The kinetics of the acid catalysed hydrolysis of

dodecyl sulphate and dodecyl ether sulphate surfactants

in concentrated micellar solutions

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ABSTRACT

The acid catalysed hydrolysis of dodecyl sulphate and dodecyl ether sulphate surfactants is catalysed by their self-micellisation. The reaction was investigated throughout the isotropic micellar phase (up to 0.6M surfactant) at $70^{O}C$. The effects of temperature, counterion, electrolytes, acid concentration and surfactant concentration on the rate of hydrolysis were studied and analysed in terms of a pseudo-phase/ion-exchange model.

CONTENTS

CHAPTER ONE

INTRODUCTION

The research upon which this thesis is based was concerned with the kinetics of the acid catalysed hydrolysis of various dodecyl and dodecyl-ether sulphate surfactants in micellar solution. These materials, which under the appropriate conditions form micelles and liquid crystalline structures in aqueous solutions, are used in detergent formulations such as shampoos.

The project is a CASE award with Albright and Wilson (Marchon Division) as the industrial collaborating body, whose interest lies in the effect of the reaction on the commercial materials while in storage. These commercial materials are prepared by the sulphation of mixtures of long chain alcohols and ether alcohols with vapourised SO_3 in a falling film reactor. The resulting acid is then neutralised with the appropriate base (e.g. NaOH, NH_3 aq., etc). To this base is then added a buffering material consisting mainly of sodium phosphates, to keep the pH of the solutions around neutral. The buffer's main use is to reduce the possibility of the hydrolysis of the surfactants, the effect of which is to render the materials unsaleable. However, despite this, hydrolysis of these materials has been encountered, particularly at high temperatures (e.g. during transportation as deck cargo, in drums, in the tropics), and hence Albright and Wilson were interested in finding means by which the reaction could be inhibited. One area of interest was the effect of multivalent cations (e.g. Fe^{3+}) which have been found to contaminate the materials.

The commercial materials are usually prepared in highly concentrated solutions (in order to reduce transportation costs) and hence industrially one would be concerned with the kinetics of the hydrolysis at these concentrations. However, at these high concentrations the materials are highly viscous and difficult to handle in small quantities and hence the practical work for this project was limited to lower concentrations. It is hoped that the results at lower

surfactant concentrations can give us an indication of the effects of the variables on the reaction at higher concentrations.

The materials used throughout the study of the reaction kinetics were pure, single chain-length surfactants, with inorganic and organic impurities (from the preparation) removed, and it is presumed that any results obtained can be used to predict effects upon the commercial materials which contain a range of chain lengths for the surfactant, plus some unreacted alcohol and inorganic salts.

As well as the industrial interest in the reaction studied, there is also academic interest from the viewpoint of the general effects of micelles on the kinetics of organic reactions. Usually the surfactant which forms the catalytic micelles does not itself take part in the reaction, but for the hydrolysis of dodecyl-sulphates it is the reacting substrate itself which forms the micelles.

The subject of micellar catalysis of organic and inorganic reactions has rapidly expanded in recent years and a number of theoretical models have been proposed. These are briefly outlined in Chapter 3 and refer mainly to dilute solutions. The model to be used in rationalising the experimental results for the reaction studied here is an ion-exchange/pseudo-phase model of micelles. In this model the micelles are regarded as forming a phase separate from the aqueous bulk and ions present in the system are assumed to compete for binding to the Stern layer of the micelles in an ion-exchange equilibrium.

The reaction studied involves an organic substrate, RSO_4^-, and a small hydrophilic ion, H^+, and it is assumed that the reaction in the micellar phase takes place solely in the Stern layer. Thus only factors which affect the composition of the Stern layer should affect the micellar catalysis of the hydrolysis. One of the main assumptions of this model is that the micellar shape should not have

any effect on the catalysis as it does not affect the Stern layer in any way. This arises from the observations that parameters such as ion-binding constants are not dependent to any significant extent upon the micellar shape.

Thus using assumptions about the physical parameters of the Stern layer and the micelles (e.g. volume, degree of ion binding, CMC, etc), but excluding any effects of micellar shape, one can predict the effect of the composition of the system upon the reaction kinetics for comparison with experimental results. We have therefore included, in Chapter 2, a brief survey of these parameters for the surfactants used. For a more extensive survey of these factors see references: Fisher and Oakenfull (1977), Elworthy et al (1968) and Romsted (1975).

Chapter 4 is a brief survey of the general effects of micelles on acid catalysed organic reactions, in particular, for comparison with the results obtained for the acid catalysed hydrolysis of the dodecyl sulphate surfactants. For a more extensive review of these reactions see references; Bunton (1973a, 1977), Cordes (1973, 1978) and Fendler and Fendler (1975).

The experimental results described in Chapter 6 cover a wide range of surfactant concentrations from just above the CMC, almost to the boundary of the liquid crystalline M phase (> 1M). Furthermore we have been interested in the effects of the acid concentration, added electrolytes and added alcohols upon the kinetics at various surfactant concentrations.

CHAPTER TWO

MICELLES

2.1   INTRODUCTION

The term micelle was first introduced by McBain (1913) and refms to the stable, dynamic aggregates formed by long chain surfactant molecules. A surfactant molecule contains both hydrophobic and hydrophilic portions and it is the interactions of these with water and with each other that provide the driving force for aggregation.

The hydrophobic portion of the surfactant is usually a hydrocarbon chain of 8-18 carbon atoms, which may include double bonds, chain branching or phenyl groups.

The hydrophilic portion may be non-ionic, anionic, cationic or zwitterionic.

Examples of surfactants:

$CH_3(CH_2)_{11}OSO_3Na$ sodium dodecyl sulphate, (SDS), (anionic)

$CH_3(CH_2)_{15}N(CH_3)_3Br$ hexadecyltrimethylammonium bromide (cationic)

$CH_3(CH_2)_{11}(OCH_2CH_2)_6OH$ hexaoxyethylenedodecanol (non-ionic)

In very dilute aqueous solution the surfactants exist as monomers, though there is some contradictory evidence for pre-micellar aggregation, and ionic surfactants behave as simple electrolytes. Above a concentration (CMC), the monomers are found to group together to form roughly spherical micelles; the aggregation number is found to be greatly dependent on a number of factors including surfactant concentration, temperature, concentration and type of added salt.

The driving force behind the aggregation is the hydrophobic repulsion of the hydrocarbon chains for the aqueous environment causing the carbon chains to group together in the core of a micelle, separated from the bulk water by the polar head groups, which make up the region called the Stern layer. In the case of ionic micelles this region also contains a fraction of the counterions in order to reduce the surface charge on the micelles. The remaining counterions are

distributed around the micelles in a Gouy-Chapman diffuse double layer.

The picture of a spherical micelle is a very simplistic one and only holds at concentrations near the CMC. At higher concentrations the micelles are better described as ellipsoids and, on increasing the surfactant concentration further or on adding electrolytes, the micelles grow into long rod-shaped aggregates, until at high concentrations liquid crystalline phases are formed, which can have any of a wide range of structures.

2.2   CRITICAL MICELLE CONCENTRATION (CMC)

One of the more fundamental, and probably most studied features of micelle formation is the CMC. The CMC is usually defined as the concentration above which micelles are formed, though they are more likely to form over a concentration region rather than at a specific concentration. The value of the CMC can be obtained from the concentration dependance of a number of physical properties, including: surface tension, conductance, emf, light scattering, solubilisation and viscosity, the CMC usually occurring at the intersection of two straight lines. The CMC is found to be dependent on a large number of parameters. The following is a brief review of some of the work done on the CMC with particular reference to the surfactants used in the kinetic studies described later (dodecyl sulphates and dodecyl ether sulphates).

2.2.1   Surfactant chain length

The relationship between the CMC of a homologous series of surfactants and the number of carbon atoms in the hydrocarbon chains was first shown by Klevens (1948).

$$\log (CMC) = A - B n$$

where A and B are constants and n is the number of carbon atoms.

Table 2.1 shows the change in CMC with number of carbon atoms for a series of alkyl sulphates.

Using theoretical treatments the change of CMC with chain length can be related to the hydrophobic and electrostatic interactions of the surfactants. The decrease in CMC with increasing chain length has been attributed to the increased hydrophobic bonding interaction of the carbon chains in the micelle (Shinoda 1953, Phillips 1955).

2.2.2 Ethoxylation of the carbon chain

The introduction of ethoxy groups ($-OCH_2CH_2-$) between the carbon chains and polar head groups of a surfactant might be expected to be somewhat analogous to increasing the chain length. However, Weil et al (1958) and Barry and Wilson (1978) showed that other factors are present, as the decrease in CMC is not as great as that for simple inclusion of methylene groups, and for inclusion of more than 4 ethoxy groups Weil et al (1958) found that the CMC began to increase again.

The discrepancies are due to the polar nature of the ethoxy groups causing an increase in the electrostatic repulsions of the head groups which destabilises the micelle, and hence increases the CMC.

Table 2.2 shows the change in CMC with the number of ethoxy groups for alkyl ethoxy sulphates.

2.2.3 Temperature

For non-ionic surfactants the CMC is found to decrease with temperature, while for ionic surfactants the CMC is found to pass through a minimum as the temperature is increased. This minimum is thought to be due to opposing temperature dependencies of the electrostatic and hydrophobic interactions of the surfactant molecules (Tanford 1973).

Table 2.1

THE EFFECT OF SURFACTANT CHAIN LENGTH ON THE CMC OF A SERIES OF SODIUM ALKYL SULPHATES (Mukerjee & Mysels 1971)

Surfactant chain	CMC (mol l^{-1})
Octyl	0.133
Decyl	0.033
Dodecyl	0.0081
Tetradecyl	0.0021
Hexadecyl	0.0004

Temperature = 25°C

Table 2.2

THE EFFECT OF ETHOXYLATION ON THE CMC OF
a) SODIUM DODECYL SULPHATE (Barry & Wilson 1978)
b) SODIUM HEXADECYL SULPHATE (Weil et al 1958)

N^o ethoxy groups	CMC $(mol\,l^{-1})^a$	CMC $(mol\,l^{-1})^b$
0	0.0081	0.0004
1	0.0045	0.00021
2	0.0028	0.00012
3		0.00007
4		0.00008

Temperature = $25°C$

The temperature dependence of the CMC for alkyl sulphates and alkyl ethoxy sulphates has been determined by Goddard and Benson (1957), Flockhart (1961) and Barry and Wilson (1978).

2.2.4 Electrolytes

The addition of electrolytes to surfactant solutions is always found to reduce the CMC due to a screening of the electrostatic repulsions of the head groups, and hence a stabilising of the micelles. The extent of the reduction in CMC is dependent on the valency, size and nature of the counterion present in the added electrolyte (i.e. the ion of opposite charge to the micelle forming moiety).

Goddard et al (1953) found that for alkyl sulphates the CMC decrease was more pronounced the smaller the size of the hydrated alkali metal ion:

$$Cs > K > Na > Li$$
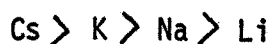
Thus the smaller the hydrated radius of the ion, the closer it can approach the micelle and the more efficient the screening of the head group charges, hence the lower the CMC.

Corrin and Harkins (1947) showed that there is a linear relation between the logarithm of the CMC and the electrolyte concentration:

$$\log (CMC) = k.\log (\text{concn. electrolyte}) + Q$$

Goddard et al (1953) found that organic ions do not behave in the same way as inorganic cations in that the larger ions produce a greater decrease in the CMC. This is due to the hydrophobic interactions which may occur between the organic cation and the micelle core leading to enhanced micelle stability and lower CMC. Thus the more hydrophobic the ion (i.e. the larger the ion), the lower the CMC.

Both Corkill and Goodman (1962) and Oko and Venable (1971) found that divalent cations reduce the CMC of sodium dodecyl sulphate (SDS) more than univalent cations, though unlike the effects for the

univalent ions the decrease is more or less independent of the size of the ions. The lower CMC on adding divalent ions is to be expected on the grounds of better screening of the head group repulsions by the larger charge of the ion. The independence of the decrease in CMC on the size of the divalent ions is more difficult to account for, but may be due to the formation of only an outer-outer sphere complex between the micelle and divalent ion whereas the monovalent ion forms an inner-inner sphere complex (Baumüller et al 1978).

2.2.5   Counterion

The effect of counterion type on the CMC has also been studied by looking at the change in CMC on changing the counterion of the surfactant, thus removing any effects due to competing ions.

The results are much the same as for the effects of added electrolytes. Mukerjee et al (1967) showed that the CMC of dodecyl sulphates was dependent on the size of the hydrated monovalent inorganic ions and on the hydrophobicity of organic ions (Table 2.3).

Hato and Shinoda (1973), Satake et al (1963) and Miyamoto (1960) showed that for divalent metal dodecyl sulphates the CMC is almost independent of the metal ion (Table 2.4).

2.3   MODEL OF MICELLE STRUCTURE

2.3.1   Introduction

The simple model of micelles, as put forward by Stigter (1964) is of a spherical aggregate of surfactant molecules. The micelle is comprised of three regions.

(a)   Hydrocarbon-like core

(b)   Stern layer

(c)   Gouy-Chapman diffuse double layer

The core of the micelle is liquid hydrocarbon-like in nature and has a radius approximately equal to the length of the

Table 2.3

THE EFFECT OF UNIVALENT COUNTERION ON THE CMC AND THE DEGREE OF DISSOCIATION(α) OF DODECYL SULPHATES (Mukerjee et al 1967)

Counterion	CMC(mol l^{-1})	α
Li	0.00877	0.30
Na	0.0081	0.28
K	0.0070	
Cs	0.00594	0.24
Me$_4$N	0.00541	0.26
Et$_4$N	0.00364	0.24
Pr$_4$N	0.00219	0.21

Temperature = 25°C

Table 2,4

THE EFFECT OF DIVALENT COUNTERION ON THE CMC OF DODECYL SULPHATES (Miyamoto 1960)

Counterion	CMC $(mol\ l^{-1})$
Co	0,0010
Mg	0,0010
Zn	0,0011
Mn	0,0012
Cu	0,0012
Ca	0,0013 [a]

Temperature = 40°C (a = 54°C)

carbon chain (extended) of the surfactant. The Stern layer consists of regularly spaced head groups and a fraction $(1-\alpha)$ of the available counterions, which reduce the charge on the micelle and screen the ionic head groups from one another. The size of the micelle is restricted by how efficient this screening of the head group charges is. The counterions and head groups both retain their hydration shells on micellization (Gustavsson and Lindman 1978, Mukerjee 1964) and the thickness of the Stern layer is found to be approximately equal to the diameter of the hydrated head group. The micelle, therefore, has a net charge αne (n = aggregation number) which is neutralised by the remaining counterions distributed about in a diffuse Gouy-Chapman electric double layer which surrounds the Stern layer.

Although this is a useful model for the micelle, particularly close to the CMC, it has a number of drawbacks. Tanford (1972), using geometric considerations, showed that the shape of the micelle at low surfactant concentrations is better described as an ellipsoid. The distinct separation of the three layers is contradicted by the large amount of evidence for a rough surface of the micelle (Stigter and Mysels 1955) and for penetration of water into the hydrocarbon core, at least to the depth of the first few methylene groups of the surfactant chain (Aniansson 1978b).

2.3.2   Size and shape of the micelle

The size and shape of micelles is found to depend on a number of parameters, though the more important ones are temperature, surfactant concentration and electrolyte concentration.

2.3.2.1   Surfactant concentration

As the concentration of surfactant is increased above the CMC, there is a region of reasonably constant micelle size and shape until one arrives at a point where one observes another change in the concentration dependence of properties used to find the CMC.

This concentration has been termed the second CMC and is a result of a change in the shape of the micelles to long rod-like structures (Kubota et al 1972, 1973). The value for the 2nd CMC of SDS, as measured by conductivity and light scattering, is 0.07M at 25°C.

In the absence of added electrolytes and non-electrolytes these rod shaped micelles will elongate as the surfactant concentration is increased further (and hence the aggregation number increases) until one observes a phase change in the system, corresponding to the formation of liquid-crystal type structures of the surfactant molecules (Skoulies 1967). Initially these consist of hexagonally packed rod-like entities, but at higher concentrations a wide range of structures can occur. In the case of SDS this phase change occurs at around 40% by weight of surfactant.

2.3.2.2   Temperature

Mazer and al. (1976, 1977) showed, using quasi-elastic light scattering techniques, that increasing the temperature resulted in a decrease in the aggregation number for SDS micelles over a range of surfactant and electrolyte concentrations. In particular they concluded that at temperatures above 60°C, the aggregation number is almost independant of the surfactant and electrolyte concentrations, and very nearly corresponds to the ideal value for a spherical micelle (n = 60).

2.3.2.3   Electrolyte concentration

The effect of NaCl on the shape and aggregation number of SDS micelles as measured using light scattering techniques, has been well documented; however, all studies have been restricted to below 0.1M SDS.

Phillips and Mysels (1955) and Emerson and Holtzer (1967) showed that the aggregation number of SDS micelles increased fairly gradually as the concentration of NaCl increased to 0.4M.

The most thorough studies are those of Mazer et al (1976, 1977) and of Turro and Yekta (1978) who looked at both the electrolyte and temperature effects in conjunction. As in other studies, they found that the aggregation number increases with the electrolyte concentration; for concentrations of NaCl above 0.5M they observed a rapid increase in the aggregation number. This rapid increase, such that at 25°C. the micelles may comprise of upward of 500 monomers, corresponds to the formation of rod-like micelles.

Fig. 2.1 shows the results of Mazer et al (1976, 1977) for the effects of both temperature and NaCl concentration on the aggregation number of SDS micelles. As noted before the most important inference from this study is that at high temperatures there is little change in the aggregation number with electrolyte concentration.

2.3.2.4 Counterion

Mysels and Princen (1959) looked at the effect of changing the counterion of dodecyl sulphate surfactant on the aggregation number using light scattering. Though the results are very limited (i.e. restricted to Na, Li, and $(CH_3)_4N$ cations) they found very little dependence of the aggregation number on the counterion used.

Satake et al (1963) obtained the aggregation numbers of divalent metal dodecyl sulphates (Cu, Ni, Mg, Co) using light scattering. Again there was not a great deal of variation, though in comparison with monovalent dodecyl sulphates the micelles seem to contain 20-30 more monomers. This will be a result of the better screening of the head group repulsions by the divalent ions allowing larger micelles to be more stable.
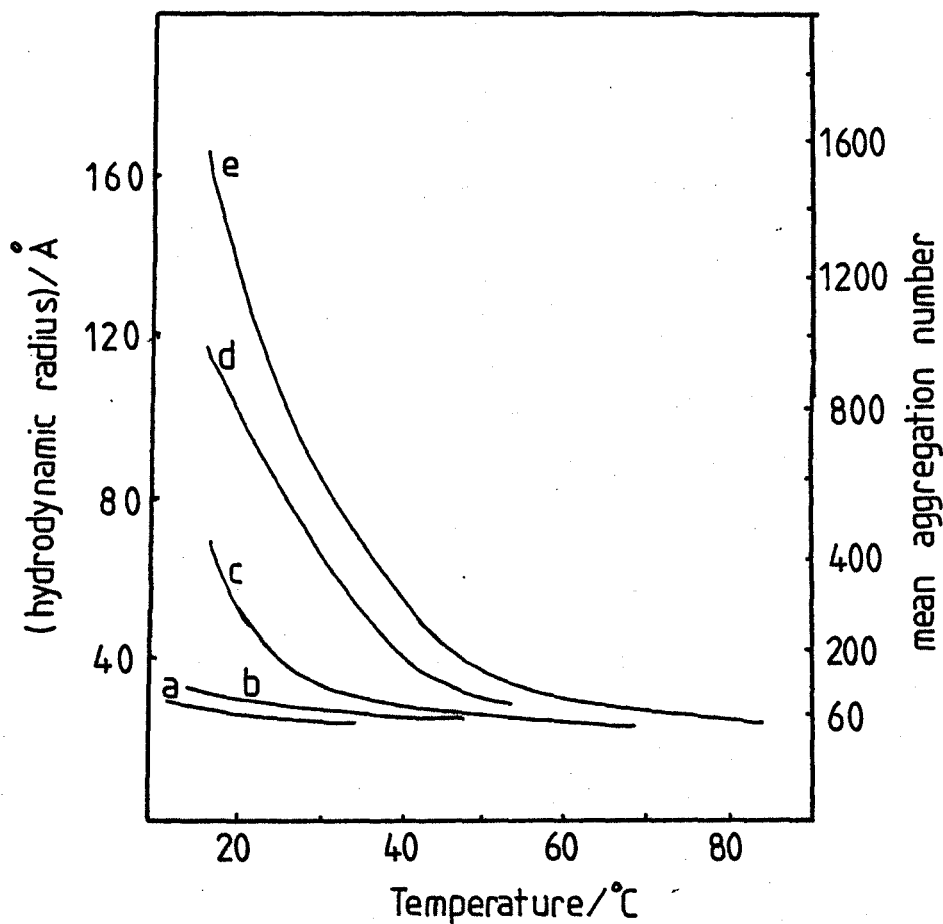
Fig. 2.1   The effect of temperature and NaCl concentration on

the size of SDS micelles at 0.069M surfactant and

a) 0.15M;   b) 0.3M;   c) 0.45M;   d) 0.55M; and e) 0.6M

NaCl concentrations.   (Mazer et al 1976, 1977).

2.3.2.5   Ethoxylation of the carbon chain

Tokiwa and Ohki (1967) used hydrodynamic data (sedimentation, viscosity, diffusion and density) to obtain the aggregation numbers of ethoxylated dodecyl sulphates. They found that increasing the number of ethoxy groups in the surfactant resulted in a decrease in the aggregation number due to increased electrostatic repulsions of the head groups, which is a result of the polar nature of the ethoxy group. However, they found the effect to be of significance only for surfactants with more than three ethoxy groups.

2.3.3   Counterion Binding

From the point of view of micellar catalysis, one of the most important features of micelles (along with their ability to solubilize organic molecules) is their ability to bind small hydrophilic ions which take part in the reaction that the micelle is catalysing (e.g. H^+, OH^-, CN^-, Ni^{2+}). In particular for the acid catalysed hydrolysis of dodecyl sulphates discussed later, where the organic substrate is also the micelle forming moiety, the binding of the H^+ ions to the micelles and any changes in that binding will be the factor which most affects the kinetics of the reaction.

The concept that micelles bind a certain fraction $(1-\alpha)$ of the available counterions initially arose from the conductance data of McBain (1913), who found that the equivalent conductance of a surfactant decreases above the CMC, whereas for fully ionised micelles it should increase.

Thus a fraction $(1-\alpha)$ of the counterions are regarded as being bound to the Stern layer of the micelles, while the remaining fraction (α) are considered as remaining free in the bulk aqueous solution (in view of this, α is often referred to as the degree of dissociation of the micelle). The bound ions are considered to be fully hydrated and to move as a kinetic unit with the micelle.

For some head groups (e.g. carboxylate), hydrogen bonding of the water in the hydration shell of ions to the head groups may be important for micelle stability (Gustavsson and Lindman 1975, Oakes 1973, Robb and Smith 1974).

The binding of counterions to micelles can be studied using a variety of experimental techniques, including nmr and esr spectra of the ions (Robb and Smith 1974, Robb 1971, Ueki and Uzu 1980), the mobility of the ion from tracer electrophoresis (Mysels and Dulin 1955), light scattering (Mukerjee et al 1967), emf measurements using ion-selective electrodes (Larsen and Magid 1974, Bunton et al 1977, Newberry 1980), as well as conductance. However, due to the various assumptions involved in the different methods, the value of α is found to vary from technique to technique.

2.3.4   The value of α

Romsted (1974) made an exhaustive survey of the variation of α with a number of factors, including method of determination, chain length, temperature, surfactant concentration, counterion, as well as electrolyte and non-electrolyte concentration. He came to the conclusion that α can be regarded as being independent of both surfactant and electrolyte concentration so long as the other factors remain constant. This leads to the concept that, since there is a virtually constant value of $(1-\alpha)$ (which is less than one), the Stern layer is regarded as being 'saturated' with respect to the counterion. In recent years this idea has become the accepted starting point, with some reservations, for the analysis of the effects of micelles on the kinetics of reactions involving small hydrophilic ions. The main point in its favour is that even where α has been found to vary with either surfactant or electrolyte concentration, the variation is small enough not to affect the kinetic analysis.

Trends in the value of α depending on a number of factors can be shown, though absolute values must not be taken too seriously, since the different techniques give somewhat different values.

2.3.4.1   Temperature

In all cases reported the value of α is found to increase as the temperature is increased. This is consistent with the negative free energy, enthalpy and entropy of the binding of ions to micelles (Larsen and Magid 1974). The results also indicate that in most cases ion-binding is controlled by the electrostatic interactions between the counterion and micelle, and by these alone.

Table 2.5 shows the variation of α with temperature for SDS and sodium diethoxy dodecyl sulphate (SDE_2S).

2.3.4.2.   Surfactant chain length

The value of α is found to decrease (i.e. an increase in the degree of ion binding) with the chain length of the surfactant (Satake et al 1969). This occurs because the volume of the micelle will increase faster than its surface area as more methylene groups are included in the carbon chain. This causes an increase in the surface-charge density due to the closer proximity of neighbouring head groups, so that a greater fraction of the counterions is needed to screen the electrostatic repulsions of the head groups.

2.3.4.3   Ethoxylation of the carbon chain

Barry and Wilson (1978) found that the inclusion of ethoxy groups in a surfactant decreases the degree of counter-ion binding (i.e. an increase in α), attributing the effect to three possible factors:

    (i)   Steric hindrance of close contact of adjacent head groups leading to a greater surface area per head group and a reduction in surface charge density.

Table 2.5

THE EFFECT OF TEMPERATURE ON THE VALUE OF α FOR SODIUM DODECYL AND DIETHOXY-DODECYL SULPHATES (Barry & Wilson 1978)

Temperature(°C)	α^a	α^b
25	0.21	0.36
30	0.23	0.36
35	0.25	0.37
40	0.29	0.38
45	0.33	0.39
50	0.38	0.40

a) sodium dodecyl sulphate (SDS)

b) sodium diethoxy-dodecyl sulphate (SDE$_2$S)

(ii)   An increase in the local dielectric constant.

(iii)   A change in micellar shape.

Table 2.6 shows the effect for a series of surfactants based on SDS.

2.3.4.4   Counterion

As for the effect of counterion on the CMC, the value of α is found to depend on the size of the hydrated counterion for hydrophilic ions and upon the hydrophobicity of the ion for organic counterions (Mukerjee et al 1967, Frahm and Diekman 1980).

Table 2.3 shows the dependence of α on the counterion for dodecyl sulphate surfactants.

The principle of counterion binding to micelles and the observation that different ions bind to different degrees is very important in micellar catalysis involving reactions with hydrophilic ions. As for most reactions in micellar systems two counterions will be present (reactive ion plus surfactant counterion), it is expected that they will compete for binding to the micelle, particularly since differences in counterion binding are not very large. This idea has led to the concept of ion-exchange in micellar systems as a basis for the understanding of micellar catalysis. This subject will be discussed in greater detail in the theoretical chapter on micellar catalysis.

2.4   SOLUBILISATION

Solubilisation refers to the process by which the solubility of a normally insoluble or only slightly soluble organic substrate in water is enhanced by the addition of a surfactant. The surfactant is found to have little effect on the solubility below its CMC, but above the CMC solubility increases in direct proportion to the surfactant concentration. Solubilisation is therefore a result of the attraction for, and binding of the substrate to the micellar pseudo-phase.

Table 2.6

THE EFFECT OF ETHOXYLATION ON THE VALUE OF α FOR SODIUM DODECYL SULPHATES (Barry & Wilson 1978)

Surfactant	α^a	α^b
$C_{12}SO_4Na$	0.21	0.33
$C_{12}E_1SO_4Na$	0.29	0.37
$C_{12}E_2SO_4Na$	0.36	0.39

a) Temperature = 25°C

b) Temperature = 45°C

In general the extent of solubilisation is dependent on the nature of the surfactant and the substrate (solubilisate), temperature, counterion and the addition of electrolytes. On a simple level, solubilisation is greater for more hydrophobic surfactants and substrates (Lindman and Wennerstrom 1980).

The micellar property of solubilisation is of great importance for the ability of micelles to enhance the rate of chemical reactions. According to the pseudo-phase model of micellar catalysis (see Chapter 3) the solubilising of substrates brings them together, in close proximity, in the small volume of the micellar phase, thus causing an increase in their relative concentrations and hence in the rate of the reaction.

The extent of solubilisation of a particular substrate by a particular surfactant can be measured in a number of ways, for example by direct solubility measurements (Bunton and Robinson 1969), by using Absorption spectra (Rehfield 1970, 1971), and NMR (Winsor 1968).

2.5   KINETICS OF MICELLE FORMATION

Although one can measure a large number of physical properties of micelles (size, aggregation number, CMC, counterion binding etc.), one must not forget that they are dynamic and not static species. That is to say, micelles are continually dissociating and re-forming at measurable rates.

Aniansson and Wall (1974, 1975) and co-workers (Aniansson 1978a, Aniansson et al 1976) have made a thorough theoretical analysis of the kinetics of micelle formation, which is found to agree very well with experimental observations.

The dynamic behaviour is determined by the equilibrium between the monomers and the micellar aggregate:

$$A_1 + A_{s-1} \underset{k_s^-}{\overset{k_s^+}{\rightleftharpoons}} A_s$$
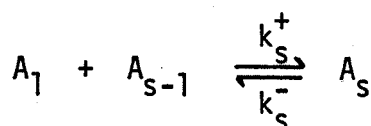
This process is co-operative and there is found to be a pronounced minimum in the size distribution curve for small micelles.

The kinetics of micelle formation are usually studied using relaxation methods, e.g. ultrasonic relaxation (Yasunaga et al 1969), stopped flow (Lang et al 1972), P-jump (Herman and Kahlweit 1973), T-jump (Takeda and Yasunaga 1973).

According to the theoretical approach, when the micelle-monomer equilibrium is subjected to a shock, the resultant relaxation back to the original position should involve a two-step process:

(a) A fast relaxation to a quasi-equilibrium where the total number of micelles remains constant.

(b) A slower process involving relaxation to the true equilibrium position coupled with a change in the total number of micelles.

This prediction is borne out by the experimental results and the relaxation times obtained can be used to find not only the rate constants for micelle formation and dissociation, but also the distribution of micelle sizes, which is found to become narrower as the chain length of the surfactant increases (Aniansson et al 1976).

The relaxation time for the fast process is found to be of the order of 10^{-6}s, whereas for the slower process it is of the order of 10^{-2}s. This slower process, which also gives an idea of the life-time of an aggregate, has been found to be strongly dependent upon the temperature and electrolyte concentration (Aniansson et al 1976), but independent of the counterion (Adair et al 1976).

CHAPTER THREE

MODELS FOR MICELLAR CATALYSIS

3.1   INTRODUCTION

Over the last twenty years or so a great deal of work has been done on the catalysis and inhibition of organic reactions by micelles. The impetus for many of the studies was a desire to obtain a simple model for enzyme catalysed reactions (Fendler and Fendler 1975) although it is now generally accepted that micelles are not very good models of enzymes.

In order to account for the deviations from enzyme-like kinetics new models have been introduced, generally based on the pseudo-phase model of micellar systems. This pseudo-phase model takes into account the possibility of rate enhancement of second and higher order reactions due to a concentrating of the reactants into the small volume of the micellar phase (Berezin et al 1973). This approach was found to work very well for reactions involving two or more organic substrates, but not for reactions between small hydrophilic ions and organic substrates. To account for the micellar effects on these types of reaction, recent studies have used the concept of ion-exchange of counterions in the micelle Stern layer in conjunction with the pseudo-phase model (Romsted 1976, Quina and Chaimovich 1979, Funasaki 1979).

3.2   GENERAL FEATURES OF MICELLAR CATALYSIS

The majority of micellar catalysed reactions studied fall into three categories;

1. Unimolecular reaction of an organic substrate

2. Bimolecular reaction between two organic substrates

3. Bimolecular reaction between an organic substrate and a small hydrophilic ion.

Recently a number of inorganic reactions have also been studied (e.g. Cho and Morawetz 1972).

The concentration profile for the rate of unimolecular reactions with respect to the surfactant concentration is such that one

observes a rapid rate enhancement as the surfactant concentration passes through the CMC, ending in a limiting value for the rate constant corresponding to complete binding of the substrate to the micelle. This observation is adequately predicted by the enzyme model of micellar catalysis.

Bimolecular reactions which are catalysed by micelles are again seen to be subject to rapid rate enhancement as the surfactant concentration passes through the CMC, however they do not show a rate plateau but a rate maximum, whereupon the reaction is found to be slowed down by further increases in the surfactant concentration.

As well as catalysis by micelles, one can also observe inhibition by them. This is generally the case for reactions involving substrates that are not solubilised by the micelles or those reactions involving ions of the same charge as the micelle forming species.

Electrolytes are found almost exclusively to inhibit any catalysis by micelles (Bunton 1973a,b), although there are some exceptions (Bunton et al 1971).

3.3   KINETIC MODELS FOR MICELLAR CATALYSIS

3.3.1   Enzyme model

This was the first and most widely used model for the catalysis of reactions by micelles (Menger and Portnoy 1967, Bunton and Robinson 1969). It assumes the formation of a complex between the organic substrate (S) and a micelle (D_n)

$$D_n + S \underset{}{\overset{K_s}{\rightleftharpoons}} D_nS \qquad 3.1$$
$$k_w[B] \bigg\downarrow \qquad \qquad \bigg\downarrow k_m[B]$$
$$PRODUCTS$$
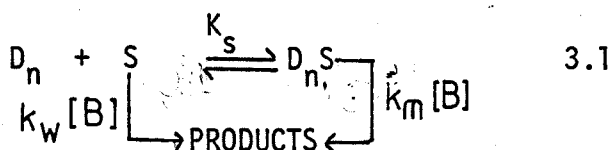
in which the substrate undergoes faster reaction.

This model also involves a number of other assumtions:

(a) A constant aggregation number (n).

(b) The micelle D_n only binds a single substrate molecule.

(c) The monomer concentration (of surfactant) remains constant above the CMC.

(d) k_w and k_m are the rate constants in the aqueous and micellar phases respectively.

(e) For bimolecular reaction, the second substrate B, is regarded as being in the aqueous phase, i.e. not bound to the micelle, and in great excess over S.

(f) The concentration of micelles is given by:

$$[D_n] = \frac{D_t - CMC}{n}$$

where D_t is the total concentration of surfactant and n the aggr. no. of the micelles.

The first order rate constant k_ψ observed for unimolecular and pseudo-first order bimolecular reaction is then given by:

$$k_\psi = \frac{k_w + k_m K_s[D_n]}{1 + K_s[D_n]} \qquad 3.2$$

where

$$K_s = \frac{[SD_n]}{[S][D_n]} \qquad 3.3$$

This predicts that for a surfactant concentration below the CMC, $k_\psi = k_w$, and for the limit of high concentration of micelles, $k_\psi = k_m$, and hence one should observe a limiting value of the observed rate constant as the surfactant concentration is increased corresponding to complete binding of the substrate. As stated before this prediction is borne out in the catalysis of unimolecular reactions (Fendler and Fendler 1975, Bunton 1973b, Cordes and Dunlap 1969), but not in the catalysis of bimolecular reactions, where one observes a rate maximum.

Bunton (1973a) included an empirical factor in equation 3.2 to account for this rate maximum, (equation 3.4).

$$k_\psi = \frac{k_w + k_m K_s [D_n]}{1 + K_s [D_n] + a[D_n]^2} \qquad 3.4$$

This inability of enzyme model to correctly predict the effects of micelles on bimolecular reactions led to the development of other kinetic models based mainly on the pseudo-phase concept of micelles.

3.3.2 Pseudo-phase model

Berezin and co-workers were the first to use the pseudo-phase model of micellar systems to account for their effects on reaction kinetics (Yatsimirskii et al 1970, 1971, Martinek et al 1973, Berezin et al 1973). This model correctly predicts the rate maxima observed for bimolecular reactions, but is restricted to reactions involving polar hydrophobic substrates and cannot be used for reactions involving small hydrophilic ions.

The pseudo-phase model treats the surfactant solution, above the CMC, as a two phase system in which the reacting substrates may be partitioned between the aqueous and micellar phases, according to a simple distribution law, e.g. for reactant A,

$$\frac{A_m}{A_w} = P_A \qquad 3.5$$

where subscript w refers to the aqueous phase and subscript m refers to the micelle phase. An analogous relation applies to reactant B.

Then the total concentrations of reactants (A_T, B_T) and the reaction velocity (υ) can be averaged over the total volume of the system.

$$A_T = A_m CV + A_w (1-CV) \qquad 3.6$$

$$\upsilon = \upsilon_m CV + \upsilon_w (1-CV) = k_{obs} A_T B_T \qquad 3.7$$

$$= k_m A_m B_m CV + k_w A_w B_w (1-CV) \qquad 3.8$$

where subscript T refers to total concentrations;

$C = C_T - CMC$ is the concentration of micellised surfactant;

A_m, B_m are the concentration of reactants in the micelle phase;

A_w, B_w are the concentration of reactants in the aqueous phase;

k_m, k_w are the second order rate constants in the micellar and aqueous phases respectively;

V = molar volume of the surfactant in micelles;

CV = volume fraction of the micellar phase;

Thus we can see that this treatment allows for the binding of both the substrates to the micelles, and for more than one substrate molecule per micelle. Using equations 3.5 to 3.8 one can derive an expression for the second order rate constant obtained by experiment (k_{obs}) in terms of the binding constants of the reactants and the surfactant concentration:

$$k_{obs} = \frac{k_m P_A P_B CV + k_w(1-CV)}{(1+K_A C)\ (1+K_B C)} \qquad 3.9$$

where $K_A = V(P_A-1)$;

$\qquad K_B = V(P_B-1)$;

(for a detailed derivation of equation 3.9 see appendix 3.1).

This scheme is most often used for dilute surfactant solution (i.e. $1-CV \simeq 1$) and for reactions involving substrates which are bound strongly to the micelles (P_A, $P_B \gg 1$) so that;-

$$k_{obs} = \frac{\bar{k}_m K_A K_B C + k_w}{(1+K_A C)\ (1+K_B C)} \qquad 3.10$$

where $\bar{k}_m = k_{m/V}$;

The most important aspect of equation 3.10 is that it predicts a maximum value for the rate constant of a bimolecular

reaction as the surfactant concentration is increased. This maximum is due to the fact that as the surfactant concentration is increased it binds more of the substrates, thus increasing their relative concentrations due to the small volume of the micelle phase, but at higher concentrations of surfactant the increased volume of the micelle phase will tend to dilute the reactants, and hence reduce the rate. Another important factor brought out by this approach is that one does not need a change in the activation energy of the reaction on going from the aqueous to the micellar phase in order to observe catalysis (i.e. k_m need not be greater than k_w), as the effect can be predicted solely as a consequence of the concentrating effect of binding the substrates to the small volume of the micellar phase (i.e. the effect would be observed even for $k_m = k_w$).

Dougherty and Berg (1974) used the pseudo-phase model to analyse the effect of SDS on the acid catalysed hydrolysis of methyl orthobenzoate. However, they were unable to obtain a suitable method to predict the concentration of H^+ ions in the micelle Stern layer, since there was poor agreement between values obtained from surface potential data and pH measurements. They did however, estimate that k_w and k_m were of the same magnitude, indicating that it is the concentration effect that is of primary importance for reactions involving hydrophilic ions.

Shirahama (1975, 1976) tried to resolve this uncertainty in the extent of binding of ions to the micelles by introducing a partition coefficient for the distribution of the hydrophilic ions between the two phases, again applying the analysis to the acid catalysed hydrolysis of methyl orthobenzoate.

The expression he obtained is very similar to Berezin's;

$$k_{obs} = \frac{k_m \mathcal{P}_{es} K_A K_I + \mathcal{P}_w k_w}{\mathcal{P}_m K_A + \mathcal{P}_w} \qquad 3.11$$

where; $\mathcal{P}_{es}$ = volume fraction of the Stern layer.

$\mathcal{P}_w$ = volume fraction of the aqueous phase.

$\mathcal{P}_m$ = volume fraction of the micellar phase.

K_A = partition coefficient for the distribution of the organic substrate.

K_I = partition coefficient for the distribution of the reactive ion.

$$K_I = e^{-\left(\frac{e\psi}{kT}\right)} = I_S/I_w$$

The treatment uses the assumption that the partition coefficient for the reactive ion decreases as the surfactant concentration increases, so that the concentration of reactive ion in the Stern layer decreases, and, while it correctly accounts for the general shape of reaction rate against concentration of surfactant profiles it does have some drawbacks:

(a) It does not allow for ion exchange of counterions in the Stern layer.

(b) It assumes that the counterion concentration decreases across the Stern layer.

(c) It regards ion binding as a sensitive function of the ionic strength, in contradiction to the relative constancy of α values found experimentally (Romsted 1975).

3.3.3   Modification of the pseudo-phase model to include Ion-Exchange in the Stern layer

The concept of ion-exchange of counterions in micellar systems was first used as a means of gaining a better understanding of the micellar catalysis of reactions involving small hydrophilic ions by Romsted (1975) in his PhD dissertation. Subsequently, a

number of other workers have used this principle, with slightly differing notation and approximations (Quina and Chaimovich 1979, Chaimovich et al 1979, Funasaki 1979, Almgren and Rydholm 1979).

Romsted adapted the pseudo-phase model of Berezin, retaining the distribution of the organic substrate between the two phases, and developing expressions for the concentrations of counterions in the micellar and aqueous phases, both for the non-reactive counterion of the surfactant and the added reactive ion.

The main assumption of Romsted's model is that the Stern layer is 'saturated' with respect to the counterions, that is the total concentration of ions in the Stern layer remains constant, independent of the ionic strength. This assumption follows from the constancy of the α values. (α = the degree of ion dissociation from micelles) found experimentally, as a function of the ionic strength and the counterion used.

$$I_m + X_m = \beta S \qquad 3.12$$

I_m = concentration of reactive ion (I) in micelle phase.

X_m = concentration of non-reactive ion (X) in micelle phase.

β = fraction of micellar charge neutralised by ions bound to Stern layer (degree of ion binding, $\beta = 1-\alpha$).

S = molar density of the micelles = $1/\bar{v}$ = molar concentration of head groups in the micelle.

In reality, α and therefore β do vary slightly with the counterion used, so that one should take β as a function of the respective mole-fractions of the reactive and non-reactive ions (X_I and X_X) and their degrees of ion binding (β_I and β_X).

$$\beta = \beta_I X_I + \beta_X X_X \qquad 3.13$$

However, the approximation of using $\beta = \beta_X$ is valid as any differences between β_I and β_X are only very small and under most

kinetic conditions $x_X \gg x_I$.

The next step is to take into account the fact that the two ions will compete for binding to the micelle Stern layer, so that one can visualise an ion-exchange equilibrium:

$$I_m + X_w = X_m + I_w \qquad 3.14$$

$$K_{I/X} = \frac{I_w X_m}{I_m X_w} \qquad 3.15$$

Then, these three equations, plus the distribution coefficient and material balance of the organic substrate (equations 3.5 and 3.6) as well as the material balance equations for the two ions:

$$I_T = I_m CV + I_w(1-CV) \qquad 3.16$$

$$X_T = X_m CV + X_w(1-CV) \qquad 3.17$$

can be used to obtain a rate expression similar to that of Berezin et al (1973), again by summing the velocity of the reaction over the total volume of the system:

$$\mathcal{V} = k_{2,obs} A_T I_T = k_m A_m I_m CV + k_w A_w I_w(1-CV) \qquad 3.18$$

The expression obtained by Romsted for the observed second order rate constant is: (for a detailed derivation see appendix 3.2)

$$k_{2,obs} = \frac{\bar{k}_m K_A \beta S(C_T-CMC)}{(K_A(C_T-CMC) + 1)(I_T + X_T K_{I/X})} + \frac{k_w}{(K_A(C_T-CMC) + 1)} \qquad 3.19$$

where $\bar{k}_m = k_m/V$

the approximations used are:

(a) Strong binding of the organic substrate, $P_A \gg 1$.

(b) $I_T \gg I_m CV$, which is most valid at low surfactant concentration, or if the reactive ion does not bind strongly to the Stern layer.

Romsted showed that equation 3.19 can be used to correctly

predict the shapes of reaction-rate profiles for micellar catalysed reactions. He produced a large number of computer generated plots of relative rate constants $(k_{2,obs}/k_w)$ against either surfactant concentration or electrolyte concentration, and looked at the effects on these of changing all the possible variables of equation 3.19. In all cases the predicted results were borne out by experimental results in the literature as well as by a number of specifically designed experiments of Romsted's. The general shape of the rate constant against surfactant plot is given by Fig. 3.1.

Components of the rate equation.

3.3.3.1   Substrate binding constant K_A

The binding constant of the substrate reflects its hydrophobicity. Increasing this is found to produce a larger value for the maximum in the rate constant, which occurs at a lower concentration of the surfactant.

3.3.3.2   CMC of the surfactant

Decreasing the CMC of the surfactant is found to produce the maximum value in the rate constant at lower surfactant concentrations (because micelles form at lower concentrations), also the value of this maximum is found to increase, as the volume fraction of the micellar phase will be smaller at these lower surfactant concentrations and hence the relative concentrations of the reactants in the micellar phase will be greater.

3.3.3.3   Concentration of reactive and non-reactive ions: I_T, X_T

Equation 3.19 shows that the observed rate constants are inversely proportional to the concentrations of both the ions present. Thus, increasing the concentration of either is found to reduce the maximum value of $k_{2,obs}$ and flattens out the shape of the profile so that at high concentrations of one of the ions one will observe a
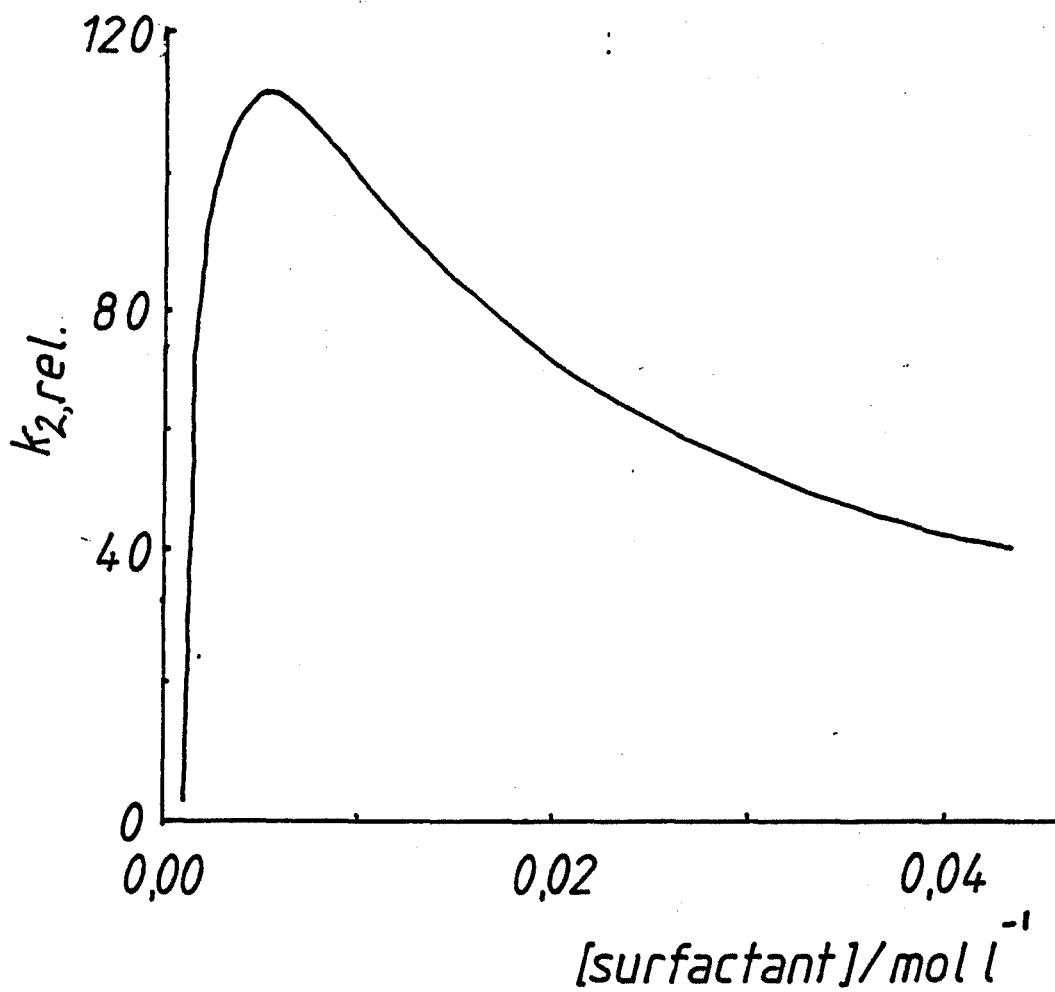
Fig. 3.1   The general shape of the relative rate constant $(k_{2,obs}/k_w)$ against surfactant concentration profile from the theory of Romsted.

plateau in the rate constant profile, and at very high ion concentration one may observe inhibition of the reaction.

3.3.3.4 Ion-exchange constant, $K_{I/X}$ (Electrolyte effects)

Due to the inverse dependence of $k_{2,obs}$ on $X_T K_{I/X}$ one would expect, as one observes in practice, that addition of the non-reactive counterion to the system will inhibit the micellar catalysis. Equation 3.19 can be used to quantify this inhibition by added electrolyte, which may include the common ion X or a second non-reactive ion Y. Romsted found that the reciprocal of $k_{2,obs}$ is a linear function of both the reactive and the non-reactive ion concentrations:

$$\frac{1}{k_{,2obs}} = \frac{I_T}{k_m \beta S} + \frac{K_{I/X} X_T}{k_m \beta S} \qquad 3.20$$

or, when a third counterion is present:

$$\frac{1}{k_{2,obs}} = \frac{(I_T + Y_T K_{I/Y})}{k_m \beta S} + \frac{K_{I/X} X_T}{k_m \beta S} \qquad 3.21$$

where, $K_{I/Y}$ is the ion exchange constant for the binding of ions I and Y to the micelle. Thus one can obtain relative values of ion-exchange constants of counterions for a given surfactant micelle, from the slopes and intercepts of plots of reciprocal rate constants against the concentrations of added electrolytes.

3.3.4 Other applications of the ion-exchange model to micellar kinetics

The model used by Romsted (1975) has also been considered by a few other workers. Quina and Chaimovich (1979) used the concept to examine not only the micellar effects on second order reactions involving small hydrophilic ions, but also:

(a) The extent of binding of the reactive ion to the micelle, both in the presence and absence of buffers.

(b) The change in the apparent pK of mildly acidic species caused by the presence of micelles.

(c) The micellar catalysis of a reaction involving the nucleophilic conjugate base of a weakly acidic species and a neutral organic substrate.

The expressions that they obtained were similar to Romsted's but more complex due to the lack of approximations and the differing notation.

$$k_{2,obs} = \frac{I_T[(k_m/V)(K_A K_{I/X})(X_m/X_w) + k_w]}{[1 + K_A(C_T-CMC)][1 + K_{I/X}X_m/X_w]} \qquad 3.22$$

where the subscripts are the same as for Romsted's equations above.

The important features to note from their results are that:

(a) The ratio of bound reactive ion concentration to the total reactive ion concentration approaches a limit as the surfactant concentration is increased and that this limit is reached sooner at lower total reactive ion concentration.

(b) The addition of electrolytes containing the surfactant counterion reduces the amount of bound reactive ion.

(c) The prediction for the variation of the observed rate constant with surfactant concentration is the same as that of Romsted.

Funasaki (1979) compared Romsted's ion-exchange model with an electro-static model of the binding of ions to the micelle. Under the conditions used he found the two models to be similar in their predictions for micellar catalysis, both in the absence and in the presence of added salts.

Bunton et al (1979) have slightly revised Romsted's approach to include the possibility of reaction occurring across the interfacial boundary between the Stern layer and the aqueous bulk.

This was to account for the non-appearance of a plateau in the rate profile for the reaction between 2,4-dinitrochlorobenzene and OH$^-$ in the presence of a quaternary ammonium hydroxide surfactant. A limit to the value of the rate constant is expected as the reactive ion is also the surfactant counterion and hence one will not get the dilution of the reactive ion in the Stern layer due to the increasing volume fraction of the micellar phase as the surfactant concentration is increased. The rate limit occurs when all the organic substrate is bound to the micelles, and this is indeed found for the acid hydrolysis of p-nitrobenzaldehyde acetals in the presence of tetradecane sulphonic acid surfactants (Bunton et al 1979). Thus the extra reaction pathway was included to account for the differences between the two reactions.

Appendix 3.1

Derivation of equation 3.9 of Berezin's pseudo-phase model of micellar catalysis.

(a) Partition of reactants (A,B) between the aqueous (w) and micellar (m) phases.

$$A_m/A_w = P_A \quad : \quad B_m/B_w = P_B \qquad 3.1.1$$

(b) Material balance equation for the reactant:

$$A_T = A_m CV + A_w(1-CV) \qquad 3.1.2$$

$$B_T = B_m CV + B_w(1-CV) \qquad 3.1.3$$

(c) Averaging of the reaction velocity (υ) over the two phases:

$$\upsilon = \upsilon_m CV + \upsilon_w(1-CV) \qquad 3.1.4$$

$$= k_m A_m B_m CV + k_w A_w B_w(1-CV) \qquad 3.1.5$$

$$k_{2,obs} A_T B_T = k_m A_m B_m CV + k_w A_w B_w(1-CV) \qquad 3.1.6$$

where, A_m, B_m are the concentration of reactants in the micellar phase.

A_w, B_w are the concentration of reactants in the aqueous phase.

P_A, P_B are the partition coefficients of the distribution of the reactants between the two phases.

$C = C_T - CMC$

CV, $(1-CV)$ are the volume fractions of the micellar and aqueous phase respectively.

$k_{2,obs}$, k_m, k_w are the observed rate constant, and the rate constants in the micellar and aqueous phases.

($k_{2,obs} = k_w$ when $C_T < CMC$)

From equation 3.1.1

$$A_m = A_w P_A \qquad 3.1.7$$

Substitute this in equation 3.1.2

$$A_T = A_w P_A CV + A_w (1-CV) \qquad\qquad 3.1.8$$

$$A_w = A_T / (P_A CV - CV + 1) \qquad\qquad 3.1.9$$

and using $K_A = (P_A - 1)V$ $\qquad\qquad$ 3.1.10

$$A_w = A_T / (1 + K_A C) \qquad\qquad 3.1.11$$

From equation 3.1.1

$$A_w = A_m / P_A \qquad\qquad 3.1.12$$

Substitute in equation 3.1.2

$$A_T = A_m CV + \frac{A_m}{P_A} (1-CV) \qquad\qquad 3.1.13$$

$$A_m = A_T P_A / (1 + K_A C) \qquad\qquad 3.1.14$$

Substituting 3.1.11 and 3.1.14 (and the analogous expression for B_m, B_w) into equation 3.1.6 we have:

$$k_{2obs} A_T B_T = \frac{k_m A_T B_T P_A P_B \ CV}{(1 + K_A C)(1 + K_B C)} + \frac{k_w A_T B_T (1-CV)}{(1 + K_A C)(1 + K_B C)} \qquad 3.1.15$$

$$k_{2obs} = \frac{k_m P_A P_B CV + k_w (1-CV)}{(1 + K_A C)(1 + K_B C)} \qquad\qquad 3.1.16$$

Appendix 3.2

Derivation of Romsted's expression for the observed second order rate constants in micellar catalysed reactions (equation 3.19).

(a) Partition of organic substrate between micellar and aqueous phases.

$$A_m/_{A_w} = P_A \qquad\qquad 3.2.1$$

$$A_T = A_m CV + A_w(1-CV) \qquad 3.2.2$$

then, as in appendix 3.1

$$A_m = \frac{A_T P_A}{1 + K_A C} \quad : \quad A_w = \frac{A_T}{1 + K_A C} \qquad 3.2.3$$

(b) Ion-exchange of reactive (I) and non-reactive (X) counterion in the Stern layer.

$$I_m + X_w \xrightleftharpoons{K_{I/X}} X_m + I_w \qquad 3.2.4$$
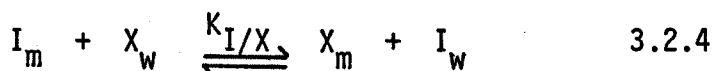
$$K_{I/X} = \frac{I_w X_m}{I_m X_m} \qquad 3.2.5$$

(c) Constant degree of ion-binding to Stern layer

$$I_m + X_m = \beta S \qquad 3.2.6$$

(d) Material balance equation for the counterion

$$I_T = I_m CV + I_w(1-CV) \qquad 3.2.7$$

$$X_T = X_m CV + X_w(1-CV) \qquad 3.2.8$$

Then, using as in appendix 3.1 the following expression for the reaction velocity:

$$k_{2obs} A_T I_T = k_m A_m I_m CV + k_w A_w I_w(1-CV) \qquad 3.2.9$$

From equation 3.2.7 we have:

$$I_w(1-CV) = I_T - I_mCV \qquad 3.2.10$$

at low concentration of surfactant the fraction of bound ion will be small so we can make the assumption:

$$I_T \gg I_mCV \qquad 3.2.11$$

so that: $I_T = I_w(1-CV)$ 3.2.12

Rearranging equation 3.2.5 gives:

$$X_w = \frac{I_w X_m}{I_m K_{I/X}} \qquad 3.2.13$$

Substitute this in equation 3.2.8

$$X_T = X_mCV + \frac{I_w X_m(1-CV)}{I_m K_{I/X}} \qquad 3.2.14$$

rearrange:

$$X_m = \frac{K_{I/X} I_m X_T}{K_{I/X} I_mCV + I_w(1-CV)} \qquad 3.2.15$$

using the assumption of equation 3.2.11 and substitute 3.2.12 into 3.2.15

$$X_m = \frac{K_{I/X} I_m X_T}{K_{I/X} I_mCV + I_T} \qquad 3.2.16$$

also from 3.2.11

$$I_T \gg K_{I/X}I_mCV \qquad 3.2.17$$

$$X_m = \frac{K_{I/X} I_m X_T}{I_T} \qquad 3.2.18$$

substituting this into equation 3.2.6

$$I_m + \frac{K_{I/X} I_m X_T}{I_T} = \beta S \qquad 3.2.19$$

rearrange $I_m = \dfrac{\beta S I_T}{I_T + K_{I/X} X_T}$ 3.2.20

Then substitute equation 3.2.3, 3.2.20 and 3.2.12 into equation 3.2.9

$$k_{2obs}\ I_T A_T = k_m\ \frac{A_T P_A}{(1 + K_A C)}\ \frac{\beta\,SI_T\,CV}{(I_T + K_{I/X}X_T)} + \frac{k_w A_T I_T}{(1 + K_A C)}$$

$$k_{2obs} = \frac{k_m P_A\,\beta\,SCV}{(1 + K_A C)\,(I_T + K_{I/X}\,X_T)} + \frac{k_w}{(1 + K_A C)}$$

then using $\quad K_A = V(P_A - 1)$

and the assumption of strong binding of substrate to the micelle

$$P_A \gg 1$$

$$k_{2obs} = \frac{k_m\,K_A\,\beta\,S\,(C_T - CMC)}{[1 + K_A(C_T - CMC)]\,[I_T + K_{I/X}X_T]} + \frac{k_w}{[1 + K_A(C_T - CMC)]}$$

CHAPTER FOUR

FEATURES OF MICELLAR CATALYSIS

4.1 INTRODUCTION

Surfactants have been widely used as catalysts for reactions between small ions and organic substrates in aqueous systems. This chapter is a brief summary of the types of reactions studied (particularly those involving H^+ ions) and of the varying factors which can affect the catalysis, i.e. the micellar charge, substrate and ion binding, added salts, etc.

The last section of the chapter deals with work done so far on the acid hydrolysis of alkyl sulphates as a preliminary to a discussion of the kinetics of this reaction in concentrated surfactant solutions, which forms the subject of this thesis.

4.2 CHARGE ON THE MICELLE

On the basis of simple electrostatics, one expects, and finds, that reactions involving positively charged ions (e.g. H^+) are catalysed by anionic micelles and inhibited by cationic micelles, whereas the reverse applies to reactions involving negatively charged ions (e.g. OH^-, CN^-)

The effects of micelles on the kinetics of many acid and base catalysed reactions have been studied. Bunton et al (1974) found that the acid catalysed hydrolysis of monoalkyl xanthates is catalysed by sodium dodecyl sulphate (SDS) micelles and inhibited by micelles of cetyltri-methylammonium bromide (CTABr). Behme et al (1965) found likewise the acid hydrolysis of methyl orthobenzoate to be catalysed by SDS and inhibited by CTABr, while the base catalysed hydrolysis of p-nitrophenyl acetate was catalysed by CTABr and inhibited by SDS.

4.3 HYDROPHOBICITY OF SUBSTRATE AND SURFACTANT

The extent of micellar catalysis of a reaction is found to be strongly dependent on the hydrophobicity of both the substrate

and the surfactant: the more hydrophobic the species, the greater the catalytic effect. This is a consequence of the binding of the substrate to the micelle, which is more effective the stronger the hydrophobic interaction between the micelle and the substrate. Alternatively the substrate may be said to be partitioned more effectively into the micelle phase and this leads to an increase in the relative concentrations of reactants.

Bunton et al (1974) showed that the micellar catalysis of the acid hydrolysis of monoalkyl xanthates by SDS increased with the length of the alkyl chain of the substrate. (Table 4.1). Berndt et al (1979) looking at the substituent effects upon the acid hydrolysis of phenylacetohydroxamines catalysed by micelles of sodium decane sulphonate, found the catalysis to increase with the hydrophobicity of the substituent:

$$p-Br > p-CH_3CH_2 > p-CH_3 > m-CH_3 > none$$
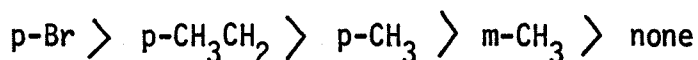
Dunlap and Cordes (1968) investigated the effects of the surfactant chain length on catalysis of the acid hydrolysis of methyl orthobenzoate by alkyl sulphate micelles. They found that the observed rate maximum increased with the surfactant chain length and that it occurred at lower surfactant concentration (due to a lowering of the CMC on increasing the surfactant chain length) (Table 4.2).

4.4   RATE MAXIMUM FOR SECOND ORDER REACTIONS

Much of the early work done on micellar catalysis observed only a limiting value of the rate as the surfactant concentration was increased. The main reason for this, in the case of second order reactions, was the fact that only low surfactant concentrations were used, not far above the CMC. It is now accepted that the value of the observed second order rate constants for reactions catalysed by micelles should pass through a maximum as the surfactant concentration is increased above the CMC.

<u>Table 4,1</u>

THE EFFECT OF ALKYL CHAIN LENGTH ON THE MICELLAR CATALYSIS OF THE ACID HYDROLYSIS OF MONOALKYL XANTHATES BY SDS (Bunton et al 1974)

Alkyl chain	k_{max}/k_0
Ethyl	1,55
n-Butyl	4,31
n-Octyl	18,97

pH = 3,70

Temperature = 25°C

k_{max} = maximum observed rate constant

k_0 = rate constant in the absence of SDS

Table 4.2

THE EFFECT OF SURFACTANT CHAIN LENGTH ON THE MICELLAR CATALYSIS OF THE ACID HYDROLYSIS OF METHYLORTHOBENZOATE BY ALKYL SULPHATES (Dunlap & Cordes 1968)

Surfactant chain	k_{max}/k_0 [a]	k_{max}/k_0 [b]
Octyl		7 (0.02M)
Decyl	15.5(0.075M)	26.8(0.075M)
Dodecyl	41.2(0.024M)	79 (0.048M)
Tetradecyl	81.5(0.030M)	92 (0.020M) [d]
Hexadecyl	86.0(0.006M) [c]	

a) Temperature = 40°C ; c) Temperature = 45°C

b) Temperature = 25°C ; d) Temperature = 30°C

The figures in brackets are the concns. of surfactant at which the rate maxima occur.

One of the earliest studies to show this phenomenon was that of Dunlap and Cordes (1968) on the acid catalysed hydrolysis of methyl orthobenzoate in the presence of SDS.

O'Connor et al (1973) observed the rate of the acid hydrolysis of both benzylidene-t-butylamine-N-oxide and 3-phenyl-2-t-butyl-oxaziridine to pass through a maximum value as the concentration of SDS increases, the maximum occurring at about 0.05M SDS.

4.5   THE EFFECT OF ADDED ELECTROLYTES

The inhibition of micellar catalysis by the addition of electrolytes is a well documented phenomenon (Fendler and Fendler 1975, Cordes 1973, Bunton 1973 a and b).

Dunlap and Cordes (1968) made an extensive survey of the effects of a wide range of cations on the acid hydrolysis of methyl orthobenzoate in the presence of SDS micelles. The cations used were split into five groups, alkali metals, alkaline earths, methyl ammoniums, mono substituted alkyl ammoniums and tetra substituted alkyl ammoniums.

For the alkali metal ions, they found that the inhibition of the micellar catalysis decreased with the size of the hydrated ion, i.e. the ions that can approach closest to the micelles inhibit the strongest.

$$Cs > Rb > NH_4 > Na > Li$$
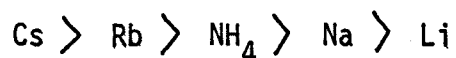
The inhibition by the alkaline earth cations was found to be almost independent of the ion, but much stronger than for the mono-valent cations.

In all cases for the alkyl substituted ammonium ions, the inhibition was found to increase with the hydrophobicity of the ion. Thus whether the ion was a mono or tetra substituted alkyl ammonium the inhibition followed the order;

$$Butyl > Propyl > Ethyl > Methyl > NH_4$$
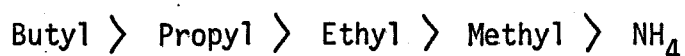
while for the methyl ammonium cations, the inhibition increased as more methyl groups were introduced into the ion.

Thus, in general, both for the organic ions and the inorganic ions, the inhibition increases as the binding ability of the ion for the micelle increases.

4.6   CONCENTRATION OF THE REACTIVE ION

Many workers have noted that rate constants obtained in micelle catalysed systems, particularly those for reactions involving small ions, are not 'true' constants but 'apparent' ones, as they are found to be dependent on the concentration of reactive ion used.

Bunton and Wolfe (1974) found that for the acid catalysed decomposition of 9-octyl purine 6-diazotate catalysed by SDS micelles, the rate enhancement (k_m/k_0) increased as the concentration of H^+ ion is decreased, and that as the H^+ ion concentration is increased, the maximum in the rate-surfactant concentration profile flattens out until it resembles the profile of a first order reaction (rate limit). Bunton and Rubin (1976) observed the same effects for the acid catalysed re-arrangement of 1,2,-diphenylhydrazine in the presence of SDS.

From the theoretical aspects of micellar catalysis, particularly those put forward by Romsted (1975), we have seen that it is not the total stoichiometric concentration of the reactive ion that is important in determining the kinetics, but the concentrations of the ion in the micellar and aqueous phases. Thus in order to obtain a better understanding of the variation in observed rate constants with reactive ion concentration, a number of people have studied the distribution of the reactive ion between the two phases.

Bunton et al (1977) investigated the binding of H^+ ions to SDS micelles using conductivity measurements and pH measurements, with both glass electrode and an unsolubilised dye method.

They assumed that one can completely distinguish between

bound and non-bound ions and that, for example, the pH measured using the glass electrode is dependent only on the concentration of the H^+ ion in the aqueous phase (i.e. those not bound). Therefore, knowing the total concentration of H^+ ions, one can find the concentration of bound H^+ ions.

The three methods were found to agree well with one another, except at high acid concentration. The fraction of ions bound to the micelle increased with surfactant concentration until a limit is reached. The limiting value of the fraction is greater at lower total H^+ ion concentration, and occurs at lower surfactant concentration, the lower the value of the total H^+ concentration (Fig 4.1).

So that assumptions did not have to be made concerning the volume of the micelles or the aggregation numbers, Bunton et al. defined a new unit for the concentration of ions bound to micelles, $m^S_{H^+}$, the number of H^+ ions bound to the micelles per micellised head group:

$$m^S_{H^+} = \frac{H^+_m}{SDS_T - CMC} \qquad 4.1$$

Over the range of acid and surfactant concentrations studied, they found this value to be a linear function of the mole fraction of the bulk concentration of H^+ ions, and they suggested that this was a reflection of the constancy of the degree of ion binding to the micelles.

$$m^S_{H^+} = 0.82 \frac{H^+_T}{H^+_T + Na^+_T} \qquad 4.2$$

Bunton and Wolfe (1973) used the concentration unit $m^S_{H^+}$ to obtain second order rate constants $(k_1/m^S_{H^+})$ for the acid catalysed hydrolysis of p-nitrobenzaldehyde diethyl acetal in the presence of SDS micelles. Unlike the second order rate constants based on k_1/H^+_T, these did not decrease at high surfactant concentration. This suggested that the rate maximum for second order reactions was indeed due to a
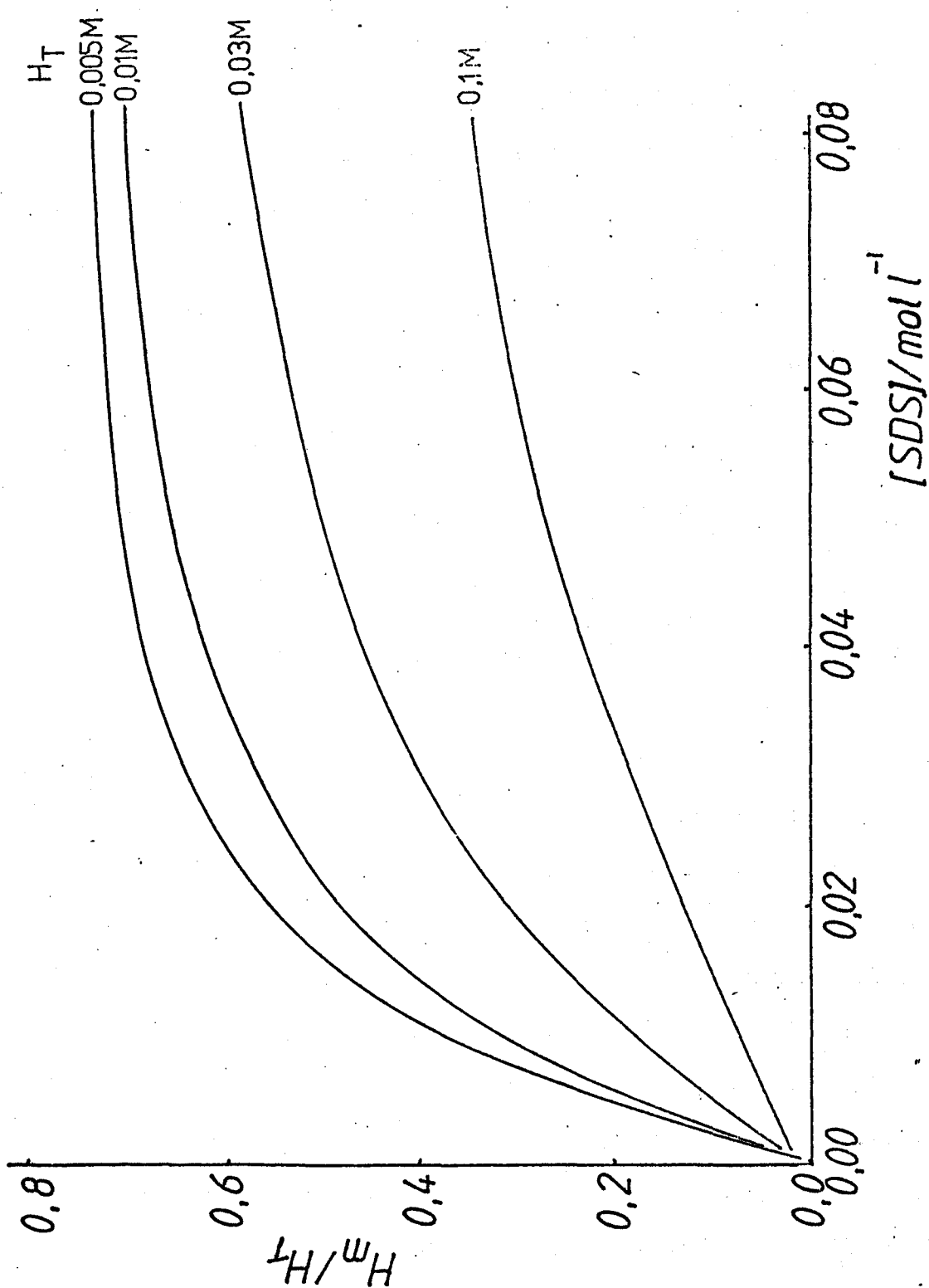
Fig. 4.1   The fraction of H^+ ions bound to SDS micelles as a
            function of the acid and surfactant concentrations
            at $25^{\circ}C$ (Bunton et al. 1977)

dilution of the H^+ ions bound to the micelles.

Almgren and Rydholm (1978) also used the same units of concentration for bound ions to investigate the effect of CTABr micelles on the reaction between p-nitrophenyl acetate and OH^- ion. This approach was used in conjunction with Romsted's ion exchange and Stern layer saturation model.

The rate of reaction using these units is then given by:-

$$\text{rate} = k'_m m^S_{OH}(\text{substrate})_m + k_w(OH^-)_w(\text{substrate})_w$$

$$k'_m = k_m/\text{molar density of surfactant in micelles.}$$

$$k_m = \text{second order rate constant at the micelle surface.}$$

They obtained iteratively calculated values of m^S_{OH} from estimated values of k'_m and $K_{Br/OH}$, and experimentally determined first order rate constants. These calculations indicated that the assumption of a constant degree of ion binding is reasonably valid, and that the values for second order rate constants at the micelle surface are similar if slightly smaller than those for the aqueous phase. This again shows that the catalytic effect of micelles is a result of the concentrating of reagents in the small volume of the micelle phase.

Chaimovich et al. (1979) used Quina and Chaimovich's (1979) ion exchange model to interpret the results for the OH^- catalysed hydrolysis of N-methyl 4-cyanopyridinium ion (MCP), which is inhibited by CTABr and tetradecyl trimethyl ammonium chloride (TTACl) micelles. This substrate is not solubilised by the micelles and the reaction takes place solely in the aqueous phase, so that they were concerned with the concentration of OH^- ions in the aqueous bulk and not in the micelle phase. They investigated the observed plots of rate constant against surfactant concentration and their agreement with calculated curves based on their expressions for the concentrations of bound and unbound ions, using estimated values of the ion exchange constants $(K_{OH/Y})$

and the degree of ion dissociation from the micelle (α), and taking into account ionic strength effects.

$$k\psi \text{ calc.} = k_\psi' (OH)_W / (OH)_T$$

$$(OH)_W = (OH)_T - (OH)_m$$

$$OH_m = \frac{-A_1 + (A_1^2 + 4(1-K_{OH/Y})OH_T K_{OH/Y}(1-\alpha)C_D)^{\frac{1}{2}}}{2(1-K_{OH/Y})} \qquad 4.3$$

$$A_1 = C_D + CMC + K_{OH/Y}OH_T + (1-\alpha)C_D K_{OH/Y}$$

k_ψ' = first order rate constant in water corrected for ionic strength effects

They found the best fits for the calculated and observed curves corresponded to $\alpha = 0.2$, $K_{OH/Br} = 0.08$, $K_{OH/Cl} = 0.14$ thus the strength of ion binding follows the series:

$$Br > Cl > OH$$

In the case of CTABr micelles the same result was obtained at two widely differing values of OH_T (20mM and 1mM). Thus reactions occurring in the aqueous phase in the presence of micelles and involving small counter ions also fit the ion exchange model.

4.7   KINETICS AND MECHANISM OF THE HYDROLYSIS OF ALKYL SULPHATES

There are three kinetically distinct pathways for the hydrolysis of alkyl sulphates, hydrogen-ion catalysed, hydroxide-ion catalysed and neutral (uncatalysed) hydrolysis. The mechanism of the three processes was elucidated some time ago by a number of workers. Burwell (1952) and Green and Kenyon (1950) showed that the slower spontaneous and hydroxide-ion catalysed hydrolyses proceed with carbon-oxygen cleavage, the hydroxide-ion pathway being direct nucleophilic displacement (Calhoun and Burwell 1955), while the

spontaneous process is midway between S_N1 and S_N2 in character. Burwell (1952) and Lieberman et al. (1948) showed that the fast acid-catalysed reaction involves sulphur-oxygen cleavage and proceeds through a protonation equilibrium of the sulphate group followed by attack of water on the sulphur.

$$ROSO_3^- + H^+ \rightleftharpoons ROSO_3H \xrightarrow{\text{ }H_2O\text{ }} ROH + HSO_4^- + H^+$$
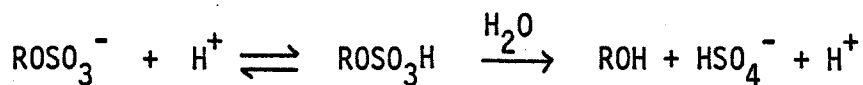
More recently the hydrogen-ion catalysed hydrolysis for the longer chain alkyl sulphates has been shown to be catalysed by the micelles which are formed by these species.

Kurz (1962) measured the rates of these three different pathways as a function of the alkyl chain length. The uncatalysed process was found to be independent of the chain length while both the acid and base catalysed processes showed sharp discontinuities on going from non-micelle forming ester to micelle forming esters. The acid catalysed process undergoes a sharp increase in reaction rate upon micellisation (Table 4.3), which Kurz attributed to a shift in the protonation equilibrium due to the high electrostatic potential of the micellar surface.

The hydroxide-ion catalysed pathway showed a sharp decrease in reaction rate upon micellisation. This was attributed to the negative charge of the micelles which would repel the hydroxyl ion whereas it would attract the positive hydrogen ion.

Kurz also showed that added electrolytes inhibit the micellar catalysed hydrolysis, this being due to a screening of the electrostatic potential of the micelles by the double layer, which reduces the shift in the protonation equilibrium.

Nogami et al (1963) showed that the acid catalysed hydrolysis of sodium dodecyl sulphate (SDS) was also catalysed by its self-micellisation, by measuring the variation in reaction rate with the

Table 4.3

THE EFFECT OF ALKYL CHAIN LENGTH ON RATE CONSTANTS FOR THE H^+ CATALYSED HYDROLYSIS OF SODIUM ALKYL SULPHATES (Kurz 1962)

Alkyl group	$k_{2\,obs}^a/10^{-5}\,l\,mol^{-1}\,s^{-1}$	$k_{2\,obs}^b/10^{-5}\,l\,mol^{-1}\,s^{-1}$
Methyl	5.0	5.47
Ethyl	7.47	5.68
Amyl	6.38	5.27
Decyl	33.7	41.3
Dodecyl	198	81.7
Tetradecyl	280	89.2
Hexadecyl	347	

a) [ester] = 0.04M, [H^+] = 0.04M

b) [ester] = 0.04M, [H^+] = 0.1M, [$NaClO_4$] = 0.37M

Temperature = 90°C

concentration of SDS. They observed a rapid increase in the rate as the concentration of SDS passed through the CMC for both 0.1M and 0.01M acid (Fig 4.2).

Nogami and Kanakubo (1963) extended this also to a study of the acid hydrolysis of sodium octyl sulphate (SOS), sodium myristyl sulphate (SMS), sodium cetyl sulphate (SCS) and sodium pentadecane-8-sulphate as a function of surfactant concentration. Again they found enhancement of the reaction rate as the surfactant concentration passed through the CMC. The enhancement was found to increase with the alkyl chain length and the branched chain sulphate was more stable to hydrolysis than the straight chain surfactants.

Motsavage and Kostenbauder (1963) also measured the rate of the acid catalysed hydrolysis of SDS, but took only two concentrations of the ester, one above and one below the CMC. They also found an enhanced reaction rate above the CMC, by a factor of 35, attributing this to the binding of solvated protons to the sulphate head groups of the micelles.

They also found that non-ionic additives, dodecanol, Pleuronic F68, and Triton WR 1339, all increased the micellar catalysed hydrolysis due to a reduction of the dielectric constant in the region of the head groups in the mixed micelle, which would increase the electrostatic interaction of the protons and head groups and hence the reaction velocity.

Barry and Shotton (1967) also studied the acid hydrolysis of SDS above the CMC and the effect upon the reaction rate of adding hexadecanol. Initially they observed an enhancement of the rate by adding the alcohol up to a mole ratio of 0.75 (alcohol: sulphate) whereupon on addition of further alcohol the rate begins to decrease again. Like Motsavage and Kostenbauder (1963), they attributed the rate increase to the change in dielectric constant, while the decrease in rate coincides with a phase change of the system.
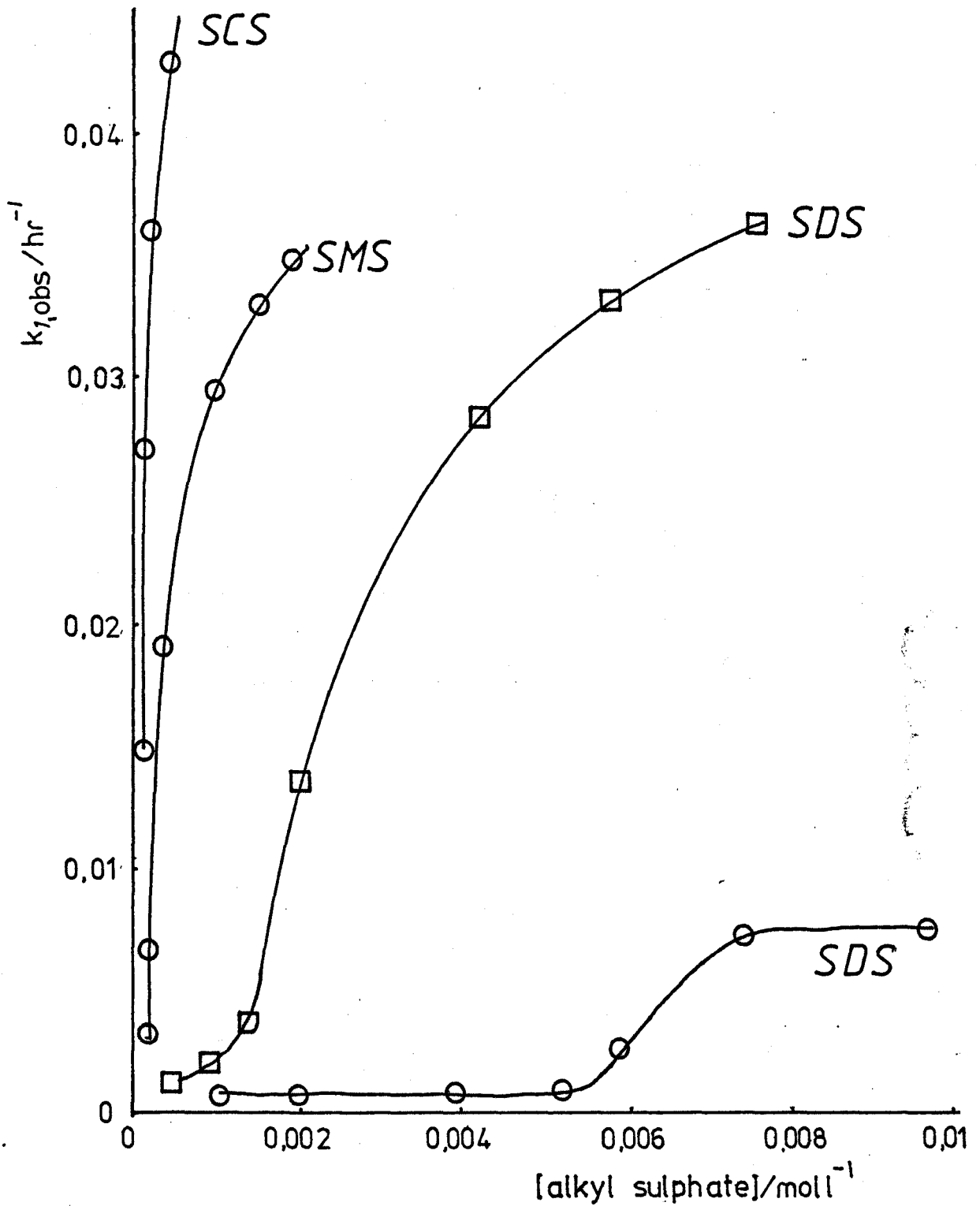
Fig. 4.2   The effect of the surfactant concentration on the
acid catalysed hydrolysis of alkyl sulphates at 70°C
(O = 0.01M HCl; □ = 0.1M HCl). Nogami et al (1963).

CHAPTER FIVE

MATERIALS AND EXPERIMENTAL

5.1   MATERIALS

The kinetic studies discussed below were carried out using five main surfactants, sodium, lithium, ammonium and magnesium dodecyl sulphates and sodium diethoxy dodecyl sulphate ($CH_3(CH_2)_{11}(OCH_2CH_2)_2^- OSO_3Na$).

5.1.1   Preparation of Dodecyl Sulphates

Sodium and lithium dodecyl sulphate were specially pure grade, obtained from BDH laboratories, and were recrystallised twice from absolute ethanol and dried under vacuum before use.

Magnesium dodecyl sulphate was precipitated from a concentrated solution of sodium dodecyl sulphate (SDS), by the addition of a concentrated solution of magnesium chloride, at 15°C. The precipitate was then recrystallised three times from ethanol and dried under vacuum.

Ammonium dodecyl sulphate was prepared from dodecan-1-ol by sulphation in a falling film apparatus using vapourised SO_3. The system consisted of two dry air streams, one containing the liquid alcohol and the other a 10% excess of vapourised SO_3, both at 35°C., which were allowed to mix as they passed down a vertical reactor tube into a post-reactor which allows complete reaction. The product dodecyl sulphuric acid was then collected and added to a neutralisation mixture, consisting of a solution of .880 ammonia in methanol. When this mixture was fully neutralised and cooled, the ammonium dodecyl sulphate precipitated out, along with the inorganic impurities, principally ammonium sulphate. The impurities were removed by recrystallisation from 90% ethanol and the surfactant was then recrystallised a further two times from absolute ethanol and dried under vacuum.

5.1.2   Preparation of Sodium diethoxy dodecyl sulphate

Sodium diethoxy dodecyl sulphate was prepared by the addition
of diethylene glycol to the dodecyl group followed by sulphation of the
resulting alcohol using chlorosulphonic acid.

5.1.2.1   Ethoxylation of dodecyl bromide (Mulley 1958, Gingras and
           Bayley 1957, 1958)

Sodium metal (one mole) was dissolved in eight equivalents
of Analar diethylene glycol, to this was added one mole of dodecyl
bromide dropwise and the mixture stirred for four hours at 220°C.
After cooling, 800ml of diethyl ether were added and the precipitated
NaBr was removed by shaking with three aliquots of 100ml of distilled
water.

The ether was then removed from the remaining organic layer
and the residue vacuum distilled to obtain the ethoxy alcohol (160°C.,
2.75mm Hg).

5.1.2.2   Sulphation of the ethoxy alcohol

0.1 mole of the ethoxy alcohol was dissolved in 150ml of
chloroform at 10°C., a 20% excess of chlorosulphonic acid was added
dropwise, and the mixture stirred at room temperature for two hours.
The mixture was then cooled to 10°C. and the acid product neutralised
with alcoholic NaOH. The inorganic precipitate which formed (NaCl)
was filtered off and the chloroform distilled off, which allowed the
ethoxy sulphate to precipitate from the remaining solution. This
precipitate was recrystallised twice from absolute ethanol and dried
under vacuum.

5.1.3   Purity of the surfactants

The purity of all the surfactants used was determined by
complete acid hydrolysis of the compound followed by determination of
the excess acid produced.

5gm of the surfactant plus 25ml of 0.5M sulphuric acid were placed in a 250ml round-bottomed flask and then refluxed under a water condenser for two hours. The mixture was then allowed to cool, and the condenser washed down with ethanol and water. The mixture was then titrated against standardised 1M NaOH solution using phenolphthalein as indicator, and the titre compared to that for a blank of 25ml of the sulphuric acid.

$$\% \text{ purity of sample} = \frac{M(A-B)S}{10w}$$

where, A = titre of sample

B = titre of blank

S = molarity of NaOH

M = molecular wt. of surfactant

w = wt. of sample

Example

A = 36,45ml ; B = 22,05ml

S = 0,957M ; M = 288,38

w = 3,9831g

% purity = 99,8

All the surfactants used were found to be better than 99.5% pure by this method.

5.2   EXPERIMENTAL DETERMINATION OF RATE CONSTANTS

5.2.1   Preparation of the reaction mixture and sampling

There are three main constituents of the reaction mixtures used, surfactant, perchloric acid, and inorganic electrolyte. The appropriate weight of surfactant, and a volume of concentrated salt solution were placed in a 100ml volumetric flask and diluted with distilled water to within 10ml of the mark. The flask was then placed in a thermostatted oil bath and allowed to equilibrate, then the appropriate volume ($\leqslant$ 5ml) of a concentrated solution of perchloric acid was added, timing started, the flask topped up to the mark and the mixture shaken. The whole was then transferred to a round-bottomed flask. Two zero-time samples were then removed using a jacketed pipette and quenched with cold distilled water; one of the samples was used to determine the initial surfactant concentration using a two-

phase titration technique (see 5.3) and the other sample was used to determine the initial acid concentration by an acid-base titration using an E.I.L. automatic titrator.

5.2.2   Following the reaction

The reaction was followed by removing 5ml samples, with a jacketed pipette, at appropriate intervals, quenching the reaction with cold distilled water and analysing the mixture. At high surfactant concentration ($> 0.02M$), the $[HSO_4^-]$ liberated on hydrolysis was sufficiently large to produce significant increases in the total acid concentration as measured by acid-base titration using an E.I.L. 7070 automatic titrator to a fixed end point. Thus the concentration of the reaction products can be found from:

$$[product] = [acid]_t - [acid]_0$$

At surfactant concentrations below 0.02M, changes in the total acid concentration were too small to be measured accurately enough, so the reaction was followed by the change in surfactant concentration using a colourimetric method (Mukerjee 1956). This involved the partition of a dye-surfactant salt between chloroform and water, followed by the measurement of the absorbance of the dye in the chloroform layer. The concentration of the surfactant can then be found from a calibration curve.

The calibration curve of absorbance of the dye against surfactant concentration covered the range in surfactant concentration from 0.02mM to 0.2mM. Thus 5ml samples removed from the reaction mixture for analysis had to be diluted down so that their surfactant concentration fell within this range. The extent of this dilution was therefore dependent on the initial concentration of surfactant in the reaction mixture and had to be taken into account when calculating the surfactant concentration present at any given time during the kinetic experiment.

The method of determining the surfactant concentration was as follows:-

$2cm^3$ of the diluted surfactant solution from the reaction mixture was placed in a stoppered centrifuge flask along with $2cm^3$ of a solution containing $0.008gcm^{-3}$ of methylene blue, $50gl^{-1}$ of Na_2SO_4, and $0.05M$ H_2SO_4, $8cm^3$ of a $0.05M$ H_2SO_4 solution and $20cm^3$ of chloroform. The flask was then shaken for 5 minutes, followed by centrifuging for 5 minutes. The absorbance of the chloroform layer was then determined at 655nm and compared to the calibration curve, obtained in the same manner using surfactant solutions of known concentration.

The concentration of surfactant in the reaction mixture was then obtained from the concentration in the diluted solution and the extent of the dilution involved.

5.2.3   Determination of rate constants from concentration-time data

For any given kinetic run we have the following:-

(a) Initial acid concentration, $(H^+)_0$

(b) Initial surfactant concentration, $(surf.)_0$

(c) The concentration of acid and surfactant at times t, $(H^+)_t$ and $(surf)_t$

The rate of reaction is dependent on both the acid and the surfactant concentrations, and as HSO_4^- is a product of the reaction, the reaction is autocatalytic.

For an autocatalytic reaction the integrated rate equation used to obtain the rate constant $k_{2,obs}$ should be:

$$k_{2,obs} \ t = \frac{1}{(H^+)_0 + (surf)_0} \times \ln\left[\frac{(H^+)_t}{(surf)_t} \ \frac{(surf)_0}{(H)_0}\right]$$

$$k_{2,obs} = \frac{(\text{slope of ln. } (H^+)_{t/(surf)_t} \text{ vs time})}{(H^+)_0 + (surf)_0}$$

However, for the acid catalysed hydrolysis of SDS these plots were found to have pronounced curvature. This is due to the weakly acidic nature of HSO_4^-, whose dissociation is suppressed by the acid already present. The results show that it is dissociated to some extent since the reaction rate does increase as the reaction proceeds, therefore, the HSO_4^- is only partially dissociated and we need to know the degree of dissociation, δ, in order to determine rate constants for the reaction. This was found empirically by plotting the integrated rate equation for a number of values of δ (Fig. 5.1) and obtaining the value of δ which yields the best straight lines and the best agreement of $k_{2,obs}$ values obtained with those obtained from the initial rate of reaction. The optimum value of δ was found to be 0.5.

Fig. 5.1   The effect of varying δ on the integrated rate constant plots.
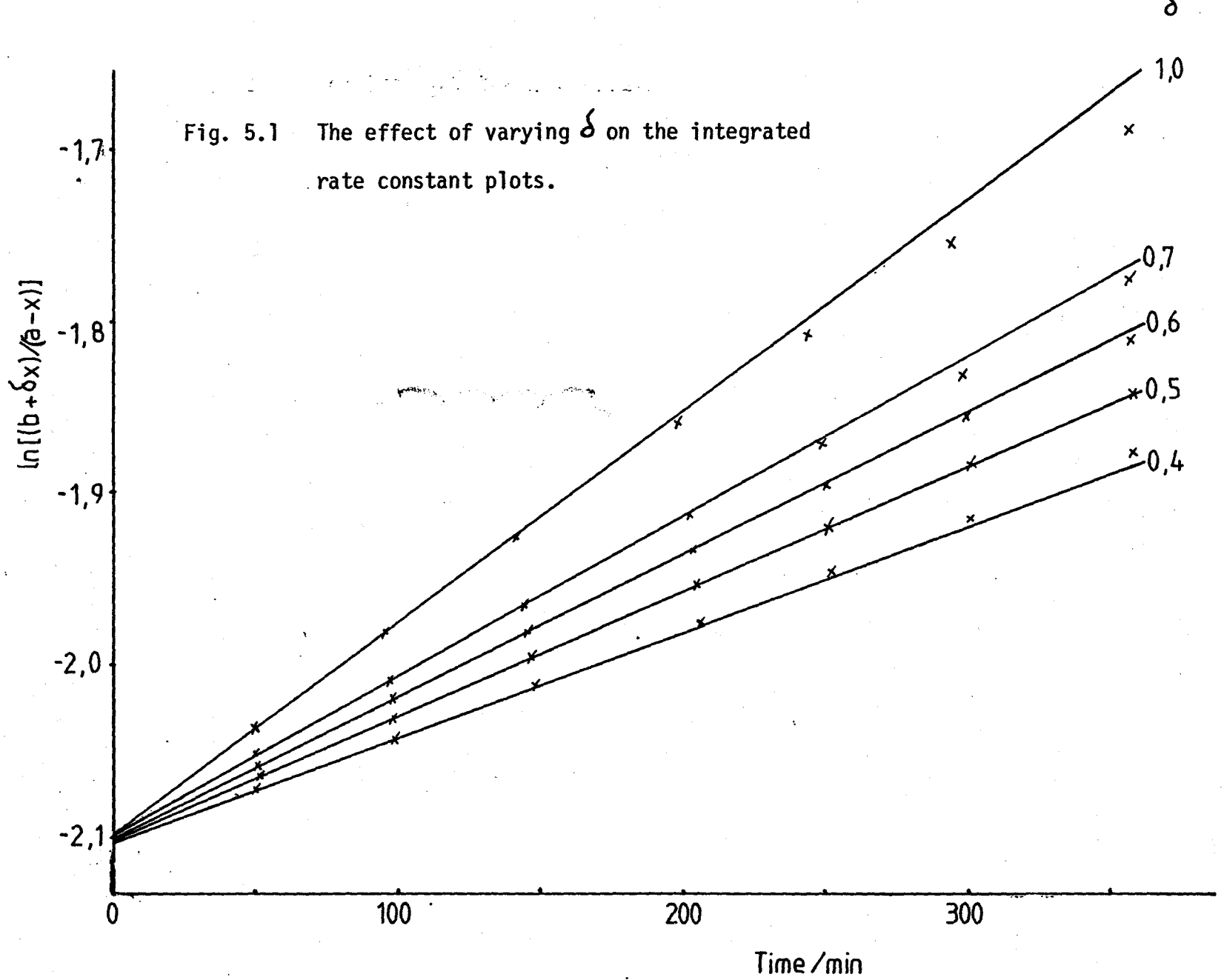
The integrated rate equation including the degree of dissociation of HSO_4^- is:

$$k_{2,obs}\, t = \frac{1}{(H^+)_0 + \delta(surf)_0} \times \ln\left[\frac{(H^+)_0 + \delta(HSO_4^-)_t}{(surf)_t} \cdot \frac{(surf)_0}{(H^+)_0}\right]$$

5.3   DETERMINATION OF ANIONIC SURFACTANT BY A TWO-PHASE TITRATION - (Reid et al 1967)

This method for determining the concentration of anionic surfactants in aqueous solution is based on the formation of salts between the anionic surfactant and large cationic organic species, which are more soluble in an organic phase than in an aqueous phase. The surfactant is titrated against a cationic titrant in the presence of a dye, which can be anionic, cationic or a mixture of anionic and cationic in nature.

5.3.1   Cationic indicator

Using a cationic dyestuff, a salt will be formed between the surfactant and the dye at the start of the titration, which is soluble in the organic layer (which will therefore be coloured). As cationic titrant is added it will replace the dye in the salt which then passes into the aqueous layer. Thus the end point of the titration is when all the colour disappears from the organic layer.

5.3.2   Anionic indicator

The anionic dye will not form a salt with the anionic surfactant, so that at the start of the titration the dye will be present in the aqueous layer. The titrant will then form a salt with the surfactant, which is colourless and soluble in the organic layer. When all the anionic surfactant has been taken up by the titrant, the excess titrant will then form a salt with the anionic dye which is coloured and soluble in the organic layer. Thus the end point occurs when the colour begins to form in the organic layer.

5.3.3   Mixed indicator

Using either anionic or cationic indicators alone does not produce a clear enough end point to the titration, so Reid et al (1967) employed a mixed indicator system containing both an anionic and a cationic dye.

Initially the surfactant forms a salt with the cationic dye to produce a coloured organic layer, while the anionic dye gives a colour to the aqueous layer. Adding the cationic titrant displaces the dye from the surfactant-dye salt to form a salt between the titrant and the surfactant, then when all the surfactant is taken up by this salt, the excess titrant then forms a coloured salt with the anionic dye which is soluble in the organic layer, while the cationic dye passes into the aqueous layer. Thus as the two dyes produce different colours, the end point occurs when the colour of the organic layer changes.

The mixed indicator method was found to be widely applicable to anionic surfactants, including alkyl sulphates, sulphonates, hydroxy-sulphates and ethoxy sulphates, and dialkyl sulphosuccinates. It is not affected by the presence of other compounds, for example alcohols, electrolytes, non-ionic detergents, etc., and is reproducible to $\pm$ 2%.

In the case of alkyl sulphate surfactants, the cationic titrant used is Hyamine 1622, the organic solvent chloroform and the mixed dye consists of Dimidium Bromide (cationic) and Disulphine Blue (anionic).
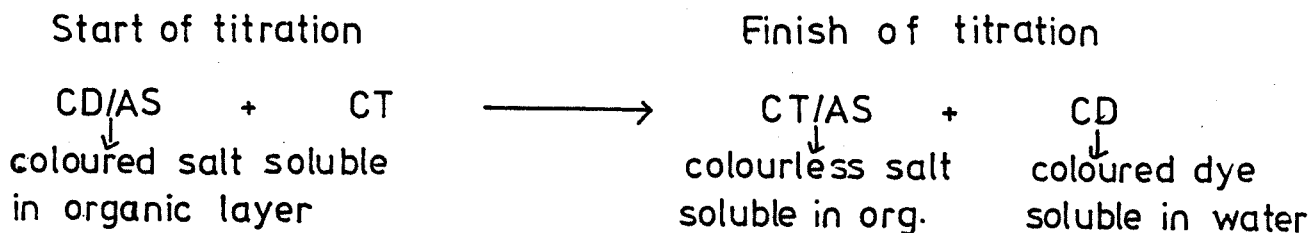
5.3.4   Method

Titrant:- 0.004M Hyamine 1622 solution.

Indicator:- 0.5gm Dimidium Bromide and 0.25gm Disulphine Blue in 250ml of solution. 20ml of this solution was added to 20ml of 2.5M H_2SO_4 and diluted to 500ml to make the working solution.

The surfactant sample was diluted to approximately 0.004M and 20ml of this was placed in a stoppered measuring cylinder along with 15ml chloroform, 10ml water and 10ml of the indicator solution. This mixture was then titrated with the Hyamine solution with vigorous shaking. As the end point approached, the emulsion formed on adding the titrant began to break easily. The end point was found when the colour of the chloroform layer changed from pink to a grey-blue.
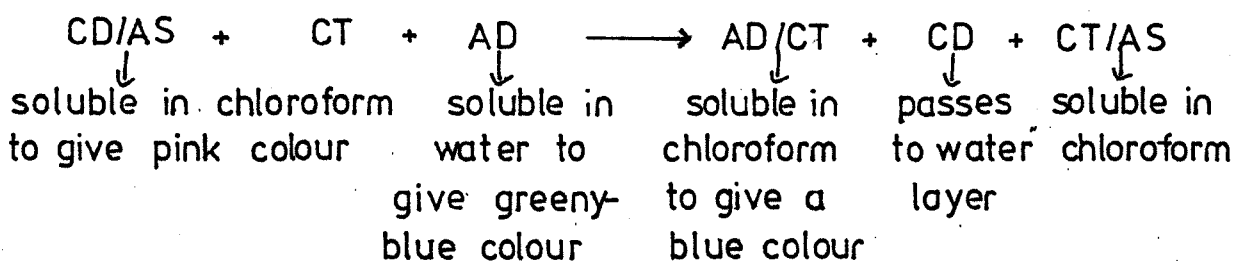
Titration with Cationic Indicator

Start of titration   Finish of titration

CD/AS   +   CT $\longrightarrow$ CT/AS   +   CD
coloured salt soluble   colourless salt   coloured dye
in organic layer   soluble in org.   soluble in water

Colour moves from organic layer to aqueous layer

Titration with Anionic Indicator

CT + AD + AS $\longrightarrow$ CT/AS   +   AD/CT
     coloured dye soluble   colourless salt   coloured salt
        in water   soluble in org.   soluble in org.
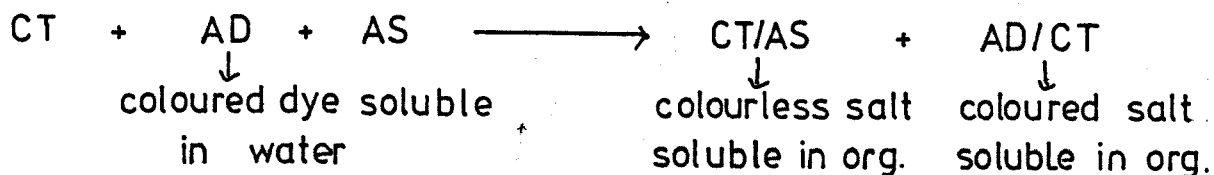
Colour moves from aqueous layer to organic layer

Titration with Mixed Indicator

CD/AS +   CT   +   AD $\longrightarrow$ AD/CT +   CD   + CT/AS
soluble in chloroform   soluble in   soluble in   passes   soluble in
to give pink colour   water to   chloroform   to water chloroform
                         give greeny-   to give a   layer
                         blue colour   blue colour

End point occurs when chloroform layer changes from pink to blue

AS = Anionic surfactant

AD = Anionic dye (disulpine blue)

CD = Cationic dye (dimidium bromide)

CT = Cationic titrant (Hyamine 1622)

APPENDIX 5,1 Example of data from a kinetic experiment

[SDS] = 0,101 M = a ; [HClO$_4$] = 0,0205 M = b

Titrant = 0,0225 M NaOH ; sample volume = 4,941 ml

Temperature = 70°C

Time (min)	Titre (ml)	[product]/10^{-3} (mol l^{-1})	$\ln \frac{b+0.5x}{a-x}$
0	4,515	0	-1,595
40	4,655	0,637	-1,573
80	4,820	1,389	-1,547
120	4,970	2,072	-1,525
180	5,200	3,119	-1,490
240	5,400	4,030	-1,481
300	5,650	5,168	-1,423
360	5,850	6,079	-1,393
410	6,055	7,013	-1,365
450	6,190	7,628	-1,346
500	6,435	8,740	-1,311
560	6,640	9,677	-1,282

x = [product] = $(T_t - T_o)$. 0,0225/4,941

initial reaction rate = 2,647 . 10^{-7} mol l^{-1} s^{-1}

integrated rate constant = 1,331 . 10^{-4} l mol^{-1} s^{-1}

$k_{2,av}$ = 1,305 . 10^{-4} l mol^{-1} s^{-1}

CHAPTER SIX

RESULTS AND DISCUSSION

6.1 INTRODUCTION

The experimental results described in this chapter relate to the acid catalysed hydrolysis of dodecyl and dodecyl-ether sulphates, which is catalysed by the self-micellisation of these species.

$$ROSO_3^- + H^+ \underset{k_2}{\overset{K}{\rightleftharpoons}} ROSO_3H \xrightarrow{H_2O} ROH + HSO_4^- + H^+$$
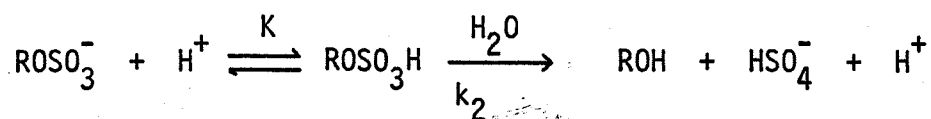
$$\text{Rate of reaction} = k_2 K [H^+][ROSO_3^-][H_2O]$$

$$k_{2,obs} = k_2 K[H_2O]$$

where

$$K = \frac{[ROSO_3H]}{[ROSO_3^-][H^+]}$$

The results are analysed in terms of Romsted's ion-exchange theory (1975), which has been modified to take into account the fact that the substrate $ROSO_3^-$ is also the micelle forming species (see section 6.2). The theory is applicable to the hydrolysis of dodecyl and dodecyl-ether sulphates as the kinetics of the reaction are chiefly determined by the concentrations of the sulphate head groups and the H^+ ions in the micellar Stern layer, as a result of the pre-equilibrium in the reaction mechanism.

The various factors we have examined in terms of their effect on the rate of hydrolysis include, temperature, acid concentration, concentration of added electrolytes, surfactant concentration, ethoxylation of the surfactant carbon chain, concentration of added hexanol and the ratio of the concentrations of the reactive and non-reactive ions.

6.2   APPLICATION OF ROMSTED'S PSEUDO-PHASE/ION-EXCHANGE MODEL TO A REACTION INVOLVING THE MICELLE FORMING SPECIES AS THE SUBSTRATE.

6.2.1   Introduction

The reaction studied is somewhat different from most organic reactions catalysed by micelles in that it is the substrate itself which is the micellar species. Thus we do not have the factor of the distribution of the organic substrate between the micellar and aqueous phases, but assume that above the CMC of the surfactant all the extra surfactant is in the micellar phase and the concentration in the aqueous phase remains constant and equal to the CMC.

As in Romsted's (1975) model we assume that the mechanism and rate determining step of the reaction are unaffected by micellisation, and that the rates of reaction in the two phases can be averaged out over the whole system such that:-

Reaction rate $= k_{2,obs} C_T H_T = k_m \overline{H}_m \overline{C}_m CV + k_w \overline{H}_w \overline{C}_w (1-CV)$ 6.1

where

C_T = total analytical concentration of surfactant

H_T =   "   "   "   acid

$\overline{H}_m$ = concentration of H^+ ions in the micelle phase

    $= H_m/CV$

$\overline{H}_w$ = concentration of H^+ ions in the aqueous phase

    $= H_w/(1-CV)$

$\overline{C}_m$ = concentration of surfactant in the micelle phase

    $= (C_T - CMC)/CV = 1/V$

$\overline{C}_w$ = concentration of surfactant in the aqueous phase

    $= CMC/(1-CV)$

C = $C_T - CMC$

V = molar volume of the surfactant in the micellar phase

Substituting these into equation 6.1 gives:-

$$k_{2,obs}C_T H_T = k_m \bar{H}_m \frac{(C_T - CMC)CV}{CV} + k_w \bar{H}_w \frac{CMC}{(1-CV)}(1-CV) \qquad 6.2$$

$$= k_m \bar{H}_m (C_T - CMC) + k_w \bar{H}_w CMC \qquad 6.3$$

$$= k_m H_m \frac{(C_T - CMC)}{CV} + k_w \frac{H_w}{(1-CV)} CMC \qquad 6.4$$

$$= k_m H_m \frac{}{V} + k_w H_w \frac{CMC}{(1-CV)} \qquad 6.5$$

hence;

$$k_{2,obs} = \frac{1}{C_T H_T} \left[\frac{k_m H_m}{V} + \frac{k_w H_w CMC}{1-CV} \right] \qquad 6.6$$

In general, organic reactions are usually regarded as taking place over the whole micellar volume. However, reactions involving hydrophilic ions will be restricted to the Stern layer of the micelle, so that the volume element for the reaction in the micellar phase should be the Stern layer volume, V_s, while the volume of the aqueous phase remains the total solution volume minus the total micellar volume, so that;

$$k_{2,obs} = \frac{1}{C_T H_T} \left[\frac{k_m H_m}{V_s} + \frac{k_w H_w CMC}{1-CV} \right] \qquad 6.7$$

In order to be able to use this expression we need to obtain values for k_m, k_w, V, V_s, CMC and an expression for H_m (using the fact that $H_T = H_m + H_w$)

6.2.2   Calculation of H_m

Expressions for the concentrations of reactive ions bound to micelles have been obtained in a number of ways (see Chapter 3), the

most suitable for this work being those of Romsted (1975) and Quina and Chaimovich (1979), which if one removes the simplifying assumptions of the Romsted approach, produce equivalent quadratic equations to calculate H_m.

6.2.2.1 Romsted's Approach

This is based on the material balance equations for the various ionic species present in a reacting system.

$$Na_T = \overline{Na}_m \, CV + \overline{Na}_w \, (1-CV) \qquad 6.8$$

$$H_T = \overline{H}_m^- \, CV + \overline{H}_w^- \, (1-CV) \qquad 6.9$$

and the saturation of the Stern layer with respect to the counterions

$$\overline{H}_m + \overline{Na}_m = \beta \, S \qquad 6.10$$

where β is the fraction of the micellar head groups neutralised by the counterions and S is the molar density of the surfactant in the micellar phase (N.B. β is assumed to be independent of the nature of the counterion).

Also taken into account is ion exchange of the counterions between the micelle and aqueous phases;

$$K_{H/Na} = \frac{\overline{H}_m \, \overline{Na}_w}{\overline{H}_w \, \overline{Na}_m} = \frac{H_m \, Na_w}{H_w \, Na_m} \qquad 6.11$$

N.B. This definition of $K_{H/Na}$ is the inverse of that used by Romsted (e.g. 3.15)

from equation 6.11

$$\overline{Na}_w = K_{H/Na} \frac{\overline{H}_w \, \overline{Na}_m}{\overline{H}_m} \qquad 6.12$$

substituting in equation 6.8

$$Na_T = \overline{Na}_m \, CV + K_{H/Na} \frac{\overline{H}_w \, \overline{Na}_m}{\overline{H}_m} \, (1-CV) \qquad 6.13$$

$$\overline{Na}_m = \frac{Na_T \overline{H}_m}{\overline{H}_m \, CV + K_{H/Na} \, \overline{H}_w \, (1-CV)} \qquad 6.14$$

However from equation 6.9

$$\overline{H}_w = \frac{H_T - \overline{H}_m \, CV}{1-CV} \qquad 6.15$$

therefore

$$\overline{Na}_m = \frac{Na_T \, \overline{H}_m}{\overline{H}_m \, CV + K_{H/Na}(H_T - \overline{H}_m \, CV)} \qquad 6.16$$

sub. this into 6.10

$$\overline{H}_m + \frac{Na_T \, \overline{H}_m}{K_{H/Na} \, H_T + \overline{H}_m \, CV(1-K_{H/Na})} = \beta S \qquad 6.17$$

then

$$\overline{H}_m^2 (1-K_{H/Na}) \, CV + \overline{H}_m \, [K_{H/Na} \, H_T + Na_T + \beta S \, CV(K_{H/Na}-1)]$$
$$- K_{H/Na} \, H_T \, \beta S = 0 \qquad 6.18$$

Therefore we can obtain $\overline{H}_m$ as the positive root of the quadratic equation 6.18

$$\overline{H}_m = \frac{-A + [A^2 + 4K_{H/Na}(1-K_{H/Na})CV \beta SH_T]^{\frac{1}{2}}}{2(1-K_{H/Na})CV} \qquad 6.19$$

but,

$$\overline{H}_m = H_m/CV$$

therefore

$$H_m = \frac{-A + [A^2 + 4K_{H/Na}(1-K_{H/Na})CV \beta SH_T]^{\frac{1}{2}}}{2(1-K_{H/Na})} \qquad 6.20$$

where

$$A = K_{H/Na} \, H_T + Na_T + \beta SCV(K_{H/Na}-1) \qquad 6.21$$

6.2.2.2 Quina and Chaimovich's approach

This approach to the calculation of H_m is based on the ion-exchange equilibrium of equation 6.11

$$K_{H/Na} \quad = \quad \frac{H_m \, Na_w}{H_w \, Na_m} \qquad\qquad 6.22$$

where

$$H_w \quad = \quad H_T - H_m$$

$$Na_m \quad = \quad (1-\alpha)C - H_m$$

$$Na_w \quad = \quad \alpha C + CMC + H_m$$

$$C \quad = \quad C_T - CMC$$

$$\alpha \quad = \quad \text{the degree of dissociation of the counterion from}$$
$$\text{the micelle } (1-\beta).$$

That is to say, Quina and Chaimovich use the same assumption as Romsted, that the Stern layer is saturated with respect to the counterions (the fraction of head groups neutralised by the counterions, $1-\alpha$, is taken as being constant) and that each H^+ ion which is bound to the micelle replaces one Na^+ ion.

By substituting the values for H_w, Na_w, and Na_m into equation 6.22 and re-arranging, we obtain

$$H_m{}^2(1-K_{H/Na}) \; + \; H_m[C(\alpha + (1-\alpha)K_{H/Na}) + K_{H/Na}H_T + CMC]$$

$$- K_{H/Na}C(1-\alpha)H_T \;\; = \;\; 0 \qquad 6.24$$

so that

$$H_m \quad = \quad \frac{-B + [B^2 + 4K_{H/Na}(1-K_{H/Na})(1-\alpha)CH_T]^{\frac{1}{2}}}{2(1-K_{H/Na})} \qquad 6.25$$

where

$$B \; = \; C(\alpha + (1-\alpha)K_{H/Na}) + K_{H/Na}H_T + CMC \qquad\qquad 6.26$$

Thus at first sight we can see that the two approaches produce very similar conclusions for the expression for H_m, in fact the only difference is one of notation and equations 6.20 and 6.26 are in effect identical, except that if one has added a salt with a common counterion to the system, one has to slightly modify equation 6.26, whereas 6.20 takes into account this possibility. Thus in 6.26 B is replaced by B' where

$$B' = B + [salt]$$

Quina and Chaimovich extended their model to include the calculation of H_m in the presence of a third ion Y due to the addition of a non-common ion salt:-

$$H_m^3(1-K_{H/Y})(1-K_{H/Na}) + H_m^2 B_1(1-K_{H/Y}) + (1-K_{H/Na})(H_T K_{H/Y} + Y_T)$$

$$+ H_m H_T K_{H/Na}(Y_T - (1-\alpha)C_T(1-K_{Na/Y})) + K_{H/Y}B_1$$

$$- K_{H/Na}(1-\alpha)CK_{H/Y}H_T^2 = 0 \qquad 6.27$$

so that one can calculate H_m using one of the methods for cubic equations.

The experimental results outlined below are discussed in conjunction with the corresponding results calculated from equations 6.7, 6.20, and 6.25, bearing in mind that in order to simplify the equations a major assumption has been made throughout the discussion, namely that the activity of water in the region of the Stern layer remains unity under all the experimental conditions. Also the parameters used for the calculations are those taken from the literature for the various surfactants used.

6.3   THE EFFECT OF TEMPERATURE ON THE ACID HYDROLYSIS OF SDS AND

        SDE_2S AT 0.035M SURFACTANT

        The temperature effect on the rate of hydrolysis of both SDS

and SDE_2S was investigated, partly to compare the results with those

previously obtained by other workers and partly to find what the effect

of ethoxylating the carbon chain of the surfactant on the activation

energy will be. In addition results at different temperatures were

used to decide upon the most convenient temperature at which to study

the other aspects of the kinetics of the reaction (surfactant

concentration effect, electrolyte effects, etc.)

        Fig. 6.1 gives Arrhenius plots (ln $k_{2,obs}$ vs. 1/Temp.)

for both SDS and SDE_2S at 0.035M surfactant. In both cases the plots

are linear over the range of temperatures used (60°C to 90°C) and

produce energies of activation for the reactions of 112 $\pm$ 2 kJ/mol.

for SDS and 126 $\pm$ 3 kJ/mol. for SDE_2S.

        The value for SDS agrees well with that obtained by Kurz (1962)

who found a value of 115 $\pm$ 1 kJ/mol. at 0.04M surfactant. These

values are less than the value found by Kurz for a non-micelle forming

alkyl sulphate (for Sodium Methyl Sulphate, Ea = 129 $\pm$ 0.5 kJ/mol.).

On the basis of this Kurz argued that the catalysis by micelles of the

surfactant was solely due to the changes in the enthalpy of activation

as the entropy of activation remains constant, though no explanation

for this was put forward.

6.4   THE EFFECT OF THE ACID CONCENTRATION (H_T) ON THE HYDROLYSIS

        OF SDS AND SDE_2S

6.4.1   Introduction

        As is generally observed for micellar catalysed reactions,

the rate constants obtained for the hydrolysis of SDS and SDE_2S are

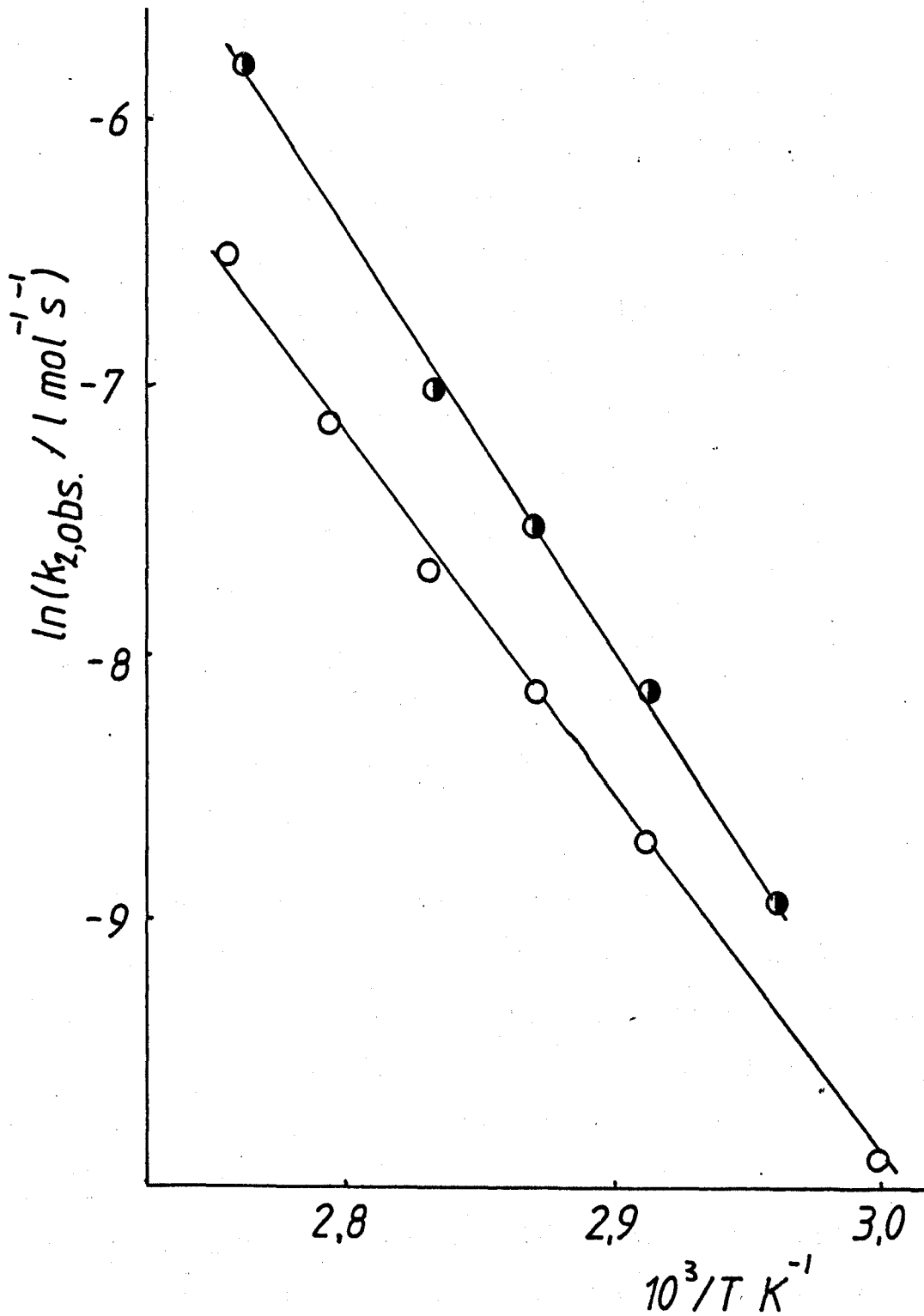not true rate constants but 'apparent' rate constants, depending on,

Fig. 6.1   The effect of temperature on the acid catalysed

hydrolysis of 0.035M SDS (o) and SDE_2S (◓) at 0.05M $HClO_4$

for example, the total acid concentration (H_T). This is due to the ability of the micelles to bind counterions, the extent of this binding depending on the degree of dissociation of the micelles, the ion-exchange constants for the competing ions, the surfactant concentration and the concentrations of the competing counterions. As a result of the micelles only binding a fraction of the available counterions, the kinetics of reactions catalysed by micelles do not depend on the total stoichiometric concentrations of the reactive ions, but on their concentrations in the micelle Stern layer and this is why the rate constants are 'apparent' only.

The effect of the acid concentration on the initial rates of reaction and on the observed rate constants for the hydrolysis of SDS and SDE_2S was studied at 0.035M surfactant and additionally at 0.35M for SDS. The observed effects are analysed in conjunction with the experimental and calculated variation in the degree of H^+ ion binding to the micelles.

6.4.2   The binding of H^+ ions to micelles of SDS

Bunton et al. (1977) have determined the extent of the binding of H^+ ions to SDS micelles experimentally, on the assumption that one can completely distinguish between bound and non-bound ions. That is, for example, if one measures the pH of a solution containing micellar SDS, only those H^+ ions which remain in the aqueous phase and are not bound to the micelles will contribute to the pH.

Fig. 6.2 illustrates the results of Bunton et al. for SDS at 25^oC, showing the fraction of the total H^+ ions available, which is bound to the micelles (i.e. H_m/H_T), as a function of the surfactant concentration.

From these experimental results they obtained an expression for the value of H_m as a function of the total ion concentrations:-
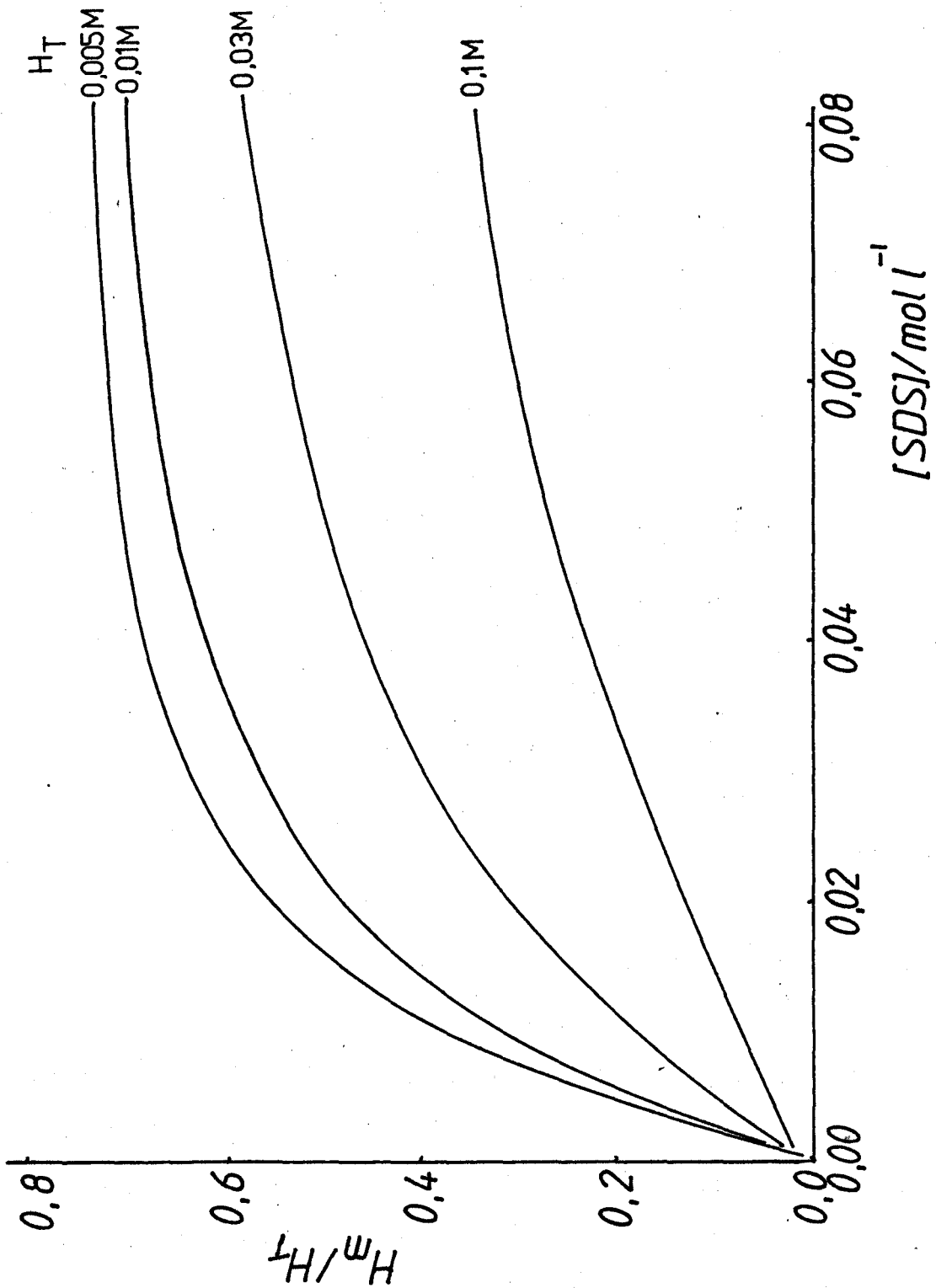
Fig. 6.2   The fraction of H^+ ions bound to SDS micelles as a function of the acid and surfactant concentrations at 25^oC (Bunton et al. 1977)

$$\frac{H_m}{C} = 0.82 \frac{H_T}{Na_T + H_T} \qquad\qquad 6.28$$

This is analogous to the expression for H_m/CV obtained by Romsted (1975) in his theoretical analysis of micellar catalysis, at the limit of low surfactant concentration.

$$\frac{H_m}{CV} = \beta S \frac{K_{H/Na} H_T}{K_{H/Na}H_T + Na_T} \qquad\qquad 6.29$$

where, $S = 1/V$.

Therefore, the expression of Bunton et al corresponds to that of Romsted with a value of $\beta = 0.82$ and the ion-exchange constant, $K_{H/Na}$, equal to unity at $25^{\circ}C$ for SDS in the range of surfactant concentration up to 0.06M.

However, in looking at the effect of the acid concentration on the rates of the hydrolysis reaction, we are more concerned with the effect of H_T on H_m rather than with the effect of C_T. Fig. 6.3 shows the variation in H_m with H_T based on the expressions of Quina and Chaimovich (1979), equation 6.25, using the appropriate values for the variable parameters for SDS under the conditions used for the kinetic experiments. The variation in the CMC with $HClO_4$ concentration is taken to be the same as that for the variation with NaCl concentration as determined by Shinoda (1955) and listed in Table 6.1. These values are used throughout this chapter. The second independent variable is the ion-exchange constant $K_{H/Na}$.

We can see that the number of H^+ ions bound to the micelles increases with the total acid concentration, H_T, to a limiting value (that is on the assumption that β remains constant and the limiting value corresponds to $H_m = \beta C$, i.e. when all the Na^+ ions bound to the micelle are replaced by H^+ ions). This limiting value in Fig. 6.3 is 0.021 mol/litre, using a value of β of 0.6 (corresponding to the
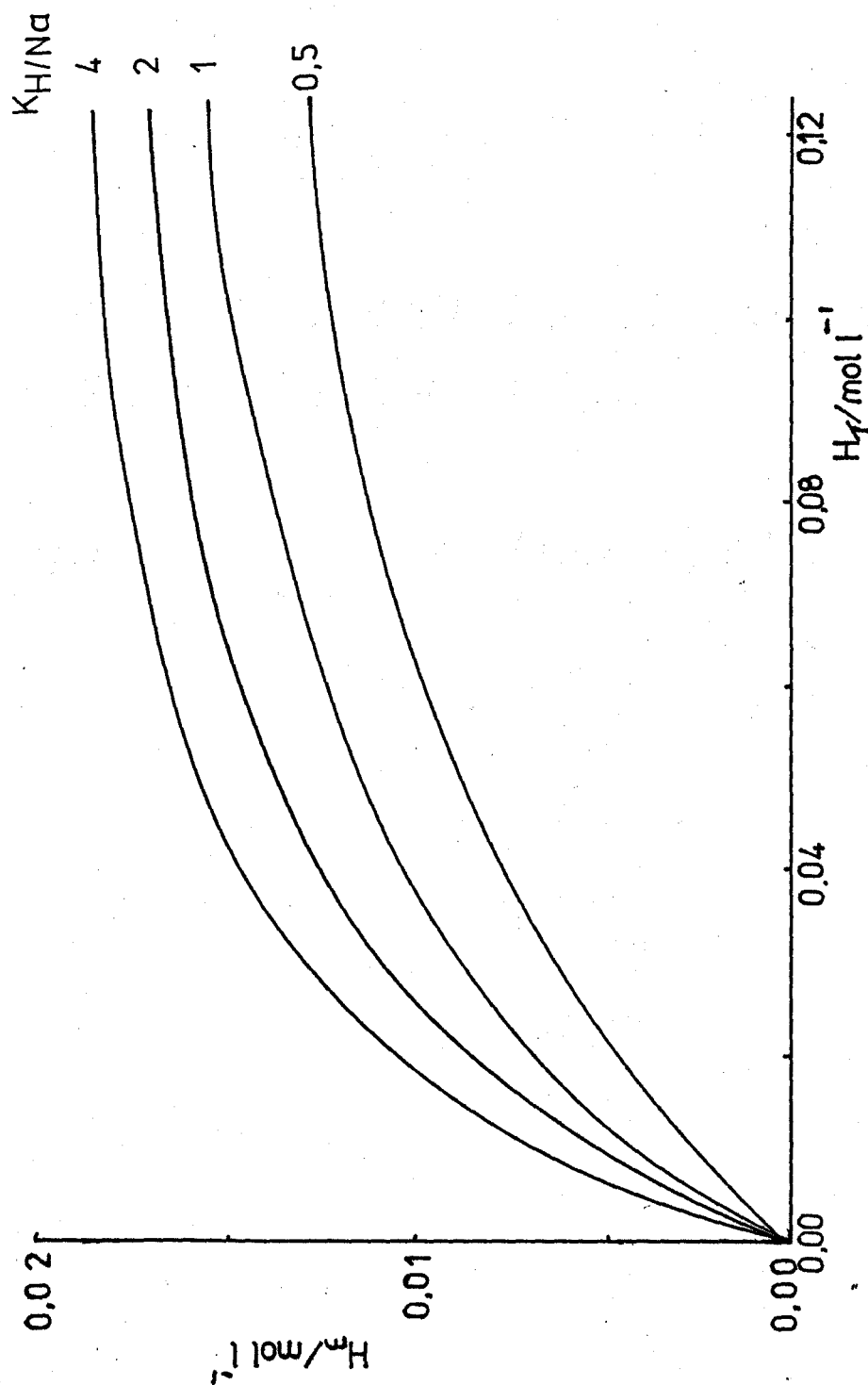
Fig. 6.3   The effect of H_T and $K_{H/Na}$ on the calculated value
of H_m, using equation No. 6.25, for 0.035M SDS at
70°C (α = 0.4, CMC varies with H_T).

Table 6.1

THE EFFECT OF ADDED NaCl ON THE CMC
OF SDS AT 70°C (Shinoda 1955)

[NaCl]/mol l^{-1}	CMC/10^{-3} mol l^{-1}
0.00	6.60
0.01	4.50
0.02	3.15
0.05	2.35
0.10	1.60
0.20	1.20
0.50	0.75

experimental data of SDS at 70°C, Barry and Wilson 1978).

6.4.3   Effect of H_T on the initial rate of hydrolysis of SDS and SDE$_2$S at 0.035M surfactant

Fig. 6.4 illustrates the effect of the total acid concentration on the initial rate of hydrolysis, at 70°C and 0.035M surfactant for both SDS and SDE$_2$S, while Fig. 6.5 shows the corresponding results for SDS at 90°C.

If one is correct in assuming that under these reaction conditions the degree of ion binding is independent of the acid concentration, then we would expect, from the variation of H_m with H_T in Fig. 6.3, that the observed initial rate of reaction should increase with the acid concentration until a limiting value is reached. The results in Figs. 6.4 and 6.5 do indeed show such tendencies, though the maximum value of H_T used, 0.16M, is obviously not high enough to obtain an actual limiting value to the rate (the achievement of an actual limit to the value of the rate will depend on both the maximum value of H_T used and upon the value of the ion exchange constant $K_{H/Na}$; the lower this value the higher the concentration of acid needed to show a limiting rate).

In order to compare the experimentally observed results and those calculated from equations 6.25 and 6.7 for the effect of H_T on the initial rate, one has to make a number of assumptions in order to obtain values for both $(H_m)_{calc.}$ and (initial rate)$_{calc.}$ The values of H_m shown in Fig. 6.3 were obtained from equation 6.25 using literature values for the CMC and β for SDS and the assumption that β is independent of the ionic strength. These values can then be used to plot the calculated variation of the initial rate with H_T using equation 6.7 and the case of dilute solutions ($1-CV \simeq 1$):-

$$\text{initial rate} = k_m H_m / V_s + k_w H_w \text{ CMC}$$
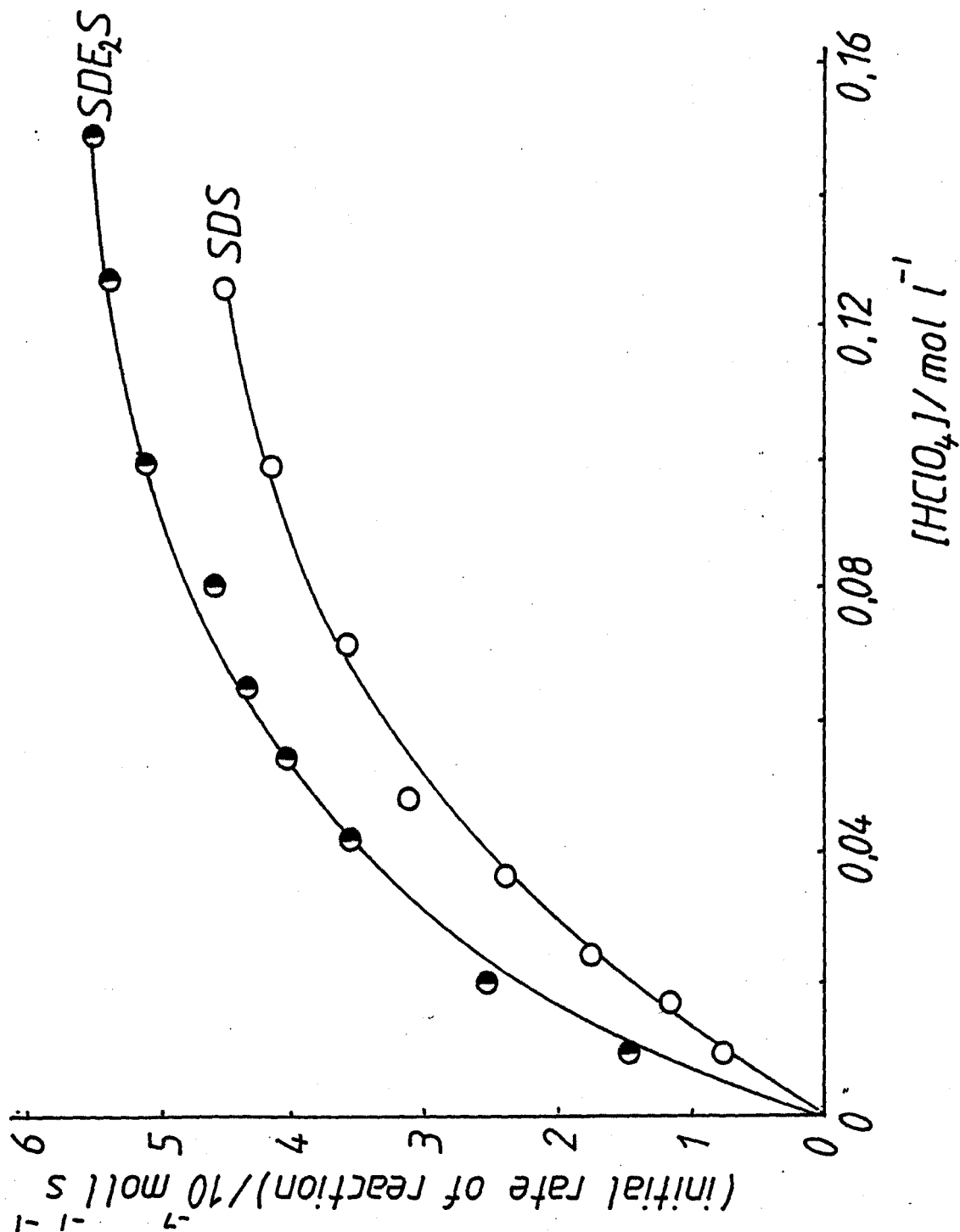
Fig. 6.4   The effect of the acid concentration on the initial
            rate of hydrolysis of 0.035M SDS (O) and 0.035M SDE$_2$S (●)
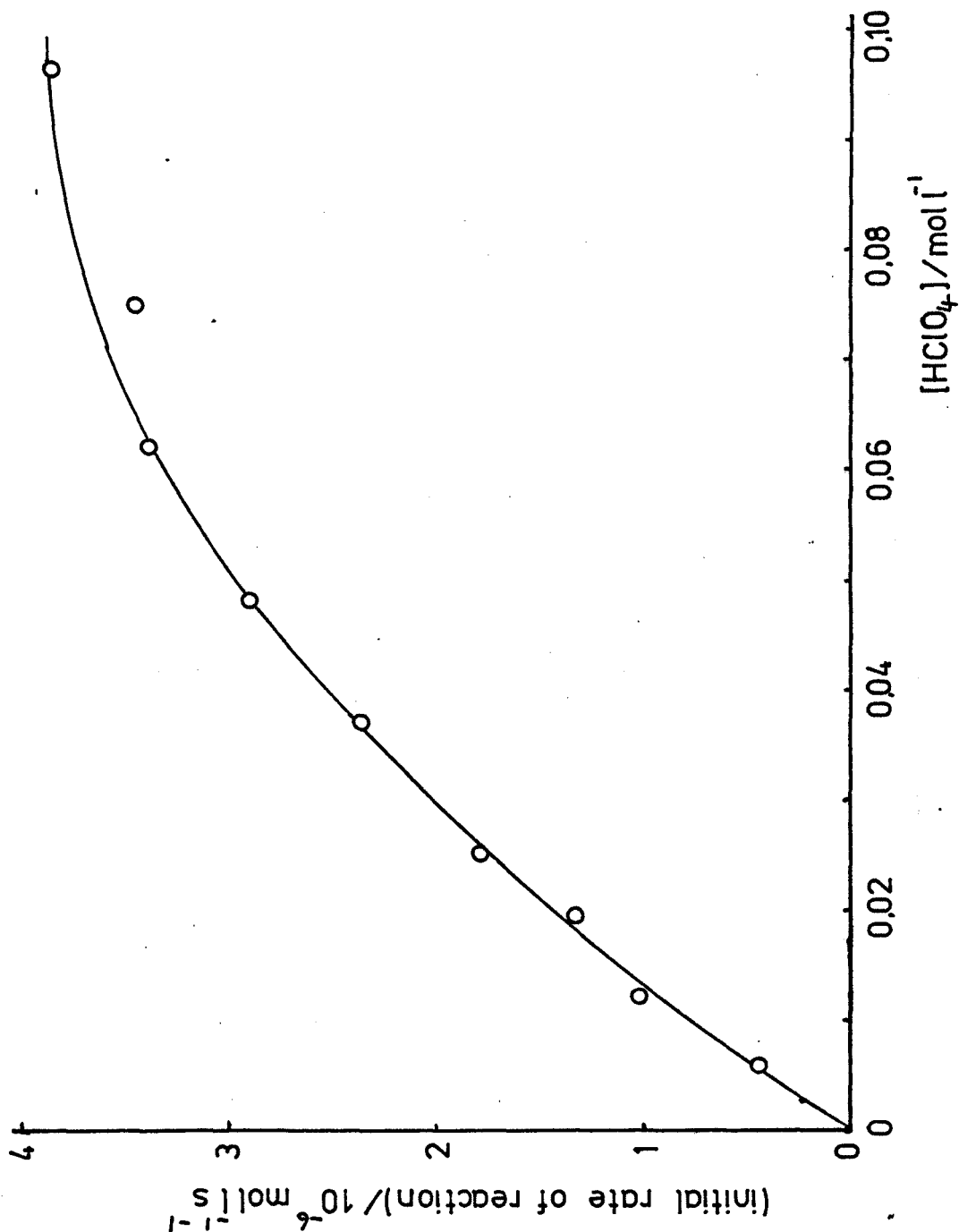   at 70°C.

Fig. 6.5   The effect of the acid concentration on the initial
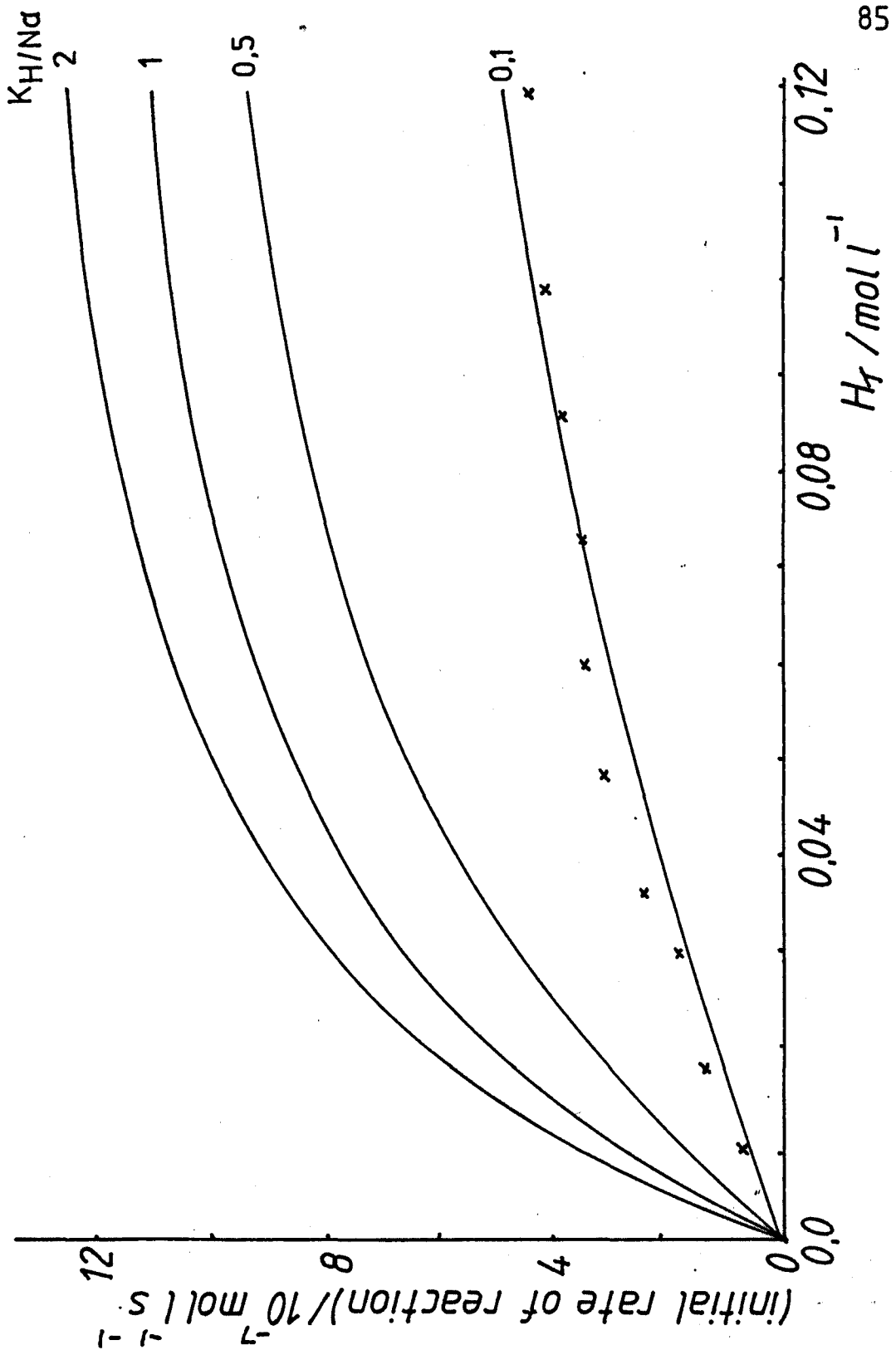rate of hydrolysis of 0.035M SDS at 90°C.

Fig. 6.6   The effect of H_T on the calculated (——) and experimental (X) values of the initial rate of hydrolysis of 0.035M SDS at $70^{\circ}C$, with $k_m/k_w = 1$.
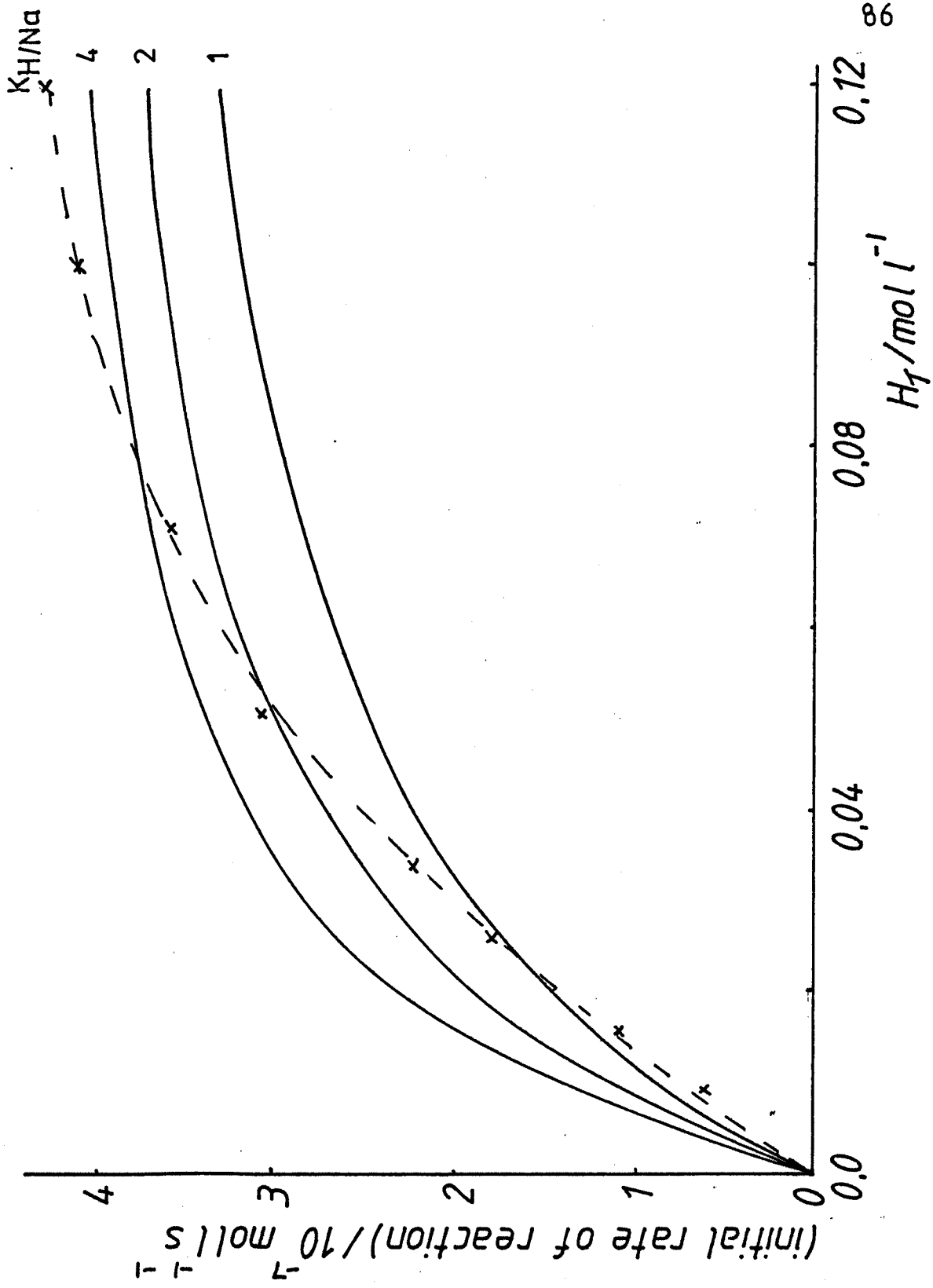
Fig. 6.7   The effect of H_T on the calculated (——) and experimental (—x—) values of the initial rates of hydrolysis of 0.035M SDS at 70°C, with $k_m/k_w = 0.3$

Thus we need to make a further assumption as to the value of the second order rate constant in the micelle phase, k_m. The value of k_w is known from measurements carried out at surfactant concentration below the CMC. We also need to obtain a value for the Stern layer volume, V_s.

The value of V_s has been determined by a number of people for SDS, though usually at low surfactant concentration and in the absence of electrolytes, which are known to increase the size of micelles. However at $70^{\circ}C$, Mazer et al. (1976), using light scattering measurements, found that micelles assume the size and shape of the small spherical micelles usually present at concentrations in the region of the CMC. This effect was found to be independent of the electrolyte concentration at surfactant concentrations up to 0.07M. Thus we may be justified in assuming that the value of V_s is that of spherical micelles and is independent of the acid concentration. Therefore we have used a value of 0.14 1 mol^{-1}, as used by Bunton et al. (1978).

Where a comparison has been made between the experimentally determined values of k_w and k_m, it has usually been found that k_m is either equal to or somewhat smaller than k_w.

The other variable used in the calculation of the value of H_m and the reaction rate is that of the ion-exchange constant, and it is this which gives rise to the different curves in Figs. 6.3 and 6.6.

Fig. 6.6 shows the variation in the calculated reaction rate with acid concentration, using the parameters for SDS at $70^{\circ}C$ and $k_m = k_w$. We can see that for the experimental results, also included, to correspond to these conditions, the ion-exchange constant must be in the region of 0.1, that is the Na^+ ions are bound more strongly than the H^+ ions. This fact is inconsistent with later results on the effects of electrolytes on the reaction rate, so that we conclude that k_m is less than k_w and Fig. 6.7 illustrates the effect of acid

concentration on the calculated and experimental reaction rates with $k_m/k_w = 0.3$. In this case we can see that the experimental results cross over those calculated using different ion-exchange constants, though they are in the region of the values for $K_{H/Na}$ being of the order of 1.0 to 4.0. The difference between the calc. and expt. curves indicates that the parameters used in the calculation may not be accurate enough, for example the value for the Stern layer volume. Also the fact that the approach to the limiting value in the rate is slower for the experimental results compared to the calculated ones could indicate that the degree of ion binding is indeed affected by the ionic strength. If the ion binding increases with the ionic strength, then the maximum value of H_m and the value of the limiting rate will increase, and the concentration of acid at which this limit is attained will also increase.

6.4.4   Effect of H_T on the initial rate of hydrolysis of SDS
at 0.35M

We also investigated the effect of the acid concentration on the rate of hydrolysis of SDS at high surfactant concentration, 0.35M (10% by wt.), and 70^oC. In this case the maximum value of the acid concentration used is much less than the surfactant concentration so that we would not expect to observe a limit to the rate of hydrolysis as the micelles will continue to take up a large proportion of the excess acid.

Fig. 6.8 shows the variation in the value of H_m, calculated using eq. 6.25, with acid concentration, again with the parameters for SDS under the reaction conditions. These results were then used to obtain Fig. 6.9 which illustrates the effect of H_T on the calculated values of the initial reaction rate, and which includes also the plot of the experimental results. In this diagram we have used $k_m/k_w = 0.3$.
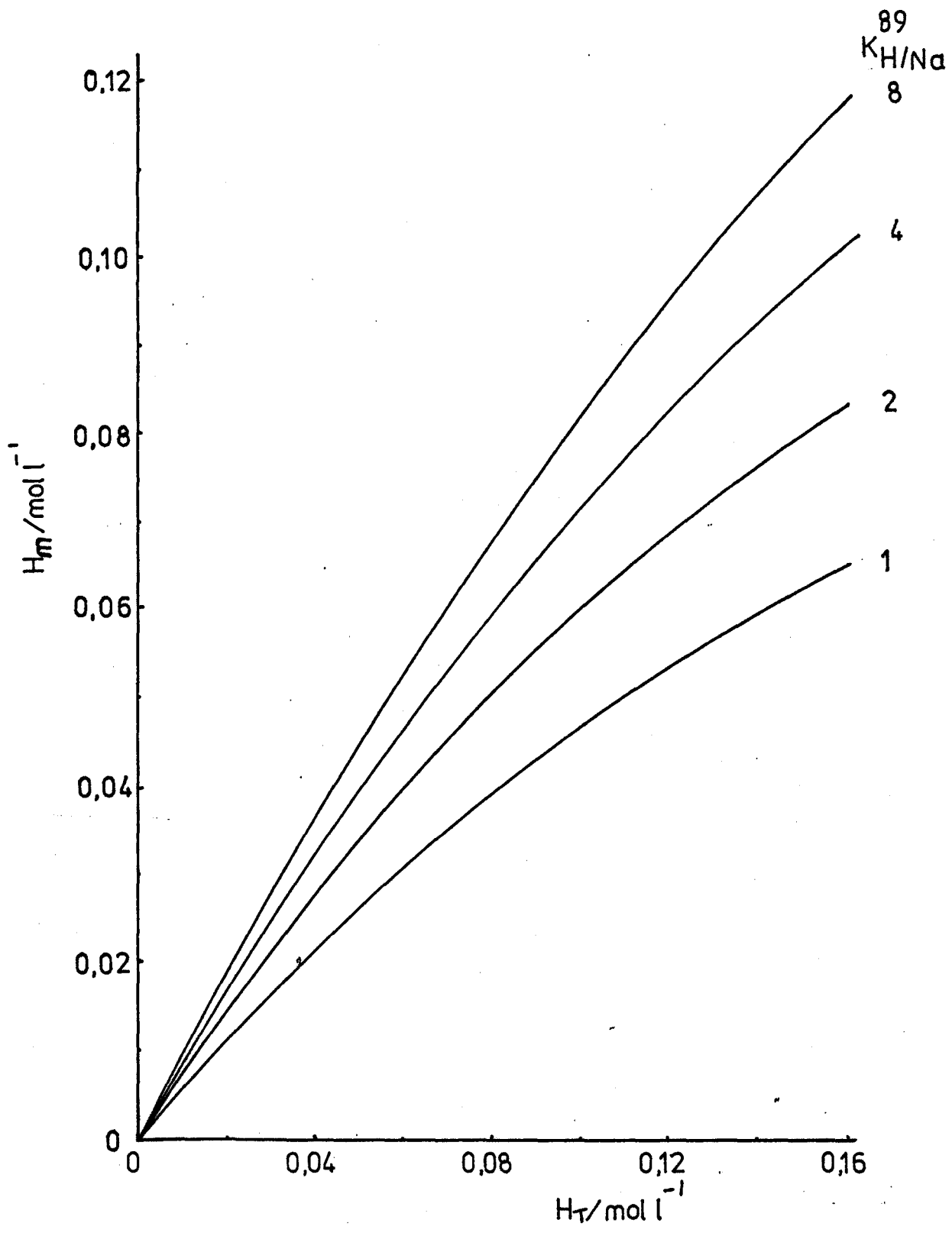
Fig. 6.8 The effect of H_T on the calculated value of H_m (using equation 6.25) for 0.35M SDS at 70°C (α = 0.4, CMC varies with H_T).
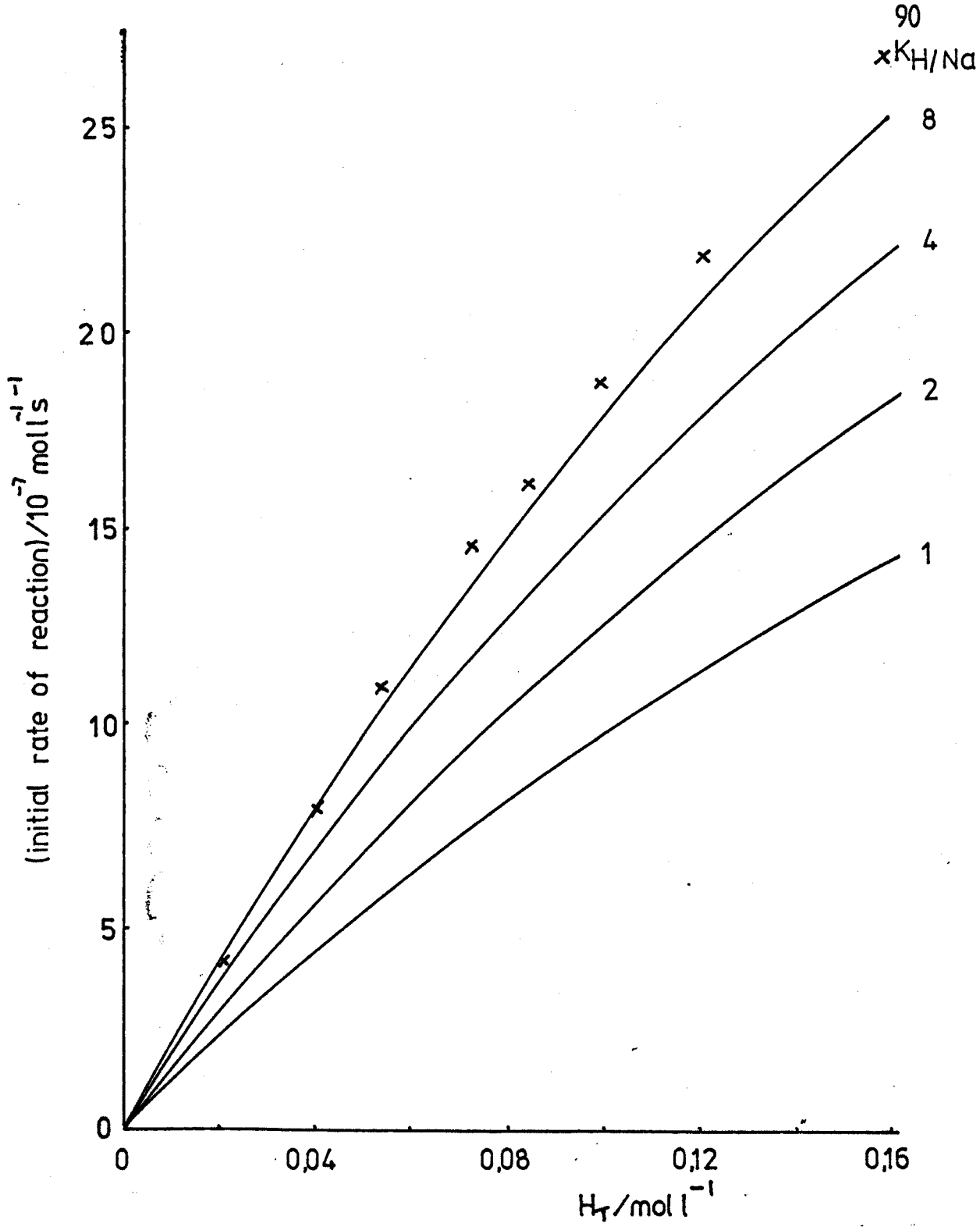
Fig. 6.9   The effect of H_T on the experimental (———) and the
calculated (x) values of the initial rate of
hydrolysis of 0.35M SDS at 70°C (k_m/k_w = 0.3).

The plots again show some curvature which increases with a decrease in the ion-exchange constant. The experimental results fit the calculated values for these conditions much better than for the lower surfactant concentration, though this agreement may well be artificial as the range of acid concentrations used is much smaller, when compared to the surfactant concentration, at this high value of the concentration of SDS (i.e. one would expect better agreement when the results are confined to the relatively linear portion of the plots).

The experimental results, using this value of k_m/k_w, indicate a high value for $K_{H/Na}$ of 8.0. In all the other experimental conditions we have not found a value of the ion-exchange constant greater than 4.0. The high value under these conditions may well be a result of the high ionic strength and the fact that $K_{H/Na}$ is a concentration constant.

If we now define a new ion-exchange constant including the activity coefficients of the species:-

$$K'_{H/Na} = \frac{H_m \, Na_w}{H_w \, Na_m} \cdot \frac{\gamma H_m}{\gamma H_w} \cdot \frac{\gamma Na_w}{\gamma Na_m}$$

$$K_{H/Na} = K'_{H/Na} \cdot \frac{\gamma Na_m}{\gamma H_m} \cdot \frac{\gamma H_w}{\gamma Na_w}$$

where $K'_{H/Na}$ will be a constant, independent of the ionic strength, then if we assume $\dfrac{\gamma Na_m}{\gamma H_m}$ will be constant as the ionic strength of the Stern layer remains constant, $K_{H/Na}$ will vary depending on the relative values of the activity coefficients of the H^+ and Na^+ ions in the aqueous bulk. These activity coefficients are both found to initially decrease with ionic strength and then to pass through a minimum value before increasing; however at all values of the ionic strength γH_w is found to be greater than γNa_w and the ratio $\gamma H_w / \gamma Na_w$ increases with ionic strength (Stokes and Robinson 1948). Thus we would expect $K_{H/Na}$ to increase with the ionic strength of the system as is observed in the experimental results.

6.4.5   The effect of H_T on $k_{2,obs.}$ at constant C_T

Fig. 6.11 illustrates the effect of the acid concentration on the second order rate constant for the hydrolysis at $70^{\circ}C$ of 0.035M SDS and SDE_2S and 0.35M SDS.

In all three cases $k_{2,obs.}$ decreases with H_T which is expected when compared to the theoretical variation obtained using eq. 6.7 and neglecting any reaction in the aqueous phase.

$$k_{2,obs} = \frac{k_m H_m}{C_T H_T V_s} \qquad\qquad 6.7a$$

We have seen earlier (see section 6.4.2 and Fig. 6.3) that at low surfactant concentration the concentration of H^+ ions on the micellar surface does not increase linearly with H_T but increases to a limit, at which all the counterions on the micellar surface have been replaced by H^+ ions. Therefore in eq. 6.7a as k_m, C_T, and V_s remain constant, $k_{2,obs.}$ is dependent on H_m/H_T which decreases with H_T.

At the higher concentration of SDS the value of $k_{2,obs.}$ is found to be almost constant, since most of the H^+ ions will always be taken up by the micelles so that H_m increases almost linearly with H_T (as shown in Fig. 6.8 for the variation of the calculated value of H_m with H_T at 0.35M SDS), therefore H_m/H_T and $k_{2,obs.}$ are almost constant.

In comparing the effect of H_T on the rate constants for 0.035M SDS and SDE_2S we find that the decrease in $k_{2,obs.}$ is more pronounced for SDE_2S than for SDS. Again if we relate this to eq. 6.7a where, at constant C_T and over the same range in H_T, the value of $k_{2,obs.}$ is determined by the value of $k_m H_m/V_s$ which must therefore be greater for SDE_2S than for SDS. Thus the concentration of H^+ ions in the Stern layer must be greater for SDE_2S than for SDS at the same value of H_T and C_T. This is consistent with a greater value of $K_{H/Na}$ for SDE_2S as compared with SDS which is found to arise in the experimentally
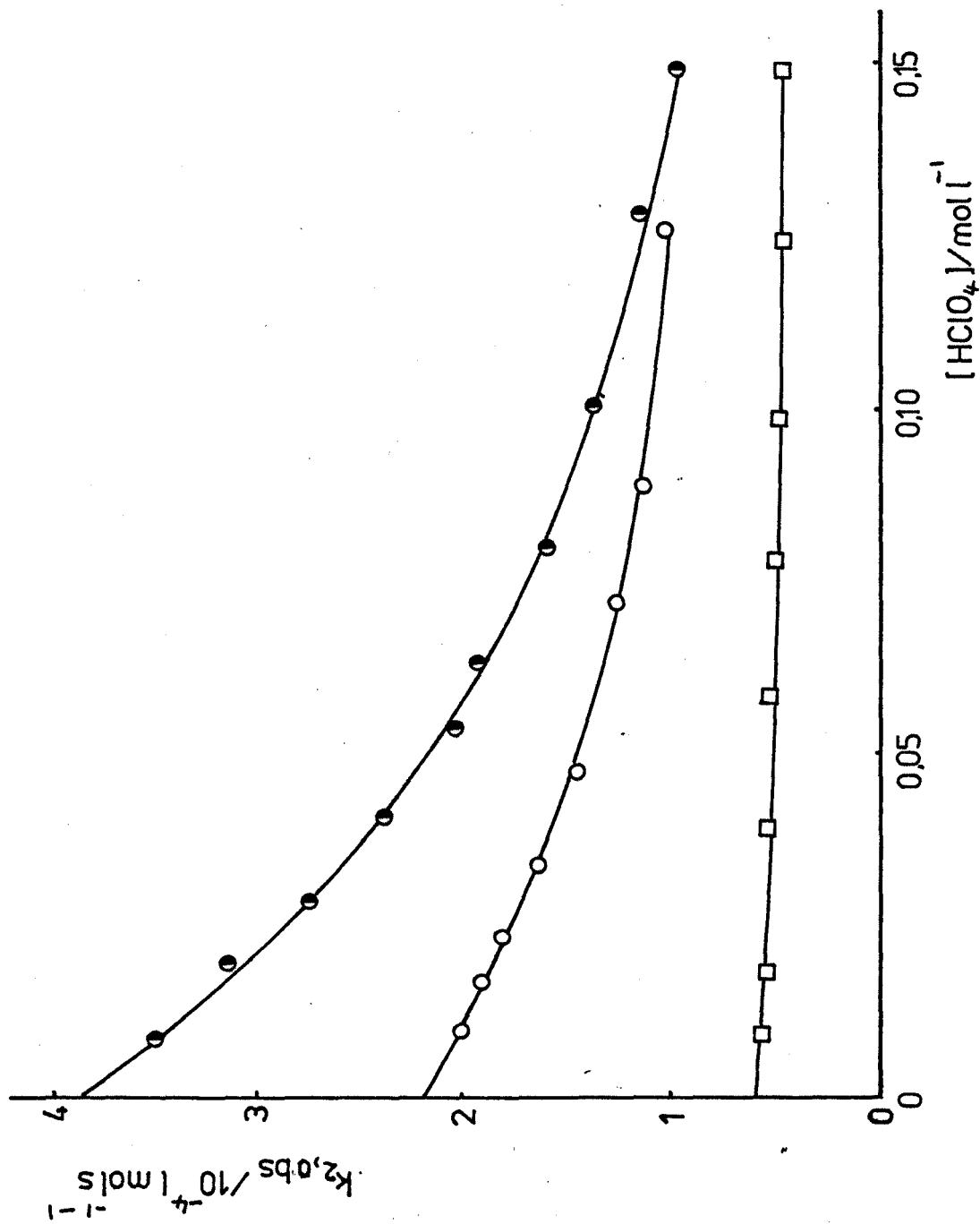
Fig. 6.11   The effect of the acid concentration on the
experimental second order rate constants for the
hydrolysis of 0.035M SDS (O), 0.035M SDE_2S (◐),
and 0.35M SDS (□) at $70^{\circ}C$.

determined values from the effects of NaCl on the rates of hydrolysis described in section 6.6 (see Tables 6.2 and 6.3). The greater preferential binding of H^+ ions by micelles of SDE_2S could be due to a co-operative effect of the ethoxy groups in H-bonding.

6.5 THE EFFECT OF THE SURFACTANT CONCENTRATION ON THE HYDROLYSIS OF SEVERAL METAL DODECYL SULPHATES, MDS, AND SDE_2S

6.5.1 Introduction

As described in Chapter 3 the general appearance of the profile for the variation in second order rate constant with surfactant concentration for a micelle catalysed reaction shows a rate enhancement above the surfactant CMC to a maximum value, followed by inhibition of the catalysis at higher surfactant concentrations. This picture is for the general case of micellar catalysis involving the reaction between a hydrophilic ion and an organic substrate, and the effects are attributed to the extent of substrate partitioning between the aqueous and micellar phases and to the binding of the reactive ion to the micelle Stern layer. In the case of the hydrolysis of dodecyl sulphates and dodecyl ether sulphates, the former effect is a constant as the substrate is also the micelle forming species, and the rate is solely dependent on the binding of the H^+ ion to the micelles.

The constancy of the distribution of the substrate between the two phases arises from the assumption that above the CMC all the additional surfactant forms micelles. Hence the distribution constant becomes:-

$$K_{dist.} = \frac{(C_T - CMC)/CV}{CMC} \qquad 6.30$$

however $C_T - CMC = C$ so that:-

$$K_{dist.} = \frac{1}{V\ CMC} \qquad 6.31$$

which is a constant. That is to say that no 'dilution' of the reactant

(surfactant head groups) can occur at higher surfactant concentration without a change in micellar structure. Their concentration remains equal to the molar density of the micelles, $S = {}^1/_V$, where V is the molar volume of the surfactant.

We have investigated the effect of the surfactant concentration on the rate of hydrolysis under a number of conditions:-

(a) The hydrolysis of SDS at constant H_T.

(b) The hydrolysis of SDS at constant H_T and Na_T.

(c) The effect of changing the counterion of the surfactant on (a) and (b).

(d) The effect of ethoxylating the carbon chain of SDS on (a) and (b).

6.5.2   The effect of surfactant concentration on the hydrolysis of SDS at constant acid concentration

By looking at equation 6.7 of the theoretical analysis of the effect of micellisation on the kinetics of the hydrolysis, we can see that the observed second order rate constant will largely be determined by the term $k_m H_m / C_T H_T V_s$ at concentrations of surfactant above the CMC. Therefore, under the condition of constant H_T and assuming that k_m and V_s are independent of C_T, the effect of C_T on the second order rate constant $k_{2,obs}$ should be a reflection of the change in $H_m/C_T V_s$ which is approximately $\overline{H}_m$, the concentration of H^+ ions in the Stern layer of the micelles.

Figs. 6.13 and 6.14 illustrate the effect of C_T on the values of H_m and $\overline{H}_m$ calculated from equations 6.20 and 6.19, the second variable being the ion-exchange constant $K_{H/Na}$. The values for V_s, β and CMC again correspond to the literature values for SDS at 70°C and an acid concentration of 0.021M, which are the conditions used in the kinetic studies.

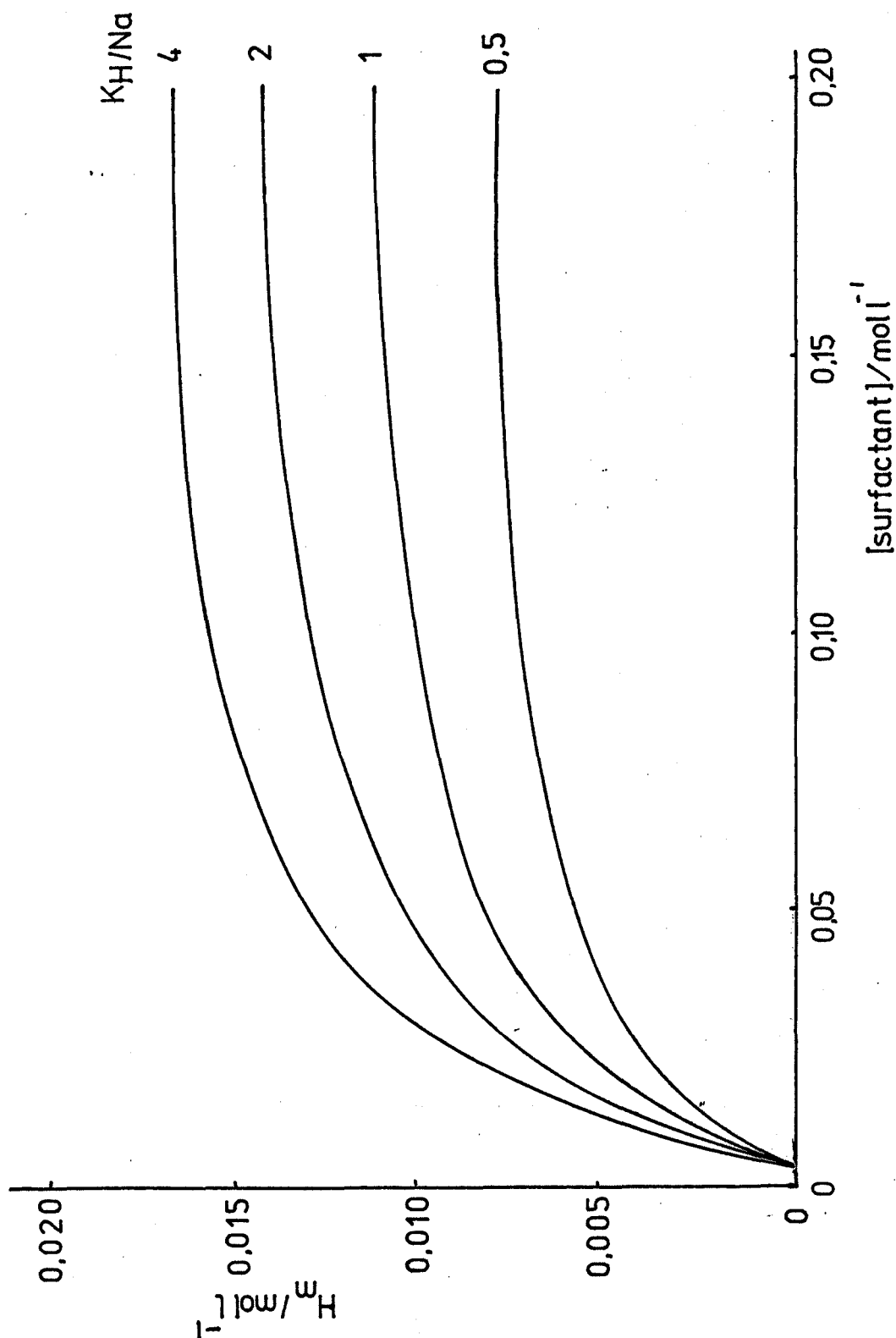The figures show that H_m increases with C_T until a limit to

Fig. 6.13   The effect of C_T and $K_{H/Na}$ on the calculated value

of H_m, using equation 6.20, for SDS at $70^{\circ}C$ and
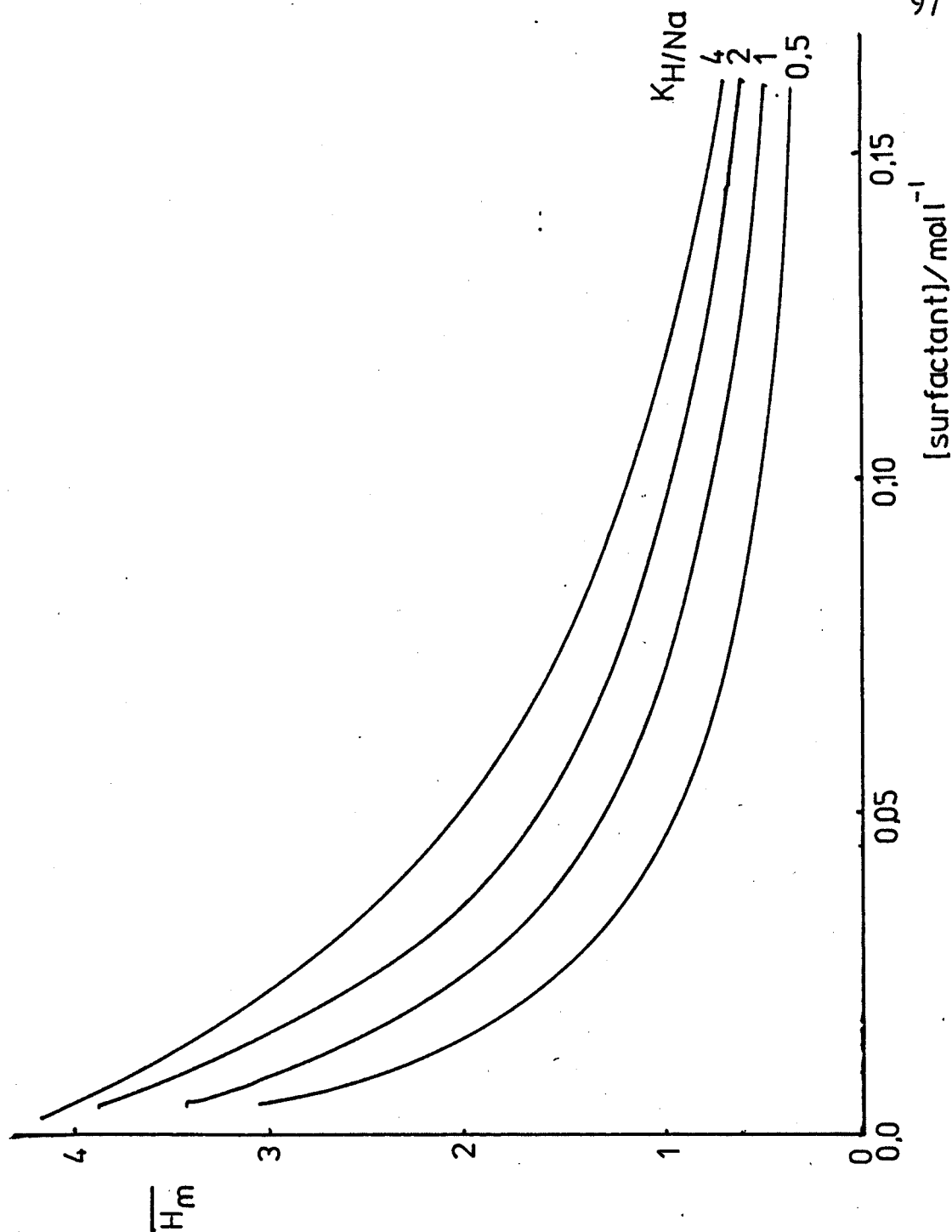
0.021M acid concentration (β = 0.6, CMC = 0.00315).

Fig. 6.14   The effect of C_T and $K_{H/Na}$ on the calculated value

of $\overline{H}_m$, using equation 6.19, for SDS at 70°C

(H_T = 0.021M, β = 0.6, CMC = 0.00315, V_s = 0.14ℓ/mol).

its value is reached, while $\overline{H}_m$ is a maximum at the CMC and thereafter decreases with C_T, that is, the total volume of the Stern layer, CV_s, increases faster than does H_m.

Figs. 6.15 and 6.16 illustrate the effect of C_T on the value of $k_{2,rel.}$ $(k_{2,obs} / k_w)$ calculated from equation 6.7: in Fig 6.15 $k_m/k_w = 1$ while in Fig. 6.16 $k_m/k_w = 0.25$, and as before the second variable is the value of $K_{H/Na}$.

In the case of the calculated curves a number of general features can be seen:-

(a) The maximum value of $k_{2,rel.}$ increases with the ion-exchange constant.

(b) The surfactant concentration at which this maximum occurs also increases with $K_{H/Na}$, and is in the region 0.01M to 0.02M (approx. 3x the CMC).

(c) At high surfactant concentrations the curves for the different values of $K_{H/Na}$ tend to merge, corresponding to all the H^+ ions being bound to the micelles $(k_{2,rel.} \rightarrow 1/C_T V_s)$.

Also included in both Figures are the results obtained experimentally for the hydrolysis of SDS. In Fig. 6.15 the expt. results fall in the general area corresponding to a low value for $K_{H/Na}$ (<1), which seems unreasonable, because H^+ ions compete successfully with Na$^+$ ions for sites on the micellar surface (Bunton et al 1977). Therefore for Fig. 6.16, we have used $k_m < k_w$, particularly at low surfactant concentrations ($< 0.08M$), the experimental results correspond reasonably well to those for a value of $K_{H/Na}$ of the order of 1.5.

It is possible to justify the use of this k_m/k_w value in order to fit the calculated to the observed results in that both rate constants include a factor for the the water activity (see section 6.1).
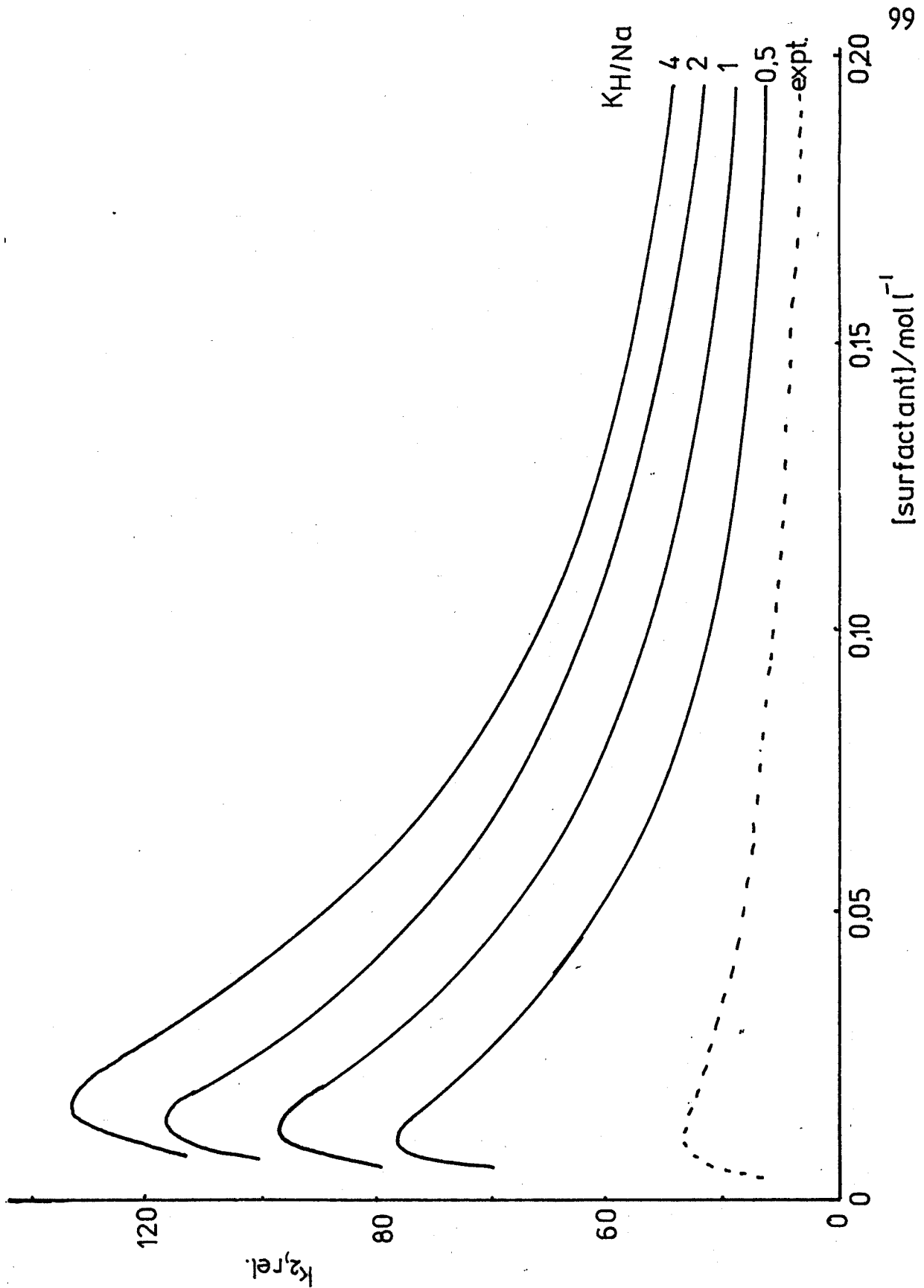
Fig. 6.15   The effect of C_T and $K_{H/Na}$ on the calculated (——),

and the effect of C_T on the experimental (---),

values of $k_{2,obs.}$ for the hydrolysis of SDS at 0.021M

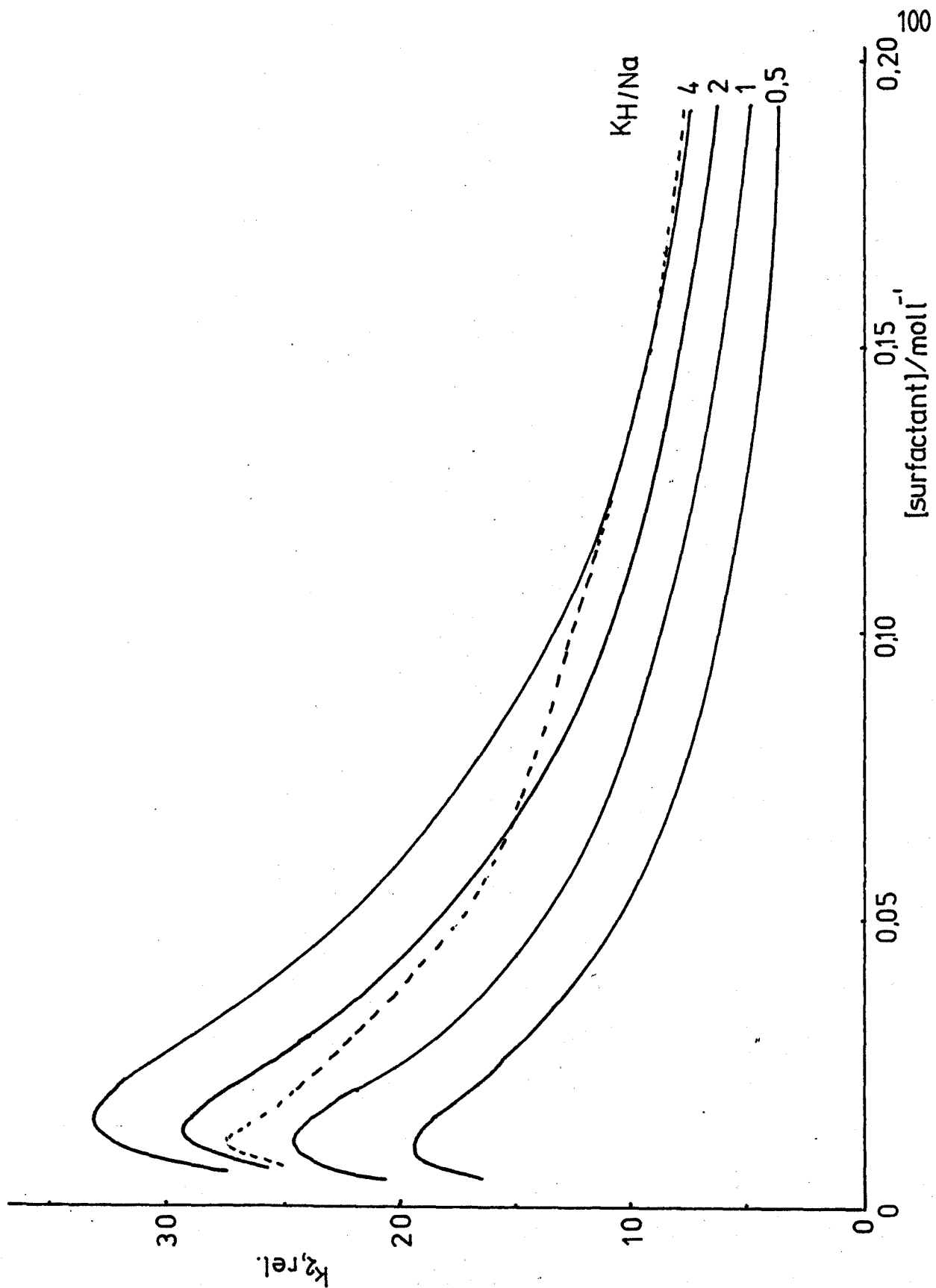acid concentration and $70^{0}C$ ($k_m = k_w$).

Fig. 6.16   The effect of C_T on the calculated (——) and experimental

(– – –) value of $k_{2,obs.}$ for the hydrolysis of SDS at 0.021M

acid concentration and $70^{\circ}C$ ($k_m/k_w = 0.25$).

The water in the Stern layer is largely water of solvation of the ions and head groups and as such will be less reactive than the aqueous bulk.

Also the ionic strength of the Stern layer is very high, of the order of 6M, which would tend to screen the oppositely charged reacting species, $ROSO_3^-$ and H^+, from one another and hence reduce the value of k_m compared to that of k_w.

6.5.4 The effect of surfactant concentration on the hydrolysis of SDS at constant H_T and Na_T

The kinetics of the hydrolysis were investigated at constant counterion concentrations ($H_T = 0.021M$, $Na_T = 0.6M$) in order to try to keep the ion-exchange effect (i.e. the ion competition for the micellar surface) constant, while increasing the amount of the micellar phase. In Romsted's (1975) theoretical analysis at low concentrations of surfactant and ideal conditions, he predicted that keeping both the concentrations of the reactive (H^+) ion and the non-reactive (Na^+) ion constant would lead to a plateau value for $k_{2,rel}$ as the surfactant concentration was increased. However conditions used in these experiments on SDS (up to 0.6M surfactant) fall outside the limits of Romsted's analysis, except for the special case of $K_{H/Na} = 1$.

Figs. 6.17 and 6.18 illustrate the effect of C_T on $k_{2,rel}$ at a constant concentration of Na^+ ion of 0.6M and the usual conditions for SDS at 70^oC (i.e. $[HClO_4] = 0.02M$, $Na_T/H_T = 30$, $\alpha = 0.4$, $V_s = 0.14$), calculated as before from equations 6.7, 6.20 and 6.25. We can see that apart from the case of $K_{H/Na} = 1$ we do not observe a plateau in the profiles. However over most of the range in surfactant concentration used, and for $0.5 < K_{H/Na} < 4.0$ the profiles are essentially linear, which is consistent with the experimentally observed results (see Fig. 6.20).
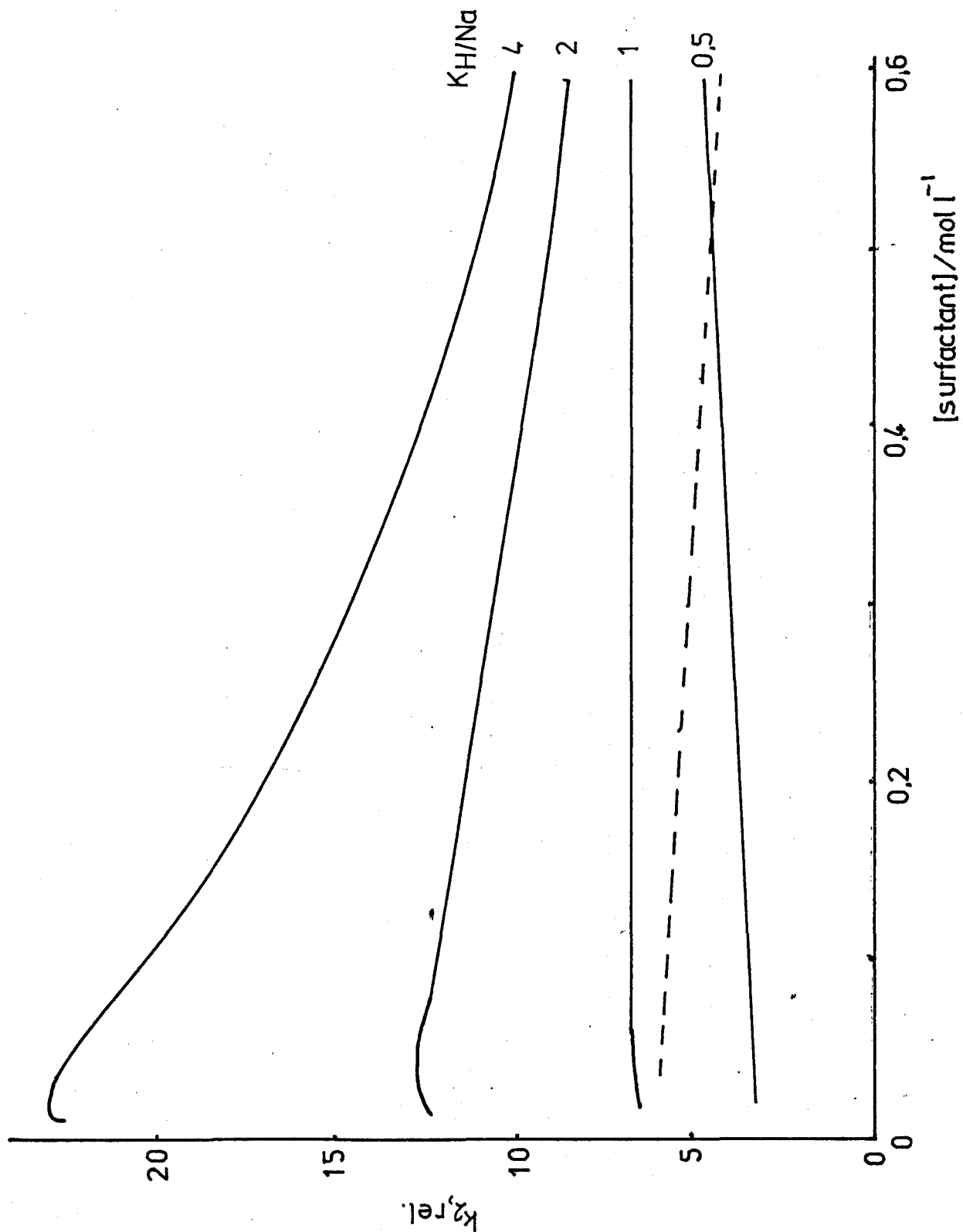
We have included in both Figs. 6.17 ($k_m = k_w$) and 6.18

Fig. 6.17   The effect of C_T on the calculated (———) and
experimental (— — —) values of $k_{2,obs.}$ for the hydrolysis
of SDS at 0.021M acid concentration, 70°C and a constant
Na$^+$ ion concentration of 0.6M ($k_m = k_w$).
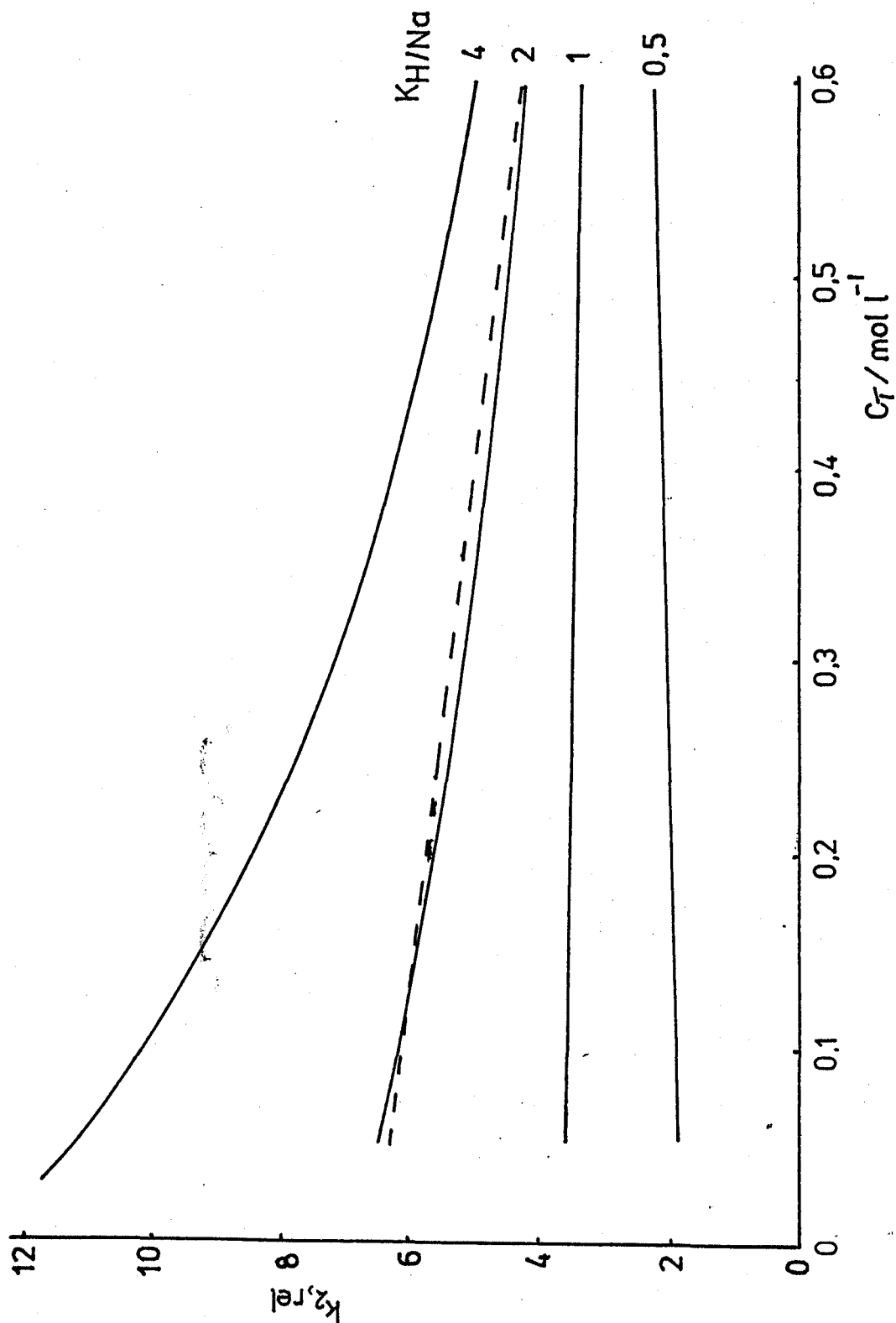
Fig. 6.18   The effect of C_T on the calculated (——) and
            experimental (---) value of $k_{2,obs.}$ for the hydrolysis
            of SDS at 0.021M acid concentration, 70°C and a
            constant Na$^+$ ion concentration of 0.6M (k_m/k_w = 0.5).

$(k_m/k_w = 0.5)$ the expt. results. The slope for the change in $k_{2,rel.}$ for SDS is -2.8, which corresponds to a value of the ion-exchange constant greater than unity (for $K_{H/Na} < 1$, the slope would be positive).

Comparing the experimental results with those calculated for Fig. 6.18 with $k_m/k_w = 0.5$ we see that they follow almost exactly the plot for $K_{H/Na} = 2.0$. However, the comparisons are not very rigorous, due to ignoring the effect of the high ionic strength and surfactant concentration on the parameters used in the calculations. If we accept the assumption that the ionic strength does not affect the ion binding to the micelles, then it is possible that k_m will be constant and independent of the ionic strength, while k_w will decrease with ionic strength due to the screening of the oppositely charged reacting species from one another. This can then be used as a justification for using the value 0.5 for k_m/k_w, rather than 0.3 which we used previously, to compare the observed and calculated results.

Taking into account these factors, the fact that $k_{2,rel}$ is almost linear over the range of surfactant concentration used indicates that:-

(a) $K_{H/Na}$ is greater than unity and of the order of 2.0.

(b) V_s and α remain constant over the range of C_T used at high ionic strength.

6.5.5 The effect of changing the counterion of the surfactant on the profiles for $k_{2,rel.}$ vs. C_T

We have also looked at the effect of C_T on the value of $k_{2,rel.}$ for lauryl sulphate surfactants with cations other than Na^+, i.e. NH_4^+, Li^+ and Mg^{2+}. In essence introducing another cation has the effect of changing the ion-exchange constant $K_{H/M}$, as different ions are bound to different degrees to the lauryl sulphate micelles (there will also be some effect due to differing values of α, but this will only be significant for Mg^{2+}).

Figs. 6.19 and 6.20 show the effect of changing the counterion on the variation of $k_{2,rel}$ with surfactant concentration. Fig. 6.19 is for the condition of constant acid concentration while Fig. 6.20 is at constant acid concentration and constant cation concentration. The two plots are consistent at first glance in that they predict the ion-exchange constants to vary in the order

$$NH_4 > Li > Na > Mg$$
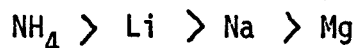
The differences in the curves in Fig. 6.19 are not great which would indicate that the values of $K_{H/M}$ do not vary very much on changing the cation, unless the cation also has an effect on the value of V_s or α which works in the opposite direction to the value of the ion-exchange constant. In Fig. 6.20 the variation of $k_{2,rel}$ with C_T at constant cation concentration is again found to produce essentially linear relationships with other counterions as with sodium. Again there are no really large differences in the values of the rate constants on changing the cations. Referring back to Fig. 6.18 it appears that the H^+ ion competes more effectively with the NH_4^+ ion ($K_{H/M} \simeq 4$) than with Li^+ ion or Na^+ ion ($K_{H/M} \simeq 2$).

6.5.6   The effect of ethoxylation of the carbon chain on the hydrolysis

Elsewhere we have described the effects of acid concentration (see section 6.4) and electrolyte concentration (see section 6.6) on the hydrolysis of both SDS and SDE_2S. We have also investigated the effects of including two ethoxy groups in the surfactant molecule on the surfactant concentration profile of the rate of the hydrolysis.

We found the general effects of both acid and electrolyte concentration on the hydrolysis of SDS and SDE_2S to be the same, except that the reaction is faster for SDE_2S. The same result is seen for the effect of surfactant concentration, shown in Fig. 6.21 : at all concentrations the rate is higher for SDE_2S, particularly at low
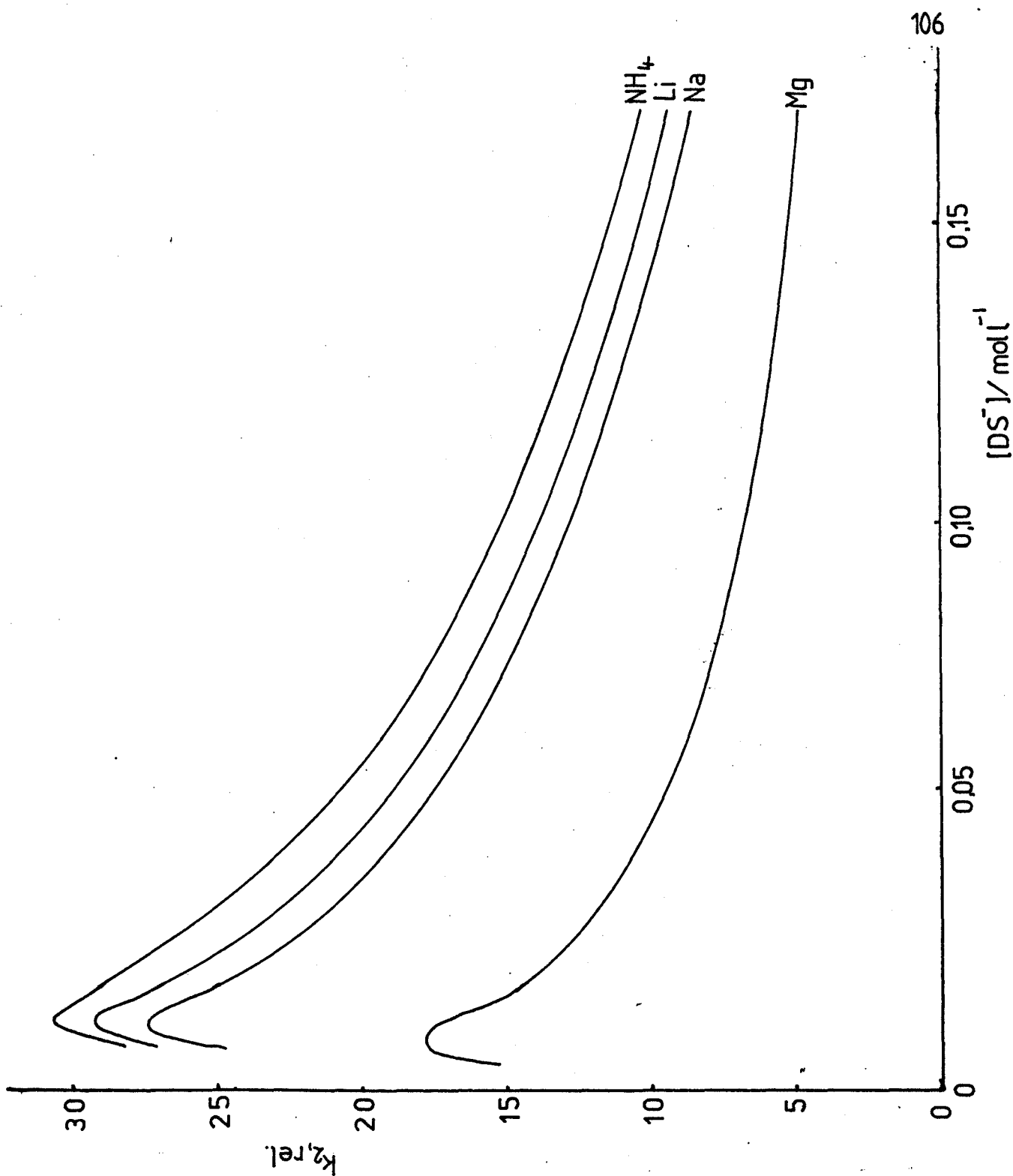
Fig. 6.19   The effect of surfactant concentration on the value

of $k_{2,obs.}$ for the hydrolysis of MDS (M = Na, Li, NH$_4$,

and Mg) at 0.021M acid concentration and 70°C.
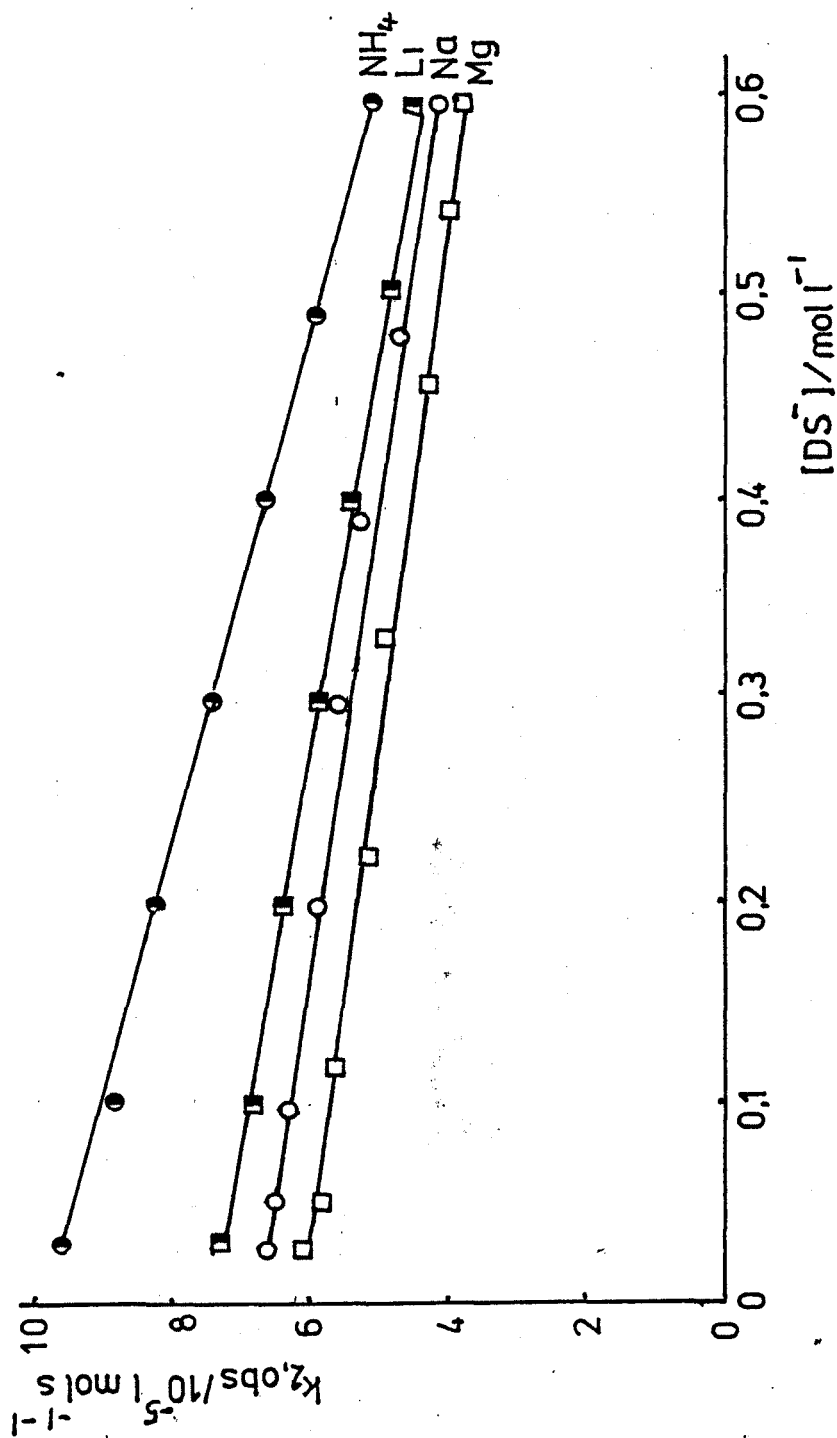
Fig. 6.20   The effect of surfactant concentration on the value

of $k_{2,obs.}$ for the hydrolysis of MDS (M = Na, Li, NH_4,

and Mg) at 0.021M $HClO_4$, $70^{o}C$ and a constant cation

concentration of 0.6M (0.3M for $MgDS_2$).
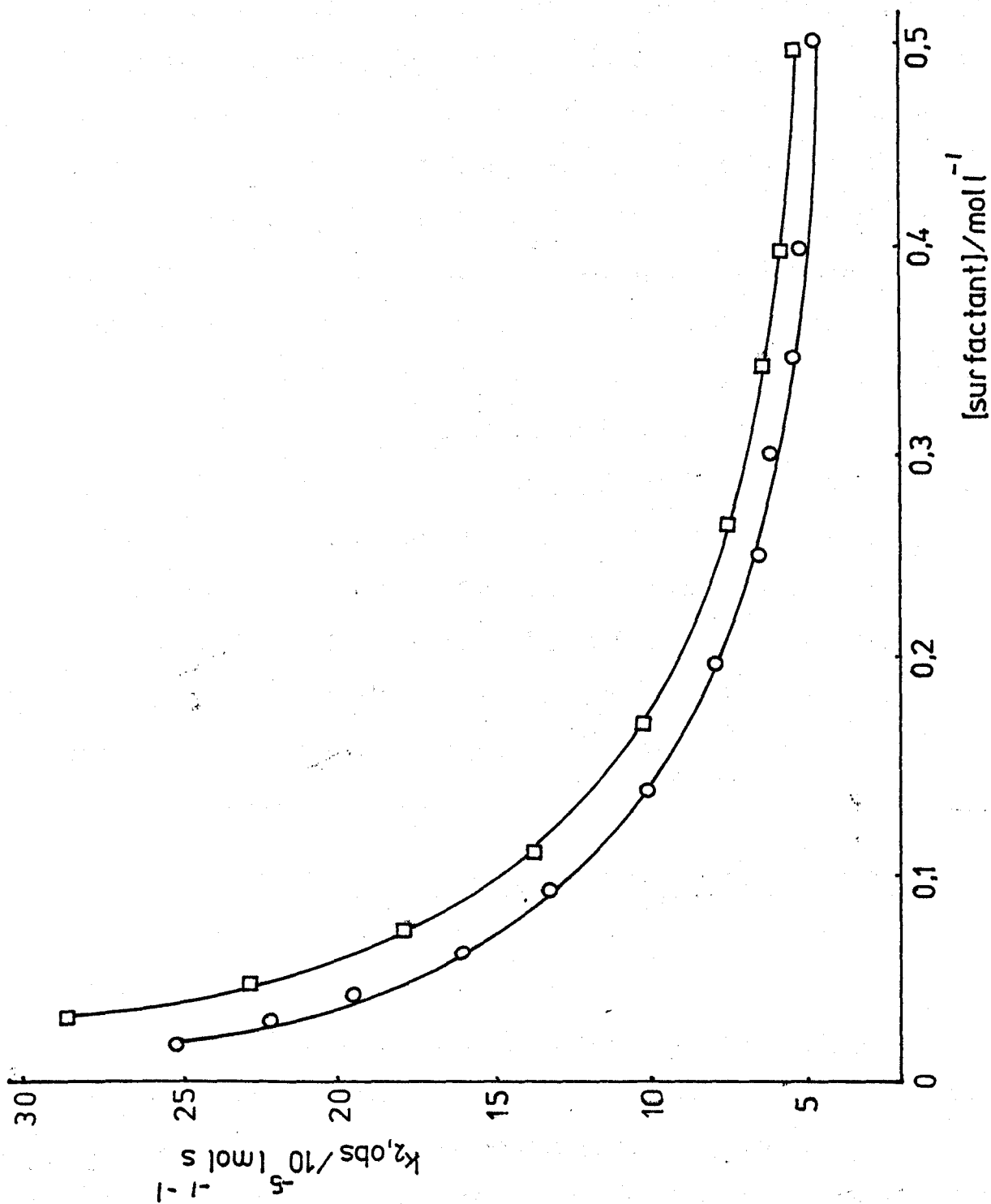
Fig. 6.21   Comparison of the effect of the surfactant

concentration on the rate of hydrolysis of SDS

(O) and SDE$_2$S (□) at 70°C and 0.021M HClO$_4$.

surfactant concentrations. A simple explanation for this could be put forward if we assume that k_w and V_s remain the same on ethoxylation of the surfactant, and that the enhanced rate is due to a higher value of the ion-exchange constant as already suggested (section 6.4.5). This is also indicated by the effects of electrolytes on the kinetics of SDE_2S described in section 6.6. Barry and Wilson (1978) have indeed shown that α is similar for the two surfactants at high temperatures. However, the value of V_s, is likely to be greater for SDE_2S due to the polar nature of the ethoxy groups, which being polar would penetrate the Stern layer to some extent. This would yield slower rates because of the dilution effect. This means that a larger value for k_m/k_w or the ion-exchange constant, or both, is needed to account for the observed results. If V_s is indeed larger and part of the solvation of H^+ ions is due to H-bonding to the ether oxygens, the reactivity of water in such an environment may be greater than in the Stern layer of SDS micelles (i.e. k_m/k_w may be greater).

6.6   THE EFFECT OF ADDED ELECTROLYTES ON THE ACID HYDROLYSIS OF SDS AND SDE_2S

6.6.1   Introduction

The addition of electrolytes has almost universally been found to inhibit the micellar catalysis of reactions involving ionic species. This is qualitatively explained as being due to the competition for binding sites on the micelles between the reactive ion and other ions present in the system due to the addition of the electrolyte. The extent of the inhibition is a reflection of the strength of the binding of the added counterion to the micelle.

For reactions involving cations as the reactive ion and anionic micelles, the inhibition follows the lyotropic series (Dunlap and Cordes, 1968), being greater for ions of smaller hydrated radius.

$$Li < Na < K < Cs < Mg < Ca$$
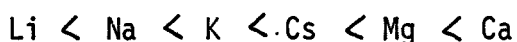
The only published instance of added electrolytes enhancing the rate of a micellar catalysed reaction is that of Bunton et al. (1971) who investigated the effects of electrolytes on the unimolecular decarboxylation of 6-nitrobenzisoxazole-3-carboxylate in the presence of CTABr micelles. Small hydrophilic ions were found to enhance the reaction rate in the order:-

$$CH_3CO_2^- \approx F < Cl < Br < SO_4^{2-}$$
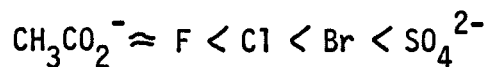
while larger anions were found to produce maxima in their reaction rate vs. electrolyte concentration profiles. These maxima, which followed the order:-

benzoate $<$ phenyl phosphate dianion $<$ tosylate

were also found to correspond to maxima found in the variation of the viscosity of the solutions with electrolyte concentration, which lead the authors to attribute the effects to changes in the shape and/or charge density of the micelles.

We have investigated the effects of added electrolytes on the hydrolysis of both SDS and SDE_2S at 0.035M surfactant concentration and for SDS at 0.35M. In the case of the lower surfactant concentration we have used the results to obtain values for the ion-exchange constants, $K_{H/X}$, where X is the added counterion.

6.6.2 Effect of added electrolytes on the hydrolysis of SDS and SDE_2S at 0.035M surfactant concentration.

The conditions used for the two surfactants are slightly different in that rate measurements were carried out at 90°C and 0.02M acid concentration for SDS, and at 70°C and 0.0425M acid concentration for SDE_2S.

Figs. 6.22 and 6.23 show the variation $k_{2,rel.}$ (rate constant in the presence of the salt divided by the rate constant in the absence of salt) as a function of electrolyte concentration for SDS and SDE_2S, respectively. In both cases the electrolytes are all found to inhibit
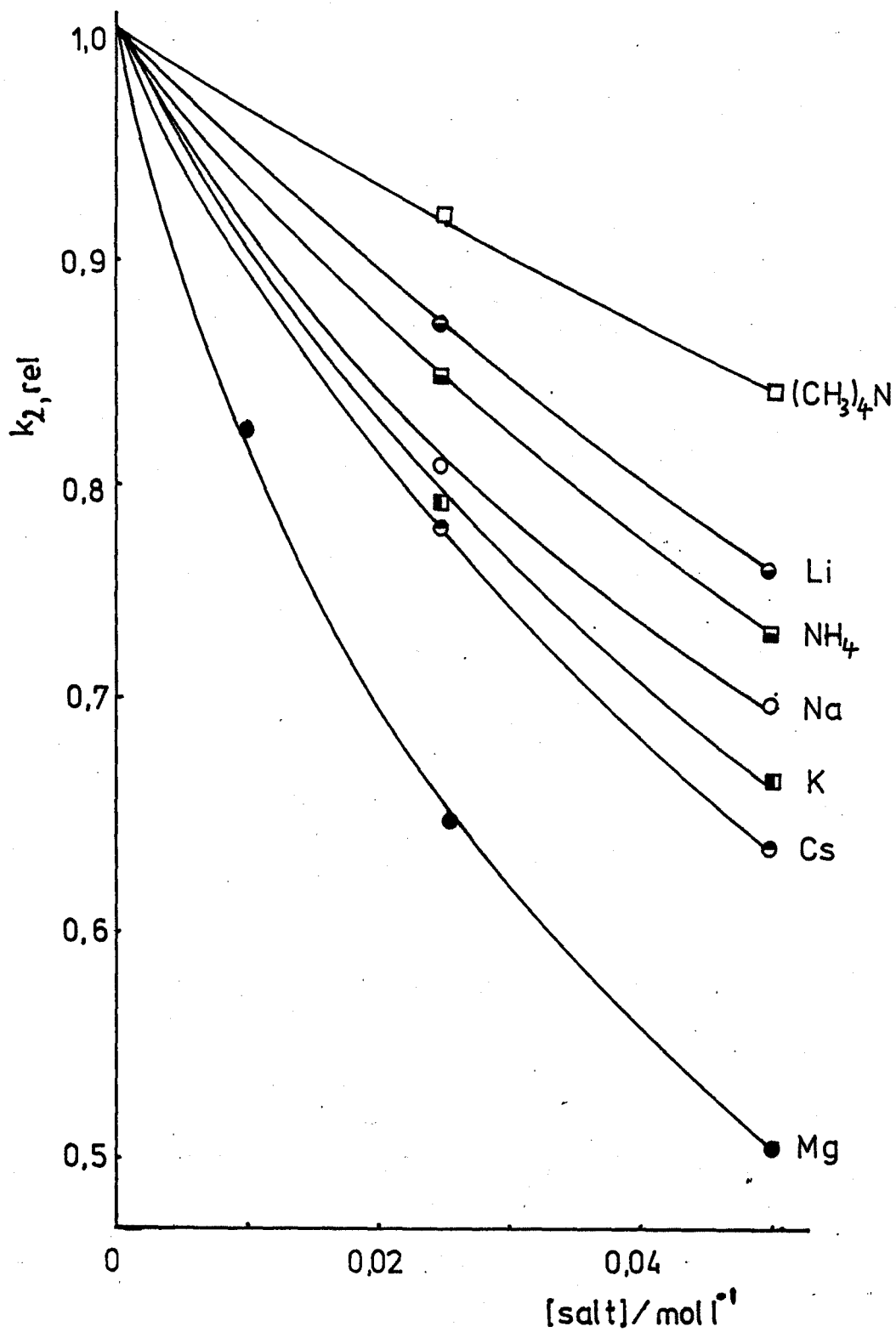
Fig. 6.22   The effect of electrolyte concentration on the
relative rate constants for the hydrolysis of
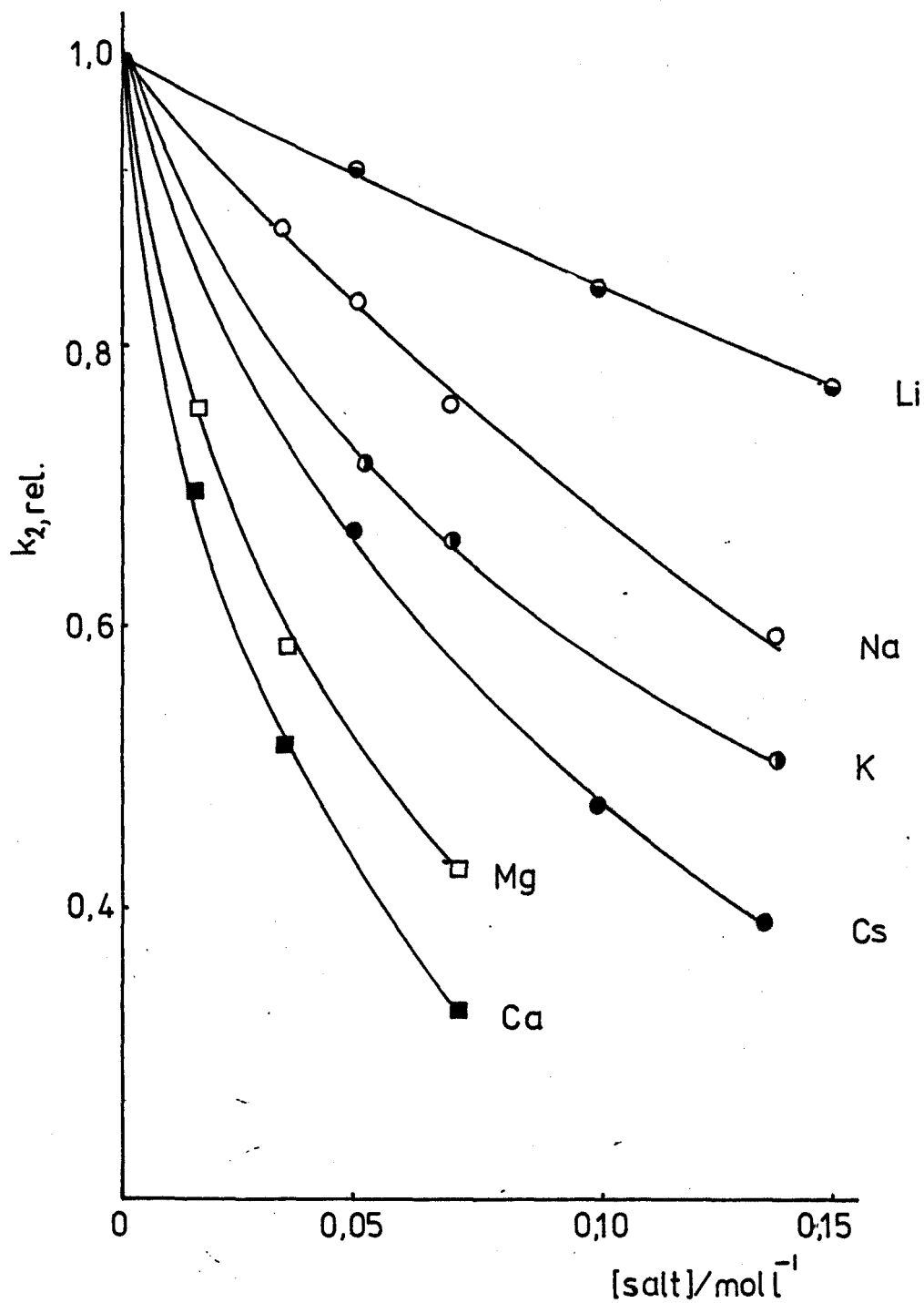0.035M SDS at 90°C and 0.02M HClO₄.

Fig. 6.23   The effect of electrolyte concentration on the

relative rate constants for the hydrolysis of

0.035M SDE_2S at $70^{\circ}C$ and 0.0425M $HClO_4$.

the hydrolysis, the effect being dependent on the cation used, following the series

$$(CH_3)_4N < Li < NH_4 < Na < K < Cs < Mg < Ca$$

This series can be correlated with the size of the hydrated ion and the charge on the ion, as is generally found for the effects of added electrolytes on micellar catalysed reactions. This is due to the fact that ions of high charge density (small size, high charge) will be more strongly attracted to the micelles and hence be more likely to displace the reactive ions bound to the micelles and hence inhibit the reaction. Thus we expect, as is observed, that for similarly charged ions the ion of smaller hydrated radius will be bound more strongly to the micelles, and that multivalent ions will bind more strongly than univalent ions (n.b. nmr results indicate that ions retain their hydration on being bound to micelles, Robb & Smith 1974).

6.6.3 Determination of ion-exchange constants from the effects of added electrolytes on the hydrolysis at low surfactant concentration

Romsted (1975) has shown that one can use the effects of added electrolytes on the rates of micellar catalysed reactions to obtain values for the ion-exchange constants for the competition for binding to the Stern layer of the counterions present. This involves a number of assumptions:-

(a) One can neglect the reaction taking place in the aqueous phase.

(b) Only a small fraction of the available reactive ion is bound to the micelles (i.e. $H_T \gg \overline{H}_m CV$)

The second approximation is then included in equation 6.17 so that we then have:-

$$\overline{H}_m + \frac{Na_T \overline{H}_m}{K_{H/Na} H_T} = \beta S \qquad 6.32$$

and we can then obtain a more simple expression for the concentration of H^+ ions in the micelle phase:-

$$\overline{H}_m = \beta \frac{S \, K_{H/Na} \, H_T}{K_{H/Na} \, H_T + Na_T} \qquad 6.33$$

Then using the first approximation for the rate equation we have

$$k_{2,obs} \, C_T \, H_T = k_m \, \overline{H}_m \, \overline{C}_m \, CV \qquad 6.34$$

$$= k_m \beta S \frac{K_{H/Na} \, C_T \, H_T}{K_{H/Na} \, H_T + Na_T} \qquad 6.35$$

If we then take the reciprocal of each side of equation 6.35 we have:-

$$\frac{1}{k_{2,obs}} = \frac{Na_T}{k_m \beta S \, K_{H/Na}} + \frac{H_T}{k_m \beta S} \qquad 6.36$$

Therefore plots of $1/k_{2,obs}$ against Na_T should be linear if the assumptions are valid, and the values of $K_{H/Na}$ and $k_m \beta S$ can be obtained from the values of the slope and intercept of the straight lines (n.b. $Na_T = C_T$ + concentration of added sodium salt).

One can also extend equation 6.36 to include the case when the added electrolyte contains a third counterion, Y, of concentration Y_T.

$$\frac{1}{k_{2,obs.}} = \frac{H_T + Na_T/K_{H/Na}}{k_m \beta S} + \frac{Y_T}{k_m \beta S \, K_{H/Y}} \qquad 6.37$$

Therefore the slopes and intercepts of plots of $1/k_{2,obs}$ vs Y_T should yield values for the ion-exchange constants $K_{H/Y}$.

Figs. 6.24 and 6.25 are plots of $1/k_{2,obs}$ vs. electrolyte concentration for the hydrolysis of SDS (at $90^\circ C$ and 0.02M H^+) and SDE_2S (at $70^\circ C$ and 0.0425M H^+) respectively, at 0.035M surfactant concentration. Both sets of results show good linearity over the range of salt concentrations used and the data for the slopes, intercepts and $K_{H/Y}$ values are given in Tables 6.3 and 6.2.
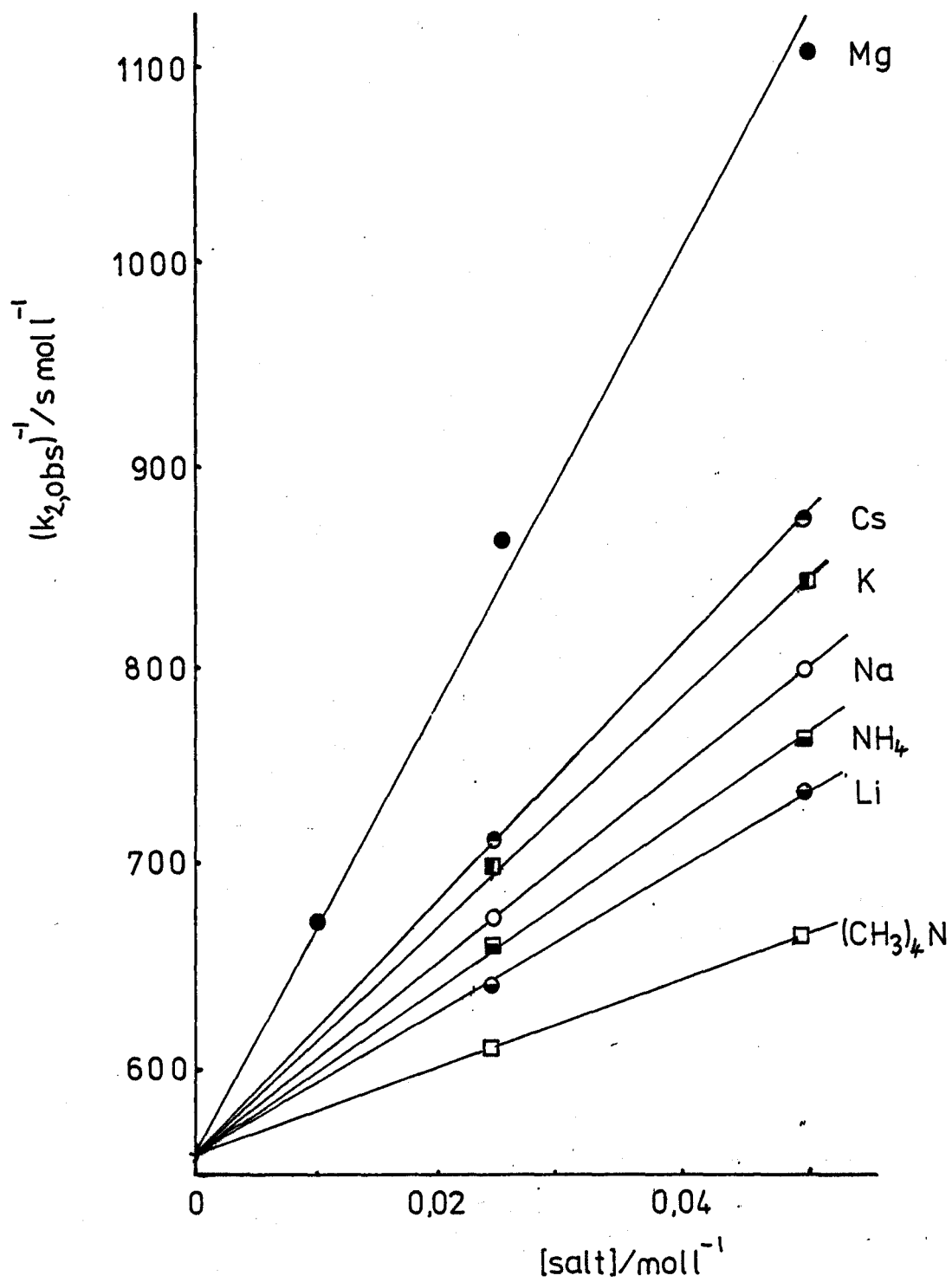
Fig. 6.24   The effect of the electrolyte concentration on the reciprocal of the observed rate constant for the hydrolysis of 0.035M SDS at 90°C and 0.021M $HClO_4$.
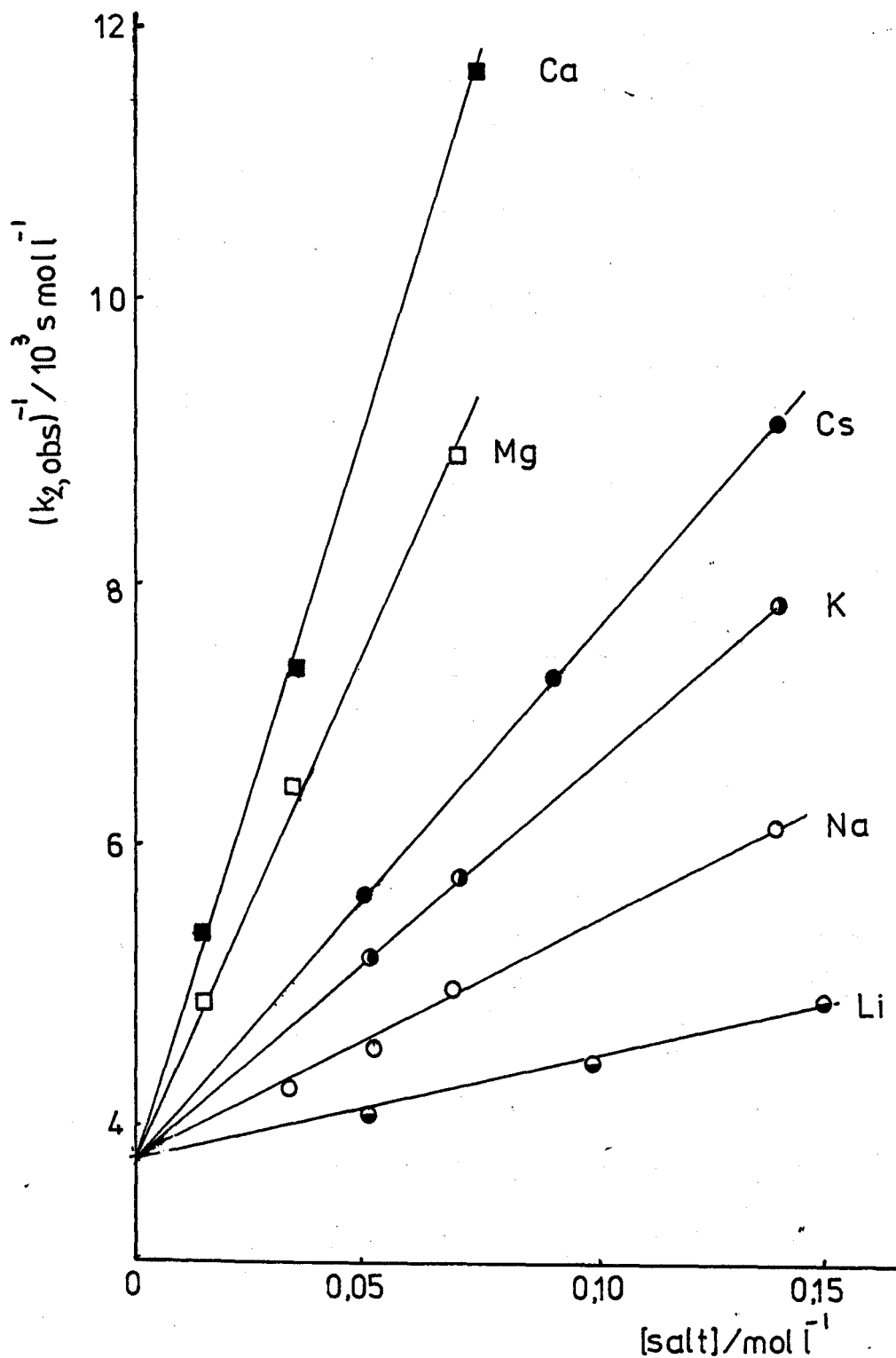
Fig. 6.25   The effect of electrolyte concentration on the

reciprocal of the observed rate constant for the

hydrolysis of 0.035M SDE_2S at $70^{\circ}C$ and 0.0425M $HClO_4$.

Table 6,2

ION-EXCHANGE CONSTANTS FOR SDS MICELLES FROM PLOTS OF $1/k_{2,obs.}$ vs [salt].

Ion	Intercept(mol.l.s)$^{-1}$	Slope(s)	$K_{H/X}$
Na	392	4800	3,89
$(CH_3)_4N$	560	2130	8,76
Li	560	3510	5,32
NH_4	560	4020	4,64
K	560	5580	3,35
Cs	560	6340	2,95
Mg	560	11300	1,65

$$k_m \beta S = 5,357 \times 10^{-5} s^{-1}$$
$$k_m = 1,25 \times 10^{-5} \, l.mol.s.^{-1} \quad (\beta = 0,6 \; ; \; S = 7,1)$$
$$k_\omega = 7,5 \times 10^{-5} \, l.mol.s.^{-1} \quad (Kurz \; 1962)$$

[SDS] = 0,035M

[$HClO_4$] = 0,021M

Temp. = 90°C

<u>Table 6.3</u>

ION-EXCHANGE CONSTANTS FOR SDE_2S MICELLES FROM PLOTS OF $1/k_{2,obs}$ vs [salt]

Ion	Intercept$(s\,mol\,l^{-1})$	Slope(s)	$K_{H/X}$
Na	3080	18040	8,11
Li	3700	7935	18,44
K	3700	29280	5,00
Cs	3700	39330	3,72
Mg	3700	75840	1,93
Ca	3700	110250	1,33

$$k_m \beta S = 6,49 \times 10^{-6} s^{-1}$$

$[SDE_2S] = 0,035M$

$[HClO_4] = 0,02M$

Temperature $= 70°C$

In all cases the values for $K_{H/Y}$ are greater than unity, indicating that the H^+ ions are bound more strongly to micelles of SDS and SDE_2S than the other counterions used, including the divalent ions (although values for ion-exchange constants for M^{2+} ions can only be taken as approximate as the expression for H_m in the presence of divalent ions should be different from that for H_m in the presence of monovalent ions to take into account the differing value of the degree of dissociation of the counterions from the micelles).

In comparing the values of $K_{H/Y}$ for micelles of SDS and SDE_2S we find that ethoxylating the carbon chain of the surfactant leads to an increase in the strength of the binding of H^+ ions relative to the other counterions (i.e. $K_{H/Y}(SDS) < K_{H/Y}(SDE_2S)$). A possible explanation for this could be the hydrogen bonding ability of the O atoms of the ethoxy groups (which are usually considered as being included in the Stern layer) which would enhance the binding of the H^+ ions, as already suggested in earlier sections.

Using equations 6.36 and 6.37 can also give us values of $k_m\beta S$ which, if taken in conjunction with assumptions about β and S, may yield an estimate of the value of k_m, the second order rate constant in the Stern layer of the micelle which can then be compared with the value of k_w, the second order rate constant in the aqueous phase.

In the case of SDS at $90^\circ C$, we have $\beta = 0.6$ (Barry and Wilson 1978) and S = 7.1 (S = $1/V_s$), thus we can obtain a value of k_m of the order of 1.25×10^{-5} $1mol^{-1}s^{-1}$ as compared with the value of k_w of 7.5×10^{-5} $1mol^{-1}s^{-1}$ (Kurz 1962). This compares well with the values used for k_m/k_w in calculating the curves for the effects of acid concentration and surfactant concentration on the hydrolysis which agree best with the experimental results.

6.6.4   The effect of electrolytes on the hydrolysis of SDS at 0.35M
         surfactant

Fig. 6.26 shows the effect of added electrolytes on the

second order relative rate constant $(k_{2,obs.}/k_{2,obs,0.})$ for the acid

hydrolysis of 0.35M SDS with 0.04M acid at 70°C.

A number of notable features can be seen in contrast to the

results found at 0.035M SDS: firstly the order of the inhibitory effect

of the cations on the reaction is reversed for monovalent ions, but

the same for divalent ions:

$$Ni > Ca > Mg > Li > Na > K > Cs$$
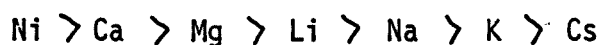
Of even more interest is the observation that as the

concentration of Cs and K salts is increased, the reaction rate passes

through a shallow minimum and beyond it the salts are found to enhance

the reaction rate.

These results could be due to a number of effects. Firstly,

the high concentration of the surfactant and the salts may lead to a

change in the size and shape of the micelles, which is greater

$(Cs > K > Na > Li)$ for ions of smaller hydrated radius (the order of

radii being $Li > Na > K > Cs$). This structural change of the micelle

could then lead to either a change in the dielectric constant of the

Stern layer (an effect on k_m), or a change in the ion binding ability

of the micelle. An overall increase in ion binding would result in an

increase in the reaction rate, as would a decrease in the dielectric

constant.

Secondly, one may be observing an effect of the high ionic

strength on the activities of the cations taking part in the ion-

exchange, which may cause preferential binding of H^+ ions to the micelle

(i.e. a change in $K_{H/M}$).

Previously we have defined the ion-exchange constants in

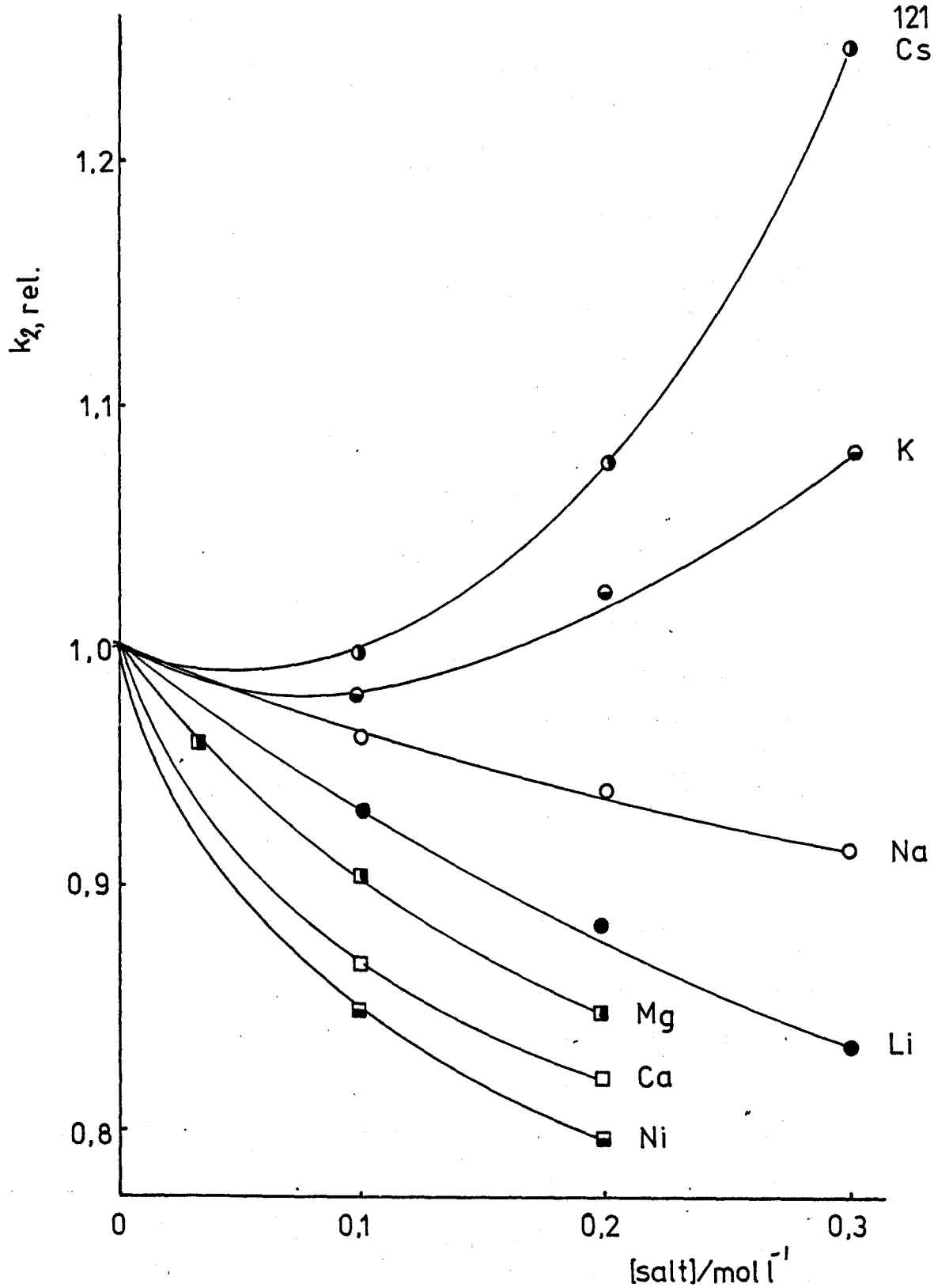terms of the concentrations of the cations in the aqueous and micellar

Fig. 6.26   The effect of electrolyte concentration on the
             relative rate constant for the hydrolysis of 0.35M
             SDS at 70°C and 0.042M HClO$_4$.

phases, which of course are not true constants, but vary with the change in activities of the ions. If we now refer to the ion-exchange constant, defined in section 6.4.4, in terms of ion activities (split into the concentration and activity coefficient terms):

$$K'_{H/M} = \frac{H_m M_w}{H_w M_m} \cdot \frac{\gamma_{H_m} \gamma_{M_w}}{\gamma_{H_w} \gamma_{M_m}} = K_{H/M} \frac{\gamma_{H_m} \gamma_{M_w}}{\gamma_{H_w} \gamma_{M_m}}$$

we shall have

$$H_m = K'_{H/M} \frac{M_m H_w}{M_w} \cdot \frac{\gamma_{M_m} \gamma_{H_w}}{\gamma_{H_m} \gamma_{M_w}}$$

Under the assumption of constant degree of ion binding (and hence a constant ionic strength of the Stern layer), the ratio $\gamma_{M_m}/\gamma_{H_m}$ will be constant. We are thus considering only the effect of high ionic strength on the ratio of activity coefficients in the aqueous phase, $\gamma_{H_w}/\gamma_{M_w}$, an increase of which will result in an increase in H_m and hence an increase in the reaction rate.

According to Stokes and Robinson (1948) as shown in Fig. 6.28, γ_{H_w} increases with ionic strength, while γ_{M_w} decreases so that the ratio $\gamma_{H_w}/\gamma_{M_w}$ must increase, which would explain our experimental results. From this Figure, the effect of varying the cation is that the ratio $\gamma_{H_w}/\gamma_{M_w}$ will increase in the order

$$Li < Na < K < Cs$$

Therefore it is quite possible that it is this effect which is producing the change in reaction rate with electrolyte concentration shown in Fig. 6.26.

6.7 THE EFFECT OF ADDED HEXANOL ON THE RATE OF HYDROLYSIS OF SDS

As one of the products of the hydrolysis of SDS is dodecanol, we were interested to find the effects of the alcohol on the rate of reaction. Dodecanol itself was found to have no significant effect on the rate at 0.35M surfactant, 0.02M acid and 70°C, which is
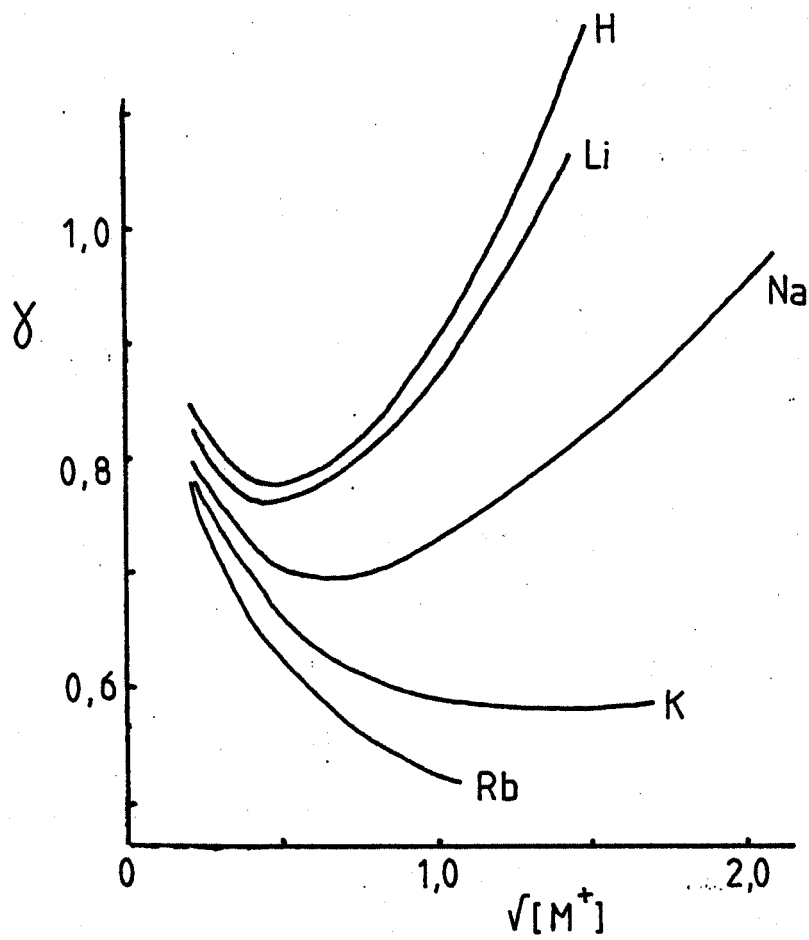
Fig. 6.28   The variation of activity coefficient (γ) with the concentration of monovalent cation chlorides. (Stokes and Robinson 1948).

inconsistent with the findings of Barry and Shotton (1967) for the effects of hexadecanol on the hydrolysis. They found that at low surfactant concentration (0.035M) the alcohol increased the reaction rate up to a mole ratio of 0.75, which is beyond the point at which a phase change occurs in the system (the liquid crystalline phase is found to occur at a mole ratio of 0.27). Beyond this point they found that any further alcohol added decreases the rate. No conclusive explanation was given for the occurrence of a maximum in the reaction rate, in particular it does not coincide with a further phase change in the system.

Having found no significant effect for dodecanol on the hydrolysis, we looked at the effect of a lower alcohol, hexanol. Fig. 6.27 shows the results for the change in relative rate constant $k_{2,rel}$ (rate constant in the presence of alcohol divided by the rate constant obtained without any alcohol) with hexanol concentration up to a mole ratio of 1.3 (alcohol:surfactant), the conditions being 0.35M SDS, 0.02M acid and $70^{\circ}C$. The alcohol is found to inhibit the hydrolysis, a 1:1 mole ratio producing a 20% drop in the rate. This inhibition is a result of the distribution of the alcohol between the micellar and aqueous phases, as determined by Hayase and Hayano (1977) using gas chromatography and yielding a distribution coefficient of 2250 for hexanol in SDS solutions. This distribution of the alcohol has an effect on the counterion binding to the Stern layer of the micelle. Lawrence and Pearson (1967) using conductance measurements found that addition of lower alcohols ($C_1 - C_7$) to 0.07M SDS solutions at $70^{\circ}C$ increased the conductance of the system as well as the Na^+ activity, indicating that ions are released into the bulk solution from the micelles. The ions are released from the micelles as the incorporation of the alcohols into the micelles reduces the surface charge density and the repulsions between adjacent head groups, so
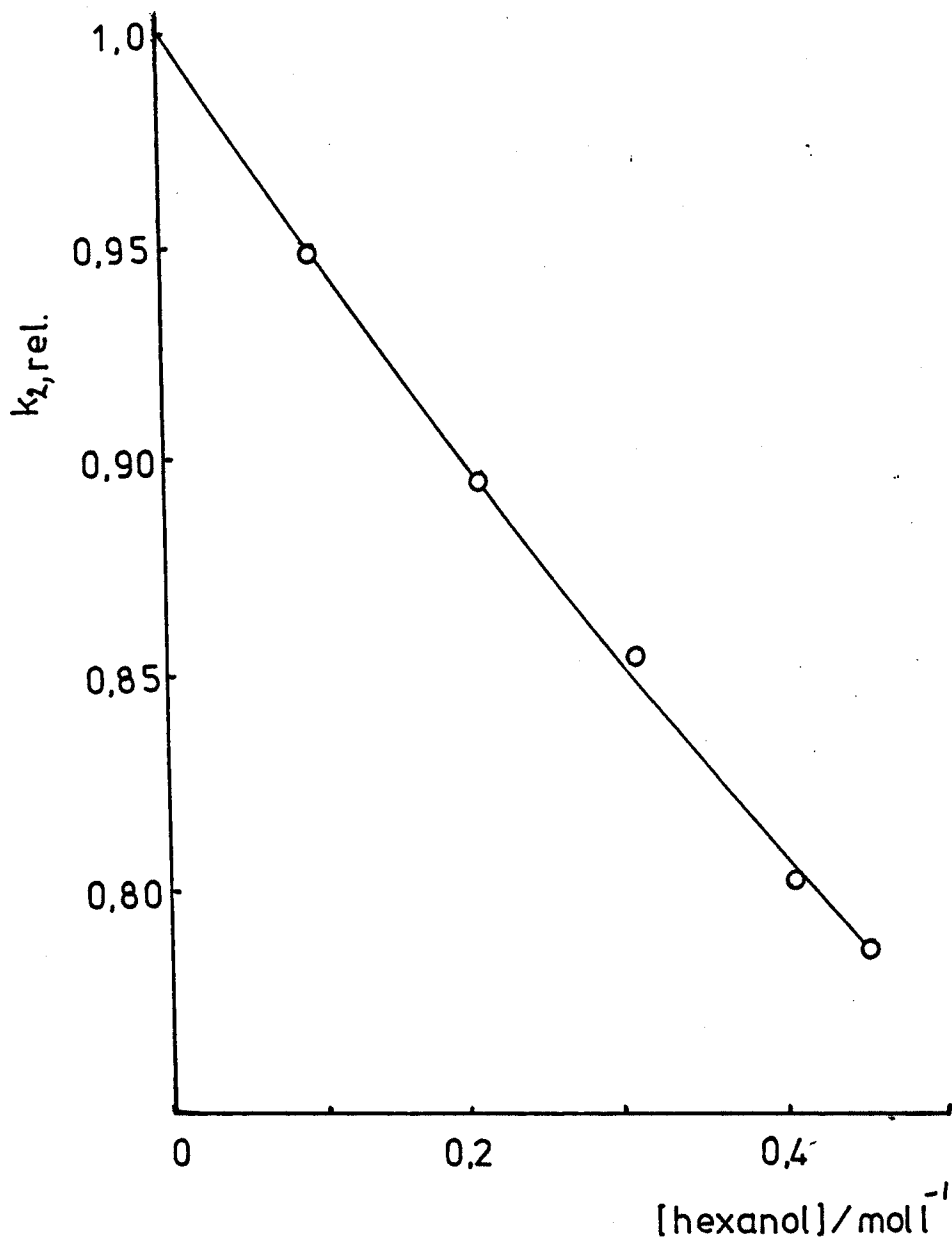
Fig. 6.27   The effect of hexanol concentration on the relative
             rate constant for the hydrolysis of 0.35M SDS at
             70°C and 0.02M $HClO_4$.

that fewer ions are required to stabilise the micellar charge. Larsen and Tepley (1974) found the same effect for short-chain alcohols on the binding of Br^- ions to CTABr micelles as determined using Br^- ion-selective electrodes.

Thus we can see that the inhibition of the hydrolysis of SDS by hexanol is a result of the decrease in the overall ion binding to the micelles, which also causes a concomitant decrease in the value of H_m which largely determines the reaction rate. In addition to this simple explanation there may be an effect of the alcohol in the micelles on the value of k_m as a result of the change in the dielectric constant of the Stern layer.

CHAPTER   SEVEN

CONCLUSIONS

7.1   INTRODUCTION

In Chapter 1 we outlined the motivation behind this research project, namely to gain a better understanding of the acid catalysed hydrolysis of dodecyl sulphate and dodecyl ether sulphate surfactants in concentrated micellar solution, with particular reference as to how the reaction may be inhibited. This objective was the basis of the industrial collaboration on this project and accompanying it was the academic interest of studying a micellar catalysed reaction in concentrated solutions of surfactants, on which the amount of literature is limited. The results of our investigation of the effects of the variable parameters of the reaction mixture on the kinetics of the hydrolysis are described in Chapter 6. We came to the conclusion that they are best explained in terms of a theoretical model due to Romsted (1975), henceforth referred to as the ion-exchange theory. In this last chapter we will attempt to bring these results together to see how well they fit the ion-exchange theory and to see if we can help Albright and Wilson in their problem of preventing or inhibiting the hydrolysis.

7.2   COMPARISON OF EXPERIMENT AND THEORY

Throughout the results section we tried to compare the experimentally observed results with those calculated using a modified form of Romsted's theory, assuming values for the various parameters involved in the equations (V_s, CMC, β, etc). In general terms, particularly at low concentrations of surfactant, the experimental results do indeed follow the expected form; however they are not completely consistent when the quantitative values of the parameters $K_{H/M}$ and k_m/k_w are examined. This does not, however, mean that the ion-exchange theory is not applicable to this system, or to micellar catalysis in general, since one would expect discrepancies due to the non-ideal nature of the system under investigation (i.e. high ionic

strength, the assumption concerning activity coefficients in micellar/ aqueous phases).

In order to obtain an overall view of the relationship between experiment and theory, we shall now survey the value of $K_{H/Na}$ found for SDS micelles in the various sections of Chapter 6. Table 7.1 lists the best values of $K_{H/Na}$ under the various conditions, using the values of the adjustable parameter k_m/k_w shown.

Firstly all the values of $K_{H/Na}$ are greater than unity, indicating that H^+ ions are bound more strongly to DS^- micelles than Na^+ ions. The overall best value of $K_{H/Na}$ would seem to be in the region of 4 (when one takes into account the argument in Chapter 6 for the variation of k_m/k_w and activity coefficients of ionic species, with surfactant concentration) which is that obtained directly from the salt effect results. According to Romsted, the determination of ion-exchange constants for micellar systems from electrolyte effects on reaction rates is probably the most reliable method. The acid catalysed hydrolysis reaction is, in a sense, a probe for the H^+ ion concentration on the micellar surface.

If we accept this hypothesis, the values for $K_{H/M}$ found from salt effects on the hydrolysis of both SDS and SDE_2S could be compared to see if the binding of ions to the micelle is affected by the introduction of ethoxy groups into the surfactant hydrocarbon chain.

Table 7.2 gives values for $K_{H/M_{rel}}$ for SDS and SDE_2S micelles. They are based on $K_{H/Na} = 1$, due to the fact that they are obtained at different temperatures. This would make them reasonably comparable. The first point to note, as stated in section 6.6 is that they follow the same order (N.B. in all cases, even for M^{2+}, $K_{H/M} > 1$)

$$Ca < Mg < Cs < K < Na < NH_4 < Li < (CH_3)_4N$$
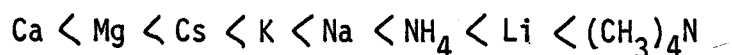
Table 7.1

EFFECT OF EXPERIMENTAL CONDITIONS ON $K_{H/Na}$ AND k_m/k_w FOR SDS MICELLES AT 70°C

Constants	Variables	k_m/k_w	$K_{H/Na}$
C_T (0.035M)	H_T	0.30	$1 < K < 4$
C_T (0.35M)	H_T	0.30	8
H_T (0.021M)	C_T	0.25	$1.5 : 1.5 < K < 4$
H_T (0.02M); Na_T (0.6M)	C_T	0.50	2
H_T (0.02M); C_T (0.035M)	Na_T	0.17^a	4

a) a value obtained experimentally at 90°C

Table 7.2

EFFECT OF ETHOXYLATION ON THE RATIO $K_{H/M}/K_{H/Na}$[a], FROM SALT EFFECTS

Ion	$K_{H/M}/K_{H/Na}^{SDS}$	$K_{H/M}/K_{H/Na}^{SDE_2S}$
Na	1	1
Li	1.36	2.25
K	0.87	0.62
Cs	0.72	0.45
Mg	0.41	0.20

a) $K_{H/M}/K_{H/Na} = K_{Na/M}$ is the equilibrium constant for the process:
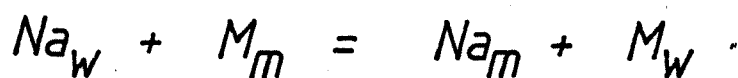
$$Na_w + M_m = Na_m + M_w$$

$$K_{Na/M} = \frac{Na_m \; M_w}{Na_w \; M_m}$$

(i.e. larger values indicate stronger binding of Na relative to M)

However the ratios $K_{H/Na}:K_{H/M}$ do not remain constant on ethoxylating the surfactant, in fact it seems that, relative to Na^+, all the ions used, with the exception of Li^+ are bound more strongly to DE_2S micelles than to DS micelles. At this stage it is not possible to put forward an explanation for this observation, but the dielectric constant of the Stern layer could be the key, as it may be lower for DE_2S micelles as a result of close involvement of ethoxy groups. This should improve the binding of ions with greater surface charge (which are in fact all less hydrated than Na^+) at the expense of those with smaller surface charge (the more hydrated Li^+).

7.3   INHIBITION OF THE HYDROLYSIS

7.3.1   Introduction

As we have stated previously in Chapter 6, the factor which will largely determine the rate of hydrolysis in micellar solution is the concentration of H^+ ions bound to the micellar surface. Therefore, in general, any factor which reduces this quantity in a given system should inhibit the rate of reaction.

7.3.2   Buffers

The first and most obvious way to achieve this is, of course, the use of buffer materials, as is in fact done in the commercial materials. Sodium phosphate buffers are used both to keep up the pH of the commercial surfactants and to act as builders. The desired pH of these systems is of the order of 6-8, which is much higher than that used in the majority of our experimental results (pH $\simeq$ 1.7). Therefore at first glance one would expect the hydrolysis of the commercial materials to be much slower than that obtained in our experiments, which leads us to wonder why there should be any problem with these materials at all, since at $20^\circ C$ and $0.02M$ H^+ we estimate the half-life of the reaction to be of the order of 400 days.

To verify this estimate a number of kinetic runs were carried out using varying amounts of buffer compounds to see if indeed the reaction was slowed down to a great extent. The results are summarised in Table 7.3. As one can see, the hydrolysis is indeed very slow in the presence of the buffers.

This leads us to the possibility that, as the reaction at pHs of the order of 7 should be almost negligible, the problems are caused by inhomogeneous neutralisation of the alkyl sulphuric acid to form the sulphate surfactant. This would lead to the formation of acid 'hot spots', where one has high local concentration of H^+ ions. At these points the hydrolysis occurs at a high rate generating acid (cf. the autocatalytic nature of the reaction) which diffuses to other regions in the mixture and hence decreases the overall pH of the material.

7.3.3   Addition of electrolyte

In section 6.6 we gave the results for the effects of added electrolytes on the hydrolysis of the two surfactants. At low concentration of surfactant (0.035M), the electrolytes, without exception, inhibited the reaction, the effect being greater for highly charged and small hydrated ions, which can be attributed to the ion-exchange phenomenon. Thus, if one could extrapolate these results to higher concentrations, one might be able to inhibit the hydrolysis of the commercial surfactants by the addition of soluble salts of highly charged ions. There are a number of drawbacks to this method however. Firstly, the critical micelle temperature (or Krafft point), which is the temperature below which the surfactant is insoluble in water, is usually quite high for M^{2+} or M^{3+} surfactants, so that one is restricted in the choice of salts (probably only to Mg^{2+}, CMT = 25^oC). Secondly, the results of our experiments at higher surfactant concentrations indicate that the effects of electrolytes are no longer so

Table 7.3

EFFECT OF BUFFER CONCENTRATION ON THE RATE OF HYDROLYSIS OF 0.35M SDS IN 0.02M $HClO_4$ AT 70°C

$[Na_2HPO_4](mol\,l^{-1})$	Initial rate($mol\,l^{-1}s^{-1}$)
0	4×10^{-7}
0.0125	3×10^{-8}
0.025	3×10^{-9}
0.05	2×10^{-9}

straightforward, as both Cs and K salts were found to enhance the rate of the reaction. However this was not observed for divalent cations.

7.3.4   Surfactant counterion

The results for hydrolysis of various metal dodecyl sulphates (section 6.5.5) again show that the nature of the counterion has an effect on the reaction rate and that the use of the divalent ion Mg^{2+} produces a large decrease in the rate of hydrolysis. Thus one would expect that commercial surfactants based on Mg^{2+} will hydrolyse much less rapidly than those based on Na^{+}, though again of course one has the limitation imposed by the Krafft point of the surfactant (this is $25^{o}C$ for $Mg(DS)_{2}$, which has to be borne in mind).

7.3.5   Addition of alcohols

It is known that the lower chain alcohols reduce the binding of ions to micelles of SDS surfactant (Lawrence and Pearson 1967) as a result of being incorporated into the micellar structure. We would then expect, as indeed observed for hexanol, that addition of lower alcohols will inhibit the hydrolysis of SDS. The effect was not found for longer chain alcohols (dodecanol), which is present in the commercial surfactants (due to incomplete sulphation of the starting materials in the manufacture), so that any use of alcohols to inhibit the reaction would have to be restricted to the shorter chain compounds.

7.4   CONCLUSIONS

The comparison of the experimental and the calculated variation in the kinetics of the hydrolysis with various adjustable parameters indicates that the system can indeed be considered as an ion-exchange one, particularly in dilute micellar solutions. At higher surfactant concentrations, a number of features will come into play to affect the kinetics, i.e. ionic strength effects on ion activities, interactions of highly charged micelles, etc. The system

could be investigated further by means other than reaction kinetics, to obtain a more complete insight into the various interactions. For example, as the main rate determining factor in the hydrolysis is the ion-exchange pre-equilibrium, the effect of the various parameters on this could be investigated in a number of ways, e.g. nmr, ion selective electrodes (pNa and pH measurements). Another useful study would involve a thorough investigation into the effects of the composition of the system on the structural parameters of the micelle (shape, size, hydration, ion-binding, etc).

As to the industrial usefulness of this project, we have shown that the reaction is in fact rather slow, particularly at high pH. While we did not investigate the reaction at very high concentrations of surfactant often encountered in the commercial materials (70% by wt), it may be reasonable to extrapolate our results at lower concentrations. This would indicate that improvement of the neutralisation process during the manufacture of the surfactants would be the best means of preventing or inhibiting the hydrolysis. One way of doing this would be to find a more efficient means of monitoring the pH of the neutralised surfactant (bearing in mind the nature of the system).

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