STUDIES OF MEMBRANE COMPOSITION AND FACTORS AFFECTING THE ANALYTICAL USE OF POTASSIUM RESPONSIVE ION-SELECTIVE ELECTRODES

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by

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ABSTRACT

In this work, optimization of the performance of potassium / PVC electrodes based on valinomycin, with respect to the composition of the membrane, i.e. the ratio of valinomycin to plasticizer, and the type of PVC matrix has been investigated, in an attempt to reduce the cost of the commercially available electrode. The behaviour of a number of PVC electrodes based on a series of novel bis-crown compounds towards potassium and sodium ions has been evaluated.

The influence of the internal reference system, particularly the internal reference solution, on the electrode charateristics was examined by varying the concentration and type of the reference solution. The presence of negative sites in the PVC membrane as an origin of the selectivity, maintaining the electroneutrality in the bulk of the membrane, has been investigated by making pH measurements on solutions in contact with the membrane constituents. The anion response of the potassium / valinomycin electrode with the variation of the concentration of valinomycin, type of plasticizer and PVC have been clarified.

Automatic calibration and selectivity determination has been carried out on the membrane using a continuous dilution method, and examination of the effect of the liquid junction potential, type of junction and concentration of the bridge solution on the response of the electrode were ascertained.

A high concentration of the valinomycin (>1% w/w) and plasticizer (<70% w/w), independent of the type of PVC and plasticizer, was found to show the best performance. The bis-crowns, except bis-naphthol crowns, did not display competitive results in the determination of potassium and sodium ions. The potentials of the internal and external surfaces of the membrane are established separately of one another, and the magnitude of the membrane potential did not simply depend on the ratio of sensed ion activity in the inner and outer solutions. There is however, strong supporting evidence that the presence of impurities in the membrane components are responsible for the selectivity and electroneutrality of the membrane.

The anion response of the membrane is shown to be influenced by the nature of membrane and concentration of valinomycin.

The source of the bias in the Corning 902 Analyser in relation to flame photometry was explained and the continuous dilution method was applied to the evaluation of the sensor instruments.

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CONTENTS

CHAPTER ONE

INTRODUCTION

1.1 INTRODUCTION AND CLASSIFICATION OF ION-SELECTIVE ELECTRODES

The introduction of new and reliable ion-selective electrodes (I.S.Es) for various cations, anions, neutral species, gases and enzymes has been a subject of intrest to many scientists in different fields. These electrochemical devices, whose potential directly corresponds to the concentration, or more correctly to the activity of particular species in solution, are rapidly replacing very sophisticated, time consuming and expensive instruments, both in research and industry. Since the publication of G.A. Rechnitz's article in 1967 [1] and later that of A.K. Covington in 1969 [2], for the first time in Great Britain, several thousand articles concerning the application of these amazing tools in various branches of chemistry such as, clinical, agricultural, envirnomental, analytical, paper industry, etc. have emerged in which their usefulness has received much attention. The understanding of the mechanism of ion transport through living cells, and its similarity to the operation of I.S.Es has encouraged physiologists and biologists to carry out detailed investigations on these devices, which led to the discovery of novel ion-selective electrodes, e.g. the potassium I.S.E. The development of I.S.Es has facilitated analysis of some species, which were difficult to detect by other techniques, such as fluoride ions and enzymes. Several magazines and scientific journals have been dedicated to news and progress about I.S.Es [3].

Ion- selective electrodes are membrane electrodes comprised of an internal reference system interfaced with a thin layer which is either solid or liquid, and might be conducting or non-conducting towards the sensed ions. It is called a membrane, and is the fundamental part of the electrode. The function and mechanism of the electrical conduction of I.S.Es is mainly related to the active material and the nature of the compounds used in the preparation of the membrane.

Initially, I.S.Es were classified according to the physical form of the membrane [2,4], i.e.

1. Solid,

2. Heterogeneous,

3. Liquid ion-exchange.

However, this classification was not valid for long, because of the possibility of utilization of active material in different configurations. Thus, a more acceptable and logical classification was presented in 1974 by A.K. Covington [5], which is based on the nature of the electroactive materials, namely:

1. Glass,

2. Insoluble inorganic salts,

3. Organic materials.

The active material in a glass membrane is silica glass. The glass I.S.E. responds to hydrogen ions, and a similar response is made towards univalent cations by altering the composition of the glass. The second group deals with solid state membranes, in which the active material is a sparingly water soluble inorganic salt such as silver chloride or lanthanum fluoride. The active materials in the last category are long chain ion-exchangers such as alkyl phosphates and complexing agents, which also include many natural antibiotics, synthetic cyclic and acyclic compounds. All these materials in different groups seem to possess an ion-exchange capacity to a certain extent. The construction and operation of various I.S.Es has been the subject of many books [6,7], reviews [8] and monographs [9,10]. Here, attempts are oriented towards the investigation of the behaviour of the PVC electrode based on neutral carriers, and the relevant aspects of these will be briefly discussed.

1.2 BRIEF HISTORICAL SURVEY OF I.S.Es

The most widely used and well known of all I.S.Es is the hydrogen-ion responsive glass electrode. It was in 1906 when Cremer [11] observed that changing the acidity of aqueous solutions affected the electrical potential of the glass membrane but it was Haber [12] who realized the usefulness of the membrane potential which developed across a glass membrane. In the investigation carried out by Klemensiewicz, the potential of the membrane was related to the hydrogen ion concentration on both sides of the membrane. However, it was around 1930, that a series of studies [13,14] on the composition of the glass membrane led to the commercial production of the glass electrodes. The observation of alkali errors in pH-responsive glass electrodes, and attempts to minimise this shortcoming, resulted in the discovery of new cation responsive glass electrodes. In this respect, investigation by Lengyel and Blum [15] in 1934, and later a more systematic research by Eisenman and co-workers [16], helped to clear the mystery of the alkali error, and shortly afterwards a series of glass electrodes for monovalent cations was fabricated.

The development of solid-form ion-selective electrodes can be traced back to the work of Tendeloo [17], and of Kolthoff and Sanders [18]. Tendeloo´s electrodes based on calcium fluoride and calcium oxalate in paraffin matrix, proved to be unsuccessful. The electrodes with active materials of silver halides as pellets and coated-wire form, which were prepared by Kolthoff and Sanders also did not produce satisfactory results. This was partly due to the light-sensitivity of these materials. However, this problem was overcome later by introducing Ag_2S into the halide pellets. The first non-glass ion-selective electrodes were prepared by Pungor and co-workers [19] in 1961, whose membranes were made of embedded silver-iodide precipitate in an inert matrix (silicone rubber). Later, they introduced a series of heterogeneous solid membrane electrodes, such as the silver and halide ion-selective electrodes. In 1966, Ross and Frant [20] discovered the fluoride electrode which was based on a single crystal of lanthanum fluoride doped with europium fluoride. Heterogeneous membranes were also made by laying compounds upon a conductive substrate, such as hydrophobic graphite (Selectrodes®) [21]. Various types of inert matrices were used in the preparation of heterogenous membranes, e.g. epoxy resin, silicone rubber, polymers, etc., of which plasticized PVC is nowadays widely used as ′inert-matrix′.

The research on the construction of calcium glass electrodes concluded with the introduction of the first liquid-membrane electrode by Ross [22], which is based on calcium didecyl phosphate with di-n-octylphenyl phosphonate. During the development of membrane electrodes, liquid membranes received great attention due to the availability of numerous ion-exchange materials. Shortly after the calcium electrode, the emergence of other liquid electrodes based on organic materials such as, nitrate, perchlorate, chloride, cupric ions, etc. followed.
Pressman [23] in 1964, discovered that valinomycin and other antibiotics facilitate the permeation of ions through living cells, and this resulted

in the discovery of a new group of permeators to be used as active materials in the membranes. The introduction of these neutral carriers extended the range of liquid membrane electrodes, and the first potassium selective electrode based on valinomycin in liquid membrane form was reported by Pioda, Stankova and Simon in 1969 [24]. This electrode, is very reliable and shows a high selectivity for potassium ions, in comparison with the glass and the other potassium responsive electrodes; this makes it of the same quality as the H^+ glass and fluoride electrodes. Due to economic factors and difficulty in purification of these naturally occurring compounds, the use of their analogues i.e. cyclic and acyclic compounds, has been promoted, although electrodes based on crown compounds are not capable of great discrimination between ions. Crowns, however, have been used and their characteristics were compared with valinomycin based electrodes [25]. The first polymeric calcium I.S.E. appeared in 1967 [26] but it was not until 1970, after the work of Moody and Thomas [27], that it attracted interest and rapidly replaced the liquid membrane electrodes. An interesting configuration of the polymeric electrode is the coated-wire I.S.E. presented [28] in 1971. In this modification platinum or silver wire, coated with a polymeric matrix containing various electroactive materials, is used.

Recently electrodes have been invented for gases and enzymes. The carbon dioxide electrode [29,30] was the first designed for the measurement of the partial pressure of carbon dioxide. Later, other gas sensors, became available for various gases such as NH_3, SO_2, NO_2, etc.

The first enzyme electrode was introduced by Clark and Lyons [31]. The principles of these electrodes are similar to gas sensing electrodes, except that the reaction takes place between a biocatalytic layer and the substances to be measured. The product of this reaction is measured by a suitable electrode [32].

Finally the latest innovation in this field is Ion-Selective Field Effect Transistors (ISFETs) [33], the membrane of which is applied directly to the gate of a field effect transistor. The performance of ISFETs as regards to the response and selectivity is the same as conventional electrodes. Due to the small size of the devices, measurement with small amount of sample and in vivo analysis is possible. Attempts at preparing multi-functional ISFET were successful in Newcastle, and for the first time Covington et al. [34] prepared a four functional ISFET for K^+, Na^+, Ca^{2+}, and H^+ . In the following sections, a brief insight into the more important carrier compounds, is given.

1.3 IONOPHORES - (THE ION-CARRIERS)

The term ionophore or ion-carrier applies to those compounds which have a tendency to bind ions selectively and increase the ion permeability of the membrane. Generally, ionophores are organic compounds with cyclic structure. However, there are also some acyclic compounds which possess similar properties, e.g. antibiotic nigercin or Simon's synthetic compounds [35]. The properties of ionophores have been summarized by Koryta [9] as follows:

1. They form complexes with univalent ions, especially with alkali metal ions.

2. They enable transport of univalent ions across lipid membranes of cells and cell organelles as well as across the so called bilayer lipid membranes and across relatively thick nonpolar solvent membranes.

3. They ion-specifically uncouple the oxidative phosphorylation in mitochondria; this is the basis of their bactericidal effect.

4. They give rise to membrane potentials in thin lipid and thick membranes.

The interesting properties of these molecules lie in their peculiar molecular structure. The cation-ionophore complex consists of two shells, namely: internal and external. The internal shell is composed of polar groups oriented towards the centre of the molecule and provide a cage for the cation. The outer or external shell consists of nonpolar and lipophilic groups, preventing interaction between the anions and solvent with the cation, and ensuring the solubility of cation-carrier complex in the apolar media of the membrane. Usually, the cation sits in the cavity of the ionophore and electrostatic or covalent bonds are induced due to the polar groups such as oxygen. The complexation is step by step or, in other words, by replacing the solvent molecules bound to the cation with oxygen atoms successively. The stability of the ionophore´s complexation with various cations depends on the structure of the ionophore, the dimension of the cation and the size of the cavity. In addition to the lipophilicity and transport properties, the ionophore molecules should have high rate of cationic loading and unloading speed at the interfaces.

Comprehensive reviews and a few publications, about the naturally occurring antibiotic ionophores have been published by Ovchinnikov et al. [36,37,38]. Reviews on the role of ionophores in biological membranes [39], synthesised ionophores [40] and structure of their complexes with metals [41], are available.

The range of ionophores is wide and can be classified into two main categories:

1. Natural ionophores,

2. Synthesised ionophores.

Naturally occurring ionophores are subdivided accordingly:

1. Cyclic,

2. Acyclic.

1.4 NATURAL IONOPHORES (CYCLIC)

1.4.1 Depsipeptides

The cyclic depsipeptides contain amino and hydroxy acid residues linked by amide, N-methyl amide and ester bonds. The prominent members of this group are valinomycin, the enniatins and monomycin. The biological action of these compounds relates to their complexing tendency with metal ions. Because of the use of valinomycin in this work as active material, further information is given below:

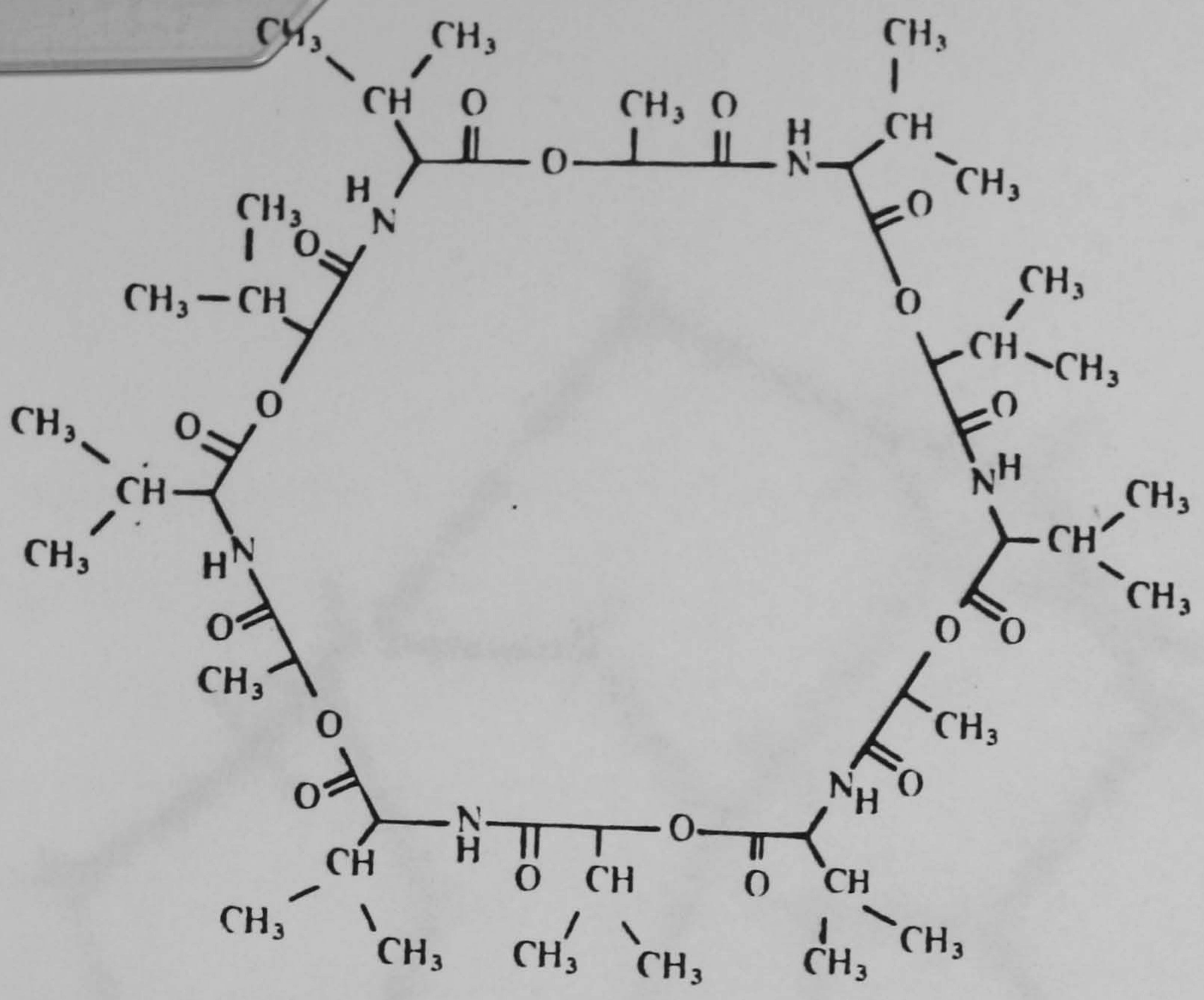
Valinomycin is the most popular and well known ionophore used in I.S.Es. It possesses high selectivity towards potassium in comparison with other antibiotics and is the active material used in potassium membrane electrode and in extraction. Valinomycin molecule contains [36] three molecules of L-valine, three molecules of D-valine, three molecules of L-lactic acid and three molecules of D-α-hydroxy-iso-valeric acid (Fig 1.1). The valinomycin has a 36 membered ring with three fold symmetry structure. Due to the existence of $>NH$ and $\overset{O}{\overset{\|}{C}}$ groups, various conformations in different solvent have been reported [42]. It has been shown that in nonpolar solvents six hydrogen bonds and in more polar solvents three hydrogen bonds exist. The number of hydrogen bonds depends on the nature of the solvent. In solution it exists in three forms (A, B, and C) in equilibrium (A: no hydrogen bonds, B: three intermolecular hydrogen bonds and C: six intermolecular hydrogen bonds). Valinomycin forms very stable complexes with K^+, Rb^+, and Cs^+ ions in methanol, but the complexes with other alkali and alkaline earth metal cations are less stable. The size of the cavity in the valinomycin molecule is sufficient to encapsulate K^+ and Na^+ ions without steric strain. The cavity diameter is 2.7-3.3 Å . It was reported that ions of larger size fitted in the cavity by increasing the size of the cavity by changing the hydrogen bond lengths [43]. The radii of some cations are given in Table 1.1 for comparison.

Table 1.1

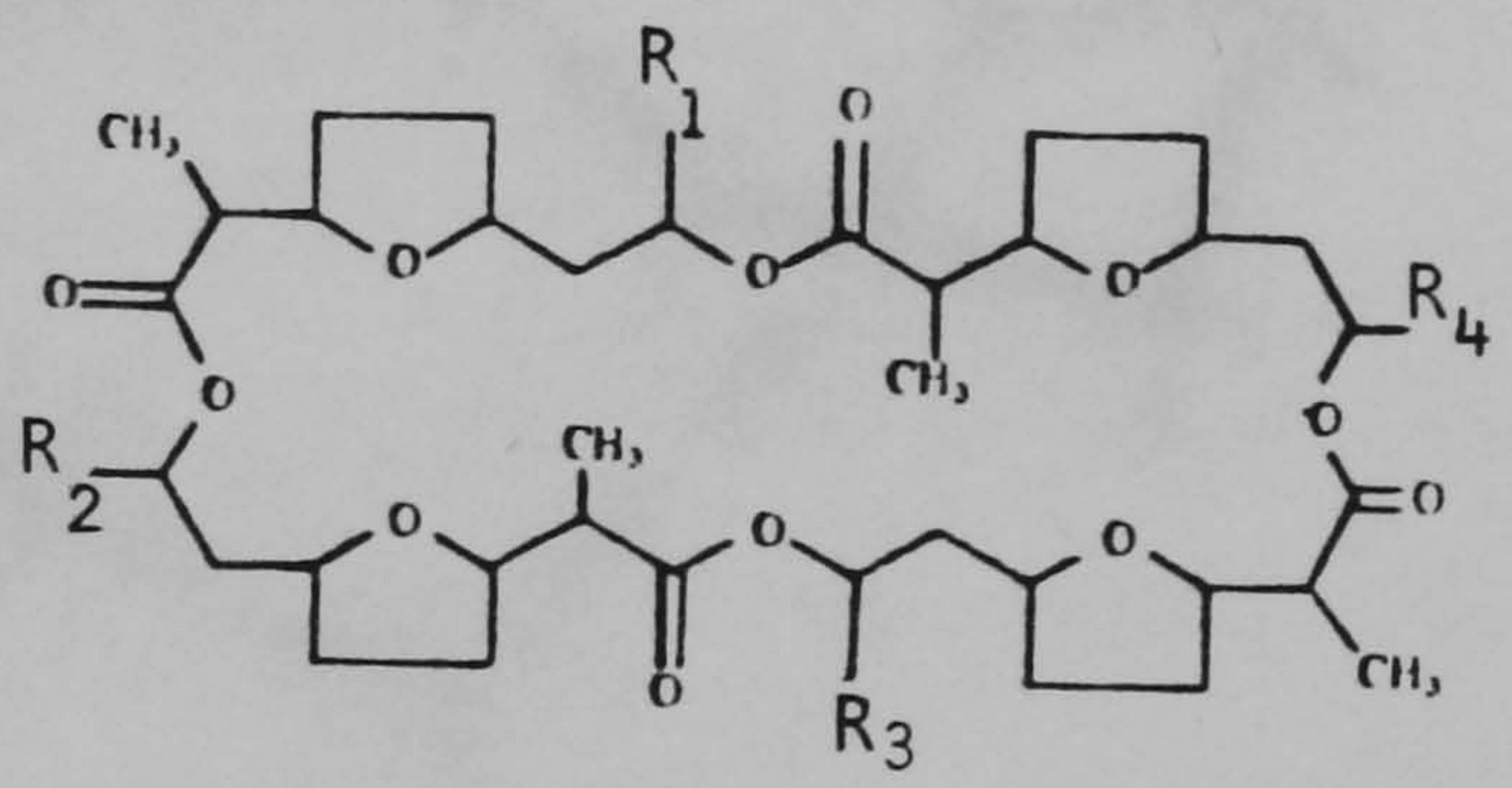
Radii of Cations /Å

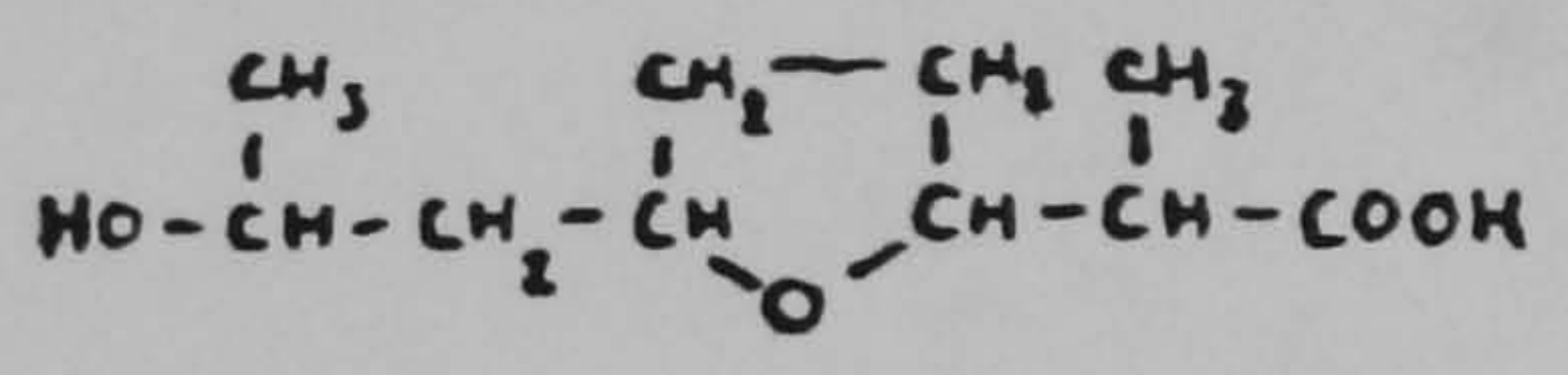
Na^+	0.95	Mg^{2+}	0.65
K^+	1.33		
Rb^+	1.48	Ca^{2+}	0.99
Cs^+	1.69		
Tl^+	1.44	Ba^{2+}	1.35

The structure of valinomycin-potassium complex is shown in Fig 1.2. Here the oxygen atoms of C groups are oriented towards the centrally situated cation. The cation is effectively screened from its interaction with solvent and the anion, by the depsipeptide skeleton and the pendant side chains. The molecular surface of the complex covered by the methyl and isopropyl groups gives the complex a high hydrophobicity. The same structure was found in the crystalline K^+-valinomycin complex [44]. Owing to the greater selectivity of valinomycin for K^+ over Na^+, it is used as an active material, when the sodium content is high (body fluid). The properties of valinomycin depend on the position of the binding units and their conformation. Replacement of any of these units leads to a decrease in the stability of the metal ion-complex [45].



Valinomycin



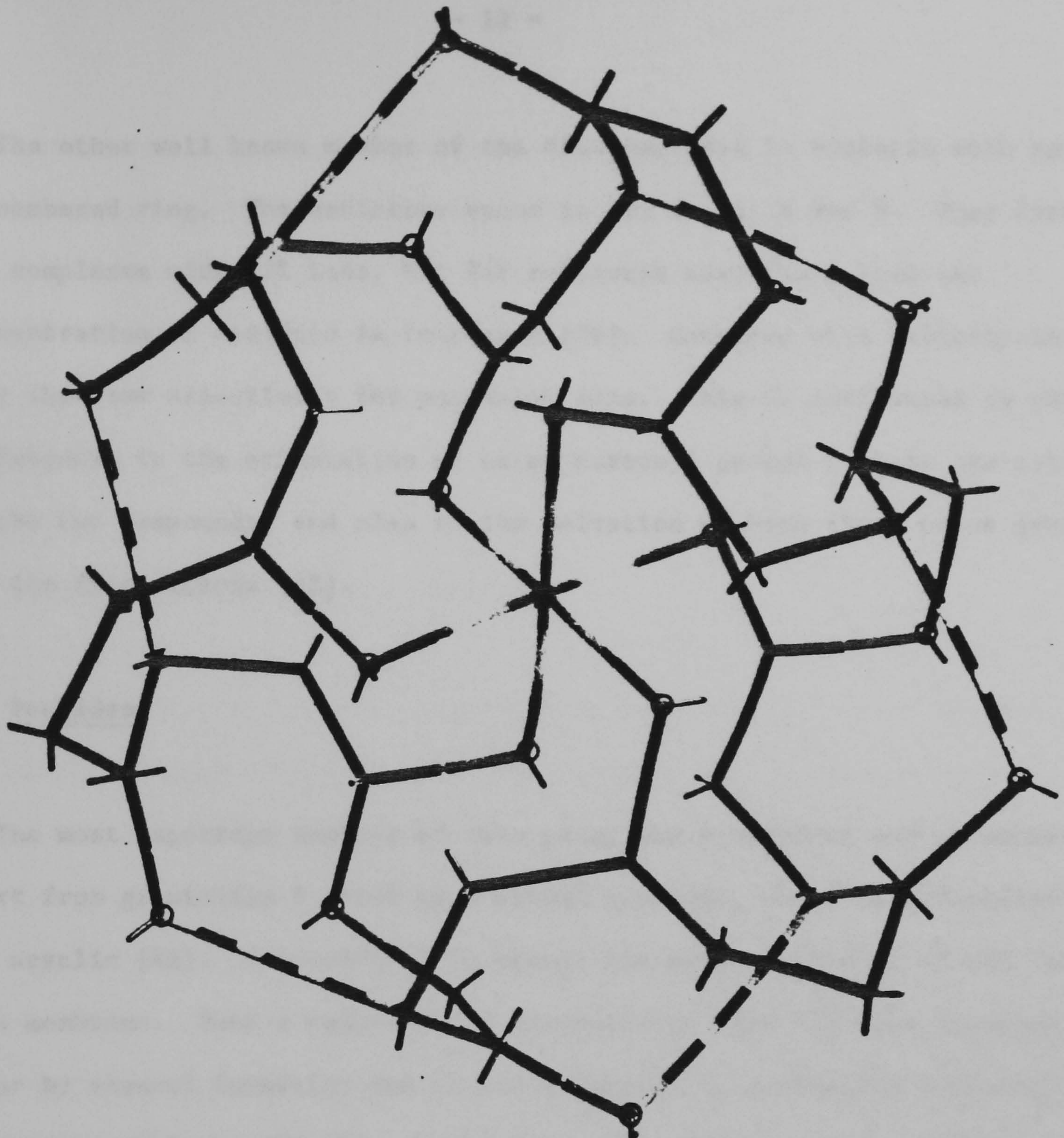


Nonactinic acid

Different nonactins

$R_1 = R_2 = R_3 = R_4 = CH_3$		Nonactin
$R_1 = R_2 = R_3 = CH_3$	$R_4 = C_2H_5$	Nonactin
$R_1 = R_2 = CH_3$	$R_2 = R_4 = C_2H_5$	Dinatin
$R_1 = CH_3$	$R_2 = R_3 = R_4 = C_2H_5$	Trinactin

Fig (1.1)



Structure of valinomycin-K$^+$ complex
Hatched bonds indicate hydrogen bonds.
Isopropyl groups are not shown [5].

Fig. (1.2)

The other well known member of the depsipeptides is enniatin with an 18-membered ring. The enniatins occur in two forms: A and B. They form 1:1 complexes with all ions, but 2:1 complexes were found when the concentration of enniatin is increased [36]. Compared with valinomycin they show low selectivity for potassium ions. This is attributed to the differences in the orientation of ester carbonyl groups towards the cation in the two compounds, and also to the solvation of both their polar groups and the free cations [42].

1.4.2 Peptides

The most important members of this group are gramicidin and alamethin. Apart from gramicidin S which is a cyclic compound, the other gramicidins are acyclic [46]. Gramicidin A increases the permeability of alkali ions in a membrane. Such a capacity for transport of ions has been proposed to occur by channel formation due to the alignment of gramicidin molecules across the membrane [47,48]. Antamanide binds sodium ions in preference to potassium. Investigations on the complexing ability of these compounds led to the synthesis of cyclic peptides, which bind the potassium ion more effectively than valinomycin [49].

1.4.3 Depsides (Macrotetrolides)

The other category of natural ionophores is the macrotetrolides. Their general formula is represented in Fig 1.1. They are derived from the nonactinic acid. Nonactin was synthesised by a stepwise condensation of four nonactinic acid molecules and subsequent cyclization. They consist of a 32-membered ring with four ether and four ester groups. They are capable of binding cations with different radii. The stability of the complex decreases by increasing the water content of the media [36]. NH_4^+ ions are more strongly bound by nonactin than valinomycin, but nonactin is less selective to potassium ions than valinomycin [50].

1.4.4 Carboxylic Acid Ionophores (Acyclic)

The last group of natural ionophores is the carboxylic acid ionophores. They include nigericin, monencin, grisorixin, x-206, x-537A and A23187. Unlike the other ionophores, which are electroneutral, these compounds form uncharged complexes. This is due to the carboxyl group in their molecules. They generally form 2:1 complexes. Nigericin which forms a stable complex with potassium ion, has a carboxylic acid group at one end, and a hydroxyl group at the other end. The presence of these groups facilitates hydrogen bond formation. Complexation is accompanied by deprotonation of -COOH group followed by a ring closure. Due to the carboxylic group the complexation is pH dependent.

The carboxylic acid ionophores form stable complexes with alkali and alkaline earth metal cations. In this respect, nigericin, monensin and A23187 prefer potassium, sodium and calcium ions repectively [52].

1.5 SYNTHETIC IONOPHORES

1.5.1 Crowns

The crowns were discovered by Pedersen in 1967 [53]. Their tendency to form complexes with various cations selectively has been attributed to the structural similarity with the natural ionophores; thus the use of these compounds instead of expensive and unstable ionophores has been encouraged. Cyclic polyethers with 3 to 20 ether oxygen atoms in their central ring have been synthesised [53]. One of the first compounds in this group was dicyclo-hexyl-18-crown-6; they all contain polar as well as non-polar groups arranged in a cyclic structure. The complexation of these compounds is such that the oxygen atoms point towards the centre of the molecule to provide a polar cavity for the cation. The non-polar groups, on the other hand, point outwards forming a lipophilic exterior. This particular arrangement allows the charged lipophilic complex to penetrate into the apolar media. Polyether compounds are capable of forming complexes with uni, di and trivalent cations. The stoichiometries of metal:ligand partly depend on the size and dimensions of the cavity in the polyether. By replacing the oxygen atoms, either fully or partially, with sulphur, nitrogen, etc., macrocyclic and macroheterocyclic compounds with different donor atoms and strong tendency towards complex formation can be synthesised [54,55]. Extensive reviews concerning the crown compounds are available [56,57]. A brief review of crown ethers is given in Chapter Three Part Two.

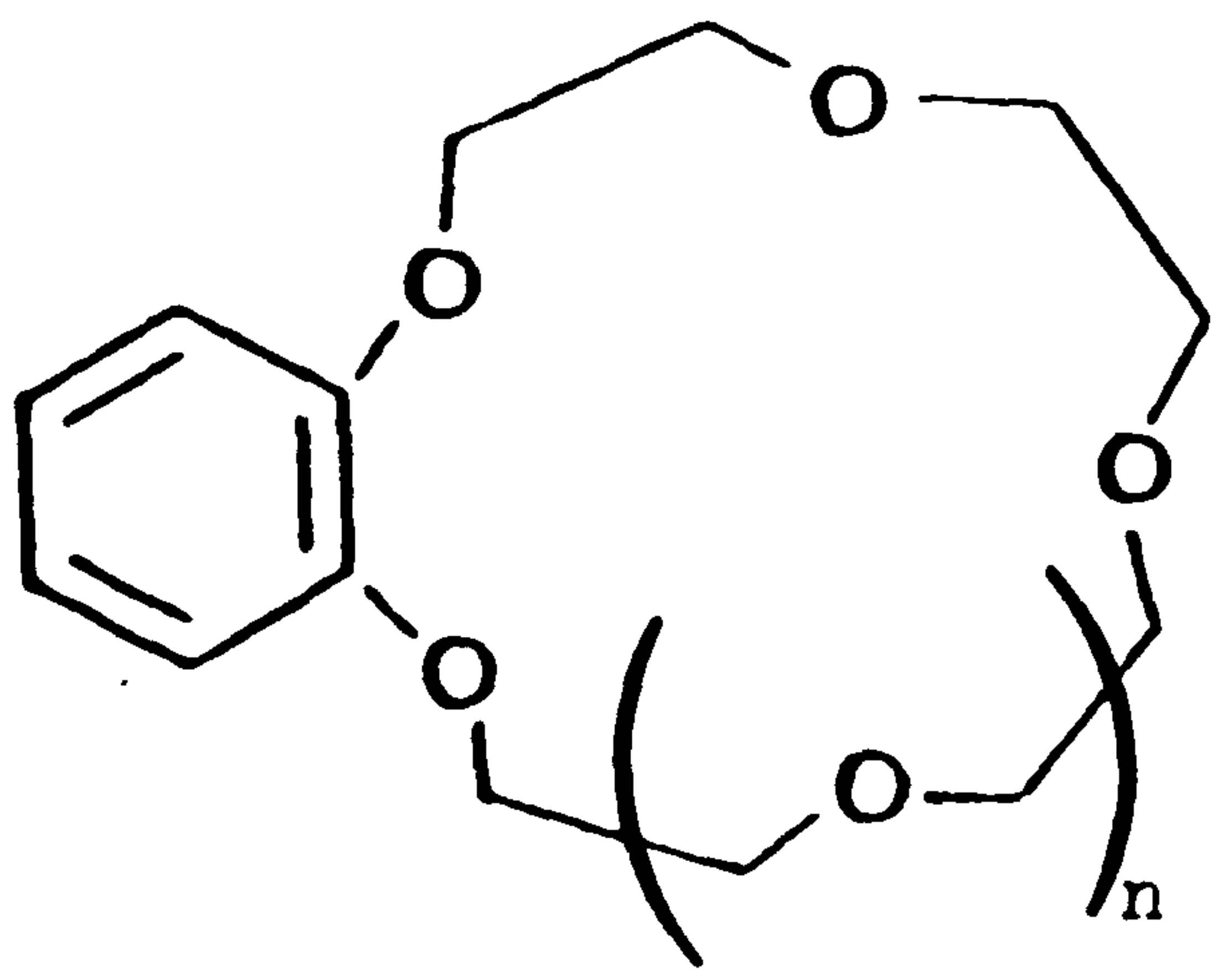
1.5.2 Macroheteropolycyclic Compounds (Cryptands)

Macrocyclic diazapolyoxa compounds were first synthesised by Lehn et al. [58], and called cryptands. A general formula for the cryptands is shown in Fig 1.3. They are not polyethers, but a combination of polyether and bicyclic diamines. Abbreviated names have been suggested for the cryptands, e.g. for m=1 and n=1 the compound is called 3.2.2 cryptand (see Fig 1.3). These compounds are capable of forming remarkably stable complexes with metal ions in both aqueous and non-aqueous solvents [59,60,61]. The cation is located within the cavity of the ligand and two bridgehead nitrogen atoms together with the ether oxygens are directed towards the inside of the cavity. The metal ion, enclosed by a hydrophobic shell, is partially hydrated or interacts with the anions [61]. The compounds demonstrate high selectivity between various metal ions. Variation in the stability and selectivity is attributed to the cavity size, the number of donor sites and the nature of the medium [62]. The selective property of cryptands has aroused the interest of analysts in ion sensor technology, but the high solubility of the species in aqueous solution and the low rate of cation release, are barriers for the use of these compounds in ion-selective electrodes. However, this hydrophilicity of cryptands has been overcome by introducting carbon bridgeheads with lipophilic branches instead of the nitrogen ones [44]. Electrodes based on these compounds have proved unsuccessful.

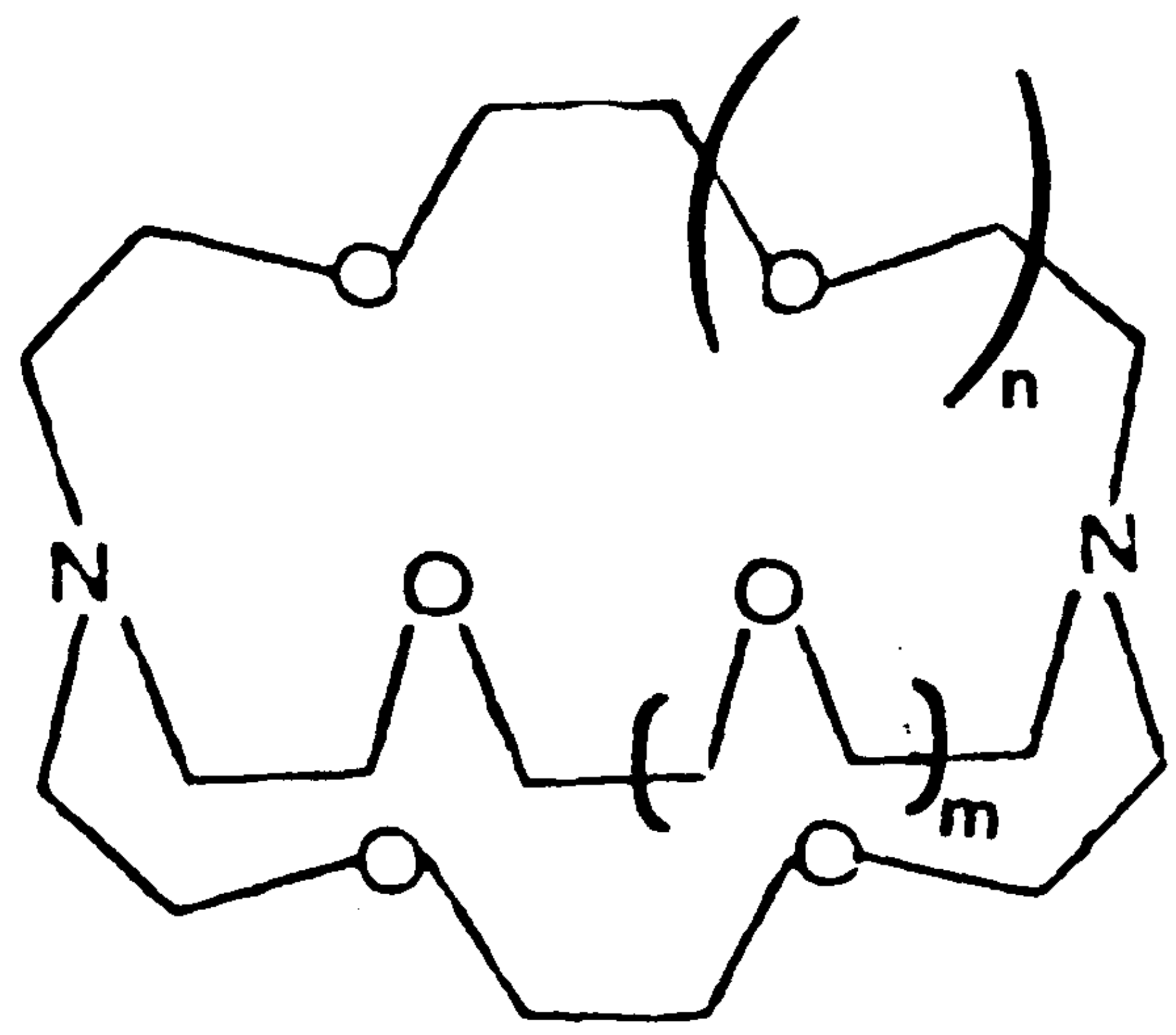
1.5.3 Bis-Crown Compounds

Pedersen [53], the discoverer of crown ethers, disclosed that benzo-15-crown-5 forms 2:1 complexes with potassium and larger cations, and he proposed a sandwich-type structure for the 2:1 stoichiometry. This idea was followed by Bourgoin et al. [63], and for the first time they synthesised a new compound in which two crowns were linked together through a short aliphatic chain. These new compounds are known as bis-crowns and they possess the ability to form complexes with cations of the appropriate size with good lipophilic property. Due to the existence of various possibilities to link two crowns of different size, the number of synthesised bis-crown ethers is growing [64,65].

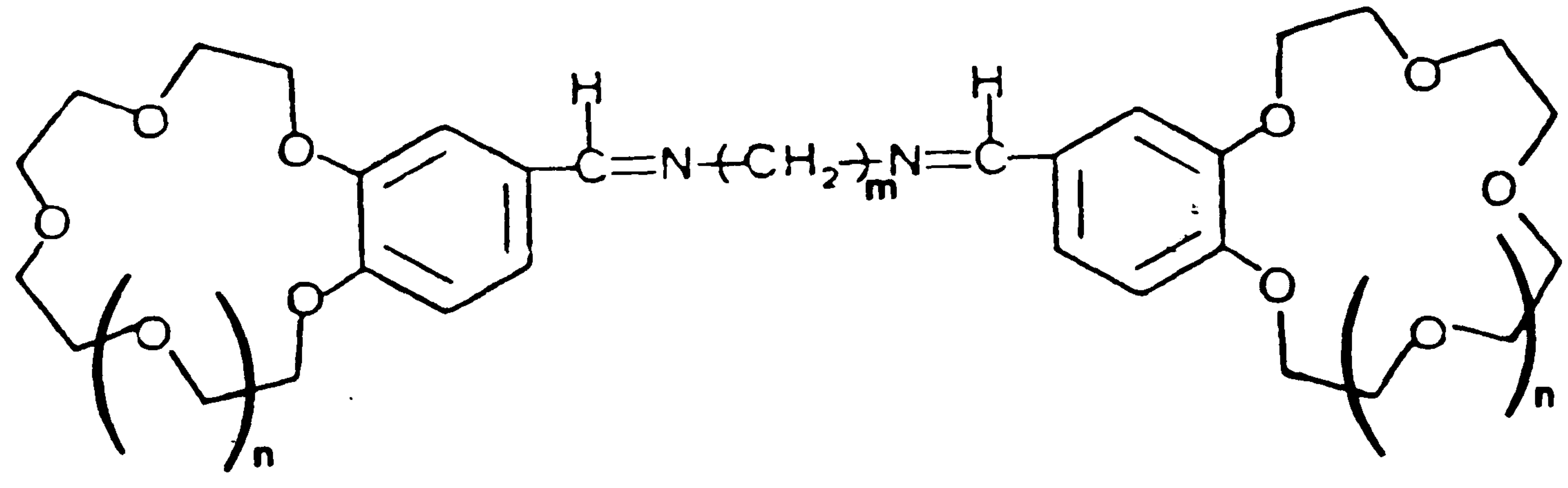
It is clear from the preceding discussion that two properties are required for an ionophore to be used as ion transporter in ion-selective electrodes. First, fast complexation and decomplexation rate, and secondly a high lipophilicity after complexation. On the basis of these criteria, bis-crown compounds have offered opportunities to synthesise ligands for a variety of ions. Japanese workers [66,67,68] and a group in Newcastle [69] have used similar types of compounds in their membranes with promising results being obtained. Detailed information about the synthesis and application of bis-crowns is given in Chapter Three Part Two.



a) Benzo Crown



b) Cryptand



c) Bis-Benzo-Crown

Fig (1.3)

1.6 IONOPHORES AS ACTIVE MATERIALS IN I.S.Es

The reversible binding and the ion transport capacity of ionophores are desirable properties for effective active materials in ion-selective electrode systems. Due to the high selectivity of natural antibiotics towards the alkali metal ions, they were used in the preparation of liquid potassium membranes [70]. Liquid membranes prepared from nonactin, monactin and monensin showed good response for potassium ions but the selectivity compared with valinomycin was inferior. However, later it was reported that the electrodes based on nonactin in di-butyl sebacate and monensin in ethylhexyl di-phenyl phosphate can be used as liquid membrane selective electrodes for ammonium and sodium ions respectively [25]. A membrane prepared from 72% nonactin and 28% monactin in tris-(2-ethylhexyl) phosphate was found to sense ammonium ions [50].

The first highly selective potassium electrode was a liquid ion-selective electrode of valinomycin dissolved in diphenyl ether and held in a porous membrane [50,71]. The very high selectivity of this electrode for potassium over sodium has rendered it useful in solutions where glass electrodes fail, particularly in biological fluids. Since the invention of the potassium / valinomycin electrode, a number of potassium electrodes of various designs have been manufactured, whose main differences are in the nature of their solvents and supports. For instance, in the Orion Research Inc. potassium liquid electrode, in conjunction with valinomycin, a nitro-aromatic solvent in a cellulose ester support was utilized [72]. The performance and selectivity of the

Orion electrode over 15 different cations has been reported [73]. There are other natural ionophores, apart from those mentioned, being used in liquid membranes for anions [50]. Vitamin B_{12}, in decanol, responds to nitrate and perchlorate ions in the range of 10^{-1} to 10^{-5} mol/dm^3 [74,75].

Liquid membrane electrodes have short lifetime, due to the loss of active material, easy contamination and other disadvantages; therefore, ionophores have been introduced into solid membranes. Numerous potassium electrodes based on valinomycin with different matrices, mostly PVC were constructed [76,77]. Again here, the main differences between the electrodes from various sources are in the nature of the plasticizer and the type of matrix used. In the absence of a plasticizer, Nernstian response cannot be obtained.

Synthesised ionophores, e.g. cyclic polyethers, have been used as active material in ion sensors. The first potassium electrodes based on the crowns: benzo-15-crown-5, dibenzo-18-crown-6, dicyclohexyl-18-crown 6 and dibenzo-30-crown-10 dissolved in nitrobenzene, did not demonstrate any high selectivity for potassium ions [78]. Comprehensive studies by Ryba and Petranek [79,80] with different crown ethers revealed that the introduction of substituent groups and their position on the aromatic ring play an important role in the selectivity and behaviour of the electrodes. On the basis of a study of complex formation constants and selectivity coefficients, Rechnitz and Eyal [78,81] suggested that in electrodes based on crown compounds, the selectivity ratio for one ion over another is approximately equal to the corresponding ratio of the complex formation constants. However, this conclusion has been criticised [82]. In

general, one can say, that electrodes based on crown compounds have so far shown low selectivity and a high detection limit.
More recently, other types of ionophores such as bis and poly-crown compounds have been used in preparation of alkali membrane electrodes [83,84,67,85]. Some of these new electrodes are approximately as effective or even superior [68] to similar electrodes based on naturally occurring ionophores. Their selectivities depend upon the bis-crown configuration and the length and nature of the connecting chains.
Apart from the aforementioned, there are some other ionophores which have been synthesised by Simon's group [36]. These compounds are non-macrocyclic possessing ionophore properties, which have been successfully employed in ion-selective electrodes [86,87].

1.7 PRINCIPLE OF OPERATION OF ION-SELECTIVE ELECTRODES BASED ON IONOPHORES

Principally, the potentials of I.S.Es arise as a result of dissimilar distribution of the charges at the interfaces between the membrane and the contacting phases. The generation of interfacial potentials differs in accordance with the type of membrane. It depends on the membrane and mainly on the active material. The assemblies to be dealt with are of the type which can be represented as:

External Reference Electrode | Solution (1) ▮ Solution (2) | Internal Reference Electrode
membrane

and are used for measurements of the potential difference of I.S.Es. The composition of the solution (2) is always kept constant. The external and internal reference electrodes are chosen in such a way that their potentials, with regard to the respective solutions, are constant and independent of the composition of the solution.

The theory for the established potential of electrodes based on neutral carriers has been developed by Eisenman and his colleagues [88,89], and more recent work has been reviewed by Simon et al. [90].

For a membrane containing an ion carrier ´S´, which separates solutions (1) and (2), possessing the ions ´I^+´ and ´J^+´, the entry of a minute amount of hydrophobic cation (cation-ligand complex) from the aqueous solution into the membrane and the selectivity of the membrane is represented as follows:

$$S_{mem} \rightleftharpoons S_{aq} \tag{1.1}$$

$$I^+_{aq} + S_{aq} \rightleftharpoons IS^+_{aq} \tag{1.2}$$

$$IS^+_{aq} \rightleftharpoons IS^+_{mem} \tag{1.3}$$

$$IS^+_{mem} + J^+_{aq} \overset{K_{ij}}{\rightleftharpoons} JS^+_{mem} + I^+_{aq} \tag{1.4}$$

Where ´mem´ denotes the membrane and ´aq´ the solution phases. Assuming that the formation of the complexes IS^+ and JS^+ in the aqueous phases is negligible and the distribution coefficients of the complexes between aqueous and organic phases are equal, the following equation (1.5) expresses the membrane potential:

$$E = E^0 + RT/F \ln\left(a_i(1) + \frac{U_{js^+}K_j}{U_{is^+}K_i}\, a_j(1)\right) \qquad (1.5)$$

Here E and E^0 are potentials, a_i and a_j are the activities of the ions 'I^+' and 'J^+' in solution (1); U_{ij^+} and U_{is^+} are the mobilities of the 'JS^+' and 'IS^+' in the membrane, and K_i and K_j are the equilibrium constants of the salt extraction reactions:

$$I^+_{aq} + X^-_{aq} + S_{mem} \xrightleftharpoons{K_i} IS^+_{mem} + X^-_{mem} \qquad (1.6)$$

$$J^+_{aq} + X^-_{aq} + S_{mem} \xrightleftharpoons{K_j} JS^+_{mem} + X^-_{mem} \qquad (1.7)$$

and R, T, F are the gas constant, the absolute temperature and the Faraday constant respectively. Usually, the mobilities of the complexes in the membrane are similar:

$$U_{ij^+} \simeq U_{is^+}$$

Thus, eqn.1.5 becomes the well known Eisenman-Nicolsky equation:

$$E = E^0 + RT/F \ln\left(a_i\ (1) + k^{pot}_{ij}\ a_j\ (1)\right) \qquad (1.8)$$

where

$$k^{pot}_{ij} = \frac{K_j}{K_i} = \frac{(K_{js^+})_{aq}}{(K_{is^+})_{aq}}$$

K_{js^+} and K_{is^+} represent the stabilities of 'JS^+' and 'IS^+' in aqueous solutions. The term k^{pot}_{ij} is called the selectivity coefficient and demonstrates the selectivity of the electrode towards the primary ions in presence of interferent ions. In the case of $a_j \ll a_i$ or $K_j \ll K_i$, the electrode is ideal for the ions I^+ and eqn.(1.8) becomes eqn.(1.9)

$$E = E^0 + RT/F \ln \left(a_i(1) \right) \qquad (1.9)$$

It should be noted that the selectivity of electrodes based on crowns is not the quotient of the stabilities of the complexes [90]. This is partly attributed to the incomplete encapsulation of the cation by the ligand and its co-ordination with the solvent.

The selectivity measurements, anion interferences and operation of membranes are discussed in detail in Chapter Two,Four and Six.

1.8 APPLICATION OF I.S.Es

Before considering the application of any ion-selective electrode to a particular situation, a number ofcharacteristics of I.S.Es must be known. They are as follows :

1. Sensitivity,

2. Selectivity,

3. Response time,

4. Stability and reproducibility.

The sensitivity of an electrode indicates the response range in which the electrode follows linearity. Outside this range, the potential of an electrode does not relate linearly to the activity of the sensed ions. The response range of an electrode varies from one to the another. It can be slightly extended by variation of the calibration procedure (see Chapter Five).

The selectivity of an electrode, as mentioned, is one of the essential parameters which restricts its use in the presence of particular ions.

The response time of an electrode is of paramount importance and it is the length of time necessary for an electrode to reach a percentage of the final potential, after a change in the contacting solution. It is sometimes referred to as 50% ($T_{1/2}$), 95% (T_{95}) and 99% (T_{99}) values of the infinite time potential [91,92]. The latest recommendation of the IUPAC is 90% (T_{90}) of the final potential [93]. There are few theoretical publications about the response time of electrodes [94,95,96].

The stability and reproducibility are the measures of reliability of the electrode´s results. Unstable and irreproducible results can be taken as a sign of an end to the useful life of the electrode.

Ion-selective electrodes measure the activity of ions in solution and they are capable of monitoring changes of ion activity continuously. Due to this property they are being used in a very wide range of applications. Generally, activity measurements are carried out by direct potentiometry and potentiometric titration techniques. The potentiometric titration provides accurate results, due to the large change of the potential at the end point. I.S.Es are used for concentration measurement by considering activity coefficients or by utilizing methods, which keep the ionic strength constant. Basically, direct potentiometric measurement in a constant background gives concentration rather than activity. I.S.Es have been used in studies of complexes, reaction kinetics and biomedical studies [97,98]. The operation of these electrodes in situations where other techniques fail or are not applicable, has recieved attention from industry and field research. In industry, monitoring of the concentration of a species under the condition of production process, is difficult and in some cases impossible. In this case, ion-selective electrodes might be useful for on-line monitoring. However, due to the effect of pressure, temperature, etc. on the internal solution of the electrode, which may result in unstable readouts, electrodes in ´all solid state form´ are preferred. In environmental studies, analysis with I.S.Es is straightforward because of their ability to function in coloured, opaque or even in solutions with suspended or colloidal particles. Continuous on-line monitoring by I.S.Es and computerised analyses are increasing in use day by day, for example, in agriculture, detergent manufacture, explosives, food processing, metallurgy and electro-plating, paper and pulp, pollution monitoring and in biomedical and clinical laboratories. The two latter fields present the widest range of application of I.S.Es. A number of automated commercial biomedical instruments based on continuous flow measurements have been designed for Na^+, K^+, Ca^{2+}, CO_2, pH and Cl^- in body fluids [99]. Numerous books and articles on the application of ion-selective electrodes in different fields are available [100,101,102].

1.9 OBJECTIVES OF THIS WORK

The purpose of this study may be presented as follows:

First, to study the influence of the membrane constituents, particularly the effect of the so called ´inert matrix´ PVC, from different sources with various physical properties, on the performance of potassium / valinomycin ion-selective electrodes. The main idea was to optimize the composition of the membrane by changing the ratio of its components in order to achieve high performance of economical electrodes.

Second, the evaluation of bis-crown compounds in PVC matrix, to produce an electrode competitive with commercially available valinomycin-based potassium electrodes. This part of the study was continuation of a previous project carried out in Newcastle in an attempt to obtain an improved potassium electrode based on synthesised reagents.

Third, the effect of internal reference system on the performance of the electrode was tested in an effort to increase the response range, selectivity and the understanding about the formation of a constant potential at the inner surface of membranes based on neutral carriers and ion-exchangers.

Fourth, the origin of selectivity and charge transport in electrodes, based on neutral carriers, and the correlations between the anion response and composition of the membrane was investigated.

Fifth, automation in selectivity coefficient measurements and aspects of the application of PVC potassium / valinomycin electrodes in biomedical analysers were examined.

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CHAPTER TWO

THEORETICAL AND PRACTICAL BACKGROUND OF THE PREPARATION AND USE OF PVC-BASED, ION-SELECTIVE ELECTRODES

2.1 INTRODUCTION

Polymer membrane electrode refers to a type of membrane, in which an electroactive material is incorporated into a polymer with an organic substance as a plasticizer. The trend to utilize the so called ′inert-matrix′ to give strength and reduce the amount of active material in the membrane dates back more than forty years ago.

The early work of Tendeloo [1] on the fabrication of a calcium electrode using calcium fluoride in paraffin wax, paved the way for further developments in utilizing support materials in membranes. In 1950, Wyllie and Patnode [2], and in 1958, Parsons [3] reported the preparation of solid disc membranes by moulding a mixture of fine particles of ion-exchangers and polymer under pressure. These membranes had poor selectivity. The development of successful membranes became possible after some progress in understanding better the nature of the membrane, and the discovery of effective ion-exchangers as active materials. The first PVC-based membrane was reported by Bloch et al. [4] in 1966 and Shatkay [5] in 1967. Since then, numerous investigations have been carried out on plasticized membranes and with the aid of polymers as binding materials, a large number of liquid membrane electrodes have been replaced by PVC-type membrane electrodes, e.g. Ca^{2+}, K^{+}, NO_3^- , ClO_4^- , etc.

The contribution of Moody et al. [6] in the development of the early polymer membranes is significant. The development of the PVC membrane electrode was the logical extention of the liquid membrane electrode, or, more generally, the desire to eliminate liquid phases in the construction of electrodes. This was the motive force for the development of solid, PVC, coated-wire and ChemFET electrodes.

The following sections give a general outline of the components, construction and usage of PVC-based ion-selective electrodes.

2.2 POLYVINYL CHLORIDE; PROPERTIES AND MANUFACTURE

Polyvinyl chloride is, in general, a white powder varying from fine dust to sand-like particles. PVC is rarely used in the uncompounded form but is normally mixed with stabilizers, lubricants and, in order to produce flexible compounds, plasticizers have to be added. PVC is a most versatile thermo-plastic material, because of its wide range of formulation and various properties it can acquire. Careful selection of the PVC and essential ingredients enables both plasticized and unplasticized PVC to be used for various purposes, e.g. electrical cables, footwear, pipes, bottles, etc.

There are three commercial processes for the manufacture of PVC:

1. Suspension polymerisation,

2. Emulsion polymerisation,

3. Mass or bulk polymerisation.

Most PVC is produced by the suspension process. By this method liquid vinyl chloride monomer, which is insoluble in water, disperses to form droplets when mechanically agitated. During the agitation, the fine droplets are kept in suspension. Polymerisation occurs in pressurised containers under the influence of heat and initiators or catalysts, both of which are soluble in the monomer. In emulsion polymerisation, surface active agents, e.g. soaps, are used to disperse the vinyl chloride in water. The size of the particles is fine and contain residues of the soaps. Unlike suspension and emulsion polymerisation, mass polymerisation occurs in the complete absence of water or emulsifying agents. The products are characterized by their regular, spherical shape, open porous structure and high bulk density.

Polymerisation comprises three steps: namely, initiation, propagation and termination. The initiation reaction occurs in two steps:- the decomposition of the initiator and the addition of the first monomer to the radical. Initiators are compounds which readily decompose to free radicals on heating or under the influence of light. Typical initiators are organic peroxides. In the propagation process, this new species is attached to a second monomer in a similar way and a single electron transfer to the side of the broken bond occurs. The chain can continue to grow by another monomer until the termination process occurs. The termination process take place in two ways, one of which is recombination and the other disproportionation. Radical polymerisation of vinyl chloride is shown below:

$$R - O - O - R \xrightarrow[\text{heat}]{\text{U.V.}} 2\,R - O^{\bullet}$$

initiation, $R - O^{\bullet} + CH_2 = CHCl \longrightarrow R - O - CH_2 - \overset{\bullet}{C}HCl$

propagation,

$$R - O - CH_2 - \overset{\bullet}{C}HCl + CH_2 = CHCl \longrightarrow R - O - CH_2 - CHCl - CH_2 - \overset{\bullet}{C}HCl$$

termination by combination,

$$- CH_2 - \overset{\bullet}{C}HCl + \overset{\bullet}{C}HCl - CH_2 - \longrightarrow - CH_2 - CHCl - CHCl - CH_2 -$$

termination by disproportination.

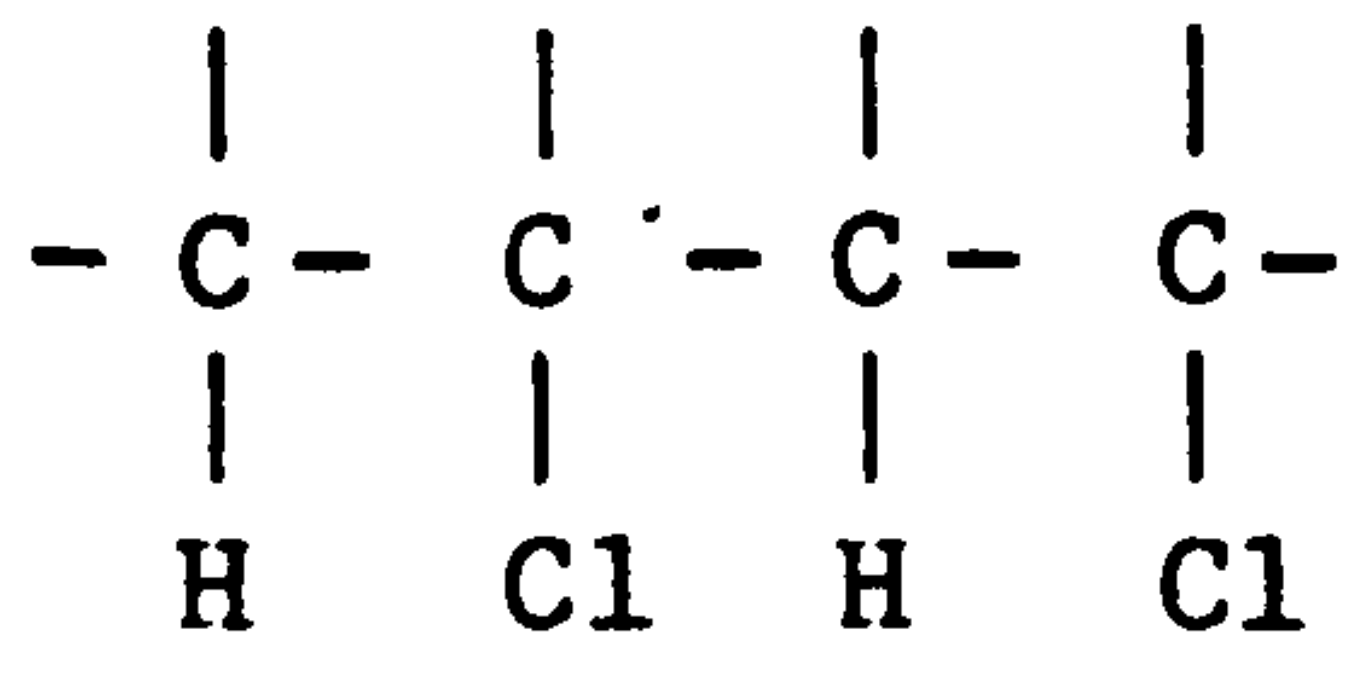
$$- CH_2 - \overset{\bullet}{C}HCl + \overset{\bullet}{C}HCl - CH_2 - \longrightarrow - CH_2 - CH_2Cl + ClCH = CH -$$

As a result of the termination steps, the chain lengths are not equal, thus assignment of a definite molecular weight to a polymer is not possible. Since the repeating unit in the PVC is asymmetric, various regular and irregular forms of configuration can be attained as follows:

a) Head to tail addition will yield a regular molecule.

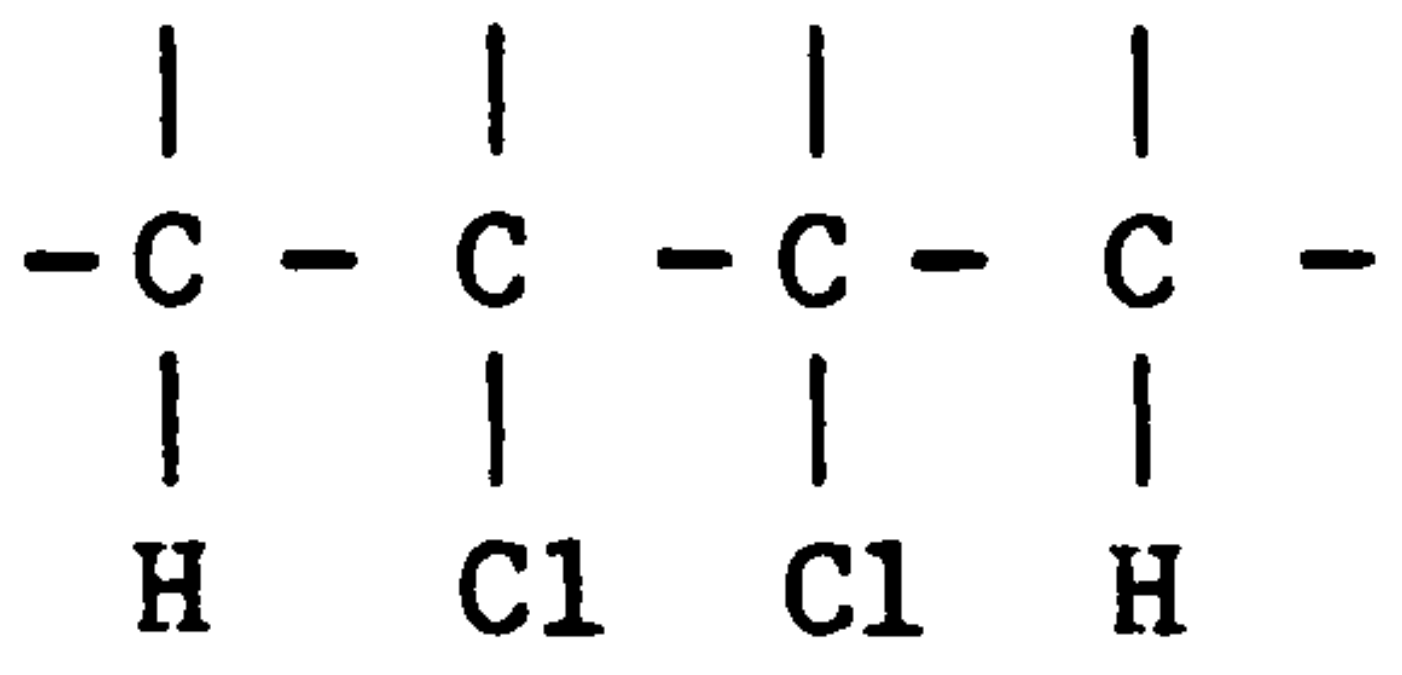
b) A random choice between head to tail, head to head and tail to tail will result in irregular molecules.

These different forms, which occur with every asymmetric monomer units, are really different chemical substances with different properties. Consequently, by changing the conditions of preparation, it may be possible to influence the forms which result. In PVC, the predominant form is usually the regular head to tail [7,8] with a small proportion of the other forms. The stereochemical arrangements are represented below.



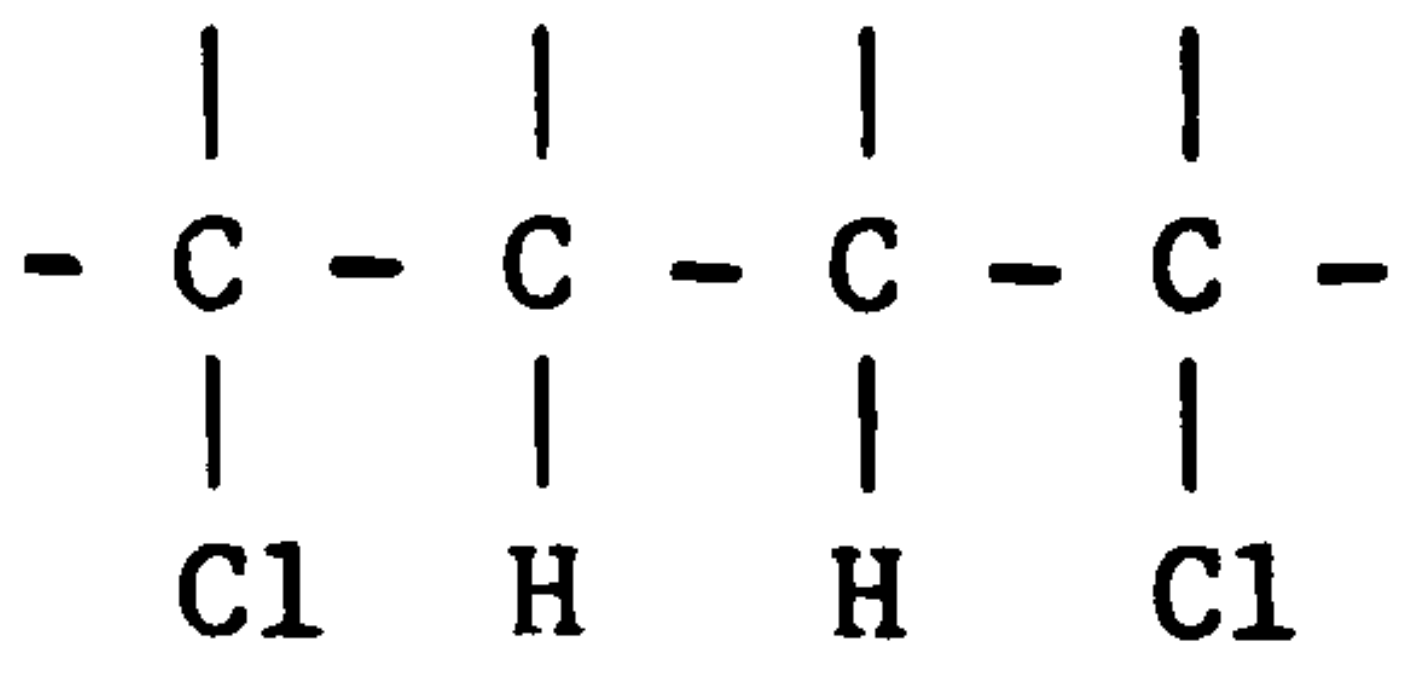
$-\underset{\mathrm{H}}{\mathrm{C}}-\underset{\mathrm{Cl}}{\mathrm{C}}-\underset{\mathrm{H}}{\mathrm{C}}-\underset{\mathrm{Cl}}{\mathrm{C}}-$

Head to Tail



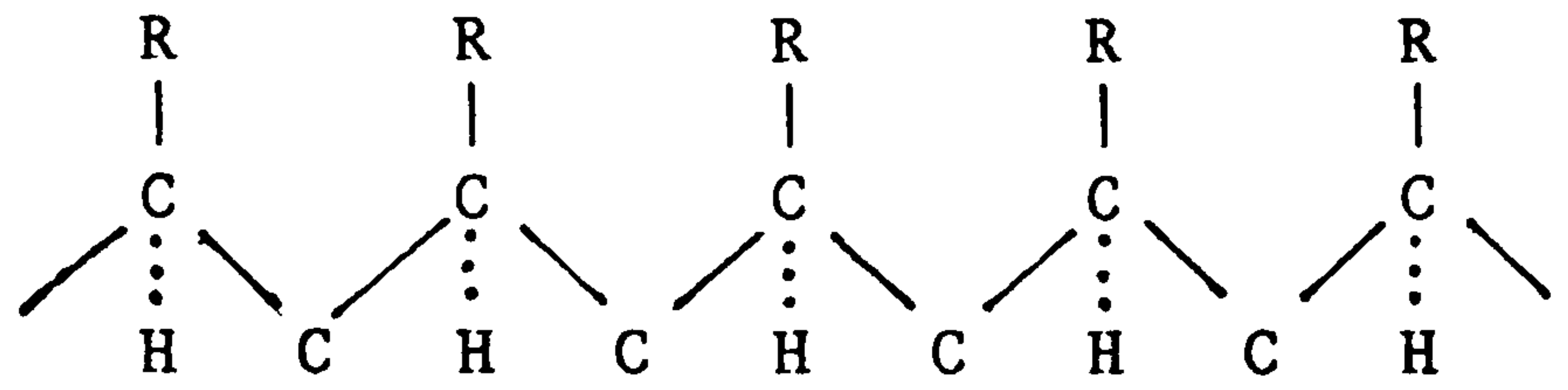
$-\underset{\mathrm{H}}{\mathrm{C}}-\underset{\mathrm{Cl}}{\mathrm{C}}-\underset{\mathrm{Cl}}{\mathrm{C}}-\underset{\mathrm{H}}{\mathrm{C}}-$

Head to Head

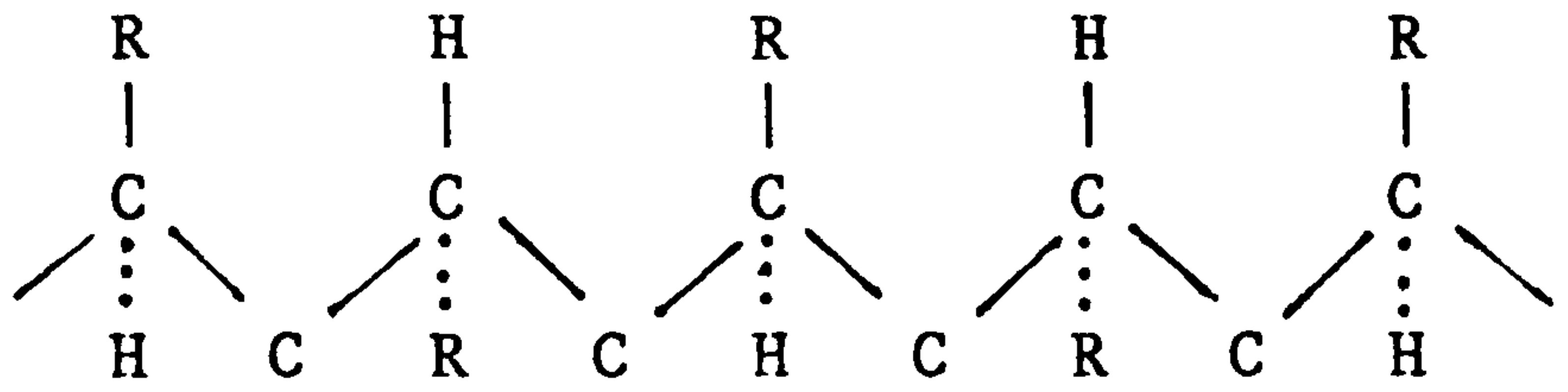


$-\underset{\mathrm{Cl}}{\mathrm{C}}-\underset{\mathrm{H}}{\mathrm{C}}-\underset{\mathrm{H}}{\mathrm{C}}-\underset{\mathrm{Cl}}{\mathrm{C}}-$

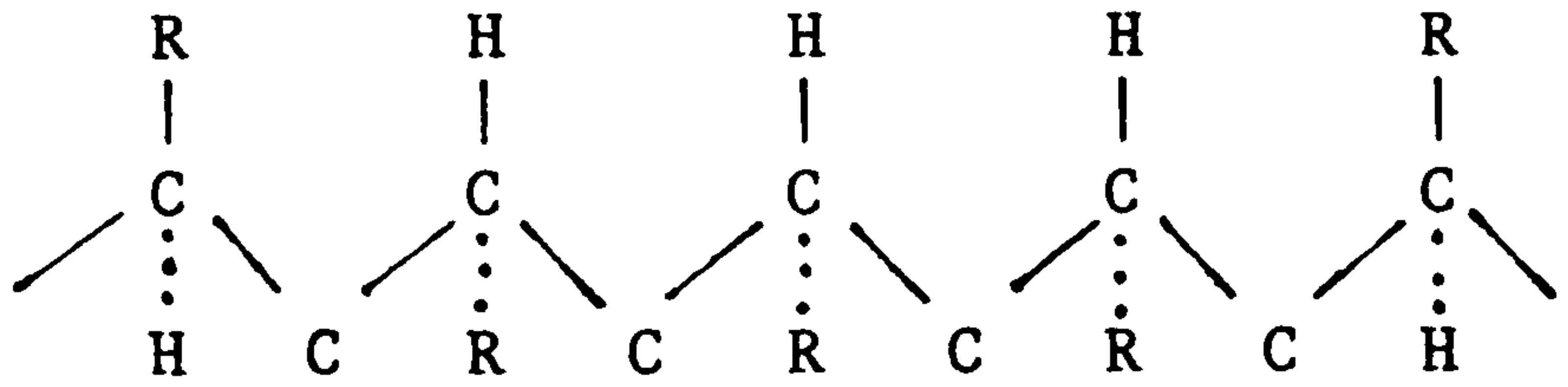
Tail to Tail



Isotactic



Syndiotactic



Atactic

For the polymer derived from monomers of the type CH_2= CHR, there are two possible stereoregular arrangements. In the first arrangement each carbon with the R group has the same configuration, but in the second alternate carbons with the R group have the same configuration. Natta [9] proposed the term isotactic for the former and syndiotactic for the latter[9].

The properties of the PVC compound depend upon the base polymer, and the nature and quantity of the other ingredients, which are added during the manufacture. For general purposes, a flexible polyvinyl chloride contains the following ingredients: polymer, plasticizer, stabilizer and lubricant.

2.3 PLASTICIZER AND GLASS TEMPERATURE

Usually, plasticizers are used to induce a flexible property and also to reduce the glass temperature of the PVC. The temperature at which the rubbery state of the polymer changes to a glassy state is called the glass-transition temperature (Tg). The nature of the monomer plays an important role in determining this temperature [10]. The value of the glass temperature varies over a large range (-120^0C to $+130^0$C) [10,11]. The main parameters which affect Tg are: the flexibility of the chains, the bulkiness of the side groups and the intermolecular interaction between substituent groups [10]. More flexibility and higher molecular weight of chains increases Tg. The plasticizers are organic compounds with high boiling points. The main asset of plasticizers is their ability to soften PVC, however, a good plasticizer should also possess a combination of the following properties: chemical inertness, low volatility, low solubility and good compatibility with the matrix. Depending on the usage of PVC, plasticizers are classified into four general groups [12]: primary, secondary, polymeric and other plasticizers. The primary and secondary plasticizers are used, when low temperature and flexibility are of prime importance, e.g. di-(2-ethylhexyl) phthalate, di-(2-ethylhexyl) sebacate. Polymeric plasticizers with high molecular weight give low volatility to the product, e.g. polypropylene adipate. The amount and type of plasticizer is very important and critical in the functioning of the PVC membrane. The effect of plasticizer on the behaviour of PVC membrane will be discussed in a separate section. It is worth mentioning here, that water is a natural plasticizer which is absorbed, to different extents, by various polymers.

2.4 STABILIZERS

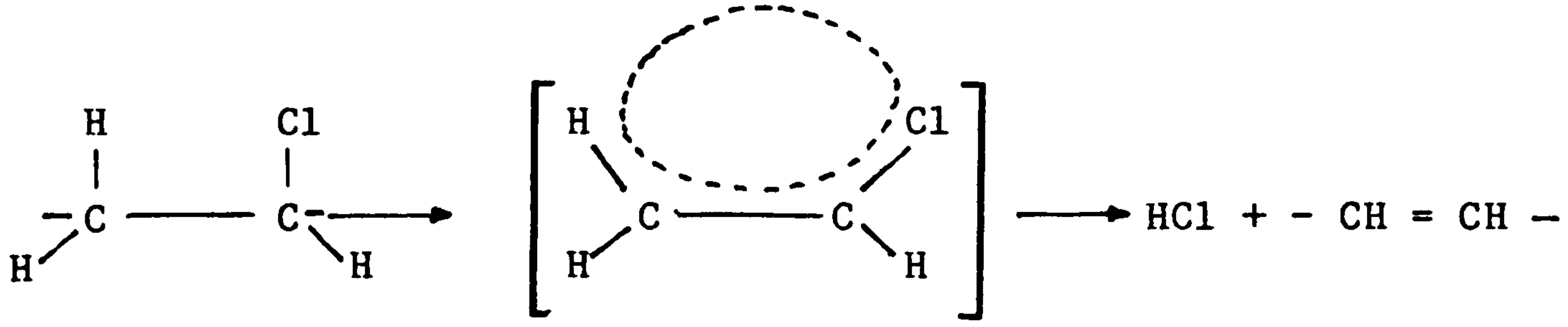
Uncompounded polyvinyl chloride has relatively poor heat and light stability compared to other polymers. Exposure of PVC to either ultra-violet light or heat, leads to degradation and as a result discolouration and change in mechanical properties occur. The degradation of polyvinyl chloride involves the liberation of hydrogen chloride which depends on the temperature. Two types of mechanism have been suggested for the dehydrochlorination process: namely, free radical [13,14] and unimolecular reaction [15]. They are represented as below:

1:

$$- CH = CH - CH_2 - CHCl - CH_2 - CHCl - + Cl^{\bullet} \longrightarrow HCl + - CH = CH - \overset{\bullet}{C}H -$$

$$- CHCl - CH_2 - CHCl \longrightarrow Cl^{\bullet} + - CH = CH - CH = CH - CH_2 - CHCl -$$

2:



The reactions are catalysed by HCl and therefore are autocatatytic reactions. The change in the colour of the polyvinyl chloride is assumed to be the result of the conjugated double bond formation. It has been shown that PVC degrades more rapidly in air than in an inert atmosphere. It is believed that, in the thermal degradation of PVC, the acid splits off in the first step, something which leaves unsaturated positions. The rate of degradation of PVC is accelerated by traces of metals such as zinc and iron. Heat and light are two main factors which limit the usefulness of the PVC; thus, addition of some materials which can prevent or minimize the effect of those factors is essential. These added materials are called stabilizers. Many compounds have been reported to lower the deterioration of the PVC but very little is known about the functioning of those substances. One possible mode of action of the stabilizers is the deactivation of the liable sites in the polymer chain. This mechanism is followed by metal carboxylate stabilizers [16]. Due to the deterioration of PVC, which starts with liberation of HCl molecules, the key function of any stabilizer must be acid acceptance. Polyvinyl chloride stabilizers may be categorised [16] as primary and secondary heat stabilizers (lead salts). Preventing of degradation of polymers by some of these is either through reflection or absorption of the light. Cadmium compounds, basic lead phosphate and tin compounds are good stabilizers. Nevertheless, final use of the PVC determines the choice of the plasticizers and stabilizers. In this work PVC samples were provided by ´BP Chemicals International Limited´, under the name of Breon.

2.5 ELECTROACTIVE MATERIALS IN MEMBRANES

Electroactive species are one of the fundamental components of ion-selective membranes. The first criterion for the selection of active material is its selective character towards the species in the solution. Ideally, it should have the capability to differentiate only one amongst the various species. The second is its compatibility with the matrix and solubility in membrane solvent and aqueous solution.

Numerous ion-exchanger systems responsive either to cations or anions, of varying charge, have been utilized as active species in membranes. Phosphate esters [17,18], tetraphenyl borate [19] and oxine [20] systems for cation sensors and quaternary ammonium salts [21,22], quaternary phosphonium salts [23,24] and many other compounds [25,26,27] have been employed in anion-selective electrodes.

Nowadays, the most widely used active materials are the neutral organic compounds, of which some naturally occur and others are prepared synthetically [28,29,30.31]. Due to their high selectivities arising from their peculiar structure, their use in ion-selective electrodes is of great importance. Because of the high prices of the natural carriers, reasons force only minimum amounts of these materials are used in the membrane preparation. It has been previously reported [32], and confirmed here, that the choice of minimum amount is very important, and will affect the response range, selectivity, response time and useful lifetime of a membrane. In the present work valinomycin is chosen as an active material for PVC potassium electrodes. The superiority of the valinomycin-based PVC electrodes over the commercially available glass [33] and ion-exchanger based potassium electrodes [34] is well documented.

2.6 SOLVENTS IN LIQUID MEMBRANES AND PLASTICIZERS IN PVC MEMBRANES

The second important component in membranes is the solvent. The role of the plasticizers in the PVC membranes, apart from softening the rigid and brittle polymer, is the contribution to the function and selectivity of the membrane. This character makes the choice of the plasticizer most critical. The solvent in a liquid membrane and the plasticizer in a polymer membrane, must be compatible with the other components, namely, the active material and the matrix. The solvent should dissolve as much active material as possible, and should have low vapour pressure and high viscosity [35,36.37]. The respose of liquid membrane ion-selective electrodes has been shown to depend closely on the nature of solvent which is used as mediator in membranes [38]. This effect is noticeable in calcium liquid ion-selective electrodes with 1-decanol or dioctylphenyl phosphonate (DOPP). With 1-decanol, the electrode does not discriminate between calcium and magnesium ions, therefore, it is suitable for determining water hardness [39,40]. The effect of solvent on the response range and selectivity of the calcium liquid membrane electrode has been clarified by the comprehensive work of Garbett and Torrance [41]. The origin of those two properties was attributed to the influence of the type of solvent on the value of the formation constant and the partition coefficient of the equilibria, which determine the ion-exchange process occurring between the calcium species in the liquid membrane and the other cations in the sample solution. Perry et al. [42], first reported that the addition of active carrier to an ion-selective electrode membrane only improves the selectivity of the electrode. For a functional potassium membrane, the solvent or plasticizer must show a response to some extent. The influence of the dielectric constant of the medium on the selectivity of the membrane has been investigated [43]. Membranes with neutral carriers as active material in low dielectric media ($\epsilon < 10$) prefer monovalent cations to divalent cations. The discrimination between cations within a given group in the periodic table was said to be insignificant. This statement of Simon et al. [43], has been followed by a theory put forward by Fiedler [44]. According to this theory, the effect of variation of the polarity of the surrounding media on the selectivity of potassium and calcium PVC electrodes is predictable. The systematic study of the influence of the organic solvent on the performance of the PVC / ion-exchanger based potassium electrodes has revealed [45] that, the chemical nature and concentration of the plasticizer primarily influences the selectivity of the electrode towards univalent cations. Thus, it has been suggested that, in the selection of plasticizer, in addition to the lowering of the glass temperature of the polymer the following factors must be taken into consideration [45]: immiscibility in water, non-volatility, good ratio of solvent to active material concentration and high viscosity. There are various organic materials used as plasticizers or solvents. Considering the above mentioned points, these substances can be categorised into three classes:

1. Diesters of dicarboxylic acids,

2. Nitro-aromatic compounds,

3. Organophosphates.

In this work, esters of o-phthalic acid and sebacic acid have been utilized and their effects upon membrane response was investigated. The specification of these substances is given below:

1. Bis-(2-ethyl hexyl) sebacate: BEHS , Fluka.

2. Di-(n-butyl) phthalate: DBP , BDH.

3. Di-(iso-octyl) phthalate: DOP , BDH.

2.7 MEMBRANES AND MATRIX MATERIALS

Sollner was the first to prepare collodion membranes, however, preparation of polyvinyl chloride membranes in their present form has been advanced by Moody and Thomas [6]. Various other materials have been introduced as membrane matrices. Apart from chemical interactions, the structure of these materials has been reported to affect the operation of the sensors [46,36].

Silicone rubber, due to its inertness, hydrophobic and flexible properties has been used as a matrix [49]. The membranes are prepared by dispersing the ground, dried active material in silicone rubber monomer and polymerising the mixture [50]. Numerous ion-selective electrodes have appeared for both cations and anions based on the silicone rubber format with different active materials [51,52]. The porous structure of silicone rubber has rendered it, virtually, obsolete.

Carbon and graphite [53] are used as matrix in the forms of paste or rod for the construction of ion-selective and redox electrodes. A variety of plastic substances has been utilized as membrane binders, e.g. polyethylene, polystyrene, epoxy resins, polyvinyl chloride, collodion, etc.
Polymers such as polystyrene and polymethacrylate with high glass temperature Tg , have been reported to be less successful [36]. Potassium electrodes constructed with block co-polymers of poly-bisphenol-A carbonate and poly-dimethylsiloxane, with sufficient cyanoethyl substitution in the latter, and impregnated with potassium valinomycin tetraphenyl borate salt showed nearly ideal Nernstian response to K^+ with more than a three years useful lifetime [54].

Cellulose ester [55] and cellulose triacetate [56] Millipore filters have been used as a support in liquid ion-exchanger based I.S.Es for the determination of calcium and potassium ions. Polymer membranes based on cellulose acetate [36], ethyl cellulose [52] and collodion [39] have shown unsatisfactory results. This malfunctional behaviour is supposed to arise from the hydrophilicity of these materials [36,39]. The same effect may occur with co-polymers which carry hydroxide groups in the network

[58,59]. It is generally accepted that the failure of liquid ion-selective membrane is the result of two factors: firstly, extension of pore size which leads to membrane losing its selectivity and secondly, loss of the active material due to the low viscosity of the media. These are avoided by the use of PVC incorporating plasticizer and active materials. In PVC-based membranes, the pore size [61] is small in contrast to Millipore filters and viscosity of the organic liquid is increased. The best matrix to use in I.S.Es has been suggested to be one which is resistant, hydrophobic and non-porous [60]. So far, there is no such material which can satisfy all these criteria, nevertheless poylyvinyl chloride is the most suitable. In this work, the effect of eight different polymer samples on the behaviour of valinomycin-based potassium electrodes, has been investigated. The typical properties of these polymers are given in Table 2.1 . The first six samples are from BP Chemicals International Limited under the trade name of Breon. The last two are from the BDH, and the only information available is about their molecular weights. The grade coding for Breon polymers is designed to describe polymer type and to indicate the more important properties. For example, Breon S 110/10 is a suspension homopolymer with an ISO viscosity number of 110, and 10 indicating the particular manufacturing process used in its preparation. Each of the Breon polymers has been designed to have particular properties e.g. Breon S 125/12 is recommended for use in cable or other electrical applications, due to its electrical properties.

Table 2.1

Typical Properties of Breon Polymers

Breon Grade	Specific Viscosity 0.5% in Cyclohexane	K Value*	Viscosity Number: ISO Method R 174 1961	Bulk Density (g/cm^3)	Particle Size μm
S. 110/10	0.56	66	111	0.53	250
S. 125/12	0.64	71	128	0.46	250
AS. 70/42	0.34	52	68	0.74	200
S. 125/14		(70-72)	(124-132)	0.460	250
S. 110/11		(65-68)	(106-116)(IS 174)	(0.53-0.57)	250
S. 110/11	57,000(MW)				
BDH	100,000(MW)				
BDH	200,000(MW)				

S = Vinyl chloride homopolymer manufactured by suspension polymerisation.
AS = Vinyl chloride/vinyl acetate copolymer manufactured by suspension polymerisation.

* The K value, characterizing the viscosity behaviour of the polymer, is related to the molecular weight.

2.8 PREPARATION OF PVC MEMBRANES

A simple and convenient method for PVC membrane preparation is by Moody et al. procedure, which is in general use [6]. In this method, the PVC powder, plasticizer and active material are dissolved in a solvent with a high evaporation rate, for instance tetrahydrofuran (THF) [47] or cyclohexanone [62]. By controlled evaporation of the solvent, a homogeneous film which is called a master membrane remains at the bottom of the container. Another method, similar to this but with pressure-controlled solvent evaporation has been suggested [48]. This method has been claimed to be useful for solid and coated-wire I.S.Es. The PVC membrane has also been constructed without a solvent [45]. In this technique, the membrane components are well mixed and cast with the help of heat in an oven. Some workers employed woven fabric in PVC membrane as a backbone for obtaining more mechanical strength. In the present work, the membrane was made by dissolving active material, PVC and plasticizer in 4 ml THF (Fluka). After shaking by an electric shaker for about 2 hours, the mixture was transferred to a circular PTFE pot with an inner diameter of 32 mm and a height of 15 mm. The base was movable as a piston inside the circular PTFE cylinder. The pot was covered with filter papers kept in place with extra weight. The solvent was allowed to evaporate completely over a period of 48 hours. A flexible membrane was thus obtained by pushing up the central piston (base) and peeling it off from the surface of the base. The thickness of the membrane was found to be around 0.3 mm. The membrane cast from the solution of THF made only with PVC was not satisfactory because it was brittle. High plasticizer content, made the membrane jelly-like, whereas low plasticizer content made it brittle again to a certain extent. The casting pot is shown in Fig 2.1. The general formulation of membrane composition was as follows (otherwise stated):

330	mg	plasticizer
5	mg	valinomycin
165	mg	polyvinyl chloride
4	ml	tetrahydrofuran

2.9 INCORPORATION OF FIXED NEGATIVE SITES

In membranes supported by cellulose acetate (Millipore) filters, negatively charged sites can be introduced as a result of sulphonic acid substituted dye within the membrane. In PVC membranes, apart from the negative sites which exist, additional ones can be introduced by adding 1.2 mg potassium tetrachlorophenyl borate or potassium tetraphenyl borate [57]. In some cases in this work, spherical glass powder has been added as a source of negative sites.

2.10 PRINCIPLE OF THE E.M.F. MEASUREMENT

In order to measure the potential of an ion-selective electrode, a suitable reference electrode in contact with the test solution is required. The potential of electrochemical cell which consists of two electrodes and a sample solution, is given by equation 2.1:

$$E_{cell} = E_2 - E_1 + \Delta E_m \qquad (2.1)$$

where E_1 and E_2 are the potential of external and internal reference electrodes respectively, and ΔE_m is that of the membrane. If, in this equation, the first and the second terms are constant, the potential difference of the cell will be the result of the membrane potential arising from the activity of the determined ion in the sample solution. Thus, the first requirement for a reference electrode is to have a stable and constant potential. It can be achieved if the concentration of the species, to which the reference electrode responds, is kept constant.

Anion-reversible reference electrodes namely Ag/AgX or Ag_2Y (X^- = halide, Y = S^{2-}) and mercury(I) salts are usually used as reference electrodes. In principle, any electrode could serve as a reference electrode but it must satisfy the following criteria: stability, reversibility, reproducibility [63] and must be non-polarizable. In addition, the choice of reference electrode is dictated by the cell design. In an electrochemical cell without a liquid junction, sensing and reference electrodes are both immersed into the same solution, so, the presence of the ionic species, to which a reference electrode responds, is necessary in the sample solution. The potential of the cell without a liquid junction will depend on both cation and anion activities, for example, consider the following cell:

$$\mathrm{Ag}\,|\,\mathrm{AgCl}\,\Big|\;\underset{1}{\mathrm{KCl}}\;\underset{\text{membrane}}{\blacksquare}\;\underset{2}{\mathrm{KCl}}\;\Big|\,\mathrm{AgCl}\,|\,\mathrm{Ag}$$

The potential of the cell is given by eqn.2.2 .

$$E = RT/F \ln \frac{[\mathrm{KCl}]_2^2}{[\mathrm{KCl}]_1^2} \qquad (2.2)$$

in which E is the cell potential while $[\mathrm{KCl}]_2$ and $[\mathrm{KCl}]_1$ are the mean activities of the external and internal solutions. The slope of the response plot will be 2 RT/F ln10, or 118 mV, but the slope will be RT/F ln10 when the calomel electrode is used as the external electrode.

In cells with a liquid junction, a saturated or 3.5 mol/dm^3 potassium chloride/calomel or silver-silver chloride electrode is often used. When the chloride or potassium ions are incompatible with the test solution, an additional salt bridge must be used. However, in either case the contribution of the single or double junction potential to the E.M.F. of the cell must not be ignored.

Conventional ion-selective electrodes consist of an internal reference electrode, usually silver-silver chloride, which is immersed in the aqueous solution in contact with the inner side of the membrane. The inner aqueous solution must contain chloride ions with the ions to which the membrane is selective. The inner electrode must have a long stability time, low temperature sensitivity and be non-polarizable. However, there are ion-selective electrodes with solid internal systems.

Throughout this study, the silver-silver chloride, because of its compactness, has been used as an internal reference electrode and was prepared in the laboratory. The calomel, more often, and fluoride, glass and silver-silver chloride electrodes, occasionally, were used as external electrodes.

2.11 PREPARATION OF THE SILVER CHLORIDE ELECTRODE

The preparation of silver-silver chloride electrodes may be in accordance with any of the following methods [63]:

1. Electrolytic,

2. Thermal,

3. Thermal-electrolytic,

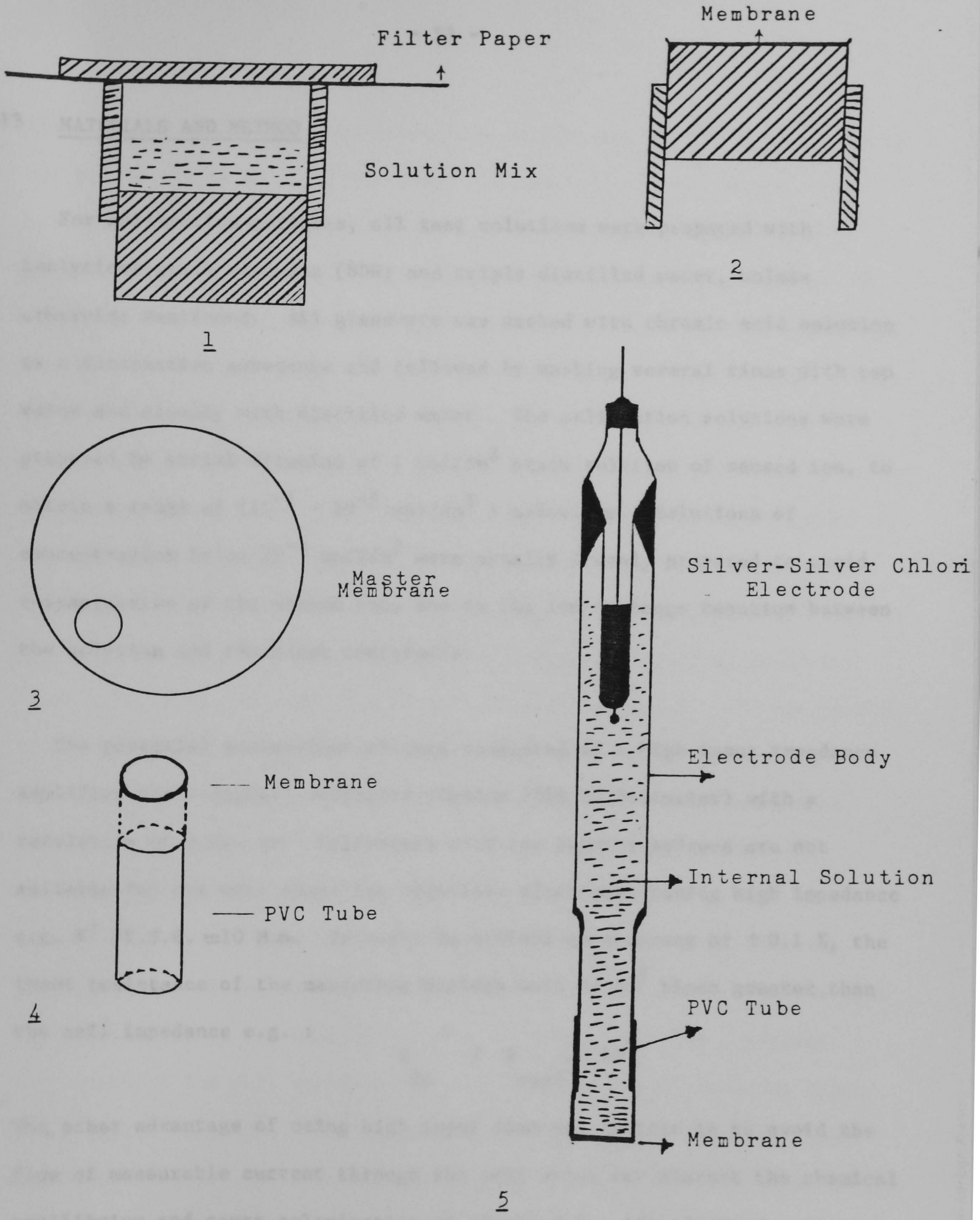
4. Other methods (such as the use of precipitated silver chloride on silver).

In the present work the electrode was prepared by the thermal-electrolytic method, as described by Bates [64]. The silver oxide paste of high purity was obtained by dropwise addition of sodium hydroxide solution to a vigorously stirred silver nitrate solution; extra NaOH was added and the resultant solution was left sitirring vigorously for 30 minutes. The precipitate was separated by decantation and washed with distilled water while vigorously stirred. This procedure was repeated more than forty times as recommended [64], for the removal of all water soluble impurities. The oxide was stored in distilled water.

Two or three cm of a platinum metal wire was sealed in to the bottom of a 6 mm. diameter soft glass tube. Before applying any Ag_2O paste to the Pt-wire, this was washed in concentrated $HNO_3$and rinsed with water several times. The wire was wound into a spiral form of 3-4 mm in diameter. In order to prevent cracking of the sphere due to its immediate exposure to the 450^0C furnace, the electrode was dried superficially with a hair dryer and then transferred to the furnace and left for 10-15 minutes until it became white. To obtain a spherical and smooth-ball silver electrode, the aforementioned process was repeated several times. In each stage, the reduction of Ag_2O occurs and the colour changes to white. The electrode was allowed to cool down and the chloridation process followed. The cell consisted of the silver electrode as the anode, a platinum electrode similar to that used as the cathode, and 0.1 mol/dm^3 HCl solution. The passage of 10 mA of current, for 45 minutes, changed small proportion of Ag to AgCl. The final electrodes were white or light grey spheres as shown in Fig 2.1 . The prepared electrodes were kept in 0.1 mol/dm^3 HCl solution while connected to each other. Before being used, the electrodes were checked against each other and sometimes against the hydrogen electrode. Those manifesting drift and high bias potentials were rejected. A small amount of mercury was poured inside the glass tube to facilitate the electrical contact between the platinum and copper wire.

2.12 PVC MATRIX MEMBRANE ELECTRODE CONSTRUCTION

The membranes were cut from the master membrane (section 2.7), using a suitable cork-borer (I.D. 8mm) and cemented onto the end of a PVC tube (3cm x 10 mm O.D.) with an adhesive of PVC/THF solution. The other end of the PVC tube was connected on to the extended glass tube of a B7 socket. To check the proper sealing of the membrane to the end of the PVC tube, the electrode was immersed in distilled water and air was blown through the electrode body. The appearance of any air bubble was the sign of improper sealing, which can be cured by changing the membrane, and repeating the glueing process. The electrode usually is completed by filling the internal reference solution (0.1 mol/dm^3 KCl) and placing the internal reference electrode (Ag/AgCl attached to a B7 cone) in the inner solution. The finished electrode needed treatment in 10^{-3} mol/dm^3 KCl solution for at least one hour before any measurement. For a better and stable response, the electrode was left in 10^{-3} mol/dm^3 KCl solution overnight. The diagramatic membrane preparation and electrode construction are shown in Fig 2.1 .



Schematic membrane preparation and electrode construction

Fig 2.1

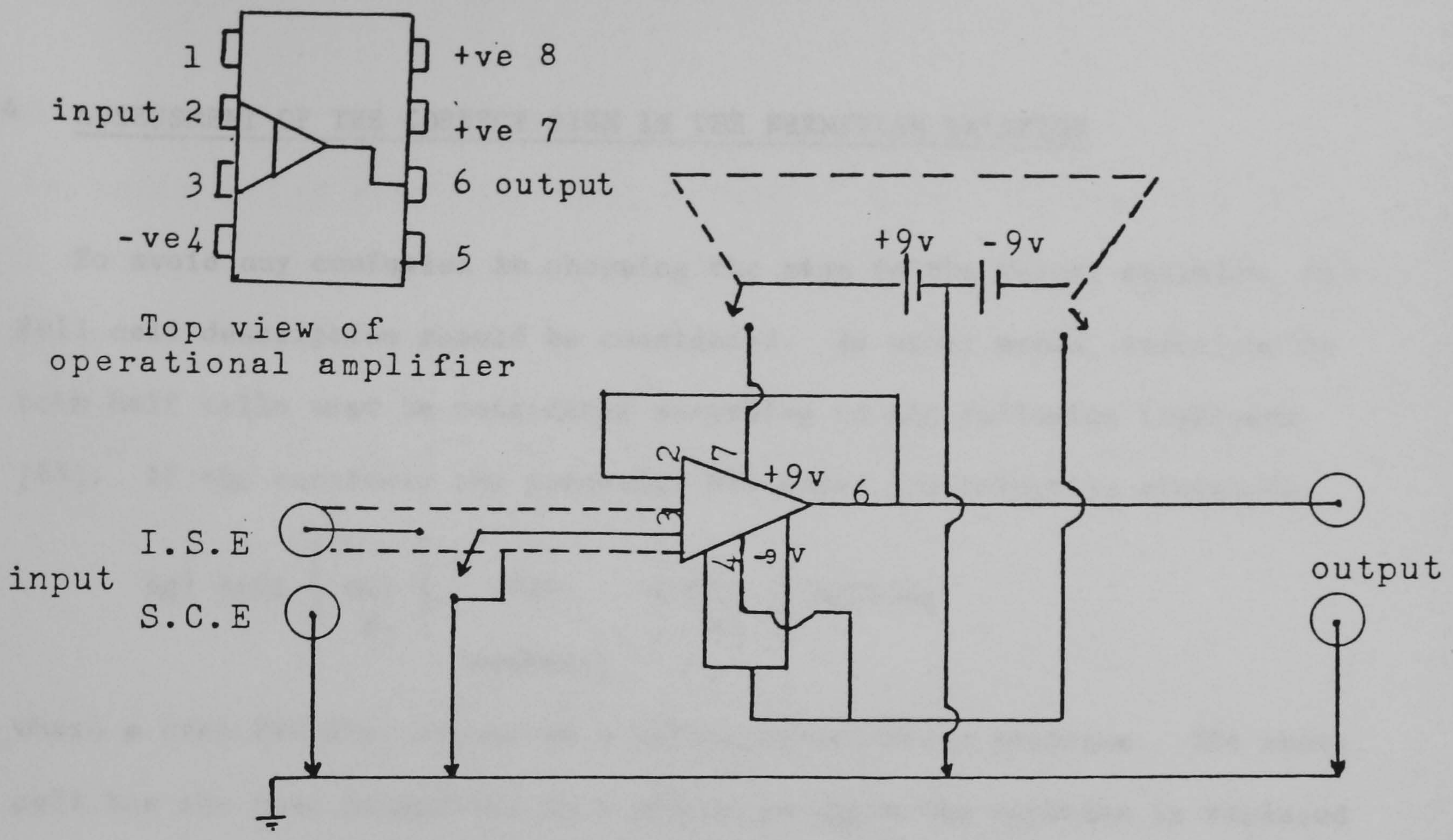
2.13 MATERIALS AND METHOD

For calibration purposes, all test solutions were prepared with Analytical-grade reagents (BDH) and triple distilled water, unless otherwise mentioned. All glassware was washed with chromic acid solution as a destructive substance and followed by washing several times with tap water and finally with distilled water. The calibration solutions were prepared by serial dilution of 1 mol/dm^3 stock solution of sensed ion, to obtain a range of (10^{-1} - 10^{-6} mol/dm^3) solutions. Solutions of concentration below 10^{-3} mol/dm^3 were usually freshly prepared to avoid contamination of the sensed ion, due to the ion-exchange reaction between the solution and the glass containers.

The potential measurement circuit consisted of a high input impedance amplifier and a digital voltmeter (Fenlow 701A DC Voltmeter) with a resolution of $\pm$ 0.1 mV. Voltmeters with low input impedance are not suitable for use with those ion-selective electrodes having high impedance e.g. K^+ /I.S.E. $\simeq 10\ M\Omega$. In order to achieve an accuracy of $\pm$ 0.1 %, the input resistance of the measuring devices must be 10^3 times greater than the cell impedance e.g. :

$$R_{in} / R_{cell} > 10^3$$

The other advantage of using high input read-out devices is to avoid the flow of measurable current through the cell which may disturb the chemical equilibrium and cause polarization of electrodes. All electrodes were connected by co-axial cable to the buffer amplifier which was interfaced with the voltmeter. The electrical circuit of the buffer amplifier is given in Fig 2.2 . The input resistance of the amplifier was $10^{12}\,\Omega$ and it was placed inside an aluminium box. The complete set-up, except the voltmeter, was placed in a Faraday cage with six sides screened, and thermostated at $25^0C \pm 0.5^0C$. To prevent electrical interference and IR drops, all connecting wires and connection points were checked regularly, and all earth connections were made to a single earth point. The arrangement for potential measurement is shown in Fig 2.2 . In the preparation of calibration plots, the ion-selective and reference electrodes, were connected to the high and to the low impedance inputs of the measuring circuit respectively. The saturated calomel reference electrode was used with an added bridging solution of 3.5 mol/dm^3 $(Me)_4NCl$ in a glass sleeve with a ceramic frit to minimise contamination of the test solution by the diffusion of the KCl from the S.C.E. All electrodes were immersed in 50 ml of standard solution to the same depth. The solution was stirred at a fixed rate throughout the whole measurement session with a Teflon coated bar over a magnetic stirrer. Due to temperature effects on the slope of the indicator electrode and the potential of the reference electrode, a thin plate of heat-insulating material (polystyrene) was used underneath the beaker to prevent the heat transfer caused by the magnetic stirrer ($5^0C = +1$ mV). The potential difference of the cell was measured in each solution in ascending order (10^{-6} to 10^{-1} mol/dm^3). The response time was faster for concentrated solutions than for the diluted solutions. The potential difference of the cell in each solution was plotted against the logarithm of sensed ion activity (concentration) to produce a calibration curve.



$E_{in} = E_{out}$ $A=1$

Circuit Diagram of single high impedance input operational amplifier

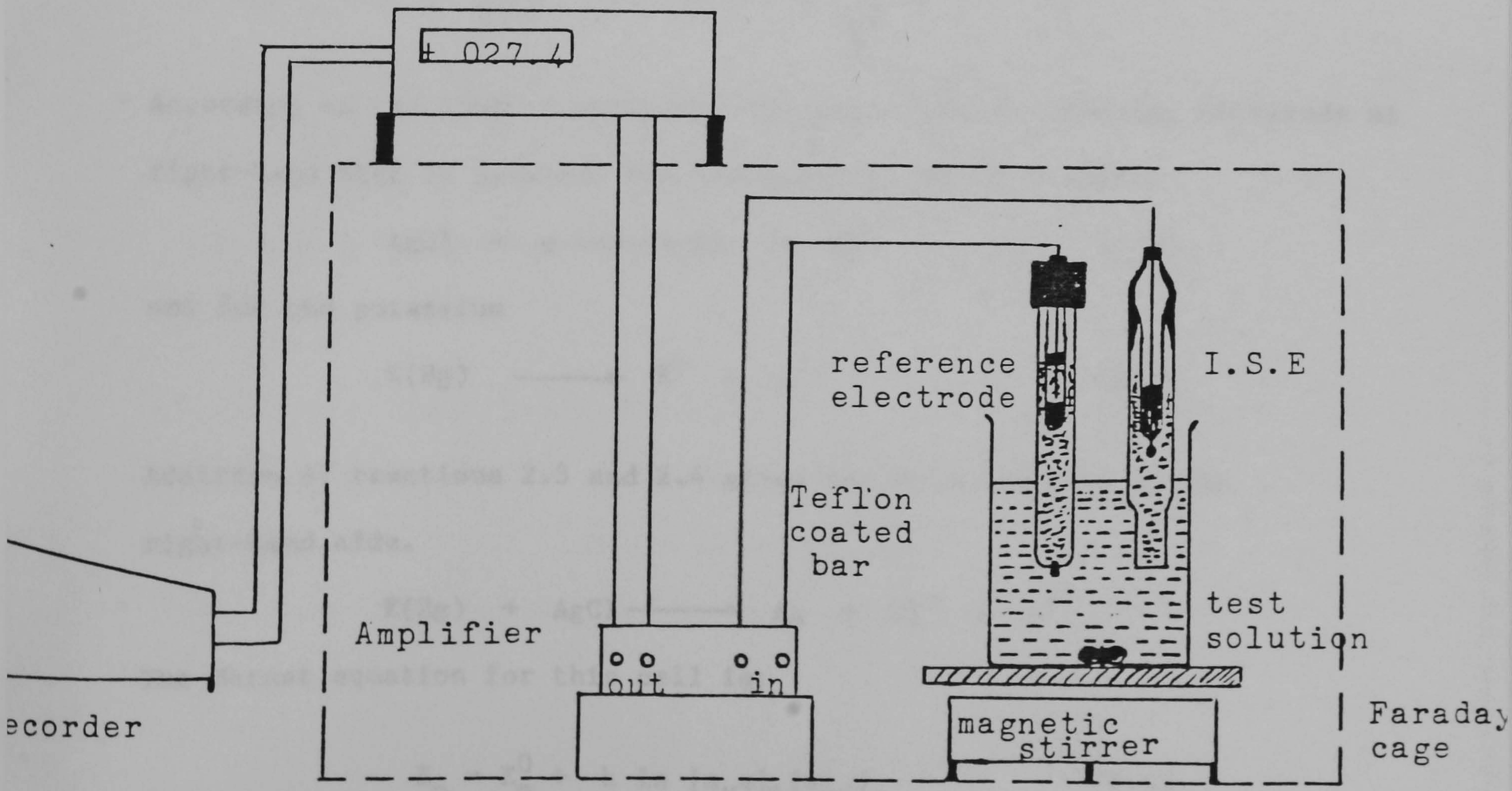


Fig 2. 2

2.14 ASSESSMENT OF THE CORRECT SIGN IN THE NERNSTIAN RELATION

To avoid any confusion in choosing the sign in the Nernst equation, the full cell description should be considered. In other words, reactions in both half cells must be considered according to the following treatment [65]. If one considers the potassium PVC based ion-selective electrode:

$$\mathrm{Ag}|\ \mathrm{AgCl}\ \Big|\ \underset{a_1}{\mathrm{KCl}}\ \Big|\ \underset{\text{membrane}}{\mathrm{PVC}}\ \Big|\ \underset{a_2}{\mathrm{KCl}}\ \Big|\ \mathrm{AgCl}|\mathrm{Ag}$$

where a cast PVC disc serves as a potassium selective membrane. The above cell has the same properties as a system in which the membrane is replaced by two potassium amalgam electrodes connected together. Thus the equivalent cell can be represented as:

$$\mathrm{Ag}|\ \mathrm{AgCl}\ \Big|\ \underset{\substack{a_1\\ L}}{\mathrm{KCl}}\ \Big|\ \mathrm{K(Hg)}\text{----}\mathrm{(Hg)K}\ \Big|\ \underset{\substack{a_2\\ R}}{\mathrm{KCl}}\ \Big|\ \mathrm{AgCl}|\mathrm{Ag}$$

According to the IUPAC convention, the silver-silver chloride electrode at right-hand side is positive and the reaction can be written:

$$\mathrm{AgCl} + e \longrightarrow \mathrm{Ag} + \mathrm{Cl}^- \qquad (2.3)$$

and for the potassium

$$\mathrm{K(Hg)} \longrightarrow \mathrm{K}^+ + e \qquad (2.4)$$

Addition of reactions 2.3 and 2.4 gives the cell reaction on the right-hand side.

$$\mathrm{K(Hg)} + \mathrm{AgCl} \longrightarrow \mathrm{Ag} + \mathrm{Cl}^- + \mathrm{K}^+$$

The Nernst equation for this cell is:

$$E_R = E_R^0 + k \ln\, [a_{K^+}]_2\, [a_{Cl^-}]_2 \qquad (2.5)$$

Where $k = RT/F$

The activities of solids are equal to unity. In the left hand side cell, a similar but reverse reaction take place, whose Nernst equation is:

$$E_L = E_L^0 + k \ln 1/ [a_{K^+}]_1 [a_{Cl^-}]_1 \qquad (2.6)$$

Subtracting eqn. 2.6 from eqn. 2.5 gives the potential difference of the whole cell:

$$\Delta E = +2 k \ln [a_{K^+}]_2 + 2 k \ln 1/ [a_{K^+}]_1$$

$$\Delta E = +2 k \ln [a_{K^+}]_2 / [a_{K^+}]_1 \qquad (2.7)$$

$$[a_+] [a_-] = a_\pm^2 ; \quad a_\pm^2 = m \gamma_\pm^2$$

$$\Delta E = 2 k \ln [m \gamma_\pm]_2 / [m \gamma_\pm]_1$$

If the concentration of the KCl on the left-hand side is kept constant, the potential of the cell will depend on the change of the KCl concentration on the right-hand side, and the Nernst slope will be 118 mV/decade.

If, instead of a silver-silver chloride, a calomel electrode is used as in the following cofiguration:

(2.8)

$$\text{Ag} | \text{AgCl} \left| \begin{matrix} \text{KCl} \\ a_1 \end{matrix} \right| \text{K(Hg)} ---- \text{(Hg)K} \left| \begin{matrix} \text{KCl} \\ a_2 \end{matrix} \underset{\substack{\text{L.J.} \\ 1}}{\Big|} \begin{matrix} 3.5 \text{ mol/dm}^3 \\ \text{T.M.A.Cl.} \end{matrix} \underset{\substack{\text{L.J.} \\ 2}}{\Big|} \text{Hg}_2\text{Cl}_2 | \text{Hg} \right.$$

Assuming the liquid junction potentials $E_{L.J._1}$ and $E_{L.J._2}$ are negligible, the potential of the cell is equal to:

$$\Delta E = k \ln [a_{K^+}]_2 / [a_{K^+}]_1$$

The Nernst slope for the cell 2.8 is now 59.16 mV at 25^0C.

2.15 CALIBRATION

The potential of an ion-selective electrode against an appropriate reference electrode in a solution containing ionic species sensed by the electrode is described by the Nernst equation:

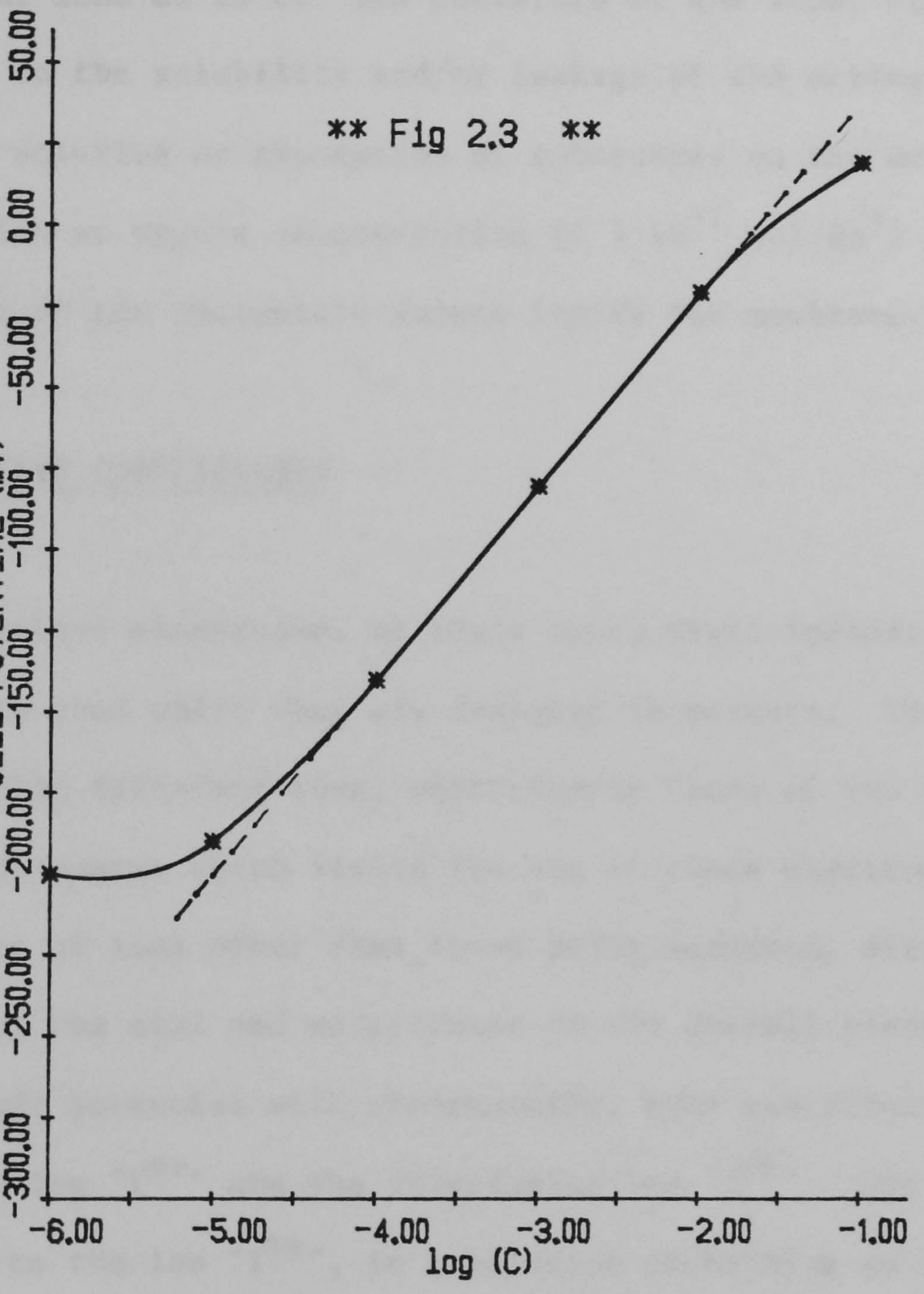
$$E = E^0 \pm k \ln [a_i] \qquad (2.9)$$

Where E is the observed potential, E^0 is a constant potential which varies with the choice of reference electrode. k is the RT/nF, a_i is the activity of the measured species, sign (+) and (-) for cations and anions respectively.

Ion-selective electrodes measure the activity of ions, which can be converted to the concentration by considering their activity coefficients. Generally, there are two methods for concentration measurement by the ion-selective electrodes:

1. Direct potentiometry, which is based on the Nernstian logarithmic relationship between cell potential and concentration.
2. Potentiometric titration.

In direct potentiometry calibration is essential. A calibration plot for an I.S.E. is a plot of the potential difference of the cell against the logarithm of the activity or concentration of the primary ion in the experimental cell. In this work, the calibration curves were produced on a concentration basis. The linearity of the slope and the response range are taken as criteria for functional electrodes. A typical calibration curve, E vs. log C , for an I.S.E. is shown in Fig 2.3 .
The slope of the straight part of the plot represents the electrode



** Fig 2.3 **

TYPICAL CALIBRATION CURVE

sensitivity in millivolts per decade of ion activity. For an ideal electrode this factor should be 59.16 mV for monovalent ions, and 29.5 mV for divalent ions at 25^0C. The curvature at the lower concentrations is attributed to the solubility and/or leakage of the active material into the sample solution or absorption of substances on the membrane surface. The deviation at higher concentration ($C > 10^{-1}$ mol/dm^3) is caused by the penetration of the lipophilic anions inside the membrane.

2.16 SELECTIVITY COEFFICIENTS

Ion-selective electrodes, as their names might indicate, are not exclusive to ions which they are designed to measure. The difficulty of distinguishing different ions, particularly those of the same sign, is an important parameter which limits the use of these electrochemical devices. The presence of ions other than those being measured, disturbs the potential of the cell and contributes to the overall electrode potential. The electrode potential will consequently, have contributions from both the primary ion 'I^{n+}' and the interfering ion '$J^{n'+}$'. For an electrode responsive to the ion 'I^{n+}', in a solution containing an interfering ion '$J^{n'+}$', the potential difference is given by the extended Nicolsky equation which is usually called Nicolsky-Eisenman equation:

$$E = E^0 + RT/nF \ln\left(a_i + k_{ij}^{pot} a_j^{n/n'}\right) \qquad (2.10)$$

Here, a_i and a_j are the activities of the 'I^{n+}' and '$J^{n'+}$' ions with charges n and n' respectively and K_{ij}^{pot} is the selectivity coefficient. For an electrode responding to the I ions only, k_{ij}^{pot} must ideally be zero, or practically very small. If, $\sum_{j}^{n} k_{ij}^{pot} \cdot a_j \ll a_i$, no significant interference exists.

The selectivity coefficient of an electrode is an index which shows how far an electrode can sense the ion of interest in the presence of a certain amount of interfering ion. For instance, if the selectivity coefficient for a potassium electrode is given by $k_{KNa}^{pot} = 10^{-4}$, this means that the electrode is 10^4 times more selective to the potassium than the sodium. In manufacturer's literature the selectivity coefficient is sometimes given as the reciprocal, e.g. $k_{NaK}^{pot} = 10^4$. It should be noted however, that selectivity coefficients are not constant, but vary with the composition of the sample solution and method of evaluation.

2.17 DETERMINATION OF SELECTIVITY COEFFICIENTS

According to the IUPAC [66] definition, the selectivity coefficient determines the capacity of the ion-selective electrodes to discriminate between different ions in solution. The various methods [60,68,69,73] for the determination of selectivity coefficients, k_{ij}^{pot} are based on potential measurements, either in separate solutions or in mixed solutions, containing primary and interfering ions.

2.18 SEPARATE SOLUTION METHODS

In this method two measurements are required. The potential of the electrode which is selective for ion ′I^+′ in pure solutions of ′I^+′ and ′J^+′ is given by eqns.2.11 and 2.12 .

$$E_1 = E^0 + RT/F \ln (a_i) \qquad (2.11)$$

$$E_2 = E^0 + RT/F \ln k_{ij}^{pot} (a_j) \qquad (2.12)$$

When the activities of a and a are equal, the electrode potential E_1 and E_2 can be related to the k_{ij}^{pot} by eqn.2.13 .

$$\frac{E_1 - E_2}{RT/F} = \ln k_{ij}^{pot} \quad \text{or} \quad k_{ij}^{pot} = \exp \frac{E_1 - E_2}{RT/F} \qquad (2.13)$$

In this method when $E_1 = E_2$, eqns.2.11 and 2.12 give

$$k_{ij}^{pot} = a_i / a_j \qquad (2.14)$$

The selectivity in this case is equal to the ratio of the activities of primary and interferent ions. Separate methods are not reliable and have been criticised by Buck [71], who recommends the mixed solution method.

2.19 MIXED SOLUTION METHODS

The potential of the electrode is measured in solutions which contain either a fixed activity for the interfering ions and a varying activity for the primary ions, or a varied activity for the interfering ions while the activity of the primary ions is kept constant. The second method is generally used when either H^+ or OH^- is the interfering ion. A typical selectivity curve is illustrated in Fig 2.4 . There are several methods for calculating k_{ij}^{pot} from this figure.

Method A: By extrapolation of the linear parts of the selectivity curve, AB and DF, where the electrode totally responds to primary ion I^+ and interfering ion J^+ respectively. The point C where the electrode is responding equally to both ions can thus be obtained at which $E_1 = E_2$ and k_{ij}^{pot} is calculated from eqn.2.14.

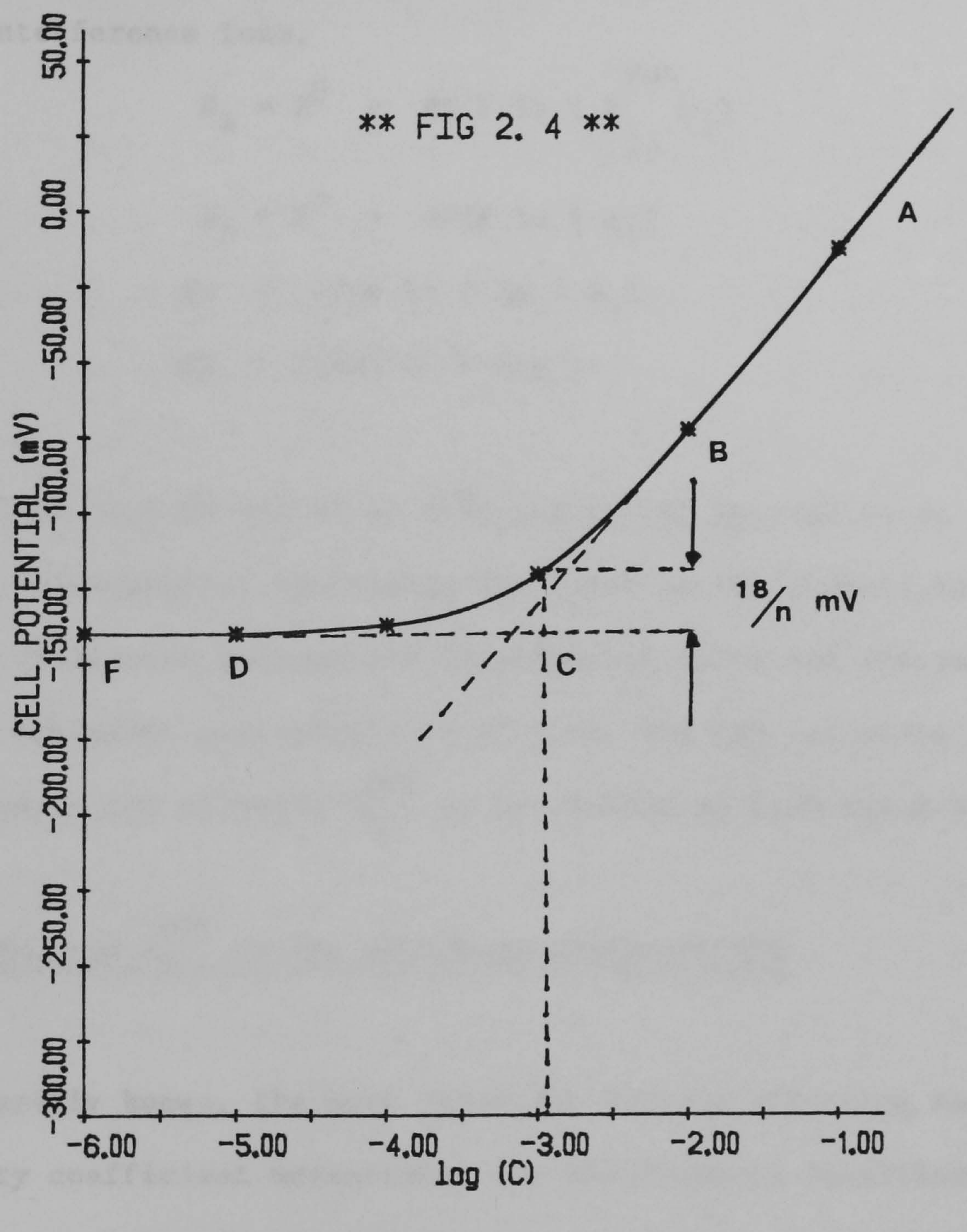
Here, a_i is the activity of the primary ion at point C and a_j is the constant activity of the interference ion. This method is only applicable when DF is a straight line, which is the case for glass and some solid state electrodes.

Method B: due to the irreproducibility and drift at lower concentration of primary ions, the DF part of the curve is not usually straight; thus it is more accurate to determine the activity of the primary ion where both ions equally contribute to the electrode response. From the Nicolsky-Eisenman equation the activity of primary ion is:

$$a_i = k_{ij}^{pot} \, a_j$$

for mixed response,

** FIG 2. 4 **



TYPICAL SELECTIVITY CURVE

$$E_1 = E^0 + RT/F \ln (a_i + k_{ij}^{pot} a_j)$$

or

$$E_1 = E^0 + RT/F \ln (2a_i)$$

and for interference ions,

$$E_2 = E^0 + RT/F \ln (k_{ij}^{pot} a_j)$$

$$E_2 = E^0 + RT/F \ln (a_i)$$

$$\Delta E = RT/F \ln (2a_i / a_i)$$

$$\Delta E = 2.303 RT/F \log 2$$

For univalent ions ΔE =18 mV at 25^0C and in the general case, it is 18/n mV. Consequently, by finding the point on the selectivity curve, where the difference between the experimental curve and the extrapolated Nernstian dependent part equals to 18/n mV, one can calculate the activity of the primary ion allowing k_{ij}^{pot} to be calculated from eqn.2.14 .

2.20 DEPENDENCE OF K_{ij}^{pot} ON THE METHOD OF DETERMINATION

As generally known, the most important factors affecting the selectivity coefficient measurement are experimental conditions such as method, activity levels of primary and interfering ions and ionic strength. The mixed solution method is more realistic and it is possible by this method to produce an environment closely resembling the sample solution. The separate solution method is not recommended, because it does not correspond to the real situation and the electrode does not exhibit a Nernstian response in interfering solution which is the common assumption in all methods. However, the selectivity coefficient will be more useful if the conditions of the measurements are stated.

2.21 RESPONSE TIME AND LIFETIME OF I.S.Es

Apart from the high selectivity, two important parameters are essential for I.S.Es, namely rapid response time and long lifetime. A rapid response becomes more important when I.S.Es are used in titration, automatic analysers and continuous measurements. The response time of an electrode may be defined as the time taken to achieve a steady-state potential within ±0.1 mV after a tenfold change in the activity of the primary ion in the solution. Nevertheless, $T_{1/2}$ and $T_{95\%}$ parameters have been defined as response times. The term $T_{1/2}$ [70,51] which is widely used, is the time which the electrode needs to obtain 50% or one half of the equilibrium potential. Due to the exponential relationship between time and potential the $T_{1/2}$ values are very short. Fleet et al. [72] proposed the $T_{95\%}$parameter which is the time required for the electrode to reach 95% of the steady-state potential after a rapid change in the activity of the primary ion.

The response time depends on many factors: the type of electrode, the magnitude and direction of the concentration change, level of interfering ion, temperature, rate of stirring, age and condition of the electrode. The range of response time varies from tenths of seconds to minutes. Generally, the response time increases for all types of electrodes with decreasing concentration of the primary ion in a solution. The response time of polyvinyl chloride matrix membrane electrodes, used in this study, was less than a minute with reproducibility within ±0.2 mV. Slow drift of ±2 mV took place over a few hours. The PVC electrode lifetime was found to be more than six months. However, the lifetime of all electrodes and, in particular, of the PVC electrode depends on the nature of the active and effective materials in the membrane [59,74]. In PVC-based electrodes, due to the dissolution and leakage of active material and plasticizer, which are not bound to the matrix (more or less free), the lifetime is short compared to the glass electrode (fixed active sites). On the other hand, the short life time for the PVC based membrane electrode cannot be a disadvantage because of the ease and inexpensiveness of the membrane replacement.

2.22 ACTIVITY, CONCENTRATION AND ACTIVITY COEFFICIENT

Since ion-selective electrodes respond to activity rather than the concentration of the single ionic species [67], it is essential to elaborate on the relationship between the activity and concentration.

The term activity is used to denote the active or effective concentration of the ion in the solution. Activity correction in very dilute solutions is not necessary but at concentrations above 10^{-2} mol/dm^3 it does become significant. The relationship between the activity and the concentration of an ion can be expressed by the equation (2.15)

$$a_i = \gamma_i c_i \tag{2.15}$$

Where a_i , c_i ,and γ_i are the activity, concentration and activity coefficient of species ´I´ respectively. It is not possible to measure the single ion activity coefficient, only the mean activity coefficient is measurable and it is defined by:

$$\gamma_{\pm}^{2} = \gamma_{+} \cdot \gamma_{-} \qquad (2.16)$$

The mean activity coefficient is related to the ionic strength of the solution ($c > 10^{-3}$ mol/dm^3) by the Debye-Hückel limiting law:

$$-\log \gamma_{\pm} = A| z_{+} z_{-} | I^{1/2} \qquad (2.17)$$

Here, A is the Debye-Hückel slope constant, which depends on the temperature and dielectric constant of the solvent, z_+ and z_- are the charges of the ions, I is the ionic strength of the solution which is given by:

$$I = 1/2 \sum_{i}^{n} z_i^2 c_i \qquad (2.18)$$

In this equation, c_i and z_i are the concentration and valency of the ions in solution. Equation 2.17 is fairly accurate at low concentrations, but at higher ionic strengths of up to 10^{-1} mol/dm^3, the extended Debye-Hückel equation is required:

$$-\log \gamma_{\pm} = A| z_{+} z_{-} | I^{1/2} / (1 + B\, a^0\, I^{1/2}) \qquad (2.19)$$

Where, B is a function of temperature and of the solvent dielectric constant, and a^0 is the ion-size parameter. At higher concentrations still, equation 2.19 has to be extended. It is possible to calculate the activity coefficient at ionic strength greater than 10^{-1} mol/dm^3 using the Robinson and Stokes's hydration theory [75].

2.23 LIQUID JUNCTIONS

At the interface between two ionic solutions, ions diffuse into each other. Diffusion with different rates (due to the different ionic mobilities) causes an electric potential gradient to develop within the junction, which is called a diffusion or liquid junction potential. Basically, for the E.M.F. measurement of an electrochemical cell, two types of cells are used: a) cells without liquid junctions, b) cells with liquid junctions. For example:

$$K^+ \ /\text{I.S.E.} \overset{\text{membrane}}{▨} \underset{S}{\text{KCl}} \;\Big|\; \text{AgCl}|\text{Ag} \qquad \text{(cell without L.J.)}$$

$$K^+ \ /\text{I.S.E.} ▨ \underset{S}{\text{KCl}} \;\underset{\text{L.J.}}{\Big|}\; \underset{\text{sat.}}{\text{KCl}} \;\Big|\; \text{AgCl}|\text{Ag} \qquad \text{(cell with one L.J.)}$$

$$K^+ \ /\text{I.S.E.} ▨ \underset{S}{\text{KCl}} \;\underset{\text{L.J. } 1}{\Big|}\; \text{T.M.A.Cl.} \;\underset{\text{L.J. } 2}{\Big|}\; \underset{\text{sat.}}{\text{KCl}} \;\Big|\; \text{Hg}_2\text{Cl}_2|\text{Hg} \qquad \text{(cell with two L.J.)}$$

The use of cells without a liquid junction is limited due to the shortage of suitable reference electrodes. For a complete electrochemical cell with one liquid junction, the E.M.F. is given by:

$$E_{\text{cell}} = E_{\text{I.S.E.}} - E_{\text{Ref.}} + E_{\text{L.J.}}$$

Where $E_{\text{I.S.E.}}$, $E_{\text{Ref.}}$ and $E_{\text{L.J.}}$ are the potentials of indicator electrode, the reference electrode and liquid junction respectively. The potential of reference electrode is independent of the sample solution composition and $E_{\text{L.J.}}$ is the potential between dissimilar solutions. The reference electrode potential is constant and the E_{LJ} under special conditions is also constant. Thus, the ion-selective electrode will be able to provide information about the activity of the ions of interest. However, in practice, problems often occur with I.S.Es systems because of variation of the liquid junction potential. The liquid junction potential contributes to the cell potential and is more pronounced when 3.5 mol/dm^3 tetramethyl ammonium chloride is used as a bridge solution. This was observed in the present work and confirmed the findings of previous work [76]. The slope was found to be as high as ≈68 mV/decade in pure KCl solutions, and ≈58 mV/decade in mixed solutions (KCl + 0.1 mol/dm^3 NaCl). Morf [77] has stated that the liquid junction potential is not independent of the sample solution and that it changes considerably. He has also demonstrated the existence of a contribution from the liquid junction potential to the slope of Ca^{2+} I.S.Es with different diluted salt bridges. The liquid junction potential depends on the mobilities and concentration of the ions in the solution, on either side of it, and on how the two solutions are brought together physically to form a junction. In the following sections, a brief discussion about the formation of a liquid junction, the determination of junction potential and also description of salt bridges is given.

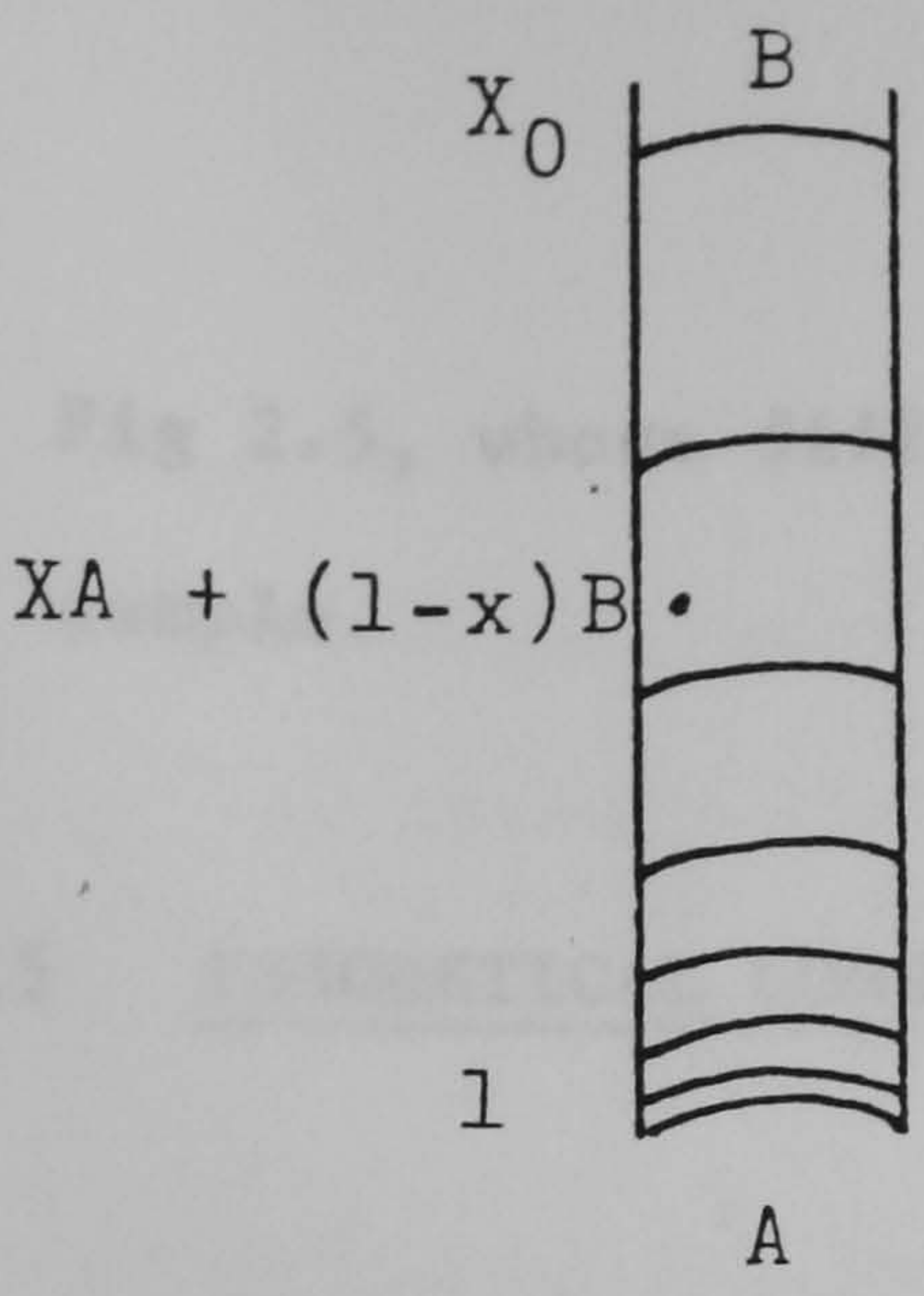
2.24 TYPES OF LIQUID JUNCTIONS

Guggenheim [78] classified junctions into five categories.

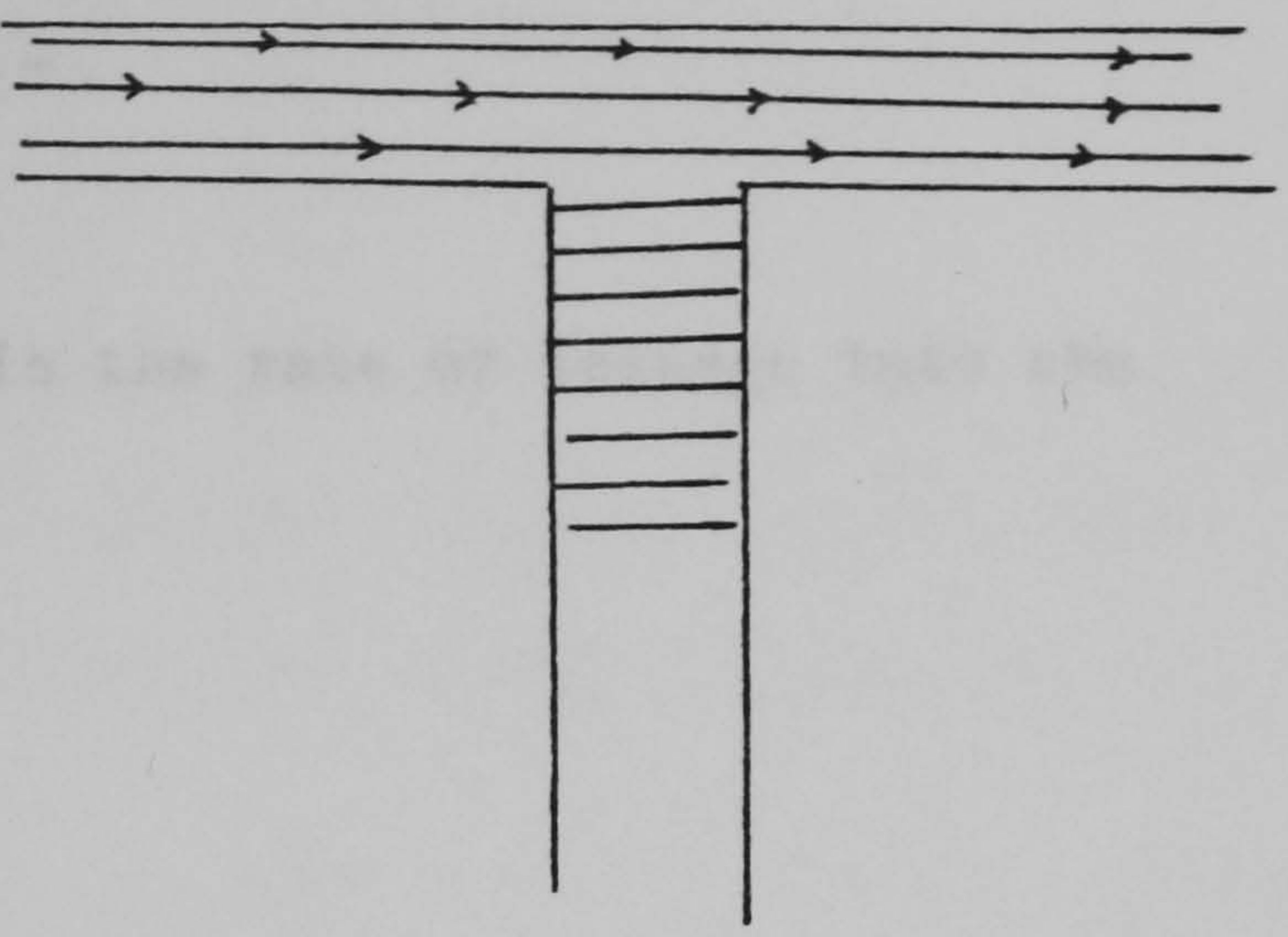
1. Continuous mixture junction,
2. Free diffusion junction,
3. Constrained diffusion junction,
4. Flowing junction,
5. Sharp or indefinite junction.

Some of these junctions are practically very difficult to obtain. Various types of junctions are shown in Fig 2.5 .

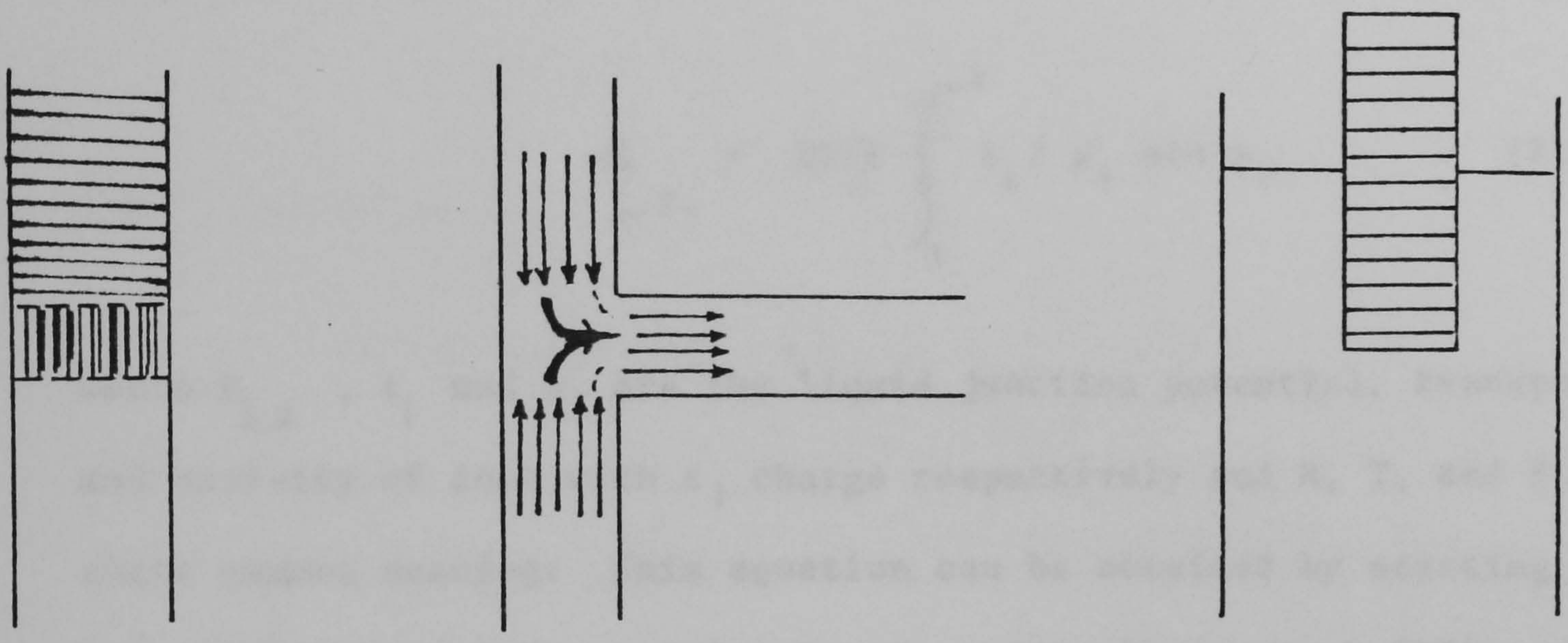
For the most precise measurements, a free diffusion junction with cylindrical symmetry has been shown to give high stability and reproducibility [79,80,81]. This type of junction, in various forms, has been used in a number of important investigations [82]. In this work a free diffusion junction in a ´T´ form was designed for the investigation of the potential of the Corning 902 analyser. However, junctions, of this type and some of other types, such as the flowing ones, are not convenient for use in routine work. The most commonly used junctions are the porous ceramic and sleeve types. Some types of restrained junctions are given in



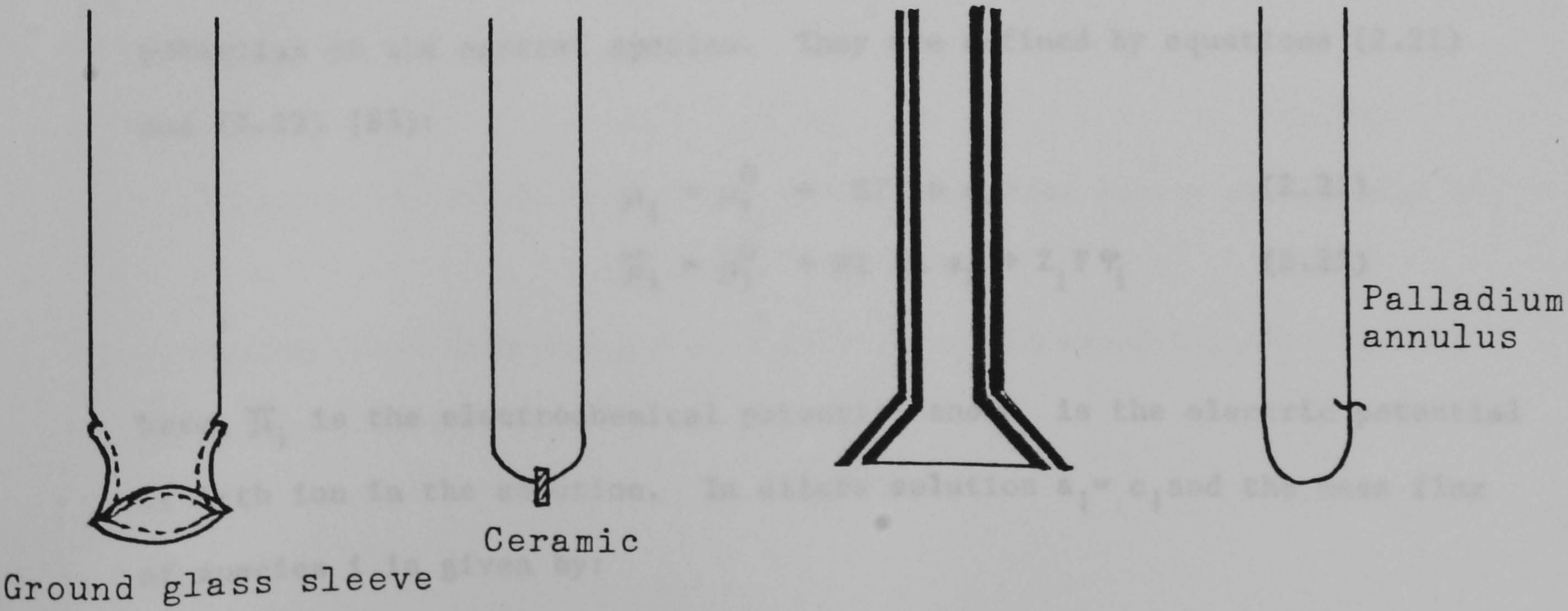
1) Continuous Mixture



2) Free diffusion



3) Constrained diffusion 4) Flowing junction 5) Sharp Junction



Various form of restrained diffusion liquid junction

Fig 2.5

Fig 2.5, whose difference lies only in the rate of leakage into the sample.

2.25 THEORETICAL CONSIDERATION

The value of liquid junction potential is given by the following equation:

$$-E_{L.J.} = RT/F \int_1^2 t_i / z_i \, d\ln a_i \qquad (2.20)$$

where $E_{L.J.}$, t_i and a_i are the liquid junction potential, transport number and activity of ions with z_i charge respectively and R, T, and F having their common meaning. This equation can be obtained by starting from the Nernst-Planck equation or via the thermodynamic approach [85].

It is clear that the driving force in the transport process is a result of the electrochemical potential of the charged species and the chemical potential of the neutral species. They are defined by equations (2.21) and (2.22) [83]:

$$\mu_i = \mu_i^0 + RT \ln a_i \qquad (2.21)$$

$$\tilde{\mu}_i = \mu_i^0 + RT \ln a_i + Z_i F \varphi_i \qquad (2.22)$$

here, $\tilde{\mu}_i$ is the electrochemical potential and φ_i is the electric potential of i-th ion in the solution. In dilute solution $a_i = c_i$ and the mass flux of species i is given by:

$$J_i = -U_i c_i \partial \bar{\mu}_i / \partial x \qquad (2.23)$$

where J_i and U_i are the mass flux and particle mobility respectively.

If no current flows across the interface the current density (I) will be zero: i.e.,

$$I = F \sum_i^n Z_i \cdot J_i = 0 \qquad (2.24)$$

Introducing the expression for the electrochemical potential into eqn.2.23 and considering eqn.2.24, eqn.2.25 will result in :

$$d\varphi / dx = -RT/F \frac{\sum_i Z_i U_i dc_i / dx}{\sum_i Z_i^2 U_i c_i} \qquad (2.25)$$

Also considering that

$$d\ln c_i = dc_i / c_i \qquad \text{and} \qquad t_i = \frac{Z_i^2 c_i U_i}{\sum_i Z_i^2 U_i c_i}$$

eqn.2.25 becomes eqn.2.20.

In the thermodynamic approach, the junction phase is assumed to consist of a continuous series of mixtures of two solutions 1 and 2, in other words, the liquid junction phase contains many transitional layers where the composition of each differs infinitesimally from the next one. The change in free energy due to the transfer of the i-th ion from $(c_i + dc_i)$ to (c_i), is given by,

$$dG = t_i / Z_i d\mu_i \qquad (2.26)$$

Considering the transfer of n ions, the total free energy change will be,

$$\Delta G = \sum_i^n t_i / Z_i d\mu_i \qquad (2.27)$$

replacing $dG = -FdE$ and $\mu_i = \mu_i^0 + RT/F \ln a_i$ in eqn.2.27, the eqn.2.20 will result again.

In order to integrate eqn.2.20, assumptions must be made about the activity of a single ion, the dependance of t on concentration and the structure of the liquid junction phase. In the Henderson approach to the integration of eqn.2.20, the following assumptions are made:

1. A continuous boundary mixture, which means, at any particular point in the liquid junction phase, the concentration c_i of the species is given by:

$$c_i = xc_i(1) + (1-x)c_i(2) \qquad 0<x<1$$

2. The activity is equal to the concentration $a_i = c_i$

3. The mobility is constant in the range c_1 to c_2 (contacting solutions).

The integration is given by eqn.2.28

$$E_{L.J.} = RT/F \frac{(U_1 - V_1) - (U_2 - V_2)}{(U_1' + V_1') - (U_2' + V_2')} \ln \frac{(U_1' + V_1')}{(U_2' + V_2')} \qquad (2.28)$$

where U_1 , U_1' and V_1 , V_1' are defined

$$U_1 = \sum_i^n (c_+u_+) \qquad V_1 = \sum_i^n (c_-u_-)$$

$$U_1' = \sum_i (c_+u_+z_+) \qquad V_1' = \sum_i (c_-u_-z_-)$$

where c_+ and c_- refer to the concentration of cations and anions, u_+ and u_- their mobilities, and z_+, z_- are the charge values; the subscript 1 refers to ions in solution 1. A similar relation hold for ions in solution 2 .

Another general solution for E has been carried out by Planck. In his approach the following assumptions were made:

1. Constrained diffusion boundary, e.g. a porous membrane

2. Ions are ideal solutes ($c_i = a_i$)

3. Mobilities are constant

Planck's integration leads to equation 2.29

$$\frac{\xi U_2 - U_1}{V_2 - \xi U_1} = \frac{\ln (c_2/c_1) - \ln \xi}{\ln (c_2/c_1) + \ln \xi} \cdot \frac{\xi c_2 - c_1}{c_2 - \xi c_1} \qquad (2.29)$$

Where U_1, U_2, V_1 and V_2 are defined as for equation 2.28, and

$$\xi = \exp \left(\frac{E_{L.J.}}{RT} \right)$$

Application of the Henderson and Planck equations to the following cases gave the same result.

a)

$$\begin{array}{c|c} \text{KCl} & \text{KCl} \\ c_1 & c_2 \end{array}$$

$$E_{L.J.} = RT/F \left(\frac{u_+ - u_-}{u_+ + u_-} \right) \ln c_2/c_1$$

b) [84]

$$\begin{array}{c|c} \text{HCl} & \text{KCl} \\ c & c \end{array}$$

$$E_{L.J.} = RT/F \ln \left(\frac{u_{H^+} + u_{Cl^-}}{u_{K^+} + u_{Cl^-}} \right)$$

This can be re-written as:

$$E_{L.J.} = RT/F \ln \frac{\Lambda_{HCl}}{\Lambda_{KCl}}$$

where Λ is the equivalent conductance of the solutions (for details see MacInnes [85] and Covington [86]). The Henderson equation is widely used for the approximate determination of the liquid junction potential and the Planck equation is frequently used in ion-selective membrane studies. A review of this equation has been given by Morf [77]. However, conditions in practice do not allow the accurate determination of the value of the liquid junction potential; thus, it is necessary to minimise or keep constant its value during the measurements.

2.26 MINIMISING LIQUID JUNCTION POTENTIALS AND THE CHOICE OF SALT BRIDGE

The liquid junction potential cannot be eliminated, but may be minimised. The most usual and effective method for minimising the liquid junction potential has been achieved by introducing a strong solution of some electrolyte between the sample solution and the reference electrode. This solution is known as the salt bridge solution.

$$\begin{array}{c} \text{Sample} \\ \text{Solution} \end{array} \underset{L.J.}{\Big|} \begin{array}{c} \text{KCl} \\ x\ \text{mol/dm}^3 \end{array} \Big| \; Hg_2Cl_2|Hg$$

Strong potassium chloride solutions are the most widely used as bridge solutions and it has been shown that as the concentration of the potassium chloride increases the liquid junction potential decreases [49]. For bridge solutions generally, salts containing cations and anions of similar mobilities are recommended [87]; e.g. KCl, KNO_3, $(KCl+KNO_3)$, NH_4NO_3. Nevertheless, the leakage of the salt bridge into the sample must be considered which will change the concentration of either primary ions or interfering ions. The use of the saturated calomel electrode will thus cause significant error in low concentrations of potassium or chloride solutions. In such cases, the best method is the use of a double junction reference electrode with a suitable solution in a second bridge. Schematically, this arrangment has the form:

$$\begin{array}{ccccccl}
\text{KCl} & | & \text{T.M.A.Cl.} & | & \text{KCl} & | & \text{Hg}_2\text{Cl}_2|\text{Hg} \\
\text{Solution} & | & 3.5\ \text{mol/dm}^3 & | & \text{sat.} & | & \\
 & \text{L.J.} & & \text{L.J.} & & & \\
 & 1 & & 2 & & &
\end{array}$$

In addition to causing a change in the constituents of the sample solution, as mentioned, the composition of the salt bridge is critical. This is due to clogging of the liquid junction with the saturated KCl salt bridge, as temperature variations can result in crystallization of KCl in the electrode tip which will lead to noisy and unstable results. Various salts were examined for salt bridges, and noticeable differences were not observed. T.M.A.Cl. was chosen as the salt bridge solution.

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CHAPTER THREE

INVESTIGATION OF THE COMPOSITION OF ELECTRODES BASED ON VALINOMYCIN AND EVALUATION OF ELECTRODES BASED ON NEW BIS-CROWN COMPOUNDS

3.1 INTRODUCTION (VALINOMYCIN) PART (I)

It is well known that liquid-membrane ion-selective electrodes suffer from some disadvantages compared to solid-state membranes. To obtain reliable results with liquid-membrane electrodes, greater skill and care are required. Those obstacles have been overcome by their counterparts, i.e. ion-selective electrodes based on a homogeneous matrix with highly improved performance, and universally accepted as good alternatives to liquid-membrane electrodes. Nowadays, all commercially available potassium and other ion-selective electrodes are manufactured in the form of a PVC matrix. Research on the finding of new ion-exchangers and neutral sequestering agents for a variety of ions has been carried out extensively. As far as matrix materials are concerned, no comprehensive study is available. Although some work on the role of various plasticizers with polyvinyl chloride and other polymers in the performance of the potassium selective electrode has been conducted [1], there has been no study on the effect of PVC with different physical properties (molecular weight, particle size, method of preparation, etc.) and different plasticizers, on the behaviour of potassium I.S.Es based on valinomycin. The purpose of this chapter is to describe the influence of the various types of PVC with three commonly used plasticizers (see

Chapter Two). Twenty-four PVC membranes were prepared and their calibration and selectivity patterns constructed. In Part Two of this chapter, the effect of newly synthesised crown compounds as active materials is explained. Three groups of bis-crown compounds have been incorporated into PVC in order to study their electrochemical characteristics. This chapter thus consists of two parts:

Part One: K^+ /PVC membranes based on valinomycin
Part Two: K^+ /PVC membranes based on bis-crowns

3.2 VARIATION OF THE TYPE OF PVC AND PLASTICIZER

Twenty-four membranes were cast using eight samples of PVC from BP and BDH, incorporating three commonly used plasticizers, according to the formulation explained in Chapter Two. The method of membrane preparation and electrode construction was outlined in Sections 2.7 and 2.11. The composition of each membrane is given in Table 3.1. For example, electrode No.20 contains: PVC S110/10, di-n-butyl phthalate, valinomycin and potassium tetrakis (p-chlorophenyl) borate. The last two compounds are common to all membranes. Electrodes were tested in the region of 10^{-1} to 10^{-5} mol/dm^3 KCl solution using a calomel electrode with an intermediate bridge solution of 3.5 mol/dm^3 tetramethylammonium chloride (T.M.A.Cl.). The sodium ion interference was evaluated in 0.1 or 0.5 mol/dm^3 NaCl solution containing 10^{-1} to 10^{-5} mol/dm^3 KCl. The electrochemical cell used is shown below (see next page).

Detailed results of the studies of the slopes of the various electrodes are shown in Tables 3.2, 3.3 and 3.4. The slopes of the calibration and

Table 3.1

Composition of The PVC Membranes

PVC samples	Plasticizers		
	Bis-(2-ethylhexyl) sebacate (Fluka)	Di-n-butyl phthalate (BDH)	Di-iso-octyl phthalate (BDH)
BDH M.W. 100,000	1	2	3
BDH M.W. 200,000	4	5	6
BP Breon S 110/10 M.W. 57000	7	8	9
BP Breon S 125/12	10	11	12
BP Breon AS 70/42	13	Membrane not usable	Membrane not usable
BP Breon S 125/14	16	17	18
BP Breon S 110/10	19	20	21
BP Breon S 110/11	22	23	24

The PB Breon AS 70/42 is a copolymer (PVC-PVA moxture). The membrane with usual percentage of plasticizer content was found too flexible but by reducing the plasticizer content to 40% a proper membrane was obtained.

Table 3.2

Response of PVC K^+ - Valinomycin Electrodes

KCl (10^{-1} to 10^{-5} mol/dm^3)

PVC Sample	Bis-(2-ethylhexyl) sebacate	Di-n-butyl phthalate	Di-iso-Octyl phthalate
BDH M.W. 100,000	53.6, 68.9, 70.3, 65.9	53.4, 68.3, 70.7, 56.8	69.0, 74.0, 61.0, 60.7
BDH M.W. 200,000	53.9, 67.4, 68.3, 64.7	60.8, 61.1, 70.3, 65.8	59.0, 64.0, 60.7, 61.8
BP Breon S 110/10 M.W. 57000	56.0, 67.5, 66.5, 62.2	37.0, 67.0, 63.9, 63.6	58.0, 74.0, 61.0, 60.5
BP Breon S 125/12	66.0, 67.0, 66.8, 62.5	37.0, 67.0, 64.0, 63.6	66.0, 57.0, 63.0, 57.4
BP Breon AS 70/42	63.0, 68.0, 66.0, 62.5	Membrane not usable	Membrane not usable
BP Breon S 125/14	61.8, 68.2, 67.5, 64.6	36.0, 67.0, 63.3, 63.7	67.0, 62.0, 62.0, 63.3
BP Breon S 110/10	60.5, 68.1, 67.4, 64.9	37.0, 66.0, 66.2, 63.3	67.0, 60.0, 63.0, 62.2
BP Breon S 110/11	61.5, 67.4, 68.4, 64.9	39.2, 56.3, 58.2, 59.3	67.0, 60.0, 63.0, 62.4

The Figures given are slopes in mixed solution in mV/dec for pK ranges 4-5, 4-3, 3-2, 2-1 respectively.

Table (3.3)

Selectivity Response of PVC K^+ - Valinomycin Electrodes

KCl (10^{-1} to 10^{-5})+0.5 mol/dm^3 NaCl

PVC Sample	Bis-(2-Ethylhexyl) Sebacate	Di-n-Butyl phthalate	Di-iso-Octyl phthalate
BDH M.W. 100,000	57.3, 56.0, 59.4, 58.3	35.5, 55.3, 58.6, 58.5	39.8, 56.1, 58.3, 58.3
BDH M.W. 200,000	39.6, 55.3, 57.1, 59.0	36.9, 55.5, 58.4, 57.7	39.8, 56.0, 58.5, 58.5
BP Breon S 110/10 M.W. 57000	38.6, 5605, 58.8, 59.6	39.0, 55.6, 58.3, 58.4	38.89 55.7, 57.9, 58.6
BP Breon S 125/12	38.5, 55.8, 58.5, 59.6	39.3, 56.0, 58.3, 58.4	28.3, 51.1, 56.5, 53.8
BP Breon AS 70/42	31.9, 55.3, 58.5, 58.5	Membrane not usable	Membrane not usable
BP Breon S 125/14	37.2, 55.3, 58.6, 59.0	39.3, 55.7, 58.4, 58.2	39.1, 55.1, 57.9, 57.8
BP Breon S 110/10	37.4, 55.7, 59.5, 58.5	38.6, 55.3, 58.0, 58.2	37.5, 54.2, 57.1, 56.8
BP Breon S 110/11	40.3, 56.0, 58.0, 58.8	57.3, 55.7, 58.5, 58.3	39.2, 55.1, 58.1, 57.8

The Figures given are slopes in mixed solution in mV/dec for pK ranges 4-5, 4-3, 3-2, 2-1 respectively.

Table 3.4

Selectivity Response of PVC K^+ - Valinomycin Electrodes

KCl (10^{-1} to 10^{-5})+0.1 mol/dm^3 NaCl

PVC Sample	Bis-(2-ethylhexyl) sebacate	Di-n-butyl phthalate	Di-iso-octyl phthalate
BDH M.W. 100,000	42.8, 56.6, 57.5, 57.7	41.6, 56.5, 57.7, 57.8	39.8, 56.3, 58.3, 59.3
BDH M.W. 200,000	40.6, 55.7, 57.7, 59.4	41.3, 56.3, 57.0, 57.3	39.9, 56.4, 58.4, 58.1
BP Breon S 110/10 M.W. 57000	39.5, 56.5, 58.8, 59.6	40.2, 56.3, 57.7, 58.3	38.9, 55.7, 57.9, 58.6
BP Breon S 125/12	39.5, 36.5, 58.5, 59.8	40.8, 56.0, 57.7, 58.3	30.2, 51.6, 55.7, 55.2
BP Breon AS 70/42	37.1, 56.6, 58.4, 59.8	Membrane not usable	Membrane not usable
BP Breon S 125/14	41.0, 56.5, 57.9, 59.2	41.0, 56.0, 57.8, 58.4	39.1, 55.1, 57.9, 57.8
BP Breon S 110/10	41.7, 56.6, 57.7, 57.7	40.9, 55.7, 57.5, 58.2	37.7, 55.2, 57.2, 58.4
BP Breon S 110/11	42.3, 56.1, 58.0, 59.4	39.2, 56.3, 58.2, 59.3	39.1, 56.2, 57.9, 59.0

The Figures given are slopes in mixed solution in mV/decade for pK ranges 4-5, 3-4, 2-3 and 2-1 respectively.

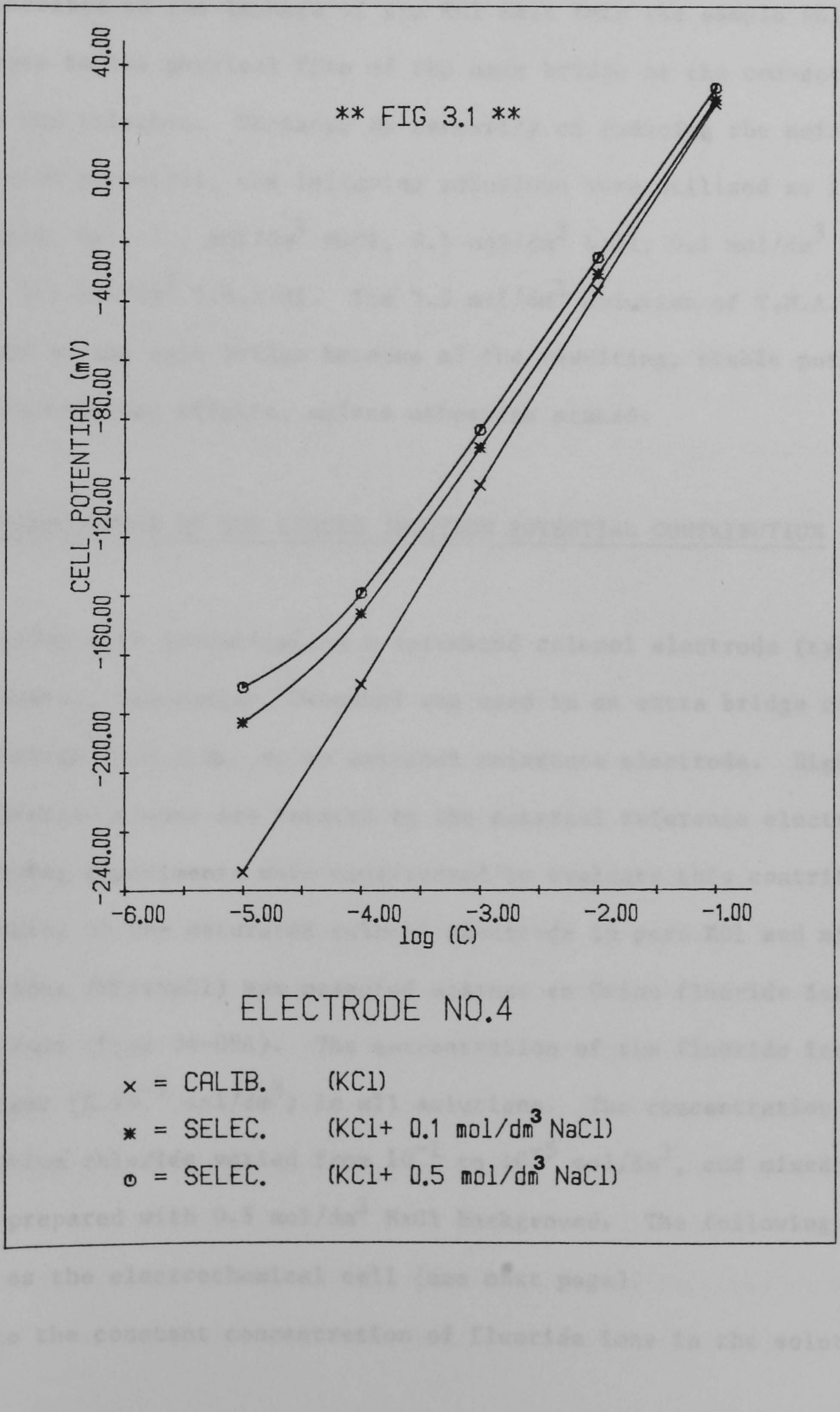
$$\mathrm{Ag|AgCl}\ \Bigg|\ \begin{matrix}\mathrm{KCl}\\ 0.1\ \mathrm{mol/dm^3}\end{matrix}\ \overset{\text{membrane}}{\blacksquare}\ \begin{matrix}\mathrm{KCl}\\ \text{or}\\ \mathrm{KCl+NaCl}\end{matrix}\ \Bigg|\ \begin{matrix}3.5\ \mathrm{mol/dm^3}\\ \mathrm{T.M.A.Cl.}\end{matrix}\ \Bigg|\ \begin{matrix}\mathrm{KCl}\\ \mathrm{(sat.)}\end{matrix}\ \Bigg|\ \mathrm{Hg_2Cl_2|Hg}$$

selectivity curves were found to be $\simeq$ 68 mV/decade and $\simeq$ 58 mV/decade respectively. The linear range was pK:1-5 for calibration and pK:1-4 for 0.5 mol/dm^3 interference curve. Comparing the calibration and selectivity results, one can infer that the electrodes based on six BP polymers with BEHS plasticizer show slightly better performance than the others. Apparently, the high slope for the calibration plots is due to the additional liquid junction potential contribution arising from the use of tetramethylammonium chloride. The determination and elimination of this potential are discussed in the following sections.

Typical calibration and selectivity curves for electrode No.4 are given in Fig 3.1.

3.3 EFFECT OF SALT BRIDGE SOLUTION ON THE SLOPES

Owing to the necessity of using a saturated calomel electrode directly in potassium ion measurements, a double junction reference electrode is required. As far as the generation of the potential and its contribution are concerned, the selection of the solution for the second junction becomes important. In an attempt to find the best solution, various concentrations of KCl were dissolved in agar and introduced into a number of tubes with different diameters. Experimentation with the use of these tubes as bridges between solution and external electrode indicated that

** FIG 3.1 **
CELL POTENTIAL (mV)
40.00
0.00
-40.00
-80.00
-120.00
-160.00
-200.00
-240.00
-6.00
-5.00
-4.00
-3.00
-2.00
-1.00
log (C)
ELECTRODE NO.4
× = CALIB. (KCl)
✱ = SELEC. (KCl+ 0.1 mol/dm3 NaCl)
⊙ = SELEC. (KCl+ 0.5 mol/dm3 NaCl)

even though it was possible to reduce the noise level at low sample concentration, the slope and selectivity were not reproducible. This can be ascribed to the leakage of the KCl salt into the sample solution and changes in the physical form of the agar bridge at the connecting point with the solution. Dictated by necessity of reducing the noise and liquid junction potential, the following solutions were utilized as intermediate bridges: 0.1, 1 , mol/dm^3 NaCl, 0.1 mol/dm^3 LiCl, 0.1 mol/dm^3 $NH_4NO_3$and 0.1, 3.5 mol/dm^3 T.M.A.Cl. The 3.5 mol/dm^3 solution of T.M.A.Cl. was chosen as the salt bridge because of the resulting, stable potential and non-interfering effects, unless otherwise stated.

3.4 DETERMINATION OF THE LIQUID JUNCTION POTENTIAL CONTRIBUTION

During this investigation a saturated calomel electrode (type-K401, Radiometer, Copenhagen, Denmark) was used in an extra bridge containing 3.5 mol/dm^3 T.M.A.Cl. as an external reference electrode. High calibration slopes are related to the external reference electrode. The following experiments were constructed to evaluate this contribution. The potential of the saturated calomel electrode in pure KCl and mixed solutions (KCl+NaCl) was measured against an Orion fluoride ion-selective electrode (type 94-09A). The concentration of the fluoride ion was kept constant (5.10^{-5} mol/dm^3) in all solutions. The concentration of potassium chloride varied from 10^{-1} to 10^{-5} mol/dm^3, and mixed solutions were prepared with 0.5 mol/dm^3 NaCl background. The following cell was used as the electrochemical cell (see next page).

Due to the constant concentration of fluoride ions in the solutions, the

$$\begin{array}{l|l|l|l}
 & & 5.10^{-5}\text{mol/dm}^3\ \text{NaF} + \text{KCl} & \text{F}^- \\
\text{S.C.E.} & (\text{Me})_4\text{NCl} & \text{"}\quad \text{"}\quad \text{"}\quad \text{"} + \text{KCl}\quad + & \text{I.S.E.} \\
 & 3.5\ \text{mol/dm}^3 & 0.5\ \text{mol/dm}^3\ \text{NaCl} & \\
 & \text{L.J.} & &
\end{array}$$

potential of the fluoride ion-selective electrode remained almost constant. As a result any change in the potential of the cell is originating at the interface between reference assembly and solutions. Six sets of experiments were carried out.

a) S.C.E. without extra bridge vs. F$^-$ /I.S.E. in pure KCl solution

b) S.C.E. without extra bridge vs. F$^-$ /I.S.E. in mixed solution (KCl + NaCl)

c) S.C.E. with extra bridge (3.5 mol/dm^3 T.M.A.Cl.) vs. F$^-$ /I.S.E. in pure KCl solution

d) S.C.E. with extra bridge (3.5 mol/dm^3 T.M.A.Cl.) vs. F$^-$ /I.S.E. in mixed solution (KCl+NaCl)

e) S.C.E. without bridge vs. F$^-$/I.S.E. in NaF solution (10^{-1} - 10^{-5} mol/dm^3)

f) S.C.E. with extra bridge vs. F$^-$ /I.S.E. in NaF solution (10^{-1} - 10^{-5} mol/dm^3)

Detailed results are given in Tables 3.5 a, b and c. Comparison of Tables 3.5a and 3.5b confirms the contribution of the liquid junction potential and demonstrates that the liquid junction contribution is not linear with increasing sample concentration as it was assumed. However, in mixed solution, the liquid junction potential is constant within the range of 10^{-1} to 10^{-4} mol/dm^3 KCl concentration in background of 0.5 mol/dm^3 NaCl, and equal to 7.4 mV. From the results in Table 3.5, one can conclude that the liquid junction potential is the result of the change in the ionic strength of the solutions. In pure solutions this change is very pronounced, while in the mixed solutions, due to the presence of high levels of interferent ions, the ionic strength remains quite constant.

However, to obtain the Nernstian slope, the liquid junction potential contribution must be considered. The calibration slopes in this study include the liquid junction potential contribution. Fig 3.2 schematically explains the consistancy and the variation of the liquid junction potential in the appropriate media.

3.5 E.M.F. MEASUREMENTS AT CONSTANT IONIC STRENGTH

The objective of most ion-selective electrode measurements is the determination of concentration. To achieve this the variation of the activity coefficient must be avoided. This is feasible when both the unknown and calibration solutions contain the same so-called ´inert electrolyte´ at the same high concentration. The presence of the ´inert electrolyte´ will reduce the liquid junction potential and it will remain unchanged. The utilization of ´inert electrolyte´ as a background medium in calibration solutions was investigated. In an effort to find an ideal ´inert electrolyte´ the following salts were used at different concentrations, and calibration and selectivity patterns were obtained: a) 0.1 mol/dm^3 Tris buffer (50 ml 0.1 mol/dm^3 Tris-(hydroxymethyl) aminomethane + 42 ml 0.1 mol/dm^3 HCl, diluted to 100 ml), which is recommended for the calibration of the I.S.Es when they are used for body fluid measurements. b) 0.15 mol/dm^3 $BaCl_2$, c) 0.15 mol/dm^3 $CaCl_2$, d) 0.1 and 0.5 mol/dm^3 $MgCl_2$, e) 0.1 and 0.15 mol/dm^3 Mg_2SO_4(M&B) and 0.1 mol/dm^3 Mg_2SO_4(BDH).

E.M.F. measurements were made by using two PVC / valinomycin electrodes with different plasticizers. Electrode No.7 with DBP and electrode No.8

Table 3.5

a) Primary ions + 5.10^{-5} mol/dm^3 NaF (KCl)

pC	E/mV one bridge	E/mV two bridges	ΔE/mV
5.0	+13.0	+46.2	30.0
4.0	+18.0	+53.2	33.5
3.0	+28.1	+58.4	29.5
2.0	+40.4	+63.0	21.5
1.0	+57.6	+72.4	14.8

b) Mixed ions + 5.10^{-5} mol/dm^3 NaF (KCl+ 0.5 mol/dm^3 NaCl)

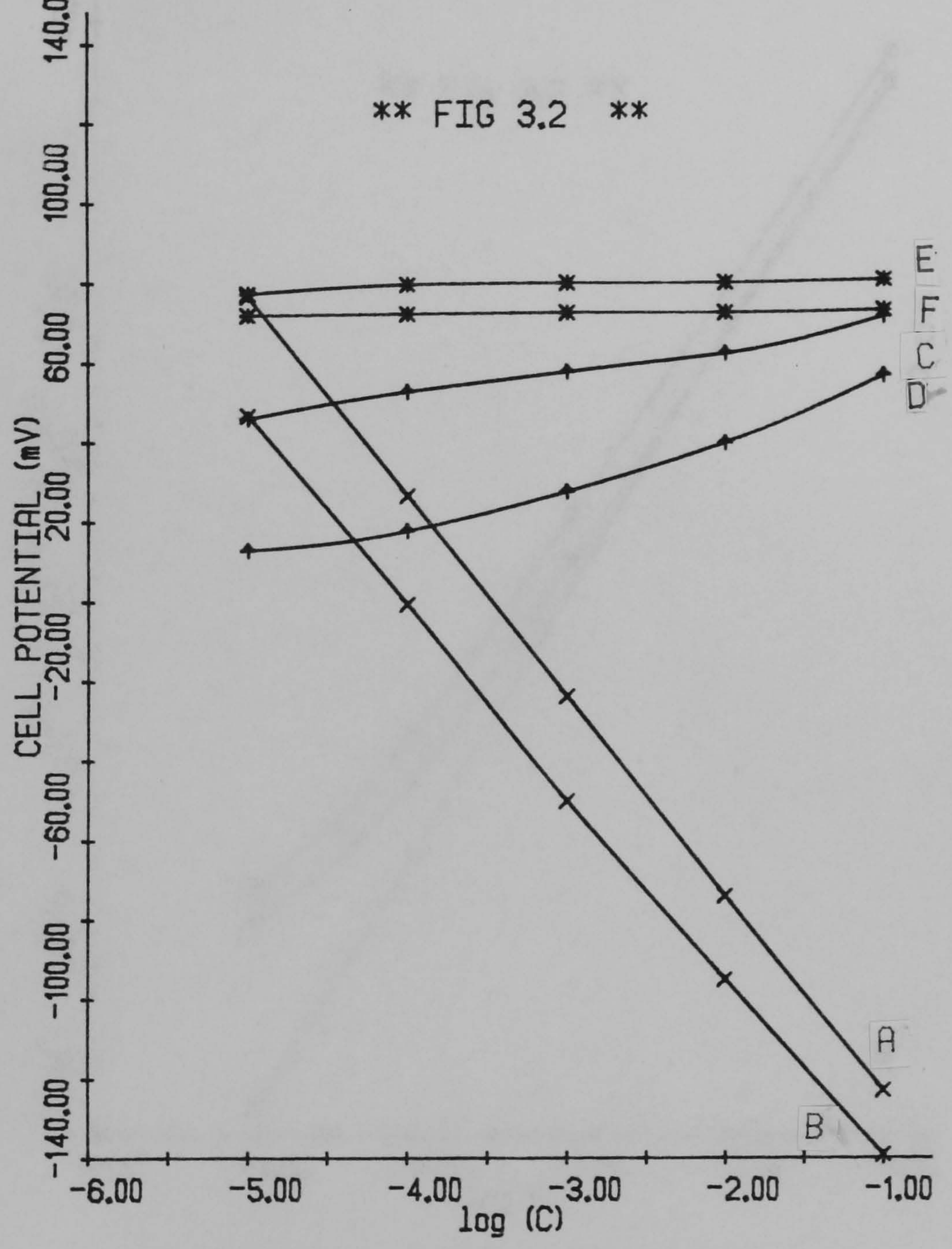
5.0	+72.7	+77.6	5.0
4.0	+72.8	+80.1	7.4
3.0	+73.3	+80.7	7.4
2.0	+73.3	+80.8	7.5
1.0	+74.0	+81.6	7.6

c) NaF Solutions

5.0	+47.0	+77.0	30.0
4.0	-00.5	+27.0	27.5
3.0	-50.0	-23.5	26.5
2.0	-95.1	-73.9	21.5
1.0	-139.2	-123.0	16.2

with BEHS. Fig 3.3 shows the calibration curve with electrode No.7 in Tris background with a slope of $\simeq$ 58 mV/decade (pK:1-4.5). A selectivity coefficient for the mixed solution of around = 15000 was obtained. The calibration curve with 0.15 mol/dm^3 $BaCl_2$ is given in Fig 3.4 with slope of $\simeq$ 58 mV/decade (pK:1-4.5). The selectivity coefficient was found to be $\simeq$ 22,500. A similar result was obtained when 0.15 mol/dm^3 $CaCl_2$ and 0.15 mol/dm^3 $MgCl_2$ were used as background solutions. The slope and response range of 58 mV/decade (pK:1-4.5) with selectivity coefficient $\simeq$ 22,500 is shown in Fig 3.5 and Fig 3.6. Comparing the three calibration curves,

** FIG 3.2 **



EFFECT OF ADDITIONAL LIQUID JUNCTION

× A = CALIB. OF F^- I.S.E. WITH ADDITIONAL L.J.

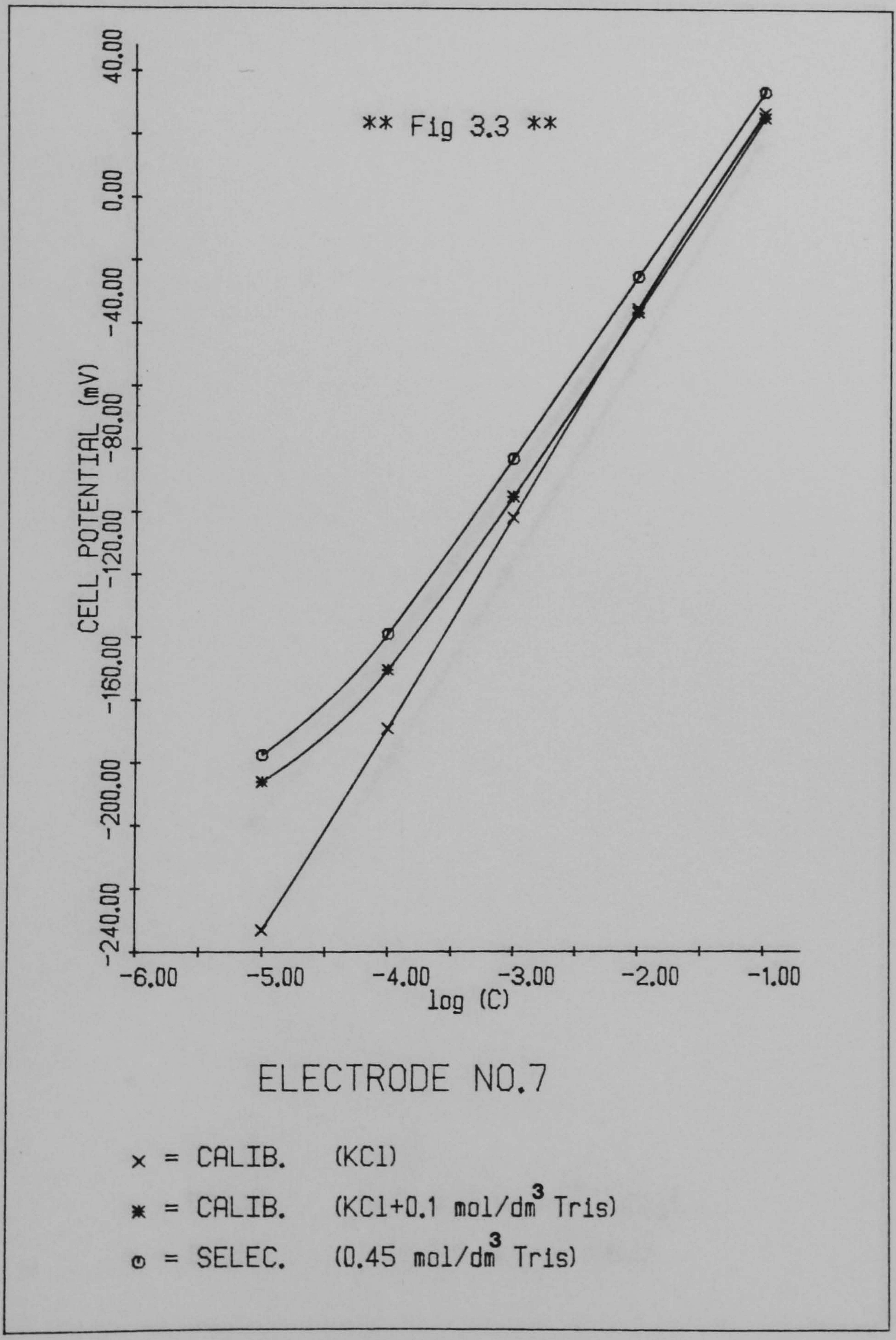
× B = CALIB. OF F^- I.S.E. WITHOUT ADDITIONAL L.J.

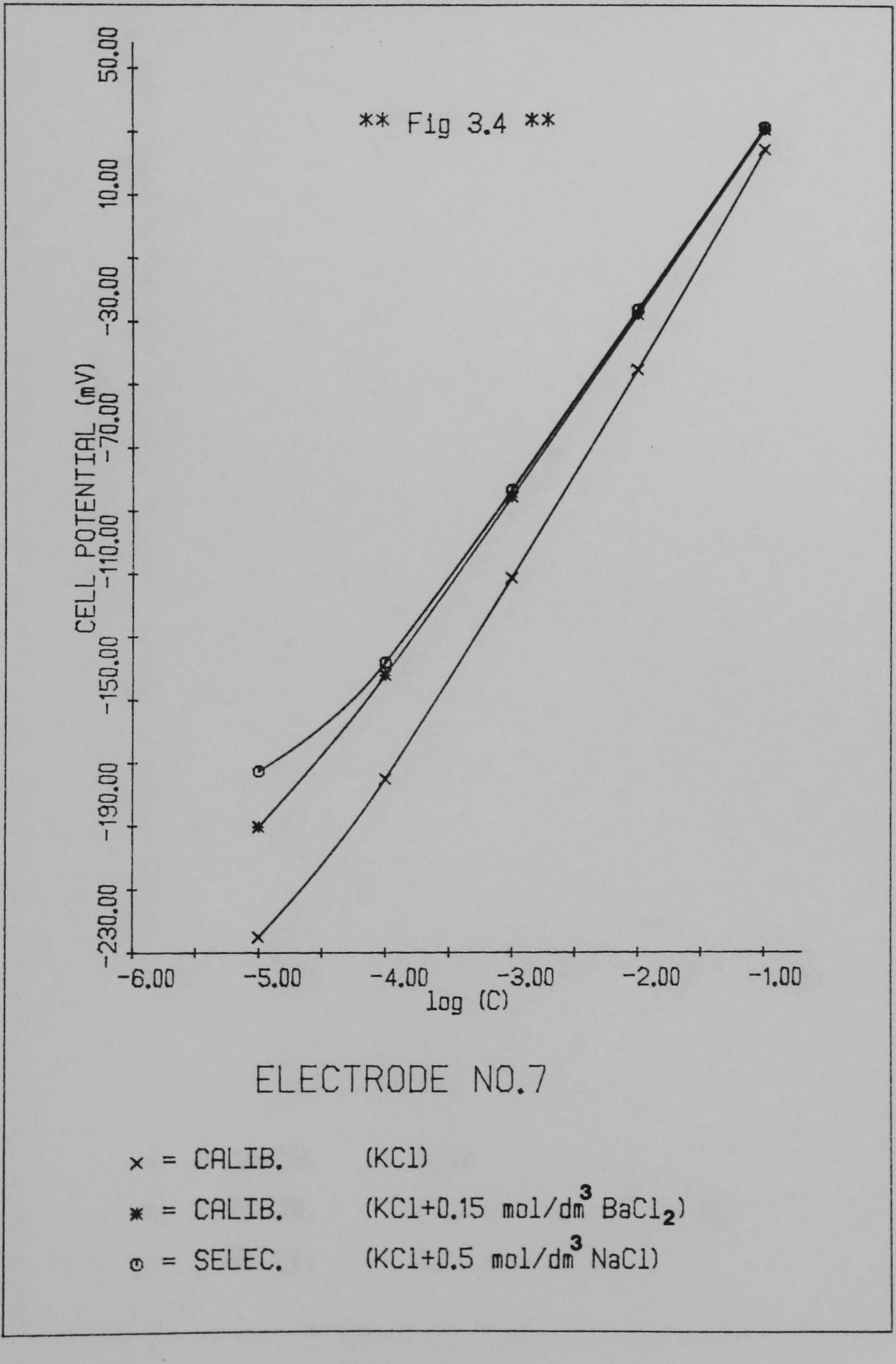
+ C = F^- I.S.E. vs. SCE WITH ADDITIONAL L.J. (KCl+F^-)

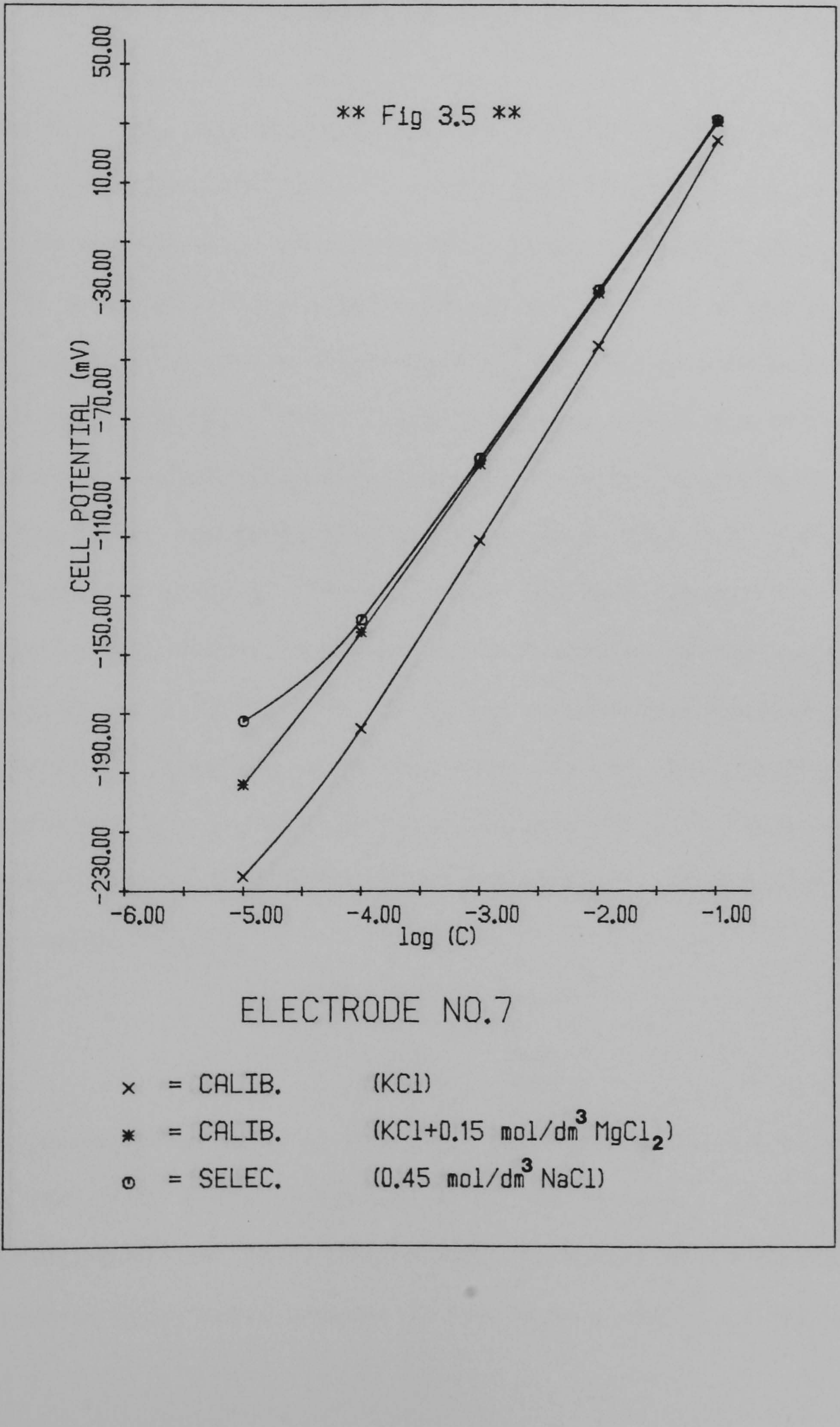
+ D = F^- I.S.E. vs. SCE WITHOUT ADDITIONAL L.J. (KCl+F^-)

✱ E = F^- I.S.E. vs. SCE WITH ADDITIONAL L.J. (KCl+F^-+NaCl)

✱ F = F^- I.S.E. vs. SCE WITHOUT ADDITIONAL L.J. (KCl+F^-+NaCl)

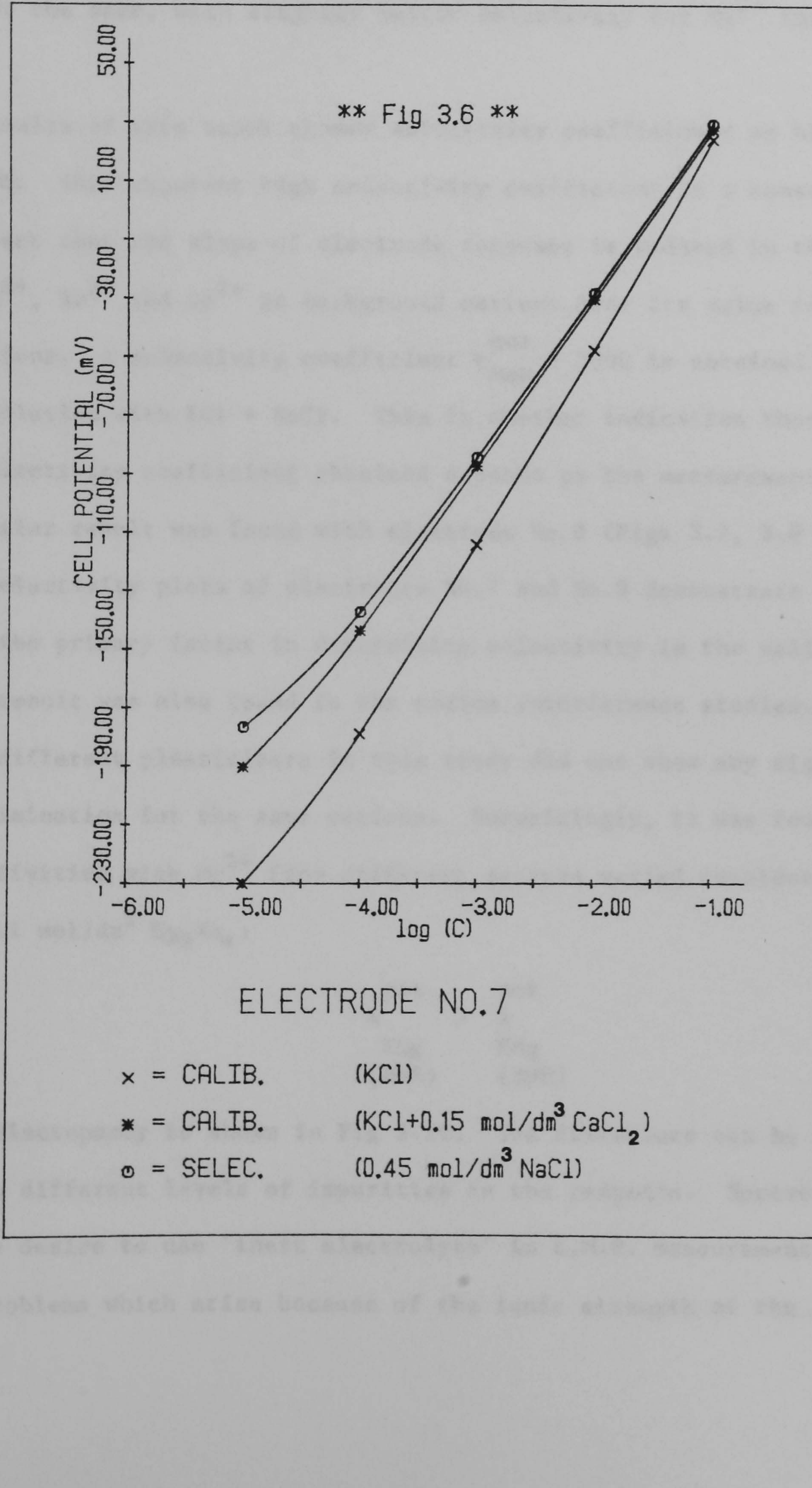

** Fig 3.3 **
CELL POTENTIAL (mV)
40.00
0.00
-40.00
-80.00
-120.00
-160.00
-200.00
-240.00
-6.00
-5.00
-4.00
-3.00
-2.00
-1.00
log (C)
ELECTRODE NO.7
× = CALIB. (KCl)
✱ = CALIB. (KCl+0.1 mol/dm^3 Tris)
⊙ = SELEC. (0.45 mol/dm^3 Tris)


** Fig 3.4 **
CELL POTENTIAL (mV)
50.00
10.00
-30.00
-70.00
-110.00
-150.00
-190.00
-230.00
-6.00
-5.00
-4.00
-3.00
-2.00
-1.00
log (C)
ELECTRODE NO.7
× = CALIB. (KCl)
✱ = CALIB. (KCl+0.15 mol/dm³ BaCl₂)
⊙ = SELEC. (KCl+0.5 mol/dm³ NaCl)



** Fig 3.5 **

ELECTRODE NO.7

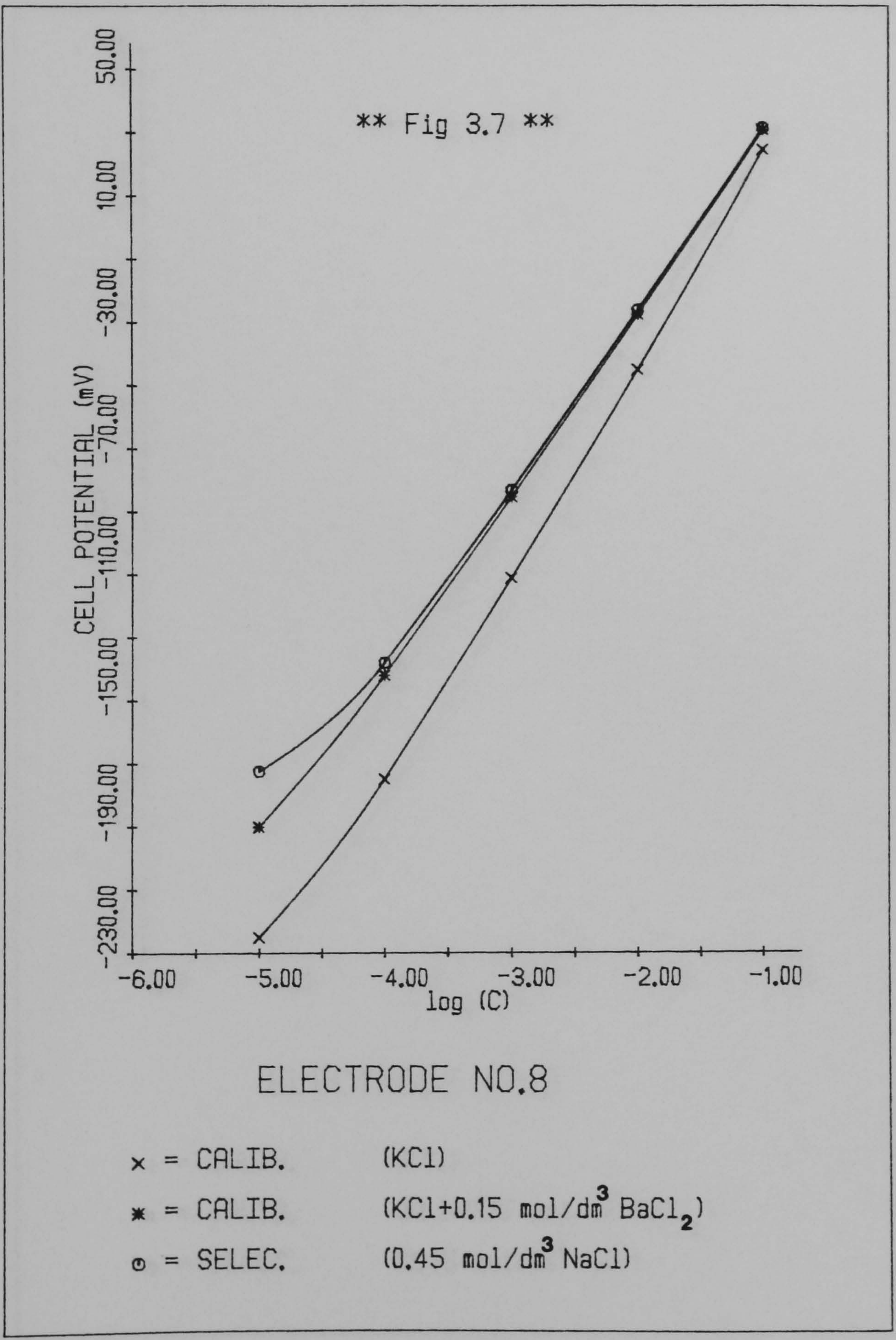

** Fig 3.6 **
CELL POTENTIAL (mV)
50.00
10.00
-30.00
-70.00
-110.00
-150.00
-190.00
-230.00
-6.00
-5.00
-4.00
-3.00
-2.00
-1.00
log (C)
ELECTRODE NO.7
× = CALIB. (KCl)
✱ = CALIB. (KCl+0.15 mol/dm³ CaCl₂)
ʘ = SELEC. (0.45 mol/dm³ NaCl)

Figs 3.4, 3.5 and 3.6, indicates that the selectivity coefficients of the potassium ion-selective electrode toward these alkaline earth metals are almost the same, with slightly better selectivity for Mg^{2+} ions.

Results of this study showed selectivity coefficients as high as k^{pot}_{NaK} = 25,000. This apparent high selectivity coefficient is a consequence of the fact that the slope of electrode response is reduced in the presence of Mg^{2+}, Ba^{2+} and Ca^{2+} as background cations over its value in pure KCl solutions. A selectivity coefficient k^{pot}_{NaK} = 5000 is obtained comparing KCl solution with KCl + NaCl. This is another indication that the value of selectivity coefficient obtained depends on the measurement conditions. A similar result was found with electrode No.8 (Figs 3.7, 3.8 and 3.9). The selectivity plots of electrodes No.7 and No.8 demonstrate the fact that the primary factor in determining selectivity is the valinomycin. This result was also found in the sodium interference studies. Electrodes with different plasticizers in this study did not show any significant discrimination for the same cations. Surprisingly, it was found that selectivities with Mg^{2+} from different sources varied considerably, e.g. for 0.1 mol/dm^3 Mg_2So_4:

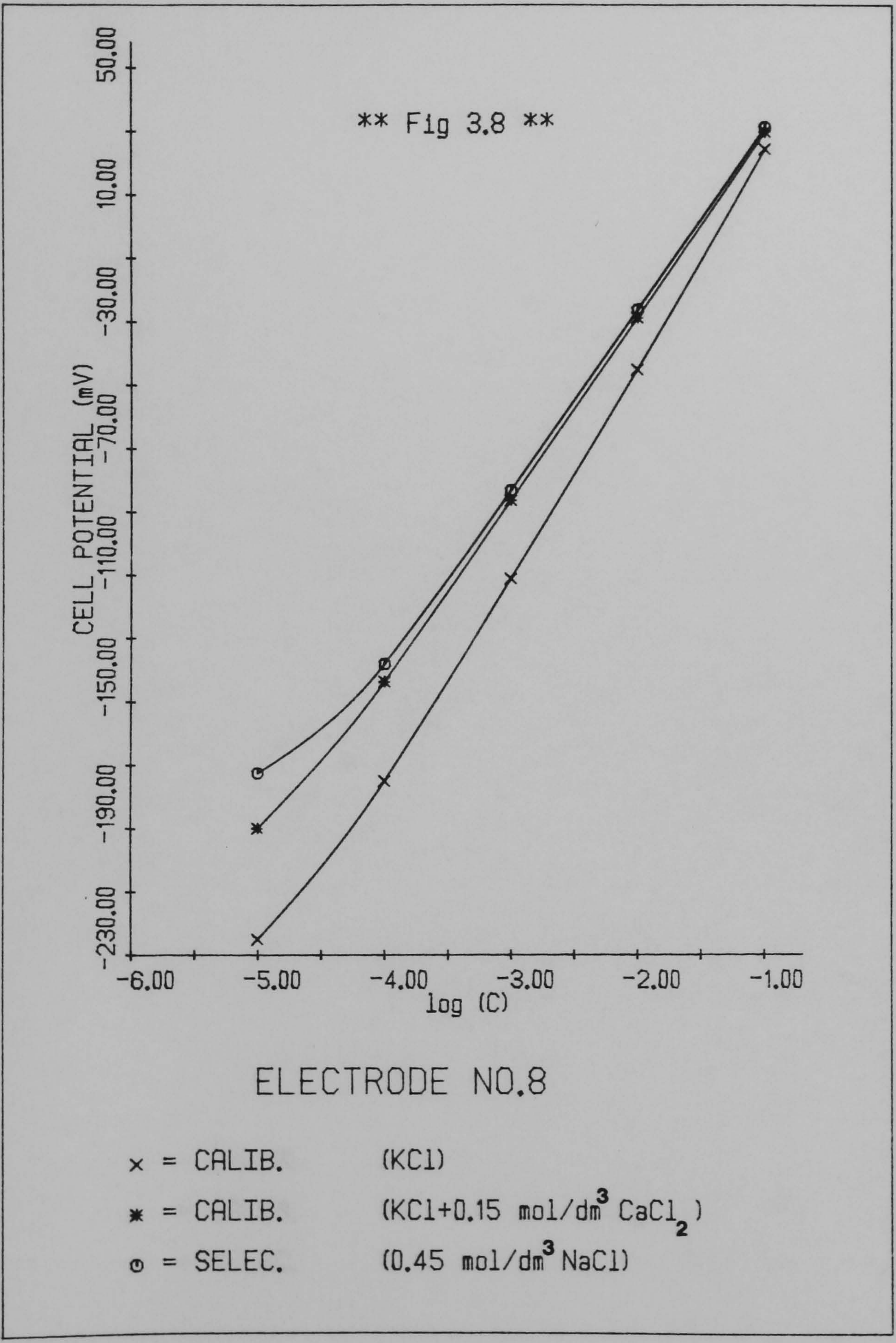
$$\underset{(M\&B)}{k^{pot}_{KMg}} > \underset{(BDH)}{k^{pot}_{KMg}}$$

This discrepancy is shown in Fig 3.10. The difference can be attributed to the different levels of impurities in the reagents. However, in spite of the desire to use ´inert electrolyte´ in E.M.F. measurements to resolve the problems which arise because of the ionic strength of the solutions,



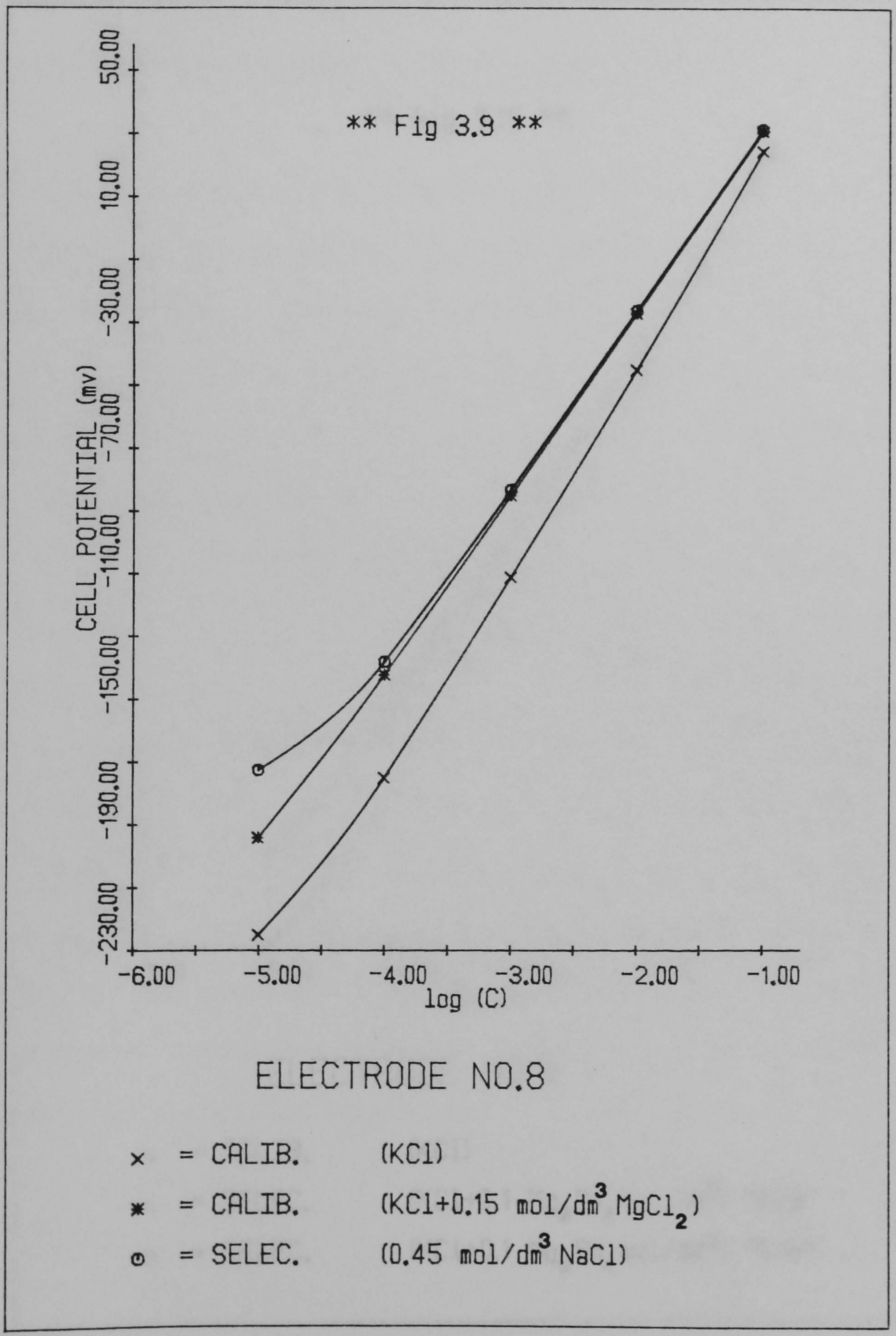
** Fig 3.7 **

ELECTRODE NO.8



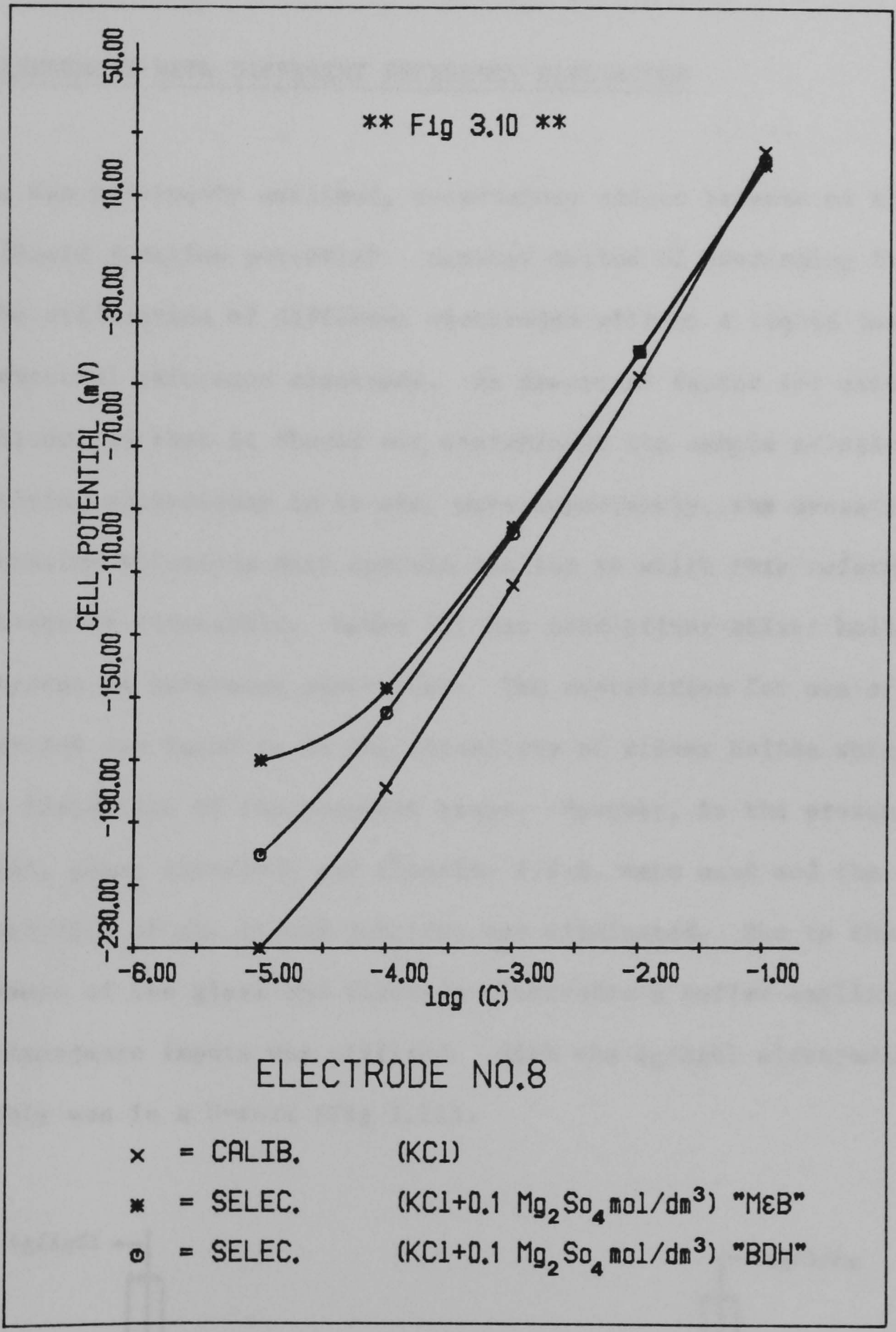
** Fig 3.8 **

ELECTRODE NO.8



** Fig 3.9 **

ELECTRODE NO.8


50.00
10.00
-30.00
-70.00
-110.00
-150.00
-190.00
-230.00
CELL POTENTIAL (mV)
-6.00
-5.00
-4.00
-3.00
-2.00
-1.00
log (C)
ELECTRODE NO.8
× = CALIB. (KCl)
✱ = SELEC. (KCl+0.1 Mg$_2$So$_4$mol/dm^3) "MεB"
⊙ = SELEC. (KCl+0.1 Mg$_2$So$_4$mol/dm^3) "BDH"

** Fig 3.10 **

it would appear that the ´inert electrolyte´ interferes practically with the potassium response of the electrodes.

3.6 MEASUREMENT WITH DIFFERENT REFERENCE ELECTRODES

As was previously outlined, uncertainty arises because of the change of the liquid junction potential. Another method of overcoming this problem is the utilization of different electrodes without a liquid junction as the external reference electrode. An important factor for using such an electrode, is that it should not contaminate the sample solution by dissolving appreciably in it and, more importantly, the measuring and the calibration solutions must contain the ion to which this reference electrode is reversible. Kumar [2] has used silver-silver halide electrodes as reference electrodes. The restriction for use of these electrodes was found to be the solubility of silver halide which will cause limitation of the response range. However, in the present work the Ag/AgCl, glass electrode and fluoride I.S.E. were used and the contribution of the liquid junction was eliminated. Due to the high impedance of the glass and fluoride electrodes a buffer amplifier with two high impedance inputs was utilized. With the Ag/AgCl electrodes the cell assembly was in a U-form (Fig 3.11).

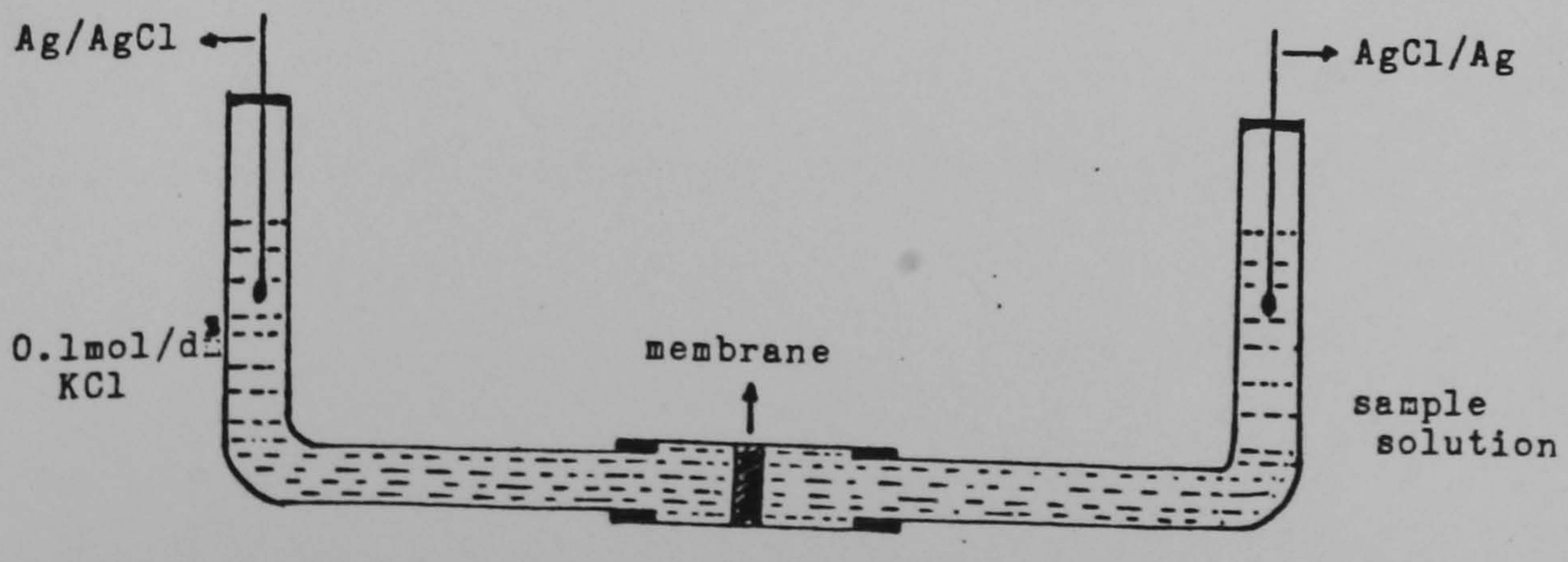
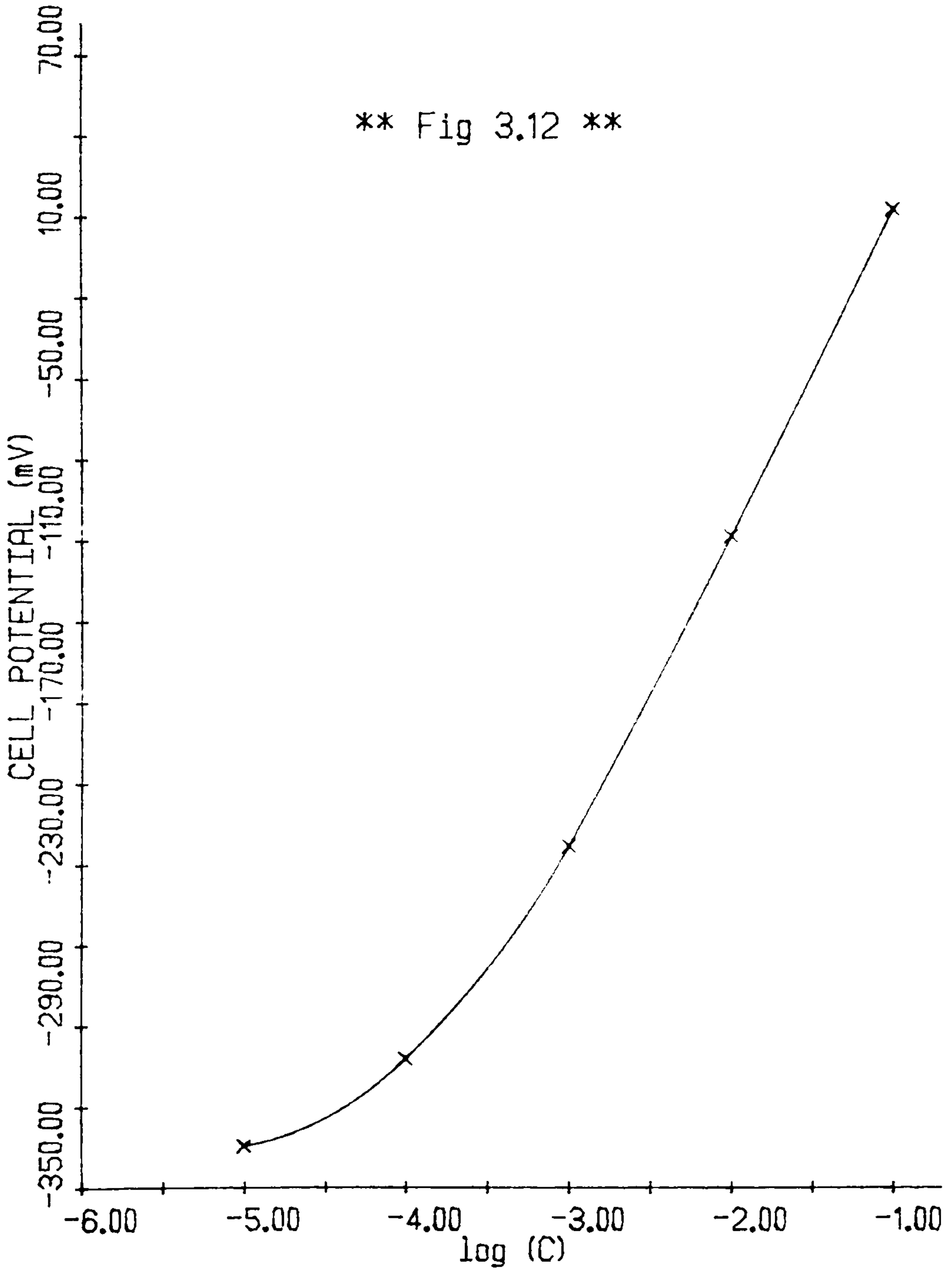


Fig 3.11

The PVC membrane was sealed cross-sectionally inside a PVC tube, the two ends of which being connected to an 'L' shaped tube. The concentration of the left hand side was kept constant (0.1 mol/dm^3 KCl), whilst on the right hand side, the concentration of the KCl electrolyte was changed after careful washing with dilute solutions. The calibration plot shown in Fig 3.12 has a slope of $\simeq$ 115 mV/decade with linear range of pK:1-3 . The response range is reduced due to the solubility of the AgCl salt. The H^+ glass electrode in solutions with background of 0.1 mol/dm^3 Tris pH:7.4, shown in Fig 3.13, gives a slope of $\simeq$ 57.8 mV/decade over pK:1-4 . Due to the absorption of CO_2 from the surrounding environment, the potential at lower concentrations was not stable. In order to utilize the F^- /I.S.E., the calibration solution was prepared in 5.10^{-5} mol/dm^3 NaF. The calibration slope after correction for the activity effect at 10^{-1} mol/dm^3 was $\simeq$ 56 mV/decade over pK:1-4 as shown in (Fig 3.14). The results of this Section clearly illustrate the liquid junction potential contribution. Due to the necessity of adding extra ions to the sample, however, deployment of these electrodes for routine determination of ion activity in solutions of unknown composition, is restricted and their utilization does not appear to offer any special advantage in the routine measurement of ion activity.

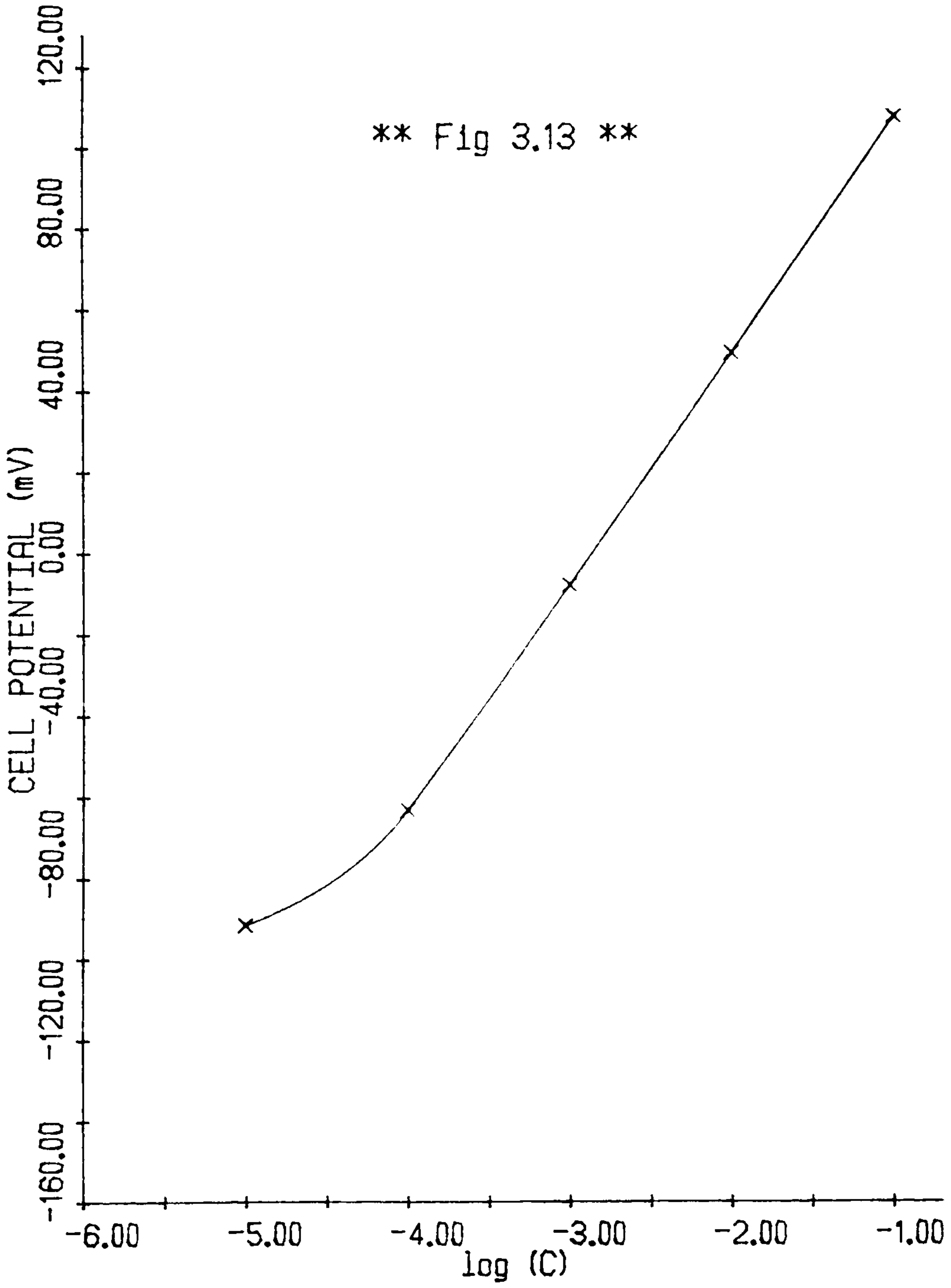


** Fig 3.12 **

ELECTRODE NO. 4

x = CALIBRATION (KCl)

EXTERNAL REFERENCE ELECTRODE: Ag/AgCl



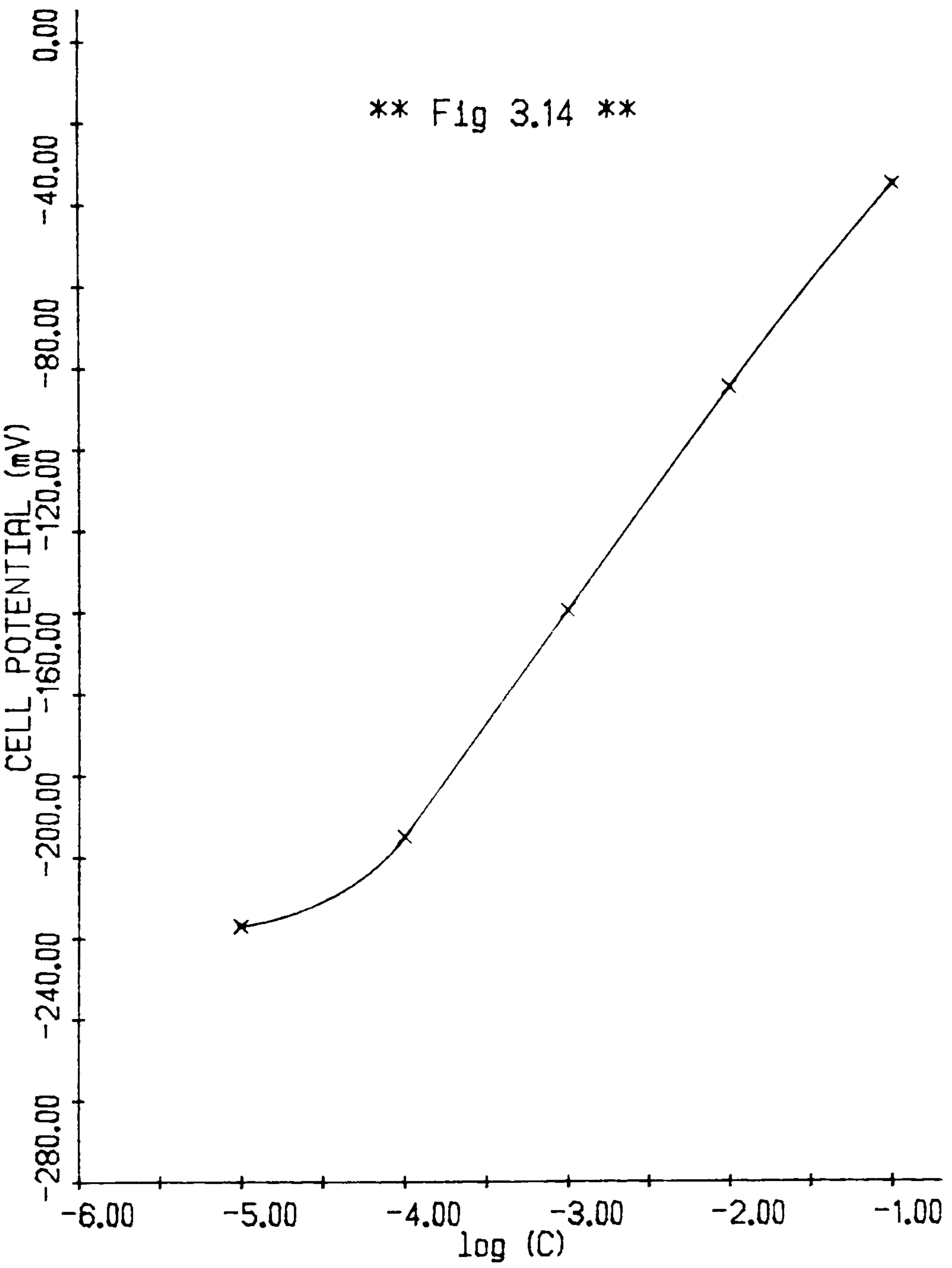
** Fig 3.13 **

ELECTRODE NO.20

x = CALIBRATION (KCl+0.1 mol/dm^3 Tris)

EXTERNAL REFERENCE ELECTRODE: GLASS I.S.E.

** Fig 3.14 **



ELECTRODE NO.23

EXTERNAL REFERENCE ELECTRODE: FLUORIDE I.S.E

× = CALIB. (KCl+5.10^{-5} mol/dm^3 NaF)

3.7 VARIATION OF THE MEMBRANE COMPOSITION

In order to obtain K^+ / valinomycin electrodes with good performance and high selectivity, whilst using the minimum amount of expensive valinomycin, two sets of experiments were carried out:

1. Variation of the amount of active material and its effect on the electrode behaviour.

2. Variation of the amount of plasticizer and its role in the physical and electrochemical characteristics of PVC membranes.

3.7.1 Variation of the Amount of Valinomycin

The membranes studied comprised of $\simeq$ 66% (w/w) of di-n-butyl phthalate, $\simeq$ 33% (w/w) Breon S110/10, 1.2 mg potassium tetrakis (p-chlorophenyl) borate (KTPCPB) with 1%, 0.5%, 0.2%, 0.1% and 0.0% (w/w) valinomycin. Results are shown in Figs 3.15, 3.16 and Tables 3.6a and b, respectively, for calibration and selectivity measurements. To avoid liquid junction potential contributions, the calibration and selectivity plots were determined by using a F^- /I.S.E. as a reference electrode. Results are given in Figs 3.17, 3.18 and Tables 3.7a and b, respectively.

Table 3.6a

Response (slope mV/decade) of the membrane with various amounts of active material

Primary Solutions (KCl)

Valinomycin Content (%w/w)	(pK) (5-4)	(4-3)	(3-2)	(2-1)
0.0	5.5	36.0	55.3	62.8
0.1	-7.0	31.0	49.0	60.9
0.2	6.0	50.0	47.3	60.8
0.5	44.0	61.0	62.0	61.3
1.0	58.0	67.0	68.1	66.1

Table 3.6b

Mixed Solutions (KCl + 0.5 mol/dm^3 NaCl)

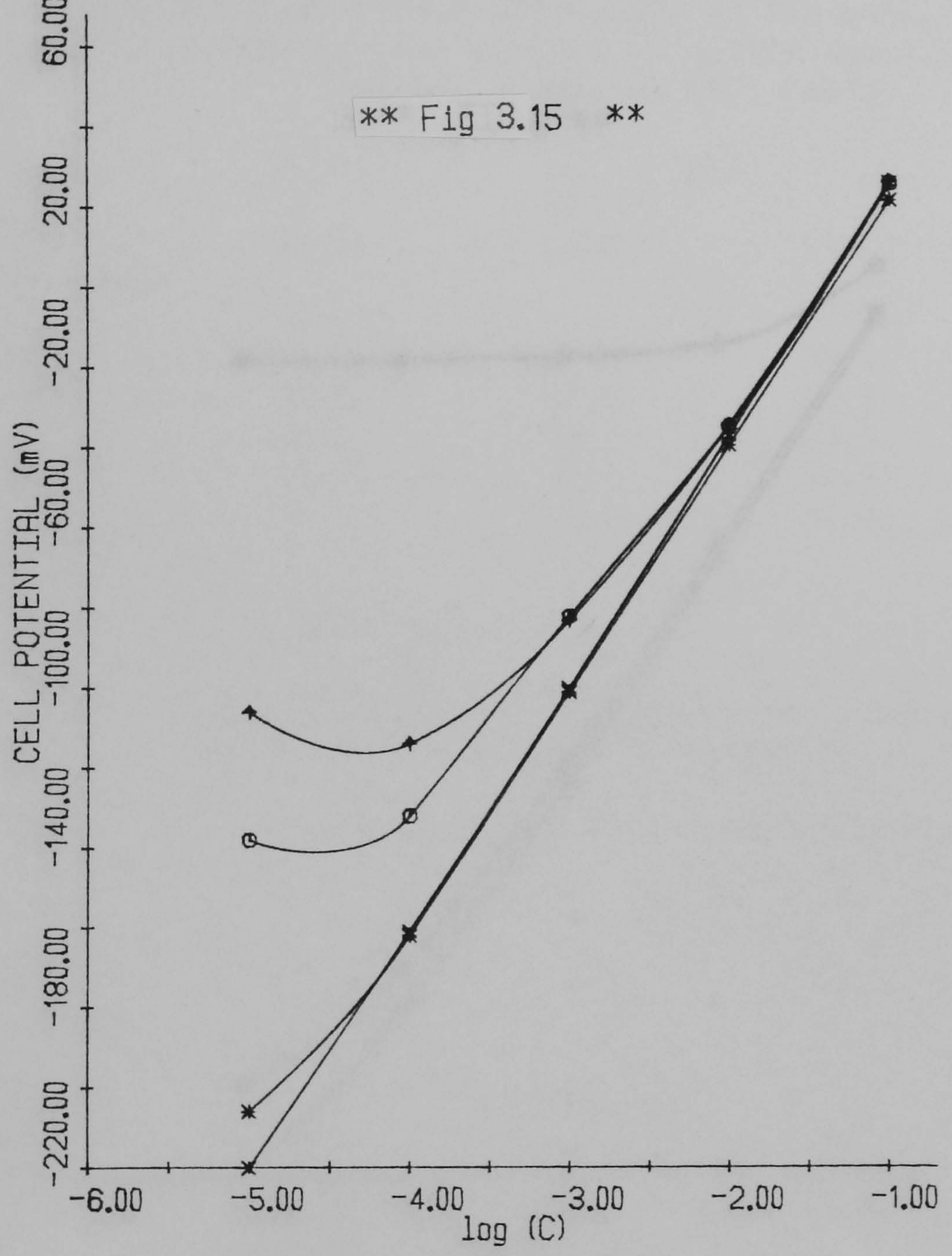
Valinomycin Content (%w/w)	(pK) (5-4)	(4-3)	(3-2)	(2-1)
0.0		no response		
0.1	0.3	0.7	3.2	18.7
0.2	0.2	0.5	3.2	18.1
0.5	28.9	49.7	56.3	58.0
1.0	39.3	55.0	58.3	59.0

These results were obtained with the following cell.

$$\begin{array}{l|ccc|c|c|l}
 & & \blacksquare & \mathrm{KCl} & & & \\
\mathrm{Ag|AgCl} & 0.1\ \mathrm{mol/dm^3} & \blacksquare & \mathrm{or} & \mathrm{T.M.A.Cl.} & \mathrm{KCl} & \mathrm{Hg_2Cl_2|Hg} \\
 & \mathrm{KCl} & \blacksquare & \mathrm{KCl{+}NaCl} & 3.5\ \mathrm{mol/dm^3} & \mathrm{(sat.)} & \\
 & & \mathrm{membrane} & & & & \\
\end{array}$$

$$\mathrm{L.J.} \qquad\qquad \mathrm{L.J.}$$

** Fig 3.15 **



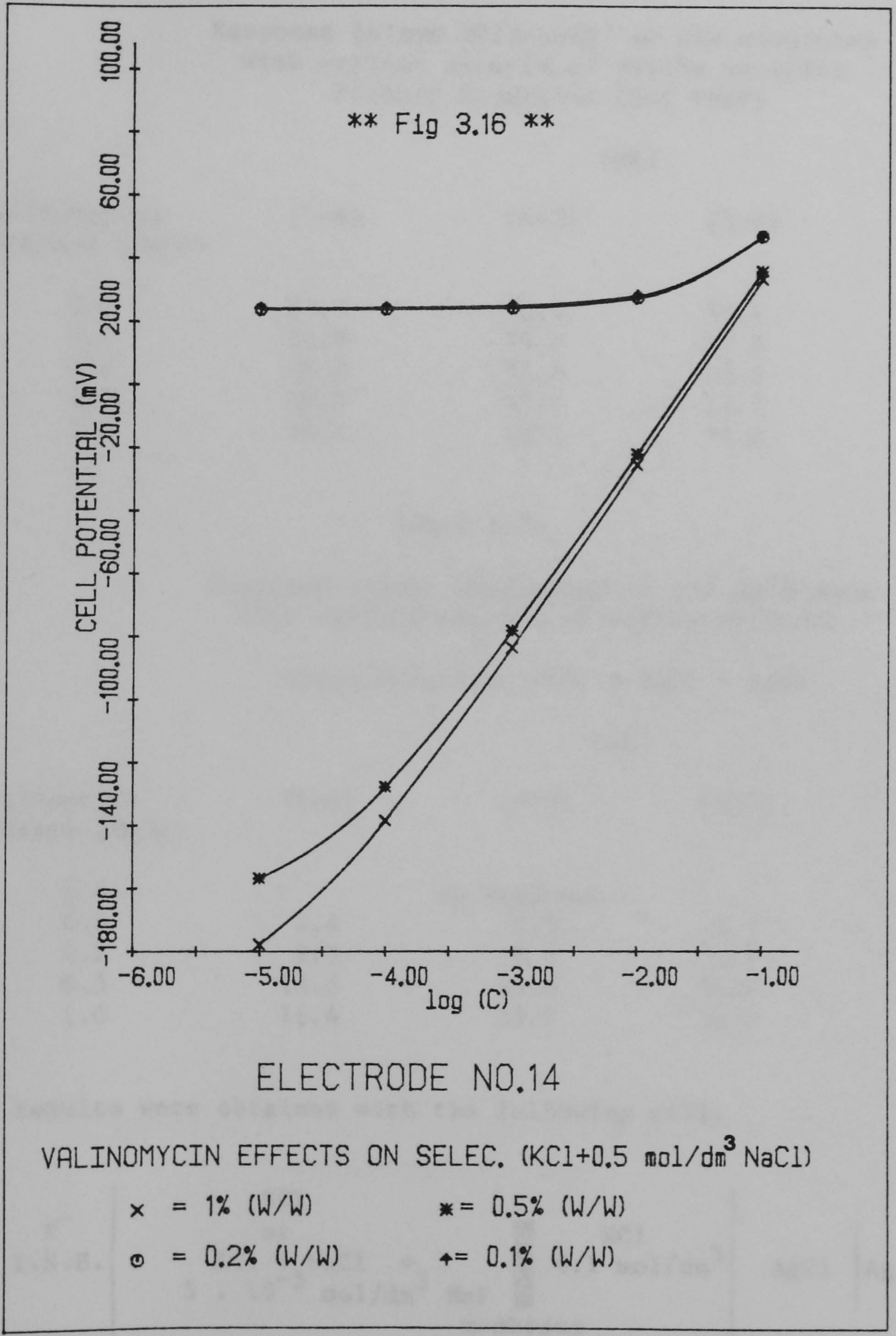
ELECTRODE NO.14

VALINOMYCIN EFFECTS ON CALIBRATION (KCl)

× = 1% (W/W) ✱= 0.5% (W/W)

⊙ = 0.2% (W/W) += 0.1% (W/W)

** Fig 3.16 **



ELECTRODE NO.14

VALINOMYCIN EFFECTS ON SELEC. (KCl+0.5 mol/dm^3 NaCl)

Table 3.7a

Response (slope mV/decade) of the membranes
with various amounts of active material
Primary Solutions (KCl +NaF)

Valinomycin Content (%w/w)	(pK) (5-4)	(pK) (4-3)	(pK) (3-2)	(pK) (2-1)
0.0	23.7	53.4	56.4	48.4
0.1	29.0	35.7	53.6	49.9
0.2	36.0	51.0	53.5	50.1
0.5	48.0	53.1	53.7	49.9
1.0	49.2	54.7	54.6	49.4

Table 3.7b

Response (slope mV/decade) of the membranes
with various amounts of active material

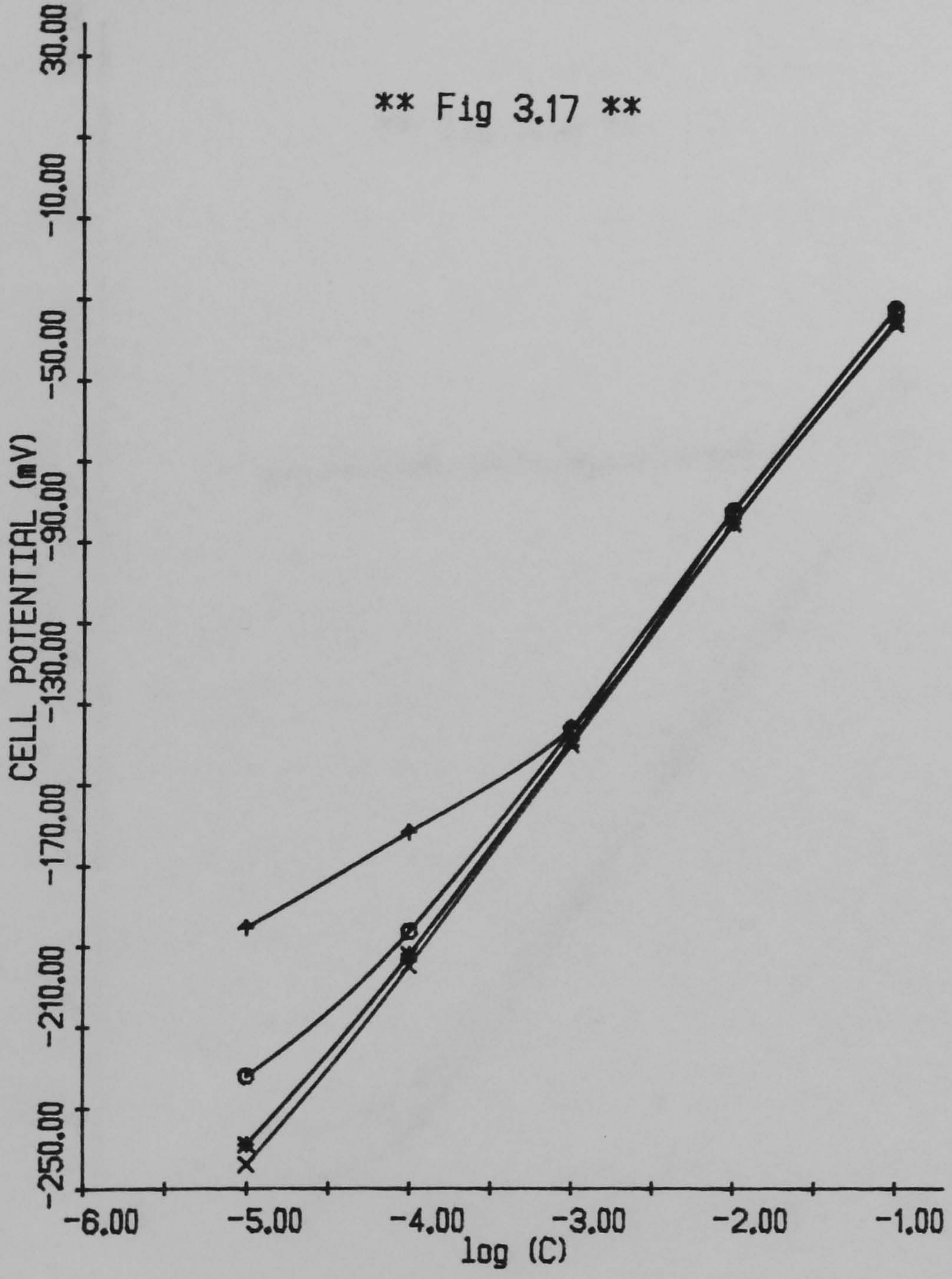
Mixed Solutions (KCl + NaCl + NaF)

Valinomycin Content (%w/w)	(pK) (5-4)	(pK) (4-3)	(pK) (3-2)	(pK) (2-1)
0.0	no response			
0.1	2.4	2.3	1.7	18.0
0.2	2.3	0.8	3.3	18.0
0.5	13.5	48.4	56.2	54.7
1.0	16.4	53.2	58.1	57.1

These results were obtained with the following cell.

F^- I.S.E.	KCl or KCl + NaCl + $5 \cdot 10^{-5}$ mol/dm^3 NaF	membrane	KCl 0.1 mol/dm^3	AgCl	Ag

** Fig 3.17 **



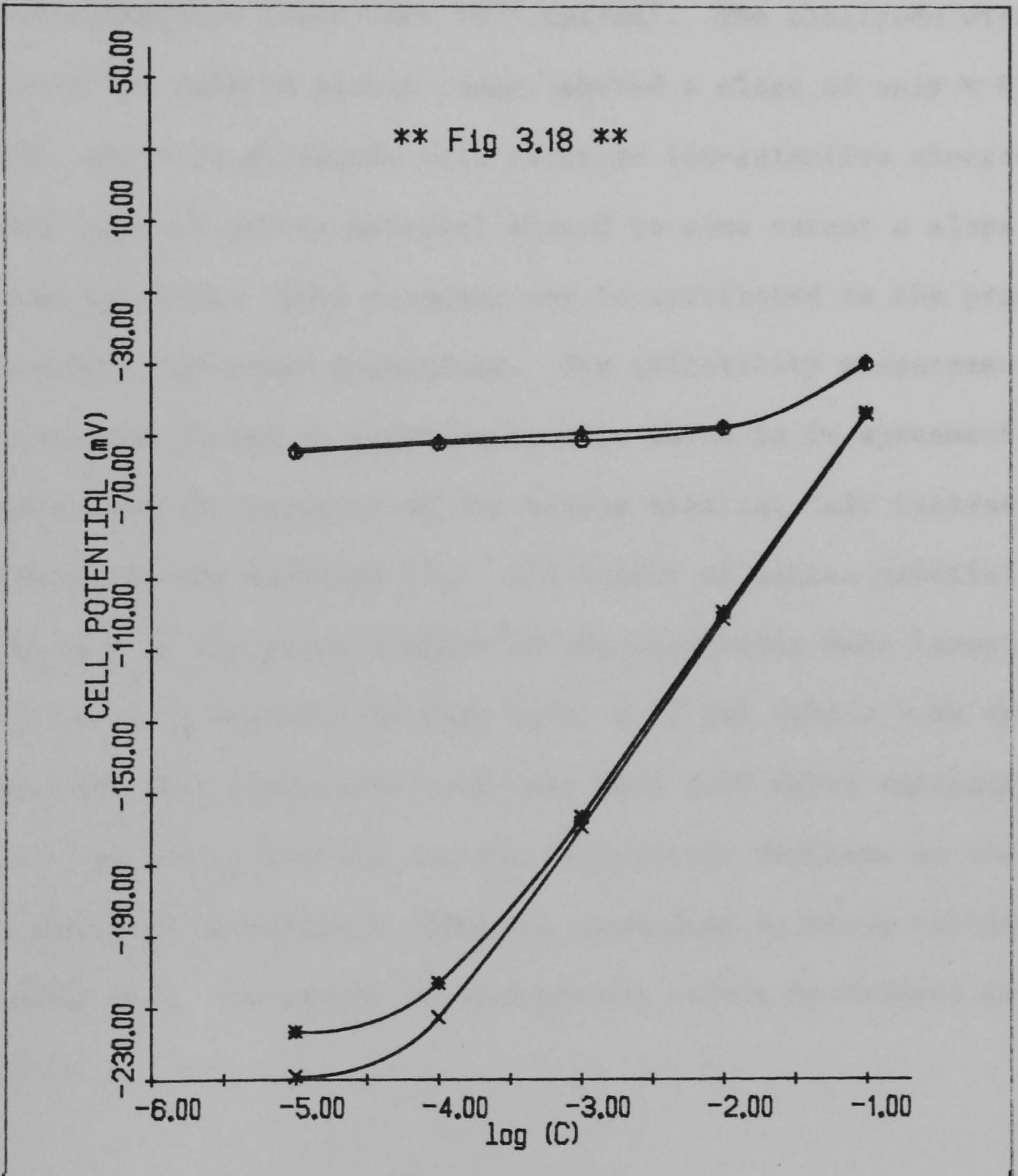
ELECTRODE NO.14

VALINOMYCIN EFFECTS ON CALIB. (KCl+5.10^{-5}mol/dm^3 NaF)

REFERENCE ELECTRODE F$^-$ I.S.E.

× = 1% (W/W) ✱= 0.5% (W/W)

⊙ = 0.2% (W/W) += 0.1% (W/W)



** Fig 3.18 **

ELECTRODE NO.14

VALINOMYCIN EFFECTS ON SELEC. (KCl+5.10^{-5}mol/dm^{3}NaF+NaCl

REFERENCE ELECTRODE F$^-$ I.S.E.

× = 1% (W/W) ✱= 0.5% (W/W)

⊚ = 0.2% (W/W) ✦= 0.1% (W/W)

It is evident from Figs 3.15 and 3.17, that at concentrations of less than 0.2% valinomycin, there is no response to K^+ ion in calibration solution with concentrations lower than 10^{-3} mol/dm^3. The electrode with 0.5%, apart from the reduced linear range, showed a slope of only ≃ 61 mV/decade (pK:1-3), and ≃ 53 mV/decade with fluoride ion-selective electrode. The electrode without active material showed to some extent a slope of ≃ 58 mV/decade (pK:1-3). This response may be attributed to the presence of 1.2 mg KTPCPB and other impurities. The selectivity measurements with this electrode showed no response at all, which is in agreement with the statement that the presence of the active material only increases the selectivity of the membrane [3]. The effect of active material was more pronounced when the selectivities of the electrodes were investigated. From the results reported in Figs 3.16, 3.18 and Tables 3.6b and 3.7b, one can conclude that electrodes with less than 0.5% (w/w) valinomycin are not selective towards potassium and the selectivity declines as the amount of active material is reduced. However, according to these results, it can be deduced that, the amount of valinomycin cannot be reduced to less than 1% (w/w).

3.7.2 Variation of the Amount of Plasticizer

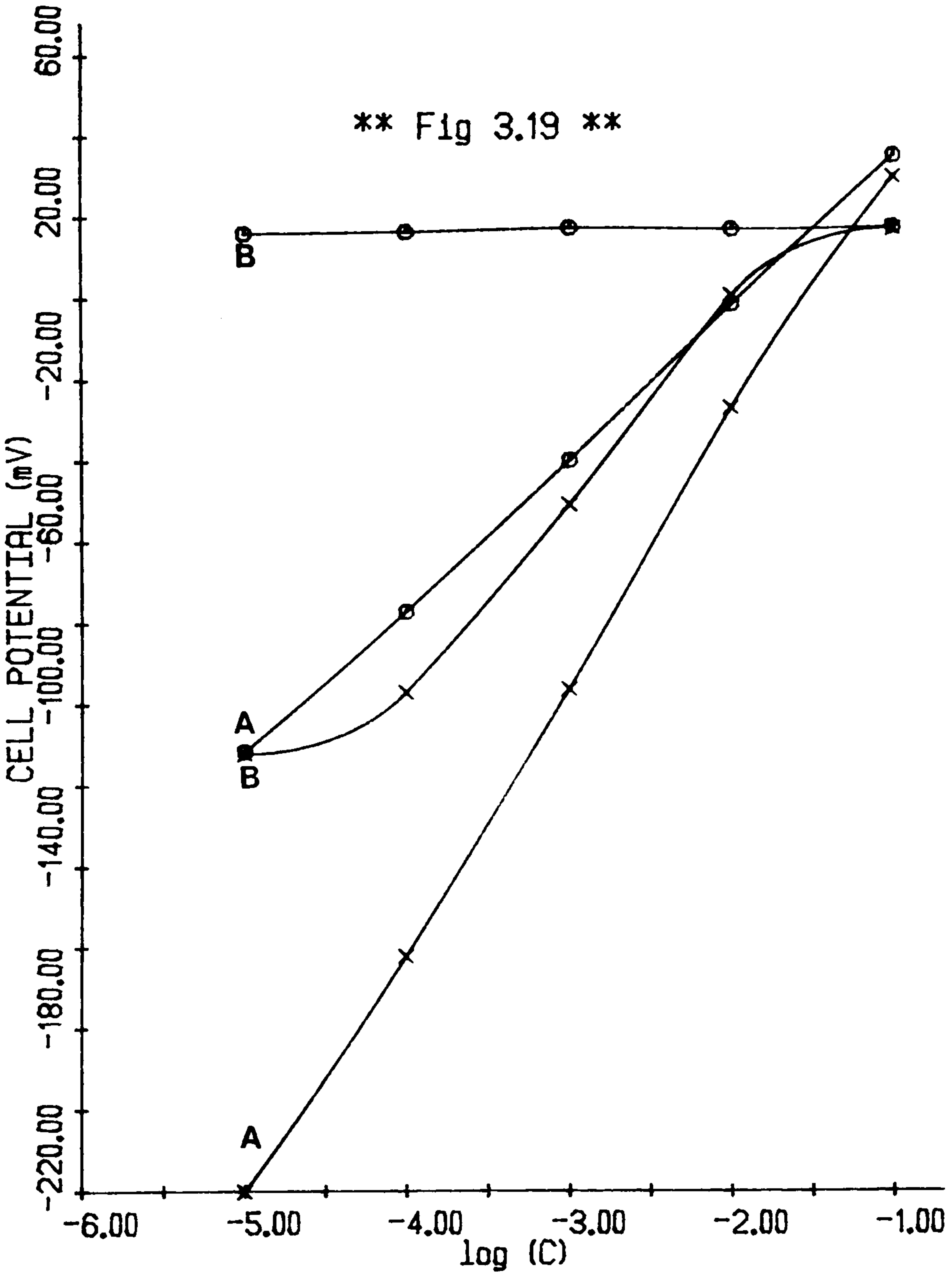
The combination of Breon S110/11 and di-n-butyl phthalate was used for this study. The plasticizer content of the membranes was chosen as 0.0%, 30%, 50%, 66% and 78% (w/w). All membranes contained the same amount of valinomycin and KTPCPB salt. Membranes without plasticizer (0.0%), as was expected, were rigid and brittle; with too much plasticizer, (more than

70%), it was jelly-like and impossible to cut. Similar experiments to those described in the previous section were carried out. The detailed results are presented in Fig 3.19 and Tables 3.8a and b. The electrode prepared with 30% plasticizer showed a slope of only ≃47 mV/decade with a linear range of pK:2-4, while that with 50% indicated a better response, nearly Nernstian (67 mV/decade for pK:2-4).

As far as the selectivity of these electrodes is concerned, the electrode with 30% did not show any response whilst that of 50% indicated a response of 38 mV in the range of pK:2-4 . One can thus conclude from Fig 3.19 and Table(3.8a and b), that electrodes with 30% and 50% plasticizer failed, either with respect to slope or selectivity as compared to those of higher formulation (see Chapter Two). Repetition of the electrode performance experiments with F^- / I.S.E. as the reference electrode, confirmed the aforementioned behaviour.

3.8 EFFECT OF THE PRESENCE OF ADDITIONAL NEGATIVE SITES

The use of potassium tetrakis (p-chlorophenyl) borate in conjunction with valinomycin, as a producer of negative sites in a membrane, was believed to reduce anion penetration into the membrane at concentrations higher than 10^{-1} mol/dm^3; this also makes the membrane selective towards cations [3,4]. Three electrodes numbered 22, 24 and 4 were prepared with, and without, KTPCPB. No differences in behaviour could be detected considering either the calibration or the selectivity slope (see Fig 3.20 for electrode No.4). A further investigation was carried out by preparing an electrode with glass powder as a source of negative sites which also



EFFECT OF PLASTICIZER CONTENT

× = CALIB. ⊙ = SELEC. (0.5 mol/dm^3 NaCl)

A MEMBRANE WITH 50% PLASTICIZER

B MEMBRANE WITH 30% PLASTICIZER

Table 3.8a

Response (slope mV/decade) of the membranes with various amounts of plasticizer

Primary Solutions (KCl)

plasticizer Content (%w/w)	(pK) (5-4)	(4-3)	(3-2)	(2-1)
0.0	10.0	36.0	49.5	49.1
30.0	15.0	46.5	51.5	16.6
50.0	58.0	66.0	69.5	56.9
66.0	58.0	67.0	69.5	66.5
78.0		unusable		

Table 3.8b

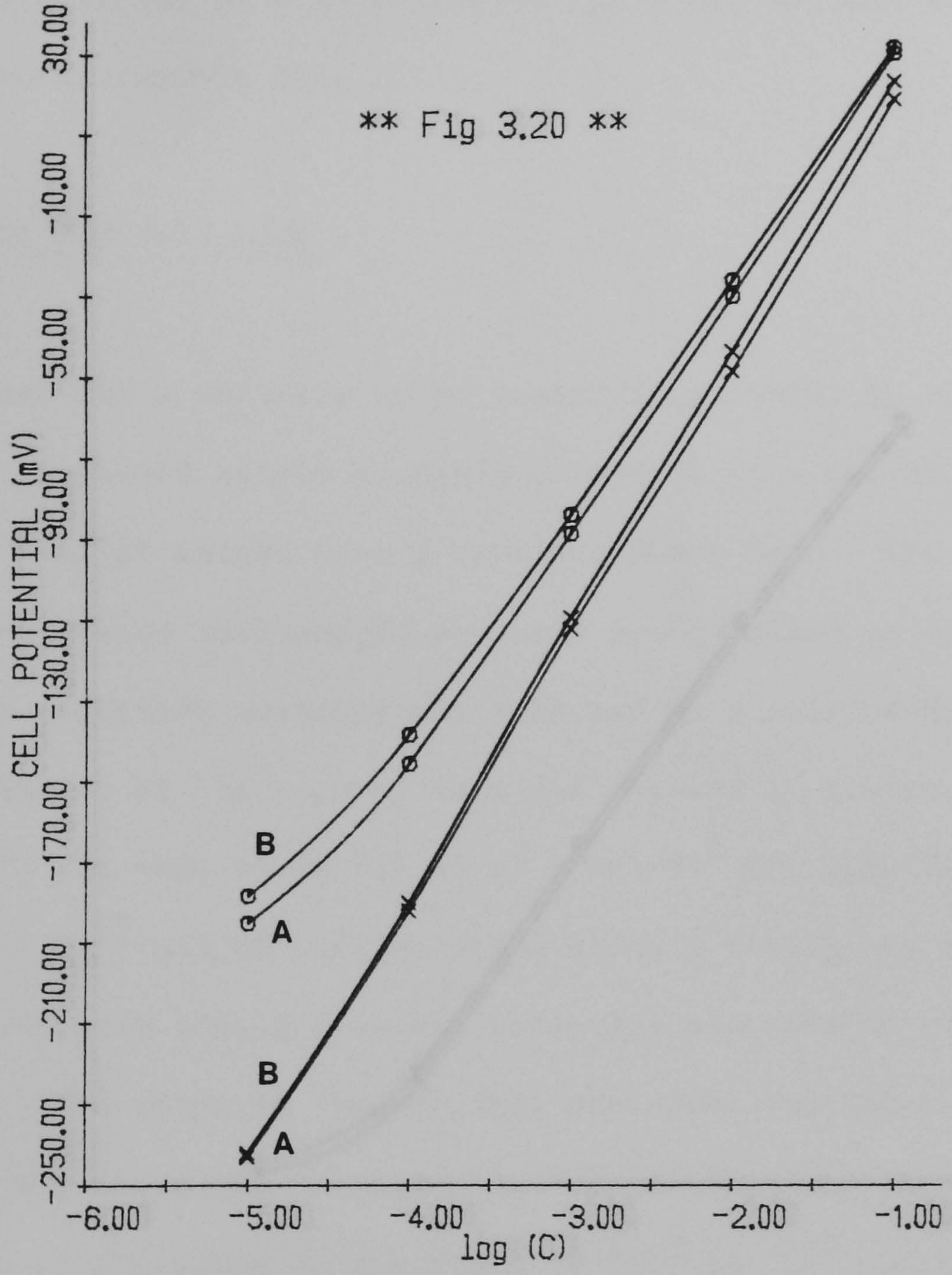
Response (slope mV/decade) of the membranes with various amounts of plasticizer

Mixed Solutions (KCl+ NaCl)

plasticizer Content (%w/w)	(pK) (5-4)	(4-3)	(3-2)	(2-1)
0.0	-0.5	-0.5	3.0	-3.0
30.0	0.5	1.0	-0.4	0.6
50.0	34.4	37.5	38.6	36.6
66.0	39.3	55.0	58.3	59.0
78.0		unusable		

showed identical performance. Fig 3.21 demonstrates the performance of electrode No. 4 in conjunction with F^- electrode, which has identical pattern to the behaviour of the same electrode in association with a reference electrode having liquid junction. From the present results, and further evidence to be discussed in detail in the following chapter, one can suggest that impurities in the matrix membrane materials, namely

** Fig 3.20 **

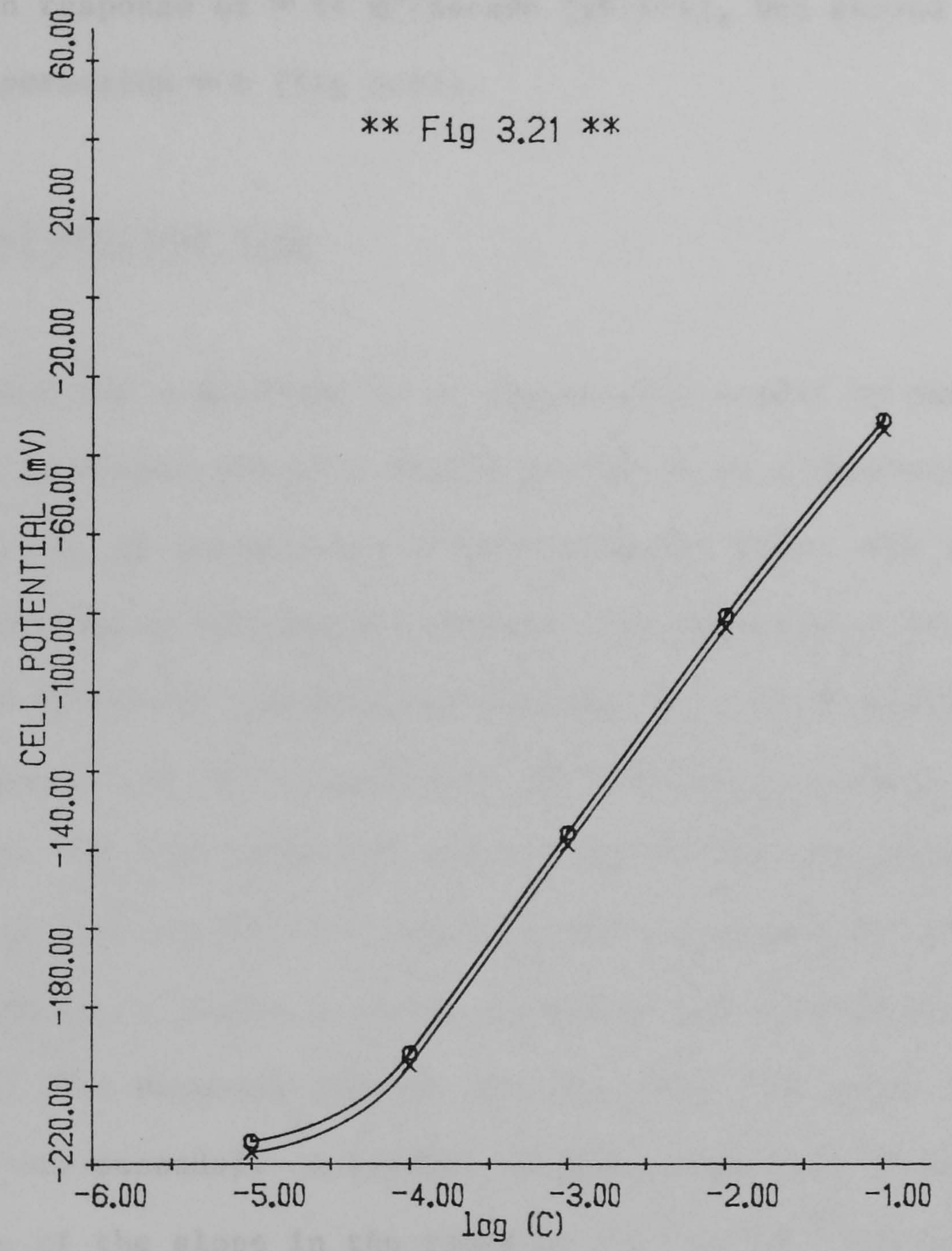


EFFECT OF KTPCPB

× = CALIB. ⊙ = SELEC. (0.5 mol/dm^3 NaCl)

A MEMBRANE WITH KTPCPB

B MEMBRANE WITHOUT KTPCPB



ELECTRODE NO. 23

EFFECT OF ADDITIONAL LIPOPHILIC ANION ON CALIB.

REFERENCE ELECTRODE: F I.S.E (KCl+5.10^{-5} mol/dm^3 NaF)

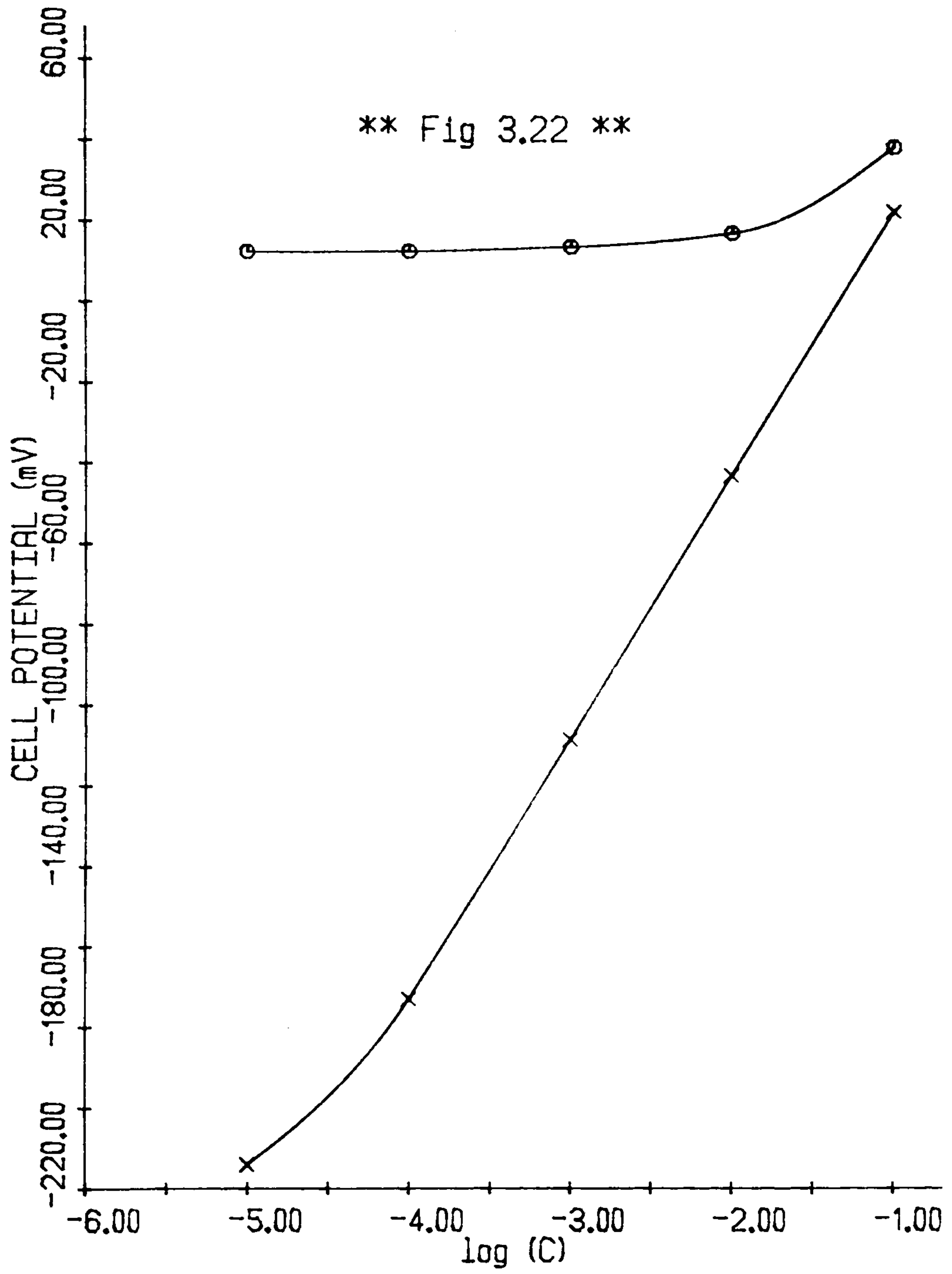
×= MEMBRANE WITH KTPCPB

⊕= MEMBRANE WITHOUT KTPCPB

plasticizer and polymer, might act as fixed negative sites. Replacing valinomycin with 10 mg of KTPCPB gave a functional electrode with a Nernstian response of ≈ 64 mV/decade (pK:1-4), but showed poor selectivity towards potassium ≈ 6 (Fig 3.22).

3.9 MEMBRANE RESPONSE TIME

In order for a membrane to be practically useful in potentiometric studies, it should attain a stable potential in a reasonably short period of time, i.e. it should have a rapid response time. The response time of the K^+ /PVC based valinomycin membrane was obtained by the jump technique, where the electrode assembly was immersed in a stirred-dilute, pure or mixed solution of the primary ions and allowed to achieve a steady potential. In this study 0.1 ml of 1 mol/dm^3 KCl solution was injected to 99.9 ml of 10^{-5} mol/dm^3 KCl solution using a syringe or micropipette, the time required to regain a stable potential was determined from the chart recorder. The response time by this procedure was found to be extremely short (a few seconds). A typical response time plot is shown in Fig 3.23. Variation of the slope in the range of 10^{-2} to 10^{-3} mol/dm^3 over a period of more than one month was investigated for different electrodes. The results are given for electrode No.5 in Fig 3.24. On the basis of these results, the slope of the calibration does not change significantly (68.9 ± 0.8 mV/decade). However, for the electrode based on ion-exchanger KTPCPB the slope is decreased. Thus, for an electrode based on valinomycin, every day calibration is not required.



** Fig 3.22 **

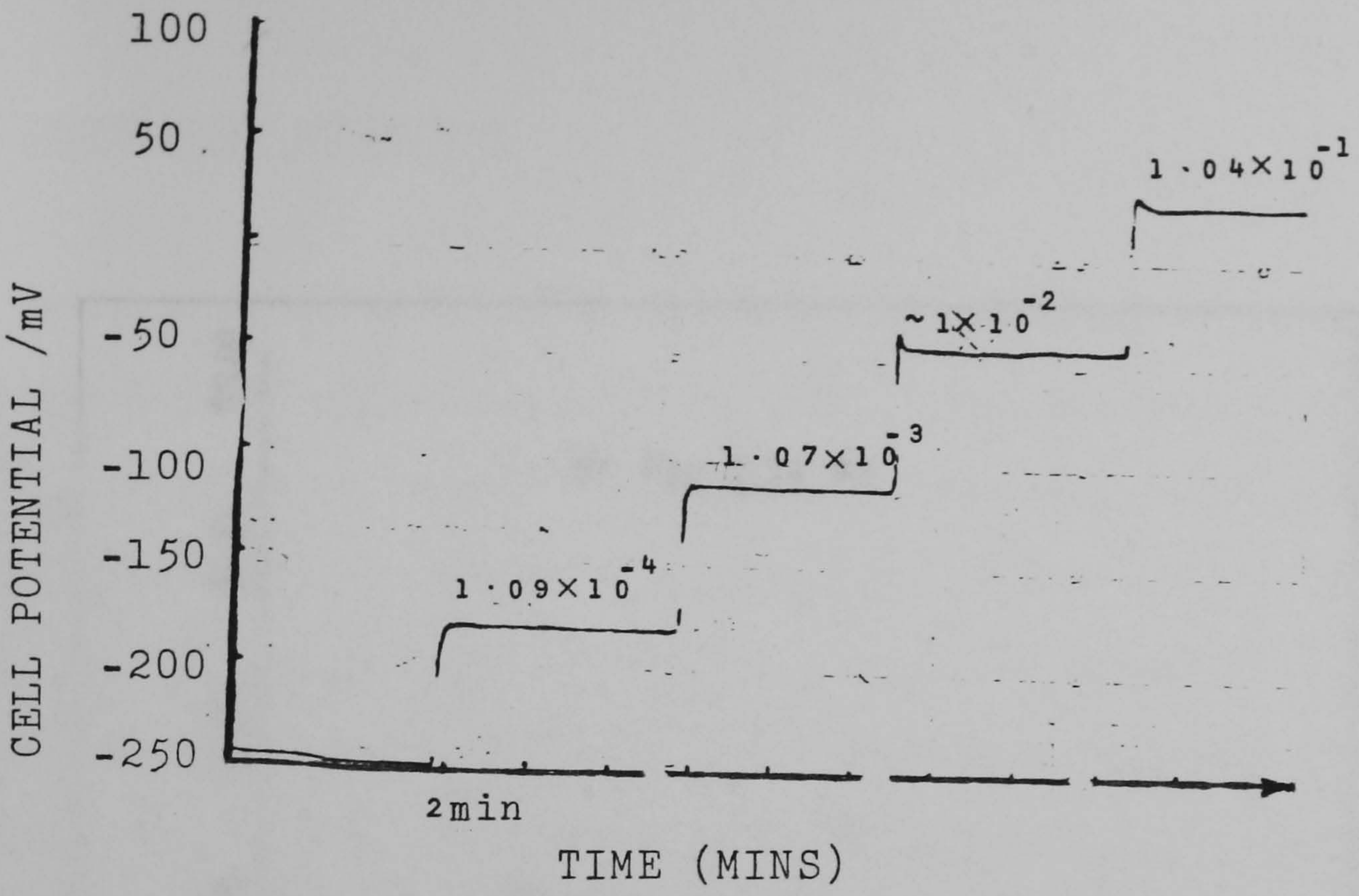
MEMBRANE BASED ON KTPCPB

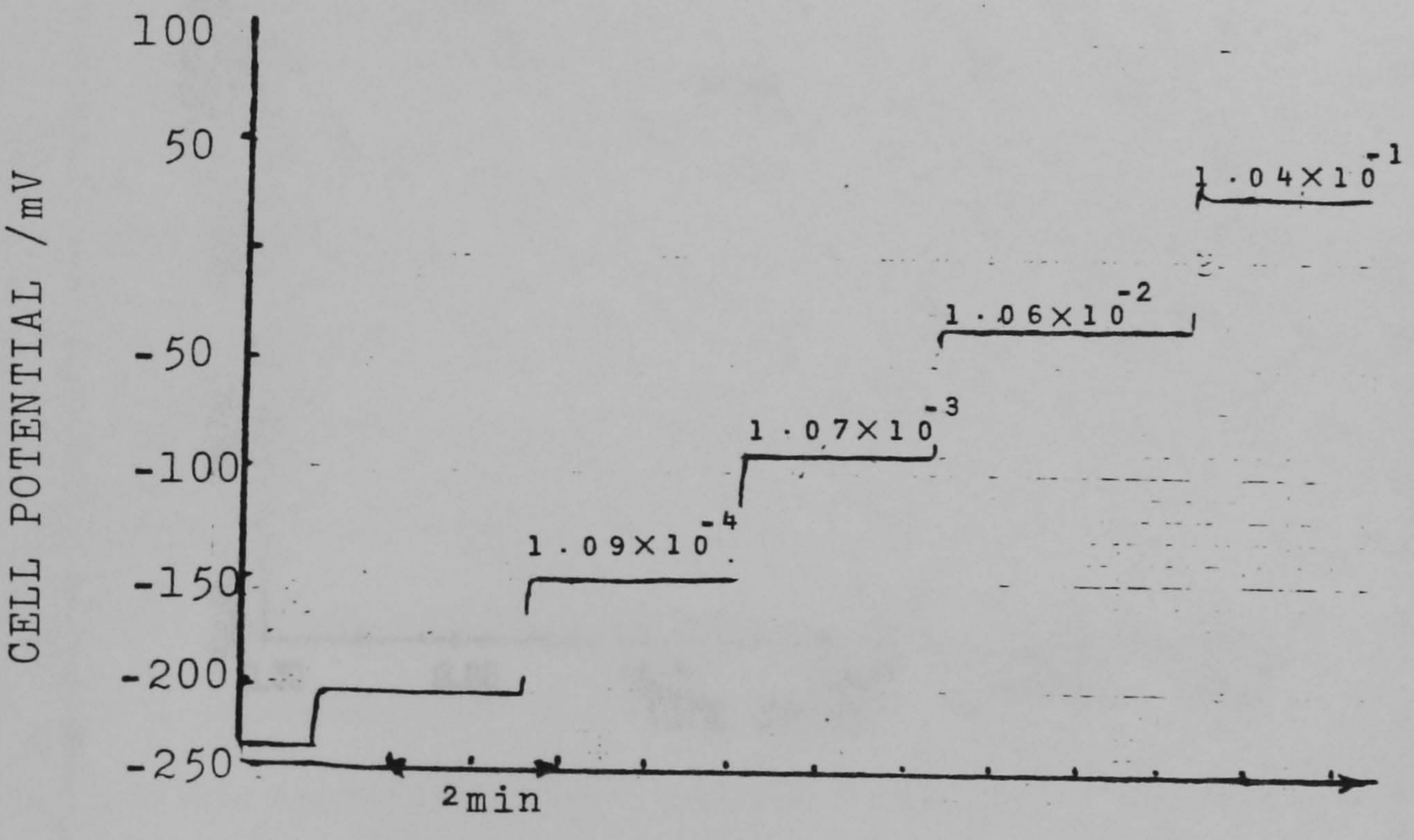
× = CALIB. (KCl)

⊕ = SELEC. (KCl + 0.5 mol/dm^3 NaCl)

RESPONSE TIME

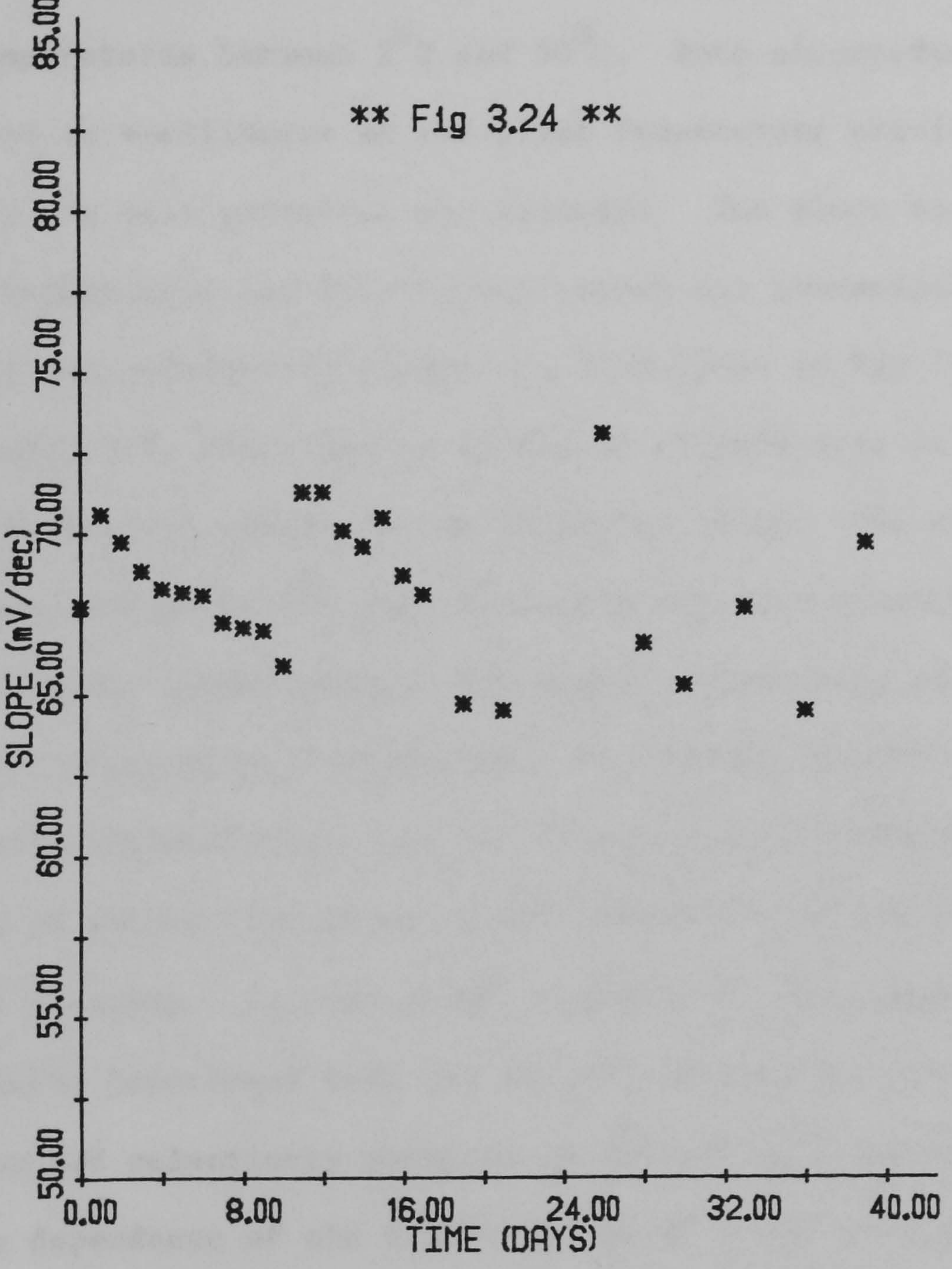
a: Response time in pure KCl solution by injection method





b: Response time in mixed solution
(KCl+0.5mol/dm^{3}NaCl)

Fig (3.23)

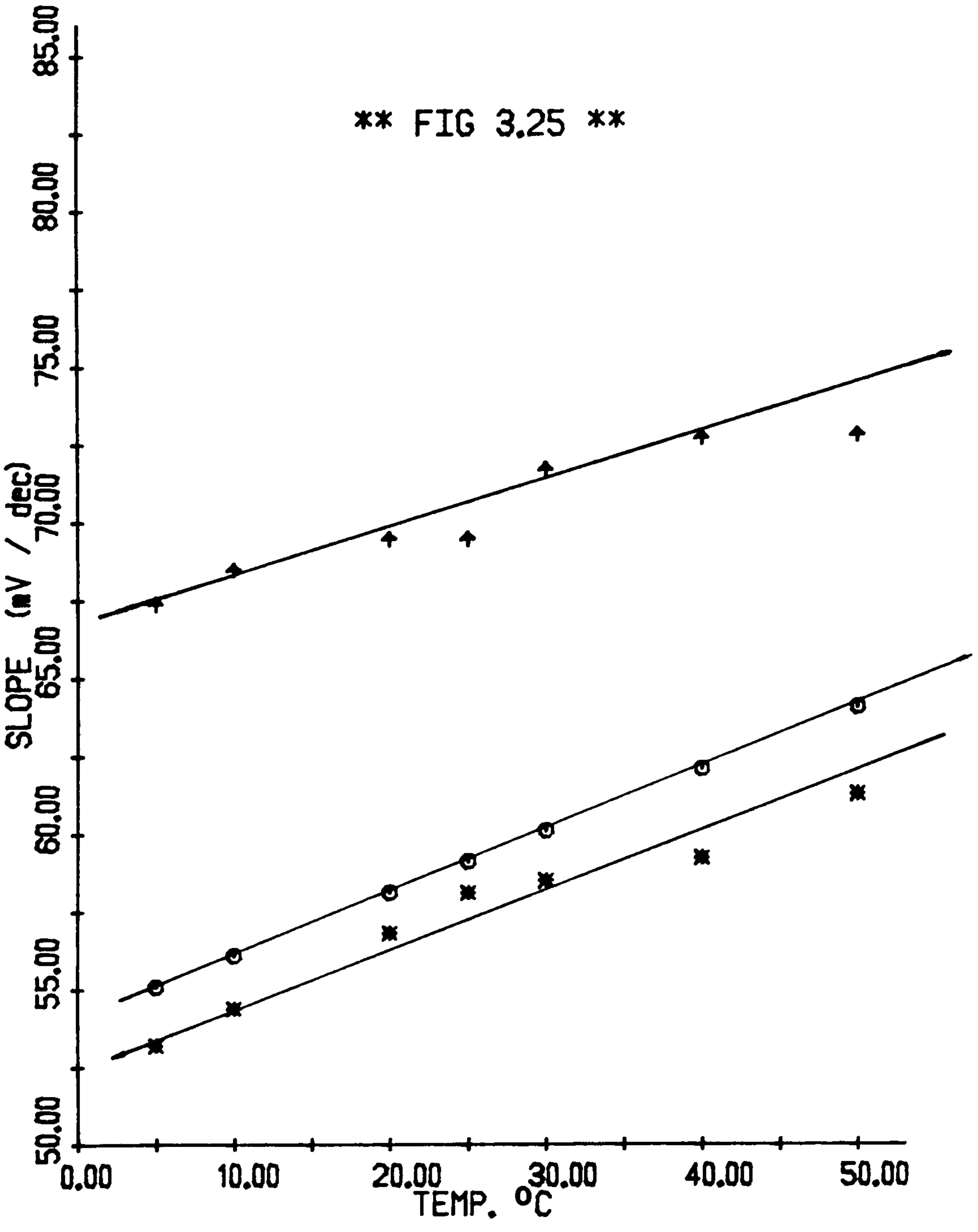


VARIATION OF SLOPE WITH TIME

3.10 TEMPERATURE DEPENDENCE

Calibration and selectivity curves were constructed in solutions for various temperatures between 5^{0}C and 50^{0}C. Both electrodes and solutions were allowed to equilibrate at the given temperature provided by a water bath before the cell potential was recorded. The slope and the linear range for calibration and selectivity curves are summarized in Table 3.9. Calibration and selectivity slopes are also shown in Fig 3.25. As one can see from Table 3.9, the slope at different temperatures is in agreement with the theoretical change in the Nernstian slope. The selectivity coefficients, except at 5^{0}C and 10^{0}C which are more than 8000, are around 4000 at all other temperatures. The higher selectivity can be attributed to the lower slope of ≃ 53 mV/decade. It has been reported that the membrane with diphenylether does not function at low temperature, which is the result of drastic reduction in the mobilities of the species in a solidified membrane. In this study, however, at the lower temperatures, the electrodes functioned well and did not deteriorate upon cooling. Calibration and selectivity patterns at 5^{0}C and 50^{0}C are shown in Fig 3.26. The dependence of the E.M.F. of the K^+ / PVC electrode on the pH at different concentrations (10^{-2} and 10^{-3} mol/dm^3) was examined. There was no effect upon the potential of the electrode between pH:2-12 .

** FIG 3.25 **

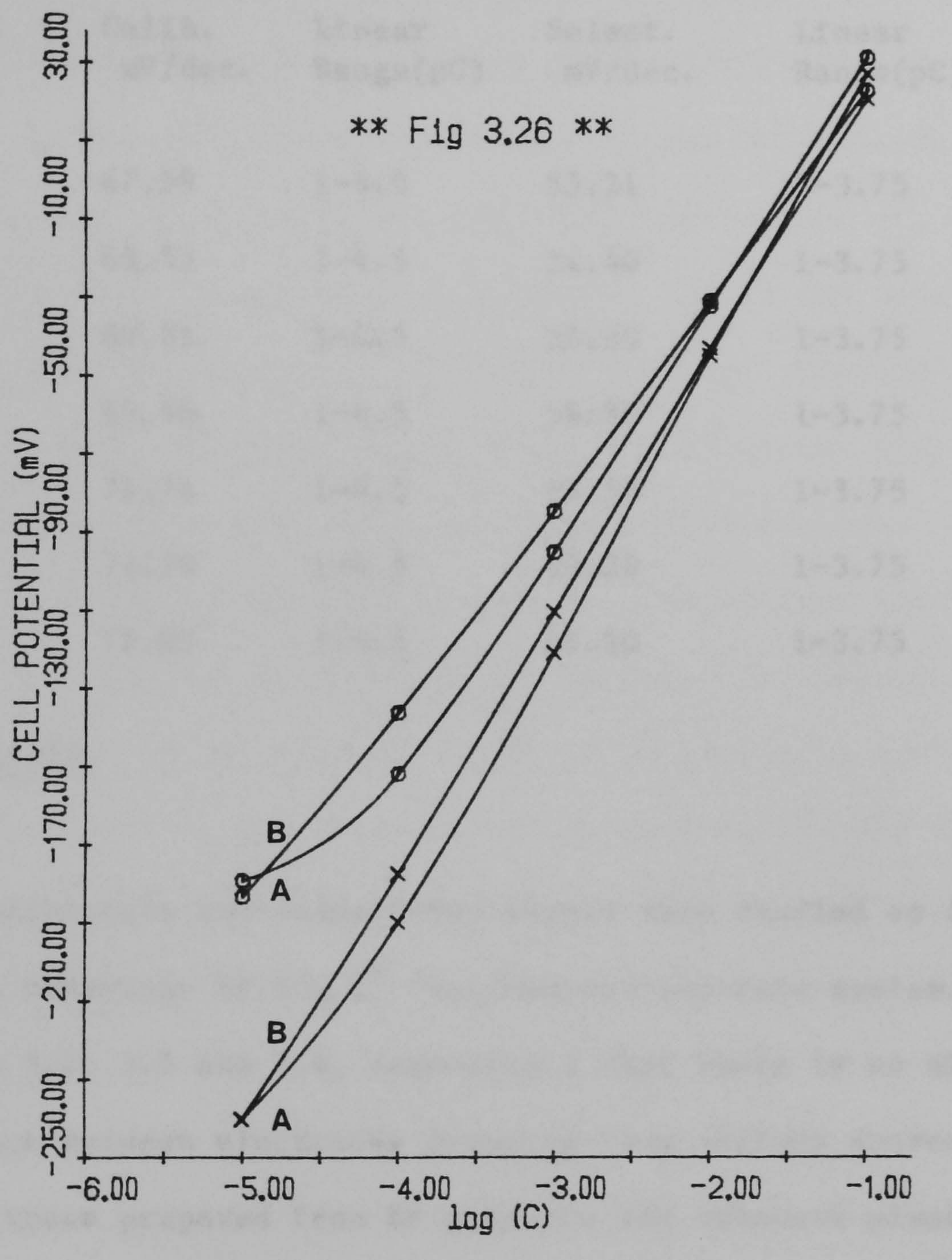


EFFECT OF TEMPERATURE ON SLOPE

+ = SLOPE OF CALIBRATION

✱ = SLOPE OF SELECTIVITY

⊙ = THEORETICAL SLOPE



EFFECT OF TEMPERATURE

× = CALIB. (KCl) ⊙= SELEC. (0.5 mol/dm^3 NaCl)

A = MEASUREMENTS AT 50 °C

B = MEASUREMENTS AT 5 °C

Table 3.9

Temperature Effect on Slope of K^+/ PVC Electrodes

Temp. ^0C	Calib. mV/dec.	Linear Range(pC)	Select. mV/dec.	Linear Range(pC)	RT/F ln 10 mV
5.0	67.39	1-4.5	53.21	1-3.75	55.1
10.0	68.52	1-4.5	54.40	1-3.75	56.1
20.0	69.51	1-4.5	56.80	1-3.75	58.1
25.0	69.50	1-4.5	56.80	1-3.75	59.1
30.0	71.74	1-4.5	58.50	1-3.75	60.1
40.0	72.75	1-4.5	59.24	1-3.75	62.1
50.0	72.85	1-4.5	61.30	1-3.75	64.1

3.11 CONCLUSION

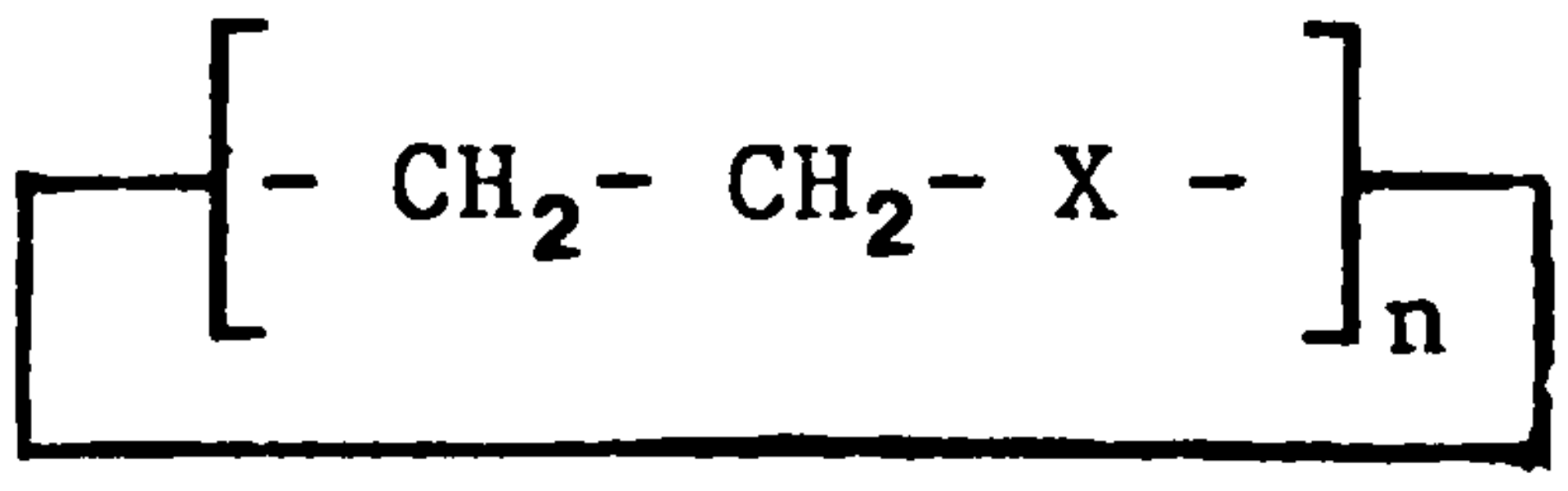
The calibration and selectivity slopes were studied to investigate the potential behaviour of the K^+ /valinomycin membrane system. The results in Tables 3.2, 3.3 and 3.4, demonstrate that there is no significant differenece between electrodes prepared from various sources of PVC. However, those prepared from BP polymers and sebacate plasticizer were marginally better. For membranes with valinomycin concentrations of 0.5% (w/w) and higher, the linear section of the curves correspond fully to potassium ions and can be seen in Fig 3.15. The linearity extends as the concentration of the membrane valinomycin content increases. The electrode properties of the membrane drastically deteriorate in a mixed solution as the valinomycin concentration is reduced to 0.2% or less. The selectivity of the electrode membranes in a mixed solution varies considerably with different concentrations of ionophore. Such observations are consistent with the conclusion that low selectivity is a result of the reduction of concentration of valinomycin, known to be responsible for the high selectivity of the electrode [3]. Therefore, it would appear unwise to economise in the amount of valinomycin less than 1% (w/w). Results with electrodes made with various amounts of plasticizer, indicate that the reduction in its content led to the loss of selectivity. For example, electrodes with 30% do not show any response in mixed solutions. This behaviour might be attributed to the drop in mobility of the species in membranes with lower plasticizer content. A formulation containing 60-70% plasticizer appears to give optimum results. The addition of negative sites, which was supposed to improve the performance of the valinomycin electrodes, could not be confirmed during the present study. However, it was found that this improvement only relates to the electrodes studied under flow conditions. Other experiments established the long lifetime of the membrane electrode as judged by the identical behaviour shown by an electrode which was prepared two months later from the edge of a master membrane rather than the middle part. Investigation of a suitable background electrolyte to keep the activity effect constant showed that the magnesium was preferable to calcium, or barium, as regard to selectivity. It was found essential to use analytical reagent chemicals for this purpose, otherwise traces of impurities with high selectivity coefficient over K^+ ions would ruin the results.

PART TWO

BIS-CROWN ETHERS
as
ACTIVE MATERIALS

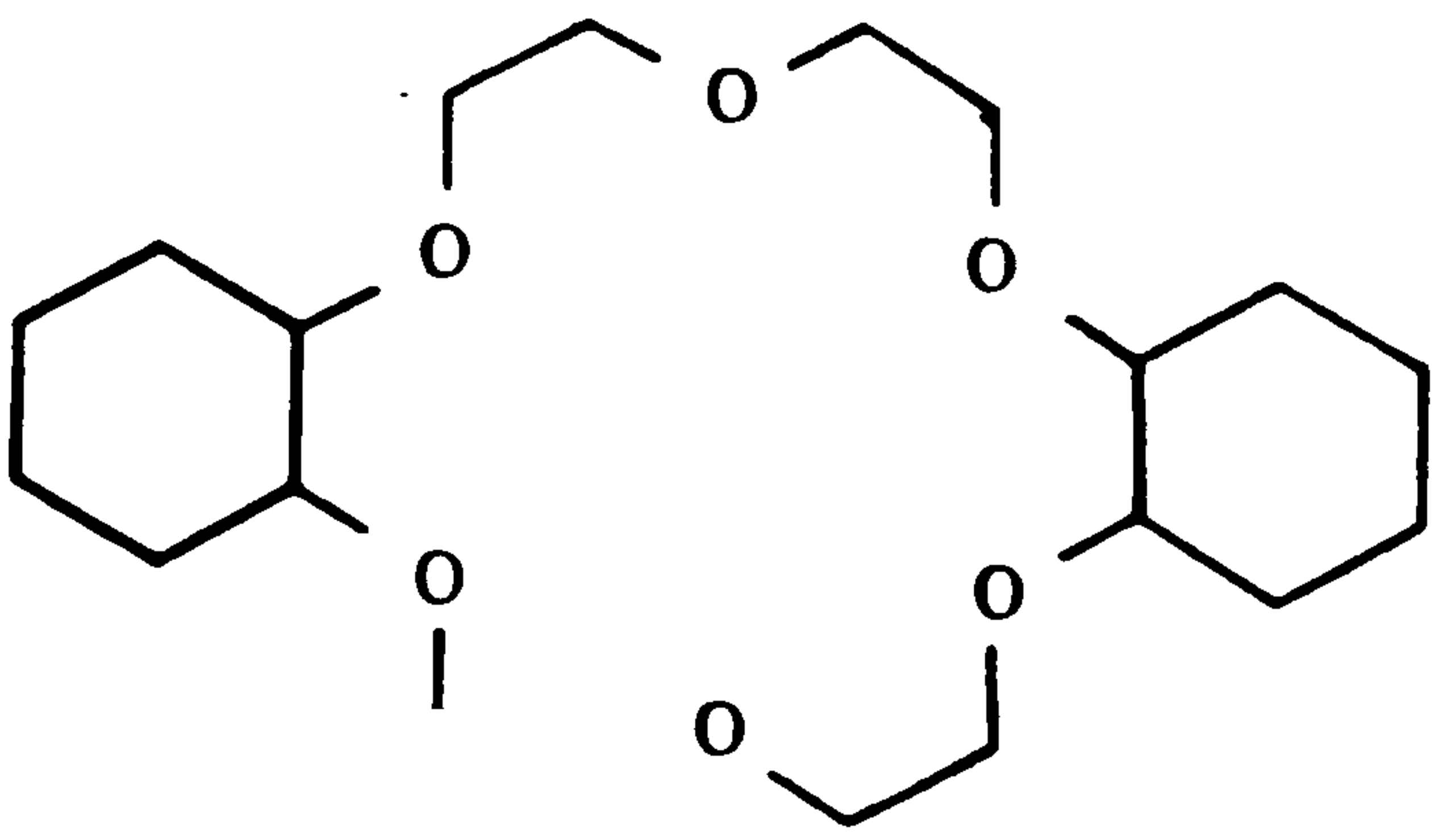
3.12 INTRODUCTION (CROWNS) PART (II)

Since the discovery of the first crown compound by accident in 1967, a number of macrocyclic polyethers have been synthesised. The tremendous ability of those compounds to complex with metal salts, particularly alkali and alkaline earth metals has been reported [5]. Since then the synthesizing of closed ring compounds which contain functional groups, capable of binding ions of suitable size and charge, has been found to be one of the ways of obtaining highly selective organic reagents. A large number of synthetic macrocyclic compounds with binding capacity towards cations and anions has been prepared and investigated, e.g. macrocyclic polyethers [5], polyamines [6], polythioethers [7] etc. The macrocyclic compounds are the derivatives of basic structure shown below:



$$\left[-\ CH_2-\ CH_2-\ X\ -\right]_n$$

where X may be O [5], N [6], S [7], P [8], etc. If X is substituted by O, the basic structure generates macrocyclic polyethers which are commonly referred to as ´Crown´ compounds. Because of the difficulty in naming these compounds according to IUPAC rules, a simplified method of nomenclature has been suggested by Pedersen which is used extensively [5]. For example, the first cyclic polyether compound (I), IUPAC´s name is 2, 3, 11, 12-dicyclohexyl-1, 4, 7, 10, 13, 16, hexacyclo-octadecane, while in Pedersen´s nomenclature it is called; dicyclohexyl-18-crown-6.

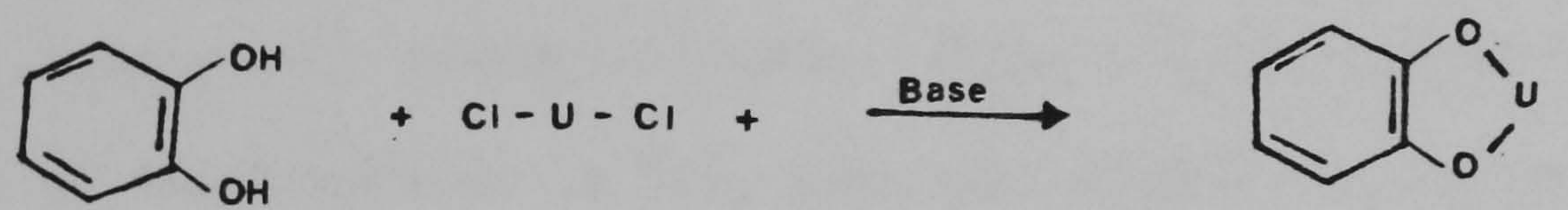


(I)

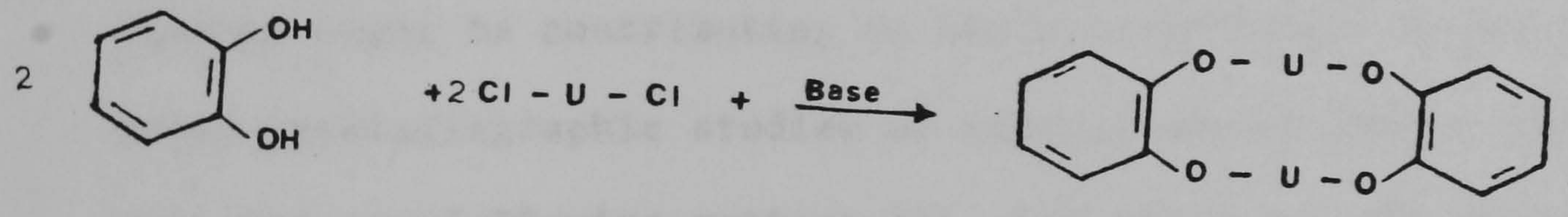
Here, the term ´crown´ represents the central ring, 18 indicates the total number of the atoms in the ring and 6 denotes the total number of donor oxygen atoms in the main ring. Although these names are simple, they are not always clear. Macrocyclic polyethers (crowns) are neutral molecules, which contain central hydrophilic cavities with electro-negative donor atoms and have hydrophobic and flexible exteriors. They possess unusual capacity to bind selectively to a wide variety of cations. Their lipophilic exterior allows them to solubilize ionic substances in non-aqueous solvents.

3.13 METHODS OF SYNTHESIZING POLYETHERS

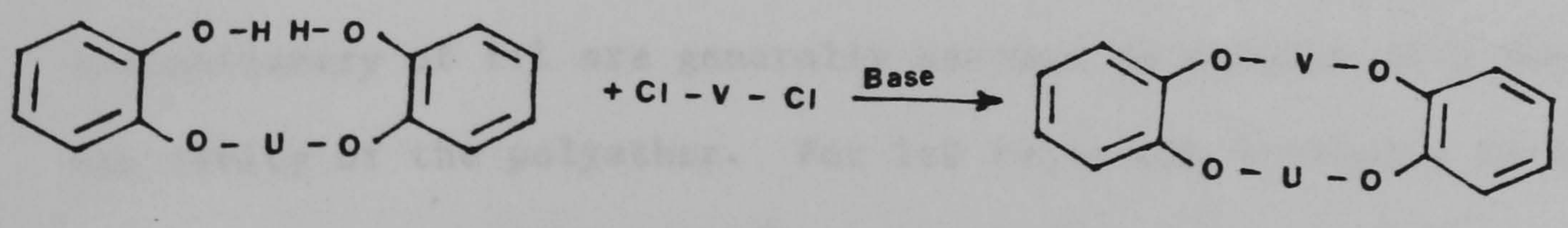
The aromatic crown polyethers are synthesized by three main methods [5,10]. These three different ways are represented by the stoichiometric equations shown below:



(1)



(2)



(3)

Where U and V represent divalent organic groups, generally of the type $-(CH_2-CH_2-O)_n-CH_2-CH_2-$. Most of those compounds were prepared through processes (1) and (2) starting with catechol or an oligo ethylene glycol and an appropriate dihalide or ditosylate (as leaving group). The solvent typically used is 1 - butanol and condensation is carried out under nitrogen at a reflux temperature for 12-24 hours. It has been found [10,11] that the yield of the product depends on the solvent, type of base and leaving group. Greene [10] ascribes the high yield of the polyethers to a ´template effect´ where a cation and a crown produce an intermediate product, thus increasing the rate of cyclization.

3.14 SALT COMPLEXES OF MONO-CROWN ETHERS

The complexation capacity of the crown ether compounds for alkali and alkaline earth cations has been well documented [5]; they are also known to bind organic and other complex cations [12,13]. One of the most interesting characteristics of these compounds is their ability to bind selectively various cations. First it was supposed that the stoichoimetry of the complexes is 1:1, i.e. one molecule of crown ether encapsulate one ion regardless of the cation valency. Later it was recognised that other factors might be contributing to the stoichiometry of the complexes. X-ray crystallographic studies of several metal-crown complexes have revealed the following ratios: 1:1, 1:2 and 2:3. The complexes with stoichiometry of 1:1 are generally assumed to consist of a metal ion in the cavity of the polyether. For 1:2 ratio the existence of sandwich structures was confirmed by the crystal structure of (KI) :(Benzo-15-Crown-5) , which had the cation located between two parallel rings consisted of five oxygen atoms [14]. A ´club sandwich´ structure has been suggested for the 2:3 complexes. Generally when the metal ion is larger than the cavity of the crown ether, complexes with 1:2 and 2:3 ratio are formed [15]. However, the structure of dibenzo-30-crown-10, as determined by X-ray diffraction, indicates that it forms a 1:1 complex with potassium iodide in which the ligand is wrapped around the K^+ cation [16,17]. Also the complexation ratio of silver cation with benzo-15-crown-5 is 1:1, where the size of cavity is smaller than the cation size. These facts demonstrate that the 1:1 stoichiometry ratio does not necessarily indicate that the metal ion is located in the cavity of the polyether, and therefore relative size is not the only parameter influencing the conformation of the complexes.

3.15 APPLICATION OF MONO-CROWN ETHERS

3.15.1 Organic Chemistry

The solubilization of metal salts by crown ethers in nonpolar solvents has aroused interest in utilization of these compounds to facilitate and enhance rates of reactions in organic solvents. During the past fifteen years an enormous amount of study has been reported concerning the use of these novel ligands in catalysing organic synthetic reactions and in probing reaction mechanisms. The complexation of $KMnO_4$ with dicyclohexyl-18-crown-6 and the solubilization of this salt in benzene provides a convenient and efficient oxidant for the oxidation of organic compounds [18]. The solubilization of alkali halides in nonpolar solvents containing crown ethers has been shown to yield effective reagents used in a wide variety of substitution and elimination reactions ('Naked' anions) [19].

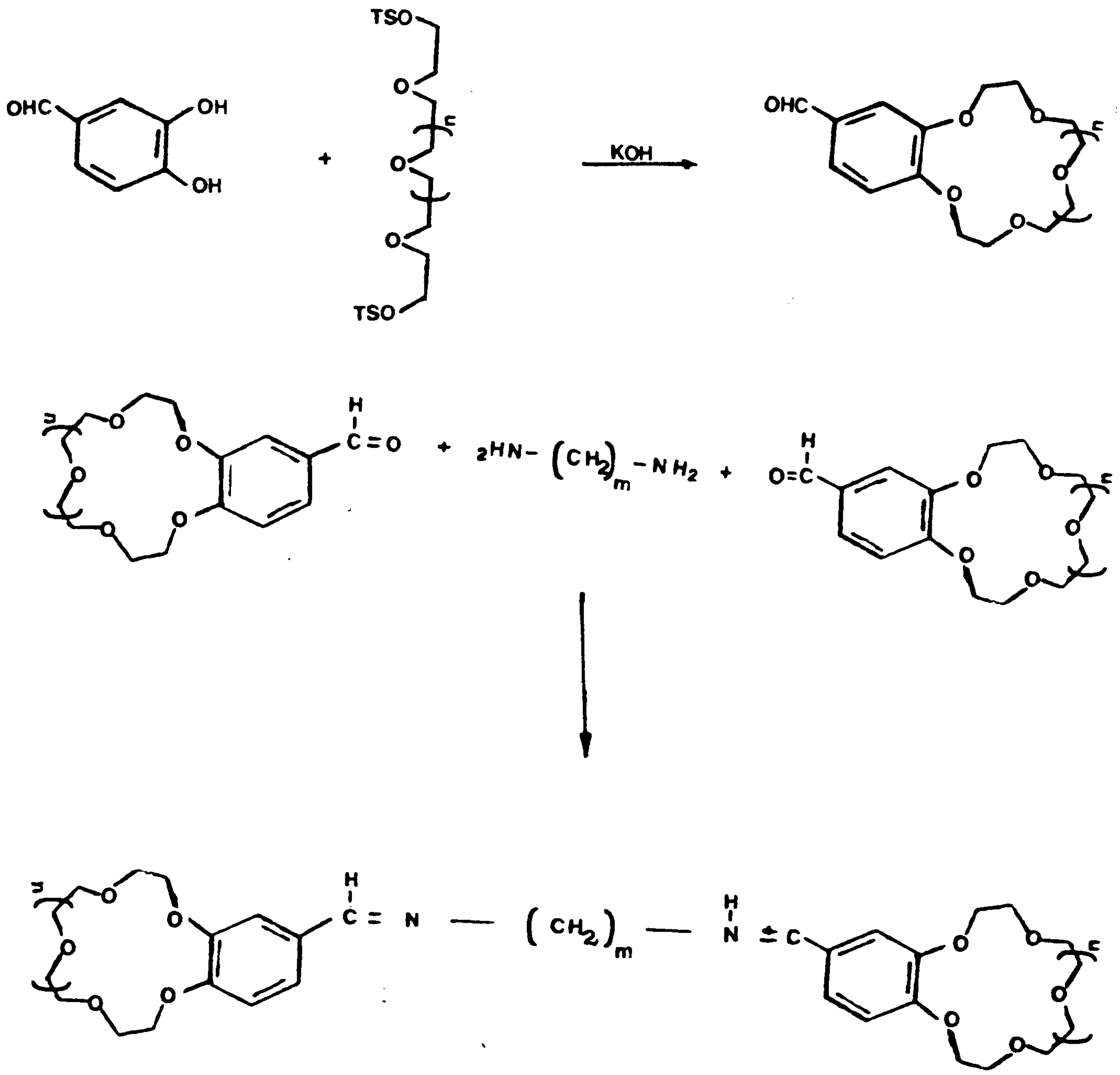
3.15.2 Analytical Chemistry

It is clear that the crown compounds should possess properties analogous to those of the macrocyclic antibiotics, e.g. the ability to form stable complexes with alkali metal cations, which have hydrophobic exterior and hydrophilic interior. They are also capable of ion-dipole interaction with the cations. Thus, they can function as an electroactive material in membranes and therefore, are important in ion-selective electrode applications. The crown compounds were used as ionophores in liquid I.S.Es, for the first time, by Rechnitz and Eyal [20,21], and later by Ryba and Petranek [22,23]. A variety of crown ethers with different ring size and varying numbers and nature of substituent groups has been tried. However, lower selectivity and narrow linear ranges compared to valinomycin and other naturally occurring antibiotics were observed. The aforementioned workers noted that by introducing substituent groups (methyl and propyl groups) into the benzene ring, the performance of the electrode was improved. This improvement was attributed to the flexibility of the ligand, resulted from the presence of those substituents which allows more favourable conformation. Davison [24] and Kumar [2] have investigated a variety of crown compounds. Promising results were achieved with electrodes based on different isomers of a tetramethyl substituents of dibenzo-18-crown-6. Nevertheless, all evidence suggest that good selectivity is not obtainable through tailoring the hole size of the crown ether or by changing the substituent groups in the crown ether molecules.

3.16 BIS-CROWNS AND THEIR USE IN ION-SELECTIVE ELETRODES

The observation that many crown ethers, e.g. benzo-15-crown-5, form ´sandwich´ type complexes with two crown moieties per cation [5] led to the preparation of bis-crown ethers and poly-crown ethers [25,26]. The former consist of two pendant crown ether moieties linked together via a bridge which contains different functional groups, e.g. ester [27], ether [28], amide [29], etc., whereas the polyethers comprise more than two units of monomers joined together through co-polymerisation of an amide or vinyl type linkage [30,26].

Recently, new types of similar compounds with various benzo crown ether moieties have been prepared [28]. By extraction and conductivity studies, Kimura et al. [31] confirmed the formation of ´sandwich´ type (2:1) complexes of bis-crown ethers and poly crown ethers with alkali metal cations. The increase in extractability and complexing ability of these compounds is attributed to the co-operative effect of the two adjacent crown ether rings. More recently, this type of compound with different linkages were impregnated into PVC matrices and their sensitivity and selectivity towards potassium [30,32] and cesium ions [31,32] were investigated. It was found that the high selectivity of bis-crown ethers over mono-crown ethers arises not only from the stability of the 2:1 complexes, but also from the lipophilicity of the bis-crown ethers. The results of these studies indicated that an appropriate design regarding ring size, variety of the heteroatoms, connectivity and flexibility of the linkage in crown ether derivatives may lead to electrodes with high selectivity, based on these compounds [32]. The long response time with poly-crown ethers and short lifetime of the bis-crown ethers with ester and amide linkage, in PVC-based electrodes, were ascribed to the low mobilities of the poly-crown ether-cation complexes, and the hydrolysis of functional groups in the bridge . Fung and Wang [30] reported a PVC electrode based on some bis-crown ethers to have selectivity comparable to the valinomycin based electrodes, i.e. 5.10^{-5} K^+/Na^+, and a cesium electrode to be more selective than existing ones. Recently, sodium selective electrodes based on bis-(12-crown-4)s have been reported. Shono et al. [33], reported a functional sodium electrode based on bis-crowns compounds by changing the internal solution of the electrode to a more concentrated solution. However, findings of the present study (Chapter Four) did not comply with their conclusion, and it appears that change of internal solution has no influence on the behaviour of the electrodes. The idea of deploying bis-crown ethers in membranes as neutral carriers was investigated in Newcastle [34] independently. Three homologous series of bis-crown ethers with different numbers of oxygen atoms in the crown ring were synthesised, and successfully characterised [35]. Two crown-ether units linked by two imine groups and a flexible alkyl chain with varying number of methylenes provided an important parameter, which can be altered, in order to optimise the electrode performance. Due to the lipophilicity of the alkyl chain the desolvation of the complex in the membrane media is enhanced. The preparation of bis-crown ethers is schematically presented below, (for details see T.Handyside's thesis[35]). Owing to the presence of the carbon-nitrogen double bond, a variety of isomers are possible; however, no isomers have been isolated [35].



n = 1 m = 5

Bis-(benzo-15-crown-5)5

The electrochemical behaviour of bis-(benzo-15-crown-5)2, 3,... and 12 in various matrices as a neutral carrier for the potassium selective electrode has been investigated [35]. Due to the time limit in the above project, the behaviour of the remaining series was examined in this work.

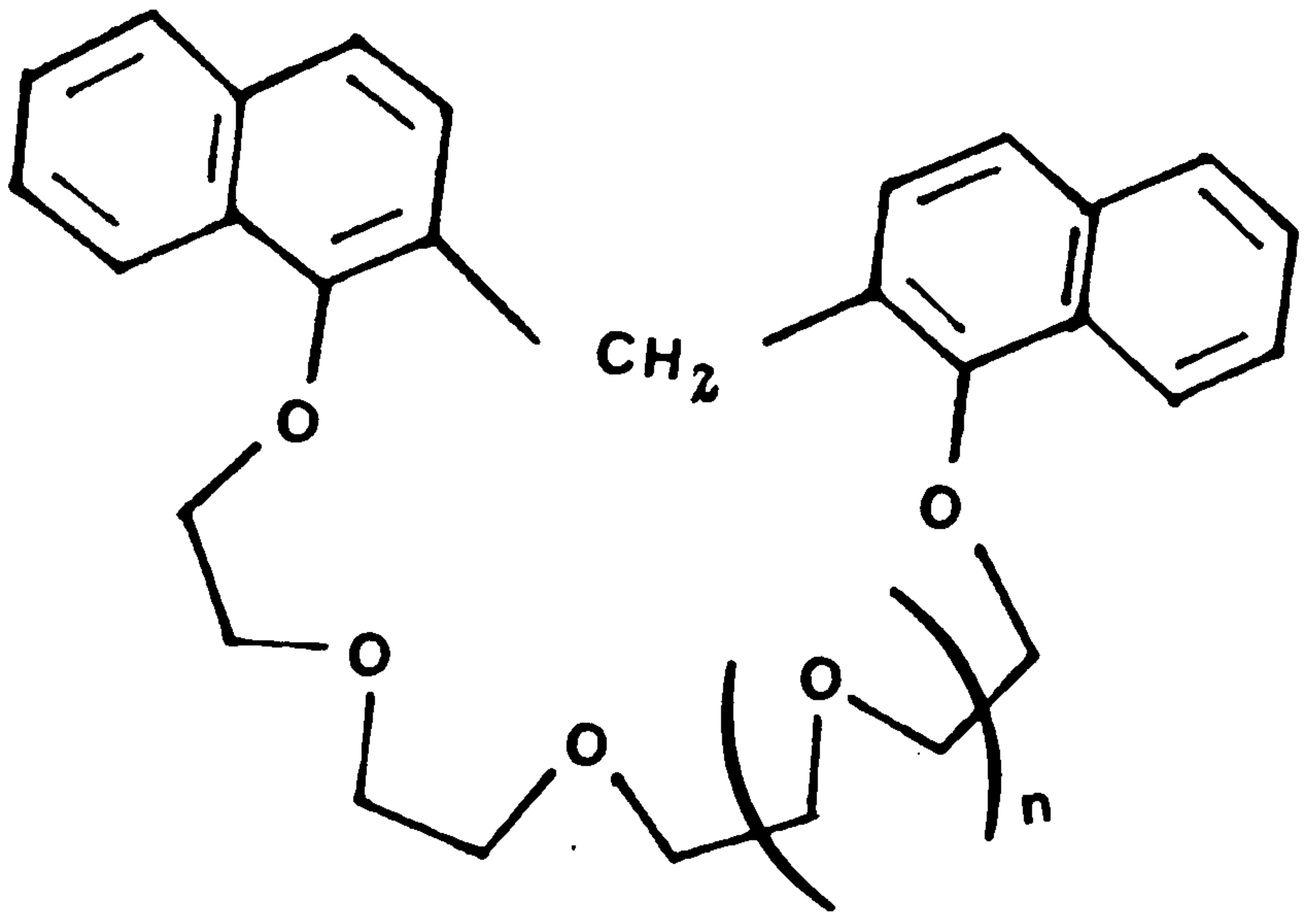
The PVC membranes were prepared by incorporating the following reagents, as active materials according to the method described in Chapter Two. The bis-benzo-crowns were:

Bis-(benzo-12-crown-4)4, 5, 7, 9 and 10

Bis-(benzo-18-crown-6)6 , 7, 8 and 9

Bis-(naphthol-crown)5, 6 and 7

The structure of bis-(naphthol-crown) is given below:



n = 1, 2 & 3

3.17 RESULTS

PVC membrane electrodes based on bis-crown ethers compounds were constructed. The electrochemical behaviour of the electrodes was examined. Calibration slopes, selectivity and response times have been taken as the criteria for good performance. Those electrodes which failed to show at least a near Nernstian slope were not investigated for selectivity and detailed studies. The electrochemical cell, and selectivity calculations have been explained in detail in Chapter Two. Experiments on the effect of the various plasticizers, in an attempt to improve the electrode performance, were carried out for some electrodes.

3.17.1 PVC Electrodes Based on Bis-(naphthol-crown)5, 6 and 7

Electrodes based on bis-(naphthol-crown)5, 6 and 7 showed Nernstian response, approximately 66 mV/decade with linear range between pK:1-3, 1-5 and 1-4.5 respectively. The selectivity coefficients for all systems were found to be small in the following order: k^{pot}_{NaK} crown7 > crown6 > crown5 . The response times were very short, less than 30 seconds. Detailed results, calibration and selectivity curves are shown in Table 3.10 and Fig 3.27.

Due to the nearer Nernstian slope and higher selectivity of the bis-(naphthol-crown)7 in comparison to the others, the effect of two different plasticizers on the behaviour of the electrode was examined (Fig 3.28). The slope and linearity did not alter, and no significant difference in the selectivity was observed (Fig 3.28).

3.17.2 PVC Electrodes Based on Bis-(benzo-18-crown-6)6, 7, 8 and 9

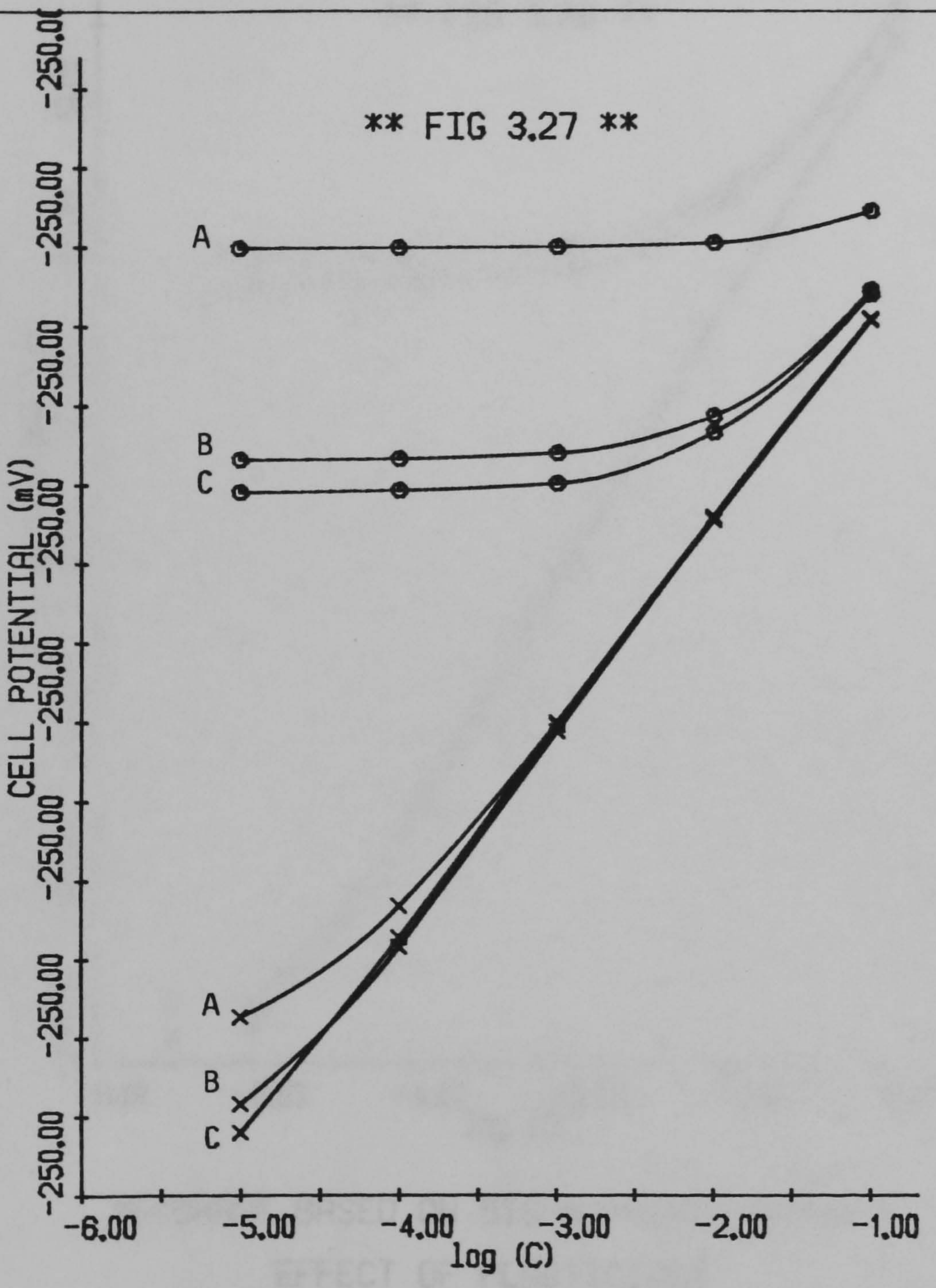
The response curves of the electrodes towards various concentration of potassium ions are shown in Fig 3.29 and their performance is summarized in Table 3.11. The primary ion calibration slope was found to be 40, 38, 38 and 46 mV/decade respectively for the above ligands. A linear range of 10^{-1} to 10^{-3} mol/dm^3 was obtained for all electrodes. Response times were very long (more than 5 minutes). The stability of the electrode potential was within ±3 mV with large drifts. The reproducibility of the electrode response for some electrodes was very poor; for example, the electrode

Table 3.10
Calibration and Selectivity
Bis-Naphthol Crowns

Bis-Naphthol Crowns (n)	Calib. KCl Slope (mV/decade)	Linear Range(pC)	Select. (KCl+NaCl) Slope (mV/decade)	Linear Range(pC)	k^{pot}_{KNa}
n = 5 DBP	35.0, 58.0, 65.0, 62.5	1 - 3.5	0.3, 0.2, 0.9, 10.0		6×10^{-1}
n = 6 DBP	62.0, 67.0, 65.0, 63.0	1 - 5.0	0.4, 1.7, 11.7, 39.6	1 - 2	6×10^{-2}
n = 7 BDP	66.0, 68.0, 68.0, 62.5	1 - 4.5	0.7, 2.1, 16.2, 43.6	1 - 2	2×10^{-2}
n = 7 BEHS	48.0, 67.0, 65.0, 61.9	1 - 4.5	.3, 3.1, 18.9, 45.8	1 - 2	2.5×10^{-2}

The figures are for pK ranges 4-5, 3-4, 2-3 and 1-2 in mV

**** FIG 3.27 ****



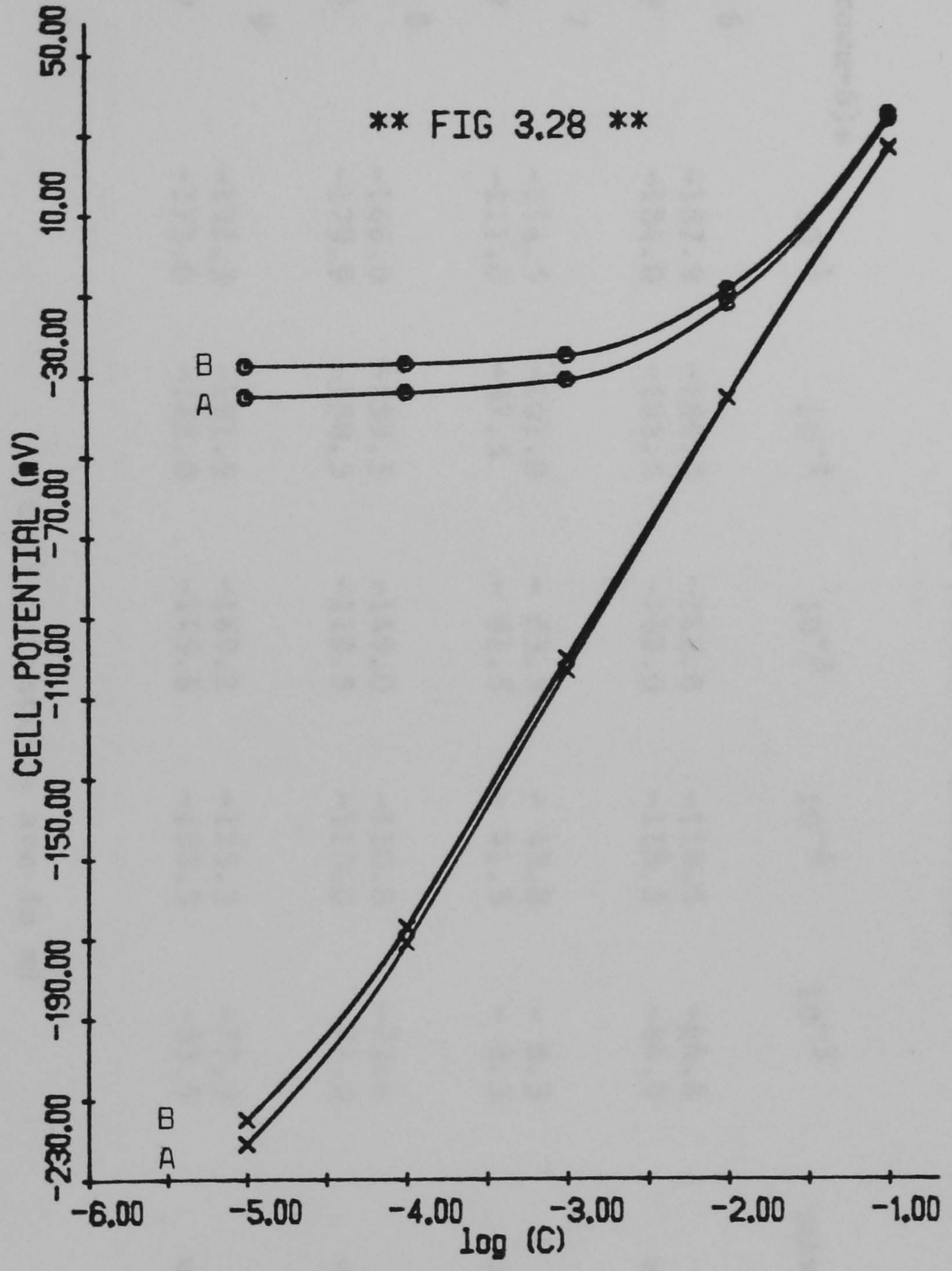
MEMBRANES BASED ON BIS-NAPHTHOL-CROWNS

× = CALIB. (KCl) ⊙ = SELEC. (0.5 mol/dm^{3}NaCl)

A = BIS-NAPHTHOL-CROWN-5

B = BIS-NAPHTHOL-CROWN-6

C = BIS-NAPHTHOL-CROWN-7



MEMBRANE BASED ON BIS-NAPHTHOL-CROWN-7

EFFECT OF PLASTICIZER

× = CALIB. (KCl) ⊙ = SELEC. (KCl+0.5 mol/dm^3 NaCl)

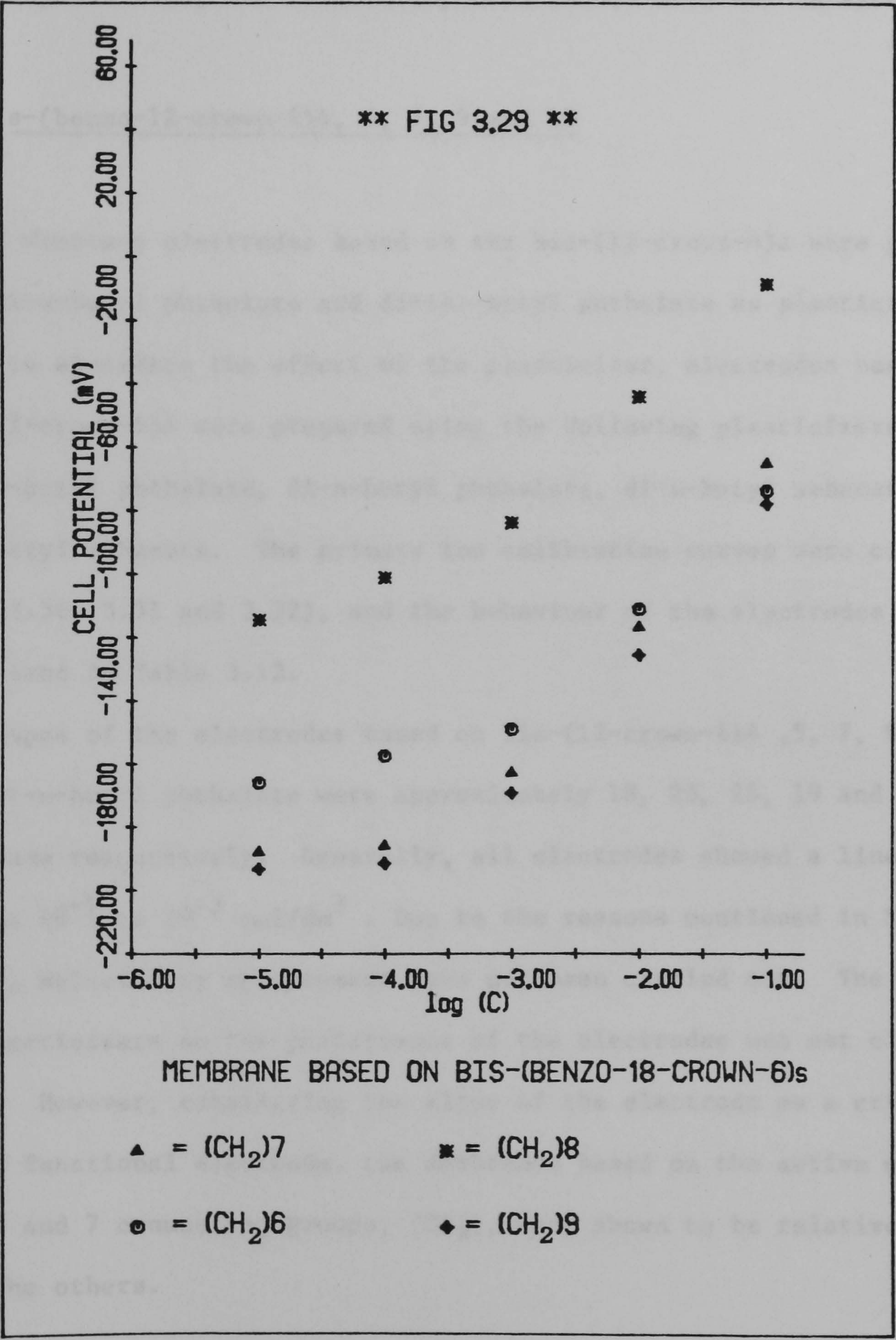
A = MEMBRANE WITH DBP

B = MEMBRANE WITH BEHS

Table 3.11
Calibration (KCl mol/dm^3)
Bis-(benzo-18-crown-6)s

Bis-(crown-6)s	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	Mixed Solution
n = 6						
	-187.9	-186.0	-162.8	-116.5	-64.8	
BDP	-184.0	-185.5	-162.0	-118.5	-64.0	unstable
n = 7						
	-114.5	-101.0	- 83.5	- 43.8	- 8.3	
DBP	-111.0	-97.5	- 81.5	- 41.5	- 8.3	unstable
n = 8						
	-166.0	-159.5	-149.0	-110.8	-73.4	
DBP	-179.9	-158.5	-119.5	-110.0	-74.0	unstable
n = 9						
	-193.3	-191.5	-169.2	-125.3	-77.5	
DBP	-173.0	-172.0	-149.8	-105.5	-53.5	unstable

Cell Potentials are in mV



** FIG 3.29 **

CELL POTENTIAL (mV)
60.00
20.00
-20.00
-60.00
-100.00
-140.00
-180.00
-220.00
-6.00
-5.00
-4.00
-3.00
-2.00
-1.00
log (C)
MEMBRANE BASED ON BIS-(BENZO-18-CROWN-6)s
▲ = $(CH_2)7$
✱ = $(CH_2)8$
⊚ = $(CH_2)6$
◆ = $(CH_2)9$

based on bis-(12-crown-6)7 . Due to the low slope, unstable potetial and long response time, the selectivity measurments were not carried out.

3.17.3 Bis-(benzo-12-crown-4)4, 5, 7, 9 and 10

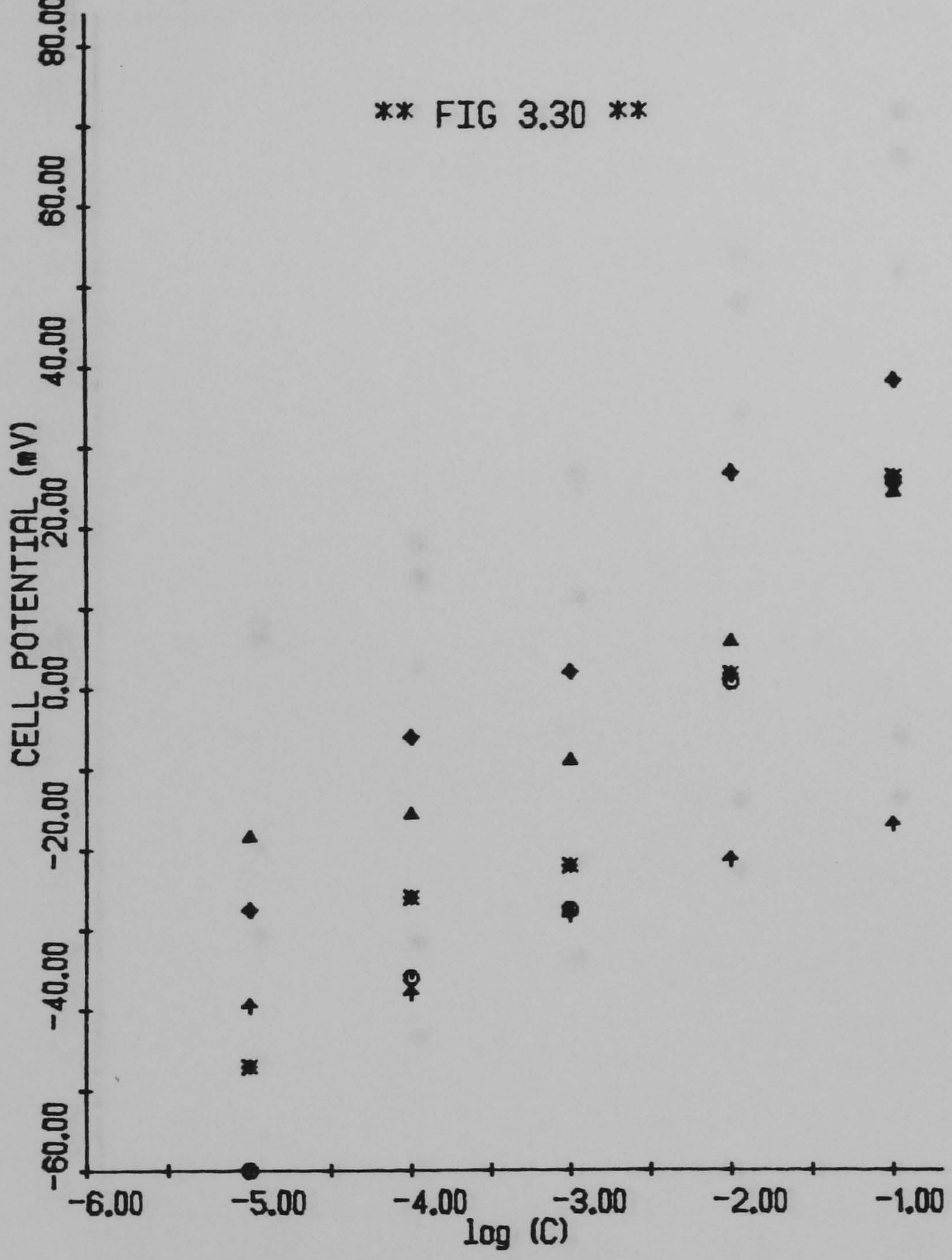
PVC membrane electrodes based on the bis-(12-crown-4)s were prepared, with di-n-butyl phthalate and di-iso-octyl phthalate as plasticizers. In order to elucidate the effect of the plasticizer, electrodes based on bis-(12-crown-4)4 were prepared using the following plasticizers: di-iso-octyl phthalate, di-n-butyl phthalate, di-n-butyl sebacate and di-n-octyl sebacate. The primary ion calibration curves were constructed (Figs 3.30, 3.31 and 3.32), and the behaviour of the electrodes is summarized in Table 3.12.

The slopes of the electrodes based on bis-(12-crown-4)4 ,5, 7, 9 and 10 with di-n-butyl phthalate were approximately 18, 25, 26, 19 and 10 mV/decade respectively. Generally, all electrodes showed a linear range between 10^{-1} to 10^{-3} mol/dm^3 . Due to the reasons mentioned in Section 3.17.2, selectivity measurement have not been carried out. The effect of the plasticizers on the performance of the electrodes was not clear (Fig 3.32). However, considering the slope of the electrode as a criterion for a good functional electrode, the membranes based on the active material with 5 and 7 connecting groups, (CH_2), were shown to be relatively better than the others.

Table 3.12
Calibration (KCl mol/dm^3)
Bis-(benzo-12-crown-4)s in Different Plasticizers

Bis-(crown-4)s	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}
n = 4 DBP	-24.5	-18.5	-15.7	-8.9	+6.0	+24.5
n = 4 DBS	-42.0	-35.0	-21.5	-8.0	+5.8	+26.8
n = 4 DOS	- 8.0	+ 3.0	+15.0	+21.0	+32.8	+51.5
n = 5 DOS	-16.0	-29.3	- 7.0	-1.5	+24.5	+42.0
n = 5 DBP	-42.0	-47.0	-26.0	-22.0	+2.0	+26.5
n = 5 DOP	- 6.0	- 2.0	+ 8.3	+17.0	+44.0	+62.0
n = 7 DBP	-51.7	-60.0	-36.0	-27.5	+1.0	+26.0
n = 7 DOP	-10.0	- 3.5	+ 4.0	+16.0	+3.8	+56.2
n = 9 DBP	-29.0	-27.5	- 6.0	+2.2	+27.0	+38.5
n = 9 DOP	-47.0	-40.5	-41.5	-31.5	-23.8	-15.7
n = 10 DBP	-46.5	-39.5	-37.0	-28.2	-21.2	-16.8
n = 10 DOP	-59.5	-56.5	-53.5	-43.5	-32.5	-23.5

Cell Potentials are in mV



** FIG 3.30 **

MEMBRANE BASED ON BIS-(BENZO-12-CROWN-4)s

WITH DBP

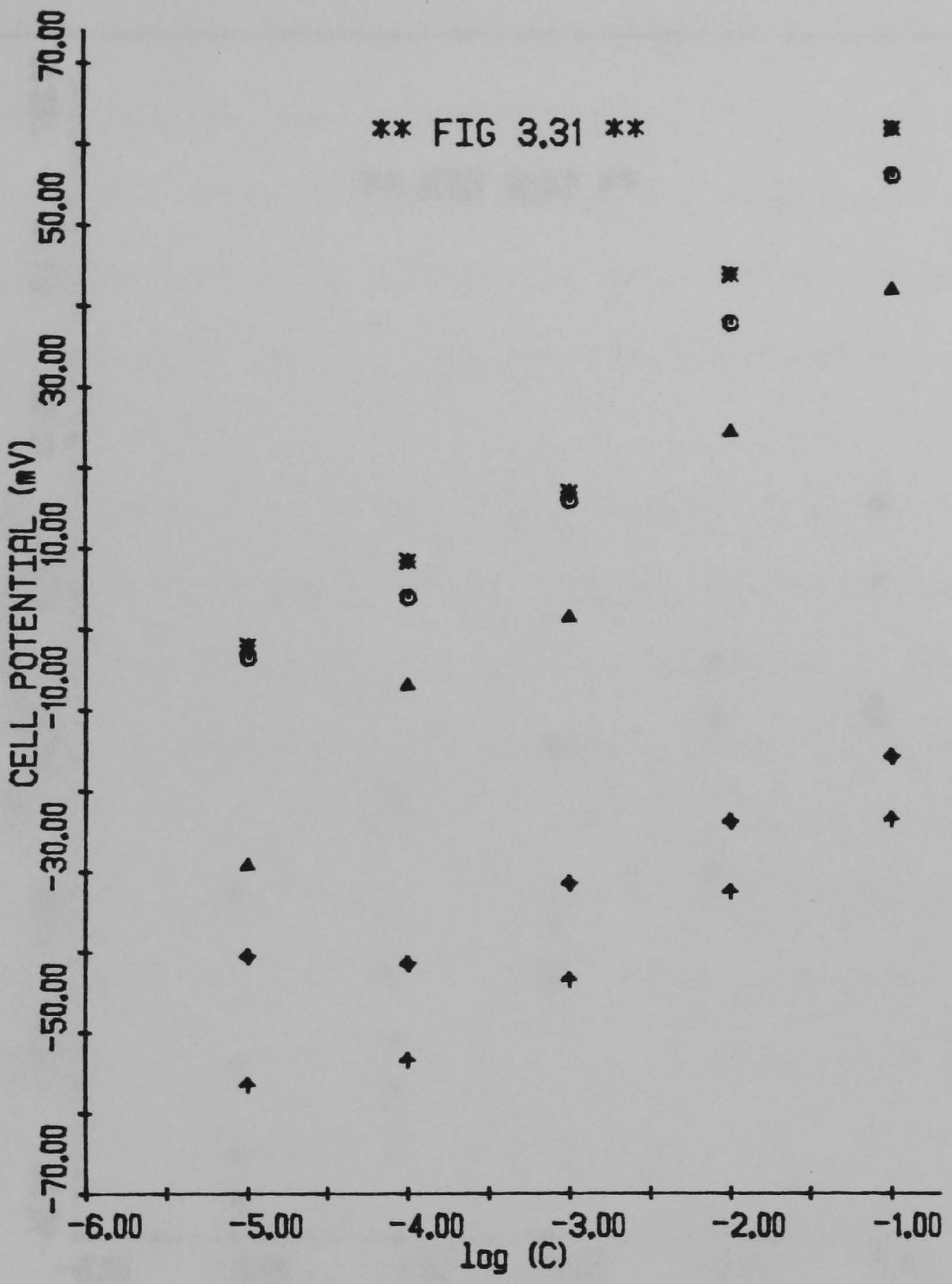
▲ = $(CH_2)4$

⊙ = $(CH_2)7$

✱ = $(CH_2)5$

◆ = $(CH_2)9$

✦ = $(CH_2)10$



** FIG 3.31 **

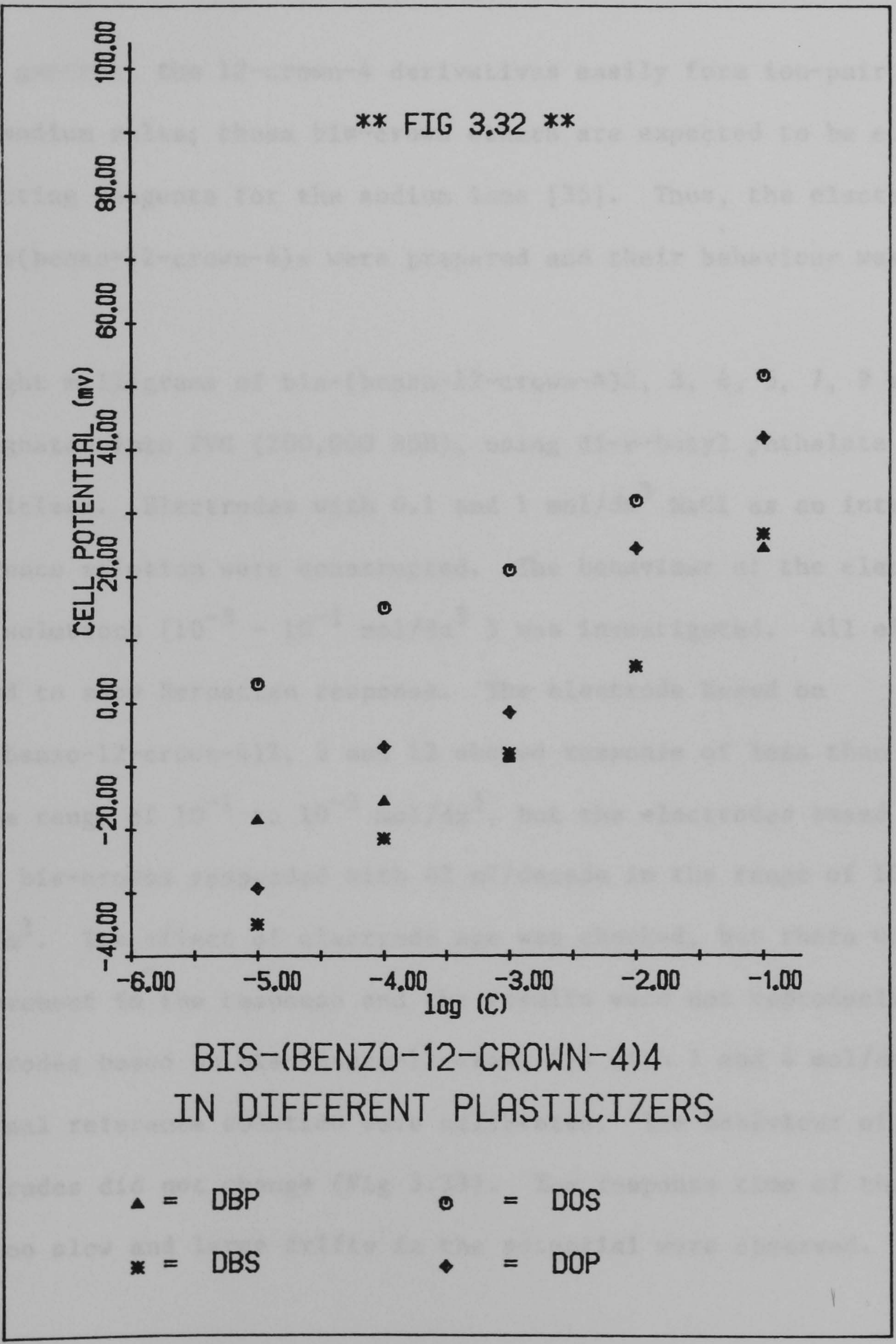
MEMBRANE BASED ON BIS-(BENZO-12-CROWN-4)s

WITH DOP

▲ = $(CH_2)4$ ⊙= $(CH_2)7$

✱ = $(CH_2)5$ ◆= $(CH_2)9$

✦ = $(CH_2)10$



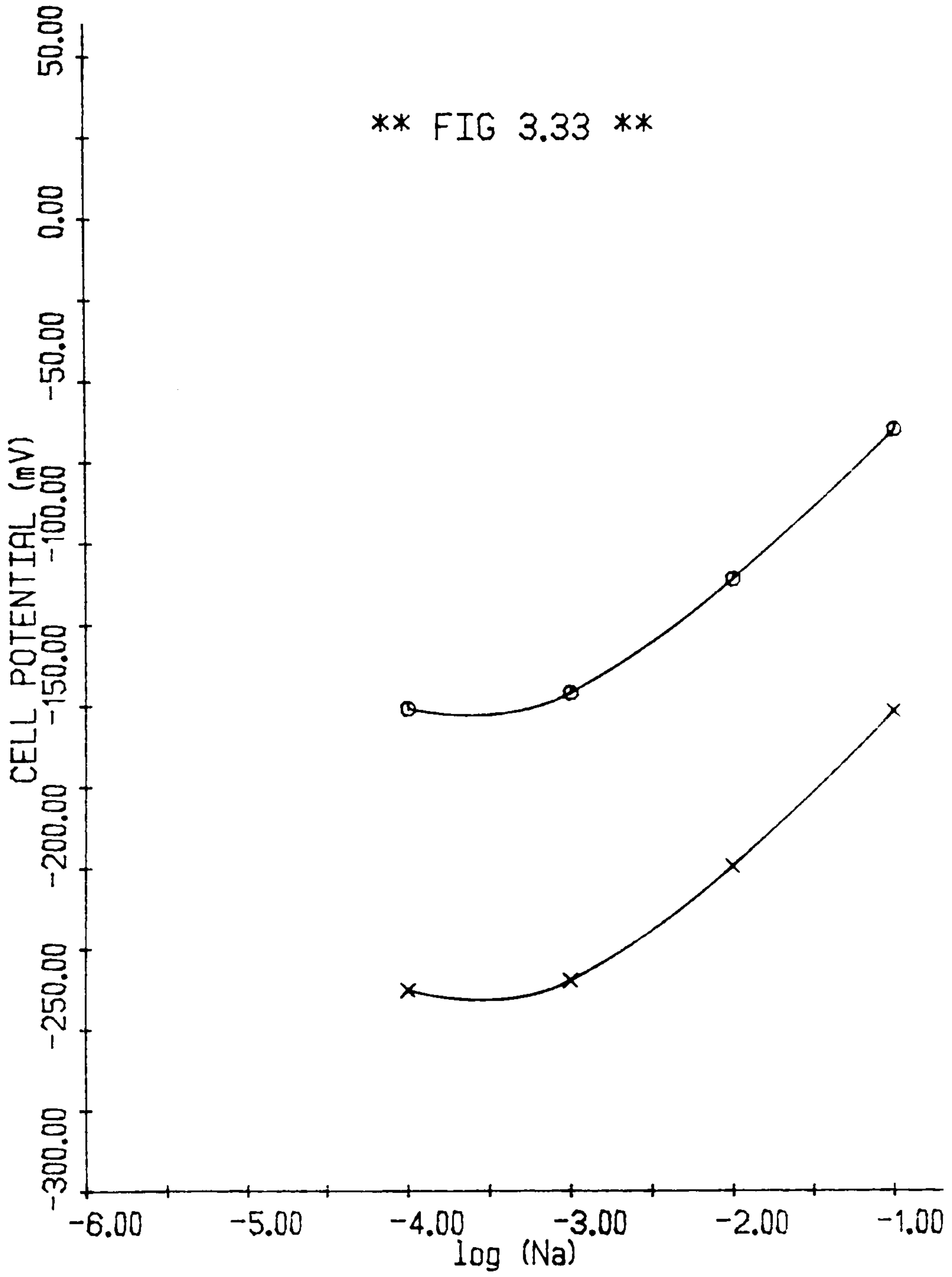
** FIG 3.32 **

BIS-(BENZO-12-CROWN-4)4
IN DIFFERENT PLASTICIZERS

3.18 SODIUM SELECTIVE PVC MEMBRANE ELECTRODE BASED ON BIS-(BENZO-12-CROWN-4)S

In general, the 12-crown-4 derivatives easily form ion-pair complexes with sodium salts; these bis-crown ethers are expected to be effective as extracting reagents for the sodium ions [35]. Thus, the electrodes based on bis(benzo-12-crown-4)s were prepared and their behaviour was examined.

Eight milligrams of bis-(benzo-12-crown-4)2, 3, 4, 5, 7, 9 and 12 was impregnated into PVC (200,000 BDH), using di-n-butyl phthalate plasticizer. Electrodes with 0.1 and 1 mol/dm^3 NaCl as an internal reference solution were constructed. The behaviour of the electrodes in NaCl solutions (10^{-5} - 10^{-1} mol/dm^3) was investigated. All electrodes failed to show Nernstian response. The electrode based on bis-(benzo-12-crown-4)2, 3 and 12 showed response of less than 10mV/decade in the range of 10^{-1} to 10^{-2} mol/dm^3, but the electrodes based on the other bis-crowns responded with 42 mV/decade in the range of 10^{-1} to 10^{-3} mol/dm^3. The effect of electrode age was checked, but there was no improvement in the response and the results were not reproducible. The electrodes based on bis-(benzo-12-crown-4)4 with 1 and 4 mol/dm^3 NaCl as internal reference solution were calibrated. The behaviour of the electrodes did not change (Fig 3.33). The response time of the electrodes was too slow and large drifts in the potential were observed.



** FIG 3.33 **

MEMBRANE BASED ON BIS-(BENZO-12-CROWN-4)4

⊙ = 1 mol/dm^3 NaCl AS INNER SOLUTION

× = 4 mol/dm^3 NaCl AS INNER SOLUTION

3.19 DISCUSSION

It is evident that poly- and bis-crown ethers can exhibit a kind of co-operative effect in the formation of a 2:1 crown-ion complex, and their ion extractability is much enhanced in comparison to that of the monocyclic crowns [37]. This extractability property depends, apart from the ring size, on the functional group on the benzo group and on the lipophilicity of the connecting groups, i.e. imine groups and the number of (CH)s, as has emerged from this study. From U.V. extraction studies, the bis-(benzo-12-crown-4)s and bis-(benzo-18-crown-6)s were not found to be very effective reagents for any alkali ions [35]. The main parameter in the structure of these compounds, which will provide a series of isomers, is the existence of the double bonds. Because of the change in conformation within the molecule, the complexation behaviour of these isomers is not the same. The domination of the unfavourable conformation might be the reason behind this unexpected behaviour in both extraction and I.S.E. studies. In I.S.E. studies, the viscosity of the PVC media reduces the mobilities of the species in the membrane. However, the electrode with bis-(naphthol-crown)5, 6 and 7 showed better response in pure KCl solution with a low selectivity towards sodium ions. The electrodes based on the bis-(benzo-18-crown-6)6, 9 with slopes around 49 mV/decade were more promising. PVC electrodes based on bis (benzo-12-crown-4)s were not functional. Further studies along the line of present study may be of value in the recognition of the effectiveness of the bis-crown compounds, provided the isomers are isolated.

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CHAPTER FOUR

INNER REFERENCE SYSTEM AND SELECTIVITY OF THE K^+ / PVC MEMBRANE

Various aspects of the valinomycin-based potassium ion-selective electrode have been studied especially, selectivity, membrane composition and anion interference [1,2,3,4,5]. There has been, however, a lack of study on the role of inner filling solutions. A greater understanding about their role might provide some information concerning the mechanism of the charge transport in electrodes based on neutral carrier materials. This chapter is concerned with the influence of the internal filling solution on the behaviour of electrodes based on neutral ionophores and ion-exchangers. In the second part of this chapter, the presence of impurities in membrane components as a source of negative sites, is proposed to be responsible for the cation selectivity and charge balance of the membrane. Finally an attempt has been made to clarify anion interference in potassium PVC / valinomycin membrane electrodes.

4.1 INTRODUCTION PART (I)

In general, classical ion-selective electrodes consist of a thin conducting or non-conducting layer at the end of a tube (glass, plastic, etc.), acting as a selective membrane, an internal reference electrode and an internal filling solution. The reference filling solution must contain the ion to which the reference electrode is reversible, and at the same time it should have the corresponding ion which would be sensed. Usually, the reliable silver-silver chloride electrode is used as a reference electrode, and the filling solution is the chloride salt, e.g. MCl, where M is the cation to which the membrane responds. The potential of M^+ ion-selective electrode is given by eqn.(4.1).

$$E = E^0 - k \ln (Cl^-)' - k \ln (M^+)' + k \ln (M^+)'' \qquad (4.1)$$

here, E^0 is the standard potential of the Ag/AgCl/Cl^- electrode. k = RT/F and Cl^- ,$(M^+)'$ and $(M^+)''$ are the activities of the anions and cations in the internal (′) and external (″) solutions. The first three terms on the right hand side of eqn.(4.1) are the components of the internal system, which account for the processes occurring at the internal reference electrode and inner surface of the membrane. It is seen from eqn.(4.1), that the reference system must be well defined and a primary requirement is to have a constant or, at least, a slowly varying potential [6]. This is the basic assumption in the theoretical treatment of all models of membrane potentials. However, other electrode variations, such as mercury-in glass electrodes [7], Selectrodes® [8] and coated-wires [9], have shown satisfactory results and good response comparable with classical electrodes. This suggests that ill-defined internal systems from a thermodynamic point of view might still be used as a reference system. Nevertheless, the use of similar solutions on both sides of the membrane has been recommended [7]. The purpose of this study is to determine whether the behaviour of electrodes could be improved by changing the inner filling solution. The present work was aimed at studying:

a) The effect of varying the concentration of the inner solution on the response range, selectivity and response time of the following electrodes:

1. K^+ / PVC I.S.E. based on valinomycin

2. K^+ / PVC I.S.E. based on KTPCPB

3. Ca^{2+} / PVC I.S.E. (Philips Ltd.)

b)The effect of various chloride salts as inner solution on the behaviour of the aforementioned electrodes.

The internal filling solutions chosen were as follows:

KCl, NaCl, LiCl, CsCl, RbCl, $MgCl_2$, $BaCl_2$, $AlCl_3$, Tris/HCl buffer, $CaCl_2$, tetraethyl ammonium chloride (T.E.A.Cl) and mercury.

4.2 EXPERIMENTAL

The experimental details described here are in addition to the general description discussed in Chapter Two. Membrane No.4 was used for the construction of K^+ /PVC electrode. The composition, preparation and construction of the electrode have been outlined in Chapters Two and Three. For each set of experiments, the internal solution was emptied and, after several washings with triple-distilled water, it was filled with the next chosen solution. Preliminary tests showed that the immediate respose of a newly filled electrode was not stable and a drift was observed. Thus, all electrodes, after replacing the inner solution, were immersed in 10^{-3} mol/dm^3 KCl solution overnight. The cell potentials were recorded every five minutes. Each set of results is the average of at least two sets of experiments. The same electrochemical cell with calomel electrode and extra salt bridge was used for the potassium electrode measurements, but for the Ca^{2+} I.S.E. the extra salt bridge was removed. The Ca^{2+} I.S.E. was constructed according to the Philips manual. The finished electrode is shown in Fig 4.1. The calibration and selectivity curves were obtained by plotting the log of the concentration of the potassium ions vs. the cell potential, but in the case of Ca^{2+} I.S.E., the log of the activity was plotted. The activity coefficients were calculated from eqn.(4.2) [11]:

$$\log \gamma = - \frac{0.51\ I^{1/2}}{1 + 1.31\ I^{1/2}} + 0.06\ I \qquad (4.2)$$

where I is the ionic strength of the sample solution. The standard potential of the electrodes (E^0) and slope of the curves were obtained by a linear regression applied to the linear part of the calibration and selectivity plots. The values are shown in Tables 4.1 to 4.6.

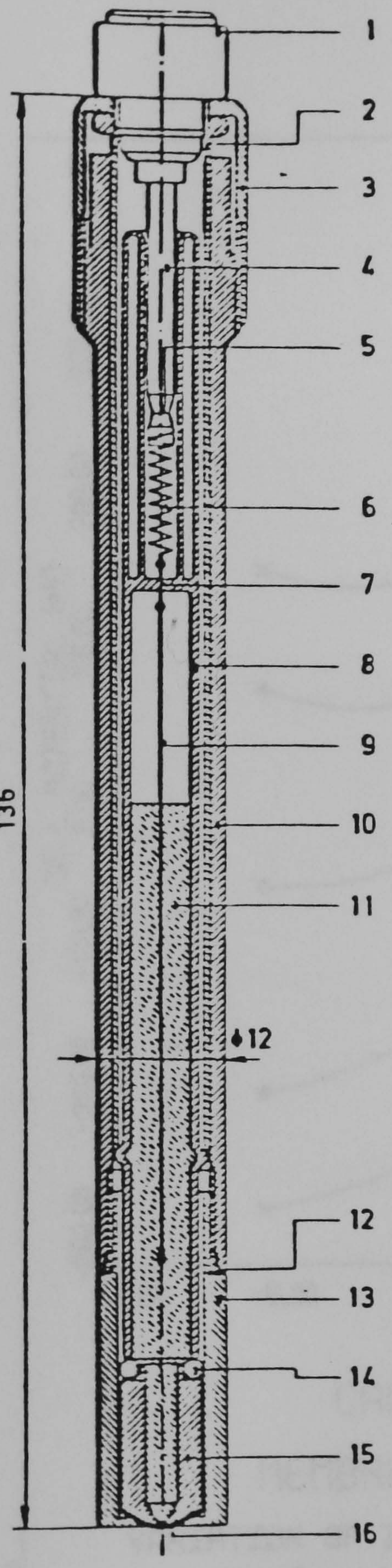
4.3 RESULTS

The following results were obtained during the calibration and selectivity measurements in pure solutions of KCl and mixed solutions (KCl + 0.45 mol/dm^3 NaCl). The valinomycin electrode with different internal solutions, either dilute filling solutions (10^{-1} - 10^{-5} mol/dm^3 KCl) or with various chloride salts, showed a Nernstian response in its dependence upon the potassium concentration. It also gave good reproducible results for measurements obtained after a long time . Even after two days, no significant change was observed in the electrode potential in the activity range of 10^{-1} to 10^{-4} mol/dm^3. The value of the slope was changed by +1 mV. The calibration and selectivity patterns are represented in Figs 4.1a, 4.1b, 4.2a, 4.2b, 4.3a and 4.3b and in the corresponding Tables 4.1, 4.2 and 4.3.

The calibration and selectivity measurements for K^+ / PVC electrodes based on the ion-exchanger also resulted in values approaching a Nernstian response. For electrodes with dilute filling solutions, less than 10^{-3} mol/dm^3, the slope diminishes on decreasing the concentration of the internal solution. For example, electrodes with 10^{-4} mol/dm^3 KCl indicate a slope of 54 mV/decade in the concentration range of 10^{-3} - 10^{-1} mol/dm^3 (Fig 4.4a and Table 4.4).

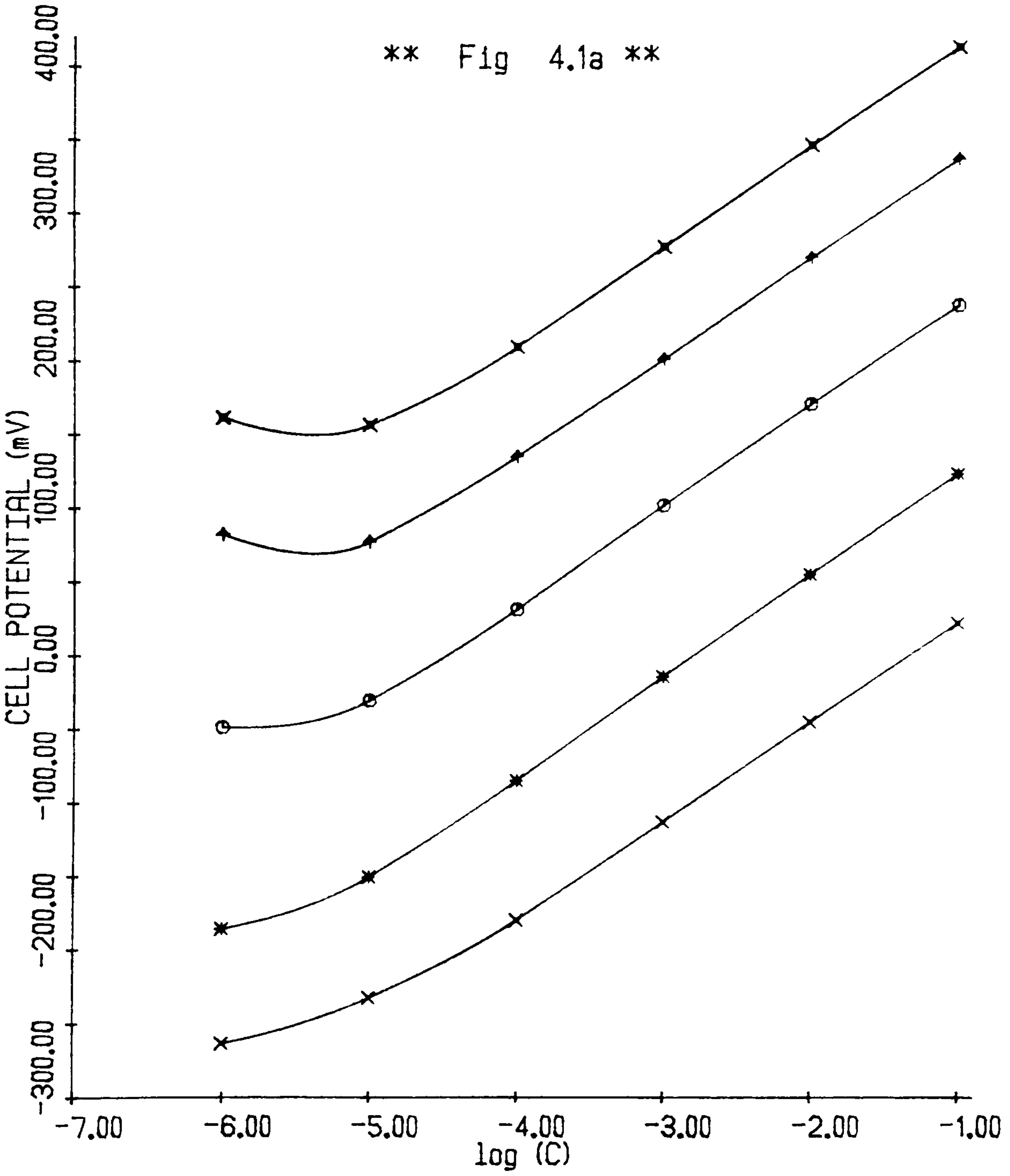
In measurements conducted over a long period of time, variations of more than 10 mV in potential in the concentration range of 10^{-4} - 10^{-1} mol/dm^3 were observed. Due to this fact, repetition of calibration of the electrode after measurements lasting longer than one day is required. As far as the behaviour of the electrodes with different chloride salts is concerned, the slope was found to be nearer to the theoretical one except for 0.1 mol/dm^3 NaCl where the slope was 54.3 mV/decade and for the RbCl it was 59.7 mV/decade in the concentration range of 10^{-3} - 10^{-1} mol/dm^3. The selectivity curves for both dilute filling solutions and various chloride salts were found to be similar and unchanged. The irreproducibility of the potential for this electrode, K^+ /ion-exchanger, might be attributed to the leakage of the ion-exchanger into the sample solutions. Detailed results are given in Figs 4.4a 4.4b, 4.5a and 4.5b and Tables 4.4 and 4.5. The response times for both electrodes were fast, but comparatively , the electrode based on the ion-exchanger showed slower response than the valinomycin-based one. Finally, a K^+ / PVC valinomycin electrode with Cu/Hg inner system was constructed. After conditioning in 10^{-3} mol/dm^3 KCl for 12 hours, the calibration curves were performed (Fig 4.7a). The reproducibility, response time and slope were found to be similar to those electrodes with other inner reference systems.

Similar experiments as for K^+ / PVC I.S.Es were carried out on the Ca^{2+} I.S.E. The effect of varying the inner concentration between 10^{-1} - 10^{-5} mol/dm^3 $CaCl_2$, and varying the chloride salts, was found to be negligible except for concentration range of 10^{-5} - 10^{-6} mol/dm^3, where the potential was not stable. A Nernstian slope of $\simeq$ 28 mV/decade in the activity range of 10^{-1} - 10^{-5} mol/dm^3 $CaCl_2$was obtained for the electrode with dilute inner solutions. The potential over a long time was stable and after two days the slope of the electrode was unchanged. The slope with different internal chloride salts was smaller but gave near Nernstian response, $\simeq$ 26 mV/decade, in the activity range of 10^{-1} - 10^{-5} mol/dm^3 $CaCl_2$. The response was fast and no noticeable differences were observed with different inner filling solutions. Detailed results are shown in Figs 4.6a, 4.6b and Table 4.6.



1. Plug for shielded cable
2. Metal shield
3. Stainless steel cap
4. Metal pin
5. Silver contacts
6. Metal spring
7. Platinum to glass seal
8. Glass insert
9. Silver wire, chlorinated
10. Hostaform C sleeve
11. 0.01 M aqueous KCl
12. O-Ring
13. Membrane support (Hostaform C)
14. O-Ring
15. Plug with cylindric cavity to fix membrane
16. PVC Membrane

Fig 4.1



** Fig 4.1a **

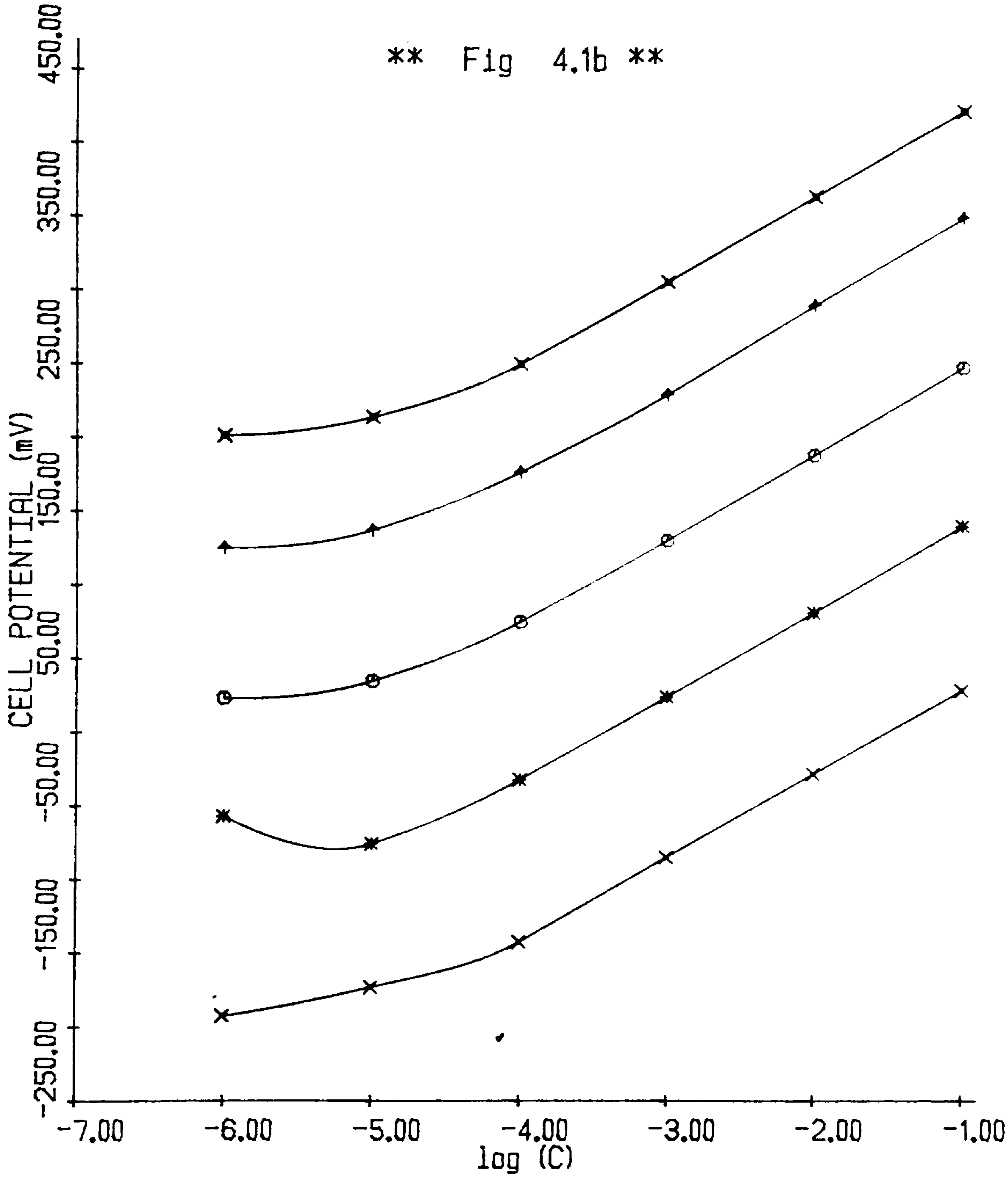
CALIBRATION CURVES

MEMBRANE: PVC/VALINOMYCIN

VARIATION OF INNER SOLUTION CONCENTRATION (KCl)

× = 10^{-1} mol/dm^3 ✱ = 10^{-2} mol/dm^3
⊙ = 10^{-3} mol/dm^3 + = 10^{-4} mol/dm^3
× = 10^{-5} mol/dm^3

** Fig 4.1b **



SELECTIVITY CURVES

MEMBRANE: PVC/VALINOMYCIN

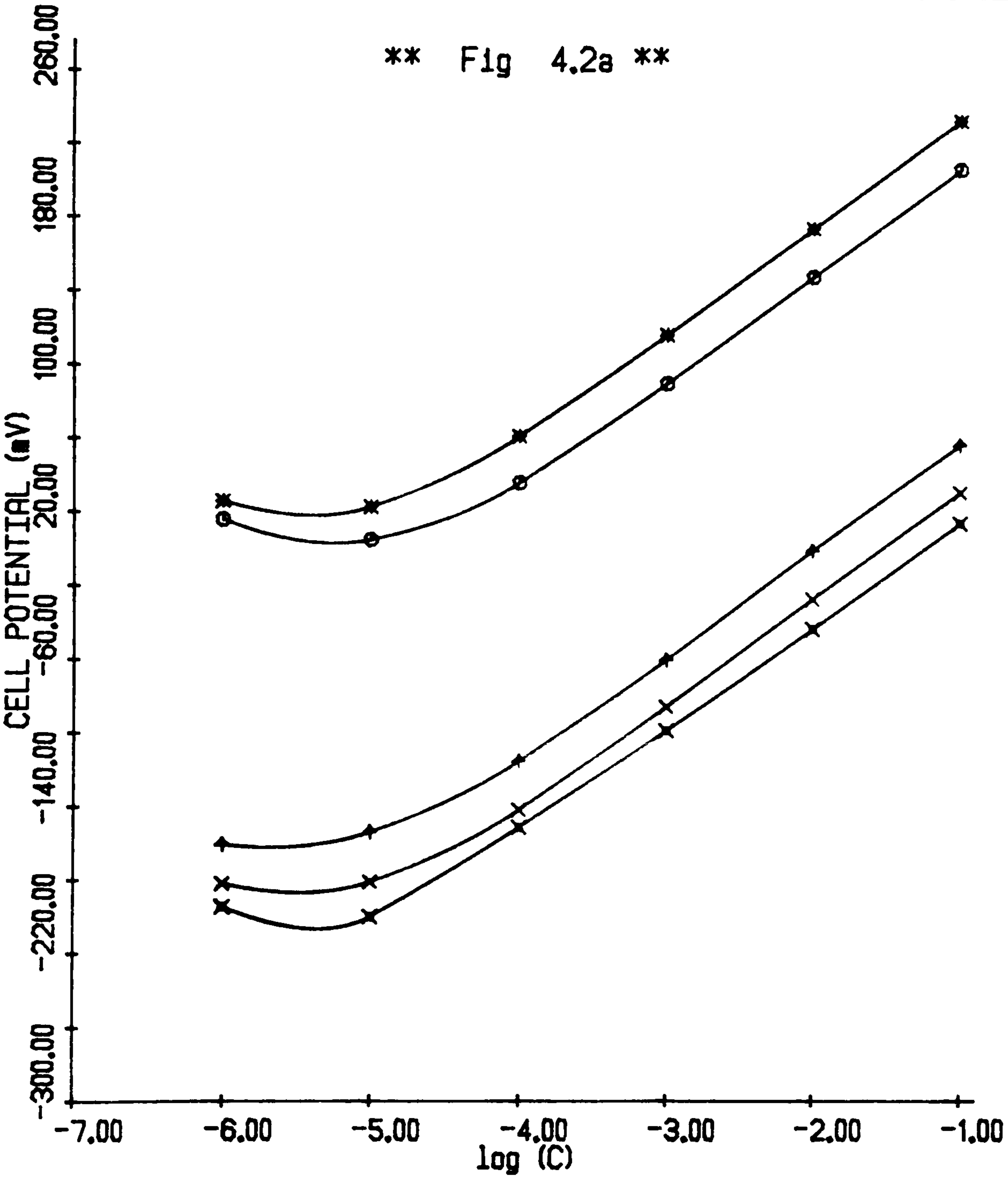
VARIATION OF INNER SOLUTION CONCENTRATION (KCl)

× = 10^{-1} mol/dm^3 ✱ = 10^{-2} mol/dm^3

⊙ = 10^{-3} mol/dm^3 + = 10^{-4} mol/dm^3

✕ = 10^{-5} mol/dm^3

** Fig 4.2a **



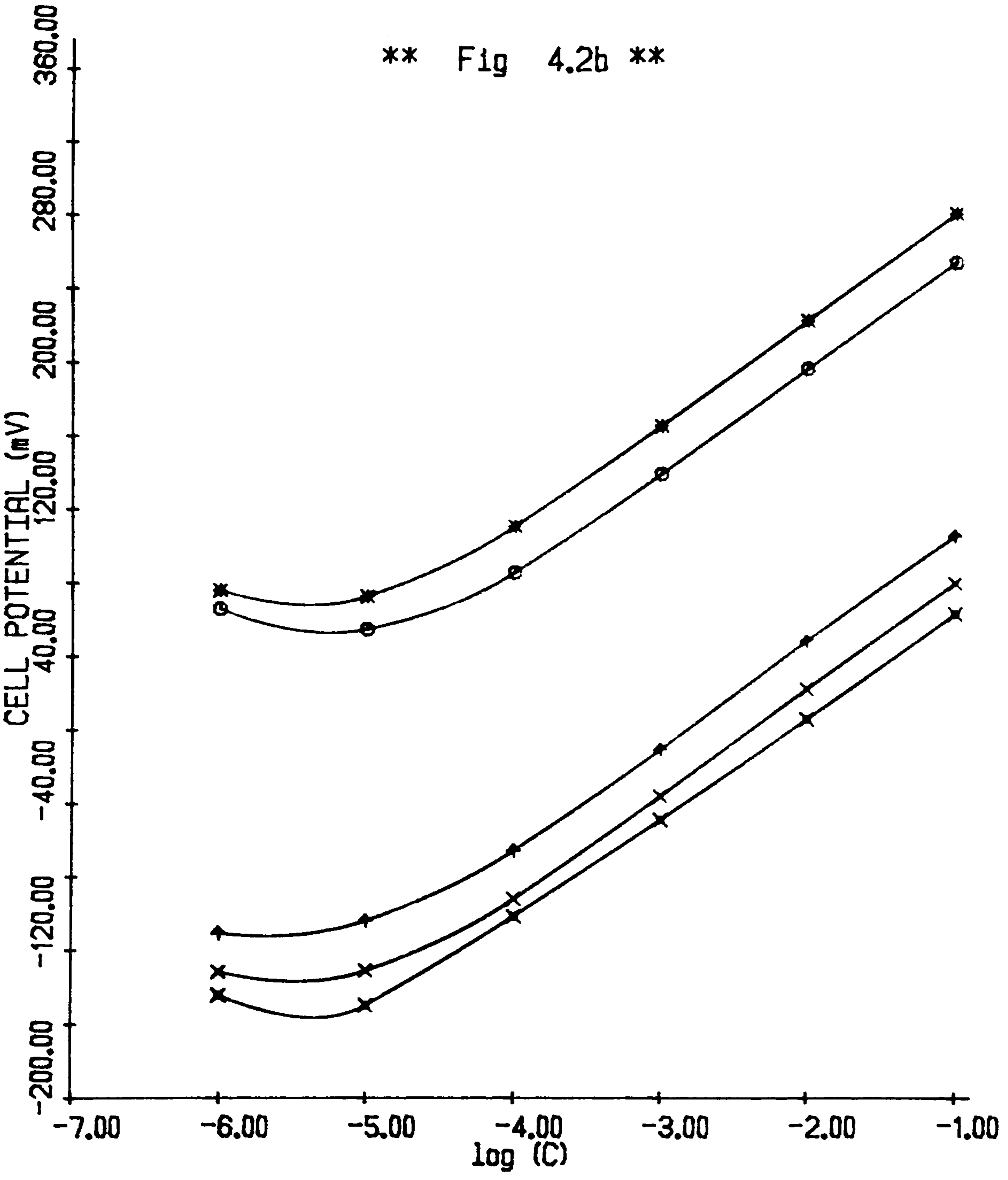
CALIBRATION CURVES

MEMBRANE: PVC/VALINOMYCIN

DIFFERENT CHLORIDE SALTS USED AS INNER SOLUTION

× = 0.1 mol/dm^{3}KCl ✱ = 0.1 mol/dm^{3}NaCl
⊙ = 0.1 mol/dm^{3}LiCl ✦ = 0.1 mol/dm^{3}CsCl
× = 0.1 mol/dm^{3}RbCl

** Fig 4.2b **

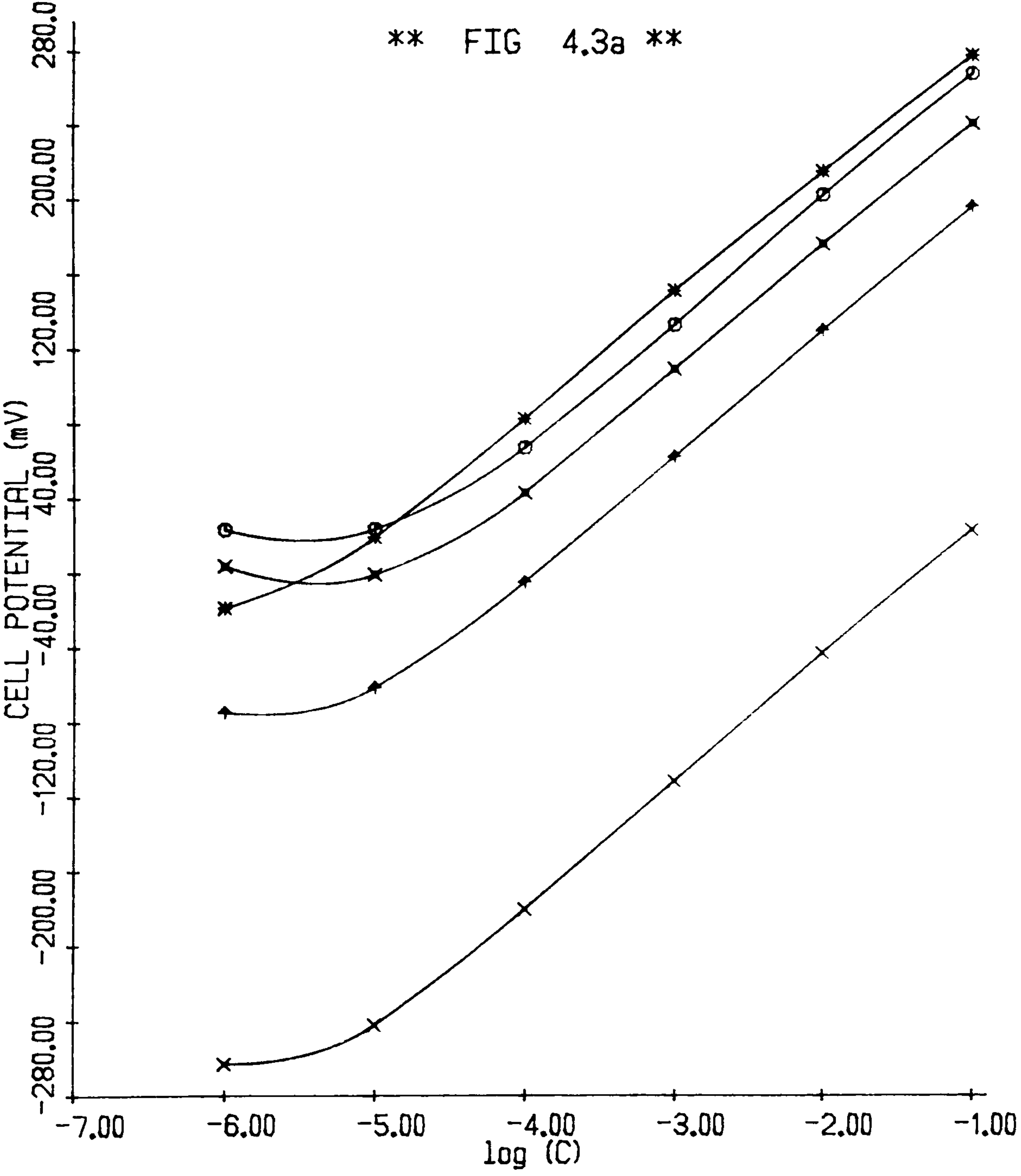


SELECTIVITY CURVES

MEMBRANE: PVC/VALINOMYCIN

DIFFERENT CHLORIDE SALTS USED AS INNER SOLUTION

× = 0.1 mol/dm^3 KCl ✱= 0.1 mol/dm^3 NaCl
⊙ = 0.1 mol/dm^3 LiCl ✦= 0.1 mol/dm^3 CsCl
✕ = 0.1 mol/dm^3 RbCl



** FIG 4.3a **

CALIBRATION CURVES

MEMBRANE: PVC/VALINOMYCIN

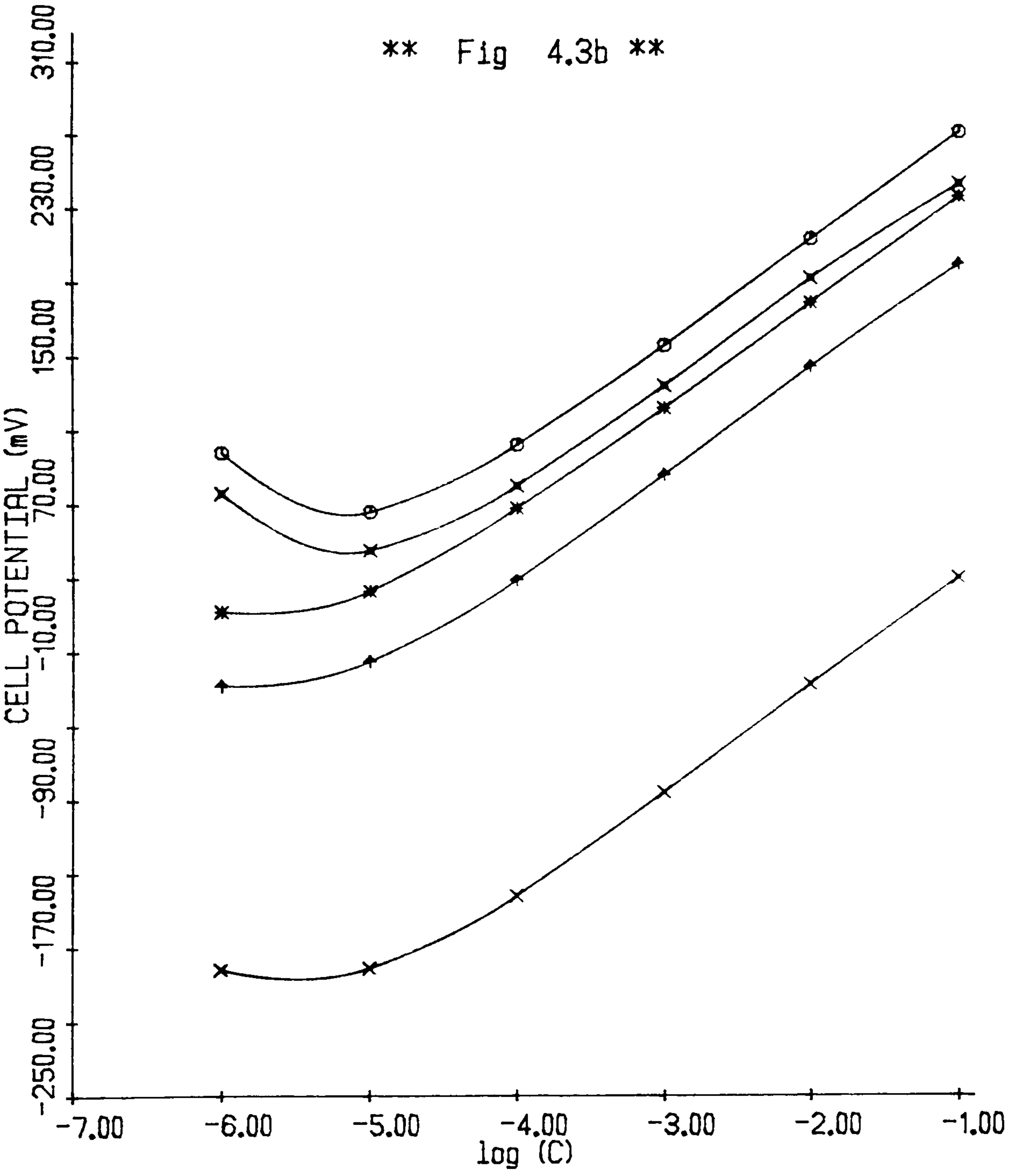
DIFFERENT CHLORIDE SALTS USED AS INNER SOLUTION

× = 0.1 mol/dm^3 KCl ✱ = 0.05 mol/dm^3 $CaCl_2$

⊙ = 0.05 mol/dm^3 $AlCl_3$ ✦ = 0.1 mol/dm^3 Tris/HCl

⨯ = 0.1 mol/dm^3 T.E.A.Cl

** Fig 4.3b **



SELECTIVITY CURVES

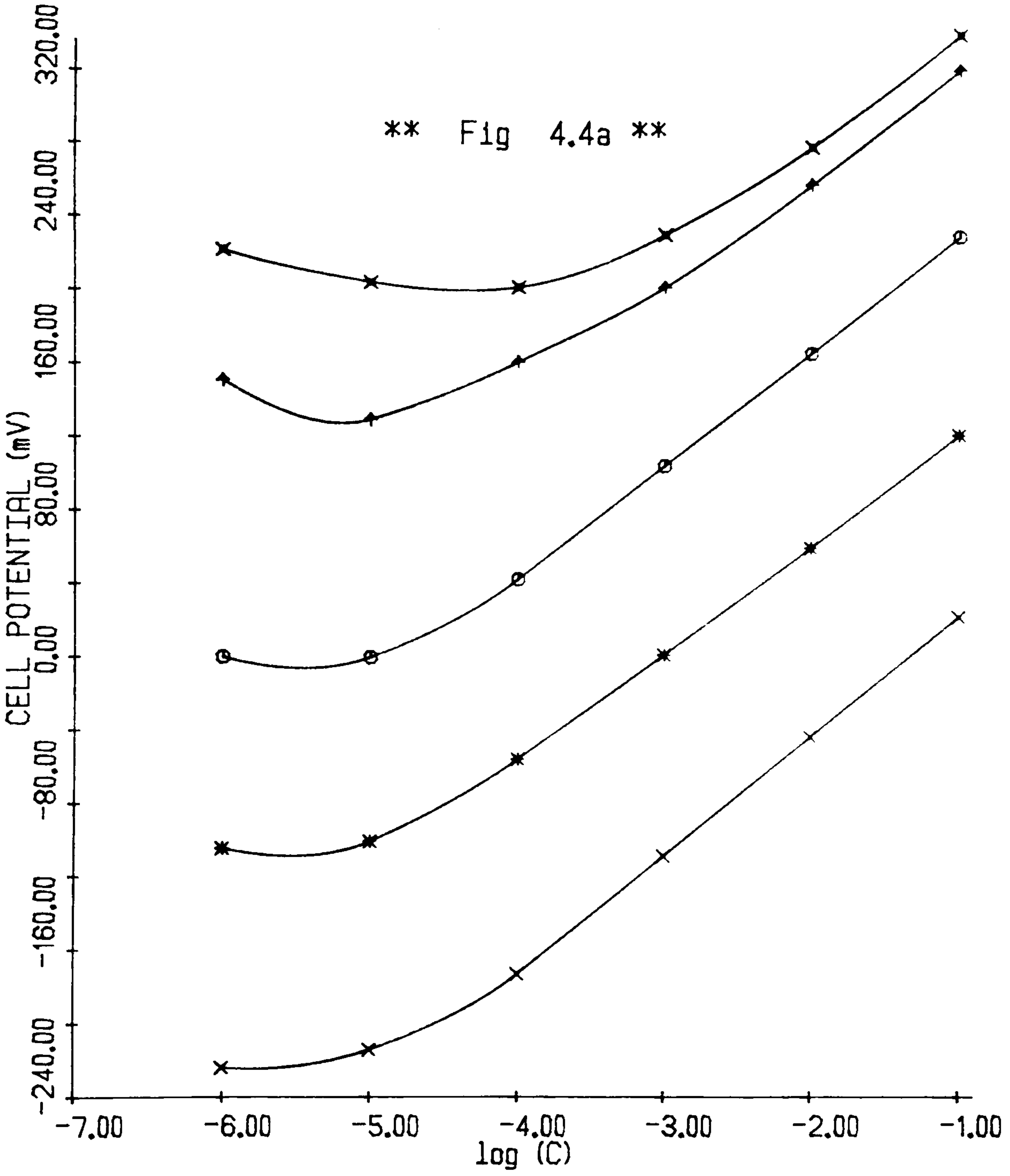
MEMBRANE: PVC/VALINOMYCIN

DIFFERENT CHLORIDE SALTS USED AS INNER SOLUTION

× = 0.1mol/dm^3 KCl ✱= 0.05mol/dm^3 $CaCl_2$

⊙ = 0.05mol/dm^3 $AlCl_3$ += 0.1mol/dm^3 Tris/HCl

× = 0.1mol/dm^3 T.E.A.CL

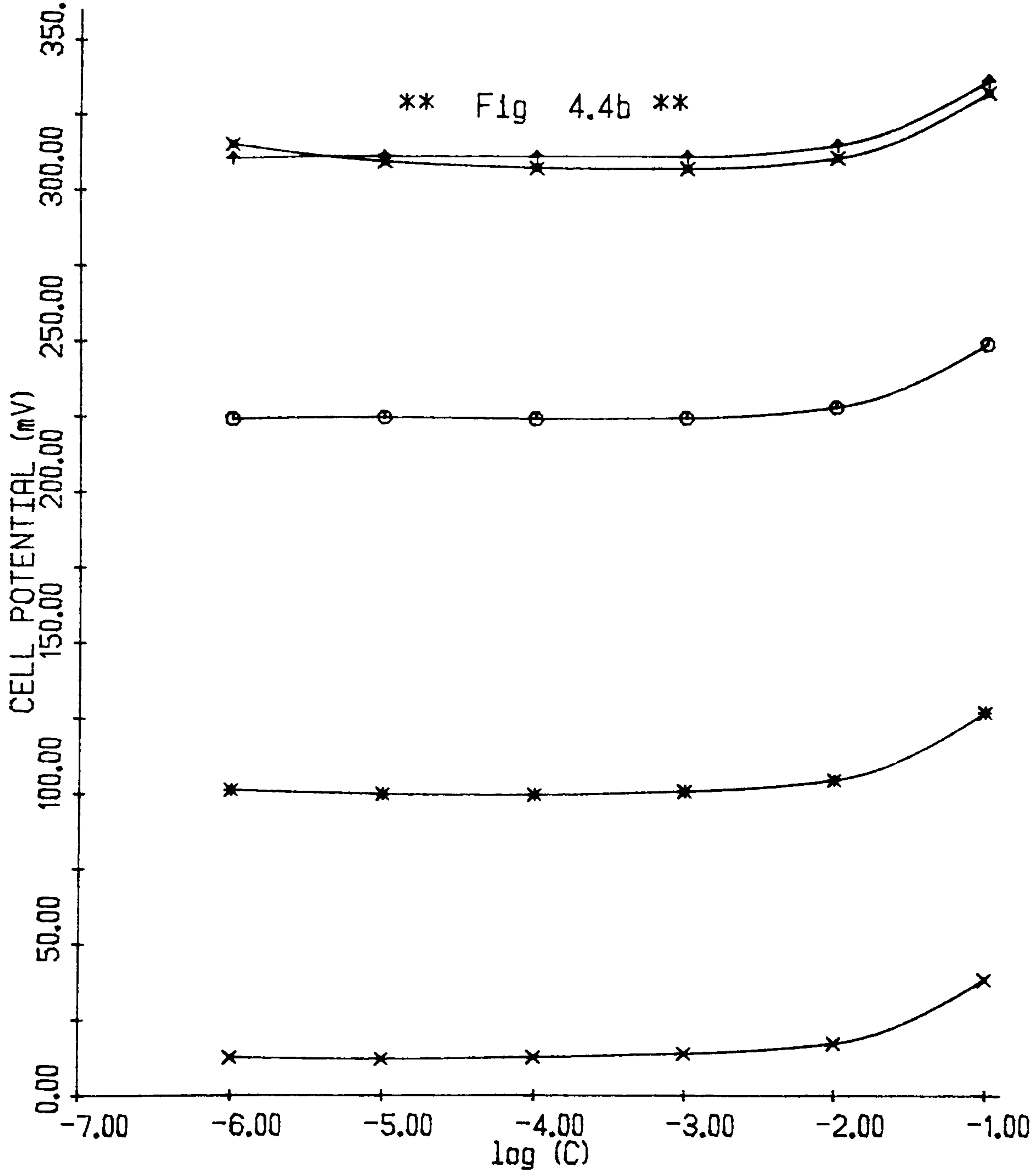


CALIBRATION CURVES

MEMBRANE: PVC/ION-EXCHANGER

VARIATION OF INNER SOLUTION CONCENTRATION (KCl)

× = 10^{-1} mol/dm^3 ✱ = 10^{-2} mol/dm^3
⊘ = 10^{-3} mol/dm^3 ✦ = 10^{-4} mol/dm^3
✕ = 10^{-5} mol/dm^3

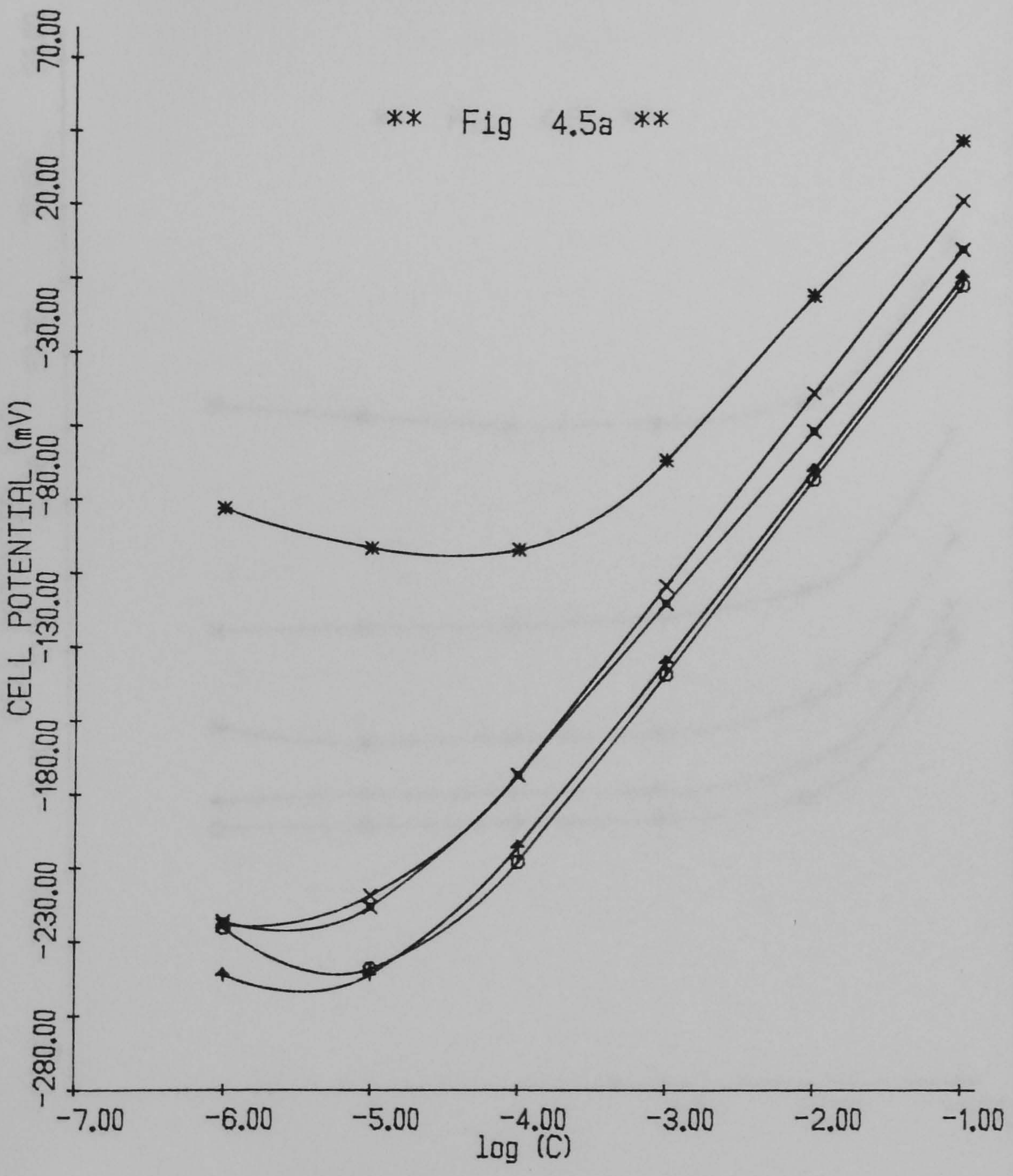


SELECTIVITY CURVES

MEMBRANE: PVC/ION-EXCHANGER

VARIATION OF INNER SOLUTION CONCENTRATION (KCl)

× = 10^{-1} mol/dm^3 ✱ = 10^{-2} mol/dm^3
⊖ = 10^{-3} mol/dm^3 + = 10^{-4} mol/dm^3
✖ = 10^{-5} mol/dm^3

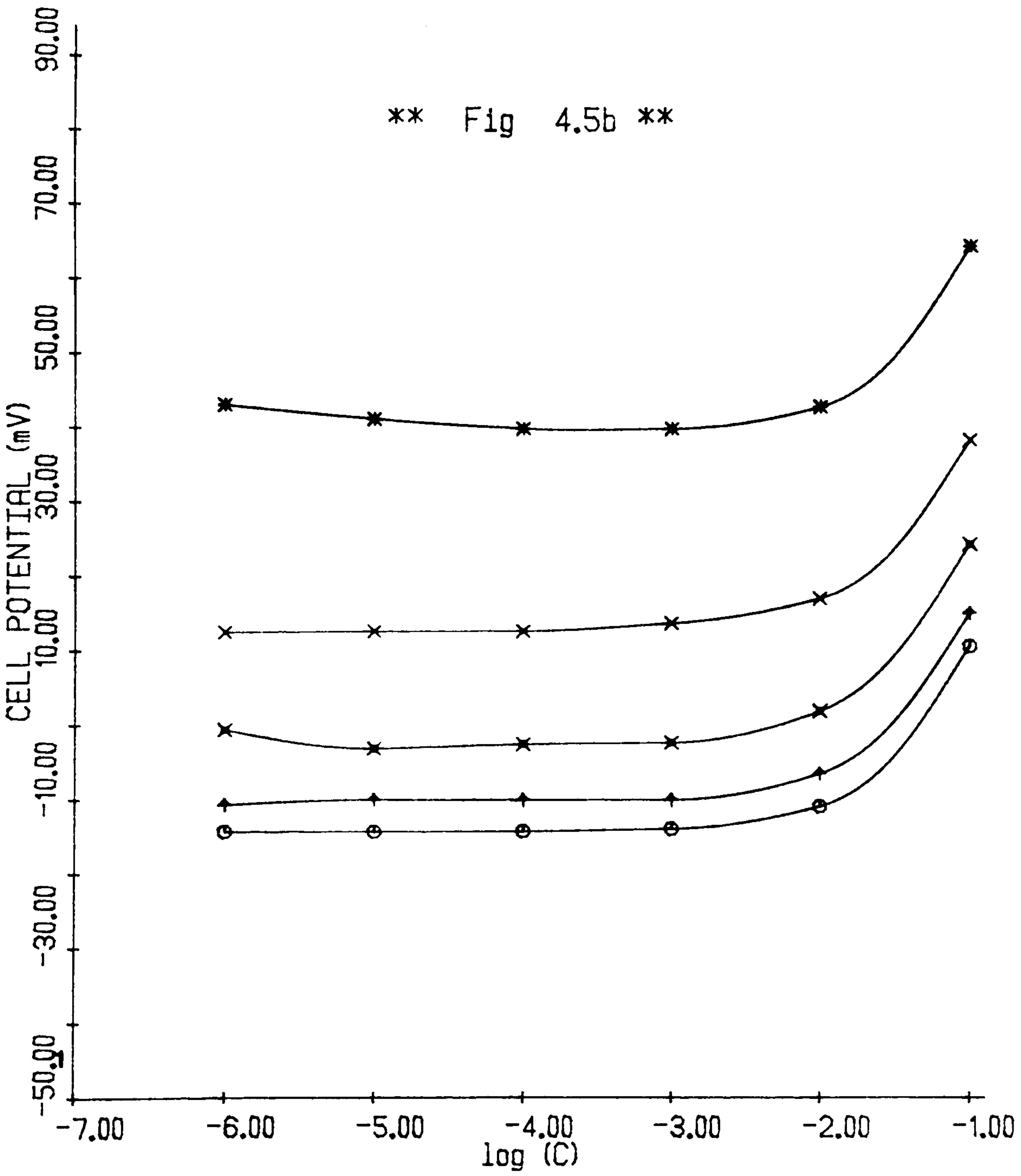


CALIBRATION CURVES

MEMBRANE: PVC/ION-EXCHANGER

DIFFERENT CHLORIDE SALTS USED AS INNER SOLUTION

× = 0.1 mol/dm^3 KCl ✱ = 0.1 mol/dm^3 NaCl
⊙ = 0.1 mol/dm^3 LiCl + = 0.1 mol/dm^3 CsCl
✕ = 0.1 mol/dm^3 RbCl



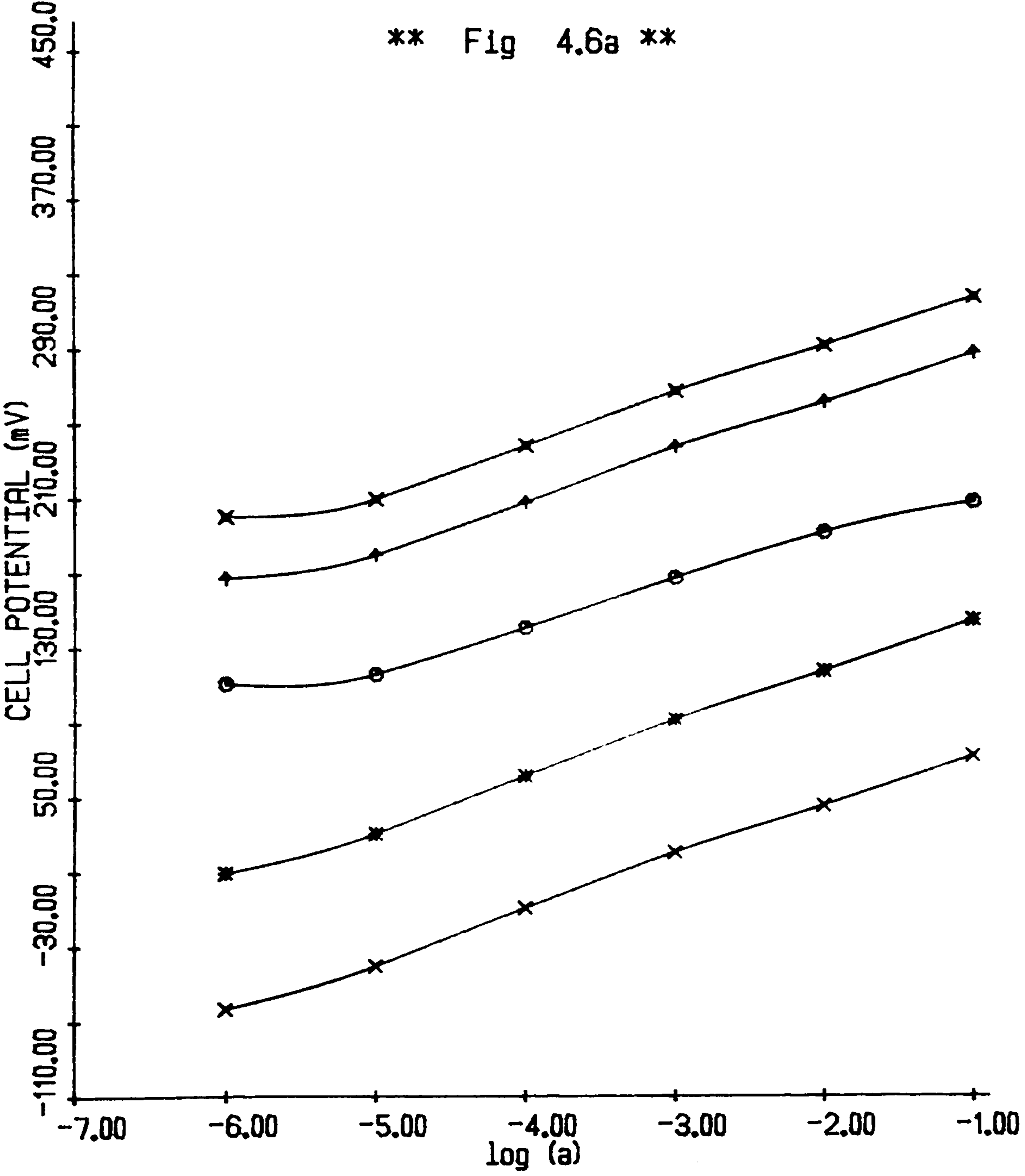
** Fig 4.5b **

SELECTIVITY CURVES

MEMBRANE: PVC/ION-EXCHANGER

DIFFERENT CHLORIDE SALTS USED AS INNER SOLUTION

× = 0.1 mol/dm^3 KCl ✱ = 0.1 mol/dm^3 NaCl
⊙ = 0.1 mol/dm^3 LiCl + = 0.1 mol/dm^3 CsCl
⨯ = 0.1 mol/dm^3 RbCl



** Fig 4.6a **

CALIBRATION CURVES

MEMBRANE: PVC /Ca^{2+} (PHILIPS Co.)

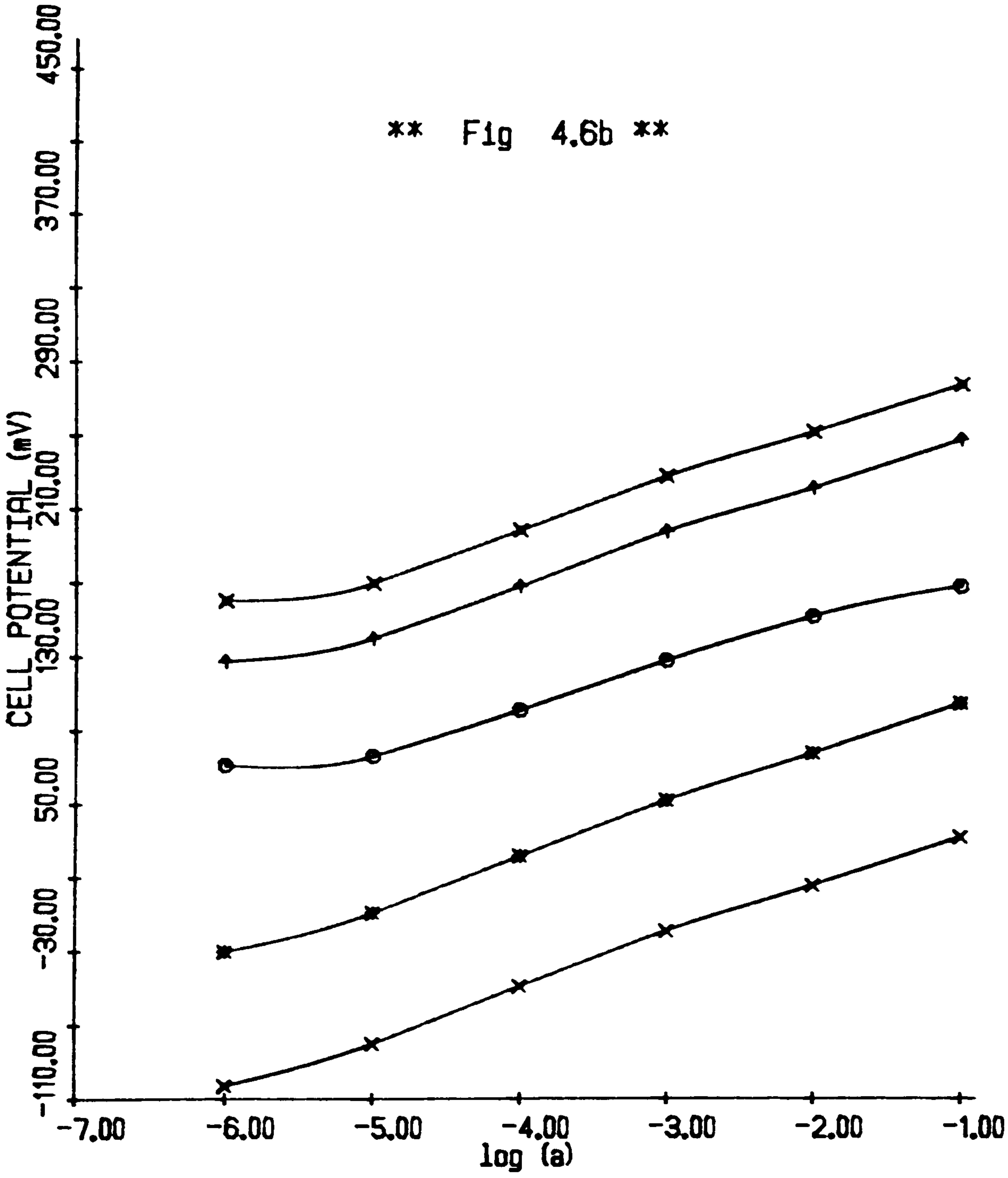
VARIATION OF INNER SOLUTION CONCENTRATION ($CaCl_2$)

⊙ = 10^{-1} mol/dm^3 ✱ = 10^{-2} mol/dm^3

⊙ = 10^{-3} mol/dm^3 + = 10^{-4} mol/dm^3

× = 10^{-5} mol/dm^3

** Fig 4.6b **



CALIBRATION CURVES

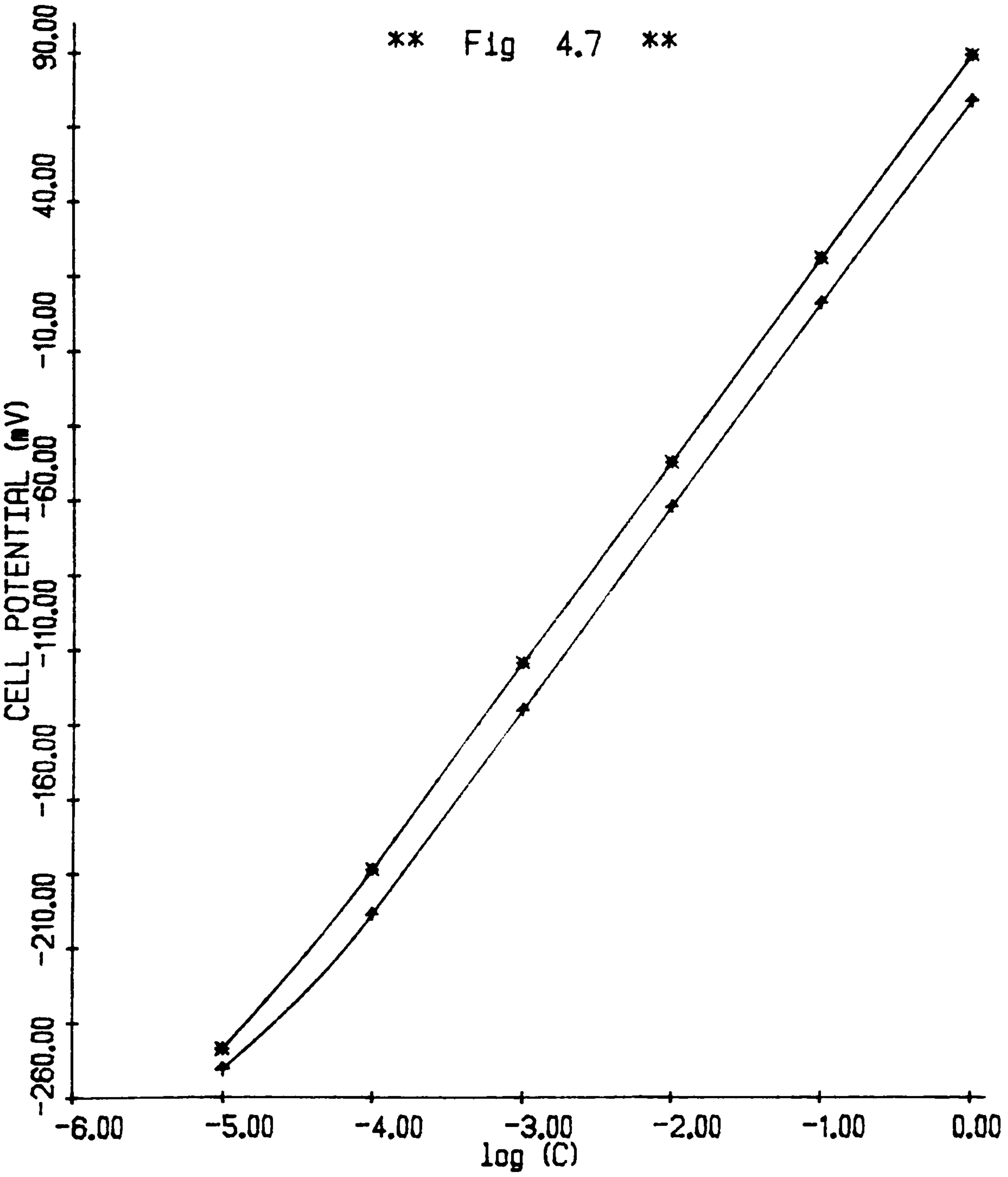
MEMBRANE: PVC/ Ca^{2+} (PHILIPS Co.)

DIFFERENT CHLORIDE SALTS USED AS INNER SOLUTION

⊖ = 0.1 mol/dm^3 $CaCl_2$ ✱ = 0.1 mol/dm^3 $AlCl_3$

⊖ = 0.1 mol/dm^3 KCl + = 0.1 mol/dm^3 $MgCl_2$

× = 0.1 mol/dm^3 $BaCl_2$



** Fig 4.7 **

CALIBRATION CURVES

MEMBRANE: PVC/VALINOMYCIN

Cu/Hg AS INNER REFERENCE SYSTEM

✱ = MEMBRABE WITH BEHS PLASTICIZER
✦ = MEMBRABE WITH DBP PLASTICIZER

Table 4.1
K^+/Valinomycin
Calibration

External Solution KCl (mol/dm^3)	Internal Solution (mol/dm^3)				
	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}
10^{-6}	-263.0	-185.0	- 48.0	+ 83.0	+162.4
10^{-5}	-232.0	-150.0	- 30.0	+ 78.0	+157.6
10^{-4}	-179.5	- 84.5	+ 32.0	+136.4	+211.0
10^{-3}	-112.5	- 13.5	+103.2	+203.0	+279.0
10^{-2}	- 44.0	+ 56.5	+172.5	+272.0	+348.3
10^{-1}	+ 23.5	+125.0	+239.8	+339.0	+415.4
E^0	+ 91.2	+195.5	+310.0	+406.8	+484.0
Slope pC (1-4)	67.8	69.2	69.0	67.7	68.2
Slope pC (4-5)	52.5	65.5	62.0	58.4	53.4

KCl + NaCl 0.45 (mol/dm^3)	Selectivity				
10^{-6}	-192.0	- 56.3	+ 23.9	+125.8	+202.0
10^{-5}	-172.5	- 75.0	+ 35.6	+138.1	+215.0
10^{-4}	-142.0	- 31.6	+ 75.6	+177.7	+251.4
10^{-3}	- 84.5	+ 24.6	+131.2	+230.7	+306.9
10^{-2}	- 27.3	+ 82.1	+189.3	+291.0	+265.0
10^{-1}	+ 29.7	+141.2	+249.0	+350.6	+423.0
E^0	+ 87.0	+198.3	+305.0	+407.2	+479.8
Slope pC (1-4)	57.3	57.6	57.8	57.9	57.3
Slope pC (4-5)	30.5	44.4	40.0	39.6	35.6

Cell Potentials and Slopes are in mV

Table 4.2
K^+/Valinomycin
Calibration

External Solution KCl (mol/dm^3)	Internal Solution (mol/dm^3)				
	0.1 KCl	0.1 NaCl	0.1 LiCl	0.1 CsCl	0.1 RbCl
10^{-6}	-263.0	- 57.8	+ 27.0	-233.0	-257.6
10^{-5}	-242.0	- 41.0	+ 63.6	-213.0	-255.0
10^{-4}	-180.0	+ 26.5	- 8.0	-153.0	-200.0
10^{-3}	-111.0	+ 95.3	+ 55.3	- 85.0	-133.0
10^{-2}	- 42.0	+163.8	+124.6	- 16.0	- 63.4
10^{-1}	- 24.2	+230.6	+194.2	+ 49.2	+ 2.9
E^0	+ 93.2	+299.2	+260.5	+116.9	+ 71.2
Slope pC (1-4)	68.1	68.0	67.6	67.6	67.8
Slope pC (4-5)	62.0	67.5	55.6	60.0	55.0

KCl + NaCl 0.45 (mol/dm^3)	Selectivity				
10^{-6}	-181.3	+ 26.5	+ 16.5	-160.3	-194.1
10^{-5}	-180.6	+ 23.3	+ 5.4	-153.6	-199.8
10^{-4}	-141.5	+ 61.8	+ 36.5	-155.1	-151.1
10^{-3}	- 85.4	+116.8	+ 90.5	- 60.0	- 98.5
10^{-2}	- 26.7	+174.3	+148.0	- 0.5	- 43.2
10^{-1}	+ 31.0	+232.7	+206.0	+ 56.7	+ 14.2
E^0	+ 89.4	+290.5	+263.3	+115.4	+ 70.2
Slope pC (1-4)	57.6	57	56.6	57.6	56.7
Slope pC (4-5)	39.1	38.5	31.1	38.5	48.7

Cell Potentials and Slopes are in mV

Table 4.3
K^+/Valinomycin
Calibration

External Solution KCl (mol/dm^3)	Internal Solution (mol/dm^3)				
	0.1 KCl	0.05 $CaCl_2$	0.05 $AlCl_3$	0.1 Tris/HCl	0.1 T.E.A.Cl
10^{-6}	-263.0	- 18.0	+ 24.0	- 74.0	+ 4.5
10^{-5}	-242.0	- 20.0	+ 24.5	- 60.5	+ 0.0
10^{-4}	-180.0	+ 84.0	+ 68.5	- 4.0	+ 44.0
10^{-3}	-111.0	+152.7	+134.5	+ 63.5	+110.8
10^{-2}	- 42.0	+216.8	+204.3	+131.5	+177.8
10^{-1}	+ 24.2	+279.6	+269.6	+198.2	+242.8
E^0	+ 93.2	+346.0	+337.5	+265.9	+309.7
Slope pC (1-4)	68.1	65.0	67.3	67.4	66.4
Slope pC (4-5)	62.0	64.5	44.6	56.5	44.0

KCl + NaCl 0.45 (mol/dm^3)			Selectivity		
10^{-6}	-181.3	+ 12.6	+ 98.8	- 27.5	+ 76.6
10^{-5}	-180.6	+ 23.8	+ 66.8	- 14.2	+ 45.9
10^{-4}	-141.5	+ 68.9	+103.4	+ 29.8	+ 81.0
10^{-3}	- 85.4	+123.2	+157.2	+ 86.8	+135.4
10^{-2}	- 26.7	+180.1	+214.6	+145.0	+193.2
10^{-1}	+ 31.0	+237.6	+272.4	+200.8	+244.5
E^0	+ 88.4	+293.2	+328.0	+258.4	+305.1
Slope pC (1-4)	57.6	56.3	56.4	57.1	56.2
Slope pC (4-5)	39.1	40.1	36.6	44.0	35.1

Cell Potentials and Slopes are in mV

Table 4.4
K^+/Ion-exchanger
Calibration

External Solution KCl (mol/dm^3)	Internal Solution (mol/dm^3)				
	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}
10^{-6}	-224.0	-104.0	+ 0.5	+151.3	+222.0
10^{-5}	-214.0	-100.4	+ 0.0	+129.8	+204.6
10^{-4}	-173.0	- 55.6	+ 42.5	+161.4	+202.0
10^{-3}	-108.6	+ 1.4	+104.6	+202.0	+230.6
10^{-2}	- 43.0	+ 60.0	+166.2	+258.2	+278.6
10^{-1}	+ 22.5	+121.5	+230.0	+321.0	+340.0
E^0	+ 87.5	+179.3	+291.8	+369.3	+392.0
Slope pC (1-4)	65.2	59.0	62.1	53.4	54.7
Slope pC (4-5)	41.0	44.8	42.5	31.6	28.6

KCl + NaCl 0.45 (mol/dm^3)	Selectivity				
10^{-6}	+ 12.6	+101.6	+224.6	-311.0	+315.6
10^{-5}	+ 12.2	+100.3	+220.4	-312.0	+310.2
10^{-4}	+ 12.7	+ 99.9	+225.0	-312.0	+308.2
10^{-3}	+ 13.8	+101.0	+225.3	-312.0	+308.0
10^{-2}	+ 17.2	+105.0	+229.0	-316.0	+311.8
10^{-1}	+ 38.5	+127.6	+250.0	-337.6	+333.8
E^0					
Slope pC (2-1)	21.3	22.6	21.0	21.6	21.7
Slope pC (3-2)	4.6	4.0	4.3	4.0	3.8

Cell Potentials and Slopes are in mV

Table 4.5
K^+/Ion-exchanger
Calibration

External Solution KCl (mol/dm^3)	Internal Solution (mol/dm^3)				
	0.1 KCl	0.1 NaCl	0.1 LiCl	0.1 CsCl	0.1 RbCl
10^{-6}	-224.0	- 82.6	-225.0	-241.0	-223.0
10^{-5}	-214.0	- 96.0	-239.0	-241.0	-218.0
10^{-4}	-173.0	- 96.4	-202.4	-197.2	-173.0
10^{-3}	-108.6	- 66.0	-130.8	-134.7	-114.7
10^{-2}	- 43.0	- 10.0	- 72.3	- 69.2	- 56.0
10^{-1}	+ 22.5	+ 42.6	- 6.2	- 3.3	+ 6.0
E^0	+ 87.5	+ 97.4	+ 58.8	+ 60.0	+ 65.0
Slope pC (1-4)	65.2	54.3	65.5	64.7	59.7
Slope pC (4-5)	41.0	4.8	36.6	43.8	35.0
KCl + NaCl 0.45 (mol/dm^3)	Selectivity				
10^{-6}	+ 12.6	+ 43.2	- 14.2	- 10.6	- 0.5
10^{-5}	+ 12.7	+ 41.3	- 14.2	- 9.9	- 3.0
10^{-4}	+ 12.7	+ 40.0	- 14.2	- 10.0	- 2.5
10^{-3}	+ 13.8	+ 40.0	- 13.9	- 10.0	- 2.3
10^{-2}	+ 17.2	+ 43.0	- 10.8	- 6.4	+ 2.0
10^{-1}	+ 38.5	+ 64.6	- 10.8	+ 15.2	+ 4.5
E^0					
Slope pC (2-1)	21.3	21.6	21.6	21.6	22.5
Slope pC (3-2)	3.4	3.0	3.0	3.6	4.3

Cell Potentials and Slopes are in mV

Table 4.6
Ca^{2+} /Philips
Calibration

External Solution CaCl (mol/dm^3)	Internal Solution (mol/dm^3)				
	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}
10^{-6}	-103.0	-30.0	+ 71.5	+128.0	+161.0
10^{-5}	- 80.0	- 9.0	+ 76.5	+104.3	+170.5
10^{-4}	- 49.0	+ 22.0	+101.5	+169.0	+199.5
10^{-3}	- 19.0	+ 52.4	+128.5	+199.0	+229.0
10^{-2}	+ 7.1	+ 79.5	+152.5	+224.0	+254.5
10^{-1}	+ 31.4	+104.5	+178.0	+248.0	+278.0
E^0	+ 66.2	+139.7	+207.5	+281.4	+311.4
Slope pC (1-5)	28.9	29.5	26.3	28.0	28.0
Slope pC (5-6)	23.0	21.0	5.0	22.5	9.5

Internal Solution CaCl (mol/dm^3)	Internal Solution (mol/dm^3)				
	0.1 $CaCl_2$	0.1 $AlCl_3$	0.1 KCl	0.1 $MgCl_2$	0.1 $BaCl_2$
10^{-6}	-103.0	+ 23.0	+ 50.7	+ 25.5	+ 7.0
10^{-5}	- 80.0	+ 30.5	+ 49.7	+ 30.0	- 10.0
10^{-4}	- 49.0	+ 54.5	+ 74.5	+ 54.0	+ 18.3
10^{-3}	- 19.0	+ 80.0	+101.6	+ 81.5	+ 43.6
10^{-2}	+ 7.1	+103.3	+125.6	+105.6	+ 71.8
10^{-1}	+ 31.4	+126.7	+149.0	+127.8	+ 93.2
E^0	+ 66.2	+155.1	+179.0	+157.8	+126.0
Slope pC (1-5)	28.9	25.0	25.9	25.6	26.9
Slope pC (5-6)	23.0	7.5	1.2	4.5	3.0

Cell Potentials and Slopes are in mV

4.4 DISCUSSION

As was outlined in previous chapters, the process by which the membrane potential is established involves the transfer of ions between the contacting solutions and membrane. The overall potential of the membrane is the contribution of two potentials: diffusion and boundary potentials, where the former is the result of the differences in the mobility of species in the membrane, and the boundary potential is the product of charge distribution in the adjacent phases; namely the aqueous and membrane phases. The boundary potential is directly involved with the activities of the species in aqueous and membrane phases (see Appendix). Thus, as expected, by changing the concentration and the type of internal solution, the boundary potential, which is the most effective factor in the membrane potential, should change, however, this did not take place. From the results in Tables 4.1, 4.4 and 4.6, the E^0 values in Table 4.7 were obtained for corresponding electrodes over the concentration range indicated. Considering the ΔE^0 change per decade, part of these potentials is due to the chloride concentration change, which would be around 60 mV/decade. The remaining potential is the inner boundary potential, which is not consistent with the concentration change of the inner filling solution. With respect to the ΔE^0 of the K^+ /I.S.Es, it appears that with higher concentration of inner solution ($c > 10^{-3}$ mol/dm^3), internal system of both electrodes respond more or less according to the Nernst law, particularly in the range of 10^{-2} to 10^{-3} mol/dm^3, where they are 114.5 and 112.5 mV for potassium/valinomycin and potassium /ion-exchanger electrodes respectively. In contrast, with low concentrations, both electrodes

Table 4.7

Internal Solution (mol/dm^3) (KCl)

	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}
K^+ /Valinomycin					
E^0 mV	91.25	195.5	310.0	406.8	484.0
ΔE^0 mV		104.3	114.5	96.8	77.2
		(60+44.3)	(60+54.50)	(60+36.8)	(60+17.2)
K^+ /Ion-exchanger					
E^0 mV	87.5	179.3	291.8	369.3	392.0
ΔE^0 mV		91.8	112.5	77.5	22.7
		(60+31.8)	(60+52.5)	(60+17.5)	(?+ ?)
Ca^{2+} /Philips					
E^0 mV	66.2	139.7	207.5	281.4	311.4
ΔE^0 mV		73.5	67.8	73.9	30.0
		(60+13.8)	(60+ 7.8)	(60+13.9)	(?+ ?)

deviate from the Nernstian relationship. This malfunctioning is more pronounced in the range of 10^{-4} to 10^{-5} mol/dm^3 especially for the K^+ /ion-exchange electrode (ΔE^0 =22.7 mV). As far as the alkaline chloride salts with 0.1 mol/dm^3 in the inner solution of K^+ /valinomycin electrode are concerned, the E^0 is changed as follows:

$$E^0_{Na^+} > E^0_{Li^+} >> E^0_{Cs^+} > E^0_{K^+} = E^0_{Rb^+}$$

Such a trend is consistent with the order of stability constants of these cations with valinomycin in methanol. The electrode with Cu/Hg inner system resembles the coated-wire electrode, where the electrode behaves as two separate interface devices with a membrane / electrolyte interface and a membrane/metal interface. Possible lack of stability of the interfacial potential at the membrane/wire (mercury) interface has been criticized by Buck [12] and Covington [13] because of an apparent absence of a well defined internal system. However, it has been suggested that in a coated-wire electrode , a metal/metal oxide system is formed at the inner interface [14]. It is possible that, electrode with mercury system work on this principle. From these results, one can conclude that functioning of electrodes based on neutral carriers is independent of the inner reference system. Due to the large difference between the complex stability of the various cations with valinomycin, e.g. the potassium and sodium ion complexes, plus the fact that the response time is too fast with all electrodes with different inner solutions, the hypothesis that the charge transport is the result of loading and unloading of the cation at the interfaces becomes questionable. It is thus reasonable to look for other means of charge transport through the membrane. The selectivity of the K^+ /PVC valinomycin electrode did not change, however, a shift in position of its curve is observed. The same pattern was demonstrated by its corresponding calibration curve. In the case of Ca^{2+} electrode, which is supposed to be based on a neutral ionophore, similar results were obtained. The E^0 should be 90 mV per decade change. However, it remained more or less constant with concentration change, except for inner solution of 10^{-4} - 10^{-5} mol/dm^3. Small change in the ΔE^0 in this range might have arisen partly from a malfunction and deterioration of the silver-silver chloride electrode at very dilute concentration (10^{-5} mol/dm^3) thus, the above argument may still applies to this electrode as well. For electrodes based on the ion-exchanger, the results support the suggestion that similar solutions on both sides of membrane might give better performance (Table 4.4 and 4.5). It seems that further experiments, such as impedance measurements and surface etching studies might provide some useful information about inner surface potential when different solutions are being used as reference solution.

Appendix Assuming that thermodynamic equilibrium exists at the interfaces between the membrane and eqeuous solution, the following equations apply for I^+ species:

$$\tilde{\mu}_{i^+(aq)} = \tilde{\mu}_{i^+(mem)}$$

$$\mu^0_{i^+(aq)} + RT \ln a'_{i^+(aq)} + F\varphi'_{i^+(aq)} = \mu^0_{i^+(mem)} + RT \ln a_{i^+(mem)} + F\varphi_{i^+(mem)}$$

$$\varphi'_{i^+(aq)} - \varphi_{i^+(mem)} = \left(\frac{\mu^0_{i^+(mem)} - \mu^0_{i^+(aq)}}{F} \right) + RT/F \ln \frac{a_{i^+(mem)}}{a'_{i^+(aq)}}$$

$$E_1 = E^0_1 + RT/F \ln \frac{a_{i^+(mem)0}}{a'_{i^+(aq)}}$$

E is the boundary potential at one interface. For the other interface similar equation is obtained.

$$E_2 = E^0_2 + RT/F \ln \frac{a'_{i^+(mem)d}}{a''_{i^+(aq)}}$$

Subscripts ′0′ and ′d′ signify thickness of the membrane.

All together, the Donnan potential will be:

$$E = E^{0} + RT/F \ln \frac{a'_{i^{+}(aq)} \cdot a_{i^{+}(mem)d}}{a''_{i^{+}(aq)} \cdot a_{i^{+}(mem)0}}$$

Generally $a_{i^{+}(mem)0} = a_{i^{+}(mem)d}$ and the boundary potential becomes:

$$\boxed{E = E^{0} + RT/F \ln \frac{a'_{i^{+}(aq)}}{a''_{i^{+}(aq)}}}$$

PART TWO

ORIGIN of NEGATIVE SITES

and

ANION INTERFERENCE in the K^+ /PVC MEMBRANES

4.5 ORIGIN OF NEGATIVE SITES IN PVC MEMBRANES PART (II)

So far, the best ion-selective electrode for potassium ions is the neutral-carrier based electrode. The mechanism of selectivity and problem of electroneutrality in these electrodes have been the subject of many studies. However, as Buck [15] stated, the mechanism in this membrane is still unclear and open to suggestions. It has been revealed [16] that, there are considerable differences between the potassium and the chloride ion concentrations in the membrane phase (0.5 mmol K^+ and 0.006 mmol Cl^-). As Covington [13] pointed out, deviation from electroneutrality over such a large distance (thick membrane) is impossible and therefore, to fulfill the electroneutrality condition in the membrane, the presence of aditional negative species is necessary. Nevertheless, the origin of these negative sites has not yet been clarified. Generally, there are three approaches to this matter:

a) Simon el al. [16] , through electrolysis and transport number measurements, concluded that water clusters involving OH^- ions are the source of the negative sites, and that the mobility of these anionic sites is likely to be low. The production of these species was attributed to the reaction between potassium ions from the aqueous solution and the water from the membrane phase. The main evidence for this hypothesis was the decrease of the pH in the contacting solutions, due to the flux of the hydrogen ion from the membrane.

b) Buck [15] suggested that the slow anion interfacial kinetics is responsible for the cation selectivity of the membrane.

c) A third group [17] believes that the anions present within the membrane, resulted from impurities in the components of the membrane, which are immobile and bound to the supporting material, are the main supply of the negative sites. The selectivity arises due to the existence of these species.

In the present work, investigation of the components of the membrane has been carried out and the pH variation from each component of the membrane constituents immersed in a sample solution was recorded. Two sets of experiments were performed: one with KCl 10^{-2} mol/dm^3 solution, and the other with triple distilled water, as external contacting solutions.

4.6 EXPERIMENTAL

Due to the small amount of the sample solution and the direct contact of the PVC powder and plasticizer with the glass and reference saturated calomel electrodes, a special cell was designed (Fig 4.8a). The two holes, large and small, were connected to each other through a capillary tube. The design of the cell will allow the use of as small as possible amount of sample solution, and more importantly it will prevent change in liquid junction potential caused by bubbling of nitrogen gas through the sample solution. It also reduces the possibility of direct contact between PVC powder and the reference electrode. An EIL glass electrode and saturated calomel electrode were used. When water was the sample solution, a Russell glass electode and double junction calomel electrode with tetramethyl ammonium chloride 3.5 mol/dm^3, to prevent contamination of the sample solution due to the penetration of potassium ions from the saturated KCl, were utilized.

Two ml of KCl solution (10^{-2} mol/dm^3), or triple distilled water, was introduced into the right hand side hole, which would flow (a small amount) through the capillary tube into the left hand side hole. The glass and reference electrodes were immersed in the right and left hole respectively. To prevent dissolution of CO_2 from the surrounding environment in the sample solution, which could cause pH variation, the sample solution was bubbled with N_2 gas during the experiments. The potentials of the cell were recorded using a digital voltmeter through a single high impedance amplifier. The temperature was kept constant at 24.5 ± 0.5^0C . The complete apparatus is shown in Fig 4.8b. The membranes with different PVC samples and plasticizers were prepared by the procedure described in Chapter Two. The following experiments were carried out:

1) 0.2 g of the master membrane was cut into small pieces and soaked in the 2 ml KCl solution or water. The potential was recorded immediately after the membrane was immersed . The results are shown in Figs 4.9a and 4.9b (for KCl and water as sample solutions) respectively.

2) The effect of the presence of valinomycin in the membrane on the pH of the sample solution was checked by repeating the above experiment by using a membrane of exactly the same composition but without valinomycin. No differences were observed.

3) 150 mg of PVC powder with different molecular weights and other particular characteristics were added to the same amounts of KCl or distilled water, and the variation of potential was monitored (Figs 4.10a and 4.10b).

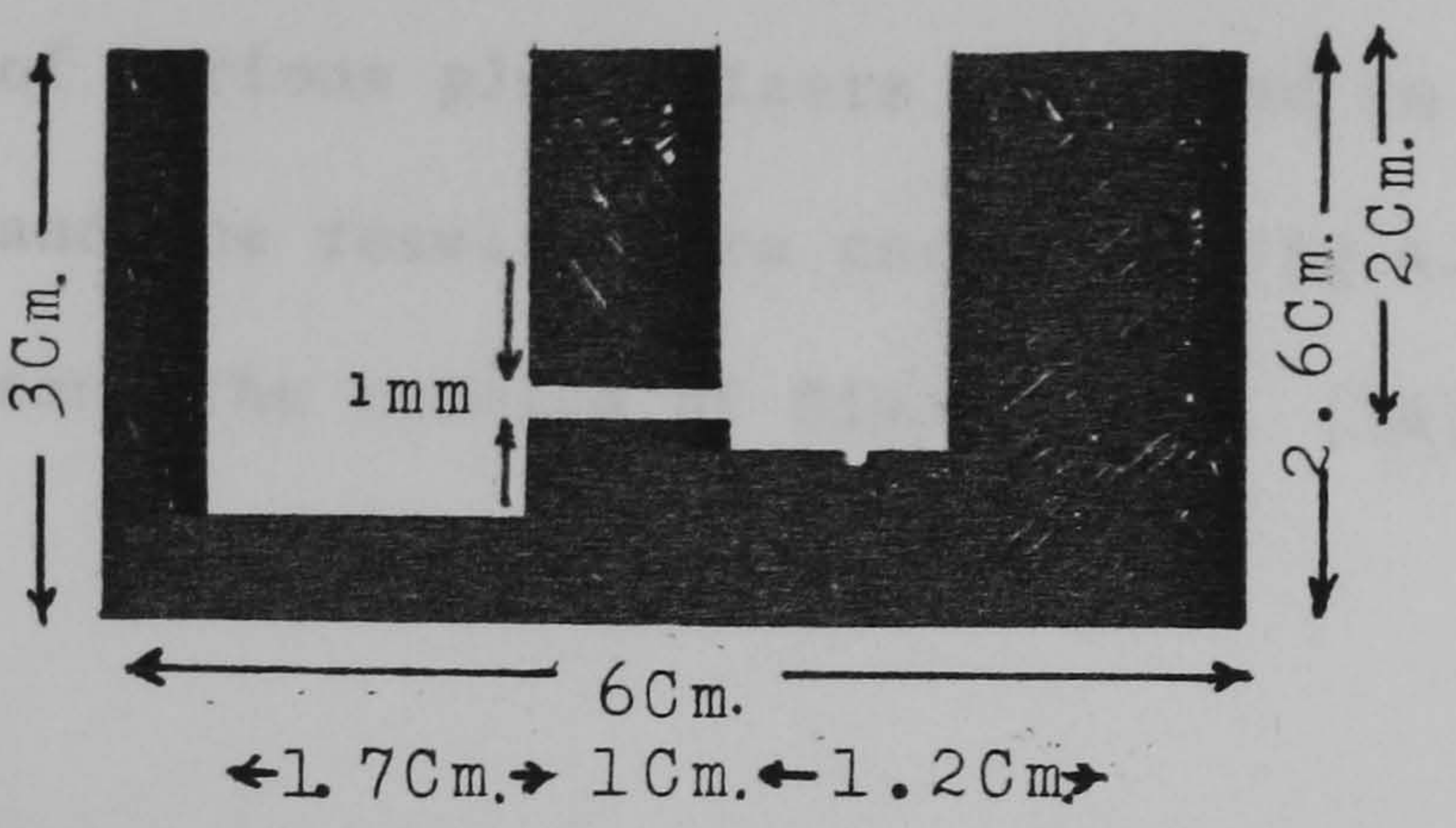


Fig 4.8a

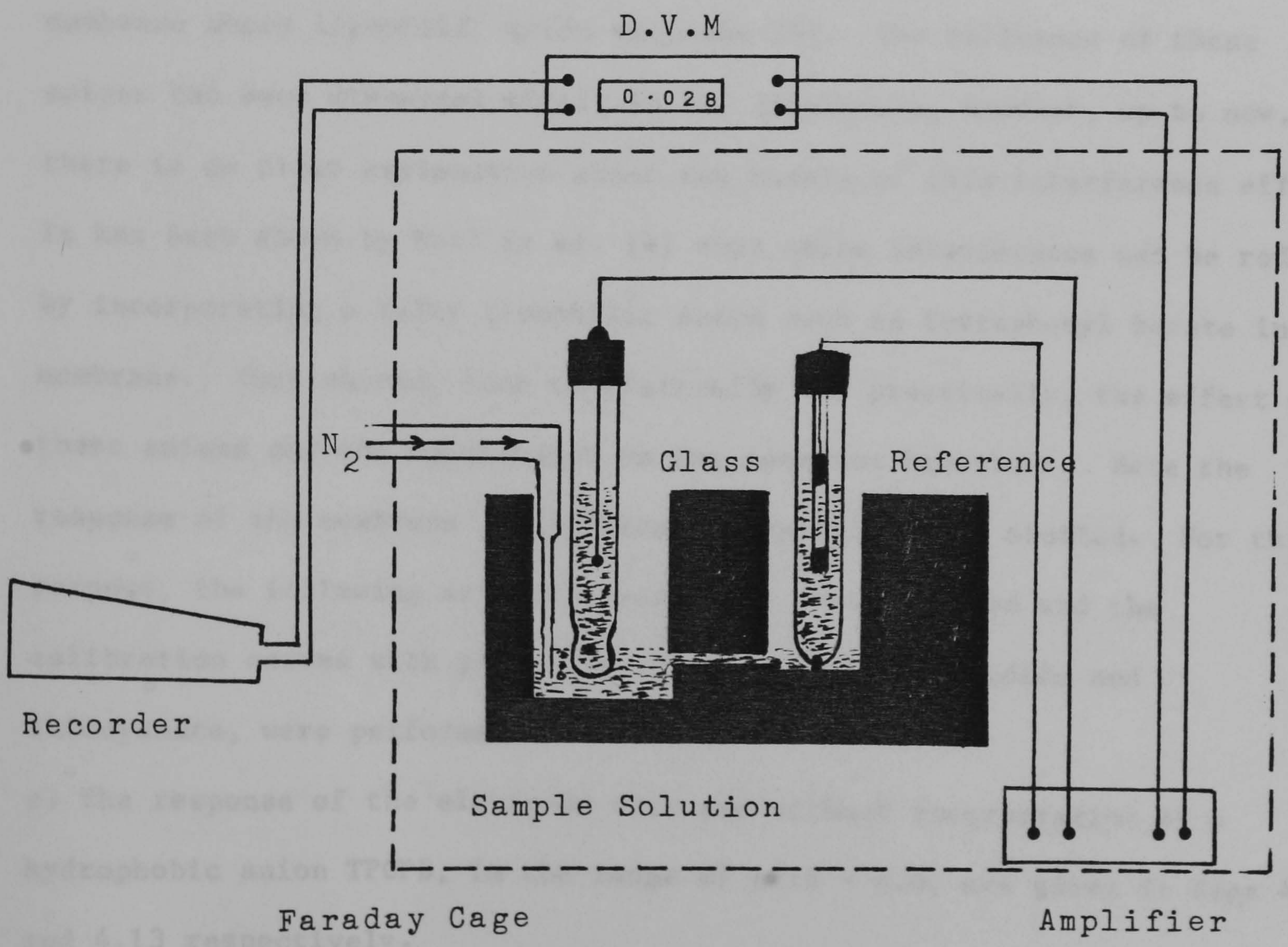
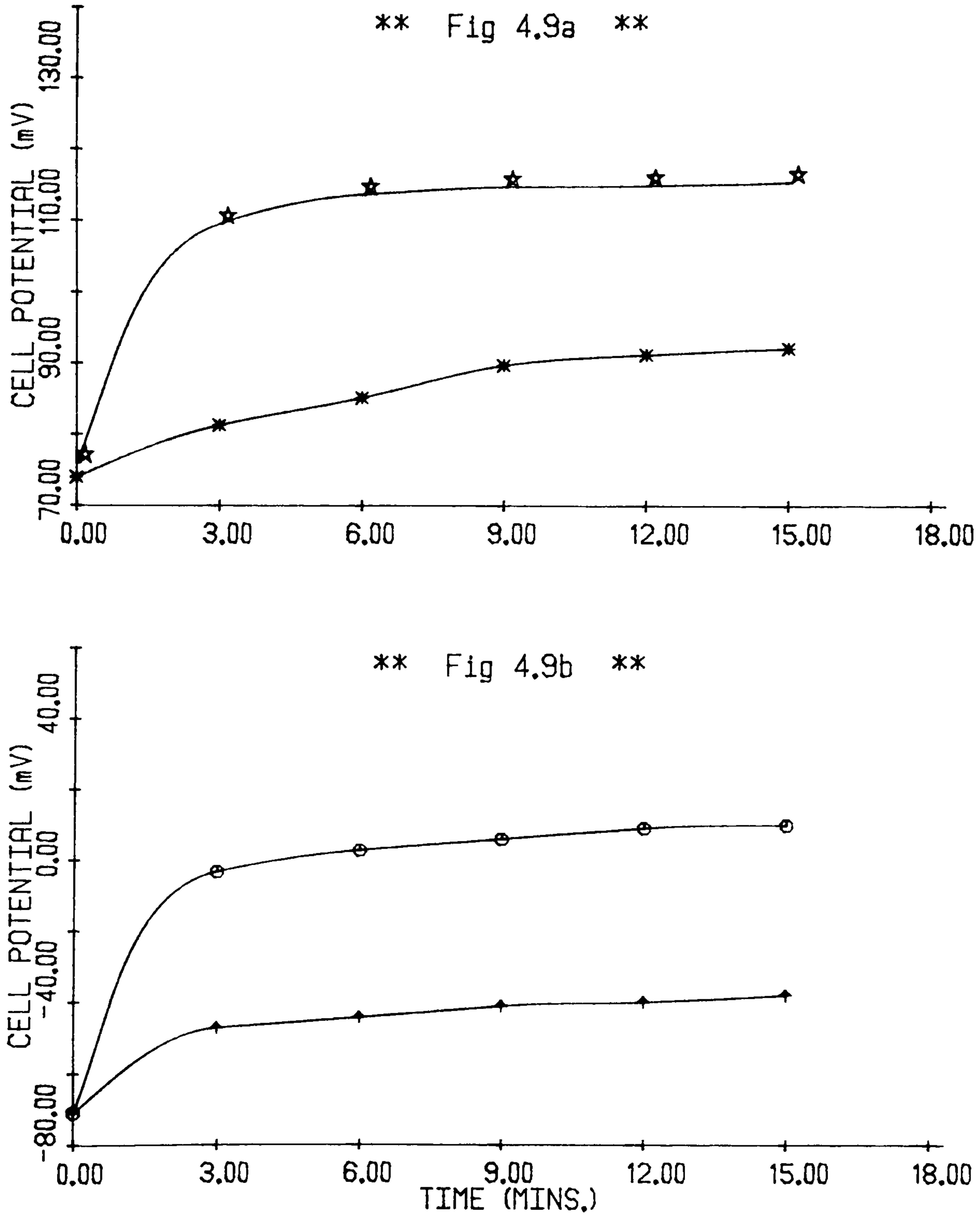


Fig 4.8b

4) 0.15 ml of various plasticizers was added to the 2 ml of KCl solution or pure water and the results were recorded (Fig 4.11a and 4.11b).
For comparison, the results of Simon et al. [16] are also shown (Fig 4.11c).

4.7 EFFECT OF LIPOPHILIC ANIONS ON THE MEMBRANE BEHAVIOUR

Generally, neutral carrier-based membrane electrodes demonstrate a Nernstian behaviour to pure chloride salt solutions, but the presence of substantial amount of strong lipophilic anions (e.g. picrate, thiocyanate, etc.) in the test solution, leads to a decline of the cationic function of the membrane. In certain cases, such as for the picrate anions, the membrane shows lipophilic anion response [5]. The influence of these anions has been discussed widely in the literature, however, up to now, there is no clear explanation about the nature of this interference effect. It has been shown by Morf et al. [4] that anion interference can be reduced by incorporating a bulky lipophilic anion such as tetraphenyl borate in the membrane. They showed, both theoretically and practically, the effect of these anions and the improvement on the membrane behaviour. Here the response of the membrane of different compositions was studied. For this purpose, the following sets of experiments were arranged and the calibration curves with potassium chloride, nitrate, iodide and thiocyanate, were performed.
a) The response of the electrode with and without incorporation of a hydrophobic anion TPCPB, in the range of pC:5 - 0.0, are given in Figs 4.12 and 4.13 respectively.

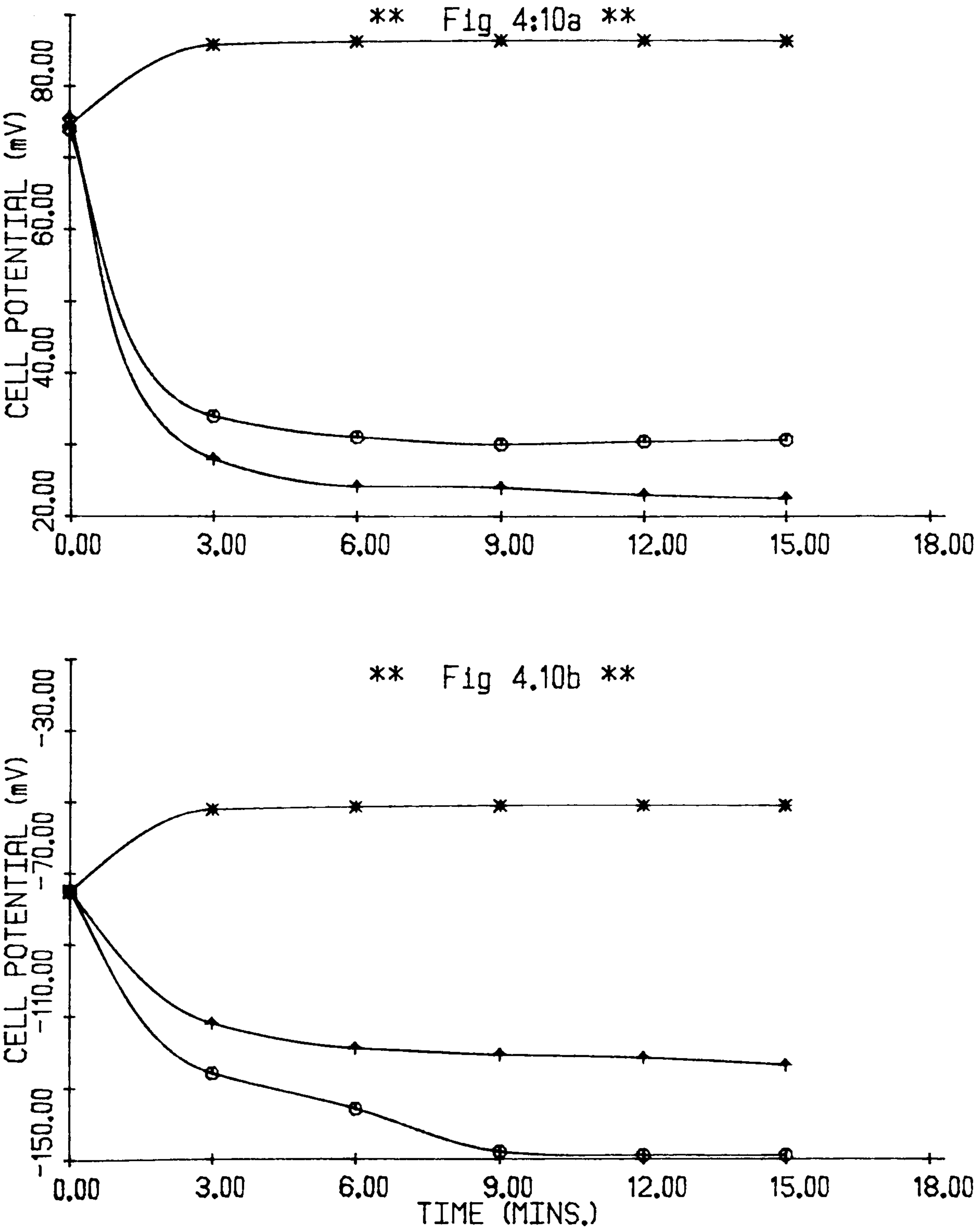


HYDROLYSIS OF IMPURITIES IN MEMBRANE

FIG 4.9a: KCl SOLUTION Fig 4.9b: H_2O SOLUTION

☆ = MEMB. No. 4 ⊖ = MEMB. No. 16

✱ = **MEMB.** No. 7 ✦ = **MEMB.** No. 8

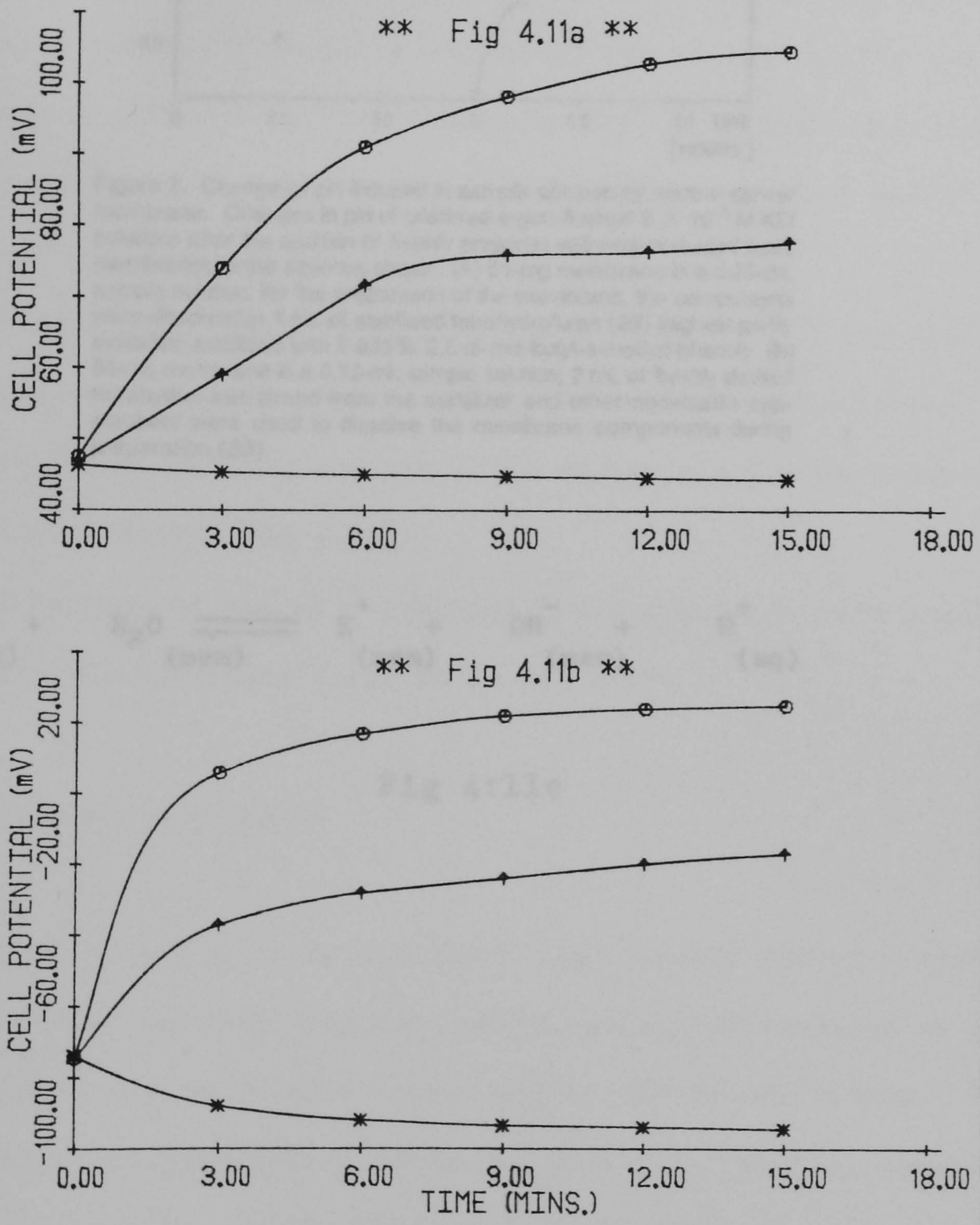


HYDROLYSIS OF IMPURITIES IN PVC SAMPLES

Fig 4.10a: KCl SOLUTION   Fig 4.10b: H_2O SOLUTION

✦ = S 125/12   ⊕ = S 110/10

✱ = BDH (MW=100,000)



HYDROLYSIS OF IMPURITIES IN PLASTICIZER

Fig 4.11a: KCl Solution Fig 4.11b: H_2O SOLUTION

+ = DOP ⊙ = DBS

✱ = DBP

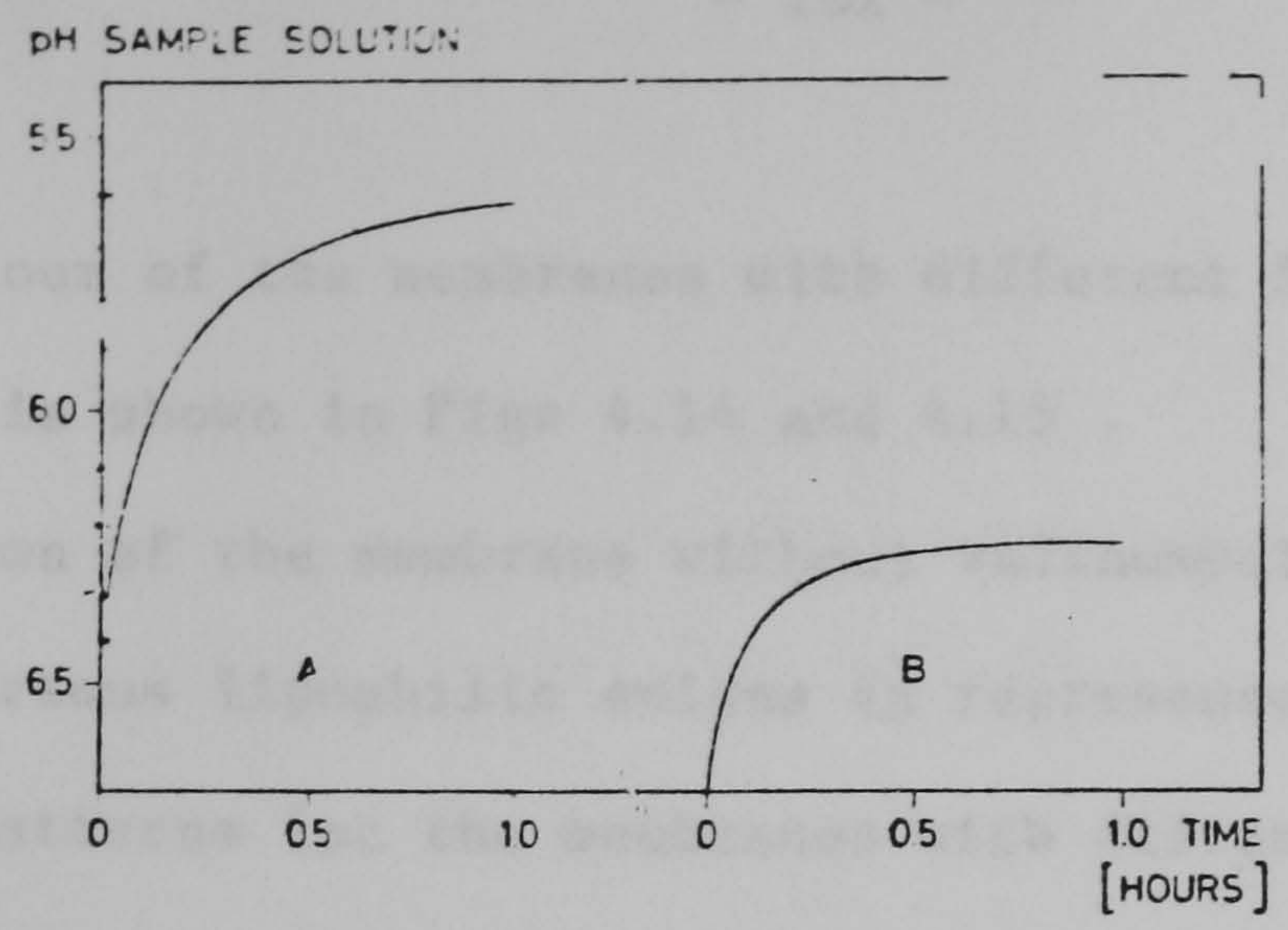


Figure 7. Change of pH induced in sample solution by neutral carrier membrane. Changes in pH of unstirred argon-flushed 9 × 10^{-3} M KCl solutions after the addition of freshly prepared valinomycin-based liquid membranes to the aqueous phase. (A) 51-mg membrane in a 0.75-mL sample solution; for the preparation of the membrane, the components were dissolved in 1 mL of stabilized tetrahydrofuran (*23*) (highest purity available; stabilized with 0.025% 2,6-di-*tert*-butyl-4-methyl-phenol). (B) 86-mg membrane in a 0.75-mL sample solution; 2 mL of freshly distilled tetrahydrofuran (freed from the stabilizer and other nonvolatile substances) were used to dissolve the membrane components during preparation (*23*)

$$\underset{(aq)}{K^+} + \underset{(mem)}{H_2O} \rightleftharpoons \underset{(mem)}{K^+} + \underset{(mem)}{OH^-} + \underset{(aq)}{H^+}$$

Fig 4:11c

b) The behaviour of the membranes with different PVC samples and different plasticizers is shown in Figs 4.14 and 4.15 .

c) The function of the membrane without valinomycin (blank) for potassium salts with various lipophilic anions is represented in Fig 4.16. Also the calibration patterns for the membranes with different contents of valinomycin, namely o.1%, 0.2% and 0.5% (w/w), for KSCN solutions, are illustrated in Fig 4.17.

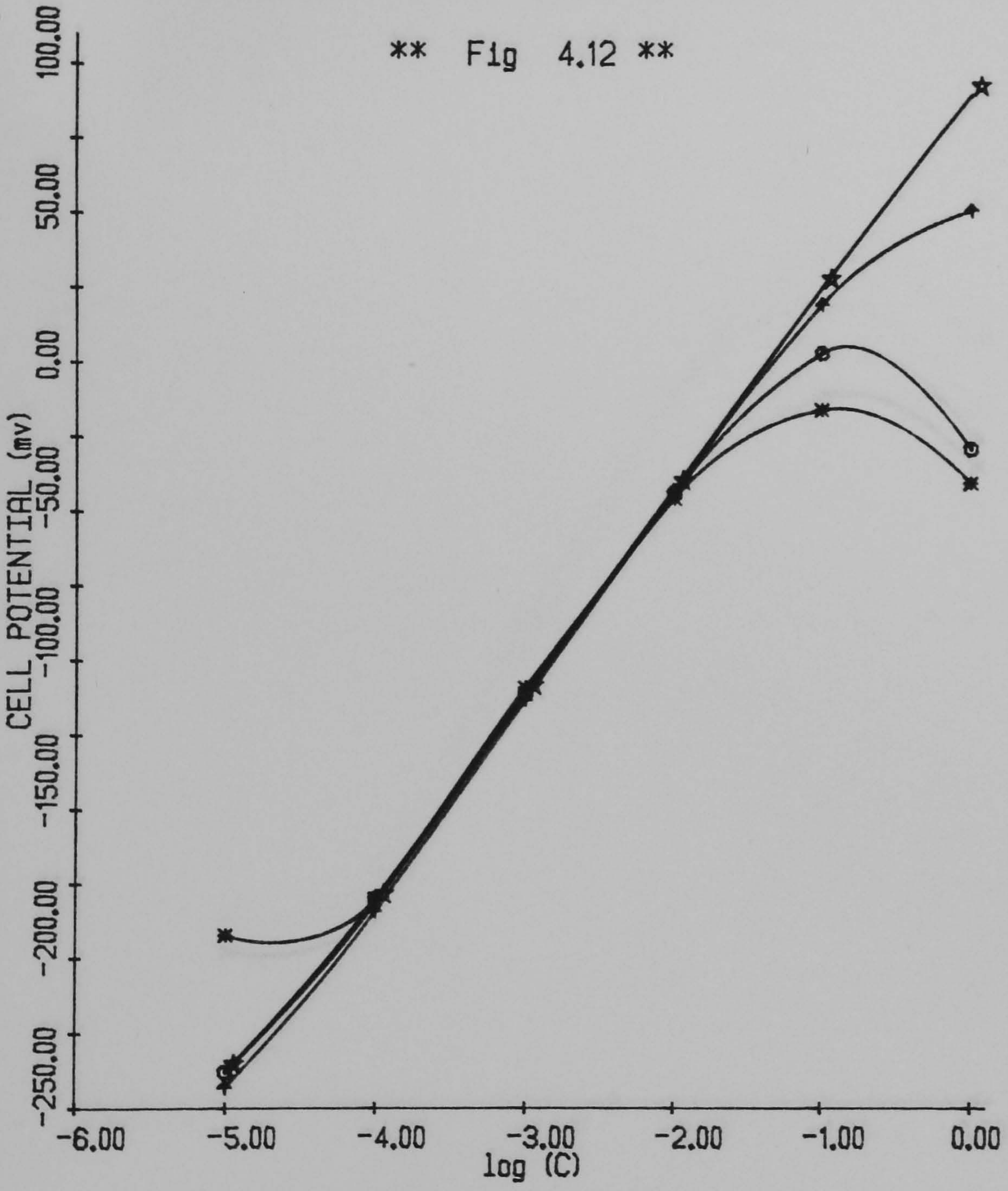
d) Membranes with solid internal systems ´Cu/Hg´ with two different plasticizers have been used for comparison of the behaviour of the conventional electrodes and the solid system electrodes towards the thiocyanate effect (Fig 4.18).

e)The behaviour of the Ca^{2+} (Philips Ltd.) electrode with calcium chloride and calcium thiocyanate is given in Fig 4.19.

4.8 RESULTS AND DISCUSSION

Once more, it has to be mentioned that freshly tested membranes were found to show unstable response, while electrodes immersed in 10^{-3} mol/dm^3 KCl and kept overnight gave rapid, stable and better slopes. The same observation was reported by Boles and Buck [5]. It was suggested that during this period, uptake of water and gel layer formation occurs [18,19]. The results of membranes with and without active material (valinomycin), indicate that the variation of the pH of the sample solution is independent of the active material, though it seems reasonable to expect some differences due to the increase in the potassium ion concentration in the membrane when valinomycin is used. Data from Fig 4.9a demonstrates that

** Fig 4.12 **



* CALIBRATION CURVES (K^+/VALINOMYCIN) *

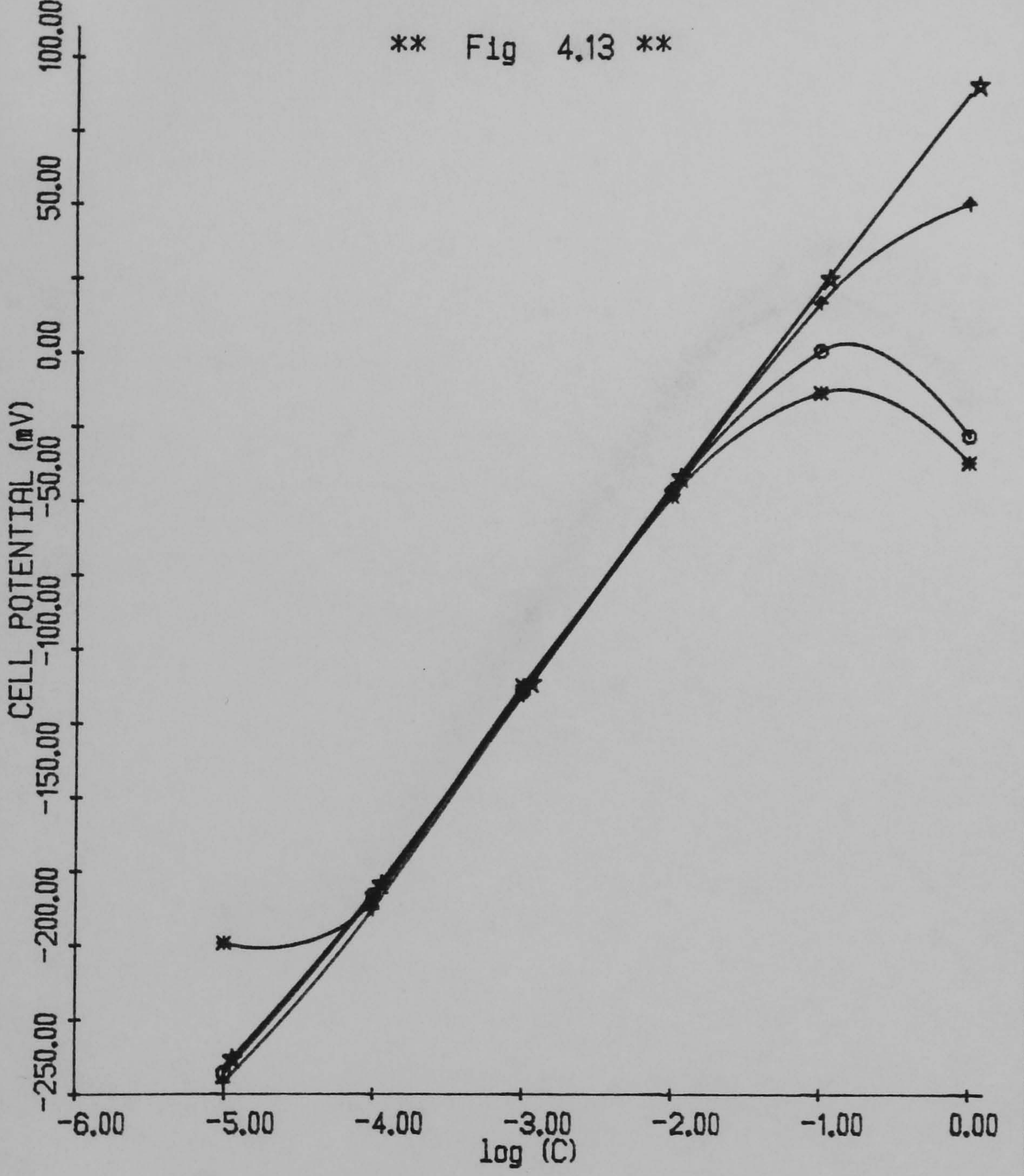
(MEMBRANE WITHOUT KTPCPB)

EFFECT OF LIPOPHILIC ANIONS

☆ = KCl ✳ = KSCN

⊙ = KI + = KNO_3

** Fig 4.13 **



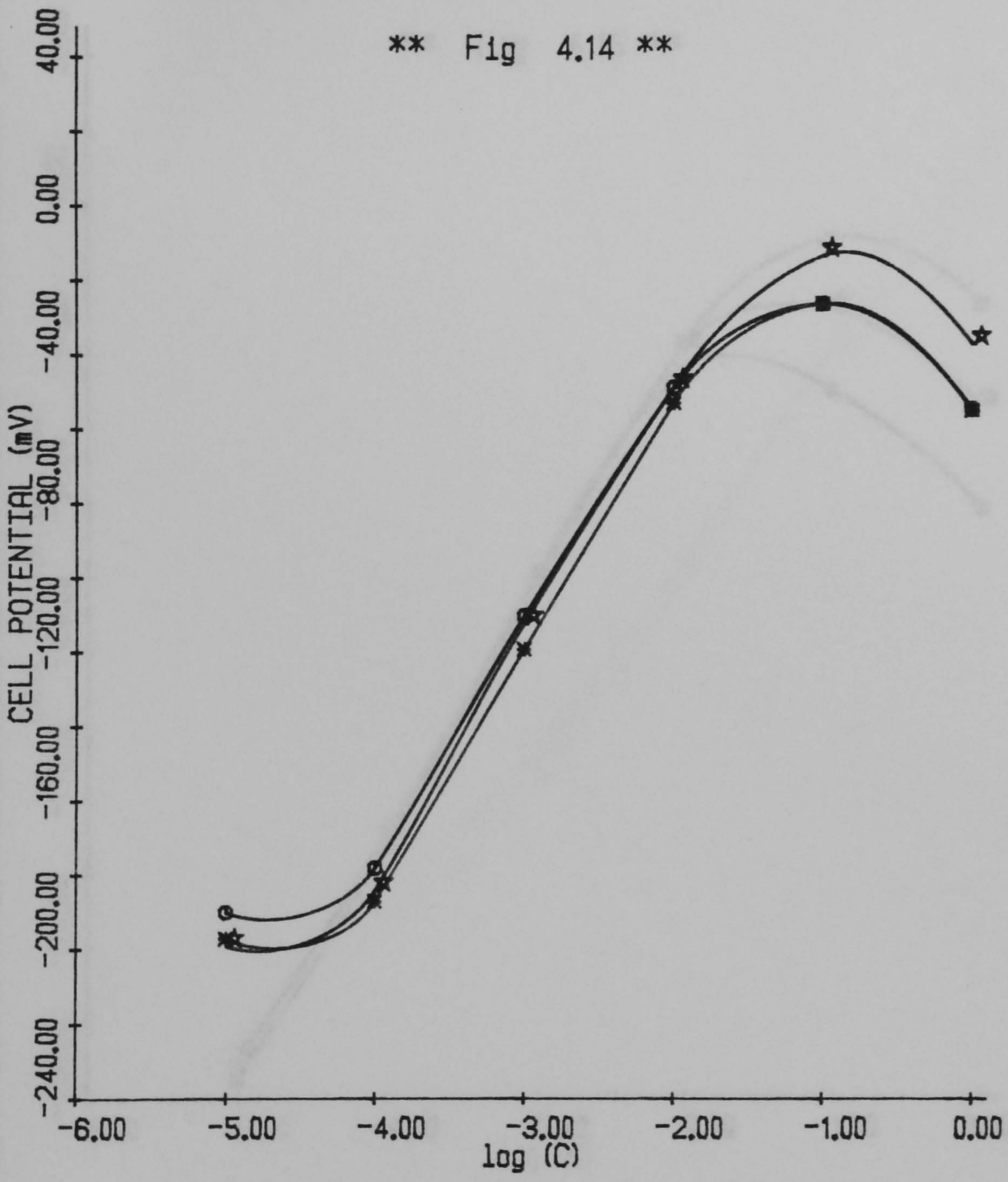
* CALIBRATION CURVES (K^+/VALINOMYCIN) *

(MEMBRANE WITH KTPCPB)

EFFECT OF LIPOPHILIC ANIONS

★ = KCl ✱ = KSCN

⊙ = KI ✦ = KNO_3



** Fig 4.14 **

* CALIBRATION CURVES (K^+ /VALINOMYCIN) *

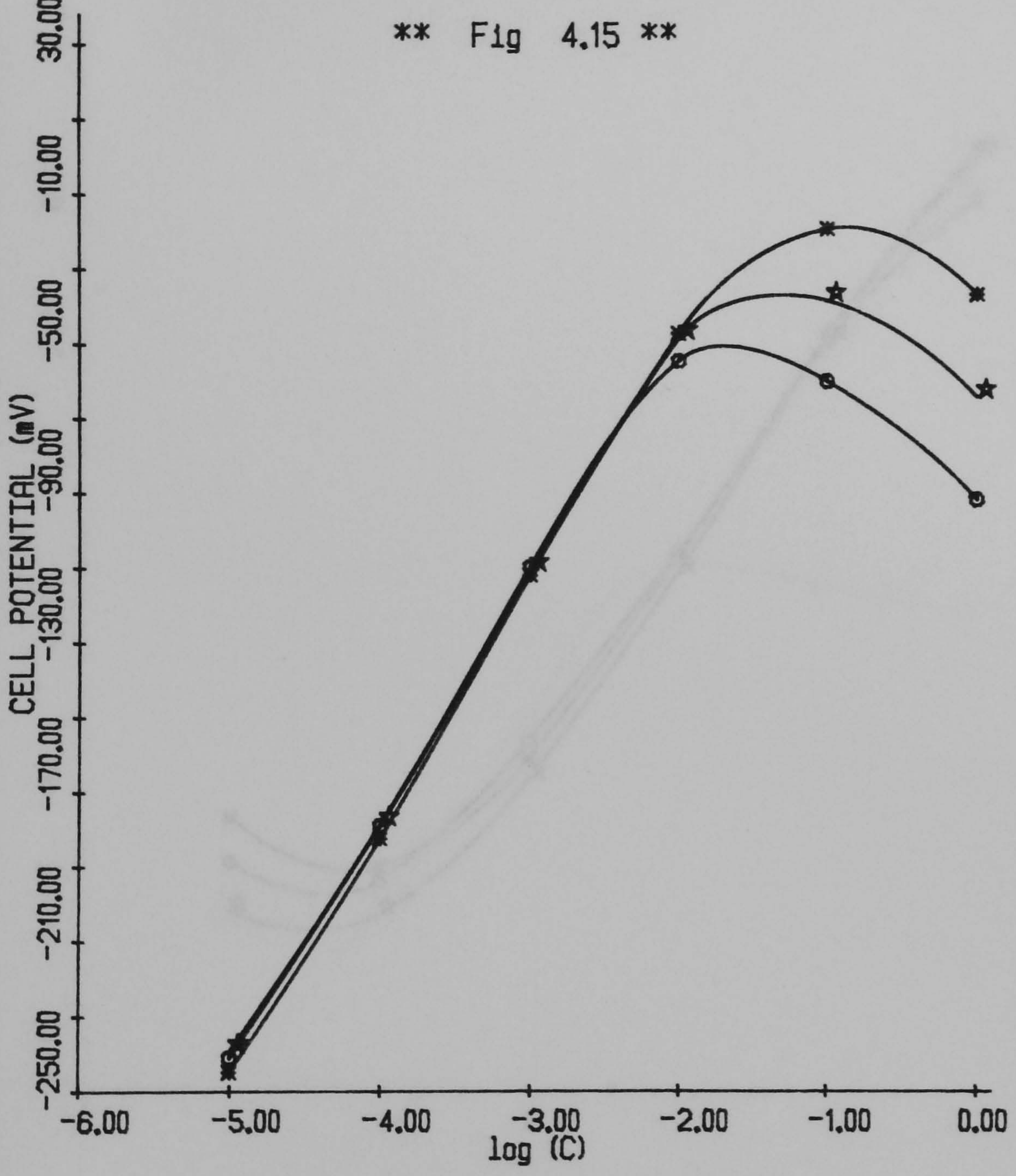
(MEMBRANES WITH DIFFERENT PVC)

EFFECT OF LIPOPHILIC ANION "SCN^-"

☆ = S 125/14 ✱ = BDH (MW=200,000)

⊙ = S 110/10 (MW=57,000)

** Fig 4.15 **



* CALIBRATION CURVES (K /VALINOMYCIN) *

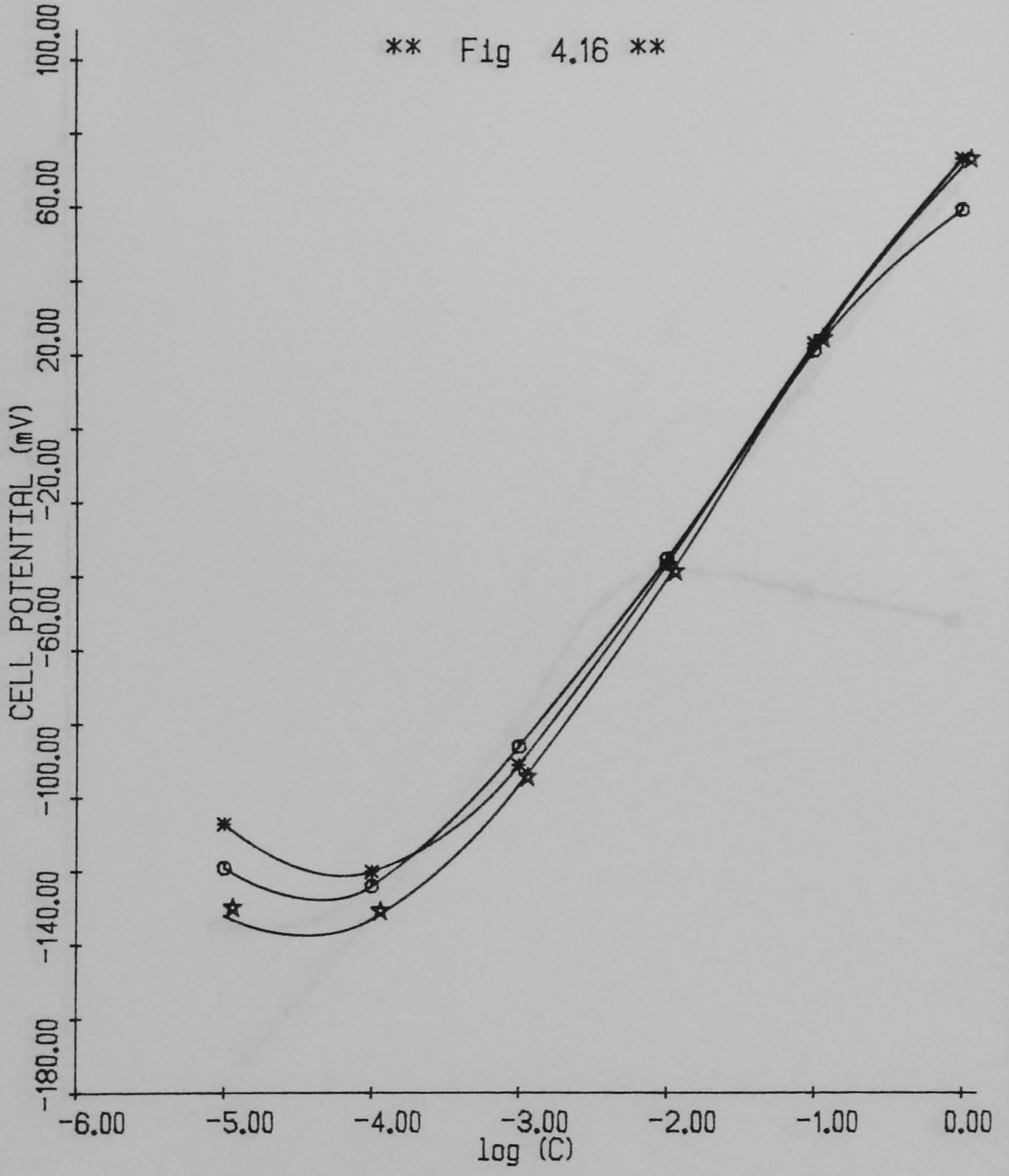
(MEMBRANES WITH DIFFERENT PLASTICIZERS)

EFFECT OF LIPOPHILIC ANION "SCN^-"

★ = DOP ✱ BEHS

⊙ = DBP

** Fig 4.16 **

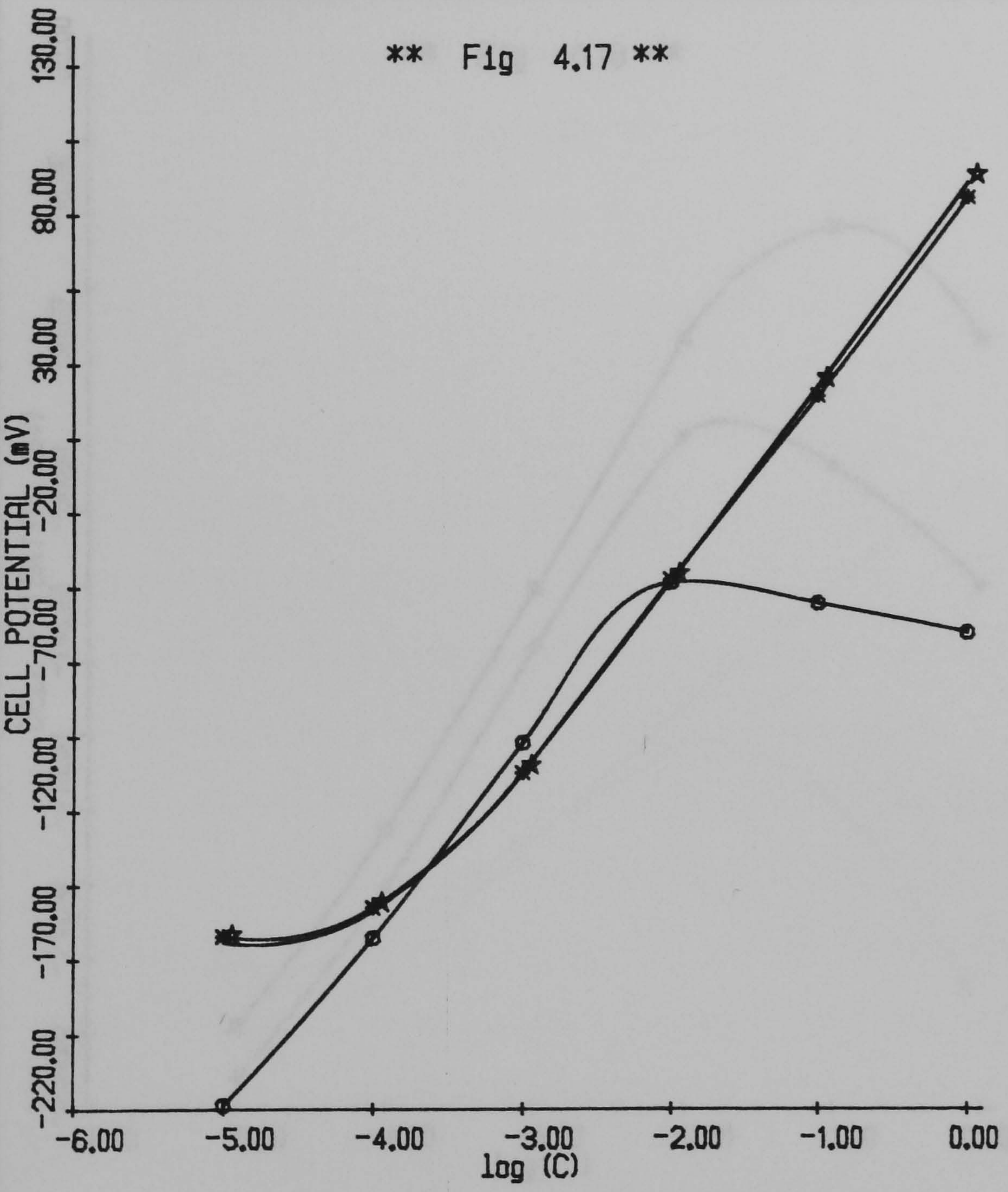


* CALIBRATION CURVES *

(MEMBRANES WITHOUT VALINOMYCIN)

EFFECT OF LIPOPHILIC ANIONS

** Fig 4.17 **



* CALIBRATION CURVES (K /VALINOMYCIN) *

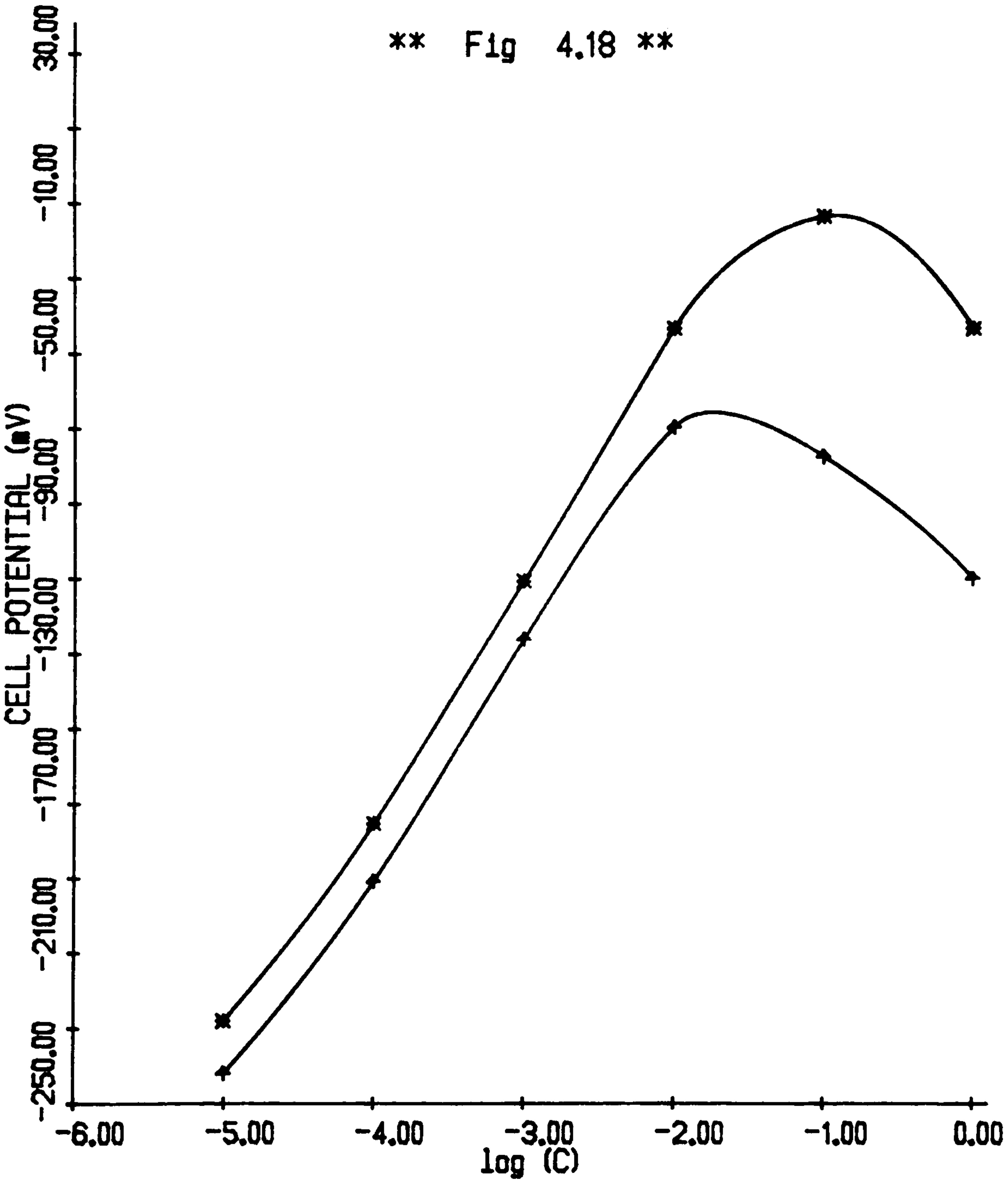
(MEMBRANE WITH DIFFERENT AMOUNT OF ACTIVE MATERIAL)

EFFECT OF LIPOPHILIC ANION "SCN^-"

★ = 0.1% (W/W) ⁎= 0.2% (W/W)

⊙ = 0.5% (W/W)

** Fig 4.18 **

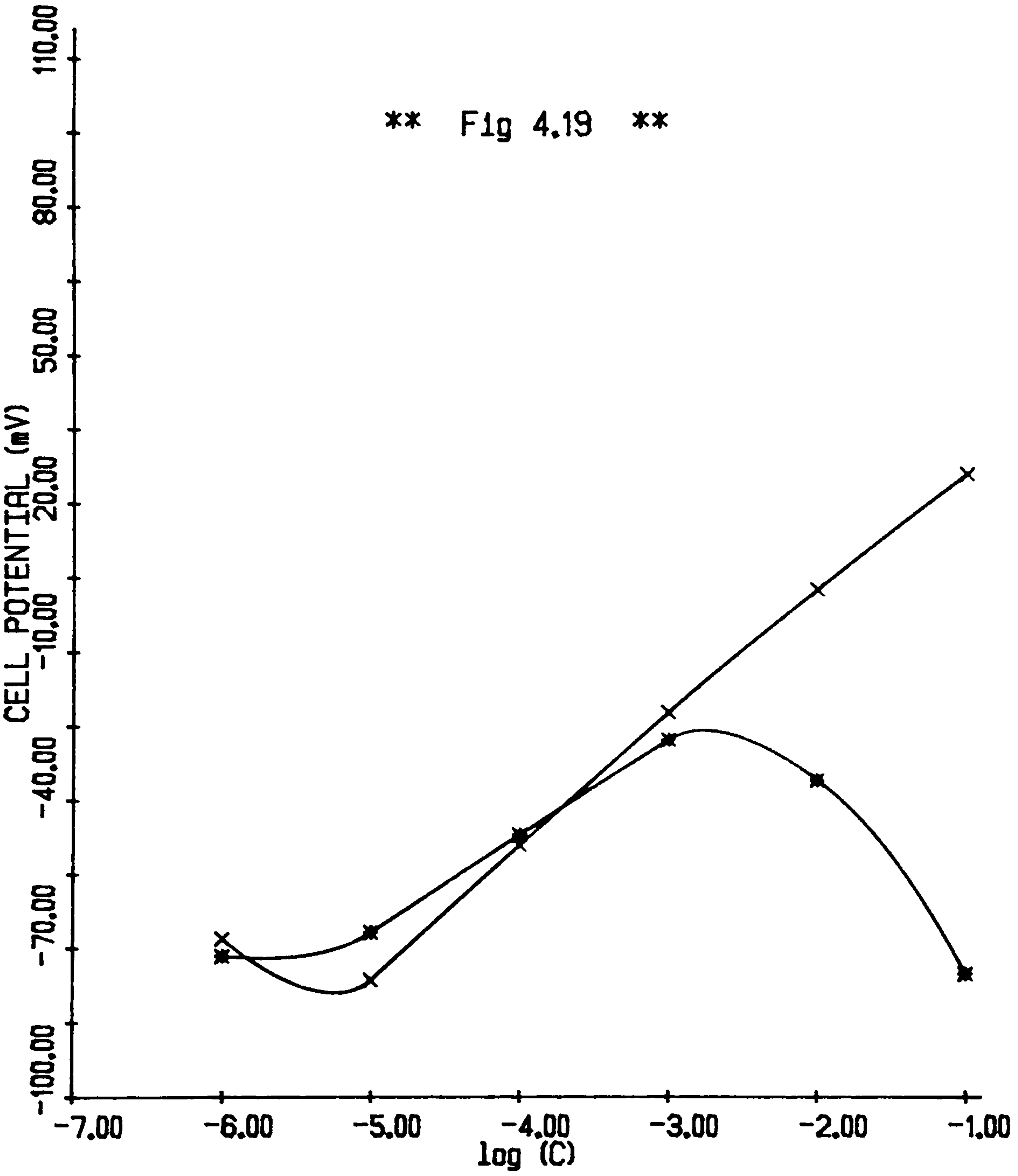


* CALIBRATION CURVES (K /VALINOMYCIN) *

Cu/Hg AS INNER REFERENCE SYSTEM

✱ = CALIBRATION WITH KSCN "BEHS"

✦ = CALIBRATION WITH KSCN "DBP"



** Fig 4.19 **

* CALIBRATION CURVES (Ca^{2+}/PHILIPS Co.) *

× = CALIBRATION CURVE: $CaCl_2$
✱ = CALIBRATION CURVE: Ca $(SCN)_2$

two similar membranes, with the only difference being in their PVC matrices, changed the pH of the external solution. The extent of this variation was not the same. The membrane with high molecular weight PVC (BDH 200,000) changed the pH rapidly and on a large scale, compared with membrane with low molecular weight (Breon 57,000). It should be noted that apart from the molecular weight, other differences must be taken into consideration (e.g. type of stabilizers). The results of experiments with water as the sample solution gave a similar pattern (Fig4.9b). However, all four membranes Numbered 4, 7, 8 and 16 with different composition, showed the same trend, decrease in the pH of the external solution, regardless of the type of contacting solution, water or KCl. These differences in the pH variation might be attributed to the differences in the ion-exchange capacity of the membrane components. This anticipation was confirmed by the results obtained from independent pH measurement with separate PVC and plasticizer samples (Figs 4.10a, 4.10b, 4.11a and 4.11b). As one can see in Figs 4.10a and 4.10b, the various types of PVC powder produce changes in the pH of the solution in different directions, e.g. acidic or basic and to different extents. This change is clearly an indication of the presence of various impurities in the different PVC samples. As far as the variation of the pH is concerned, it is independent of the nature of the sample solution (water or KCl). Similar results were obtained when different plasticizers were examined (Figs 4.11a and 4.11b). Some of the PVC powders and plasticizers changed the pH of the solution in the opposite direction, in other words the solution turned basic. Thus, in view of these results, it seems logical to suggest that the decrease of the pH in external solutions is the result of a combination of effects of membrane components, including impurities. The results of these sets of experiments, which were shown in Figs 4.9a, 4.9b, 4.10, 4.10b, 4.11a and 4.11b, strongly reject the Simon et al. [16] hypothesis that the origin of immobile sites rests in the occurrence of the following exchange reaction:

$$\underset{\text{aq}}{K^+} + \underset{\text{mem}}{H_2O} \rightleftharpoons \underset{\text{mem}}{K^+} + \underset{\text{mem}}{OH^-} + \underset{\text{aq}}{H^+} \qquad (4.3)$$

It is clear that the presence of potassium in the aqueous solution is essential for this exchange reaction. It is quite reasonable to assume that in the absence of potassium ion, the flux of the hydrogen ion will not occur, or at least only to a very small extent. The experiments with triple distilled water gave exactly the same variation pattern (Figs 4,9b,4.10b and 4.11b). Thus, one can surely conclude, that if there is any exchange reaction, it would not necessarily be the above reaction (4.3). The exchange reaction most likely to occur is the hydrolysis of impurities in the membrane constituents, e.g. PVC, plasticizer, etc. The lipophilic anion interference data from Figs 4.12 and 4.13 clearly indicate that the presence of the KTPCPB, at least in the amounts which were used in the preparation of the membranes in this study (1.2 mg), does not prevent the penetration of hydrophobic anions. At high concentrations of sample solution pC:1 - 0.0, membranes with and without additional lipophilic anion do not prevent the anion response. Anionic responses were observed according to the following order:

$$SCN^- > I^- > NO_3^- > Cl^-$$

However, the introduction of KTPCPB at high levels might show significant differences. Concerning the anion interference in the membrane with various amount of valinomycin (Figs 4.16 and 4.17), it can be shown that up to 0.2% active material does not give any significant anion response, whereas, the membrane with 0.5% valinomycin creates a maximum around pC=2 with very low anion response. A comparison of Figs 4.12, 4.13, 4.16 and 4.17 indicates that it is the presence of the valinomycin which helps the penetration of the lipophilic anions and facilitate the anion response of the membrane. The membrane with 1% valinomycin gives higher anion response in the range of pC:1 - 0.0. This contribution to the anion response might arise due to the anion pair complex formation. This observation is in good agreement with the work of Seto et al. [20] who used polynactin as neutral carrier. Thus, one way of reducing the anion interference is the reduction of the active material, while on the other hand, as explained in Chapter Three, and as can be seen from Fig 4.17, this reduction will cause losses of the membrane selectivity and reduction in the response range. However, it is plausible to utilize a membrane with low active material content for potassium measurements with strong lipophilic anions. Results for the membranes with various plasticizers (Fig 4.15) demonstrate some discrepancy as the position of the maxima are not the same. The membrane based on DBP shows anion response below pC:2 - 0.0, while the membrane made of BEHS shows it below pC:1 - 0.0. This behaviour may be firstly attributed to the extractibility of the membrane media, which is the result of the polarity and ion-exchange capacity of the membranes. The high polar media extract more lipophilic anions. Secondly this difference may arise due to the differences in the mobility of the anions in the membrane. Another method of either reducing or eliminating the anion interference is to use a low polar plasticizer with no ion-exchange capacity. Following the ion-exchange capacity of the membrane components, Fig 4.14 reveals that membranes with the same composition made of different PVC samples, showed different extents of distortion in the response curve of potassium thiocyanate solution. This may be the direct result of the impurities in the PVC samples which provide a different ion-exchange capacity in the membranes

Fig 4.18 shows the SCN^- effect on the membranes with different plasticizers BEHS and DBP with solid internal system (Cu/Hg). By comparing Figs 4.18 and 4.15 it can be seen that both types of electrodes give similar deviation from linearity at concentration above 10^{-2} mol/dm^3 for the membrane with BDP and 10^{-1} mol/dm^3 for the membrane based on BEHS. From this observation, one can say that anion interference is independent of the internal reference system and more likely is related to the membrane composition. The SCN^- response for the Ca^{2+} membrane (Philips Ltd.) was found above 10^{-3} mol/dm^3. This result is in contradiction with Morf's [21] finding, where he reported a slope about 100mV. He stated this response to be the result of both divalent cation and monovalent anion. However, in this study this was not observed (Fig 4.19).

From these findings it is very difficult to attribute the distortion of the membrane response, at higher concentrations of the lipophilic anions, to the complete consumption of the neutral carrier. If this were the case, it should be expected that the blank and membranes with lower valinomycin (0.1% and 0.2%) should show strong anion responses; however, this was not the case. It is evident from the results that all components of the membrane are involved in the anion interference. To overcome this shortcoming, investigation of the nature of the processes determining the electrode properties is required. In the meantime, proper active materials, plasticizers and inert matrices must become available. The results of this study are consistent with the assumption that the PVC membrane contained negative sites, and selectivity of membrane is the result of the presence of such sites. Electroneutrality of the membrane is preserved due to the existence of those negative sites. In conclusion, it seems reasonable to assume that cations from the external solution do not cross the membrane but only penetrate the interface of the membrane. However, anions in the bulk of the membrane appear more likely to be responsible for the charge transfer through the membrane.

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CHAPTER FIVE

THE BIAS OF THE CORNING 902 NA^+/ K^+ ANALYSER AND A CONTINUOUS DILUTION METHOD FOR CALIBRATION OF I.S.Es

5.1 INTRODUCTION PART (I)

Automatic instruments, based on ion-selective electrodes which measure potassium, sodium and calcium ions levels in whole blood, serum, plasma and urine, as well as pH meters and gas analysers, are replacing flame photometers and other time consuming devices. The flame system suffers from a number of disadvantages especially in intensive care units, where quick Na^+ and K^+ analyses are required. The most unfavourable condition is that the whole blood can only be analysed when separated and diluted. In contrast, instruments based on ion-selective electrodes can be easily and quickly operated on small quantities, and still more possible is the development of electrodes capable of determining species which are impossible to measure with other methods. In fact, ion-selective electrodes measure the activity of ions in the sample solutions; that is the ions which are free and not complexed. This property is in some cases an advantage and in others a disadvantage. For instance, a change in extra-cellular potassium level affects both the heart rhythm and its strength, and potassium activity is the important factor here [1]. The characteristics and specifications of some available electrochemical devices have been given by Covington [2].

However, bias has been observed with these devices, which mainly arises from liquid junction variations and interferents. Only small potential differences are associated with the normal variation of ion concentrations in body fluids. For example, the normal range for plasma sodium is between 138 to 151 mmol/dm^3 and for potassium, 3.4 to 5.2 mmol/dm^3 . This variation corresponds to 2.4 mV and 11.3 mV changes in membrane potential of the sodium and potassium electrodes respectively. Covington et al.[4] recently, through liquid junction geometry studies, found that 2 mV/decade change is common. To overcome the source of error, a better understanding of liquid junction formation and standard solutions is required. Preliminary measurements with the Corning 902 Na$^+$/ K$^+$ analyser revealed that the results are not reproducible and some discrepancy occurred (Table 5.1). In this work the possible origin of this bias has been explored.

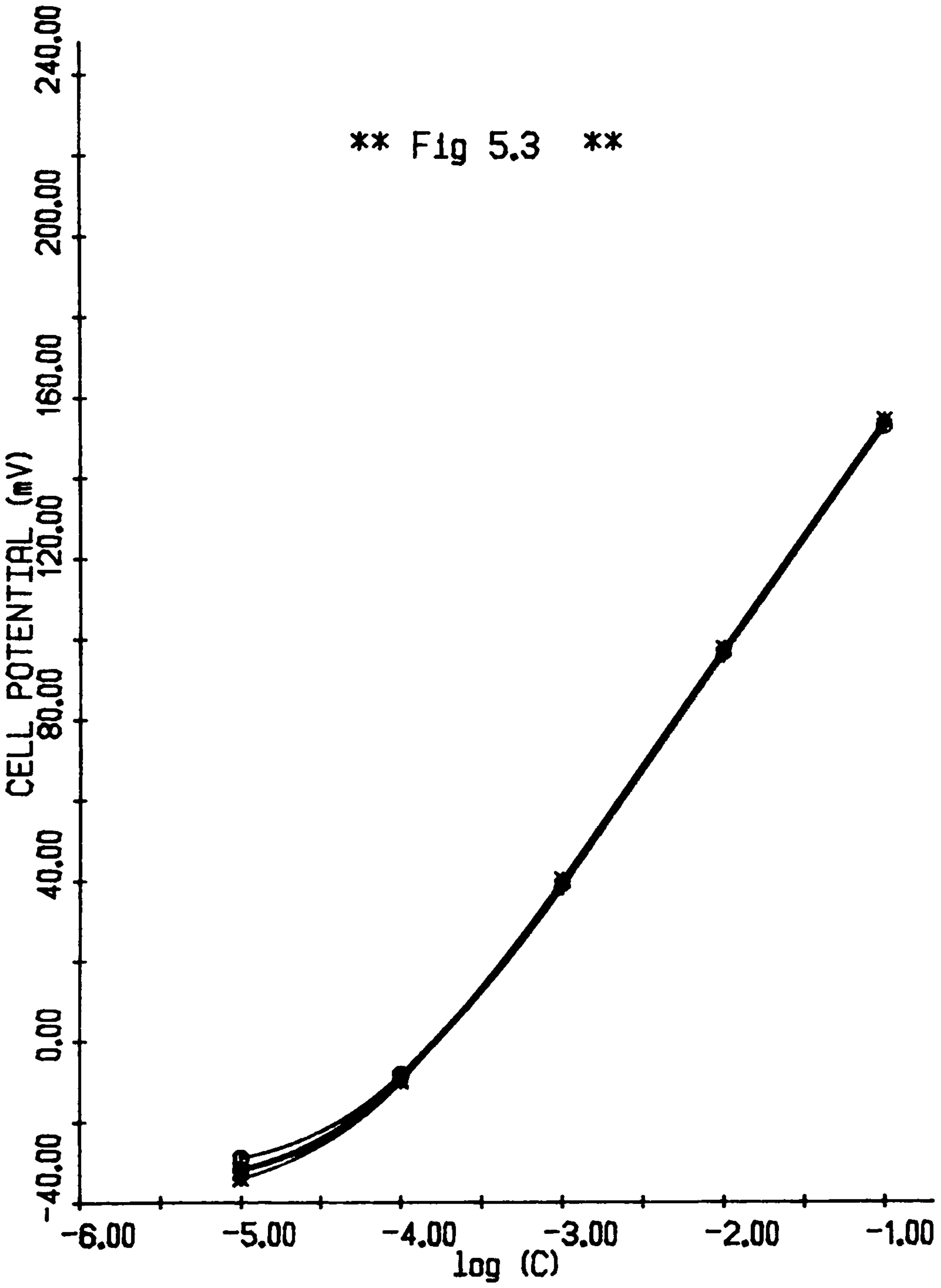
Table 5.1

KCl Conc.(mmol/dm^3)	Measured by Corning 902
1.0	1.09, 1.07, 1.09, 1.07 1.09 1.08
2.0	2.01, 2.01, 1.98, 1.98, 2.06 2.06
3.0	2.93, 2.94, 2.94, 2.92, 3.03, 3.00
4.0	3.96, 3.96, 3.91, 3.92, 3.99, 3.99
5.0	4.96, 4.99, 4.88, 4.89, 4.89, 4.87
6.0	5.97, 5.98, 6.0, 5.88, 5.89 5.91
7.0	7.08, 7.09, 7.06, 7.05, 6.92, 6.91

5.2 POSSIBLE LIQUID JUNCTION POTENTIAL VARIATION DUE TO TRITON X-100

To find the sources of the bias, calibration curves for electrodes from the Corning analyser were produced independently. It was found that the results were not reproducible. This can be taken as a sign that the irreproducibility is not originating from the electrical circuits of the analyser; thus, there must be other sources for this discrepancy. The calibration curves are shown in Figs 5.3 and 5.4 for K^+ and Na^+ ions respectively. As was mentioned earlier, the origin of irreproducibility might rest mainly with the variation of liquid junction potential between the reference electrode and sample solution. Another possibility may be the interference of some species with the membrane, which will alter the electrode potential difference. Consequently, the effect of two factors, namely liquid junction potential variation and interference of the non-ionic detergent Triton X-100, added to the standard solutions by Corning, was assessed.

The potential, which arises across liquid phase interfaces due to differences in the mobilities of the charged particles, is called the liquid junction potential. It is a well known fact that some uncertainty in I.S.E. measurements comes from the variation of liquid junction potentials. These are extremely difficult to reproduce in practice, due to different geometric forms, stirring, flow effects and memory effects. The latter is brought about by the ionic diffusion into the bridge solution from the previously used standard or sample solutions. To overcome all these problems, it is important to take into account all parameters which

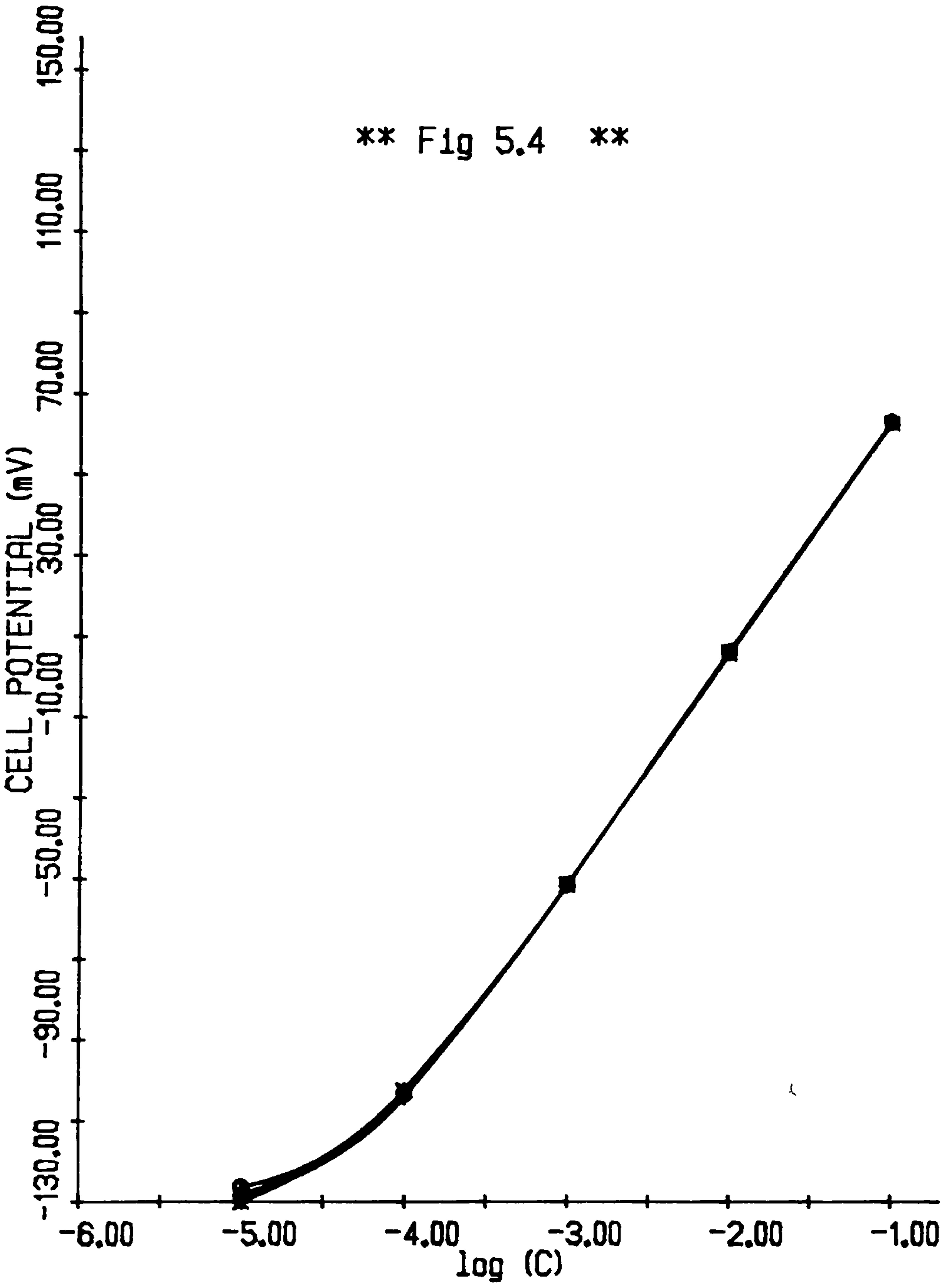


** Fig 5.3 **

CORNING FLOW CELL

REPRODUCIBILITY OF THE POTASSIUM ELECTRODE

** Fig 5.4 **



CORNING FLOW CELL

REPRODUCIBILITY OF THE SODIUM ELECTRODE

might affect the mobility of the species and geometry of the formation of the liquid junction. If parameters such as pH, T, and ionic strength are kept constant, the only factors which might affect the liquid junction potential should be, firstly, the amount of the Triton X-100 in the solutions, and, secondly, the memory effect of the reference electrode. To obtain information about the effect of the Triton X-100 on the potential of the cell, two series of experiments were arranged.

a) The effect of Triton X-100 on the reference electrode.($E_{L.J.}$)

b) The effect of Triton X-100 on the K^+ / PVC electrode.

5.3 EXPERIMENTAL PROCEDURE

The electrochemical cell of the 902 analyser was dismantled and is represented in Fig 5.2A. It consists of three separate electrodes: Ag/AgCl acting as external reference, sodium glass electrode and K^+ / PVC electrode as indicator electrodes. The composition of the PVC potassium membrane provided in the analyser is supposed to be the same as that described in Chapter Two. Similar results were obtained when a home-made membrane was used.

All experiments were carried out using the cell arrangement, shown in (Fig 5.1). Part A is the cell block of the analyser. Part B of the cell is designed to check the effect of liquid junction formation and also compare the K^+ / I.S.E. potential against the S.C.E. The reason for choosing the 'T' form of junction was that after a number of experiments with different form of liquid junction geometries, carried out in this laboratory, it was found that stable and reproducible results could only be obtained by using this form of junction. An important feature of using this form of junction is the elimination of memory effects found in commercial porous plug junctions(S.C.E.). A new junction can be easily formed by injecting fresh solution. A syringe was employed in part B to achieve this renewal procedure. All solutions were prepared in constant ionic background by serial dilution. The composition of the background solution is given below and it was adjusted to pH = 7.4 by addition of HCl solution.

Composition of Background Solution

6.055 g	Tris
42 ml	1 mol/dm^3 HCl
8.1816 g	NaCl (to give 140 mmol/dm^3)
500 ppm	Triton X-100 (Iso-octyl phenoxy polyethoxy-ethanol) $\simeq$10 ethoxy units
500 ppm	Biocide (Bronidox)
3 D Water	to one liter

A hydrostatic head was used to effect the flow of solution through the cell. The rate of flow was controlled by varying the height of the beaker on the stand.


Sample Solution
Ag/AgCl
'T' Junction
Waste
Syringe
S.C.E
4mol/dm KCl
4mol/dm³ KCl
Stand
P.V.C K⁺ I.S.E
Capillary Na⁺ glass
Dialysis membrane
A
B

5.4 RESULTS

5.4.1 Effect of Triton X-100 on the Calibration Curves

500 ppm Triton X-100 was added to the calibration solutions (10^{-1} - 10^{-5} mol/dm^3) KCl. The results are shown in Table 5.2. They are the average of 5 runs and in some cases 10 runs.

Table 5.2

	KCl Conc. mol/dm^3	E/mV (flow cell)	E/mV (T. junction)	ΔE/mV
	10^{-5}	-33.0	-71.8	38.8
500 pmm	10^{-4}	-11.8	-49.8	38.0
Triton	10^{-3}	+37.7	- 2.0	39.7
X-100	10^{-2}	+92.2	+53.8	38.4
	10^{-1}	+146.5	+108.7	37.8

In the absence of Triton X-100, and using the same solution (4 mol/dm^3 KCl) in the reference electrodes, the results in Table 5.3 were obtained.

Table 5.3

	KCl Conc. mol/dm^3	E/mV (flow cell)	E/mV (T. junction)	ΔE/mV
	10^{-5}	-27.0	-67.3	40.3
No	10^{-4}	- 6.5	-45.2	38.7
Triton	10^{-3}	+38.5	+ 0.2	38.3
X-100	10^{-2}	+93.4	+55.0	38.4
	10^{-1}	+147.5	+109.3	38.2

With the calibration solution as above, but with 500 ppm Triton X-100 in the inner solution of the reference electrodes, the results in Table 5.4 were obtained.

Table 5.4

	KCl Conc. mol/dm^3	E/mV (flow cell)	E/mV (T. junction)	ΔE/mV
	10^{-5}	-33.0	-71.8	38.8
No	10^{-4}	-11.8	-49.8	38.0
Triton	10^{-3}	+41.5	- 0.5	42.0
X-100	10^{-2}	+90.8	+52.3	38.5
	10^{-1}	+143.9	+105.6	38.3

When 500 ppm Triton X-100 was added to both calibration and reference solutions, the results in Table 5.5 were found.

Table 5.5

	KCl Conc. mol/dm^3	E/mV (flow cell)	E/mV (T. junction)	ΔE/mV
	10^{-5}	- 5.0	-43.7	38.7
500 ppm	10^{-4}	- 7.0	-45.0	38.0
Triton	10^{-3}	+40.0	+ 1.5	38.5
X-100	10^{-2}	+92.2	+53.4	38.8
	10^{-1}	+145.6	+106.7	38.9

Next the amount of Triton X-100 in the calibration solution was changed to 2000 ppm, while reference electrodes contained no Triton X-100 (see Table 5.6).

Table 5.6

	KCl Conc. (mol/dm^3)	E/mV (flow cell)
2000 ppm	10^{-5}	-27.2
Triton	10^{-4}	- 7.0
X-100	10^{-3}	+40.1
	10^{-2}	+96.6
	10^{-1}	+152.9

Finally, the calibration solutions contained 500 ppm Triton X-100, while the inner solution of the reference electrode was 4 mol/dm^3 KCl + 2000 ppm Triton X-100 (see Table 5.7).

Table 5.7

	KCl Conc. (mol/dm^3)	E/mV (flow cell)
500 ppm	10^{-5}	-27.2
Triton	10^{-4}	- 7.0
X-100	10^{-3}	+40.1
	10^{-2}	+96.6
	10^{-1}	+152.9

5.4.2 Effect of Triton X-100 on Reference Electrodes

The Corning reference electrode was checked against a S.C.E. The experiments were carried out with the same cell used for above experiments (Fig 5.1). The results given in Table 5.8 correspond to the effect of the presence of Triton X-100 in calibration solutions on the potential differences between Ag/AgCl of Corning analyser and T-junction S.C.E. The internal solution of both electrodes was 4 mol/dm^3 KCl.

Table 5.8

	KCl Conc. (mol/dm^3)	ΔE/mV
	10^{-5}	39.9
500 ppm	10^{-4}	39.9
Triton	10^{-3}	40.0
X-100	10^{-2}	40.0
	10^{-1}	40.0
2000 ppm	10^{-2}	40.0
Triton	10^{-1}	40.0
X-100		

By adding 2000 ppm Triton X-100 to the inner solution of the reference electrode (Ag/AgCl), the effect of the presence of Triton on the electrode potential vs. S.C.E. was examined; the results are shown in Table 5.9.

Table 5.9

	KCl Conc. (mol/dm^3)	ΔE/mV
	10^{-5}	39.8
500 ppm	10^{-4}	39.8
Triton	10^{-3}	39.8
X-100	10^{-2}	39.8
	10^{-1}	39.8
2000 ppm Triton	10^{-2}	39.9
X-100	10^{-1}	39.8

Finally, the effect of the presence of Triton X-100 in the filling solutions of both electrodes, while the calibration solutions had no Triton X-100, was studied. The potential differences for Ag/AgCl vs. T-junction S.C.E. are given in Table 5.10 .

Table 5.10

KCl Conc. (mol/dm^3)	ΔE/mV	
10^{-5}	40.1	
10^{-4}	40.1	500 ppm
10^{-3}	40.0	Triton X-100
10^{-2}	40.0	in Inner Solution
10^{-1}	39.9	
10^{-2}	40.0	2000 ppm
10^{-1}	40.0	Triton X-100
		in Inner Solution

A similar set of experiments was carried out by replacing the S.C.E. with a second Ag/AgCl electrode in the cell as shown in Fig 5.2B with results which are given in Table 5.11 .

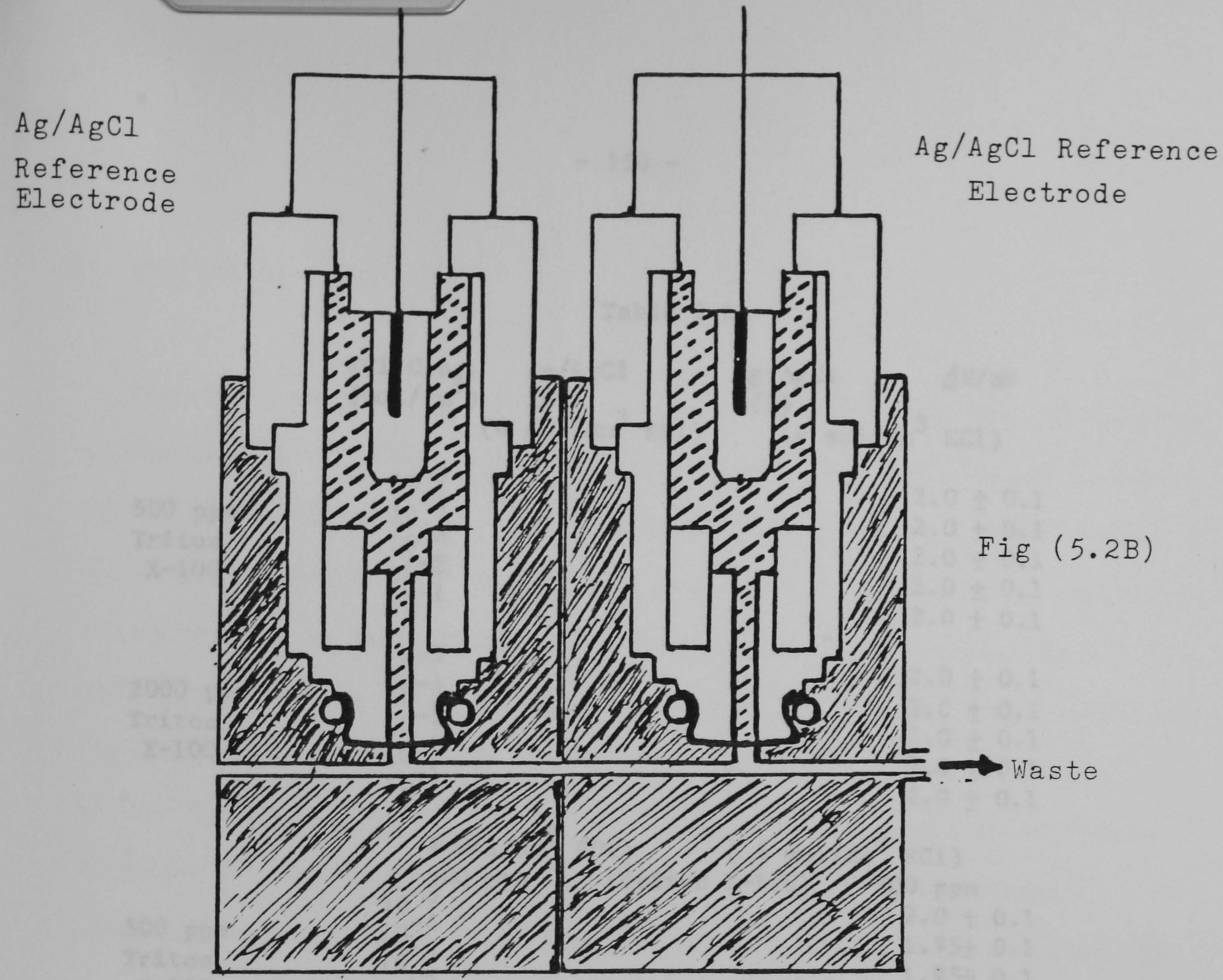


Fig (5.2B)

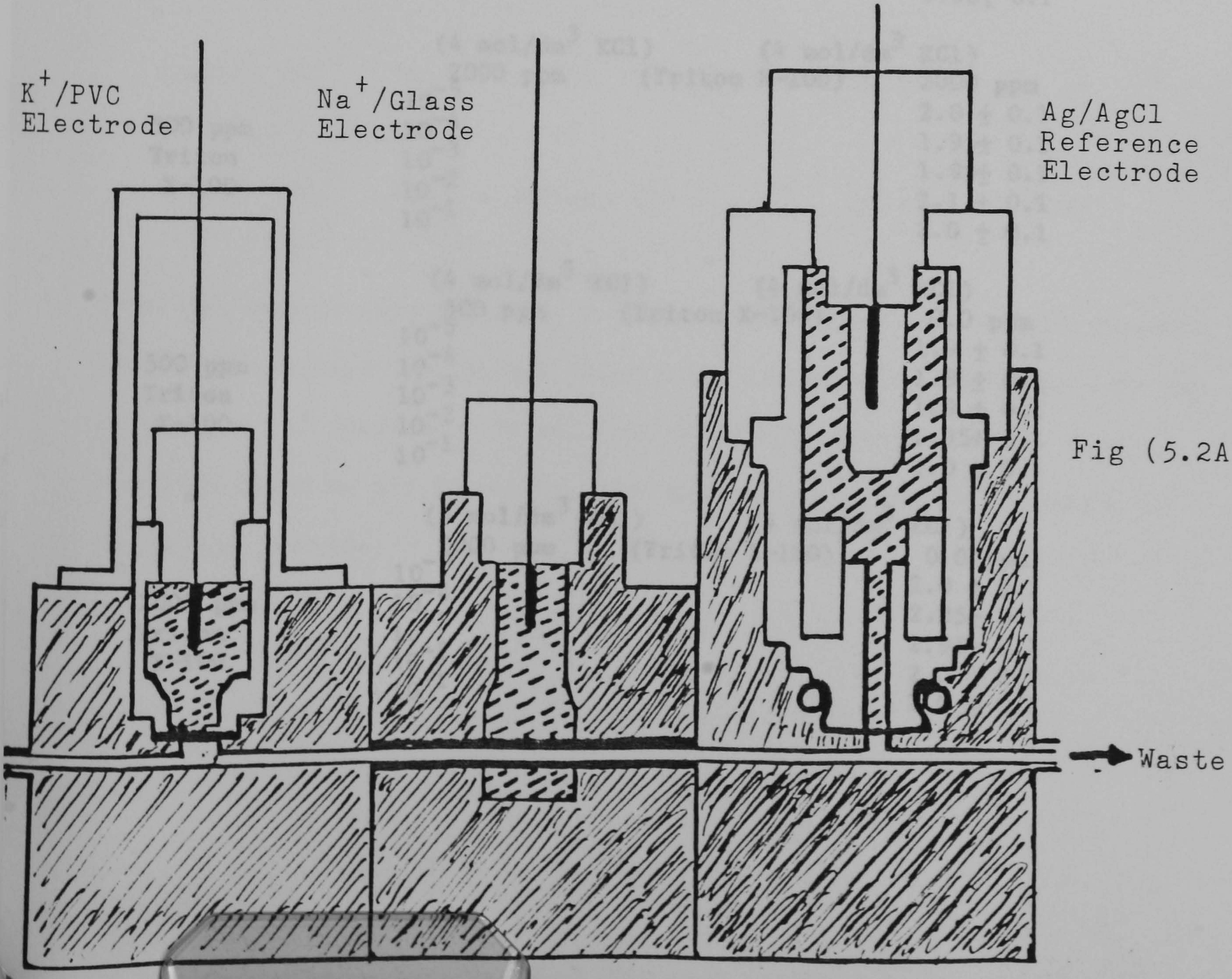


Fig (5.2A)

Table 5.11

	KCl Conc. (mol/dm^3)	Ag/AgCl (A) (4 mol/dm^3 KCl)	Ag/AgCl (B) (4 mol/dm^3 KCl)	ΔE/mV
500 ppm Triton X-100	10^{-5}			2.0 ± 0.1
	10^{-4}			2.0 ± 0.1
	10^{-3}			2.0 ± 0.1
	10^{-2}			2.0 ± 0.1
	10^{-1}			2.0 ± 0.1
		"	"	
2000 ppm Triton X-100	10^{-5}			2.0 ± 0.1
	10^{-4}			2.0 ± 0.1
	10^{-3}			2.0 ± 0.1
	10^{-2}			2.0 ± 0.1
	10^{-1}			2.0 ± 0.1
		4 mol/dm^3 KCl)	(4 mol/dm^3 KCl)	
		500 ppm	(Triton X-100)	500 ppm
500 ppm Triton X-100	10^{-5}			2.0 ± 0.1
	10^{-4}			1.95± 0.1
	10^{-3}			1.95± 0.1
	10^{-2}			1.9 ± 0.1
	10^{-1}			1.98± 0.1
		(4 mol/dm^3 KCl)	(4 mol/dm^3 KCl)	
		2000 ppm	(Triton X-100)	2000 ppm
500 ppm Triton X-100	10^{-5}			2.0 ± 0.1
	10^{-4}			1.95± 0.1
	10^{-3}			1.95± 0.1
	10^{-2}			2.1 ± 0.1
	10^{-1}			2.0 ± 0.1
		(4 mol/dm^3 KCl)	(4 mol/dm^3 KCl)	
		500 ppm	(Triton X-100)	0.0 ppm
500 ppm Triton X-100	10^{-5}			1.9 ± 0.1
	10^{-4}			1.9 ± 0.1
	10^{-3}			1.9 ± 0.1
	10^{-2}			1.95+ 0.1
	10^{-1}			2.0 ± 0.1
		(4 mol/dm^3 KCl)	(4 mol/dm^3 KCl)	
		2000 ppm	(Triton X-100)	0.0 ppm
2000 ppm Triton X-100	10^{-5}			2.0 ± 0.1
	10^{-4}			2.05± 0.1
	10^{-3}			1.95+ 0.1
	10^{-2}			2.0 ± 0.1
	10^{-1}			2.0 ± 0.1

5.5 DISCUSSION

From the results in Tables 5.2 - 5.7, the slopes of all the calibration curves regardless of the junction geometry, are 54 ± 1 mV/ decade (range pK:1-4). Therefore, there is no regular pattern of change in the actual values of the potential differences. This makes it difficult to attribute irregularities to variations in the liquid junction potential. As a result, no distinct relation can exist between the values of the slopes and the presence of Triton X-100 or the variation in the amount of Triton X-100. Results in Tables 5.8 - 5.11 demonstrate that addition of Triton X-100 to the internal solution of the electrode or to the external calibration solution, or both, does not produce significant effect on the behaviour of the electrode. The potential differences observed were:

Ag/AgCl (A) vs. S.C.E. (T-junction) $\Delta E = 40 \pm 0.1$ mV

Ag/AgCl (A) vs. Ag/AgCl (B) $\Delta E = 2 \pm 0.1$ mV

These differences were expected, because of the differences in the standard potentials of S.C.E. and Ag/AgCl electrodes and also the differences in the geometry of the junction. In the case of Ag/AgCl electrodes, the bias potential might be attributed to their manufacturing and the formation of the liquid junction.

5.6 SOLVENT EXTRACTION STUDIES ON THE COMPLEX FORMATION OF TRITON X-100 WITH ALKALI CATIONS

It is a well known fact that compounds containing certain functional groups are capable of forming complexes with cations. This property has been well documented for the polyether or crown compounds [3]. The complex formation is the result of ion-dipole ´electrostatic interaction´ or the covalent bonds between M^+ and the unshared electron pairs of donor atoms. Comparing the stability constants of crown compounds with open chain polyethers reveals that, the open chain polyethers, e.g. pentaglyme, forms much less stable complexes with alkali metal than its cyclic analogue. In this context, due to the existence of functional groups in the molecular structure of Triton X-100, the possible complexation property of Triton X-100 was considered, and a preliminary investigation was carried out.

5.7 SOLVENT EXTRACTION

Complexes in a solution can be detected in many different ways such as spectral changes, conductivity measurements or potentiometric titrations. Solvent extraction methods have been adopted by several workers [5.6], and applied in the present study. In this method an aqueous solution containing various cationic salts of the coloured picrate anion is shaken with an organic solvent (immiscible in water). This organic phase contains Triton X-100 as the cation binding substance. The optical absorbance of the organic phase was measured to determine the amount of the metal-Triton X-100 picrate. The following reaction corresponds to the salt extraction equilibrium:

$$\begin{array}{ccccccccc}
\text{Monovalent} & + & \text{Complexing} & + & \text{Picrate} & \longrightarrow & \text{Cation-complexing} & + & \text{Picrate} \\
\text{Cation} & & \text{Substance} & & \text{Anion} & & \text{Substance} & & \text{Anion} \\
\text{(aq)} & & \text{(org)} & & \text{(aq)} & & \text{(org)} & & \text{(org)}
\end{array}$$

(aq) and (org) designate aqueous and organic phases.

Accordingly, the capability of Triton X-100 to form complexes with alkali metal cations (Li^+, Na^+, K^+, Cs^+ and Rb^+) was investigated by this method.

5.8 EXTRACTION PROCEDURE

Triton X-100 was used without purification. Picric acid solution (BDH, reagent grade), and all hydroxides were BDH Analar grade chemicals except cesium and rubidium hydroxide (Koch-Light Lab. Ltd.). They were prepared with triple distilled water. Dichloromethane was BDH reagent grade. The organic layer was made up from 0.5 ml Triton X-100 in 1 dm^3 dichloromethane (CH_2Cl_2). The aqueous solution contained a known initial concentration of metal hydroxide 0.1 mol/dm^3, and $5.23 \cdot 10^{-5}$ mol/dm^3 picric acid. Equal volumes of the two solutions (20 ml) were vigorously shaken for 5 minutes in a separating funnel (50 ml) at room temperature (21 ± 1^0C). The funnel was left for about 20-30 minutes until the phases separated; no noticeable difference in the absorbance was found when the two phases were left for a longer time (5 hours).

5.9 RESULTS AND DISCUSSION

The absorbance of picrate ion, in each separated phase was determined with a Unicam spectrophotometer (model SP 800). The U.V. spectra are shown in Fig 5.5; the maximum absorption in the organic phase was found at 372 nm for the picrate associated with the complexed metal ion. Maximum absorption of aqueous phases were found at 354 nm for the picrate anion regardless of the metal ion. Bourgain et al. [5], have found that salts of picric acid in low polarity media exhibit significant shifts in their optical spectra in the presence of crown ethers. These shifts occur when a tight ion-pair is converted into a loose pair by a cation chelating compound, or in other words, when complexation leads to a significant increase in the inter-ionic distance of the tight ion-pairs. Here, in agreement with the Bourgain's [5] conclusion, all spectra showed that the picrate maximum at 354 nm in aqueous solution had moved to 372 nm in the organic layer. This can be taken as indication of the presence of loose ion-pairs of metal complexes. The height of the absorbance in the organic phase is a measure of the extent of the complex formation. The absorbance (A) of picrate in the organic layer is given in Table 5.12. From Table 5.12, one can conclude that the tendency of Triton X-100 to form complexes with alkali metal ions is in the following sequence:

$$Rb^+ = K^+ = Cs^+ > Na^+ > Li^+$$


(2): Organic phase
(3): KP before extraction
A
1·4
1·2
1·0
0·8
0·6
0·4
0·2
0
225
250
275
300
325
350
400
wavelength millimicrons
1
2
3

Fig 5.5


K$^+$ with Triton X- 100
(1): Aqueous phase
(2): Organic phase
(3): KP before extraction
A
1·4
1·2
1·0
0·8
0·6
0·4
0·2
0
225
250
275
300
325
350
400
wavelength millimicrons
3
2
1

Fig 5.5

Table 5.12

(Triton X-100-M^+) Picrate	Li^+	Na^+	K^+	Cs^+	Rb^+
Absorbance (org)	0.05	0.14	0.5	0.48	0.52
$\frac{A_{M^+}}{A_{K^+}}$ (relative absobance)	1/10	1/3	1	1	1

5.10 CONCLUSION

The main objective of this section was to assess the origin of the bias in the Corning 902 analyser. From the results of the extraction study, there is evidence that the presence of Triton X-100 in sample solutions, would lead to variation of the potassium and sodium activities, due to its complexation capacity. It is, however, supposed that Triton X-100 is a surfactant material, which might affect the surface of the membrane. As far as the source of bias is concerned, with respect to the present findings it would appear reasonable to suggest that: the presence of Triton X-100 and the type of liquid junction are involved. It is thus, advisable to replace Triton X-100 with better substitutes, and a ´T´ form junction rather than ceramic junctions is to be utilized.

PART TWO

CONTINUOUS DILUTION METHOD

5.11 INTRODUCTION PART (II)

The prime step in the utilization of ion-selective electrodes in any field of research is to make sure of their response towards particular ions. To achieve this, the easiest and universally accepted method is to calibrate electrodes. This is provided by measuring the electrode's potential differences in solutions containing different levels of the sensed ions. With regard to the conventional method, an electrode is required to be immersed in a series of standard solutions, which is a cumbersome and time-consuming process. However, apart from the difficulty in preparation of the solutions, calibration curves with only a few points are not accurate or informative and may introduce some errors. These two disadvantages could be overcome by introducing the logarithmic dilution method [7,8].

5.12 LOGARITHMIC DILUTION METHOD

In this method, a vessel is filled with a known volume of sensed ion salt solution, which is stirred vigorously with a Teflon-coated magnetic bar. A constant flow of diluent is delivered to the vessel, while exactly the same volume is displaced. By this means, the concentrated solution in the vessel is diluted with respect to one of the species which responds to the potential of the electrode. Considering the initial concentration of species (I) as c^0 with an initial volume of V^0, diluted by a constant rate (V) per unit of time, the concentration of (I) species after (t) elapse of time can be obtained from equation (5.1).

$$c = c^0 e^{-Vt/V^0} \qquad (5.1)$$

by inserting eqn. (5.1) into the Nernst equation (5.2), equation (5.3) can be obtained

$$E = E^0 + k \ln c \qquad (5.2)$$

$$E = E^{0\prime} - Vkt/V^0 \qquad (5.3)$$

Where E is the potential difference of the cell at time t and $E^{0\prime}$ the constant potential

$$E^{0\prime} = E^0 + k \ln c^0$$

$k = RT/F$

From eqn. 5.3, the output potential of the cell (E) is a function of elapsed time. Eqn. 5.1 makes it possible to obtain a potential curve against log C of the ion of interest. This can be achieved by rescaling the (t) axis of the E vs. t curves. If a chart recorder moves y cm per minute, for one decade change in concentration of sensed ions the paper on the chart recorder would shift $2.303 \cdot (V^0/V)\ Y$ cm .

Taking logarithms of both sides of $c/c^0 = e^{-Vt/V^0}$

gives $$\ln c/c^0 = -Vt/V^0 \quad .$$

if $c = 1/10\ c^0$ then

$$2.303 \log 1/10 = -Vt/V^0 \quad \text{or} \quad t = 2.303 \; V^0/V$$

therefore 1 min. Y cm. shift

$$2.303 \; V^0/V \qquad x = 2.303 \; (V^0/ V).Y$$

As far as the application of this method to the calibration of I.S.Es is concerned, the following points must be taken into consideration:

1) The initial volume of the solution has to kept constant during the measurements.

2) The electrode response has to keep up with the pace of dilution.

3) Throughout the calibration period a homogeneous mixture is required, so the solution has to be rapidly stirred in a specially designed cell.

5.13 DESIGN OF THE VESSEL

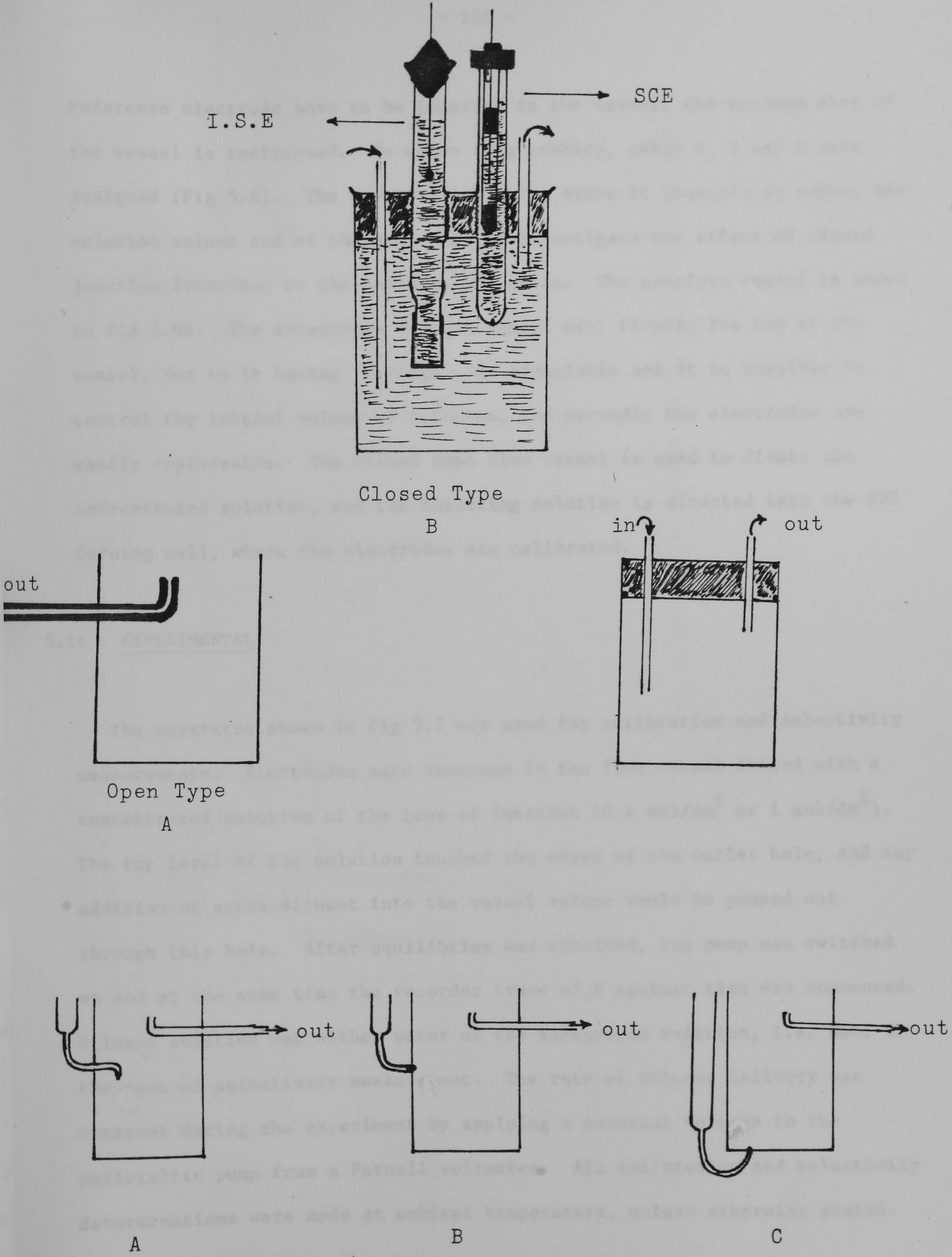
As was already mentioned, during the dilution the volume of the solution must be kept constant. For this purpose two types of vessel were designed:

a) Open type flow cell.

b) Closed type flow cell.

The vessels, which were used in this study for different purposes, are shown in Fig 5.6.

A reference electrode made contact with the solution through a ceramic plug. From eqn. 5.1, to reduce the calibration time, a small initial volume of sensed ion solution is essential. Since the I.S.E. and the



(5.6)

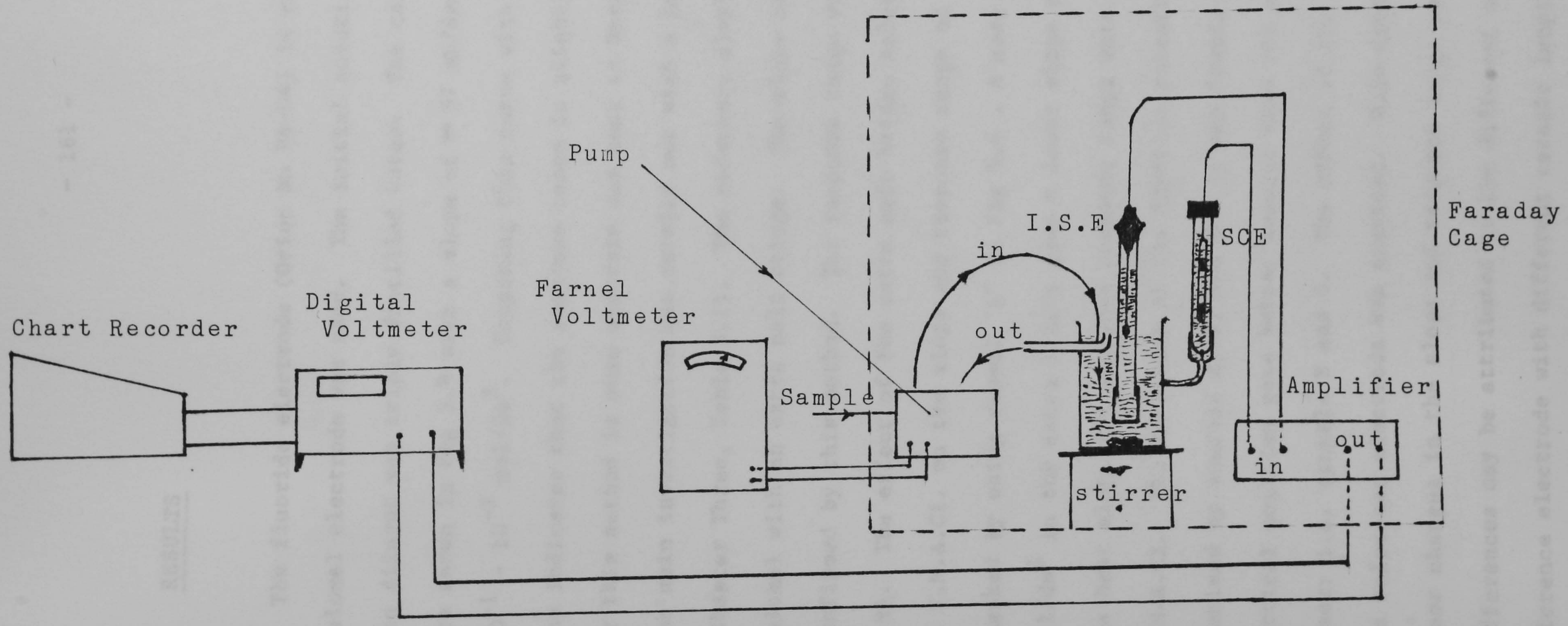
reference electrode have to be immersed in the vessel, the minimum size of the vessel is restricted. To solve this problem, cells A, B and C were designed (Fig 5.6). The use of these cells makes it possible to reduce the solution volume and at the same time to investigate the effect of liquid junction formation on the calibration curves. The complete vessel is shown in Fig 5.6B. The advantages of this vessel are: firstly the top of the vessel, due to it having ˊ0 ringsˊ, is adjustable and it is possible to control the initial volume of solution, and secondly the electrodes are easily replaceable. The closed type flow vessel is used to dilute the concentrated solution, and the resulting solution is directed into the 902 Corning cell, where the electrodes are calibrated.

5.14 EXPERIMENTAL

The apparatus shown in Fig 5.7 was used for calibration and selectivity measurements. Electrodes were immersed in the flow vessel filled with a concentrated solution of the ions of interest (0.1 mol/dm^3 or 1 mol/dm^3). The top level of the solution touched the edges of the outlet hole, and any addition of extra diluent into the vessel volume would be pumped out through this hole. After equilibrium was attained, the pump was switched on and at the same time the recorder trace of E against time was commenced. Diluent solution was either water or the background solution, i.e. NaCl in the case of selectivity measurement. The rate of diluent delivery was constant during the experiment by applying a constant voltage to the peristaltic pump from a Farnell voltmeter. All calibration and selectivity determinations were made at ambient temperature, unless otherwise stated.

Schematic diagram of apparatus for calibrations of I.S.Es by continuous dilution method

Fig.(5.7)

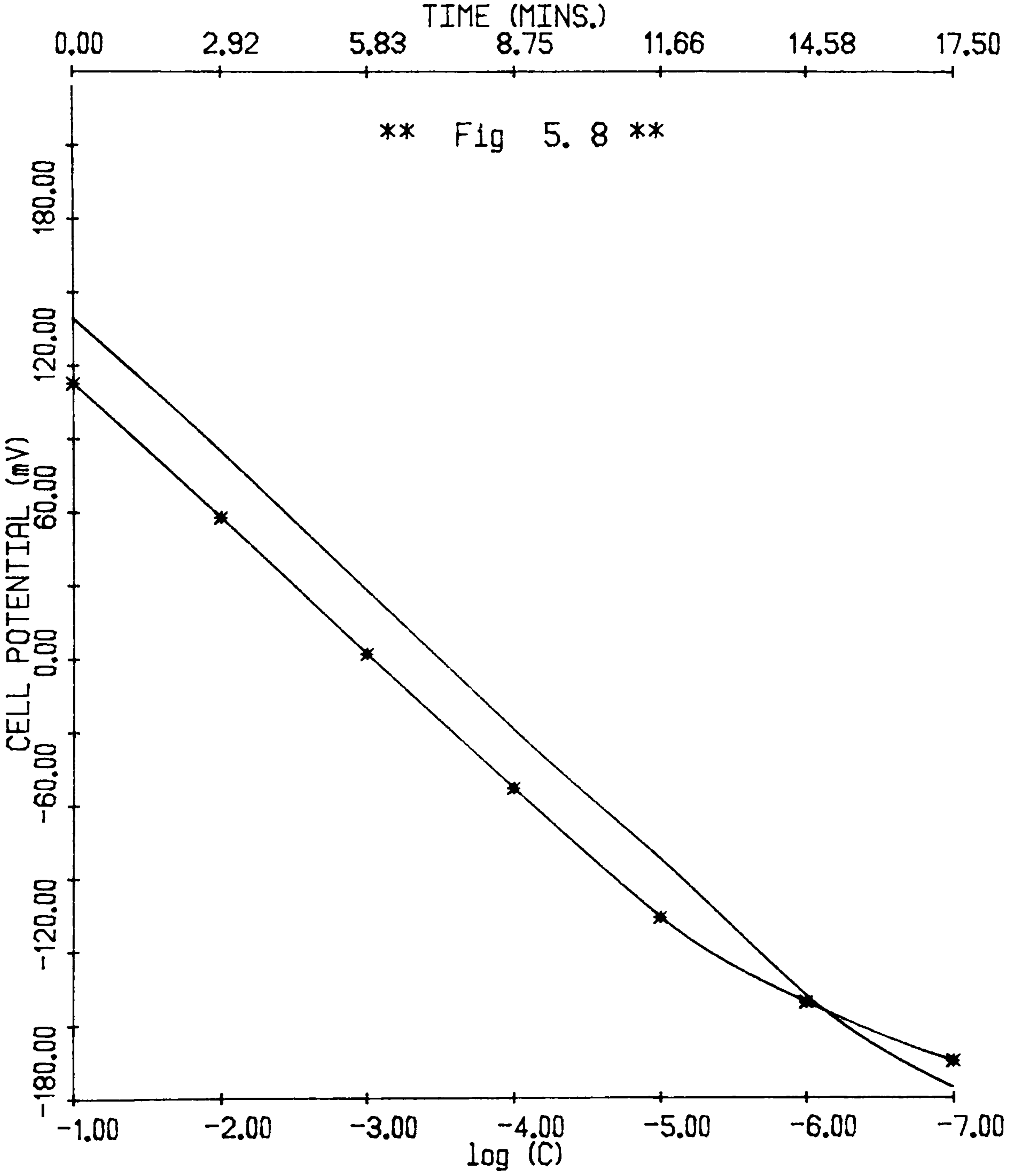


5.15 RESULTS

The fluoride electrode (Orion No 94-04) in conjunction with a saturated calomel electrode was used. The initial solution was 0.1 NaF mol/dm^3 and the diluent was triple distilled water. The calibration curves obtained are shown in Fig 5.8 with a slope of ≃ 57 mV/decade and a response range of 10^{-1} - 10^{-7} mol/dm^3. Comparing this curve with a conventionally determined one indicates that the response range is slightly increased and the slope by this method is more accurate and near to Nernstian.

The main investigation was carried out with a home-made potassium electrode (Chapter Three, Table 3.1). The reference electrode was a saturated calomel with an extra salt bridge. The slope of 68 ± 1 mV/decade was confirmed by this method. The response range was slightly extended (Fig 5.9). The effect of the extra salt bridge solution, i.e. the concentration of T.M.A.Cl. on the slope and response range of the potassium electrode was checked by using vessel ´A´ in Fig 5.6 . A more dilute solution, 0.35 mol/dm^3 in the extra brigde gave a lower slope and shorter response range. The best slope and extended response range were obtained with 3.5 mol/dm^3 T.M.A.Cl. The formation of the junction potential and its effect was examined by vessels A, B, and C. It was found, that the junction in the vertical position gave better results than the side and bottom contact cases: i.e. vessels B and C. The effect of the length of the ceramic on the reference electrode was examined. With different lengths of ceramic, minor changes in the slope and response range were observed. These differences may be attributed to the different memory effect of the reference electrode with different ceramic lengths. This finding is in

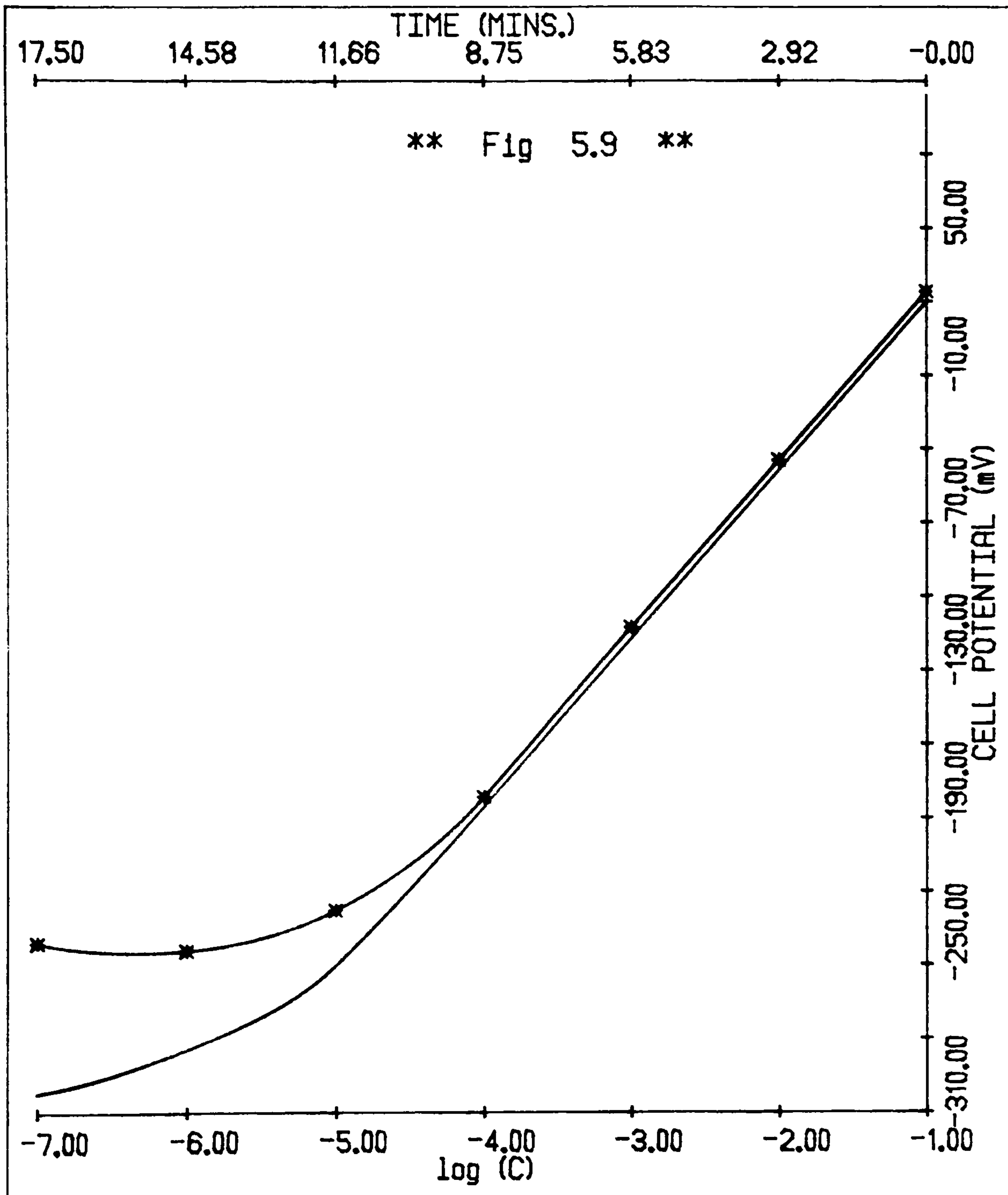
** Fig 5. 8 **



* CALIBRATION CURVES FOR FLUORIDE I.S.E. *

TOP CURVE IS OBTAINED BY CONTINUOUS METHOD

BOTTOM CURVE IS OBTAINED BY CONVENTIONAL METHOD



** Fig 5.9 **

* CALIBRATION CURVES FOR POTASSIUM I.S.E. *

TOP CURVE IS OBTAINED BY CONVENTIONAL METHOD

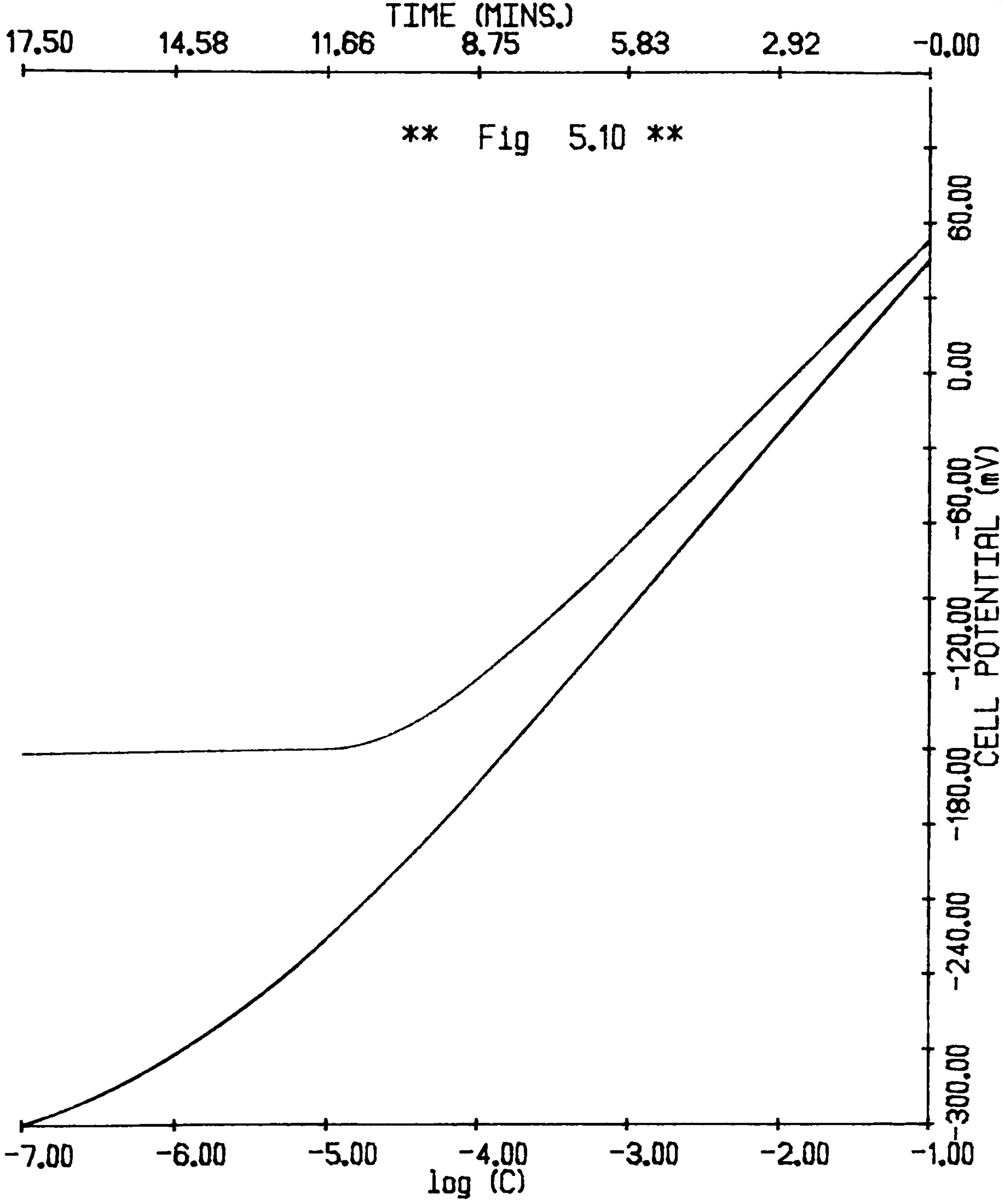
BOTTOM CURVE IS OBTAINED BY CONTINUOUS METHOD agreement with the results of Whalley [9], which were obtained by pH measurements. Typical calibration curves for K^+ / PVC I.S.E. vs. S.C.E. with, and without, the extra salt bridge are shown in Fig 5.10, from which it is clear that an additional salt bridge is necessary for preventing potassium ion contamination from the reference electrode. The contribution of liquid junction potential to the slope of the potassium electrode was reaffirmed. The cell without a junction was arranged by using the fluoride electrode as reference electrode. The electrodes were used in vessel A in Fig 5.6 with 0.1 mol/dm^3 KCl + 10^{-4} mol/dm^3 NaF as starting solution. The diluent solution was 10^{-4} mol/dm^3 NaF. Calibration curves are given in Fig 5.11. The slope was ≈ 58.1 mV/decade and the lower limit to the range of 10^{-4} mol/dm^3 was obtained.

In addition to the potassium electrode, the pH glass (Russell), sodium (EIL) and Ca^{2+} /PVC (Philips) electrodes were calibrated by the aforesaid method. All of these electrodes showed similar response curves as they did by a conventional method.

5.16 SELECTIVITY MEASUREMENTS

The selectivity of the potassium electrode towards Na^+ ions, at different concentrations, was carried out (Figs 5.12 and 5.13). Selectivity coefficients were calculated without considering the liquid junction contribution (Table 4.13). As was mentioned in previous chapters, it is necessary to declare the method of measurement, the concentration of interferents and other factors when the selectivity coefficient is given. Due to observed interference from the NH_4^+ ions in potassium-based

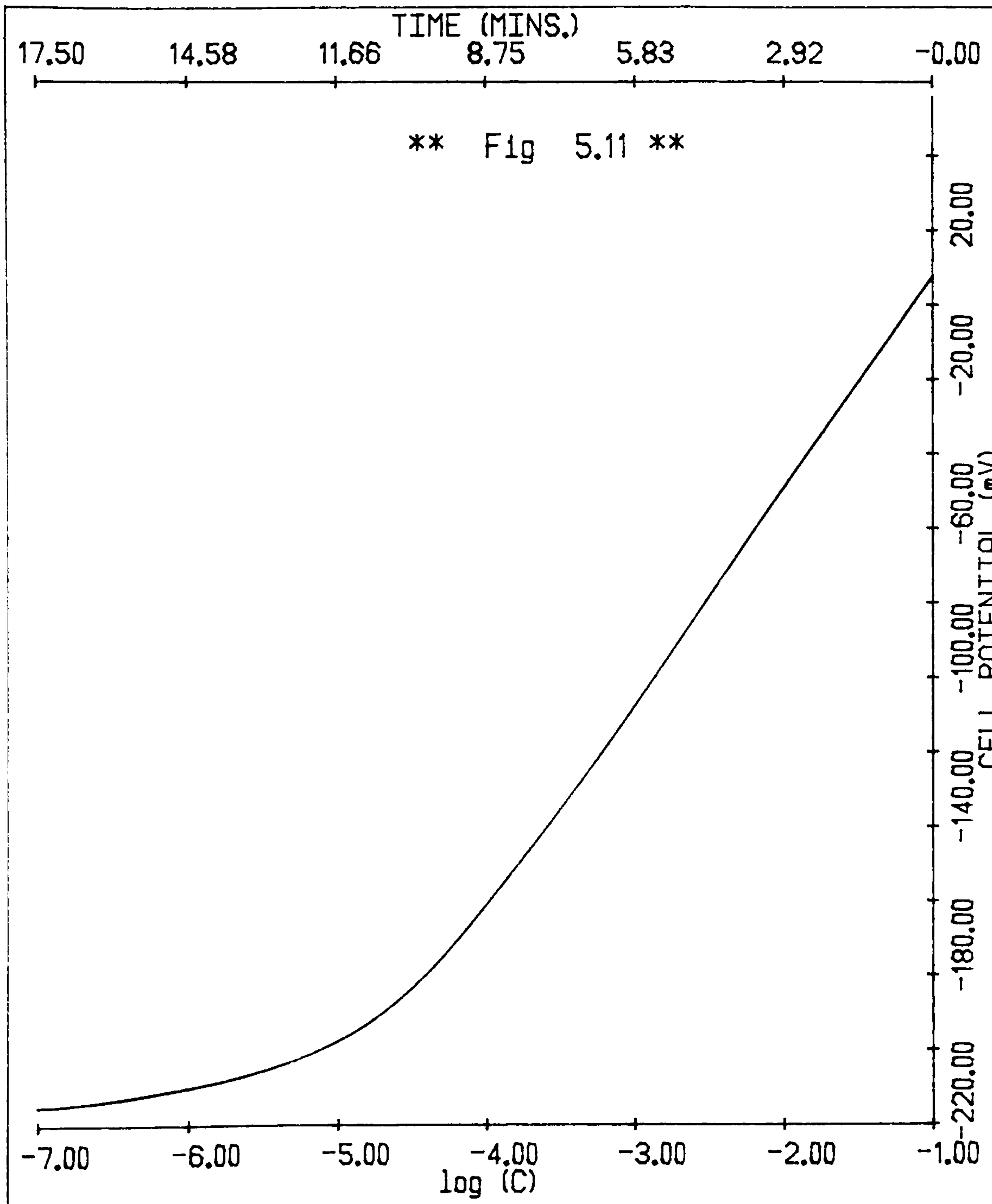
** Fig 5.10 **



* CURVES ARE OBTAINED BY CONTINUOUS METHOD*

TOP CURVE IS OBTAINED WITHOUT SALT BRIDGE

BOTTOM CURVE IS OBTAINED WITH SALT BRIDGE



** Fig 5.11 **

* CALIBRATION CURVE FOR POTASSIUM I.S.E. *

CURVE IS OBTAINED BY CONVENTIONAL METHOD

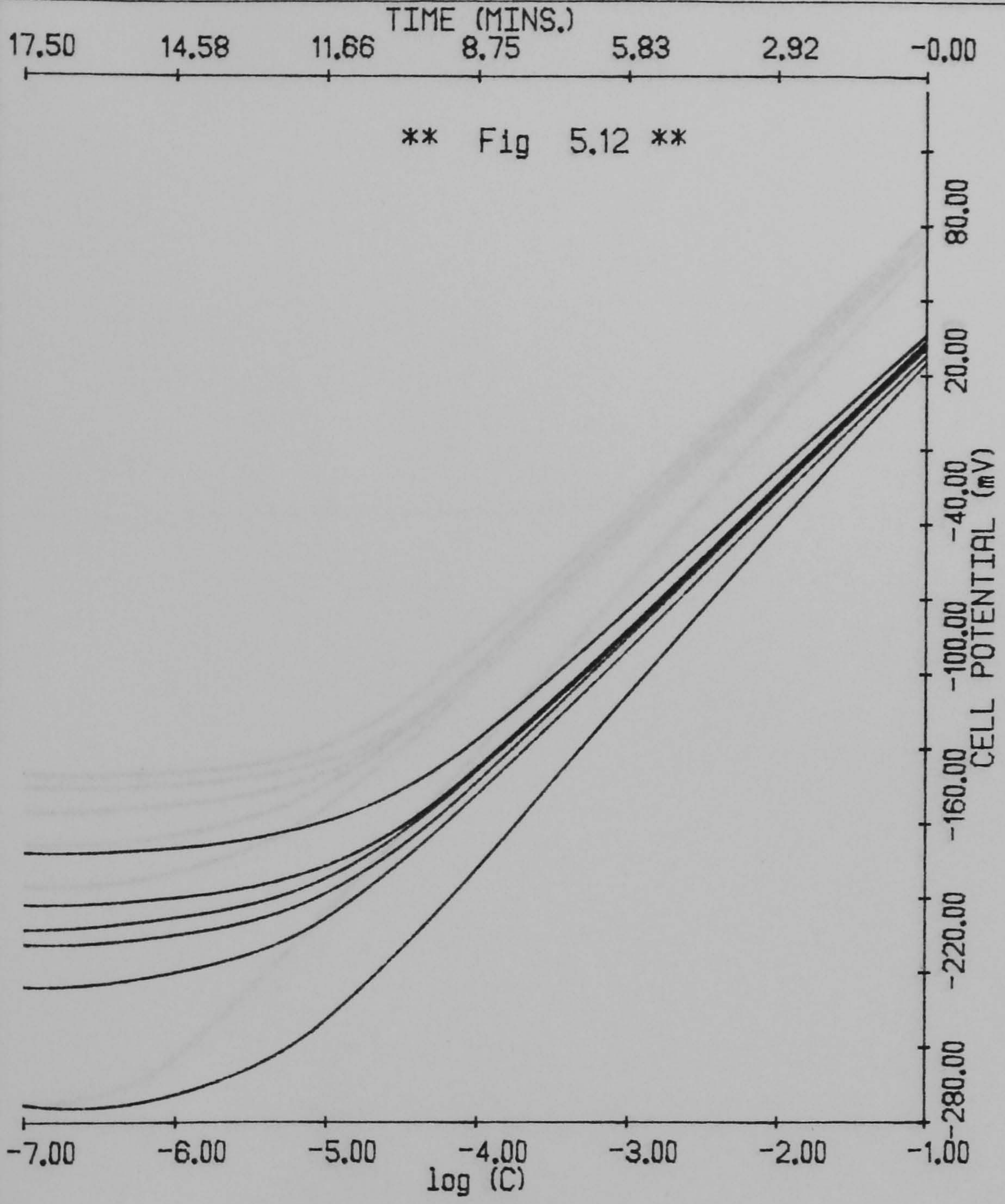
POTASSIUM ELECTRODE vs. FLUORIDE ELECTRODE valinomycin electrode, the selectivity of the electrode towards this ion was determined and it was approximately the same as in conventional method (Fig 5.14). It should be mentioned here that in measuring the selectivity , potassium solutions were prepared with a background of interfering ion solution. The diluent was the background solution,for instance, when the initial sample solution was 0.1 KCl + 0.7 mol/dm^3 NaCl, a 0.7 mol/dm^3 NaCl solution was used.

Table 5.13

Concentration of Sodium Chloride (mol/dm^3)	$k^{pot}_{NaK} \times 10^3$
0.1	10.0
0.2	7.5
0.3	6.6
0.4	7.2
0.5	6.0
0.6	6.6
0.7	5.7
0.8	6.8
0.9	6.6
1.0	7.0

5.17 CORNING ANALYSER AND THE CONTINUOUS DILUTION METHOD

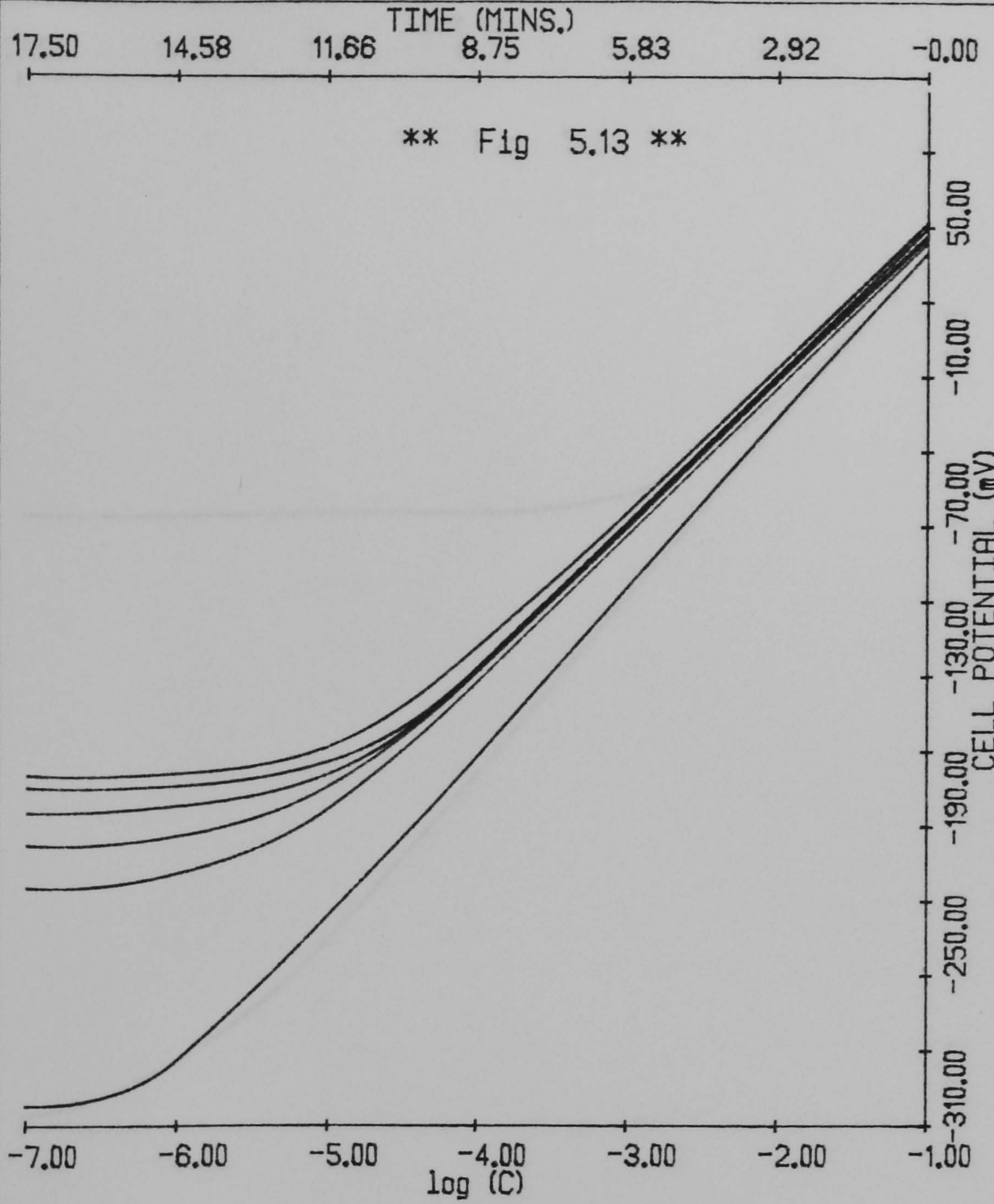
In the Corning 902 analyser, a two point calibration method is used for the calibration of electrodes, which is obviously not accurate. Thus, the logarithmic dilution method which is fast and capable of on line calibration was adapted to this instrument. The closed flow vessel was used as a diluent cell and the outlet of the vessel was connected to the electrode block of the Corning 902 by silicone rubber tubing. The whole apparatus was shown in Fig 5.16. By this method, the potassium and sodium



** Fig 5.12 **

* SELECTIVITY CURVES FOR POTASSIUM I.S.E. *
WITH CONTINUOUS METHOD

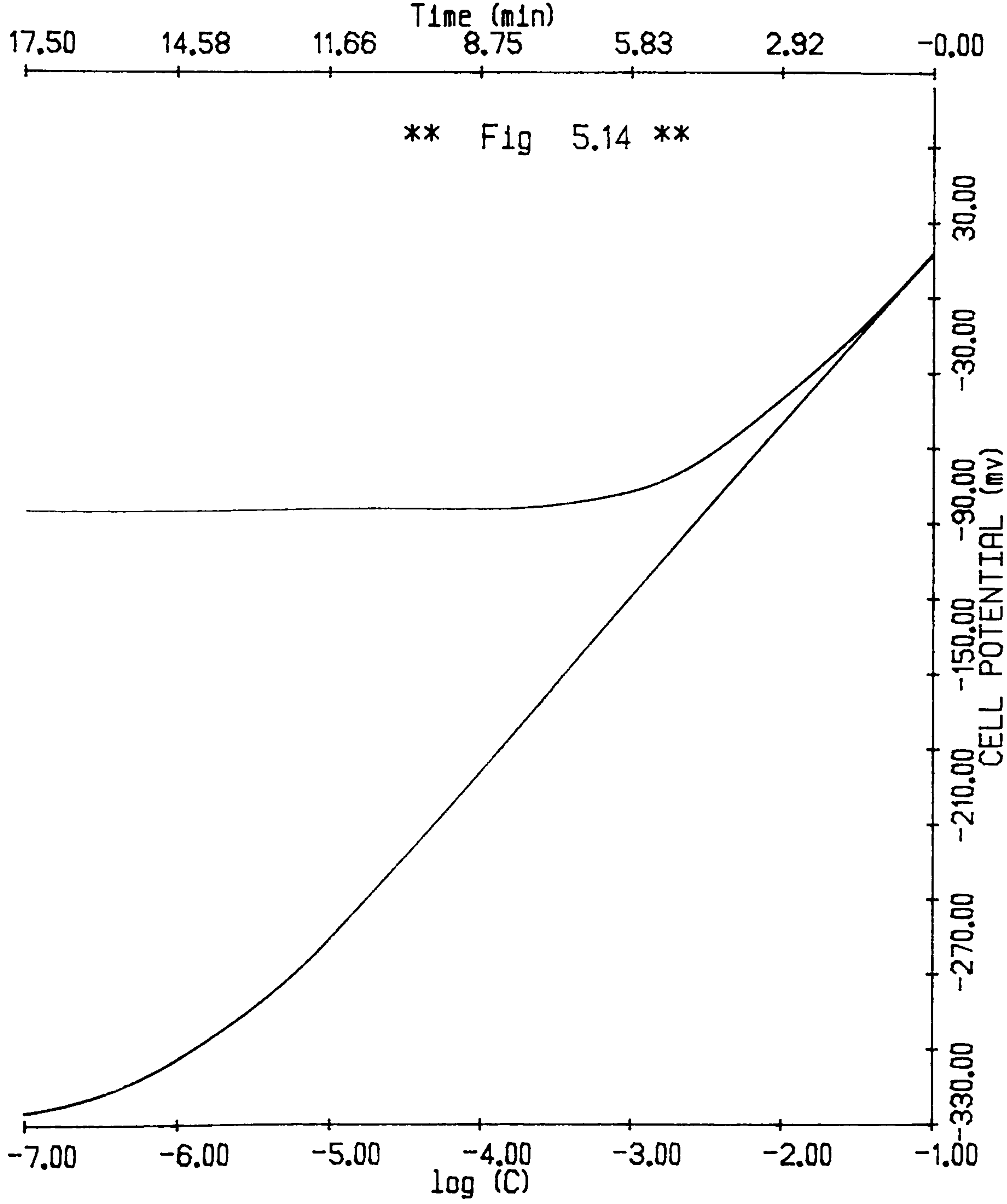
CONCENTRATION OF SODIUM CHLORIDE IS 0.0, 0.1, 0.3, 0.5, 0.7, 0.9 mol/dm^3 FROM BOTTOM TO TOP RESPECTIVELY.



** Fig 5.13 **

* SELECTIVITY CURVES FOR POTASSIUM I.S.E. *
WITH CONTINUOUS METHOD

CONCENTRATION OF SODIUM CHLORIDE IS 0.0, 0.2, 0.4, 0.6, 0.8, 1.0 mol/dm^3 FROM BOTTOM TO TOP RESPECTIVELY.

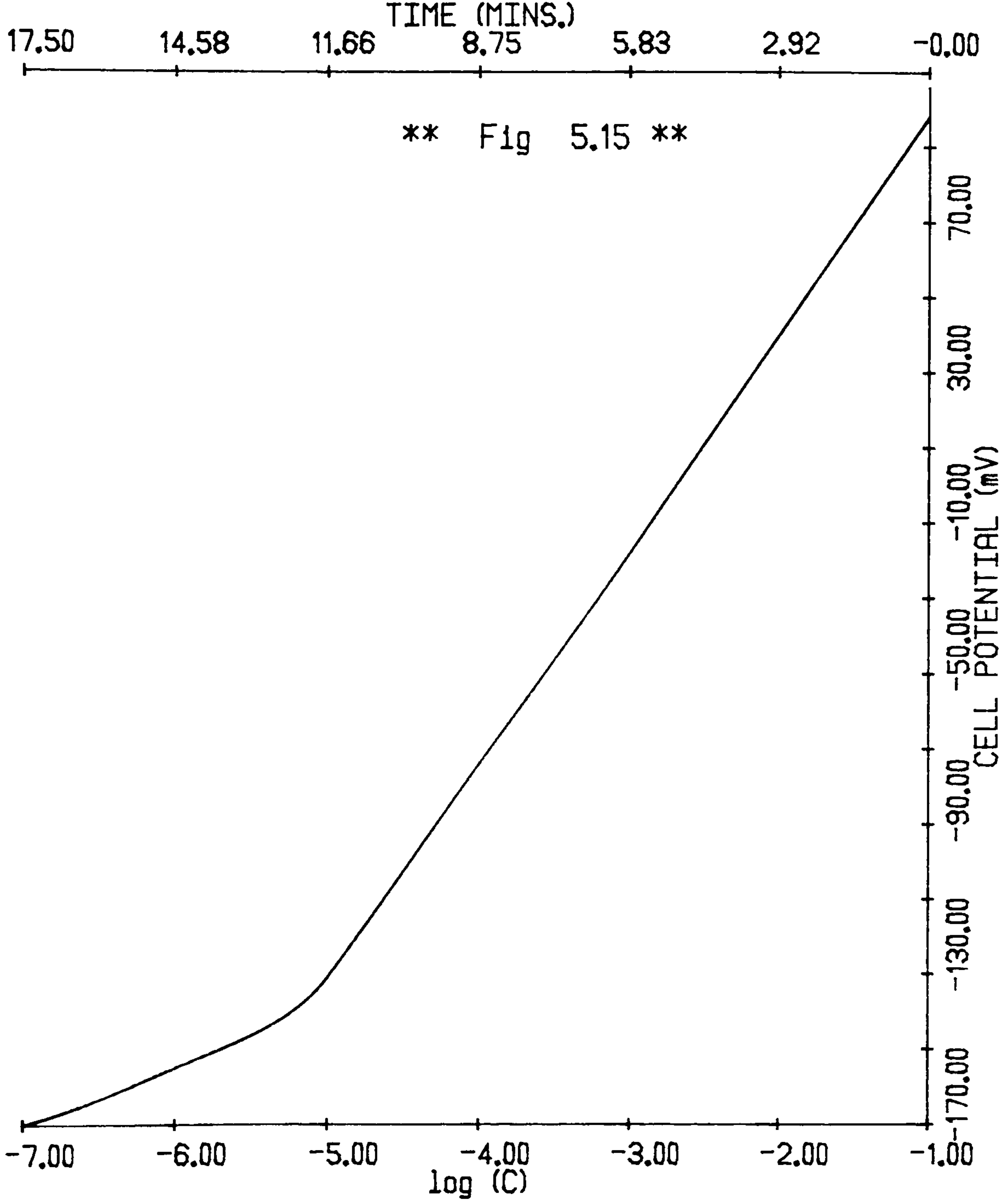


** Fig 5.14 **

* SELECTIVITY CURVES BY DILUTION METHOD *

TOP CURVE IS SELECTIVITY (0.1 mol/dm^3 NH_4Cl + KCl)

BOTTOM CURVE IS CALIBRATION (KCl)



* CALIBRATION BY CONTINUOUS METHOD *

K^+/PVC I.S.E OF CORNING 902 ANALYZER

Schematic diagram of apparatus for calibrating Corning 902 electrodes by logarithmic dilution method

Fig. (5.16)

glass electrodes were calibrated. The calibration curve for potassium electrode is given in (Fig 5.15). The slope was 54 ± 1 mV/decade for potassium electrode and 51 ± 1 mV/decade for the sodium electrode.

5.18 DISCUSSION

It should be mentioned that the method was adapted to the calibration of ion-selective electrodes out of necessity based on Pebler abstract [8]. However, during the course of the work, it was realized that Pungor et al. [7] had already utilized this method to calibrate silver iodide-based silicone rubber electrodes.

However, the results found are similar to those of Pungor et al. [7], though with different electrodes. At the lower concentrations, the slope of the calibration curve by conventional method measurements decreases very sharply (see Figs 5.8 and 5.9). The calibration curves by both methods are parallel till 10^{-5} mol/dm^3. The shift in the curves, either positive or negative could have arisen from a difference in standard potential or a difference in the formation of liquid junction potential between the two methods.

It was noted that a change in the flow rate and stirrer speed can cause distinguishable differences at lower concentration, this effect might be attributed to the variation of reaction rate at the membrane surface. Calibration is only possible when starting from high concentrations for practical reasons. The outstanding advantages of this method are in its simplicity, speed effectively, an infinite number of calibration points and capability to calibrate several electrodes at the same time. Finally, as Pungor et al. suggested, this method can be easily applied with an automatic control.

5.19 REFERENCES

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CHAPTER SIX

MECHANISTIC CONSIDERATION OF ION-SELECTIVE MEMBRANES

6.1 THE MEMBRANE POTENTIAL

The aim of this chapter is to review the works so far being carried out on the potential generation, permeability, and charge transportation in membranes.

A membrane may be defined as a phase, which is immiscible in the contacting solutions, and which itself might conduct an ion from one solution to the other. The conductivity towards the ions of interest is not essential, but a surface or interfacial equilibrium on both sides of the membrane is required [1].

The origin of the potential difference is the distribution of charge in the membrane, which may be the result of adding an active material into the membrane or the conducting solutions.

In the absence of an active material, the membrane potential would be a liquid junction potential or diffusion potential, which arises as a consequence of dissimilarity of mobilities of various species inside the membrane. The liquid junction potential was calculated [2,3,4,5] by integrating the Nernst-Planck equation, which is given by eqn.6.1:

$$E = \left[\frac{U_+ - U_-}{U_+ + U_-}\right] RT/F \ln a''/a' \qquad (6.1)$$

Where U_+ and U_- are the mobilities of cation and anion, a' and a'' are the activities of ions on both sides solutions and R, T, F are the gas constant, absolute temperature and Faraday constant respectively.

Addition of active material into the membrane facilitates the entrance of particular ions into the membrane, which results in the formation of a boundary potential (Donnan potential). The membrane potential may thus, be considered as the combination of two potentials: boundary and interdiffusional, i.e.,

$$E_m = E_B + E_D \qquad (6.2)$$

where E_m , E_B and E_D are membrane, boundary and interdiffusion potentials respectively.

The electrochemical cell which is used for the determination of the membrane potential is shown below:

Donnan potential Donnan potential

Reference Electrode	Solution (S)	Membrane	Solution (X)	Reference Electrode

Diffusion potential

The current hypotheses for membrane potentials may be roughly divided into three categories: firstly, theories based on the Nernst-Planck equation or classical thermodynamics , secondly, those of irreversible thermodynamics and thirdly, the theories based on the transition state theory (rate processes). The common assumption in all those approaches is that, a local equilibrium exists.
The theory of the first category is by far the most widely used. By integration of the Nernst-Planck equation for the movement of species between the membrane and membrane solution interfaces, the relationship between the concentration(activity) of permeating species and driving force of these species is obtained.

It is usually assumed that thermodynamic equilibrium exists across the interfaces and that the system is in a steady state, so the flux is constant throughout the membrane. The difference between the various treatments in this category arises from different assumptions as regards the integration of the Nernst-Planck equation. Nevertheless, in the Nernst-Planck approach, the interaction of different permeating species is ignored.

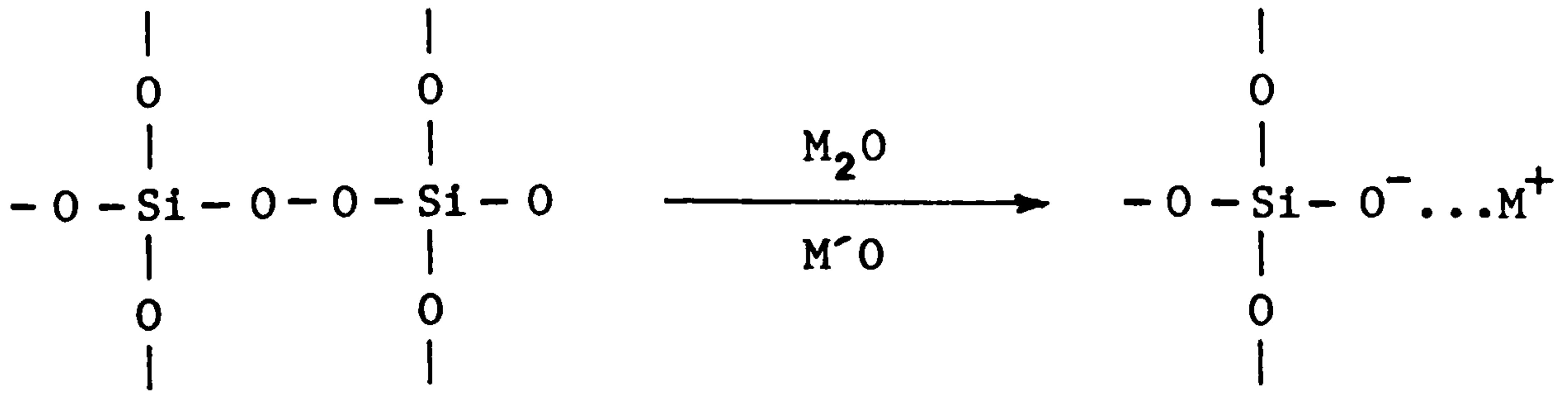
The second theory has been used frequently for biological membranes where structural and mechanistic information are often unavailable.

The third theory is in good agreement with the aforementioned two, however, due to the requirement of detailed information about the structure and some other complicated parameters of the membrane, this last approach is not frequently used.

However, there is no general approach to the mechanism of the membrane electrodes, due to their various and complicated structures and composition. Therefore, the mechanistic aspects of the major types will only be briefly explained in the following sections. Much attention has been directed to the mechanism of membranes based on neutral carriers.

6.2 THE GLASS ELECTRODES

The works of Hughes [6], MacInnes, Dole [7], and Perley [8], demonstrated that the composition of glass plays an essential role in the ion-specific behaviour of glass electrodes. Due to the high resistance and non-hygroscopic property of pyrex and quartz, electrodes made of them show no response to cations. Addition of alkali and alkaline earth metal oxides to pure glass(100% SiO) produces negative fixed ion-exchange sites. Basically such negative sites are responsible for the electrode behaviour.



$$-O-Si-O-O-Si-O \xrightarrow[M'O]{M_2O} -O-Si-O^-...M^+$$

The composition alteration of the glass by adding Al_2O_3 or B_2O_3 or both, led to the discovery of Na^+ and other alkali metal sensitive glass electrodes [9,10]. The development of the potential and selectivity is determined by the composition and structure of the glass membrane. X-ray experiments have confirmed the theory of Zachariasen [11] for the structure of the silicate glasses. According to this theory, each silicon atom is surrounded by four oxygen atoms, and each bridging oxygen is bound by two silicon atoms. The structure of the network is three dimensional, due to the silicon atom hybridisation. The alkali metal and alkaline earth cations are fitted in the holes of continuous, random network. As regards to the glass property, cationic characteristics, in particular the size of cation, play an important role. The transport of a minute amount of current through the membrane is supposed to be carried out by the alkali cations; however, the attribution of charge transfer to such cations is not widely accepted [12].

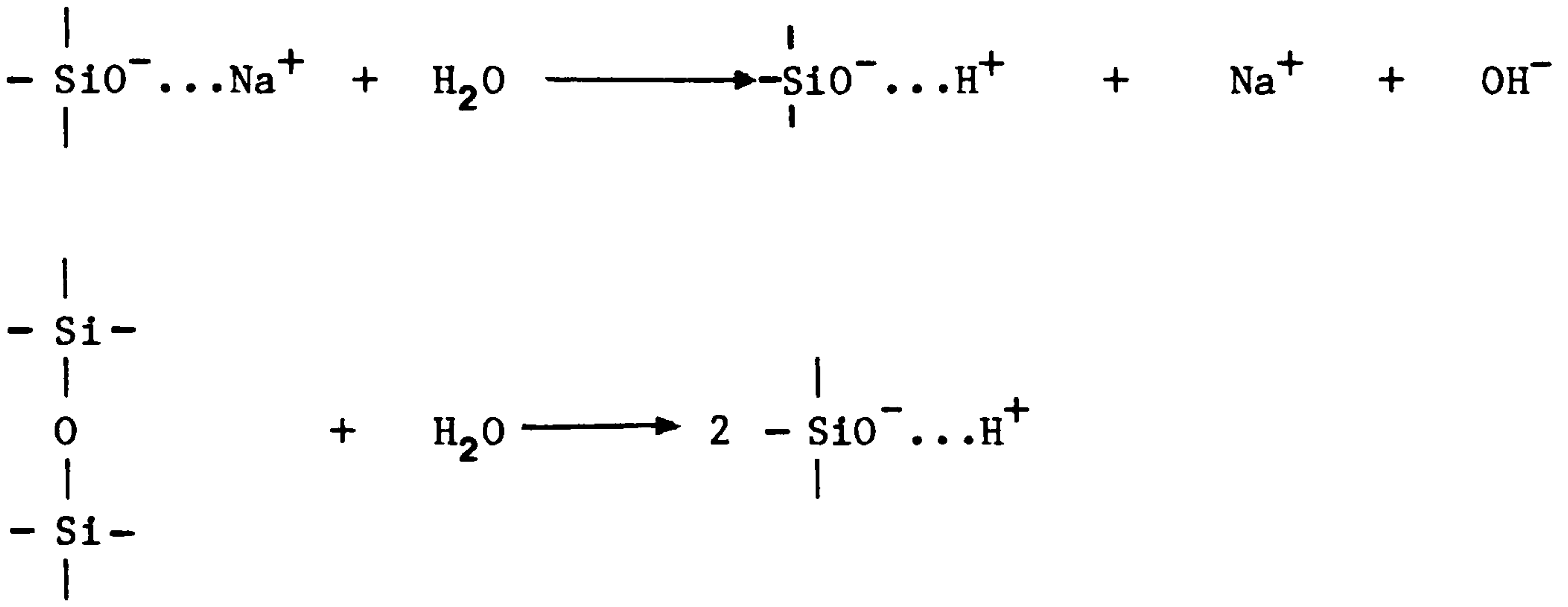
The glass membrane can be assumed to consist of three distinct regions: two thin gel layers on the inner and outer surface, and an unchanged bulk layer between these two layers. Radiotracers and ion-beam etching studies have confirmed the above mentioned structure, and indicated that the hydration process is accompanied by a chemical reaction, in which certain compounds of the glass membrane and solution take part in an exchange reaction.

The ion-exchange reaction for the pH electrode can be written as eqn.(6.3):

$$\underset{\text{glass}}{M^+} + \underset{\text{solution}}{H^+} \rightleftharpoons \underset{\text{glass}}{H^+} + \underset{\text{solution}}{M^+} \qquad (6.3)$$

It has been shown that the surface of a glass membrane must be hydrated in order to show a response to cations [13].

Experiments carried out by Csakavi et al. , Wikby, and Baucke [14,15,16], have revealed the thickness and composition of the gel layers. According to their work, various hydrolysis and dissolution reactions occur when a freshly made electrode is allowed to stand in an aqueous solution, e.g. :



$$-\mathrm{SiO^-}\ldots\mathrm{Na^+} + \mathrm{H_2O} \longrightarrow -\mathrm{SiO^-}\ldots\mathrm{H^+} + \mathrm{Na^+} + \mathrm{OH^-}$$

$$\begin{array}{c} | \\ -\mathrm{Si}- \\ | \\ \mathrm{O} \\ | \\ -\mathrm{Si}- \\ | \end{array} + \mathrm{H_2O} \longrightarrow 2\ -\mathrm{SiO^-}\ldots\mathrm{H^+}$$

Various theories have been proposed for the operation of the glass electrode [17,18,19,20,21], however, the ion-exchange mechanism is the most acceptable. This theory was extended by Eisenman, and there is an excellent book edited by him [22]. According to this theory, the potential arises from two contributions: the boundary potential and the diffusion potential. The boundary potential is the result of the ion-exchange reaction (eqn.6.3) at the gel layers and it depends upon the cation activity ratio in the solution and membrane. The cation activity in the membrane depends on the ion-exchange equilibrium described by eqn. 6.3. For a long time there was disagreement between two schools of thought about the contribution of the diffusion potential. Interference problems of the glass electrode, particularly the alkali error of the pH glass electrode, were attributed to eqn.6.3 in which M^+ is the Na^+ ion.

The proceeding of this reation to the left would lead to reduction of H^+ concentration in the outer gel layer.

6.3 SOLID STATE ELECTRODES

The solid state electrodes are based either on inorganic salts or solid ion-exchanging materials. With regard to the inorganic salts, they could be single or mixed crystals embedded in a suitable matrix, for example:

LaF_3 , $AgCl + Ag_2S$, $AgCl + Ag_2S + PVC$

The low solubility of the crystal in aqueous solution and conductivity are the two basic characteristics for suitable materials for membranes in this type of electrodes. The operation of the electrode is mainly interpreted by ion-exchange theory [23,24,25]. However, this theory is incapable of explaining the electrochemical properties of all types of solid state electrodes [27]. Buck presented a theory considering rapid reversible ion-exchange at the membrane interface and mobile defects (Frenkel mechanism) within the membrane crystal. The potential of the membrane may be considered as arising from the contribution of two Donnan potentials and a diffusion potential. Due to the fixed negative ion-exchange sites, the diffusion potential for the zero current is zero [24,25,26], therefore, the membrane potential is given by the Donnan terms alone. Impedance studies [29] on the lanthanum fluoride and silver chloride membranes indicated the existence of a thin film, probably lanthanum hydroxide on the surface of crystal. However, with silver chloride such films were not present. According to these results, to explain the behaviour of the solid type electrode in the same way as glass electrodes is unrealistic [30]. The same principle might be applicable to heterogeneous membrane electrodes. Radiotracer experiments have provided evidence for the exchange of iodide ions in a silver iodide silicone rubber matrix. It is assumed that the ion adsorption process at the membrane surface may be the primary factor in the ion-exchange mechanism [32]. The method of membrane preparation, amount and nature of impurities [28], and mechanical pretreatment [31] have been reported to have significant effect on the electrical properties of solid electrodes.

6.4 LIQUID ION-EXCHANGER BASED ELECTRODES

A liquid membrane consists of a thin, porous, inert support, saturated with an ion-exchanging material in the liquid phase. The substances must have an extraction and selective binding capacity towards the ions of interest in contacting solutions. In contrast to the glass and solid state electrodes, the active sites in the liquid membranes may be mobile. The potential of the membrane is the result of two processes: firstly, a rapid ion-exchange or extraction equilibrium at the membrane-solution interface, where the ion from the external solution exchanges the ion bound to the ion-exchanger sites in the membrane. Secondly, the diffusion process, which takes place due to the differences in the mobility of various species inside the membrane. The ion-exchange theory has been mainly established by Eisenman and Sandblom [10,33,34] in collaboration with Conti and Walker [35,36]. Their theory is based on the ion-transport and ion-exchange theory of Teorall, Meyer and Sievers (T.M.S) [37,38].

According to Eisenman et al. , the potential difference across the membrane based on ion-exchanger is given by the following (equation 6.4):

$$E_m = (RT/Z_i F)\ln \frac{\sum_i u_i\ K_i\ a''_i}{\sum_i u_i\ K_i\ a'_i} - \underset{1}{\int_0^d} - \underset{2}{\int_0^d} \qquad (6.4)$$

where E is the potential of the solid or liquid ion-exchange membrane; z is the valence of the counter ion (i); a and a are activities of ions in contacting solutions on each side of the membrane; u is the mobility of the i-th ion inside the membrane and K is a constant which is defined as:

$$K_i = \exp\left(\frac{u^0_{i(aq)} - u^0_{i(mem)}}{RT} \right) \qquad (6.5)$$

$u^0_{i(aq)}$ and $u^0_{i(mem)}$ are the standard chemical potentials of the i-th ions in aqueous and membrane phases respectively. The two integrals $\int_1$ and $\int_2$ are terms which are functions of mobility of species in the membrane and are defined as:

$$\int_1 = \int_0^d t\ d\ln \frac{\sum_i \frac{u_{is}\ c_i}{K_i}}{\sum_i u_i\ c_i} \qquad (6.6)$$

$$\int_2 = \int_0^d \frac{\frac{u_s\ J^*_s}{RT}}{\left(u_s + \sum_i \frac{u_{is}}{K_i} c_i \right) \sum_i u_i c_i + u_s c_s \sum_i \frac{u_{is}}{K_i} c_i} \qquad (6.7)$$

Here the subscript 's' refer to the dissociated site species, 'is' refer to the associated ion pairs, 'K_i' is the dissociation constant of the ion-pair, 'c_i' is the concentration of the species, 'J_s^*' is the total flux of sites and 't' is given by eqn.6.8

$$t = \frac{u_s c_s}{\left(\dfrac{u_s c_s}{\sum_i u_{is} c_{is}} + 1 \right) \sum_i u_i c_i + u_s c_s} \qquad (6.8)$$

which varies between 0 in the case of complete dissociation and

$$\frac{(\quad u_s c_s \quad)}{(\; u_s c_s + \sum_i u_i c_i \;)}$$

for the case of strong association.

In the solid membrane, the ion-exchange sites are spatially fixed, and the mobility is zero, so both $\int_1$ and $\int_2$ become zero and eqn.6.4 reduces to the Eisenman-Nicolsky equation:-

$$E_m = (RT/Z\ F) \ln \frac{\sum u_i K_i a_i''}{\sum_i u_i K_i a_i'} \qquad (6.9)$$

All the above equations emphasize that the behaviour of the electrodes based on the ion-exchanger, not only depends on the activities of the ions in the solution and the membrane, but also on the equilibrium constant of the ion-exchange process, as well as mobility of the species in the membrane. Ionic migration has been assumed to be responsible for the passage of a small amount of current through the membrane [38]. However, impedance measurements [28], have indicated that ionic transport is not the only means of conveying the electrochemical information.

6.5 ELECTRODES BASED ON NEUTRAL CARRIERS

The discovery and utilization of macrocyclic ligands as active materials in the artificial membranes was the result of investigating of body cells. Ob servations [39] on potassium ion transport in mitochondria guided Stefanac and Simon [40] to develop potassium ion-selective electrode based on valinomycin.
There are two distinct membranes containing neutral carriers: thin and thick membranes. Thin or bilayer membranes are those whose thickness is smaller or equal to Debye thickness (50 - 100 Å) and electroneutrality inside this type of membrane is not necessary. Thick membranes are those which are thicker than the Debye length and as Covington pointed out [41], the violation of electroneutrality over such large distance is unjustifiable, and electroneutrality must be maintained at least in the bulk of the membrane. There are also structural differences between these membranes. Thick membranes may be regarded as a solution of neutral carriers. Thin membranes, similar in structure to biological membranes, are arranged in such a fashion that lipophilic parts of their molecules are inwardly situated, while the hydrophobic parts are oriented towards the external aqueous solutions. Accordingly, the conductivity mechanisms in thin and thick membranes are different. Here more attention is paid to the behaviour of thick membranes, due to the fact that the theory for the thick membrane is the extension and modification of the thin membrane.

Different theories and models have been proposed to explain the potential response and cation selectivity of membranes based on neutral carriers. The simplest model is the one suggested by Delevi and co-workers [42,43] for thin membranes, where membrane contains only one type of charged species.

The Ciani, Eisenman and Szabo [44] model of bilayer membranes applies to thin membranes, however, the results obtained with ion-selective electrodes are frequently interpreted by this theory. In this model, exclusion of free anions is assumed, and the following species are considered to exist in the membrane phase: cations, cation-carrier complexes, anion-pairs and free carriers.

The distortion of the potential response of the membrane is attributed to penetration of the anions into the membrane. This deviation becomes significant at higher concentrations of the electrolyte and at high values of the ion-pair formation constant. According to this model the permeation of anions changes the concentration of the cation at the inner surface of the membrane. The membrane potential is given by eqn. 6.10:

$$E = RT/ZF \ln \left[\frac{a''_{i^+}}{a'_{i^+}}\right] + RT/ZF \ln \left[\frac{c''^{tot}_{s}}{c'^{tot}_{s}}\right] + RT/F \ln \left[\frac{D'_{in}}{D''_{ex}}\right] \qquad (6.10)$$

where $$D = 1 + K_{is^+} . a_{i^+} . K_{isx} . a_{i^+} . a_{x^-} \qquad (6.11)$$

Here E is the membrane potential, a''_{i^+} and a'_{i^+} are the cation activities in external and internal solutions, c''^{tot}_{s} and c'^{tot}_{s} are the concentrations of the carrier in external and internal solutions, K_{is^+} and K_{isx} are the equilibrium constants of the following reactions:

$$I^{+}_{aq} + S_{mem} \xrightleftharpoons{K_{is^{+}}} IS^{+}_{mem} \tag{6.12}$$

$$IS^{+}_{mem} + X^{-}_{mem} \xrightleftharpoons{K_{isx}} ISX_{mem} \tag{6.13}$$

Due to the large deviation from electroneutrality, the application of this model to thicks membrane without considering the electroneutrality condition is questionable, therefore, for thick membranes modification of this model is required.

The extension and generalization of thin membrane theory for thick membranes has been carried out by Boles and Buck [45]. In this model, electroneutrality is regarded to exist at high salt activity in the bulk of the membrane and deviation from the electroneutrality occurs within the membrane (space charge control at low activity). The membrane components consist of free anions, free cations, free carriers, cation-carrier complexes and anion-pairs.

The difference between the two treatments is that, in the latter, two extra assumptions are suggested: the existence of the anions and the electroneutrality in the bulk of the membrane. Maxima in response plot and anion response at high salt activity depend on the mobility of the anion and anion-pair formation constant. Buck [46] informally suggested that deviations in the response plot is attributed to the change in the rate of anion interfacial kinetics.

In the model proposed by Morf and Simon [47], Nernstian response is obtained when the anions are immobile. It has been shown that anion interference can be reduced, at least at the low concentration of the salt by incorporating large lipophilic anions such as potassium or sodium tetraphenyl borate in the membrane. According to this model, the position of the maxium and the reversal response depends on the extraction constant of the reaction (eqn. 6.14) and the mobility of the anions.

$$I^+_{aq} + X^-_{aq} + S_{mem} \xrightarrow{K_{ex}} IS^+_{mem} + X^-_{mem} \qquad (6.14)$$

Here I^+, X^-, S and IS^+ are cation, anion, carrier and cation-carrier complex respectively, ´aq´ and ´mem´ subscripts are for the aqeuous and membrane phase. The maximum occurs because of the full consumption of the carriers. The complete consumption of the carriers is not in agreement with the results obtained on resistance measurements [48] and also the present study (Chapter Four Section 4.6).

The last, but not the least, important model is that suggested by Kedem et al. [49]. They believe that fixed negative charge sites must be presented in the matrix, and the cation-carrier complexes act in the membrane as counter-ions of the negative sites. There is enough evidence to support this hypothesis, e.g. the ion-exchange capacity of the polymer matrix [50]. This hypothesis was investigated by Seto et al. [51], and they derived an equation on the basis of T.M.S theory (fixed negative charge sites), where, the behaviour of the membrane in relation to components of the membrane was predicted. The position of the maximum is proportional to $c^{-1/2}$ and also proportional to the concentration of the lipophilic fixed negative sites, where, ′c′ is the total concentration of the neutral carrier.

pH measurements described in present study on the role of membrane components (PVC, plasticizer, etc.), revealed that impurities in the membrane matrix introduce negative sites into the structure. The effect of a number of lipophilic anions on K^+ / PVC valinomycin based membrane was shown in Fig 4.12 . The cation response range is greater for KF and decreases as the lipophilicity of anions increases.

6.6 TRANSPORT PROCESS AND SELECTIVITY

The electrochemical information must be conveyed through the membrane. However, the exact nature of processes involved in membrane potential formation is not clear. Many models of membrane transport have used the Nernst-Planck equation and Fick′s law to describe the relation between the flow of permeating species and the force acting on the system. The driving force in the membranes is provided by electrochemical potentials of the charged species. For neutral species, chemical potential should be considered. An alternative theory for transport is the Eyring jump mechanism, where the charged species jump over two symmetrical energy barriers. This model is only applicable to membranes whose thickness is four times greater than the diameter of the carrier molecules.

The model presented by Reusch and Cussler [52] is a simple description of the carrier mediated transport mechanism for the neutral carriers present in liquid organic phases (Fig 6.1).

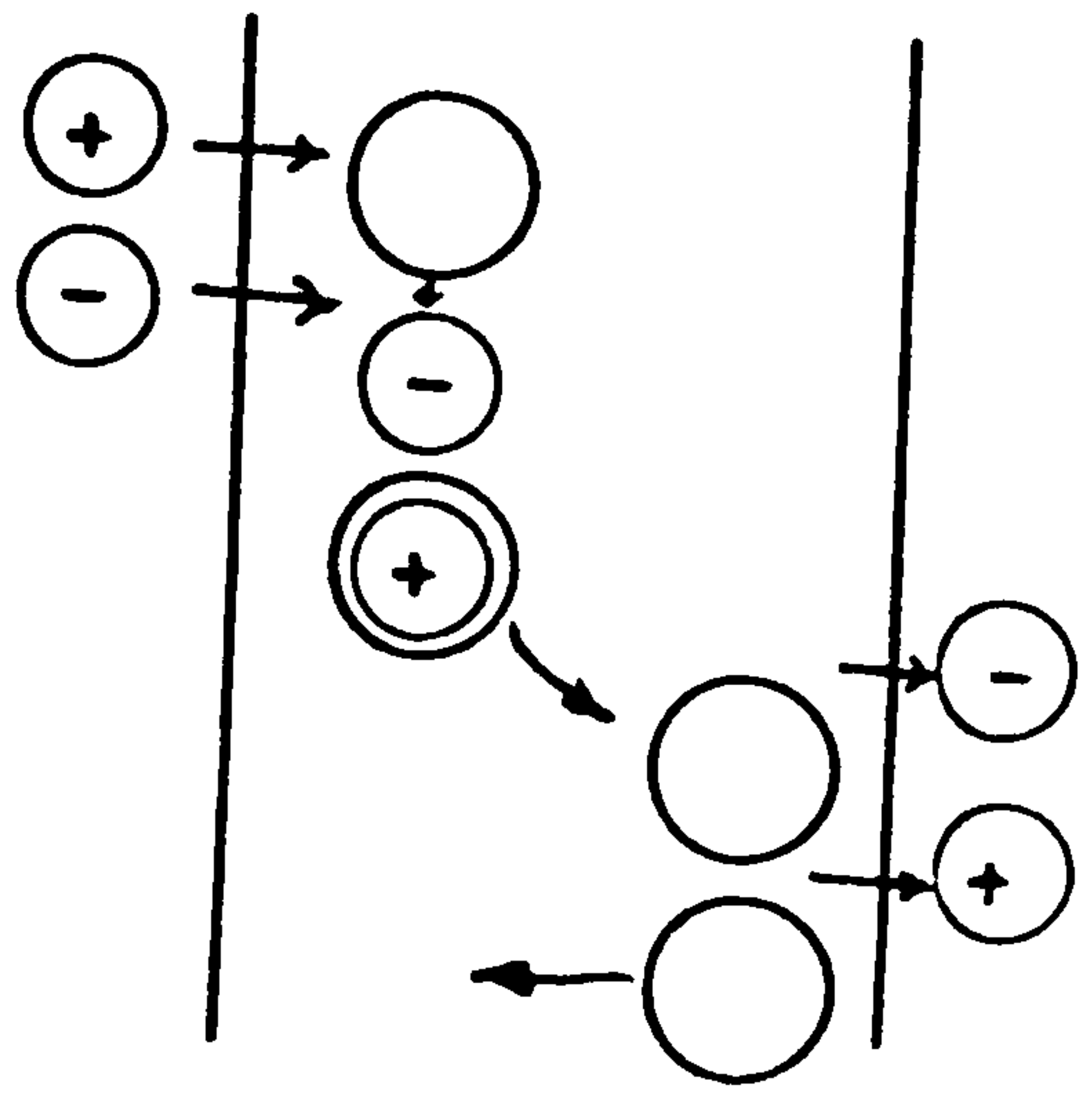


Fig 6.1

1)Ion forms complex with carrier in the membrane-solution interface.
2)The complex diffuses across the membrane.
3)Decomplexation occurs at the other interface, releasing ions.
4)Free carrier returns.

In this model, the carrier molecule forms a complex with a cation by surrounding it with an electronegative environment of oxygen atoms and isolating the cation from the surrounding solvent [53]. The organic phase is not permselective to cations, therefore, an ion-pair is formed and travels towards the low concentration. The mechanism consists of four steps: the first and third steps are the very rapid ion-exchange (extraction) reactions, where loading and unloading of cation at the membrane-solution interfaces occur. The second step is a slow diffusion of anion-pair complex across the membrane; and finally the free carrier returns to its former position to undergo further complexation. According to the results obtained by Covington et al. [54] with a U-tube (over 20 cm long), the applicability of this model to thick membranes which would have very slow diffusion, is questionable.

Experiments on membranes without negative sites have revealed [55] that the response and selectivity of the membrane depends on the presence of negative sites. The presence of those sites allows the membrane to be selective to cations, and the ionophore contributes to the selectivity when selectivity already exists.

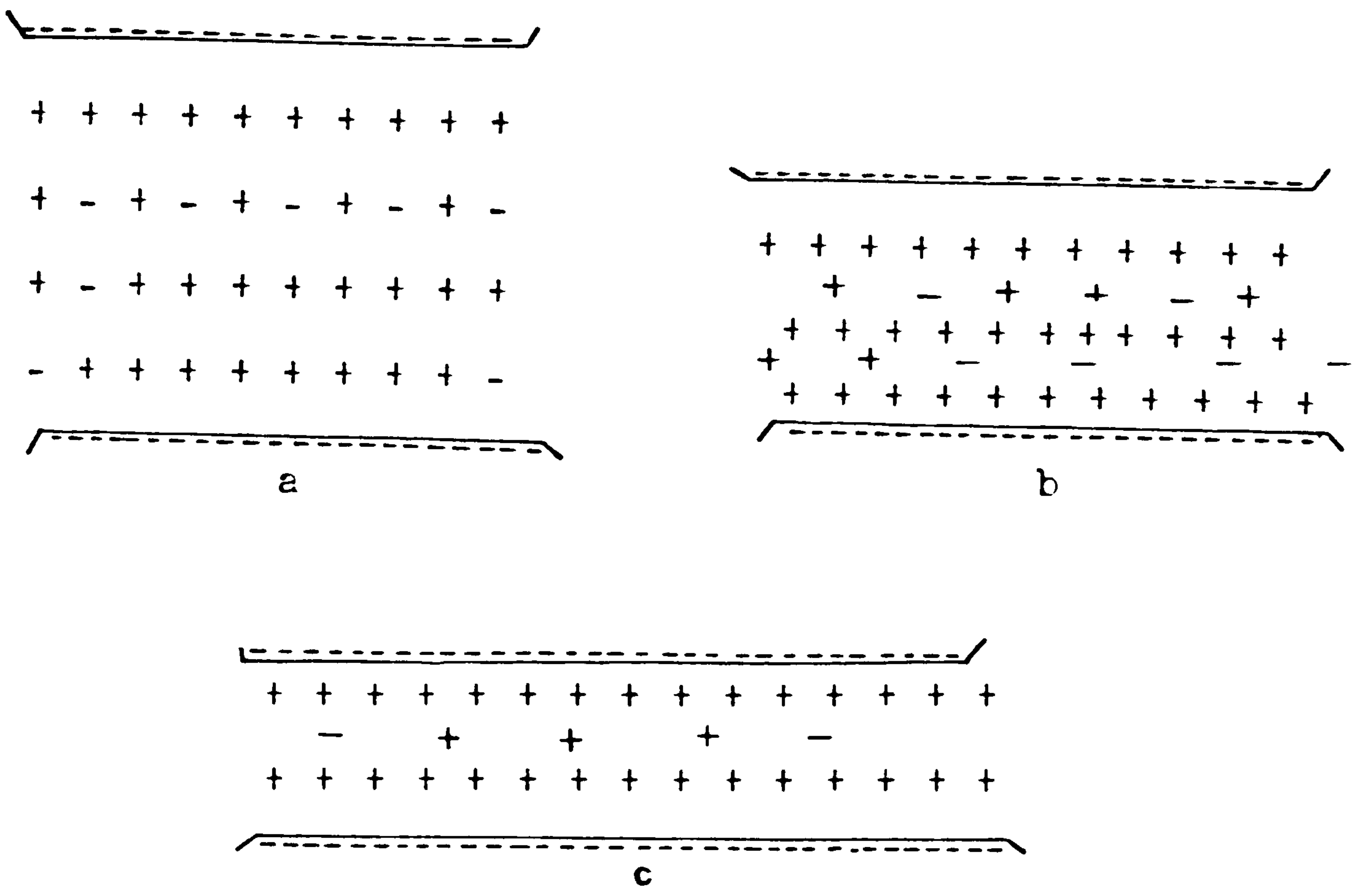
The supports are usually ´Millipore´ filter porous discs made of cellulose acetate [56] or cellulose accetate and nitrate. It has been found that these supports possess an ion-exchange capacity which enable the membrane to be selective [57]. PVC membranes made with various plasticizers showed different selectivity. This inconsistancy may be attributed to the possession of different extents of fixed negative sites[58].

From radiotracer studies, Simon and co-workers [59] have put forward new proposals about the nature of these negative sites. They believe that a flux of protons migrate out of the membrane and leaves hydroxyl ions behind (eqn.4.3).

$$\underset{aq}{K^+} + \underset{mem}{H_2O} \rightleftharpoons \underset{mem}{K^+} + \underset{mem}{OH^-} + \underset{aq}{H^+} \qquad (4.3)$$

They concluded that the low mobility of the hydroxide ions is due to water cluster formation, and therefore, the preference for K^+ ions over Cl^- is attributed to the presence of these negative sites within the membrane. This finding is in agreement with theoretical treatment of membrane response by Morf and Simon [47].

Ion distribution in a porous membrane with fixed negative sites and correlation of pore diameter and selectivity are shown in a schematized manner in Fig 6.2a-6.2c.



a

b

c

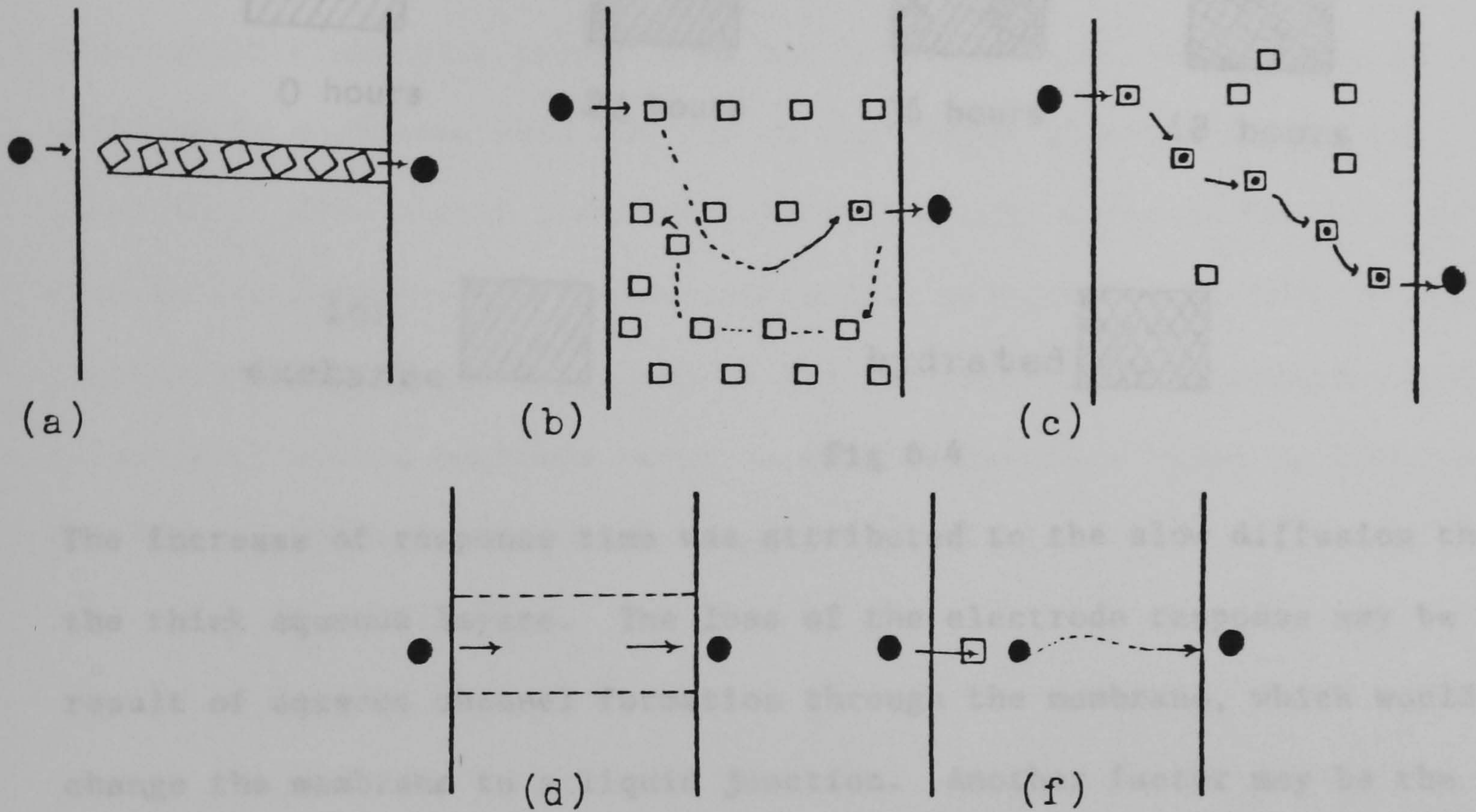
Fig (6.2)

The negative sites will give rise to an electric double layer in the vicinity of the pore surface. The permeability of the membrane will depend on the diameter of these double layers. By changing the pore size and double layer thickness, the membrane properties can be altered from a liquid junction to a selective membrane. Negative sites may be introduced by chemical reaction or by the incorporation of a large lipophilic anion into the membrane.

Several mechanisms of charge transfer across the membrane are illustrated in Fig 6.3 . The carrier mediated transport mechanism, which involves initial complex formation between the neutral carrier and cation followed by its transport in the cavity of the carrier, has been accepted [44,28]. Stark and Benz´s [61] findings on bilayer membranes, that the conductivity of the membrane is proportional to the concentration of a neutral carrier, is in agreement with the carrier mediated mechanism. They believe, however, that the transport of MS^+ is not a simple diffusion process and explained this by Eyring jump model. It is probable that an ion remains bound to a single carrier in a thin membrane where the diffusion is very rapid. However, in thick membranes the charge transfer across the membrane by diffusion of MS^+ species is unlikely.

Experiments carried out by Wipf et al. using ^{14}C labelled macrotetralide [62] and valinomycin [63] have shown that the transport of the potassium ion across the membrane is accompanied by an equal number of neutral carriers within the membrane which is consistent with 1:1 complexation process (cation:carrier). The exchange of ligands is shown to occur during the transport process, so a carrier-relay mechanism was proposed for the diffusion of charge in the bulk of the membrane.
A drastic decrease in the slope and selectivity of the thick membrane was taken as an indication that channel formation through the membrane did not occur [64]. The effect of temperature [65] on the conductivity of a thin membrane was demonstrated to be high, above 40^0C. However, the conductivity sharply decreases at the point of transition to solid state, which suggest that in both type of membranes the possibility of channel

formation by a group of antibiotic molecules is unlikely (except for gramicidin [66]).



□ : Carrier

● :Cation

(Fig 6.3)

a: Channel b:Carrier c:Carrier relay d:Pores f:Lipophilic

An important study on the impedance and time dependence of the PVC-Aliquat nitrate system has revealed, interesting results concerning the effect of water uptake (hydration) by the membrane on the behaviour of the electrode. Buck et al. [67,68] concluded that uptake of water by a liquid membrane must be associated with a change of the support (hydration) and not changes in the transport properties of the dissolved species. They proposed a three-layer model similar to the glass electrode. Fig 6.4 demonstrates the hydration of the membrane with time.

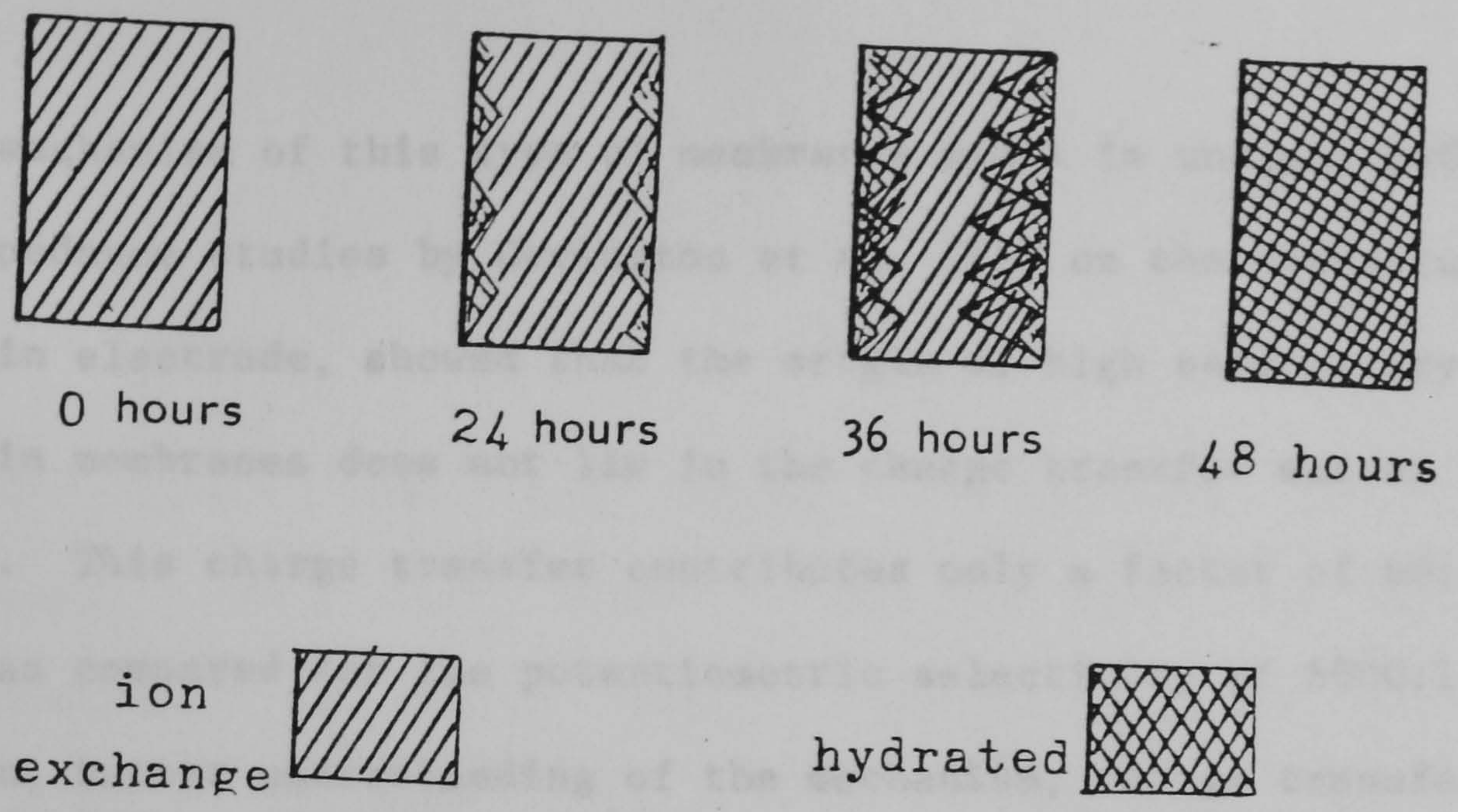


Fig 6.4

The increase of response time was attributed to the slow diffusion through the thick aqueous layers. The loss of the electrode response may be the result of aqueous channel formation through the membrane, which would change the membrane to a liquid junction. Another factor may be the expulsion of ion-exchange material by extension of the hydration layers. The transport of charge in this model may be explained by the model proposed by Shohami and Ilani [69]. According to their hypothesis, the negative fixed sites are located in a narrow aqueous channel, surrounded by a solvent of low dielectric constant. The lipophilic ion-carrier complexes are assumed to enter the membrane from both organic and aqueous phases. The mechanism of the charge transfer is considered to be a jumping process, where cations from doubly-occupied sites jump to nearby singly-occupied sites, and from singly-occupied sites to vacancies.

The transport of charge in PVC membrane based on valinomycin seem more likely to be interpreted by this theory, and a three layer fixed charged sites model is the most realistic [67,54,70]. However, as Buck pointed out, the mechanism of this type of membranes still is unclear [46]. Recent impedance studies by Covington et al. [71] on the potassium-based valinomycin electrode, showed that the origin of high selectivity of valinomycin membranes does not lie in the charge transfer across the interface. This charge transfer contributes only a factor of 60:1 for K^+ over Na^+ as compared for the potentiometric selectivity of 6000:1. In conclusion, better understanding of the mechanism, charge transfer and selectivity of the membrane based on neutral carriers could be achieved if the bulk of the membrane is thoroughly investigated

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CHAPTER SEVEN

CONCLUSIONS AND SUMMARY

In this chapter, a summary of experimental results (chapters 3, 4 and 5) is presented, and a general conclusion is derived based on the findings of the present study. An attempt is being made to compare results with those available in the literature.

7.1 COMPOSITION OF A PVC MEMBRANE

7.1.1 Plasticizer

A variety of plasticizers is used in PVC-supported membranes, e.g. sebacic esters, phthalic esters, etc. The prime role of the plasticizer is to reduce the glass temperature of the rigid PVC in order to produce a flexible and more useful membrane. In Chapter Three, Section 3.6, results of the effect of added plasticizer on the response range and selectivity of the membrane were given. The first and most obvious effect was that an electrode without plasticizer could not give stable results, and thus addition of plasticizer is essential for obtaining functional electrodes. The results in Table 3.8 indicated that for satisfactory electrodes the content of plasticizer must be controlled. Electrodes with concentrations lower than 30% (w/w) of plasticizer showed a poorer response, particularly in mixed solutions, when a membrane with 30% (w/w) plasticizer content failed completely to demonstrate any response. On the other hand, increasing the plasticizer content to 70% (w/w), improved selectivity, slope and response range of an electrode (see Table 3.8 and Fig 3.19). However, this trend ceased as the plasticizer content was increased to 78% (w/w), which produced a gel-like and unusable membrane. As regards the effect of the plasticizer content, it seems to change the mobility ratio of the ions concerned. Results obtained with the valinomycin / PVC electrodes were in agreement with the work of Baum and Lynn [1] as far as the content of the plasticizer is concerned: the active material in their membrane was the ion-exchanger potassium tetra (p-chlorophenyl) borate. They reported a significant influence on the electrode behaviour due to the change of the type of plasticizer. This could be attributed to the interaction of the plasticizer molecules with the ion-exchanger and cations. In this study, as results in Tables 3.2, 3.3 and 3.4 demonstrate, the type of plasticizer does not show any significant effect, except in the electrodes based on bis-(benzo-12-crown-4)s, (Table 3.12 and Fig 3.32). The influence of different plasticizers on membranes based on bis-naphthol-crown-7 and valinomycin was negligible. These observations support the view that, membranes composed of valinomycin and also those ligands which encapsulate the cation properly to the extent of preventing interactions between cation and plasticizer as well as cation with anions, the type of plasticizer is not significant. Nevertheless, the plasticizer must possess the properties which were previously explained (Chapter Two Section 2.2). This finding is in agreement with the results of Mascini et al. [2] and Fiedler [3]. In general, as Simon et al. [4] stated, the effect of the plasticizer type (dielectric constant) will be more outstanding in discriminating between mono and divalent cations. However, the effects of plasticizer were found to be more pronounced on electrode behaviour when salts with lipophilic anions were used, e.g. KSCN (see Fig 4.15). This distortion at a higher concentration might be partly due to the different viscosity and polarity of the membrane medium. Such a difference could be attributed to the plasticizer type, which allows the penetration of the lipophilic anions to various extents.

7.1.2 Active Material

Two types of active materials were utilized in the present study: valinomycin and bis-crown compounds. As the results in Chapter Three Section 3.7 demonstrate, addition of active material is essential to obtain a selective electrode. This observation is in agreement with the finding of Kedem et al. [5] that: the selectivity is induced because of the presence of active material. Membrane without active material did not distinguish between the primary and interferent ions. Results in Table 3.6 and Fig 3.15 indicate that, in order to obtain electrodes with good selectivity and slopes, the amount of valinomycin must not fall below a certain level (1% w/w). The effect of the amount of active material is more obvious when electrodes are used in mixed solutions, e.g. NaCl+KCl (see Fig 3.16). Consequently, attempts to reduce the amount of valinomycin to economize on the membrane cost were not successful in cases where interfering ions, particularly sodium ions were concerned. On the other hand, deviation from the linearity at higher concentration levels of lipophilic salts is increased by increasing the concentration of the valinomycin in the membrane(Fig 4.17). Membranes based on different bis-crown compounds with different concentrations did not show any improvement in the slope of their calibration curves. As far as the comparison of the slopes is concerned, the behaviour of electrodes based on bis-naphthol-crown-5, 6 and 7 was interesting. Nevertheless, these electrodes showed very low selectivity towards the sodium ions. From solvent extraction and U.V. studies, the complexation properties of these ligands with alkali metals indicated the following order: [6]

Bis-naphthol-crown-5 $Na^+ > Rb^+ > Cs^+ > K^+$

Bis-naphthol-crown-6 $K^+ > Rb^+ > Cs^+ > Na^+$

Bis-naphthol-crown-7 $Cs^+ > Rb^+ > Na^+$

These results are not unexpected as far as the size of the cavity is concerned. But, surprisingly, all PVC membranes based on these ligands showed Nernstian response towards the potassium ions (Table 3.10 and Fig 3.27). This behaviour could not be interpreted only in terms of ring size alone. A knowledge of conformational flexibility might be helpful in understanding the aforementioned behaviour. The selectivity values of bis-naphthol crown-5, 6 and 7 are comparable to the mono and bis-benzo-15-crown-5, which have selectivity coefficients approximately in the range of 20-30 [7,8,9]. However, their selectivities are inferior compared to the membranes based on dimethyldibenzo-30-crown-10 and dibenzo-30-crown-10 where $k^{pot}_{NaK} = 400$. The performance of electrodes based on bis-(benzo-18-crown-6)s and bis-(benzo-12-crown-4)s was less impressive. As far as the behaviour of the blank electrodes is concerned, it looks as though the presence of those ligands changes the nature of the membrane through the interaction between the plasticizer molecules and other components. Apart from these, the viscous PVC membranes might restrict the movement of the ligand and the loading and unloading processes. Japanese workers [10,11] have obtained reasonable results with the electrodes based on bis-crown compounds. As compared with results of the present study, there is a clear indication that the dominant factor in the operation of these ligands in the membrane, is the nature of their linking groups providing favourable conformation for a particular cation. In contrast, when dealing with bis-crown compounds where linkage is provided by imine groups as used here, one might expect a number of isomers being produced each possessing different complexing capacity toward the alkali metal ions. As such, certain factors contributing unfavourably to the membrane behaviour might be attributed to the existence of various isomers in these compounds.

Membranes with KTPCPB only as active material produced a near Nernstian response. However, addition of small amounts of the same compound to membrane based on valinomycin to prevent anion penetration showed no improvement. From the results in Chapter Three (Tables 3.6 and 3.8) one can also conclude that, optimum performance could be achieved by employing higher valinomycin and plasticizer ($<70\%$ w/w) concentrations in the PVC potassium ion-selective membrane formulation.

7.1.3 Matrix

The criterion for the selection of matrix for a membrane is its compatibility with other components of the membrane. A comprehensive study [12] on the pore size of the membrane in liquid membrane electrodes, revealed that the most suitable diameters are 0.01 to 0.2 μm. Upon increasing the pore diameter, the membrane potential will become a liquid junction potential. In PVC membranes, the pore diameters are very small compared to liquid membranes and water channel formation across the membrane is less possible. The type of polymer plays an important role in the response of the electrodes. Membrane matrices with different polymers, e.g. polyurethane or polymethylmethacrylate, were not successful [2]. The polyvinyl chloride matrix has been found to be more satisfactory with a variety of plasticizers. The results of the present study (Chapter Three Table 3.2) showed that there is no significant difference between the behaviour of the electrodes with different PVC matrices. However, pH measurements, and anion responses (Fig 4.14) proved that the different samples of PVC, which are supposed to be inert, include some impurities which may be the residue of the addition of components during the manufacturing process.

7.2 INTERNAL REFERENCE SYSTEM IN I.S.Es

As pointed out in Chapter Four, an ion-selective electrode system requires an internal reference system, i.e. internal solution and internal reference electrode. Principally, in order to obtain a thermodynamically defined reversible electrode, the internal reference system must contain a reversible couple which facilitates ionic to electrical charge conversion. In the present study these were the Ag/AgCl electrode and the potassium chloride solution.

7.2.1 Change in the Concentration of KCl in Inner Reference System

Results in Table 4.1 and Figs 4.1a and 4.1b demonstrate that changes in the concentration of the internal reference solution in the range of 10^{-1} to 10^{-5} mol/dm^3 KCl, do not affect the slope, selectivity, response range and response time. Similar conclutions can be drawn for the calcium electrode (Philips Ltd.). For membranes based on ion-exchangers, however, a decrease in the concentration below 10^{-3} mol/dm^3 results in the decline of the slope and the response range (Table 4.4 and Figs 4.4a and 4.4b). In this context, it is worthwhile to note that Shatkay [13] have also remarked that an increase in the concentration of inner solution of a Ca^{2+} responsive electrode, based on ion-exchanger in PVC, resulted in the extension of response range. Generally, the only influence of the variation of the concentration was the difference in the extent of displacement of successive curves, e.g. distance between the curves for internal solution of 10^{-2} and 10^{-3} mol/dm^3 was 114.5 mV, while for the curves of 10^{-3} and 10^{-4} mol/dm^3 it was 96.8 mV (Table 4.1). Ideally, displacement of curves with different internal solutions, should be proportional. In theory, a displacement of 120 mV is expected per one decade change of the internal solution (10^{-1} to 10^{-2} mol/dm^3 KCl), which is the result of 60 mV due to the change of the potential of internal reference electrode (Ag/AgCl) and 60 mV change contributed by the inner surface of the membrane. Comparison of ΔE^0 values in Table 4.7 indicates that, they do not follow this pattern. It seems that at low concentrations, either the silver-silver chloride electrode or the inner surface of the membrane do not obey Nernstian law, especially in the concentration range of 10^{-4} to 10^{-5} mol/dm^3 (ΔE^0 = 77.2 mV). Jalkanen and Virtanen [14] reported exactly the same trend as was found here with membranes based on valinomycin. This is to be compared with potassium electrode based on an ion-exchanger, where a decrease in the concentration of the inner solution somewhat reduced the range of funtionality of the membrane (Table 4.4). However, this effect was slight, and even with inner solution of 10^{-4} and 10^{-5} mol/dm^3 KCl, the electrode ceased to be useful at about 10^{-3} mol/dm^3 KCl (Fig 4.4a). Apart from the above mentioned reasons, this behaviour may be also due to a decrease in the ion-exchange rate.

The results for the sodium electrode based on bis-(benzo-12-crown-4)s of the present study (Fig 3.33) disagree with the findings of Shono et al. [11]. According to their work, changes in the inner solution leads to a functional sodium electrode, while in the present work, change of the inner solution from 1 mol/dm^3 to 4 mol/dm^3 NaCl shows a pattern similar to the valinomycin based electrode. In other words, only a shift in the position of calibration curves occurs. However, there is not enough evidence to support their findings and current hypotheses would apparently not justifiy such an improvement.

7.2.2 Changes in the Type of Inner Solution Salts

As stated previously, the internal reference solution must contain the ion of interest as well as a counter ion which is sensed by the internal reference electrode. In this work, these were potassium and calcium as sensed ions for corresponding electrodes with chloride as their counter ions. A set of experiments in Chapter Four proved that the type of cation in the inner solution of the electrodes based on the neutral ionophore did not influence the behaviour of the electrodes and that the only distinguishable difference was a shift in the electrode's potential, as follows (see Tables 4.2, 4.3, 4.5 and 4.6):

K^+ /PVC based on valinomycin

E^0 $Na^+ > Li^+ > Cs^+ > K^+ > Rb^+$

$Al^{3+} > (T.E.A)^+ > Ca^{2+} >$ Tris/HCl $>> K^+$

K^+ /PVC based on ion-exchanger

E^0 $Na^+ > K^+ > Rb^+ > Cs^+ > Li^+$

Ca^{2+} /PVC (Philips Ltd.)

E^0 $K^+ > Al^{3+} > Mg^{2+} > Ba^{2+} > Ca^{2+}$

These results suggest the absence of a relationship between inner and outer surface potentials. As far as thermodynamic reversibility is concerned, there should be a partition of cations between aqueous and membrane phases. At the same time, and to a certain extent, complexation occurs between cation and ligand from the membrane phase. On the other hand, electrodes with Cu/Hg inner systems suggest that there is no relationship between the behaviour of the electrode and the presence of the ion of interest in the internal system. In other words, thermodynamically ill-defined electrodes work satisfactorily. With regard to the data from the variation of internal solution experiments, the hypothesis of a cycle of loading, transporting, unloading of the ion of interest by the ligand through the thick membrane, and the return of carrier to its former position does not apply. Another reason for the non-applicability of the above hypothesis rests on the fact that response times of all electrodes with different inner solutions were registered over a short period of time (seconds), while according to the same hypothesis the response takes a longer time. Therefore, one might conclude that contribution to the membrane potential from the bulk of the membrane i.e. diffusion is unlikely to occur. A state of thermodynamic equilibrium should still apply in this situation too, in which case there must be means to provide a stable potential at the inner surface and also means to allow the transport of minute amounts of current through the membrane.

7.3 MECHANISTIC CONSIDERATIONS

In Chapter Six, the contemporary hypotheses of the operation of membranes based on the neutral carriers were outlined. As was noted, there is no general agreement on the operation, ion transportation and selectivity of these electrodes. Data produced in the present study might however contribute towards the clarification of this uncertainty.

7.3.1 Origin of the Selectivity in PVC/ Valinomycin Based Electrodes

It has been shown that membranes become highly selective with respect to cations, if they contain a small amount of negative sites [15]. The existence of these negative sites, apart from providing selectivity, is necessary that the electroneutrality condition prevails in the bulk of a thick membrane. As for the source of the negative sites in the PVC membranes, the results in Chapter Four (Part Two) support the view that impurities from the manufacturing and purification processes of the membrane components are responsible for the existence of those sites. Results of the first set of pH measurements on potassium chloride solutions 10^{-2} mol/dm^3, in which membrane and membrane components (PVC and plasticizer) were immersed, showed changes of pH (Fig 4.9a, 4.10a and 4.11a). This can be taken as an indication that hydrolysis of the impurities occurs in each component indiscriminantly and changes in the pH of the solution are the result of all those reactions. In the second set of experiments which differed only in their contacting solutions (triple distilled water) a similar pattern was observed. Therefore, the change in the pH is not the consequence of reaction 4.3 which was proposed by Simon et al. [16]. In their hypothesis, presence of potassium ions in aqueous solution is essential for reaction with water molecules from the membrane in order to induce a flux of hydrogen ions from the membrane, leaving behind water clusters of hydroxide ions (Fig 4.11c). Data in Figs 4.9b, 4.10b and 4.11b explicitly demonstrate that, in the absence of potassium, ions the pH of the external solution is changed. Therefore, the variation of the pH is independent of potassium ions and arises from the reaction of impurities in the membrane with water molecules. Our results give some indications of impurities in membrane constituents, which are responsible for the electroneutrality and selectivity of the membrane. These findings are in agreement with the work of other research groups [15].

7.3.2 PVC Membrane and the Anion Response with Respect to Membrane Composition

It has been reported that , at high concentration of lipophilic anions, the valinomycin-based electrode loses its response due to the penetration of the those anions into the membrane [17]. Evidence presented in this work complies with the results obtained by a number of authors for potassium salts containing lipophilic anions (Fig 4.12). This trend appears to be in accord with the Hofmeister lipophilic series. Morf et al. [18] have suggested that incorporation of tetraphenyl borate, in the form of its potassium and sodium salts, improves the behaviour of potassium-based valinomycin electrode. This improvement is ascribed to the large lipophilic anions remaining in the membrane, while potassium or sodium cations leach into the sample solution. However, according to the results obtained here, there is no significant difference in the behaviour of electrodes either with or without lipophilic salt towards the potassium ions in conjunction with various lipophilic anions (Figs 4.12 and 4.13). There is indication of some improvement when electrodes with additional lipophilic salts are used in flow cells. It might be possible to prevent the entry of the anions into the membrane by introducing higher concentrations of a lipophilic salt (more than 1.2 mg). The behaviour of electrodes made of different types of plasticizers, and of electrodes composed of various types of PVC (Figs 4.14 and 4.15), indicates that the anionic response varies with changes in the type of membrane components. This behaviour could be attributed to the differences in the ion-exchange capability, viscosity, polarity, etc. of the membranes, which might have resulted from the participation of different plasticizers and polyvinyl chlorides. These observations, therefore, support the idea that the different ion-exchange capacity of the membrane constituents is partly due to the presence of the impurities. In the light of this evidence, and results of the pH measurements (Section 4.5), the origin of negative sites, as being due to impurities, is tenable. Data presented in Fig 4.17 demonstrate that an increase in the concentration of the valinomycin in the membrane increases its anionic response. This finding, does not support the suggestion of full consumption of valinomycin being the reason for the anion response of the membrane [18]. It is possible to conclude that an increase in the valinomycin might increase the amount of anion-K^+ /valinomycin and anion/potassium ion-pairs which could result in a further reduction of potassium and potassium-valinomycin complex mobilities.

However, on the basis of this set of results alone, it is difficult to arrive at a concrete conclusion. Therefore, further systematic investigations are required. Electrodes with a Cu/Hg internal system, with different plasticizers, confirmed the results obtained with conventional electrodes (Fig 4.18). From these results one might infer that the anion response of the electrode is independent of the internal reference system. The shift of the maxima towards the high potassium ion concentration with membrane prepared with BEHS plasticizer might be attributed partly to the decrease in the extractibility of the medium. Since a similar trend was found by the variation in the type of membrane components, the extent of the anionic response of the membrane would depend on the nature of anions, the nature of the medium and the level of valinomycin. Finally, on the basis of these observations, consideration of the following points might be useful in constructing a PVC-potassium electrode with less anionic response:

a) Concentration of valinomycin,
b) Polarity of the plasticizer or, more generally, membrane medium,
c) Purity and ion-exchange capacity of the membrane components.

7.4 APPLICATION OF K^+/PVC AND AUTOMATIC CALIBRATION OF ELECTRODES

The results obtained with the Corning Analyser had poor reproducibility and showed bias with respect to the flame photometer. In Chapter Five Part One, the sources of this bias have been investigated and in Part Two of the same chapter, a new method for calibration of electrodes both independently and also in conjunction with the Corning 902 has been described.

7.4.1 The Sources of Bias in the Corning 902 Analyzer

Results given in Chapter Five indicate that there are two possible sources:

a) Variation of liquid junction potential,

b) Interference from Triton X-100

Data in the present study are in agreement with the work of Whalley [19] i.e., a 2 mV change in the liquid junction potential is not unlikely. This change in liquid junction potential with respect to that of membrane potential in the concentration range of potassium and sodium ions in body fluids is significant. On the basis of results with different junction types, the use of 'T' form junction is recommended. A special design of 'T' junction can overcome the memory effects of the reference electrode (Fig 5.16), though there are some practical restrictions on the utilization of this type of junction. The amount of Triton X-100 in the sample solution and inner solution of the reference electrode did not produce regular change in the liquid junction potential. Due to surfactant property and complexation ability of Triton X-100 with alkali metals as shown in section 5.10, its presence in sample solution may lead to irreproducible results. In the light of the above findings, the following points are recommended:

1) Utilization of 'T' form junction of renewable type,

2) Replacement of Triton X-100 by another suitable material.

7.4.2 Automatic Calibration

The calibration and selectivity curves in Chapter Five, Part Two, manifested that the logarithmic dilution method is more rapid, simple and yields accurate results in comparison with the conventional method. Automatic calibration of electrodes is rendered possible by this method. According to the results obtained, the effect of the extra liquid junction, its contribution and the role of the liquid junction type were confirmed. Since the direction of dilution is from a higher to lower concentration, the memory effect on the reference and the sensed electrodes may cause some problems in special cases. However, application of the method in industry and on-line monitoring by means of a computer is feasible. In the present study, the method was successfully applied to the calibration of the electrodes of the 902 Corning Analyser.

7.5 SUGGESTIONS FOR FUTURE WORK

In the light of the findings of the present study, a number of suggestions leading to the clarification of the behaviour of membrane electrodes are proposed. Bis-crowns discussed in Chapter Three as active materials are of considerable interest and deserve further study. The complexing ability of these compounds has to be closely investigated as membranes based on all bis-naphthol-crowns showed similar responses towards the potassium ion, while extraction studies indicate various affinities with other ions. An evaluation of bis-crown compounds, particularly bis-naphthol-crowns, because of their good response to potassium ion, in conjunction with valinomycin, may improve the selectivity of the electrode. The co-operative effects of valinomycin and other active materials with bis-crowns are worth investigating. The effect of substituent groups on the ring and connecting chain needs to be evaluated in order to decide whether the effect is as marked as with that of tetramethyl dibenzo-18-crown-6 [7]. An appraisal of the favourable conformation of bis-crowns towards the alkali ions in different solvents is not yet available. A knowledge of the conformation and differentiating abilities of the favourable conformations might result in preparation of improved electrodes. More information on the charge transport, development of potential and operation of membranes concerned with this study is possible through systematic a.c. impedance studies. Finally, further elaboration of the continuous dilution method can lay the basis for establishing standard conditions with regard to the determination and comparison of selectivity coefficients.

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