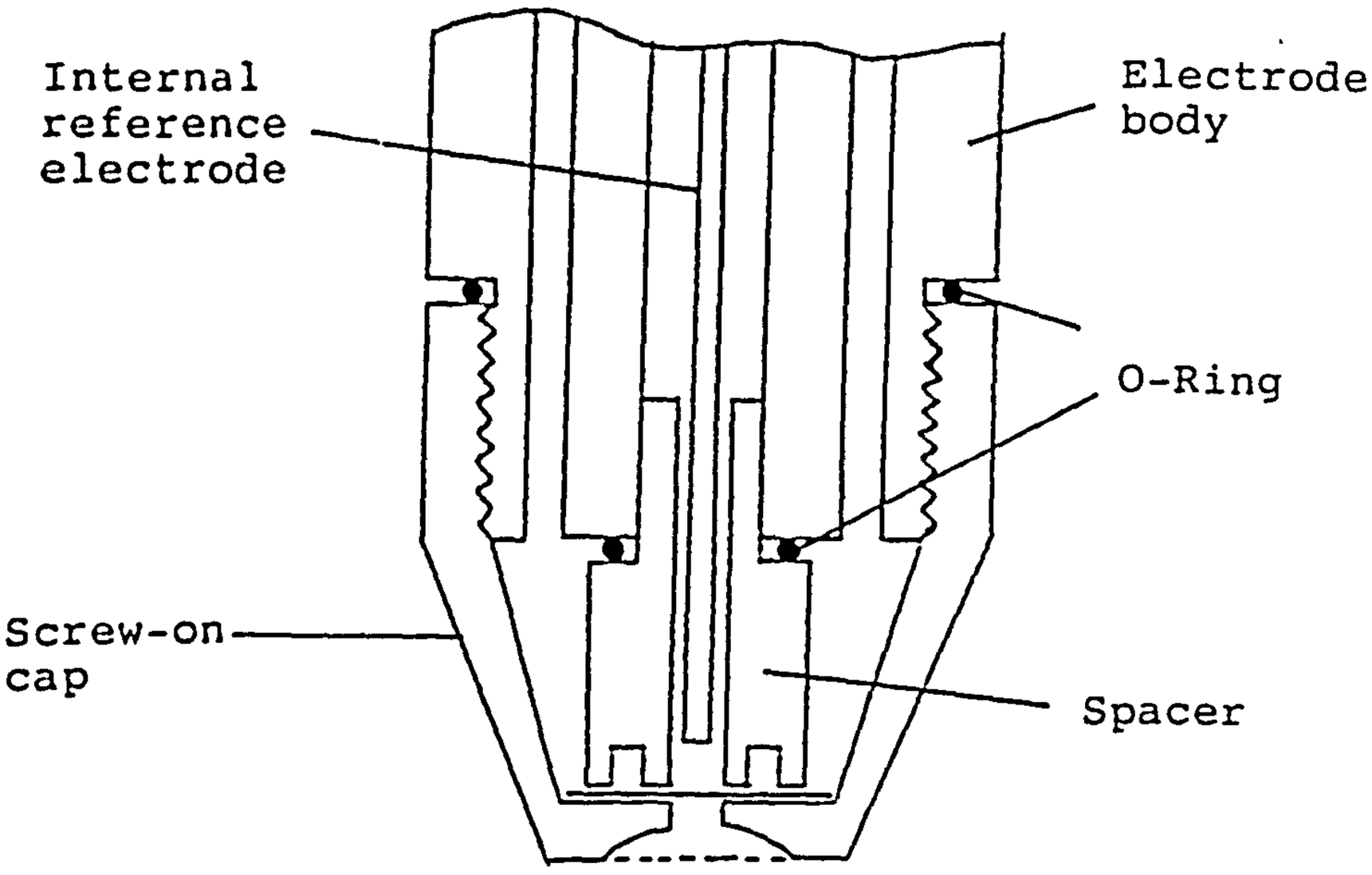
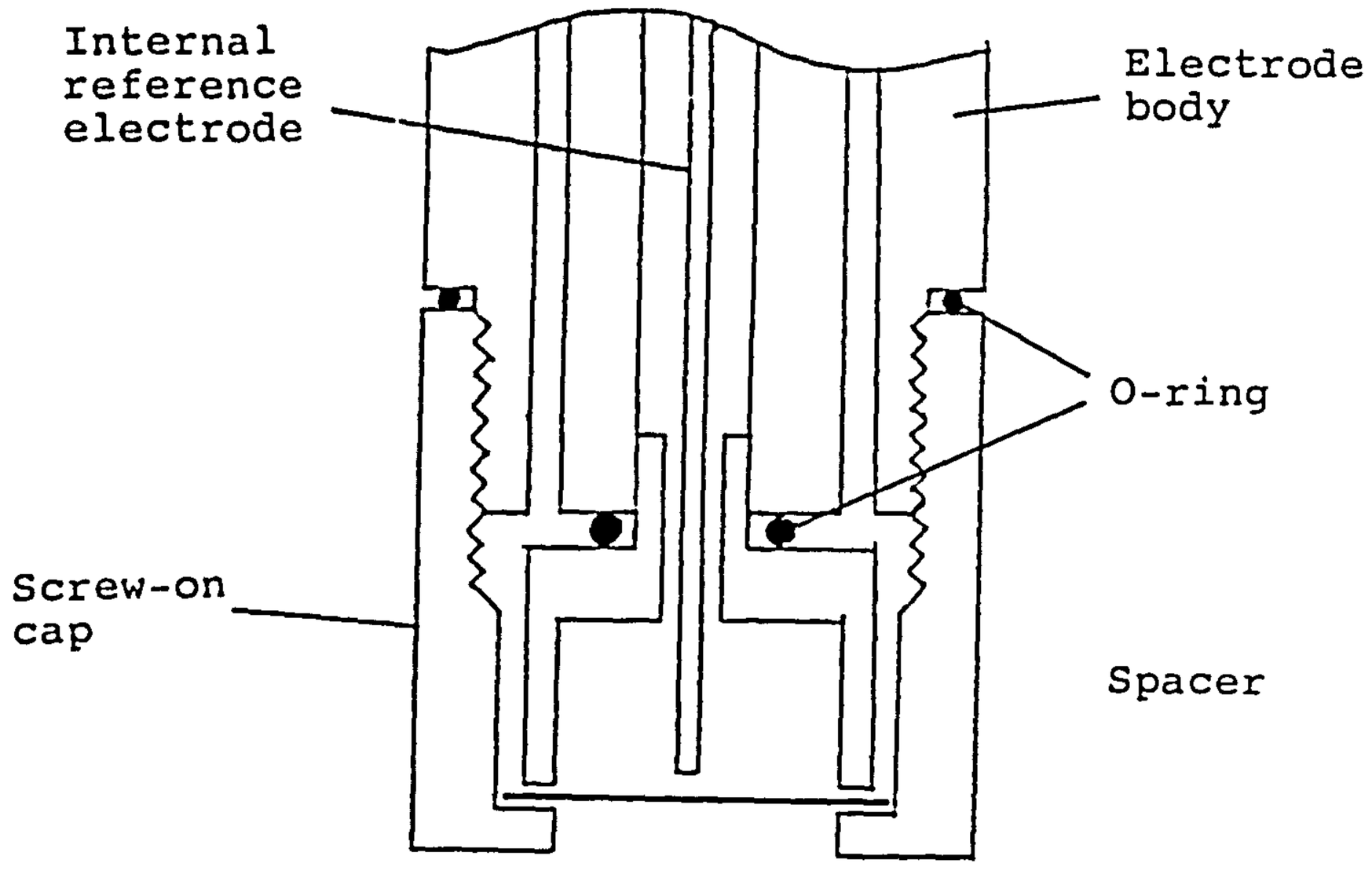


Fig 4.0b: Modified Orion cap giving larger membrane surface area.



Using the modified Orion cap, similar results were obtained, although in this case, the solution reservoir was available to the membrane. The surface area of the membrane exposed to the aqueous solutions in this situation was approximately five times greater than with the original Orion cap, and this increase appears to be sufficient for discontinuities to appear in the membrane resulting in its loss of function.

Cell impedances were measured for membranes contacted by solutions of either 0.1 mol dm^{-3} KCl or NaCl. For all the electrodes studied, the membrane impedance was measured at regular intervals in order to investigate the time-dependence of the bulk membrane resistance and capacitance, and the charge transfer resistance and double layer capacitances, after exposure to the aqueous solutions.

Initially, measurements were made using a two-electrode configuration as discussed in Chapter 2, but a four-electrode system was adopted as soon as the necessary hardware became available. Some restrictions on the use of four-electrode cell configurations for impedance measurements were found and these are discussed later in this chapter.

The procedure adopted for the measurements on all liquid membranes was as follows. Firstly, the membrane solution was allowed to achieve room temperature (all samples were stored desiccated at 0^{O} C to minimise degradation of the valinomycin). The electrode was assembled as outlined in Chapter 2, and all impedance measurements were then carried out. Single-ion responses and other potential measurements were made after all impedance measurements were completed, finally being followed by the determinaton of the mixed-ion response. In this way, electrodes were exposed only to a single cationic species for

all measurements, prior to the assessment of the mixed ion response, so that no contamination or memory effects from interferent ions could occur which would invalidate any of the results.

The time dependence of all electrodes was followed for a period of three days (72 hours) after initial solution contact to ensure that any variation in the cell impedance had ceased and that a steady state had been reached. The low frequency impedance spectrum was then recorded. Periodically electrodes were not disassembled after measurements were completed, and the membrane impedance was measured after several weeks to ensure that the final steady state had in fact been achieved. In all cases three days was found to be a sufficient length of time for this to be achieved.

4.3 Liquid membranes: Expected Equivalent Circuits

The general equivalent circuit which might be expected for an ion selective membrane is discussed in Chapter 1. It is suggested that at the high frequency end of the impedance spectrum, a single semicircle would be expected to appear, representing the parallel combination of the bulk resistance, R_b, and the geometric capacitance, C_g. For a supported liquid membrane it is possible that the situation may be more complex, due to the presence of the support material. If the dielectric constant and resistivity of the support material differs greatly from those of the membrane solvent, then it is possible that the bulk of the membrane would give rise to two semicircular features in the complex plane, one due to the solvent which occupies the pores in the membrane, and another due to the

membrane material itself. The extent to which these two possible features would be separated depends on the difference between the time constants for the two networks (this is discussed in Chapter 1). If both the solvent and support had similar time constants, then it is unlikely that both features could be deconvoluted, and only a single arc would be present, having a resistance which was the sum of the solvent and support resistances.

Even this may not adequately describe the membrane. Buck (4.8) has suggested that hydration of the support material occurs once the electrode is exposed to the aqueous solutions, but the effects of this hydration are not clearly defined. Permeation of the organic phase within the membrane pores by water from the aqueous solutions could also be involved. If this was not accompanied by the permeation of ionic species, the net result would be an increase in the dielectric constant of the organic phase resulting in an increase in the capacitance. It seems unlikely, however, that such permeation would take place without the concomitant uptake of ionic species by the membrane.

It is necessary to assume an idealised model of the membrane based on the following assumptions. For the sake of simplicity, it must be assumed that the membrane contains cylindrically symmetrical pores which are filled by the organic membrane solution and travel all the way through the membrane from one surface to the other. It must also be assumed that the rest of the membrane consists of a smooth sheet of the cellulose acetate material of uniform thickness.

Initially, on first contact with the aqueous solutions, the filter support will be completely unhydrated (ignoring hydration

from atmospheric water) as illustrated in Fig 4.1a. In this case, the equivalent circuit would be expected to be as shown in Fig 4.1b, with two parallel RC networks in parallel with each other. It is reasonable to assume that as hydration occurs, the thickness of the membrane as a whole will increase due to swelling of the hydrated regions which will in turn result in an increase in the length of the pores. Assuming that the support material does not swell inwards and reduce the pore diameters, this will cause an increase in the total volume of the pores, which will remain filled by replenishment from the reservoir of membrane solution. The result of this process would be a decrease in the capacitance, and an increase in the resistance of the material in the pores due to the increase in thickness. As these are purely geometric changes, and resistance and capacitance vary inversely with each other, the time constant for the R_1/C_1 parallel network representing the liquid in the pores would remain unchanged (assuming that there is no water uptake by the 2,3-dimethylnitrobenzene, and consequently no change in the resistivity of the material).

The effect of hydration on the other half of the circuit, will be to introduce a second parallel network in series with the R_2/C_2 network as shown in Fig 4.2a and 4.2b. Initially, as the hydrated layer will be very thin, its resistance will be very small and its capacitance will be large. As the thickness of the hydrated layer increases, the thickness of the unhydrated region will decrease, but the net result would be an overall increase in the thickness of the membrane as a whole.

The effect of these processes on the total impedance of the membrane is not easy to determine except in general terms. The resistance of the hydrated layer will increase with its

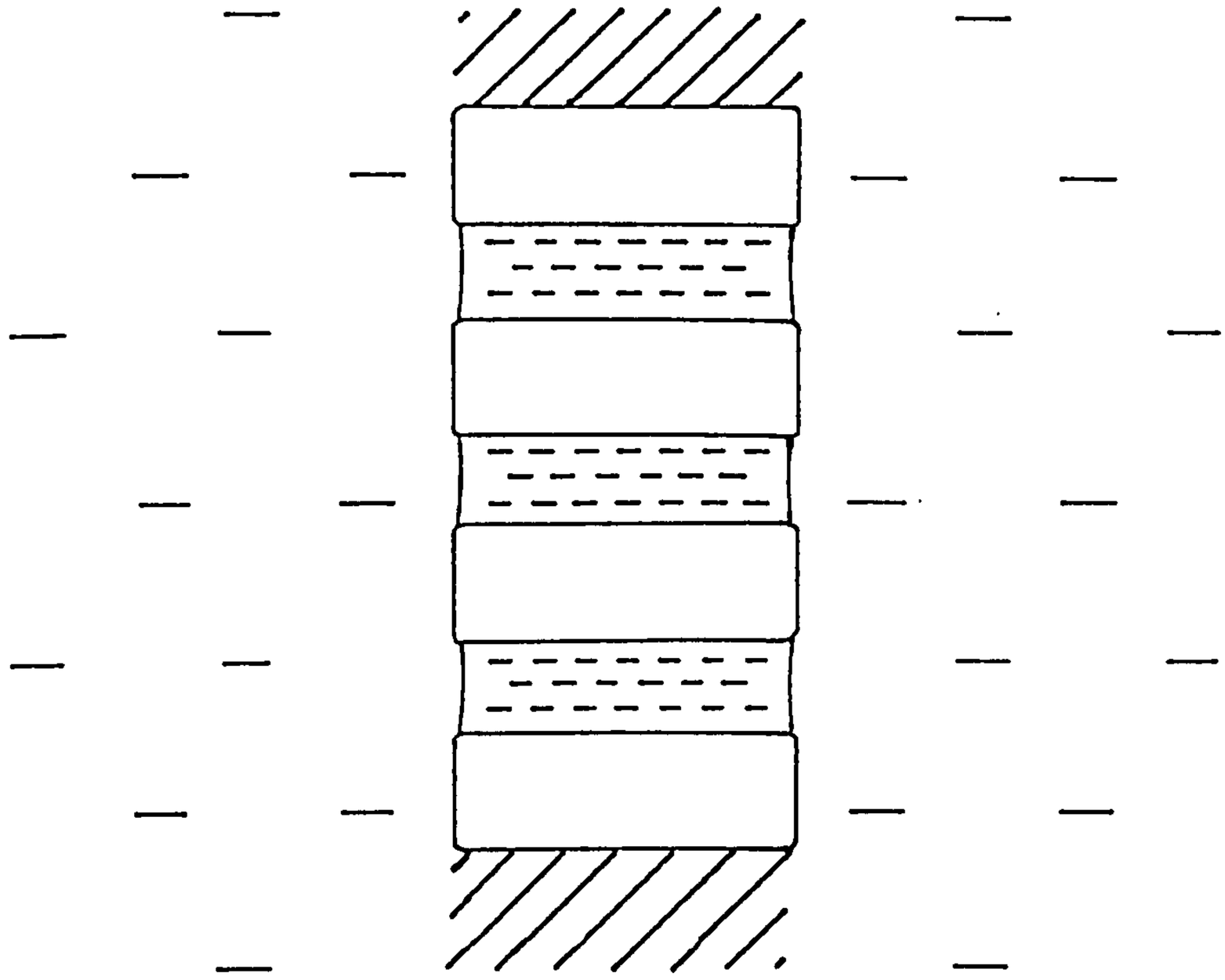


Fig 4.1a: Schematic diagram of a porous cellulose acetate membrane, with pores filled with an organic solvent.

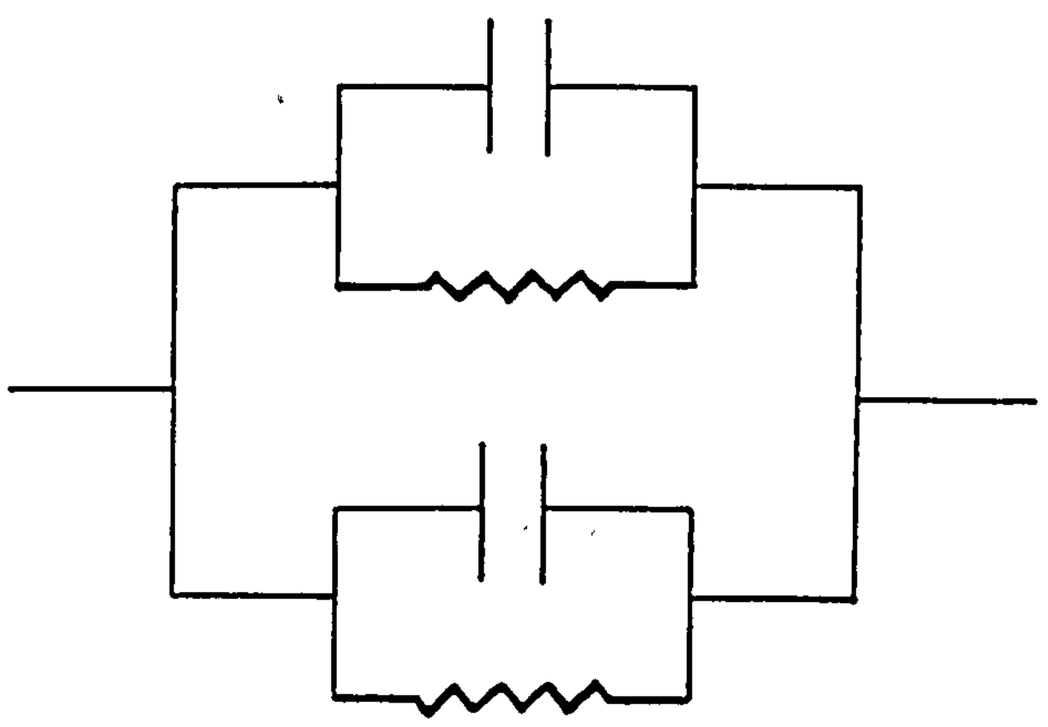


Fig 4.1b: Equivalent circuit for the system shown in Fig 4.1a.

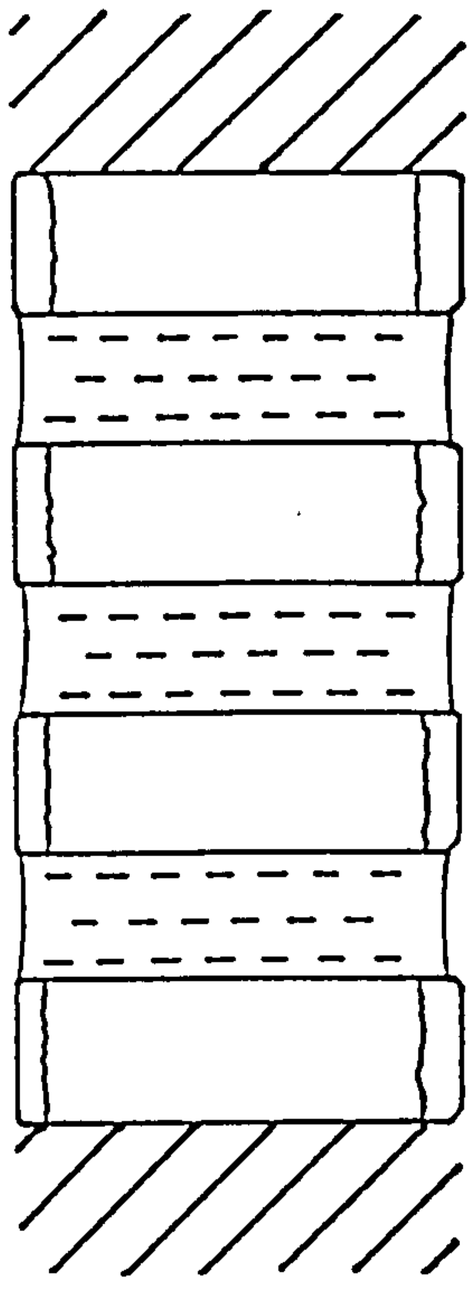


Fig 4.2a: Schematic diagram of a porous cellulose acetate membrane with hydrated surface layers and pores filled with an organic solvent.

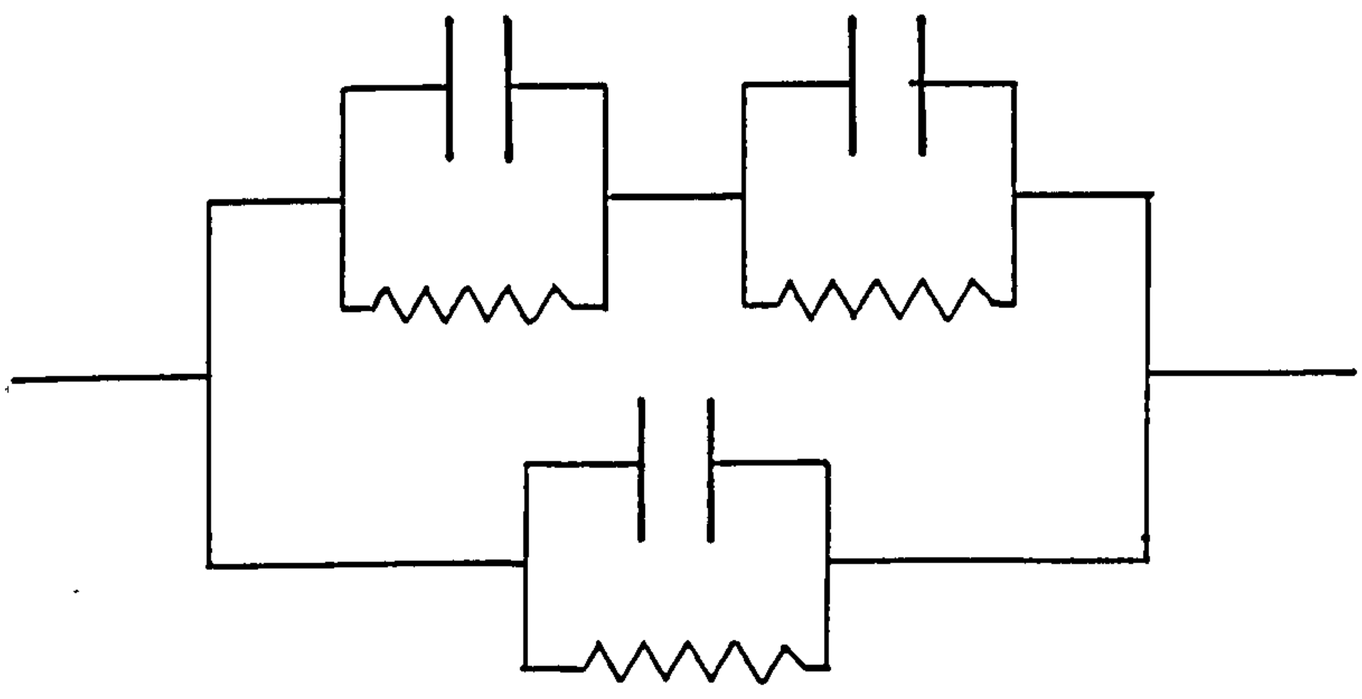


Fig 4.2b: Equivalent circuit for the system shown in Fig 4.2a.

thickness and its capacitance will decrease, whereas the resistance of the unhydrated bulk region will decrease, and its capacitance will increase with time. To assign absolute values to these effects is very difficult, as the magnitude of each change depends on the extent to which the cellulose acetate swells on hydrating, the resistivity of the hydrated layer compared to that of the dry acetate, and the actual thickness of the hydrated layer. It is likely that the time constants for all three processes will be sufficiently close for it to be difficult to resolve the separate features in the complex plane plot. As a result, it is unlikely that detailed information about this aspect of the membrane structure can be obtained from impedance measurements.

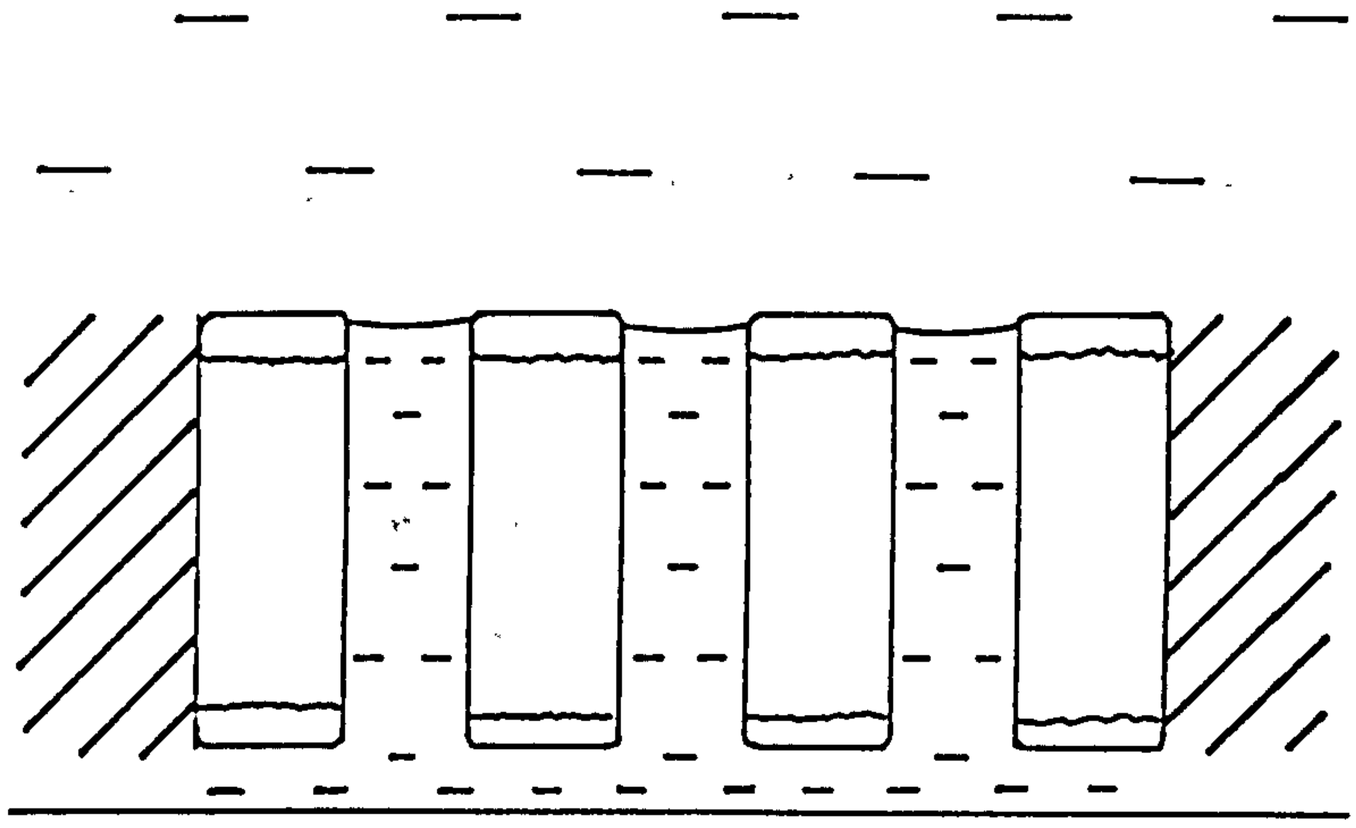
A further complication could also arise from the fact that the vertical orientation of the membrane cell is likely to give rise to a layer of nitrobenzene solution on the underside of the filter (Fig 4.3), which would further affect the impedance of the R_1/C_1 network representing the nitrobenzene phase, although the equivalent circuit would probably still be similar to that shown in Fig 4.2b.

The general predictions of this model are as follows:

i. If hydration of the membrane support does occur, then it is likely that this will be evident in the impedance behaviour of the membrane. Due to the thickening of the membrane as a whole, the most easily identifiable effect on the membrane impedance will be an increase in the total membrane resistance.

ii. In view of the complicated nature of the equivalent circuits discussed above, it is unlikely that all (if any) of the processes associated with swelling of the membrane will be separately identifiable, and that the abovementioned increase in

Fig 4.3: Schematic diagram of a horizontally-orientated porous cellulose acetate membrane with hydrated surface layers and pores filled with an organic solvent.



resistance will be the only result of this effect which can be clearly detected from the complex plane impedance plot.

Considering the membrane-solution interfaces, the expected impedance behaviour depends solely on the extent to which charge transfer across the interface occurs. If the interface acts in the same way as a classical blocking electrode and no ions can traverse the boundary between the two phases, then the interface should appear as a pure capacitor in the impedance plot. If the passage of ions does occur to any extent however, the charge transfer processes will manifest themselves as a parallel network as discussed in Chapter 1.

4.4 Results of Measurements on Membranes Comprising 2,3-DMNB Alone

Results of both potentiometric and impedance measurements on pure solvent (2,3-dimethylnitrobenzene) are given in this section.

The resistance of the pure solvent membranes is sufficiently large to be at the limit of the range of the FRA. As a result of this, it would be unwise to attempt a highly detailed analysis of the data for these membranes, as these results are inevitably subject to larger errors than would be present with systems possessing a lower resistance, although interpretation of the data in general terms can yield useful information.

4.4.1 Potential Response

The potential response of the membranes containing no valinomycin was not studied in detail, however several

electrodes were fabricated for the purpose of limited potential measurements, and single-ion responses were measured with KCl solutions. The reference electrode used for the potential measurement was a saturated calomel electrode with a 3 mol dm^{-3} tetramethylammonium chloride salt bridge.

The response of the pure solvent membranes was found to be poor, with slopes of only 30-35 mV/decade over the range 10^{-1} - 10^{-3} mol dm^{-3} KCl. Handyside (4.9) reported a wide range of slopes for pure solvent membranes, and found an apparent dependence on the type of experimental arrangement used. It was suggested that the controlling factor in the absence of valinomycin is the extent to which the support material can provide negative sites to achieve good anion exclusion, although a high degree of variability was reported.

4.4.2 Impedance Measurements

Figs 4.4a and 4.4b show typical steady-state impedance plots obtained for membranes contacted by 0.1 mol dm^{-3} KCl, after three days. Fig 4.4a shows a plot obtained using the two-electrode cell connected to the 1174 alone and Fig 4.4b shows the continuation of this run down to a low frequency using the 1186 coupled to the 1174 in a four-electrode configuration. The apparent difference in bulk resistance between the two runs is due to the time dependence discussed below, there being a necessary time delay between the commencement of the high frequency runs and the low frequency run. Fig 4.5 shows a complete spectrum obtained for a membrane contacted by 0.1 mol dm^{-3} NaCl. In both cases, the magnitude of the bulk impedance is sufficiently high to exceed the range of the FRA, although

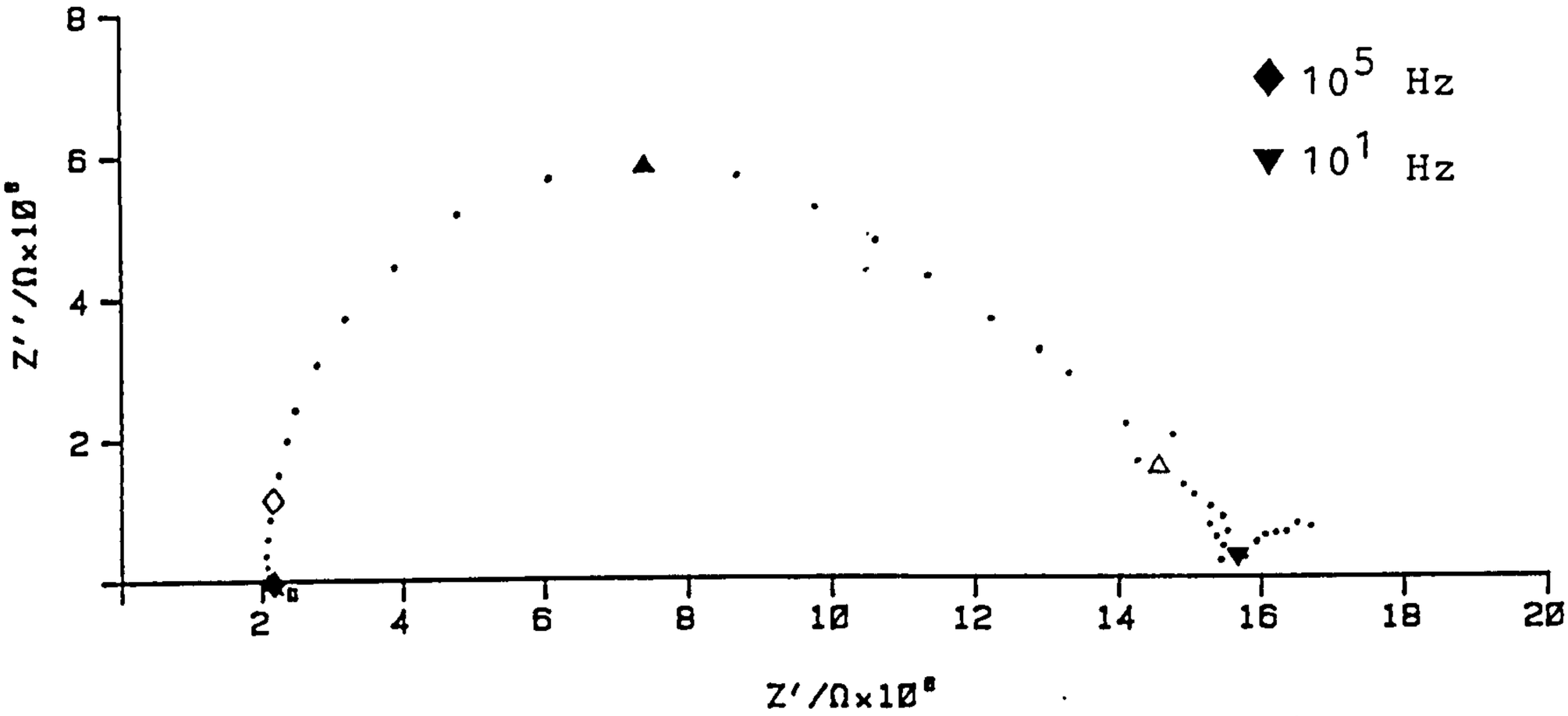


Fig 4.4a: Two-electrode Impedance spectrum for a pure 2,3-DMNB membrane contacted by 0.1 mol dm^{-3} KCl solutions.

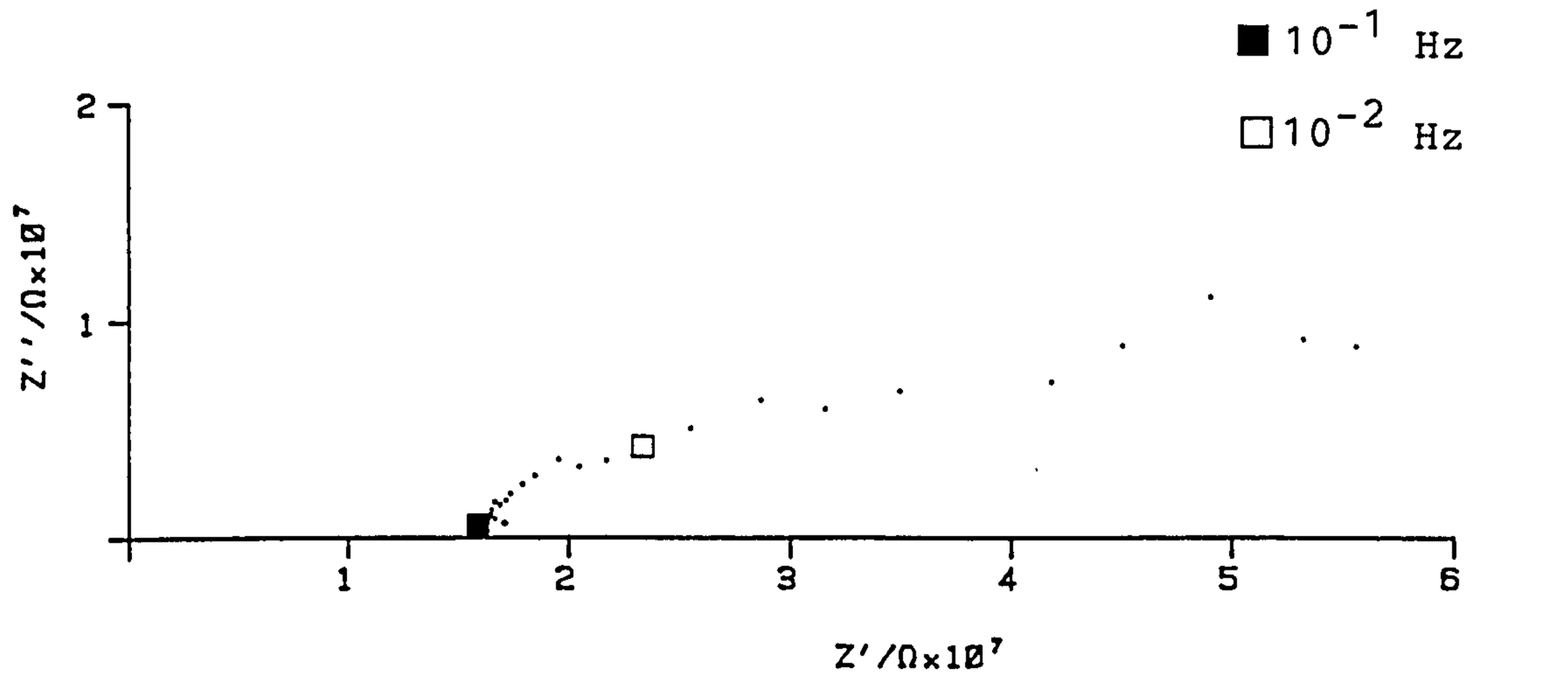


Fig 4.4b: Four-electrode Impedance spectrum for a pure 2,3-DMNB membrane contacted by 0.1 mol dm^{-3} KCl solutions.

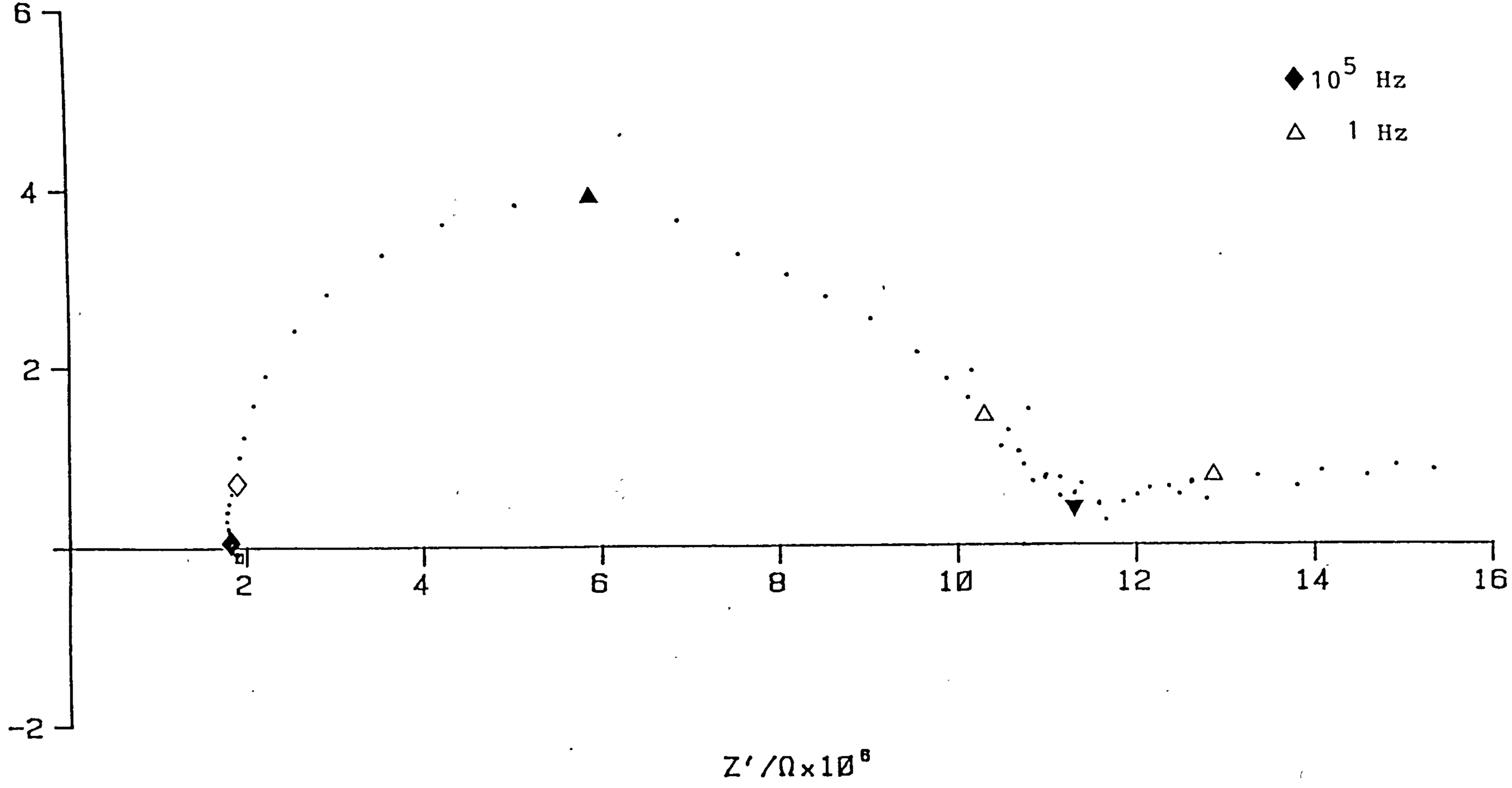


Fig 4.5: Composite spectrum (two- and four-electrode) for a pure 2,3-DMNB membrane contacted by 0.1 mol dm^{-3} NaCl solutions.

the use of the 1186 coupled to the 1174 allows measurements to be made beyond the normal range of the 1174 alone. Using this facility and a four-electrode configuration, the impedance of the membrane system could be followed until a steady state was reached. This also allowed the low frequency behaviour of the membranes to be recorded, although as can be seen, Figs 4.4 and 4.5 show that the low frequency regions of the spectra are not well defined.

From Figs 4.4 and 4.5, it can be seen that there are two main features in the impedance spectrum (apart from the solution resistance), a feature at higher frequencies which is attributable to the membrane bulk and one at lower frequencies which can be attributed to the processes occurring at the membrane/solution interface. It is apparent that the time constants for the separate regions present in the bulk membrane are very similar as suggested in section 4.3, and that resolution of the bulk membrane features into separate semicircles is not possible. In view of this, no definite conclusion can be drawn concerning the exact structure of the bulk membrane, as discussed above. It is reasonable, however, to take the point where the impedance locus returns to the real axis as representing the total membrane resistance and on this basis several conclusions can be drawn.

For both the membranes contacted by KCl, and those contacted by NaCl, there is an increase in the total bulk resistance with time, and this supports the suggestion proposed in section 4.3, that hydration of the membrane support material occurs, possibly with other associated processes which cannot be resolved from the impedance data.

From the very high bulk resistance, it can be concluded that

the pure solvent membrane contains few free charge carriers, even after equilibration with the aqueous solutions. If there were any appreciable level of charge-carrying species within the membrane, the bulk resistance would be expected to be several orders of magnitude lower. The idea that there are few charge carriers present within the membrane is also supported by the low frequency data, from which it can be seen that the charge transfer resistance is very high, with both K^+ and Na^+ as the cationic species in the aqueous solutions. This indicates that the exchange current for the transfer of both sodium and potassium across the membrane solution interface is very low, and that little exchange (if any) is occurring either initially, or after the equilibration period. This result is in agreement with Shoami et al. (4.10), who found that the energetics of ion transfer for alkali metal ions from aqueous solutions to an organic medium, such as nitrobenzene derivatives, is very unfavourable and that such transfer is unlikely to take place.

4.5 Results of Measurements On Membranes Containing Valinomycin

Membranes were fabricated as previously, but with concentrations of valinomycin of 0.009 mol dm^{-3}, 0.0045 mol dm^{-3}, 0.002 mol dm^{-3} and 0.0009 mol dm^{-3} (0.009 mol dm^{-3} being the concentration used by Pioda et al (4.5) in their original work on valinomycin-based liquid membranes). For all the membranes, the single- and mixed-ion responses were assessed, and the cell impedance was measured at regular intervals over a period of time, to establish the time-dependence of the equivalent circuit parameters. Results of these measurements are given in separate sections below.

4.5.1 Potential Response

The K^+ single-ion response of the membranes containing valinomycin was investigated using a saturated calomel reference electrode and a tetramethylammonium chloride bridge, and similar results were found for all concentrations of valinomycin used. The membranes showed slopes of approximately 55mV/decade over the range 10^{-2} - 10^{-4} mol dm^{-3} KCl as found by Handyside (4.9).

The mixed-ion response of the membranes containing valinomycin was also investigated with 0.1 mol dm^{-3} NaCl interferent, and although the slopes of the potential vs log(K^+) plots were poorer than for the calibration plots, the mixed-ion response was still found to be quite good over a limited range (55mv/decade over the range pK^+ 1.5 - 3.5).

4.5.2 Impedance Measurements On Membranes Contacted by KCl Solutions

Figs 4.6-4.9 show the impedance spectra obtained for membranes with valinomycin at the above concentrations, in contact with 0.1 mol dm^{-3} KCl. All the data shown are the final, steady-state spectra obtained three days after first solution contact, and Tables 4.1-4.4 show the variation of the membrane equivalent circuit parameters with time for the four different membranes.

Fig 4.6 shows the impedance spectrum taken after 72 hours for the membrane containing 0.009 mol dm^{-3} valinomycin. The spectrum shows a single semicircle at high frequency, covering the approximate range 999.9 kHz to 0.1 Hz, and in the lower-frequency region of the plot which runs down to 10^{-2} Hz a

Fig 4.6: Final steady-state four-electrode impedance spectrum for the membrane containing 0.0090 mol dm^{-3} valinomycin, contacted by 0.1 mol dm^{-3} KCl solutions.

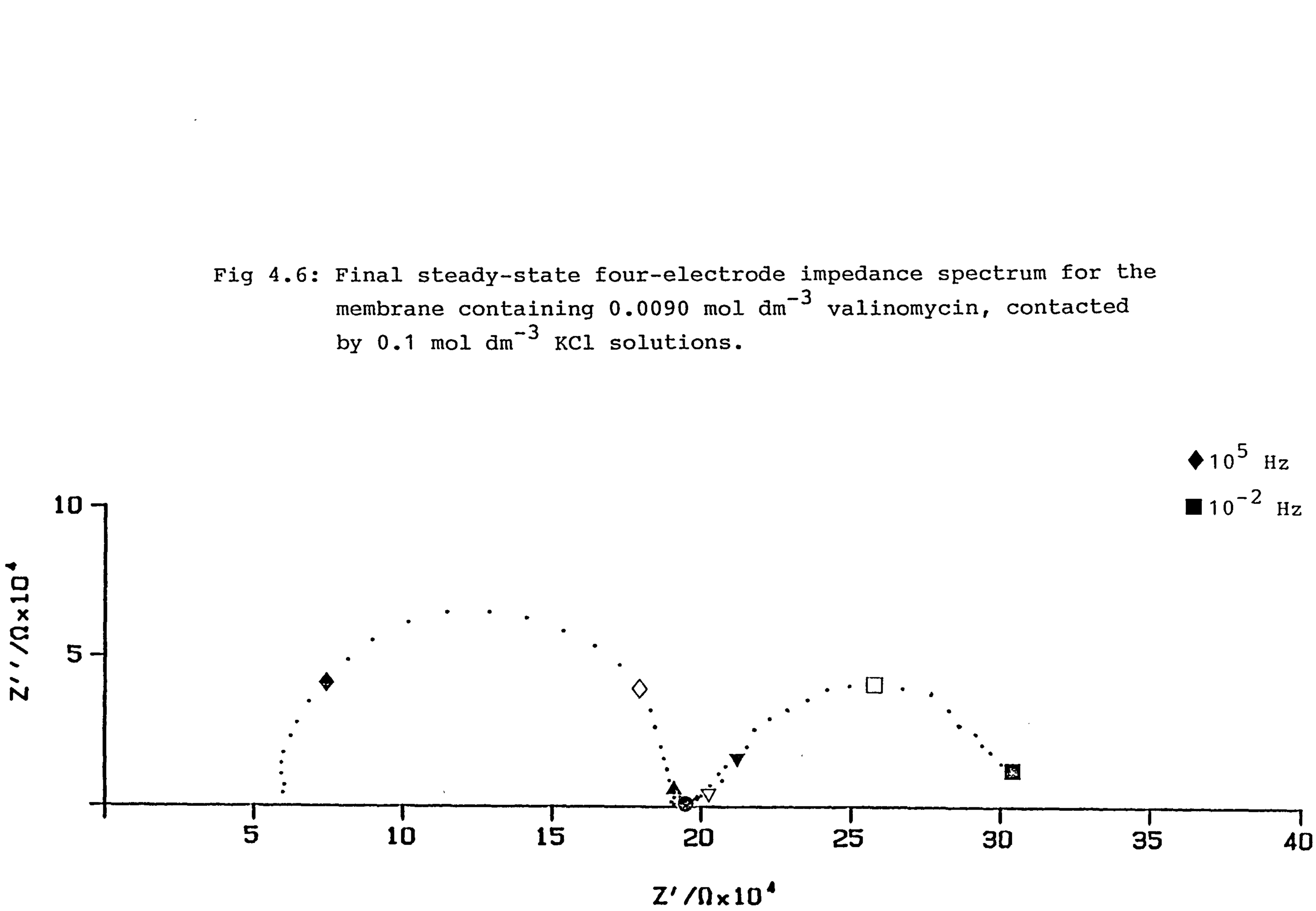


Table 4.1: Time Dependence Of Membrane Impedance For 2,3-DMNB Membrane Containing 0.009 mol dm^{-3} Valinomycin

t/hours	$R_b/10^5\Omega$	$\omega_1{}^*{}_{max}$/Hz
1	2.32	25040
2	2.18	"
3	2.09	"
4	1.94	"
5[+]	1.91	"
72	1.92	"

[+] After five hours the membrane resistance did not show any further change.

second feature is clearly visible. From the discussion in section 4.3, and the results presented in section 4.4, the high frequency feature can be identified as being due to the bulk membrane, and the lower frequency one as being due to the interfacial processes. The bulk resistance of the membrane was found to decrease with time, after contact with the aqueous solutions, and from Table 4.1 it can be calculated that the overall decrease in R_b over the 72-hour period was approximately 17%.

Fig 4.7 shows the spectrum for the second membrane, containing 0.0045 mol dm^{-3} valinomycin. This plot differs from that shown in Fig 4.6 in that a distortion is visible in the bulk semicircle, towards its low-frequency end, and also in that a second feature is visible at intermediate frequency. The low-frequency region of the spectrum is similar to the corresponding region of Fig 4.6, although the charge-transfer semicircle has a larger resistive component. As with the membrane containing 0.009 mol dm^{-3} valinomycin, a reduction in the total bulk resistance with time was found, and, as can be seen from Table 4.2, the magnitude of the reduction in this case was approximately 30%. The initial and final bulk resistance of the membrane are also higher than the corresponding values for the previous membrane.

Fig 4.8 shows the spectrum for the membrane containing 0.002 mol dm^{-3} valinomycin, which shows features similar to those exhibited in Fig 4.7, although this particular spectrum was not continued to sufficiently low frequency for the charge-transfer semicircle to be fully resolved. In this case, the bulk resistance fell by 37% from its initial value over the three-day period, and the initial and final bulk resistances were found to

Fig 4.7: Final steady-state four-electrode impedance spectrum for the membrane containing 0.0045 mol dm-3 valinomycin, contacted by 0.1 mol dm^{-3} KCl solutions.

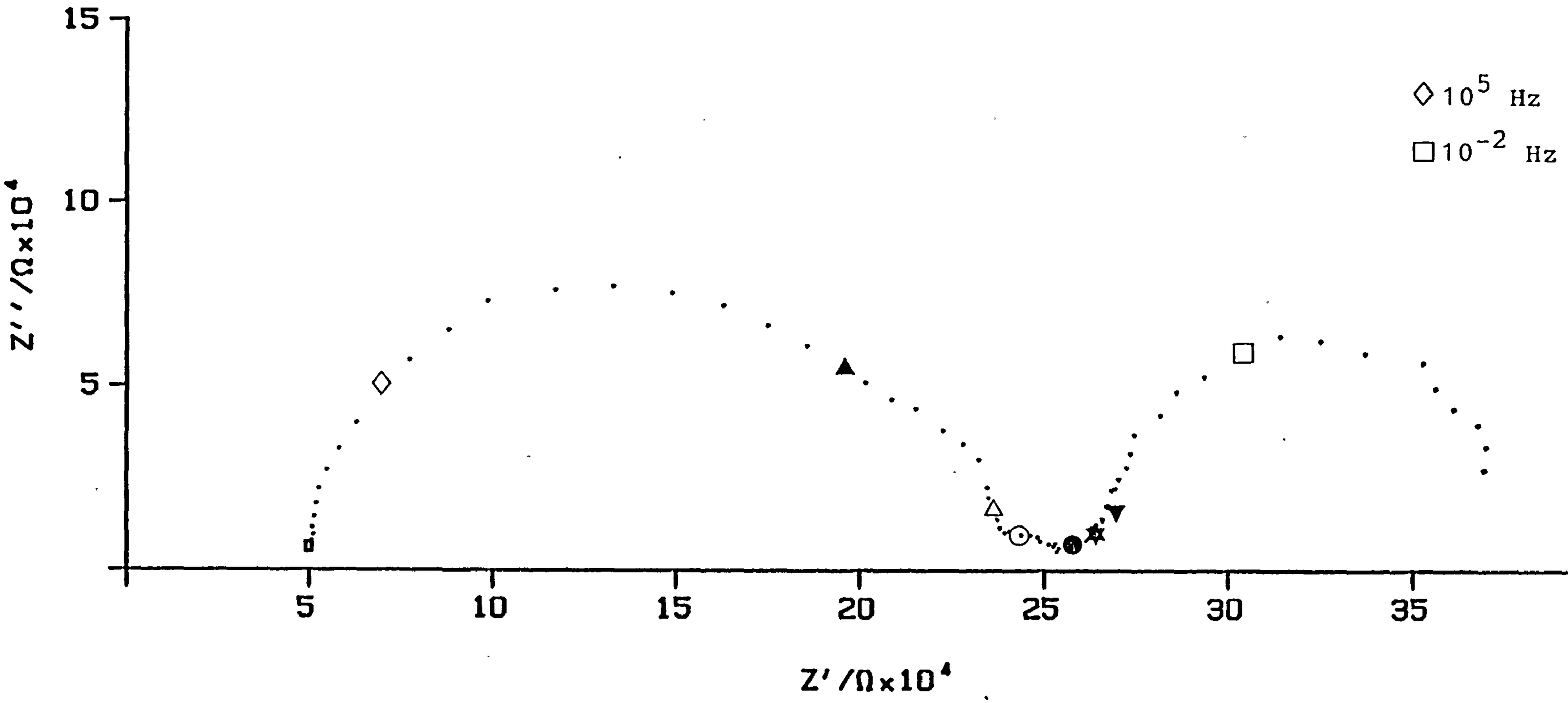


Table 4.2: Time Dependence Of Membrane Impedance For 2,3-DMNB Membrane Containing 0.0045 mol dm^{-3} Valinomycin

t/hours	$R_b/10^5\Omega$	$\omega_{1\,max}^*$/Hz
1	3.60	15780
2	3.55	"
3	3.37	"
4	3.22	"
5	3.11	"
6	3.04	"
7	2.94	"
8	2.89	"
9	2.84	"
10	2.80	"
11	2.72	"
12	2.71	"
13	2.70	"
14	2.68	"
15	2.66	"
16	2.66	"
17	2.64	"
18	2.60	31510
19	2.58	"
20	2.56	"
21	2.57	"
22	2.56	"
23	"	"
24	"	"
72	"	"

Fig 4.8: Final steady-state four-electrode impedance spectrum for the membrane containing 0.0020 mol dm^{-3} valinomycin, contacted by 0.1 mol dm^{-3} KCl solutions.

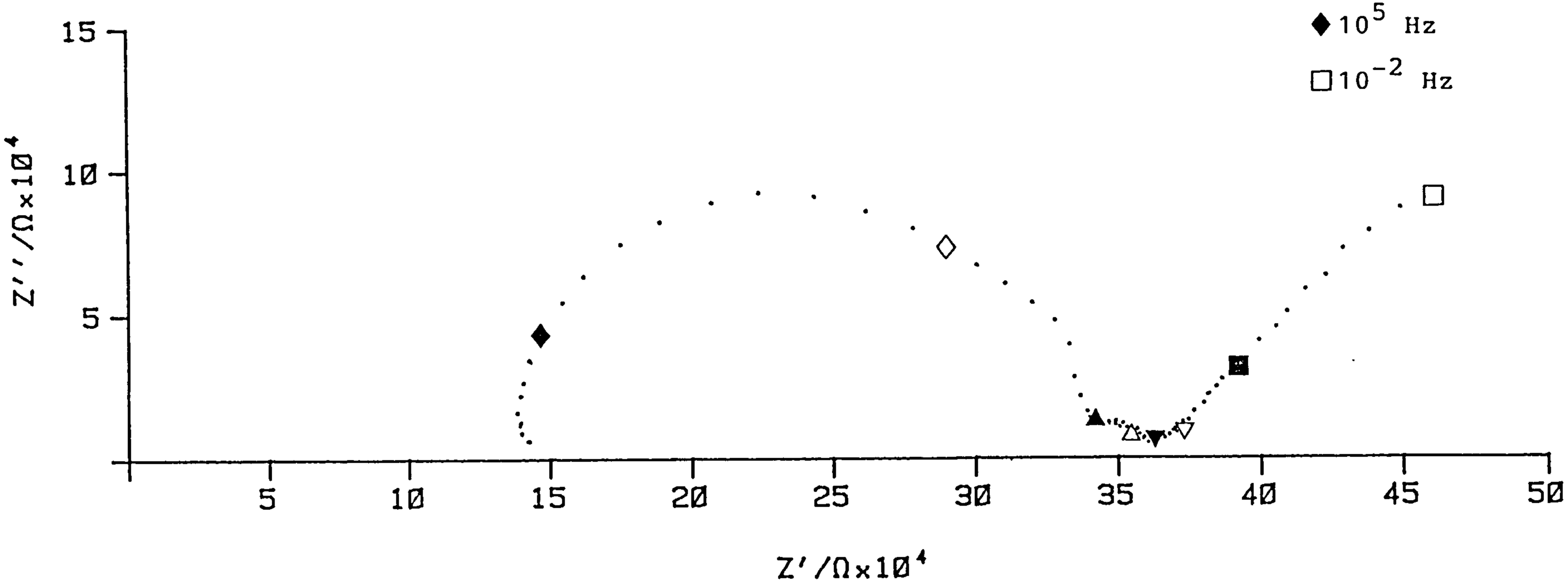


Table 4.3: Time Dependence Of Membrane Impedance For 2,3-DMNB Membrane Containing 0.002 mol dm^{-3} Valinomycin

t/hours	$R_b/10^5\ \Omega$	$\omega_{1\,max}^*$/Hz
1	5.81	15800
2	4.96	"
3	4.91	"
4	4.67	"
5	4.47	"
6	4.38	"
7	4.29	"
8	4.14	"
9	4.05	"
10	3.93	"
11	4.01	"
12	3.87	"
13	3.59	25040
14	3.80	"
15	3.74	15800
16	3.65	"
17	"	"
18	3.62	"
19	3.59	"
20	3.56	"
21	3.50	"
22	"	"
23	"	"
24	"	"
72	"	"

be greater than for both the previous two cases.

Fig 4.9 shows the spectrum for the membrane containing 0.0009 mol dm^{-3} valinomycin. Similar features are present in this plot as found with the previous two membranes, and the bulk resistance was again found to decrease with time. The percentage decrease in R_b was found to be 37%, as for the membrane containing 0.002 mol dm^{-3} valinomycin, although the initial and final bulk resistance values were higher than for all the other membranes. The value of the charge-transfer resistance is also clearly much greater for this membrane. These results are discussed below.

4.5.2a <u>High Frequency Features: The Bulk Membrane</u>

The bulk resistance values obtained for the membranes in contact with 0.1 mol dm^{-3} KCl solutions are summarised in Table 4.5. These data show several interesting features, from which a number of conclusions may be drawn.

Firstly, these results show that there is a decrease in bulk resistance with time for all the membranes studied. This is in complete contrast to the membranes which contained no valinomycin, which showed an increase in R_b with time. From the data presented in this section, for the membranes containing the ionophore, it seems to be the case that the increase in R_b which is exhibited by the blank membranes is offset completely by a decrease due to the uptake of potassium into the membrane, completely masking the geometrical effects.

A second interesting aspect of the variation of the bulk resistance with time, is the fact that as the concentration of valinomycin in the membrane was reduced, the percentage decrease

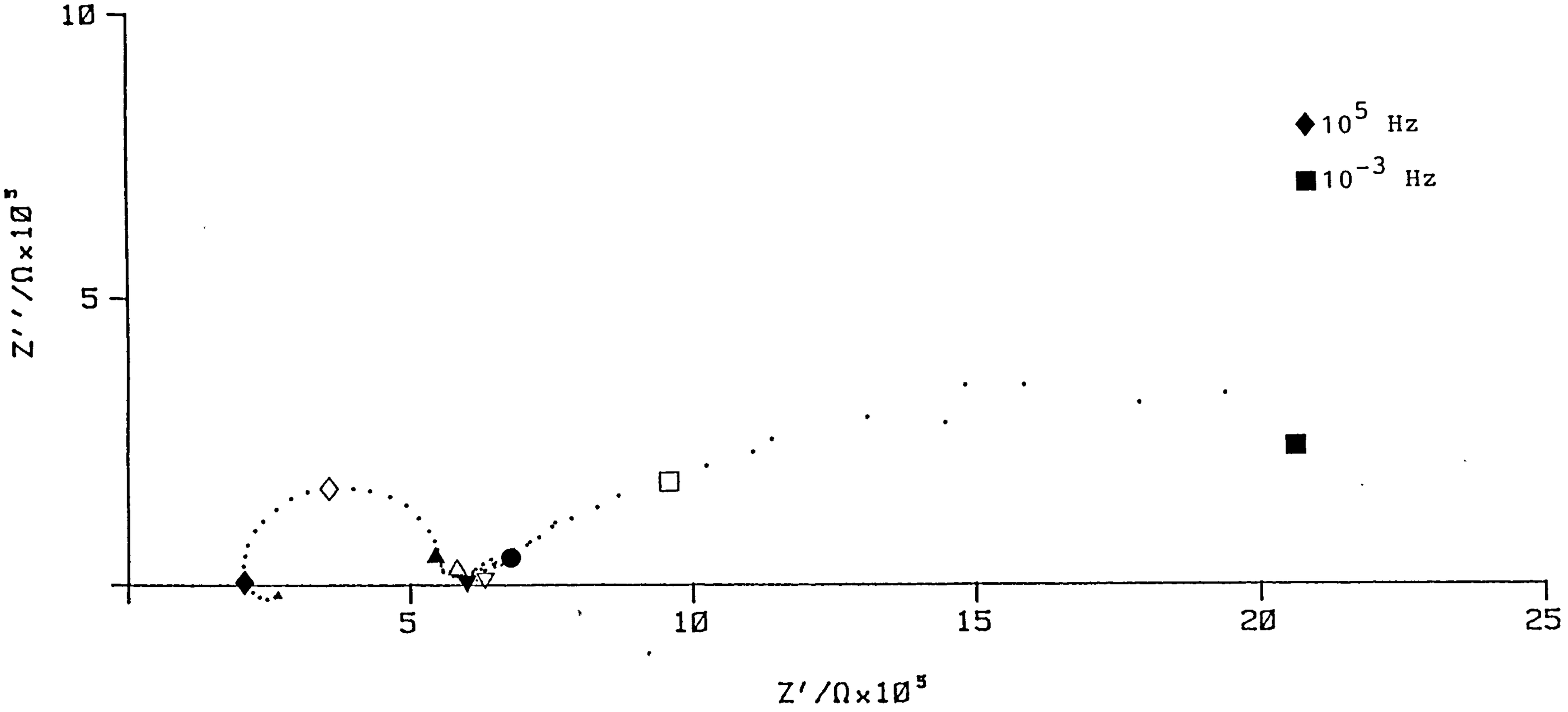


Fig 4.9: Final steady-state four-electrode impedance spectrum for the membrane containing 0.0009 mol dm^{-3} valinomycin, contacted by 0.1 mol dm^{-3} KCl solutions.

Table 4.4: Time Dependence Of Membrane Impedance For 2,3-DMNB Membrane Containing 0.0009 mol dm^{-3} Valinomycin

t/hours	$R_b/10^5\ \Omega$	$\omega_{1\ max}^*$/Hz
1	8.52	9980
2	6.69	"
3	6.01	"
4	5.63	"
5	5.48	"
6	5.39	"
7	5.37	"
8	5.32	"
9	5.28	"
10	5.28	"
11	5.27	"
12	"	"
13	"	"
14	"	"
15	"	"
16	"	"
17	"	"
18	"	"
19	"	"
20	"	"
21	"	"
22	"	"
23	"	"
24	"	"
72	"	"

Table 4.5: Summary of Initial and Final, Steady-State Bulk Resistance Values For 2,3-DMNB Membranes Contacted By 0.1 mol dm^{-3} KCl Solutions

Val	Relative [Val]	$R_b$init/Ω	$R_b$fin/Ω	% Decrease	Rel. $R_b$init	Rel. $R_b$fin
0.0090	10.0	2.3 x10^5	1.9 x10^5	17	1.0	1.0
0.0045	5.0	3.6 x10^5	2.5 x10^5	30	1.6	1.3
0.0020	2.2	5.8 x10^5	3.6 x10^5	37	2.5	1.9
0.0009	1.0	8.5 x10^5	5.3 x10^5	37	3.7	2.9

in R_b became greater. This seems to indicate that the higher the valinomycin concentration, the faster the membrane reaches equilibrium with the aqueous solutions, so that with the highest concentration, the equilibration process was largely complete when the first impedance measurements were made. This is also supported by the fact that the time taken to reach equilibrium with the contacting solutions increased with decreasing valinomycin concentration. The exception to these observations was the membrane with the lowest valinomycin concentration, which showed a percentage reduction in R_b similar to that of the membrane with approximately double the concentration of valinomycin, although the final bulk membrane resistance was reached more quickly than with the next highest valinomycin concentration. A likely explanation for this anomaly, is that with the lowest concentration of valinomycin, the inherent increase in R_b shown by the membranes in the absence of the ionophore is not completely masked, resulting in the percentage reduction in R_b being less than expected. This would also result in the equilibrium with the aqueous solutions appearing to be reached in a shorter time.

Finally, it can be seen that as the concentration of the valinomycin in the membrane is reduced, both the initial and final bulk resistance of the membrane become larger. The initial and final values for R_b are shown plotted against the concentration of valinomycin in the membrane, in Fig 4.10a, and Fig 4.10b shows $\ln (R_b)$ vs. the valinomycin concentration. From these plots, it is clear that no simple relationship holds between these two variables, which is perhaps not surprising when the complexity of the membrane structure is considered. The fact that there is a decrease in bulk resistance with

Fig 4.10a: Variation of Rb with Valinomycin concentration for membranes contacted by 0.1 mol dm^{-3} KCl solutions.

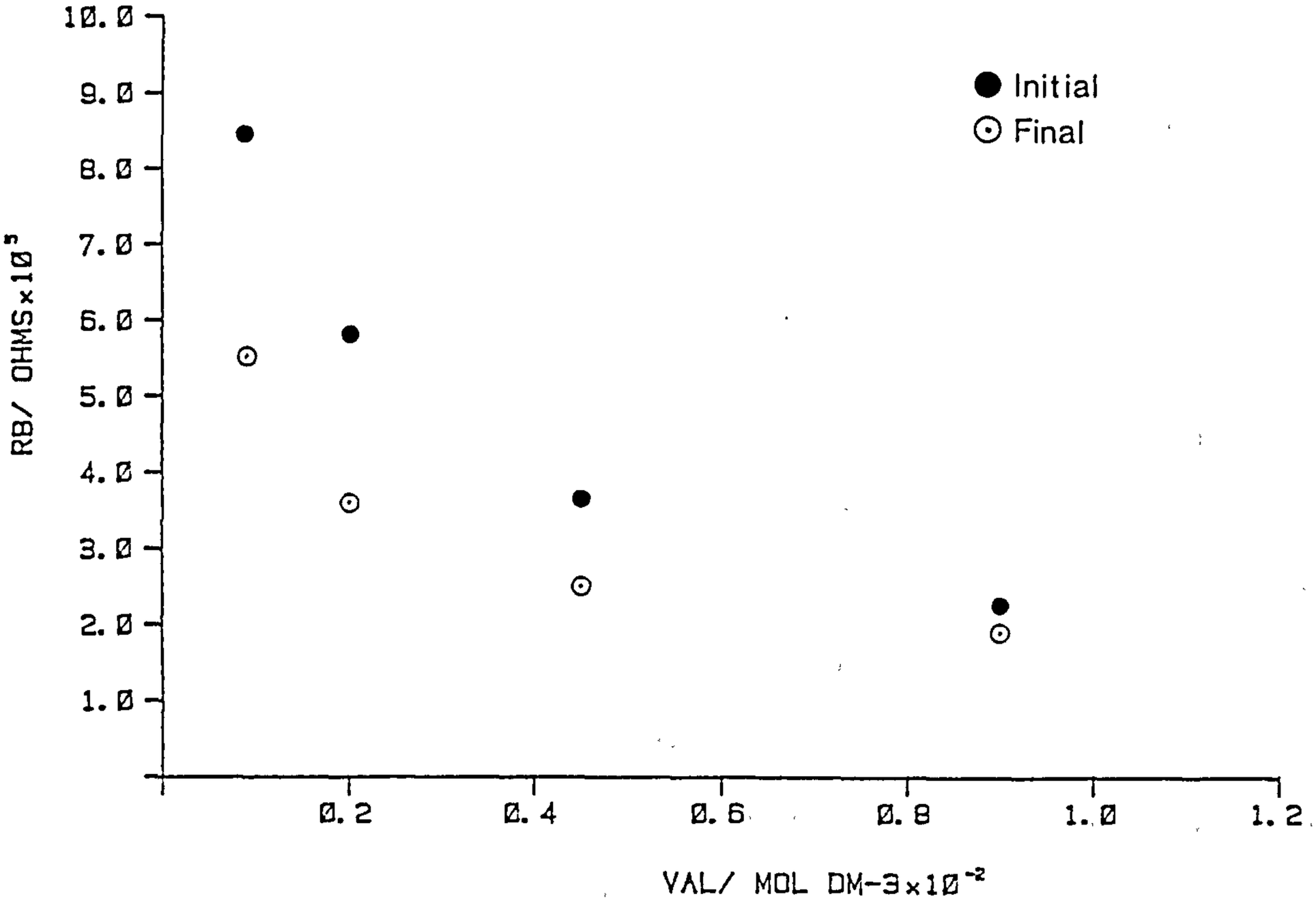
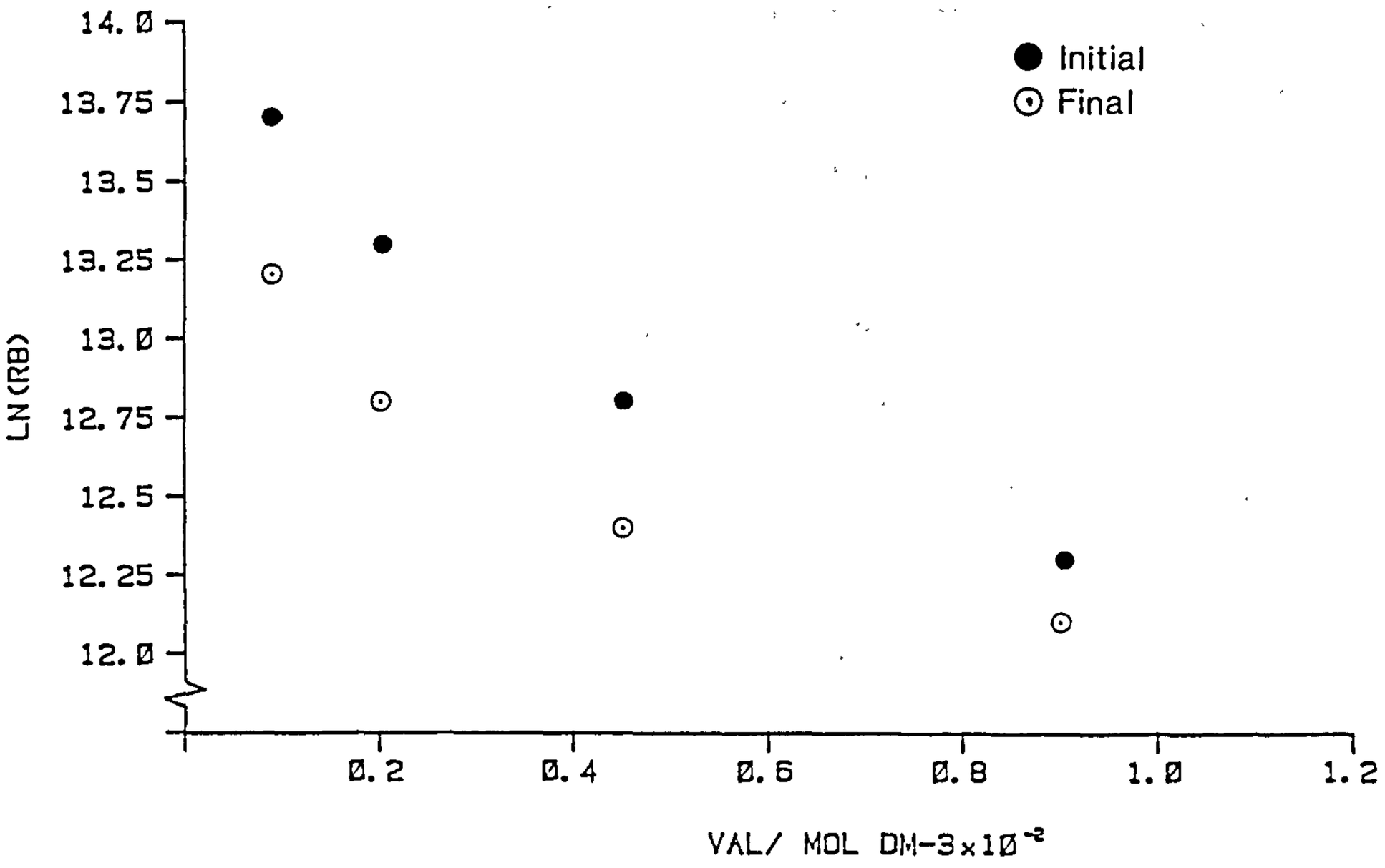


Fig 4.10b: Variation of Ln(Rb) with valinomycin concentration for membranes contacted by 0.1 mol dm^{-3} KCl solutions.



increasing valinomycin concentration can be explained on the basis of the assumption that the greater the valinomycin concentration, the more potassium can enter the membrane, and therefore, a larger number of charge carriers are present. It would be expected that the R_b values would approach a limiting value similar to the value obtained for the membranes containing no valinomycin, and this appears to be the case from Fig 4.10a. It is possible that the apparent non-linearity of the relationship between R_b and the concentration of the valinomycin is due to the geometric effects cancelling out or being insufficiently masked by the decrease due to potassium uptake.

The nature of the separate bulk membrane features which are manifest at high frequencies in the membranes with all but the highest valinomycin concentration, can be explained by the model proposed in section 4.3. The question of which of these features in the impedance plot relates to which of the bulk membrane phase regions, is not easy to resolve. Fig 4.11a shows the impedance spectrum for the membrane containing 0.0045 mol dm^{-3} valinomycin as measured after 24 hours, with a possible fit of three semicircles to the experimental data. A theoretical plot for three parallel networks in series is shown in Fig 4.11b, but, as suggested in section 4.3, it is possible that the equivalent circuit consists of two parallel networks in series which are in parallel as a whole with a third network (Fig 4.2b).

Further, detailed, analysis of the structural implications of these data is not practical beyond assigning time constants to the three processes identified, due to the uncertainty in the membrane thickness when in the cell and the amount of the membrane surface area associated with each region.

Fig 4.11a: Visual fit for three semicircles to Fig 4.7.

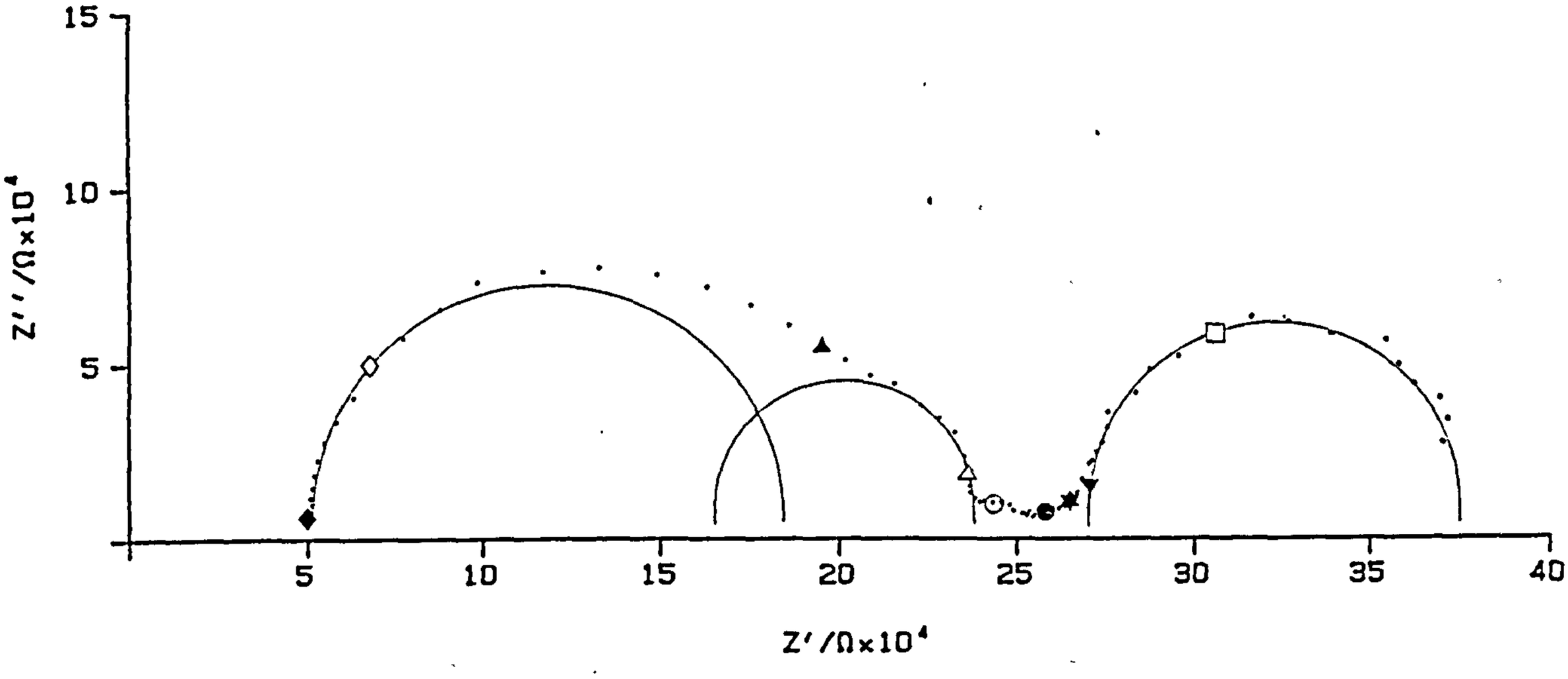
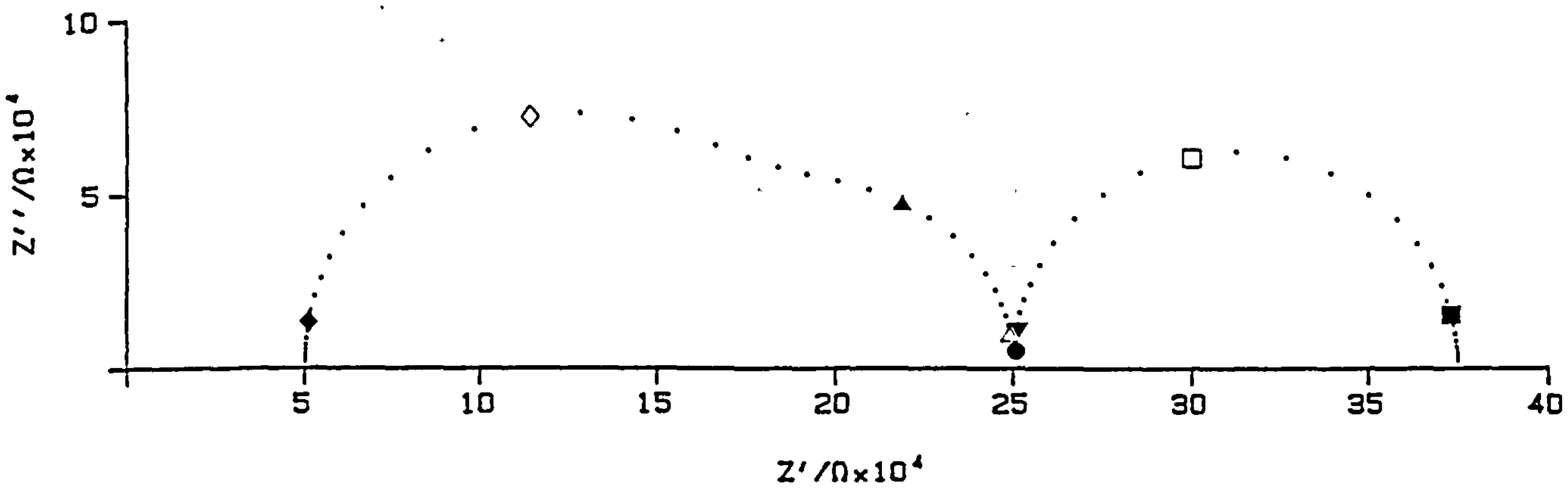


Fig 4.11b: Theoretical impedance locus for the equivalent circuit calculated for Fig 4.7.



Theoretically, the dielectric constant for each region can be calculated from the following equation,

$$E = \frac{Cl}{E_o A} \qquad 4.1$$

where E is the dielectric constant of the medium, E_o is the permittivity of free space, C is the measured capacitance, l is the membrane thickness, and A is its' area, but without detailed knowledge of l and A, calculations are of little use.

Time constants for the various processes shown in Fig 4.11 are given in table 4.6.

4.5.2b Low Frequency Features: Interfacial Processes

As discussed in the previous section, there is a low frequency structure present in all the spectra for all four membrane types, and this can be related to the interfacial processes. Fig 4.6 shows that the charge-transfer resistance for the membrane with the highest valinomycin concentration is approximately 10^5 ohms. For the membrane with 0.0045 mol dm^{-3} valinomycin, the value is larger, approximately 1.2×10^5 ohms.

For the two membranes with lower valinomycin concentrations, the charge transfer resistance is much larger. For the membrane containing 0.002 mol dm^{-3} valinomycin, the region is less well defined, but the value is evidently larger than for the two higher concentrations. For the lowest concentration R_{ct} has increased to a value of approximately 1 Mohm.

Table 4.7 gives a summary of the measured R_{ct} values obtained from these four plots, and the data are shown graphically in Fig 4.12.

Table 4.6: Equivalent Circuit Parameters for Fig 4.11b

R/Ω	C/F
1.30×10^{5}	1.25×10^{-10}
7.00×10^{4}	2.00×10^{-9}
1.25×10^{4}	1.50×10^{-6}

Table 4.7: Summary of Final, Steady-State R_{ct} Values for 2,3-DMNB Membranes Containing Valinomycin Contacted By 0.1 mol dm^{-3} KCl Solutions

[Val]	Ratio Val.	R_{ct}fin/Ω	Rel. R_{ct}fin/Ω
0.0090	10	1.0×10^5	1
0.0045	5	1.2×10^5	1.2
0.002	2.2	5.0×10^5	5.0
0.0009	1	$>1.0 \times 10^6$	10.0

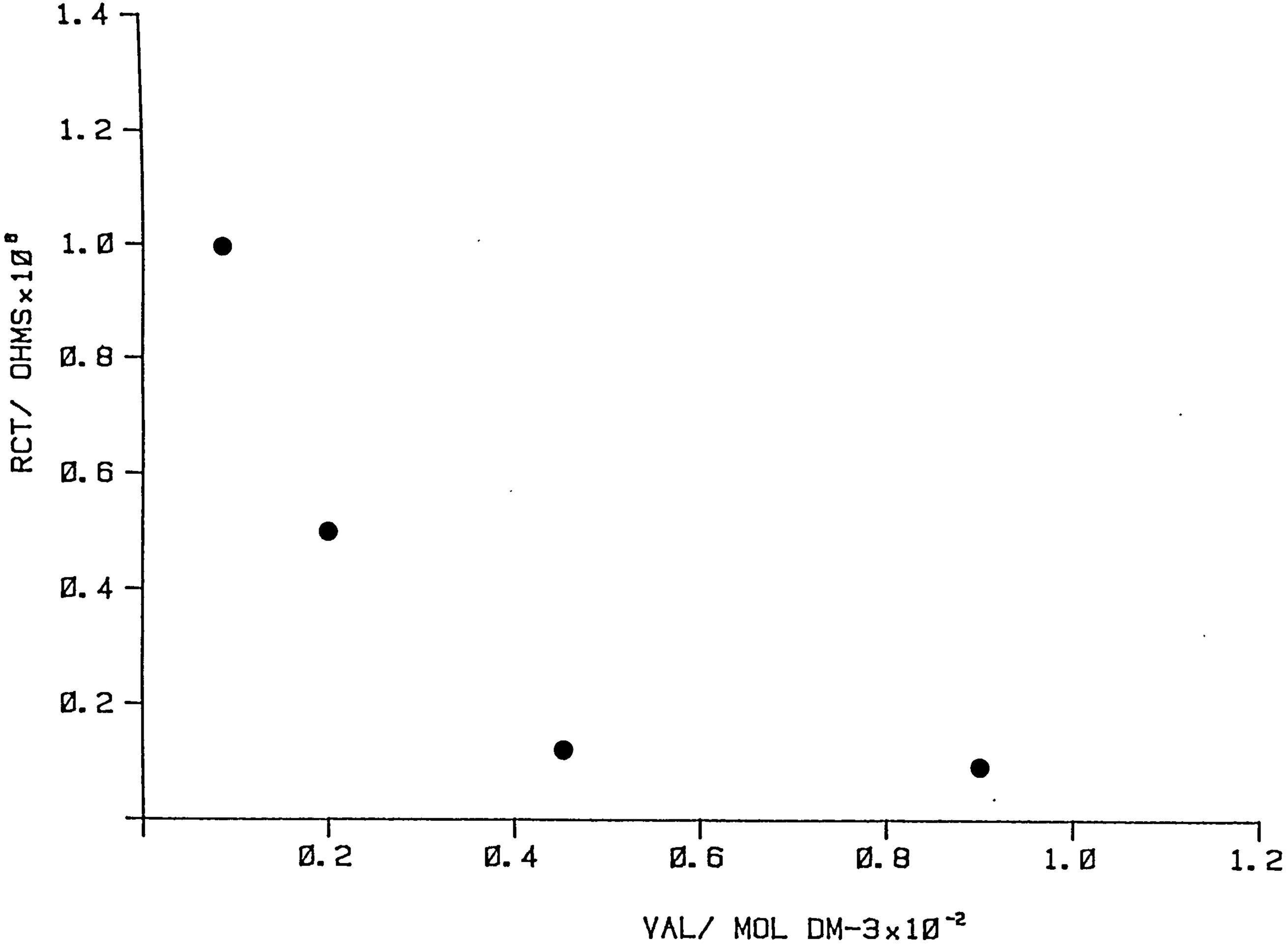


Fig 4.12: Variation of Rct with valinomycin concentration for membranes contacted by 0.1 mol dm^{-3} KCl solutions.

As might be expected, increasing the valinomycin concentration in the membrane appears to increase the rate at which charge transfer occurs across the membrane-solution interface, and, in fact, it is apparent that a tenfold increase in valinomycin concentration results in a tenfold increase in the exchange current, and a simple linear relationship holds. The fact that the R_{ct} value for the 0.0045 mol dm^{-3} membrane is not exactly twice that of the 0.009 mol dm^{-3} membrane can reasonably be put down to experimental error. These results are discussed further in the final summary presented in section 4.8

4.5.3 Impedance Measurements On Membranes Contacted by NaCl Solutions

In addition to the measurement of the potentiometric response of the 2,3-dimethylnitrobenzene/valinomycin membrane and investigation of its impedance behaviour in contact with solutions of the primary ion, a series of experiments was performed to establish the impedance of the system when in contact with solutions of the interferent ion, sodium, alone.

Membranes were studied with two different valinomycin concentrations, corresponding to two of the membranes used for measurements with KCl contacts. The concentrations used were 0.009 mol dm^{-3} and 0.0045 mol dm^{-3} valinomycin and the membranes were contacted by 0.1 mol dm^{-3} NaCl solutions. The membranes were fabricated as previously described, and the time dependence of the cell impedance was followed as for the membranes with KCl contacts.

Figure 4.13 shows the final, steady-state spectrum recorded after three days for the membrane with the higher valinomycin

Fig 4.13: Final steady-state four-electrode impedance spectrum for the membrane containing 0.0090 mol dm^{-3} valinomycin, contacted both sides by 0.1 mol dm^{-3} NaCl solutions.

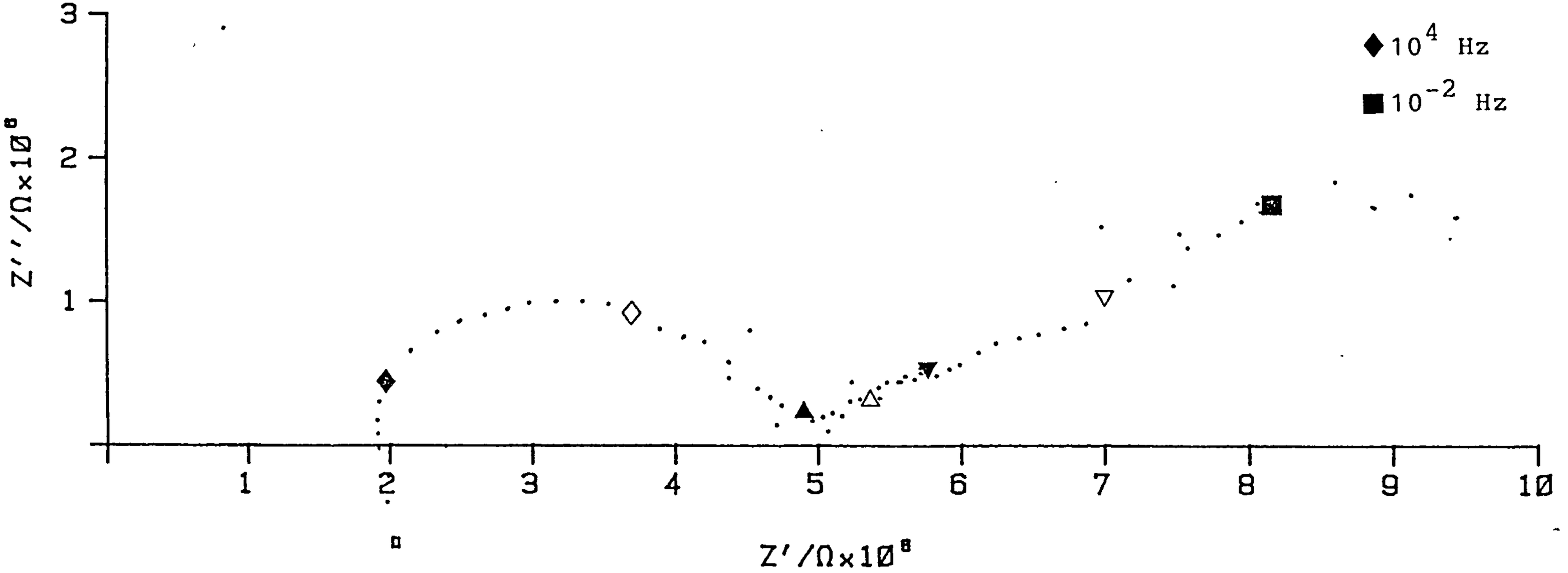


Table 4.8: Time Dependence Of Membrane Impedance For 2,3-DMNB Membrane Containing 0.009 mol dm^{-3} Valinomycin With 0.1 mol dm^{-3} NaCl Contacts.

t/hours	$R_b/10^6\Omega$	$\omega_{1\,max}^*$/Hz
1	1.88	6298
2	2.77	3971
3	3.22	"
4	3.47	"
5	3.56	"
6	3.72	"
7	3.80	"
8	3.93	"
9	4.05	"
10	4.11	"
11	4.14	"
12	4.15	"
13	4.16	"
14	4.17	"
15	4.16	"
16	4.18	"
17	4.16	"
18	4.18	"
19	4.19	"
20	4.20	"
21	4.19	"
22	4.20	"
23	4.20	"
24	4.21	"
72	4.50	"

concentration, and Fig 4.14 shows the corresponding spectrum for the membrane containing 0.0045 mol dm^{-3} valinomycin.

The general features of the spectra for the two membranes are similar to those of the valinomycin-containing membranes when contacted by KCl solutions, a large semicircle at high frequency, and a second structure at lower frequency. These features can be interpreted in the same way as for the membranes contacted by KCl, with the high frequency feature representing the bulk membrane, and the low-frequency feature, the interfacial charge-transfer processes.

4.5.3a High Frequency Features: The Bulk Membrane

Tables 4.8 and 4.9 show the variation of the bulk resistance with time for both membranes, from which it can be seen that in contrast to the corresponding membranes contacted by KCl solutions, in both cases there is an increase in R_b with time. For the higher valinomycin concentration, the increase is of the order of 180%, and for the lower concentration, the increase is approximately 60%.

There are also other differences between these spectra and those obtained for the corresponding membranes contacted by KCl solutions. In the present case, the membrane bulk resistance is approximately one order of magnitude larger than for the situation where KCl contacting solutions were employed. This indicates that there are fewer charge carriers present within the membrane when it is contacted by NaCl. From this, it appears that ions from the NaCl solutions do not enter the membrane to such a great extent as those from the KCl, if at all.

Fig 4.14: Final steady-state four-electrode impedance spectrum for the membrane containing 0.0045 mol dm^{-3} valinomycin, contacted by 0.1 mol dm^{-3} NaCl solutions.

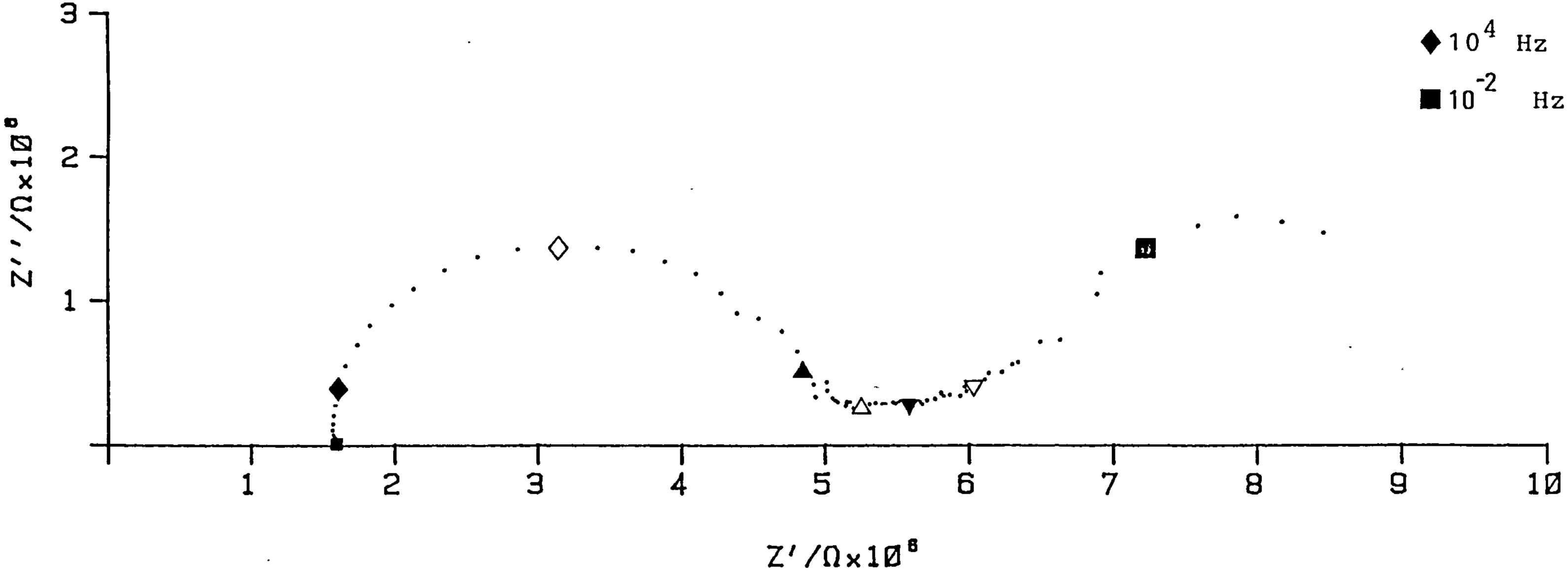


Table 4.9: Time Dependence Of Membrane Impedance For 2,3-DMNB Membrane Containing 0.0045 mol dm^{-3} Valinomycin With 0.1 mol dm^{-3} NaCl Contacts.

t/hours	$R_b/10^6\Omega$	$\omega_{1\,max}^*$/Hz
1	3.63	10^2
2	4.27	"
3	4.63	"
4	4.78	"
5	4.84	"
6	4.88	"
7	4.93	"
8	4.98	"
9	4.97	"
10	5.01	"
11	4.99	"
12	5.06	"
13	5.05	"
14	5.07	"
15	5.10	"
16	5.09	"
17	5.10	"
18	5.10	"
19	5.11	"
20	5.12	"
21	5.06	"
22	5.11	"
23	5.12	"
24	5.12	"
72	5.08	"

The increase in bulk resistance is similar to that found for membranes containing no valinomycin, but it is not clear why one membrane should experience a much larger increase relative to its initial resistance than the other. It is possible, however, that trace impurities of potassium in the sodium chloride solutions could affect the results for these membranes, although every effort was made to exclude potassium from the cells.

The membrane with the higher valinomycin concentration shows a lower bulk resistance, as was found for the membranes contacted by KCl, although in this case, the resistance of the membrane is still much higher than the corresponding membrane when contacted by KCl solutions. In the latter case, this reduction in resistance was attributed to the presence of more charge carriers due to greater take-up of potassium by the membrane in the presence of a higher valinomycin concentration. If this were the case for the membrane when in contact with NaCl solutions, the charge-transfer resistance should reflect the greater rate of exchange of ions between the membrane and the aqueous phases.

4.5.3b Low Frequency Features: Interfacial Processes

For both membranes investigated, the magnitude of the charge-transfer resistance is in excess of 1×10^6 ohm. These results are similar to those found for the membranes containing no valinomycin, and in complete contrast to the results for the membranes with KCl contacts. From the high value of R_{ct}, it is apparent that the sodium ions cannot enter the membrane with any greater ease when valinomycin is present than when there is no valinomycin in the membrane, and this is as would be expected

from the relative formation constants for the two complexes concerned.

The bulk resistance is lower than for the pure solvent membrane, however, and this must be due to an increase in the number of charge-carrying species within the organic phase. In the present case where the membrane shows such a high charge-transfer resistance, it seems unlikely that this reduction is due to the uptake of sodium ions, and the fact that the membrane shows lower resistance with the higher valinomycin concentration suggests that the valinomycin itself is a possible source of charge-carriers.

4.5.4 Summary

From the above results several conclusions can be drawn. The reduction in the bulk resistance of the membrane when contacted by solutions of the primary ion agrees with results reported by Buck (4.11) who found a similar effect for nitrate-selective membranes, and would be expected for a membrane taking up charge-carrying species from solution.

From the difference in charge transfer resistance and bulk resistance for the membranes when contacted with KCl compared to when they are contacted by NaCl, it appears that the potassium can enter the membrane with much greater ease than the sodium ions. The extent to which the sodium ions are taken up by the membrane is not clearly defined, as impurities in the valinomycin or in the sodium solutions could account for the difference between the membranes containing valinomycin when contacted by NaCl and the corresponding membranes containing no valinomycin.

The ratio of the charge transfer resistances appears to reflect the selectivity of the membrane for potassium over sodium, and it seems that this can therefore be explained largely on the basis that very few ions can enter the organic phase without the aid of the neutral carrier. The carrier must act at the membrane solution/interface and allow solubilisation of the potassium in the organic phase, as is generally supposed in theoretical treatments of the liquid membrane electrodes, whilst not having any effect on the sodium ions due to the low stability of the Na^+/valinomycin complex.

The mechanism whereby the potassium is balanced electrically within the membrane is not clear. Handyside (4.9) suggested that hydration of the filter support gives rise to negative sites on the support itself, which balance the positive charge of the valinomycin complex as discussed in Chapter 3. It would seem that, from the impedance measurements, hydration of the support does occur, applying the model proposed in section 4.3, and so it is possible that this is the source of the balancing charge, although it is also possible that the valinomycin itself may introduce charge-carrying species into the membrane. Another likely source of balancing charge is from chloride ions entering the organic phase along with the potassium. If this were the case, then slopes of less than the theoretical Nernstian 59 mV/decade would be expected. From the selectivity data given, where sub-Nernstian calibration slopes were found, it seems possible that this mechanism also plays a part in the charge balancing process, although the extent to which each possible mechanism contributes to the electroneutrality cannot be precisely determined.

4.6 Membranes with Treated Millipore Filter Supports

From the impedance and potentiometric data presented above, it seems likely that both hydration of the membrane support and uptake of chloride ions from the aqueous solutions are involved in the mechanism by which the electroneutrality of the membrane interior is maintained. In view of this, attempts were made to improve the anion exclusion properties of the membrane. The commercial Orion series 92 potassium electrode incorporates a special filter support for use with the potassium liquid-membrane solution, although the precise nature of the support is unknown. It has been suggested (4.12) that the support material is pre-treated with valinomycin or with some material which would assist in the exclusion of anionic species from the membrane and consequently improve the performance.

Davidson (4.12b) attempted to treat Millipore filters with salts of the tetraphenylborate anion to improve the slope of the calibration curve for various liquid membranes with some degree of success although the results were not conclusive.

In this section, impedance spectra are reported for membranes comprising valinomycin in 2,3-dimethylnitrobenzene, with different types of support other than the Millipore filter. The supports used were the Orion Series 92 potassium-selective membrane support, and a variety of Millipore filters treated in different ways with tetraphenylborate anions.

4.6.1 Orion Valinomycin Membrane Support

The potentiometric response of the Orion potassium electrode was found to be as reported elsewhere, with a near-Nernstian

response (a slope of approximately 60 mV/ decade) over a wide range of primary ion concentrations (10^{-1} - 10^{-4} mol dm^{-3}).

The impedance spectrum of the electrode was investigated by Handyside using the standard Orion body with two electrodes. The low-frequency region of the spectra was not well defined however, and from spectra obtained for silver/silver chloride electrodes shown in section 2.8, it would appear that much of the low frequency behaviour reported previously could be attributed to the internal reference electrode and counter electrode.

Fig 4.15 shows the spectrum as measured with a four-electrode cell, which clearly shows two semicircular structures at high frequency, and there is also evidence of a third, low-frequency structure. The time dependence of this electrode in contact with KCl was similar to that found for the membranes with an untreated Millipore support, in that there is a reduction in the bulk impedance of the membrane with increasing time. Even with four-electrode measurements, the low frequency region is less well defined than for the untreated filter support electrode. The interpretation of the results is discussed with the results of measurements on the membranes with other supports in section 4.6.3.

4.6.2 Millipore Filters Treated with Tetraphenylborate Salts

Various methods were investigated for treating the filter with tetraphenylborate. These were as follows.

i. Immersion of the filter in a saturated aqueous solution of the sodium salt of the anion, followed by drying in a desiccator over silica gel.

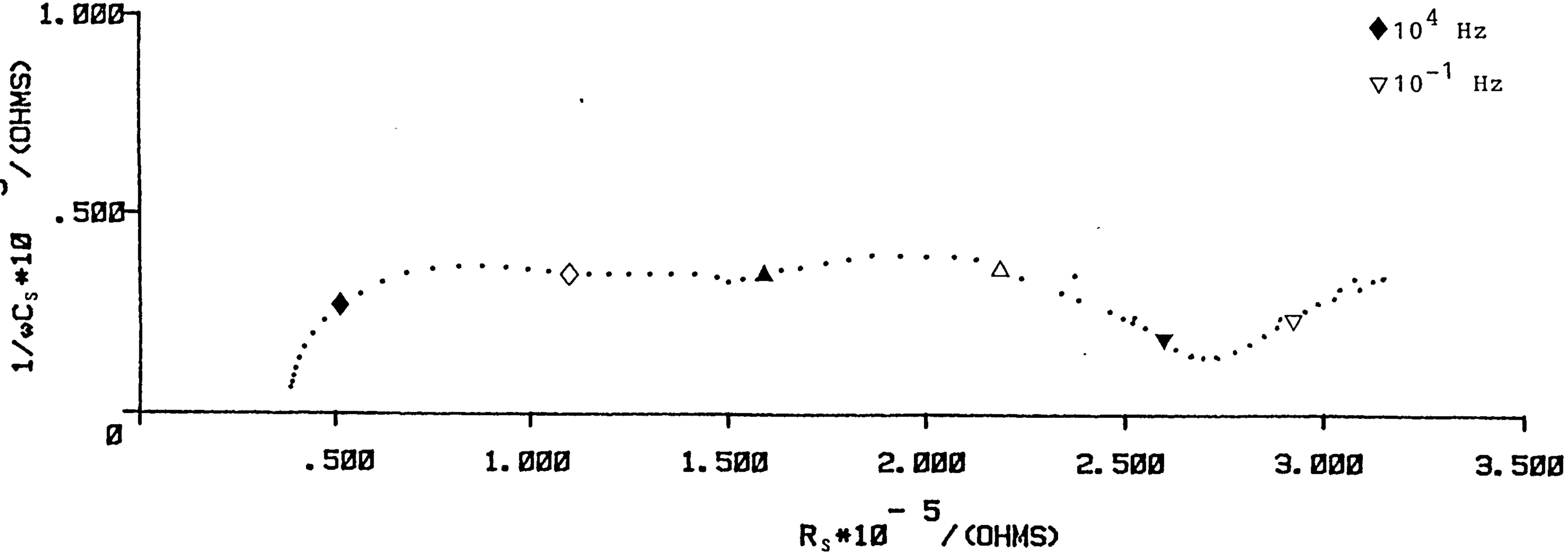


Fig 4.15: Final steady-state four-electrode impedance spectrum for a membrane containing 0.009 mol dm^{-3} valinomycin with an Orion K^+ -selective membrane filter support, contacted by 0.1 mol dm^{-3} KCl solutions.

ii. Repeated application of single drops of saturated aqueous $NaBPh_4$ solution to the filter followed by drying after the addition of each drop.

iii. Treating the filter in a similar way to that described in ii. but using a solution of the anion ten times more dilute.

iv. Treating the filter with a solution of the potassium salt of the membrane in solution in diethylether as in ii. and iii. above.

It was found that the solutions of the potassium salt caused discoloration and appeared to distort the filter. Attempts were made to fabricate electrodes using these supports but it was found that the electrodes leaked, presumably due to damage to the filters. Of the methods used for sodium tetraphenylborate treatment, it was found that the most successful method was iii. above. The other methods produced discoloured membranes which had a layer of the salt on the surface which was visible to the naked eye, and it was apparent that the solution had not permeated the filters to the same extent as for those which had been completely immersed. It appeared that the solution evaporated before the liquid had fully permeated the support. The filters which were immersed in the solution were left for 48 hours before drying, and, surprisingly there was no evidence of a surface layer of the salt.

Attempts were also made to exchange the sodium in these filters for potassium by soaking them in 0.1 mol dm^{-3} KCl solution. For the filters which had been immersed in the saturated solution of the salt, this resulted in the growth of crystalline dendrites from the membrane surface rendering the filters unusable, although using very dilute potassium solutions reduced this effect considerably. For the filters prepared

using the more dilute salt solution, better results were achieved, and the exchange did not give rise to any dendrites.

In view of these findings, only electrodes fabricated using the sodium-treated membranes were further investigated. The mixed-ion potential response of the cell after equilibration with 0.1 mol dm^{-3} KCl was found to be greatly improved by the treatment of the support material, electrodes typically showing Nernstian responses over a large concentration range similar to those found for the Orion electrode.

A typical final, steady-state impedance spectrum for a membrane with a treated Millipore support is shown in Fig 4.16. This spectrum was measured with the membrane in contact with 0.1 mol dm^{-3} KCl solutions on both sides, and was of necessity measured after equilibration with KCl solutions of the same concentration.

4.6.3 Discussion

From the spectra shown for both the membranes treated with sodium tetraphenylborate and the Orion potassium filters it can be seen that two clearly identifiable structures are visible at the high frequency end of the spectrum. From the model suggested earlier, it can be deduced that these two features are due to the bulk membrane and that the bulk resistance is given by the real component of the impedance at the point where the impedance locus returns to the real axis after the second semicircle. It can be seen that the membrane bulk resistance is similar to that found for the Millipore filter alone using a membrane solution containing the same concentration (0.009 mol dm^{-3}) of valinomycin. The presence of the second high frequency

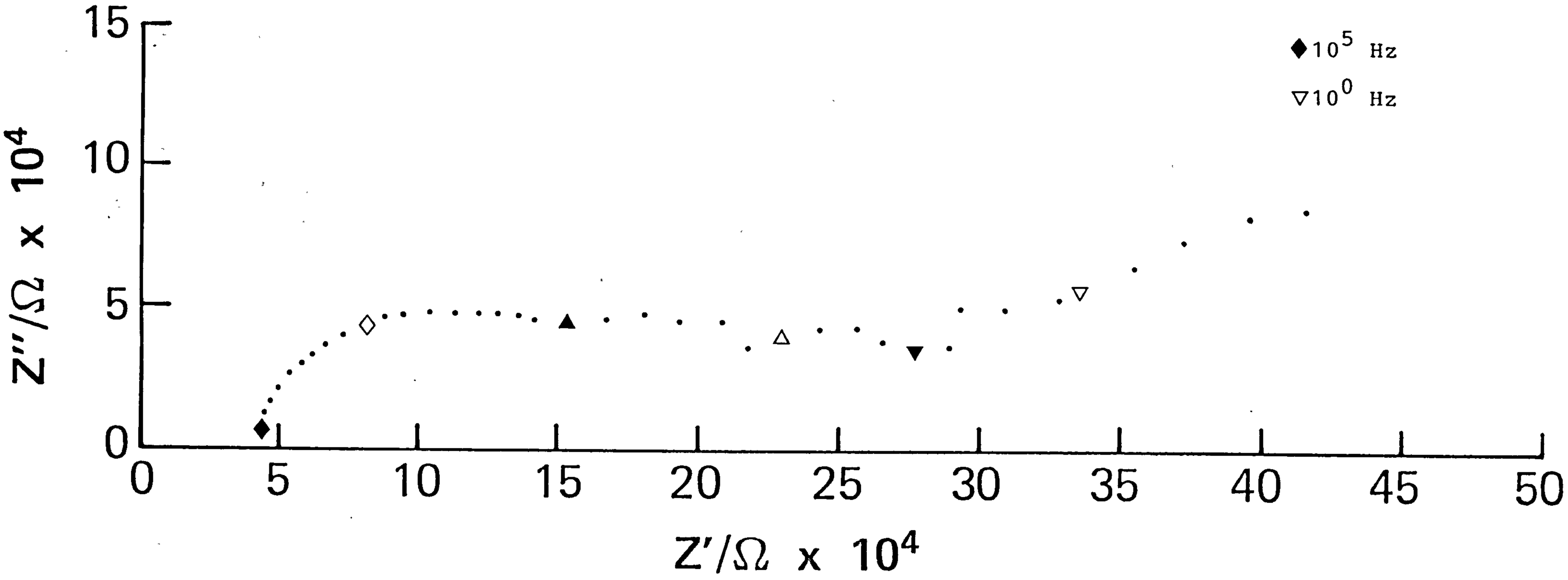


Fig 4.16: Final steady-state four-electrode impedance spectrum for a membrane containing 0.009 mol dm^{-3} valinomycin with a $NaBPh_4^-$ treated Millipore filter support, contacted by 0.1 mol dm^{-3} KCl solutions.

structure is clearly attributable to the addition of the tetraphenylborate to the filter support. In view of the model discussed, it is likely that the second feature has appeared due to the tetraphenylborate forming a separate bulk membrane phase. Considering the method of treatment used, it is reasonable to assume that this crystalline phase is present both in the membrane pores, and on its surface, although the pores are apparently not constricted by this process to such an extent that the electrode will not function.

The improvement in the slope and linear range of the response curves for these membranes, compared to those with untreated supports, indicates that the treatment improves the anion exclusion properties of the electrode. The fact that these results are closely similar to those obtained with the Orion electrode lends support to the suggestion that the Orion filter support has been pre-treated. The precise nature of the Orion treatment must, however, remain unresolved as these results do not indicate specifically that the treatment applied is in the form of tetraphenylborate or similar salts, only that there is a distinct separate phase present in the Orion support due to the addition of some material.

Interestingly, the treatment of the filter appears to have increased the charge-transfer resistance of the membrane, implying that is is more difficult for the potassium to enter the organic phase in the presence of the tetraphenylborate, although considering the appearance of the new bulk phase, it seems likely that this apparent change in R_{ct} is due to a difference in membrane geometry brought about by the treatment process, and does not actually reflect a true decrease in the exchange current.

4.7 Summary and Conclusions

From the impedance measurements reported in this chapter (summarised in Table 4.10), it is apparent that the operation of the liquid membrane electrode based on valinomycin can be explained largely on the grounds that the potassium is preferentially solubilised in the organic phase by the valinomycin and that this is the basis of the cation selectivity of the electrode. For the membranes containing valinomycin, the exchange currents calculated from the charge-transfer resistance reflect the selectivity of the membrane for potassium over sodium.

This is in agreement with Rechnitz and Eyal (4.14), who were of the opinion that the potentiometric selectivity of liquid-membrane electrodes depends on the interfacial processes alone.

Camman (4.13) also reported values for the exchange current for the potassium ion in a similar system, calculated from dc resistance measurements. The values given here are considerably smaller, but the method of estimating the charge transfer resistance from the dc resistance of the entire system, used by Camman, involves a number of assumptions which are difficult to verify, and cannot achieve the accuracy obtained with direct measurement of the R_{ct} from impedance measurements.

The treatment of the membrane support improves the Nernstian response of the electrode and it is therefore reasonable to assume that the electrode based on the Millipore filter as membrane support relies on the uptake of chloride ions from the aqueous solutions to provide a certain amount of the balancing charge for the potassium-valinomycin complex, although hydration

Table 4.10: Summary Of Parameters From Impedance Measurements For Liquid Membranes

Solns *	Val. Concn.	R_b /Ω	C_g/F	R_{ct} /Ωcm^2	i_o /μAcm^{-2}	C_{dl} /Fcm^{-2}
KCl	-	10^7	-	10^7	-	-
NaCl	-	10^7	-	10^7	-	-
KCl	9.0×10^{-4}	5.3×10^5	2.9×10^{-11}	8.8×10^3	2.9	2.1×10^{-2}
KCl	9.0×10^{-3}	1.9×10^5	2.1×10^{-11}	9.7×10^2	26.5	7.2×10^{-3}
NaCl	9.0×10^{-3}	4.2×10^6	1.5×10^{-11}	$>10^6$	-	-
KCl	$^+9.0 \times 10^{-3}$	2.5×10^5	2.7×10^{-10}	-	-	-

* All solutions 0.1 mol dm^{-3}

+ Filter treated with $NaBPh_4$

of the filter support is also likely to be involved. It also seems probable that the successful operation of the Orion liquid membrane electrode relies on a similar treatment of the support.

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Chapter 5

PVC Membrane Electrodes

5.1 Introduction

PVC matrix membranes have been used in ion-selective electrodes for a number of years, particularly for the construction of neutral-carrier based electrodes. The polymer membrane is more physically robust, is considerably easier to handle than the original liquid membranes, and permits more flexibility in cell design and application than do supported liquid films. The results reported in this chapter concern the nature of the PVC matrix when cast as an electrode membrane. Results of measurements on the individual components of the membrane are also included, in order to attempt to fully characterise the behaviour of the material.

The physical properties of cast membranes were also investigated by electron microscopy.

5.2 The PVC Matrix

It is generally assumed that the PVC membrane behaves in exactly the same way as the liquid membrane, and can be treated merely as a liquid membrane of high viscosity (5.1), although there are several reasons why this approach can be faulted. Specifically, it is doubtful that the behaviour of ligands and ionophores within the PVC matrix can be compared to that within a liquid solvent, which possesses no rigid structure like that of the polymer. A second important factor is that the PVC

itself is not a 'clean' compound of well characterised composition (5.2-5.4), and that in addition to the plasticiser deliberately incorporated, the membrane contains various other compounds added to the PVC during manufacture which act as stabilisers to slow down the degradation of the material (5.5,5.6). Under the influence of heat (5.2), or ultra-violet light (5.3), PVC decomposes producing HCl. The mechanism by which this degradation occurs is.not well defined or understood, but is thought to occur in two stages. Firstly hydrogen chloride cleaves from the polymer leaving unsaturated hydrocarbon residues, and secondly, oxidation occurs at the unsaturated sites. The HCl produced has an autocatalytic function, promoting further degradation of the PVC, and metals, particularly iron, increase this catalytic activity. The eventual result of the degradation is a carbon chain possessing a high degree of unsaturation, giving rise to a conjugated system known as a polyene. Polyenes are very unstable in the presence of heat and UV light and as a result oxidation occurs, causing the polymer chains to become cleaved, and the formation of carbonyl groups on the chain fragments. Thus the degradation process produces a number of ionic species, and also carbonyl groups, which may act as sites for further reaction.

In view of the above mechanism, all stabilisers used in the manufacture and processing of PVC are hydrogen chloride acceptors. A wide variety of such compounds is used, many having been in use for a long time. New stabilisers are found generally by trial and error as it is very difficult to predict the action of the material within the polymer matrix from theoretical grounds.

The stabilisers used can be categorised as follows (5.5)

Primary heat stabilisers

Heavy metal soaps, Organotin compounds, Lead salts

Secondary heat stabilisers

Organics, Organophosphites, Epoxys

Light stabilisers

All the above compounds are effective light stabilisers, but the use of two or more stabilisers in the PVC can result in enhanced effectiveness.

In view of these various additives, the possibilty for ion-exchange to occur is much greater than with a pure liquid membrane, and the generation of negative sites via these additives becomes a more likely process. The plasticiser is also a likely source of charged species (5.6), and is unlikely to behave simply as an inert solvent (5.7-5.11).

5.2.1 The Membrane Surface: Physical Uniformity

As suggested in Chapter 1, it is possible that surface roughness could give rise to distortions of the complex plane impedance plot due to the creation of large numbers of parallel RC networks at the interface, making interpretation of data more problematical. To investigate the nature of the PVC surface, and to see whether multiple RC networks were a likely feature with PVC membranes, membranes were cast as for normal use, and samples were examined by electron microscopy.

Figs 5.1 and 5.2 show a series of electron micrographs of the upper and lower surfaces of a PVC membrane containing valinomycin, plasticised with dioctyl sebacate. The upper surface is the top surface of the membrane when cast in the

Fig 5.1: Electron micrographs of the upper surface of a PVC/dioctyl sebacate/valinomycin membrane.

a. x500

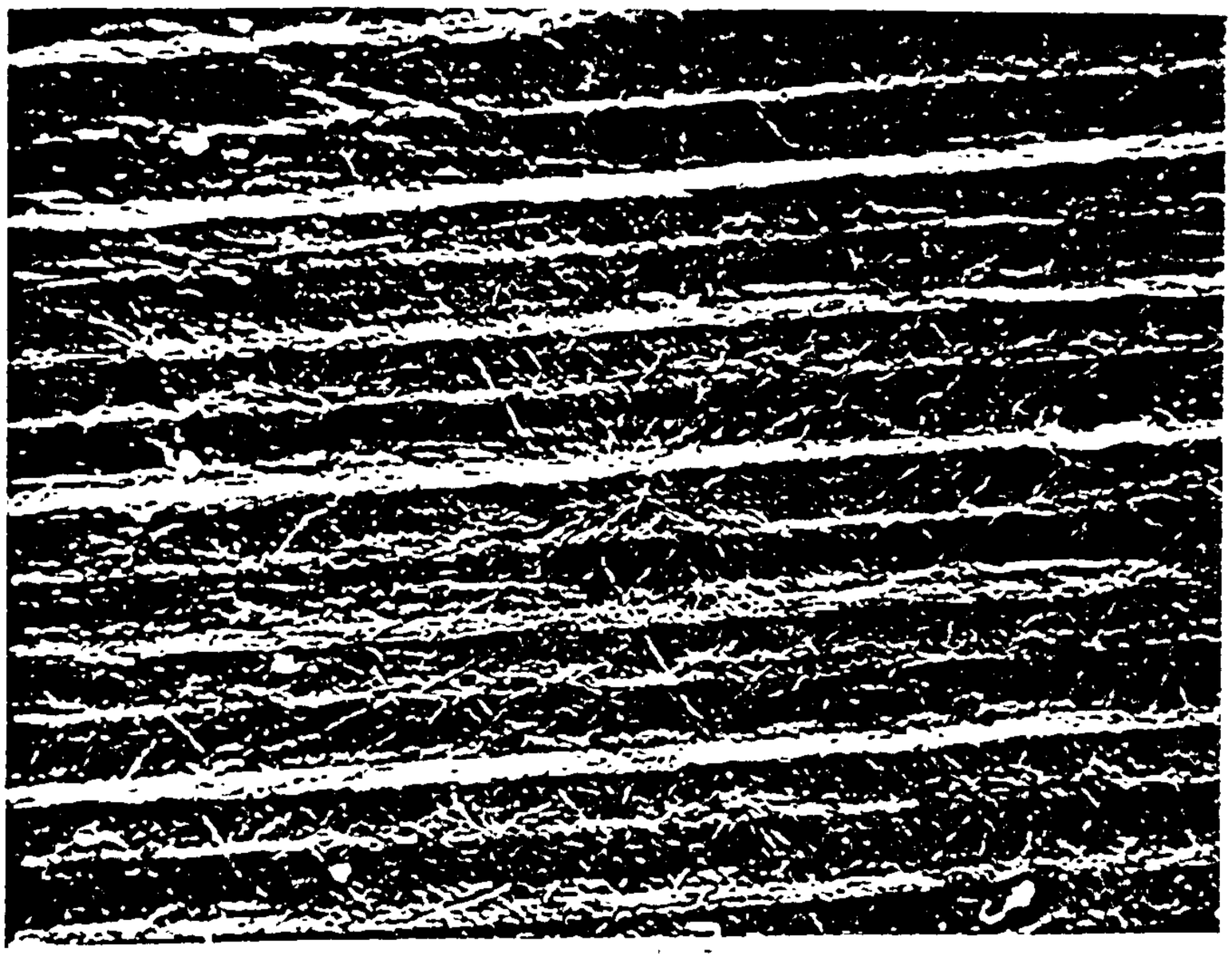
b. x2000

c. x10000

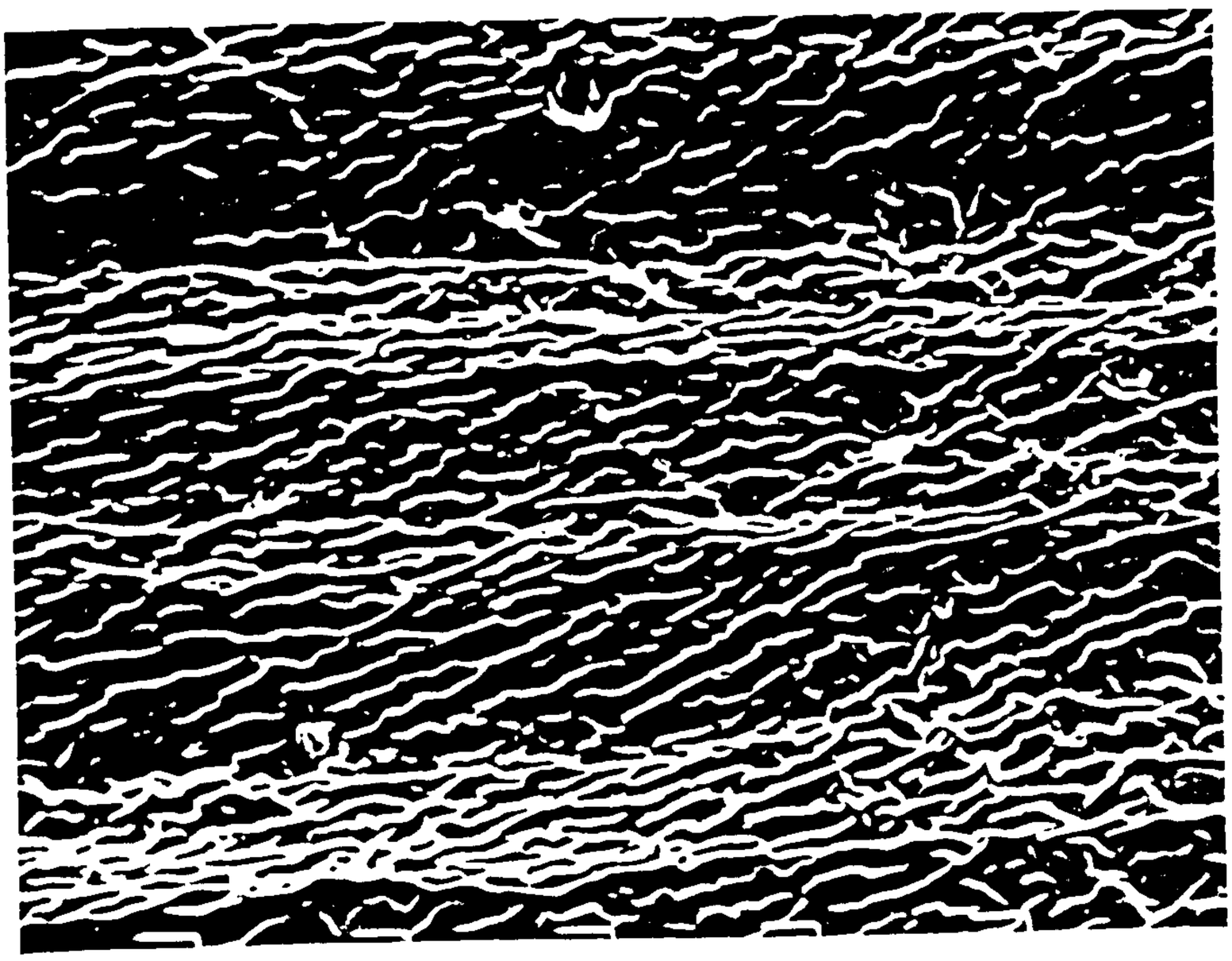
d. x20000

e. x30000

a

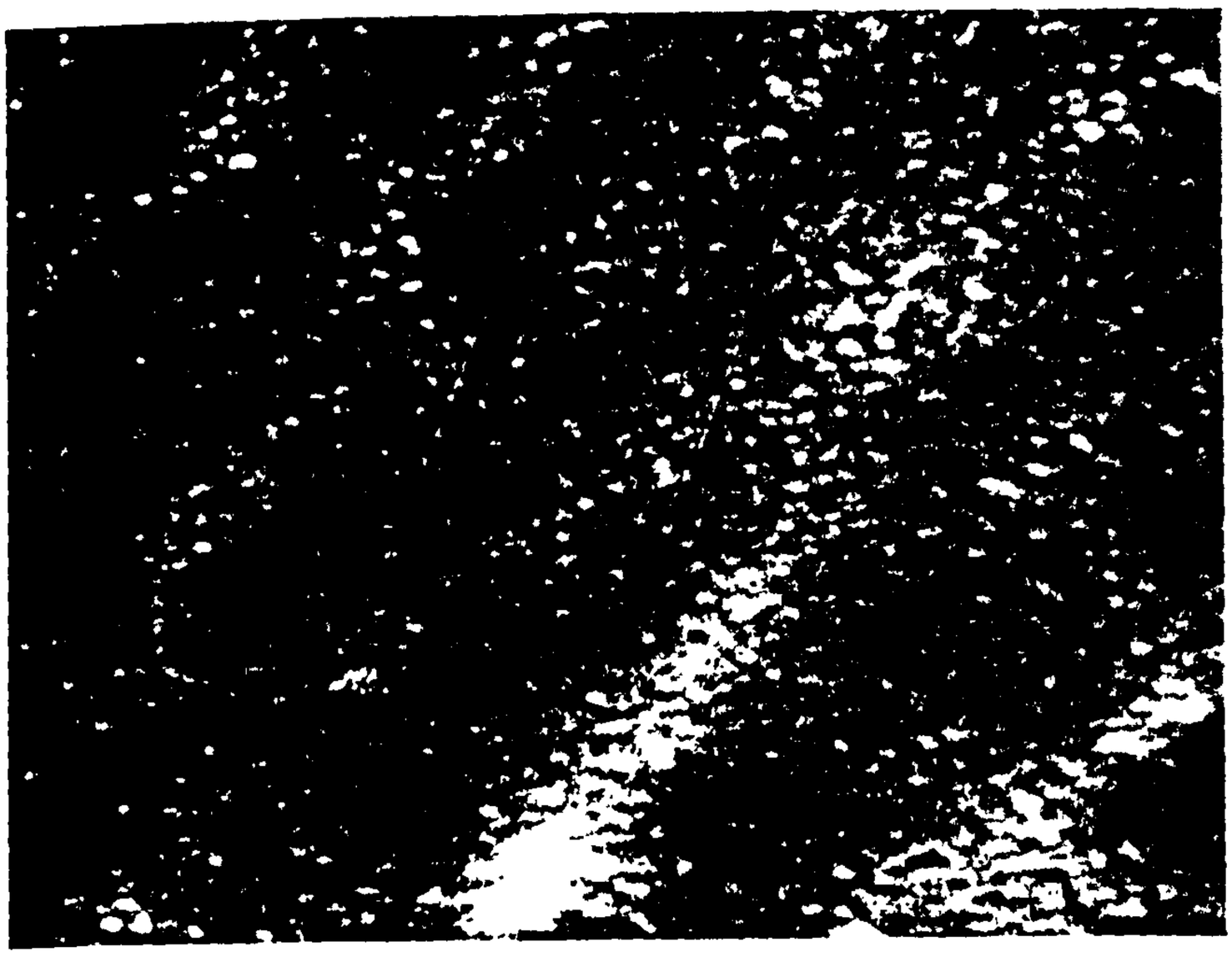


b



c

d



e

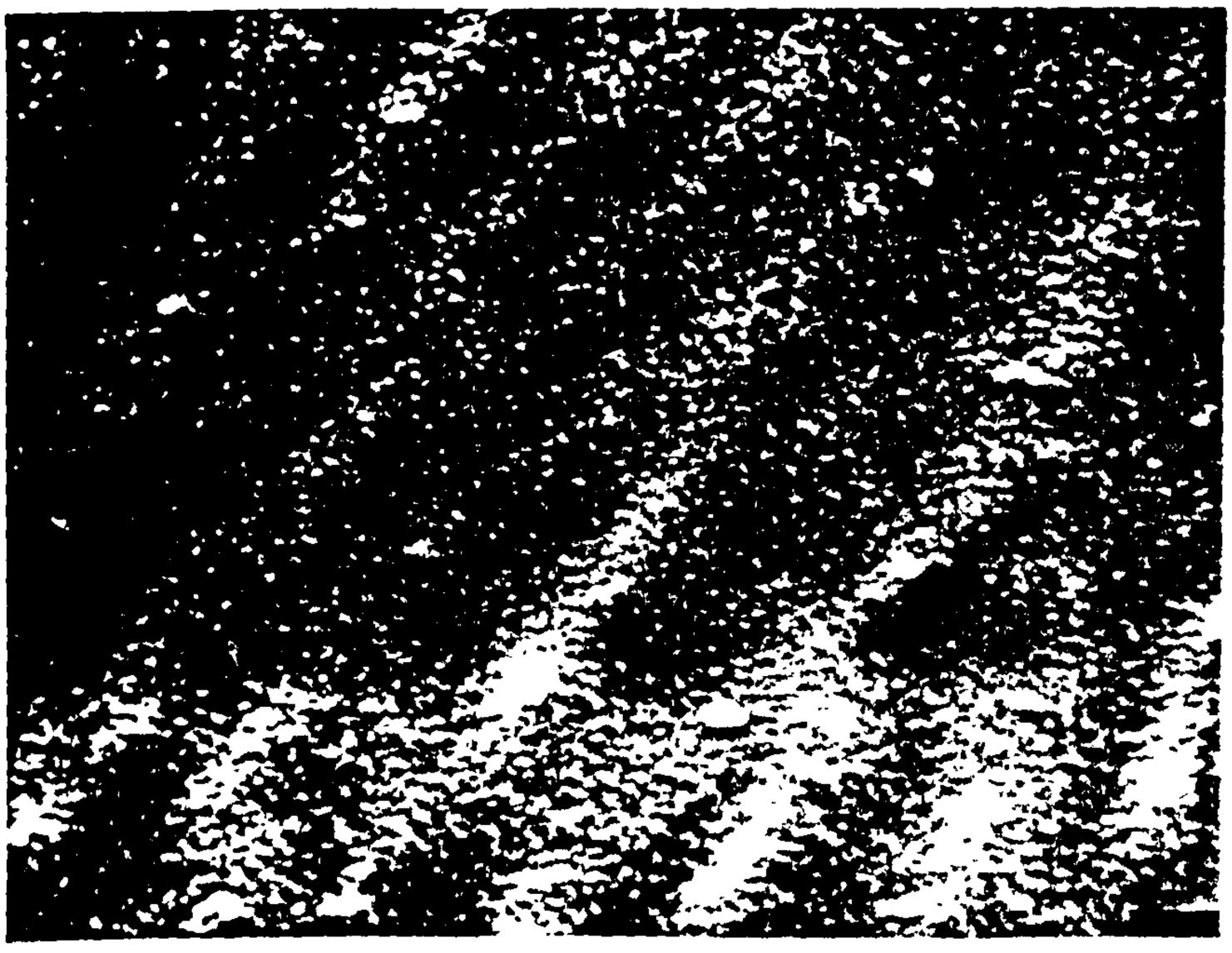


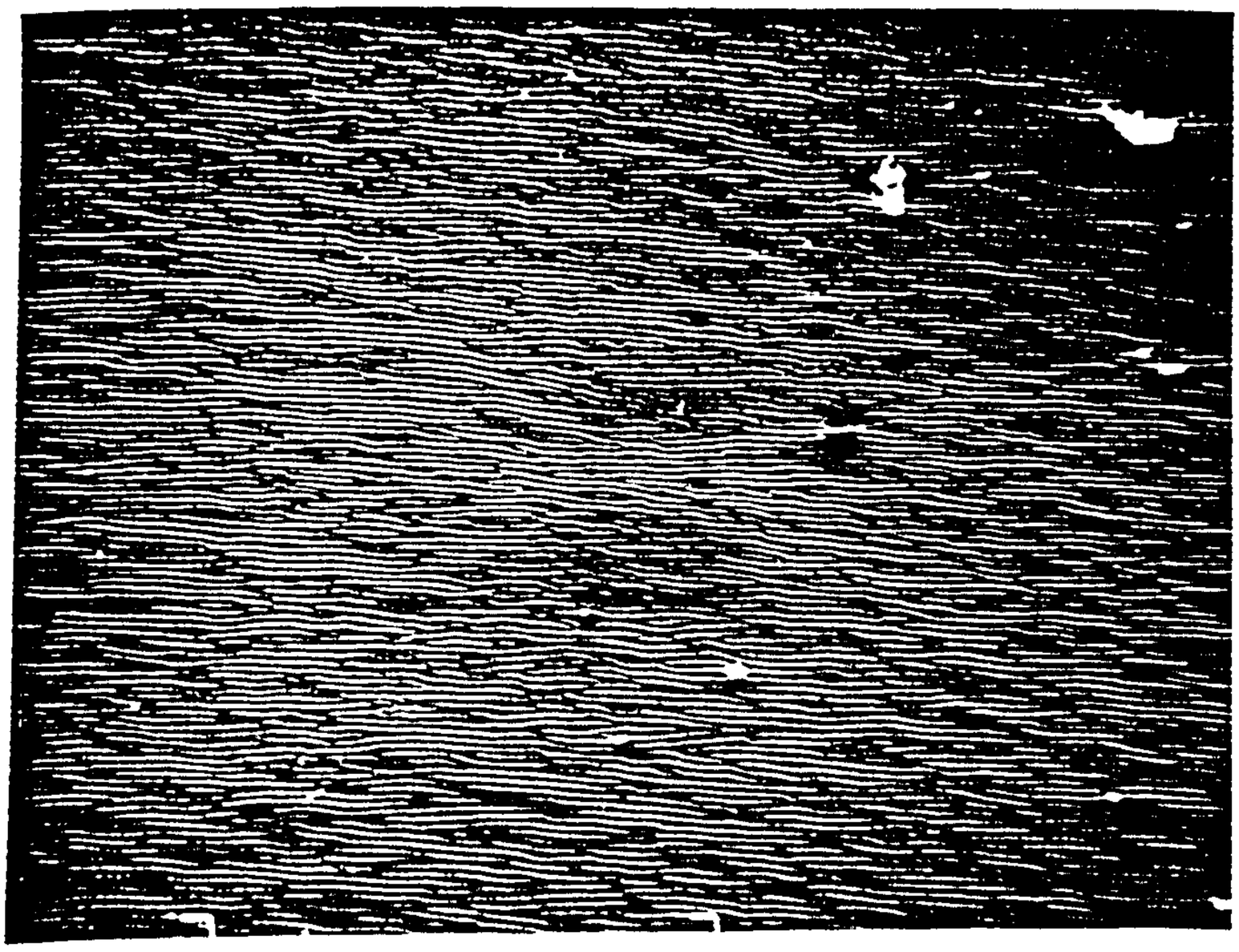
Fig 5.2: Electron micrographs of the lower surface of a PVC/dioctyl sebacate/valinomycin membrane.

a.x500

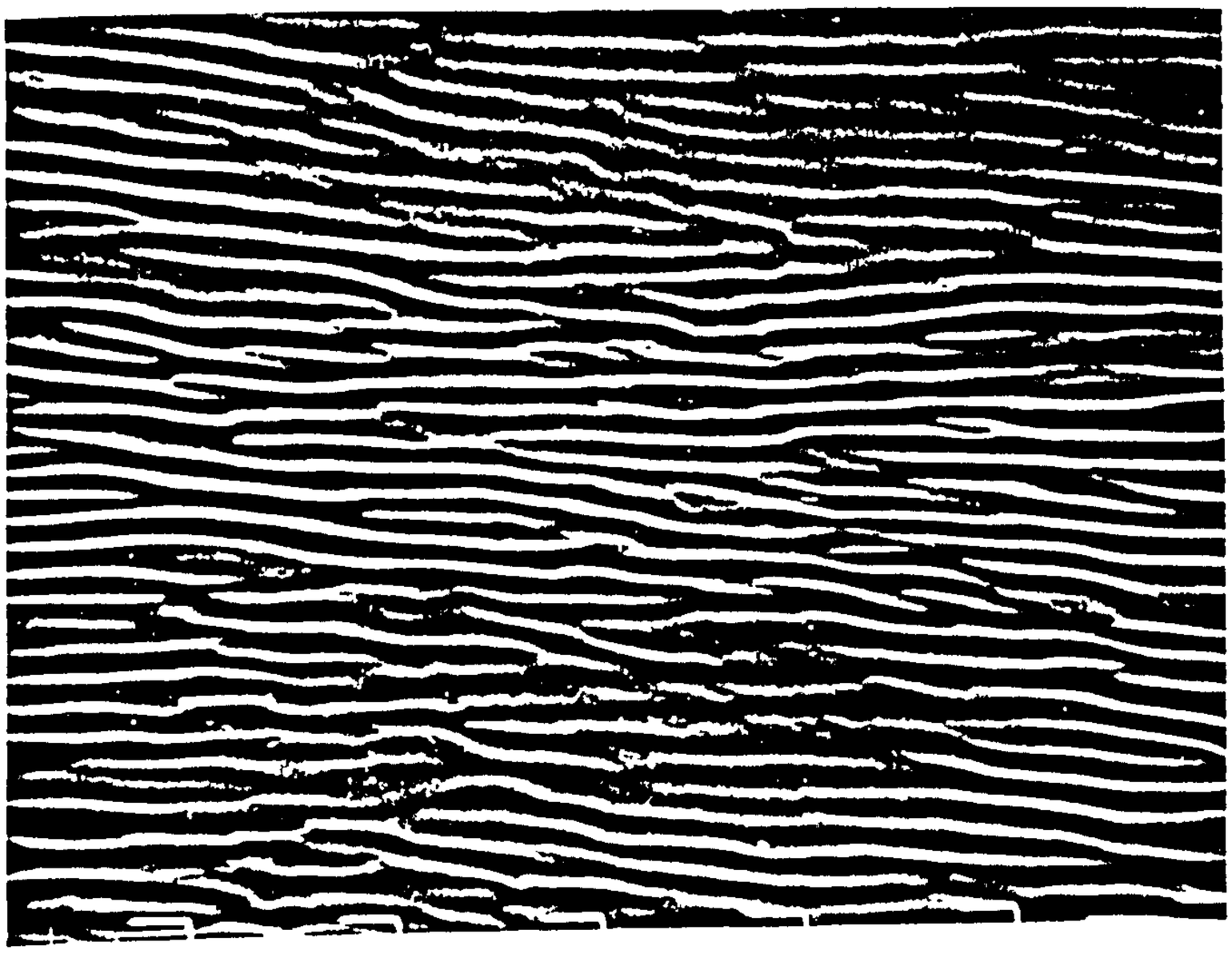
b.x2000

c.x10000

a



b



c

mould. This surface was exposed only to the atmosphere, having had no contact with any solid surfaces during casting, whilst the lower surface was formed in contact with the PTFE mould. Fig 5.1 shows images of the upper membrane surface, and the images shown on Fig 5.2 are of the lower membrane surface.

Fig 5.1a is the image of the upper surface x500 magnification. The membrane shows a uniform pattern of approximately parallel ridges running across the picture, giving a general wrinkled appearance. Figs 5.1b and 5.1c show the surface at magnifications of x2000 and x10000 respectively, from which the wrinkling effect can be seen to be quite regular and uninterrupted even at such high magnification. Attempts were made to achieve higher magnifications of this upper surface, and the results are shown in Figs 5.1d and 5.1e. The microscope begins to lose definition at these magnifications and the images are less clear, but it is still possible to see the regularity of the wrinkling, and that there is no evidence of any other features.

Fig 5.2a shows the x500 image of the lower membrane surface. This surface also shows wrinkling, but with a much higher degree of irregularity in the pattern. In addition there is a second series of regular marks on a much larger scale running across the membrane surface. Fig 5.2b and 5.2c show the surface at x2000 and x10000 magnification. In Fig 5.2b, the large scale features are still clearly visible, and the highly irregular nature of the smaller scale features is apparent. In contrast to the gentler undulations on the upper surface (Fig 5.1b), these smaller features appear as deeper folds where the membrane has crumpled, creating crevices and pockets. Fig 5.2c shows this in greater detail.

The large scale regular features on the lower side of the membrane can be attributed to the machine marks left on the moulds in construction, which would result in a mirror image imprinted into the surface of the membrane. The nature of the smaller scale features is not so easy to establish, although it is quite possible that they have arisen due to stretching of the membrane material during mounting in preparation for electron microscopy, and that the difference in the two surfaces is merely due to the membrane being stretched differently in different mountings. If this is the case, then the only difference between the two surfaces is the presence of the mould machine marks on the lower surface. Neither surface shows any evidence of pores or other features giving access into the membrane interior, and apart from the wrinkling, the surfaces are surprisingly uniform. It is not clear to what extent the wrinkling exists when a membrane is mounted for normal use in an ion-selective electrode, but the membranes are not usually mounted in a state of tension, and so it is reasonable to assume that a certain degree of irregularity exists.

The effect of the wrinkling and the mould marks seen in Figs 5.1 and 5.2, on the impedance spectra of the membranes is not easy to ascertain other than in qualitative terms. To attempt to quantify their effects would be unreasonable in view of the number of variable factors involved. It is clear however, that one membrane surface is roughened as a result of the casting process, and that the membrane does not present a uniform even surface in contact with the aqueous solutions. In addition, the wrinkling and folding of the membrane which is apparent in the electron microscope images is also likely to be present when the membrane is mounted in an ISE cell. On this basis, it seems

possible that this low-level of irregularity could give rise to some distortion of the ac impedance spectrum, manifesting itself in the region of the spectrum representing the interfacial processes.

5.2.2 PVC Membranes: Expected Equivalent Circuit

The equivalent circuit proposed for the liquid membranes in Chapter 4 is necessarily complex due to the presence of the two separate membrane phases, the support and the membrane liquid itself. As the PVC membranes are assumed to be chemically and physically homogeneous, the equivalent circuit would be expected to be much closer to the ideal circuit proposed in Chapter 1, with the bulk membrane phase appearing in the complex plane plot as a single parallel RC network. It is possible, however, that in addition uptake of water into the membrane surface could occur, giving rise to a hydrated layer similar to that found in glass membranes (5.12). In this case, provided that the time constants for the two processes were sufficiently separated, then a second RC network could be expected, in series with the first, giving rise to a second semicircle in the complex plane plot.

The interfacial charge-transfer processes would be expected to manifest themselves in the impedance plot in a similar way to that reported for the liquid membranes in Chapter 4, i.e. as a single semicircle at low frequencies. As discussed above, this low-frequency data could possibly be distorted due to surface roughness, but it should still be possible to resolve the feature providing that the time constant for the process is sufficiently removed from that of the bulk membrane.

5.3 Dry PVC Membranes

In view of the various mechanisms proposed for the origin of negative sites or mobile anions within the membrane, discussed in Chapter 3, a series of measurements were made on dry PVC membranes to assess the level of conductivity inherent in the membrane after fabrication. Measurements were made using stainless steel electrodes contacting directly on to the membrane surfaces, using the cell described in Chapter 2, and in this way the impedance of membranes could be measured, which had not contacted any aqueous solutions (other than as described below). The pressure applied to the electrodes in clamping the membrane was monitored via a statimeter gauge, and was just sufficient to ensure good contact between the membrane and the electrodes.

Fig 5.3 shows the impedance spectrum of a membrane comprising PVC, dioctyl sebacate (DOS) and valinomycin, measured as described above. The plot shows a single semicircle at high frequency, similar to that seen with the liquid membranes, which terminates in a near vertical straight line at lower frequency. This complex plane plot corresponds to an equivalent circuit consisting of a parallel RC network, representing the membrane, with a resistive component of approximately 2.0×10^6 (3.45×10^6 Ohm cm^{-2}), in series with a pure capacitor. This capacitive behaviour is due to the fact that no charge transfer can occur across the membrane/steel interface, as would be expected.

Fig 5.4 shows the impedance spectrum of the membrane (contacted by stainless steel electrodes, as previously) after immersion in triply-distilled water for 24 hours. The membrane was dried by repeated compression between clean sheets of filter

Fig 5.3: Impedance spectrum of a dry PVC/dioctyl sebacate/ valinomycin membrane contacted by stainless steel electrodes.

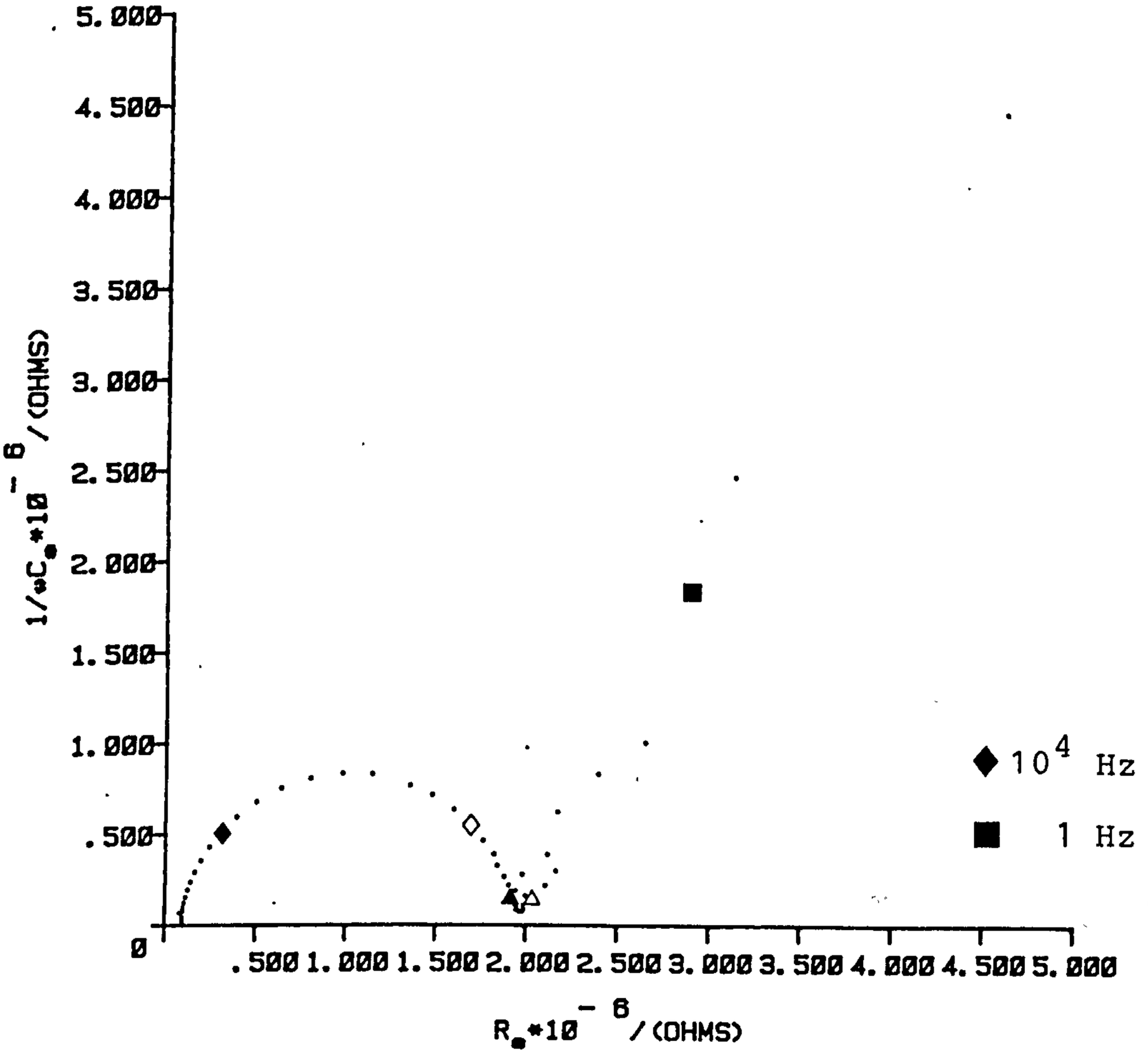
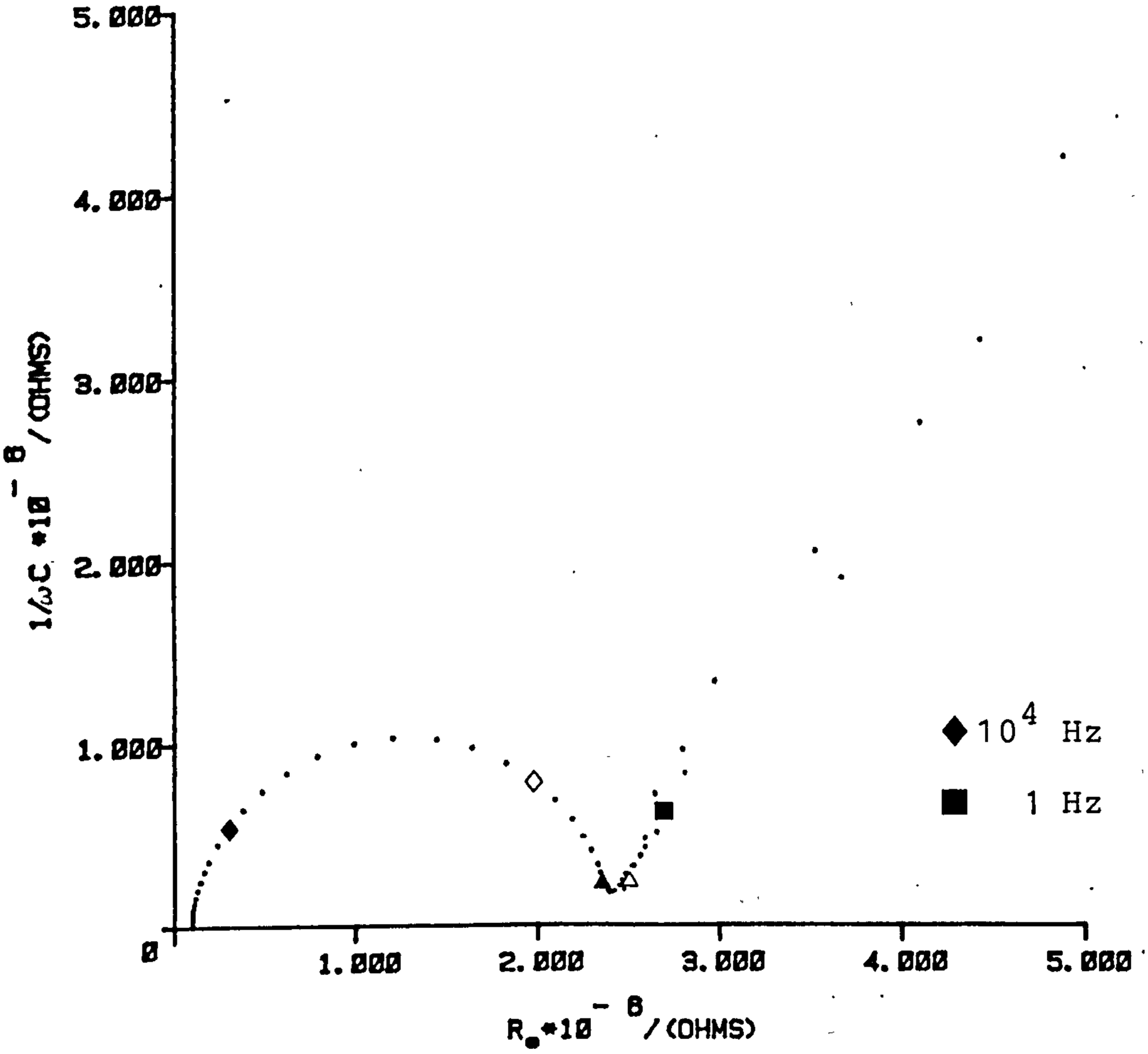


Fig 5.4: Impedance spectrum of the dry PVC/dioctyl sebacate/ valinomycin membrane after immersion in triply-distilled water for 24 hours.



paper until no traces of water were visible on the papers. In this way, surface water was removed, but any water which had been taken up into the PVC matrix during immersion should still be present. The complex plane plot shows similar features to that obtained for the membrane prior to contact with the water, except that the bulk resistance of the membrane has increased to 2.4 x 10^6 Ohm (an increase of approximately 19%) as a result of the water treatment.

Fig 5.5 shows the impedance spectrum of the membrane after immersion in 0.1 mol dm^{-3} KCl solution for 24 hours, the membrane being dried, as outlined above, before being loaded into the cell. From this plot, it can be seen that the spectrum is of the same form as found previously, with a parallel RC network at high frequency and capacitive behaviour in the low frequency region and that the membrane resistance has again increased, in this instance by approximately 15% over the 24 hour period.

A further series of measurements was carried out on dry membranes in the same cell, but under higher pressures, in order to investigate the effect of clamping the membrane in the cell, and to follow the geometric changes which must occur under these conditions. Fig 5.6 shows a composite impedance spectrum for a membrane clamped at pressures of 100kg, 200kg and 300kg. It can be seen quite clearly that as the pressure is increased, the membrane resistance falls, presumably due to the reduction in the membrane thickness, although above a certain pressure, the membrane cannot easily be further compressed and the resistance reaches a final steady value.

Table 5.1 gives a summary of all the results obtained for the membranes contacted by stainless steel electrodes.

Fig 5.5: Impedance spectrum of the dry PVC/dioctyl sebacate/10^{-3} valinomycin membrane after immersion in 0.1 mol dm^{-3} KCl solution for 24 hours.

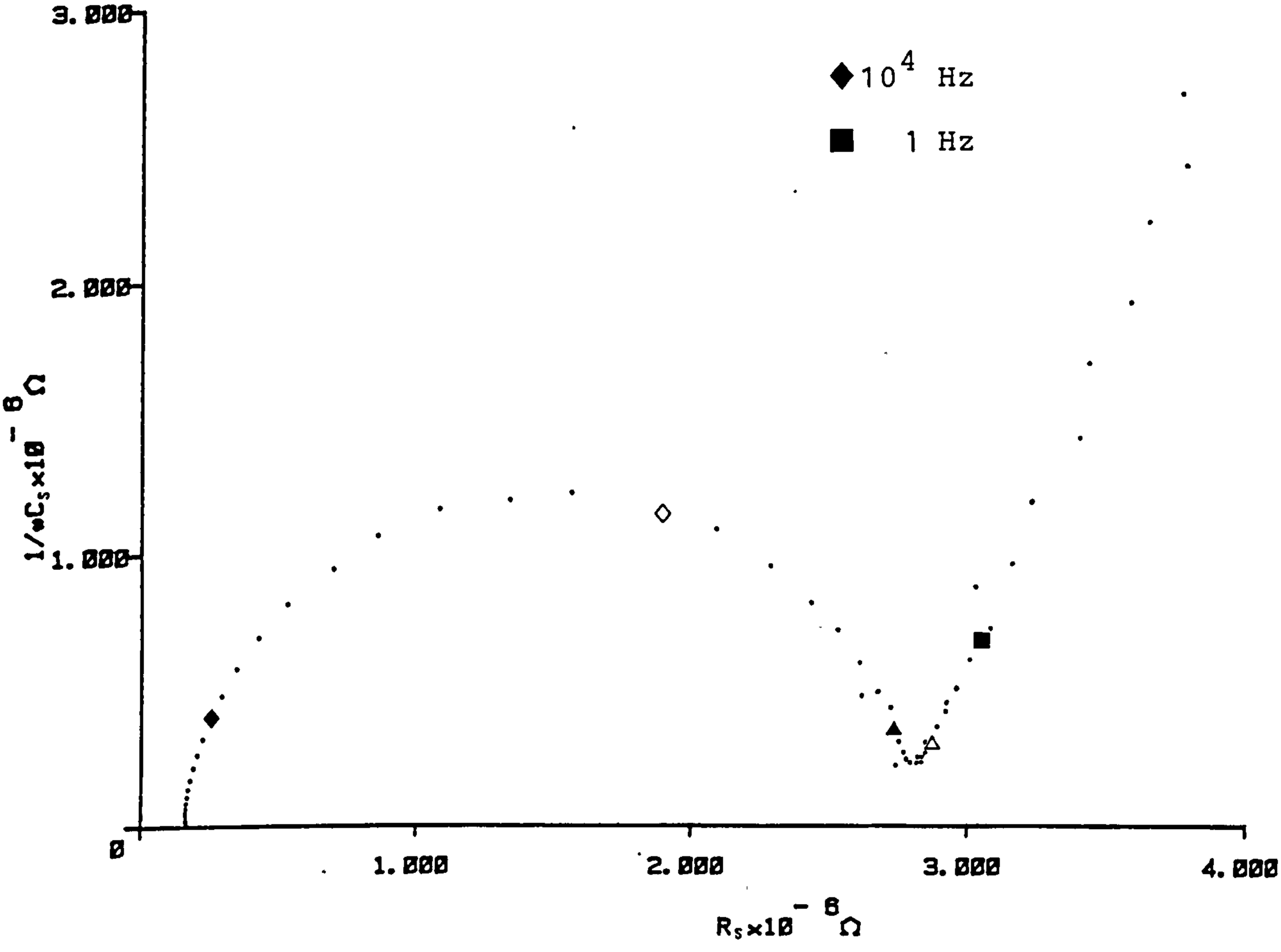


Fig 5.6: Impedance spectrum of a dry PVC/dioctyl sebacate/ valinomycin membrane under various pressures.

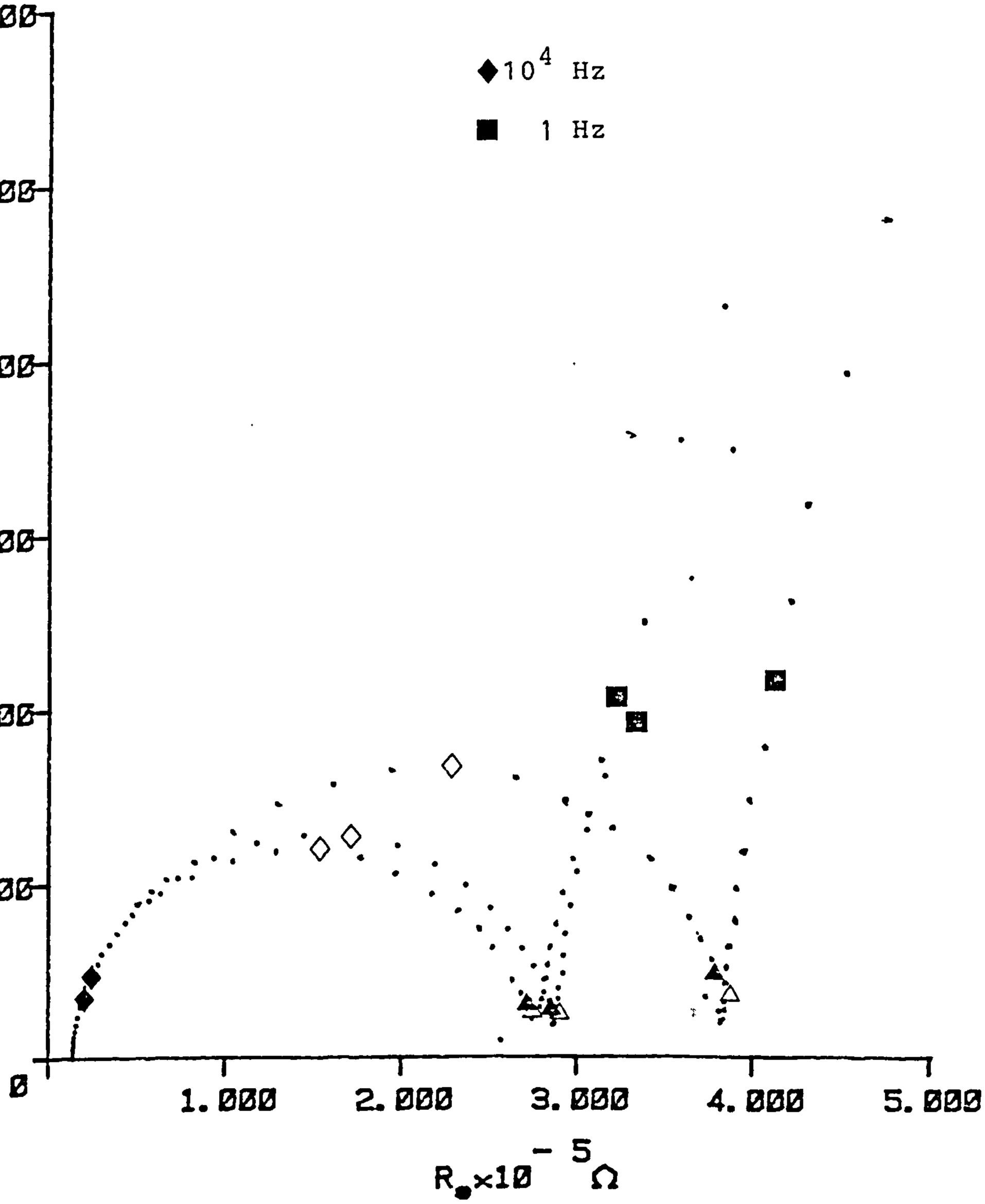


Table 5.1: Summary Of Results For Dry Membranes

Conditioning Treatment	Electrode Pressure/cm^2	ω^*/Hz	R/Ω	C/F	RC/s
None	Holding	3.151×10^{2}	2.0×10^{6}	2.5×10^{-10}	5.0×10^{-4}
Water (24hrs)	Holding	2.504×10^{2}	2.4×10^{6}	2.6×10^{-10}	6.4×10^{-4}
KCl (24hrs)	Holding	1.989×10^{2}	2.7×10^{6}	3.0×10^{-10}	8.0×10^{-4}
None	100kg	9.980×10^{2}	3.8×10^{5}	4.2×10^{-10}	1.6×10^{-4}
None	200kg	9.980×10^{2}	2.9×10^{5}	5.6×10^{-10}	1.6×10^{-4}
None	300kg	9.980×10^{2}	2.8×10^{5}	5.8×10^{-10}	1.6×10^{-4}

The value of R_b measured for the dry membrane prior to contact with any solutions is not as large as would be expected for an insulator which contained no charge-carrying species, and indicates the presence of a number of charge carriers inherent within the polymer matrix. This result is not surprising in view of the presence of the various additives discussed above. Unfortunately, it is impossible to obtain from the manufacturers the precise composition of the PVC, and so no definite conclusions can be drawn as to the nature of these charge carriers. It is also possible that the degradation process is more important as a source of charged species than the added stabilisers although a third possible source of such species is the valinomycin itself, as suggested for the liquid membranes studied in Chapter 4. The valinomycin used was not purified in any way, and no details of sample purity were available from the suppliers. It is therefore possible that significant levels of impurities were present in the samples of ionophore used in the fabrication of membranes. Whether the amount of such impurities would be sufficient to account for all the charged species inherent within the PVC membrane is not clear, although this seems unlikely in the light of the above discussion.

The measurements on the membrane after exposure to aqueous solutions show several interesting features, indicating that there has been some interaction between the two.

Several possible effects of water uptake by the membrane could be expected, these are:

i. The water would cause swelling of the PVC matrix similar to that found in the cellulose acetate membrane supports discussed in Chapter 4. In this case, the measured resistance

of the membrane would increase along with the membrane thickness. If the effects were purely geometric, i.e. no change in the resistivity of the membrane had occurred, then the increase in resistance would be accompanied by a decrease in the geometric capacitance and the time constant for the bulk membrane parallel RC network would remain unchanged.

ii. Uptake of water could cause the creation of charge carrying species in the membrane due to reaction with the water. This could be due to the formation of OH^- conglomerates as suggested by Simon (5.1), or due to the H_2O-induced dissociation of species already present within the membrane. Either process would produce a change in the resistivity of the membrane. This generation of charge carriers would not necessarily cause a fall in the membrane resistance, if the reduction in resistance was offset by geometric effects (swelling).

iii. Exposure to water could actually increase the resistivity of the membrane by extracting charge carriers from the membrane. This partitioning would result in a change in the conductivity of the water, and would lead to an increase in membrane resistance, which could be exacerbated by swelling.

From Table 5.1 it can be seen that the resistance of the dry membrane did increase on exposure to water, and that the time constant for the bulk membrane processes also increased, indicating that the change in resistance is not due solely to geometric effects. Which of the mechanisms suggested above is occurring is not clear, but the fact that there is an increase in the membrane resistance with time suggests that there is a swelling of the membrane material on exposure to the water, and the change in the time constant for the membrane also suggests

that this swelling is accompanied by some process as outlined above. Equilibration with atmospheric water must occur during the casting process, but the extent of this water uptake is evidently not sufficient to achieve a saturation level.

The results for the membrane after exposure to the KCl solution, are more surprising. In view of the fact that the potassium solution to which the membrane was exposed contained large numbers of charge-carriers, it would be expected that the membrane would take up ionic species from the aqueous solution, and that such a process would result in a reduction of the membrane resistance. From the data given above, it is clear that this process cannot be occurring to a sufficient extent to offset the increase in bulk resistance shown by the membrane after exposure to water. This is all the more surprising considering that the valinomycin in the membrane should promote the uptake of the potassium, more than with any other species. What seems to be more likely, is that an ion-exchange process is occurring, whereby charge carriers present in the membrane are exchanged for potassium, rather than the membrane being initially low in charge carriers and then taking them up from the solution.

5.4 Impedance Measurements on Membrane Components

Whilst the results presented earlier in this chapter give some insight into the behaviour of PVC membranes, it is not clear to what extent the individual components affect the operation of the membrane as a whole, although some workers have tried to assess the optimum composition (5.13-5.14). Previously, work has been carried out to try investigate the

origin of the charge carrying species within the PVC membrane by way of pH measurements (5.15), using an experimental set-up whereby a quantity of the plasticiser could be contacted by a small amount of water, and the pH of the water could be monitored. It was found that some plasticisers produced a negative change in pH of the water, whilst others produced a positive change, with no apparent rationale which could be applied to account for these changes in terms of the operation of the plasticised membrane in an ISE. Similar experiments were carried out with a variety of types of PVC, and again, both positive and negative pH changes were produced. In the present work an attempt was made to investigate this further by way of impedance measurements. The various membrane components were exposed to triply distilled water, and the conductivity (via the change of the cell impedance) were followed for both components of the mixture. Measurements were carried out using a tightly-stoppered standard conductivity cell with platinised platinum electrodes, as shown diagrammatically in Fig 5.7, thermostatted at $25^{o}C$.

5.4.1 Results and Discussion

Fig 5.8a shows the impedance spectrum obtained with pure DOS in the conductivity cell, prior to contact with the triply-distilled water, which shows almost pure capacitive behaviour (the apparent resistive offset is an artefact due to the large comparison resistor used), and is not resolved into a semicircle. From this it can be deduced that the plasticiser has a sufficiently high resistance to be outside the range which the 1174 can accurately measure - greater than 10^{7} ohm).

Fig 5.7: Diagram of the conductivity cell used for impedance measurements on plasticiser and aqueous phases.

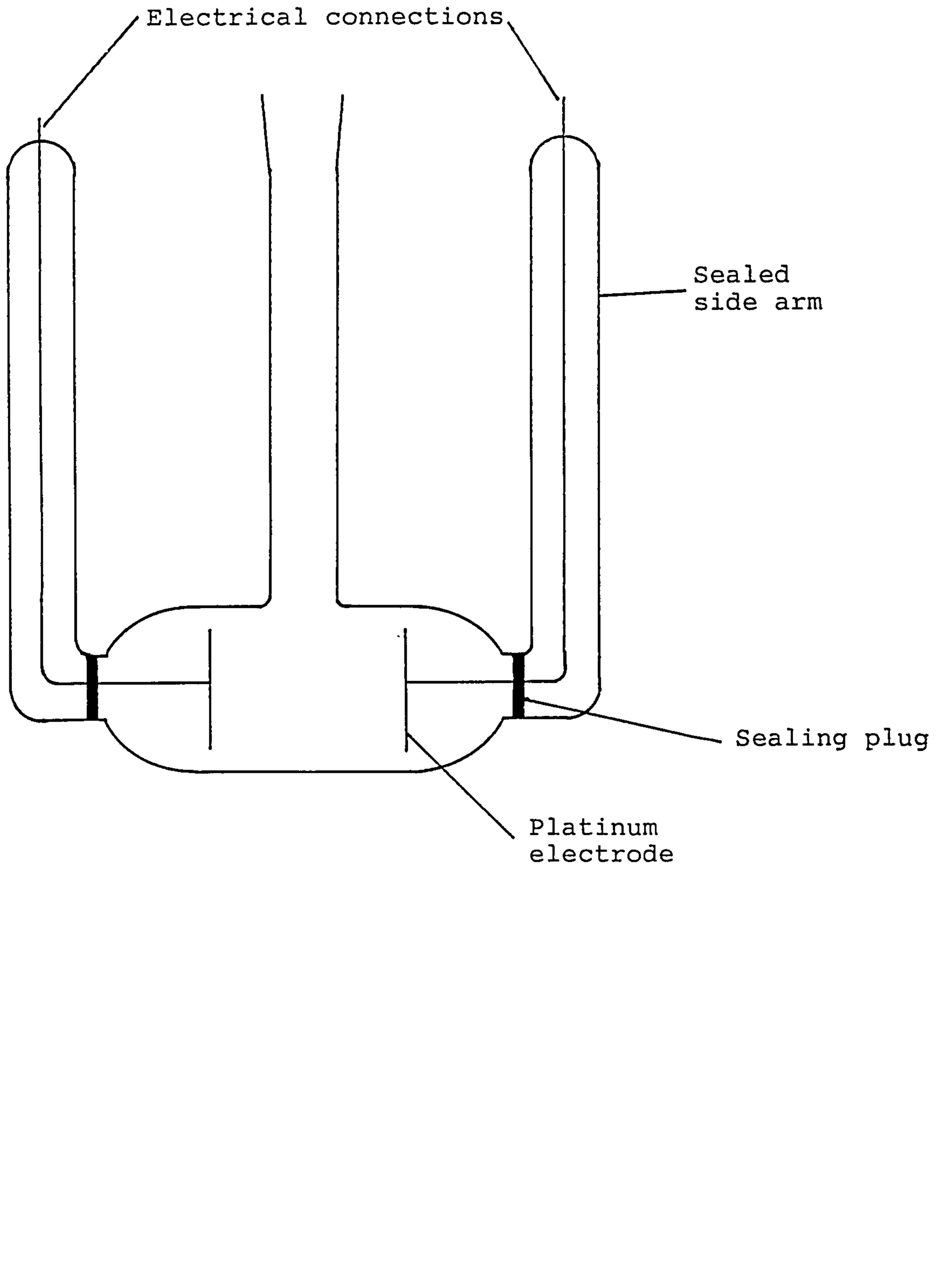
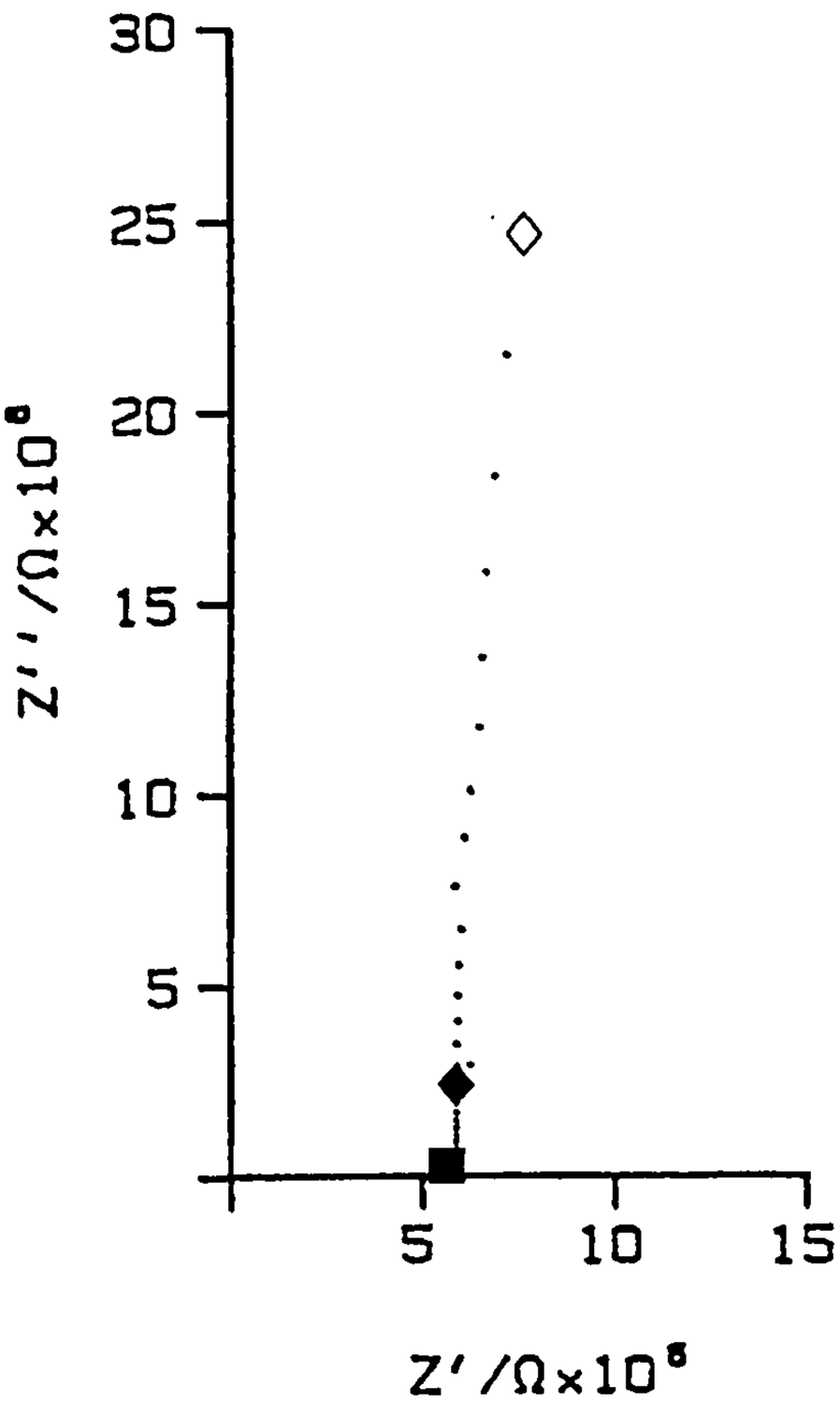


Fig 5.8a: Impedance spectrum obtained with pure DOS in the conductivity cell, prior to contact with triply-distilled water.



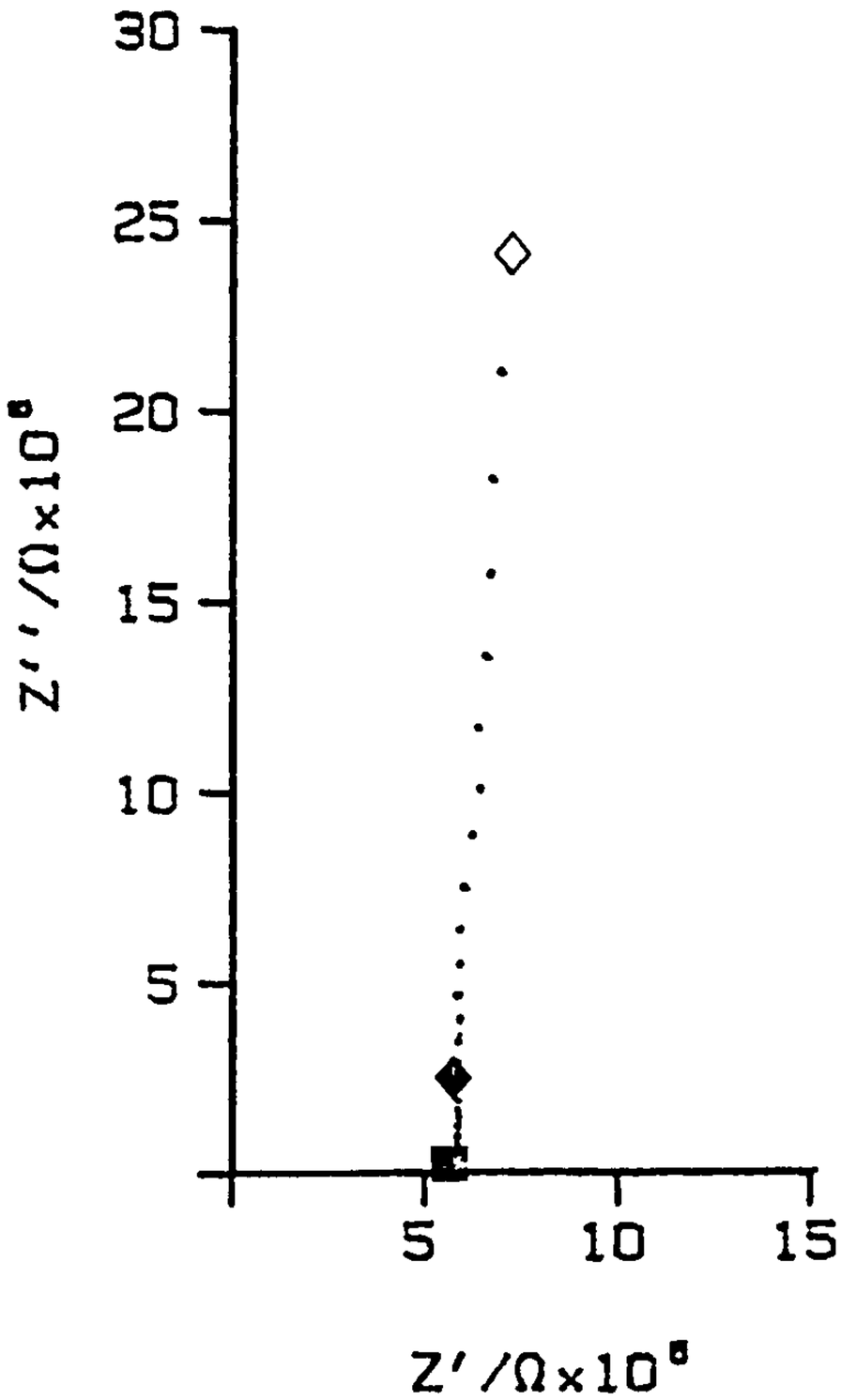


Fig 5.8b: Impedance spectrum of the DOS after a 24-hour period of equilibration with triply-distilled water.

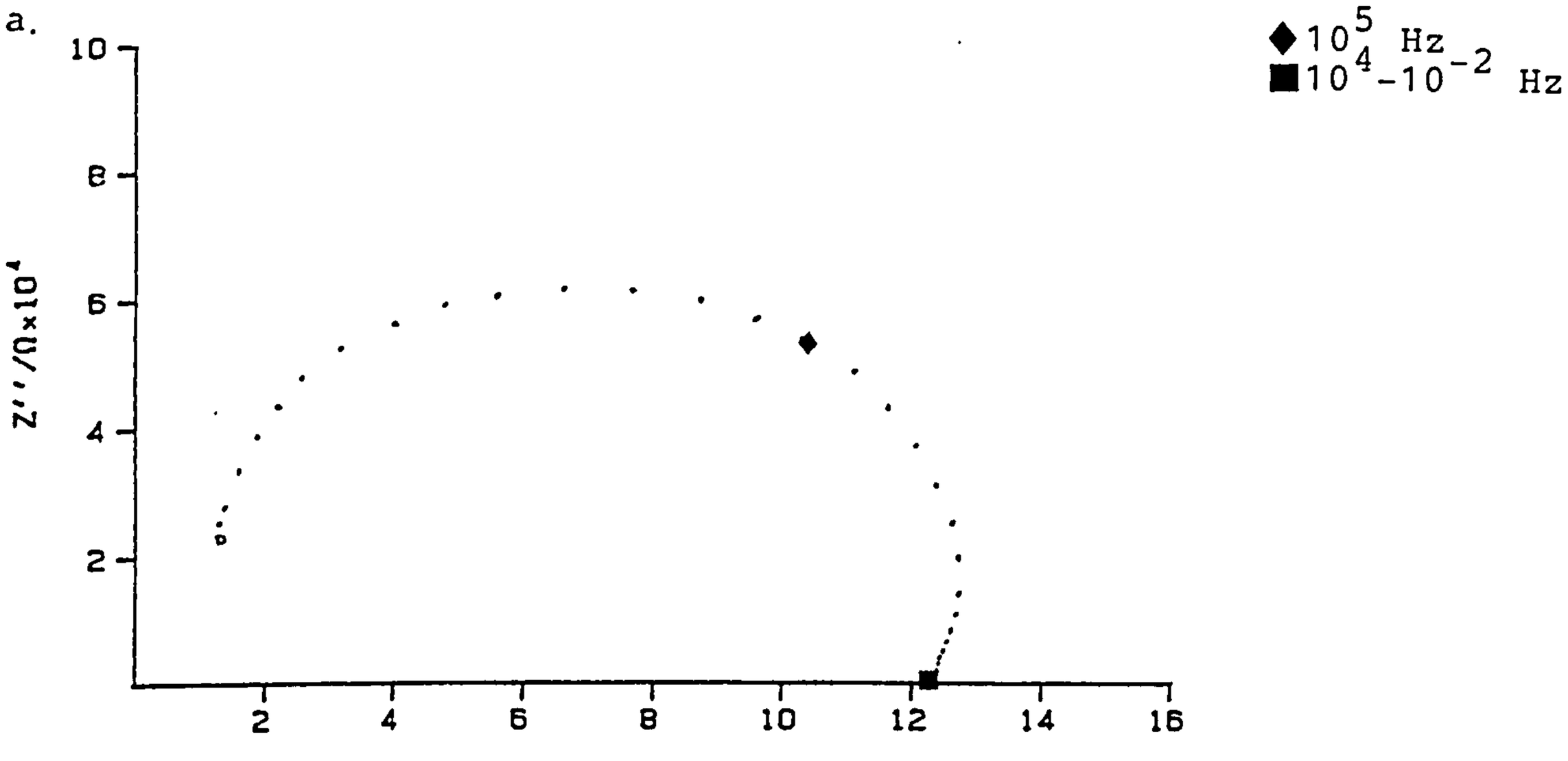
The cell impedance was followed for twenty-four hours, during which there was no visible change in the spectrum. After this period, the DOS was removed from the cell and added to an equal quantity of triply distilled water in a separating funnel. The mixture was then shaken for one hour and left to separate for a further 24 hours, after which the impedance spectrum of each component was separately determined. Fig 5.8b shows the impedance spectrum of the DOS after the period of equilibration with the water. This spectrum shows similar features to the spectrum of the plasticiser, before contact with the water.

Fig 5.9 a and 5.9 b show the impedance spectra measured for the water before and after the equilibration with the platiciser respectively. The initial spectrum shows a semicircular feature, with a resistive component of approximately 1.20 $x10^5$ ohm, representing the resistance of the water between the electrodes. The second spectrum, measured after exposure to the plasticiser, clearly shows that the resistance of the water has fallen by a factor of approximately three.

Similar experiments were carried out, using 0.1 mol dm^{-3} solutions of KCl, NaCl and CsCl in place of the triply-distilled water. In all three cases, the spectra for the plasticiser showed no change on exposure to the aqueous solution, nor was any change apparent in the spectra of the chloride solutions after contact with the DOS, indicating that under these conditions, there was no change in the resistance of either the aqueous solutions or the plasticiser.

The lowering of the resistance of the triply-distilled water after contact with the plasticiser evidently indicates

Fig 5.9: Impedance spectra measured for triply-distilled water a) before and b) after the equilibration with the plasticiser respectively.



the creation of charge-carrying species within the aqueous phase. It is possible that some charge-carriers would be created by equilibration of the water with atmospheric carbon dioxide, but the water was given ample time to reach such an equilibrium prior to the commencement of the experiment. On this basis, it must be assumed that the additional ionic species within the water arise as a result of the mixing with the DOS. The nature of such species is open to conjecture, although considering that the plasticiser is an ester, it seems likely that an equilibrium of the following form would exist between it and the water;

$$\text{ester} + H_2O = H^+(aq) + \text{ester anion}$$

Due to the high resistance of the plasticiser, it is impossible to say whether there has been any reduction in its magnitude after exposure to the water, and so it is not clear to what extent the charge-carrying species are partitioned between the aqueous and organic phases. Similarly, the very low resistance and high concentration of charge-carriers of the chloride solutions make it impossible to detect any small change in the solution composition, though it is of interest that even on exposure to the relatively high concentration of ions in the chloride solutions, the plasticiser does not appear to have taken up any charged species.

In a separate experiment, the conductivity cell was filled with triply distilled water and was left for 24 hours to achieve thermal equilibrium in a water bath, after which 200mg of PVC powder was added to the cell. The impedance of the cell was then measured hourly for 24 hours, and the resistance of

the water was obtained from the impedance spectrum as previously. In this case, no change in the impedance spectrum was found over the 24 hour period as a result of the addition of the PVC. Although this result is in contrast to the findings of Arami, in the earlier study very small quantities of water were used, for which a given quantity of ionic species arising from the PVC would produce a greater change in pH or conductivity. It does seem however, on the basis of the measurements reported here, that the greatest interaction is between the plasticiser and the water.

5.5 Conclusions

From the results presented in this chapter, it is clear that there is an interaction between the membrane matrix and any aqueous phase with which it may be in contact, although it is not clear on the basis of these measurements alone, whether this interaction plays any part in the operation of the membrane in an ISE. It is also evident however, that the membrane phase when cast into a film contains a significant number of charge-carrying species, and that ionic species are an integral part of the PVC matrix. The implications of these results on the mechanism of anion exclusion which operates when the membrane is used in an ion-selective electrode are clear. Both anionic and cationic sites are clearly present within the membrane even in the absence of deliberately added, large (and supposedly immobile) anions, and can provide an inherent source of balancing charge within the membrane. This is in contrast to the results found with the liquid membranes, where in the absence of the added ionophore, the membrane support and

solvent appear to be free of charged species, whilst the PVC membrane when in contact with aqueous solutions, can undergo ion exchange even in the absence of any complexing agent.

Chapter 5 References

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Chapter 6

PVC Membranes - The PVC/Valinomycin System

6.1 Introduction

Prior to the commencement of this project the small amount of work published covering impedance measurements on ion-selective electrodes had involved the use of liquid membrane, and solid-state electrodes alone, and no work had been published on the impedance of PVC-matrix electrode membranes (see Chapter 1). The object of the current work was to extend the measurements on liquid membranes presented in Chapter 4, and on the PVC matrix given in Chapter 5 to cover the impedance of PVC membranes in contact with aqueous solutions, in order to characterise in detail the whole system as a basis for further work.

The work presented in this chapter covers not only membranes as normally fabricated for use in electrodes but also a number of membranes containing various individual components, so as to obtain a detailed picture of the PVC membrane system in contact with aqueous solutions. The results of both potential and impedance measurements are presented for each type of membrane in separate sections, where the general features and interpretation of the results are discussed. In section 6.3, results are presented for membranes containing no active material, and also for membranes containing valinomycin as the sole additive. In section 6.4, data are given for membranes containing salts of the tetraphenylborate ion, but with no ionophore in the matrix. This is followed in section 6.5 by

results of work on membranes containing both the ionophore and added salts and in section 6.6, a comparison is made between the Cs^+ ion and K^+ ion in PVC membranes. A summary is presented at the end of the chapter in section 6.7, in which all the results are discussed in more detail, and a theory is proposed on the basis of these data encompassing the different membrane formulations, to account for the cation-selectivity, and anion-exclusion properties of the PVC membranes containing valinomycin.

6.2 Expected equivalent Circuits and General Details

The details of the basic equivalent circuits expected for PVC membranes are discussed in Chapter 5, where it is concluded that the impedance spectra for PVC membranes should be essentially similar to those obtained for liquid membranes, with two semicircular features in the complex plane, corresponding to the bulk membrane and interfacial processes.

Despite their measurable conductivity PVC membranes have a resistance which is high in comparison to systems studied in classical electrochemistry, (10^5- 10^6 Ohm as opposed to 0 - 10^2 Ohm), and this presents the main problem in making impedance measurements on them. The accuracy of the measurements depends to a large extent on the magnitude of the impedance being measured, greater accuracy being achieved the lower the value of the resistive component. It is therefore desirable to reduce the membrane resistance as much as possible, and the most obvious way to do this is to reduce its thickness. The membranes normally used in ion-selective electrodes are cast with thicknesses of the order of 1 mm as this provides good

physical strength, and is a convenient (although arbitrary) size for casting small quantities of membrane material. For the current work, attempts were made to cast membranes to a variety of thicknesses smaller than 1mm, but it was found that if the thickness was reduced below about 0.1 mm, the membrane lacked physical strength, and could not be handled and loaded into cells without sustaining damage. Membranes cast to approximately 0.1mm, were found to function quite satisfactorily in ion-selective electrodes despite their reduced thickness, and, also as expected, to have resistances which were considerably lower (by a factor of approximately ten) than those of the standard membranes. Fortunately, none of these thinner membranes were found to have resistances in excess of the upper limit of the measuring system, and the choice of 0.1mm for the thickness appears to be satisfactory in all respects.

An alternative way of reducing the membrane resistance is to use membranes of a larger surface area. With liquid membranes, attempts to increase the surface area were unsuccessful due to the loss of membrane solution from the filter support, for which no simple remedy could be found. This problem obviously does not arise with PVC membranes although no information is available relating to the effect of changing the membrane area on the operation of the membrane in an electrode. It can be assumed that a point will be reached where the membrane will distort or rupture due its physical size, but, apart from this, there is no theoretical limit for the size of membrane used, and the use of membranes of 0.5 cm^2 in laboratory electrodes seems to be an arbitrary decision. Two cells were therefore constructed for the PVC membranes, allowing the use of membranes of different surface areas (the design of the PTFE cells used

for measurements on the PVC membranes is discussed in detail in Chapter 2). One cell was made with an internal bore of 0.5 cm, giving a cross sectional area of 0.196 cm^2, and the second cell was made with a bore of 1 cm, giving a cross sectional area of 0.785 cm^2.

After preliminary measurements, it was found that in certain situations, the low frequency regions of the impedance spectra for PVC membranes were not clearly defined. This is due partly to the compromise between selecting a fast integration time, so as to measure the whole spectrum quickly whilst it is undergoing time dependent changes, and partly due to the high resistance of the systems under study. In some cases, the low frequency features occurred at frequencies where resonance with the electrical mains supply occurs and were subject to interference as a result. In cases where the low frequency limit was in any doubt, the DC resistance of the system was obtained, via the 1186 ECI. This is achieved by applying a potential across the membrane and monitoring the current flowing in the cell as a result. The resistance can then be calculated using Ohms' law. This method provides a useful technique to verify the values obtained with the frequency response analyser.

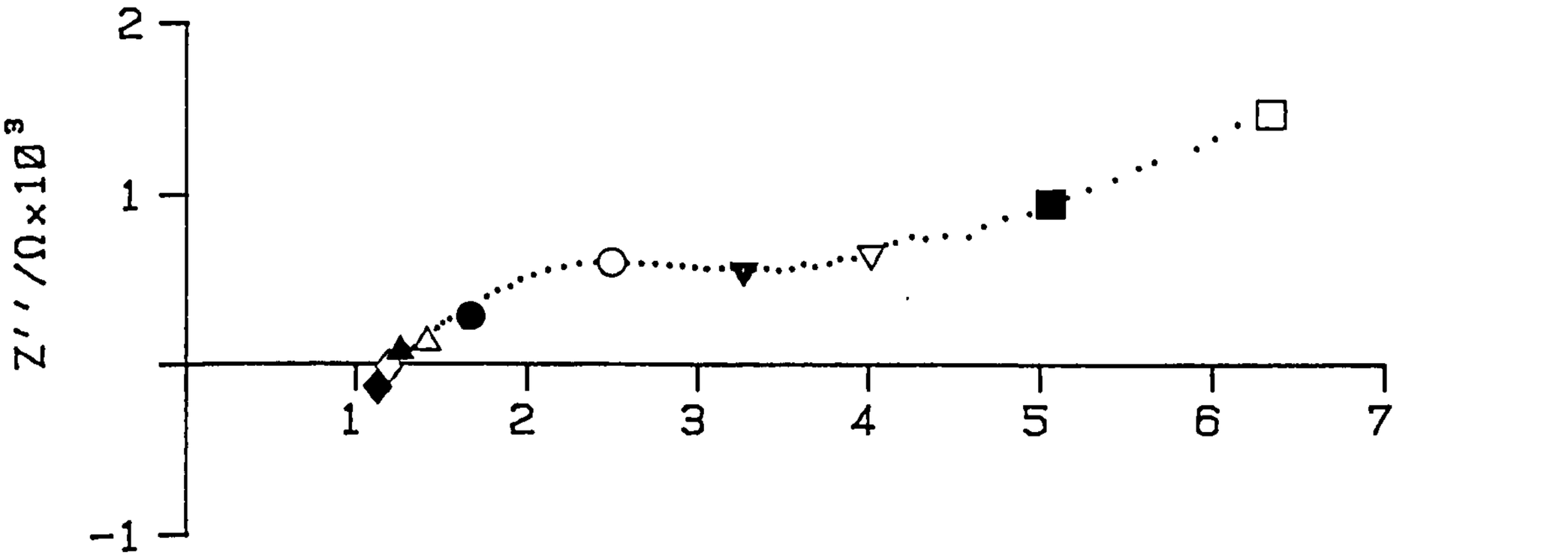
6.2.1 The PTFE Cell Impedance

The impedance of the cells was measured when filled with 0.1 mol dm^{-3} KCl, with no membrane present, in order to assess the contribution from the cell and its electrodes to the measured impedance. As discussed in Chapter 2, the use of the four-electrode system should eliminate this contribution, however, as it was necessary to use some two-electrode

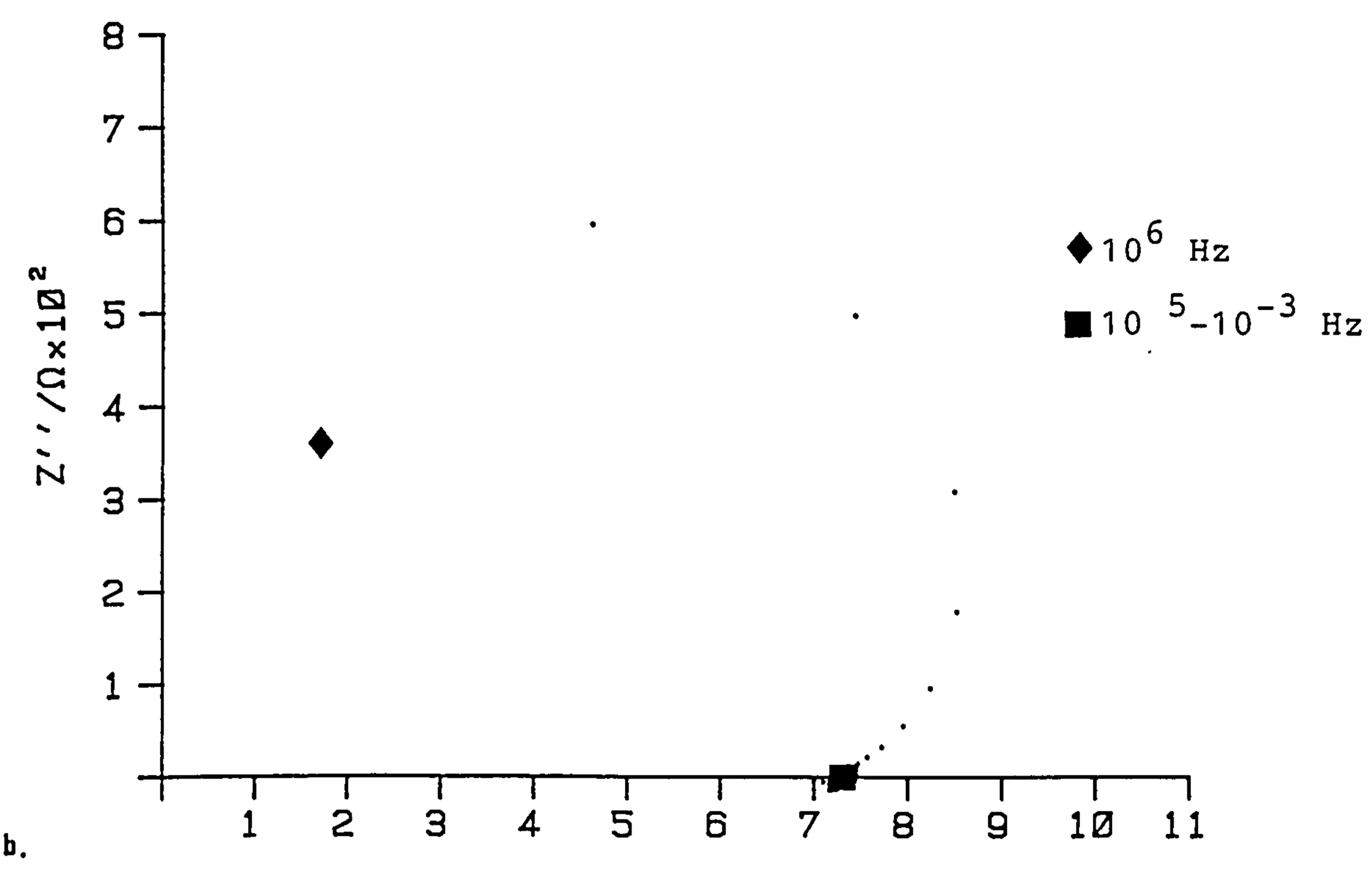
measurements, it was of interest to determine the cell impedance.

Fig 6.1a shows the impedance spectrum of the cell filled with KCl, in a two electrode configuration, over the range 1 MHz - 0.1 mHz. This spectrum is similar to those shown for the Orion silver choride electrodes in section 2.8, and shows an offset along the real axis of approximately 1.1 x 10^3 ohm, corresponding to the solution resistance, and a poorly defined high frequency semicircle tailing off towards lower frequency. This spectrum can be interpreted as previously, with a parallel RC network representing the AgCl layer on the electrode surface, resonating at high frequency, in series with one or more networks representing the interfacial processes occurring at the electrode surface, appearing at lower frequencies. The low frequency region of the spectrum where the interfacial impedance occurs, is again complicated by surface roughness, effectively leading to multiple RC networks.

Fig. 6.1b shows the impedance spectrum over the same frequency range obtained with the cell in a four-electrode configuration. This spectrum shows a marked difference to the one obtained using two electrodes, and illustrates the advantages of the four-electrode arrangement. Below 100 kHz, the plot shows a single point representing a pure resistance with a value of approximately 720 Ohm. Above this frequency, the spectrum shows a structure which is normally interpreted as an inductance. In this case, this inductive loop is an artefact of the system due to a phase shift induced by the 1186 circuitry at high frequencies, and it is for this reason that the 1174 is used alone under these conditions. The remaining pure resistive offset along the real axis represents the resistance of the KCl



a.



b.

Fig 6.1: Impedance plot for the PTFE cell with no membrane, filled with 0.1 mol dm^{-3} KCl measured in (a), a two-electrode, and (b), a four electrode configuration.

filling solution between the reference electrodes alone, and can be used to obtain a value for the conductivity of the KCl solution, providing a useful check on the accuracy of the system. Alternatively, using a standard value for the KCl conductivity an estimate of the spacing between the electrodes can be obtained, which again can be used as a check on the system. Taking the conductivity of 0.1 mol dm^{-3} KCl to be 1.29 S m^{-1} (i.e. a resistivity of 77.52 ohm cm) the spacing between the electrodes can be calculated to be 9.23 cm which compares very favourably with the measured length of 9.25 cm.

6.2.2 Potential Measurements Using The PTFE Cell

The PTFE cells present an experimental arrangement for measuring the membrane potential which is essentially different from that normally used in work on ISEs. To assess single or mixed ion potential responses, the membrane would normally be housed as a dip-type electrode in one form or another, and its potential would be measured against a standard calomel electrode, generally with an intervening salt bridge. As the use of symmetrical cells is required for accurate impedance measurements, this arrangement cannot be used. One solution to this problem is to measure the membrane impedance in the PTFE cell, and then transfer the membrane to a standard B7 glass tube electrode (Fig 2.5), where the potential response could be assessed in the normal way. Again this is not an entirely satisfactory arrangement as the removal of the membrane from the PTFE cell, followed by its attachment to the standard glass holder, are likely to result in damage to the membrane and allow possible contamination by external agents.

An alternative is to measure the potential response with the membrane remaining resident in the PTFE cell. This is obviously preferable from the point of view of keeping the membrane in the same environment for all measurements, but presents the problem of measuring the membrane response with two Ag/AgCl electrodes. When measuring the single ion response in this way, the two Ag/AgCl electrodes produce a potential difference due to the difference in Cl^- concentration on the two sides of the membrane. The total cell potential as measured therefore represents the sum of this reference electrode potential and the membrane potential, and to assess correctly the latter, the response characteristics of the Ag/AgCl electrodes must either be known or assumed.

In the present work, this question was resolved by adopting the following regime. Portions of membranes were cut and their potential response was assessed in the normal way by glueing them with a PVC/THF paste on to a glass holder. The response of further portions of the same membrane was then measured in the PTFE cell using the Ag/AgCl electrodes, and the two sets of measurements were then compared. It was found that, within the limits of experimental error, the Ag/AgCl electrodes were behaving ideally (ie giving a contribution to the total potential of approximately 59 mV/decade at $25^{o}C$).

The function of the potential measurements in this work was to verify that a given membrane was behaving in general as expected, rather than to attempt highly accurate, detailed potential measurements (with the exception of the results concerning relative ionic mobilities discussed below). In view of this, and the fact that the Ag/AgCl electrodes behave in a predictable manner, potential measurements were carried out with

the membrane remaining in situ in the PTFE cell, and corrections were made for the Ag/AgCl electrode contribution accordingly.

6.2.3 Relative Mobilities of Species from Potential Measurements

Using standard electrochemical principles, and considering the diffusion potential across the membrane, it is possible to calculate the relative mobilities of the positive and negative charge carriers within the membrane. This argument is based on classical ideas of electrochemistry, where the carriage of charge through the membrane must necessarily be shared between the cationic and anionic species in the membrane bulk. The extent to which each type of species contributes to the overall charge-transfer process depends on the relative ease with which each class of ions can move through the membrane matrix. This is expressed by the transport number, t (with a subscript + or - representing cations or anions respectively), where

$$t_+ + t_- = 1 \qquad 6.1$$

At equilibrium, the following equation holds:-

$$E = (t_+ - t_-) \frac{RT}{F} \ln\left(\frac{a_1}{a_2}\right) \qquad 6.2$$

where E is the potential arising from the difference in mobility of cations and anions, and a_1 and a_2 are the mean activities for solutions on either side of the membrane.

From equation 6.2 it can be seen that when $t_+ = t_-$, E becomes zero, and when $t_+ = 1$, equation 6.2 reduces to,

$$E = \frac{RT}{F} \ln\left(\frac{a_1}{a_2}\right) \qquad 6.3$$

It is necessary to modify this expression in the present case due to the configuration of the PTFE cell. If one side of the cell is filled with 0.1 mol dm^{-3} KCl (or NaCl), and the other chamber is filled with a solution of the same salt, but with an activity smaller by a factor of ten, there will be a contribution to the overall measured potential from the Ag/AgCl electrodes equivalent to

$$E_{(AgCl)} = \frac{RT}{F} \ln\left(\frac{a_1}{a_2}\right) \qquad 6.4$$

The measured potential then becomes

$$E = \frac{2RT}{F} \ln\left(\frac{a_1}{a_2}\right) \qquad 6.5$$

This expression evaluates to 110.6 mV for KCl solutions, and 110.0 mV for NaCl solutions.

With the PTFE cell arrangement, the assumption must necessarily be made that the Ag/AgCl electrodes are behaving ideally, but as discussed earlier, this appears to be a reasonable assumption, although even if the electrodes are not behaving ideally, a comparison can be obtained between potassium and sodium as the cation. This is because the Ag/AgCl electrodes must respond to the Cl^- activity in the same way for both solutions, and the electrodes in each side of the cell are exposed to Cl^- at closely similar activities regardless of the cation present.

6.3 The Basic Valinomycin Membrane

The valinomycin PVC membrane as originally formulated is cast containing only plasticised PVC and valinomycin (6.1,6.2).

and the potentiometric response of such membranes has been reported to be Nernstian over a large concentration range (6.1).

In this section, results of impedance and potential measurements are reported for membranes comprising plasticised PVC alone, and also with valinomycin as the only additive. The object of this section of the work is to establish the parameters of the PVC membrane system in contact with aqueous solutions, and further investigate the presence of inherent charge carrying species.

6.3.1 The PVC/Dioctyl Sebacate Membrane

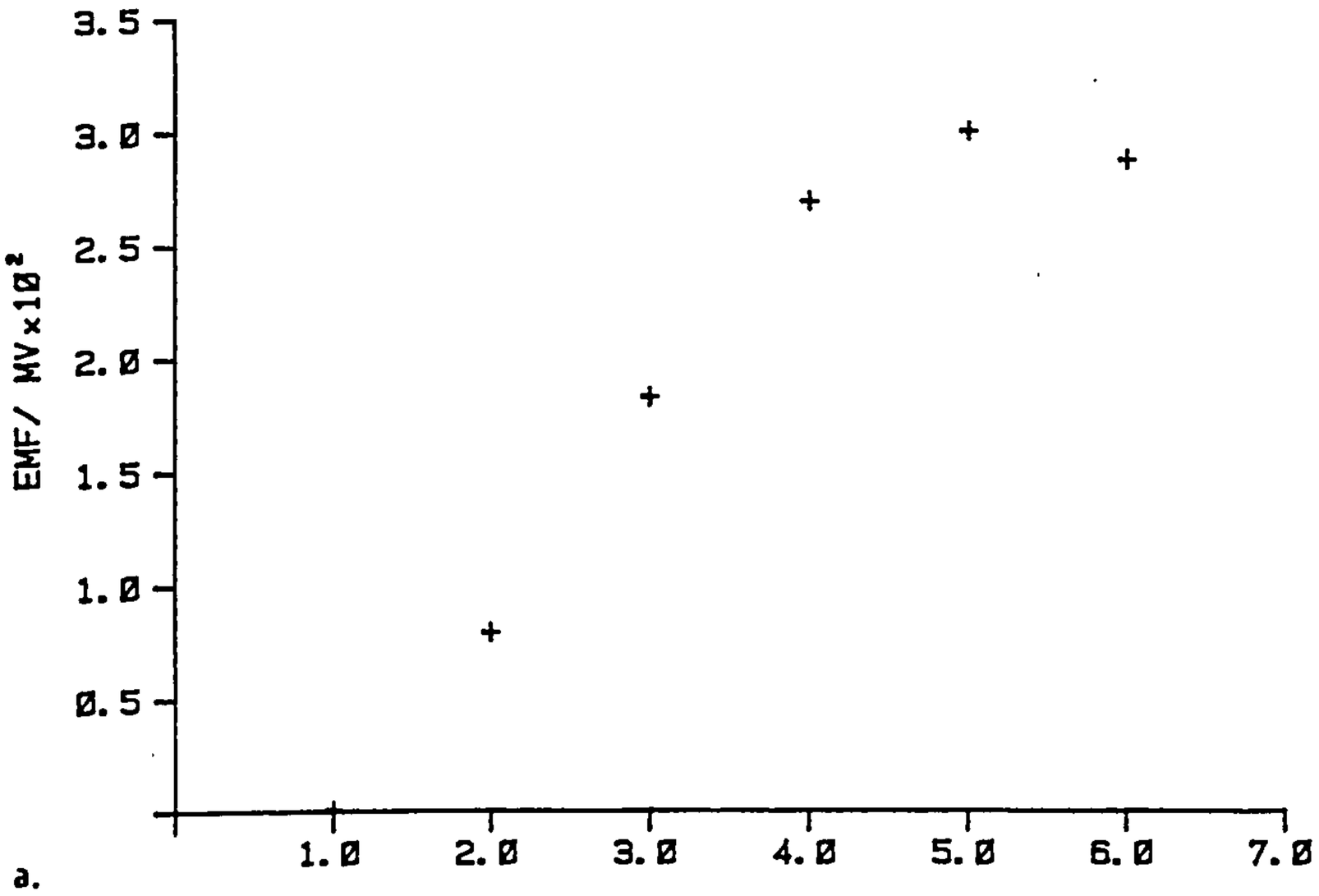
It is to be expected that the membrane containing no valinomycin would reflect the basic features of the PVC matrix, in terms of time-dependent effects and the resistance of the membrane material. The membrane should show no selectivity for one type of cation over another, although the membranes should exhibit a single-ion response. The typical membrane composition was 150mg PVC/300mg DOS, and the potential response and impedance behaviour of the membranes are discussed below.

6.3.1a Potential Response

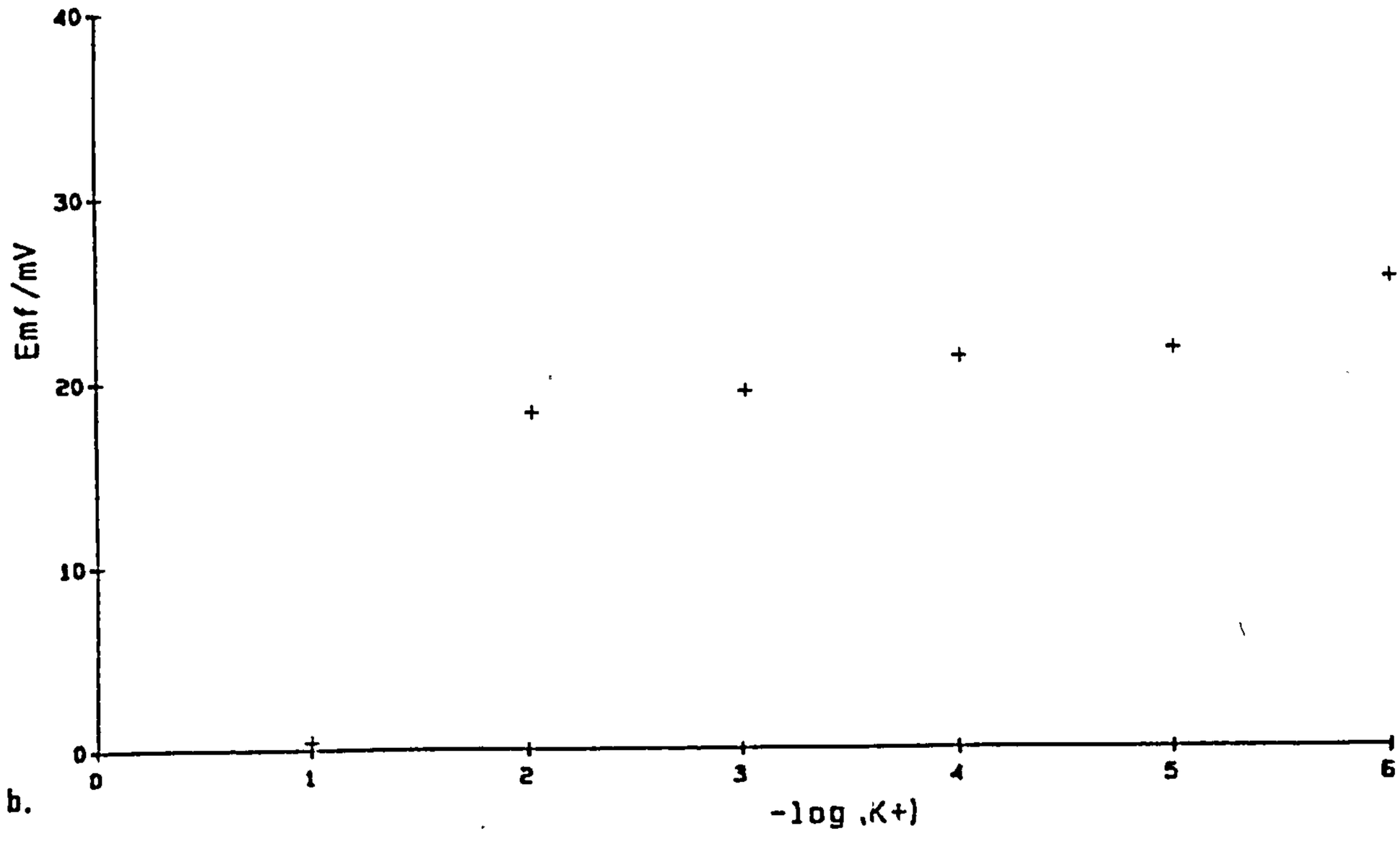
Fig 6.2a shows the calibration curve (single-ion response) for a typical membrane and Fig 6.2b shows the potential response of the membrane as determined by the mixed solution method with 0.1 mol dm^{-3} NaCl constant interferent concentration.

It can be seen that the membrane shows a limited single ion response over the whole concentration range. If the cation and anion mobilities were equal, the potential should reflect only

Fig 6.2: (a) Calibration (K^+ single-ion response) and (b) selectivity (K^+/Na^+ mixed-ion response) plots for a PVC/DOS membrane measured with a 0.1 mol dm^{-3} KCl reference solution.



a.



b.

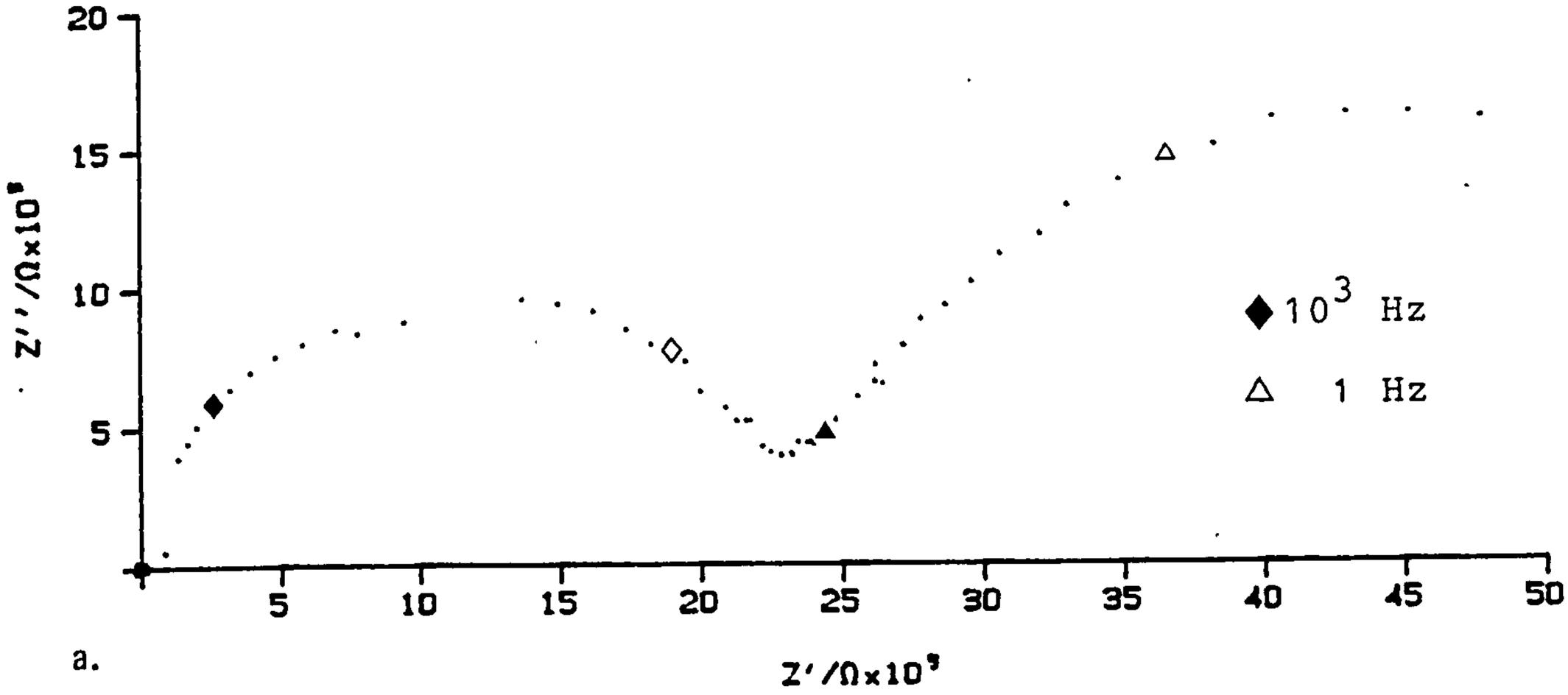
the difference in potential of the Ag/AgCl electrodes in the two bathing solutions. In this case, the slope of the plot should be Nernstian, and the potential measured with a tenfold concentration difference should be 59.18mV. The measured potential at this point is in fact 78.8mV, indicating that the two mobilities are not equal, and that the membrane exhibits a low level of selectivity for cations over anions, although there is no evidence of any inherent selectivity of the membrane for one type of cation over another as is clear from Fig 6.2b.

6.3.1b Impedance Measurements

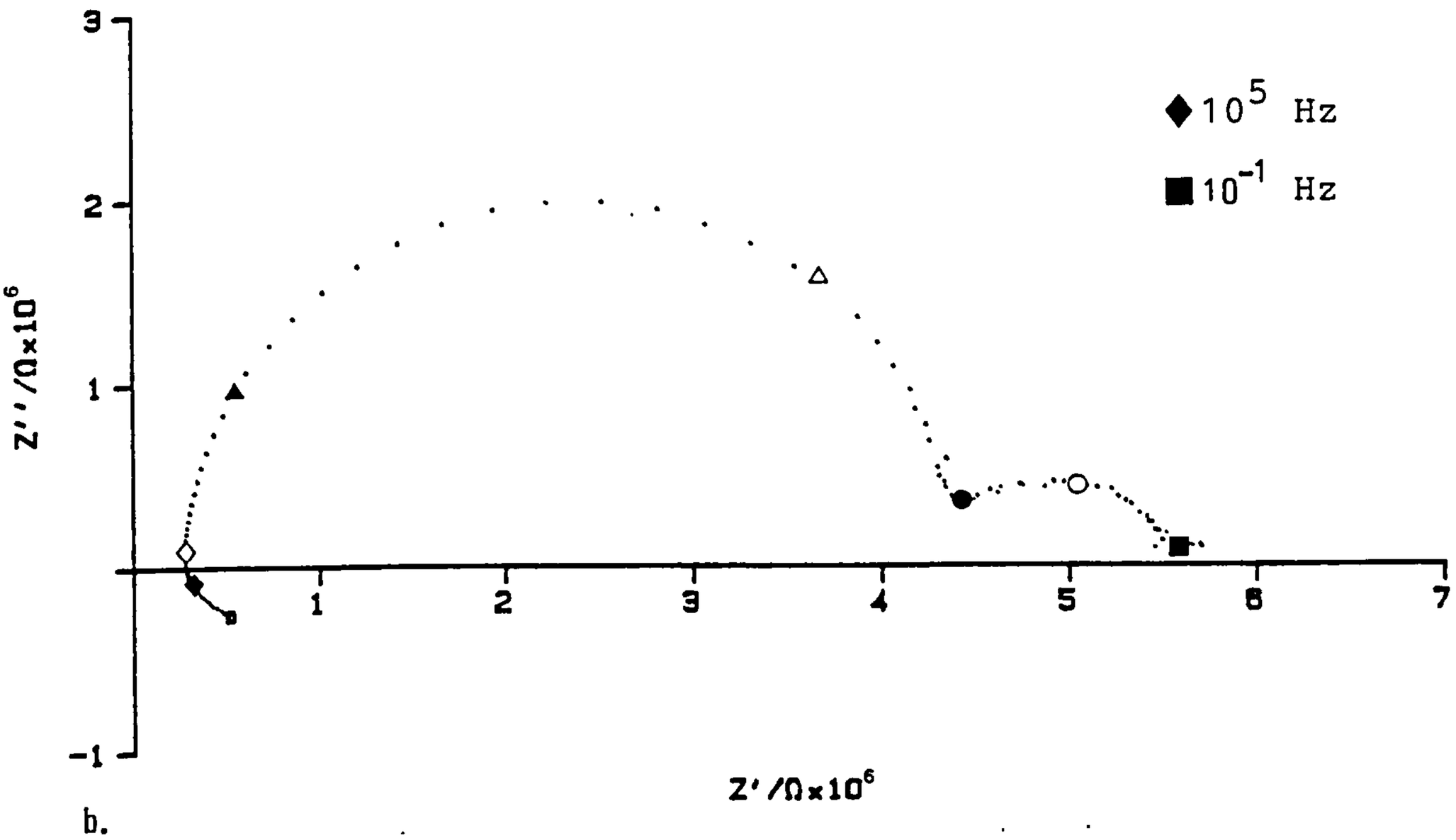
Fig 6.3a shows the impedance spectrum obtained with 0.1 mol dm^{-3} KCl contacting solutions, the first measurement being made approximately five minutes after the membrane was first contacted by the aqueous solutions. The spectrum shows two features similar to those found with liquid membranes; a high frequency semicircle, and a second feature at lower frequency. The high frequency feature can be attributed to the parallel combination of the bulk membrane resistance R_b, and the geometric capacitance C_g, and the low frequency feature can be attributed to the combination of the charge-transfer resistance R_{ct}, and the double-layer capacitance C_{dl}, as was the case with the liquid membranes. The bulk resistance of the membrane was initially 2.28 $x10^6$ Ohm, from which the capacitance of the membrane can be calculated to be 2.03 $x10^{-10}$ F.

The lower frequency feature, although not fully resolved, shows a large portion of a second semicircle, representing the charge-transfer processes at the membrane solution interface. Extrapolating the curve to meet the real axis of the plot

Fig 6.3: Initial (a) and final (b) impedance spectra for a PVC/DOS membrane, measured with 0.1 mol dm^{-3} KCl contacting solutions.



a.



b.

Table 6.1: Time Dependence of the Impedance of a PVC/DOS Membrane (0.1 mol dm^{-3} KCl Contacting Solns.)

t/hours	$R_b/10^6\,\Omega$	$\omega_{1\,max}^*$/Hz	$R_{ct}/10^6\,\Omega$	$\omega_{2\,max}^*$/Hz
1	2.28	343.1	4.40	0.638
2	2.70	"	2.81	"
3	2.90	294.4	2.58	0.744
4	3.15	"	2.25	1.009
5	3.26	"	2.18	"
6	3.49	"	1.86	"
7	3.68	"	1.80	1.177
8	3.79	"	1.72	"
9	3.98	"	1.43	"
10	4.00	252.4	1.40	1.372
11	4.00	"	1.40	"
12	4.13	"	1.43	"
13	4.20	"	1.28	1.865
14	4.20	"	1.30	"
15	4.20	"	1.30	1.599
16	4.31	216.5	1.24	1.865
17	4.40	"	1.15	"
18	4.40	"	1.24	"
19	4.44	"	1.24	"
20	4.58	"	1.16	"
21	4.62	"	1.07	"
22	4.62	"	1.07	"
23	4.71	"	1.07	"
24	4.70	"	1.08	"
72	4.50	"	1.07	2.174

shown in Fig 6.3a, gives a value of 4.40 x10^6 Ohm for the resistive component of the network, and a capacitance of 6.60 x10^{-8} F. Fig 6.3b shows the impedance spectrum of the membrane determined 72 hours after the first spectrum was measured, which shows that the bulk resistance of the membrane has increased markedly, and that the charge transfer resistance has become greatly reduced. Table 6.1 gives the variation of R_b and R_{ct} over the 72-hour period, from which it can be seen that the value of R_{ct} reduces to a final value of approximately 10^6 Ohms and the bulk resistance stabilises at 4.50 x10^6 Ohms.

Figs 6.4a and 6.4b show the corresponding spectra for the membrane contacted by 0.1 mol dm^{-3} NaCl solutions. In this case, the charge-transfer semicircle is more clearly defined initially, and is of a similar order of magnitude to that found with the KCl solutions. Table 6.2 shows the time dependence of the impedance as followed over a period of 24 hours. As with the membrane contacted by KCl solutions, R_{ct} is seen to decrease with time, and R_b shows a gradual increase over the same period.

For both membranes, the time constant for the membrane bulk decreases slightly over the 24 hour period, by a factor of approximately two, corresponding to the increase in R_b. This indicates that the increase in resistance cannot be purely due to geometric factors, and that there must be a change in the resistivity of the membrane, rather than just an increase in the membrane thickness.

6.3.2 The PVC/Dioctyl Sebacate/Valinomycin Membrane

In this section, results for membranes containing valinomycin as the only additive are presented, the typical

Fig 6.4: Initial (a) and final (b) impedance spectra for a PVC/DOS membrane, measured with 0.1 mol dm^{-3} NaCl contacting solutions.

a.

b.

Table 6.2: Time Dependence of the Impedance of a PVC/DOS Membrane (0.1 mol dm^{-3} NaCl Contacting Solns.)

t/hours	$R_b/10^6\ \Omega$	$\omega_{1\,max}^*$/Hz	$R_{ct}/10^5\ \Omega$	$\omega_{2\,max}^*$/Hz
1	2.56	1003	41.4	2.174
2	3.71	"	28.5	"
3	4.10	"	24.4	"
4	4.34	"	21.3	"
5	4.73	543.7	17.3	5.464
6	4.73	"	17.3	"
7	4.85	"	15.8	4.019
8	4.73	"	17.3	6.374
9	5.12	"	12.6	"
10	5.24	"	11.8	"
11	5.32	"	10.6	"
12	5.32	"	9.86	"
13	5.51	"	7.88	"
14	5.51	"	7.88	"
15	5.52	466.5	7.86	7.429
16	5.50	"	7.84	"
17	5.51	"	7.82	"
18	5.53	"	6.70	"
19	5.51	"	5.91	6.374
20	5.51	"	5.91	7.429
21	5.52	"	5.90	"
22	5.51	"	5.87	"
23	5.51	"	4.73	8.658
24	5.51	"	5.52	"
72	5.51	"	5.52	"

composition for the membrane being 150mg PVC/300mg dioctyl sebacate/6.5mg valinomycin. Potential difference measurements (single and mixed-ion potential responses) were carried out as previously, and impedance measurements were also made on membranes in contact with aqueous solutions containing either 0.1 mol dm^{-3} KCl or 0.1 mol dm^{-3} NaCl.

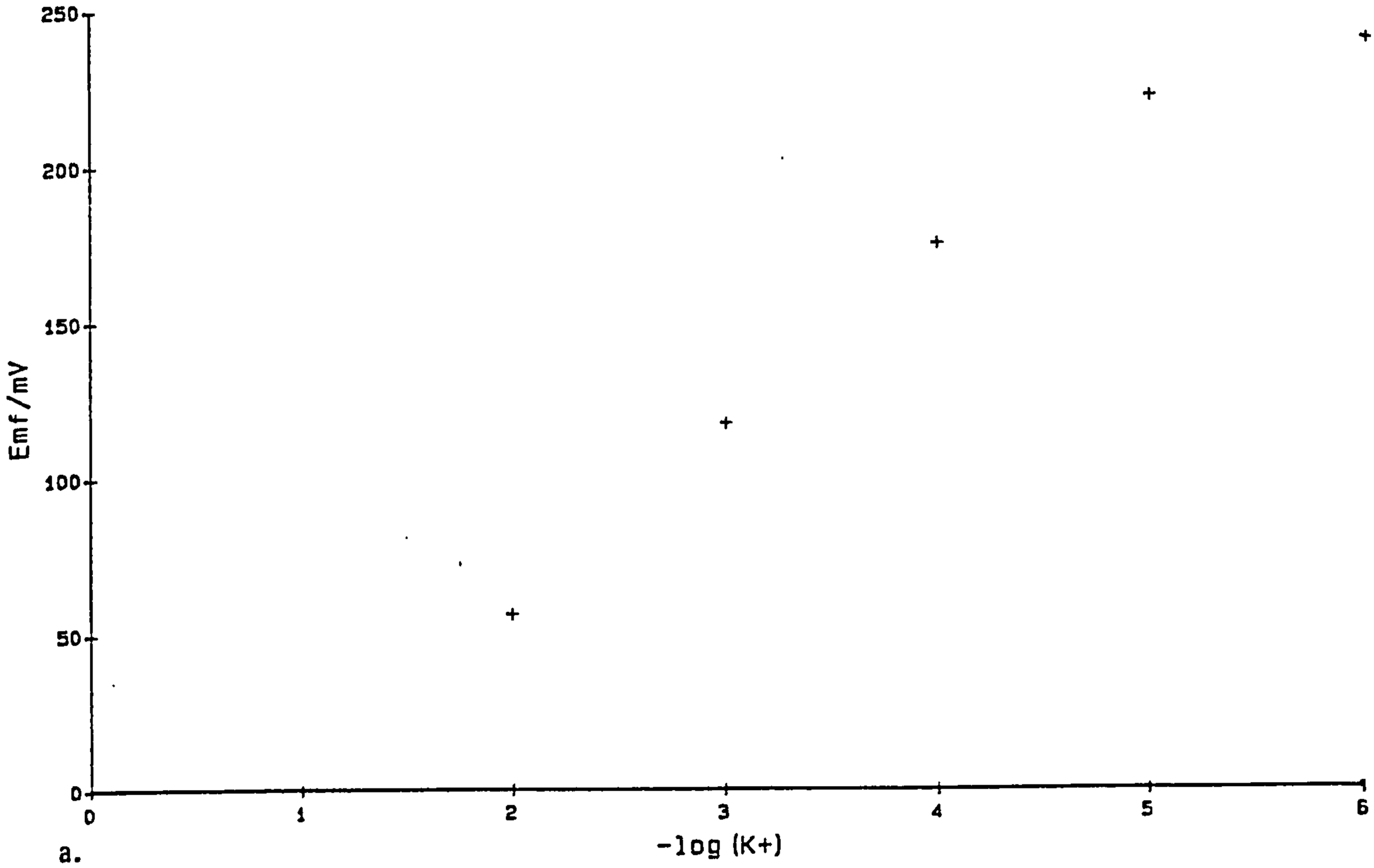
6.3.2a Potential Response

Typical calibration curves (single ion response) and selectivity plots (mixed ion response) for membranes containing valinomycin are shown in Figs. 6.5a and 6.5b, respectively. As would be expected, both the single ion and mixed ion responses show slopes of near 59mV over the concentration range 10^{-1} - 10^{-4}. Some membranes were found to show poorer responses with slopes for the mixed-ion response as low as 45mV/decade, although this was so for only about 10% of membranes cast. The possible reasons for this poor response are discussed in section 6.3.3.

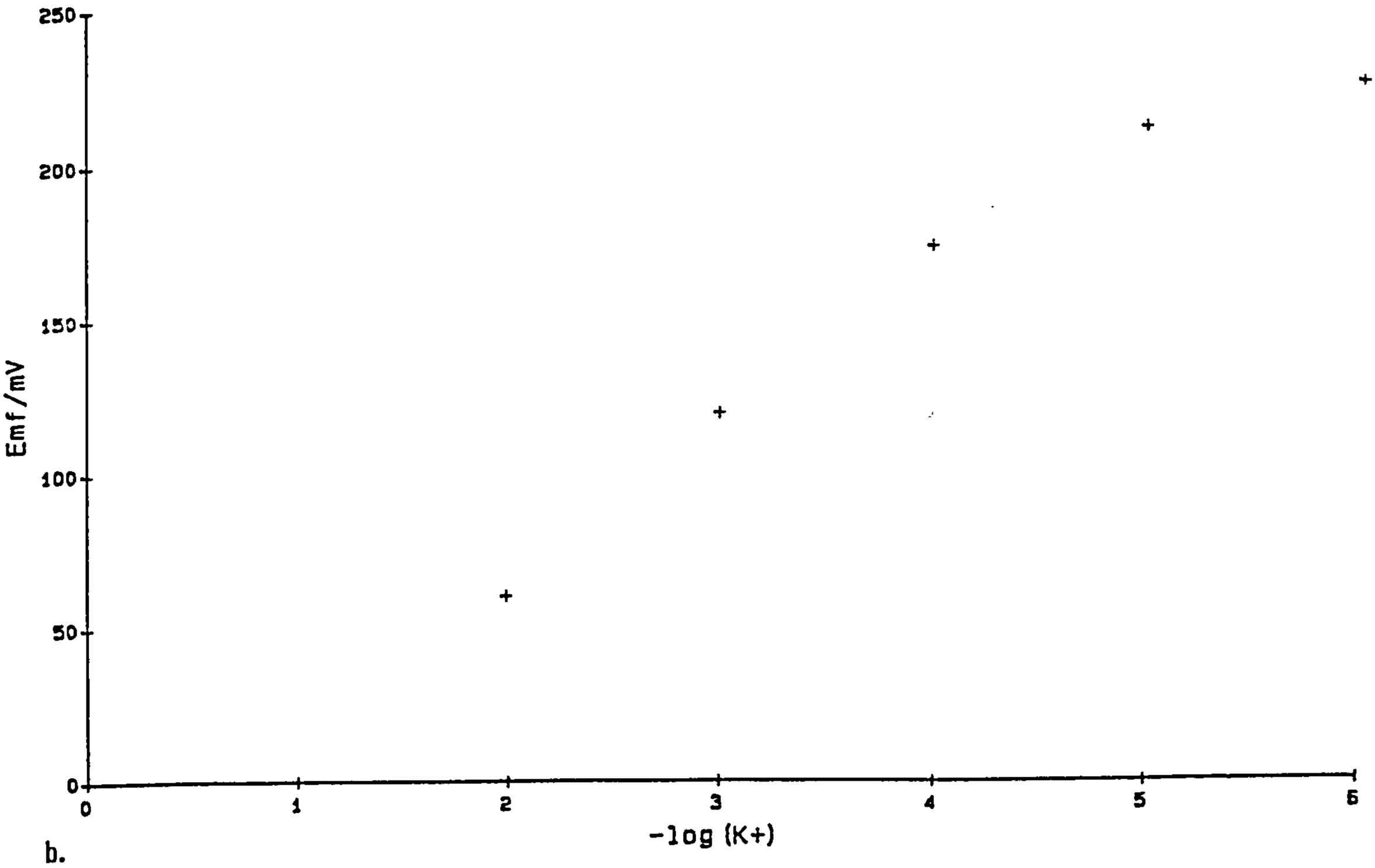
6.3.2b Impedance Measurements

The impedance of the membranes was measured when in contact with both 0.1 mol dm^{-3} KCl alone and 0.1 mol dm^{-3} NaCl alone. It would be expected that the spectra obtained in these two situations would illustrate in some way the preference shown by the membrane from potentiometric measurements. From a simple viewpoint, it might be expected that the selectivity would be reflected in the interfacial ionic transfer rates i.e. that potassium will enter the membrane with much greater ease than

Fig 6.5: (a) Calibration (K^+ single-ion response) and (b) selectivity (K^+/Na^+ mixed-ion response) plots for a PVC/DOS/valinomycin membrane measured with a 0.1 mol dm^{-3} KCl reference solution.



a.



b.

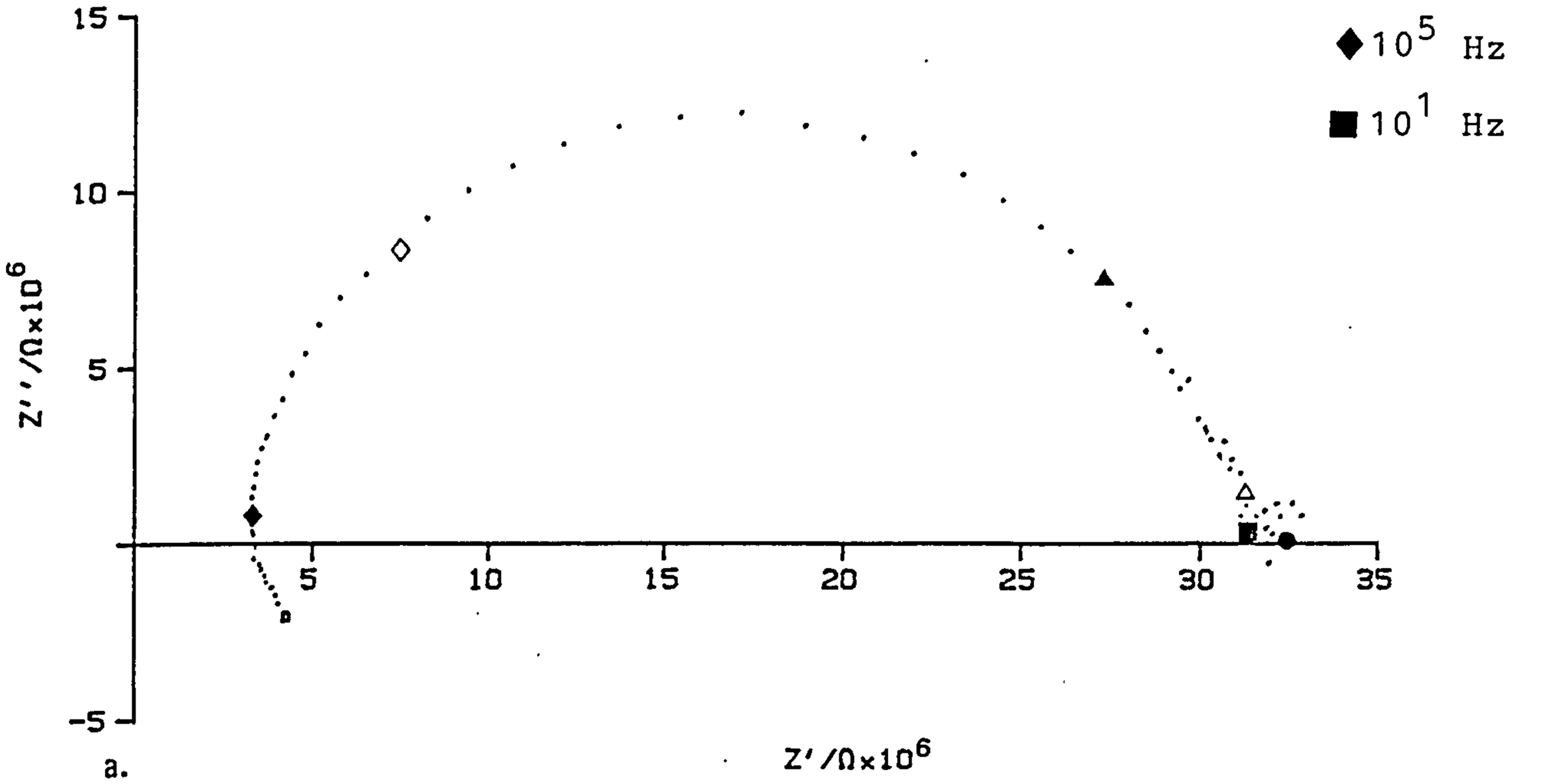
the sodium. If this were the case, then the impedance spectrum obtained with sodium contacting solutions should show a much larger charge transfer semicircle than when potassium contacting solutions were present, and the difference in magnitude should be of the same order of magnitude as the selectivity coefficient. i.e. 10^3 - 10^4.

Figs. 6.6a and 6.6b show spectra obtained after three days for membranes contacted by 0.1 mol dm^{-3} KCl and 0.1 mol dm^{-3} NaCl respectively. The spectra show a high frequency semicircle similar to that found with the membranes containing no valinomycin. The low frequency data for these membranes were poorly defined, and the DC resistance points determined as outlined in section 6.2 are included for clarity. The time dependence of the impedance of these membranes is shown in Tables 6.3 and 6.4.

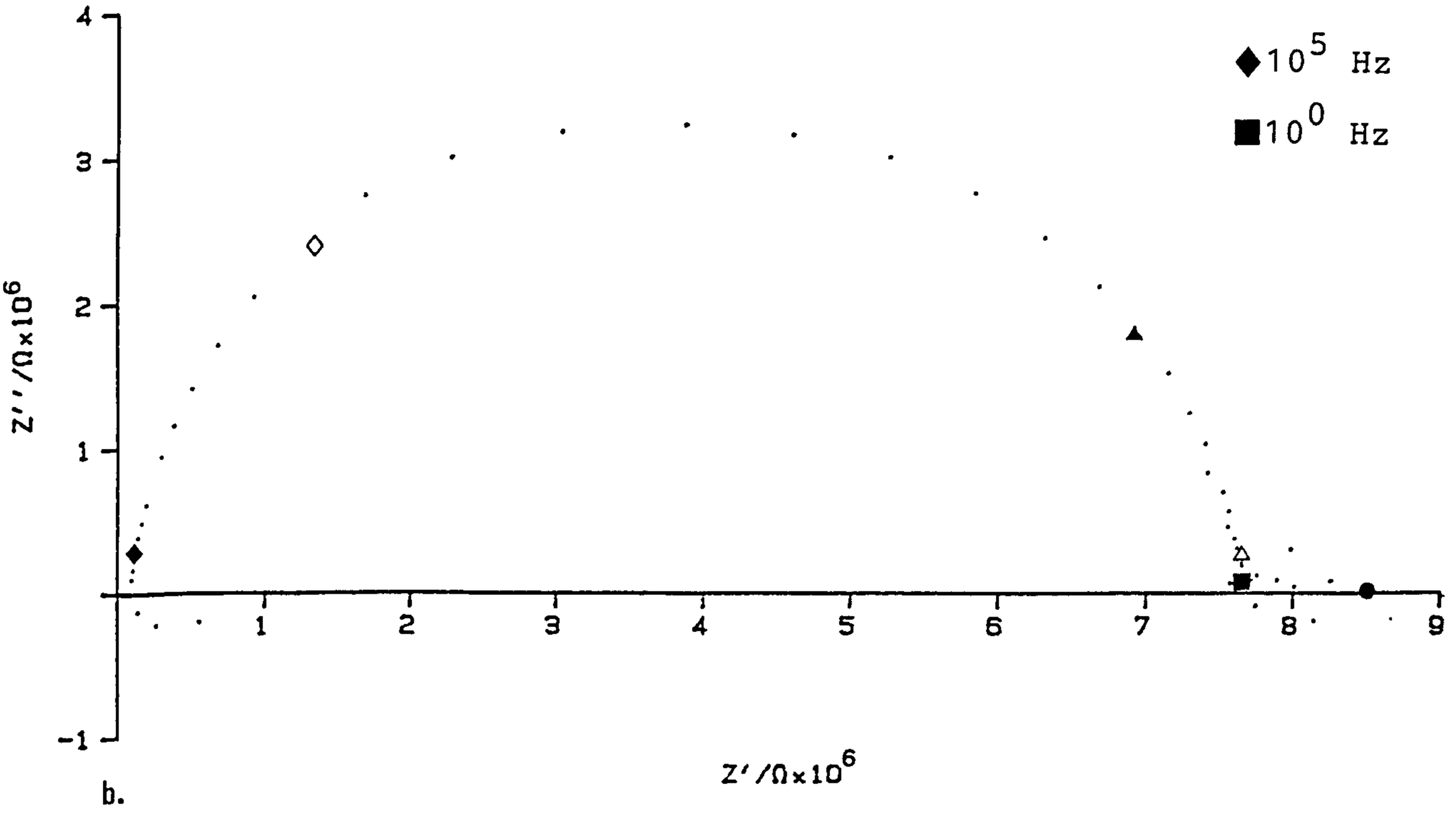
6.3.3 Discussion

Although the PVC/valinomycin system will generally yield a membrane which gives a good mixed-ion potential response with sodium chloride as the interferent, workers in these laboratories have often found the response to be sub-Nernstian. There is also a lack of consistency between membranes fabricated using materials from different batches from suppliers. The reasons for this variability are not clear, but as discussed in Chapter 5, there is considerable evidence from measurements on dry membranes, that the PVC contains charge-carrying species inherent in the matrix prior to contact with aqueous solutions. It is possible that these adventitious species are involved in the mechanism of operation of the membrane, and that variations

Fig 6.6: Final impedance spectra (measured after 72-hours) for a PVC/DOS/valinomycin membrane, with (a) 0.1 mol dm^{-3} KCl and (b) 0.1 mol dm^{-3} NaCl contacting solns.



a.



b.

Table 6.3: Time Dependence of Membrane Impedance for PVC/DOS/Val Membrane With 0.1 mol dm^{-3} KCl Contacting Solutions

t/hours	$R_b/10^6\ \Omega$	$\omega_1^*{}_{max}$/Hz
1	1.89	3975
2	2.37	"
3	2.54	"
4	2.65	"
5	2.75	2506
6	2.81	"
7	2.84	"
8	2.83	"
9	2.94	"
10	2.99	"
11	3.02	"
12	3.04	"
13	3.07	"
14	3.10	"
15	3.09	"
16	3.10	"
17	3.11	"
18	3.10	"
19	3.09	"
20	3.12	"
21	3.10	"
22	3.11	"
23	3.12	"
24	3.11	"
72	3.11	"

Table 6.4: Time Dependence of Membrane Impedance for PVC/DOS/Val Membrane With 0.1 mol dm^{-3} NaCl Contacting Solutions

t/hours	$R_b/10^6\ \Omega$	$\omega_1^*{}_{max}$/Hz
1	4.83	6374
2	5.31	"
3	5.84	"
4	6.37	"
5	6.49	"
6	6.77	"
7	6.89	"
8	7.09	5464
9	7.21	"
10	7.25	"
11	7.34	"
12	7.42	"
13	7.46	"
14	7.44	"
15	7.54	"
16	7.66	"
17	7.58	"
18	7.70	"
19	7.62	"
20	7.71	"
21	7.74	"
22	7.70	"
23	7.74	"
24	7.72	"
72	7.76	"

in their concentration can explain the differing electrode responses.

The large initial values for R_{ct} found for the membranes with no added ionophore indicate that the membrane at first takes up ions from the solutions only slowly, but the decrease in R_{ct} with time which is seen both when KCl contacting solutions are used and also with NaCl solutions, can only be interpreted as indicating that the rate of exchange increases with time, requiring a corresponding increase in the number of ionic species at the membrane surface available for exchange with ions in solution. Such an increase would be the inevitable result of the initial period of exchange, whereby a gradual permeation of the membrane by species from the solutions occurs, but could also be due to the formation of ionic species in the membrane as a result of water uptake.

Table 6.5 summarises the final bulk and charge transfer resistances for these membranes, and also for membranes containing valinomycin. These results permit several conclusions to be drawn.

Firstly, considering the bulk resistance of the membranes, from Table 6.5 it can be seen that for membranes both with and without added valinomycin, R_b is larger when the contacting solutions contain sodium chloride than when they contain potassium chloride. This suggests that in the absence of added charge carriers, the potassium ion is inherently more mobile in the PVC matrix than the sodium ion, although the mobility of both species must be of the same order of magnitude. Whilst the sodium is the smaller of the two ions, and as a result might be expected to be the more mobile, it has a much higher charge density than the potassium ion (Table 6.6) and therefore

Table 6.5: Summary of Impedance Data for PVC/Dioctyl Sebacate Membranes Both With and Without Valinomyin

Membrane Composition	Solutions (a)	R_b / MOhm cm^2	R_{ct} / kOhm cm^2	R_{ct} Na^+ / R_{ct} K^+	Exchange Current /μA cm^{-2}
No Val	KCl	3.51	834	0.51	3.1×10^{-2}
"	NaCl	4.29	430		6.0×10^{-2}
Val	KCl	2.43	74	7.24	3.5×10^{-1}
"	NaCl	6.05	536		4.8×10^{-2}

a - All solutions 0.1 mol dm^{-3}

Table 6.6: Radii and Charge Densities Of Alkali Metal Cations

	r/A	Chge D./ 10^{20} C A^{-3}
Na^+	0.95	12.1
K^+	1.33	1.62
Cs^+	1.69	0.79

electrostatic interactions between the ion and the PVC matrix would be expected to affect the sodium ion more than the potassium. Such weak interactions with the matrix are a possible explanation for the difference in bulk resistance found for the two ions.

It is also interesting to note that the addition of valinomycin to the membrane reduces the bulk resistance of the membrane, when KCl contacting solutions are used, but produces an increase in R_b relative to the resistance of the membrane containing no valinomycin when NaCl contacts are employed. This implies that the valinomycin either increases the mobility or number of potassium ions within the membrane, but produces the opposite effect on sodium ions.

Comparing the bulk resistance of membranes in contact with aqueous solutions with the measurements made on dry membranes reported in Chapter 5, it can be seen that R_b is of the same order of magnitude when direct contact is made as when solution contacts are employed. This is further evidence that the PVC matrix contains large numbers of inherent charge carriers (presumably mobile cations).

From Table 6.5, it can be seen that in the absence of valinomycin, the charge transfer resistance is of a similar order of magnitude regardless of which cation (sodium or potassium) is present in the solution. This is as expected assuming that the charge transfer resistance reflects the ease with which the cation can enter the membrane, in which case, in the absence of the ionophore, the value of R_{ct} should be approximately the same for both sodium and potassium.

Table 6.5 also shows that when the membrane contains valinomycin, the ratio of charge transfer resistance is

increased only marginally, such that R_{ct} is only about ten times greater for sodium than for potassium. This result is in contrast to what would be expected if the selectivity of the membrane arises purely out of the relative ease with which the cation can cross the membrane/solution interface. In view of this, it must be concluded that the selectivity of the membrane does not arise solely at this interface, and that a simple mechanism like that of the liquid membranes does not operate, where potassium ions are made soluble in the membrane phase whilst sodium ions are not.

6.4 The Use of Negative Sites

In the early 1970's Band, (6.3) proposed the incorporation of salts of large anions into the PVC matrix of valinomycin-based electrodes to improve the anion exclusion properties of the membranes. Assuming that anions from the aqueous solutions are excluded largely due to electrostatic repulsion and poor solubility in the membrane phase, this should produce a measureable improvement in the slope and possibly the linear range of the electrode. At the time, no further explanation was provided for the mechanism by which anion exclusion was supposedly enhanced although it was noted that inclusion of such negative sites also reduced the membrane resistance.

In this section, results are reported for measurements on membranes containing various quantities of the tetraphenylborate anion (either as the potassium or sodium salt) and no valinomycin. Such membranes should yield information on the interaction between the added salt and the PVC matrix.

6.4.1 Potassium Tetraphenylborate

Membranes were cast by the normal method except that, as membranes were required containing low concentrations of $KBPh_4$, to ensure accuracy and consistency between castings, solutions of $KBPh_4$ were made up in UV grade THF (containing no stabilisers) in volumetric glassware, and these solutions were then used as the solvent for casting the membranes. Solutions were made up to concentrations such that after casting, the membrane contained the desired level of $KBPh_4$.

The most dilute solution was made up to give a level of $KBPh_4$ in the membrane which was equal to that used by Band (0.015 mg $KBPh_4$ per mg of valinomycin). Although no valinomycin was used in the current study the membranes were cast to contain this quantity of the salt, so as to give a direct comparison with other membranes containing both the salt and the ionophore. Four other KBPh4 concentrations were used, i.e. approximately five, ten, thirty-five and one hundred times the concentration recommended by Band (the precise compositions of the membranes are given in Table 6.7). The lower concentrations were achieved by serial dilution of the THF solutions at 25^{o}C (the THF was allowed to achieve room temperature, after removal from cold storage, before solutions were made up).

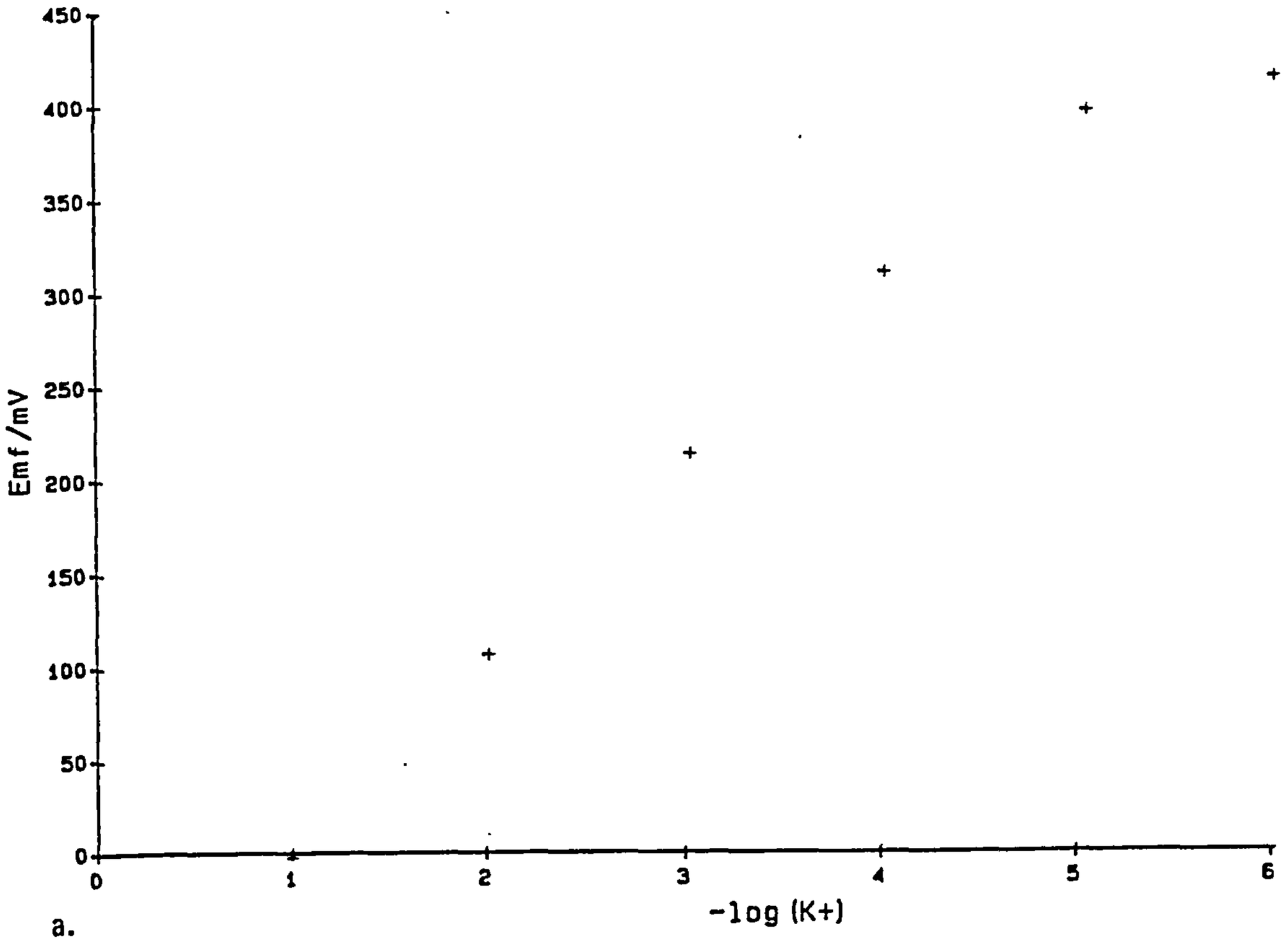
6.4.1a Potential Response

Single and mixed ion responses were measured for all membranes as described previously. Similar responses were found for all the membranes; typical results are shown graphically Fig 6.7 (membrane with the salt at the same concentration as used by

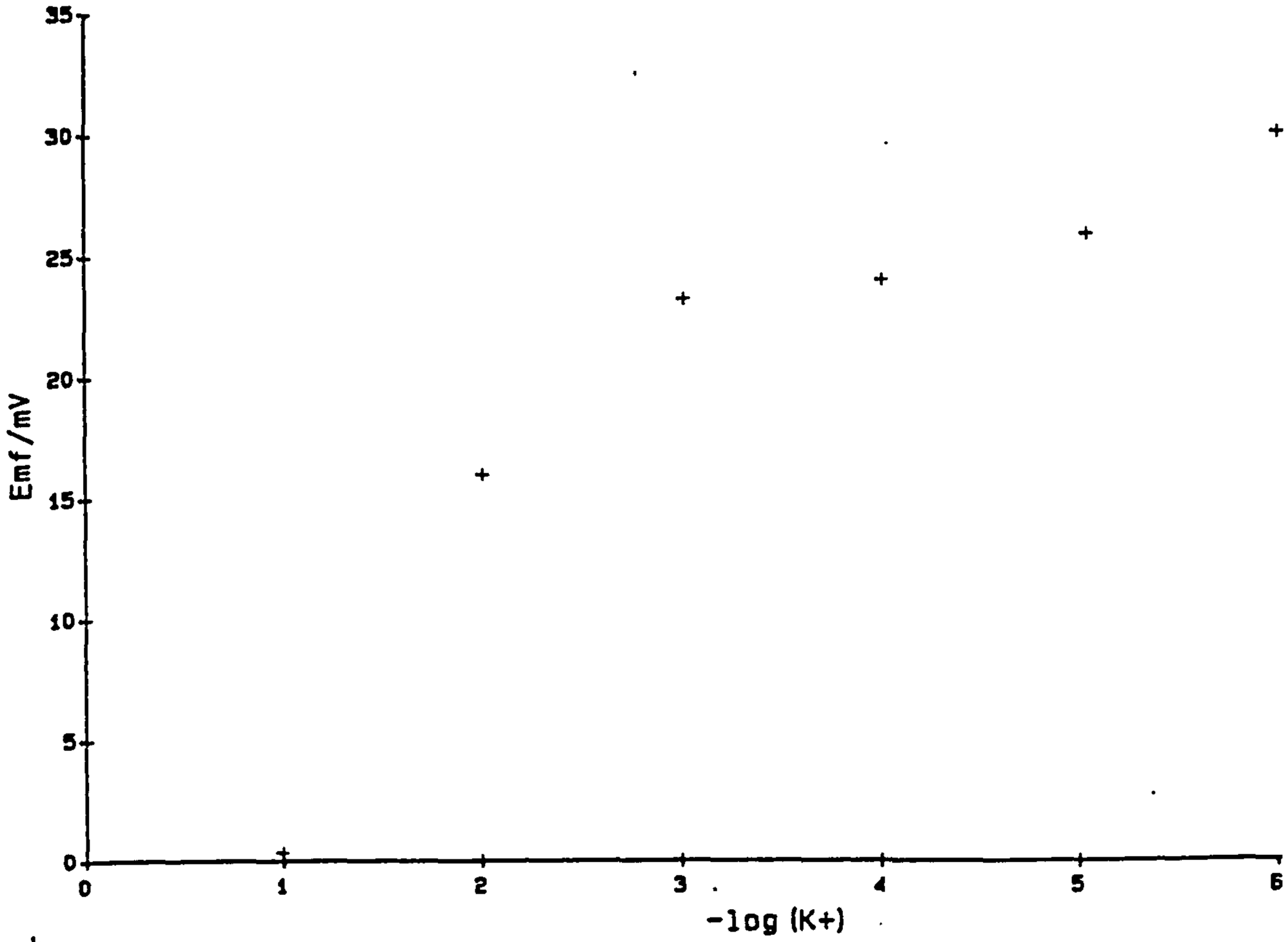
Table 6.7: Composition Of Membranes Containing Potassium Tetraphenylborate Alone

No.	PVC/mg	DOS/mg	$KBPh_4$/mg	mass% $KBPh_4$	Relative Concentrn.
1	151.0	294.0	4.92×10^{-2}	1.1×10^{-2}	1.0
2	153.4	308.1	2.50×10^{-1}	5.0×10^{-2}	5.1
3	150.0	295.7	4.49×10^{-1}	1.1×10^{-1}	9.2
4	155.0	308.0	1.7	4.0×10^{-1}	34.5
5	148.3	97.3	4.898	1.40	99.5

Fig 6.7: (a) Calibration (K^+ single-ion response) and (b) selectivity (K^+/Na^+ mixed-ion response) plots for a PVC/DOS membrane containing a similar level of BPh_4^- as used by Band, measured with a 0.1 mol dm^{-3} KCl reference solution.



a.



b.

Band). The membrane containing the highest concentration of $KBPh_4$ showed evidence of precipitation in the PVC matrix, although this did not appear to affect the response.

From Fig 6.7a it is clear that the membranes show a good single-ion response over a wide concentration range, and from Fig 6.7b, it can be seen that there is no evidence of any degree of selectivity for potassium over sodium. These results are as expected for a membrane containing no ionphore, although, in contrast to the results presented here, it has been reported that membranes containing $KBPh_4$ exhibit a limited selectivity for potassium over other alkali metal ions (6.4).

6.4.1b Impedance Measurements

Impedance measurements were made on the membranes using the same regime as previously, i.e. the time-dependance of the impedance spectra was followed for the first 24 hours and subsequently measured after three days. Fig 6.8a shows the impedance spectrum for the membrane with the lowest concentration of $KBPh_4$ as measured approximately five minutes after first contact by 0.1 mol dm^{-3} KCl solutions. The spectrum shows a large semicircular feature at high frequency, similar to that found for the membranes containing valinomycin alone, but differs from the earlier spectra, in that a second feature is visible as a small distortion at the low frequency end of the main semicircle.

Fig 6.8b shows the final, steady-state spectrum recorded after three days for the same membrane. From this second spectrum, it is clear that the same two features are present as in the initial measurement, but close inspection reveals that

Fig 6.8: Initial (a) and final (b) impedance spectra for $KBPh_4$ membrane No.1, (Table 6.7), measured with 0.1 mol dm^{-3} KCl contacting solutions.

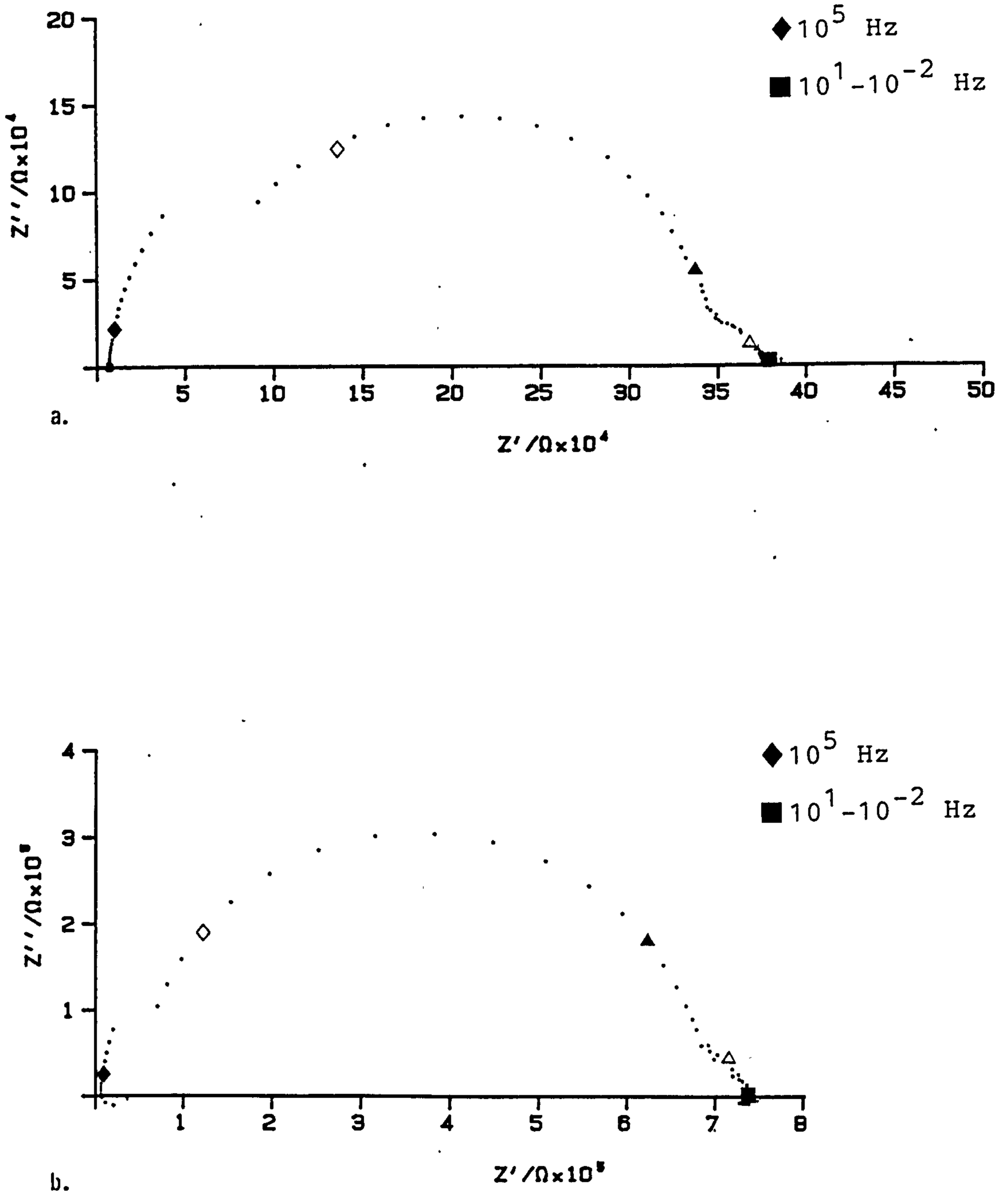


Table 6.8: Time Dependence of Membrane Impedance for Membrane No.1 (With 0.1 mol dm^{-3} KCl Contacting Solutions)

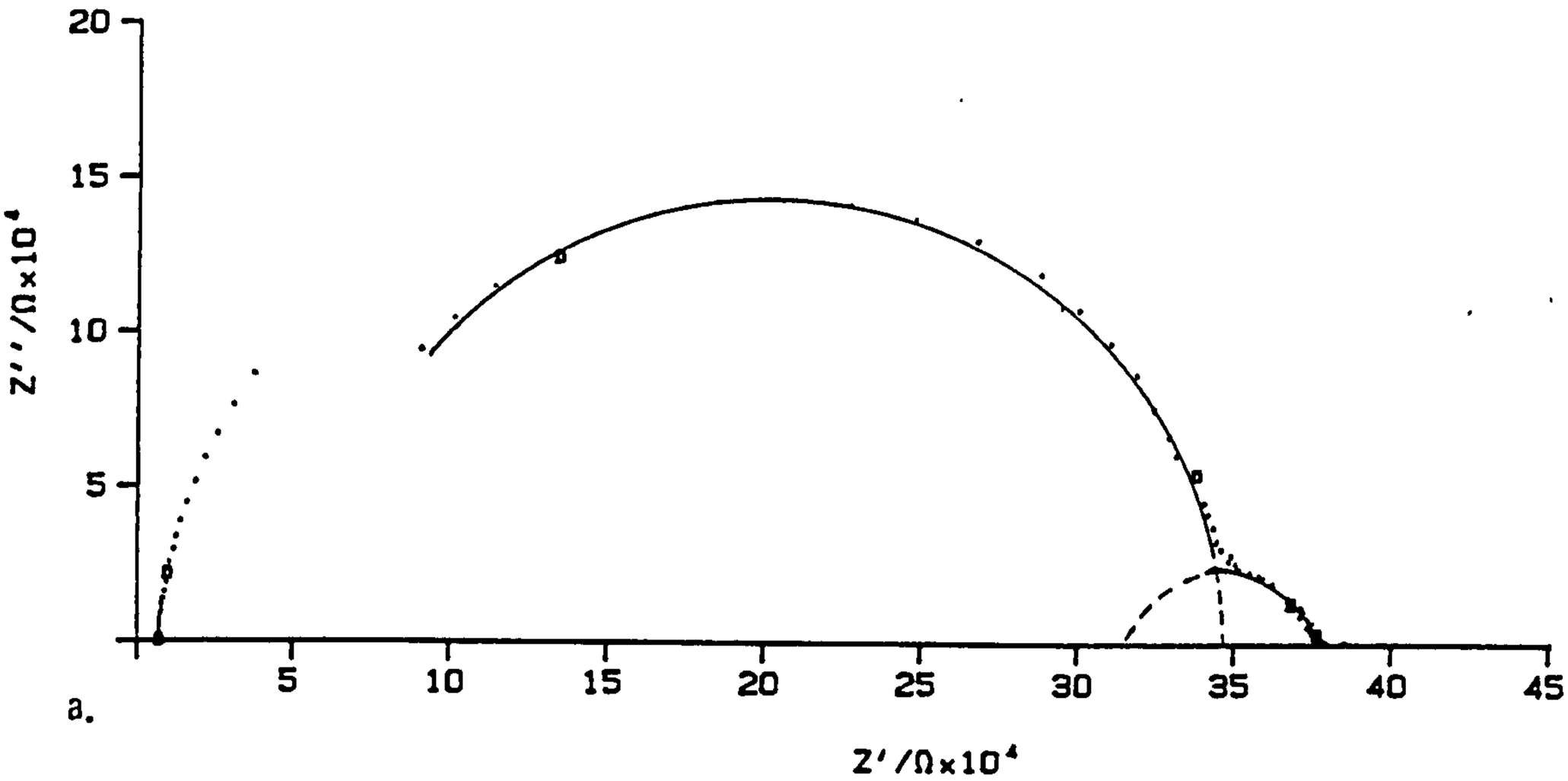
t/hours	$R_b/10^5\ \Omega$	ω^*_{max}/Hz	$R_{ct}/10^4\ \Omega$
1	3.26	5426	4.92
2	4.12	4656	5.53
3	4.28	5426	3.75
4	4.75	4656	8.00
5	5.20	3991	7.75
6	5.47	3991	7.75
7	5.91	"	8.13
8	6.23	"	8.26
9	6.34	3151	8.28
10	6.44	"	8.63
11	6.59	"	8.56
12	6.62	"	8.80
13	6.69	"	9.11
14	6.68	"	9.30
15	6.69	"	9.41
16	6.74	"	9.50
17	6.78	"	9.51
18	6.75	"	9.73
19	6.77	"	9.98
20	6.81	"	9.92
21	6.78	"	10.00
22	6.80	"	10.20
23	6.80	"	10.00
24	6.80	"	10.50
72	6.80	"	11.00

there has been an increase in the resistive component of both features. As the two features overlap to a large extent, and the lower frequency one is considerably smaller than the one at high frequency, it is more difficult to assign an accurate value for the resistive component of the smaller semicircle. Comparing both spectra, however, it is clear that the magnitude of the smaller semicircle has increased with time. Fig 6.9 shows visual best semicircle fits for the two spectra. These spectra can be interpreted as previously, attributing the high frequency part of the spectrum to the membrane bulk (R_b/C_g) parallel network, and in this instance, it is evident that R_b has approximately doubled over the three-day period.

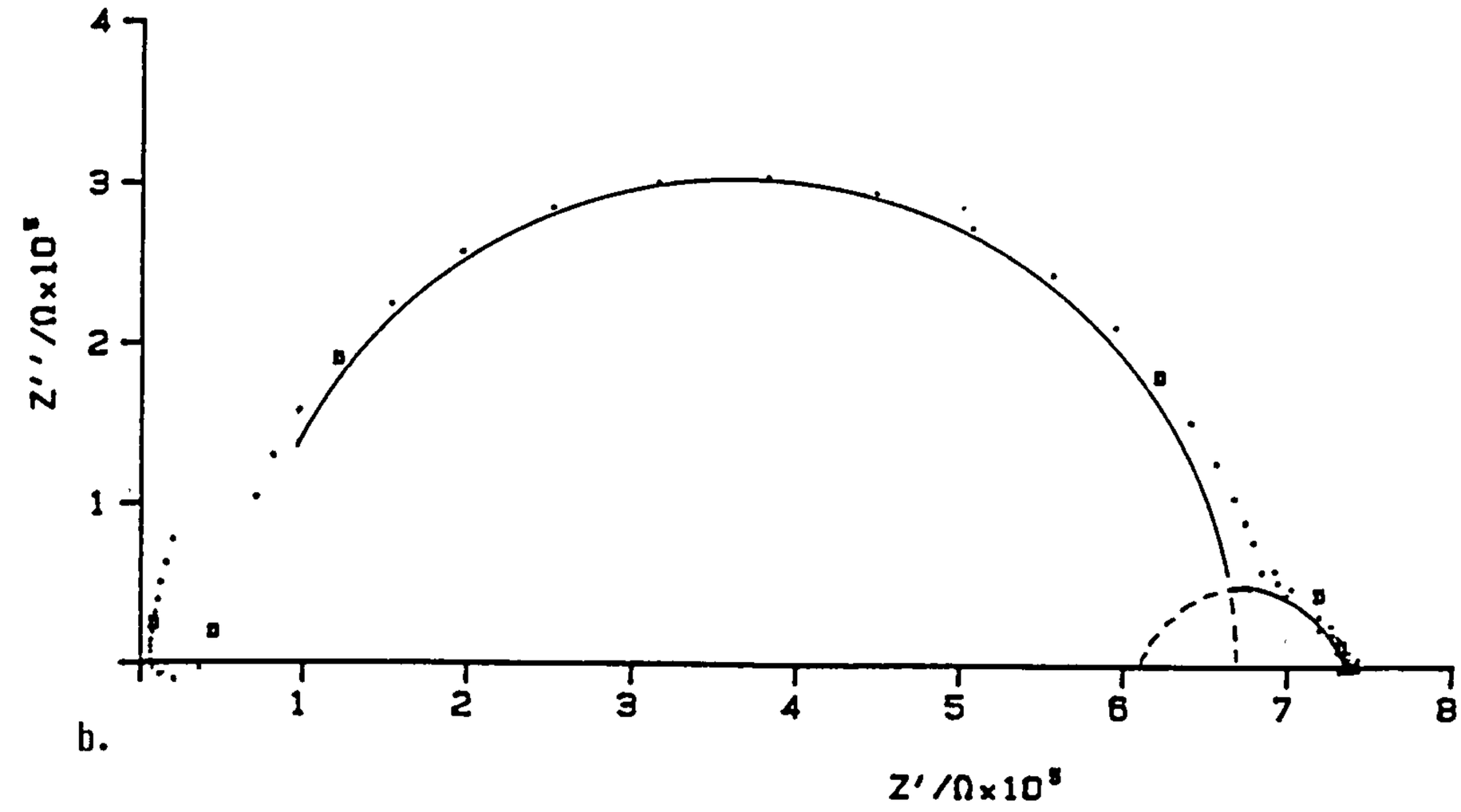
Figs 6.10a and 6.10b show the corresponding initial and final spectra for the membrane containing the second lowest $KBPh_4$ concentration (membrane no. 2 in Table 6.7). The initial spectrum for this membrane is similar to the corresponding run for the previous membrane, and shows the bulk semicircle. There is some evidence of the second feature at low frequencies, but this is less clear than for the membrane with the lowest $KBPh_4$ concentration and even in the steady state spectrum run down to 1 mHz, this second feature is poorly defined.

Figs 6.11 - 6.13 show the initial and final spectra for the membranes containing the three highest concentrations of $KBPh_4$. All three sets of spectra show features similar to those found for the membranes containing the lower concentrations of the tetraphenylborate salt, although in all of the plots, the lower-frequency feature is not clearly-defined. The full time dependence of the membrane impedance is given for all five membranes in Tables 6.8 - 6.12.

Fig 6.9: Visual best fits of two semicircles for Figs 6.8a, and 6.8b



a.



b.

Fig 6.10: Initial (a) and final (b) impedance spectra for $KBPh_4$ membrane No.2, (Table 6.7), measured with 0.1 mol dm^{-3} KCl contacting solutions.

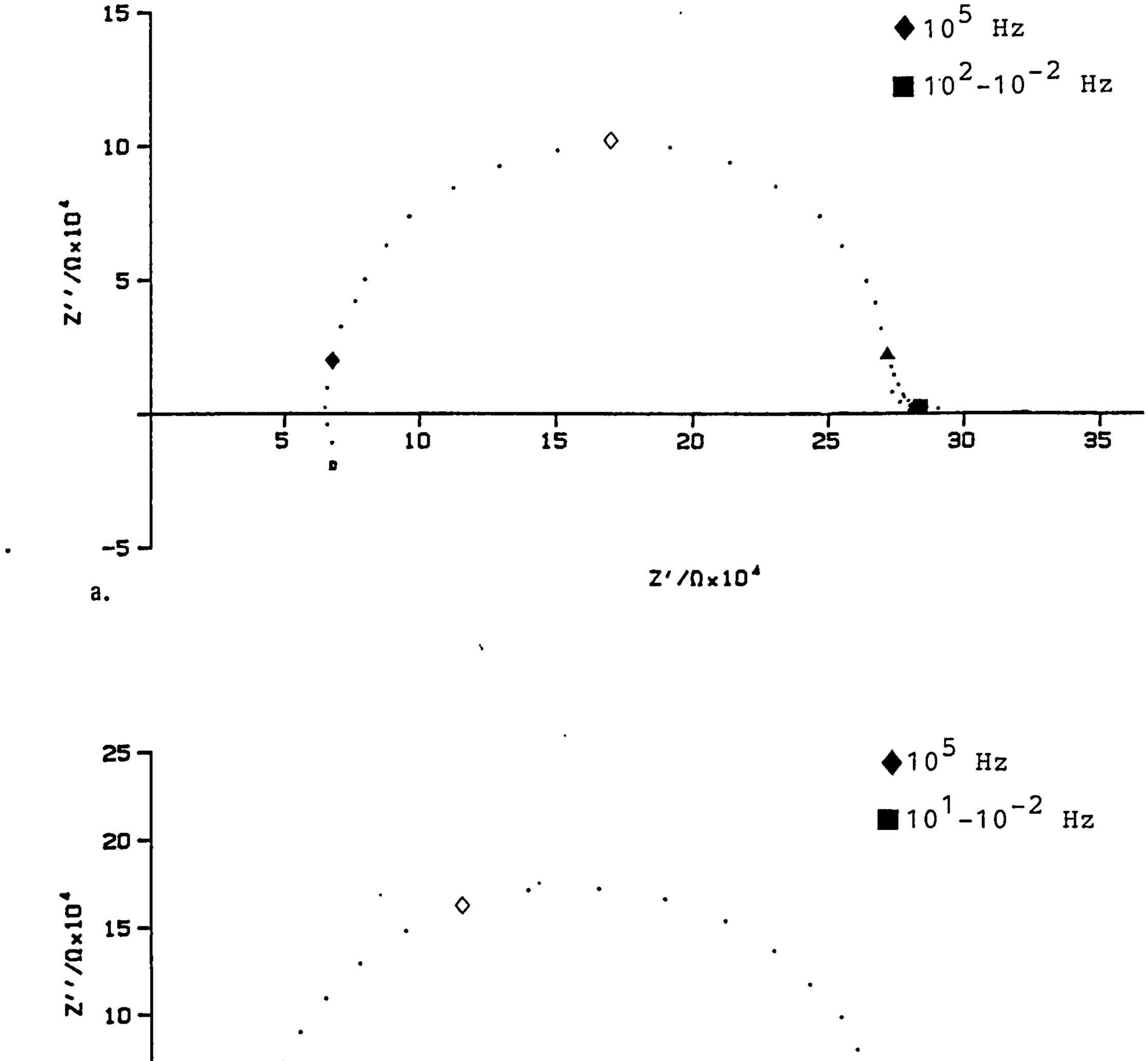


Table 6.9: Time Dependence of Membrane Impedance for Membrane No.2 (With 0.1 mol dm^{-3} KCl Contacting Solutions)

t/hours	$R_b/10^5\ \Omega$	$\omega_{1\,max}^*$/Hz
1	2.79	9980
2	3.16	"
3	3.49	6298
4	3.62	"
5	3.65	"
6	3.73	"
7	3.79	"
8	3.80	"
9	3.83	"
10	3.85	"
11	3.89	"
12	3.91	"
13	3.95	"
14	3.98	"
15	4.01	"
16	4.05	"
17	4.08	"
18	4.09	"
19	4.08	"
20	4.11	"
21	4.12	"
22	4.10	"
23	4.14	"
24	4.17	"
72	4.15	"

Fig 6.11: Initial (a) and final (b) impedance spectra for $KBPh_4$ membrane No.3, (Table 6.7), measured with 0.1 mol dm^{-3} KCl contacting solutions.

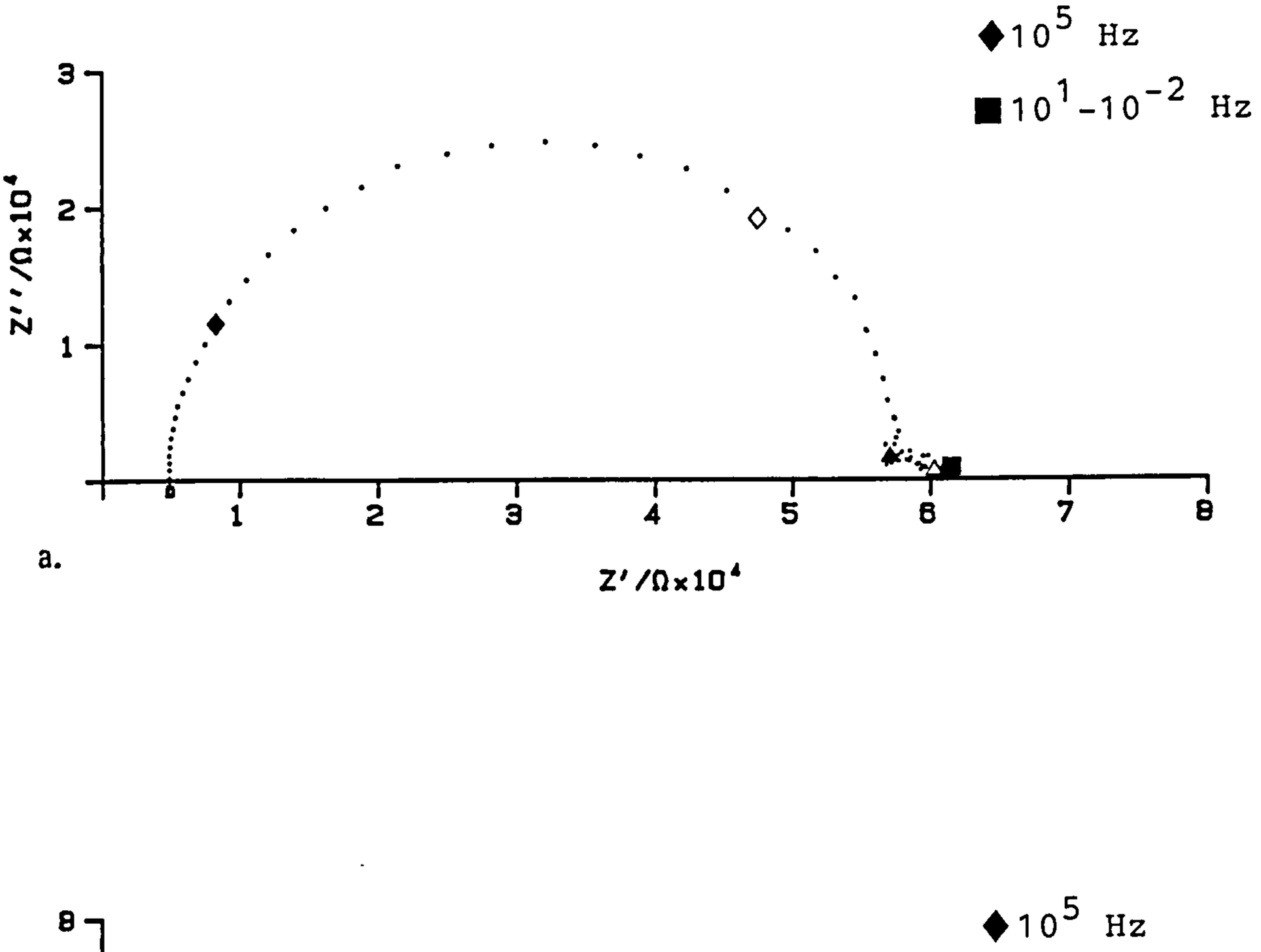


Table 6.10: Time Dependence of Membrane Impedance for Membrane No.3 (With 0.1 mol dm^{-3} KCl Contacting Solutions)

t/hours	$R_b/10^5\ \Omega$	$\omega_{1\,max}^*$/Hz
1	0.57	21550
2	0.60	"
3	0.68	18490
4	0.78	"
5	0.86	15860
6	0.93	"
7	1.02	"
8	1.07	13600
9	1.04	11650
10	1.07	"
11	1.04	10000
12	1.05	"
13	1.07	"
14	1.07	"
15	1.07	"
16	1.14	"
17	1.17	"
18	1.20	"
19	1.20	"
20	1.35	"
21	1.40	"
22	1.47	"
23	1.48	"
24	1.51	"
72	1.51	"

Fig 6.12: Initial (a) and final (b) impedance spectra for $KBPh_4$ membrane No.4, (Table 6.7), measured with 0.1 mol dm^{-3} KCl contacting solutions.

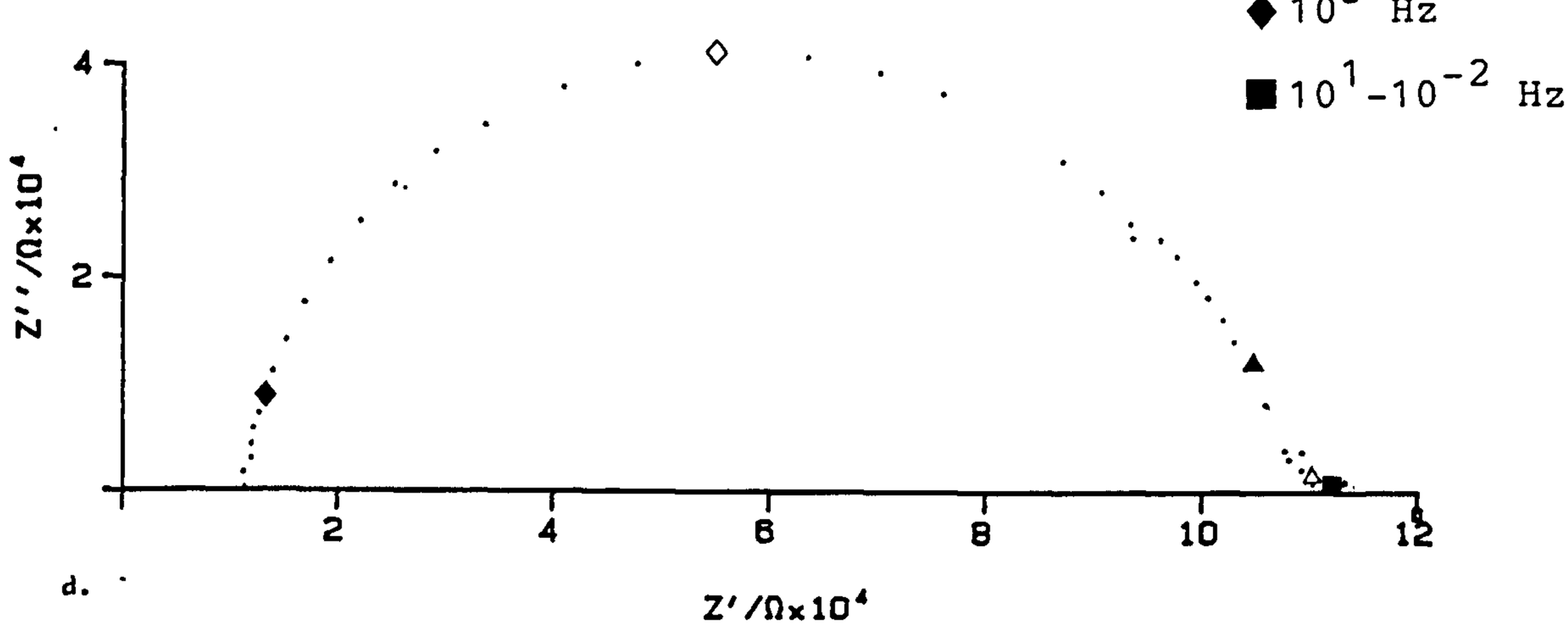
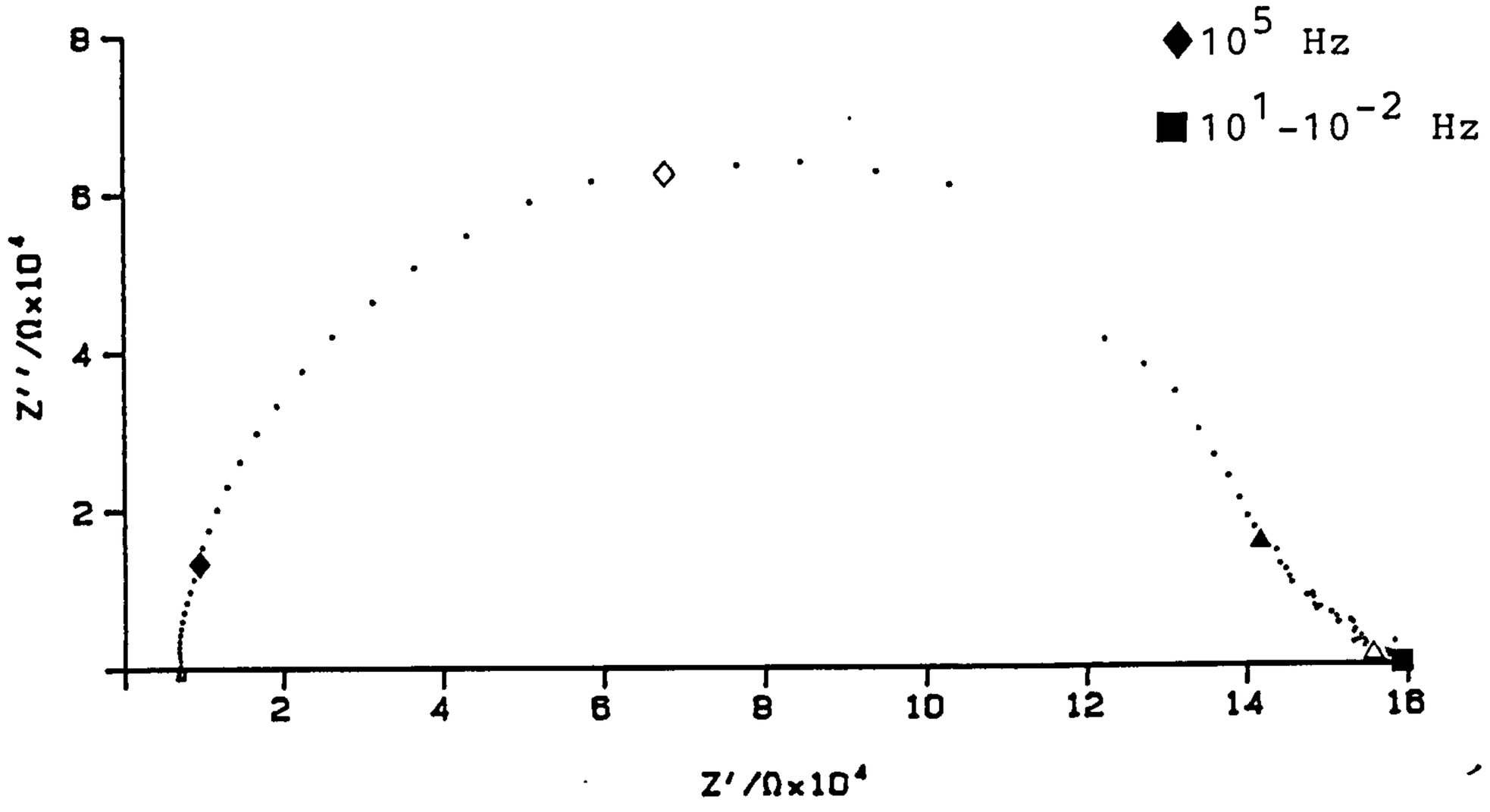


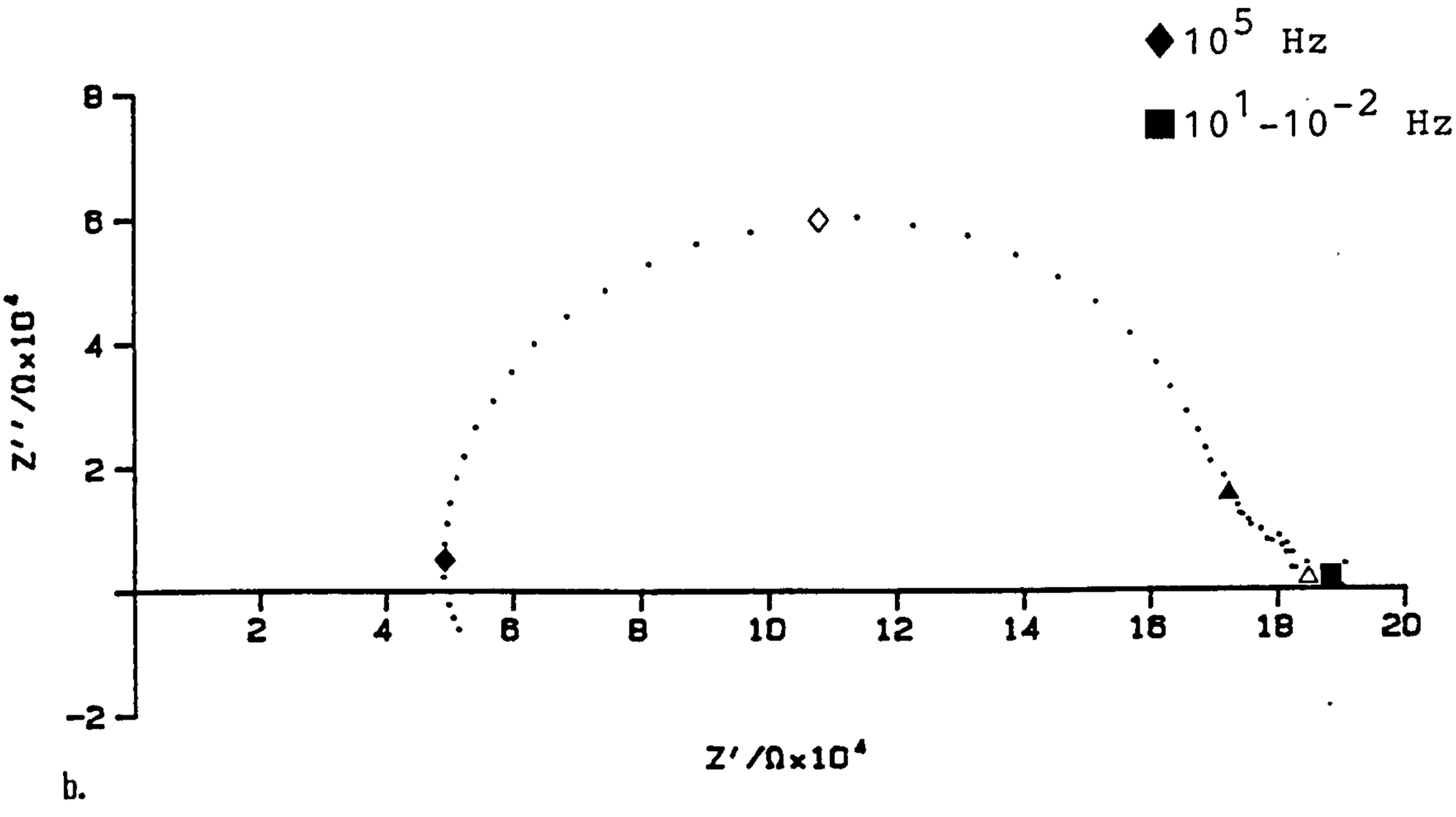
Table 6.11: Time Dependence of Membrane Impedance for Membrane No.4 (With 0.1 mol dm^{-3} KCl Contacting Solutions)

t/hours	$R_b/10^5\Omega$	$\omega_{1\,max}^*$/Hz
1	1.10	9980
2	1.15	"
3	1.17	"
4	1.12	"
5	1.18	"
6	1.20	"
7	1.18	"
8	1.19	"
9	1.20	"
10	1.21	"
11	1.23	"
12	1.28	"
13	1.30	"
14	1.36	"
15	1.41	"
16	1.46	"
17	1.49	"
18	1.53	"
19	1.52	"
20	1.55	"
21	1.58	"
22	1.57	"
23	1.59	"
24	1.59	12540
72	1.59	

Fig 6.13: Initial (a) and final (b) impedance spectra for $KBPh_4$ membrane No.5, (Table 6.7), measured with 0.1 mol dm^{-3} KCl contacting solutions.



a.



b.

Table 6.12: Time Dependence of Membrane Impedance for Membrane No.5 (With 0.1 mol dm^{-3} KCl Contacting Solutions)

t/hours	$R_b/10^5\ \Omega$	$\omega_{1\,max}^*$/Hz
1	1.42	7377
2	1.35	"
3	1.29	"
4	1.31	"
5	1.38	"
6	1.40	"
7	1.42	"
8	1.46	"
9	1.50	"
10	1.53	"
11	1.56	"
12	1.56	"
13	1.60	"
14	1.60	"
15	1.63	"
16	1.64	"
17	1.67	"
18	1.69	"
19	1.69	"
20	1.73	"
21	1.71	"
22	1.72	"
23	1.73	"
24	1.73	"
72	1.71	"

6.4.2 Sodium Tetraphenylborate

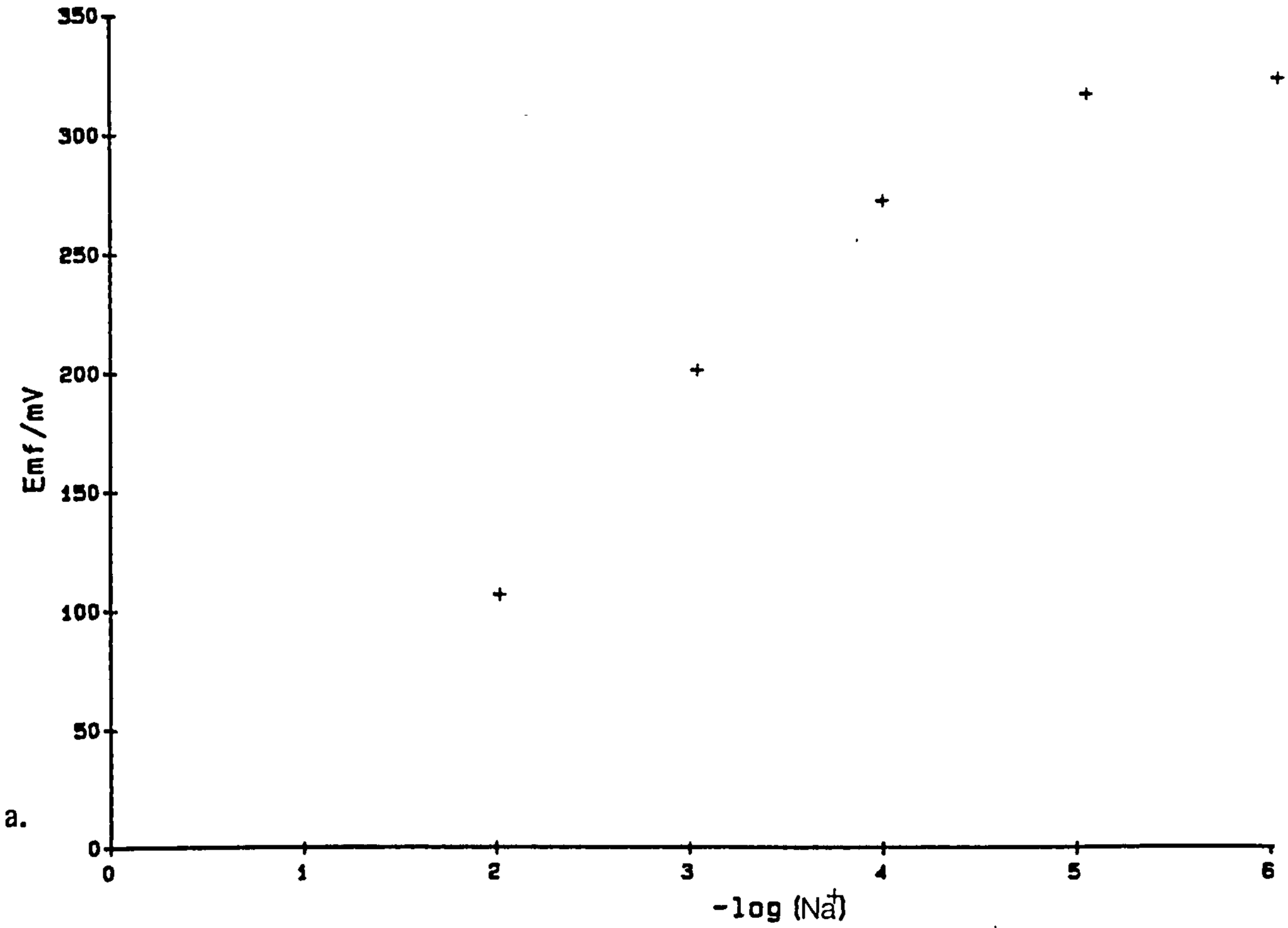
Originally, the incorporation of negative sites into PVC membranes was achieved by the addition of the sodium salt of the tetraphenylborate anion. The membrane was then conditioned by exposure to KCl solutions for a period prior to use, during which time it was supposed that exchange between the sodium in the membrane and potassium in the aqueous solutions occurred. Thus the end result was the effective incorporation of the potassium salt into the membrane. The sodium salt is more readily available from suppliers than the potassium salt, and is in fact used in potassium assays, relying on the marked preferential complexation of potassium rather than sodium.

Membranes were cast to two formulations, corresponding to the potassium salt concentration used by Band et al. (5.0×10^{-2} mg $NaBPh_4$), and to ten times this concentration (5.0×10^{-1} mg $NaBPh_4$), and the impedance behaviour and potential response were investigated. Impedance measurements were also carried out to observe the changes occurring in the membrane when exposed to aqueous potassium solutions.

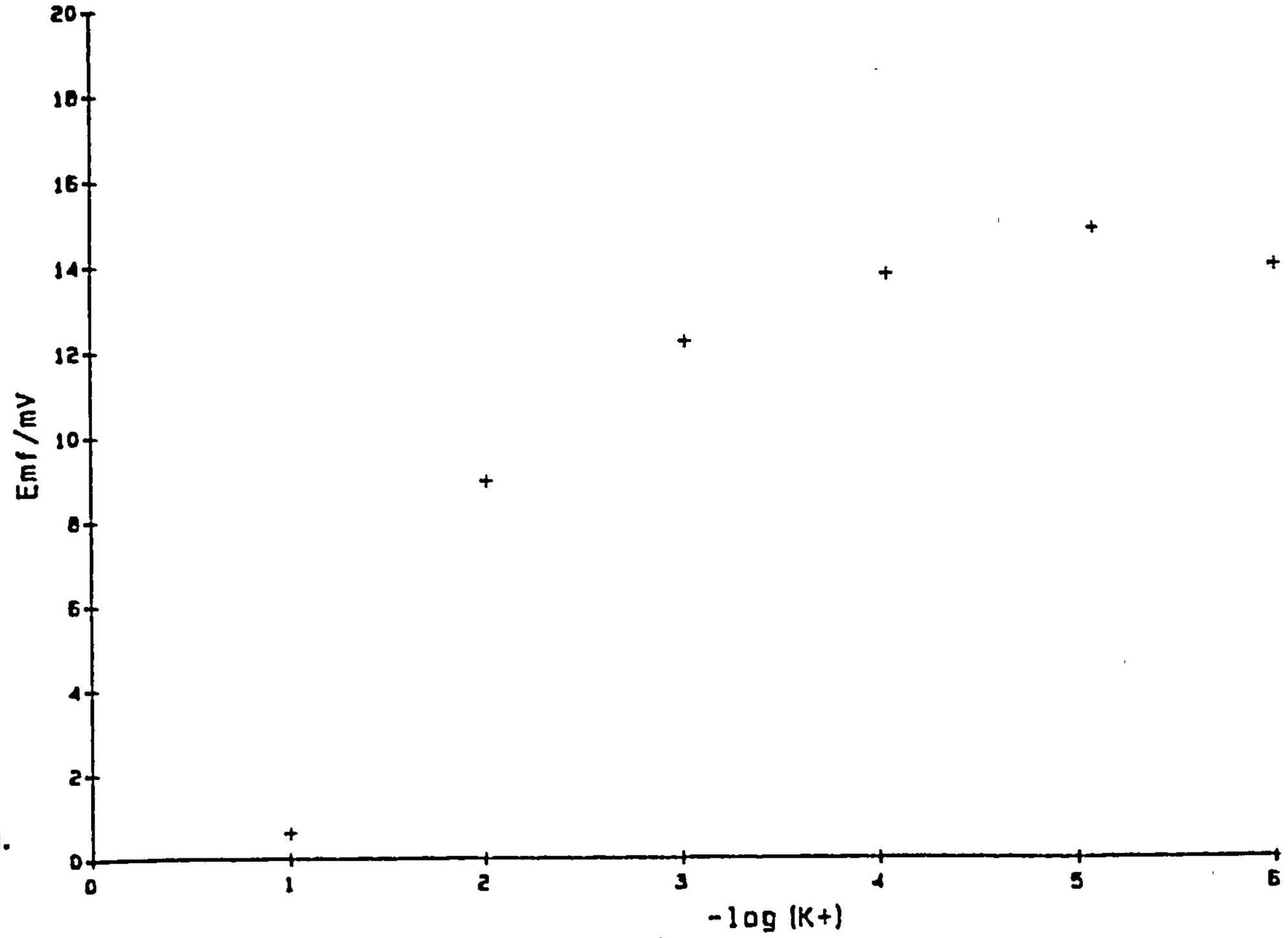
6.4.2a Potential Response

Calibration (single-ion response) plots were constructed for the membranes in contact with sodium solutions, and typical results are shown in Fig 6.14a. It is evident that the response of these membranes to the sodium ion is similar to the response of the membranes containing the potassium salt to potassium ions.

Fig 6.14: (a) Calibration (Na^+ single-ion response) and (b) selectivity (K^+/Na^+ mixed-ion response) plots for a membrane containing 5.0 $X10^{-2}$ mg $NaBPh_4$



a.



b.

The selectivity of the membranes was also investigated, but this was necessarily carried out after a conditioning period in KCl solutions. Had this conditioning not been carried out, and a steady state not been established prior to the measurements in mixed solutions, the take-up of potassium during the selectivity determination would have invalidated the results obtained. The mixed ion response for both membranes was found to be similar, with no selectivity for potassium over sodium, and the response of the membrane containing 5.04 $x10^{-2}$ mg $NaBPh_4$ is shown in Fig 6.14b.

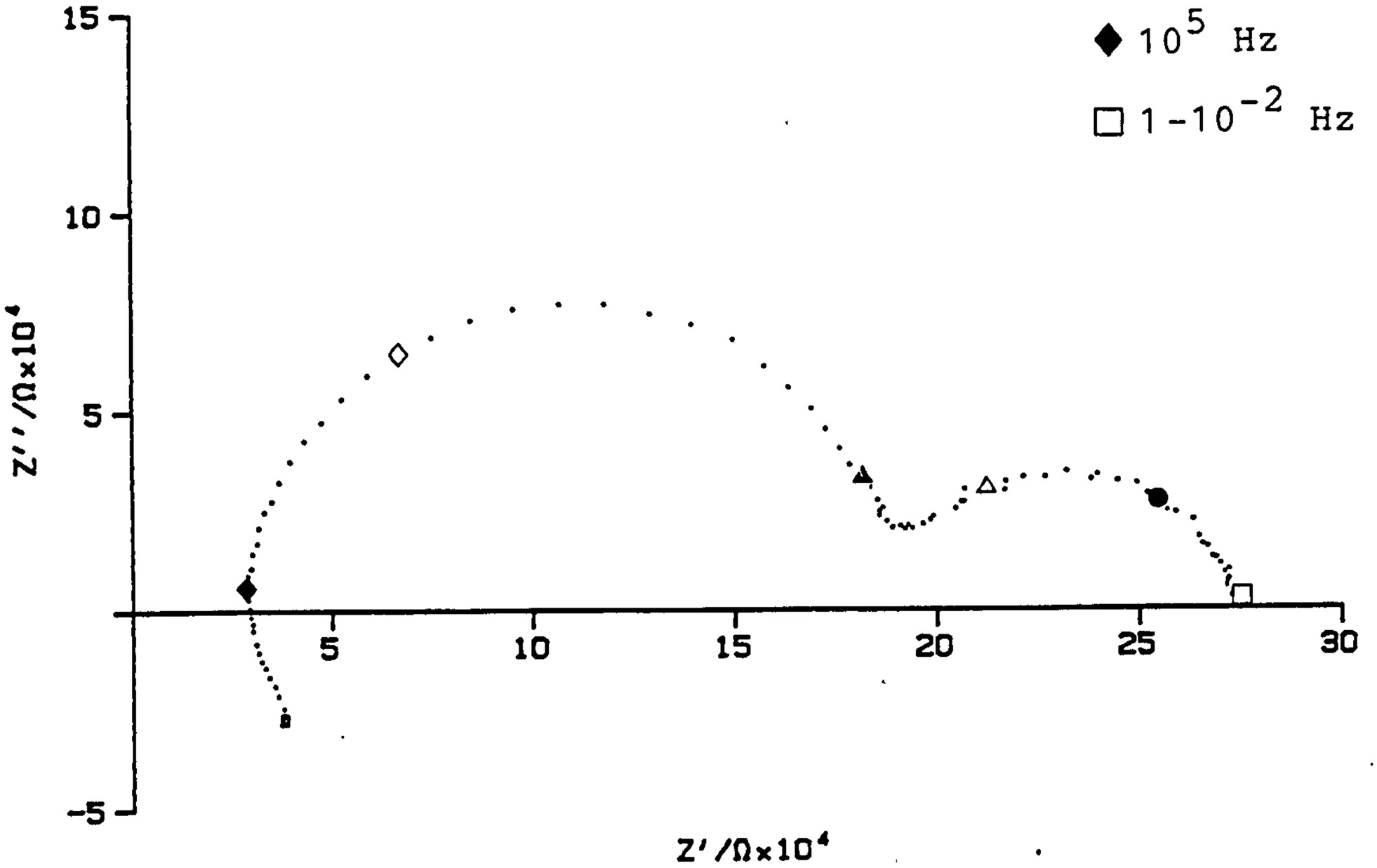
6.4.2b Impedance Measurements

The impedance spectra for the two membranes were measured with 0.1 mol dm^{-3} NaCl contacting solutions, with both two-and four-electrode configurations, as previously.

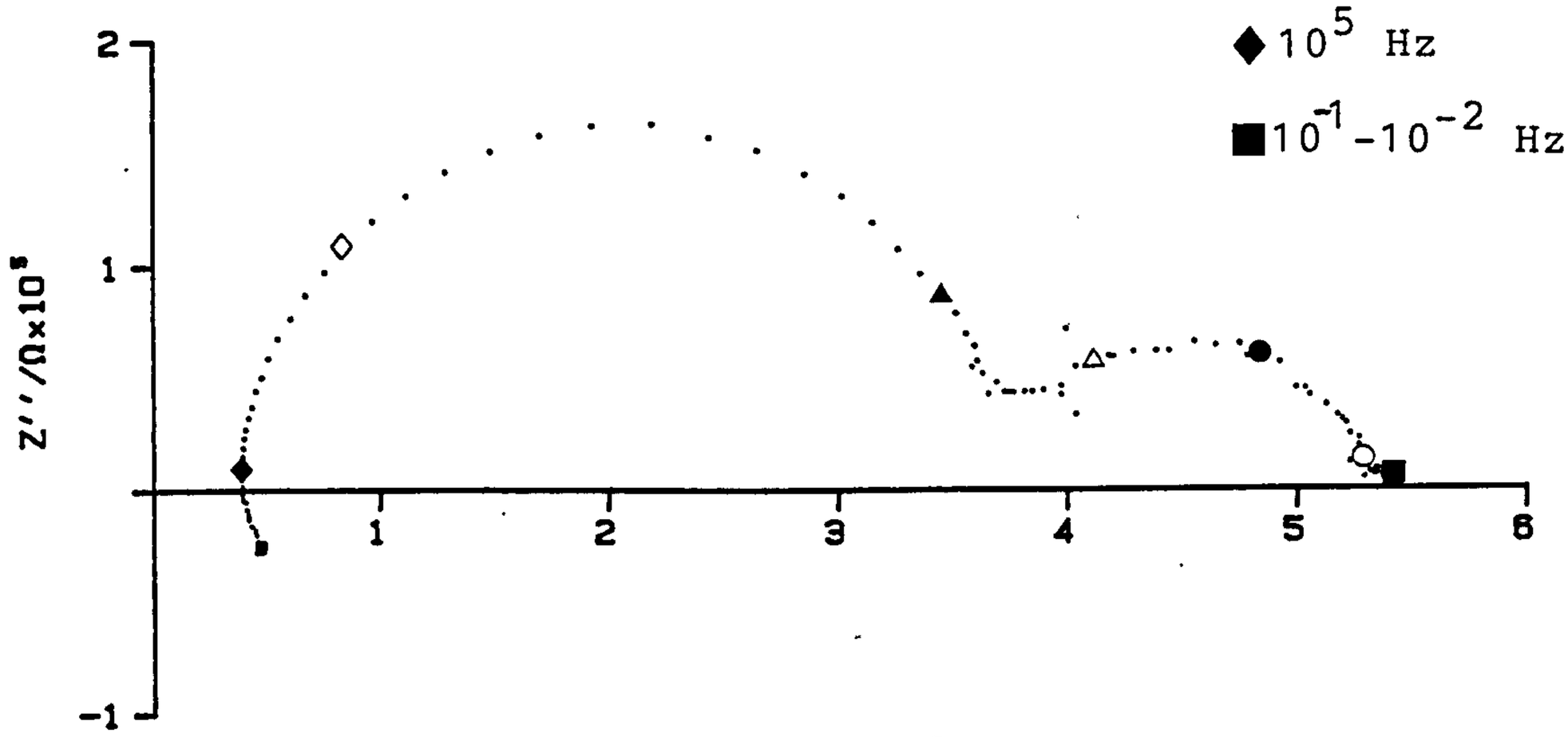
Fig 6.15a shows the initial spectrum taken for the membrane with the lower concentration of $NaBPh_4$, measured approximately five minutes after the membrane was first contacted by the aqueous solutions. The spectrum is at first sight different from the corresponding spectrum for the membrane containing $KBPh_4$, in that two clearly defined semicircles are visible, whereas in the former case, there was poor separation of the two features. Although there is apparently greater separation of time constants for the two semicircles in the present case, the spectra are generally of the form already established with previous measurements, with a high frequency semicircle representing the membrane bulk, and a lower frequency semicircle attributable to the interfacial processes.

As with the membranes containing $KBPh_4$, the time dependence

Fig 6.15: Initial (a) and final (b) impedance spectra for a membrane containing 5.0 x10-2 mg $NaBPh_4$, measured with 0.1 mol dm^{-3} NaCl contacting solutions.



a.



b.

Table 6.13: Time Dependence of Impedance for the Membrane Containing the Lower Level Of $NaBPh_4$ ($0.1\ mol\ dm^{-3}$ NaCl Contacting Solutions)

t/hours	$R_b/10^5\ \Omega$	$\omega_{1\,max}^*$/Hz	$R_{ct}/10^5\ \Omega$	$\omega_{2\,max}^*$/Hz
1	1.91	5437	0.86	$10-10^2$
2	2.08	"	0.76	"
3	2.23	"	1.09	"
4	2.35	"	1.06	"
5	2.43	"	1.11	"
6	2.53	"	1.11	"
7	2.53	"	1.15	"
8	2.75	"	1.27	"
9	2.87	"	1.30	"
10	2.90	"	1.36	"
11	3.09	"	1.35	"
12	3.15	"	1.41	"
13	3.24	"	1.48	"
14	3.33	"	1.45	"
15	3.42	"	1.48	"
16	3.46	"	1.48	"
17	3.56	3424	1.53	"
18	3.53	"	1.57	"
19	3.68	"	1.65	"
20	3.83	"	1.58	"
21	3.85	"	1.58	"
22	3.81	"	1.57	"
23	3.86	"	1.55	"
24	3.83	"	1.58	"
72	3.84	"	1.57	"

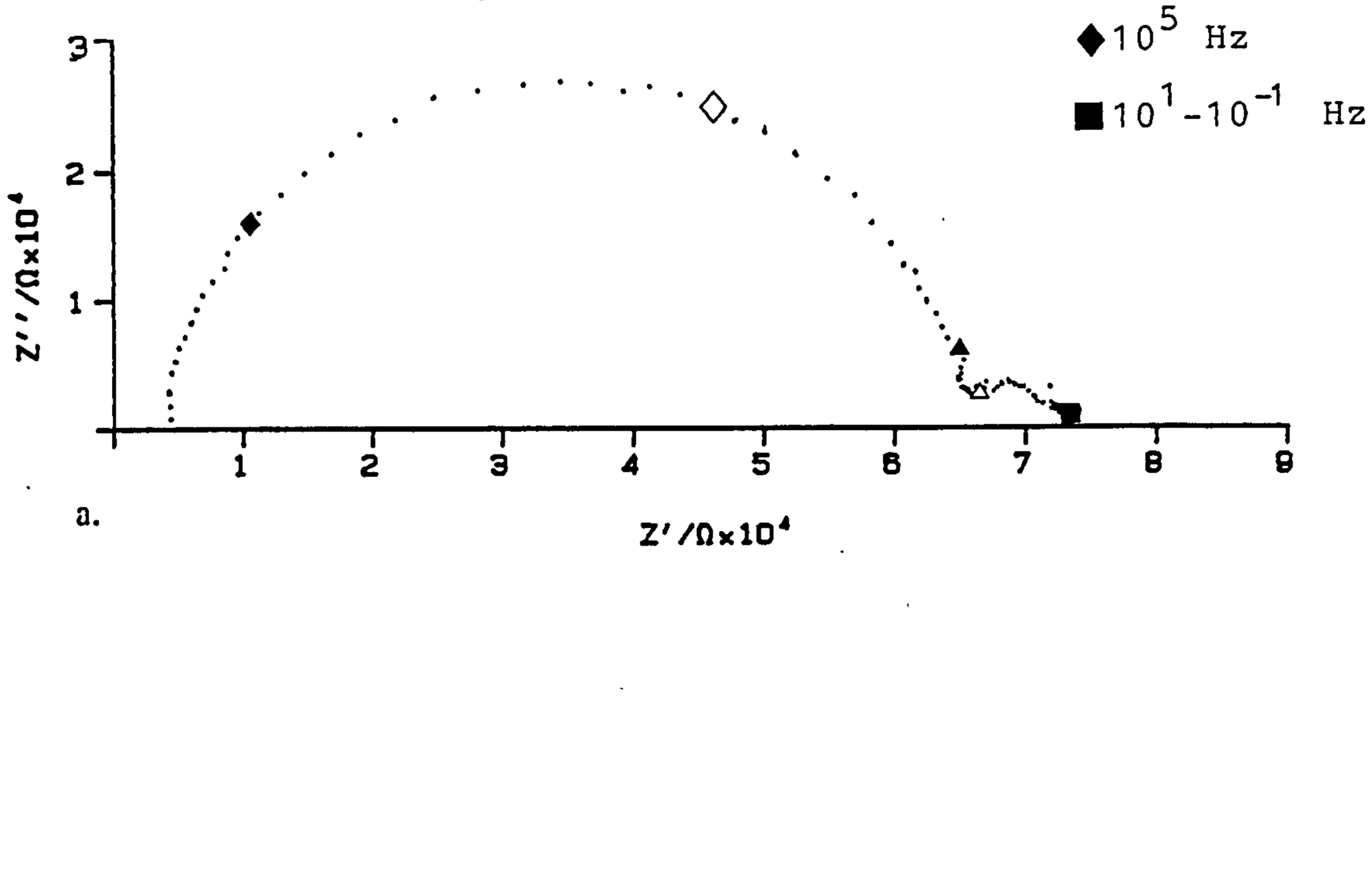
of the impedance was followed, and Fig 6.15b shows the final steady state spectrum measured after three days. The value of R_b has increased from approximately 1.91×10^5 Ohms to approximately 3.83×10^5 Ohms over this period, and R_{ct} has increased from 8.6×10^4 Ohms to 1.58×10^5 Ohms. The full time dependence of the impedance is given in Table 6.13, where the values obtained for the various equivalent circuit parameters are shown.

Fig 6.16a shows the initial spectrum measured for the membrane containing 5.04×10^{-1} mg of $NaBPh_4$ taken approximately five minutes after first solution contact. From this spectrum it is clear that the value of R_b is smaller by a factor of approximately three than for the membrane with the lower concentration of the salt, and that R_{ct} is also reduced by a factor of approximately ten. Fig 6.16b shows the steady-state spectrum recorded three days after the initial solution contact, and the detailed time dependence is given in Table 6.14.

6.4.3 Discussion

The origin of the lower frequency feature found in the spectra for the membranes containing the potassium salt, is most likely to be the interfacial charge-transfer processes, as with the previous membranes discussed, although it is possible that it represents a second bulk phase arising due to the partial crystallisation of $KBPh_4$ within the membrane. If this were the case, and two separate phases were present in such membranes, increasing the $KBPh_4$ concentration should result in a concomitant increase in the size of the second semicircle

Fig 6.16: Initial (a) and final (b) impedance spectra for a membrane containing 5.0 x10^{-1} mg $NaBPh_4$, measured with 0.1 mol dm^{-3} NaCl contacting solutions.



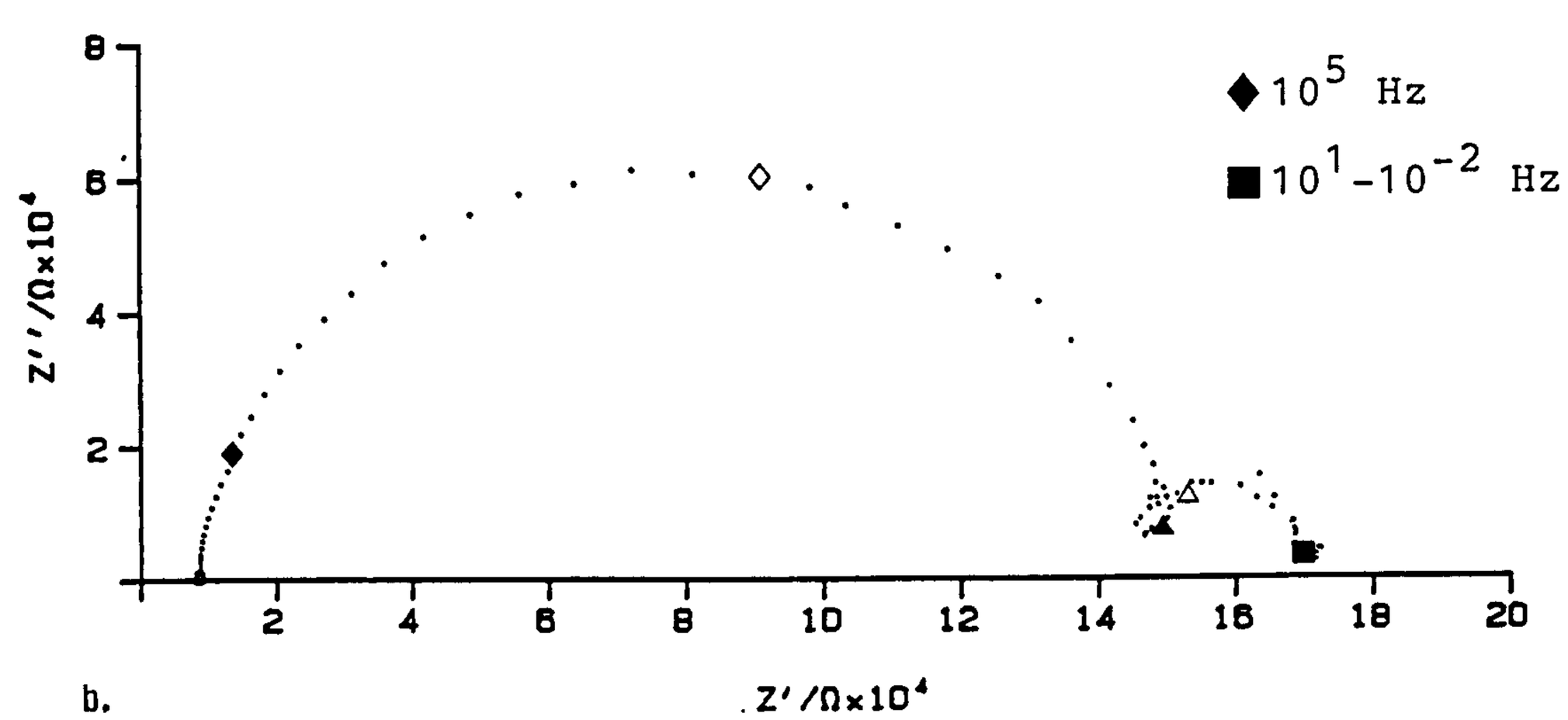


Table 6.14: Time Dependence of Impedance for the Membrane Containing the Higher Level Of $NaBPh_4$ ($0.1\ mol\ dm^{-3}$ NaCl Contacting Solutions)

t/hours	$R_b/10^5\ \Omega$	$\omega_{1\,max}^*$/Hz	$R_{ct}/10^4\ \Omega$	$\omega_{2\,max}^*$/Hz
1	0.65	18490	0.80	10^1-10^2
2	0.67	21550	0.97	"
3	0.72	"	0.98	"
4	0.77	"	1.11	"
5	0.81	"	0.86	"
6	0.87	10000	1.04	"
7	0.91	18490	1.11	"
8	0.93	"	1.21	"
9	0.97	"	1.31	"
10	1.00	15850	1.42	"
11	1.05	13600	1.82	"
12	1.08	15850	1.62	"
13	1.11	"	1.62	"
14	1.13	13600	1.62	"
15	1.17	"	1.62	"
16	1.18	10000	1.72	"
17	1.21	"	1.82	"
18	1.26	"	1.69	"
19	1.27	"	1.85	"
20	1.29	"	2.02	"
21	1.30	"	2.20	"
22	1.37	"	2.00	"
23	1.47	"	2.35	"
24	1.53	"	2.47	"
72	1.52	"	2.47	"

relative to the first, as more $KBPh_4$ was precipitated due to its solubility product being exceeded. If the smaller semi-circle is interpreted in this way, then the spectra show no evidence of interfacial processes, in which case any charge-transfer must be occurring at a much higher rate than found for the membranes with no added salt, such that R_{ct} is indetectably small.

As with the membranes containing no additives, the bulk resistance of the membranes containing potassium tetraphenyl-borate shows an increase over a period of several hours. The extent of this increase seems to vary from membrane to membrane and does not appear to be directly related to the membrane composition. The cause of the increase must be attributed to the interaction of the membrane with the aqueous solutions, possibly due to the uptake of water, resulting in a swelling of the membrane and an increase in the apparent resistance. It is possible that this uptake of water would be accompanied by the uptake of additional ionic species from the solutions, although such an influx of ions would reasonably be expected to produce a decrease in the membrane resistance. This is evidently not the case, although it is possible that such an uptake is occurring but the effect is masked by the effects of swelling due to water uptake.

The initial and final bulk resistance for the five membrane compositions are summarised in Table 6.15, from which it can be seen that the membrane containing the lowest concentration of tetraphenylborate shows a final bulk resistance of 6.8×10^5 Ohms. This is smaller by a factor of approximately 6.6 than the resistance of the membrane containing no additives when in contact with KCl solutions. Table 6.15 also shows that the

Table 6.15: Summary of Equivalent Circuit Parameters for Membranes Containing $KBPh_4$

Membrane	Rel Concn. $KBPh_4$	R_b init $/10^5\ \Omega$	R_b fin $/10^5\ \Omega$
1	1.0	3.26	6.80
2	5.1	2.79	4.17
3	9.2	0.57	1.51
4	34.5	1.10	1.59
5	99.5	1.42	1.73

resistance of the membranes decreases as the concentration of $KBPh_4$ is increased, up to a point, whereafter a small increase in R_b occurs with further increases in $KBPh_4$ concentration. The initial decrease would be expected due to an increase in the number of ionic species within the membrane, but the cause of the reversal of this trend is less clear. The solution to this problem is most likely to lie in the precipitation of the potassium salt within the membrane.

The membrane containing the highest concentration of $KBPh_4$ when cast showed visible evidence of crystallisation of the salt within the membrane matrix. The effect of this on the impedance is likely to be twofold. If the dielectric constant of the crystalline phase is sufficiently different from that of the PVC matrix, and a sufficiently large amount of this separate phase is present within the membrane, a second bulk semicircle would be expected in the impedance plot. For these two features to be resolved requires a separation between the time constants of greater than a factor of one hundred (as discussed earlier). The second possible effect of the crystallisation will be to reduce the effective membrane area and therefore increase the membrane resistance. Thus initially increasing the salt concentration will result in a greater number of charge carriers within the membrane, but at a certain point, the solubility of the salt will reach its limit, and the further addition of salt will not produce any further increase in the number of charge carriers. After this point, the precipitation of the salt will tend to reduce the effective area of the membrane and increase its resistance, which appears to be the case for the membranes studied.

The spectra obtained for the membranes containing the

sodium salt are similar to those found with the other membranes investigated, in that R_b is seen to increase with time after exposure to the aqueous solutions, and that there is also an increase in R_{ct}. The values for R_b and R_{ct} are of similar order of magnitude to those found for the membranes containing $KBPh_4$ for similar salt concentrations, and the time constants for the bulk and interfacial processes are also similar. It can be seen that again, as with the membranes containing the potassium salt, a tenfold change in the salt concentration produces a much smaller change in R_b. It is clear that with regard to the environment of the PVC matrix, there is little difference between the sodium salt and potassium salt of the BPh_4^- anion when in contact with aqueous solutions of the corresponding cation. This is in contrast to the membranes containing no additives, which display a higher resistance when in contact with sodium solutions than when in contact with potassium solutions. The presence of the anion evidently overcomes any differences in solubility or mobility for the two cations which are inherent in the membrane.

6.5 Valinomycin-containing Membranes With Added BPh_4^-

From the results reported in sections 6.4.1 and 6.4.2, it is apparent that the addition of tetraphenylborate salts to the PVC matrix produces marked changes in the impedance behaviour of the membrane. The bulk resistance of the membrane is lowered by an amount dependent on the BPh_4^- concentration, and the charge transfer resistance is also substantially lowered, allowing control of R_b and R_{ct} to any desired magnitude (the upper limit on this control being the solubility limit of the

salt within the membrane, and the lower limit being the level of inherent charge carriers in the membrane). In view of this, the addition of BPh_4^- would be expected to affect the ion-selective behaviour of membranes containing valinomycin, particularly from the point of view of the interfacial charge transfer processes.

To investigate the effect of adding tetraphenylborate salts to the PVC membrane under these conditions, membranes were cast containing either the potassium or sodium salt of the anion in addition to valinomycin, and the results of potential and impedance measurements on these membranes are reported and discussed below. Membranes were cast to the formulation used by Band, (containing 0.015 mg $KBPh_4$ per mg of valinomycin, or the equivalent quantity of the sodium salt) so as to correspond with the series of membranes containing no valinomycin.

6.5.1 Potential Response

Fig 6.17a shows the single-ion calibration plot for a typical membrane containing valinomycin and potassium tetraphenylborate. The slope of the plot is approximately 115mV/decade, which is close to the theoretical value found for the majority of membranes containing valinomycin alone. The mixed-ion response is shown in Fig 6.17b. This plot has a slope of 59mV mV/decade over the K+ activity range 10^{-1} - 10^{-4}. With the levels of salt employed in the membranes studied, there did not appear to be any appreciable dependence (ie greater than the possible experimental errors) of the response on the salt concentration.

Fig 6.18 shows a typical single-ion response and mixed-ion

Fig 6.17: (a) Calibration (K^+ single-ion response) and (b) selectivity (K^+/Na^+ mixed-ion response) plots for a PVC/DOS/valinomycin/$KBPh_4$ membrane measured with a 0.1 mol dm^{-3} KCl reference solution.

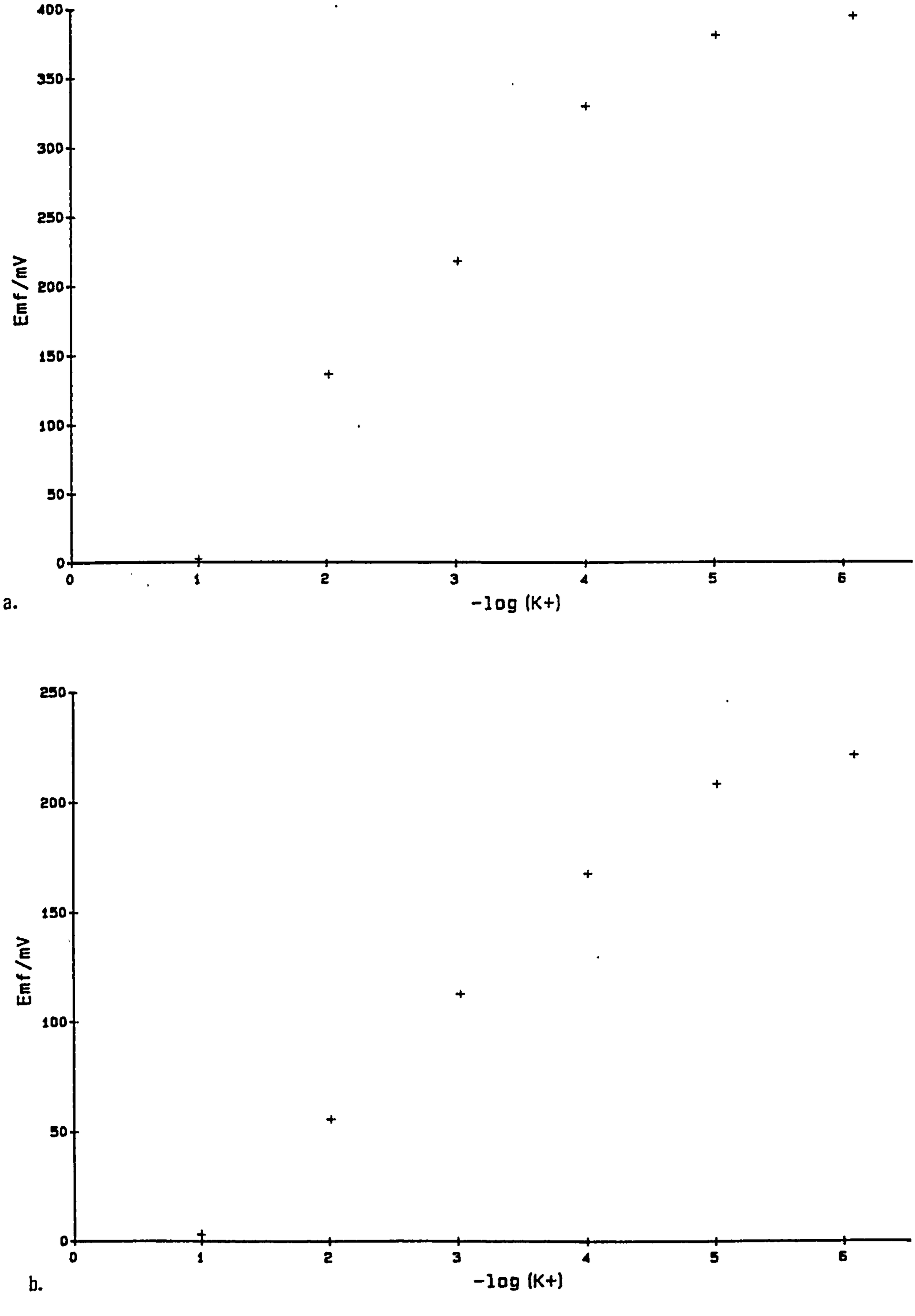
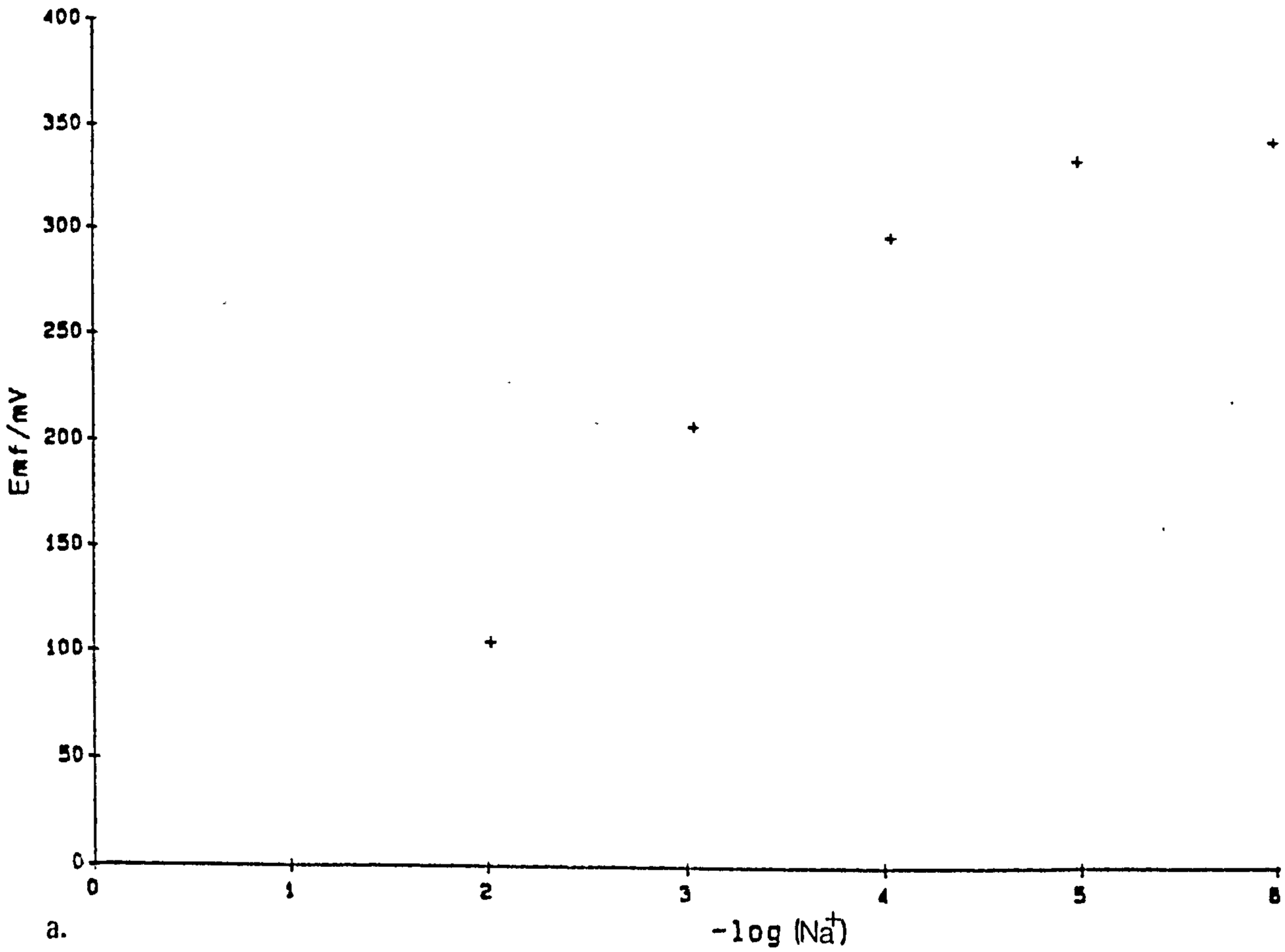
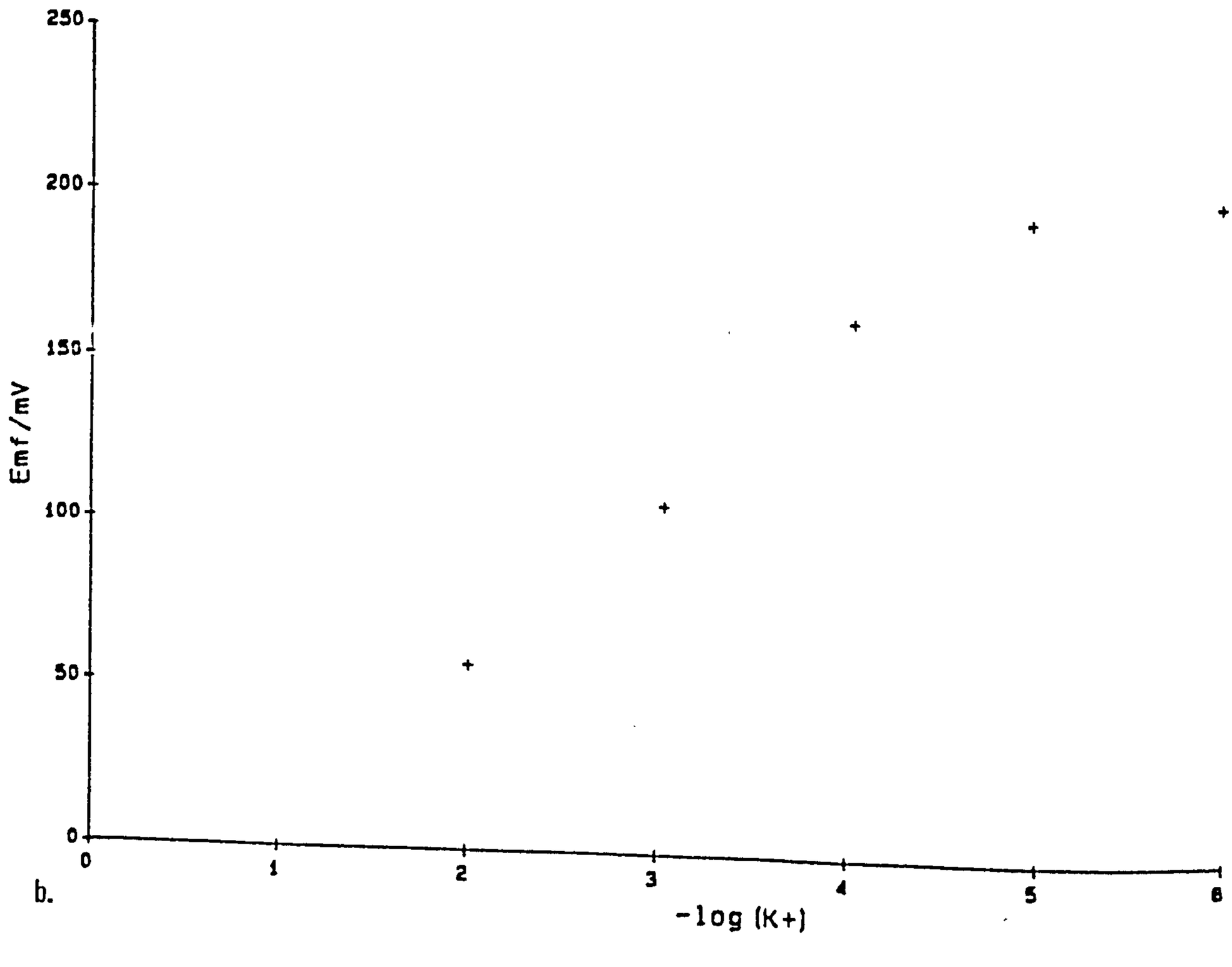


Fig 6.18: (a) Calibration (Na^+ single-ion response) and (b) selectivity (K^+/Na^+ mixed-ion response) plots for a PVC/DOS/valinomycin/$NaBPh_4$ membrane



a.



b.

response (sodium plus potassium after a period of conditioning in 0.1 mol dm^{-3} potassium chloride solutions) respectively, for a membrane containing sodium tetraphenylborate and valinomycin.

It is clearly evident that the response of these electrodes is close to theoretical, with slopes of approximately 59mV/ decade. These results are in keeping with those found by previous workers (6.3), and also with the membranes containing potassium tetraphenylborate.

6.5.2 Impedance Measurements

The impedance of the membranes in contact with o.1 mol dm-3 solutions of the relevant cation, was followed over a three-day period, as previously. A typical steady-state impedance spectrum for a membrane containing valinomycin and $KBPh_4$, in contact with 0.1 mol dm^{-3} KCl solutions is shown in Fig 6.19, with the time-dependence of the impedance over the 72-hour period given in Table 6.16. The final, steady-state spectrum for the membrane containing the sodium salt is shown in Fig 6.20, and the full time-dependence is given in Table 6.17.

The spectrum for the membrane containing potassium is of the same form found with the membranes containing $KBPh_4$ alone, with a clearly-defined bulk semicircle, but with the semicircle due to the interfacial charge-transfer processes very poorly resolved. This low frequency feature is visible only as a distortion of the bulk semicircle, as found previously. From Table 6.16, it can be seen that the time dependence of the impedance is essentially similar to that of the membranes containing valinomycin alone, and those with the BPh_4^- salt as the only additive. The bulk resistance shows an increase over

Fig 6.19: Final impedance spectrum (measured after 72-hours) for a PVC/DOS/valinomycin/$KBPh_4$ membrane, measured with 0.1 mol dm^{-3} KCl contacting solutions.

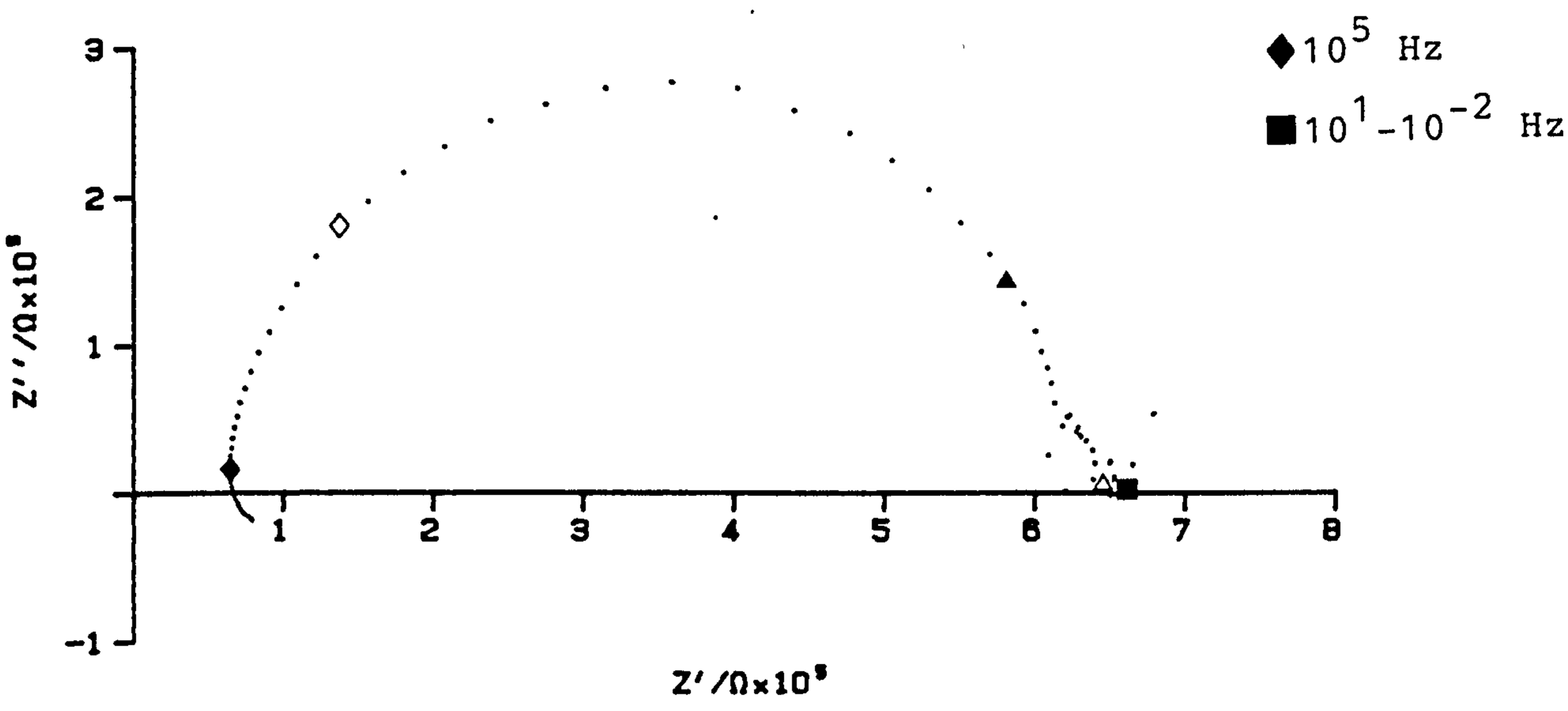


Fig 6.20: Final impedance spectrum (measured after 72-hours) for a PVC/DOS/valinomycin/$NaBPh_4$ membrane, measured with 0.1 mol dm^{-3} NaCl contacting solutions.

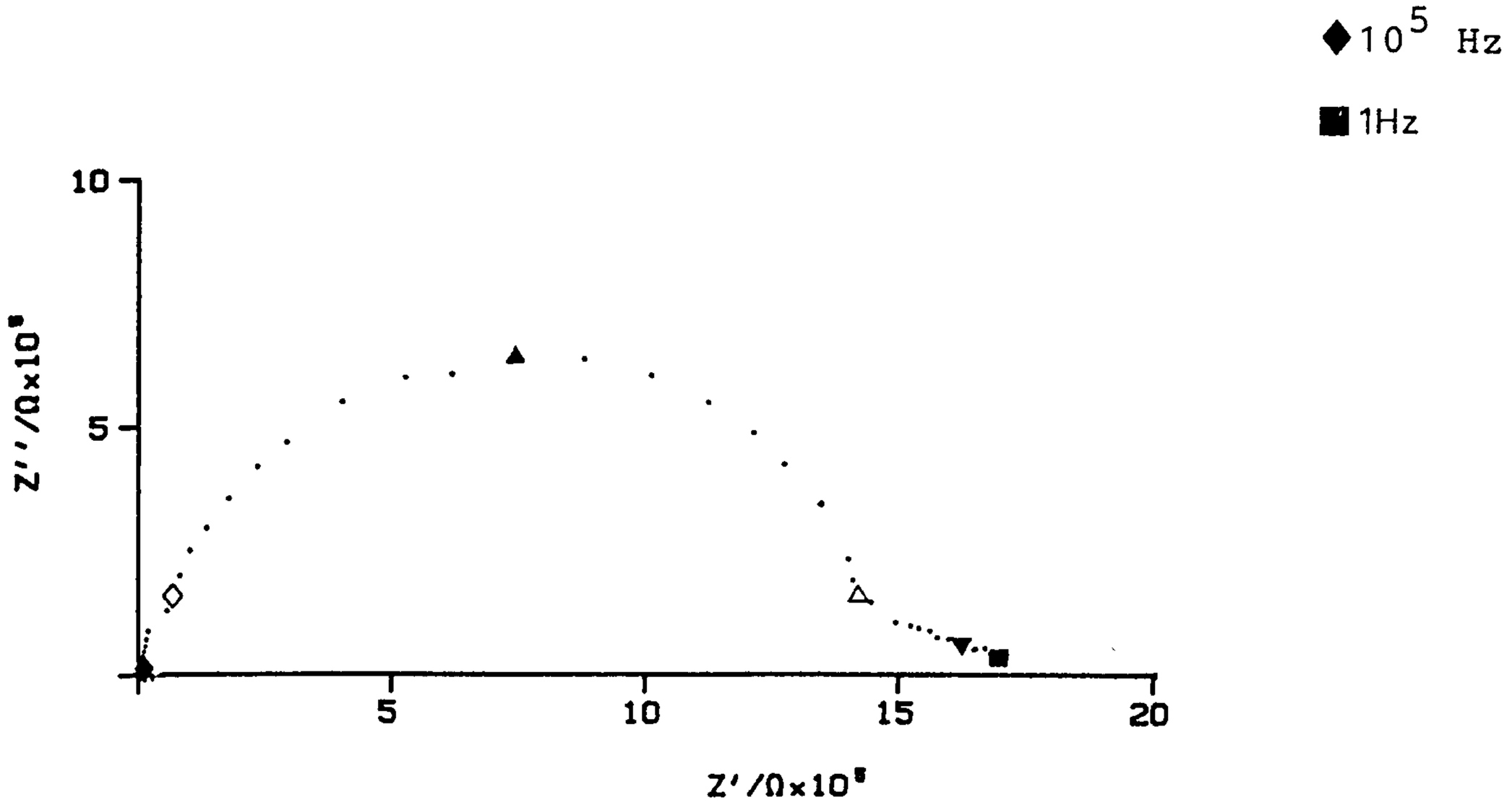


Table 6.16: Time Dependence of Impedance for PVC/DOS/$KBPh_4$ /Valinomycin Membrane With 0.1 mol dm^{-3} KCl Contacting Solutions

t/hours	$R_b/10^5\ \Omega$	$\omega_1^*{}_{max}$/Hz
1	4.33	2159
2	5.17	"
3	5.17	"
4	5.09	"
5	4.85	"
6	4.96	"
7	5.07	"
8	5.13	"
9	5.22	3424
10	5.39	"
11	5.57	"
12	5.66	"
13	5.75	"
14	5.90	"
15	6.05	"
16	6.10	"
17	6.15	"
18	6.15	"
19	6.15	"
20	6.18	"
21	6.20	"
22	6.18	"
23	6.20	"
24	6.20	"
72	6.21	"

Table 6.17: Time Dependence of Impedance for $PVC/DOS/NaBPh_4$ /Valinomycin Membrane With 0.1 mol dm^{-3} NaCl Contacting Solutions

t/hours	$R_b/10^6\ \Omega$	$\omega_1^*{}_{max}$/Hz
1	0.98	1169
2	1.21	"
3	1.29	"
4	1.37	"
5	1.40	1000
6	1.41	"
7	1.45	"
8	1.47	"
9	1.47	"
10	1.48	"
11	1.47	"
12	1.48	"
13	1.49	"
14	1.51	"
15	1.49	"
16	1.50	"
17	1.50	"
18	1.51	"
19	1.48	"
20	1.51	"
21	1.53	"
22	1.52	"
23	1.53	"
24	1.53	"
72	1.52	"

the first 24 hours which continues to a constant value, reached by the end of the 72 hour period. The magnitude of the final bulk resistance is similar to that of the corresponding membrane containing no valinomycin, but with a similar amount of added salt.

For the membrane containing the sodium salt, the spectrum is essentially similar, except that the bulk resistance of the membrane is higher than that of the corresponding membrane containing no valinomycin, and also higher than for the membrane containing $KBPh_4$ and valinomycin. The low frequency data is not well-defined in this case, but the charge-transfer resistance is evidently of the order of 10^5 Ohms.

6.5.3 Discussion

Both types of membrane produced good selectivities for potassium over sodium, as expected, this being the most effective formulation for PVC membranes to have been reported. It is interesting to note however, that for the membrane containing the potassium, the addition of the valinomycin does not at first sight appear to have had a marked effect on the bulk resistance of the membrane. This is in contrast to the membranes containing no salt, where it was found that the valinomycin did produce a reduction in the bulk resistance. On closer inspection, however, the data show that the initial value of R_b for the membrane containing the ionophore is larger than that for the corresponding membrane containing only the salt. The percentage increase in R_b seen for this latter membrane is greater than for the former, resulting in the final R_b values being much closer together. This result is unusual,

as it implies that the inclusion of the ionophore actually decreases the mobility of the potassium within the membrane. This could be taken to indicate that the ionophore 'pins' the potassium ion in a potential well, which would otherwise be absent, and that the potassium can then only move by hopping from valinomycin molecule to valinomycin molecule.

For the membrane containing the sodium salt, it would seem that the incorporation of valinomycin, as previously, has also markedly reduced the mobility of the cation. In view of the low stability of the Na^+/valinomycin complex it seems less likely that this is due to a direct interaction between the two, but it is not obvious by what mechanism this reduction in mobility occurs. It is clear though, that the bulk resistance is lower than for the membrane containing valinomycin and no salt, and so the presence of the salt has caused some increase in the number of charge-carriers.

6.6 A Comparison Between Potassium and Caesium For The PVC/Valinomycin System

The sequence of selectivities exhibited by membranes containing valinomycin, show that they give approximately equal responses to potassium and caesium (relative to the marked selectivity against sodium). In view of this, a series of membranes was fabricated containing the caesium salt of the tetraphenylborate ion, both with and without valinomycin, in an attempt to obtain a comparison between potassium and caesium, both in terms of the potentiometric response, and the impedance behaviour of the membranes. Also, it is suggested in section 6.3.3 that the difference in mobility between K^+ and Na^+, as

perceived through the bulk membrane resistance, could be related to the charge density on the metal ion. The incorporation of Cs^+ into the membrane should yield additional information to test this hypothesis, the charge density on Cs^+ being somewhat lower than that on potassium (Table 6.6).

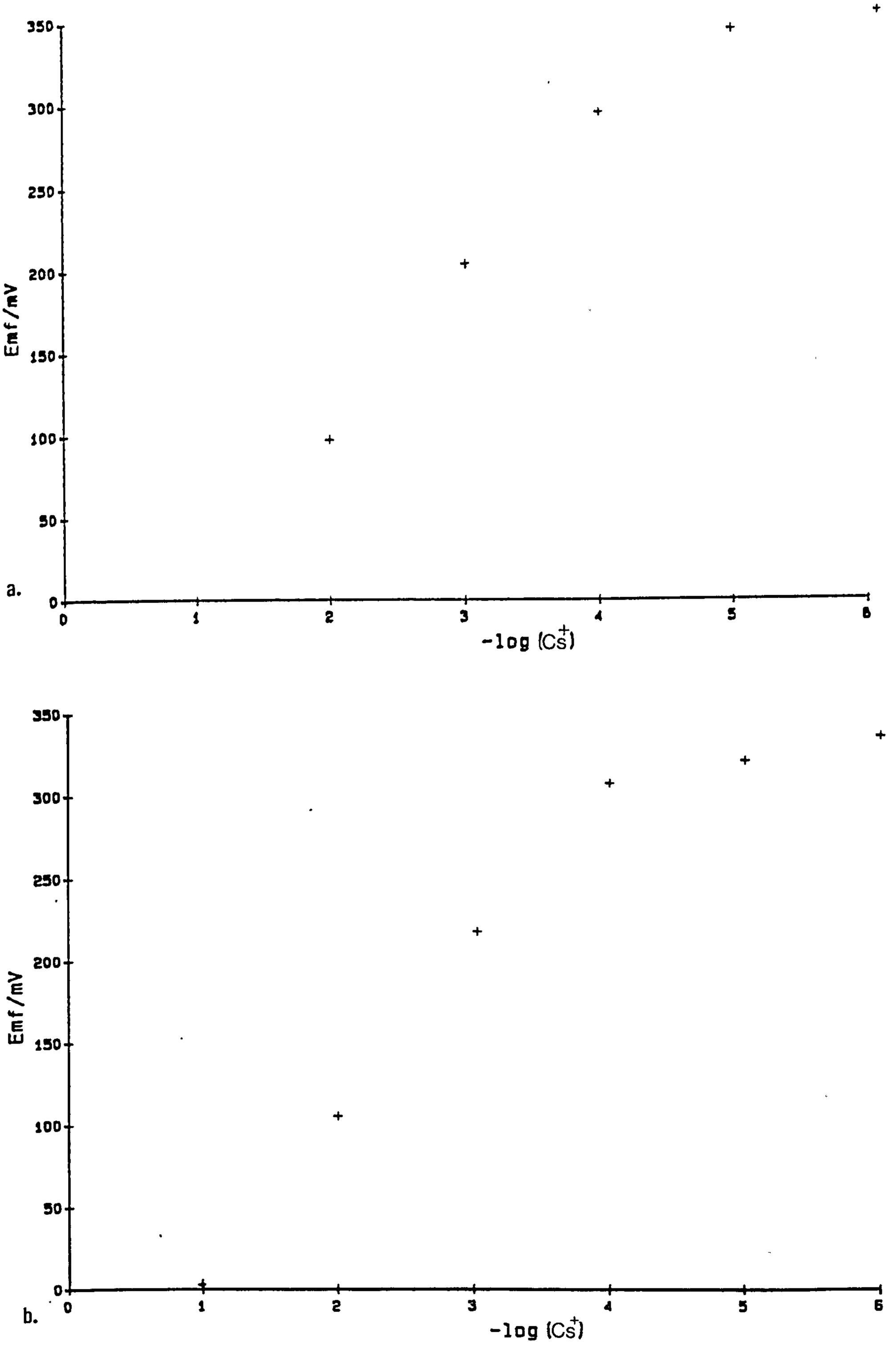
Membranes were cast as previously, and accuracy and consistency in the quantity of $CsBPh_4$ incorporated into the membranes was achieved using solutions of $CsBPh_4$ in THF, as with previous membranes containing salts. A similar concentration of the BPh_4^- salt was used as previously, giving a typical composition of 150mg PVC/300mg dioctyl sebacate/ 6.2 $x10^{-2}$mg $CsBPh_4$. For membranes containing the ionophore, a similar concentration of valinomycin was used as previously.

6.6.1 Potential Response

The single-ion response of all the membranes was determined using solutions of caesium chloride, and Fig 6.21a shows a typical response curve for a membrane containing only the salt, for which the potential response is close to Nernstian and is similar to the corresponding plots for the membranes containing $KBPh_4$ or $NaBPh_4$ alone, in contact with solutions containing only the corresponding cation.

The single-ion response of a membrane containing valinomycin is shown in Fig 6.21b. The response is slightly poorer than for the corresponding membranes containing the sodium and potassium salts, with a slope of approximately 112mV over the range 10^{-1} - 10^{-4} mol dm^{-3} CsCl. The fact that the reponse is sub-Nernstian would indicate that anion exclusion is possibly incomplete with the caesium salt in the membrane.

Fig 6.21: Calibration (Cs^+ single-ion response) plots for (a) PVC/DOS/$CsBPh_4$ and (b) PVC/DOS/$CsBPh_4$/ valinomycin membranes measured with a 0.1 mol dm^{-3} CsCl reference soln.



The mixed-ion response of all of the membranes was also investigated with 0.1 mol dm^{-3} NaCl as the interferent. The response of a membrane with no added ionophore is shown in Fig 6.22a, from which it is evident that the membrane shows no selectivity for caesium in the absence of valinomycin, as would be expected.

A typical mixed-ion response curve for a membrane containing the ionophore is shown in Fig 6.22b. In this case, the plot shows a slope of approximately 58mV/decade over the Cs^+ concentration range 10^{-1} - $10^{-3.8}$, as expected, indicating that the membrane does exhibit a high degree of selectivity for caesium in the presence of sodium.

6.6.2 Impedance Behaviour

The impedance of the membranes was measured in contact with 0.1 mol dm^{-3} CsCl solutions, as a comparison with membranes with added $KBPh_4$ and $NaBPh_4$, when in contact with solutions of K^+ or Na^+ respectively.

Fig 6.23a shows the initial spectrum for a membrane containing no valinomycin, measurements being commenced approximately five minutes after first solution contact. The plot shows similar features to the membranes studied previously, with a high-frequency semicircle due to the membrane bulk and a lower frequency arc representing the interfacial processes. The two features are well separated, and in common with the membranes containing $NaBPh_4$, are more clearly defined than those found with several of the membranes with $KBPh_4$ as the additive. The initial bulk resistance is approximately 12.3×10^4 Ohms, and the initial charge-transfer

Fig 6.22: Selectivity (Cs^+/Na^+ mixed-ion response) plots for (a) PVC/DOS/$CsBPh_4$ and (b) PVC/DOS/$CsBPh_4$/ valinomycin membranes measured with a 0.1 mol dm^{-3} CsCl reference soln.

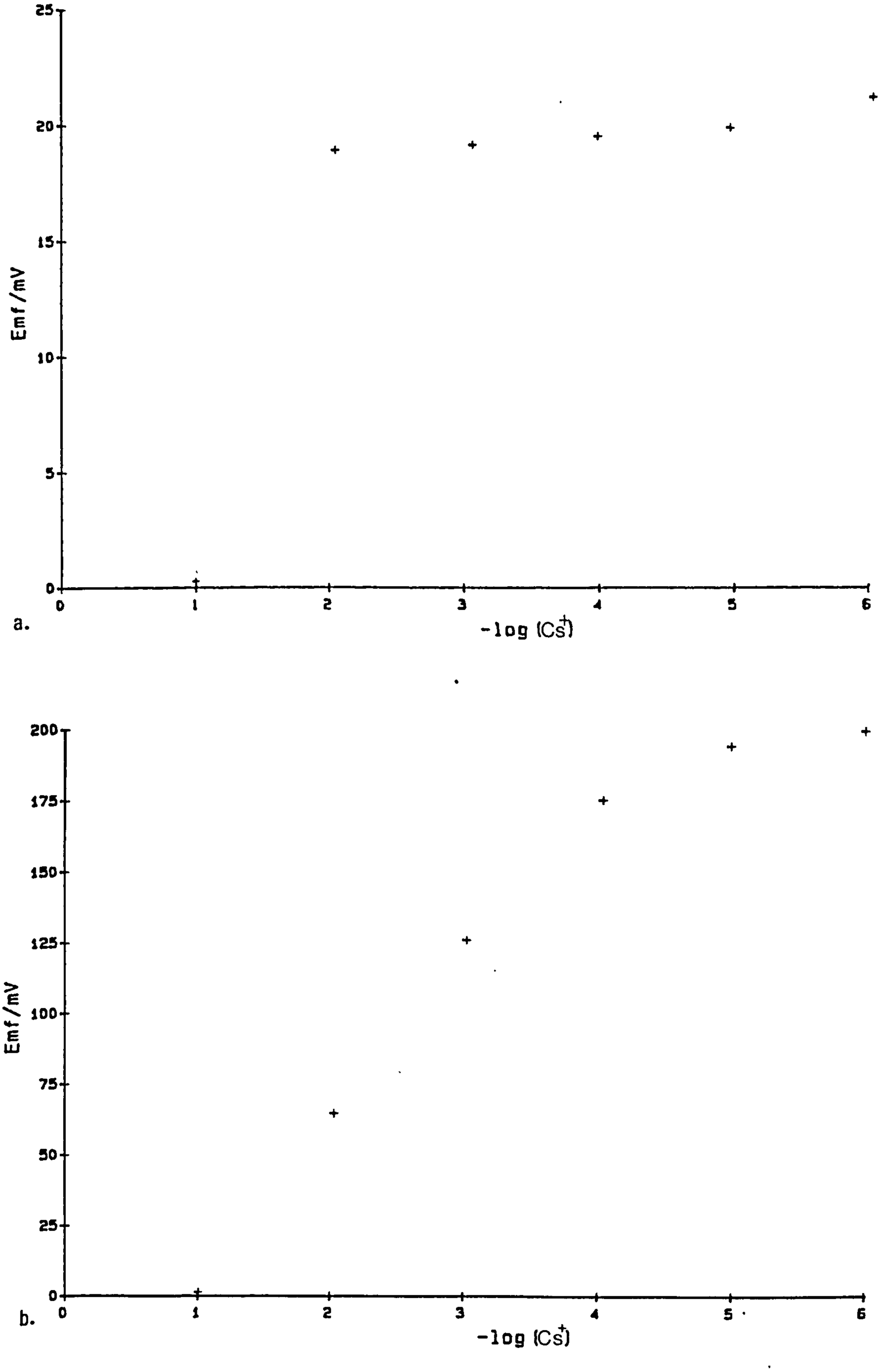
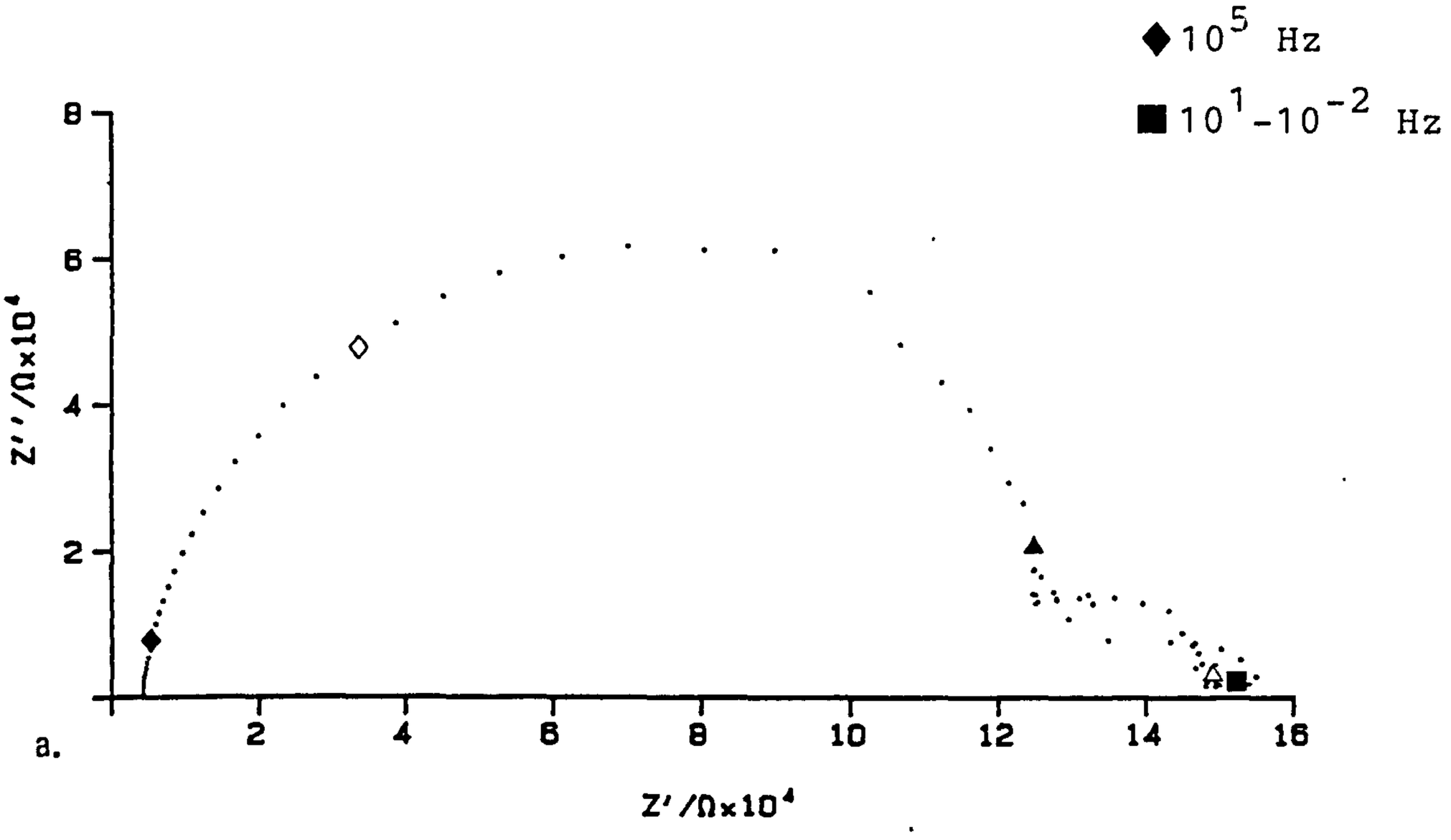


Fig 6.23: Initial (a) and final (b) impedance spectra for a membrane containing 6.02 x10-2 mg $CsBPh_4$, measured with 0.1 mol dm^{-3} CsCl contacting solutions.



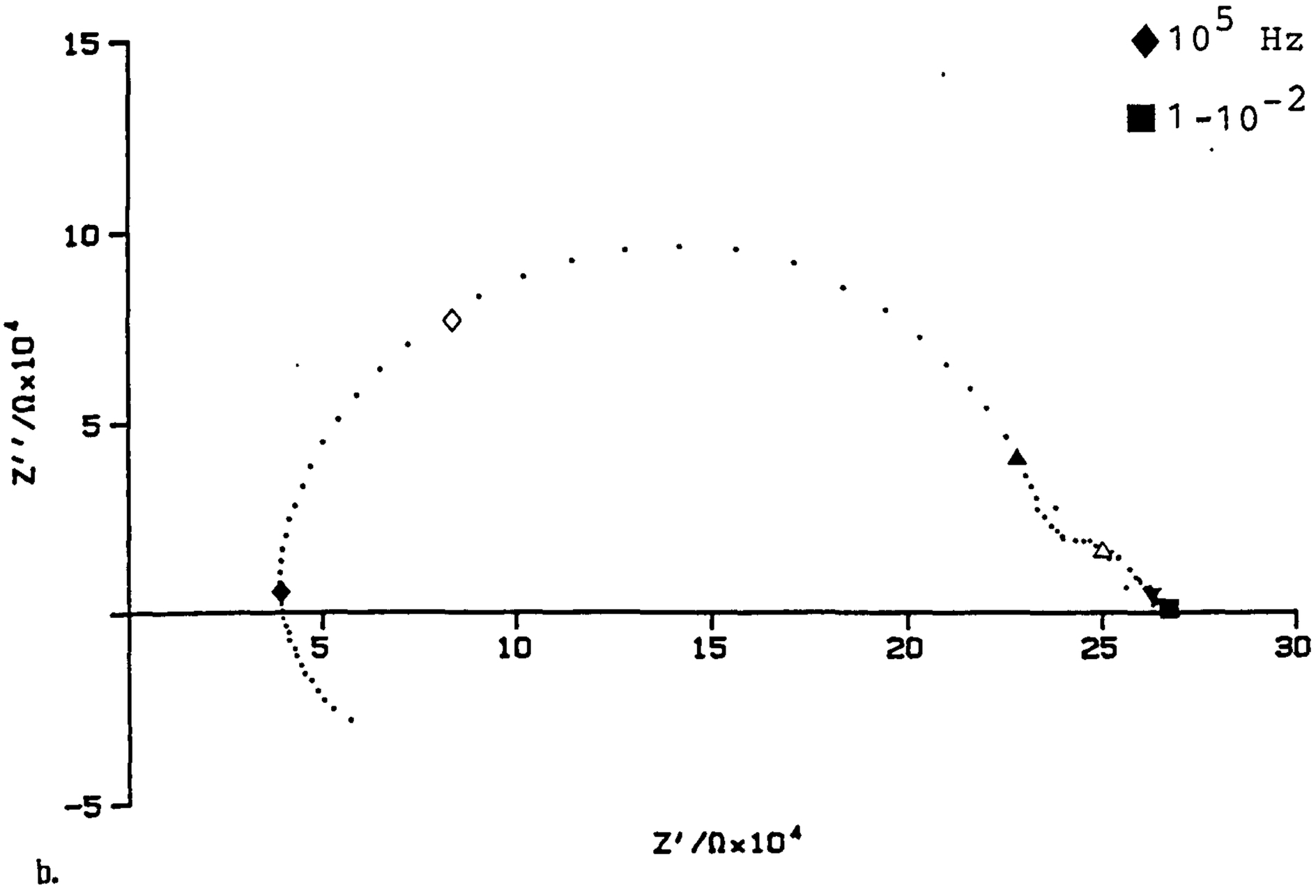


Table 6.18: Time Dependence of Impedance for the Membrane Containing PVC/DOS/$CsBPh_4$ (With 0.1 mol dm^{-3} CsCl Contacting Solutions)

t/hours	$R_b/10^5\ \Omega$	$\omega_{1\,max}^*$/Hz	$R_{ct}/10^4\ \Omega$	$\omega_{2\,max}^*$/Hz
1	1.26	4656	2.42	10^2-10^3
2	1.41	"	"	"
3	1.53	"	2.40	"
4	1.65	"	"	"
5	1.74	"	"	"
6	1.83	"	"	"
7	1.91	"	"	"
8	1.99	"	"	"
9	2.05	"	2.34	"
10	2.11	"	3.01	"
11	2.16	"	3.39	"
12	2.22	"	"	"
13	2.27	"	"	"
14	2.32	"	"	"
15	2.35	"	"	"
16	2.40	"	"	"
17	2.39	"	"	"
18	2.44	"	"	"
19	2.42	"	"	"
20	2.43	"	"	"
10	2.44	"	"	"
21	2.45	"	"	"
22	2.42	"	"	"
23	2.45	"	"	"
24	2.44	"	"	"
72	2.45	"	"	"

resistance has a value of approximately 2.5 x 10^4 Ohms. The time dependent behaviour of the membrane impedance was followed and Fig 6.23b shows the spectrum recorded three days after first solution contact. The detailed time dependence of the membrane is given in Table 6.18.

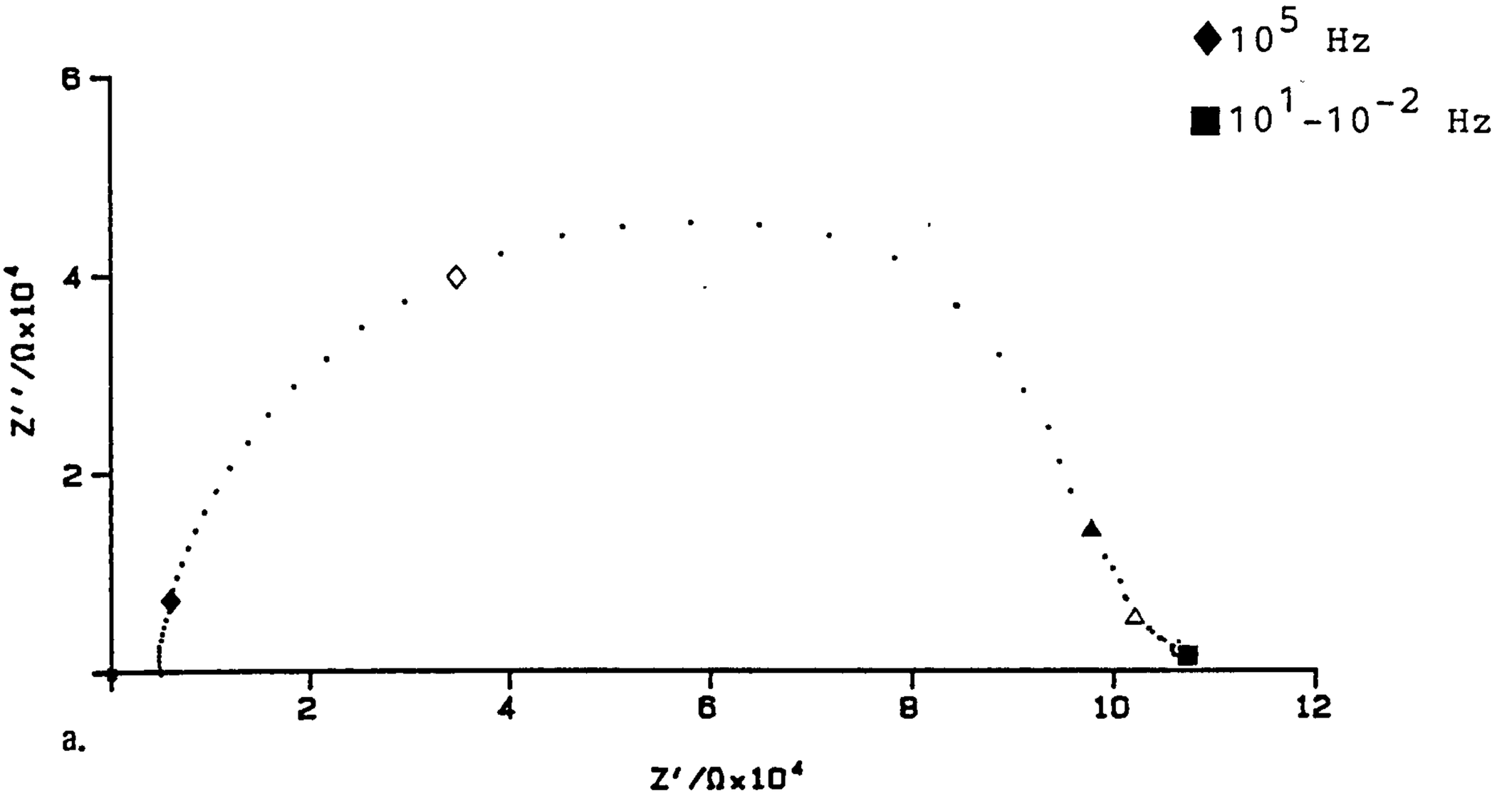
Fig 6.24a shows the initial spectrum, recorded approximately five minutes after first solution contact, for a membrane containing the caesium salt, and valinomycin. This plot again shows the high frequency semicircle due to the bulk membrane, and the charge-transfer semicircle which has not been greatly affected by the inclusion of valinomycin into the membrane, but is poorly-defined. The final, steady-state spectrum is shown in Fig 6.24b, and the time dependence of the membrane impedance is given in Table 6.19.

6.6.3 Discussion

Considering first the membranes containing no ionophore, the most notable feature of the impedance is that the final bulk resistance is appreciably lower than that for the corresponding membranes containing K^+ and Na^+ (i.e. membranes with equivalent concentrations of those ions). A comparison of the value of R_b for all the membranes containing only salts of the BPh_4^- ion is given in Table 6.20.

The fact that R_b is lower for caesium would appear to support the theory that the mobility of the cation within the membrane is dependent on the charge density on the ion. When compared to the value of R_b for the membrane containing $KBPh_4$ however, it can be seen that the latter exhibits a higher resistance than the corresponding Na^+- containing membrane. It

Fig 6.24: Initial (a) and final (b) impedance spectra for a PVC/DOS/$CsBPh_4$/valinomycin membrane, measured with 0.1 mol dm^{-3} CsCl contacting solutions.



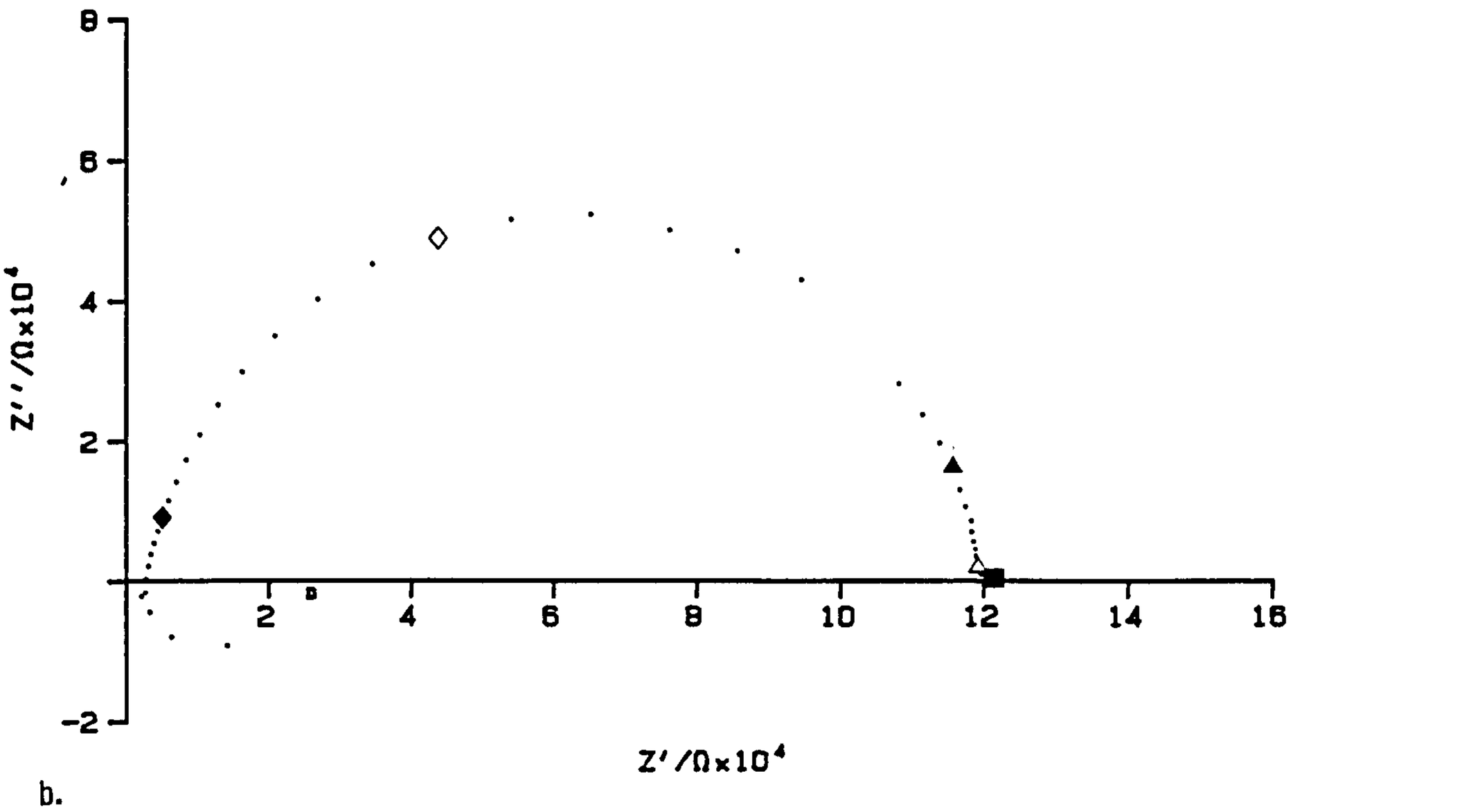


Table 6.19: Time Dependence of Impedance for PVC/DOS/$CsBPh_4$ /Valinomycin Membrane With 0.1 mol dm^{-3} CsCl Contacting Solutions

t/hours	$R_b/10^5\,\Omega$	$\omega_1^*{}_{max}$/Hz
1	1.01	5426
2	1.02	"
3	1.05	"
4	1.06	"
5	1.08	"
6	1.09	"
7	1.10	"
8	1.12	"
9	1.12	"
10	1.12	"
11	1.13	"
12	1.15	"
13	1.15	"
14	1.15	"
15	1.16	"
16	1.17	"
17	1.17	"
18	1.18	7377
19	1.19	"
20	1.20	"
21	1.21	"
22	1.21	"
23	1.22	"
24	1.22	"
72	1.23	"

Table 6.20: Summary of Bulk Resistance Values For PVC Membranes With Added $BPh4^-$ Salts

Additive	mass%	Contacts	R_b init	R_b fin
None	-	KCl	2.28×10^{6}	4.50×10^{6}
None	-	NaCl	2.56×10^{6}	5.51×10^{6}
KBPh4	1.1×10^{-2}	KCl	3.26×10^{5}	6.80×10^{5}
KBPh4	5.0×10^{-2}	KCl	2.79×10^{5}	4.17×10^{5}
KBPh4	1.1×10^{-1}	KCl	5.70×10^{4}	1.51×10^{5}
KBPh4	4.0×10^{-1}	KCl	1.10×10^{4}	1.59×10^{5}
KBPh4	4.9	KCl	1.42×10^{5}	1.73×10^{5}
NaBPh4	1.1×10^{-2}	NaCl	1.91×10^{5}	3.84×10^{5}
NaBPh4	1.1×10^{-1}	NaCl	6.53×10^{4}	1.53×10^{5}
CsBPh4	1.1×10^{-2}	CsCl	1.26×10^{5}	2.45×10^{5}

only 20 mV for a five decade change in K+ concentration in the sample solution (although all membranes produced some degree of single-ion response with the relevant primary ion, either Na^+, K^+ or Cs^+). For membranes containing valinomycin, the selectivities were in the range 10^3- 10^4 for potassium over sodium (as determined by the mixed solution method) and calibration curve slopes of near to the theoretical value of 59.2 mV/decade were found for membranes containing both valinomycin and added tetraphenylborate salts. In the absence of BPh_4^-, although linear responses were found, the slopes of the primary ion activity versus potential plots were sometimes sub-Nernstian, though generally better than 55mV/decade.

Evidence has been produced by other techniques (6.6-6.11) suggesting that the membrane is electroneutral, but that the anions present in the membrane bulk are immobile relative to the cations. The immobility of the anions could be a result of chemical bonding to the membrane support (6.9), poor water solubility (6.10), or merely due to a very low anion transport number (6.7,6.12). It appears that the improved response found for the membranes in sections 6.4 and 6.5 is attributable to the presence of the anions within the membrane, rather than the concomitant increase in concentration of the primary ion, and that the response is improved due to electrostatic repulsion between the BPh_4^- ions within the membrane and the Cl^- ions in the solution.

The relative ionic mobilities for the cation and anion were calculated from potentiometric data (with a tenfold difference of concentration in the two contacting solutions) for selected membranes, as outlined in section 6.3.3, and shown in Table 6.21.

Table6.21: Measured P.D. Values for a Tenfold Difference In Concentration Across PVC Membranes

$KBPh_4$ /mg	$NaBPh_4$ /mg	Ligand /mg	Contacts	P.D /mV	Theoretical
0.05	0	0	KCl	109.2	110.16
0	0.05	0	NaCl	103.8	110.61
0.05	0	4.4	KCl	108.9	110.16
0	0.05	4.4	NaCl	(a)	110.61

a - This value could not be accurately determined due to K^+ uptake as a result of impurities in the NaCl solutions.

The potential difference values measured for the membranes containing $KBPh_4$ are close to those which would be anticipated on theoretical grounds for membranes in which the anion is immobile with respect to the cation. The membranes containing $NaBPh_4$ produced slightly lower potential difference values than the $KBPh_4$-containing membranes, indicating that the relative mobility of the anions is greater in the membranes containing the sodium salt. This may be due to greater penetration of the membranes by chloride ions, or due to differing degrees of interaction between the cation and the PVC matrix. The cation transport number in both cases, is however, close to unity, and from these results, it appears that the membranes must depend on the presence of anions which are relatively immobile if a Nernstian response to K^+ is to be expected, as with no added salt or valinomycin in the membrane and a tenfold difference in K^+ concentration, a potential difference of only 92.8 mV is produced, indicating a considerable degree of Cl^- penetration. In the absence of deliberately added tetraphenylborates however, it is by no means certain that adventitious immobile anions will be present in the PVC matrix, although it seems likely that some will be incorporated as impurities into a membrane from its components, or otherwise, when it is fabricated. This would explain the variable results found for membranes containing no added salts. It has been suggested (6.11), that the anion arises from carbonyl groups in the plasticiser, and this is supported by the data presented in Chapter 5.

For all membranes containing valinomycin, excluding those containing $CsBPh_4$, the bulk resistance and charge-transfer resistance were found to be higher when the bathing solutions

were 0.1 mol dm^{-3} NaCl than when they were 0.1 mol dm^{-3} KCl, and with all membranes studied, the impedance spectra were found to be time-dependent, showing an increase in bulk resistance with time.

The fact that the bulk resistance of the membranes with sodium contacting solutions was higher than with potassium chloride solutions would appear to reflect the greater mobility of the potassium ions within the membrane compared with that of sodium ions, although in the absence of valinomycin this discrepancy was not found. The similarity between the bulk resistance of the dry membranes reported in Chapter 5 and the corresponding membranes in contact with aqueous solutions strongly suggests that the membranes as formed have mobile ions (presumably mobile cations) present within them although it must be emphasised that the 'dry' membranes were as normally prepared, i.e. they were prepared in the open atmosphere with no special precautions being taken to exclude moisture, and so may have taken up water from the atmosphere during fabrication.

It is apparent from the results reported in sections 6.3 and 6.4 that membranes prepared without any added salt undergo ion-exchange with the aqueous contacting solutions to some extent, so that their composition in terms of charged species, is time-dependent, and a function of the particular contacting solution.

Exchange currents calculated for the exchange of both potassium and sodium ions across the membrane/solution interface for membranes containing valinomycin do not reflect the selectivity ratio found for the same membranes via potential measurements. The results given in section 6.3 show that the ratio of charge transfer resistance, $R_{ct}(Na^+)/R_{ct}(K^+)$,

is several orders of magnitude lower than the value of the selectivity coefficient (10^3 - 10^4), and it is therefore apparent that the selectivity does not arise wholly at the membrane solution interface. If this were the case, the charge transfer ratio, which reflects the ease with which the ions can enter the membrane, would also be expected to be in the region of 1000:1, so it must be assumed that the selectivity arises, in part, from deeper into the membrane than the thickness of the electrical double-layer (30 nm).

It has been suggested (6.13) that significant deviations from electroneutrality within the bulk of the membrane occur using the assumption that the cation-carrier complex is the only charged species present in the membrane interior. In this case, potassium ions are complexed by the valinomycin and the cation is transported through the membrane in the cavity of the valinomycin which acts as a carrier. This view, also taken by others (6.9,6.13,6.14), is strictly applicable only to thin liquid membranes, although extended to thicker membranes (6.15), and is unlikely to apply to the membranes used in the present study, due to the greater thickness (as discussed in Chapter 3), and the deliberate incorporation of salts into the matrix.

In section 6.5, results are given for membranes where the initial salt levels in the membranes are such as to swamp the effects of any inherent ionic impurities, and the possibility of ion-exchange with the initial solutions was also much reduced by contacting membranes containing K^+, with only KCl solutions, and those containing Na^+, with only NaCl solutions. It is reasonable to assume that under these circumstances, the ionic composition of the membranes containing added salts is

essentially unchanged during the course of the experiments, as when salts are added, the internal concentrations of charged species will undergo smaller percentage changes with time. The results obtained for these membranes are summarised in Table 6.22 and 6.23, and on the basis of these results, a mechanism for the operation of the PVC membranes can be proposed based on the assumption that the bulk of the membrane is electrically neutral.

Table 6.22 shows that addition of salts to the membrane results in a bulk resistance appreciably lower than in the absence of the additive. It can also be seen that a tenfold change in additive concentration does not produce a tenfold change in the bulk resistance of the membrane, which would seem to indicate that at higher tetraphenylborate concentrations, there is association between the anions and cations in the membrane.

From Table 6.23, it is clear that when salts are added to the membrane, there is a fast equilibrium between K^+ in the aqueous phase and K^+ in the membrane, both in the presence and absence of valinomycin, and that in the absence of valinomycin a similar situation exists for sodium ions.

Using the values in Table 6.22, and assuming that the membrane conductivity arises almost exclusively from cation conduction, a table of relative ionic mobilities can be constructed (Table 6.24). From this table, it is apparent that Na^+ and K^+, in the absence of valinomycin, have comparable mobilities and that the presence of valinomycin causes a greater reduction in Na^+ mobility than K^+ mobility. Since it seems likely that the valinomycin molecules are immobilised in the membrane and that very little free K^+ is present when there

Table 6.22: Summary of Bulk Membrane Resistance Values for PVC Membranes (normalised to 1 cm^2 Area)

$KBPh_4$ /mg	$NaBPh_4$ /mg	Ligand /mg	Contacts *	R_b init/Ω	R_b fin/Ω
0	0	0	Stainless Steel	3.45×10^6	3.45×10^6
0	0	0	KCl	1.78×10^6	3.51×10^6
0.05	0	0	KCl	2.56×10^5	5.34×10^5
0.50	0	0	KCl	4.47×10^4	1.19×10^5
0	0.05	0	NaCl	1.50×10^5	3.00×10^5
0.05	0	4.4	KCl	3.40×10^5	4.87×10^5
0	0.05	4.4	NaCl	7.70×10^5	1.20×10^6

* All solutions 0.1 mol dm^{-3}

Table 6.23: Summary of Charge Transfer Resistances for PVC Membranes (Normalised to 1 cm^2 Area)

$KBPh_4$ /mg	$NaBPh_4$ /mg	Ligand /mg	Contacts *	R_{ct} init/Ω	R_{ct} fin/Ω
0	0	0	KCl	3.43×10^6	8.35×10^5
0.05	0	0	KCl	3.84×10^4	8.58×10^4
0	0.05	0	NaCl	6.71×10^4	1.23×10^5
0.05	0	4.4	KCl	$<3.90 \times 10^4$	$<3.90 \times 10^4$
0	0.05	4.4	NaCl	$<3.90 \times 10^5$	$<3.90 \times 10^5$

* All solutions 0.1 mol dm^{-3}

Table 6.24: Relative Mobilities Of Species Within PVC Membranes

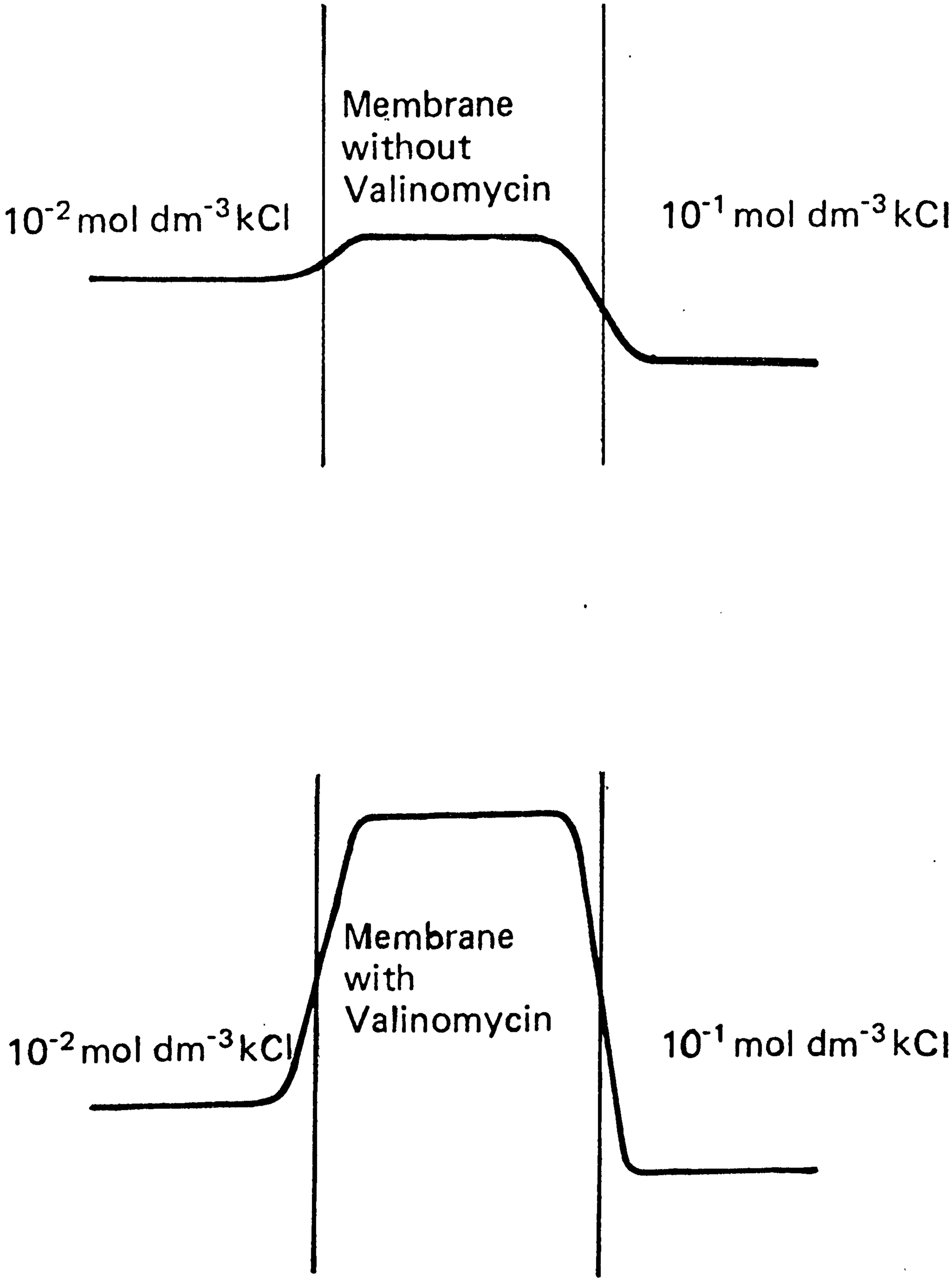
Species	Initial	After Equilib. With Water
K^+	1.00	1.00
Na^+	1.70 $\pm$ 0.3	1.78 $\pm$ 0.2
K^+ (Valinomycin Present)	0.75 $\pm$ 0.1	1.10 $\pm$ 0.2
Na^+ (Valinomycin Present)	0.30 $\pm$ 0.1	*

* This value was uncertain due to the takeup of K^+ as impurities in the NaCl solutions

is an excess of valinomycin, it is reasonable to assume that K^+ ions can exchange rapidly between valinomycin molecules.

The selectivity of the membranes in the presence of valinomycin evidently does not arise from a change in the relative mobility of K^+ over Na^+, since this change is much less than the measured selectivity (a ratio of approximately 2:1 compared to a selectivity of greater than 1000:1). The selectivity appears to arise because the equilibrium concentration of sodium ions in the membrane in equilibrium with a sodium chloride solution, is extremely small, due to the large increase in the electrostatic potential in the bulk of the membrane resulting from the presence of valinomycin (as depicted in Fig 6.25). Thus, when no valinomycin is present in the membrane, sodium ions in an aqueous solution in contact with the PVC matrix will readily undergo ion-exchange with potassium ions in the membrane until the Na^+ and K^+ are both in equilibrium across the interface. With valinomycin incorporated into ther membrane howéver, there will be very little ion-exchange between sodium ions in the aqueous solutions and potassium ions in the membrane, unless the activity ratio of Na+/K+ in the aqueous phase is greater than 10^3:1.

Fig 6.25: Variation of electrostatic potential with distance through a membrane containing valinomycin in contact with solutions containing potassium.



Chapter 6 References

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Chapter 7

PVC Membranes - Alternative Potassium Ligands

7.1 Introduction

As discussed in Chapter 3, for several years attempts have been made to synthesise compounds which will mimic the ion-selective properties of the naturally occurring ionophores. The main motivation for this being the difficulties of extraction and purification of the natural products, although some of these have been synthesised in the laboratory (7.1). Since the discovery of the crowns by Pederson in 1971 (7.2), many compounds have been produced which exhibit a degree of ion-selective behaviour (Chapters 1 & 3), and in this chapter results of both potential and impedance measurements are reported for several of these synthetic alternatives which have been reported elsewhere to show potassium selective behaviour.

7.2 Expected Equivalent Circuits

Whilst the synthetic ionophores do not show as high a degree of ion-selectivity as valinomycin, if it is assumed that the basis of their lower level of selectivity is the same as for the valinomycin system, then it would be reasonable to expect that the impedance behaviour of membranes containing these compounds would be similar to that of membranes containing valinomycin.

The general form of the impedance spectra should be as found with all other PVC membranes studied, with a bulk membrane semicircle, and a second semicircle at lower frequency

representing the interfacial charge-transfer processes, but it is less certain to what extent these features will have similar characteristics, (i.e. values of R_b, R_{ct}, C_g and C_{dl}). It is likely that any differences in selectivity or other behaviour between the synthetic ionophores and their natural counterpart will be reflected in their impedance spectra, particularly in the lower-frequency region. Impedance measurements may therefore yield further information on the criteria necessary for an ionophore to exhibit a high degree of selectivity.

7.3 Dibenzo-18-Crown-6

As the crowns were the first synthetic ionophores produced, and have received a great deal of attention from workers worldwide, despite their relatively poor selectivity for alkali metal ions, a member of the crowns was included in this study. Dibenzo-18-C-6 was selected as a typical crown since it has been reported to show a limited degree of selectivity for potassium over sodium, particularly from extraction studies (7.3).

Membranes were cast containing either sodium or potassium tetraphenylborate in order to maximise the anion exclusion properties of the membrane as with the valinomycin system, and using a similar ratio of ionophore to BPh_4^-, as previously (i.e. approximately 5.0 $x10^{-2}$mg salt/150 mg PVC/300mg plasticiser).

7.3.1 Potential Response

The single-ion response of the membranes was determined using solutions of the appropriate cation (either K^+ or Na^+) as previously. The mixed ion response for the membranes containing

the potassium salt was determined directly after impedance measurements were completed, but as for the previous membranes containing the sodium salt, equilibration with potassium was necessary before the mixed ion response could be measured. The data for the sodium-containing membranes were therefore measured after a 24-hour immersion in 0.1 mol dm^{-3} KCl solution.

Figures 7.1a and 7.1b show typical single-ion responses for the two membrane formulations. The membrane containing potassium tetraphenylborate gives a sub-Nernstian response (108mV/decade) over the range 10^{-1} - $10^{-3.5}$ mol dm^{-3} KCl, and the single-ion response for the membrane containing the sodium salt is similar with a slope of 107mV/decade over the range 10^{-1} - 10^{-4} mol dm^{-3} NaCl.

The mixed-ion response of the membrane containing $KBPh_4$ is shown in Fig 7.2a, and that for the membrane containing $NaBPh_4$ (after conditioning) is shown in Fig 7.2b. The response is clearly poor for both membranes, although they show a limited response over the first two decades of change in primary ion concentration, which flattens out to a constant potential at lower K^+ concentrations. Values for $K_{K/Na}$ calculated from these plots are 4.5×10^{-2} for the K^+ membrane and 7.6×10^{-2} for the Na^+ membrane which are similar to the values of approximately 7.7×10^{-2} reported in the literature (7.3).

7.3.2 Impedance Measurements

The impedance spectra of the membranes in contact with either 0.1 mol dm^{-3} KCl or NaCl solutions were recorded, and the time dependence of the membrane impedance was followed as for the valinomycin-containing membranes.

Fig 7.1: Calibration (K^+ or Na^+ single-ion response) plots for (a) PVC/DOS/$KBPh_4$/dibenzo-18-C-6, and (b) PVC/DOS/$NaBPh_4$/dibenzo-18-C-6 membranes, measured with 0.1 mol dm^{-3} solution of the relevant cation as reference.

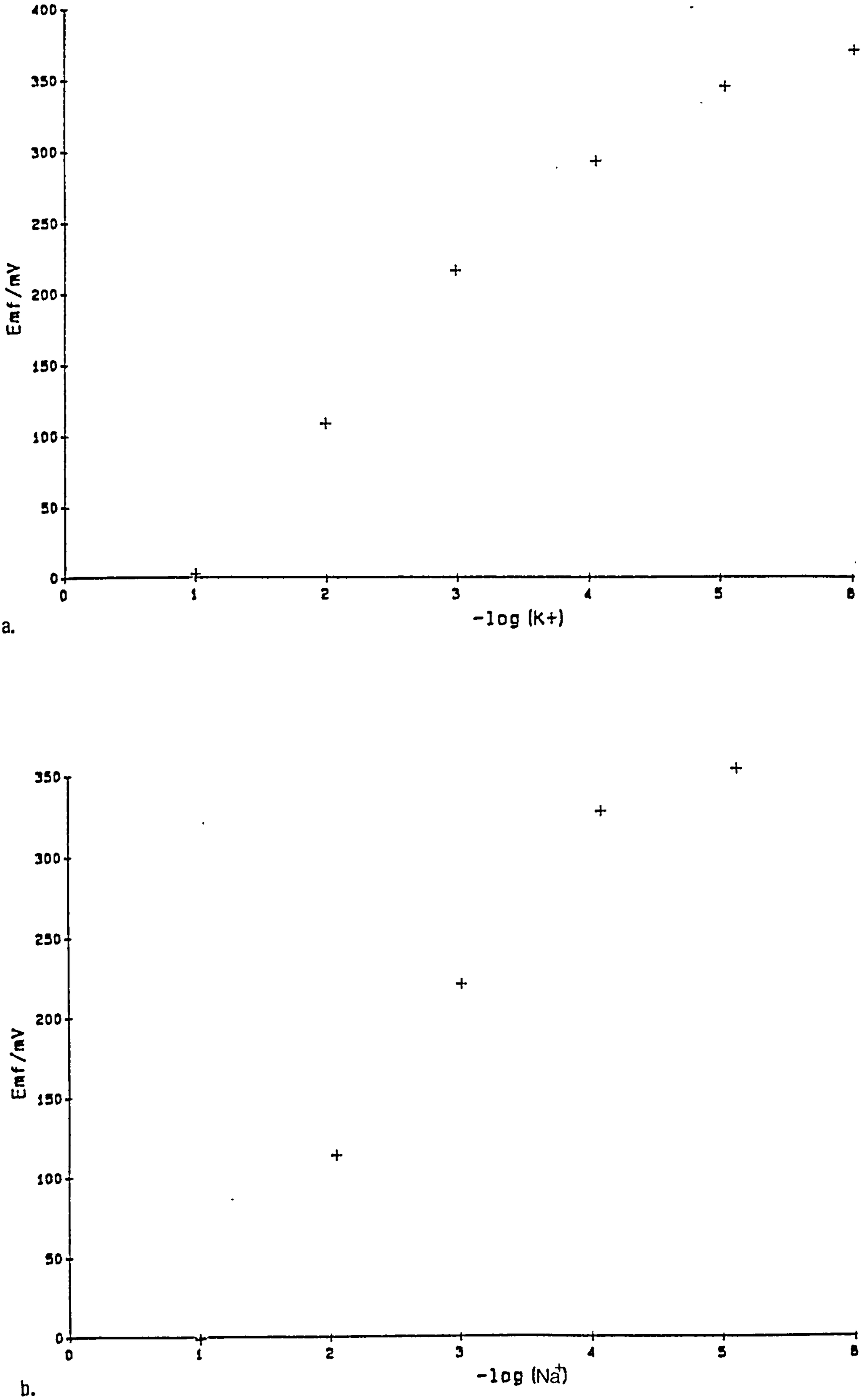


Fig 7.2: Selectivity (K^+/Na^+ mixed-ion response) plots for (a) PVC/DOS/$KBPh_4$/dibenzo-18-C-6, and (b) PVC/DOS/$NaBPh_4$/dibenzo-18-C-6 membranes, measured with a 0.1 mol dm^{-3} KCl solution as reference.

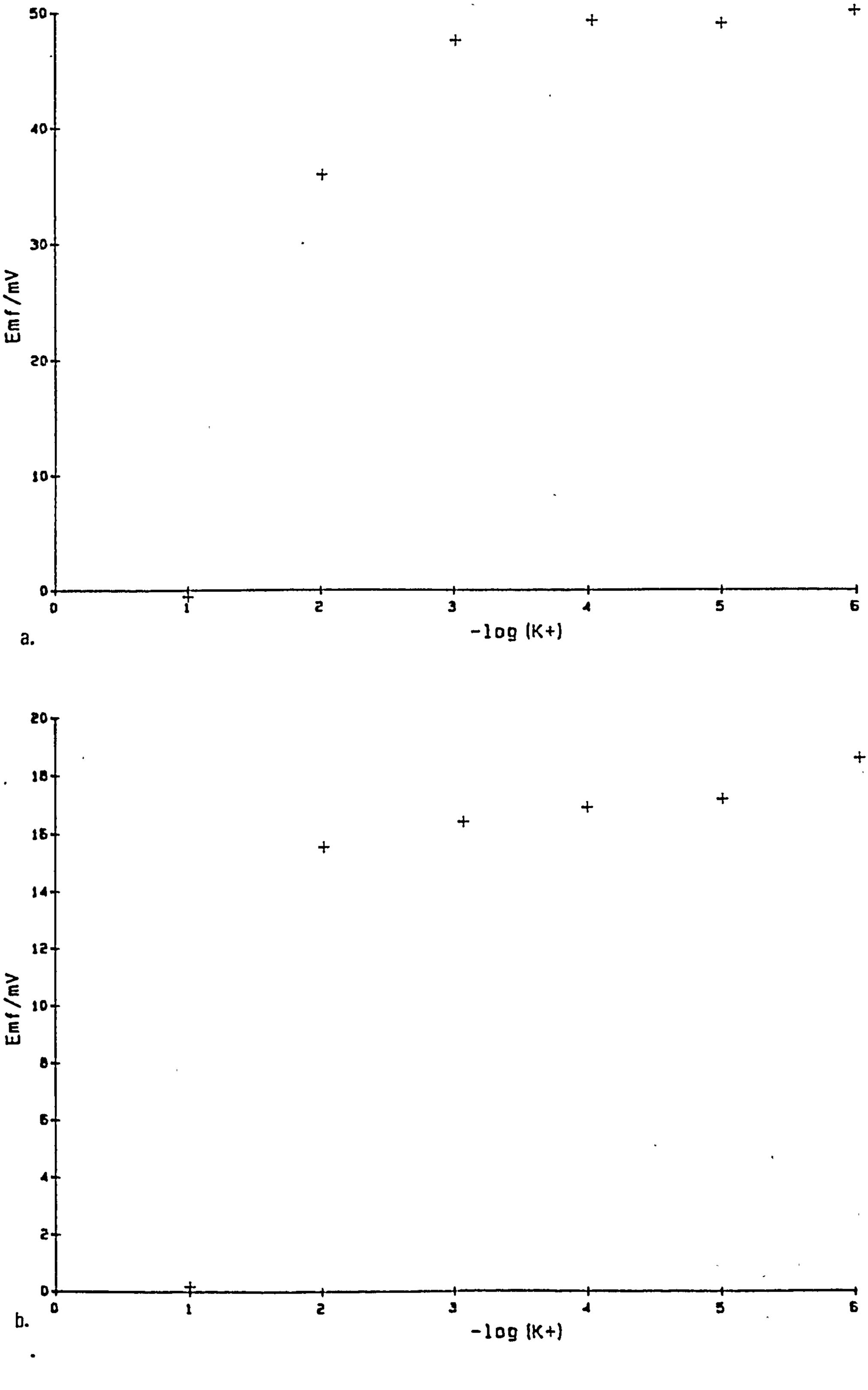


Fig 7.3a shows the initial spectrum obtained for the membrane with added $KBPh_4$, approximately ten minutes after first contact with the aqueous 0.1 mol dm^{-3} KCl solutions. The spectrum shows the bulk membrane semicircle, but little evidence of a second feature at lower frequency. Figs 7.3b and 7.3c show the spectra recorded one and two hours after the initial run from which it is clear that the bulk membrane resistance is increasing with time, although there is still no clearly-resolved feature at lower frequency. Fig 7.3d shows the final, steady-state spectrum recorded for the dibenzo-18-C-6/$KBPh_4$ membrane. In this spectrum, run down to low frequency (10mHz), there is clear evidence of a second feature, although this is not completely resolved into a semicircle. It is difficult to achieve complete resolution of such features at very low frequencies due to the limitations of using a practical integration time, and signal voltage as discussed in previously. The spectrum is sufficiently clear however to show that the resisitive component of the second feature is in excess of 2.0×10^5 Ohms. The detailed time-dependence of the impedance is given in Table 7.1.

The corresponding series of spectra for the $NaBPh_4$/dibenzo-18-C-6 membrane in contact with 0.1 mol dm^{-3} NaCl solutions are shown in Figs 7.4a - 7.4d, and Table 7.2 shows the variation of the membrane equivalent circuit parameters with time, measured hourly for the first twenty-four hours, and finally after 72 hours. These spectra show close similarity to those obtained for the membranes containing the potassium salt and dibenzo crown, with a second feature becoming visible when the spectrum was measured down to very low frequency, with a resistive component of a similar magnitude to that found for the membrane

Fig 7.3: (a) Initial impedance spectrum and (b) spectrum measured after 1 hour for a PVC/DOS/$KBPh_4$/dibenzo-18-C-6 membrane, measured with 0.1 mol dm^{-3} KCl contacting solutions.

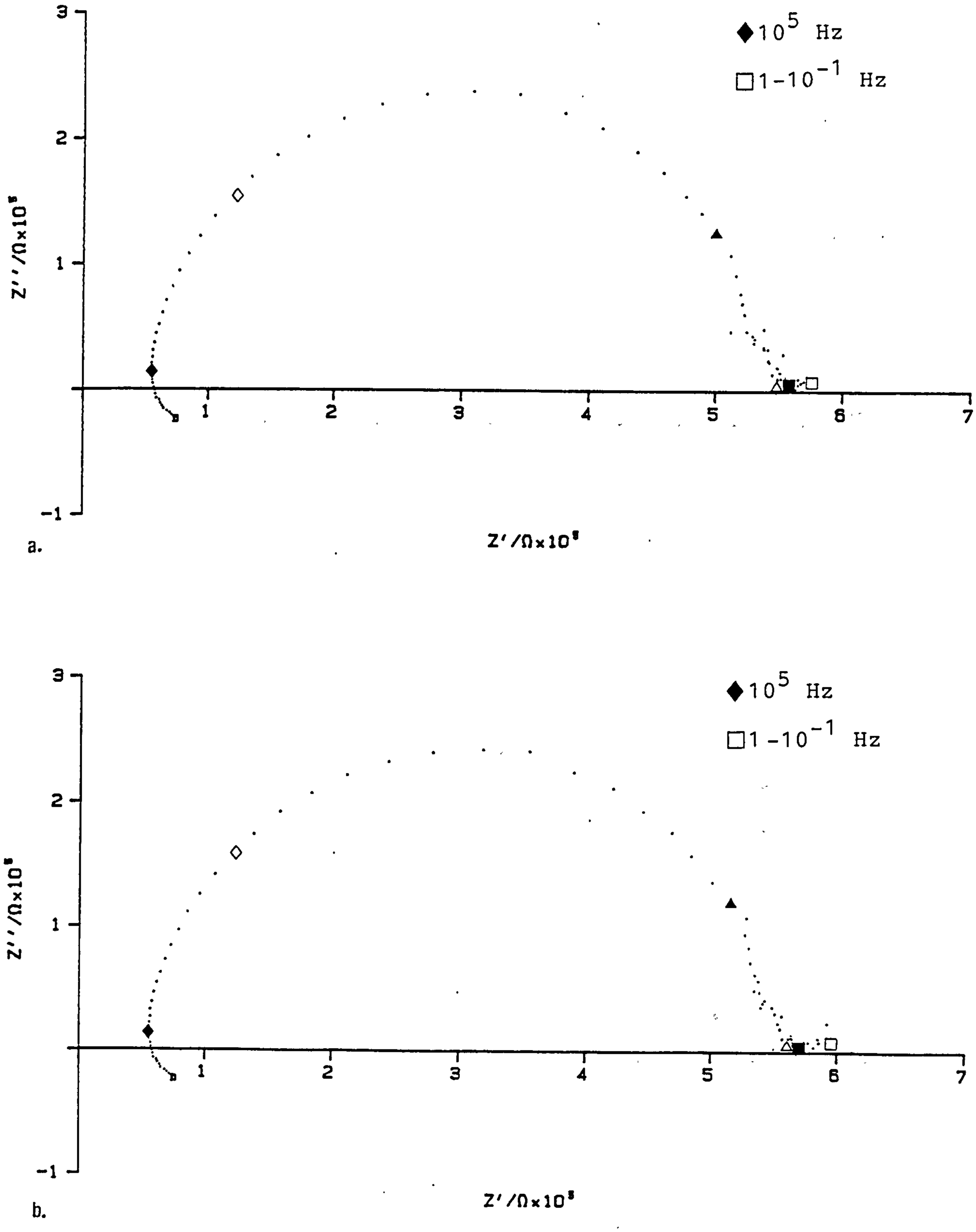
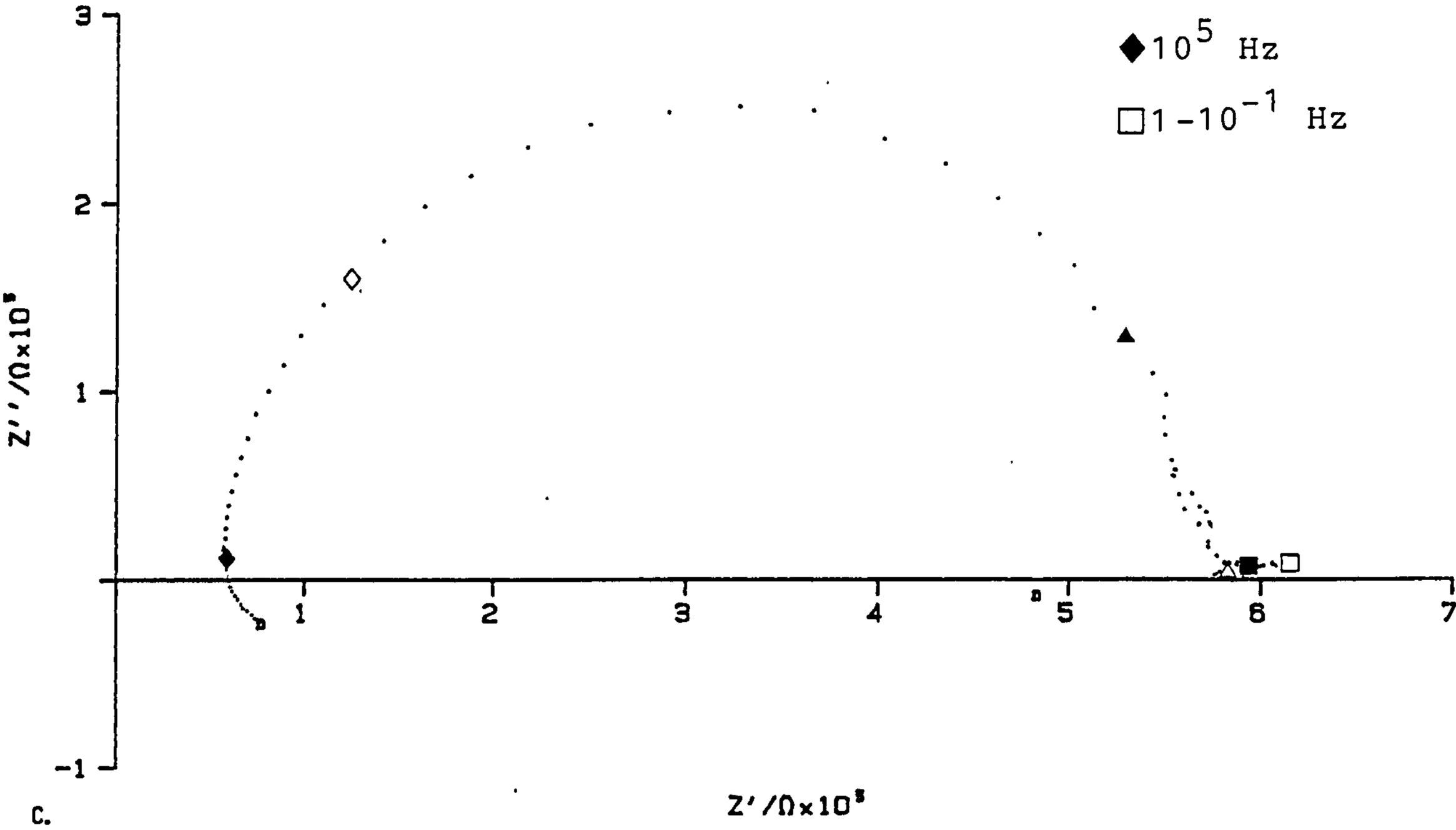
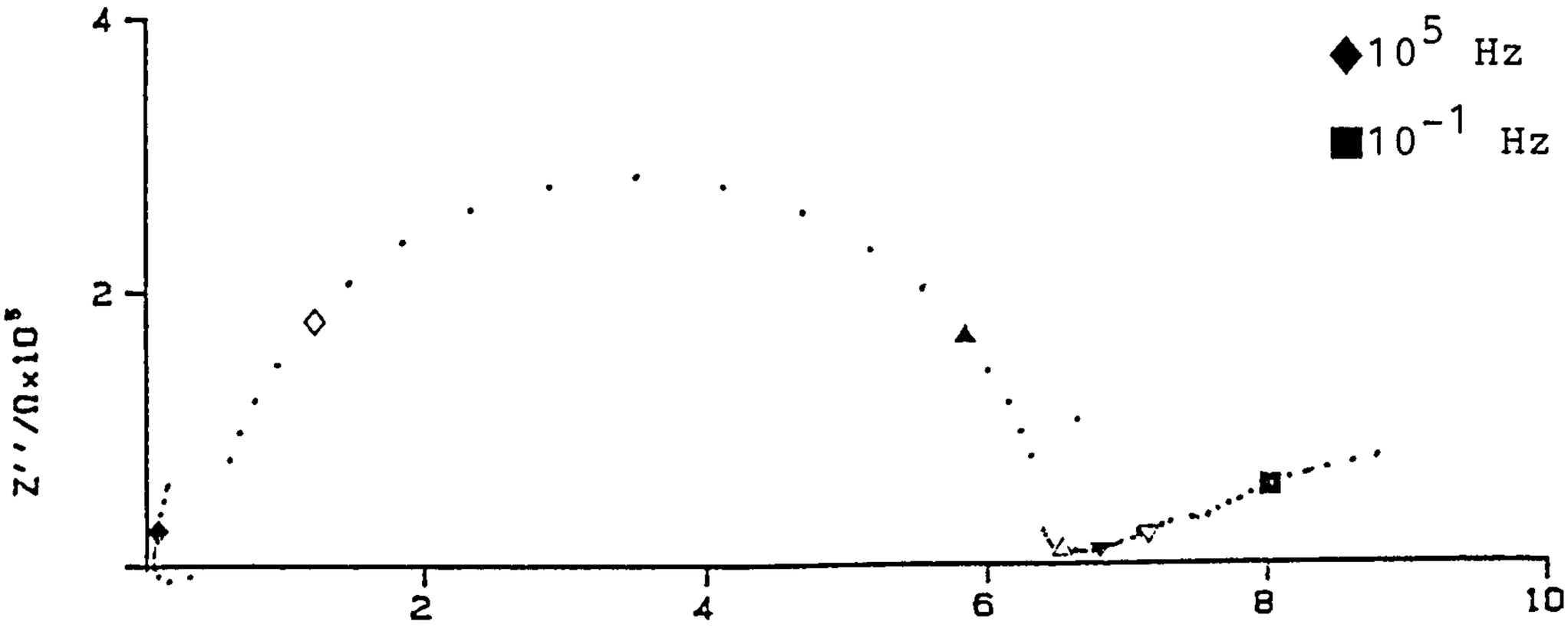


Fig 7.3: Impedance spectra for a PVC/DOS/$KBPh_4$/dibenzo-18-C-6 membrane, measured after (c) 2 hours and (d) 72 hours with 0.1 mol dm^{-3} KCl contacting solutions.



c.



d.

Z'/Ω×10⁵

Table 7.1: Time Dependence of Impedance for Membrane Containing Dibenzo-18-C-6 and $KBPh_4$ with 0.1 mol dm^{-3} KCl Contacting Solutions

t/hours	$R_b/10^5\ \Omega$	$\omega_{1\,max}^*$ /Hz
1	5.19	2935
2	5.37	"
3	5.50	"
4	5.68	"
5	5.89	"
6	6.11	"
7	6.12	"
8	6.28	"
9	6.46	"
10	6.45	"
11	6.45	"
12	6.46	"
13	6.47	"
14	6.47	"
15	6.47	"
16	6.48	"
17	6.48	"
18	6.47	"
19	6.49	"
20	6.48	"
21	6.50	"
22	6.50	"
23	6.51	"
24	6.53	"
72	6.51	"

Fig 7.4: (a) Initial impedance spectrum and (b) spectrum measured after 1 hour for a PVC/DOS/$NaBPh_4$/dibenzo-18-C-6 membrane, measured with 0.1 mol dm^{-3} NaCl contacting solutions.

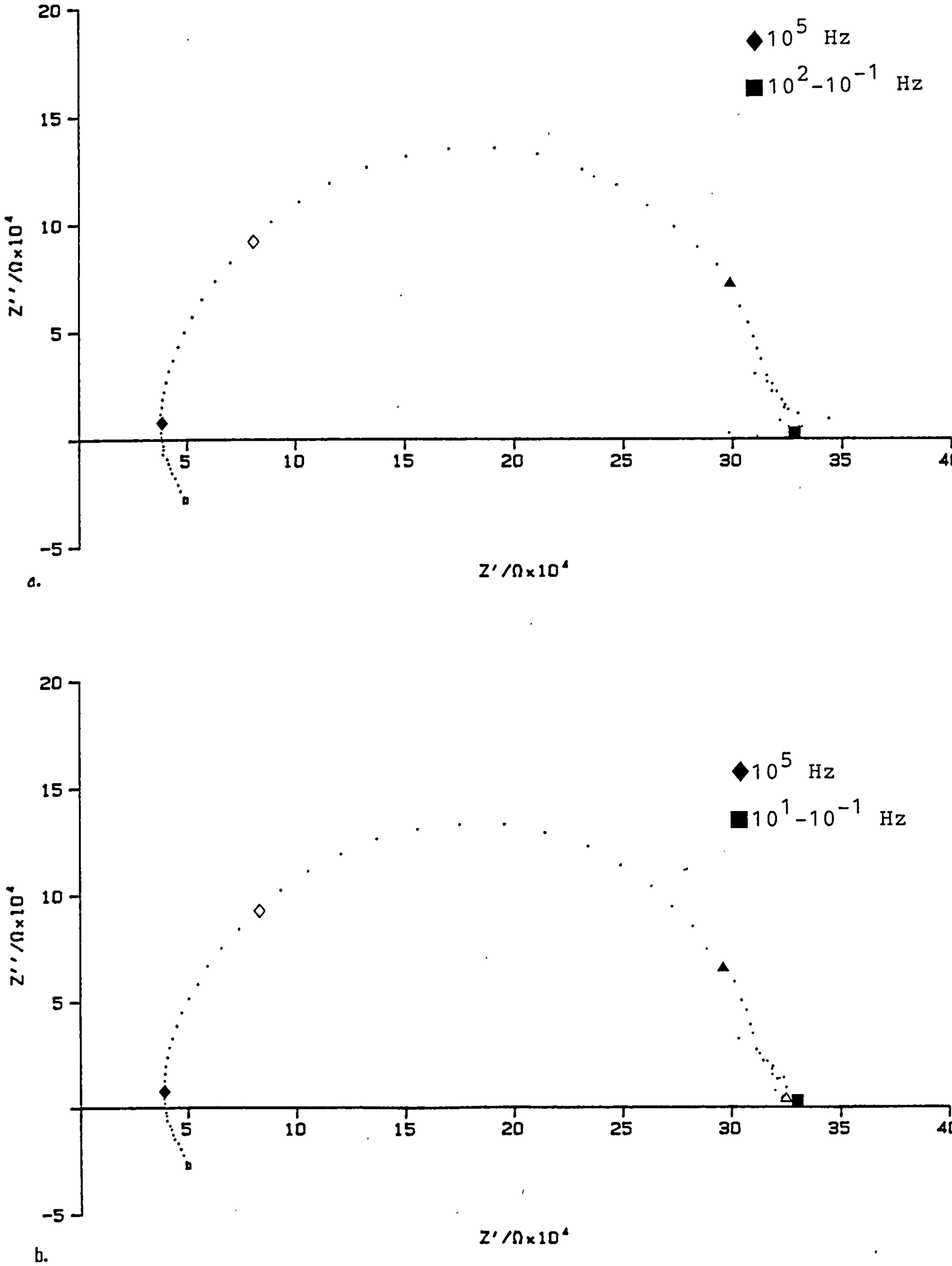


Fig 7.4: Impedance spectra for a PVC/DOS/$KBPh_4$/dibenzo-18-C-6 membrane, measured after (c) 2 hours and (d) 72 hours with 0.1 mol dm^{-3} KCl contacting solutions.

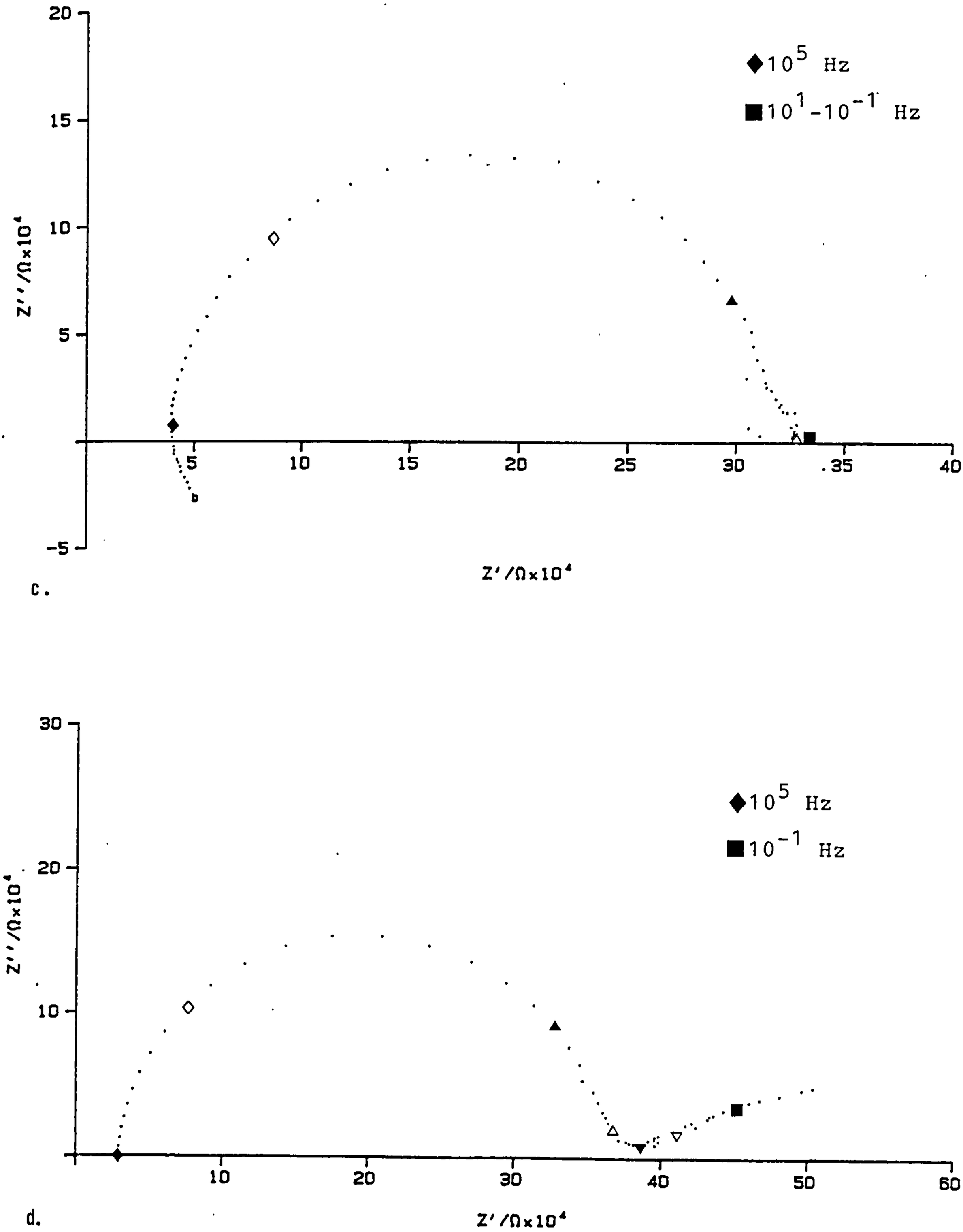


Table 7.2: Time Dependence of Impedance for Membrane Containing Dibenzo-18-C-6 and $NaBPh_4$ with 0.1 mol dm^{-3} NaCl Contacting Solutions

t/hours	$R_b/10^5\ \Omega$	$\omega_1^*{}_{max}$/Hz
1	3.24	1852
2	3.25	"
3	3.39	"
4	3.26	"
5	3.32	"
6	3.33	"
7	3.37	"
8	3.42	"
9	3.44	"
10	3.47	"
11	3.51	"
12	3.56	"
13	3.65	"
14	3.68	"
15	3.66	"
16	3.71	"
17	3.72	"
18	3.76	"
19	3.77	"
20	3.75	"
21	3.77	"
22	3.76	"
23	3.79	"
24	3.81	"
72	3.79	"

containing the potassium salt and dibenzo crown.

7.3.3 Discussion

The single-ion response of the membranes is quite poor in comparison to the membranes containing valinomycin and the corresponding tetraphenylborate salts. It seems that in the present case, the transport number for the anion as determined from the potential difference measurements (measured with a tenfold difference in concentration across the membrane) is much higher than that found for the valinomycin membranes, and indeed for the membranes containing the salt, but no ionophore. It can only be assumed that the crown is in some way reducing, or interfering with the transport of the cation within the membrane, resulting in the increased anion transport number.

The final steady-state impedance spectra measured using a four-electrode configuration, down to low frequency (10mHz) for both membranes show clearly a low frequency feature due to the interfacial charge-transfer processes, which is more well-defined than in the spectra for the corresponding valinomycin-containing membranes. The value of R_{ct} which can be read from the plots for the membranes containing the crown is of the order of 2.0×10^5 Ohms. For a membrane containing the potassium salt, in the absence of any ionophore, the addition of the BPh_4^- appreciably reduces the charge transfer resistance of the membrane, to well below this level, and with the inclusion of valinomycin in the membrane formulation, R_{ct} remains comparitively small. In the present case, however, the addition of the dibenzo crown results in an increase of R_{ct} relative to that found for membranes containing no ligand, specifically for

the membrane containing the potassium salt, although this is also true to a lesser extent for the membrane containing $NaBPh_4$. The reduction of the rate of interfacial charge transfer suggests that some process is occurring which inhibits the exchange of ions across the membrane/solution interface and this will evidently have an effect on the operation of the membrane in an ion-selective electrode. A possible explanation for this behaviour is that the crown binds the cation strongly and that the associated decomplexation rates are slow, in which case, the membrane will be unable to respond to changes in the solution concentration of the primary ion, as the concentration and electrochemical potential of the cation in the surface regions of the membrane will show little variation. From the potential measurements, this would also appear to be the case, as evidenced by the relatively large anion transport number. The effect of this strong and relatively irreversible complexation on the response of the electrode would also be to reduce the effective range over which the membrane. Although it was suggested for membranes containing only valinomycin, that the interfacial processes do not appear directly involved in the mechanism of cation selectivity, in this case, it is possible that the poor interfacial kinetics indicate that the ionophore does not allow a sufficiently fast decomplexation for a good electrode response.

In view of the relatively small selectivity coefficient exhibited by the crown, the similarity of the spectra for the two types of membrane (with added $KBPh_4$ or $NaBPh_4$) is not surprising. It is interesting however that the values of the bulk resistance show dissimilarities. Both types of membrane show higher bulk resistances than the corresponding ones with no

ionophore, which, as for the valinomycin, appears to indicate that the ionophore reduces the mobility of both primary cation and interferent in the membrane. For the dibenzo crown however, unlike the valinomycin, the membrane seems to have a more marked effect on the K^+ than on the Na^+, which supports the suggestion that the ionophore binds more effectively and irreversibly with K^+ than Na^+.

7.4 2,2,2-Cryptand

The group of ionophores known as the cryptands differ from the crowns in that they have a structure which is basically three-dimensional, with a bicyclic configuration, whereas the crowns possess a two-dimensional ring structure (at least in the uncomplexed form). The structure of the cryptand molecules and their complexes with alkali metal cations is discussed in detail in Chapter 3. Due to this cage-like structure, these molecules should provide better encapsulation of the complexed ion than the planar crowns, and give an environment which is more similar to that found with valinomycin than is possible with the smaller members of the series of crowns. It has been noted (7.4), that the three-dimensional structure of the whole series of cryptands is illustrated by the comparatively large stability constants of their complexes with a number of cations. Typically these stability constants are as much as 10^6 times larger than those of the crowns (7.5), and are even larger than those of many of the naturally occurring ionophores (e.g. valinomycin). In extraction studies, the ready-formed cavity of the cryptand requires comparatively little conformational rearrangement (7.6), and permits the optimum degree of replacement of the

inner co-ordination sphere of solvent molecules around the cation, via a multi-step mechanism as described by Lockhart (7.6a), although the solvent strongly affects the magnitude of the stability constant (7.7).

Membranes were fabricated containing 2,2,2-cryptand as a typical member of the group, which is reported from extraction studies to exhibit a high degree of selectivity for potassium. The membranes were cast as previously, containing either $KBPh_4$ or $NaBPh_4$, in order to overcome any variation in quantity of adventitious negative sites, and hopefully to improve the potential response of the fabricated electrode. The selectivity with respect to sodium over potassium and the impedance behaviour of the membranes was investigated as previously, and the time dependence of the impedance was followed over a period of three days.

7.4.1 Potential Response

Figure 7.5a shows the single ion response as determined for a membrane containing 2,2,2-cryptand and $KBPh_4$. The response is clearly very poor, with a slope of 85 mV/decade over the concentration range 10^{-1} - 10^{-4}. Figure 7.5b shows the mixed ion response for the same membrane, determined with a 0.1 mol dm^{-3} NaCl constant interferent concentration from which it can be seen that the membrane exhibits no appreciable selectivity for potassium over sodium at all.

The single-ion and mixed-ion responses are shown for the corresponding membrane containing $NaBPh_4$ in figures 7.6a and 7.6b. The single-ion response is again very poor, and similar to the results for the potassium membrane, the membrane shows

Fig 7.5: (a) Calibration (K^+ single-ion response) and (b) selectivity (K^+/Na^+ mixed-ion response) plots for a PVC/DOS/2,2,2-cryptand/$KBPh_4$ membrane measured with a 0.1 mol dm^{-3} KCl reference solution.

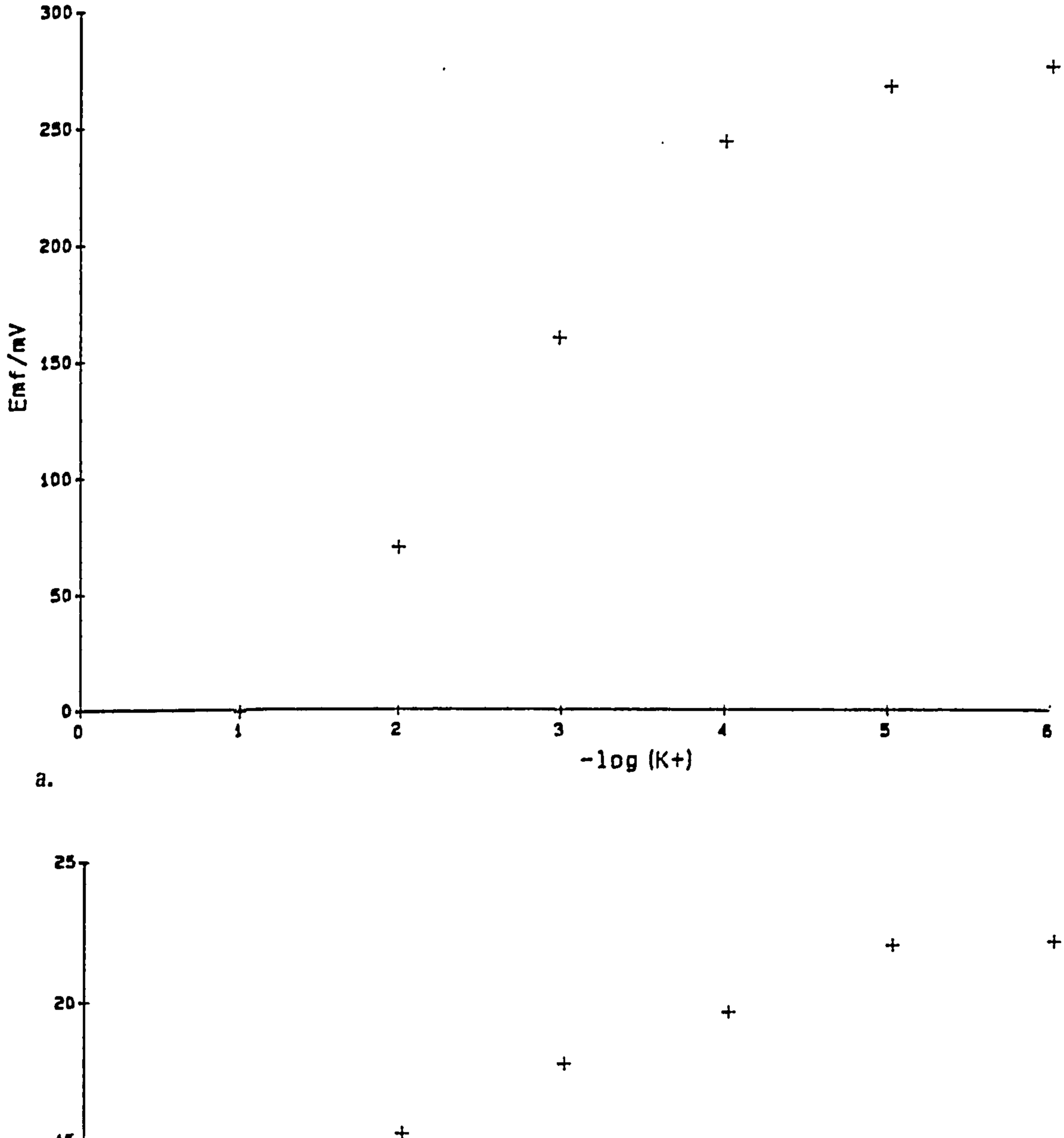
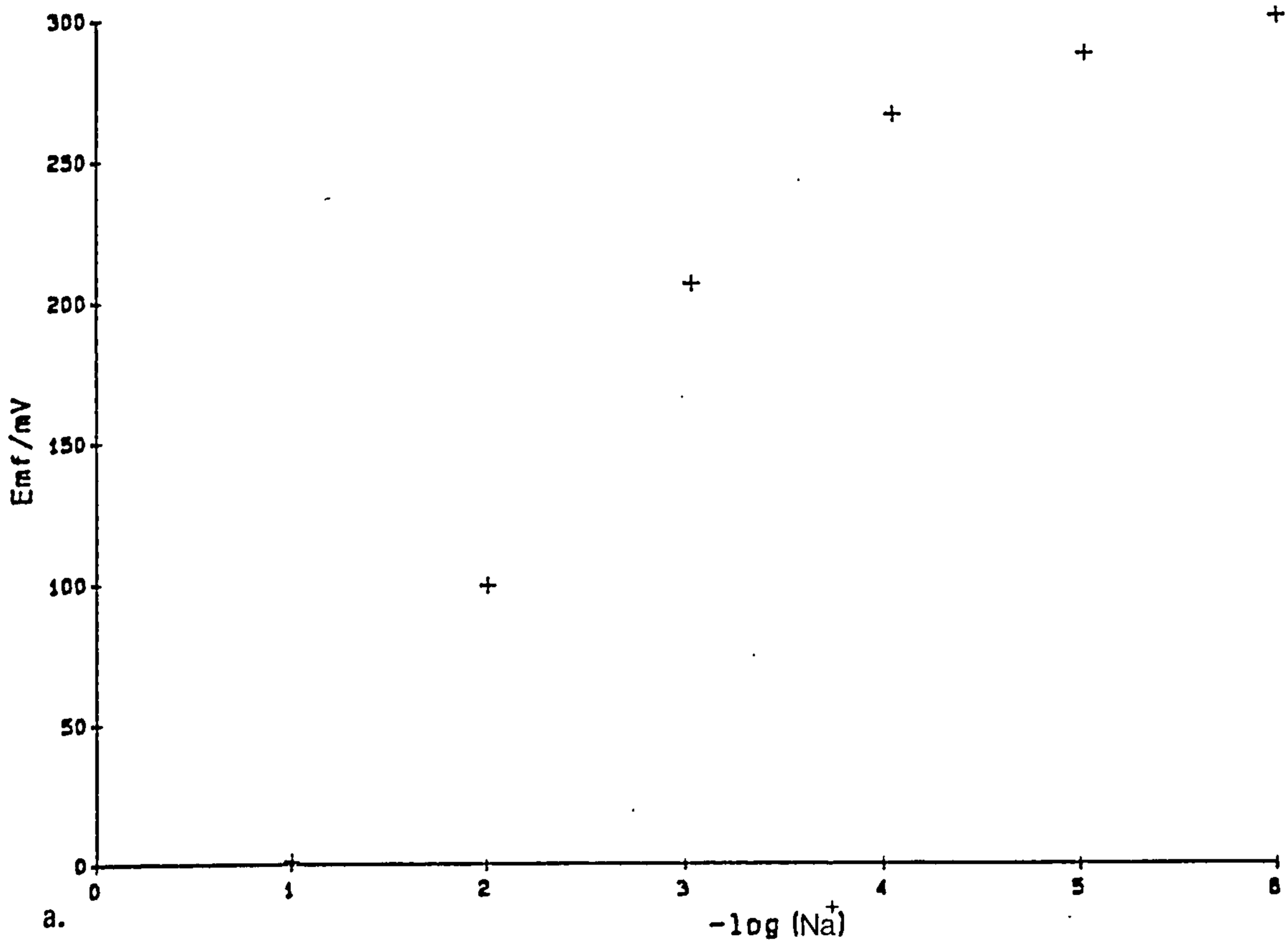


Fig 7.6: (a) Calibration (Na^+ single-ion response) and (b) selectivity (K^+/Na^+ mixed-ion response) plots for a PVC/DOS/2,2,2-cryptand/$NaBPh_4$ membrane with 0.1 mol dm^{-3} NaCl and KCl reference solutions respectively.



almost no selectivity for potassium over sodium, after the necessary conditioning period.

7.4.2 Impedance Measurements

The impedance behaviour of the two types of membrane was studied as described previously. Fig 7.7a shows the initial impedance spectrum for the membrane containing 2,2,2-cryptand and $KBPh_4$ measured immediately after first contact on both sides with 0.1 mol dm^{-3} KCl solutions. The spectrum shows the familiar bulk semicircle, with R_b = 2.7 $x10^5$ and C_g = 1.0 $x10^{-10}$ F. The spectrum also shows the presence of low frequency features, which are not fully resolved at the mimimum frequency used for time-dependence runs.

Fig 7.7b shows the spectrum taken one hour after that shown in Fig 7.7a, and Fig 7.7c shows the spectrum taken after two hours. The final steady-state spectrum taken after three days is shown in Fig 7.7d. It is evident that the bulk resistance undergoes an increase with time, a fact which is consistent with the results obtained for the other PVC membranes studied. Table 7.3 shows the variation of the equivalent circuit parameters with time over the first twenty-four hours, and the final, steady state value measured after three days.

Figure 7.8a shows the spectrum recorded approximately ten minutes after first solution contact for the membrane containing 2,2,2-cryptand and $NaBPh_4$. The spectrum shows the bulk membrane feature as found previously, with approximate parameters R_b = 3.0 $x10^5$ Ohm and a capacitance of 2.1 $x10^{-10}$ F. Figs 7.8b and 7.8c show the spectra for the same membrane measured one and two hours respectively after that shown in

Fig 7.7: (a) Initial impedance spectrum and (b) spectrum measured after 1 hour for a PVC/DOS/$KBPh_4$/2,2,2-cryptand membrane, measured with 0.1 mol dm^{-3} KCl contacting solutions.

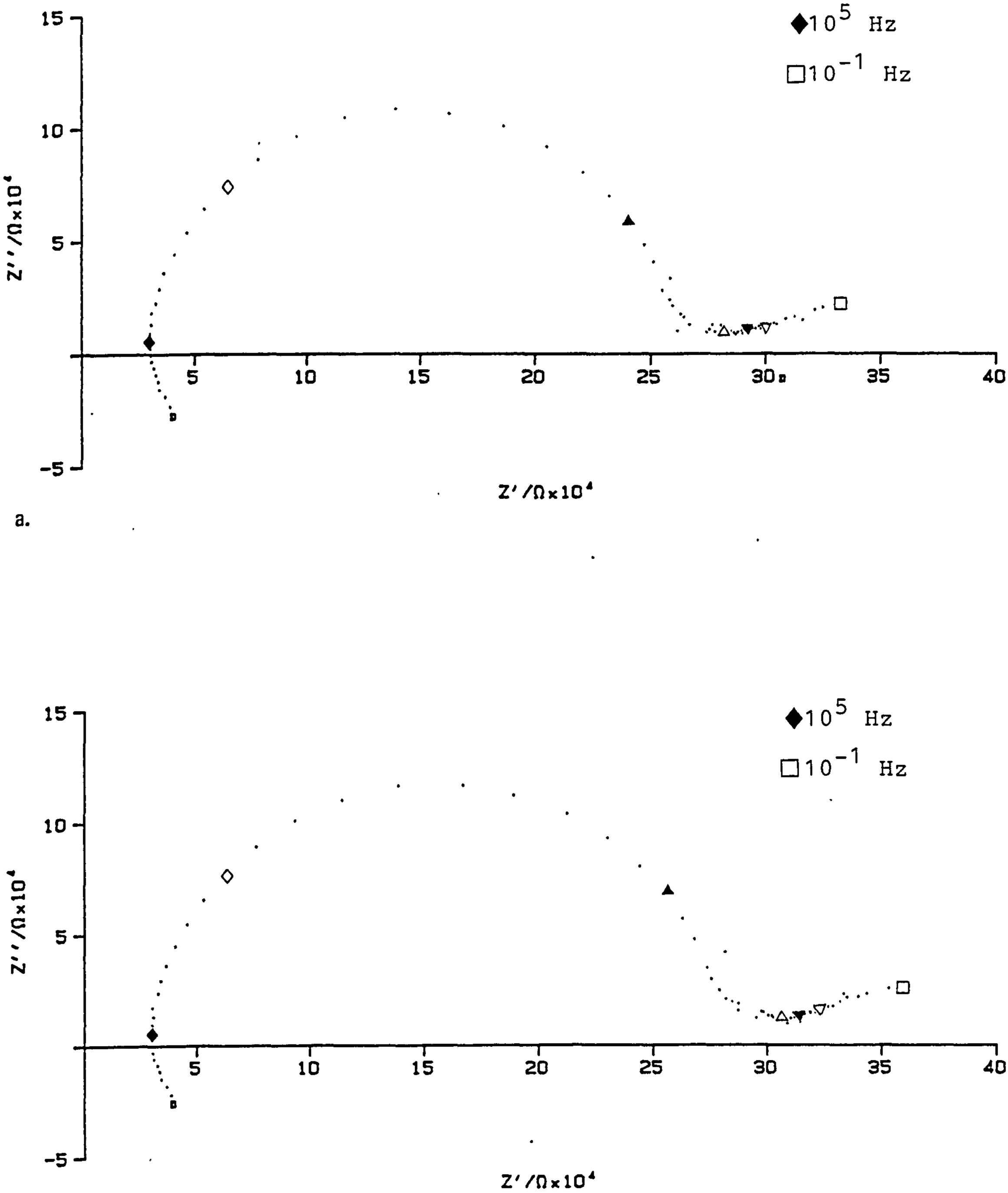
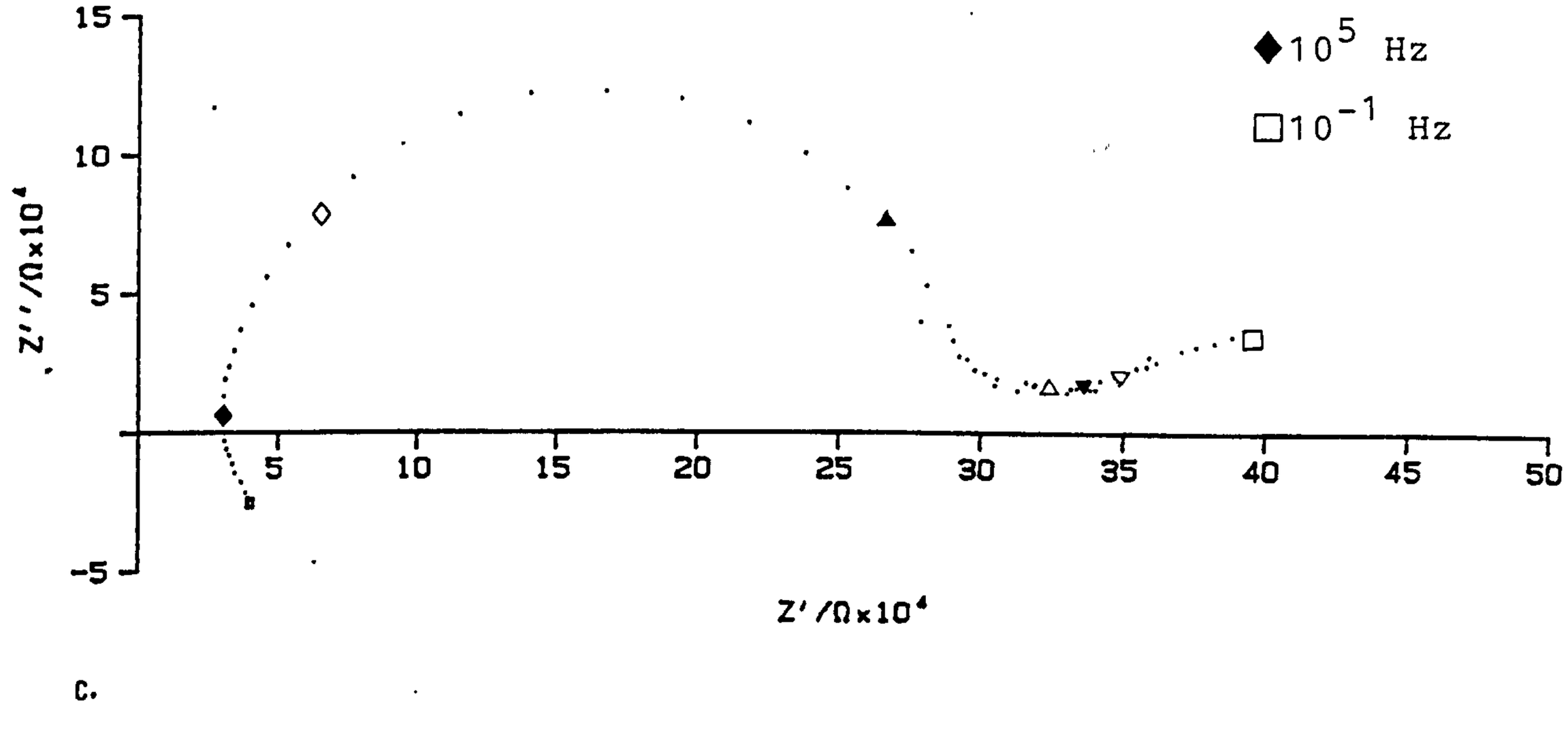
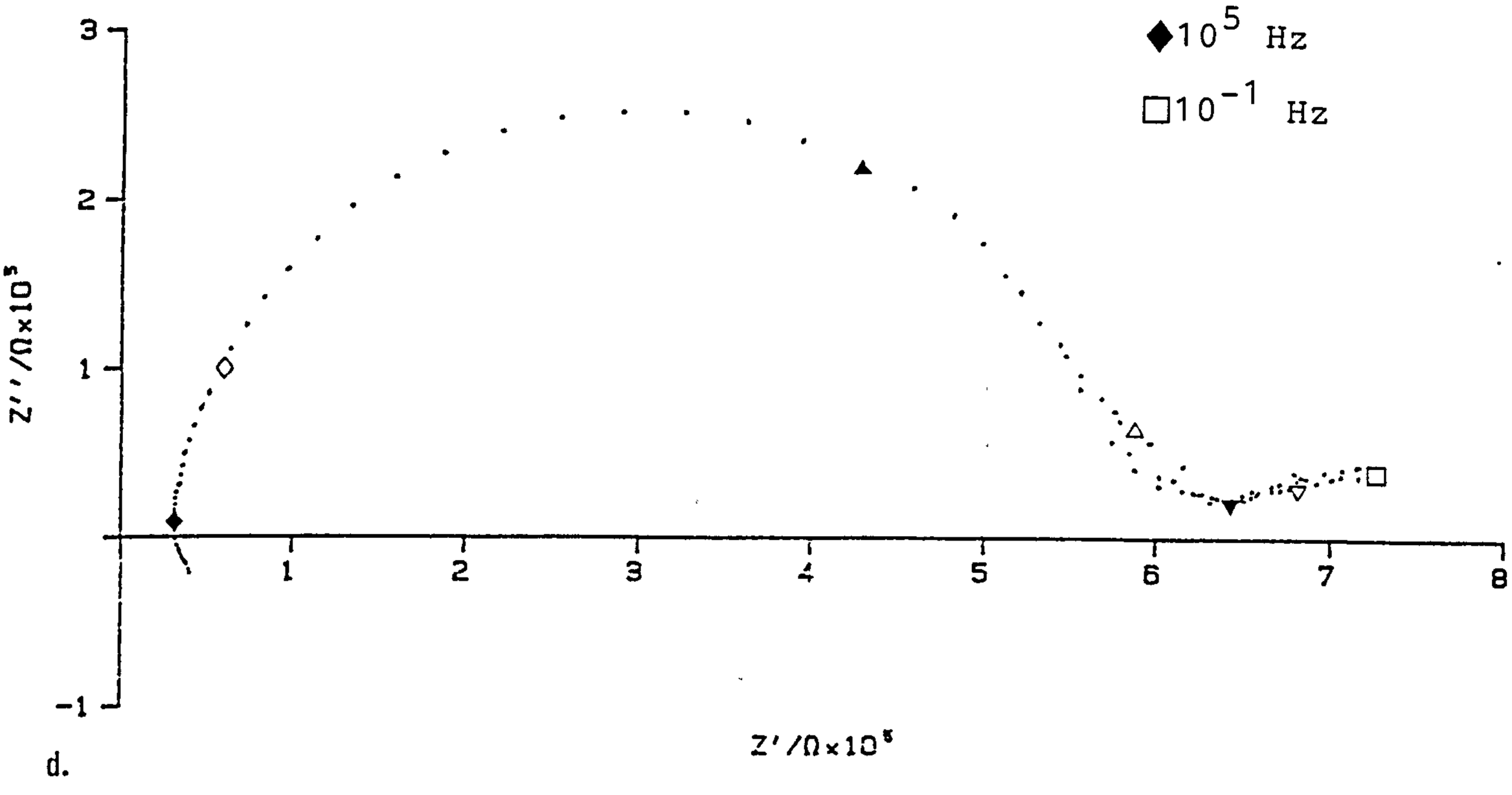


Fig 7.7: Impedance spectra for a PVC/DOS/$KBPh_4$/2,2,2-cryptand membrane, measured after (c) 2 hours and (d) 72 hours with 0.1 mol dm^{-3} KCl contacting solutions.



c.



d.

Table 7.3: Time Dependence of Impedance for Membrane Containing 2,2,2-Cryptand and $KBPh_4$ with 0.1 mol dm^{-3} KCl Contacting Solutions

t/hours	$R_b/10^5\ \Omega$	$\omega_{1\,max}^*$/Hz
1	2.67	10^3-10^4
2	2.87	"
3	3.04	"
4	3.19	"
5	3.44	"
6	3.68	"
7	3.77	"
8	4.04	"
9	4.18	"
10	4.40	"
11	4.84	"
12	4.93	"
13	5.11	"
14	5.20	"
15	5.27	"
16	5.48	"
17	5.43	"
18	5.43	"
19	5.62	"
20	5.83	"
21	5.84	"
22	5.90	"
23	5.92	"
24	5.92	"
72	5.91	"

Fig 7.8: (a) Initial impedance spectrum and (b) spectrum measured after 1 hour for a PVC/DOS/$NaBPh_4$/2,2,2-cryptand membrane, measured with 0.1 mol dm^{-3} NaCl contacting solutions.

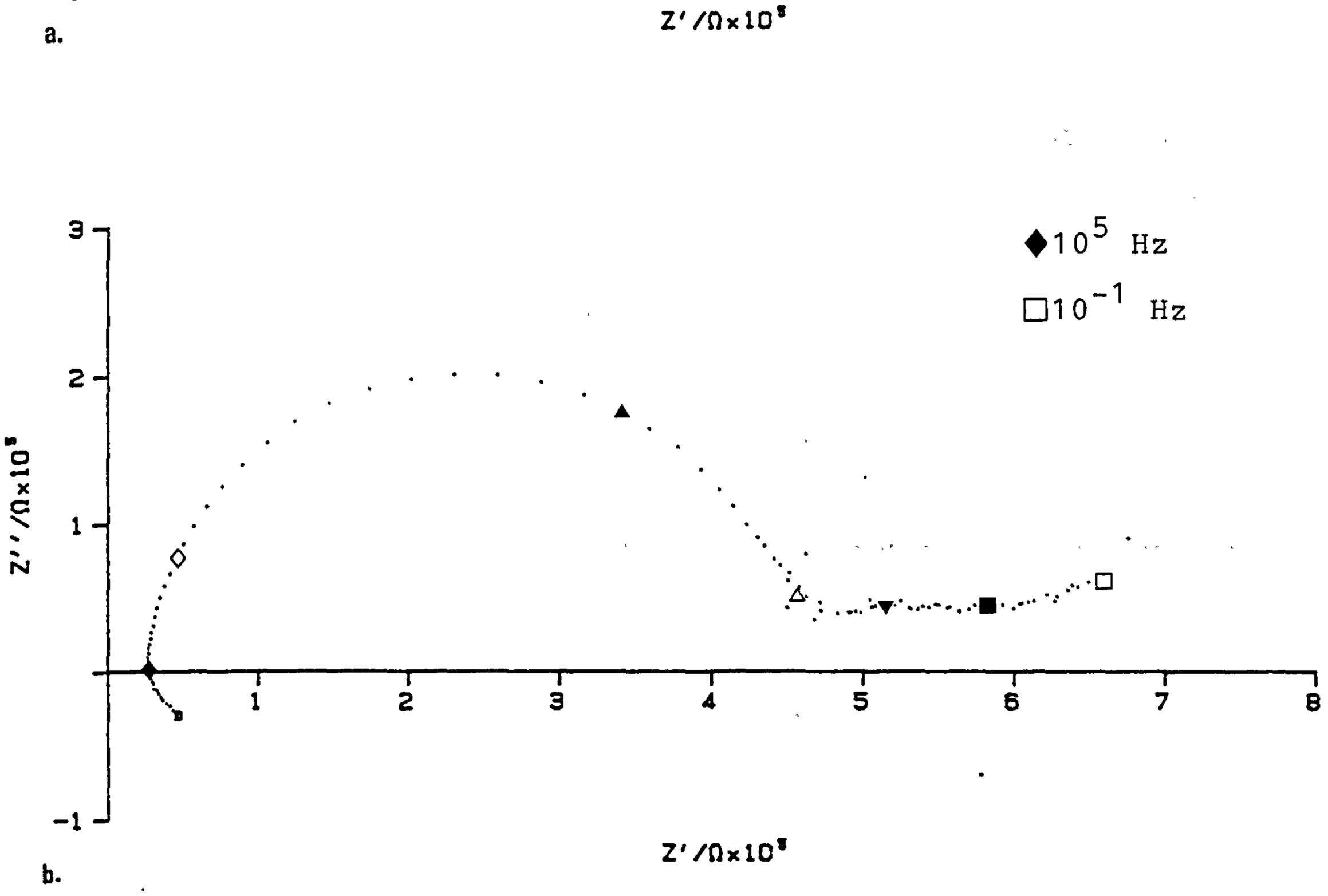


Fig 7.8: Impedance spectra for a PVC/DOS/$NaBPh_4$/2,2,2-cryptand membrane, measured after (c) 2 hours and (d) 72 hours with 0.1 mol dm^{-3} NaCl contacting solutions.

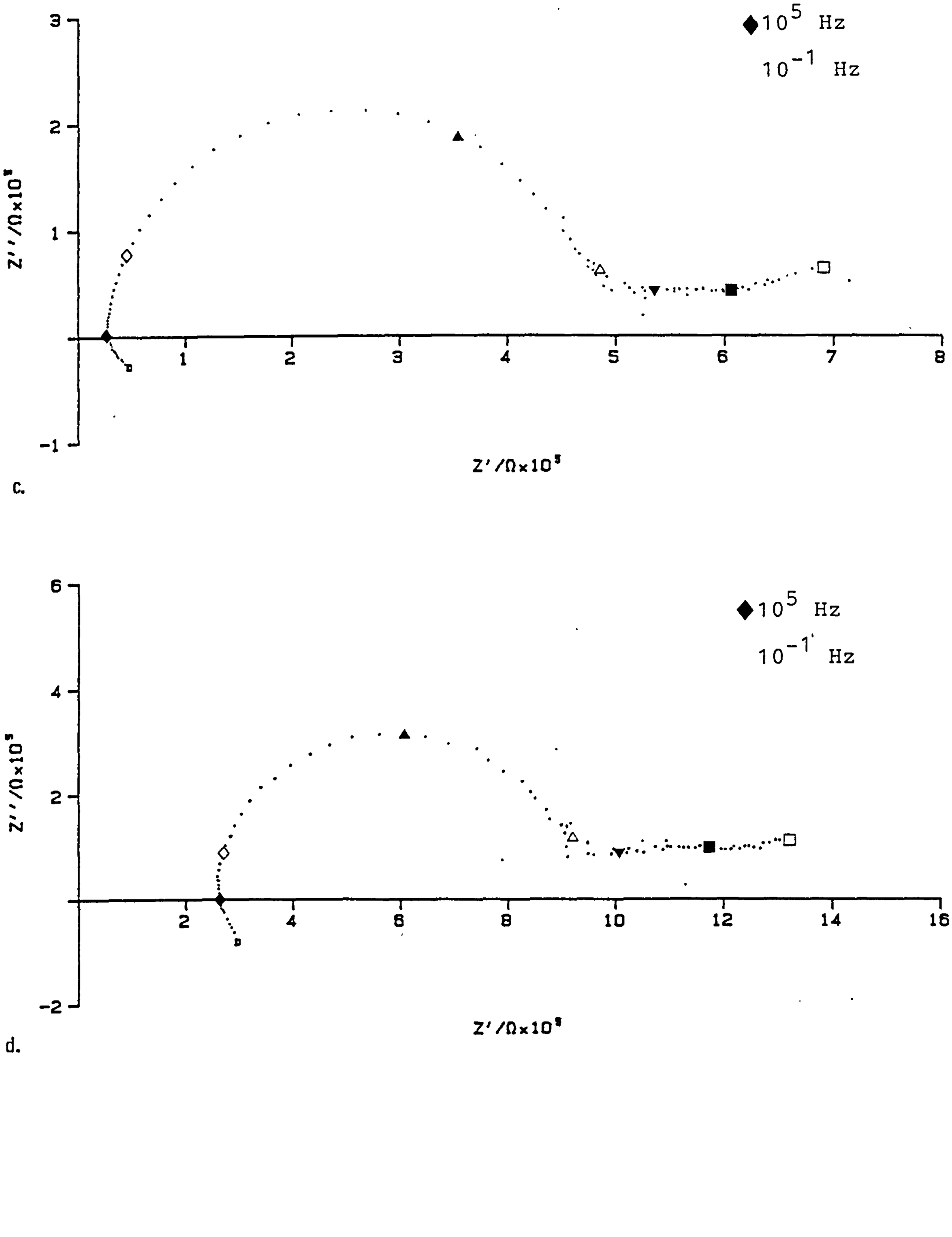


Table 7.4: Time Dependence of the Impedance of a Membrane Containing 2,2,2-Cryptand and $NaBPh_4$ with 0.1 mol dm^{-3} NaCl Contacting Solutions

t/hours	$R_b/10^5\ \Omega$	$\omega_{1\,max}^*$/Hz
1	4.32	2519
2	4.40	1589
3	4.63	1852
4	5.00	1589
5	5.21	"
6	5.83	"
7	6.07	"
8	6.56	1362
9	6.63	"
10	6.68	"
11	6.71	1169
12	7.30	1362
13	7.45	1169
14	7.54	"
15	7.68	"
16	7.78	"
17	7.89	"
18	8.05	"
19	8.30	"
20	8.86	"
21	8.96	"
22	9.26	"
23	9.16	"
24	9.26	"
72	9.21	"

Fig7.8a, and Fig 7.8d shows the final steady-state spectrum recorded after three days. The time dependence of the membrane impedance is given in Table 7.4.

7.4.3 Discussion

From the above results, it is apparent that there are several differences between the membranes containing 2,2,2-cryptand and the corresponding membranes containing valinomycin. The most obvious difference is the fact that, even with the presence of the added salt, the membrane in contact with KCl solutions still shows a relatively high charge transfer resistance, as with the dibenzo crown. For the corresponding membrane containing valinomycin, the addition of the salt results in a much lower value for R_{ct}, similar to that found in the absence of the ionophore. From these facts, it must be concluded that the cryptand is affecting the exchange of ions across the interface in a way quite dissimilar from the manner in which it is affected by valinomycin, but apparently similar to the effect of the crown. It has been suggested elsewhere (7.8) that the controlling factor in the stability of alkali metal cryptates is the dissociation rate of the complex, and that very strong binding is evidenced by slow decomplexation rates. As for the dibenzo crown, whilst resulting in an apparently high degree of selectivity as determined by extraction studies, the slow decomplexation would permit ion-exchange processes to occur only slowly. The inhibition of such exchange processes would again result in a correspondingly poor response for an ion-selective electrode fabricated using these ionophores. From the impedance spectra,

and potentiometric data presented above, it appears that this is the case, and that whilst the K^+ complex of the 2,2,2-cryptand has a much larger stability constant than the Na^+ complex (7.7a), it has proven to be a less efficient carrier in membrane systems than valinomycin. In work on simple liquid model membranes (7.6a), it has been found that approximately four times as much sodium as potassium is actually transported through the membrane, reflecting the slower dissociation process (7.7b). As found with the membranes containing dibenzo-18-C-6, the effect of this is manifested in the low exchange current.

The potential difference data recorded also show a similarity with those for the crown, in that the anion transport number is again apparently very high compared to that for membranes containing valinomycin, and the same interpretation can be applied here. That is that the ligand binds the cation sufficiently strongly to inhibit its participation in ion exchange under normal circumstances and results in a very poor response.

There are also other differences between the impedance spectra obtained for these membranes and those discussed in earlier chapters. For the membrane containing sodium tetraphenylborate, a second feature at intermediate frequencies is present, which can be interpreted as representing a second bulk membrane phase. The reason why a membrane containing the cryptand should produce a second distinct phase with a time constant sufficiently removed from that of the main phase, when previous membranes did not, is not clear. Nor is it obvious why the membrane does not show this intermediate frequency feature when it contains the potassium salt, in contact with potassium solutions. It is possible though, that the cryptand promotes

the precipitation of the sodium salt within the membrane, although the bulk resistance is again similar to that found in the absence of the ionophore, but with a similar level of the added salt.

A further difference is that for the membranes containing the cryptand, the relative values for the bulk resistance are similar to those found with membranes containing valinomycin, in that the membrane containing the K^+ salt shows a lower bulk resistance than the one containing $NaBPh_4$, in contrast to the results found for the crown, where the opposite was true. To interpret this data as previously, implies that despite the more effective binding between K^+ and the cryptand, the process of transport of charged species within the membrane bulk, is more facile with the K^+ salt. It must be concluded from this that a carrier mechanism operates whereby the cation/ionophore complex is relatively mobile within the membrane, although this is in contrast to the findings from liquid membrane studies (7.8) where sodium transport was found to be more effective as a result of the slow K^+-cryptand decomplexation. These results give further evidence to suggest that the liquid and PVC membranes cannot necessarily be treated as merely different forms of the same system.

From the results for the cryptand, it would seem that whilst being an effective chelating agent for potassium, due to the kinetics of the ion-binding and decomplexation process, it is unlikely to be of any utility in ISE systems in its present form (without alteration to the structure), although preliminary work (7.9), has shown that certain anions can catalyse the dissociation of some cryptands (acid catalysis has also been identified (7.6a)), and it is possible that this might afford a

route to improve the response of ISEs incorporating these compounds.

7.5 COD-I: A New Type Of Potassium Ionophore

In the search for new ionophores with improved selectivity compared to that of the simpler crowns and related compounds, many different approaches have been adopted, focussing both on cyclic and acyclic molecules. In the closing stages of this project, samples of a new ionophore became available, named COD-I. This molecule has a macrocyclic structure, differing from previous ionophores in that the ring contains two 6-membered carbon rings in the main ring structure, and also a sulphur group. The structure of the molecule is as shown in Fig 7.9.

Little work has been carried out with this molecule other than its characterisation, and at the date of writing, no work has been published concerning its ion-selective properties. In view of the lack of data concerning this ionophore, the same procedure was followed as used in the work with valinomycin, the dibenzo crown and the cryptand. Membranes were therefore cast containing the potassium salt of the tetraphenylborate ion, at a similar concentration to that used for previous membranes, and the selectivity, single-ion response and impedance behaviour of the membrane were investigated. The results of this work are presented below.

7.5.1 Potential Measurements

Figure 7.10a shows the single ion reponse of the COD-I

Fig 7.9: schematic representation of the structure of the COD-I molecule.

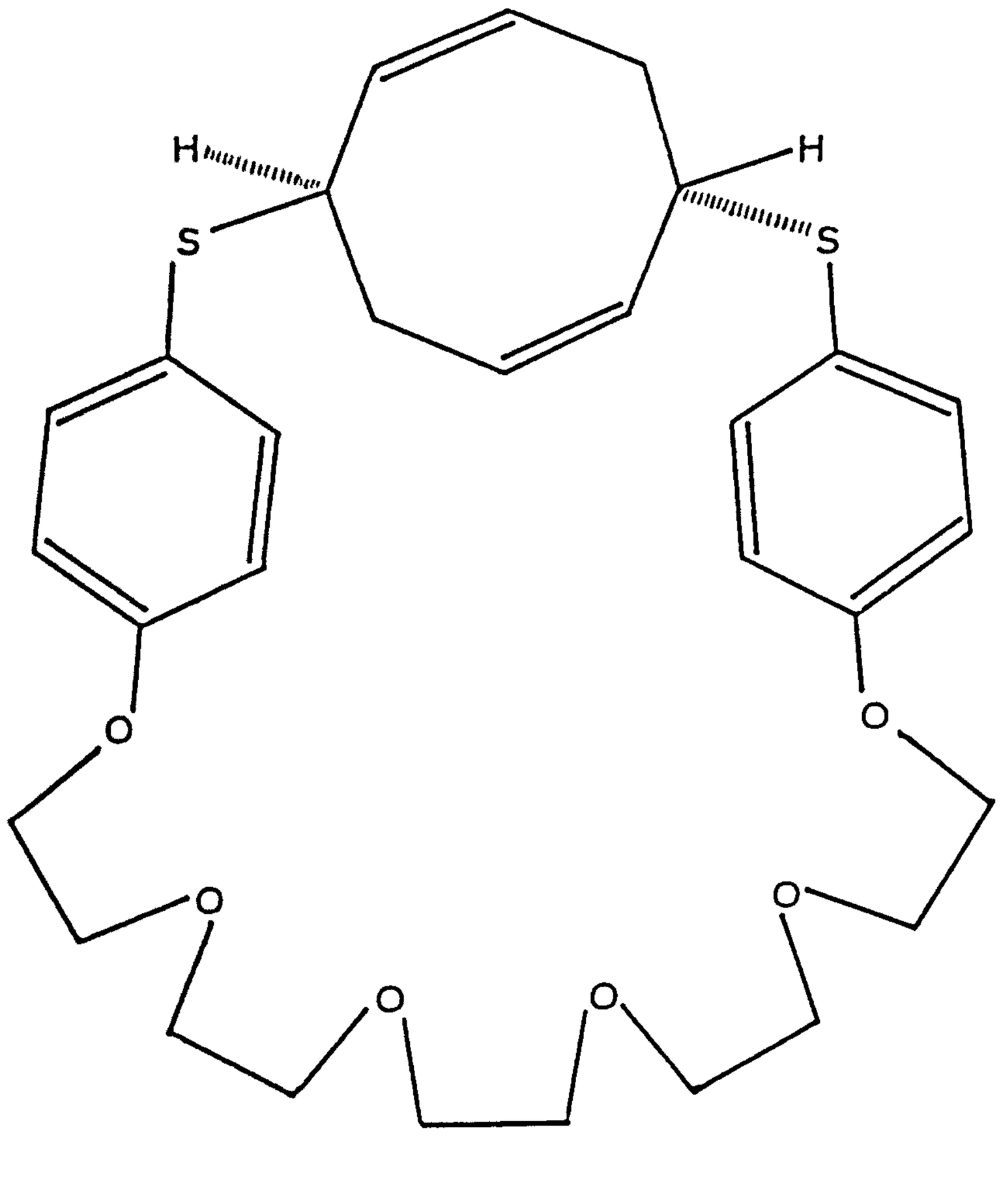
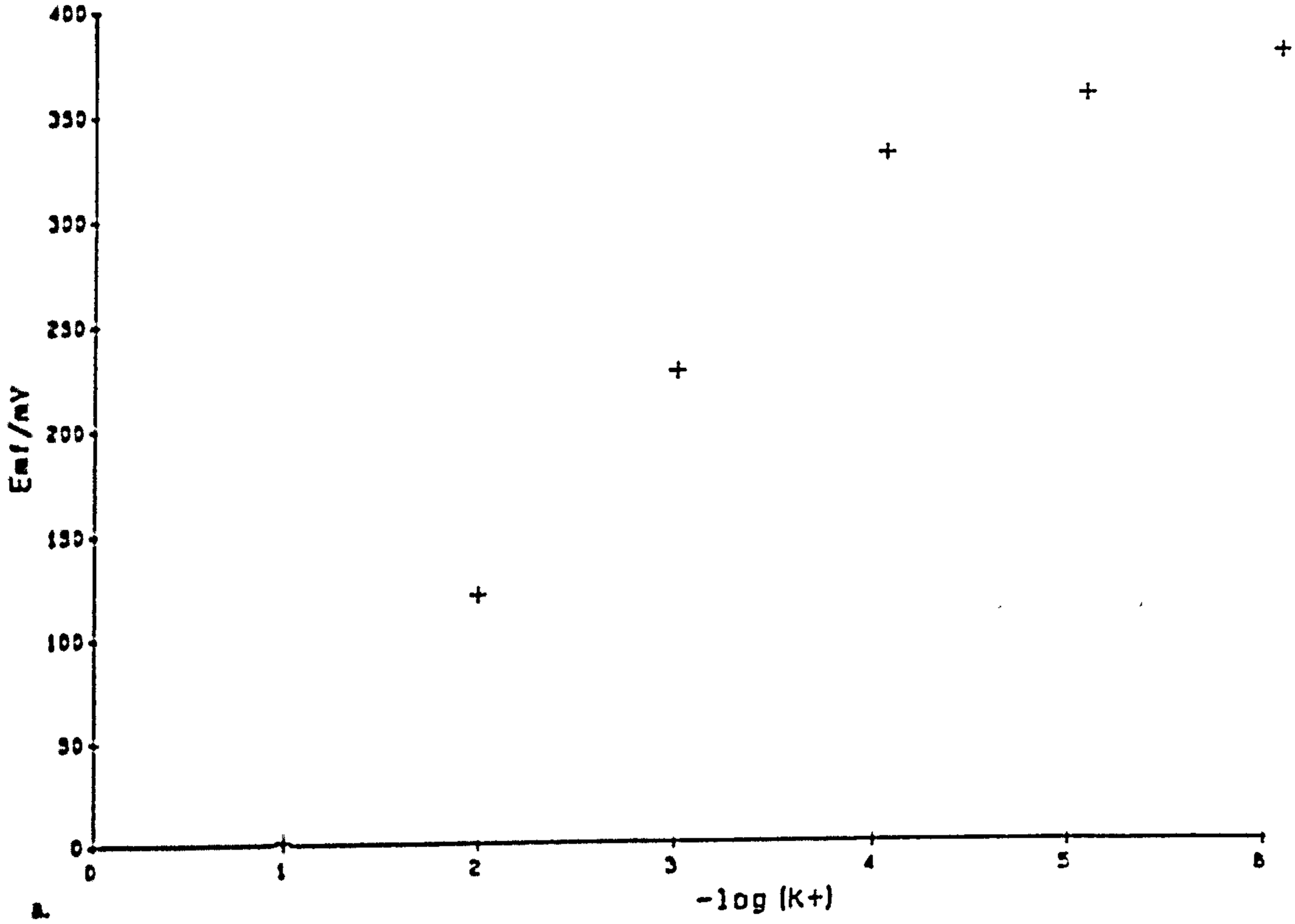


Fig 7.10: (a) Calibration (K^+ single-ion response) and (b) selectivity (K^+/Na^+ mixed-ion response) plots for a PVC/DOS/COD-I/$KBPh_4$ membrane measured with a 0.1 mol dm^{-3} KCl reference solution.



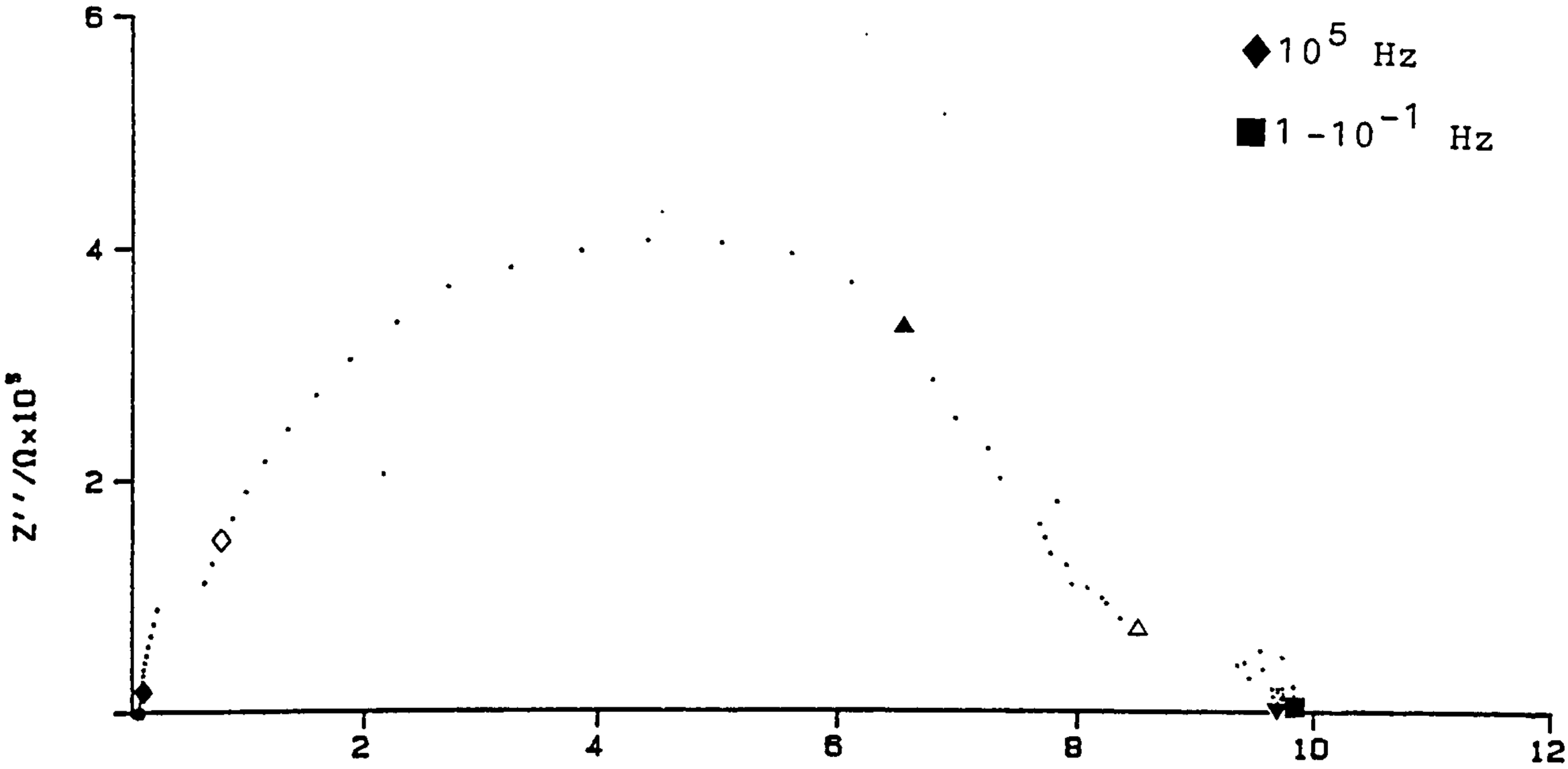
membrane in contact with KCl solutions. The plot has a slope of 114mV/decade, which is much closer to that found for the valinomycin-containing membranes than found for the crown and cryptand. The response is near Nernstian, particularly at higher potassium ion concentrations. The mixed-ion response, determined with a constant 0.1 mol dm^{-3} NaCl background concentration, is shown graphically in Fig 7.10b.

This response shows that the ionophore does not yield a membrane which is highly selective for potassium over a large concentration range, although there is a limited response over the range 10^{-1} - 10^{-3} mol dm^{-3} K^{+} concentration. The slope of the plot is far from Nernstian, however, the best slope being that of 47 mV between 10^{-1} and 10^{-2} mol dm^{-3} potassium.

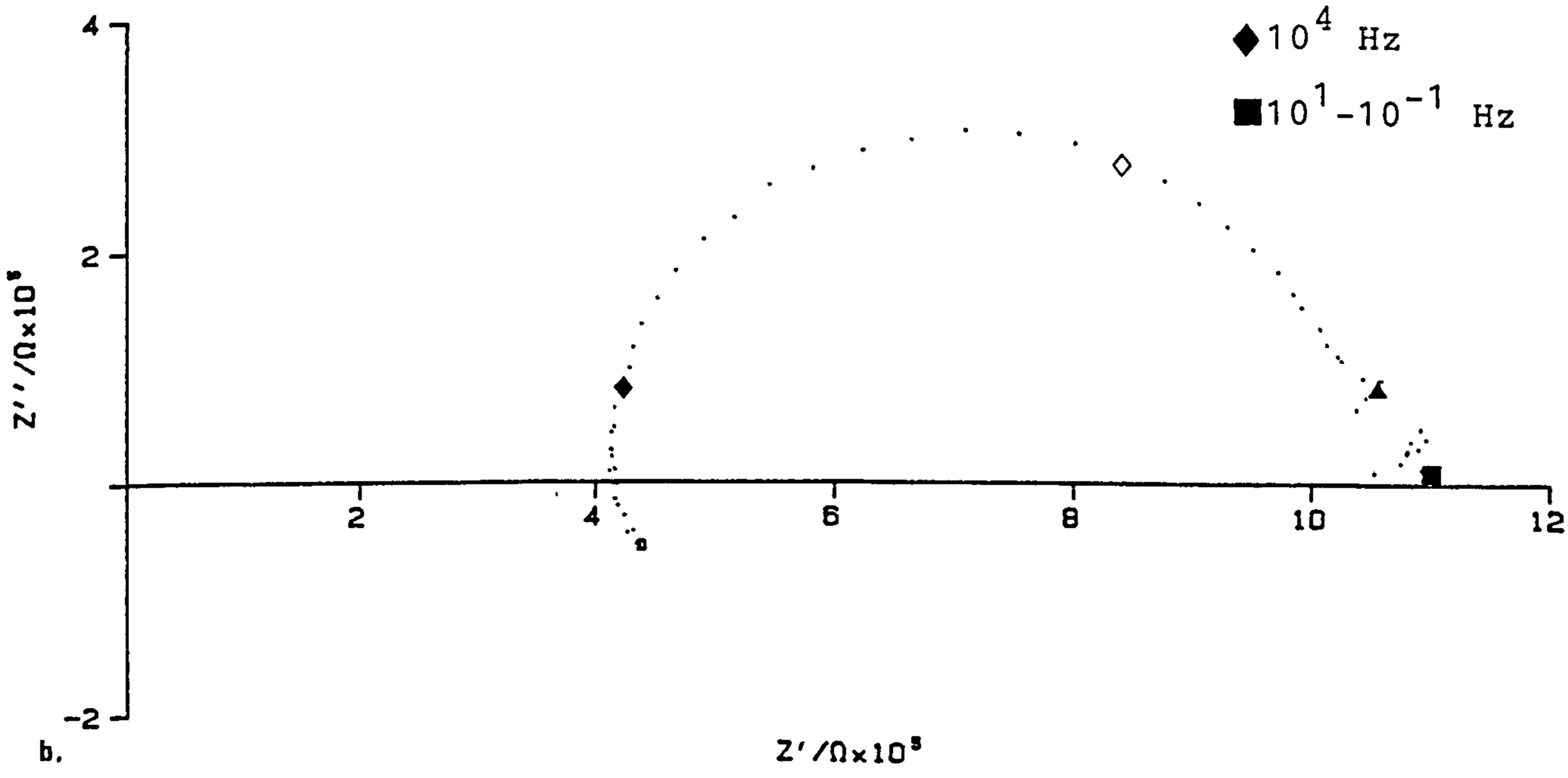
7.5.2 Impedance Measurements

Figure 7.11a shows the impedance spectrum of the COD-I-containing membrane immediately after first solution contact. The bulk semicircle found for previous membranes is clearly visible at high frequencies, as is a second lower-frequency feature, which is distorted in this plot due to a change in current-measuring resistor. Figs 7.11b and 7.11c show the spectra measured one and two hours respectively after first solution contact. These spectra show similar features to those found in the initial run, and it can be seen that the bulk resistance undergoes an increase with time. The detailed variation of the bulk membrane equivalent circuit parameters with time is given in Table 7.5, and the final spectrum recorded after 72 hours, is shown in Fig 7.11d, in which the low frequency region of the spectrum is fully resolved.

Fig 7.11: (a) Initial impedance spectrum and (b) spectrum measured after 1 hour for a PVC/DOS/COD-I/$KBPh_4$ membrane, measured with 0.1 mol dm^{-3} KCl contacting solutions.

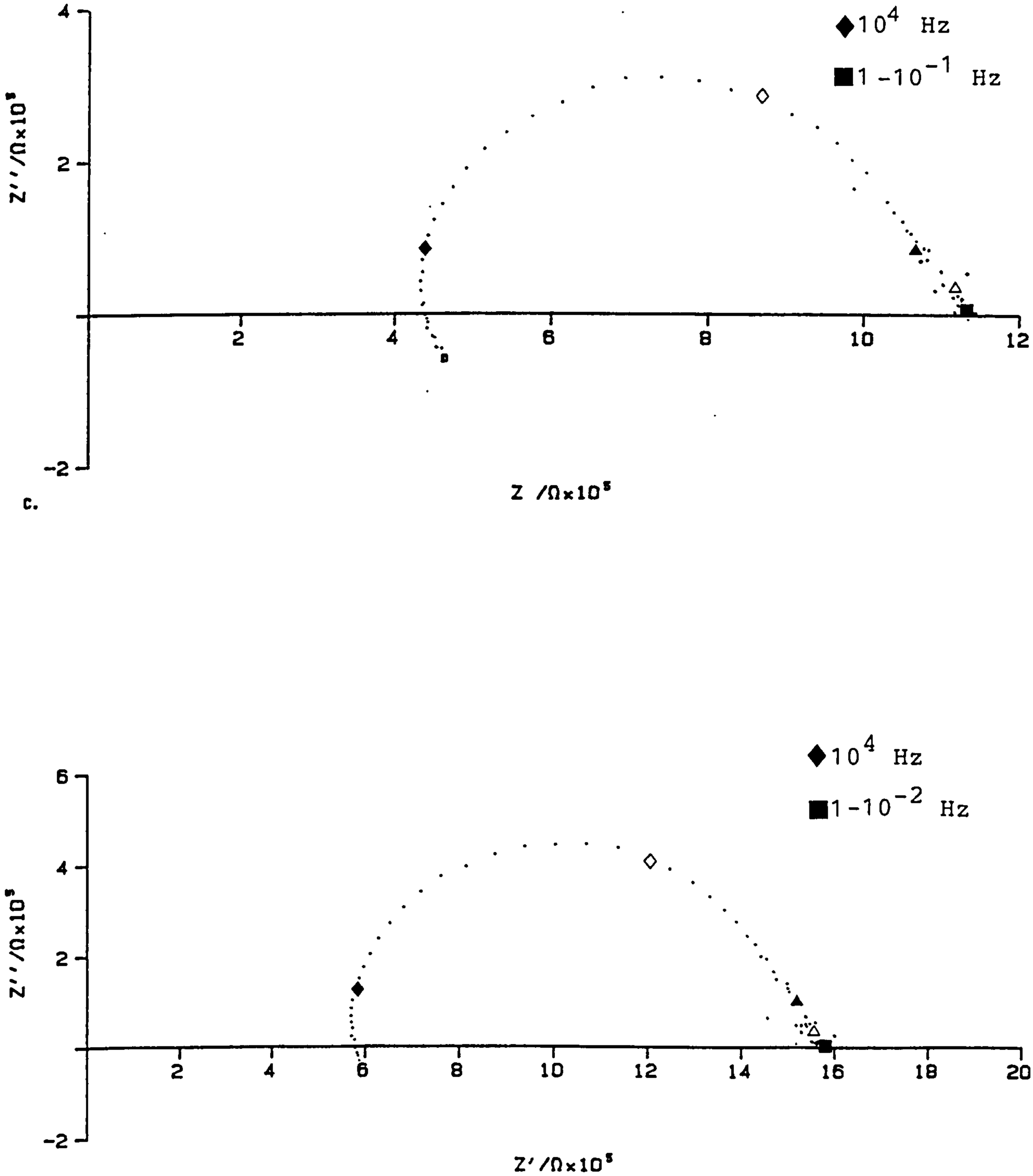


a.



b.

Fig 7.11: Impedance spectra for a PVC/DOS/COD-I/$KBPh_4$ membrane, measured after (c) 2 hours and (d) 72 hours with 0.1 mol dm^{-3} KCl contacting solutions.



c.

d.

Table 7.5: Time Dependence of Impedance for Membrane Containing COD-I and $KBPh_4$ with 0.1 mol dm^{-3} KCl Contacting Solutions

t/hours	$R_b/10^5\ \Omega$	$\omega_{1\,max}^*$ /Hz
1	0.97	4656
2	1.11	3991
3	11.2	"
4	11.6	"
5	11.9	"
6	12.1	4656
7	12.2	3991
8	12.4	"
9	12.9	"
10	13.0	"
11	13.3	"
12	13.3	4656
13	13.5	3991
14	13.5	"
15	13.7	"
16	13.8	"
17	14.6	"
18	15.0	"
19	15.0	"
20	15.1	"
21	15.3	"
22	15.3	"
23	15.4	"
24	15.6	"
72	15.6	"

7.5.3 Discussion

The potentiometric data for the COD-I membrane show clearly that the ionophore does not produce a membrane with ion-selective properties comparable to those achieved with valinomycin-containing membranes. The response is, however, much closer to that found for valinomycin membranes than any of the other ligands investigated.

The impedance spectra for the membrane show no evidence of the large charge-transfer resistance seen in the spectra for the dibenzo crown and the cryptand, and to this extent, the COD-I appears similar to valinomycin. The spectra are different, however, in that they show a much larger bulk resistance than found for any of the other ionophores in a membrane containing $KBPh_4$. It must be concluded that despite more facile charge-transfer kinetics, the mobility of the cation/carrier complex is less than for the other ionophores studied, although the potentiometric data suggest that the relative mobility of the cationic species is greater than for the anion.

On the basis of these results, it appears that the COD-I is capable of selectively complexing the potassium ion within the membrane, even in the presence of sodium, and does so in a way similar to valinomycin. The molecule evidently does not show a high a degree of selectivity as the natural ionophore but it is possible that this type of molecule could yield a more effective ligand, with variation of some of the constituent groups whilst retaining the basic structure as has been achieved for other synthetic ligands.

7.6 Conclusions

The problem of finding new ionophores for determining potassium in the presence of sodium has proved a more intractable problem than synthesising ionophores selective to other ions, particularly calcium, where several successes have been achieved, although despite the apparent lack of success, a great deal of information has been collected concerning the desirable properties for a functional ionophore, and the results reported here can be used to further this knowledge.

From the potentiometric data presented above, it is apparent that none of the synthetic ionophores studied can be said to offer performance (as judged by mixed ion response) equivalent to that of the natural material valinomycin, and this has been noted in previous studies, but the impedance data reported here, can throw new light on some aspects of the behaviour of the ionophores in the environment of the PVC matrix.

The lack of selectivity found for the dibenzo crown by potentiometric means is illustrated in the impedance spectra of the compounds, where it can be seen that there is little difference between the spectra obtained from membranes containing sodium and those containing potassium, and in contrast to the results for valinomycin, there appears to be almost no degree of selectivity occurring at the membrane /solution interface. The cryptand shows results similar to those found for the crown, and also shows some evidence of a more complex bulk membrane phase, whilst the new ligand, COD-I, shows a single-ion response comparable to that found for membranes containing valinomycin, but shows only a

limited mixed ion response. The response is, however, a marked improvement on that found for the crown or cryptand and it is possible that this type of ligand offers a new direction for the design of synthetic ligands.

The most interesting feature of the impedance spectra for these membranes is the relative values for the bulk membrane resistance, which do not show simple trends which can easily be related to the operation of the ionophore in an ISE. For the cryptand, which exhibits poor interfacial kinetics, the value of R_b is similar to that found for the corresponding membrane containing valinomycin, whilst the COD-I, which shows relatively rapid interfacial charge-transfer processes R_b is much higher. It would seem from these data that the interaction between the PVC matrix and the species in the membrane is complex, and that the process of charge transport within the membrane is not simply related to the interfacial processes as might otherwise be supposed.

Table 7.6: Summary of Bulk Resistance Values for PVC Membranes With Added BPh_4^- Salts

Ligand	Additive	(wt%)	Contacts	R_b init/ $10^5\ \Omega$	R_b fin/ $10^5\ \Omega$
None	None	-	KCl	22.8	45.0
Dibenzo-18-C-6	KBPh4	1.1×10^{-2}	KCl	5.19	6.51
"	NaBPh4	4.7×10^{-2}	NaCl	3.24	3.79
2,2,2-cryptand	KBPh4	1.1×10^{-1}	KCl	2.67	5.91
"	NaBPh4	4.0×10^{-1}	NaCl	3.00	9.21
COD-I	KBPh4	4.9×10^{-1}	KCl	0.97	15.6

Chapter 7 References

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Chapter 8

Summary and Conclusions

A study of various ion-selective electrode membranes has been successfully carried out, utilising ac impedance measurements. Both liquid and PVC matrix membranes containing valinomycin were studied, and several other ligands have also been investigated in PVC membranes. To achieve the highest possible quality of impedance data whilst preserving the essential features of the normal operating conditions of the membrane, a new cell for the study of PVC membranes was perfected. This cell was found to function well for both impedance and potentiometric measurements and provides a useful alternative housing to the more usual glass tube employed with PVC membranes, although to be fully practical in general work, a different reference electrode would be required for the sample chamber.

The use of four electrode impedance measurements on ion-selective electrodes has not been reported elsewhere, and this approach, coupled with high-quality measuring equipment, allowing a large range of frequencies to be covered, has yielded data for both the liquid and PVC membranes of a quality only previously found for solid-state electrodes. The employment of a computer controlled system also allowed a much greater degree of flexibility and detail of measurement than previously possible.

The measurements on liquid membranes containing valinomycin as the ionophore, carried out with both sodium and potassium contacting solutions, and using Millipore filters as the

membrane support, allow a clear picture of the operation of the electrode membrane to be deduced. It is apparent that the selectivity of the membranes in this situation depends entirely on the exclusion of interferents and counter ions from the membrane. In the absence of the ionophore, the membranes show very little permeability for either potassium or sodium, as measured by the exchange current determined from the impedance spectra. When valinomycin is added to the membrane, the exchange current for potassium is greatly increased, whilst that for sodium is essentially unchanged, the valinomycin acting to preferentially solvate the potassium in the membrane phase. These membranes, produced with an untreated Millipore filter as the support material, were found not to have ideal anion exclusion properties, as evidenced by the sub-Nernstian calibration curve slopes for all such membranes. Using the commercially-produced Orion potassium membrane support yielded electrodes with greatly improved slopes although the impedance spectra of such electrodes showed a more complicated structure, giving support to the suggestion that the Orion membranes are pre-treated with either the ionophore or some other material, added specifically to improve anion exclusion. This is supported further by the data for membranes treated with sodium tetraphenylborate, which gave electrodes with greatly improved slopes, and also impedance spectra showing evidence of a second bulk membrane phase similar to that found with membranes utilising the Orion K+ support. From these findings, it does seem likely that the Orion treatment involves some material similar to the tetraphenylborate salt.

A second interesting aspect of the liquid membrane electrodes, is that the surface area of the membrane could not

be increased from the size used in the Orion series 92 body without loss of electrode function. This is of relevance to the further use of impedance measurements, where it would be preferable to increase the membrane area to reduce the resistive component of the impedance.

In view of the close correlation between the ratio of exchange currents for different ions and their selectivity coefficients found for the liquid membranes, it would be practical to use the impedance technique as a method for determining the effectiveness of a given ionophore as a membrane-active agent. Although this method obviously requires sophisticated apparatus, a very well-defined measure of electrode performance can be achieved. It is also possible to assess whether or not a membrane is damaged, from the magnitude of its bulk resistance, which is substantially lowered if the membrane support is cracked, or leakage of the membrane solution occurs permitting direct contact of internal and external solutions. In this respect, the impedance technique presents a reliable and relatively quick method to check assembled electrodes for correct functioning.

It would be of interest to broaden the scope of the work on liquid membranes to cover other electrode systems, and also to investigate fully the effect of possible interferents on the valinomycin membrane having fully characterised the system in terms of the major interferent, sodium.

For the PVC membranes, which in recent years have become the preferred form for valinomycin electrodes, a considerably more complicated situation appears to exist. Whilst a limited correlation between the ratio of charge transfer resistance for primary and interferent ions, and the selectivity coefficient

is apparent, from the impedance measurements, it is clear that this is not sufficiently large to fully explain the cation-selectivity of the membrane. The basis of the selectivity appears to be the increase in effective primary ion concentration within the membrane, which is raised far higher in the presence of the ionophore than is the interferent ion concentration. Although the vast majority of the primary ion thus incorporated into the membrane bulk is complexed by the ionophore, the effect is that of a comparatively large bulk concentration of K^+, whilst the sodium concentration is limited by the exchange with free cations present in the matrix.

The data for the PVC membranes were found to be complicated by the apparent presence of a relatively high level of charge-carrying species within the matrix, seen in the absence of any additives other than the ionophore. The origin of these adventitious ionic species is not fully resolved, as, from the data given in Chapter 5, the plasticiser and PVC both appear to be possible sources. It also seems from the impedance measurements, that the valinomycin may itself provide some ionic impurities. The incorporation of salts of a large anion into the membrane matrix swamps the level of inherent charge carriers and permits a high degree of control over the interfacial charge transfer rate, without disrupting the ion-selective behaviour of the membrane, indicating further that the basis of selectivity in the PVC membrane can not be a simple exclusion process occurring at the membrane/solution interface as found with the liquid membranes. The addition of such salts also appears to aid the anion exclusion properties of the membrane, producing membranes which have slopes closer to the 59.2mV/ decade predicted by the Nernst equation. It

seems that in the absence of such additives the inherent ionic species provide the neccesary source of balancing charge for the cation/ionophore complex.

The results presented in Chapter 7 cover the extension of the work on PVC membranes to include several other ionophores, selected to be representative of their class of compounds. In agreement with earlier work, none of the materials studied produced membranes with selectivity coefficients comparable to those found for valinomycin, but the lack of selectivity can be interpreted from the impedance spectra and potentiometric data obtained. For the dibenzo-18-crown-6 membrane, the spectra reveal very little difference between the situation where the membrane is exposed to sodium and where it is exposed to potassium. In both cases, large charge transfer resistances are found, suggesting slow interfacial kinetics, compared to the valinomycin membrane. It seems that in this case, the ionophore behaves in a similar manner to both primary ion and interferent, and no selectivity results. This appears to be connected to the slow decomplexation of the cation by the ligand within the membrane. From the potential difference measurements, it seems that the cation transport number is greatly reduced by the presence of the ligand.

Very similar results were obtained for the membranes containing 2,2,2-cryptand, and these two types of ligand, whilst possessing quite different structures, appear to behave in many respects, in a similar manner within the membrane, as far as is evidenced by their electrical properties.

The results for the new ligand, COD-I, based on a sulphur containing macrocycle, suggest that this ionophore behaves in a way more similar to the behaviour of the valinomycin in a PVC

membrane than the more familiar types of ionophore, as exemplified by the crown and cryptand. From the data for these potassium ionophores, one aspect of their operation in a PVC membrane is not fully resolved. For the valinomycin, the bulk resistance measurements apear to be fully self-consistent, with potassium being more mobile within the membrane than sodium, in the presence of the ionophore. For the dibenzo-crown and cryptand however, this does not seem to be the case, whilst the data for the COD-I appear to agree with those for valinomycin, but are of a higher order of magnitude. There does not appear to be a direct correlation between the effectiveness of the ligand as an ion-selective agent in a membrane, and the mobility of species within the membrane phase, and it would be interesting to investigate this aspect of the PVC membranes further.

The impedance method has been shown to be a useful technique for gaining further insight into the mechanism and details of operation of ion-selective membranes, both as liquid and PVC membranes. Further work with new ionophores, and extending the present work to cover the systems studied in more detail, is warranted with a view to the insight into the membrane mechanism which the technique allows. A more detailed study of the relationship between the concentration of negative sites and the ionophore within the membrane may yield useful information about the interaction between the ionophore and the PVC matrix. A point must be reached, where the concentration of the cation in the membrane exceeds the concentration of the available ionophore molecules, and at this point, a clear change in the impedance spectra should become visible.

An extention of the work to cover other ligands would also

be of interest, to investigate to what extent the impedance behaviour of the valinomycin in both liquid and PVC matrix membranes is mimicked by ionophores selective for ions other than potassium.

Appendix A

System Software - The Impedance Data Control System (C)

Program Descriptions

1. START-UP

This is the main program in the package. The majority of the program is concerned with selecting values for the FRA front panel controls all of which are set using START-UP. These parameters include the maximum and minimum freqencies for the run, number of points per decade change in frequency, and the output voltage to be used.

The operator is given the option of adding to a previously collected set of data by loading into the data array prior to the run, the new data then following it in the array. If this option is selected, old data files can be reviewed before loading to find the desired one. Another option available is to set-up the new run using the same parameters (but not the data) from a previous run.

The operator is prompted at the beginning of the program for a variety of experimental details, including temperature, electrode area, electrode materials and solution compositions. All this information is saved at the end of the run in the description file.

2. DCOLLECT

This programme controls the FRA, setting all pre-selected parameters and collecting (and displaying) the data. The system

was designed to run unattended for long periods, so the interaction between the operator and the computer is mimimal during data collection. The only point at which input via the computer is necessary is when the comparison resistance (CMR) is changed. This is achieved by pressing the 'HOLD' button on the FRA. At the end of the current measurement, the computer will detect that 'HOLD' has been pressed and prompt for the new CMR value. Alternatively at this point the operator has the option of terminating the run.

The program runs with FRA in local mode with all front panel controls active as discussed above. This means that parameters such as the integration time and measurement delay can be altered whilst the run is in progress without needing to interrupt the run via the computer. This does not alter the preset values as stored in the computer however, and subsequent runs in a multiple run will use the preset values. When a multiple run has been pre-programmed, a machine-code timing routine is called after each individual run, giving the delay selected. Any delay length can be programmed from one second upwards. During the delay loop, the monitor screen shows the name of the operator, the number of the next run and the length of the delay being executed. During a multiple run data are saved after each individual run for maximum data security.

3.ANALYSIS 1

This program is for routine analysis of data collected using DCOLLECT. The data can be plotted, and re-plotted changing the axis scales if required, until the user is satisfied with the plot after which the plot can be output to a dot-matrix printer

or graphics plotter. The data can be dumped onto the printer as a numeric listing if required, along with all details contained in the description file. Several data files can be plotted on the same set of axes for comparisons, up to a limit of ten files per plot. After the analysis is complete, control can be passed back to START-UP, or further analysis can be carried out using ANALYSIS 2.

4. ANALYSIS 2

This program allows further processing of data after it has been plotted using ANALYSIS 1. Data points can be deleted from the plot and sections of the plot can be expanded. Linear least squares regression can be carried out over a selected portion of the plot. As with ANALYSIS 1, plot can be output to the printer or plotter.

5. HPPLOTTER

This program allows any plot from ANALYSIS 1 or ANALYSIS 2 to be plotted on the HP 7225A graphics plotter. All axis scales and labels are defined in the relevant analysis program and are passed to HPPLOTTER to reproduce the plot. The program is loaded and run by the analysis programs, and the relevant program is re-loaded and run when plotting is completed, with all variables preserved.

6. BSHAPE

All the machine code routines used by the programs above are

contained in BSHAPE, in addition to the shape table required by the computer for displaying graphics. Once loaded, BSHAPE remains resident in memory and is unaffected by the presence or absence of the BASIC programs. It is therefore loaded automatically when the computer is powered up and can be used by the BASIC programs as required. The various routines included in BSHAPE are listed below.

i. Shape table.

ii. Data loading/saving routines.

iii. Catalog/file selection routine.

iv. Print formatting routine (used for formatting output both on-screen and for the printer). This enables the output to be of a standard format on any printer, as no routines in the printer interface or printer itself are utilised.

v. Chain function for loading and running other programs direct.

Start-Up

```
9000  IF Z1 <  > 0 THEN 10000
9100  HIMEM: 34643
10000 RR$ = "ENTER NUMBER ":CD$ = ""
10010 E1$ = CD$ + "IN#0":E2$ = CD$ + "PR#0":E3$ = CD$ + "PR#3"
10020 H = 37904: ONERR  GOTO 12050
10030  IF Z1 <  > 0 THEN 10110
10040  GOSUB 13100
10045  IF  PEEK (37296) = 169 AND  PEEK (37396) = 201 THEN 10060
10050  PRINT CD$;"BLOADBSHAPE7,D1": POKE 232,104: POKE 233,142
10060  HOME : VTAB 10: PRINT  TAB( 15): PRINT "APPLE/1174": PRINT : PRINT
     TAB( 10): PRINT "REMOTE CONTROL SYSTEM": FOR I = 1 TO 2000: NEXT I
10070 DT = 0:RNZ = 1
10080  DIM PS(24),DA(2,500)
10090 PS(0) = 1:PS(2) = 1:PS(4) = 1:PS(6) = 2:PS(7) = 4:PS(8) = 2:PS(9) =
    8:PS(12) = 3:PS(13) = 1:PS(16) = 999900:PS(17) = 0.1:PS(18) = 1:PS(19
    ) = 1:PS(20) = 0.01:PS(21) = 0.01:PS(22) = 15:PS(23) = 15
10100  GOTO 10240
10110  HOME : VTAB 7: PRINT : PRINT "PROGRAM OPTIONS ARE :"
10120  PRINT : PRINT "1: EXIT PROGRAM"
10130  PRINT : PRINT "2: PROCESS DATA FOR OUTPUT"
10140  PRINT : PRINT "3: COMMENCE ANOTHER RUN"
10150  IF P6 <  > 0 THEN 10170
10160  PRINT : PRINT "4: ADD TO PRESENT DATA"
10170  PRINT : PRINT RR$;: INPUT Q$:Q =  VAL (Q$): IF Q < 1 OR Q > 4 THEN
     CALL H: GOTO 10110
10180  ON Q GOTO 10190,10220,10218,14000
10190  HOME : PRINT "PROGRAM ENDED": END
10218  CLEAR : GOTO 9100
10220  HOME : VTAB 12: HTAB 10: INVERSE : PRINT "LOADING ANALYSIS PROGRAM
    ": PRINT CD$;"RUNANALYSIS 1.V3,D1"
10240  HOME : VTAB 2: HTAB 6: INVERSE : PRINT "CREATION OF INFORMATION FI
    LE": NORMAL : VTAB 4: HTAB 6: PRINT "(<CR> WILL CATALOG DRIVE #2)":DE
     = 1
10250  PRINT : PRINT : INPUT "ENTER FILENAME :";B$: IF B$ <  > "" THEN 10
    256
10252  CALL 35424: FOR I = 0 TO 29:DI =  PEEK (35456 + I) - 128:CH$ =  CHR$
    (DI):B$ = B$ + CH$: NEXT I: IF  PEEK (35436) = 141 THEN 10240
10256 FC$ =  MID$ (B$,1,1):FC =  ASC (FC$): IF FC > 48 AND FC < 57 THEN  PRINT
    : INVERSE : PRINT "FIRST CHARACTER OF FILENAME IS NUMERIC": NORMAL :C
    A = 1: CALL H: GOTO 10250
10257  IF CA = 1 THEN  PRINT : HOME : VTAB 2: HTAB 6: INVERSE : PRINT "CR
    EATION OF INFORMATION FILE": NORMAL : VTAB 7: PRINT "FILENAME : ";B$
10258  VTAB 9: INPUT "MAX NO. OF RUNS WITH THIS NAME :";RN$:RNZ =  INT ( ABS
    ( VAL (RN$))): IF RNZ = 0 THEN RNZ = 1
10260  IF DT = 0 THEN  PRINT CD$;"DELETED";B$;",D2"
10270 DT = 0:K = K + 1: IF K = RNZ THEN RNZ = 1:RN$ = "": GOTO 10300
10280  IF DT = 0 THEN  PRINT CD$;"DELETED";B$ +  STR$ (K)
10290  GOTO 10270
10300 L1$ = "INFORMATION FILE: " + B$:L1 =  INT (20 - ( LEN (L1$) / 2))
10302  IF L1 <  = 0 THEN L1 = 14:L1$ = "INFORMATION FILE"
10304  HOME : PRINT  TAB( L1): INVERSE : PRINT L1$: NORMAL
10305 B1$ = B$: VTAB (3)
10310  INPUT "OPERATOR    : ";A$
10320  INPUT "RUN NO      : ";C$
10330  INPUT "DATE        : ";D$
10340  INPUT "TEMPERATURE : ";E$
10350  INPUT "PRESSURE    : ";F$
10370  INPUT "MEMBRANE NO : ";G$
10380  INPUT "AREA IN CM2 : ";G1$:G1 =  VAL (G1$): IF G1 = 0 OR G1 < 0 THEN
    G1 = 1
10390  INPUT "SOLUTION 1  : ";H$
10400  INPUT "SOLUTION 2  : ";I$
10410  INPUT "ELECTRODES  : ";J$
10452  HOME : PRINT  TAB( 14): INVERSE : PRINT "INFORMATION FILE": NORMAL
10460  VTAB 3: PRINT "DESCRIPTION STRINGS :(MAX 5 X 80 CHRS.)"
10470  PRINT : PRINT
10500  INPUT K$: IF K$ = "" THEN 10550
10510  INPUT L$: IF L$ = "" THEN 10550
10520  INPUT M$: IF M$ = "" THEN 10550
10530  INPUT N$: IF N$ = "" THEN 10550
10540  INPUT O$
10550  VTAB 21: INPUT "ALTER DESCRIPTION ?";Q$: IF Q$ = "Y" THEN 10300
10552  IF Q$ = "N" OR Q$ = "" THEN DE = 0: GOTO 10556
10554  CALL H: GOTO 10550
10556  IF DD = 1 THEN 10590
10560  HOME : PRINT  TAB( 14): INVERSE : PRINT "GENERATOR CONTROL": NORMAL
    :DD = 0
10565  VTAB 4: PRINT "DATA ORIGIN:": PRINT : PRINT "1: FROM 1174": PRINT
    : PRINT "2: FROM DISK": PRINT
10570  PRINT RR$;: INPUT ":";Q$:R =  VAL (Q$): IF R < 1 OR R > 2 OR R <  >
     INT (R) THEN  CALL H: GOTO 10560
10580  ON R GOTO 10590,10950
10590  IF DD = 1 THEN  PRINT : HOME : VTAB 2: HTAB 14: INVERSE : PRINT "G
    ENERATOR CONTROL": NORMAL : VTAB 4: GOTO 10592
10591  VTAB 13
10592  PRINT "SET UP 1174:": PRINT : PRINT "1: IN LOCAL": PRINT : PRINT "
    2: AS WITH A PREVIOUS RUN"
10600  PRINT : PRINT "3: WITH PROGRAMMED PARAMETERS": PRINT : PRINT RR$;:
     INPUT ":";Q$:R =  VAL (Q$): IF R < 1 OR R > 3 OR R <  >  INT (R) THEN
     CALL H: GOTO 10590
10610  ON R GOTO 11670,11180,10620
10620  HOME : PRINT  TAB( 11): INVERSE : PRINT "MEASUREMENT PARAMETERS": NORMAL

10625  VTAB 4: INPUT "USE PRESENT VALUES ?:";R1$: IF R1$ = "Y" THEN 11310

10630  IF R1$ = "N" THEN 10650
10640  CALL H: GOTO 10620
10650  HOME : PRINT  TAB( 11): INVERSE : PRINT "MEASUREMENT PARAMETERS": NORMAL

10655  VTAB 4:DV = PS(15) + 1: PRINT "INTEGRATION TIME :";DV: PRINT : PRINT
    "1: MIN": PRINT : PRINT "2: X10": PRINT : PRINT "3: X100": PRINT : PRINT
    "4: X1000": PRINT
10660  PRINT RR$;: INPUT ":";Q$:R =  INT ( VAL (Q$))
10670  IF R < 0 OR R > 4 THEN  CALL H: GOTO 10650
10680  IF R = 0 THEN 10700
10690 PS(15) = R - 1
10700  HOME : PRINT  TAB( 11): INVERSE : PRINT "MEASUREMENT PARAMETERS": NORMAL

10705  VTAB 4:DV = PS(14) + 1: PRINT "MEASUREMENT DELAY:";DV: PRINT : PRINT
    "1: 0.1 SECONDS": PRINT : PRINT "2: 1 SECOND"
10710  PRINT : PRINT "3: 10 SECONDS": PRINT : PRINT "4: 100 SECONDS": PRINT

10720  PRINT RR$;: INPUT ":";Q$:R =  VAL (Q$): IF R = 0 THEN 10760
10730  IF R < 1 OR R > 4 THEN 10700
10740 PS(14) = R - 1
10750 DV = 1: IF PS(2) = 3 THEN DV = 2
10760  VTAB 17: PRINT "INPUT REJECT :";DV: PRINT : PRINT "1: OFF": PRINT
    : PRINT "2: ON": PRINT
10770  PRINT RR$;: INPUT ":";Q$:R =  VAL (Q$): IF R = 0 THEN 10800
10780  IF R < 1 OR R > 2 THEN 10760
10790 PS(2) = 0: IF R = 2 THEN PS(2) = 3
10800  HOME : PRINT  TAB( 11): INVERSE : PRINT "MEASUREMENT PARAMETERS": NORMAL

10802  VTAB 4: PRINT "DISPLAY MODE :";PS(13) + 1: PRINT : PRINT "1: R,THE
    TA": PRINT : PRINT "2: A,B": PRINT : PRINT "3: LOGR,THETA": PRINT
10804  PRINT RR$;: INPUT ":";Q$:R =  VAL (Q$): IF R = 0 THEN 10809
10806 PS(13) = R - 1
10809  VTAB 14: PRINT "INPUT CHANNEL :";PS(12): PRINT : PRINT "1: X": PRINT
    : PRINT "2: Y": PRINT : PRINT "3: Y/X": PRINT
```

```
10810  PRINT RR$;: INPUT ":";Q$:R =  VAL (Q$): IF R = 0 THEN 10840
10820  IF R < 1 OR R > 3 THEN 10800
10830 PS(12) = R
10840 DV = PS(9) - 1: IF PS(9) = 0 THEN DV = 6
10850  HOME : PRINT  TAB( 11): INVERSE : PRINT "MEASUREMENT PARAMETERS": NORMAL

10855  VTAB 4: PRINT "INPUT RANGE :";DV: PRINT : PRINT "1: 0.01 VOLTS": PRINT
    : PRINT "2: 0.1 VOLTS": PRINT
10860  PRINT "3: 1 VOLT": PRINT : PRINT "4: 10 VOLTS": PRINT : PRINT "5:
    100 VOLTS": PRINT : PRINT "6: AUTORANGING": PRINT
10870  PRINT RR$;: INPUT ":";Q$:R =  VAL (Q$): IF R = 0 THEN 10910
10880  IF R < 1 OR R > 6 OR R <  > INT (R) THEN  CALL H: GOTO 10850
10890  IF R = 6 THEN R = 7
10900 PS(9) = R + 1
10910  VTAB 22: PRINT "VOLTS OUT  (";PS(20);")  ";: INPUT ":";Q$:R =  VAL
    (Q$): IF R = 0 THEN 10940
10920  IF R < 0 OR R > 9.99 THEN 10910
10930 PS(20) = R:PS(21) = R
10940  GOTO 11310
10950 DD = 1
10952  HOME : VTAB (2): HTAB 14: INVERSE : PRINT "DISK DATA LOAD": NORMAL
    : VTAB 4: HTAB 6: PRINT "(<CR> WILL CATALOG DRIVE #2)": VTAB 6
10960  INPUT "ENTER FILENAME :";FF$: IF FF$ <  > "" THEN 10965
10961  PRINT  CHR$ (4);"VERIFY HELLO,D2"
10962 CA = 1: CALL 35424: FOR I = 0 TO 29:DI =  PEEK (35456 + I) - 128:CH
    $ =  CHR$ (DI):FF$ = FF$ + CH$: NEXT I: IF  PEEK (35436) = 141 THEN 1
    0952
10965 FC$ =  MID$ (FF$,1,1):FC =  ASC (FC$): IF FC > 48 AND FC < 57 THEN
     PRINT : INVERSE : PRINT "FIRST CHARACTER OF FILENAME IS NUMERIC": NORMAL
    :CA = 1: CALL H: PRINT : GOTO 10960
10970  PRINT CD$;"VERIFY";FF$;",D2"
10980  PRINT CD$;"VERIFYD";FF$;",D2"
11044  IF CA = 1 THEN  PRINT : HOME : VTAB 2: HTAB 14: INVERSE : PRINT "D
    ISK DATA LOAD": NORMAL
11046  VTAB 3: PRINT  TAB( 40): VTAB 3: HTAB 12: INVERSE : PRINT "LOADING
    : DATA FILE": NORMAL
11048  POKE 29,68: POKE 30,65: CALL 38144
11050  PRINT CD$;"BLOAD";FF$;",A";  PEEK (27) +  PEEK (28) * 256 + 9;",D2"

11051  IF DA(0,0) <  > 0 THEN  CALL H: HOME : VTAB 3: HTAB 10: FLASH : PRINT
    "SINGLE-FREQUENCY DATA": NORMAL :DD = 0: FOR L = 1 TO 2000: NEXT L: GOTO
    10560
11052  VTAB 3: PRINT  TAB( 40): VTAB 3: HTAB 9: INVERSE : PRINT "LOADING:
     DESCRIPTION FILE": NORMAL : PRINT CD$;"OPEND";FF$;",D2": PRINT CD$;"
    READD";FF$
11054  FOR L = 0 TO 24: INPUT PS(L): NEXT L: INPUT A1$,C1$,D1$,E4$,F1$,G2
    $,H1$,I1$,J1$,K1$,L1$,M1$,N1$,O1$,CR,O: PRINT CD$;"CLOSE": PRINT CD$
11056  VTAB 3: PRINT  TAB( 40): PRINT : VTAB 9: IF CA = 1 THEN  PRINT : HOME
    : VTAB 2: HTAB 14: INVERSE : PRINT "DISK DATA LOAD": NORMAL : VTAB 5:
    CA = 0
11057 DAZ = DA(1,0): INPUT "REVIEW THIS FILE ? :";Q$: IF Q$ = "Y" THEN  GOSUB
    13200
11060  GOTO 10590
11070  REM  LOCAL SET-UP
11080  PRINT E3$: PRINT "@72:'S001'": PRINT "@72"; CHR$ (1);":": PRINT E1
    $: PRINT E2$
11090  HOME : VTAB 6: PRINT  TAB( 14): INVERSE : PRINT "LOCAL SET-UP": NORMAL

11100  VTAB (12): PRINT  TAB( 14);"SET CONTROLS": PRINT : PRINT  TAB( 18)
    ;"AND": PRINT
11110  PRINT : PRINT  TAB( 8);"PRESS RETURN WHEN READY": PRINT : PRINT  TAB(
    14): INPUT "TO CONTINUE";Q$: PRINT E3$
11120  FOR I = 1 TO 15
11130  PRINT "@72:'T4"; CHR$ (I + 48);"'": PRINT "@"; CHR$ (95);"R:"
11140  INPUT LV:PS(I) = LV: NEXT I
11150  PRINT E2$: PRINT E1$
11160  FOR I = 16 TO 24:AAZ = I: GOSUB 12200:PS(I) = W1: NEXT I
11170  GOTO 11540
11180  REM PRESET LOAD
11190  HOME : VTAB 2: HTAB 13: INVERSE : PRINT "DISK PARAMETER LOAD":DP =
    1: NORMAL : VTAB 4: HTAB 6: PRINT "(<CR> WILL CATALOG DRIVE #2)": VTAB
    6
11260  INPUT "ENTER FILENAME :";FF$: IF FF$ <  > "" THEN 11262
11261 CA = 1: CALL 35424: FOR I = 0 TO 29:DI =  PEEK (35456 + I) - 128:CH
    $ =  CHR$ (DI):FF$ = FF$ + CH$: NEXT I: IF  PEEK (35436) = 141 THEN 1
    1190
11262 FC$ =  MID$ (FF$,1,1):FC =  ASC (FC$): IF FC > 48 AND FC < 57 THEN
     PRINT : INVERSE : PRINT "FIRST CHARACTER OF FILENAME IS NUMERIC": NORMAL
    :CA = 1: CALL H: PRINT : GOTO 11260
11264  PRINT CD$;"DELETED";FF$;",D2"
11270  PRINT CD$;"OPEND";FF$;",D2"
11280  PRINT CD$;"READD";FF$
11290  FOR L = 0 TO 24: INPUT PS(L): NEXT L
11300  PRINT CD$;"CLOSE": PRINT CD$:DP = 0
11310  REM GENERATOR SETTINGS
11320  HOME : PRINT  TAB( 14): INVERSE : PRINT "GENERATOR CONTROL": NORMAL
    : VTAB 4:SR = 0
11330  PRINT "GENERATOR :": PRINT : PRINT "1: FREQUENCY SWEEP": PRINT : PRINT
    "2: SINGLE FREQUENCY": PRINT : PRINT RR$;: INPUT Q$:R =  VAL (Q$)
11340  IF R < 1 OR R > 2 OR R <  > INT (R) THEN  CALL H: GOTO 11310
11350  IF R = 2 THEN 11640
11360  REM  FREQ. SWEEP SBR
11370 DV = 1: IF PS(7) = 0 THEN DV = 2
11380  VTAB 13: PRINT "SWEEP MODE (";DV;"):": PRINT : PRINT "1: LOG ": PRINT
    : PRINT "2: LIN ": PRINT : PRINT RR$;: INPUT Q$
11390 R9 =  VAL (Q$): IF R9 = 0 THEN 11411
11400  IF R9 = 1 THEN PS(7) = 4
11410  IF R9 = 2 THEN PS(7) = 0
11411  HOME : PRINT  TAB( 14): INVERSE : PRINT "GENERATOR CONTROL": NORMAL
    : VTAB 4
11412  PRINT "FREQUENCY SWEEP :": PRINT : PRINT "1: UP": PRINT : PRINT "2
    : DOWN": PRINT : PRINT RR$;: INPUT Q$:PS(8) = 2
11414 R =  VAL (Q$): IF R < 1 OR R > 2 OR R <  > INT (R) THEN  CALL H: GOTO
    11411
11416  IF R = 2 THEN PS(8) = 3
11420  VTAB 13: PRINT "F MAX  (";PS(16);")",: INPUT ":";Q$:R =  VAL (Q$):
     IF R = 0 THEN 11450
11430  IF R < 0.001 OR R > 999900 THEN  CALL H: GOTO 11420
11440 PS(16) = R
11450  VTAB 15: PRINT "F MIN  (";PS(17);")",: INPUT ":";Q$:R =  VAL (Q$):
     IF R = 0 THEN 11480
11460  IF R < 0.0001 OR R > 999900 THEN  CALL H: GOTO 11450
11470 PS(17) = R
11480  VTAB 17: PRINT "DELTA F (";: IF R9 = 2 THEN  PRINT PS(22);: GOTO 1
    1500
11490  PRINT PS(23);
11500  PRINT ")",: INPUT ":";Q$:R =  VAL (Q$): IF R = 0 THEN 11540
11510  IF R < 1 OR R > 99 THEN  CALL H: GOTO 11480
11520  IF PS(7) = 4 THEN PS(23) = R: GOTO 11540
11530  IF PS(7) = 0 THEN PS(22) = R: GOTO 11540
11540  HOME : PRINT  TAB( 11): INVERSE : PRINT "MULTIPLE RUN FACILITY": NORMAL

11545  VTAB 4: INPUT "IS THIS TO BE A MULTIPLE RUN :";Q$
11580  IF Q$ = "N" THEN Z1 = 1:RNZ = 1: GOTO 11920
11590  IF Q$ = "Y" THEN Z1 = 2: GOTO 11610
11600  CALL H: GOTO 11540
11610  VTAB 7: INPUT "ENTER TOTAL NO. OF RUNS :";RN$:RNZ =  VAL (RN$): IF
    RNZ < 1 OR RNZ <  > INT (RNZ) THEN  CALL H: GOTO 11610
11620  VTAB 8: PRINT : INPUT "TIME DELAY (MINUTES) :";TD$:TD =  VAL (TD$)
    : IF TD < 1 / 60 THEN  CALL H: GOTO 11620
11630 TD = TD * 60: GOTO 11870
11640  REM  SINGLE FREQ.
```

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11650  HOME : PRINT  TAB( 14): INVERSE : PRINT "SINGLE FREQUENCY": NORMAL
    : VTAB 4
11655  INPUT "OPERATING FREQ. :";Q$:R =  VAL (Q$): IF R < 0.0001 OR R > 9
    99900 THEN 11650
11660 PS(19) = R:PS(8) = 2:PS(16) = 999900:PS(17) = R:PS(23) = 1:PS(22) =
    0:PS(7) = 0:PS(14) = 0:DA(0,0) = PS(19)
11670  VTAB 7: PRINT "WHICH MODE DISPLAY  (1)"
11680  PRINT : PRINT "      Z' / TIME  (1)"
11690  PRINT : PRINT "      Z''/ TIME  (2)"
11700  PRINT : PRINT "    C.D.L/ TIME  (3)"
11710  PRINT : PRINT RR$;: INPUT Q$:P6 =  VAL (Q$): IF P6 <  >  INT (P6) OR
    P6 < 0 OR P6 > 3 THEN  CALL H: GOTO 11670
11720  IF P6 = 0 THEN P6 = 1
11730 RNZ = 1:Z1 = 1: VTAB 18: PRINT "ENTER THE TOTAL NO OF READINGS :";:
     INPUT N1:N1 = N1 + DAZ: IF N1 < 1 OR N1 > 500 THEN  CALL H: GOTO 117
    30
11740  VTAB 20: INPUT "TIME INTERVAL (S) :";TD: IF TD < 2.2 OR TD > 84000
     THEN  CALL H: GOTO 11740
11750 TI = 2 / PS(19)
11760  IF PS(19) >  = 10 THEN 11780
11770 TI = TI * (10 ^ PS(15)) + 0.3: GOTO 11860
11780  IF PS(19) >  = 100 THEN 11820
11790  ON PS(15) + 1 GOTO 11800,11840,11850,11810
11800 TI =  INT (.1 / TI + 1) * TI + 1: GOTO 11860
11810 TI = 201: GOTO 11860
11820  ON PS(15) + 1 GOTO 11830,11840,11850,11850
11830 TI = 2.2: GOTO 11860
11840 TI = 3: GOTO 11860
11850 TI = 21
11860 TD = TD - TI: IF TD < 0 THEN  PRINT : PRINT "DELAY < MEASUREMENT TI
    ME ": CALL H: GOTO 11740
11870 T1 = TD * 16124:T6 = 256
11880 T2 = T1 -  INT (T1 / T6) * T6:T1 =  INT (T1 / T6)
11890 T3 = T1 -  INT (T1 / T6) * T6:T1 =  INT (T1 / T6)
11900 T4 = T1 -  INT (T1 / T6) * T6:T1 =  INT (T1 / T6)
11910 T5 = T1 -  INT (T1 / T6) * T6
11920  HOME : VTAB 2: HTAB 9: INVERSE : PRINT "COMPARISON RESISTANCE": NORMAL

11922  VTAB 4: INPUT "ENTER CMR VALUE :";CR$:CR =  VAL (CR$): IF CR < 1 OR
    CR > 10000000 THEN  CALL H: GOTO 11920
11930 RS = 1: VTAB 6: INPUT "SUBTRACT FROM REAL   :";Q$: IF Q$ = "N" THEN
    RS = 0
12004  VTAB 12: INPUT "REVIEW SETTINGS ? :";Q$: IF Q$ = "Y" THEN  GOSUB 1
    2940: GOTO 12010
12006  IF Q$ = "N" OR Q$ = "" THEN 12010
12008  CALL H: GOTO 12004
12010  VTAB 14: IF SR = 1 THEN  PRINT : HOME : VTAB 4
12014  INVERSE : PRINT "ALTER SETTINGS :": NORMAL : PRINT : PRINT "1: GEN
    ERATOR ONLY": PRINT : PRINT "2: ALL": PRINT : PRINT "3: NONE": PRINT
    : PRINT RR$;: INPUT ":";Q$
12016 Q =  VAL (Q$): IF Q < 1 OR Q > 3 OR Q <  >  INT (Q) THEN  CALL H: GOTO
    12010
12018  HOME : ON Q GOTO 11310,10560,12026
12026 DA(2,0) = G1
12028 DD = 0:SR = 0:A1$ = "":B1$ = "":C1$ = "":D1$ = "":F1$ = "":G2$ = ""
    :H1$ = "":I1$ = "":J1$ = "":K1$ = "":L1$ = "":M1$ = "":N1$ = "":O1$ =
    "":E4$ = "":FF =  FRE (0):B1$ = B$
12030  HOME : VTAB 12: PRINT  TAB( 6): INVERSE : PRINT "LOADING DATA COLL
    ECTION PROGRAM": NORMAL : PRINT CD$;"BLOAD CHAIN,A520,D1"
12040  CALL 520"DCOLLECT.V3"
12050 ER =  PEEK (222):EN =  PEEK (218) +  PEEK (219) * 256
12060  IF ER = 6 THEN EM$ = "FILE NOT FOUND"
12080  IF ER = 4 THEN EM$ = "WRITE PROTECTED DISC"
12084  IF ER = 7 THEN EM$ = "VOLUME NO. MISMATCH"
12090  IF ER = 8 THEN EM$ = "I/O ERROR "
12100  IF ER = 9 THEN EM$ = "DISK IS FULL"
12101  IF ER = 10 THEN EM$ = "FILE ALREADY EXISTS"
12106  IF ER = 13 THEN EM$ = "FILE TYPE MISMATCH"
12120  IF ER = 254 THEN EM$ = "BAD INPUT RESPONSE"
12128  IF DE <  > 1 THEN 12132
12129  IF ER = 6 THEN DT = 1: RESUME
12130  VTAB 23: PRINT  TAB( 40): IF CA <  > 1 THEN  PRINT : VTAB 3
12131  IF ER = 4 OR ER = 8 OR ER = 9 OR ER = 10 OR ER = 7 OR ER = 13 OR E
    R = 254 THEN  CALL H:TB = 20 - ( INT ( LEN (EM$) / 2)): HTAB TB: FLASH
    : PRINT EM$: FOR I = 1 TO 3000: NEXT I: NORMAL :CA = 0: GOTO 10240
12132  IF DP <  > 1 THEN 12136
12133  IF ER = 10 THEN 11270
12134  VTAB 23: PRINT  TAB( 40): IF CA <  > 1 THEN  PRINT : VTAB 3
12135  IF ER = 4 OR ER = 6 OR ER = 7 OR ER = 8 OR ER = 9 OR ER = 13 OR ER
    = 254 THEN  CALL H:TB = 20 - ( INT ( LEN (EM$) / 2)): HTAB TB: FLASH
    : PRINT EM$: FOR I = 1 TO 3000: NEXT I: NORMAL :CA = 0: GOTO 11190
12136  IF DD <  > 1 THEN 12140
12138  VTAB 23: PRINT  TAB( 40): IF CA <  > 1 THEN  PRINT : VTAB 3
12139  IF ER = 4 OR ER = 6 OR ER = 7 OR ER = 8 OR ER = 9 OR ER = 13 OR ER
    = 254 THEN  CALL H: VTAB 3:TB = 20 - ( INT ( LEN (EM$) / 2)): HTAB T
    B: FLASH : PRINT EM$: FOR I = 1 TO 3000: NEXT I: NORMAL :CA = 0: GOTO
    10952
12140  IF ER = 255 THEN  NORMAL : STOP : RESUME
12150  TEXT : PRINT E3$: PRINT "@?2"; CHR$ (1);":": PRINT E1$: PRINT E2$:
    HOME
12152 TB = 20 - ( INT ( LEN (EM$) / 2)): VTAB 8: HTAB TB: FLASH : PRINT E
    M$: NORMAL
12160  VTAB 12: HTAB 14: INVERSE : PRINT "ERROR NO. ";ER;" HAS OCCURED": NORMAL
12162  VTAB 13: HTAB 16: INVERSE : PRINT "IN LINE ";EN: NORMAL
12164  STOP
12200  REM  MOS  STORE READ
12210  PRINT E3$: PRINT "@?2"
12220  ON AA% - 15 GOTO 12250,12260,12270,12280,12290
12230  ON AA% - 20 GOTO 12320,12350,12380,12410
12240  PRINT ":'T3;'": GOSUB 12610: GOSUB 12520:W1 = P: GOTO 12500
12250  PRINT ":'T3F'": GOTO 12470
12260  PRINT ":'T3N'": GOTO 12470
12270  PRINT ":'T36'": GOTO 12470
12280  PRINT ":'T37'": GOTO 12470
12290  PRINT ":'T3G'": GOSUB 12610:W1 = P * 10 ^ ( - 5 + (R - ( INT (R /
    10) * 10))): IF W1 < 0.01 THEN W1 = 0.01
12300  IF W1 > 9.99 THEN W1 = 9.99
12310  GOTO 12500
12320  PRINT ":'T33'": GOSUB 12610:W1 = P / 1000: IF W1 < 0.01 THEN W1 =
    0.01
12330  IF W1 > 9.99 THEN W1 = 9.99
12340  GOTO 12500
12350  PRINT ":'T3>'": GOSUB 12610:W1 = P * 10 ^ ((R - ( INT (R / 10) * 1
    0)) - 7): IF W1 < 1E - 7 THEN W1 = 1E - 7
12360  IF W1 > 999900 THEN W1 = 999900
12370  GOTO 12500
12380  PRINT ":'T37'": GOSUB 12610:W1 = P / 100: IF W1 < 0.2 THEN W1 = 0.
    2
12390  IF W1 > 99.99 THEN W1 = 99.99
12400  GOTO 12500
12410  PRINT ":'T3C'": GOSUB 12610:W3 =  INT ((R -  INT (R / 100) * 100) /
    10)
12420  IF W3 = 1 THEN P = P +  - 1
12430 W1 = P / 100: IF  ABS (W1) < 0.01 THEN W1 = 0.01: GOTO 12450
12440  IF  ABS (W1) > 9.99 THEN W1 = 9.99
12450  IF W3 = 1 THEN W1 = W1 +  - 1
12460  GOTO 12500
12470  GOSUB 12610: GOSUB 12510:W1 = P
12480  IF W1 < 1E - 4 THEN W1 = 1E - 4
12490  IF W1 > 999900 THEN W1 = 999900
12500  PRINT E1$: PRINT E2$: RETURN
```

```
12510 MM = 1
12520 W2 = ((P * 100) +  INT (R / 100)) / 100000
12530  IF MM = 1 THEN 12560
12540 W3 =  INT ((R -  INT (R / 100) * 100) / 10)
12550  IF W3 = 1 OR W3 = 5 THEN W2 = W2 *  - 1
12560 P = W2 * 10 ^ ((R - ( INT (R / 10) * 10)) - 4):MM = 0: RETURN
12570  REM  LATCH STORE READ
12580  PRINT E3$: PRINT "@?2;'T4"; CHR$ (AAZ + 48);"'": PRINT "@"; CHR$ (
    95);"R;"
12590  INPUT LV:PS(AAZ) = LV
12600  PRINT CD$;"PR#0": PRINT CD$;"IN#0": RETURN
12610  PRINT "@"; CHR$ (95);"R;": PRINT E2$: INPUT P,R$:R =  VAL (R$): PRINT
    E3$: RETURN
12620  PRINT "@"; CHR$ (95);"R;": PRINT E2$: INPUT P: PRINT E3$: RETURN
12630  REM  LATCH STORE WRITE
12640  PRINT E3$: PRINT "@?2"
12650  FOR K = 1 TO 15
12660  IF K = 5 OR K = 10 THEN 12680
12670 AAZ = K:S1$ =  CHR$ (48 + AAZ):S2 = PS(AAZ):SS$ = ";'T2" + S1$ +  STR$
    (S2) + "'": PRINT SS$
12680  NEXT K
12690 U3 = 6:U4 = 4:X = 16:MA$ = "F": GOSUB 12880
12700 MA$ = "N": GOSUB 12880:MA$ = "6": GOSUB 12880:MA$ = "7": GOSUB 1288
    0:X = 22
12710 MA$ = ">": GOSUB 12880:X = 20
12720 U3 = 5:U4 = 3:MA$ = "G0": IF PS(20) = 0 THEN MA$ = "G"
12730  GOSUB 12880
12740 MA$ = "3": IF PS(21) = 0 THEN  GOSUB 12880: GOTO 12790
12750 U1 =  INT ( LOG (PS(21)) /  LOG (10) + 1E - 6)
12760 U2 =  INT (PS(21) * 10 ^ 3) * 10 ^ 4: IF U2 = 0 THEN U2 = 1E - 6
12770 U2$ = "": IF U1 <  > 0 THEN  FOR K = 1 TO  ABS (U1):U2$ = U2$ + "0"
    : NEXT K
12780 U2$ = U2$ +  STR$ (U2): GOSUB 12920
12790 MA$ = "?": IF PS(23) = 0 THEN  GOSUB 12880: GOTO 12840
12800 U2$ =  STR$ (PS(23) * 10 ^ 6)
12810  IF  LEN (U2$) = 6 THEN U2$ = "00" + U2$
12820  IF  LEN (U2$) = 7 THEN U2$ = "0" + U2$
12830  GOSUB 12920
12840 MA$ = "C":X = 24: IF PS(24) = 0 THEN  GOSUB 12880: GOTO 12870
12850 MA$ = "C0":U4$ = "00": IF PS(24) < 0 THEN U4$ = "10"
12860 U2$ =  STR$ ( ABS (PS(24)) * 10 ^ 4) + U4$: GOSUB 12920
12870  PRINT CD$;"PR#0": PRINT CD$;"IN#0": RETURN
12880  IF PS(X) = 0 THEN U2$ = "00000000": GOTO 12920
12890 U1 =  INT ( LOG (PS(X)) /  LOG (10) + 1E - 6)
12900 U2 =  INT (PS(X) * 10 ^ (U3 - U1))
12910 U2$ =  STR$ (U2) +  STR$ (U1 + U4):X = X + 1
12920  PRINT ";'T1";MA$;U2$;"'"
12930  RETURN
12940  REM  REVIEW SETTINGS
12950 SR = 1: HOME : PRINT  TAB( 11): INVERSE : PRINT "1174 SETTINGS": NORMAL
    : PRINT : PRINT "DATA ORIGIN",: IF DD = 1 THEN  PRINT ": DISK": GOTO
    12970
12960  PRINT ": 1174"
12970  PRINT "INT. TIME",: IF PS(15) = 0 THEN  PRINT ": MIN": GOTO 12990
12980 IT = 10 ^ PS(15): PRINT ": ";IT
12990  PRINT "MEAS. DELAY",: IF PS(14) = 0 THEN  PRINT ": 1 SEC": GOTO 13
    010
13000 MD = 10 ^ (PS(14) - 1): PRINT ": ";MD
13010  PRINT "INPUT REJECT",: IF PS(2) = 3 THEN  PRINT ": ON": GOTO 13030

13020  PRINT ": OFF"
13030  PRINT "MODE",: IF PS(12) = 1 THEN  PRINT ": X": GOTO 13060
13040  IF PS(12) = 2 THEN  PRINT ": Y": GOTO 13060
13050  PRINT ": Y/X"
13060  PRINT "INP. RANGE",: IF PS(9) < 8 THEN IR = 10 ^ (PS(9) - 4): PRINT
    ":";IR
13070  PRINT ": AUTORANGING"
13080  PRINT "V OUT",": ";PS(20)
13082  PRINT "COMP. RES.",": ";CR
13083  PRINT : PRINT "GENERATOR: ";: IF P6 <  > 0 THEN  PRINT " SINGLE FR
    EQUENCY": PRINT : GOTO 13091
13085  IF PS(7) = 4 THEN  PRINT "LOG ";: GOTO 13088
13086  IF PS(7) = 0 THEN  PRINT "LIN ";: GOTO 13088
13087  CALL H: STOP
13088  PRINT "SWEEP": PRINT : PRINT " DIRECTION: ";: IF PS(8) = 3 THEN  PRINT
    "DOWN": GOTO 13091
13089  IF PS(8) = 2 THEN  PRINT "UP": GOTO 13091
13090  CALL H: STOP
13091  IF P6 <  > 0 THEN  PRINT "FREQUENCY : ";PS(17): PRINT : GOTO 13096

13092  PRINT " F MAX    : ";PS(16): PRINT " F MIN    : ";PS(17): PRINT "
    DELTA F  : ";: IF PS(7) = 4 THEN  PRINT PS(23): GOTO 13094
13093  PRINT PS(22)
13094  IF P6 = 0 THEN  PRINT " ";RNZ;" RUN";: IF RNZ > 1 THEN  PRINT "S W
    ITH ";TD / 60;" MINUTE DELAY"
13095  IF P6 = 0 THEN 13098
13096  PRINT N1;" READINGS WITH ";TD;" SECOND DELAY"
13098  PRINT : PRINT : INPUT "PRESS RETURN TO CONTINUE :";Q$: HOME
13099  RETURN
13100  REM  INITIALISATION
13110  PRINT E3$: PRINT "@?2";CD$;":": PRINT "@?2"; CHR$ (1);":": PRINT E
    1$: PRINT E2$: RETURN
13200  REM  DATA FILE LOAD REVIEW
13210  HOME : VTAB 2: HTAB 12: INVERSE : PRINT "LOADED DATA REVIEW": NORMAL
    : VTAB 4
13212 TB = 2
13214  PRINT  TAB( TB);"FILENAME",":";FF$
13220  PRINT  TAB( TB);"OPERATOR",":";A1$
13230  PRINT  TAB( TB);"RUN NO.",":";C1$
13240  PRINT  TAB( TB);"DATE",":";D1$
13250  PRINT  TAB( TB);"TEMPERATURE",":";E4$
13260  PRINT  TAB( TB);"PRESSURE",":";F1$
13280  PRINT  TAB( TB);"MEMBRANE NO.",":";G2$
13300  PRINT  TAB( TB);"SOLUTION 1",":";H1$
13310  PRINT  TAB( TB);"SOLUTION 2",":";I1$
13330  PRINT  TAB(  STORE B);"ELECTRODES",":";J1$
13340  PRINT  TAB( TB);"AREA (CM2)",":";DA(2,0)
13360  PRINT : PRINT K1$: PRINT L1$: PRINT M1$: PRINT N1$: PRINT O1$
13370  INPUT "PRESS RETURN TO CONTINUE :";Q$: HOME : VTAB 2: HTAB 12: INVERSE
    : PRINT "LOADED DATA REVIEW": NORMAL : VTAB 4: PRINT  TAB( TB);"FILEN
    AME",":";FF$
13380  PRINT  TAB( TB);"INPUT CHANNEL",":";: IF PS(12) = 1 THEN  PRINT "X
    "
13382  IF PS(12) = 2 THEN  PRINT "Y"
13384  IF PS(12) = 3 THEN  PRINT "Y/X"
13390  PRINT : PRINT  TAB( TB);"DISPLAY MODE",":";: IF PS(13) = 0 THEN  PRINT
    "R,THETA"
13392  IF PS(13) = 1 THEN  PRINT "A,B"
13394  IF PS(13) = 2 THEN  PRINT "LOG R, THETA"
13500  VTAB 12: INPUT "LIST DATA ?:";Q$: IF Q$ = "N" OR Q$ = "" THEN 1360
    0
13510  IF Q$ <  > "Y" THEN  CALL H: GOTO 13500
13520  VTAB 14: INPUT "LIST ON E(PSON) OR V(DU) ?: ";Q$: IF Q$ <  > "E" THEN
     PRINT  CHR$ (12): GOTO 13570
13530  PRINT  CHR$ (4);"PR#1": POKE 1657,96
13540  PRINT "Filename : ";FF$: PRINT : PRINT
13570  HTAB 2: INVERSE : PRINT "FREQUENCY";: NORMAL : HTAB 20: INVERSE : PRINT
    "X";: NORMAL : HTAB 34: INVERSE : PRINT "Y": NORMAL : PRINT
13575  FOR CC = 1 TO DAZ
13580  CALL 34644:DA(0,CC);E4,"    ",DA(1,CC);E4,"    ",DA(2,CC), CHR$ (1
    3);
13581  IF Q$ = "E" THEN 13584
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13582  IF  INT (CC / 18) = CC / 18 THEN  PRINT : INPUT "PRESS RETURN TO C
   ONTINUE :";CC$: HOME : PRINT  CHR$ (12): HTAB 2: INVERSE : PRINT "FRE
   QUENCY";: NORMAL : HTAB 20: INVERSE : PRINT "I";: NORMAL : HTAB 34: INVERSE
   : PRINT "Y": NORMAL
13584  NEXT CC
13590  PRINT : PRINT  TAB( TB);"CHR",":";CR
13592  PRINT  TAB( TB);"FREQ. MAX.",":";PS(16);"HZ"
13594  PRINT  TAB( TB);"FREQ. MIN.",":";PS(17);"HZ"
13596  PRINT  TAB( TB);"SEMI. MAX.",":";0;"HZ"
13597  PRINT : PRINT DAI;" POINTS IN FILE": IF Q$ = "E" THEN  PRINT  CHR$
   (12)
13598  PRINT  CHR$ (4);"PR#0": PRINT : INPUT "PRESS RETURN TO CONTINUE PR
   OGRAM :";Q$
13600  RETURN
14000 N2 = N2 + 1:B$ = B$ + " (+" +  STR$ (N2) + ")": GOTO 10550
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DCollect

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2  ONERR  GOTO 3386
4  CALL 38048
6  POKE 232,104: POKE 233,142
8 H = 37984:CD$ = ""
10  SCALE= 1: ROT= 0: HCOLOR= 3
12 E3$ = CD$ + "PR#3":E2$ = CD$ + "PR#0":E1$ = CD$ + "IN#0"
14  HGR2 : TEXT
15  POKE 222,0: POKE 218,0: POKE 219,0
17  PRINT  CHR$ (4);"FR#1": PRINT  CHR$ (4);"PR#0"
18  GOSUB 3402
20  HOME : VTAB 12: HTAB 14: PRINT "SETTING FRA"
22  GOSUB 100: REM  WRITE PARAMS
23  HOME : VTAB 8: HTAB 5: INVERSE : PRINT "FRA COLLECTING FIRST DATA POI
    NT": NORMAL : VTAB 10: HTAB 6: PRINT "CTRL-T = NUMERIC DATA DISPLAY"
24  VTAB 12: HTAB 6: PRINT "CTRL-P = GRAPHICS PLOT": VTAB 14: HTAB 6: PRINT
    "DEFAULT IS REAL-TIME GRAPHICS"
26  PRINT E3$
28  GOSUB 460
30 DA(1,0) = DAZ:NO = NO + 1
32  TEXT : HOME : VTAB 12: PRINT  TAB( 15): INVERSE : PRINT "SAVING DATA"
    : NORMAL
34  IF Z1 = 1 OR P6 <  > 0 THEN 38
36 B$ = B1$ +  STR$ (NO)
38  IF DA(0,0) <  > 0 THEN 50
40  FOR J = 1 TO DA(1,0)
42  IF DA(0,J) < .1 THEN 46
44  IF DA(2,J) > D1 THEN D1 = DA(2,J):D = DA(0,J)
46  NEXT J
48 PS(1) = DA(1,0)
50  PRINT CD$;"OPEND";B$;",D2"
52  PRINT CD$;"WRITED";B$
54  FOR L = 0 TO 24: PRINT PS(L): NEXT L
56  PRINT A$: PRINT C$: PRINT D$: PRINT E$: PRINT F$
58  PRINT G$: PRINT H$: PRINT I$: PRINT J$
60  PRINT K$: PRINT L$: PRINT M$: PRINT N$: PRINT O$
62  PRINT CR: PRINT D
64  PRINT CD$;"CLOSE"
66  PRINT CD$;"LOCKD";B$: PRINT CD$
68  POKE 29,68: POKE 30,65: CALL 38144
70  PRINT CD$;"BSAVE";B$;",A"; PEEK (27) +  PEEK (28) * 256 + 9;",L";15 *
    (DA(1,0) + 1);",D2"
72  PRINT CD$;"LOCK";B$
74  IF NO >  = RNZ OR ER = 107 THEN 90
76  REM  TIME DELAY
78  GOSUB 3402: HOME : GOSUB 3406
80  HOME : VTAB 6: HTAB 13: INVERSE : PRINT "OPERATOR :";A$: NORMAL
82  VTAB 9: HTAB 12: INVERSE : PRINT "NEXT RUN = NO.:";NO + 1: NORMAL
84  VTAB 12: HTAB 9: INVERSE
86  PRINT "EXECUTING";: NORMAL : PRINT TD / 60;: INVERSE : PRINT "MINUTE
    DELAY": NORMAL
88  GOSUB 3418: GOTO 14
90 CD$ =  CHR$ (4)
92 NO = 0:Z1 = 1: PRINT E3$: PRINT "@72"; CHR$ (1);":": PRINT E2$: PRINT
    E1$
94  VTAB 12: HTAB 9: INVERSE : PRINT "MEASUREMENTS  COMPLETED": NORMAL
96  PRINT CD$;"BLOADCHAIN,D1,A520"
98  CALL 520"START-UP.V3"
100  REM
102  PRINT E3$: PRINT "@72"
104  FOR K = 1 TO 15
106  IF K = 5 OR K = 10 THEN 110
108 AAZ = K:S1$ =  CHR$ (48 + AAZ):S2 = PS(AAZ):SS$ = ":'T2" + S1$ +  STR$
    (S2) + "'": PRINT SS$
110  NEXT K
112 U3 = 6:U4 = 4:X = 16:MA$ = "F": GOSUB 150
114 MA$ = "N": GOSUB 150:MA$ = "6": GOSUB 150:MA$ = "7": GOSUB 150:X = 22

116 MA$ = ")": GOSUB 150:X = 20
118 U3 = 5:U4 = 3:MA$ = "60": IF PS(20) = 0 THEN MA$ = "6"
120  GOSUB 150
122 MA$ = "3": IF PS(21) = 0 THEN  GOSUB 150: GOTO 132
124 U1 =  INT ( LOG (PS(21)) /  LOG (10) + 1E - 6)
126 U2 =  INT (PS(21) * 10 ^ 3) * 10 ^ 4: IF U2 = 0 THEN U2 = 1E - 6
128 U2$ = "": IF U1 <  > 0 THEN  FOR K = 1 TO  ABS (U1):U2$ = U2$ + "0": NEXT
    K
130 U2$ = U2$ +  STR$ (U2): GOSUB 158
132 MA$ = "7": IF PS(23) = 0 THEN  GOSUB 150: GOTO 142
134 U2$ =  STR$ (PS(23) * 10 ^ 6)
136  IF  LEN (U2$) = 6 THEN U2$ = "00" + U2$
138  IF  LEN (U2$) = 7 THEN U2$ = "0" + U2$
140  GOSUB 158
142 MA$ = "C":X = 24: IF PS(24) = 0 THEN  GOSUB 150: GOTO 148
144 MA$ = "C0":U4$ = "00": IF PS(24) < 0 THEN U4$ = "10"
146 U2$ =  STR$ ( ABS (PS(24)) * 10 ^ 4) + U4$: GOSUB 158
148  PRINT CD$;"PR#0": PRINT CD$;"IN#0": RETURN
150  IF PS(X) = 0 THEN U2$ = "00000000": GOTO 158
152 U1 =  INT ( LOG (PS(X)) /  LOG (10) + 1E - 6)
154 U2 =  INT (PS(X) * 10 ^ (U3 - U1))
156 U2$ =  STR$ (U2) +  STR$ (U1 + U4):X = X + 1
158  PRINT ":'T1";MA$;U2$;"'"
160  RETURN
460  REM
470 TT$ = "@" +  CHR$ (95) + "R:"
480  PRINT  CHR$ (4);"PR#3": PRINT "@72:'T4('": PRINT TT$
490  PRINT  CHR$ (4);"PR#0": VTAB 1: HTAB 38: INPUT IC$:IC =  VAL (IC$)
500  PRINT  CHR$ (4);"PR#3": PRINT "@72:'T4='": PRINT TT$
510  PRINT  CHR$ (4);"PR#0": VTAB 1: HTAB 38: INPUT DM$:DM =  VAL (DM$)
520  IF IC <  > 1 AND IC <  > 2 AND IC <  > 3 THEN EM$ = "INPUT CHANNEL E
    RROR":EN = 520: GOTO 3400
524  IF DM <  > 0 AND DM <  > 1 AND DM <  > 2 THEN EM$ = "DISPLAY MODE ER
    ROR":EN = 524: GOTO 3400
530  ON DM GOTO 540,550
532 T2$ = "THET/DEG":T3$ = "THET/RAD"
534  IF IC = 1 THEN A1$ = "H":A2$ = "L":TI$ = "R & THETA (X) INPUT":T1$ =
    "R/MV (X)"
536  IF IC = 2 THEN A1$ = "0":A2$ = "4":TI$ = "R & THETA (Y) INPUT":T1$ =
    "R/MV (Y)"
538  IF IC = 3 THEN A1$ = "8":A2$ = "(":TI$ = "R & THETA (Y/X) INPUT":T1$
     = " R (Y/X)"
539  GOTO 570
540 T3$ = "": IF IC = 1 THEN A1$ = "I":A2$ = "M":TI$ = "A & B (X) INPUT":
    T1$ = " A/MV (X)":T2$ = " B/MV (X)"
542  IF IC = 2 THEN A1$ = "1":A2$ = "5":TI$ = "A & B (Y) INPUT":T1$ = " A
    /MV (Y)":T2$ = " B/MV (Y)"
546  IF IC = 3 THEN A1$ = "9":A2$ = "=":TI$ = "A & B (Y/X) INPUT":T1$ = "
     Z'/OHMS ":T2$ = " Z''/OHMS"
548  GOTO 570
550 T1$ = "LOGR /DB":T2$ = "THET/DEG":T3$ = "THET/RAD": IF IC = 1 THEN A1
    $ = "J":A2$ = "L":TI$ = "LOGR & THETA (X) INPUT"
552  IF IC = 2 THEN A1$ = "2":A2$ = "4":TI$ = "LOGR & THETA (Y) INPUT"
554  IF IC = 3 THEN A1$ = ":":A2$ = "(":TI$ = "LOGR & THETA (Y/X) INPUT"
556  GOTO 570
570  CALL 38048
572  POKE 232,104: POKE 233,142
575 DAZ = DAZ + 1: PRINT E3$
580  PRINT "@72:'S111T2;0T2;2'": PRINT "@72"; CHR$ (1)
582  IF  PEEK ( - 16384) - 128 = 20 THEN  POKE  - 16368,0: TEXT
584  IF  PEEK ( - 16384) - 128 = 16 THEN  POKE  - 16368,0: POKE  - 16297,
    0: POKE  - 16304,0: POKE  - 16299,0
590 QQ =  PEEK (49331): IF  PEEK (49331) < 64 THEN 582
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600  GOSUB 2200
610  PRINT E3$: PRINT "@72;'T48'": GOSUB 3082
620  IF P = 1 THEN  GOSUB 3422: GOTO 580
630  IF DAZ >  = 500 THEN P = 0
640  PRINT "@72;'S111T2;0T2;2'": PRINT "@72"; CHR$ (1)
644  IF DAZ = 1 THEN EX =  - TD
646  IF DAZ = 2 THEN EX = 2 *  - TD
648  IF DAZ = 3 THEN EX = EX + 21
650  IF P6 <  > 0 THEN DA(0,DAZ) = DAZ * (TD + TI) + EX
660  ON DM + 1 GOTO 1030,1340,1840
680  IF P6 = 0 OR IC <  > 3 THEN 710
690  IF DAZ >  = N1 THEN 720
700  GOSUB 3418
710  IF P <  > 0 THEN DAZ = DAZ + 1: GOTO 582
720  PRINT "@72;'T2;0'"
730  PRINT E2$: PRINT E1$
740  RETURN
1020  REM  R & THETA
1030  PRINT E2$
1040  IF DAZ = 1 THEN  PRINT : HOME
1060 EE = I2 -  INT (I2 / 10) * 10
1070 DD =  INT (I2 / 100):SB = (I2 - 100 * DD - EE) / 10
1080 DA(1,DAZ) = (I1 / 1000 + DD / 100000) * 10 ^ (EE - 4)
1100  IF SB = 1 OR SB = 5 THEN DA(1,DAZ) =  - 1 * DA(1,DAZ)
1110  IF IC <  > 3 THEN DA(1,DAZ) = DA(1,DAZ) * 1000
1130 DA(2,DAZ) = I3 / 10
1140  IF DAZ = 1 OR (DAZ - RD) / 18 =  INT ((DAZ - RD) / 18) THEN  GOSUB
   6000: PRINT : GOSUB 6040
1150  IF DAZ >  = 18 OR RD <  > 0 THEN 1170
1160  VTAB (4 + DAZ - RD - ( INT ((DAZ - RD) / 18) * 18)): GOTO 1180
1170  VTAB (5 + DAZ - RD - ( INT ((DAZ - RD) / 18) * 18))
1180  CALL 34644:DA(0,DAZ);E3,DA(1,DAZ),DA(2,DAZ),I4 / 1000, CHR$ (13):
1200  PRINT E3$: GOTO 680
1340  REM  A & B INPUT
1350  PRINT E2$
1500  IF DAZ = 1 THEN  PRINT : HOME
1520 EE =  - 5 + (I2 - ( INT (I2 / 10) * 10)) - 4
1540 SB =  INT (I2 / 10):SB = SB - ( INT (SB / 10) * 10): IF SB > 3 THEN
   DA(1,DAZ) = 10E20: GOTO 1600
1560 DA(1,DAZ) = ((I1 * 100) +  INT (I2 / 100)) * 10 ^ EE
1570  IF IC <  > 3 THEN CR = 1000:RS = 0
1580 DA(1,DAZ) = DA(1,DAZ) * CR: IF RS = 1 THEN DA(1,DAZ) = DA(1,DAZ) - C
   R
1600  IF SB = 1 OR SB = 5 THEN DA(1,DAZ) = DA(1,DAZ) *  - 1
1620 EE =  - 5 + (I4 - ( INT (I4 / 10) * 10)) - 4
1640 SB =  INT (I4 / 10):SB = SB - ( INT (SB / 10) * 10): IF SB > 3 THEN
   DA(2,DAZ) = 10E20: GOTO 1700
1660 DA(2,DAZ) = ((I3 * 100) +  INT (I4 / 100)) * 10 ^ EE
1680 DA(2,DAZ) = DA(2,DAZ) * CR
1700  IF SB = 1 OR SB = 5 THEN DA(2,DAZ) = DA(2,DAZ) *  - 1
1702 DA(2,DAZ) = DA(2,DAZ) *  - 1
1708  IF DAZ = 1 OR (DAZ - RD) / 18 =  INT ((DAZ - RD) / 18) THEN  GOSUB
   6000: PRINT : GOSUB 6040
1716  IF DAZ >  = 18 OR RD <  > 0 THEN 1732
1724  VTAB (4 + DAZ - RD - ( INT ((DAZ - RD) / 18) * 18)): GOTO 1740
1732  VTAB (5 + DAZ - RD - ( INT ((DAZ - RD) / 18) * 18))
1740  CALL 34644:"  ",DA(0,DAZ);E4," ",DA(1,DAZ)," ",DA(2,DAZ), CHR$ (1
   3):
1745  IF IC = 3 THEN  GOSUB 3084
1750  PRINT E3$: GOTO 680
1840  REM  LOGR & THETA INPUT
1850  PRINT E2$
2020 DD =  INT (I2 / 100):SB =  INT (I2 - D1 * 100) / 10
2030 : IF SB = 4 THEN DA(1,DAZ) = 10E20: GOTO 2100
2040  IF SB = 5 THEN DA(1,DAZ) =  - 10E20: GOTO 2100
2060 DA(1,DAZ) = (I1 / 10) +  INT (I2 / 100) / 1000
2080  IF SB = 1 THEN DA(1,DAZ) =  - 1 * DA(1,DAZ)
2100 DA(2,DAZ) = I3 / 10
2108  IF DAZ = 1 OR (DAZ - RD) / 18 =  INT ((DAZ - RD) / 18) THEN  GOSUB
   6000: PRINT : GOSUB 6040
2116  IF DAZ >  = 18 OR RD <  > 0 THEN 2132
2124  VTAB (4 + DAZ - RD - ( INT ((DAZ - RD) / 18) * 18)): GOTO 2140
2132  VTAB (5 + DAZ - RD - ( INT ((DAZ - RD) / 18) * 18))
2140  CALL 34644:DA(0,DAZ);E3,DA(1,DAZ),DA(2,DAZ),I4 / 1000, CHR$ (13):
2150  PRINT E3$: GOTO 680
2240  REM READ DATA
2280  PRINT "@72;'T37'": PRINT TT$: PRINT E2$: VTAB 1: INPUT F1$,F2$: PRINT
   E3$: PRINT "@72;'T3K'": PRINT TT$: PRINT E2$: VTAB 1: INPUT F3$,F4$
2300 F1 =  VAL (F1$):F2 =  VAL (F2$)
2320 DA(0,DAZ) = (F1 / 1000) * 10 ^ (F2 - ( INT (F2 / 10) * 10) - 4): IF
   DA(0,DAZ) < 50.5 AND DA(0,DAZ) > 49.5 THEN DAZ = DAZ - 1
2340 LF =  VAL (F3$) + ( VAL (F4$) / 1000) - 4
2360 M1$ = "@72;'T3" + A1$ + "'":M2$ = "@72;'T3" + A2$ + "'"
2380  PRINT E3$: PRINT M1$: PRINT TT$: PRINT E2$: VTAB 1: INPUT I1$,I2$
2400  PRINT E3$: PRINT M2$: PRINT TT$: PRINT E2$: VTAB 1: INPUT I3$,I4$
2420 I1 =  VAL (I1$):I2 =  VAL (I2$):I3 =  VAL (I3$):I4 =  VAL (I4$)
2440  RETURN
3080  PRINT TT$: PRINT E2$: VTAB 1: INPUT P,R$:R =  VAL (R$): PRINT E3$: RETURN
                              ..
3082  PRINT TT$: PRINT E2$: VTAB 1: INPUT P: PRINT E3$: RETURN
3084  REM  REAL-TIME PLOTTING
3086  SCALE= 1: ROT= 0: HCOLOR= 3
3088  PRINT E2$
3089  POKE 232,104: POKE 233,142
3090  IF DA(1,0) + 1 = DAZ AND NO > 0 THEN  GOSUB 3117: GOTO 3094
3092  IF DA(1,0) + 1 = DAZ THEN  GOSUB 3110
3094  ON P6 + 1 GOTO 3096,3098,3100,3102
3096 X = DA(1,DAZ) * S3 + 40 + M8 * PU:Y = 167 - M4 * PU - DA(2,DAZ) * S3
   : GOTO 3104
3098 X = DA(0,DAZ) * S4 + 40:Y = 167 - DA(1,DAZ) * S3 + (M4 - 1) * YP: GOTO
   3104
3100 X = DA(0,DAZ) * S4 + 40:Y = 167 - DA(2,DAZ) * S3 + (M4 - M5) * YP: GOTO
   3104
3102 X = DA(0,DAZ) * S4 + 40:Y = 167 - S3 / (DA(2,DAZ) * W) + (M4 - 1) *
   YP
3104  IF X < 2 OR Y < 2 OR X > 278 OR Y > 189 THEN  GOSUB 3114
3106  IF P6 = 0 AND Q <  >  INT ( LOG (Q9 * DA(0,DAZ)) / 2.302585) THEN Q =
   INT ( LOG (Q9 * DA(0,DAZ)) / 2.302585): DRAW 4 AT X,Y
3108  HPLOT X,Y: PRINT E3$: RETURN
3110  CALL 38048
3112 Q9 = 1.011: IF PS(8) = 3 THEN Q9 = .99
3114 EX = EX + I3 + DAZ * .1:B2 = DA(2,1):B6 = DA(1,1)
3117  FOR L = 1 TO DAZ
3118  IF DA(1,L) > B1 THEN B1 = DA(1,L)
3120  IF DA(2,L) > B3 THEN B3 = DA(2,L)
3122  IF DA(2,L) < B2 THEN B2 = DA(2,L)
3124  IF DA(1,L) < B6 THEN B6 = DA(1,L)
3126  NEXT L
3128 B4 = ((TI + TD) * N1 + EX) * 1.15:B5 = B2: IF P6 = 1 THEN B3 = B1:B2
   = B6
3130  IF X > 278 THEN B1 = B1 * 1.4:B4 = B4 * 1.4
3132  IF Y < 2 AND B3 > 0 THEN B3 = B3 * 1.4
3134  IF Y < 2 AND B3 < 0 THEN B3 = B3 * .7
3136  IF Y > 189 AND B2 > 0 THEN B2 = B2 * .7
3138  IF Y > 189 AND B2 < 0 THEN B2 = B2 * 1.4
3140  IF B3 < 0 THEN B3 = 0
3142  IF P6 <  > 0 THEN 3242
3144  IF B3 < .4 * B1 THEN B3 = .5 * B1
3146  IF B2 > 0 THEN B2 = 0
3148  IF B6 > 0 THEN B6 = 0
3150  IF B1 < 0 THEN B1 = 0
3152 M1 = B3 - B2:M2 =  - B2 / M1:S1 = (B1 - B6) * 1.2:S5 = S1: IF S1 < .
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   3 * CR THEN S1 = .5 * CR:B1 = S1:S5 = B1: IF B4 < 0 THEN B4 =  - B1
3154  IF M1 / S5 * 23 > 16 THEN S1 = M1 * 1.2
3156 M6 =  INT ( LOG (S1) / 2.30258):S1 = S1 / 10 ^ M6: IF S1 < 1.95 THEN
   S2 = 2:P =  INT ((S1 + .2) / .4) * 2:M6 = M6 - 1: GOTO 3162
3158  IF S1 < 4.85 THEN S2 = 5:P =  INT (S1 + .5) * 2:M6 = M6 - 1: GOTO 3
   162
3160 S2 = 1:P =  INT (S1 + 1)
3162  IF P < 5 THEN P = P + 1
3164  IF M1 / S5 * 23 > 16 THEN PU =  INT (160 / P):M4 =  INT (P * M2 + .
   8):M3 = P - M4:R =  INT (230 / PU): HGR2 :M8 =  -  INT (B4 / S5 * R +
   .1):R = R - M8: GOTO 3168
3166 PU =  INT (230 / P):M3 =  INT (160 / PU):M4 =  INT (M3 * M2 + .8):M3
    = M3 - M4:R = P: HGR2 :M8 =  -  INT (B4 / S5 * R + .1):R = R - M8
3168  FOR J = 0 TO M3 + M4: HPLOT M8 * PU + 35,167 - J * PU TO 40 + M8 *
   PU,167 - J * PU: NEXT J
3170  HPLOT 40 + M8 * PU,167 TO 40 + M8 * PU,167 - (M3 + M4) * PU
3172  FOR J = 0 TO R + M8: HPLOT J * PU + 40,167 - M4 * PU TO J * PU + 40
   ,172 - M4 * PU: NEXT J
3174  HPLOT 40,167 - M4 * PU TO 40 + (R + M8) * PU,167 - M4 * PU:P$ = "IM
   PEDANCE PLOT":PX = 108:PY = 165 - (M4 + M3) * PU - PU: IF PY < 0 THEN
   PY = 0
3176  HPLOT PX - 2,PY + 9 TO PX + 98,PY + 9: GOSUB 3216
3178  FOR J =  - M8 TO R
3180  IF J = 0 AND M4 <  > 0 THEN 3188
3182 P$ =  STR$ (J * S2):PX = (J + M8) * PU + 38:PY = 174 - M4 * PU: IF J
    * S2 > 9 OR J * S2 < 0 THEN PX = PX - 3: IF J * S2 <  - 9 THEN PX =
   PX - 4
3186  GOSUB 3216
3188  NEXT J
3190  FOR J = 1 TO M4 + M3 + 1
3192 P$ =  STR$ ((J - 1 - M4) * S2):PY = 164 - (J - 1) * PU:PX = M8 * PU +
   34 -  LEN (P$) * 7
3194  IF M8 <  > 0 AND (J - 1 - M4) = 0 THEN 3198
3196  GOSUB 3216
3198  NEXT J
3200 P$ = "Z' /(OHMS) X 10" +  STR$ (M6):PX = 108:PY = 185: GOSUB 3216
3202 P$ = "Z''/(OHMS) X 10" +  STR$ (M6):PX = 149:PY = 2: ROT= 48:UP = 1:
    GOSUB 3216: ROT= 0:UP = 0
3204 S3 = PU / (S2 * 10 ^ M6)
3206  FOR L = 1 TO DAZ:X = DA(1,L) * S3 + M8 * PU + 40:Y = 167 - M4 * PU -
   DA(2,L) * S3
3208  IF Q <  >  INT ( LOG (Q9 * DA(0,L)) / 2.30258) THEN Q =  INT ( LOG
   (Q9 * DA(0,L)) / 2.30258): DRAW 4 AT X,Y
3210  HPLOT X,Y
3212  NEXT L
3214  RETURN
3216 RU = PX:P4 =  - 32
3218  FOR RR = 1 TO  LEN (P$)
3220 S =  ASC ( MID$ (P$,RR,1)): IF S >  = 128 THEN S = S - 128
3222  IF S = 32 THEN 3234
3224  IF S = 20 THEN P4 = 27: GOTO 3238
3226  IF PY < 0 THEN PY = 0
3228  IF UP = 1 THEN  DRAW S + P4 AT PY,RU:P4 =  - 32:RU = RU - 7: GOTO 3
   238
3230  IF S + P4 = 44 THEN RU = RU - 1
3232  DRAW S + P4 AT RU,PY:P4 =  - 32
3234 RU = RU + 7: IF UP = 1 THEN RU = RU - 14
3236  IF S + P4 = 44 THEN RU = RU - 1
3238  NEXT RR
3240  RETURN
3242  IF B3 = B2 THEN 3250
3244  IF DA(1,0) + 1 <  > DAZ THEN 3248
3246  IF B2 < 0 THEN B2 = 1.3 * B2
3248  IF B2 > 0 AND B2 < 0.35 * B3 THEN B2 = 0
3250 B1 = B4: IF P6 <  > 3 THEN 3256
3252  IF B2 < 0 THEN  PRINT E1$: PRINT E2$: HOME : PRINT "NEGATIVE VALUES
   OF I'' INVALIDATE COMPUTATION OF COL "; END
3254 B2 = 1 / (DA(0,0) * B3 * 6.2831852 * DA(2,0)):B3 = 1 / (DA(0,0) * B5
    * DA(2,0) * 6.2831852)
3256  IF B2 = B3 THEN B2 = .7 * B2:B3 = B3 * 1.3: IF B2 < 0 THEN B2 = B2 *
   1.86:B3 = B3 * .538
3258  IF P6 = 3 AND B2 < .35 * B3 THEN B2 = 0
3260 M1 = B3 - B2:M6 =  INT ( LOG (M1) / 2.30258):M1 = M1 / (10 ^ M6):M4 =
   1:S1 = .2:P = 6
3262  IF M1 > 1.18 THEN P = 8
3264  IF M1 > 1.58 THEN P = 4:S1 = .5
3266  IF M1 > 1.98 THEN P = 5
3268  IF M1 > 2.48 THEN P = 6
3270  IF M1 > 2.98 THEN P = 8
3272  IF M1 > 3.98 THEN S1 = 1:P =  INT (M1 * 1.5)
3274  IF M1 > 7.48 THEN S1 = 2:P = 5
3276  IF S1 <  = .5 THEN S1 = S1 * 10:M6 = M6 - 1
3278 M5 = 1: IF B2 < 0 THEN M5 =  INT (P *  - B2 / (B3 - B2)):M4 = 0
3280  IF B2 > .35 * B3 THEN P = P + 1
3282 M7 =  INT ( LOG (B1) / 2.30258):M2 = B1 / (10 ^ M7)
3284 S2 = .2:R = 6: IF M2 > 1.18 THEN R = 8
3286  IF M2 > 1.58 THEN R = 10
3288  IF M2 > 1.98 THEN R = 6:S2 = .5
3290  IF M2 > 3.98 THEN R = 10
3292  IF M2 > 4.98 THEN S2 = 1:R =  INT (M2) + 2: IF R = 11 THEN S2 = 2:R
    = 6
3294  IF S2 <  = .5 THEN S2 = S2 * 10:M7 = M7 - 1
3296 YP =  INT (160 / P):XR =  INT (230 / R): HGR2
3298  FOR J = 0 TO P: HPLOT 35,167 - J * YP TO 40,167 - J * YP: NEXT J
3300  IF B3 > 0 THEN  IF B2 / B3 > 0.35 THEN  HPLOT 40,167 TO 43,164 TO 3
   7,158 TO 40,155 TO 40,167 - P * YP:M4 = 1 +  INT ((B2 / 10 ^ M6) / S1
   ): GOTO 3304
3302  HPLOT 40,167 TO 40,167 - P * YP
3304  FOR J = 0 TO R
3306  HPLOT J * XR + 40,167 - (M5 - 1) * YP TO J * XR + 40,172 - (M5 - 1)
    * YP
3308  NEXT J
3310  HPLOT 40,167 - (M5 - 1) * YP TO 40 + R * XR,167 - (M5 - 1) * YP
3312 S3 = YP / (S1 * 10 ^ M6):S4 = XR / (S2 * 10 ^ M7):W = 6.2831852 * DA
   (0,0) * DA(2,0)
3314  ON P6 GOTO 3316,3324,3334
3316 P$ = "RESISTANCE VERSUS TIME":PX = 82:PY = 0: IF M5 / P > .5 THEN PY
    = 181
3317  HPLOT PX - 2,PY + 9 TO PX + 153,PY + 9: GOSUB 3216
3318 P$ = "Z' /(OHMS) X 10": IF M6 < 0 THEN P$ = P$ +  CHR$ (93) + " " +
    STR$ ( ABS (M6)): GOTO 3322
3320 P$ = P$ +  STR$ (M6)
3322 PX = 136:PY = 2: ROT= 48:UP = 1: GOSUB 3216: ROT= 0:UP = 0: GOTO 334
   0
3324 P$ = "IMAGINARY VERSUS TIME":PX = 87:PY = 0: IF M5 / P > .5 THEN PY =
    181
3326  HPLOT PX - 1,PY + 9 TO PX + 145,PY + 9: GOSUB 3216
3328 P$ = "Z''/(OHMS) X 10": IF M6 < 0 THEN P$ = P$ +  CHR$ (93) + " " +
    STR$ ( ABS (M6)): GOTO 3332
3330 P$ = P$ +  STR$ (M6)
3332 PX = 136:PY = 2: ROT= 48:UP = 1: GOSUB 3216: ROT= 0:UP = 0: GOTO 334
   0
3334 P$ = "D.L.C VERSUS TIME":PX = 102:PY = 0: HPLOT PX - 2,PY + 9 TO PX +
   117,PY + 9: GOSUB 3216
3336 P$ = "D.L.C/FCM" +  CHR$ (93) + "2X 10" +  CHR$ (93) + " ":P$ = P$ +
    MID$ ( STR$ ( ABS (M6)),1,1): IF  LEN ( STR$ ( ABS (M6))) > 1 THEN P
   $ = P$ + " " +  MID$ ( STR$ ( ABS (M6)),2,1)
3338 PX = 143:PY = 2: ROT= 48:UP = 1: GOSUB 3216: ROT= 0:UP = 0
3340  FOR J = 1 TO R
3342 P$ =  STR$ (J * S2):PX = J * XR + 38:PY = 174 - (M5 - 1) * YP: IF J *
   S2 > 9 THEN PX = PX - 3: IF J * S2 > 99 THEN PX = PX - 4
3344  GOSUB 3216
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3146  NEXT J
3148  M3 = 1: IF M4 = 0 THEN M3 = 0
3150  FOR J = M4 TO P + M4 - M3
3152  P4 = STR$ ((J - M3 + 1) * 51):PX = 27:PY = 164 - (J - M4 + M3) * YP
      : IF (J - M3 + 1) * 51 > = 10 OR (J - M3 + 1) * 51 <.0 THEN PX = 20
3154  IF (J - M3 + 1) * 51 > = 100 THEN PX = 12: IF (J - M3 + 1) * 51 >
      = 1000 OR (J - M3 + 1) * 51 < = - 100 THEN PX = 6
3156  IF (J - M3 + 1) * 51 < = - 10 THEN PX = 12
3158  GOSUB 3216
3160  NEXT J
3162  P4 = "TIME /S X 10" + STR$ (M7):PX = 109:PY = 185: IF M3 / P > .5 THEN
      PY = 2
3164  GOSUB 3216: IF M3 > 1 THEN M4 = 1
3166  FOR L = 1 TO DAZ
3168  X = DA(0,L) * 54 + 40
3170  ON P6 GOTO 3372,3374,3376
3172  Y = 167 - DA(1,L) * 53 + (M4 - 1) * YP: GOTO 3378
3174  Y = 167 + (M4 - M3) * YP - DA(2,L) * 53: GOTO 3378
3176  Y = 167 - 53 / (DA(2,L) * H) + (M4 - 1) * YP
3178  IF X > 2 AND X < 278 AND Y > 2 AND Y < 189 THEN  HPLOT X,Y
3180  NEXT L
3182  RETURN
3184  PRINT "PROGRAM ENDED": END
3186  ER = PEEK (222):EL = PEEK (218) * 256 + PEEK (219): PRINT  CHR$ (
      4):"PR#0": PRINT  CHR$ (4);"IN#0"
3188  INVERSE : IF ER = 107 THEN  PRINT : NORMAL
3190  IF ER = 6 THEN  PRINT "FILE NOT FOUND": NORMAL : CALL H: RESUME
3192  IF ER = 9 THEN  GOSUB 4000: GOTO 32
3194  IF ER = 254 THEN  PRINT "BAD INPUT RESPONSE": NORMAL : CALL H: RESUME
3196  IF ER = 255 THEN  CALL H: STOP : RESUME
3198  TEXT : PRINT E3$: PRINT "@22";CHR$ (1);"";
3200  PRINT E1$: PRINT E2$: PRINT "ERROR NO. ";ER;" IN LINE "; PEEK (218)
      + PEEK (219) * 256: NORMAL : CALL H: STOP
3202  REM  INITIALISE
3204  PRINT E3$: PRINT "@22";CD$;"";: PRINT "@22"; CHR$ (1);"";: PRINT E2$
      : PRINT E1$: RETURN
3206  REM   RESET ARRAY
3208  VTAB 13: HTAB 11: INVERSE : PRINT "RE-SETTING DATA ARRAY": NORMAL
3212  FOR I = 1 TO DAZ:DA(0,I) = 0:DA(1,I) = 0:DA(2,I) = 0: NEXT I:DAZ =
      0:DA(1,0) = 0
3216  RETURN
3218  REM  TIME DELAY
3220  POKE 28,72: POKE 29,73: POKE 30,14: POKE 31,75: CALL 32802: RETURN

3222  PRINT E1$: PRINT E2$: IF P6 < > 0 THEN DAZ = DAZ - 1: GOTO 30

3224  REM  RUN INTERRUPT
3250  TEXT : HOME : INVERSE : VTAB 2: PRINT "                RUN INTERRUPTED
                                            ": NORMAL
3260  POKE 34,3:RD = DAZ: VTAB 7: INPUT "E(ND RUN) OR A(LTER SETTINGS) :"
      ;D$: IF D$ = "E" THEN DAZ = DAZ - 1: GOTO 30
3490  IF D$ < > "A" THEN  CALL H: GOTO 3424
3500  VTAB 9: INPUT "CHANGE CHR ?";D$: IF D$ < > "Y" AND D$ < > "N" THEN
      3700
3510  IF D$ = "N" THEN 3760
3700  HOME : VTAB 9: INPUT "NEW CHR :";CR$:CR = VAL (CR$): IF CR < > INT
      (CR) OR CR > 1000000 OR CR < 1 THEN  CALL H: GOTO 3700
3760  VT = 11: IF TD < > 0 THEN  GOSUB 5000
3850  VTAB VT: CALL - 868: INPUT "CHANGE LIMITS ?";D$: IF D$ < > "Y" AND
      D$ < > "N" THEN 3850
3854  IF D$ = "N" OR D$ = "" THEN 3910
3858  POKE 34,16: HOME : VTAB VT: CALL - 868: PRINT "F MAX (";PS(16);")"
      ;"";: INPUT D$: IF D$ = "" THEN 3870
3860  D = VAL (D$): IF D < 10E - 4 OR D > 999900 THEN 3858
3862  PS(16) = D
3870  VTAB (VT + 2): PRINT "F MIN (";PS(17);")";"";: INPUT D$: IF D$ = "
      " THEN 3880
3872  D = VAL (D$): IF D < 10E - 4 OR D > PS(16) THEN 3870
3874  PS(17) = D
3876  VTAB (VT + 4): PRINT "DELTA F (";PS(23);")";"";: INPUT D$: IF D$ =
      "" THEN 3886
3882  D = VAL (D$): IF D < 1 OR D > 99 THEN 3880
3884  PS(22) = D:PS(23) = D
3886  PRINT E3$: PRINT "@72"
3890  US = &14 + 4:X = 16:M4 = "F": GOSUB 150
3892  M4 = "N": GOSUB 150
3894  X = 22:M4 = ")": GOSUB 150
3896  M4 = "?":US = STR$ (PS(23) * 10 ^ 6): IF  LEN (US) = 6 THEN US =
      "00" + US
3898  IF  LEN (US) = 7 THEN US = "0" + US
3900  GOSUB 158
3910  AX = 8: GOSUB 3920
3914  POKE  - 16297,0: POKE  - 16299,0: POKE  - 16304,0: RETURN
3920  PRINT E3$: PRINT "@72";S1$ =  CHR$ (48 + AX):S2 = PS(AX):SS$ = "
      ?" + S1$ + STR$ (S2) + "";: PRINT SS$: RETURN
4000  REM  DATA DISK FULL
4020  IF DK = 1 THEN
4100  TEXT : HOME : VTAB 10: HTAB 11: FLASH : PRINT "ERROR IN SAVING DATA
      ": VTAB 12: HTAB 14: PRINT "DATA DISK FULL"
4120  INVERSE : VTAB 14: HTAB 12: PRINT "INSERT A  NEW DISK": VTAB 16: HTAB
      9: INPUT "PRESS RETURN WHEN READY";D$: NORMAL
4140  RETURN
5000  REM  CHANGE MULT RUN
5120  VTAB 11: INPUT "CHANGE TIME DELAY ?";D$: IF D$ < > "Y" AND D$ < >
      "N" THEN 5120
5130  IF D$ = "N" THEN VT = 11: GOTO 5240
5140  VT = 17: VTAB 13: INPUT "ENTER TOTAL NO. OF RUNS :";RN$:RN2 = VAL (
      RN$): IF RN2 < 1 OR RN2 < > INT (RN2) THEN  CALL H: GOTO 5140
5160  VTAB 15: INPUT "TIME DELAY (MINUTES) :";TD$:TD = VAL (TD$): IF TD <
      1 / 60 THEN  CALL H: GOTO 5140
5180  TD = TD * 60
5184  T1 = TD * 16124:T6 = 256
5188  T2 = T1 -  INT (T1 / T6) * T6:T1 =  INT (T1 / T6)
5192  T3 = T1 -  INT (T1 / T6) * T6:T1 =  INT (T1 / T6)
5196  T4 = T1 -  INT (T1 / T6) * T6:T1 =  INT (T1 / T6)
5200  T5 = T1 -  INT (T1 / T6) * T6
5240  RETURN
6000  REM   TITLE SUBROUTINE
6020  HOME : VTAB 2: HTAB (20 - ( INT ( LEN (T1$) / 2))): INVERSE : PRINT
      T1$: NORMAL : RETURN
6040  REM   DISPLAY TITLES
6062  T0$ = "FREQ. /HZ": IF P6 < > 0 THEN T0$ = " TIME /S "
6080  VTAB 4: HTAB 2: INVERSE : PRINT T0$;: NORMAL : HTAB 11: INVERSE : PRINT
      T1$;: NORMAL : HTAB 20: INVERSE : PRINT T2$;: NORMAL : HTAB 29: INVERSE
      : PRINT T3$;: NORMAL : PRINT
6082  GOTO 6100
6090  VTAB 4: HTAB 4: INVERSE : PRINT T0$;: NORMAL : HTAB 16: INVERSE : PRINT
      T1$;: NORMAL : HTAB 28: INVERSE : PRINT T2$;: NORMAL : PRINT
6100  RETURN
```

Analysis I

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1  CLEAR
2  IF Z1 = 0 THEN  HIMEM: 34643: LOMEM: 24576
12  ONERR  GOTO 804
14 PP = 1:H = 37984:A6 = 7:A7 = 0: IF Z1 <  > 0 THEN FM$(1,1) = B$: GOTO
    22
16  DIM PS(24),SY(7,1),DA(2,500)
17  DIM FM$(7,1):CD$ =  CHR$ (4)
22  IF  PEEK (35424) = 76 AND  PEEK (35425) = 199 THEN 25
24  PRINT CD$;"BLOADBSHAPE7,A$8754,D1"
25  CALL 38048: POKE 232,104: POKE 233,142: PRINT CD$;"BLOADLCF": CALL 76
    9
26 ST = 1:B1 = 0:B2 = 0:B3 = 0:B4 = 0:A1 = 0:A6 = 7:B5 = 0:B6 = 0:A7 = 0:
    P6 = 0:T4 = 0:T5 = 0:M9 = 0:M8 = 0:M4 = 0:M3 = 0:E3 = 1:E2 = 1:E1 = 0
    : IF Z1 <  > 1 OR P1 = 2 THEN 322
28  SCALE= 1: ROT= 0: HCOLOR= 3: GOTO 386
32  HOME : VTAB 9: HTAB 7: INVERSE : PRINT "EVALUATING  PLOTTING DATA": NORMAL

36  REM
38  PRINT : PRINT : HTAB 8: PRINT "PRESS RETURN AFTER PLOT"
40 B1 = DA(1,1):B2 = DA(2,1):B3 = B2:B6 = B1
42  FOR I = 1 TO DA(1,0): IF I = SY(E3,0) THEN E3 = E3 + 1: GOTO 54
44  IF DA(1,I) > B1 THEN B1 = DA(1,I)
46  IF DA(2,I) > B3 THEN B3 = DA(2,I)
48  IF DA(2,I) < B2 THEN B2 = DA(2,I)
50  IF DA(1,I) < B6 THEN B6 = DA(1,I)
52  IF DA(0,I) > B4 THEN B4 = DA(0,I)
54  NEXT I
55 E3 = 1
56  IF B1 < 0 THEN B1 = 0
58 B5 = B2: IF DA(0,0) <  > 0 THEN 614
62  IF B3 < 0 THEN B3 = 0
64  IF B2 > 0 THEN B2 = 0
66  IF B6 > 0 THEN B6 = 0
68 S1 = (B1 - B6):AV = 160: IF  - B6 / S1 > .25 OR  - B6 / S1 > .75 THEN
    AV = 152
69 M1 = B3 - B2:M2 =  - B2 / M1:S5 = S1: IF M2 < 1 / 32 OR B3 < M1 / 32 THEN
    108
74  IF M1 / S1 * 230 > AV THEN S1 = M1: GOTO 76
76 M6 =  INT ( LOG (S1) / 2.30258):S1 = S1 / (10 ^ M6)
78 M4 = 0
80 S2 = .2:P = 6: IF S1 > 1.18 THEN P = 8
82  IF S1 > 1.58 THEN P = 10: IF S1 * 10 ^ M6 = M1 THEN S2 = .5:P = 4
84  IF S1 > 1.95 THEN S2 = .5:P = 5: IF S1 > 2.45 THEN P = 6
86  IF S1 > 2.95 THEN P = 8
88  IF S1 > 3.95 THEN P = 10: IF S1 * 10 ^ M6 = M1 THEN S2 = 1:P = 5
90  IF S1 > 4.98 THEN S2 = 1:P =  INT (S1 + 1.5): IF P = 11 THEN S2 = 2:P
    = 6
92  IF P > 8 AND S1 * 10 ^ M6 = M1 THEN S2 = 2:P =  INT ((S1 / 2) + 1.3)
94  IF S1 <  = 5 THEN S1 = S1 * 10:S2 = S2 * 10:M6 = M6 - 1
96  IF M1 / S5 * 230 > AV THEN 100
98 M3 =  INT (M1 / (S2 * 10 ^ M6 + 1)) + 1:M4 =  INT (M3 * M2) + 1:R = P:
    M3 = M3 - M4 + 1: GOTO 138
100 M4 =  INT (P * M2) + 1:M3 = P + 1 - M4:R =  INT (S5 / (S2 * 10 ^ M6) +
    1.5): GOTO 138
108  IF M1 / S5 * 230 > AV THEN S1 = M1: GOTO 112
110 S1 = S5
112 M6 =  INT ( LOG (S1) / 2.30258):S1 = S1 / (10 ^ M6)
114 M4 = 0:S2 = .2:P = 6: IF S1 > 1.18 THEN P = 8
116  IF S1 > 1.58 THEN P = 10: IF S1 * 10 ^ M6 = M1 THEN S2 = .5:P = 4
118  IF S1 > 1.95 THEN S2 = .5:P = 5: IF S1 > 2.45 THEN P = 6
120  IF S1 > 2.95 THEN P = 8
122  IF S1 > 3.95 THEN P = 10: IF S1 * 10 ^ M6 = M1 THEN S2 = 1:P = 5
124  IF S1 > 4.98 THEN S2 = 1:P =  INT (S1) + 2: IF P = 11 THEN S2 = 2:P =
    6
126  IF P > 8 AND S1 * 10 ^ M6 = M1 THEN S2 = 2:P =  INT ((S1 / 2) + 1.3)

128  IF S1 <  = 5 THEN S1 = S1 * 10:S2 = S2 * 10:M6 = M6 - 1
130  IF M1 / S5 * 230 > AV THEN 136
132 M3 =  INT (M1 / (S2 * 10 ^ M6) + .5) + 1:R = P: IF B3 < M1 / 32 THEN
    M4 = M3:M3 = 0
134  GOTO 138
136 M3 = P:R =  INT (S5 / (S2 * 10 ^ M6) + 1.5): IF B3 = 0 THEN M4 = M3:M
    3 = 0
138  IF M1 / S5 * 230 > AV THEN PU =  INT (AV / (M3 + M4)): GOTO 141
140 PU =  INT (230 / R): IF PU * (M3 + M4) > AV THEN M3 =  INT (AV / PU):
    M4 =  INT (M3 * M2 + .85):M3 = M3 - M4: GOTO 142
141 R = R + 1: IF R * PU > 230 THEN R =  INT (230 / PU)
142  IF B3 < M1 / 32 THEN M4 = M3 + M4:M3 = 0
143  IF B6 >  - .04 * (S5) THEN 146
144 M8 =  INT ( - B6 / S5 * R + .5):R = R - M8: IF R < 0 THEN M8 = M8 + R
    :R = 0
145  IF PU * (M8 + R) > 230 THEN M8 = M8 - 1: GOTO 145
146  HGR2 : IF M8 > R THEN T4 =  - 206 + (M8 + R) * PU:T5 = T4 - 8
147 T3 = 167: IF M4 > M3 THEN T3 = 175: IF M3 = 0 THEN T3 = 183: IF  - B6
    / S5 > .25 OR  - B6 / S5 > .75 THEN T3 = 177
148  FOR J = 0 TO M3 + M4
150  IF A1 <  > 3 THEN 154
152  IF J > 0 AND J < M3 + M4 THEN 160
154  IF M8 > R THEN 158
156  HPLOT 35 + A7 - T4 + M8 * PU,T3 - J * PU TO 40 - T4 + M8 * PU,T3 - J
    * PU: GOTO 160
158  HPLOT 40 - T4 + M8 * PU,T3 - J * PU TO 45 - T4 - A7 + M8 * PU,T3 - J
    * PU
160  NEXT J
162  HPLOT 40 - T4 + M8 * PU,T3 TO 40 - T4 + M8 * PU,T3 - (M3 + M4) * PU
164  FOR J = 0 TO R + M8
166  IF A1 <  > 3 THEN 170
168  IF J > 0 AND J < M8 + R THEN 176
170  IF M4 > M3 THEN 174
172  HPLOT J * PU + 40 - T4,T3 - M4 * PU TO J * PU + 40 - T4,T3 + 5 - M4 *
    PU - A7: GOTO 176
174  HPLOT J * PU + 40 - T4,T3 - M4 * PU TO J * PU + 40 - T4,T3 - 5 - M4 *
    PU + A7
176  NEXT J
178  HPLOT 40 - T4,T3 - M4 * PU TO 40 - T4 + (M8 + R) * PU,T3 - M4 * PU
180 S3 = PU / (S2 * 10 ^ M6):ST = 1:E3 = 1
181 E3 = 1:Q = 0:Q9 = 1.011: IF PS(8) = 3 THEN Q9 = .99
182  FOR J = ST TO DA(1,0): IF J = SY(E3,0) THEN E3 = E3 + 1: GOTO 196
184 X = DA(1,J) * S3 + 40 - T4 + M8 * PU
186 Y = T3 - DA(2,J) * S3 - M4 * PU
188  IF X < 2 OR X > 278 OR Y < 2 OR Y > 189 THEN  POKE 38016,6: POKE 380
    17,5: CALL 38018: GOTO 196
190  IF SY(E3,1) < 3 THEN 194
192  IF Q =  INT ( LOG (Q9 * DA(0,J)) / 2.30258) THEN 194
193 Q =  INT ( LOG (Q9 * DA(0,J)) / 2.30258): DRAW SY(E3,1) AT X,Y
194  HPLOT X,Y
196  NEXT J
197  IF E1 = 2 THEN E1 = 1: GOTO 390
198 P$ = "IMPEDANCE PLOT":PX = 100:PY = 165 - (M4 + M3 + 1) * PU: IF M4 >
    M3 THEN PY = 182
200  IF PY < 0 THEN PY = 0
202  HPLOT PX - 1,PY + 9 TO PX + 96,PY + 9: GOSUB 262: IF M8 <  > 0 THEN
    M9 = 1
204 A9 = 1: IF M4 = 0 OR M3 = 0 THEN  IF M8 = 0 THEN A9 = 0
206  FOR J = A9 TO R + M8 + M9
208  IF A1 <  > 3 THEN 212
210  IF J = A9 AND M8 <  > 0 OR J = R + M8 + M9 OR J = 0 AND A9 = 0 THEN
    212
211  GOTO 220
212 P$ =  STR$ ((J - M8 - M9) * S2):PX = (J - M9) * PU + 38 - T4 - .5 * (
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    LEN (P$) - 1) * A6: IF J - M9 - M8 = 0 AND M4 <  > 0 AND M3 <  > 0 THEN
    220
214 PY = T3 + 7 - M4 * PU
216  IF M4 > M3 THEN PY = T3 - 13 - M4 * PU + 3 * A7
217  IF PU < 3 * A6 + 2 AND  INT ((J - A9) / 2) <  > (J - A9) / 2 AND J -
    M8 - M9 < 0 THEN 220
218  GOSUB 262
220  NEXT J
224  FOR J = 0 TO M4 + M3
226  IF A1 <  > 3 THEN 230
228  IF J > 0 AND J < M4 + M3 THEN 238
230 P$ =  STR$ ((J - M4) * S2):PX = M8 * PU - T4 + 34 -  LEN (P$) * A6 +
    .5 * A7: IF M8 > R THEN PX = M8 * PU + 42 - T5
232 PY = T3 - 3 - J * PU + 1.5 * A7
234  IF M8 <  > 0 AND R <  > 0 AND J - M4 = 0 THEN 238
236  GOSUB 262
238  NEXT J
239 A1 = 1
240 P$ = "I"/(DIMS) X 10": IF M6 < 0 THEN P$ = P$ +  CHR$ (93) + ""
242 P$ = P$ +  STR$ ( ABS (M6)):PX = 100:PY = 185: IF M4 > M3 THEN PY = 1
    65 - (M4 + M3 + 1) * PU: IF PY < 2 THEN PY = 2
244  GOSUB 262: ROT= 48:UP = 1
246 P$ = "I""/(DIMS) X"10": IF M6 < 0 THEN P$ = P$ +  CHR$ (93) + ""
248 P$ = P$ +  STR$ ( ABS (M6)):PX = T3 + 53 - (J - 1) / 2 * PU:PY = 2: IF
    PX > 191 THEN PX = 191
249  IF M8 > R THEN PY = 273
250  GOSUB 262: ROT= 0:UP = 0
254  RETURN
262 RU = PX:P4 =  - 32
266  FOR RR = 1 TO  LEN (P$)
268 S =  ASC ( MID$ (P$,RR,1))
270  IF S >  = 128 THEN S = S - 128
272  IF S = 19 THEN P4 = 27: GOTO 292
274  IF S = 32 THEN 286
276  IF PY < 0 THEN PY = 0
278 A8 = 7: IF A1 = 2 AND S > 47 AND S < 58 THEN P4 = 27:A8 = 5
279  IF UP = 1 THEN  DRAW S + P4 AT PY,RU:P4 =  - 32:RU = RU - 7: GOTO 29
    2
280  IF S + P4 = 44 THEN RU = RU - 1
282  IF S = 45 AND A1 = 2 THEN  DRAW S + P4 AT RU,PY - 3:P4 =  - 32: GOTO
    286
284  DRAW S + P4 AT RU,PY:P4 =  - 32
286 RU = RU + A8: IF UP = 1 THEN RU = RU - 2 * A8
290  IF S + P4 = 44 THEN RU = RU - 1
292  NEXT
294  RETURN
322  HOME : VTAB 2: HTAB 10: INVERSE : PRINT "DATA PROCESSING PROGRAM": NORMAL
    : VTAB 5: HTAB 9: PRINT "(<CR> WILL CATALOG DISK )"
326  PRINT : INPUT "ENTER FILENAME :";B$: IF B$ <  > "" THEN 330
328  CALL 35424: FOR I = 29 TO 0 STEP  - 1:DI =  PEEK (35456 + I) - 128: IF
    DI = 32 THEN  NEXT I
329  FOR J = 0 TO I:DI =  PEEK (35456 + J) - 128:B$ = B$ +  CHR$ (DI): NEXT
    J:FM$(E2 + 1,1) = B$: IF  PEEK (35436) = 141 THEN 322
330  PRINT CD$;"VERIFY";B$;",D2"
332  PRINT CD$;"VERIFYD";B$;",D2"
333 FM$(1,1) = B$:FF =  FRE (0)
334  GOSUB 548
335  VTAB 4: PRINT  TAB( 40): VTAB 4: HTAB 13: INVERSE : PRINT "LOADING D
    ATA FILE": NORMAL
336  POKE 29,68: POKE 30,65: CALL 38144: PRINT CD$;"BLOAD";B$;",A"; PEEK
    (27) +  PEEK (28) * 256 + 9;",D2":P1 = 2: GOTO 28
342  GOTO 386
343 A1 =  VAL (A1$): IF A1 <  - 90 THEN A1 =  - 90
344  IF A1 > 1000 THEN A1 = 1000
345  RETURN
346  HOME : PRINT "ENTER CHANGED MAXIMA FOR AXES IN +/- %": PRINT : PRINT
    "A BLEEP INDICATES AN OFFSCREEN POINT": IF P6 = 0 THEN 360
354  PRINT : PRINT : INPUT "TIME AXIS       ";A1$: GOSUB 343:B1 = B1 + B1 /
    100 * A1
356  PRINT : INPUT "Y AXIS MAX      ";A1$: GOSUB 343:B3 = B3 + B3 / 100 *
    A1: PRINT : INPUT "Y AXIS MIN      ";A1$: GOSUB 343:B2 = B5 + B5 / 100
    * A1: IF B2 <  > 0 THEN B5 = B2
357  IF B2 > B3 THEN B2 = B3:B3 = B5
358  IF B2 = B3 THEN B2 = B3 - B3 / 20:B3 = B3 + B3 / 20
359  GOTO 376
360  PRINT : PRINT : INPUT "+IVE REAL AXIS  ";A1$: GOSUB 343:B1 = B1 + B1
     / 100 * A1: PRINT : INPUT "-IVE REAL AXIS  ";A1$: GOSUB 343:B6 = B6 +
    B6 / 100 * A1: PRINT : INPUT "+IVE IMAGINARY ";A1$: GOSUB 343:B3 = B3
     + B3 / 100 * A1: PRINT : INPUT "-IVE IMAGINARY ";A1$: GOSUB 343:B2 =
    B2 + B2 / 100 * A1
368  HOME : VTAB 2: HTAB 12: INVERSE : PRINT "PLOTTING OPTIONS": NORMAL
369  VTAB 6: INPUT "MARKING EVERY DECADE ?:";P$: IF P$ <  > "Y" THEN SY(E
    2,1) = 2: GOTO 374
370  VTAB 8: PRINT " WHICH SYMBOL ?:": PRINT : PRINT "  1: SQUARE": PRINT
     : PRINT "  2: DIAMOND": PRINT : PRINT "  3: CIRCLE": PRINT : PRINT "
     4: SOLID DIAMOND": PRINT : PRINT "  5: SOLID SQUARE": PRINT : INPUT
    " ENTER NUMBER :";P$
371 P7 =  VAL (P$): IF P7 <  > INT (P7) OR P7 < 0 OR P7 > 5 THEN  CALL H
    : GOTO 370
372 P7 = P7 + 2:SY(E2,1) = P7: IF P7 > 5 THEN P7 = P7 + 55:SY(E2,1) = P7
373  IF P7 = 5 THEN SY(E2,1) = 32
374  IF E1 = 2 THEN  POKE  - 16299,0: POKE  - 16304,0:SY(E3,0) = DA(1,0) -
    PS(1): GOTO 182
376  HOME : VTAB 2: HTAB 12: INVERSE : PRINT "PLOTTING OPTIONS": NORMAL
377  VTAB 6: PRINT "AXIS LABELING:": VTAB 8: PRINT " 1: NORMAL": PRINT : PRINT
     " 2: REDUCED SIZE": PRINT : PRINT " 3: LIMITS ONLY": PRINT : INPUT "E
    NTER OPTION :"A1$:A1 =  VAL (A1$): IF A1 <  > 2 AND A1 <  > 3 THEN A
    1 = 1
378 A6 = 7:A7 = 0: IF A1 = 2 THEN A6 = 5:A7 = 2
380  IF P6 <  > 0 THEN  GOSUB 614: GOTO 390
382  IF P1 = 3 THEN  CALL 38048:T4 = 0:T3 = 0:T5 = 0: GOSUB 68: GOTO 390
383  IF E1 = 1 THEN 388
384  IF P1 <  > 3 THEN  RETURN
386  IF DA(0,0) = 0 THEN  GOSUB 368: CALL 38048: GOSUB 32: GOTO 390
388  CALL 38048: GOSUB 32
390  GET Q$
392  TEXT : HOME : GOSUB 572
394  GET Q$
396  HOME : VTAB 2: HTAB 12: INVERSE : PRINT "PROGRAM OPTIONS": NORMAL : VTAB
    4: PRINT " 1: DISPLAY LAST GRAPH": VTAB 6: PRINT " 2: RE-PLOT GRAPH":
     VTAB 8: PRINT " 3: LIST DATA ":A4 = 9: VTAB 10: PRINT " 4: EXIT PROG
    RAM"
398  PRINT : PRINT " 5: OUTPUT PLOT TO EPSON": PRINT : PRINT " 6: COMMENC
    E A NEW RUN"
409  IF E2 > 6 THEN A4 = 6: GOTO 416
410  PRINT : PRINT " 7: PLOT A NEW FILE": PRINT : PRINT " 8: OUTPUT TO HP
     PLOTTER"
414  IF E2 > 1 THEN A4 = 8: GOTO 416
415  PRINT : PRINT " 9: PLOT ANALYSIS"
416  POKE 232,104: POKE 233,142:P1 = 3
418  VTAB 22: INPUT "  ENTER NUMBER :";P$:P =  VAL (P$): IF P <  >  INT
    (P) OR P < 1 OR P > A4 THEN  CALL H: GOTO 418
420  IF P <  > 7 THEN 426
422  HOME : VTAB 2: HTAB 14: INVERSE : PRINT "PLOT NEW FILE": NORMAL : VTAB
    4: INPUT "ADD TO PRESENT DATA ?";Q$: IF Q$ <  > "Y" AND Q$ <  > "N" THEN
    422
424 P1 = 2: IF Q$ = "Y" THEN P = 10:E1 = 1: PRINT : INPUT "RETAIN AXES ?
    ";Q$: IF Q$ = "Y" THEN E1 = 2
426  ON P GOTO 432,346,486,427,428,436,26,446,815,900
427  HOME : PRINT "PROGRAM ENDED": END
428  GOSUB 462
430  GOTO 396
```

```
432  POKE  - 16299,0: POKE  - 16304,0: POKE  - 16297,0: GOTO 390
436  PRINT CD$;"RUN START-UP.V3,D1"
446  HOME : VTAB 12: PRINT  TAB( 12): INVERSE : PRINT "LOADING HPPLOTTER"
     : NORMAL
448  IF P6 > 0 THEN 452
450 I2 = PU:I1 = PU:IP = R:IN = M8:YP = M3:YN = M4:YE = M6:IE = M6:IF = S
    2:YF = S2:YS = 0: GOTO 454
452 I2 = IR:I1 = YP:IP = R:IN = 0:YP = P - M5:YN = M5:YE = M6:IE = M7:IF =
    S2:YF = S1:YS = M4
454  CALL 38048
456  PRINT CD$;"BLOADCHAIN,A520,D1"
458  CALL 520"HPPLOTTER.V2"
462  HOME : VTAB 2: HTAB 15: INVERSE : PRINT "EPSON OUTPUT": NORMAL
463  VTAB 4: PRINT "IS THE EPSON READY ";: INPUT PQ$: IF PQ$ <  > "Y" THEN
     463
464  VTAB 6: PRINT "(S)MALL OR (L)ARGE PLOT ";: INPUT PQ$: IF PQ$ = "S" OR
     PQ$ = "L" THEN 468
466  CALL H: GOTO 464
468  PRINT CD$;"PR#";  STR$ (PP): PRINT : POKE (1656 + PP),96: POKE (1912 +
     PP),66: IF PQ$ = "S" THEN  POKE (1912 + PP),2
470  PRINT  CHR$ (17): PRINT : POKE 53247,0: PRINT : PRINT : IF E2 = 1 THEN
      GOSUB 572: PRINT  CHR$ (12): PRINT CD$;"PR#0": RETURN
475  PRINT : PRINT : PRINT "          Filenames : ";FH$(1,1)
477  FOR I = 2 TO E2
479  PRINT "                      ";FH$(I,1)
480  NEXT : IF FF = 19 THEN  PRINT : PRINT : RETURN
481  PRINT  CHR$ (12): PRINT CD$;"PR#0": RETURN
486 CD$ =  CHR$ (4): HOME : VTAB 2: HTAB 16: INVERSE : PRINT "DATA LISTIN
    G": NORMAL
487  IF P6 = 1 OR P6 = 2 THEN A1$ = " TIME /S ":A2$ = "Z'/ (OHMS)":A3$ =
     "Z''/(OHMS)"
488  IF P6 = 0 THEN A1$ = "FREQUENCY":A2$ = "Z'/ (OHMS)":A3$ = "Z''/(OHMS
     )"
489  IF P6 = 3 THEN A1$ = " TIME /S ":A2$ = "CDL/ FCM-2":A3$ = "Z''/(OHMS
     )"
490  VTAB 4: PRINT "OUTPUT ON:": VTAB 6: HTAB 4: PRINT "1: VDU": VTAB 8: HTAB
     4: PRINT "2: EPSON PRINTER"
495  VTAB 12: INPUT "ENTER RESPONSE :";P$
496  PRINT CD$;"PR#";  STR$ (PP): PRINT CD$;"PR#0": IF P$ = "2" THEN 522
498  HOME
506  VTAB 2: HTAB 2: INVERSE : PRINT A1$;: NORMAL : HTAB 13: INVERSE : PRINT
     A2$;: NORMAL : HTAB 24: INVERSE : PRINT A3$: NORMAL : PRINT
507 E3 = 1
508  FOR L = 1 TO DA(1,0): IF L = SY(E3,0) THEN E3 = E3 + 1: GOTO 516
510 P8 = DA(1,L) + .00001:P9 = DA(2,L) + .00001: IF P6 = 3 THEN P8 = YP /
    (DA(2,L) * W1)
512  CALL 34644:DA(0,L);E4,"  ",P8;E3,"  ",P9, CHR$ (13);
514  IF  INT ((L + 1 - E3) / 20) = (L + 1 - E3) / 20 THEN  INPUT "PRESS R
    ETURN TO CONTINUE ";Q$: HOME : VTAB 2: HTAB 2: INVERSE : PRINT A1$;: NORMAL
     : HTAB 13: INVERSE : PRINT A2$;: NORMAL : HTAB 24: INVERSE : PRINT A3
    $: NORMAL : PRINT
516  NEXT
518  INPUT "PRESS RETURN TO CONTINUE ";Q$: GOTO 396
522  HOME : VTAB 2: HTAB 14: INVERSE : PRINT "EPSON OUTPUT": NORMAL : VTAB
     4: INPUT "IS THE EPSON READY ?";Q$: IF Q$ <  > "Y" THEN 522
524  PRINT CD$;"PR#";  STR$ (PP): PRINT  CHR$ (4): POKE (1656 + PP),96: IF
     E2 > 1 THEN FF = 19: GOSUB 475:FF = 0: GOTO 528
526  PRINT "          Filename :";B$: PRINT : PRINT
528  VTAB 2: HTAB 3: PRINT A1$;: HTAB 14: PRINT A2$;: HTAB 25: PRINT A3$:
     PRINT
533 E3 = 1
534  FOR L = 1 TO DA(1,0): IF L = SY(E3,0) THEN E3 = E3 + 1: GOTO 540
536 P8 = DA(1,L) + .00001:P9 = DA(2,L) + .00001: IF P6 = 3 THEN P8 = YP /
    (DA(2,0) * W1)
538  CALL 34644:DA(0,L);E4,"  ",P8;E3,"  ",P9, CHR$ (13);
540  NEXT L
542  PRINT  CHR$ (12): PRINT CD$;"PR#0": GOTO 396
548  HOME : VTAB 5: PRINT  TAB( 40): VTAB 4: HTAB (9): INVERSE : PRINT "L
    OADING  DESCRIPTION FILE": NORMAL : PRINT CD$;"OPEN";B$;",D2"
550  PRINT CD$;"READ0";B$
552  FOR L = 0 TO 24: INPUT P$(L): NEXT L
558  INPUT A$,C$,D$,E$,F$,G$,H$,I$,J$,K$,L$,M$,N$,O$,CR,O
568  PRINT CD$;"CLOSED";B$
570  RETURN
572  HTAB 8: PRINT "Operator     : ";A$: HTAB 8: PRINT "Filename     : ";B$
     : HTAB 8: PRINT "Date         : ";D$: HTAB 8: PRINT "Temperature : ";E
     $: HTAB 8: PRINT "Pressure     : ";F$
584  HTAB 8: PRINT "Membrane No : ";G$: HTAB 8: PRINT "Surface Area: ";DA
    (2,0);" cm2": HTAB 8: PRINT "Solution 1  : ";H$: HTAB 8: PRINT "Solut-e     ion 2  : ";I$
592  HTAB 8: PRINT "Electrodes  : ";J$
598  HTAB 8: PRINT "C.M.R        : ";CR;" Ohms"
600  IF DA(0,0) <  > 0 THEN  PRINT "       Freq         : ";DA(0,0);" Hz":
     GOTO 608
602  HTAB 8: PRINT "Freq Max     : ";PS(16);" Hz": HTAB 8: PRINT "Freq Min-e         : ";PS(17)
Hz": HTAB 8: PRINT "Seel Max     : ";O;" Hz"
608  PRINT : PRINT
610  PRINT K$: PRINT L$: PRINT M$: PRINT N$: PRINT O$
612  RETURN
614  IF P1 = 3 AND P7 <  > P6 THEN P7 = P6: GOTO 628
616  HOME : VTAB 9: PRINT "WHICH TYPE OF SINGLE FREQUENCY PLOT ": PRINT :
     PRINT " Z' / TIME   (1) ": PRINT : PRINT " Z''/ TIME   (2) ": PRINT : PRINT
     " DLC/ TIME   (3) "
618  VTAB 17: INPUT "ENTER NUMBER ? ";P$:P6 =  INT ( VAL (P$)): IF P6 < 1
     OR P6 > 3 THEN  CALL H: GOTO 618
620  HOME : VTAB 9: PRINT  TAB( 12);: INVERSE : PRINT "MORE CALCULATING":
     NORMAL
622  IF P1 = 3 AND P7 <  > P6 THEN 28
624 P7 = P6
626  IF P1 = 3 THEN 640
628  IF P6 = 1 THEN B3 = B1:B2 = B6:B1 = B4:B5 = B2
630  IF P6 = 2 THEN B1 = B4
632  IF P6 <  > 3 THEN 640
636 W1 = 6.2831852 * DA(0,0) * DA(2,0):B2 = 1 / (W1 * B3):B1 = B4:B3 = 1 /
    (W1 * B5):B5 = B2
638  IF B2 < 0 THEN  HOME : PRINT "NEGATIVE CDL !!": CALL H: FOR K = 1 TO
     1000: NEXT : GOTO 396
640  IF P6 = 3 AND B2 < .35 * B3 THEN B2 = 0
642  IF P6 <  > 2 AND B2 > B3 THEN B2 = .99 * B3
644  IF B3 < 0 THEN B3 = 0
646 M1 = (B3 - B2) * 1.1:M6 =  INT ( LOG (M1) / 2.30258):M1 = M1 / (10 ^
    M6):M4 = 1:S1 = .2:P = 6
648  IF M1 > 1.18 THEN P = 8
650  IF M1 > 1.58 THEN P = 4:S1 = .5
652  IF M1 > 1.98 THEN P = 5
654  IF M1 > 2.48 THEN P = 6
656  IF M1 > 2.98 THEN P = 8
658  IF M1 > 3.98 THEN S1 = 1:P =  INT (M1 + 1.5)
660  IF M1 > 7.48 THEN S1 = 2:P = 5
662  IF S1 <  = .5 THEN S1 = S1 * 10:M6 = M6 - 1
664 M7 =  INT ( LOG (B1) / 2.30258):M2 = B1 / (10 ^ M7):M5 = 1: IF B2 < 0
     THEN M5 =  INT (1.1 * P *  - B2 / (B3 - B2)):M4 = 1
666 S2 = .2:R = 6: IF M2 > 1.18 THEN R = 8
668  IF M2 > 1.58 THEN R = 10
670  IF M2 > 1.98 THEN R = 5:S2 = .5
672  IF M2 > 2.48 THEN R = 6
674  IF M2 > 2.98 THEN R = 8
676  IF M2 > 3.98 THEN R = 10
678  IF M2 > 4.98 THEN S2 = 1:R =  INT (M2) + 2: IF R = 11 THEN S2 = 2:R =
    6
680  IF S2 <  = .5 THEN S2 = S2 * 10:M7 = M7 - 1
682  IF B3 > 0 THEN  IF B2 / B3 > 0.35 THEN M4 = 1 +  INT ((B2 / 10 ^ M6)
     / S1)
```

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684 L3 = 0:L2 =  LEN ( STR$ ((P + M4 - M3 - M5 + 1) * S1)): IF L2 = 4 THEN
    L3 = 5
686  IF L2 > 4 THEN L3 = A6 * (L2 - 4) + 5
688 YP =  INT (160 / P):XR =  INT ((230 - L3) / R)
690  HGR2
692 A9 = 0: IF M4 > 1 THEN A9 = 1
694  FOR J = 0 TO P
696  IF A1 <  > 3 THEN 700
698  IF J > A9 AND J < P THEN 702
700  HPLOT 35 + A7 + L3,167 - J * YP TO 40 + L3,167 - J * YP
702  NEXT J
704  IF B3 > 0 THEN  IF B2 / B3 > 0.35 THEN  HPLOT 40 + L3,167 TO 43 + L3
    ,164 TO L3 + 37,158 TO L3 + 40,155 TO L3 + 40,167 - P * YP: GOTO 708
706  HPLOT L3 + 40,167 TO L3 + 40,167 - P * YP
708  FOR J = 0 TO R
710  IF A1 <  > 3 THEN 714
712  IF J > 0 AND J < R THEN 716
714  HPLOT J * XR + L3 + 40,167 - (M5 - 1) * YP TO J * XR + L3 + 40,172 -
    (M5 - 1) * YP - A7
716  NEXT J
718  HPLOT L3 + 40,167 - (M5 - 1) * YP TO L3 + 40 + R * XR,167 - (M5 - 1)
     * YP
720 S3 = YP / (S1 * 10 ^ M6):S4 = XR / (S2 * 10 ^ M7)
722  ON P6 GOTO 726,734,744
726 P$ = "RESISTANCE VERSUS TIME":PX = B2 + L3:PY = 0: HPLOT PX - 2,PY +
    9 TO PX + 153,PY + 9: GOSUB 262
728 P$ = "Z' /(OHMS) X 10": IF M6 < 0 THEN P$ = P$ +  CHR$ (93) + ""
730 P$ = P$ +  STR$ ( ABS (M6)):PX = 136:PY = 2: ROT= 48:UP = 1: GOSUB 26
    2:UP = 0: ROT= 0: GOTO 754
734 P$ = "IMAGINARY VERSUS TIME":PX = L3 + 87:PY = 0: IF M5 / P > .5 THEN
    PY = 181
736  HPLOT PX - 1,PY + 9 TO PX + 145,PY + 9: GOSUB 262
738 P$ = "Z''/(OHMS) X 10": IF M6 < 0 THEN P$ = P$ +  CHR$ (93) + ""
740 P$ = P$ +  STR$ ( ABS (M6)):PX = 136:PY = 2: ROT= 48:UP = 1: GOSUB 26
    2:UP = 0: ROT= 0: GOTO 754
744 P$ = "D.L.C VERSUS TIME":PX = L3 + 102:PY = 0: HPLOT PX - 2,PY + 9 TO
    PX + 117,PY + 9: GOSUB 262
746 P$ = "D.L.C/FCM" +  CHR$ (93) + "2X 10": IF M6 < 0 THEN P$ = P$ +  CHR$
    (93) + ""
748 P$ = P$ +  MID$ ( STR$ ( ABS (M6)),1,1): IF  LEN ( STR$ ( ABS (M6))) >
    1 THEN P$ = P$ + "" +  MID$ ( STR$ ( ABS (M6)),2,1)
750 PX = 143:PY = 2: ROT= 48:UP = 1: GOSUB 262:UP = 0: ROT= 0
752 A9 = 1: IF M5 = 0 OR P + M4 - M3 - M5 + 1 = 0 THEN A9 = 0
754  FOR J = A9 TO R
755  IF J = 0 AND M5 > 1 THEN 764
756  IF A1 <  > 3 THEN 760
758  IF J > 0 AND J < R THEN 764
760 P$ =  STR$ (J * S2):PX = J * XR + L3 + 38 + .5 * A7 - .5 * ( LEN (P$)
    - 1) * A6:PY = 174 - (M5 - 1) * YP
762  GOSUB 262
764  NEXT J
766 M3 = 1:A9 = 0: IF M4 = 1 THEN A9 = 1
768  FOR J = M4 - A9 TO P + M4 - M3
770  IF A1 <  > 3 THEN 774
772  IF J > M4 AND J < P + M4 - M3 OR J = 1 THEN 778
774 P$ =  STR$ ((J - M5 + 1) * S1):PY = 164 - (J - M4 + M3) * YP + A7 * 1
    .5:PX = L3 + 36 - A6 *  LEN (P$)
776  GOSUB 262
778  NEXT J
780 P$ = "TIME /S X 10" +  STR$ (M7):PX = 109 + L3:PY = 185: IF M5 / P >
    .5 THEN PY = 2
782  GOSUB 262
784  FOR L = ST TO DA(1,0)
786 X = DA(0,L) * S4 + 40 + L3
788  ON P6 GOTO 790,792,794
790 Y = 167 - DA(1,L) * S3 + (M4 - M5) * YP: GOTO 796
792 Y = 167 + (M4 - M5) * YP - DA(2,L) * S3: GOTO 796
794 Y = 167 - S3 / (DA(2,L) * W1) + (M4 - 1) * YP
796  IF X < 0 OR Y < 0 OR Y > 191 OR X > 279 THEN  POKE 38016,6: POKE 380
    17,5: CALL 38018: GOTO 800
798  HPLOT X,Y
800  NEXT L
801  IF E1 = 2 THEN E1 = 1: GOTO 390
802  RETURN
804 ER =  PEEK (222):EM =  PEEK (218) +  PEEK (219) * 256: IF ER = 6 OR E
    R = 9 THEN EM$ = "FILE NOT FOUND": GOSUB 981: IF E1 = 0 THEN 322
806  IF ER = 8 THEN EM$ = "I/O ERROR": GOSUB 981: IF E1 = 0 THEN  VTAB 9:
    GOTO 322
807  IF ER = 11 THEN EM$ = "NAME BEGINS WITH A NUMBER": GOSUB 981: IF E1 =
    0 THEN 322
808  IF ER = 13 THEN EM$ = "FILE TYPE MISMATCH": GOSUB 981: IF E1 = 0 THEN
    VTAB 9: GOTO 322
809  IF E1 <  > 0 THEN  IF ER = 6 OR ER = 11 OR ER = 8 OR ER = 13 THEN 90
    0
810  IF ER = 254 THEN EM$ = "BAD INPUT RESPONSE": GOSUB 981: NORMAL : RESUME

812  IF ER = 255 THEN EM$ = "CONTROL C-STOP  (-CONT TO CONTINUE)": STOP :
    RESUME
814  INVERSE : PRINT "ERROR NO "; PEEK (222);" IN LINE "|: CALL H: NORMAL
    : PRINT  PEEK (218) +  PEEK (219) * 256: TEXT : STOP : RESUME
815  HOME : VTAB (9): PRINT  TAB( 10);: INVERSE : PRINT "LOADING ANALYSIS
    PROGRAM": NORMAL :T3 = T3 - 167
816  IF  PEEK (768) = 1 THEN  CALL 37354: GOTO 818
817  PRINT  CHR$ (4);"BSAVEGRAPH,A$4000,L$2000,D1"
818  PRINT CD$;"BLOADCHAIN,A520,D1"
820  CALL 520"ANALYSIS 2.V3"
900  HOME : INVERSE : VTAB 2: HTAB 10: PRINT "ADD TO PRESENT DATA": PRINT
    : NORMAL : PRINT "FILES :";: INVERSE : PRINT FM$(1,1): IF E2 > 1 THEN
     FOR I = 2 TO E2: HTAB 8: PRINT FM$(I,1): NEXT : NORMAL
901  NORMAL
905  IF E2 > 6 THEN  PRINT : PRINT : PRINT "MAX NO OF FILES IS PLOTTED": PRINT
    : INPUT "PRESS RETURN TO CONT ";Q$: GOTO 368
910  PRINT : PRINT : PRINT "(<CR> WILL CATALOG DISC #2)": PRINT : INPUT "
    ENTER NEXT FILENAME ? ";FM$(E2 + 1,1)
920  IF FM$(E2 + 1,1) <  > "" THEN 930
925  CALL 35424: FOR I = 29 TO 0 STEP  - 1:DI =  PEEK (35456 + I) - 128: IF
    DI = 32 THEN  NEXT I
926 B$ = "": FOR J = 0 TO I:DI =  PEEK (35456 + J) - 128:B$ = B$ +  CHR$
    (DI): NEXT J:FM$(E2 + 1,1) = B$: IF  PEEK (35436) = 141 THEN 900
930  PRINT CD$;"VERIFY";FM$(E2 + 1,1);",D2"
932  PRINT CD$;"VERIFYD";FM$(E2 + 1,1);",D2"
940  PRINT CD$;"OPEND";FM$(E2 + 1,1);",D2"
950  PRINT CD$;"READD";FM$(E2 + 1,1)
960  FOR I = 0 TO 24: INPUT PS(I): NEXT
962  PRINT CD$;"CLOSE"
964  IF P6 = 0 AND PS(8) = 2 THEN  HOME : VTAB 2: HTAB 10: INVERSE : PRINT
    "DATA INCOMPATABLE": NORMAL : CALL H: FOR I = 1 TO 1500: NEXT : GOTO
    900
966  IF P6 <  > 0 AND PS(8) <  > 2 THEN  HOME : VTAB 2: HTAB 10: INVERSE
    : PRINT "DATA INCOMPATABLE": NORMAL : CALL H: FOR I = 1 TO 1500: NEXT
    : GOTO 900
967 Q$ = ""
968  IF DA(1,0) + PS(1) > 500 THEN  HOME : VTAB 2: HTAB 10: INVERSE : PRINT
    "TOO MUCH DATA": NORMAL : CALL H: PRINT : INPUT "DO YOU WISH TO TRY A
    NOTHER FILE ? ";Q$: IF Q$ <  > "Y" AND Q$ <  > "N" THEN 968
970  IF Q$ = "Y" THEN 900
972  IF Q$ = "N" THEN 396
973  POKE 29,68: POKE 30,65: CALL 38144: PRINT CD$;"BLOAD";FM$(E2 + 1,1);
    ",A"; PEEK (27) +  PEEK (28) * 256 + 9 + 15 * (1 + DA(1,0));",D2":P1 =
    2:E2 = E2 + 1
974 ST = 1:SY(E2 - 1,0) = DA(1,0) + 1:DA(1,0) = DA(1,0) + 1 + PS(1): IF E
    1 = 2 THEN ST = DA(1,0) + 2 - PS(1)
```

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976  IF E1 = 2 THEN E3 = E2: GOTO 368
978 E3 = 1: IF P6 = 0 THEN 368
980  GOTO 388
981  CALL H: VTAB 3: HTAB (21 - ( INT ( LEN (EM$) / 2))): FLASH : PRINT E
    M$: NORMAL : FOR I = 1 TO 4000: NEXT : RETURN
```

Analysis 2

```
1 F3 = 167 + (M4 - M5) * YP:F4 = 167 + (M4 - 1) * YP:YU = YP
2  IF P6 > 0 THEN 4
3 XP = R:XN = M8:YP = M3:YN = M4:YE = M6:XE = M6:YF = S2:XF = S2:AL = A1:
   YS = 0: GOTO 5
4 XP = R:XN = 0:YP = P - M5:YN = M5:AL = A1:YE = M6:XE = M7:XF = S2:YF =
   S1:YS = M4
5  ONERR  GOTO 10000
6 MX = 40 - T4:YM = 167 + T3:XM = (M8 + R) * PU + 40 - T4:MY = 167 + T3 -
   (M3 + M4) * PU: IF P6 <  > 0 THEN XM = 40 + L3 + R * XR:MY = 11:MX =
   40 + L3:T3 = 0:YM = 167
7  DIM XY(4,2)
100  CALL 38048: SCALE= 1: ROT= 0: HCOLOR= 3:A1 = 1: POKE 233,142: POKE 2
   32,104
130  PRINT  CHR$ (4);"BLOADLCF": CALL 769: POKE 35453,0: IF  PEEK (768) =
   1 THEN  POKE 35453,1: CALL 37583: GOTO 640
140  PRINT  CHR$ (4);"BLOADGRAPH,D1": GOTO 640
160 RU = PX:P4 =  - 32
190  FOR RR = 1 TO  LEN (P$)
220 T =  ASC ( MID$ (P$,RR,1))
250  IF T >  = 128 THEN T = T - 128
280  IF T = 19 THEN P4 = 27: GOTO 580
310  IF T = 32 THEN 520
340  IF PY < 0 THEN PY = 0
370 A8 = 7: IF A1 = 2 AND S > 47 AND T < 58 AND  LEN (P$) < 4 THEN P4 = 2
   7:A8 = 5
400  IF UP = 1 THEN  DRAW T + P4 AT PY,RU:P4 =  - 32:RU = RU - 7: GOTO 58
   0
430  IF T + P4 = 44 THEN RU = RU - 1
460  IF T = 45 AND A1 = 2 THEN  DRAW T + P4 AT RU,PY - 3:P4 =  - 32: GOTO
   520
470  IF RU < 0 THEN RU = 0
480  IF RU > 273 OR RU < 0 OR PY < 0 OR PY > 184 THEN P4 =  - 32: GOTO 52
   0
490  DRAW T + P4 AT RU,PY:P4 =  - 32
520 RU = RU + A8: IF UP = 1 THEN RU = RU - 2 * A8
550  IF T + P4 = 44 THEN RU = RU - 1
580  NEXT
610  RETURN
640  HOME : PRINT "GRAPH ENHANCEMENT :-": PRINT : PRINT "THIS SECTION ALL
   OWS YOU TO EXPAND ANY  PORTION OF THE PLOT."
650 C = 1:C3 = 10:FF = 0:TT = 0:T7 = 0:T6 = 0: IF DA(1,0) < 10 THEN C3 =
   1
670  PRINT : PRINT : PRINT "THE PLOT IS REDISPLAYED WITH THE CURSOR INDIC
   ATED BY (+). CURSOR CONTROL IS  WITH THE ARROW KEYS.": PRINT "'H'
   SETS THE EXPANSION RANGE LIMITS ": PRINT "'J' JUMPS 10 POINTS ON NEXT
    MOVE"
700  PRINT "'D' DELETES POINT FROM SCREEN"
730  PRINT : PRINT : INPUT "DISPLAYING DATA ON SCREEN ? ";Q$: PRINT : PRINT
   "PRESS RETURN AFTER PLOT TO CONTINUE"
760  FOR I = 1 TO 1000: NEXT
790  IF Q$ <  > "Y" THEN 1060
820  HCOLOR= 0
850  FOR K = 167 TO 191: HPLOT 204,K TO 279,K: NEXT K
880  HCOLOR= 3: HPLOT 206,191 TO 206,166 TO 279,166 TO 279,191 TO 206,191

910  ON P6 + 1 GOTO 940,970,1000,1030
940 P$ = "Z' =":PX = 209:PY = 168: GOSUB 160:P$ = "Z''=":PX = 209:PY = 17
   6: GOSUB 160:P$ = "F=  HZ":PX = 209:PY = 184: GOSUB 160: GOTO 106
   0
970 P$ = "Z'=":PX = 209:PY = 168: GOSUB 160:P$ = "T =":PX = 209:PY = 176:
    GOSUB 160: GOTO 1060
1000 P$ = "Z''=":PX = 209:PY = 168: GOSUB 160:P$ = "T  =":PX = 209:PY = 1
   76: GOSUB 160: GOTO 1060
1030 P$ = "CDL=":PX = 209:PY = 168: GOSUB 160:P$ = "T  =":PX = 209:PY = 1
   76: GOSUB 160
1060  POKE  - 16299,0: POKE  - 16304,0: POKE  - 16297,0
1090 F = L3 + 40 - T4 + M8 * PU:F2 = 167 + T3 - M4 * PU
1120 J =  INT (DA(1,0) / 2):F7 = J - 1 - C:F8 = J + 1 + C
1150  GOTO 1570
1180  GET S$:S =  ASC (S$): IF S <  > 74 THEN 1200
1190 C = C3: GOTO 1180
1200  IF S = 8 OR S = 21 OR S = 68 OR S = 72 THEN 1210
1205  GOTO 1180
1210  IF S = 72 AND F9 <  > 0 THEN 1990
1240  IF S = 72 THEN F9 = J:B7 = DA(0,J): IF 2 < X1 AND 2 < Y1 AND 278 >
   X1 AND 189 > Y1 THEN  DRAW 118 AT X1,Y1
1270  IF S = 8 THEN J = J - C: IF J < 1 THEN J = DA(1,0) + J
1280  IF S = 8 AND DA(0,J) = 0 AND J > 0 THEN C = 1: GOTO 1270
1300  IF S = 21 THEN J = J + C: IF J > DA(1,0) THEN J = J - DA(1,0)
1310  IF S = 21 AND DA(0,J) = 0 AND J < DA(1,0) THEN C = 1: GOTO 1300
1330  IF J < 1 THEN J = DA(1,0) - J
1360  IF J > DA(1,0) THEN J = J - DA(1,0)
1390 F7 = J - 1 - C:F8 = J + 1 + C
1420  IF S = 69 THEN 2020
1450 B8 = DA(0,J): IF S = 68 THEN DD = 2: IF DA(0,J) <  > 0 THEN ND = ND +
   1:DA(0,J) = 0: IF 2 < X1 AND 2 < Y1 AND 278 > X1 AND 189 > Y1 THEN  HCOLOR=
   0: HPLOT X1,Y1: HCOLOR= 3
1455  IF ND = DA(1,0) THEN B3 = B2: GOTO 2292
1460  IF S = 68 THEN 1180
1480  IF 2 < X1 AND 2 < Y1 AND 278 > X1 AND 189 > Y1 THEN  XDRAW 119 AT X
   1,Y1: IF DA(0,L) > 0 THEN  HPLOT X1,Y1
1570  FOR K = F7 TO F8
1572 V = K: IF V < 1 THEN V = DA(1,0) - V
1575  IF V > DA(1,0) THEN V = V - DA(1,0)
1600  IF P6 <  > 0 THEN 1660
1630 X = DA(1,V) * S3 + F:Y = F2 - DA(2,V) * S3: GOTO 1810
1660 X = DA(0,V) * S4 + 40 + L3
1690  ON P6 GOTO 1720,1750,1780
1720 Y =  - DA(1,V) * S3 + F3: GOTO 1810
1750 Y =  - DA(2,V) * S3 + F3: GOTO 1810
1780 Y = F4 - S3 / (DA(2,V) * W1)
1810  IF X > 2 AND X < 278 AND Y > 2 AND Y < 189 THEN 1840
1820  IF V = J THEN  POKE 38016,6: POKE 38017,5: CALL 38018
1830  GOTO 1900
1840  IF DA(0,V) = 0 THEN 1900
1870  HPLOT X,Y: IF V = J THEN  DRAW 119 AT X,Y
1900  IF V = J THEN X1 = X:Y1 = Y
1910  NEXT K
1930 L = J: IF Q$ = "Y" THEN  GOSUB 2920
1960 C = 1: GOTO 1180
1990  IF J = F9 THEN F9 = 1:J = DA(1,0)
2000 F8 = J: IF DA(0,J) = 0 THEN F8 = F9
2020 B1 = DA(1,F8):B2 = DA(2,F8):B6 = B1:B3 = B2:B7 = DA(0,F8):B8 = B7: IF
   F9 > J THEN F8 = F9:F9 = J:J = F8
2050  FOR K = F9 TO J: IF DA(0,K) = 0 THEN 2200
2080  IF DA(1,K) > B1 THEN B1 = DA(1,K):XY(3,0) = B1:XY(3,1) = DA(2,K):XY
   (2,2) = DA(0,K)
2110  IF DA(1,K) < B6 THEN B6 = DA(1,K):XY(1,0) = B6:XY(1,1) = DA(2,K):XY
   (1,2) = DA(0,K)
2140  IF DA(2,K) < B2 THEN B2 = DA(2,K):XY(2,1) = B2:XY(2,0) = DA(1,K):XY
   (2,2) = DA(0,K)
2170  IF DA(2,K) > B3 THEN B3 = DA(2,K):XY(4,1) = B3:XY(4,0) = DA(1,K):XY
   (4,2) = DA(0,K)
2180  IF DA(0,K) < B8 THEN B8 = DA(0,K)
2190  IF DA(0,K) > B7 THEN B7 = DA(0,K)
2200  NEXT
2230  IF P6 = 1 THEN B2 = B6:B3 = B1:XY(2,0) = XY(1,2):XY(2,1) = B6:XY(2,
   2) = XY(1,2):XY(4,0) = XY(2,2):XY(4,1) = B1:XY(4,2) = XY(2,2)
2260  IF P6 = 3 THEN B5 = B2:B2 = 1 / (W1 * B3):B3 = 1 / (W1 * B5):XY(2,1
   ) = B2:XY(2,0) = XY(2,2):XY(4,1) = B3:XY(4,0) = XY(4,2)
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2270  IF P6 = 2 THEN XY(2,0) = XY(2,2):XY(4,0) = XY(4,2)
2290  IF P6 <  > 0 THEN B1 = B7:B6 = B8
2292  IF B3 = B2 THEN  TEXT : HOME : VTAB 3: HTAB 10: FLASH : PRINT "INSU
    FFICIENT DATA": NORMAL : CALL H: FOR I = 1 TO 4000: NEXT :Q = 1: GOTO
    2894
2294 M1 = B3 - B2:M2 = B1 - B6:M6 =  INT ( LOG (M1) / 2.30258):M7 =  INT
    ( LOG (M2) / 2.30258):M1 = M1 / (10 ^ M6):M2 = M2 / (10 ^ M7):S1 = .2
    :S2 = .2
2296  IF M1 > 1.58 THEN S1 = .5: IF M1 > 3.98 THEN S1 = 1: IF M1 > 7.48 THEN
    S1 = 2
2298  IF M2 > 1.98 THEN S2 = .5: IF M2 > 4.98 THEN S2 = 1: IF M2 > 8.98 THEN
    S2 = 2
2300  IF S1 < 1 THEN S1 = S1 * 10:M6 = M6 - 1
2302  IF S2 < 1 THEN S2 = S2 * 10:M7 = M7 - 1
2303 R =  INT ((B1 - B6) / (S2 * 10 ^ M7) + 1.5):P =  INT ((B3 - B2) / (S
    1 * 10 ^ M6) + 1.7)
2304 XI =  INT (230 / R):YI =  INT (160 / P): IF P6 <  > 0 THEN 2308
2305 YI = XI: IF  INT (160 / XI) * S2 * 10 ^ M7 < P * S1 * 10 ^ M6 THEN Y
    I =  INT (160 / P):XI = YI:M7 = M6:S2 = S1: GOTO 2308
2307 S1 = S2:M6 = M7
2308  IF B2 >  = 0 OR B3 <  = 0 THEN XA = 172
2309  IF B1 <  = 0 THEN YA = 240
2310  IF B6 >  = 0 THEN YA = 40
2311 XL =  INT (B6 / (S2 * 10 ^ M7)) * S2
2312 YL =  INT (B2 / (S1 * 10 ^ M6)) * S1
2313 XH =  INT (230 / XI * S2 + XL):YH =  INT (160 / YI * S1 + YL)
2314  IF XL < 0 AND XH > 0 THEN YA =  - XL / (XH - XL) * 230 + 40
2315  IF YL < 0 AND YH > 0 THEN XA = YL / (YH - YL) * 160 + 172
2316 LX = XL: IF XH < 0 THEN LX = XH
2317  IF YA = 240 THEN T7 =  - 30
2318  HGR2 : HPLOT 40 + T7,XA TO 270 + T7,XA: HPLOT YA,172 TO YA,12
2320  IF YL < 0 AND YH > 0 AND YL / (YL - YH) > .5 AND XA <  > 172 THEN 2
    324
2322  HPLOT 40 + T7,XA + 5 TO 40 + T7,XA: HPLOT 270 + T7,XA + 5 TO 270 +
    T7,XA: GOTO 2326
2324  HPLOT 40 + T7,XA - 5 TO 40 + T7,XA: HPLOT 270 + T7,XA - 5 TO 270 +
    T7,XA
2326  IF XL / (XL - XH) > .5 AND XL < 0 AND XH > 0 AND YA <  > 40 THEN 23
    30
2327  IF XH < 0 THEN 2330
2328  HPLOT YA - 5,172 TO YA,172: HPLOT YA - 5,12 TO YA,12: GOTO 2331
2330  HPLOT YA + 5,172 TO YA,172: HPLOT YA + 5,12 TO YA,12
2331 S5 = YI / (S1 * 10 ^ M6):S6 = XI / (S2 * 10 ^ M7):Q = 0: IF XL < 0 AND
    XH > 0 THEN LX = 0
2332 LY = YL: IF YL < 0 AND YH > 0 THEN LY = 0
2333  FOR I = F9 TO J: IF P6 <  > 0 THEN 2338
2334 X = YA + S6 * (DA(1,I) - LX * 10 ^ M7):Y = XA - S5 * (DA(2,I) - LY *
    10 ^ M6): IF SY(1,1) = 2 THEN 2350
2335  IF DA(0,I) = 0 THEN 2360
2336  IF Q =  INT ( LOG (Q9 * DA(0,I)) / 2.30258) THEN 2350
2337 Q =  INT ( LOG (Q9 * DA(0,I)) / 2.30258): DRAW SY(1,1) AT X,Y: GOTO
    2350
2338 X = YA + S6 * (DA(0,I) - LX * 10 ^ M7): IF DA(0,I) = 0 THEN 2360
2339  ON P6 GOTO 2340,2342,2344
2340 Y = XA - (DA(1,I) - LY * 10 ^ M6) * S5: GOTO 2350
2342 Y = XA - (DA(2,I) - LY * 10 ^ M6) * S5: GOTO 2350
2344 Y = XA - (1 / (DA(2,I) * W1) - LY * 10 ^ M6) * S5
2350  IF DA(0,I) = 0 THEN 2360
2351  IF X < 2 OR Y < 2 OR Y > 189 OR X > 278 THEN  POKE 38016,6: POKE 38
    017,5: CALL 38018: GOTO 2360
2352  HPLOT X,Y
2360  NEXT I
2408  IF XH < 0 THEN 2415
2410 P$ =  STR$ ( INT (XH * 100) / 100):PX = 272 - 3.5 *  LEN (P$):PY = X
    A + 7
2411  IF YL < 0 AND YH > 0 AND YL / (YL - YH) > .5 AND XA <  > 172 THEN P
    Y = XA - 13
2412  IF  LEN (P$) > 2 THEN PX = PX - 7 * ( LEN (P$) - 2)
2413  GOSUB 160: GOTO 2440
2415 P$ =  STR$ ( INT (XL * 100) / 100):PX = 12 - 3.5 *  LEN (P$):PY = XA
    + 7: IF YL < 0 AND YH > 0 AND YL / (YL - YH) > .5 AND XA <  > 172 THEN
    PY = XA - 13
2416  GOSUB 160: GOTO 2443
2440 P$ =  STR$ ( INT (XL * 100) / 100):PX = 42 - 3.5 *  LEN (P$):PY = XA
    + 7: IF YL < 0 AND YH > 0 THEN  IF XL > 0 THEN 2450
2441  IF YL < 0 AND YH > 0 AND YL / (YL - YH) > .5 AND XA <  > 172 THEN P
    Y = XA - 13
2442  IF XL <  > 0 OR YL >  = 0 THEN  GOSUB 160
2443  IF YL < 0 AND YH > 0 AND XH < 0 THEN T6 = 12::P$ =  STR$ ( INT (XH *
    100) / 100): GOTO 2450
2444  IF XH < 0 THEN P$ =  STR$ ( INT (XH * 100) / 100):PX = YA - 3.5 *  LEN
    (P$):PY = XA + 7: GOSUB 160: GOTO 2470
2445  GOTO 2470
2450 P$ = "(" + P$ + ")":PY = YA - 10 + T6:PX = XA + 3.5 *  LEN (P$) - 1:
    ROT= 48:UP = 1: GOSUB 160: ROT= 0:UP = 0
2470 P$ =  STR$ ( INT (YL * 100) / 100): IF XL < 0 AND XH > 0 AND YL = 0 THEN
    2500
2473  IF XL < 0 AND XH > 0 AND XA = 172 AND YL <  > 0 THEN PY = XA + 2:P$
    = "(" + P$ + ")":PX = YA - 3.5 *  LEN (P$) + 2: GOSUB 160: GOTO 2500

2474 PY = 157:PX = YA - 7 - 7 *  LEN (P$): IF XL < 0 AND XH > 0 AND XL /
    (XL - XH) > .5 THEN PX = YA + 7
2475  IF XH <  = 0 THEN PX = YA + 7
2476  GOSUB 160: GOTO 2500
2477  GOSUB 160
2500 P$ =  STR$ ( INT (YH * 100) / 100):PX = YA - 7 *  LEN (P$) - 7:PY =
    9
2503  IF XL < 0 AND XH > 0 AND XL / (XL - XH) > .5 THEN PX = YA + 7
2504  IF XH <  = 0 THEN PX = YA + 7
2505  IF XL < 0 AND XH > 0 AND YH < 0 AND XA <  > 172 THEN P$ = "(" + P$ +
    ")":PX = YA - 3.5 *  LEN (P$):PY = 6
2506  GOSUB 160
2530  IF P6 <  > 0 THEN 2620
2560 P$ = "Z' /(OHMS) X 10": IF M6 < 0 THEN P$ = P$ +  CHR$ (93) + ""
2590 P$ = P$ +  STR$ ( ABS (M6)):PX = 110:PY = 184: GOSUB 160: GOTO 2650
2620 P$ = "TIME /S X 10" +  STR$ (M7):PX = 115:PY = 184: GOSUB 160
2650 UP = 1: ROT= 48: ON P6 + 1 GOTO 2680,2740,2680,2800
2680 P$ = "Z''/(OHMS) X 10": IF M6 < 0 THEN P$ = P$ +  CHR$ (93) + ""
2710 P$ = P$ +  STR$ ( ABS (M6)):PX = 140:PY = 2: GOTO 2862
2740 P$ = "Z' /(OHMS) X 10": IF M6 < 0 THEN P$ = P$ +  CHR$ (93) + ""
2770 P$ = P$ +  STR$ ( ABS (M6)):PX = 140:PY = 2: GOTO 2862
2800 P$ = "D.L.C/FCM" +  CHR$ (93) + "2X 10": IF M6 < 0 THEN P$ = P$ +  CHR$
    (93) + ""
2830 P$ = P$ +  MID$ ( STR$ ( ABS (M6)),1,1): IF  LEN ( STR$ ( ABS (M6)))
    > 1 THEN P$ = P$ + "" +  MID$ ( STR$ ( ABS (M6)),2,1)
2860 PX = 155:PY = 2
2862  IF YA = 240 THEN PY = 273
2863  GOSUB 160
2865  ROT= 0:UP = 0
2870 C4 = DA(0,F9): IF C4 = 0 THEN F9 = F9 + 1: GOTO 2870
2875 C5 = DA(0,J): IF C5 = 0 THEN J = J - 1: GOTO 2875
2877 P$ = "RANGE " +  STR$ (C4) + " TO " +  STR$ (C5): IF P6 = 0 THEN P$ =
    P$ + " HZ": GOTO 2880
2878 P$ = P$ + " S "
2880 PY = 0:PX = 160 - 3.5 *  LEN (P$): GOSUB 160
2890  GET Q$
2891  TEXT : HOME : VTAB 4: HTAB 12: INVERSE : PRINT "PROGRAM OPTIONS": NORMAL
    : PRINT
2892  PRINT : PRINT "1: REPLOT EXPANSION": PRINT : PRINT "2: LINEAR REGRE
    SSION": PRINT : PRINT "3: PRINTOUT ON EPSON"
2893  PRINT : PRINT "4: EXIT PROGRAM ": PRINT : PRINT "5: PLOT A NEW FILE
    ": PRINT : INPUT "ENTER REQUIRED NUMBER :";Q$:Q =  INT ( ABS ( VAL (Q
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   $))): IF Q < 1 OR Q > 5 THEN  CALL H: GOTO 2891
2894  ON Q GOTO 2895,5000,2901,2899,2900
2895  IF DD <  > 0 THEN  HOME : VTAB 3: HTAB 13: INVERSE : PRINT "RELOAD
   ING DATA": NORMAL : POKE 29,68: POKE 30,65: CALL 38144: PRINT  CHR$ (
   4);"BLOAD";B$;",A"; PEEK (27) +  PEEK (28) * 256 + 9;",D2":DD = 0:ND =
   0
2896  IF  PEEK (33453) = 1 THEN  CALL 37583: GOTO 2898
2897  PRINT  CHR$ (4);"BLOADGRAPH,D1"
2898 F9 = 0:F8 = 0:B1 = 0:B2 = 0:B3 = 0:B4 = 0:B6 = 0:B7 = 0:B8 = 0:B9 =
   0:R = 0:P = 0: GOTO 640
2899  HOME : PRINT "PROGRAM EXITED": END
2900  PRINT  CHR$ (4);"BLOADCHAIN,A520,D1": CALL 520"ANALYSIS 1.V3"
2901  HOME : VTAB 2: HTAB 14: INVERSE : PRINT "EPSON OUTPUT": NORMAL : VTAB
   6: INPUT "IS EPSON READY ?";Q$: IF Q$ <  > "Y" THEN 2901
2902  VTAB 8: INPUT "L(ARGE) OR S(MALL) PLOT ? ";Q$:Q = 2: IF Q$ = "L" THEN
   Q = 66
2905  PRINT  CHR$ (4);"PR#";PP: POKE (1656 + PP),96: PRINT "FILENAME : ";
   B$;" -EXPANDED PLOT": PRINT : PRINT : PRINT : POKE (1912 + PP),Q: PRINT
    CHR$ (17); CHR$ (12): PRINT  CHR$ (4);"PR#0"
2910  GOTO 2891
2920  HCOLOR= 0
2950  FOR I = 167 TO 182: HPLOT 237,I TO 278,I: NEXT I
2980  IF P6 = 0 THEN  FOR I = 183 TO 190: HPLOT 223,I TO 262,I: NEXT
3010  HCOLOR= 3: ON P6 + 1 GOTO 3040,3100,3130,3160
3040 P$ =  STR$ ( INT (DA(1,J) / 10 ^ M6 * 100) / 100):PX = 237:PY = 168:
    GOSUB 160:P$ =  STR$ ( INT (DA(2,J) / 10 ^ M6 * 100) / 100):PX = 237
   :PY = 176: GOSUB 160
3041  IF DA(0,J) < 0.01 THEN 3044
3042 P$ =  STR$ (DA(0,J)): IF DA(0,J) > 1000 THEN P$ =  STR$ ( INT (DA(0,
   J)))
3043  GOTO 3070
3044 FR$ =  STR$ ( INT (DA(0,J) * 10000))
3046 FR$ = "0.00" + FR$:P$ = FR$
3070 PX = 265 - 7 *  LEN (P$):PY = 184: GOSUB 160: GOTO 3220
3100 P$ =  STR$ ( INT (DA(1,J) / 10 ^ M6 * 100) / 100):PX = 237:PY = 168:
    GOSUB 160: GOTO 3190
3130 P$ =  STR$ ( INT (DA(2,J) / 10 ^ M6 * 100) / 100):PX = 237:PY = 168:
    GOSUB 160: GOTO 3190
3160 P$ =  STR$ ( INT (1 / (DA(2,J) * 10 ^ M6 * W1) * 100) / 100):PX = 23
   7:PY = 168: GOSUB 160
3190 P$ =  STR$ ( INT (DA(0,J) / 10 ^ M7 * 10) / 10):PX = 237:PY = 176: GOSUB
    160
3220  RETURN
5000  HOME : VTAB 12: PRINT  TAB( 6);: INVERSE : PRINT "EVALUATING LINEAR
    REGRESSION": NORMAL
5080 XA = 167 + T3 - M4 * PU:YA = 40 - T4 + M8 * PU: IF P6 <  > 0 THEN XA
    = 167 + T3 - (M5 - 1) * YU:YA = 40 + L3: IF M4 <  > 1 THEN XA = 167 +
   T3 - (M3 - M4) * YU
5090 XX = 0:YY = 0:XY = 0:YX = 0:X2 = 0:N = 0:Q8 = 6.283123 * DA(2,0) * D
   A(0,0)
5100  FOR I = F9 TO J
5110  IF DA(0,I) = 0 THEN 5200
5120  ON P6 GOTO 5140,5150,5160
5130 XX = XX + DA(1,I):YY = YY + DA(2,I):XY = XY + DA(1,I) * DA(2,I):X2 =
   X2 + DA(1,I) * DA(1,I): GOTO 5190
5140 XX = XX + DA(0,I):YY = YY + DA(1,I):XY = XY + DA(0,I) * DA(1,I):X2 =
   X2 + DA(0,I) * DA(0,I): GOTO 5190
5150 XX = XX + DA(0,I):YY = YY + DA(2,I):XY = XY + DA(0,I) * DA(2,I):X2 =
   X2 + DA(0,I) * DA(0,I): GOTO 5190
5160 XX = XX + DA(0,I):YY = YY + 1 / (Q8 * DA(2,I)):XY = XY + DA(0,I) / (
   Q8 * DA(2,I)):X2 = X2 + DA(0,I) * DA(0,I)
5190 N = N + 1
5200  NEXT
5210 XB = XX / N:YB = YY / N:B = (XY - XX * YY / N) / (X2 - XX * XX / N):
    IN = YB - XB * B:X4 = 0:Y4 = 0
5211 AN =  COS ( ATN (B))
5212  IF  ABS (B) <  = .5 THEN Y = B1 * B + IN:Y1 = B6 * B + IN:LL =  SQR
   ((B1 - B6) * (B1 - B6) + (Y - Y1) * (Y - Y1)): GOTO 5230
5213 X = (B3 - IN) / B:X1 = (B2 - IN) / B:LL =  SQR ((B3 - B2) * (B3 - B2
   ) + (X - X1) * (X - X1))
5230  FOR I = F9 TO J
5231  IF DA(0,I) = 0 THEN 5300
5240  IF P6 <  > 0 THEN 5248
5244 Y1 = DA(2,I) - B * DA(1,I) - IN:TT =  ABS (AN * Y1) + TT: GOTO 5300
5248  IF P6 = 1 THEN Y1 = DA(1,I) - B * DA(0,I) - IN:TT =  ABS (AN * Y1) +
   TT: GOTO 5300
5250  IF P6 = 2 THEN Y1 = DA(2,I) - B * DA(0,I) - IN:TT =  ABS (AN * Y1) +
   TT: GOTO 5300
5255 Y1 = 1 / (Q8 * DA(2,I)) - B * DA(0,I) - IN:TT = TT +  ABS (AN * Y1)
5300  NEXT
5302 X4 = LL / (LL + TT)
5303 D4 =  - B:D5 = IN * S3:D5 =  - D4 * YA - D5 + XA: IF P6 <  > 0 THEN
   D4 =  - B * S3 / S4:D5 =  - IN * S3 + XA - D4 * YA
5315 XY(1,1) = D4 * MX + D5:XY(2,1) = D4 * XM + D5:XY(1,0) = MX:XY(2,0) =
   XM
5316 XY(3,0) = (YM - D5) / D4:XY(4,0) = (MY - D5) / D4:XY(3,1) = YM:XY(4,
   1) = MY
5317  GOTO 5320
5318  TEXT : HOME : VTAB 12: HTAB 8: INVERSE : PRINT "LINE OUTSIDE SCREEN
    LIMITS": NORMAL : VTAB 14: HTAB 12: INVERSE : PRINT "USE LARGER SCAL
   ES": NORMAL : VTAB 16: HTAB 2: INPUT "HIT ANY KEY TO REPLOT ORIGINAL
   GRAPH";Q$
5319  PRINT  CHR$ (4);"RUNANALYSIS 1.V3,D1"
5320  FOR L = 1 TO 4: IF XY(L,0) < MX OR XY(L,0) > XM THEN 5324
5321  IF XY(L,1) < MY OR XY(L,1) > 167 + T3 THEN 5324
5322  IF FF = 0 THEN X = XY(L,0):Y = XY(L,1):FF = 1: GOTO 5324
5323 X1 = XY(L,0):Y1 = XY(L,1)
5324  NEXT L
5325  IF X < 2 OR X1 < 2 OR X > 278 OR X1 > 278 OR Y < 2 OR Y1 < 2 OR Y >
   189 OR Y1 > 189 THEN 5318
5327  IF  PEEK (33453) = 1 THEN  CALL 37583: GOTO 5329
5328  PRINT  CHR$ (4);"BLOADGRAPH,D1"
5329  POKE  - 16304,0: POKE  - 16299,0: HPLOT X,Y TO X1,Y1: GET Q$: TEXT
   : HOME
5330  PRINT " COEFF OF FIT "; INT (1000 * X4) / 1000
5331 P$ = "": IF P6 <  > 0 THEN P$ = "Ohms / s"
5332  IF P6 = 3 THEN P$ = "F /(cm2 s)"
5333 SG = 1:I2 =  - IN / B: IF IN < 0 THEN SG =  - 1
5334  PRINT " SLOPE         "; INT (B * 1000) / 1000;" ";P$
5335  IF IN = 0 THEN 5340
5336 PW =  INT ( LOG ( ABS (IN)) / 2.302585):IN =  INT (1000 * IN / 10 ^
   PW) / 1000 * SG * 10 ^ PW:SG = 1: IF I2 < 0 THEN SG =  - 1
5337 PW =  INT ( LOG ( ABS (I2)) / 2.302585):I2 =  INT (1000 * I2 / 10 ^
   PW) / 1000 * SG * 10 ^ PW
5340  PRINT " Y INTERCEPT  ";IN;P$:P$ = " OHMS": IF P6 <  > 0 THEN P$ = "
    S "
5342  PRINT " X INTERCEPT  ";I2;P$: IF FF = 17 THEN 6100
5348  GET Q$
5350  TEXT : HOME : VTAB 2: HTAB 14: INVERSE : PRINT "PROGRAM OPTIONS": NORMAL

5352  VTAB 6: PRINT : PRINT "1: REVIEW LAST PLOT": PRINT : PRINT "2: REPL
   OT EXPANSION ": PRINT : PRINT "3: PRINT ON EPSON": PRINT : PRINT "4:
   PLOT A NEW FILE": PRINT : PRINT "5: EXIT PROGRAM": PRINT
5354  PRINT "6: RETURN TO MAIN PROGRAM": PRINT : PRINT "7: PLOT ON HPPLOT
   TER": PRINT : INPUT "ENTER REQUIRED NUMBER :";Q$:Q =  INT ( ABS ( VAL
   (Q$))): IF Q > 7 THEN  CALL 37984: GOTO 5350
5356  ON Q GOTO 5358,5357,6000,5360,5370,5375,7500
5357 Q = 1: GOTO 2894
5358  POKE  - 16299,0: POKE  - 16304,0: GOTO 5329
5360  IF Q = 4 THEN  HOME : HTAB 11: VTAB 3: INVERSE : PRINT "LOADING ANA
   LYSIS 1": NORMAL : PRINT  CHR$ (4);"RUNANALYSIS 1.V3,D1"
5365  REM  IF Q=5 THEN 5375
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5370  HOME : PRINT "PROGRAM ENDED": END
5375  PRINT  CHR$ (4);"RUN START-UP.V3,D1"
6000  HOME : VTAB 2: HTAB 14: INVERSE : PRINT "EPSON OUTPUT": NORMAL
6004  VTAB 5: INPUT "IS EPSON READY ? ";Q$: IF Q$ < > "Y" THEN 5330
6005  VTAB 7: INPUT "L(ARGE) OR S(MALL) PLOT ";Q$: PRINT  CHR$ (4);"PR#";
    PP: PRINT  CHR$ (4);"PR#0": PRINT  CHR$ (4);"PR#";PP: POKE (1912 + PP
    ),2: POKE (1656 + PP),96: IF Q$ = "L" THEN  POKE (1912 + PP),66
6010  PRINT "Linear regression from ";C4;" to ";C5;: IF P6 = 0 THEN  PRINT
     " Hz ";
6020  IF P6 < > 0 THEN  PRINT " s ";
6030  PRINT N;" data points"
6040 FF = 17: GOTO 5330
6100 FF = 0: PRINT  CHR$ (17)
6120  PRINT "       Operator    : ";A$
6125  PRINT "       Filename    : ";B$
6130  PRINT "       Date        : ";D$
6135  PRINT "       Temperature : ";E$
6140  PRINT "       Pressure    : ";F$
6145  IF A$ < > "GARY" THEN 6170
6150  PRINT "       Membrane no : ";G$
6155  PRINT "       Surface area: ";DA(2,0);" cm2"
6160  PRINT "       Solution 1  : ";H$
6165  PRINT "       Solution 2  : ";I$
6170  PRINT "       Electrodes  : ";J$
6175  IF A$ = "GARY" THEN 6185
6180  PRINT "       Surface area: ";DA(2,0);" cm2"
6185  PRINT "       C.M.R       : ";CR;" Ohms"
6190  IF DA(0,0) < > 0 THEN  PRINT "       Freq        : ";DA(0,0);" Hz"
    : GOTO 6210
6195  PRINT "       Freq max    : ";PS(16);" Hz"
6200  PRINT "       Freq min    : ";PS(17);" Hz"
6205  PRINT "       Semi max    : ";O;" Hz"
6210  PRINT : PRINT
6215  PRINT K$: PRINT L$: PRINT M$: PRINT N$: PRINT O$
6216  PRINT  CHR$ (12): PRINT  CHR$ (4);"PR#0": GOTO 5330
7500 I1 = PU:A1 = AL:I2 = PU: IF P6 > 0 THEN I1 = XR:I2 = YU
7505 R2 = (YM - Y - YN * I2) / S3:R4 = (YM - Y1 - YN * I2) / S3:R1 = (X -
    MX - XN * I1) / S3:R3 = (X1 - MX - XN * I1) / S3
7510  HOME : VTAB 3: HTAB 12: INVERSE : PRINT "LOADING HP PROGRAM": NORMAL
    : CALL 38048: PRINT CD$;"BLOADCHAIN,A520,D1": CALL 520"HPPLOTTER.V2"
10000  TEXT : PRINT "ERROR NO "; PEEK (222);" IN LINE "; PEEK (218) +  PEEK
    (219) * 256: STOP
30000  IF Q = 1 AND DD < > 0 THEN  HOME : VTAB 3: HTAB 13:: INVERSE : PRINT
    "RELOADING DATA": NORMAL : POKE 29,68: POKE 30,65: CALL 38144: PRINT
     CHR$ (4);"BLOAD";B$;",A"; PEEK (27) +  PEEK (28) * 256 + 9;",D2":DD =
    0:ND = 0
30010  IF Q = 1 THEN  PRINT  CHR$ (4);"BLOADGRAPH,D1":F9 = 0:F8 = 0:B1 =
    0:B2 = 0:B3 = 0:B4 = 0:B6 = 0:B7 = 0:B8 = 0:B9 = 0:R = 0:P = 0: GOTO
    640
```

HP Plotter

```
10000  SPEED= 255
10002  HOME : VTAB 2: HTAB 10: INVERSE : PRINT "HP PLOTTER PROGRAM": NORMAL

10010  VTAB 3: HTAB 9: INVERSE : PRINT "INITIALISING PLOTTER": NORMAL
10020  GOSUB 11910
10030  ONERR  GOTO 12350
10040 NY = YP + YN:NX = XP + XN:LO = 0
10042  IF A1 = 3 THEN LO = 1
10050 AP$ = ":'UC -99,2,8,99,-1,-3,-99;'"
10060 OM$ = ":'UC 99,1,0,-1,3,0,3,1,2,2,0,1,-2,0,-3,-1,-3,1,0,-99;'"
10070 XX$ = ":'UC 99,3,4,-99,-3,0,99,3,-4,-99;'"
10080 SL$ = ":'LB/" +  CHR$ (3) + ";'"
10090 TE$ = ":'LB10" +  CHR$ (3) + ";'"
10092 CS$ = ":'CP-.33,-.25;'"
10100 H = 37984:RO = 0
10110  HOME : VTAB 2: HTAB 10: INVERSE : PRINT "HP PLOTTER PROGRAM": NORMAL
    : VTAB 5: INPUT "DO YOU WANT A 90° ROT PLOT ?";R1$: IF R1$ = "Y" THEN
    RO = 1
10120  REM  ASK FOR PARAMETERS
10130 FF = 9000: IF RO = 1 THEN FF = 5500
10140 : VTAB 7: INPUT "ENTER PLOT SCALE (%):";PE$:PE =  VAL (PE$): IF PE =
    0 OR PE > 100 THEN PE = 100: GOTO 10160
10150 SF =  INT ((PE / 100) * FF): GOTO 10170
10160 SF = FF
10170  PRINT : PRINT "ENTER STARTING POSITION:"
10180  INPUT "X (MAX 10000) ";P1$:P1 =  INT ( VAL (P1$)): IF P1 < 1000 OR
    P1 > 10000 THEN P1 = 1500
10190  INPUT "Y (MAX 7000)  ";P2$:P2 =  INT ( VAL (P2$)): IF P2 < 1000 OR
    P2 > 7000 THEN P2 = 1500
10200  IF P6 = 0 THEN YI =  INT ((I1 / 230) * SF):XI =  INT ((I2 / 230) *
    SF): GOTO 10220
10202 A1 = (I1 / 160) * NY:A2 = (I2 / 230) * NX:RT = A1 / A2
10204  IF RT > 1 THEN 10208
10206 SF =  INT ((PE / 100) * 9000): IF RO = 1 THEN SF =  INT ((PE / 100)
    * 5500): GOTO 10210
10208 SF =  INT ((PE / 100) * 5500): IF RO = 1 THEN SF =  INT ((PE / 100)
    * 9000)
10210 YI =  INT ((I1 / 160) * SF):XI =  INT ((I2 / 230) * SF)
10220 SP$ = ":'PU;PA" +  STR$ (P1) + "," +  STR$ (P2) + ";PU;'"
10230  IF RO = 1 THEN 10260
10240  IF YI * NY + P2 < 7200 AND XI * NX + P1 < 10500 THEN 10310
10250  GOTO 10270
10260  IF P1 - YI * NY > 500 AND XI * NX + P2 < 7200 THEN 10310
10270  HOME : VTAB 12: PRINT  TAB( 8): FLASH : PRINT "SCALE FACTOR/STARTI
    NG POINT"
10280  NORMAL : PRINT  TAB( 14): FLASH : PRINT "MISMATCH ERROR": NORMAL
10290  PRINT : PRINT  TAB( 13): PRINT "PLEASE  RE-ENTER"
10300  FOR JJ = 1 TO 1000: NEXT JJ: GOTO 10110
10310 C2 = 1: IF SY(1,0) = 0 THEN  GOSUB 12210
10312  GOSUB 10490
10320  REM  RETURN OR FINISH
10330  HOME : VTAB (4)
10340  PRINT "PROGRAM OPTIONS ARE :-"
10350  PRINT : PRINT " 1: RETURN TO MAIN PROG."
10360  PRINT : PRINT " 2: RETURN TO 'ANALYSIS 1'"
10370  PRINT : PRINT " 3: EXIT FROM PROGRAM"
10380  PRINT : PRINT " 4: REPLOT LAST GRAPH"
10390  PRINT : PRINT " 5: PLOT ANOTHER FILE ON THESE AXES"
10400  VTAB 19: INPUT "ENTER NUMBER :";NN
10410  IF NN < 1 OR NN > 5 OR NN <  > INT (NN) THEN  CALL H: GOTO 10400
10420  ON NN GOTO 10430,10450,10480,10100,11750
10430  PRINT  CHR$ (4);"RUN START-UP.V3,D1"
10450 ZR(3) = 2
10460  PRINT  CHR$ (4);"RUN ANALYSIS 1.V3,D1"
10480  END
10490  REM  *** COMMENCE PLOT ***
10500  PRINT  CHR$ (4);"PR#3"
10510  PRINT "@7Z;'IN;'": PRINT SP$
10520  REM  PLOT AXES
10530  REM  Y-AXIS
10540 U1 =  INT (YI / 9): IF RO = 1 THEN U1 = U1 *  - 1
10550 U1$ =  STR$ (U1)
10560 U2 = 3 *  INT (YI / 9): IF RO = 1 THEN U2 = U2 *  - 1
10570 U2$ =  STR$ (U2)
10580 U3 =  INT (YI -  ABS (2 * U2)): IF RO = 1 THEN U3 = U3 *  - 1
10590 U3$ =  STR$ (U3)
10600 A1$ =  STR$ (P1 + (YN * YI))
10610 A2 =  -  INT (YI / 4): IF RO = 1 THEN A2 = A2 *  - 1
10620 A2$ =  STR$ (A2)
10630 A3 = 2 *  INT (YI / 4): IF RO = 1 THEN A3 = A3 *  - 1
10640 A3$ =  STR$ (A3)
10650 YZ$ = ":'PR" +  STR$ (0) + "," + U2$ + "," + A2$ + "," + U1$ + "," +
    A3$ + "," + U1$ + "," + A2$ + "," + U1$ + "," +  STR$ (0) + "," + U3$
     + ";'"
10660  IF RO = 1 THEN YZ$ = ":'PR" + U2$ + "," +  STR$ (0) + "," + U1$ +
    "," + A2$ + "," + U1$ + "," + A3$ + "," + U1$ + "," + A2$ + "," + U3$
    + "," +  STR$ (0) + ";'"
10670 T1 =  - 100:T2 = 0: IF RO = 1 THEN T1 = 0:T2 =  - 100
10680  IF XN > XP THEN T1 =  - T1:T2 =  - T2
10690  FOR J = 0 TO NY
10692  IF LO = 0 THEN 10700
10694  IF J = 0 OR J = NY THEN 10700
10696 TY$ = ":'PR0,0;'": GOTO 10710
10700 TY$ = ":'PR" +  STR$ (T1) + "," +  STR$ (T2) + "," +  STR$ ( - T1) +
    "," +  STR$ ( - T2) + ";'"
10710 AY$ = ":'PA" +  STR$ (P1 + (XN * XI)) + "," +  STR$ ((YI * J) + P2)
    + ";'"
10720  IF RO = 1 THEN AY$ = ":'PA" +  STR$ (P1 - (J * YI)) + "," +  STR$
    (P2 + (XN * XI)) + ";'"
10730  IF YS <  > 0 AND YN = 0 AND J = 1 THEN  PRINT YZ$;TY$: GOTO 10770
10740  IF YS <  > 0 AND YP = 0 AND J = NY THEN  PRINT YZ$;TY$: GOTO 10770

10750  PRINT AY$;: IF J = 0 THEN  PRINT ":'PD;'"
10760  PRINT TY$
10770  NEXT J: PRINT ":'PU;'"
10780  REM  X-AXIS
10790 U1 =  INT (XI / 9)
10800 U1$ =  STR$ (U1)
10810 U2 = 3 *  INT (XI / 9)
10820 U2$ =  STR$ (U2)
10830 U3 =  INT (XI -  ABS (2 * U2))
10840 U3$ =  STR$ (U3)
10850 A1$ =  STR$ (P1 + (YN * YI))
10860 A2 =  -  INT (XI / 4): IF RO = 1 THEN A2 = A2 *  - 1
10870 A2$ =  STR$ (A2)
10880 A3 = 2 *  INT (XI / 4): IF RO = 1 THEN A3 = A3 *  - 1
10890 A3$ =  STR$ (A3)
10900 XI$ = ":'PR" + U2$ + "," +  STR$ (0) + "," + U1$ + "," + A2$ + "," +
    U1$ + "," + A3$ + "," + U1$ + "," + A2$ + "," + U3$ + "," +  STR$ (0)
     + ";'"
10910  IF RO = 1 THEN XI$ = ":'PR" +  STR$ (0) + "," + U2$ + "," + A2$ +
    "," + U1$ + "," + A3$ + "," + U1$ + "," + A2$ + "," + U1$ + "," +  STR$
    (0) + "," + U3$ + ";'"
10920 T1 = 0:T2 =  - 100: IF RO = 1 THEN T1 = 100:T2 = 0
10930  IF YN > YP THEN T1 =  - T1:T2 =  - T2
10940  FOR J = 0 TO NX
10942  IF LO = 0 THEN 10950
10944  IF J = 0 OR J = NX THEN 10950
10946 TX$ = ":'PR0,0;'": GOTO 10960
10950 TX$ = ":'PR" +  STR$ (T1) + "," +  STR$ (T2) + "," +  STR$ ( - T1) +
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   "," + STR$ ( - T2) + ";'"
10960 AX$ = ":'PA" + STR$ ((XI * J) + P1) + "," + STR$ (P2 + (YI * YN))
   + ";'"
10970 IF RO = 1 THEN AX$ = ":'PA" + STR$ (P1 - (YN * YI)) + "," + STR$
   (P2 + (XI * J)) + ";'"
10980 IF XS < > 0 AND XN = 0 AND J = 1 THEN PRINT XZ$;TX$: GOTO 11020
10990 IF XS < > 0 AND XP = 0 AND J = NX THEN PRINT XZ$;TX$: GOTO 11020

11000 PRINT AX$;: IF J = 0 THEN PRINT ":'PD;'"
11010 PRINT TX$
11020 NEXT J: PRINT ":'PU;'"
11030 REM TICK LABELS
11040 REM Y-AXIS
11050 IF RO = 1 THEN PRINT ":'DI0,1;'"
11060 LS = 0: IF YS < > 0 THEN LS = 1
11070 K = - YN: IF YS < > 0 THEN K = YS
11080 FOR J = LS TO NY
11082 IF LO = 0 THEN 11090
11084 IF J = 0 OR J = NY THEN 11090
11086 GOTO 11340
11090 IF K = 0 THEN 11180
11100 YL$ = STR$ (K * YF):OX = LEN (YL$) * 114 + 150: IF XN > XP THEN O
   X = - 150
11110 IF ABS (MM) < ABS (OX) THEN MM = ABS (OX)
11120 OY = 54: IF RO = 1 THEN OY = OX:OX = - 54
11130 S1$ = ":'PU;PA" + STR$ (P1 + (XN * XI)) + "," + STR$ (P2 + (YI *
   J)) + ";'"
11140 IF RO = 1 THEN S1$ = ":'PU;PA" + STR$ (P1 - (J * YI)) + "," + STR$
   (P2 + (XI * XN)) + ";'"
11150 S2$ = ":'PR " + STR$ ( - OX) + "," + STR$ ( - OY) + ";'"
11160 PRINT S1$;S2$
11170 PRINT ":'LB" + YL$ + CHR$ (3) + ";'"
11180 K = K + 1: NEXT J
11190 REM X-AXIS
11200 IF RO = 1 THEN PRINT ":'DI0,1;'"
11210 LS = 0: IF XS < > 0 AND XP < > 0 THEN LS = 1
11220 IF XP = 0 THEN NX = NX - 1
11230 K = - XN: IF XS < > 0 THEN K = XS
11240 FOR J = LS TO NX
11242 IF LO = 0 THEN 11250
11244 IF J = 0 OR J = NX THEN 11250
11246 GOTO 11340
11250 IF K = 0 THEN 11340
11260 XL$ = STR$ (K * XF):OX = ( LEN (XL$) * 114) / 2: IF K < 0 THEN OX =
   OX - 57
11270 OY = 275: IF YN > YP THEN OY = - 150
11280 IF RO = 1 THEN OY = OX:OX = - 275: IF YN > YP THEN OX = 150
11290 S1$ = ":'PU;PA" + STR$ (P1 + (J * XI)) + "," + STR$ (P2 + (YN * Y
   I)) + ";'"
11300 IF RO = 1 THEN S1$ = ":'PU;PA" + STR$ (P1 - (YI * YN)) + "," + STR$
   (P2 + (J * XI)) + ";'"
11310 S2$ = ":'PR" + STR$ ( - OX) + "," + STR$ ( - OY) + ";'"
11320 PRINT S1$;S2$
11330 PRINT ":'LB" + XL$ + CHR$ (3) + ";'"
11340 K = K + 1: NEXT J
11342 PRINT SP$
11350 REM *** Y-AXIS LABEL ***
11360 IF XN = 0 THEN L1 = MM + 200:L2 = L1
11370 IF XP = 0 THEN L1 = - ((XN * XI) + MM + 400):L2 = L1: GOTO 11400
11380 IF XN < > 0 AND XN < = XP THEN L1 = 150:L2 = 0
11390 IF XN < > 0 AND XN > XP THEN L1 = - ((XN + XP) * XI + 150):L2 =
   L1
11400 ON P6 GOTO 11420,11410,11430
11410 YL = 340: GOTO 11440
11420 YL = 300: GOTO 11440
11430 YL = 730
11440 YC = (YI * NY) / 2
11450 IF RO = 1 THEN LS$ = ":'PA" + STR$ ( INT (P1 - YC + YL)) + "," +
   STR$ ( INT (P2 - L1)) + ";DI-1,0;'": GOTO 11470
11460 LS$ = ":'PA" + STR$ ( INT (P1 - L2)) + "," + STR$ ( INT (P2 + YC -
   YL)) + ";" + "DI0,1;'"
11470 PRINT LS$: ON P6 GOTO 11490,11480,11500
11480 GOSUB 12030: GOTO 11510
11490 GOSUB 12000: GOTO 11510
11500 GOSUB 12060
11510 REM *** X-AXIS LABEL ***
11520 XL = 340: IF P6 < > 0 THEN XL = 410
11530 XC = (XI * (XP + XN) / 2)
11540 IF YN = 0 THEN L1 = 700:L2 = 700
11550 IF YP = 0 THEN L1 = - ((YN * YI) + 400):L2 = L1: GOTO 11580
11560 IF YN < > 0 AND YN < YP THEN L1 = 300:L2 = 300
11570 IF YN < > 0 AND YN > YP THEN L1 = - ((YN + YP) * YI + 150):L2 =
   L1
11580 IF RO = 1 THEN PRINT ":'PA" + STR$ ( INT (P1 + L1)) + "," + STR$
   ( INT (P2 + XC - XL)) + ";" + "DI0,1;'": GOTO 11600
11590 PRINT ":'PA" + STR$ ( INT (P1 + XC - XL)) + "," + STR$ ( INT (P2
   - L2)) + ";" + "DI1,0;'"
11600 IF P6 < > 0 THEN GOSUB 11970: GOTO 11620
11610 GOSUB 12000
11620 REM PLOTTING DATA POINTS
11630 C3 = C1:M = 1
11640 FOR J = 1 TO DA(1,0)
11650 XX = INT ((DA(1,J) / (XF * 10 ^ XE) * XI) + (XN * XI) - (XS * XI))

11660 YY = INT ((DA(2,J) / (YF * 10 ^ YE) * YI) + (YN * YI) - (YS * YI))

11670 D1 = XX:D2 = YY: IF RO = 1 THEN D1 = - YY:D2 = XX
11680 PRINT ":'PA" + STR$ (P1 + D1) + "," + STR$ (P2 + D2) + ";'"
11682 IF SY(M,0) = 0 THEN 11690
11684 IF J = SY(M,0) THEN C2 = C2 + 1:M = M + 1: GOTO 11702
11686 IF DA(0,J) = 0 THEN 11702
11690 IF P6 = 0 AND DA(0,J) / (10 ^ INT ( LOG (.99 * DA(0,J)) / 2.30258
   )) + .05 > 10 THEN C1 = C2
11700 GOSUB 12090
11702 NEXT J
11704 IF R1 < > 0 OR R2 < > 0 OR R3 < > 0 OR R4 < > 0 THEN GOSUB 12
   500
11710 PRINT ":'PU;IN;'"
11720 PRINT CHR$ (4);"PR#0"
11730 PRINT CHR$ (4);"IN#0"
11740 C1 = 0:C2 = 0:C3 = 0: RETURN
11750 REM PLOT ANOTHER FILE ON
11760 REM THE SAME SET OF AXES
11762 HOME : VTAB 2: HTAB 16: INVERSE : PRINT "HP PLOTTER": NORMAL : VTAB
   5: HTAB 9: PRINT "(<CR> WILL CATALOG DISK )"
11764 PRINT : INPUT "ENTER FILENAME :";F$: IF F$ < > "" THEN 11850
11766 CALL 35424: FOR I = 29 TO 0 STEP - 1:DI = PEEK (35456 + I) - 128
   : IF DI = 32 THEN NEXT I
11768 B$ = "": FOR J = 0 TO I:DI = PEEK (35456 + J) - 128:B$ = B$ + CHR$
   (DI): NEXT J:F$ = B$: IF PEEK (35436) = 141 THEN 11750
11850 POKE 29,68: POKE 30,65: CALL 38144
11860 PRINT CHR$ (4);"BLOAD";F$;",A" PEEK (27) + PEEK (28) * 256 + 9;"
   ,D2"
11870 GOSUB 12210
11880 PRINT CHR$ (4);"PR#3"
11890 PRINT "@7%";":'IN;'"
11900 PRINT SP$: GOSUB 11620: GOTO 10320
11910 REM INIT. SBR
11920 PRINT CHR$ (4);"PR#3"
11930 PRINT "@7%";":'IN;'"
11940 PRINT CHR$ (4);"PR#0"
11950 PRINT CHR$ (4);"IN#0"
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11960  RETURN
11970  REM  TIME
11980  PRINT "'LB" +  CHR$ (84) +  CHR$ (105) +  CHR$ (109) +  CHR$ (101)
     + "/ " +  CHR$ (115) +  CHR$ (3) + ";""
11990 EE = XE: GOSUB 12320: PRINT SP$: RETURN
12000  REM  Z'
12010  PRINT "'LBZ" +  CHR$ (3) + ";"": PRINT AP$
12020  PRINT SL$;DM$:EE = XE: GOSUB 12320: PRINT SP$: RETURN
12030  REM  Z''
12040  PRINT ":'LBZ" +  CHR$ (3) + ";"": PRINT AP$;AP$
12050  PRINT SL$;DM$:EE = YE: GOSUB 12320: PRINT SP$: RETURN
12060  REM  DLC/FCM2
12070  PRINT ":'LB D.L.C/ F" +  CHR$ (99) +  CHR$ (109) +  CHR$ (3) + ";C
    P 0.4,0.5;SI0.1,0.16;LB-2" +  CHR$ (3) + ";SI;CP-0.4,-0.5;""
12080 EE = YE: GOSUB 12320: PRINT SP$: RETURN
12090  REM  PLOT POINT SYMBOL
12100  PRINT ":'DI 1,0;""
12110  IF RO = 1 THEN  PRINT ":'DI 0,1;""
12120  IF C1 <  > 1 THEN  PRINT CS$
12128  ON C1 GOTO 12130,12140,12150,12160,12170,12180,12190
12130  PRINT ":'PD;PU;"": GOTO 12200
12140  PRINT ":'UC-99,2,1,99,0,6,-99,-2,-1,99,4,-4,-99,0,4,99,-4,-4,-99;'
    ": GOTO 12200
12150  PRINT ":'UC -99,2,1,99,0,6,-99,-2,-3,99,4,0,-99;"": GOTO 12200
12160  PRINT ":'UC-99,1,2,99,0,4,2,0,0,-4,-2,0,-99;"": GOTO 12200
12170  PRINT ":'UC-99,1,3,99,1,2,1,-2,-2,0, -99;"": GOTO 12200
12180  PRINT ":'UC-99,1,1,99,2,0,1,1,0,4,-1,1,-2,0,-1,-1,0,-4,1,-1,-99;""
    : GOTO 12200
12190  PRINT ":'UC-99,1,2,99,-1,2,2,2,2,-2,-1,-2,-2,0,-99;"": GOTO 12200
12200  PRINT ":'SI;DI 1,0;"":C1 = C3: RETURN
12210  REM   ASK PLOT SYMBOL
12220  HOME : VTAB 5: PRINT "WHICH PLOTTING SYMBOL :"
12230  PRINT : PRINT "1: DOTS ": PRINT : PRINT "2: ASTERISKS (*)": PRINT
    : PRINT "3: CROSSES (+)": PRINT : PRINT "4: SMALL SQUARES"
12240  PRINT : PRINT "5 :TRIANGLE ": PRINT : PRINT "6: LARGE SQUARES": PRINT
    : PRINT "7: PENTAGONS"
12250  VTAB (21): INPUT "ENTER NUMBER :";CC$:CC =  VAL (CC$): IF CC < 1 OR
    CC > 7 OR CC <  > INT (CC) THEN  CALL H: GOTO 12250
12260  IF C1 = 0 THEN C1 = CC: GOTO 12280
12270 C2 = CC: GOTO 12310
12280  VTAB 23: INPUT "DECADE MARKING ?:";Q$: IF Q$ = "N" OR Q$ = "" THEN
    C2 = C1: GOTO 12310
12290  IF Q$ = "Y" THEN 12210
12300  CALL H: GOTO 12280
12310  RETURN
12320  REM  X10 EY
12330  PRINT ":'CP 0.25,0;"": PRINT XX$;TE$
12340  PRINT ":'CP 0.25,0.4;SI0.1 ,0.16;"": PRINT ":'LB" +  STR$ (EE) +  CHR$
    (3) + ";SI;"": RETURN
12350  REM    ERROR SBR
12360  PRINT  CHR$ (4);"PR#3"
12370  PRINT "@7%";":'IN;""
12380  PRINT  CHR$ (4);"PR#0"
12390  PRINT  CHR$ (4);"IN#0"
12400 ER =  PEEK (222):EN =  PEEK (218) +  PEEK (219) * 256
12410  INVERSE : PRINT "ERROR ";ER;" HAS OCCURED": NORMAL : PRINT "  ";EN

12420  STOP : TRACE : RESUME
12500  REM  LINEAR REGRESSION
12510 XA =  INT ((R1 / (XF * 10 ^ XE) * XI) + (XN * XI) - (XS * XI))
12514 XB =  INT ((R3 / (XF * 10 ^ XE) * XI) + (XN * XI) - (XS * XI))
12520 YA =  INT ((R2 / (YF * 10 ^ YE) * YI) + (YN * YI) - (YS * YI))
12524 YB =  INT ((R4 / (YF * 10 ^ YE) * YI) + (YN * YI) - (YS * YI))
12530 D1 = XA:D2 = YA:D3 = XB:D4 = YB: IF RO = 1 THEN D1 =  - YA:D2 = XA:
    D3 =  - YB:D2 = XB
12540  PRINT ":'PA" +  STR$ (P1 + D1) + "," +  STR$ (P2 + D2) + ";""
12550  PRINT ":'PD;"": PRINT ":'PA" +  STR$ (P1 + D3) + "," +  STR$ (P2 +
    D4) + ";""
12560  PRINT ":'PU;""
12570  RETURN
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Simplot

```
10  GOTO 10000
66  PRINT CD$;"LOCK,D";B$: PRINT CD$
68  POKE 29,68: POKE 30,65: CALL 38144
70  PRINT CD$;"BSAVE";B$;",A";PEEK (27) + PEEK (28) * 256 + 9;",L";15 *
    (DA(1,0) + 1);",D1"
72  PRINT CD$;"LOCK";B$
10000  ONERR  GOTO 17660
10004  HIMEM: 34643
10010  LOMEM: 24576
10020  DIM DS$(20),DS(2),PS(24),DA(2,200)
10024 PS(0) = 1:PS(2) = 1:PS(4) = 1:PS(6) = 2:PS(7) = 4:PS(8) = 2:PS(9) =
    8:PS(12) = 3:PS(13) = 1:PS(16) = 999900:PS(17) = 0.1:PS(18) = 1:PS(19
    ) = 1:PS(20) = 0.01:PS(21) = 0.01:PS(22) = 15:PS(23) = 15
10030 FF =  FRE (0): TEXT : HOME
10032  CALL 38048
10040  POKE 232,104: POKE 233,142
10050 H = 37984:CD$ =  CHR$ (4): SCALE= 1: ROT= 0: HCOLOR= 3: POKE 222,0:
     POKE 216,0: POKE 219.0
10130 A1$ = "FREQUENCY":A2$ = "Z'/ (OHMS)":A3$ = "Z''/(OHMS)"
10140 TB = 13:TI$ = "PROGRAM OPTIONS": GOSUB 18140
10150  VTAB 4: PRINT "1: CALCULATE NEW DATA": PRINT : PRINT "2: LIST DATA
     ON MONITOR": PRINT : PRINT "3: LIST DATA ON PRINTER": PRINT : PRINT
    "4: PLOT DATA": PRINT : PRINT "5: SAVE DATA"
10154  PRINT : PRINT "6: VIEW GRAPHICS PAGE": PRINT : PRINT "7: DUMP PLOT
     TO PRINTER": PRINT : PRINT "8: EXIT PROGRAM"
10160  VTAB 21: INPUT "ENTER NUMBER :";O$: IF O$ = "" THEN 10160
10170 O =  VAL (O$): IF O < 1 OR O > 8 OR O <  >  INT (O) THEN 10160
10200  ON O GOSUB 10950,21100,21200,14000,20000,18000,21000,10400
10210  GOTO 10030
10400  REM  FINISH
10410 TB = 12:TI$ = "PROGRAM FINISHED": GOSUB 18140
10420  END
10950  REM CALC NEW DATA
10960  GOSUB 11000: REM SET PARAMS
10970  GOSUB 12000: REM CALC DATA
10980  RETURN
11000  REM  GET PARAMETERS
11010 TB = 11:TI$ = "IMPEDANCE SIMULATION": GOSUB 18140
11020  VTAB 4: INPUT "F MAX   :";O$: IF O$ = "" THEN 11020
11030 O =  VAL (O$): IF O < 1E - 4 OR O > 999900 THEN 11050
11040 PS(16) = O
11050  VTAB 6: INPUT "F MIN   :";O$: IF O$ = "" THEN 11050
11052 O =  VAL (O$): IF O < 1E - 4 OR O > 999900 THEN 11050
11054 PS(17) = O: IF O = 1 THEN PS(17) = 1.1
11060  VTAB 8: INPUT "DELTA F :";O$: IF O$ = "" THEN 11060
11070 O =  VAL (O$): IF O < 1 OR O > 99 THEN 11060
11080 PS(22) = O:PS(23) = O: HGR2 : TEXT : GOTO 11350
11204  DRAW 92 AT 2,37
11210  HPLOT 10,40 TO 30,40
11220 XX = 30:YY = 40: GOSUB 19000
11240  GOSUB 19300: HPLOT XX,YY TO XX + 20,YY
11260  DRAW 93 AT 2,97
11280  HPLOT 10,100 TO 30,100
11300 XX = 30:YY = 100: GOSUB 19000
11320  GOSUB 19300: HPLOT XX,YY TO XX + 15,YY:XX = XX + 15: GOSUB 19300: HPLOT
    XX,YY TO XX + 10,YY
11340 XX = XX + 10: GOSUB 19000: HPLOT  TO XX + 20,YY
11350  TEXT : VTAB 11: INPUT "SOLUTION RESISTANCE :";O$: IF O$ = "" THEN
    11350
11360 O =  VAL (O$): IF O <  = 0 OR O  1E6 THEN 11350
11370 RS = O: POKE 34,11: HOME
11390  TEXT : VTAB 11: INPUT "HOW MANY PARALLEL NETWORKS ?";O$: IF O$ = "
    " THEN 11350
11400 O =  VAL (O$): IF O  = O OR O > 3 THEN 11350
11410 NP = O: FOR I = 1 TO 3:R(I) = 0:C(I) = 0: NEXT
11420  POKE 34,10
11430  FOR I = 1 TO NP
11434 TB = (I * 12) - 11: VTAB 13: HTAB TB: INPUT "R :";O$: IF O$ = "" THEN
    11434
11438 O =  VAL (O$): IF O < 1 OR O > 1E8 THEN 11434
11440 R(I) = O:TB = (I * 12) - 11: VTAB 14: HTAB TB: INPUT "C :";O$: IF O
    $ = "" THEN 11440
11444 O =  VAL (O$): IF O < 1E - 12 OR O > 1 THEN 11440
11448 C(I) = O
11450  NEXT : HOME : PRINT
11460  CALL 34644;"  R1:",R(1);E3, CHR$ (13):
11464  CALL 34644;"  C1:",C(1);E3, CHR$ (13):
11468  PRINT : CALL 34644;"  R2:",R(2);E3, CHR$ (13):
11472  CALL 34644;"  C2:",C(2);E3, CHR$ (13):
11476  PRINT : CALL 34644;"  R3:",R(3);E3, CHR$ (13):
11480  CALL 34644;"  C3:",C(3);E3, CHR$ (13):
11488  VTAB 22: INPUT "VALUES OK ?";O$: IF O$ = "" THEN 11488
11490  IF O$ = "N" THEN  PRINT : HOME : GOTO 11350
11500  POKE 34,0
11510 R1 = R(1):R2 = R(2):R3 = R(3):C1 = C(1):C2 = C(2):C3 = C(3)
11700  RETURN
12000  REM  CALC DATA
12100 D =  LOG (10) / PS(22)
12110 A1 = 39.48 * C1 * C1 * R1 * R1
12120 A2 = 39.48 * C2 * C2 * R2 * R2
12124 A3 = 39.48 * C3 * C3 * R3 * R3
12130 P2 = 2 * 3.14159:J = 1
12140  VTAB 10: HTAB 12: INVERSE : PRINT "POINTS EVALUATED": NORMAL
12200 F =  EXP ( LOG (PS(17)) + D * J)
12210  IF F > PS(16) THEN 12254
12220 Z1 = R1 / (1 + F * F * A1) + RS: IF NP > 1 THEN Z1 = Z1 + R2 / (1 +
    A2 * F * F): IF NP = 3 THEN Z1 = Z1 + R3 / (1 + A3 * F * F)
12230 Z2 = (P2 * F * C1 * R1 * R1) / (1 + A1 * F * F): IF NP > 1 THEN Z2 =
    Z2 + (P2 * F * C2 * R2 * R2) / (1 + A2 * F * F): IF NP = 3 THEN Z2 =
    Z2 + (P2 * F * C3 * R3 * R3) / (1 + A3 * F * F)
12240 DA(0,J) = F:DA(1,J) = Z1:DA(2,J) = Z2
12250 J = J + 1: VTAB 10: HTAB 29: PRINT J: GOTO 12200
12254 DAZ = J - 1:DA(1,0) = DAZ
12260  GOSUB 13000
12300  RETURN
13000  REM  GET SEMIMAX
13010  POKE 34,20: HOME : POKE 34,0: VTAB 21: HTAB 8: FLASH : PRINT "CALC
    ULATING TIME CONSTANTS": NORMAL
13100  FOR I = 1 TO DAZ
13110 M1 = DA(2,I):M2 = DA(2,I + 1):M3 = DA(2,I + 2)
13130  IF M1 = M2 OR M1 > M2 THEN  IF M1 > M3 THEN F1(1) = DA(0,I):F2(1) =
    DA(1,I):F3(1) = DA(2,I):J = I:I = DAZ
13140  NEXT
13150  FOR I = J TO DAZ
13160 M1 = DA(2,I):M2 = DA(2,I + 1):M3 = DA(2,I + 2):M4 = DA(2,I + 3)
13170  IF M1 > M2 AND M3 > M2 AND M4 > M3 THEN J = I:I = DAZ
13190  NEXT
13200  FOR I = J TO DAZ
13210 M1 = DA(2,I):M2 = DA(2,I + 1):M3 = DA(2,I + 2)
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```
13220  IF (M1 - M2) > 0 AND (M2 - M3)  0 AND (M3 - M4) < 0 THEN 13240
13230  IF M1 = M2 OR M1  M2 THEN  IF M1  M3 THEN F1(J) = DA(0,I):F2(J
    ) = DA(1,I):F3(J) = DA(2,I):J = J+1:I = DAZ
13240  NEXT
13250  FOR I = J TO DAZ
13260 M1 = DA(2,I):M2 = DA(2,I + 1):M3 = DA(2,I + 2):M4 = DA(2,I + 3)
13270  IF M1 > M2 AND M3 > M2 AND M4  M3 THEN J = I:I = DAZ
13280  NEXT
13290  FOR I = J TO DAZ
13300 M1 = DA(2,I):M2 = DA(2,I + 1):M3 = DA(2,I + 2)
13310  IF (M1 - M2) > 0 AND (M2 - M3) < 0 AND (M3 - M4) < 0 THEN 13390
13320  IF M1 = M2 OR M1 > M2 THEN  IF M1 > M3 THEN F1(J) = DA(0,I):F2(J)
     = DA(1,I):F3(J) = DA(2,I):I = DAZ
13390  NEXT : HOME
13400  RETURN
14000  REM  PLOTTING LOOP
14010  SCALE= 1: ROT= 0: HCOLOR= 3
14020  POKE 232,104: POKE 233,142
14030 B1 = 0:B2 = 0:B3 = 0:B6 = 0
14040  GOSUB 14100
14042  GOTO 14098
14060 X = DA(1,DAZ) * S3 + 40 + M8 * PU:Y = 167 - M4 * PU - DA(2,DAZ) * S
    3
14080  IF X < 2 OR Y < 2 OR X > 278 OR Y > 189 THEN  GOSUB 14130
14090  IF Q <  >  INT ( LOG (Q9 * DA(0,DAZ)) / 2.30258) THEN Q =  INT ( LOG
    (Q9 * DA(0,DAZ)) / 2.30258): DRAW 4 AT X,Y
14094  HPLOT X,Y: RETURN
14098  GET Q$: TEXT : RETURN
14100  CALL 38048
14120 Q9 = 1.011: IF PS(8) = 3 THEN Q9 = .99
14130 EX = EX + 13 + DAZ * .1:B2 = DA(2,1):B6 = DA(1,1)
14140  FOR L = 1 TO DAZ
14150  IF DA(1,L) > B1 THEN B1 = DA(1,L)
14160  IF DA(2,L) > B3 THEN B3 = DA(2,L)
14170  IF DA(2,L) < B2 THEN B2 = DA(2,L)
14180  IF DA(1,L) < B6 THEN B6 = DA(1,L)
14190  NEXT L
14200 B4 = ((TI + TD) * N1 + EX) * 1.15:B5 = B2
15100  IF X > 278 THEN B1 = B1 * 1.4:B4 = B4 * 1.4
15120  IF Y < 2 AND B3 > 0 THEN B3 = B3 * 1.4
15140  IF Y < 2 AND B3 < 0 THEN B3 = B2 * .7
15160  IF Y > 189 AND B2 > 0 THEN B2 = B2 * .7
15180  IF Y > 189 AND B2 < 0 THEN B2 = B2 * 1.4
15200  IF B3 < 0 THEN B3 = 0
15240  IF B3 < .4 * B1 THEN B3 = .5 * B1
15260  IF B2 > 0 THEN B2 = 0
15280  IF B6 > 0 THEN B6 = 0
15300  IF B1 < 0 THEN B1 = 0
15320 M1 = B3 - B2:M2 =  - B2 / M1:S1 = (B1 - B6) * 1.2:S5 = S1: IF S1 <
    .3 * CR THEN S1 = .5 * CR:B1 = S1:S5 = B1:  IF B6 < 0 THEN B6 =  - B1
15340  IF M1 / S5 * 23 > 16 THEN S1 = M1 * 1.2
15360 M6 =  INT ( LOG (S1) / 2.30258):S1 = S1 / 10 ^ M6: IF S1 < 1.95 THEN
    S2 = 2:P =  INT ((S1 + .2) / .4) * 2:M6 = M6 - 1: GOTO 15420
15380  IF S1 < 4.85 THEN S2 = 5:P =  INT (S1 + .5) * 2:M6 = M6 - 1: GOTO
    15420
15400 S2 = 1:P =  INT (S1 + 1)
15420  IF P < 5 THEN P = P + 1
15440  IF M1 / S5 * 23 > 16 THEN PU =  INT (160 / P):M4 =  INT (P * M2 +
    .8):M3 = P - M4:R =  INT (230 / PU): HGR2 :M8 =  -  INT (B6 / S5 * R +
    .1):R = R - M8: GOTO 15480
15460 PU =  INT (230 / P):M3 =  INT (160 / PU):M4 =  INT (M3 * M2 + .9):M
    3 = M3 - M4:R = P: HGR2 :M8 =  -  INT (B6 / S5 * R + .1):R = R - M8
15480  FOR J = 0 TO 5 + M8: HPLOT M8 * PU + 35.167 - J * PU TO 40 + M8 *
    PU,167 - J * PU: NEXT J
15500  HPLOT 40 + M8 * PU,167 TO 40 + M8 * PU,167 - (M3 + M4) * PU
15520  FOR J = 0 TO 5 + M8: HPLOT J * PU + 40,167 - M4 * PU TO J * PU + J
    0,172 - M4 * PU: NEXT J
15540  HPLOT 40,167 - M4 * PU TO 40 + (R + M8) * PU,167 - M4 * PU:P$ =  CHR$
    (20) + "IMPEDANCE " +  CHR$ (20) + "PLOT":PX = 106:PY = 165 - (M4 + M
    3) * PU - PU: IF PY < 0 THEN PY = 0
15560  HPLOT PX - 2,PY + 9 TO PX + 96,PY + 9: GOSUB 15940
15580  FOR J =  - M8 TO R
15600  IF J = 0 AND M4 <  > 0 THEN 15660
15620 P$ =  STR$ (J * S2):PX = (J + M8) * PU + 38:PY = 174 - M4 * PU: IF
    J * S2 > 9 OR J * S2 < 0 THEN PX = PX - 3: IF J * S2 <  - 9 THEN PX =
    PX - 4
15640  GOSUB 15940
15660  NEXT J
15680  FOR J = 1 TO M4 + M3 + 1
15700 P$ =  STR$ ((J - 1 - M4) * S2):PY = 164 - (J - 1) * PU:PX = M8 * PU
     + 34 -  LEN (P$) * 7
15720  IF M8 <  > 0 AND (J - 1 - M4) = 0 THEN 15760
15740  GOSUB 15940
15760  NEXT J
15770 P$ =  CHR$ (20) + "Z' /(" +  CHR$ (20) + "OHMS) X 10" +  CHR$ (20) +
     STR$ (M6):PX = 108:PY = 185: GOSUB 15940
15780 P$ =  CHR$ (20) + "Z''/(" +  CHR$ (20) + "OHMS) X 10" +  CHR$ (20) +
     STR$ (M6):PX = 149:PY = 2: ROT= 48:UP = 1: GOSUB 15940: ROT= 0:UP =
     0
15820 S5 = PU / (S2 * 10 ^ M6)
15830  FOR L = 1 TO DAZ
15840 X = DA(1,L) * S3 + M8 * PU + 40:Y = 167 - M4 * PU - DA(2,L) * S5
15860  IF Q <  >  INT ( LOG (Q9 * DA(0,L)) / 2.30258) THEN Q =  INT ( LOG
    (Q9 * DA(0,L)) / 2.30258): DRAW 4 AT X,Y
15880  HPLOT X,Y
15900  NEXT L
15920  RETURN
15940 RU = PX:P4 =  - 32
15960  FOR RR = 1 TO  LEN (P$)
15980 S =  ASC ( MID$ (P$,RR,1)): IF S >  = 128 THEN S = S - 128
16000  IF S = 32 THEN 16120
16020  IF S = 20 THEN P4 = 27: GOTO 16160
16040  IF PY < 0 THEN PY = 0
16060  IF UP = 1 THEN  DRAW S + P4 AT PY,RU:P4 =  - 32:RU = RU - 7: GOTO
    16160
16080  IF S + P4 = 44 THEN RU = RU - 1
16100  DRAW S + P4 AT RU,PY:P4 =  - 32
16120 RU = RU + 7: IF UP = 1 THEN RU = RU - 14
16140  IF S + P4 = 44 THEN RU = RU - 1
16160  NEXT RR
16180  RETURN
17640  PRINT "PROGRAM ENDED": END
17660 EN =  PEEK (222):EL =  PEEK (218) +  PEEK (219) * 256
17780  TEXT
17800  PRINT "ERROR NO. ";EN;" IN LINE ";EL: NORMAL : STOP
17860  REM  RESET ARRAY
17880  VTAB 13: PRINT  TAB( 11): INVERSE : PRINT "RE-SETTING DATA ARRAY":
    NORMAL
17900 DAZ = 0:DA(1,0) = 0
17920  FOR I = 1 TO MN
17940 DA(0,I) = 0:DA(1,I) = 0:DA(2,I) = 0: NEXT I
17960  RETURN
18000  REM  VIEW GRAPHICS PAGE
18020  POKE  - 16297,0: POKE  - 16299,0: POKE  - 16304,0
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18030  GET D$
18040  TEXT :TB = 14:TI$ = "DATA PARAMETERS": GOSUB 18140: VTAB 4
18050  HTAB 2: PRINT "F MAX   :";PS(16): PRINT : HTAB 2: PRINT "F MIN   :
    ";PS(17): PRINT : HTAB 2: PRINT "DELTA F :";PS(22)
18054  PRINT : HTAB 2: PRINT "RS :";RS
18057  PRINT : HTAB 2: PRINT "R1 :";R1; TAB( 15);"R2 :";R2; TAB( 30);"R3
    :";R3: HTAB 2: PRINT "C1 :";C1; TAB( 15);"C2 :";C2; TAB( 30);"C3 :";C
    3
18060  VTAB 15: HTAB 14: INVERSE : PRINT "TIME  CONSTANTS": VTAB 17: HTAB
    4: PRINT "FREQUENCY":: HTAB 17: PRINT "Z'  (OHMS)":: HTAB 28: PRINT "
    Z'' (OHMS)": NORMAL
18070  CALL 34644;"  ",F1(1);E4,"    ",F2(1);E3,"  ",F3(1), CHR$ (13):
18074  CALL 34644;"  ",F1(2);E4,"    ",F2(2);E3,"  ",F3(2), CHR$ (13):
18078  CALL 34644;"  ",F1(3);E4,"    ",F2(3);E3,"  ",F3(3), CHR$ (13):
18080  VTAB 22
18096  GET D$
18098  RETURN
18120  REM   TITLE SUBROUTINE
18140  HOME : VTAB 2: HTAB TB: INVERSE : PRINT TI$: NORMAL : RETURN
19000  REM  DRAW RES
19020  FOR K = 3 TO 21 STEP 6
19030  HPLOT  TO XX + K,YY - 2 TO XX + K + 3,YY + 3
19040  NEXT
19044  HPLOT  TO XX + K - 1,YY:XX = XX + K - 1
19050  RETURN
19200  REM  DRAW CAP
19220  HPLOT XX,YY TO XX + 10,YY:XX = XX + 10
19240  HPLOT XX,YY - 8 TO XX,YY + 8:XX = XX + 1
19244  HPLOT XX,YY - 8 TO XX,YY + 8:XX = XX + 4
19248  HPLOT XX,YY - 8 TO XX,YY + 8:XX = XX + 1
19252  HPLOT XX,YY - 8 TO XX,YY + 8
19260  HPLOT XX,YY TO XX + 10,YY
19270 XX = XX + 10:YY = YY + 12
19290  RETURN
19300  HPLOT  TO XX + 15,YY:XX = XX + 15
19320  HPLOT XX,YY - 12 TO XX,YY + 12
19340  HPLOT XX,YY - 12 TO XX + 10,YY - 12: HPLOT XX,YY + 12 TO XX + 10,Y
    Y + 12
19360 XX = XX + 10:YY = YY + 12: GOSUB 19000
19380 XX = XX - 25:YY = YY - 24: GOSUB 19200
19400  HPLOT XX,YY - 12 TO XX + 10,YY - 12: HPLOT XX,YY + 12 TO XX + 10,Y
    Y + 12:XX = XX + 10
19420  HPLOT XX,YY - 12 TO XX,YY + 12
19440  RETURN
20000  REM  SAVE DATA
20450 TB = 6:TI$ = "CREATION OF INFORMATION FILE": GOSUB 18140: VTAB 4: HTAB
    6: PRINT "(<CR> WILL CATALOG DRIVE #2)"
20460  PRINT : PRINT : INPUT "ENTER FILENAME :";B$: IF B$ <  > "" THEN 20
    480
20470  CALL 35424: FOR I = 0 TO 29:DI =  PEEK (35456 + I) - 128:CH$ =  CHR$
    (DI):B$ = B$ + CH$: NEXT I: IF  PEEK (35436) = 141 THEN 20450
20480 FC$ =  MID$ (B$,1,1):FC =  ASC (FC$): IF FC > 48 AND FC < 57 THEN  PRINT
    : INVERSE : PRINT "FIRST CHARACTER OF FILENAME IS NUMERIC": NORMAL :C
    A = 1: CALL H: GOTO 20460
20490  IF CA = 1 THEN  GOSUB 18140: VTAB 7: PRINT "FILENAME : ";B$
20550 L1$ = "INFORMATION FILE: " + B$:L1 =  INT (20 - ( LEN (L1$) / 2))
20560  IF L1 <  = 0 THEN L1 = 14:L1$ = "INFORMATION FILE"
20570  HOME : HTAB L1: INVERSE : PRINT L1$: NORMAL
20580 DS$(1) = B$: VTAB 3
20590  INPUT "OPERATOR    : ";DS$(2)
20600 DS$(3) = "SIMULATED DATA"
20610  INPUT "DATE        : ";DS$(4)
20620 DS$(5) = "SIMULATION"
20630 DS$(6) = "SIMULATION"
20640 DS$(7) = "SIMULATION"
20650 DS$(8) = "1":S1 = 1
20660 DS$(9) = "SIMULATION"
20670 DS$(10) = "SIMULATION"
20680 DS$(12) = "SIMULATION"
20690  GOSUB 18140
20700  VTAB 3: PRINT "DESCRIPTION STRINGS :(MAX 5 X 80 CHRS.)"
20710  PRINT : PRINT
20720  FOR K = 13 TO 16
20730  INPUT DS$(K): IF DS$(K) = "" THEN 20770
20760  NEXT
20770  VTAB 21: INPUT "ALTER DESCRIPTION ?";C$: IF C$ = "Y" THEN 20550
20780  IF C$ = "N" OR C$ = "" THEN : GOTO 20890
20790  CALL H: GOTO 20770
20800  REM SAVE DATA
20810 DA(1,0) = DAZ
20820  TEXT : HOME : VTAB 12: HTAB 15: INVERSE : PRINT "SAVING DATA": NORMAL

20840  FOR J = 1 TO DA(1,0)
20850  IF DA(0,J) < .1 THEN 20870
20860  IF DA(2,J) > 01 THEN 01 = DA(2,J):C = DA(0,J)
20870  NEXT J
20880 PS(1) = DA(1,0)
20890  PRINT CD$;"OPEND";B$;",D1"
20900  PRINT CD$;"WRITED";B$
20910  FOR L = 0 TO 24
20916  PRINT PS(L)
20918  NEXT L
20920  FOR L = 0 TO 13
20922  PRINT DS$(L)
20924  NEXT
20930  PRINT DS(1): PRINT DS(2)
20940  PRINT CD$;"CLOSE"
20950  PRINT CD$;"LOCKD";DS$(1)
20952  PRINT CD$
20960  POKE 29,68: POKE 30,65: CALL 38144
20964  PRINT CD$;"BSAVE";B$;",A"; PEEK (27) +  PEEK (28) * 256 + 9;",L";1
    5 * (DA(1,0) + 1);",D1"
20980  PRINT CD$;"LOCK";B$
20990  RETURN
21000  REM  PLOT DUMP (EPSON)
21004 B = 15:TI$ = "EPSON OUTPUT": GOSUB 18140
21010  VTAB 4: PRINT "IS THE EPSON READY ";: INPUT PO$: IF PO$ <  > "Y" THEN
    21010
21020  VTAB 6: PRINT "(S)MALL OR (L)ARGE PLOT ";: INPUT PO$: IF PO$ = "S"
    OR PO$ = "L" THEN 21040
21030  CALL H: GOTO 21020
21040  PRINT CD$;"PR#1": PRINT : POKE 1657,96: POKE 1913,66: IF PO$ = "S"
    THEN  POKE 1913,2
21050  PRINT  CHR$ (17): PRINT : PRINT : PRINT
21060  HTAB 4: PRINT  CHR$ (27); CHR$ (45); CHR$ (1);"SIMULATED PLOT"; CHR$
    (27); CHR$ (45); CHR$ (0)
21064  PRINT : HTAB 6: PRINT "RS :";RS: PRINT : HTAB 6: PRINT "R1 :";R1;:
    HTAB 30: PRINT "W1# :";:W1 = 1 / (R1 * C1): CALL 34644:W1;E4, CHR$ (
    13):
21072  HTAB 6: PRINT "C1 :";C1: PRINT : HTAB 6: PRINT "R2 :";R2;: HTAB 30
    : PRINT "W2# :";:W2 = 1 / (R2 * C2): CALL 34644:W2;E4, CHR$ (13):
21076  HTAB 6: PRINT "C2 :";C2: PRINT : HTAB 6: PRINT "R3 :";R3;: HTAB 30
    : PRINT "W3# :";:W3 = 1 / (R3 * C3): CALL 34644:W3;E4, CHR$ (13):
21078  HTAB 6: PRINT "C3 :";C2: PRINT
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21080  HTAB 14: PRINT  CHR$ (27): CHR$ (45): CHR$ (1);"CALCULATED TIME CO
    NSTANTS"; CHR$ (27): CHR$ (45): CHR$ (0): PRINT : PRINT
21084  PRINT "   FREQUENCY";"     ";"Z'  (OHMS)";"  ";"Z'' (OHMS)"
21090  CALL 34644;"  ",F1(1);E4,"     ",F2(1),"  ",F3(1), CHR$ (13);
21094  CALL 34644;"  ",F1(2);E4,"     ",F2(2),"  ",F3(2), CHR$ (13);
21096  CALL 34644;"  ",F1(3);E4,"     ",F2(3),"  ",F3(3), CHR$ (13);
21098  PRINT  CHR$ (12): PRINT CD$;"PR£0": RETURN
21100  REM DATA LISTING (SCREEN)
21110 CD$ =  CHR$ (4):TB = 16:TI$ = "DATA LISTING": GOSUB 18140
21120  GOSUB 21190: FOR L = 1 TO DAZ
21130  CALL 34644;L;I3," ",DA(0,L);E4,"  ",DA(1,L);E3,"  ",DA(2,L), CHR$
    (13);
21140  IF  INT ((L) / 15) = (L) / 15 THEN  PRINT : PRINT : INPUT "PRESS R
    ETURN TO CONTINUE ";D$: GOSUB 21190
21150  NEXT : VTAB 22
21160  INPUT "PRESS RETURN TO CONTINUE ";D$: RETURN
21190  HOME : VTAB 2: HTAB 7: INVERSE : PRINT A1$;: NORMAL : HTAB 18: INVERSE
    : PRINT A2$;: NORMAL : HTAB 29: INVERSE : PRINT A3$: NORMAL : PRINT :
     RETURN
21200  REM DATA LISTING (EPSON)
21210 TB = 14:TI$ = "EPSON OUTPUT": GOSUB 18140: VTAB 4: INPUT "IS THE EP
    SON READY ?";D$: IF D$ <  > "Y" THEN 21210
21220  PRINT CD$;"PR£1": PRINT  CHR$ (4): POKE 1657,96
21230  PRINT "FILENAME :";DS$(1): PRINT : PRINT
21240  VTAB 2: HTAB 8: PRINT A1$;: HTAB 19: PRINT A2$;: HTAB 30: PRINT A3
    $: PRINT
21250  FOR L = 1 TO DAZ
21260  CALL 34644;L;I3," ",DA(0,L);E4,"  ",DA(1,L);E3,"  ",DA(2,L), CHR$
    (13);
21270  NEXT L
21280  PRINT  CHR$ (12): PRINT CD$;"PR£0"
21290  RETURN
22000  HOME : VTAB 12: PRINT  TAB( 12): INVERSE : PRINT "LOADING HPPLOTTE
    R": NORMAL
22020  IF P6 > 0 THEN 22060
22040 I2 = PU:I1 = PU:XP = R:XN = M8:YP = M3:YN = M4:YE = M6:XE = M6:XF =
    S2:YF = S2:YS = 0: GOTO 22080
22060 I2 = XR:I1 = YP:XP = R:XN = 0:YP = P - M5:YN = M5:YE = M6:XE = M7:X
    F = S2:YF = S1:YS = M4
22080  CALL 38048
22100  PRINT CD$;"BLOADCHAIN,A520,D1"
22120  CALL 520"HPPLOTTER.V2"
```
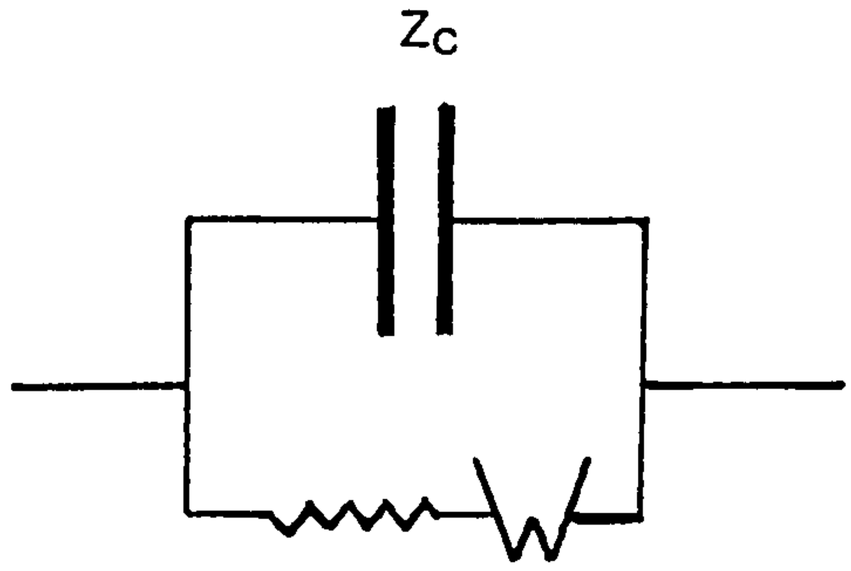

Appendix B

Derivation of the Total ac Impedance of a Parallel Network Containing a Warburg Impedance.

For the parallel network,



the total circuit impedance can be derived as follows.

$$\frac{1}{Z} = \frac{1}{Z_c} + \frac{1}{Z_r + Z_w}$$

$$= \frac{1}{1/j\omega C} + \left[\frac{1}{R + \sigma\omega^{-1/2} - j\sigma\omega^{-1/2}}\right]$$

$$Z = 1 \Big/ \left[j\omega C + \frac{1}{R + \sigma\omega^{-1/2} - j\sigma\omega^{-1/2}}\right]$$

$$= 1 \Big/ \left[\frac{j\omega CR + j\omega^{1/2}\sigma C + \sigma\omega^{1/2}C + 1}{R + \sigma\omega^{-1/2} - j\sigma\omega^{-1/2}}\right]$$

$$= \frac{R + \sigma\omega^{-1/2} - j\sigma\omega^{-1/2}}{j\sigma CR + j\omega^{1/2}C\sigma + \sigma\omega^{1/2}C + 1}$$

Multiplying both numerator and denominator by the complex conjugate of the denominator leaves terms containing j only in the numerator.

i.e. multipling by $(1 + \sigma\omega^{1/2}C - j\sigma CR - j\omega^{1/2}C\sigma)$ gives,

Numerator:

$$R + \sigma\omega^{1/2}CR - j\omega CR^2 - j\sigma\omega^{1/2}CR + \sigma\omega^{-1/2} + \sigma^2C$$
$$- j\sigma\omega^{1/2}CR - j\sigma^2C - j\sigma\omega^{-1/2} - j\sigma^2C - \sigma\omega^{1/2}CR - \sigma^2C$$

Denominator:

$$j\omega CR + j\sigma\omega^{3/2}C^2R + \omega^2C^2R^2 + \sigma\omega^{3/2}C^2R + j\sigma\omega^{1/2}C$$
$$+ j\sigma^2\omega C^2 + \sigma\omega^{3/2}C^2R + \sigma^2\omega C^2 + \sigma\omega^{1/2}C + \sigma^2\omega C^2$$
$$- j\sigma\omega^{3/2}C^2R - j\sigma^2\omega C^2 + 1 + \sigma\omega^{1/2}C - j\omega CR - j\sigma\omega^{1/2}C$$

Collecting like terms and cancelling, this becomes;

$$\frac{R - j\omega CR^2 - 2j\sigma\omega^{1/2}CR + \sigma\omega^{-1/2} - 2j\sigma^2C - j\sigma\omega^{-1/2}}{\omega^2C^2R^2 + 2\sigma\omega^{3/2}C^2R + 2\sigma^2\omega C^2 + 2\sigma\omega^{1/2}C + 1}$$

Thus,

$$Z = \frac{R + \sigma\omega^{-1/2} - j(\omega CR^2 + 2\sigma\omega^{-1/2}CR + 2\sigma^2C + \sigma\omega^{-1/2})}{1 + 2\sigma\omega^{1/2}C + 2\sigma^2\omega C^2 + 2\sigma\omega^{3/2}C^2R + \omega^2C^2R^2}$$

$$= \frac{R + \sigma\omega^{-1/2} - j(\omega C(R + \sigma\omega^{-1/2})^2 + \sigma^2C + \sigma\omega^{-1/2})}{\omega^2C^2(R + \sigma\omega^{-1/2})^2 + \sigma^2\omega C^2 + 2\sigma\omega^{1/2}C + 1}$$

$$= \frac{R + \sigma\omega^{-1/2} - j[(\omega C(R + \sigma\omega^{-1/2})^2 + \sigma\omega^{-1/2}(1 + \sigma\omega^{1/2}C)}{\omega^2C^2(R + \sigma\omega^{-1/2})^2 + (1 + \sigma\omega^{1/2}C)^2}$$

Therefore,

$$Z' = \frac{R + \sigma\omega^{-1/2}}{\omega^2C^2(R + \sigma\omega^{-1/2})^2 + (1 + \sigma\omega^{1/2}C)^2}$$

and

$$Z'' = \frac{j(\omega C(R + \sigma\omega^{-1/2})^2 + s^2C\ (1 + \sigma\omega^{-1/2}C)}{\omega^2C^2(R + \sigma\omega^{-1/2})^2 + (1 + \sigma\omega^{1/2}C)^2}$$

Table of Symbols

(aq) - denotes aqueous medium

a_i - activity of species i

A - area

C - Various capacitances (see below)

C_{dl} - double layer capacitance

C_g - geometric capacitance

c_i - concentration of species i

C_p - parallel capacitance

C_s - series capacitance

Cw - psuedo capacitance due to charge separation from ions moving at difference velocities

e - sinusoidal voltage

E - various voltages or potential differences

E - magnitude of voltage vector

E - voltage phasor

E_b - total interfacial (boundary) potential

E_c - voltage drop across a capacitance

E_d - diffusion potential

E_j - junction potential

E_m - total membrane potential

E_o - standard potential of cell

E^o - standard electrode potential

E_r - voltage drop across a resistance

E_r - reference electrode potential

E_{cell} - total cell potential

f - frequency

F - Faraday constant

i - current

i,j - subscripts denoting primary (i) and interferent (j) species

Table of Symbols (continued)

I_r - current through a resistance

I_c - current through a capacitance

I - current phasor

I - magnitude of current vector

j - root minus one

J_i - total flux density for species i

k_i - distribution coefficient

k_i - forward rate constant for species i

k_i - backward rate constant for species i

K_ij - selectivity coefficient

K_{ij}Pot - potentiometric selectivity coefficient

l - length or thickness

(m) - denotes membrane phase

p - asymmetry factor (alpha)

R - resistance

R - gas constant

R_b - bulk membrane resistance

$R_b$init - initial bulk resistance

$R_b$fin - final bulk resistance

R_{ct} - charge transfer resistance

R_{ct}init - initial charge transfer resistance

R_{ct}fin - final charge transfer resistance

R_p - parallel resistance

R_s - series resistance

R_s - solution resistance

Rw - resistive component of Warburg impedance

s - Nernst factor (RT/F)ln10

t - time

T - temperature

Table of Symbols (continued)

u_i, u_j - relative mobility of species i and j

U_m, U_x - mobility of species m, or x

v_i - flow velocity for species i

z_i - charge on ion i

Z - impedance vector

Z_r - impedance of a resistance

Z_c - impedance of a capacitance

Z' - real component of impedance vector

Z" - imaginary component of impedance vector

ω - angular frequency

ω^*_{max} - angular frequency of semicircle maximum

ϕ - potential difference

μ_i - chemical potential of species i

$\overline{\mu_i}$ - electrochemical potential of special i

μ_i^o - standard chemical potential of species i

χ - capacitive reactance