

# Kinetics of the Acid-catalysed Hydrolysis of Dodecylsulphate and Dodecyldiethoxysulphate Surfactants in Concentrated Micellar Solutions

Part 1.—Effects of Acid and Surfactant Concentrations and of the Nature and Concentration of Counterions

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The rates of the acid-catalysed hydrolysis of sodium dodecylsulphate (SDS) and sodium dodecyldiethoxysulphate (SDE<sub>2</sub>S) have been investigated in concentrated surfactant solutions (0.035-0.6 mol dm<sup>-3</sup>). The acid concentration dependence of the initial rates shows a 'saturation' effect, whereas increasing surfactant concentrations above the c.m.c. lead to a maximum in the  $k_{2,obs}$  values, beyond which they decrease sharply. These results are discussed in terms of the ion-exchange pseudophase model of the micellar reaction. The nature of the counterion has an effect on  $k_{2,obs}$ , the values following the sequence NH<sub>4</sub> > Li > Na ≫ Mg. This has been ascribed to differences in the ion-exchange constants,  $K_{H/X}$ , of these cations in the Stern layer of the micelles with the hydrogen ion. Maintaining the total counterion concentration and the ratio of concentrations of surfactant counterion to the concentration of hydrogen ion constant (at 30, *i.e.* 0.6:0.02 mol dm<sup>-3</sup>) largely eliminates the decrease in the  $k_{2,obs}$  values with increasing surfactant concentration, as expected from the pseudo-phase ion-exchange model. Quantitative agreement between theory and experiment is less good, however, owing at least partly to deviations from ideality in solutions of high ionic strength.

The fact that the acid-catalysed hydrolysis of long-chain alkyl sulphates in relatively dilute micellar solutions is also micellar catalysed was established in 1962 by Kurz.<sup>1</sup> Later work<sup>2</sup> demonstrated that the rates of this reaction show the familiar sigmoid dependence on surfactant concentration for sodium dodecylsulphate, with rate constants approaching 'limiting' values just above the c.m.c. The dependence of these limiting values on acid concentration indicated, however, that the reaction is not simply first order with respect to the hydrogen ion, since their ratio in 0.1 and 0.01 mol dm<sup>-3</sup> hydrochloric acid was rather less than 10:1.

Dodecylsulphate surfactants are now manufactured as salts of sodium, lithium, magnesium, ammonium *etc.* in highly concentrated solutions or as pure solids, and their ethoxylated analogues ('ether' sulphates) mainly as concentrated solutions.<sup>3</sup> We have therefore undertaken to investigate<sup>4</sup> the acid-catalysed hydrolysis in concentrated solutions of sodium and several other dodecylsulphates and of sodium dodecyldiethoxysulphate, up to concentrations as high as practicable, in view of increasing viscosity. In these systems the surfactant is both the micelle former and the substrate of the reaction. The reaction also involves a small hydrophilic ion, the hydrogen ion,

as catalyst, and therefore our results are best accounted for in terms of the pseudophase ion-exchange model of micellar catalysis of Berezin *et al.*<sup>5</sup> and Romsted,<sup>6</sup> rather than in terms of the more frequently invoked 'enzyme' model.<sup>7</sup>

## EXPERIMENTAL

### MATERIALS

Sodium and lithium dodecylsulphates were of specially pure grade (B.D.H.) and were recrystallised twice from absolute ethanol and dried under vacuum before use.

Magnesium dodecylsulphate was precipitated from a concentrated solution of sodium dodecylsulphate 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 dodecylsulphate was prepared from dodecan-1-ol by sulphation and neutralisation of the dodecylsulphuric acid with ammonia. The sulphation was carried out in a falling film apparatus using vaporised sulphur trioxide. The product was recrystallised first from 90% ethanol and then twice from absolute ethanol and finally dried under vacuum.

Sodium diethoxydodecylsulphate was prepared by ethoxylation of dodecyl bromide with diethylene glycol, sulphation of the alcohol with chlorosulphonic acid and neutralisation of the acid obtained with alcoholic sodium hydroxide, following procedures in the literature.<sup>8-10</sup> The product was recrystallised twice from absolute ethanol and dried under vacuum.

The purity of all the surfactants was checked by complete acid hydrolysis of the compounds, followed by the determination of the excess acid produced.

Perchloric acid (AnalaR) was used as the catalyst.

### PREPARATION OF THE REACTION MIXTURES

Since the kinetic runs were carried out at high temperatures, the solutions of the surfactant and the added salt (in experiments containing an excess of common counterion) and the concentrated perchloric acid solution were brought separately to the temperature of the thermostat prior to the addition of the acid to the surfactant solution. The final volume of the solution (100 cm<sup>3</sup>) was made up with distilled water also brought to the reaction temperature.

### KINETICS

Immediately after mixing the reactants, two zero-time samples were removed using a jacketed pipette and quenched with cold distilled water. One of the samples was used to check the initial surfactant concentration using the two-phase titration technique of Reid *et al.*<sup>11</sup> and the other sample was used to check the initial acid concentration by an acid-base titration using an E.I.L. automatic titrator (model 7070).

The reaction was followed by removing 5 cm<sup>3</sup> samples with a jacketed pipette at appropriate intervals, quenching the reaction with cold distilled water and analysing the mixture. At high surfactant concentrations (> 0.02 mol dm<sup>-3</sup>), the concentration of HSO<sub>4</sub><sup>-</sup> ions liberated on hydrolysis was sufficiently large to produce significant increases in total acid concentration, so that the concentration of the reaction products could be found from [acid]<sub>t</sub> - [acid]<sub>0</sub>. At surfactant concentrations below 0.02 mol dm<sup>-3</sup>, changes in the total acid concentration were too small to be measured accurately enough and so the reaction was followed by the change in surfactant concentration using a colorimetric method.<sup>12</sup>

### DETERMINATION OF RATE CONSTANTS FROM CONCENTRATION - TIME DATA

The rate of the reaction depends both on the acid and the surfactant concentrations, and as HSO<sub>4</sub><sup>-</sup> is a product of the reaction, the reaction is autocatalytic. The autocatalysis is negligible in dilute solutions of surfactants and in the presence of relatively high concentrations of perchloric acid, as in the experiments of Kurz,<sup>1</sup> but is appreciable in concentrated solutions of surfactants (up to 0.6 mol dm<sup>-3</sup> in the present work). The acid concentration against time curves show an upward curvature, even though the reaction could not be followed to more than *ca.* 10% in most mixtures, because the solutions become inhomogeneous due to the appearance of a liquid-crystalline phase, induced by the reaction product dodecanol. Neither the first-order

plots, assuming no contribution of the  $\text{HSO}_4^-$  ions to catalysis (the assumption made by Kurz<sup>1</sup> and valid for his experimental conditions), nor the second-order plots, assuming full ionisation of  $\text{HSO}_4^-$ , were linear. The ionisation constant of  $\text{HSO}_4^-$  ions in fairly concentrated surfactant solutions, and in the presence of additional electrolytes in some experiments, is not known. We have therefore introduced a 'degree of dissociation' ( $\delta$ ) of  $\text{HSO}_4^-$  ions as an empirical parameter and have adjusted its value until the plots of

$$\ln \{([\text{H}^+]_0 + \delta[\text{HSO}_4^-]_t)/[\text{surfactant}]_t\}$$

against time were linear. An optimum value of  $\delta = 0.5$  was found in most experiments. The rate constants,  $k_{2,\text{obs}}$ , obtained from such plots were found to be in good agreement with values obtained from initial rates. The reported  $k_{2,\text{obs}}$  values are, in fact, averages from the two methods and are accurate to  $\pm 2\%$ .

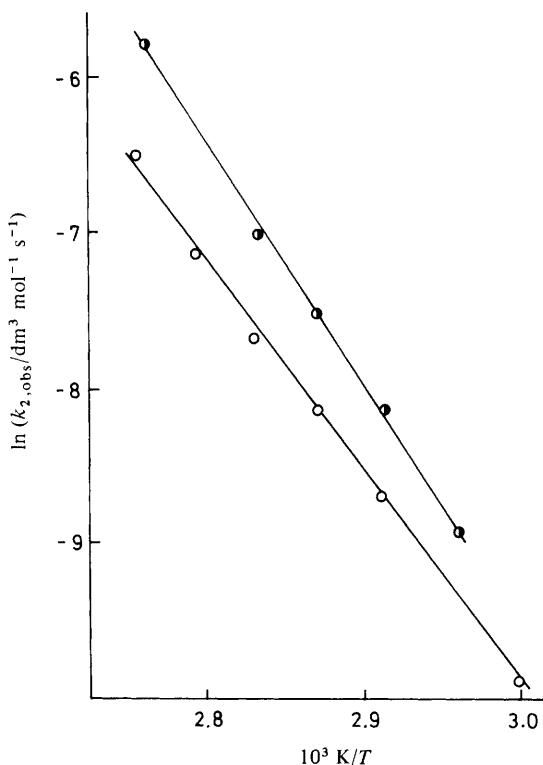


Fig. 1.—Arrhenius plots of second-order rate constants for SDS (O) and SDE<sub>2</sub>S (●).

## RESULTS

We first studied the effects of temperature and acid concentration at low surfactant concentrations (*ca.* 1%) in order to compare our results with those found earlier for SDS<sup>1, 2</sup> and in order to choose the most convenient temperature and acid concentration for work at higher surfactant concentrations.

The effect of temperature was studied in 0.035 mol dm<sup>-3</sup> solutions for both SDS and SDE<sub>2</sub>S over the temperature range 60–90 °C, using 0.02 mol dm<sup>-3</sup> perchloric acid as catalyst. The Arrhenius plots obtained are satisfactory (fig. 1) and the activation energy for SDS is  $112 \pm 2$  kJ mol<sup>-1</sup>, which is in good agreement with the value

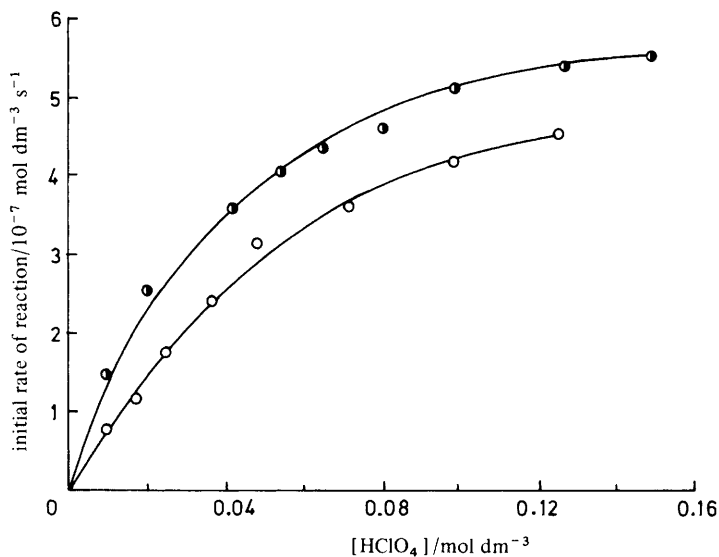


FIG. 2.—Effect of acid concentration on the initial rates of hydrolysis of 0.035 mol dm<sup>-3</sup> SDS (○) and 0.035 mol dm<sup>-3</sup> SDE<sub>2</sub>S (●) at 70 °C.

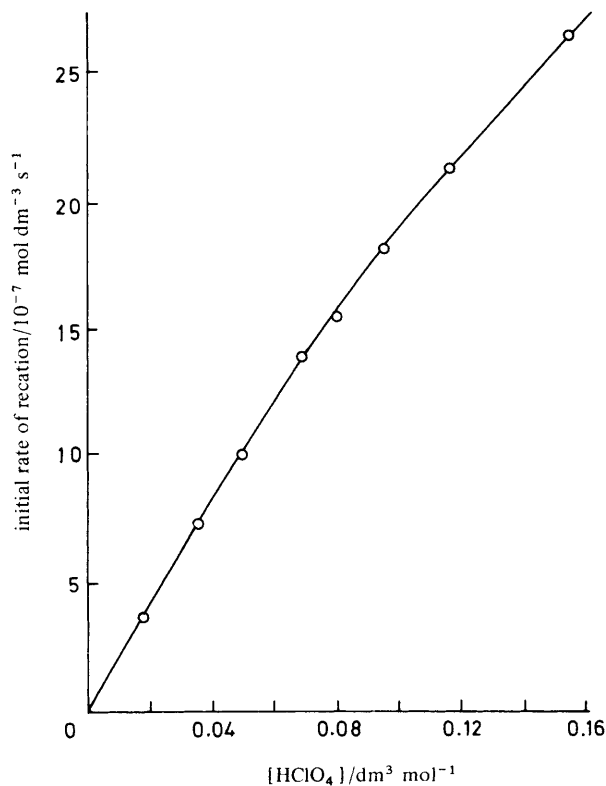


FIG. 3.—Effect of acid concentration on the initial rates of hydrolysis of 0.35 mol dm<sup>-3</sup> SDS at 70 °C.

$115 \pm 1$  kJ mol<sup>-1</sup> found by Kurz<sup>1</sup> for this surfactant. The value for SDE<sub>2</sub>S is higher,  $126 \pm 3$  kJ mol<sup>-1</sup>. The value found by Kurz<sup>1</sup> for a non-micelle-forming alkyl sulphate (sodium methylsulphate) is higher still,  $129 \pm 0.5$  kJ mol<sup>-1</sup>. Thus catalysis by micelles reduces the observed activation energy of the reaction, as already noted by Kurz.<sup>1</sup>

The effect of acid concentration was studied at surfactant concentrations of 0.035 mol dm<sup>-3</sup> for both SDS and SDE<sub>2</sub>S at 70 °C and for SDS at 90 °C. Plots of initial rates against the concentration of perchloric acid at 70 °C are shown in fig. 2. The plot for 0.035 mol dm<sup>-3</sup> SDS at 90 °C is like the plot for 70 °C, except that the initial rates are exactly ten-fold higher. These results can be compared with Kurz's results at 90 °C. Our value of  $k_{2,obs}$  obtained for 0.035 mol dm<sup>-3</sup> SDS and an acid concentration of 0.04 mol dm<sup>-3</sup> is  $1.78 \times 10^{-3}$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>, which compares favourably with Kurz's value of  $1.987 \times 10^{-3}$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>, obtained using 0.04 mol dm<sup>-3</sup> surfactant and the same acid concentration.

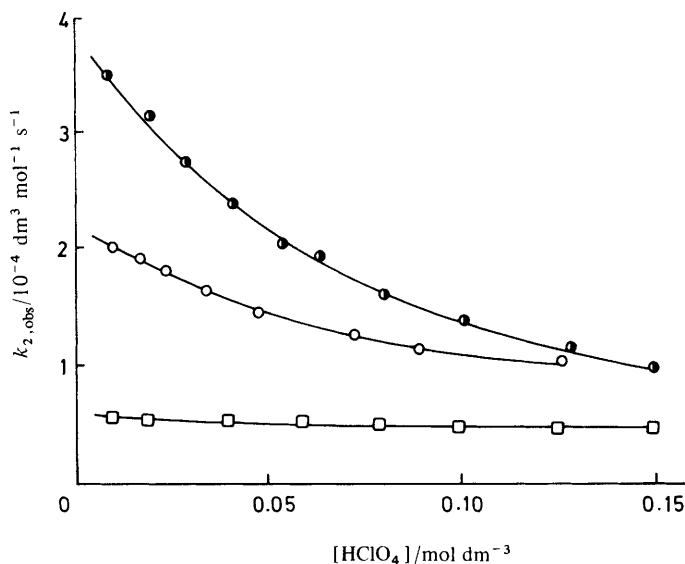


FIG. 4.—Effect of acid concentration on the second-order rate constants for the hydrolysis of 0.035 mol dm<sup>-3</sup> SDS (○) and SDE<sub>2</sub>S (●) and of 0.35 mol dm<sup>-3</sup> SDS (□) at 70 °C.

The rate of hydrolysis of SDS was also measured at a surfactant concentration of 0.35 mol dm<sup>-3</sup> (ca. 10%) and acid concentrations up to 0.16 mol dm<sup>-3</sup> at 70 °C (fig. 3). The results in fig. 2 and 3 are in agreement with Nogami's findings<sup>2</sup> that the micellar catalysed rates are non-linear in the total hydrogen ion concentration. Thus the reaction is not first order in the total hydrogen ion concentration, so the values of  $k_{2,obs}$  obtained at various acid concentrations are apparent only. The variation of  $k_{2,obs}$  with acid concentration for the rates in fig. 2 and 3 is shown in fig. 4.

The effect of surfactant concentration on the observed rate constant at constant acid concentration was examined for both SDS and SDE<sub>2</sub>S at 70 °C (fig. 5). We also examined the effect of the nature of the surfactant counterion at 70 °C. The results are shown as  $k_{2,rel}$  ( $= k_{2,obs}/k_w$ , where  $k_w$  is the rate constant for the reaction below the critical micelle concentration) in fig. 6 for sodium, lithium, ammonium and magnesium dodecylsulphates. Finally, we examined the effect of surfactant concen-

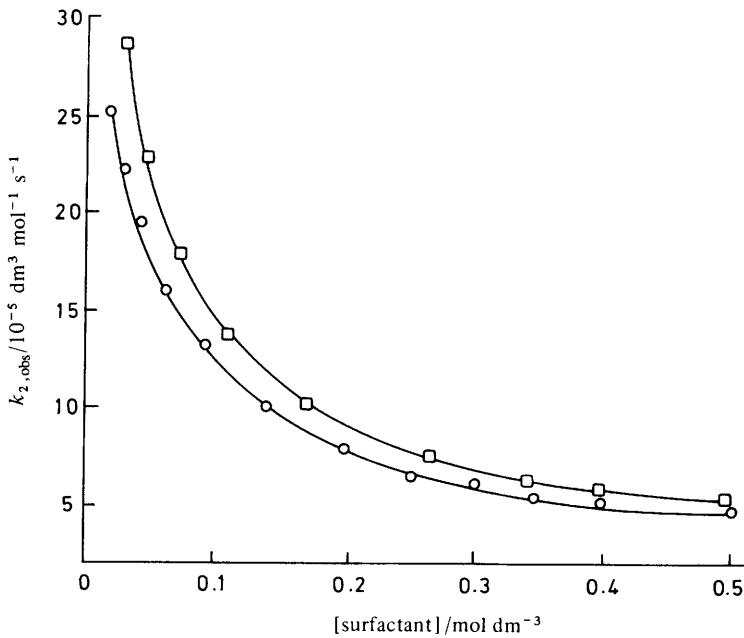


FIG. 5.—Comparison of the effect of surfactant concentration on the rate of hydrolysis of SDS (○) and SDE<sub>2</sub>S (□) at 70 °C and 0.021 mol dm<sup>-3</sup> HClO<sub>4</sub>.

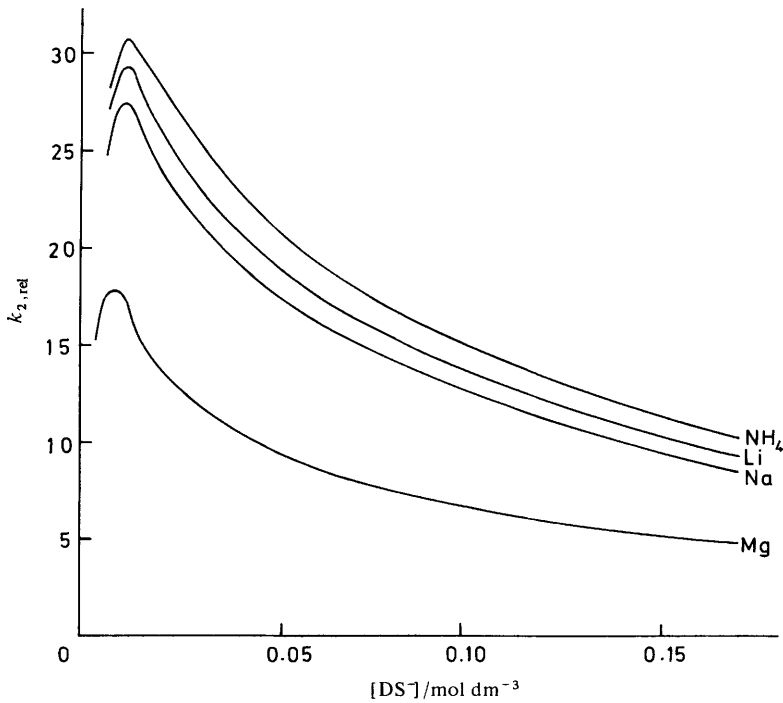


FIG. 6.—Effect of the nature of the counterion on the relative rate constant ( $k_{2,rel} = k_{2,obs}/k_w$ ) against surfactant concentration profile for the hydrolysis of MDS (M = Na, Li, NH<sub>4</sub> and  $\frac{1}{2}$ Mg) at 0.021 mol dm<sup>-3</sup> HClO<sub>4</sub> and 70 °C.

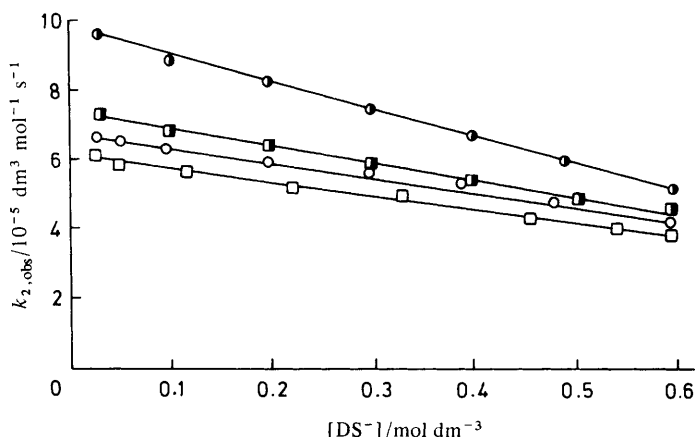


FIG. 7.—Effect of surfactant concentration on the value of  $k_{2,\text{obs}}$  for the hydrolysis of MDS [ $M = \text{Na}$  (○),  $\text{Li}$  (◼),  $\text{NH}_4$  (●) and  $\frac{1}{2}\text{Mg}$  (◻)] at  $0.021 \text{ mol dm}^{-3} \text{ HClO}_4$ ,  $70^\circ\text{C}$  and a constant cation concentration of  $0.6 \text{ mol dm}^{-3}$ .

tration at  $70^\circ\text{C}$  at a constant total hydrogen ion concentration of  $0.021 \text{ mol dm}^{-3}$  and a constant total counterion equivalent concentration of  $0.6 \text{ mol dm}^{-3}$  for the counterions  $\text{Na}^+$ ,  $\text{Li}^+$ ,  $\text{NH}_4^+$  and  $\text{Mg}^{2+}$  (fig. 7).

## DISCUSSION

### THEORETICAL INTRODUCTION

The acid-catalysed hydrolysis of alkyl sulphates has been shown by Burwell<sup>13</sup> and Lieberman *et al.*<sup>14</sup> to involve sulphur–oxygen bond cleavage and to proceed through the pre-equilibrium protonation of the sulphate group, followed by attack of water on the sulphur



The rate of the reaction is therefore given by

$$\text{rate} = k_2 K [\text{H}^+] [\text{ROSO}_3^-] [\text{H}_2\text{O}] = k_{2,\text{obs}} [\text{H}^+] [\text{ROSO}_3^-] \quad (2)$$

where

$$K = \frac{[\text{ROSO}_3\text{H}]}{[\text{ROSO}_3^-][\text{H}^+]} \quad (3)$$

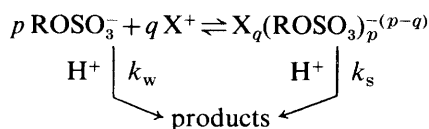
and

$$k_{2,\text{obs}} = k_2 K [\text{H}_2\text{O}]. \quad (4)$$

For the acid-catalysed hydrolysis of lower alkyl sulphates in non-micellar solutions, the values reported by Kurz for  $k_{2,\text{obs}}$  ( $k_{\text{H}}$  in his notation)<sup>1</sup> are independent of the alkyl-chain length, but depend on the ionic strength of the solutions. Thus, at  $90^\circ\text{C}$ , an increase of ionic strength from 0.081 to 0.51 reduces  $k_{2,\text{obs}}$  from  $7.2 (\pm 0.5) \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  to  $5.2 (\pm 0.3) \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . This is the direction of change expected for a reaction between oppositely charged ions.

For long-chain alkyl sulphates, the reaction is also catalysed by the self-micellisation

of these species<sup>1, 2, 15-17</sup> and so occurs by two parallel pathways, as shown in scheme 1.



SCHEME 1

In scheme 1  $k_w$  and  $k_s$  are the effective second-order rate constants for the reaction in the aqueous and micellar pseudo-phases, respectively. The values of  $k_w$ , which is identical with  $k_{2,\text{obs}}$  defined by eqn (4), are obtainable from measurements of the reaction rate at concentrations below the critical micelle concentrations (c.m.c.) of the alkyl sulphates. We use the symbol  $k_s$  for the effective rate constant of the micellar reaction, since the latter takes place exclusively in the Stern layer of the micelles<sup>5</sup> in the systems under discussion. The observed rate of reaction is thus given by

$$\text{rate} = k_{2,\text{obs}} C_T H_T = k_w \bar{H}_w \bar{C}_w (1 - CV) + k_s \bar{H}_s \bar{C}_s CV_s \quad (5)$$

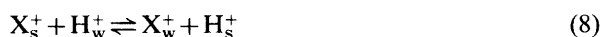
where  $C_T$  and  $H_T$  are, respectively, the total concentrations of surfactant and hydrogen ion in the solution,  $C (= C_T - \text{c.m.c.})$  is the concentration of surfactant in micellised form,  $V_s$  is the molar volume of the surfactant head groups in the Stern layer and  $V$  that of the surfactant [thus  $(1 - CV)$  and  $CV_s$  are the volumes of the aqueous pseudo-phase and of the Stern layer, respectively, in unit volume of the solution],  $\bar{H}_w$  is the concentration of hydrogen ions and  $\bar{C}_w$  that of surfactant monomers in the aqueous pseudo-phase and  $\bar{H}_s$  and  $\bar{C}_s$  are the corresponding concentrations in the Stern layer. Since  $\bar{C}_w = \text{c.m.c.}/(1 - CV)$ ,  $\bar{C}_s = C/CV_s = 1/V_s$ ,  $\bar{H}_w = H_w/(1 - CV)$  and  $\bar{H}_s = H_s/CV_s$ , it follows that

$$\text{rate} = k_{2,\text{obs}} C_T H_T = k_w H_w \text{c.m.c.}/(1 - CV) + k_s H_s/V_s \quad (6)$$

where  $H_w$  and  $H_s$  are the concentrations in the solution as a whole of free hydrogen ions and hydrogen ions bound in the Stern layer, respectively. In concentrated surfactant solutions only the second term in eqn (6) makes a significant contribution. Dividing through by  $k_w C_T H_T$  and ignoring the first term, we obtain an expression for the observed second-order rate constant relative to the rate constant in pure water

$$k_{2,\text{rel}} = \frac{k_{2,\text{obs}}}{k_w} = \frac{k_s}{k_w} \frac{1}{C_T V_s} \frac{H_s}{H_T} \quad (7)$$

In scheme 1,  $q/p = \beta$  is the degree of counterion binding by the micelles and, *e.g.* for SDS at ordinary temperatures, has the value of  $0.75 \pm 0.1$ , according to estimates made by a variety of methods.<sup>18</sup> Data collected by Romsted<sup>6</sup> show that, to a good approximation,  $\beta$  is independent of the nature and concentration of the counterion for ions of the same charge type. Romsted<sup>6</sup> has therefore argued that reactive ions in micellar-catalysed reactions enter the Stern layer mainly by ion exchange with surfactant counterions, rather than by additional binding to the micellar surface. Thus in the systems under discussion, the hydrogen ions will be assumed to enter the Stern layer by exchange with the counterions  $\text{X}^+$





where the subscripts w and s denote the aqueous pseudo-phase and the Stern layer, respectively. The distribution of the hydrogen ions between the aqueous pseudo-phase and Stern layer is thus governed by the ion-exchange constant  $K_{H/X}$

$$K_{H/X} = \frac{H_s X_w}{X_s H_w} = \frac{\bar{H}_s \bar{X}_w}{\bar{X}_s \bar{H}_w} \quad (9)$$

where  $H_w$  and  $H_s$  have been defined already and  $X_w$  and  $X_s$  are the corresponding concentrations of surfactant counterions. The reactive ion,  $H^+$ , and the surfactant counterion,  $X^+$ , together neutralize a fraction  $\beta$  of the total charge of the micellised surfactant head groups

$$\bar{H}_s + \bar{X}_s = \beta \bar{C}_s \quad (10)$$

In addition, the total concentrations of hydrogen ions,  $H_T$ , and surfactant counterions,  $X_T$ , must satisfy the material balance equations

$$H_T = \bar{H}_s CV_s + \bar{H}_w(1 - CV) \quad (11)$$

$$X_T = \bar{X}_s CV_s + \bar{X}_w(1 - CV) \quad (12)$$

Eqn (9)-(12) lead to a quadratic equation for  $H_s$  (see Appendix), which can be solved to give  $H_s$  as a function of the variables  $H_T$ ,  $X_T$ ,  $C$  and  $K_{H/X}$

$$H_s = \frac{-A \pm [A^2 + 4K_{H/X}(1 - K_{H/X})\beta CH_T]^{\frac{1}{2}}}{2(1 - K_{H/X})} \quad (13)$$

where  $A = K_{H/X}H_T + X_T + \beta C(K_{H/X} - 1)$  and only the positive root has physical significance.

Eqn (13) shows that if all other variables remain constant,  $H_s$  increases as a complicated function of  $H_T$ . It then follows from eqn (7) that the micellar reaction should not be first order in  $H_T$ , and  $k_{2,obs}$  values obtained from initial rates in individual experiments (for given  $H_T$ ,  $C_T$  and  $X_T$ ) should be apparent constants only.

The value of the ratio  $k_s/k_w$  in eqn (7) will depend on the relative ionic strengths of the Stern layer and aqueous pseudo-phase. Geometric considerations of the micellar surface<sup>6</sup> show that the Stern layer volume per micelle is constant, but  $\bar{C}_s$  depends on the packing of monomers in the micelle (*i.e.* on the aggregation number) and is estimated to be between 5 and 7 mol dm<sup>-3</sup> (for aggregation numbers between 62 and 87, assuming spherical micelles). This corresponds to molar volumes of head groups in the Stern layer,  $V_s$ , between 0.20 and 0.14 dm<sup>3</sup> mol<sup>-1</sup> (Bunton *et al.*<sup>19</sup> have expressed a preference for the latter value as the most realistic at ordinary temperatures). The high molar concentration of head groups in the Stern layer thus implies a high ionic strength in that layer. In view of this it is reasonable to assume that  $k_s/k_w < 1$ .

A theoretical treatment similar to Romsted's has been given by Quina and Chaimovich,<sup>20</sup> but the final equation requires modification if a salt with a common counterion is added to the system, whereas eqn (13) accommodates this without modification. Accordingly we shall discuss our experimental results in terms of eqn (7) and (13).

#### EFFECT OF ACID CONCENTRATION

The results in fig. 2 and 3 confirm the theoretical prediction that the micellar-catalysed reaction should not be first order in the total hydrogen-ion concentration. As fig. 2 shows, the rate approaches a limiting value at sufficiently high acid concentrations.

In terms of the theory, this can be ascribed to progressive replacement of  $\text{Na}^+$  by  $\text{H}^+$  ions in the Stern layer. The replacement appears to be almost complete at a ratio  $H_T/\text{Na}_T$  of ca. 4. The higher rates of hydrolysis and more pronounced curvature of the plot for  $\text{SDE}_2\text{S}$  (fig. 2) imply a larger value of  $K_{\text{H}/\text{Na}}$  for  $\text{SDE}_2\text{S}$  than for SDS.

The dependence of the observed rate constant on acid concentration (fig. 4) is qualitatively as expected from eqn (7). Thus, at constant surfactant concentration, the fraction of bound hydrogen ions,  $H_s/H_T$ , will decrease with increasing total acid concentration,  $H_T$ , an effect demonstrated experimentally by Bunton *et al.*<sup>21</sup> Therefore  $k_{2,\text{obs}}$  is expected to decrease with increasing  $H_T$  at low surfactant concentrations, as observed. At the higher concentration of SDS ( $0.35 \text{ mol dm}^{-3}$ ), the initial rate is approximately linear in  $H_T$  (fig. 3), so that the reaction under these conditions is approximately first order in  $H_T$ , and  $k_{2,\text{obs}}$  is almost constant (fig. 4). This is also expected, since most of the hydrogen ions will be taken up by the micelles ( $H_s/H_T \rightarrow 1$ ) when the surfactant concentration considerably exceeds the total acid concentration, especially if  $K_{\text{H}/\text{Na}} > 1$ . Evidence that  $K_{\text{H}/\text{Na}} > 1$  for SDS comes from c.m.c. measurements at  $25^\circ\text{C}$ , which show that the c.m.c. of SDS has considerably smaller values in the presence of hydrochloric acid<sup>22</sup> than in the presence of sodium chloride.<sup>23, 24</sup> The much smaller values of  $k_{2,\text{obs}}$  at the higher surfactant concentration are consistent with the predicted inverse dependence of  $k_{2,\text{obs}}$  on  $C_T$  [eqn (7)].

In terms of eqn (7), the more pronounced decrease in  $k_{2,\text{obs}}$  with increasing acid concentration under the same experimental conditions ( $C_T = 0.035 \text{ mol dm}^{-3}$ ) for  $\text{SDE}_2\text{S}$  than for SDS (fig. 4) implies a greater value of  $k_s H_s/V_s$  for the former. Thus, the concentration of  $\text{H}^+$  ions in the Stern layer must be greater for  $\text{SDE}_2\text{S}$  than for SDS at the same values of  $C_T$  and  $H_T$ , or  $k_s$  must be greater, or both. The first possibility implies a greater value of  $K_{\text{H}/\text{Na}}$  for  $\text{SDE}_2\text{S}$  than for SDS, which is consistent with the effect of added sodium chloride on the rates of hydrolysis (see Part 2). The greater tendency of  $\text{SDE}_2\text{S}$  micelles to bind  $\text{H}^+$  ions could be due to their binding by the ether oxygens. A greater value of  $k_s$  is also possible if the dielectric constant of the Stern layer containing the ethoxy groups is less than that of the purely aqueous Stern layer, since  $K$  [eqn (3)] should be greater in a medium of lower dielectric constant. (Barry and Wilson<sup>25</sup> suggest, on the contrary, that the dielectric constant of the Stern layer containing ethoxy groups could be greater, but this seems unlikely since ethers have lower dielectric constants than water.)

For quantitative comparison of theory with experiment,<sup>4</sup> the c.m.c. values of SDS in dilute acid solutions were taken to be the same as those in dilute sodium chloride at  $70^\circ\text{C}$ , as determined by Shinoda,<sup>26</sup> although as already noted at  $25^\circ\text{C}$  the c.m.c. has much smaller values in dilute HCl than in sodium chloride solutions.<sup>22-24</sup> This introduces only a minor uncertainty at high surfactant concentrations, however. The degree of ion binding,  $\beta$ , was taken to be 0.6 at  $70^\circ\text{C}$ , following the findings of Barry and Wilson<sup>25</sup> which show that counterion binding decreases with temperature ( $\beta = 0.79$  at  $25^\circ\text{C}$  and 0.67 and  $45^\circ\text{C}$ ).

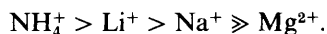
These values for the c.m.c. and  $\beta$ , a value of 0.3 for  $k_s/k_w$  and values between 2 and 4 for  $K_{\text{H}/\text{Na}}$ , were then used to generate from eqn (7) and (13) curves of initial rate against hydrogen ion concentration. These curves show a more pronounced curvature than the experimental curves for SDS in fig. 2, and the predicted limiting rates at high acid concentration are lower than those experimentally observed. This is probably because  $\beta$  is not in fact constant, as assumed, but increases as hydrogen ions replace sodium ions in the Stern layer, thus leading to greater experimental rates. An increase in  $\beta$  with increasing acid concentration would be expected to occur if the  $\text{H}^+$  ion is bound more strongly than the  $\text{Na}^+$  ion by the micelles, as the c.m.c. determinations<sup>21-24</sup> indicate.

## EFFECT OF SURFACTANT CONCENTRATION

In micellar-catalysed reactions involving an organic substrate and a small hydrophilic ion, the observed second-order rate constant generally decreases steadily with increasing surfactant concentration from a maximum value at just above the c.m.c.<sup>6</sup> This effect has been attributed to dilution of the reactants, which are largely bound to the micelles at surfactant concentrations just above the c.m.c., by the progressively increasing volume of the micellar phase. The steady decrease in the observed rate constant is also clearly observed in the hydrolysis of SDS and SDE<sub>2</sub>S (fig. 5 and 6), although the dilution of the organic substrate, which is also the micelle former, does not occur. The decrease in the rate constant must therefore be due solely to a decreasing concentration of hydrogen ions in the Stern layer. Curves calculated from eqn (7) and (13), using the previously mentioned values of c.m.c.,  $\beta$ ,  $k_s/k_w$  and  $K_{H/Na}$ , do in fact agree reasonably well with the experimental curves in fig. 5 up to a concentration of  $0.05 \text{ mol dm}^{-3}$ , but at higher surfactant concentrations the theoretical values of  $k_{2,obs}$  are less than the observed values.<sup>4</sup> This may be an ionic strength effect, because it must be borne in mind that  $K$  [eqn (3)] and  $K_{H/Na}$  [eqn (9)] have been defined as 'concentration' equilibrium constants. Evidence for the importance of ionic strength effects will be presented in Part 2.

## EFFECT OF THE NATURE OF THE COUNTERION

The relative rate constants in fig. 6 fall in the sequence



In terms of the theory this implies that the value of the ion-exchange constant  $K_{H/X}$  decreases in the same sequence and that the  $\text{Mg}^{2+}$  ion is therefore much more strongly bound to the micellar surface than the monovalent counterions. This is plausible in view of the much greater charge density of the  $\text{Mg}^{2+}$  ion and is also consistent with the much lower c.m.c. value for magnesium dodecylsulphate ( $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ )<sup>27</sup> than for SDS ( $8.1 \times 10^{-3} \text{ mol dm}^{-3}$ ).<sup>7</sup>

## EFFECT OF SURFACTANT CONCENTRATION AT CONSTANT TOTAL HYDROGEN AND TOTAL COUNTERION EQUIVALENT CONCENTRATIONS

Romsted<sup>6</sup> claimed that, at low surfactant concentration and assuming ideal solution behaviour, a constant ratio of reactive to non-reactive ion concentrations ( $H_T/X_T = \text{constant}$ ) would lead to a plateau value of  $k_{2,obs}$  as the surfactant concentration is increased. The results in fig. 7 show no plateau, but a decrease with increasing surfactant concentration, although this is much less pronounced than in the absence of added salt. Qualitatively, this is not readily accounted for, but theoretical curves<sup>4</sup> generated using eqn (7) and (13) indicate that negative slopes should be expected for  $K_{H/X} > 1$  and positive slopes for  $K_{H/X} < 1$  [for  $K_{H/X} = 1$ , the quotient on the r.h.s. of eqn (13) becomes indeterminate, but logically Romsted's prediction ought to hold]. For values of  $K_{H/X} > 2$ , the generated lines show curvature due mainly to the inverse relationship between  $k_{2,obs}$  and  $C_T$  [eqn (7)]. The trend in fig. 7 with change of cation is again consistent with values of  $K_{H/X}$  decreasing in the order  $\text{NH}_4^+ > \text{Li}^+ > \text{Na}^+ > \text{Mg}^{2+}$ .

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## APPENDIX

In order to obtain an equation for  $H_s$  in terms of  $H_T$  and  $X_T$ , eqn (9) is first solved for  $\bar{X}_w$ , and this is substituted into eqn (12), giving

$$X_T = \bar{X}_s CV_s + K_{H/X} \frac{\bar{H}_w \bar{X}_s}{\bar{H}_s} (1 - CV) \quad (\text{A } 1)$$

from which

$$\bar{X}_s = \frac{X_T \bar{H}_s}{\bar{H}_s CV_s + K_{H/X} \bar{H}_w (1 - CV)} \quad (\text{A } 2)$$

is obtained.  $\bar{H}_w$  is now eliminated from eqn (A 2) using its value from eqn (11) to give

$$\bar{X}_s = \frac{X_T \bar{H}_s}{\bar{H}_s CV_s + K_{H/X} (H_T - \bar{H}_s CV_s)} \quad (\text{A } 3)$$

This quantity is now substituted into eqn (10), giving

$$\bar{H}_s + \frac{X_T \bar{H}_s}{K_{H/X} H_T + \bar{H}_s CV_s (1 - K_{H/X})} = \beta \bar{C}_s \quad (\text{A } 4)$$

which, making use of the relationships  $\bar{H}_s = H_s / CV_s$  and  $\bar{C}_s = 1 / V_s$ , can be simplified to

$$H_s + \frac{X_T H_s}{K_{H/X} H_T + H_s (1 - K_{H/X})} = \beta C \quad (\text{A } 5)$$

the quadratic equation in  $H_s$ , whose solution is given in eqn (13).

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