The hydrolysis of C_{12} primary alkyl sulfates in concentrated aqueous solutions. Part 2. Influence of alkyl structure on hydrolytic reactivity in concentrated aqueous mixtures of sodium primary alkyl sulfates: 1-benzoyl-3-phenyl-1,2,4-triazole as a probe of water activity

Donald Bethell,[a] Roger E. Fessey,[a] Jan B. F. N. Engberts[b] and David W. Roberts[c]

[a] *Department of Chemistry, University of Liverpool, Liverpool, UK L69 3BX*
[b] *Department of Organic Chemistry, University of Groningen, Zernikelaan, Groningen, The Netherlands*
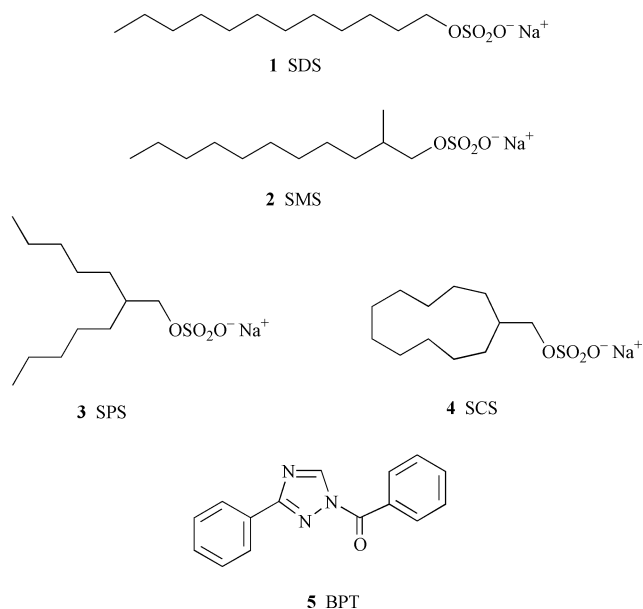[c] *Unilever Research, Port Sunlight Laboratory, Quarry Road East, Bebington, Wirral, UK CH63 3JW*

The kinetics of the hydrolysis of aqueous solutions of three sodium C_{12}-alkyl sulfates (SXS), sodium 2-methylundecyl sulfate (SMS), sodium cycloundecylmethyl sulfate (SCS) and sodium 2-pentylheptyl sulfate (SPS), has been investigated at concentrations up to 70% and compared with the behaviour of sodium dodecyl sulfate (SDS). The same kinetic form as previously described for SDS was observed, namely, autocatalysis by protons generated *via* hydrogen sulfate ion, but there were substantial variations in the reactivity as the alkyl structure changed; β-branching reduced the reactivity, particularly for SMS which was the least reactive of the surfactants studied. The patterns of reactivity by the uncatalysed and hydrogen-ion catalysed pathways for the different SXS were rather similar, but it is argued that the results are consistent with an S_N2 mechanism for uncatalysed hydrolysis and the concerted SO_3 cleavage (or transfer to a pre-associated water molecule)/proton transfer mechanism for the catalytic route, as previously proposed for SDS. Changes in the microenvironment of the sulfate group in aggregates formed from the different SXS are seen as being responsible for much of the rate variation. Attempts have been made to establish the dependence of observed rate constants in dilute solutions of SXS above the c.m.c. on the water activity as indicated empirically by the rate of pH-independent hydrolysis of 1-benzoyl-3-phenyl-1,2,4-triazole (BPT) in the same solutions. It appears, however, that BPT hydrolysis is not a useful guide to water activity in SXS solutions and values of $d(\ln k)/d(\ln [H_2O])$ are generally much larger than expected on the basis of simple ideas of transition state composition. The effects of surfactant aggregation on the microenvironment in which chemical reactions take place are suggested to be the dominant kinetic influence both on SXS and BPT hydrolysis.

Introduction

In a previous paper[1] we reported on the kinetics of hydrolysis of sodium dodecyl sulfate (**1**: SDS) in aqueous solutions containing from 1 to 70% by weight (0.035–2.4 mol kg⁻¹) of the surfactant. The hydrolysis of SDS is an autocatalytic reaction; it was shown that, in initially neutral aqueous solution, a slow uncatalysed hydrolysis generates hydrogen sulfate anions which cause a decrease in pH and thereby allow the incursion of an acid-catalysed pathway which soon dominates. The observed first order rate constants for uncatalysed hydrolysis (k_2) and the second order rate constants for the catalysed process (k_3) varied in quite complex ways as the initial surfactant concentration was changed. This phenomenon was even more pronounced in reaction mixtures containing initially added sulfuric acid. There appeared to be no simple correlation of k_2 and k_3 with the formal water concentration over the whole range of surfactant solutions; in the more dilute solutions however, ratios k_2/k_3 at a given surfactant concentration decreased sharply as the water concentration decreased, and this was taken to indicate that the catalysed rates were less dependent on the availability of water than the uncatalysed rates. It was argued that the uncatalysed hydrolysis was probably a result of S_N2 attack by water on the α-carbon atom of the dodecyl group, but that the proton-catalysed process appeared to involve rate-limiting extrusion of sulfur trioxide from O-protonated SDS, dodecyl hydrogen sulfade ($C_{12}H_{25}OSO_2OH$), coupled with proton transfer from the terminal oxygen atom to the alkylated oxygen. The possibility that the process concerted with proton transfer was a transfer of SO_3 to a preassociated water molecule was also considered possible. The investigation left open the question of the complex dependence of rate constants on [SDS], although it was suspected that changes in the aggregates formed by SDS were responsible, giving rise to changing reaction microenvironments.

Commercial primary alkyl sulfate (PAS) surfactants contain mixtures of sodium salts of primary alkyl hydrogen sulfates having alkyl groups differing in chain length and branching. To throw light on the effect of structure on hydrolytic stability, we report now studies on the hydrolysis of the sodium salts of three further C_{12} primary alkyl hydrogen sulfates, sodium 2-methylundecyl sulfate (**2**; SMS), sodium 2-pentylheptyl sulfate (**3**; SPS) and sodium cycloundecylmethyl sulfate (**4**; SCS) over a wide concentration range in aqueous colloidal solution. Collectively, we will symbolise the surfactants SXS. Because compounds (**2–4**) have alkyl structures quite different from that in SDS, it was expected that their reactivity would be different not only as a direct consequence of the change in molecular structure, but also because of differing aggregation behaviour as the surfactant concentration changes. This in turn might lead

$OSO_2O^- Na^+$

1 SDS

$OSO_2O^- Na^+$

2 SMS

$OSO_2O^- Na^+$

3 SPS

$OSO_2O^- Na^+$

4 SCS

5 BPT

SXS	c.m.c./mM	
	Experiment	QSAR Prediction[a]
SDS **1**	8.6[b]	6.6
SMS **2**	12.0[c]	9.3
SPS **3**	18.2[c]	17.8
SCS **4**		25.6

[a] Ref. 5. [b] Ref. 6. [c] Ref. 7.

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

$$RCH_2OSO_3^- \xrightarrow{k_2} RCH_2OH + HSO_4^-$$

$$RCH_2OSO_3^- \xrightarrow[H_3O^+]{k_3} RCH_2OH + HSO_4^-$$

Scheme 1

to changes in the availability of water at the reactive centres with superimposed local medium effects. Rather than address this tricky problem directly, the pH-independent hydrolysis of 1-benzoyl-3-phenyl-1,2,4-triazole (**5**; BPT) has been investigated in the presence of a range of concentrations of **1**–**4** as a probe of the microenvironment in the vicinity of the surfactant head-groups in these solutions. Earlier work has established that in aqueous solution at pH 4 BPT undergoes a neutral, water-catalysed hydrolysis with two water molecules involved in the transition state.[2] The observed hydrolysis rate is therefore very sensitive to the water activity, but it is also subject to the effects that cosolvents or other solutes have on the water structure and by their interactions with the initial state BPT (electrically neutral) and the transition state for its hydrolysis (very polar). The use of BPT to probe the microenvironment of alkyl sulfate groups has already been investigated for non-micellar sodium n-alkyl sulfates having chain lengths from C_1 to C_8.[3] The success of the present approach in surfactant solutions above the c.m.c. is, of course, dependent on the probe molecule being located on average in the relevant environment. Arguments and evidence have already been presented suggesting that the probe molecule is indeed bound in the Stern layer of micelles formed in SDS solutions at concentrations from the c.m.c. to 0.12 M.[4]

Results

Kinetics of hydrolysis of primary alkyl sulfates SMS, SPS and SMS, 2–4
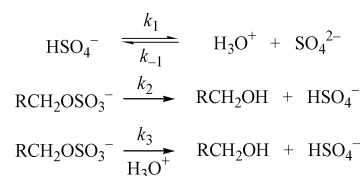
The studies of the hydrolysis of primary alkyl sulfates were carried out at concentrations in water that ranged from just above the c.m.c. to around 2.4 mol kg^{-1} and at temperatures such that the aqueous mixtures all formed macroscopically homogeneous solutions. Values of the c.m.c.'s for the surfactants taken from the literature are in Table 1.

As previously described for SDS **1**,[1] the rates of hydrolysis of **2**–**4** were followed in initially neutral solutions by acidimetric titration. In all cases the progress of the reaction was slow in the initial stages, but progressively accelerated and finally slowed as hydrolysis of the reactant neared completion. This auto-catalytic form was analysed in its initial stages (up to 10% conversion) by fitting the observations to a computer model of the reactions in Scheme 1 in which the variables were the first order rate coefficient for an uncatalysed process and a second order rate coefficient for the process catalysed by the protons resulting from hydrogen sulfate ions produced in the hydrolysis. As for our study of SDS hydrolysis, a fixed value of the acid dissoci-

ation constant of hydrogen sulfate ions ($pK_a = 1.78$, the measured value in dilute aqueous solution at 25 °C) was used throughout, although it is known to change somewhat in SDS solutions above the c.m.c., and will be presumably changed in solutions containing SXS. Reactions were followed at 100 °C, except for SMS for which it was necessary to use a substantially higher temperature of 140 °C in order to obtain results on a convenient timescale. Values of the derived rate coefficients are in Table 2, and average values at each initial surfactant concentration (expressed in mol kg^{-1}) are shown in Fig. 1a and b.

The four surfactants studied all show patterns of kinetic behaviour that are consistent with the reactions set out in Scheme 1, although the derived rate coefficients for uncatalysed and proton-catalysed pathways show substantial variation from one reactant to another. SDS is clearly the most readily hydrolysed by both routes, while SMS is the least reactive, necessitating studies on it to be conducted at a temperature forty degrees higher than for the other three SXS. Leaving aside the absolute values of the rate coefficients, the patterns of their variation as a function of the initial [SXS] are remarkably similar. Thus, for the uncatalysed hydrolysis, values of k_2 decrease with increasing [SXS] up to 10% by weight, whereafter they show a modest increase up to 70% by weight. In the acid-catalysed process, the patterns, while rather similar from one SXS to another, are more complicated. Two minima were usually displayed in the ranges 2–5% and 15–20% by weight of surfactant, with a weakly defined maximum at *ca.* 10%; rate coefficients at the highest [SXS] were comparable with or even higher than in the 1% solutions. Acid-catalysed hydrolysis of SPS showed the least variation in rate coefficient with surfactant concentration of all the reactions studied.

Kinetics of hydrolysis of BPT in aqueous SXS solutions

In an attempt to identify the cause or causes of the variations of k_2 and k_3 values with [SXS] and to throw more light on the mechanisms of the uncatalysed and catalysed hydrolysis pathways, we have used the rate of the well understood neutral hydrolysis of BPT as a probe reaction. The rate of hydrolysis of BPT is conveniently measured spectrophotometrically, typically at 25 °C. In an effort to make the reaction conditions more relevant to those of the SXS hydrolysis, the present kinetic study was for the most part conducted at 45 °C; at 100 °C, BPT hydrolysis is too rapid for accurate measurement by conventional means, but the lower temperature reduces the maximum [SXS] that can be investigated to about 30%, since at higher concentrations reaction mixtures are no longer homogeneous liquids.

Table 2 Rate coefficients for uncatalysed (k_2/s^{-1}) and acid-catalysed (k_3/kg mol^{-1} s^{-1}) hydrolysis of primary alkyl sulfates (SXS) **1–4** in water

[SXS]	SDS[a,b]		SMS[c]		SPS[a]		SCS[a]	
(weight%)	$10^7 k_2$	$10^4 k_3$	$10^7 k_2$	$10^4 k_3$	$10^7 k_2$	$10^4 k_3$	$10^7 k_2$	$10^4 k_3$
1	25	32	3.0	16	1.8	3.3	6.0	10
			4.0	18	2.2	3.7	8.0	12
2	20	27	1.7	12	1.4	2.8	4.0	5.0
			2.5	16	1.6	3.0	5.0	6.0
5	11	25	1.0	23	0.7	2.8	2.5	6.0
			1.2	27	0.7	3.2	2.9	8.0
10	0.7	28	1.0	23	0.10	2.7	0.18	0.70
			1.2	27	0.10	2.7	0.22	0.70
15	0.5	17	1.0	20	0.08	1.8	0.10	0.70
			1.4	22	0.12	2.2	0.20	0.70
20	1.8	17	1.0	18	0.15	1.8	0.30	0.35
			1.4	20	0.25	2.2	0.40	0.45
30	1.5	22	1.0	27	0.18	2.0	0.25	0.80
			1.2	31	0.22	2.4	0.35	1.0
40	4.7	20	1.1	28	0.20	2.3	0.60	0.90
			1.5	32	0.30	2.7	0.80	1.1
50	5.9	22	1.4	32	0.20	2.0	1.0	0.90
			1.6	34	0.30	2.2	1.2	1.1
60	5.7	26	1.4	30	0.22	1.8	1.0	1.0
			1.8	34	0.28	2.4	1.4	1.4
70	5.5	26	1.4	33	0.25	2.2	1.7	1.0
			1.6	35	0.25	2.2	1.7	1.4

[a] At 100 °C. [b] Average values taken from ref. 1. [c] At 140 °C.
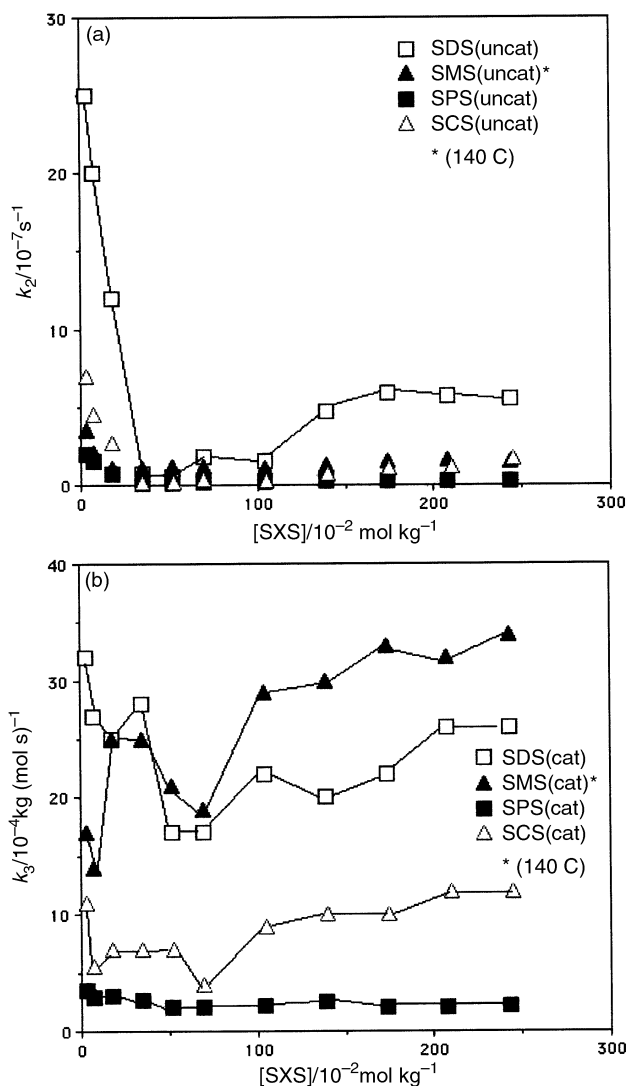
Fig. 1 Rate coefficients for SXS hydrolysis as a function of initial concentration at 100 °C: (a) uncatalysed hydrolysis; (b) acid-catalysed hydrolysis.

For SDS solutions, the reaction was followed at temperatures of 25, 30, 40 and 45 °C; values of the observed rate constants, k, are in Table 3. For SMS, SPS and SCS solutions, BPT hydrolysis was examined only at 45 °C and these k values are in Table 4, together with results for sodium butyl sulfate (SBS) chosen to represent an SXS with a much reduced tendency to aggregate. The results on SDS at 25 °C are broadly in agreement with earlier studies over a shorter surfactant concentration range.[4,8] It should be noted that the presence of the surfactant had no evident effect on the reaction mechanism. The kinetic form was the same throughout, and, in the case of SDS solutions, the observed kinetic solvent deuterium isotope effect at 30 °C was 3.15 in 1% SDS and 4.33 at 20% SDS; typical values for 3-substituted 1-acyl-1,2,4-triazoles in aqueous solution are reported to be in the range 2.40 to 4.15 at 25 °C.[1a,9]

In all cases, as [SXS] increased, the rate coefficient (k) for BPT hydrolysis decreased rapidly from the value in pure water (k^0), as has been previously observed.[4,8] The observed results for BPT hydrolysis in the presence of SBS are broadly consistent with the results of Noordman *et al.*[3] for comparable experiments using sodium propyl sulfate and sodium pentyl sulfate; the present data fall close to the previously reported regression line of log (k^0/k) *vs.* SXS molality as shown by the line labelled B in Fig. 2. Compared with this, however, k decreased much more rapidly from the value in pure water in solutions of all the C_{12}-sulfates. The results for SDS make it clear that k^0 is more than halved as [SXS] passes through the c.m.c., with further reduction to around 10% of k^0 when [SDS] reaches 4 times the c.m.c. Thereafter only modest further decreases were observed. A rather similar pattern of behaviour was found for SMS, SCS and SPS. The initial, roughly linear plot of log (k^0/k) *vs.* SXS molality was maintained well beyond the c.m.c. of SXS, and the slope decreased in the sequence SDS > SMS > SCS > SPS >> SBS. Thereafter in each case the downward trend in k continued much less steeply (Fig. 2) and, particularly in the case of SMS, with considerable scatter of the data (which exceeds the experimental uncertainty of the rate measurements). This reduced dependency of k on [SXS] at concentrations above about 0.2 mol kg^{-1} is quite different from the observations of Noordman *et al.*[3] for solutions of sodium heptyl and sodium octyl sulfates which showed upward, rather than downward,

**Table 3** Rate constants (k_P/s^{-1}) for BPT hydrolysis in aqueous SDS solutions

[SDS] (weight%)	[SDS]/ 10^{-2} mol kg^{-1}	$k/10^{-5}$ s^{-1} 25 °C	30 °C	40 °C	45 °C
0	0	127, 123, 126	164, 178, 168	352, 318, 358	425, 384, 392
0.3	1.04	37.6, 41.0, 39.5	51.1, 51.4, 50.5	173, 172, 173	186, 187, 201
1 [a]	3.47	9.70, 9.78, 9.33	14.1, 12.6, 12.3	26.9, 27.1, 27.0	31.5, 31.9, 30.9
2	6.94	6.75, 6.65, 7.16	12.2, 14.3, 11.5	20.1, 20.3, 20.7	29.5, 26.6, 25.4
5	17.4	5.73, 5.59	8.01, 7.95, 8.10	15.4, 15.4, 15.9	20.6, 20.5, 20.3
10	34.7	4.06, 4.20	6.24, 6.29	9.97, 11.7, 10.8	20.1, 20.3, 20.5
12	41.7	4.51, 4.00	5.47, 5.25	11.6, 11.9, 12.2	15.6, 16.5, 16.5
15	52.1	4.63, 4.14, 4.86	5.60, 5.24, 5.32	11.9, 10.5, 11.4	14.7, 15.0, 14.7
20 [b]	69.4	3.19, 3.40	5.11, 4.85	10.7, 10.5, 10.3	15.4, 16.0, 15.4
25	86.8			9.22, 9.24, 9.12	14.5, 14.1, 14.3
30	104.2			8.00, 8.77	11.9, 11.5

[a] In D$_2$O at 30 °C, values of $k_P/10^{-5}$ s^{-1} were: 4.07, 4.11, 4.21. [b] In D$_2$O at 30 °C, values of $k_P/10^{-5}$ s^{-1} were: 1.10, 1.20.

Table 4 Rate constants (k/s^{-1}) for BPT hydrolysis in aqueous SMS, SPS and SCS solutions at 45 °C

[SXS] (weight%)	SDS[a]	$k/10^{-5}$ s^{-1} SMS	SPS	SCS	SBS[b]
0	400	(400)	(400)	(400)	(400)
1	31.4	160, 217	340, 350	318, 298	370
2	27.2	88.9, 70.8	200, 220	155, 157	364
5	20.5	129, 111	160, 180	93.3, 90.9	340
10	20.3	98.1, 86.5	150, 170	121, 161	340
12	16.2	40.4, 45.7	105, 115	78.7, 70.7	332
15	14.8	30.3, 34.7	80, 100	68.2, 70.7	345
20	15.6	68.9, 72.7	80, 100	62.8, 54.7	271
25	14.3	40.7, 48.2	60, 80		
30	11.7	32.4, 38.7	45, 55		

[a] Average values taken from Table 2. [b] Sodium butyl sulfate; values interpolated from measurements at other concentrations.
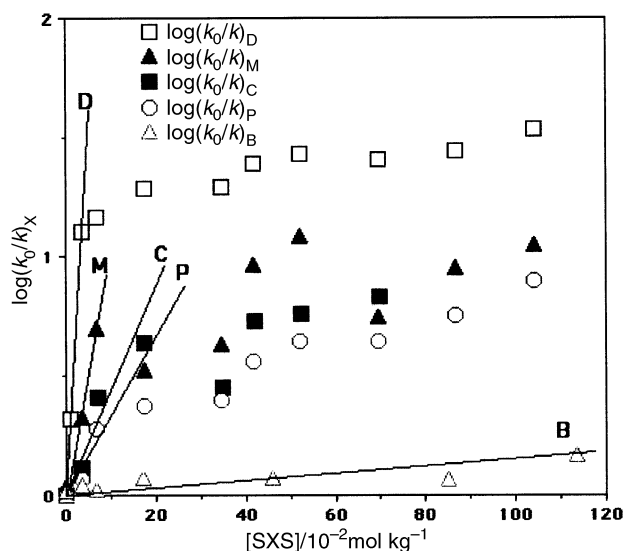
Fig. 2 Effect of SXS molality on the rate coefficient for BPT hydrolysis in aqueous solution at 45 °C. The solid straight lines, labelled X to signify the SXS to which they refer, are drawn through the first three experimental points. The line labelled B is drawn with the slope reported in ref. 3 for BPT hydrolysis in solutions of sodium propyl and sodium pentyl sulfates.

deviations from the extrapolation of the linear plots of log (k^0/k) *vs.* [SXS] obtained at <0.1 mol kg^{-1}.

It has previously been argued that the decrease in the rate of BPT hydrolysis in SDS solutions up to 0.12 M can be attributed to the high concentration of head-groups in the Stern layer of the micelles present under these conditions and in which the BPT molecules are located. Similar kinetic effects can be

achieved in solutions of sodium methyl sulfate, but much higher concentrations of this are required in the absence of aggregation in order to match the rate reductions with SDS. The present results seem to imply that, well above the c.m.c. of all the surfactants used in the present study, BPT undergoes hydrolysis in environments that change much less rapidly with surfactant molality than in the concentration region around the surfactant's c.m.c. This does not seem unreasonable if, under these conditions, essentially all the BPT is held within the Stern layer of the surfactant aggregates where medium effects and the local water activity remains fairly constant until a major change in the aggregation behaviour of the surfactant supervenes. The apparent inconsistency of the experimental findings for the C$_{12}$-primary alkyl sulfates and the heptyl and octyl sulfates remains; further, more detailed studies will be required to resolve it.

Discussion

We have previously argued that, for SDS hydrolysis, values of the rate coefficient for the uncatalysed process probably refer to nucleophilic attack by water on the α-carbon atom of the dodecyl sulfate ion and that values of k_2 therefore incorporate the water activity in the solutions. By contrast the rate-limiting step in the hydronium ion-catalysed pathway was suggested to be either cleavage of SO$_3$ from the corresponding dodecyl hydrogen sulfate with concerted intramolecular proton transfer to the alkyl-bound oxygen atom or transfer of SO$_3$ to a pre-associated water molecule, again with concerted proton transfer; in either case, k_3 was believed not to incorporate the water activity. Variation of k_2 with [SXS] was thus expected to arise from changes in the water activity in the microenvironment in which the reaction takes place together with medium effects arising from the interaction of initial states and transition states with surrounding molecules in the solution. For k_3 only variations arising from medium effects on the relevant initial and transition states, were anticipated and these were expected to be different from those involved in the uncatalysed process. In the case of the neutral hydrolysis of BPT, it has previously been established that the observed rate coefficients depend on the square of the water activity together with medium effects that have been analysed in terms of pairwise solute–solute interactions for a wide diversity of cosolutes.[10]

SXS Structural effects on the rate of hydrolysis

To what extent are the variations in the rate coefficients for uncatalysed and acid-catalysed hydrolysis in Table 2 consistent with the mechanisms proposed for SDS hydrolysis? Bearing in mind the complications that are likely to arise from differences in aggregation behaviour as the hydrophobic alkyl group changes from a straight chain to branched chains and then to a medium ring structure, comparison is made at the 1% concentration where all SXS are expected to form simple, largely

**Table 5** Structural effects of the alkyl group on the hydrolysis of sodium alkyl sulfates

	Relative reactivity at 100 °C	
Alkyl group	Uncatalysed hydrolysis	Catalysed hydrolysis
SDS $CH_3(CH_2)_{10}CH_2$-	(100)	(100)
SMS $CH_3(CH_2)_8CHMeCH_2$-	0.2[a]	0.7[a]
SPS $[CH_3(CH_2)_4]_2CHCH_2$-	8	11
SCS cyclo-$[(CH_2)_{10}CH]CH_2$-	28	34

[a] At 140 °C.

spherical micelles. For each SXS, approximate rate coefficients for the two hydrolysis pathways relative to SDS (=100) at 100 °C are given in Table 5. In the case of SMS, allowance has to be made for the effect of the increased hydrolysis temperature. This has been done by estimating the rate of hydrolysis of SDS at 140 °C using the previously obtained activation parameters[1] so that the relative rate values are at that temperature in this case. The effect of the β-branching in the alkyl group brings about a substantial decrease in the rate coefficient, and the pattern is remarkably similar in the catalysed and uncatalysed reactions. In the case of the uncatalysed pathway, if it were a simple S_N2-displacement, β-branching would be expected to have such a rate-retarding effect. However, the introduction of just a methyl branch in SMS has an unusually large (>500-fold) retarding effect. This is much larger than has been reported for the effect of β-methyl substitution on rates of known S_N2-displacements in simpler, non-aggregating substrates. For example, the relative reactivity of 2-methylpropyl iodide compared to propyl iodide in reaction with iodide ion at 50 °C[11] or with ethoxide ion at 55 °C in ethanol[12] is 0.1. The value is comparable to the present observations for SPS and SCS, suggesting that the uncatalysed hydrolysis may indeed be an S_N2 reaction. If that is the case then there must be an additional rate-retarding influence in the case of SMS. We suggest that the explanation may lie in packing considerations;[13] the very fact that the chain branch is so small prevents it from being involved with the central hydrocarbon core of the aggregates and makes its influence in reducing the water activity and ion-solvating power within the Stern layer particularly marked, compared with SCS and SPS. For the uncatalysed reactions, it is tempting to suggest that the similarity of the pattern of structural effects on rate signifies a similarity in mechanism. The acid-catalysed pathway cannot, however, be an S_N2 displacement of hydrogen sulfate ion since we have established that in this reaction the C–O bond in the reactant dodecyl sulfate is retained in the dodecanol produced.[1] It should be borne in mind that, in the light of our demonstration that the catalytic hydrolysis shows specific hydrogen-ion catalysis, the values of k_3 are the product of an equilibrium constant for O-protonation of the sulfate and a rate constant for the subsequent rate limiting step. Any structural effect on the protonation pre-equilibrium might be expected to be small in the absence of aggregation, but above the c.m.c. the sulfate head-group could find itself in very different environments in micelles formed from the different SXS. For the subsequent step, formulated as a cleavage or transfer of SO_3 with concurrent proton transfer transforming S–O–H to C–O–H, structural effects on the rate constant in the absence of aggregation are again likely to be small. Our inference, then, from the results in Table 5 is that the dominant influence of alkyl structure on the hydrolysis rate by the catalysed and uncatalysed pathway is by modifying the environment in the vicinity of the sulfate head-groups.

The influence of water concentration

As exemplified by Fig. 3 for the case of SPS, by plotting logarithmically the rate coefficients k_2 and k_3 for SXS hydrolysis
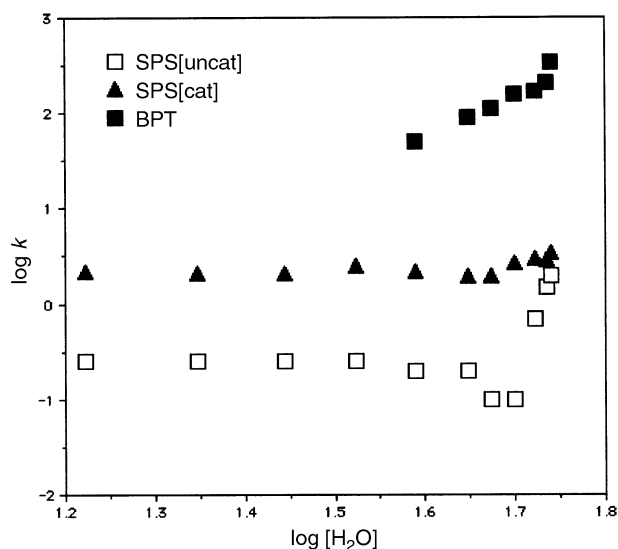
Fig. 3 Dependence of rate coefficients for SPS hydrolysis (100 °C) and BPT hydrolysis (45 °C) on the formal molality of water in the reaction mixture.

and k for BPT hydrolysis against the logarithm of the formal water concentration in the reaction mixture $[H_2O]$ (expressed in mol kg^{-1}), it is observed that the most marked dependence of rate on water concentration is found when the water concentration is highest, that is to say in dilute SXS solutions with SXS concentrations from just above the c.m.c. to around 20% by weight. At higher [SXS] (lower $[H_2O]$), k_2 decreases fairly slowly with decreasing water concentration, while k_3 shows little change. For BPT hydrolysis, values of k decrease continuously with decreasing $[H_2O]$ over the accessible concentration range.

Although the slopes of these logarithmic plots formally represent orders of reaction with respect to water, as with any studies of organic reactions in mixed aqueous–organic solvents, such a simplistic interpretation is to be avoided. This is particularly true as regards SXS hydrolysis where under some of the conditions studied, the reactants, SXS and water are major components of the reaction mixture. Kinetic effects of changes in the interaction of the reactants with the solvent cannot be separated from the effects of changing concentration of water as a reactant. The problem is exacerbated in situations in which both reactants are major components of the reaction mixtures and where micelles and other aggregates are present. In the present investigation, a remarkable feature of the pattern of behaviour seen with all four SXS is that, in the most dilute SXS solutions studied, the dependence of reaction rate on $[H_2O]$ is greatest for uncatalysed SXS hydrolysis and least for the catalysed process; BPT hydrolysis maintains a rather constant dependence of rate on $[H_2O]$ over the whole range examined. That the slopes of the logarithmic dependence of observed rate coefficient and $[H_2O]$ should not be equated with kinetic order in H_2O is demonstrated by the apparent kinetic orders for neutral hydrolysis of BPT in SXS solutions; these were 1.3 for SBS, 2.6 for SDS, 3.8 for SMS, 4.8 for SPS, and 5.9 for SCS, which should be compared with the value of 2 expected on the basis of earlier mechanistic work in dilute aqueous solution containing non-aggregating solutes. For the catalytic pathway for SXS hydrolysis, the slope of the logarithmic plot is about 3. We shall resist the temptation to suggest that this might signify that, in the proposed SO_3-cleavage/transfer mechanism, the concomitant proton transfer is mediated by a water molecule, even though the transformation of the electrically neutral alkyl hydrogen sulfate to a molecule of dodecanol and one of SO_3 (or H_2SO_4 in the SO_3-transfer mechanism) would probably require little change in the need for charge solvation, and medium effects

would be likely to be small. The apparent kinetic orders with respect to water for the uncatalysed hydrolysis of the C_{12} SXS in solutions of concentration 1–20% are much higher, typically around 30 (see Fig. 3), and bear no relation to expectation on the basis of the simple S_N2 mechanism proposed earlier. A possible explanation for the steep dependence may be that, as [SXS] increases, the reactant, whether the sulfate head-group of SXS or the benzoyl group of BPT, occupies an environment which becomes increasingly hydrophobic, thereby experiencing a lower reactant water activity than indicated by [H_2O], the macroscopic water concentration calculated from the composition of the whole reaction mixture. In addition, the hydrophobic microenvironment will exert a substantial medium effect by virtue of its reduced charge solvating capability; indeed, in the case of the putative S_N2 displacement of sulfate ion by a molecule of water in the uncatalysed SXS hydrolysis, not only will there be the development of two additional charges in the transition state, but there will also be an additional, developing electrostatic repulsion between the departing sulfate ion and the negatively charged Stern layer of the micellar aggregates.

Conclusions

The pattern of kinetic behaviour observed in the hydrolysis of aqueous sodium C_{12}-alkyl sulfates at concentrations up to 70% is broadly the same as previously described for SDS. The same kinetic form—autocatalysis by protons generated as hydrogen sulfate is produced—is observed, but there are substantial variations in the reactivity as the alkyl structure changes; β-branching reduces the reactivity, an effect that is particularly pronounced in SMS. Notwithstanding the similarity of the patterns of reactivity for the different SXS hydrolysing by the uncatalysed and hydrogen-ion catalysed pathways, it is argued that the results are consistent with an S_N2 mechanism for uncatalysed hydrolysis and the concerted SO_3-cleavage (-transfer)/proton transfer mechanism for the catalytic route. Changes in the microenvironment of the sulfate group in aggregates formed from the different SXS are seen as being responsible for much of the rate variation. Using the formal water concentration in SXS solutions at concentrations just above the c.m.c. leads to values of $\Delta(\log k)/\Delta(\log [H_2O])$ that are much larger than reaction orders in H_2O expected on the basis of the proposed mechanisms. Neutral BPT hydrolysis appears not to be a useful guide to water activity in SXS solutions; again the apparent orders of reaction are generally much larger than the value of 2, expected on the basis of the well-established reaction mechanism, as a result of the superimposed medium effect, particularly of the sulfate head-groups in the Stern layer of the surfactant aggregates, which changes substantially from one SXS to another. The effects of surfactant aggregation on the microenvironment in which chemical reactions take place appear to be the dominant kinetic influence.

Experimental

Materials

Water was repeatedly distilled in an all glass apparatus and was free of CO_2 contamination. BPT was a pure sample available from earlier studies in the Groningen laboratory.

Sodium 2-methylundecyl sulfate (SMS). SMS was prepared by dropwise treatment of 2-methylundecanol (obtained by reduction of commercial 2-methylundecanal with ethanolic sodium borohydride) with a dichloromethane solution of chlorosulfonic acid at 0 °C, followed by careful neutralisation using ethanolic sodium hydroxide. Removal of the solvents *in vacuo*, followed by washing of the solid salt with a little dichloromethane and three recrystallisations from propan-2-ol

afforded SMS as colourless crystals in 70% yield. Analysis: found C 49.98, H 8.74%; $C_{12}H_{25}SO_4Na$ requires C 49.77, H 8.77%.

Sodium cycloundecylmethyl sulfate (SCS). The commercial alcohol was purified by distillation under reduced pressure and sulfated as described for the preparation of SMS. After recrystallisation the product SCS (51% yield) was in the form of colourless crystals. Analysis: found C 49.70, H 7.80%; $C_{12}H_{23}SO_4Na$ requires C 50.33, H 8.10%.

Sodium 2-pentylheptyl sulfate (SPS). Iodopentane (2.2 molar equivalents) was added to a cooled ethanol solution in which diethyl malonate had been converted into its sodium salt using a 7-fold excess of sodium ethoxide; the mixture was refluxed for 16 hours. Excess aqueous sodium hydroxide was then added and refluxing continued for a further 4 hours. After cooling to room temperature the mixture was carefully acidified with concentrated hydrochloric acid, and most of the ethanol was removed under reduced pressure until crude 2,2-dipentyl-malonic acid precipitated as a yellow solid. Decarboxylation by heating of the solid at 170 °C for 24 hours afforded crude 2-pentylheptanoic acid which was distilled; the fraction of the distillate collected at 170 °C/7 mmHg was a colourless liquid. Analysis: found C 71.74, H 11.97%; $C_{12}H_{24}O_2$ requires C 71.94, H 12.08%. Reduction of the acid was achieved using lithium aluminium hydride in diethyl ether first at room temperature and then at reflux overnight. An aqueous work-up, followed by ether extraction and distillation under reduced pressure yielded the pure 2-pentylheptanol as a colourless liquid, bp 170 °C/1 mmHg. Analysis: found C 77.20, H 14.17%; $C_{12}H_{26}O$ requires C 77.34, H 14.07%. Sulfation of the alcohol to produce SPS was achieved in 50% yield as described above for SMS. Analysis: found C 49.70, H 8.70; $C_{12}H_{25}SO_4Na$ requires C 49.77, H 8.77%.

Kinetic measurements

The procedures for following the hydrolysis of SMS, SPS and SCS and the computer modelling method for extracting the rate coefficients for the uncatalysed and catalysed reactions were as previously described for SDS.[1]

The hydrolysis of BPT was initiated by injection of a small volume of an acetonitrile solution of the triazole into the SXS solution whose pH had been adjusted to 4 by addition of a small volume of dilute aqueous hydrogen chloride. The progress of the reaction was followed by the decreasing absorbance (*A*) of BPT at 273 nm. Plots of ln (*A*) *vs.* time were accurately linear over five half-lives, and first order rate constants (*k*) were derived by linear regression analysis. Reactions were conducted in duplicate or triplicate and, for SDS solutions, reproducibility of rate coefficients was good (within 2% of the mean); for the other SXS, the reproducibility was unaccountably somewhat poorer, but usually rate coefficients were within 5% of the mean value.

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