The hydrolysis of C_{12} primary alkyl sulfates in concentrated aqueous solutions. Part 1. General features, kinetic form and mode of catalysis in sodium dodecyl sulfate hydrolysis †

Donald Bethell,*[a] **Roger E. Fessey,**[a] **Ernest Namwindwa**[a] **and David W. Roberts**[b]

[a] *Department of Chemistry, University of Liverpool, Liverpool, UK L69 3BX*
[b] *Unilever Research, Port Sunlight Laboratory, Bebington, Wirral, UK CH63 3JW*

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As part of an investigation into the observed rapid hydrolysis of sodium primary alkyl sulfates in commercial concentrated aqueous mixtures (typically 70% by weight of surfactant) at 80 °C, the rate of hydrolysis of sodium dodecyl sulfate (SDS) in water has been followed acidimetrically over a wide range of initial SDS concentrations in aqueous buffers, in the presence of added sulfuric acid (0.20 mol kg^{-1}) and also in unbuffered, initially neutral solution. First order rate coefficients derived from the initial rates of sulfuric acid-catalysed reactions showed unexpected, non-monotonic variations with increasing initial [SDS] at constant [H_2SO_4] and with [H_2SO_4] at 70% SDS. Reactions in initially neutral solutions were found to have an autocatalytic form arising from the existence of both an uncatalysed and an acid catalysed pathway from reactants to products. Both pathways are characterised by rate coefficients (derived by computer simulation of the initial phase of the hydrolysis) that vary with the initial [SDS]; those for the acid-catalysed pathway show similar but less dramatic variation than observed in reactions in the presence of sulfuric acid. Possible reasons for the difference in behaviour are discussed. The autocatalysis observed in initially neutral solutions is shown to arise from the production of hydrogen sulfate ions during the hydrolysis, but experiments in buffer solutions at both high and low SDS concentrations show the characteristics of specific hydrogen ion catalysis. Solvent kinetic deuterium isotope effects on both pathways are, however, small. Examination of the dodecanol produced by SDS hydrolysis at low and high initial concentrations in ^{18}O-enriched water showed no incorporation of the label, signifying exclusive S–O cleavage in the acid-catalysed pathway. It is argued that the results, taken in conjunction with literature data, are consistent with an S_N2 displacement of sulfate ion by water in the uncatalysed hydrolysis pathway. While, for the hydrogen ion catalysed pathway, a previously suggested unimolecular cleavage of SO_3 from dodecyl hydrogen sulfate, with concerted intramolecular proton transfer, appears more consistent with the observations, proton transfer concerted with direct transfer of SO_3 to a preassociated water molecule is a plausible alternative.

Introduction

Long chain primary alkyl sulfuric acids, usually as their sodium salts, are important commercial surfactants. They are normally produced commercially by treatment of mixtures of naturally produced fatty alcohols with sulfur trioxide, followed by neutralisation of the sulfated product with sodium hydroxide. From this process is obtained a neutral mixture of sodium primary alkyl sulfates (PAS), containing around 70% by weight of PAS with chain lengths in the range C_{12} to C_{14}, in the form of a viscous paste at ambient temperatures. This paste becomes a free-flowing, and therefore more easily handled, liquid at higher temperatures, typically around 80 °C. Prolonged storage of the material at such elevated temperature, however, leads to complete hydrolysis according to the formal reaction (1).

$$RCH_2OSO_3^-Na^+ + H_2O \rightarrow RCH_2OH + HSO_4^-Na^+ \quad (1)$$

Notwithstanding variations in the alkyl-chain composition of different batches of PAS, complete hydrolysis usually occurs in about 12 hours at 80 °C. The kinetic and mechanistic investigation described in this and an accompanying paper was undertaken to throw more light on this situation, particularly to examine the possibility that the high reactivity might be associated with the state of aggregation of the surfactant at high concentration. Our starting point was the hydrolysis of sodium dodecyl sulfate (SDS), a material that features commonly in academic studies of surfactant behaviour and which is found to the extent of 40 to 70% by weight in commercial PAS preparations.

Although there is a substantial literature on the hydrolysis of aryl sulfates as a consequence of their biological significance, there are relatively few reports in the open literature on the hydrolysis of primary alkyl sulfates. Much of what has appeared has been concerned with the differences in the kinetics of hydrolysis of SDS when conducted below and just above the critical micelle concentration (c.m.c = 8.6 mM at 40 °C[1]). Thus Kurz,[2] Motsavage and Kostenbauder[3] and Nogami *et al.*[4] demonstrated from initial rate measurements the occurrence of an uncatalysed and a proton-catalysed hydrolysis pathway. They showed that micellisation of SDS, for example, led to a 30- to 40-fold increase in rate constants for the acid-catalysed hydrolysis, but that there was a negligible effect on the uncatalysed reaction. Mixed micelles of SDS and non-ionic additives, particularly dodecanol, showed substantial rate enhancements,[3] further complicating the kinetic form of SDS hydrolysis. Although in these early investigations the term specific acid catalysis was used in connection with the hydrolysis, the precise form of the catalysis was not explicitly studied using buffer solutions of varying concentration,

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† Dedicated to the memory of Lennart Eberson in gratitude for his friendship and in recognition of his many contributions to Physical Organic Chemistry.

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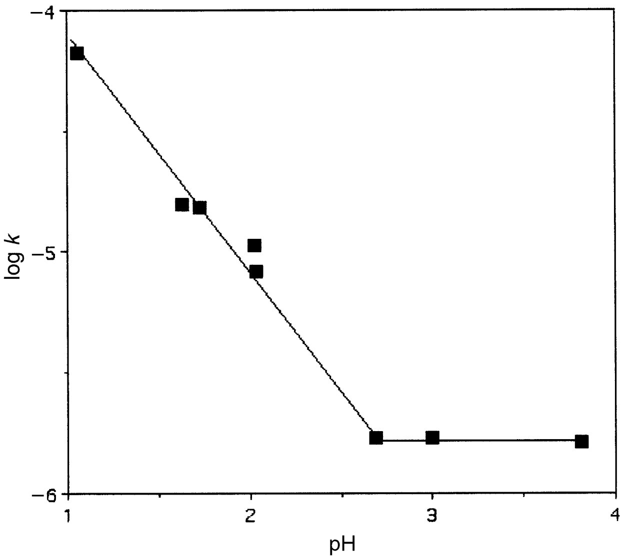


Fig. 1 pH-Dependence of the initial first order rate coefficients for hydrolysis of SDS (0.1 M = 2.8 weight%) in aqueous sulfate buffers at 100 °C. Ionic strength 0.4 M.

reliance being placed on the approximate proportionality of observed rate constants and [H_3O^+].[3] Subsequently it was reported that the proportionality was not exact[4a] and that a 'saturation' effect was evident; this was interpreted[5] in terms of the pseudophase ion-exchange model of micellar behaviour.[6] The effect on rate constants for hydrolysis of increasing the surfactant concentration substantially beyond the c.m.c. has received relatively little attention. Garnett *et al.*[5] reported a *ca.* 30% linear decrease in rate constants for perchloric acid catalysed hydrolysis of SDS on increasing the concentration from 0.02 to 0.6 mol dm^{-3} (*i.e.* up to ca. 18% by weight), an effect attributed to dilution of the hydrogen-ion concentration in the Stern layer of the micelles, offset by ionic strength effects.

The present investigation addresses the following aspects of SDS hydrolysis: the effects on the rate of hydrolysis of increasing the reactant/surfactant concentration from a little above the c.m.c. to a value comparable with the PAS concentration in commercial pastes, the nature of catalysis involved in the hydrolysis, and possible changes in the reaction mechanisms over the concentration range studied. In a subsequent paper we shall discuss certain properties of concentrated SDS solutions that throw light on the origin of the kinetic behaviour described here, and also compare the behaviour of SDS with other C_{12} PAS.

Results and discussion

Preliminary kinetic experiments and hydrolysis in the presence of added sulfuric acid

In all cases, initial rates of hydrolysis at 80–100 °C were followed by titration at 25 °C of aliquots of reaction mixtures to pH 7 using an autotitrator, yielding the total acid (H_3O^+ and HSO_4^-) produced and hence the residual SDS concentration.

Preliminary experiments were carried out on SDS (0.025 M) in aqueous sulfate buffer solutions with measured initial pH-values, determined at 25 °C, in the range from 3.8 to 1.0 and at a constant ionic strength adjusted to 0.4 M by the addition of sodium chloride. From the results for hydrolysis at 100 °C, initial first order rate coefficients were evaluated from plots of ln [SDS] *vs.* time and these are shown in Fig. 1 as a function of pH. Clearly, at the higher pH values, down to *ca.* 2.7, the initial rate coefficient is invariant with changing pH, but in more acidic solutions values increase; a line of unit slope has been drawn in Fig. 1 and fits the results satisfactorily. Fig. 2 shows the time-variation of the concentration of SDS in reactions in two solutions, initially at pH 7, one containing 1% by weight of SDS (0.035 mol kg^{-1}) and the other 10% SDS (0.347 mol kg^{-1}) with no other additives. In both instances the course of the reaction is sigmoidal, characterized by an initial slow phase followed by a rapid acceleration and a final slowing down as the hydrolysis approaches completion. It should be noted that the time to complete hydrolysis is very much shorter in the more concentrated SDS solution. These results are entirely consistent with earlier views of SDS hydrolysis as involving two pathways, one a slow, uncatalysed hydrolysis and the other an acid-catalysed process. The hydrolysis shows the characteristic autocatalytic form, the catalysis presumably arising from the production of hydrogen sulfate ions according to reaction (1).

Table 1 Relationship of instantaneous rate of SDS hydrolysis and sodium hydrogen sulfate concentration at 80 °C

SDS concentration (weight%)	Conversion (%)	Instantaneous rate/M s^{-1}	[$NaHSO_4$]/M	Exp. initial rate/M s^{-1}
5	4	2.7	0.00694[a]	2.5, 2.9
	8	4.0	0.0139[a]	4.3, 4.7
	22	8.1	0.0381[a]	8.0, 9.8
	40	11	0.0694[a]	11, 12
10	4	8.0	0.0142[b]	8.1, 9.5
	8	14	0.0282[b]	12, 16
	21	20	0.0741[b]	18, 24
	41	37	0.1428[b]	34, 40
70	4	4.5	0.10[c]	4.0, 5.0
	8	7.0	0.20[c]	6.2, 7.8
	21	14	0.50[c]	12, 16
	41	17	1.0[c]	15, 19

[a] Constant ionic strength (NaCl) 0.24 M. [b] Ionic strength (NaCl) 0.49 M. [c] Ionic strength (NaCl) 3.43 M.

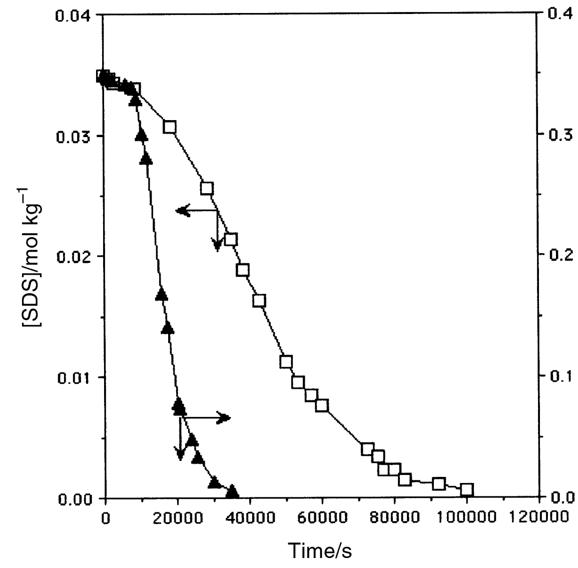


Fig. 2 Variation of SDS concentration with time in the hydrolysis of SDS at 100 °C in initially neutral aqueous solution: (□) curve A, 1% SDS; (▲) curve B, 10% SDS.

This interpretation was confirmed by measuring initial rates of SDS hydrolysis at 80 °C in 5, 10 and 70% SDS solutions to which had been added concentrations of hydrogen sulfate ion corresponding to *ca.* 5, 10, 20 and 40% conversion according to reaction (1). The experimental results are compared in Table 1 with instantaneous rates of hydrolysis of SDS in analogous reactions when no sodium hydrogen sulfate had been added initially and determined from the conversion/time curves at the appropriate time by differentiation with respect to time of the second order binomial expression that fitted the experimental [SDS] *vs.* time curve. The agreement is well within the limits of

Table 2 Initial first order rate coefficients[a] for SDS hydrolysis at 100 °C in the presence of added H_2SO_4 (0.2 mol kg^{-1})

SDS conc. (weight%)	$k_0/10^{-4}$ s^{-1}	ΔH/kJ mol^{-1} (ΔS/J K^{-1} mol^{-1})[b]	SDS conc. (weight%)	$k_0/10^{-4}$ s^{-1}	ΔH/kJ mol^{-1} (ΔS/J K^{-1} mol^{-1})[b]
1	4.0, 3.8 (6.5)[c]	112 (−15)	25	2.7, 2.7	119 (+5)
2	2.1, 1.7 (5.5)	114 (−16)	30	2.9, 3.2 (4.5)	115 (−5)
5	4.4, 4.7 (5.1)	108 (−10)	40	3.0, 3.1 (4.1)	129 (+38)
10	4.5, 4.6 (5.7)	142 (+60)	50	4.0, 4.3 (4.5)	120 (+20)
12	4.5, 4.7	147 (+70)	60	4.3, 4.2 (5.3)	112 (−20)
15	4.0, 4.3 (3.5)	151 (+77)	65	4.2, 4.4	116 (−10)
20	3.0, 3.0 (3.5)	129 (+40)	70	4.2, 4.2 (5.3)	120 (−5)

[a] Initial 7% reaction. [b] Average estimated uncertainties: in ΔH ± 5 kJ mol^{-1}; in ΔS ± 12 J K^{-1} mol^{-1}. [c] Average values of $k_1 \times [H_2SO_4]$ at the same SDS concentration are in parentheses.

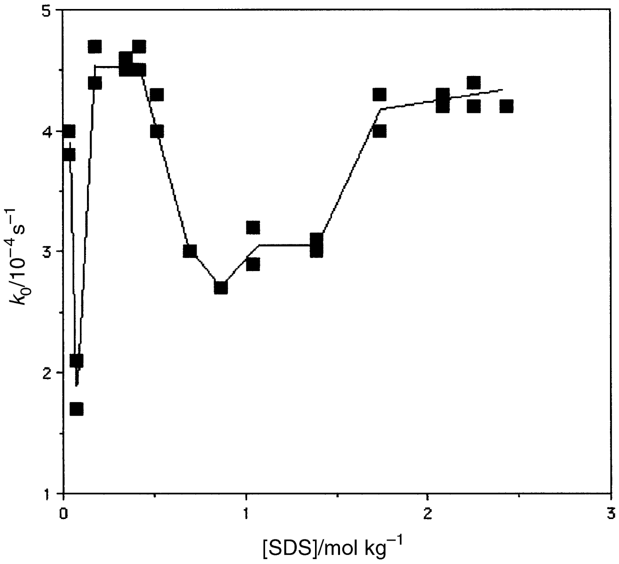


Fig. 3 Variation with SDS molality of observed first order rate coefficients at 100 °C for the hydrolysis of SDS in aqueous solutions containing 2% by weight of sulfuric acid.

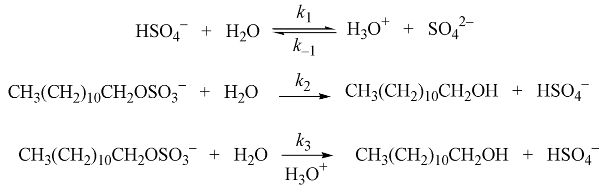
accuracy of the two data sets, confirming that hydrogen sulfate ions are responsible for the catalysis. The presence of the product ions leads to an increased acidity in the reaction mixture, and we show later that the autocatalysis arises solely from the increasing hydrogen ion concentration and does not involve the hydrogen sulfate ions *per se*, that is, as general acids.

The sigmoidal form of [SDS] *versus* time curves was absent when the hydrolysis was carried out in the presence of added sulfuric acid (2% by weight = 0.204 mol kg^{-1}); only the acid-catalysed pathway was observable. Initial first order rate coefficients (k_0) were determined in duplicate runs from plots of ln [SDS] against time over the early stages of reaction (≤7% hydrolysis) which were linear ($r \geq 0.99$); values were determined at temperatures 80, 85, 90 and 100 °C over the range of SDS concentrations from 1 to 70 weight% (0.035 to 2.43 mol kg^{-1}). Reproducibility of rate coefficients was usually ±5%. Activation parameters, derived using the Eyring equation from excellent linear plots of ln k_0 *vs.* T^{-1}, and rate coefficients at 100 °C are in Table 2. The values of k_0 vary in an unexpected way with [SDS] (see Fig. 3); the initial decrease is similar to that previously reported in perchloric acid-catalysed hydrolyses, but the most remarkable features are minima at 2 and *ca.* 25% SDS separated by a prominent maximum at 12% SDS. This behaviour would seem to be a consequence of the complex nature of the surfactant solutions and the nature of the aggregates within which hydrolysis takes place.

In a further set of experiments, the effect of changing the concentration of sulfuric acid initially present in reaction mixtures containing initially 70% by weight of SDS was investigated using the same procedures. Values of k_0 so obtained are in Table 3, from which it can be seen that they increase in a manner that is also not monotonic. Up to around 2% H_2SO_4, rate coefficients increase linearly with the concentration of added acid, but a rate maximum is reached at around 2.5% sulfuric acid, k_0 values decreasing to a minimum at *ca.* 4 weight% H_2SO_4 whereafter the values increase again. This result, unforeseen on the basis of previously described acidity dependences in dilute SDS solutions, is presumably a consequence of electrolyte effects on SDS aggregation,[8] but it prompted an investigation of the mode of acid catalysis of SDS hydrolysis in aqueous solutions from 5 to 70% SDS.

Hydrolysis in unbuffered, initially neutral solution

The unusual variations in k_0 values with [SDS] observed in sulfuric acid-catalysed reactions discouraged attempts to analyse curves such as those in Fig. 2 over the whole course of the reaction. Instead recourse was made to kinetics simulation based on the program Kinetics (Chemistry Courseware Consortium, University of Liverpool) applied to data obtained over the first 10% of hydrolysis. The program requires the input of the initial concentrations of all species in the reaction scheme and the simplified version in Scheme 1 was adopted



$$HSO_4^- + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_3O^+ + SO_4^{2-}$$

$$CH_3(CH_2)_{10}CH_2OSO_3^- + H_2O \xrightarrow{k_2} CH_3(CH_2)_{10}CH_2OH + HSO_4^-$$

$$CH_3(CH_2)_{10}CH_2OSO_3^- + H_2O \xrightarrow[H_3O^+]{k_3} CH_3(CH_2)_{10}CH_2OH + HSO_4^-$$

Scheme 1

throughout. Note that the concentration of water was not explicitly included, so that the derived rate constants contain where appropriate the (constant) concentration of water (see below). For the purposes of the simulation, a value of pK_a for hydrogen sulfate ion of 1.78, experimentally determined at 25 °C,[7] was assumed to apply under all reaction conditions. We justify this on the grounds that we could not directly measure pK_a under the range of conditions of the SDS hydrolysis, but we recognise that any variation in the pK_avalue for hydrogen sulfate ion as the [SDS] changes will be reflected in the derived rate coefficient for the acid-catalysed reaction. We shall return to this matter later. Since the simulation program requires the pK_a-value to be introduced in the form of rate constants for the forward and reverse reactions, k_{-1} was arbitrarily fixed at 1×10^{10} s^{-1} with k_1 then 1.66×10^8 mol kg^{-1} s^{-1}. Changing these values by an order of magnitude while maintaining the ratio constant did not influence the outcome of the simulation.

Experimental data were simulated by adjustment of the two remaining parameters in Scheme 1, the rate coefficients for the uncatalysed (k_2) and catalysed (k_3) processes. All hydrolyses were run in duplicate and separately simulated; values of the derived rate coefficients generally agreed within ±5–10% of the mean for k_3 for which changes of this magnitude could readily be detected by the simulation procedure. Rather larger

Table 3 Influence of the concentration of added H_2SO_4 on the initial rate coefficients for SDS hydrolysis in 70% solution at 100 °C

$[H_2SO_4]$ (weight%)	0	1.2	1.8	1.9	2.0	2.4	2.6	3.2	4.6	6.4
$10^4\ k_0/s^{-1}$	Small	2.1	3.6	3.9	4.2	4.6	3.4	2.7	3.1	7.9

Table 4 Rate coefficients for SDS hydrolysis in initially neutral solution from computer simulations according to Scheme 1 of experimental [SDS] *versus* time curves[a]

	$k_2/10^{-7}\ s^{-1}$			$k_3/10^{-4}\ M^{-1}\ s^{-1}$		
(weight%)	80 °C	100 °C	$(\Delta S/J\ K^{-1}\ mol^{-1})$[b]	80 °C	100 °C	$(\Delta S/J\ K^{-1}\ mol^{-1})$[b]
1	2.3, 3.0	21, 29 (26)[c]	120 (−30)	3.6, 3.9	30, 34 (1.7)[c]	120 (20)
2	1.9, 2.2	16, 24	130 (0)	2.6, 2.9	25, 29	120 (50)
5	0.74, 0.80	10, 12 (10)[d]	150 (10)	2.9, 3.2	23, 27 (28)[d]	110 (10)
10	0.055, 0.085	0.7, 0.7 (0.8;[c] 0.7[d])	130 (−50)	2.4, 3.2	26, 30 (14;[c] 31[d])	120 (40)
15	0.05, 0.09	0.6, 0.4	110 (−100)	2.3, 2.7	15, 19	100 (−20)
20	0.11, 0.17	1.4, 2.2 (1.8;[c] 2.0[d])	140 (−3)	2.2, 2.6	15, 19 (9;[c] 19[d])	100 (−20)
30	0.21, 0.29	1.3, 1.6	90 (−130)	1.5, 1.9	20, 24	140 (80)
40	0.30, 0.40	4.5, 4.9	140 (10)	1.8, 2.2	18, 22	120 (40)
50	0.43, 0.47	5.7, 6.1	140 (10)	1.8, 2.2	20, 24	130 (60)
60	0.80, 1.0	5.5, 5.9	100 (−100)	2.9, 3.2	24, 28	110 (10)
70	1.1, 1.2	5.3, 5.7 (5.5;[c] 5.5[d])	90 (−130)	5.7, 6.1	24, 28 (12;[c] 28[d])	80 (−80)

[a] Initial 10% reaction. [b] Estimated uncertainties: in $\Delta H \pm 20\ kJ\ mol^{-1}$; in $\Delta S \pm 50\ J\ K^{-1}\ mol^{-1}$. [c] Reactions using LDS; average values from two experiments. [d] Reactions carried out in D_2O; average values from two experiments.

differences were obtained in repeat determinations of k_2, especially when the values were very low.

Results obtained at 80 and 100 °C for SDS concentrations in the range 1 to 70 weight% are compiled in Table 4 from which it can be seen that there are variations in values of both k_2 and k_3. It may be noted that k_3 values turn out to be of similar magnitude to values of $k_0/[H_2SO_4]$ taken from Table 2. The results in Table 4 show that, for the uncatalysed process, rate coefficients pass through a clear minimum in the concentration range 10–15 weight% SDS at both 80 and 100 °C. Variations in the values of k_3 are smaller and less clearly defined, but a minimum is discernible around 30 weight% SDS at 80 °C, and in the range 15–20% at 100 °C. Values of the apparent activation enthalpies and entropies were evaluated from the kinetic results at 80 and 100 °C for both the catalysed and uncatalysed reaction; the precision is necessarily not high, but, taken at face value, the results in both series show interesting but different fluctuations as the initial SDS concentration varies. Detailed analysis is not warranted, but such complexity is to be expected from a superposition of temperature effects on rate processes and temperature effects on surfactant aggregation.

In a separate series of experiments, the influence of the reaction product dodecanol on the rate coefficients derived from simulations of the initial 10% of hydrolysis was examined. Reaction mixtures contained an amount of dodecanol corresponding to that which would have been formed after 50% hydrolysis. It was established that dodecanol had no effect within the experimental error on values of k_2 over the whole range of initial SDS concentrations. For k_3, however, values increased uniformly by *ca.* 50%.

The effect on values of k_2 and k_3 of replacing water in the reaction mixtures by deuterium oxide was also investigated. Over the whole range of SDS concentrations, the solvent isotope effects were small, falling well within the experimental uncertainty of the rate constants derived by the simulation method; average values for k_2^H/k_2^D in solutions containing 5, 10, 20 and 70% SDS at 100 °C were 1.0, and for k_3^H/k_3^D 0.9.

Comparison of values of k_2 and k_3 with values obtained using lithium dodecyl sulfate (LDS) at 1, 10, 20 and 70% by weight showed that the change of counter-cation had little effect on k_2, but that k_3 for SDS was roughly twice that for the lithium salt at all concentrations (neglecting the small difference in mol kg^{-1}). These observations contrast with earlier results on the hydrolysis of LDS (up to *ca.* 5% by weight) catalysed by 0.021 M perchloric acid in water at 70 °C for which observed second order rate constants exceeded those for SDS by around 10%.[5] However, the effect of added NaCl and LiCl on the perchloric acid catalysed hydrolysis of SDS at higher concentrations (0.35 mol dm^{-3}) was a rate enhancement that was greater for Na than Li and this reversal of the effect observed at lower [SDS] has been ascribed to an activity coefficient effect superimposed on the ion-exchange equilibrium in which hydrogen ions are displaced by alkali-metal cations in the micellar Stern layer. As we saw, SDS hydrolysis catalysed by added mineral acid shows somewhat different characteristics from the autocatalysed process, and this can be ascribed in part to electrolyte effects on surfactant aggregation. For the present, suffice it to say that the change in counter-ion affects only the acid-catalysed pathway, presumably by altering the acidity experienced by sulfate head-groups in the SDS aggregates which are expected to be quite different at 1 and 70% SDS.

Acid catalysis of SDS at low and high concentrations in aqueous solution

The mode of acid catalysis by hydrogen sulfate ions in aqueous solution was investigated at two SDS concentrations, 1 and 70 weight%, by the use of sulfate buffer solutions of varying concentration. In the experiments at the lower SDS concentration, the ionic strength was maintained constant by the addition of NaCl. In the far from ideal concentrated SDS solutions no additional salts were added; formal ionic strengths were calculated assuming that all the salts were fully dissociated. Initial rates of hydrolysis were measured as before; the results are in Table 5.

It can be seen from the results that at both low and high SDS concentrations the measured initial rates of hydrolysis increase as the ratio $[HSO_4^-]/[SO_4^{2-}]$ increases and the pH decreases, but remains essentially unchanged when $[HSO_4^-]$ increases at constant buffer ratio. This is the characteristic of reactions showing specific hydrogen-ion catalysis and indicates that the hydrolysis of dodecyl sulfate ions at both low and high concentrations in water has a rate-limiting step involving a rapidly formed adduct of the anion and a proton.[9] Two different types of basic site for proton attachment exist in alkyl sulfate anions, namely the oxygen atoms bearing the formal negative charge (protonation of which would yield the alkyl hydrogen sulfate) and the oxygen atom directly attached to the alkyl group (protonation of which

Table 5 Initial rates of SDS hydrolysis in aqueous sulfate buffers at 80 °C

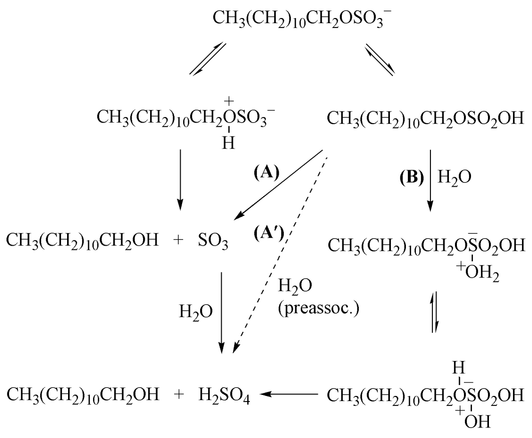
SDS (weight%)	$[HSO_4^-]$/mol kg^{-1}	$[SO_4^{2-}]$/mol kg^{-1}	Ionic strength/mol kg^{-1}	pH[a]	$v_0/10^{-7}$ mol kg^{-1} s^{-1}
1.0	0.0354	0.00354	0.106	1.79	2.1
	0.0354	0.00886	0.106	1.82	2.1
	0.0354	0.01770	0.106	1.90	1.6
	0.0354	0.02655	0.106	1.96	1.4
	0.0354	0.03540	0.106	2.02	1.1
	0.0177	0.01770	0.106	2.15	1.1
	0.0089	0.00886	0.106	2.25	1.15
70	0.200	0.020	2.69	1.37	520
	0.200	0.050	2.78	1.47	290
	0.200	0.100	2.93	1.62	250
	0.200	0.150	3.08	1.76	195
	0.200	0.200	3.23	1.84	205
	0.100	0.100	2.83	1.89	200
	0.050	0.050	2.63	1.97	170

[a] Values measured at 25 °C for 1% SDS solutions; values at 25 °C for 70% SDS solutions calculated from $[HSO_4^-]$ and $[SO_4^{2-}]$, taking pK_a for HSO_4^- as 1.78.

would give a zwitterion). Both protonated forms have been discussed as possible intermediates in the hydrolysis, and the experimental finding is consistent with a number of reaction pathways for each. Some pathways can be eliminated on the basis of oxygen labelling studies.

Oxygen labelling studies on SDS hydrolysis

One criterion of the constancy of reaction mechanism in SDS hydrolysis is that the origin of the oxygen atom in the product dodecanol, whether the sulfate group in the SDS reactant or the water, should be constant throughout the range of SDS concentrations. Accordingly, SDS solutions in water that contained 10 atom% ^{18}O and that were initially neutral were subjected to complete hydrolysis at 100 °C and the dodecanol produced was extracted from the diluted reaction mixture using diethyl ether and examined by mass spectrometry. Reactions were conducted on 10, 20, and 70 weight% SDS solutions. In all cases the dodecanol showed no ^{18}O enrichment over natural abundance. Under the conditions of the experiments, the percentage of hydrolysis by the uncatalysed pathway is negligible, so the inference is that acid-catalysed hydrolysis proceeds at all concentrations by a mechanism involving S–O bond cleavage. Several such possibilities that have been discussed are shown in Scheme 2.



Scheme 2

Variations in rate coefficients for SDS hydrolysis with initial [SDS]

On the basis of the results presented here, it is evident that the hydrolysis of SDS in the temperature range 80 to 100 °C over the concentration range 1 to 70% by weight proceeds by two pathways, one uncatalysed and rather slow, the other catalysed by protons generated *via* the hydrogen sulfate ions produced in the hydrolysis. There appear to be no mechanistic changes with SDS concentration and the variations in the observed rate constants must therefore be ascribed to changes in the reaction medium. Such changes are likely to embrace the state of aggregation of the reactant SDS, changes in water activity, and medium effects on equilibria (most notably the dissociation of hydrogen sulfate ions to generate solvated protons) and on initial- and transition-state energies. We have investigated the effect of changing [SDS] on the apparent pK_a value of hydrogen sulfate ion experimentally by direct titration of 0.005 and 0.010 M $NaHSO_4$ in SDS solutions up to 20% by weight. The results so obtained are in Fig. 4 as averages of duplicate determinations, agreeing in most cases within 0.02 pK units and never by more than 0.04 pK units, at the two hydrogen sulfate concentrations. There appears to be little change in pK_a at SDS concentrations up to and a little beyond the c.m.c, whereafter an abrupt increase of about 0.3 pK units is observed which then drops only to rise again in the range 10 to 20% SDS. These findings go some way towards explaining the relative insensitivity of k_3 values to [SDS] when compared with k_0 values; the measured acidity of hydrogen sulfate at SDS concentrations from the c.m.c. to *ca.* 0.15 mol kg^{-1} and in the range 0.4 to 0.5 mol kg^{-1} is lower than was assumed in the simulations, and this would suppress the values of k_3 in these concentration ranges.

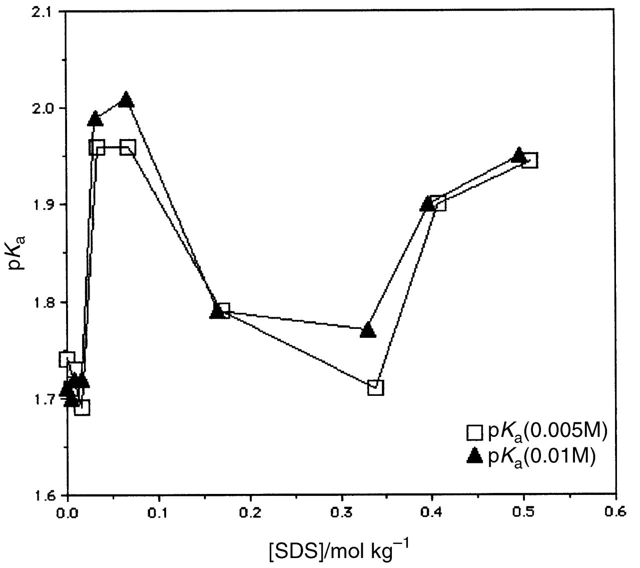


Fig. 4 Effect of SDS molality on apparent pK_a values for sodium hydrogen sulfate in aqueous solutions at 25 °C.

Mechanisms of SDS hydrolysis

Uncatalysed hydrolysis. We can offer no direct evidence to establish the mechanism of the uncatalysed process, There is, however, ample evidence in the literature,[10] based on studies of sodium salts of secondary alkyl sulfates in neutral or basic solutions, that demonstrates that hydrolysis occurs with complete inversion of configuration at the secondary carbon atom, indicative of nucleophilic attack on the α-carbon atom in an S_N2 process; the availability of an even faster S_N2 process for primary alkyl sulfates is to be expected. The present findings, especially the absence of a solvent deuterium isotope effect, are consistent with the occurrence of uncatalysed hydrolysis of SDS by the same mechanism. The appropriate kinetic form was assumed in Scheme 1, but the derived k_2 values then incorporate the water activity in the vicinity of the surfactant's sulfate head-groups. In the more dilute SDS solutions above the c.m.c., where aggregation of SDS into simple micelles occurs, water activity is likely to be a major influence on k_2 which does indeed show a steady decline (we shall return to this aspect of surfactant solutions in a future paper). The subsequent upturn in k_2 must, on the basis of an S_N2 process throughout the SDS concentration range, be indicative of an accelerating influence associated with concentrated SDS solutions that overrides the effect of declining water activity. Further, although an S_N2 process would be expected to lead to incorporation of ^{18}O atoms into the dodecanol produced by this pathway in reaction mixtures containing isotopically enriched water, the proportion of dodecanol produced in this way in the present experiments is negligible in comparison with that produced by the acid-catalysed pathway. It is to be noted that Guthrie's interpretation of the uncatalysed hydrolysis of aryl sulfate ions, in terms of rapid pre-equilibrium formation of a phenoxide/SO_3 'encounter complex' and rate-determining trapping of SO_3 by water, seems a much less plausible mechanism for primary alkyl sulfates because of the availability of the S_N2-pathway at carbon and the poorer nucleofugality of alkoxides compared with aryl oxides.

Acid-catalysed hydrolysis. The acid-catalysed pathway clearly involves specific acid catalysis and S–O bond fission, the latter conclusion previously arrived at on the basis of the stereochemistry of the products of acid-catalysed hydrolysis of secondary alkyl (steroidal) hydrogen sulfates.[11] Pre-equilibrium protonation of the alkyl sulfate anion must be involved, but the question then arises of the site of protonation leading to hydrolysis and when the water molecule becomes involved, as indicated in Scheme 2. Guthrie[12] has presented a convincing argument against reaction through the zwitterionic form of protonated arylsulfate anions[11b] on the basis of estimates of pK_a values for the zwitterion and alkyl hydrogen sulfate of −20.9 and −5.66 respectively. Using a Marcus analysis of the experimental rate and estimated equilibrium data for the hydrolysis, he concluded that, for acid-catalysed hydrolysis, the rate-limiting step of the reaction is cleavage of SO_3 from the alkyl hydrogen sulfate (necessarily involving a proton transfer concerted with S–O bond cleavage), followed by rapid hydration of SO_3. Methyl sulfate was included in Guthrie's treatment, but most data referred to aryl sulfates and all of these systems necessarily do not involve the complicating feature of aggregation. The formation of such an electrophilic species as SO_3 as a discrete intermediate in aqueous solutions has, however, been specifically excluded in a number of instances. Using aryl sulfate ions rendered chiral at sulfur by incorporation of isotopic oxygen, the stereospecificity of enzyme catalysed SO_3-transfer between aryl oxides indicates that a direct transfer takes place,[13] confirming earlier structure–reactivity studies on SO_3-transfer between heterocyclic *N*-sulfonates and *N*- and *O*-centred nucleophiles.[14] The consensus here is that free SO_3 is not formed, but that transfer takes place through a loose, 'exploded', in-line transition state with rather weak binding of sulfur to the outgoing and incoming centres.[15]

The present findings, based on k_3 and k_0 values are consistent with rate-limiting cleavage or transfer of SO_3 from the alkyl hydrogen sulfate [Routes **(A)** or **(A′)** in Scheme 2]. Thus the ^{18}O-labelling studies confirm S–O bond cleavage, and the solvent deuterium isotope effect of 0.9 would be expected if the rate-limiting cleavage were associated with a proton transfer, the normal kinetic isotope effect on which offsets the expected inverse effect on the pre-equilibrium protonation of SDS. If Route **(A)** is the case, then k_3 values, unlike k_2, will not incorporate the water activity, and, ignoring associated medium effects, their values should vary differently with [SDS] as the initial SDS concentration increases and the water activity decreases. This could be the case in the more dilute SDS solutions where k_2 decreases much more rapidly than k_3. The ratio k_2/k_3 at 100 °C goes from 0.78 mM at 1% SDS to 0.74 (2% SDS), 0.44 (5% SDS) and 0.025 (10% SDS), and this pattern of behaviour is maintained even if the k_3 values in Table 4 are corrected for the use of too low a pK_a for hydrogen sulfate in the kinetic simulation. The decreases in the ratio are greater than might have been expected if the ratio were directly proportional to the formal water concentration in these solutions and is suggestive of a more complex state of affairs. Nevertheless, SO_3 cleavage from the alkyl hydrogen sulfate seems preferable to the alternative mechanism for acid-catalysed hydrolysis in which the rate-limiting step is attack of a water molecule on the sulfur atom of the alkyl hydrogen sulfate [Route **(B)** in Scheme 2], for which k_3 would incorporate the water activity near the sulfuric acid group and k_2/k_3 might have been expected to be more nearly constant. It may be relevant that the apparent entropies of activation in Table 2, although very imprecise, nevertheless are almost invariably more negative for the uncatalysed reaction than for the acid-catalysed process, as would be expected since a molecule of water is 'frozen' in the transition state of the S_N2-process.

The situation is made less certain, however, by the possibility of preassociation[16] with the reaction centre of a water molecule which can act as the receptor of a transferred molecule of SO_3 [Route **(A′)** in Scheme 2]. The availability of such a preassociated solvent molecule would not be represented by the formal water concentration in the solution as a whole. It is to be concluded that, while the observations in this study appear to fit the SO_3-cleavage/proton transfer mechanism, a concerted SO_3-transfer process to a preassociated water molecule cannot be ruled out and has the added virtue of circumventing the problem of the lifetime of free SO_3 in an aqueous medium. Transfer of SO_3 from the alkyl hydrogen sulfate to a preassociated water molecule concerted with proton transfers might imply a rather ordered transition state; more detailed attention to entropies of activation may prove illuminating.

It has to be recognised that medium effects on the rates of catalysed and uncatalysed pathways are likely to be very different not only on the basis of the mechanisms proposed here, but also because of the complex nature of surfactant solutions. Nevertheless, the concentration range up to 10% SDS is by general agreement one in which only simple aggregation into micelles occurs, the effect of increasing concentration above the c.m.c. being principally to distort the shape of the micelles from spherical around the c.m.c. to elongated, ellipsoidal forms at higher concentrations. Changes to more complex lyotropic liquid crystalline phases are to be expected only at higher concentrations and these are presumed to be responsible for the subsequent effects both on k_2 and k_3. The effects of surfactant concentration on certain measureable parameters that might provide empirical correlations to rationalise the rate variations are presented in the accompanying paper.

Experimental

Materials

Water was repeatedly distilled in an all glass apparatus and was protected from CO_2 contamination. SDS was in most experiments a commercial sample (Aldrich) which gave results indistinguishable from those obtained with material synthesised from dodecanol. [Dodecanol was treated in dichloromethane solution with chlorosulfuric acid for one hour, followed by removal of HCl by passage of a stream of argon. Addition of ethanolic sodium hydroxide to the resultant solution with cooling and then evaporation of the solvent yielded SDS which was recrystallised from aqueous propan-2-ol.] LDS was a commercial sample (Aldrich) and the sodium salts used were of analytical reagent grade.

Kinetic procedures

Reaction mixtures were prepared by weight from the solutes, SDS, water and, where appropriate, salts and dodecanol, and divided into 1.000 g aliquots, typically 20, each contained in a screw-capped glass reaction tube. The tubes were brought to the chosen reaction temperature [(80–100) ± 0.1 °C; thermostatic bath, Grant W14] within five minutes after which the first tube was removed as the zero-time sample and placed in an ice bath to stop hydrolysis in readiness for acidimetry. Further samples were then removed at appropriate intervals, mostly during the initial phases of the reaction.

Acidimetric titration was carried out on each sample after dilution with water (50 cm^3) and adjustment of the temperature to 25 ± 0.1 °C. Titrations to pH 7.00 were carried out automatically at this temperature in a jacketed vessel, protected from the ingress of atmospheric CO_2 and around which water from a Grant Y38 thermostat was circulated. A Metrohm 691 pH meter was used in conjunction with a Model 665 Dosimat and Model 614 Impulsomat. The titrant used was aqueous sodium hydroxide, a concentration of 0.1 mM being used for samples with an initial pH > 4.00 and 100 mM for more acidic samples. Concentrations of SDS (in mols per kg of solution) were evaluated as a function of time from the known initial concentration and the concentration of acid produced. In those reactions in which sulfuric acid was present initially, this concentration had to be subtracted in each case from the total acid concentration measured; this procedure necessarily introduced additional uncertainty into initial rate determinations, but the fit of data to a first order kinetic law and the reproducibility of repeat determinations of k_0 was satisfactory as indicated in Tables 2 and 4.

Determination of the pK_a of sodium hydrogen sulfate in aqueous SDS

Solutions of SDS in purified water were prepared with concentrations ranging from just below the c.m.c. to approximately 20% by weight (0.7 mol kg^{-1}) and containing sodium hydrogen sulfate (0.005 or 0.010 mol kg^{-1}). The solution (*ca.* 50 cm^3) was thermostated (25 °C) and the pH determined using a glass electrode. To this magnetically stirred solution were added aliquots of standardised aqueous NaOH (0.1 M), typically 0.25 cm^3, but decreasing as the end-point was approached, and the pH was determined after each addition. The pK_a value was obtained by interpolation at the half-neutralisation point. Duplicate determinations at the same [$NaHSO_4$] agreed to within 0.02 pK units. The concentration values in Fig. 4 have been corrected for the change in [SDS] due to the added water at half neutralisation.

^{18}O-Labelling experiments

Solutions of SDS in ^{18}O-labelled water (10 atom% excess) were prepared in screw-capped glass reaction tubes. Reaction mixtures were initially at pH 7 and the SDS concentrations were 1, 10, 20 and 70%. After standing at room temperature for 5 minutes, the tubes were placed in a thermostat bath at 80 ± 0.1 °C for a period known from earlier kinetic experiments to correspond to >98% hydrolysis of the surfactant at that concentration. The tubes and their contents were then cooled in ice and the reaction mixture poured into water (50 cm^3) and extracted with ether (3 × 50 cm^3). The combined extracts were washed with water and dried ($MgSO_4$), removal of the solvent yielding dodecanol as a colourless liquid in 70% yield. Chemical ionisation mass spectrometric analysis (VG 7070E) and comparison with results from a commercial sample of dodecanol showed that in all four cases the dodecanol produced by hydrolysis only contained ^{18}O at natural abundance. Control experiments established that, under comparable reaction conditions [$NaHSO_4$ in ^{18}O-labelled water (10 atom% excess)], there was no incorporation of the label into dodecanol, indicating that any label introduced during SDS hydrolysis could not have been removed by exchange during subsequent exposure to the reaction conditions nor during work-up of the products.

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