Effects of micellar head group structure on the spontaneous hydrolysis of methyl naphthalene-2-sulfonate. The role of perchlorate ion

Lucia Brinchi,[a] Pietro Di Profio,[a] Raimondo Germani,[a] Gianfranco Savelli,[a] Nicoletta Spreti[b] and Clifford A. Bunton[c]

[a] *Dipartimento di Chimica, Università di Perugia, 06100 Perugia, Italy*
[b] *Dipartimento di Chimica, Ingegneria Chimica e Materiali, Università di L'Aquila, 67010 L'Aquila, Italy*
[c] *Department of Chemistry, University of California, Santa Barbara, CA 93106, USA*

The spontaneous (S_N2) hydrolysis of methyl naphthalene-2-sulfonate (MeONs) in water is inhibited by cationic, anionic and zwitterionic micelles of the following surfactants, CTAOMs, n-$C_{16}H_{33}N^+Me_3MeSO_3^-$; CTPAOMs, n-$C_{16}H_{33}N^+Pr_3MeSO_3^-$; SDS, $C_{12}H_{25}OSO_3^-Na^+$; SB3-14, n-$C_{14}H_{29}N^+Me_2(CH_2)_3SO_3^-$;- SBBu3-14, n-$C_{14}H_{29}N^+Bu_2(CH_2)_3SO_3^-$; DMMAO, n-$C_{14}H_{29}N^+Me_2O^-$; DPMAO, n-$C_{14}H_{29}N^+Pr_2O^-$. Rate constants, k_{rel}, relative to those in water, are in the range 0.55–0.63 for all the cationic and zwitterionic micelles including the protonated amine oxides. The value of k_{rel} in anionic micelles of SDS is 0.22, but $NaClO_4$ sharply decreases k_{rel} in SB3-14 from 0.56 to 0.15. These rate effects are not related to variations in substrate binding but depend upon interactions of the head groups with the initial and transition states.

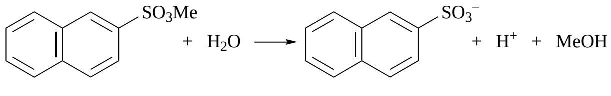
Introduction

Aqueous micelles affect rates of nonsolvolytic bimolecular reactions by controlling concentrations of the two reagents at the micelle–water interface. Therefore overall rate constants depend upon transfer equilibria between water and micelles and second-order rate constants in each region.[1] Nucleophilic reactions have been widely studied and second-order rate constants at micelle–water interfaces are typically similar to, or slightly lower than, those in water. For S_N2 reactions of Br^- or Cl^- mediated by cationic micelles of quaternary ammonium ion surfactants rate constants at the micelle–water interface increase modestly with increasing head-group bulk of the surfactant,[2] but the effect is inverted for reactions of OH^-.[3] Rates of intramolecular S_N2-like cyclisations at micellar surfaces also increase modestly with increasing head group size.[4]

Spontaneous, bimolecular, hydrolyses of alkyl halides and sulfonate esters are mechanistically simple, because the solvent, *e.g.*, water, participates only nucleophilically and by solvating leaving groups, and not as a general acid–base catalyst as in some deacylations. In the transition state positive charge develops on the nucleophilic water molecule and is dispersed into the solvent by hydrogen-bonding. However, despite involvement of water molecules as nucleophiles or general bases, aqueous micelles do not strongly affect rates of either deacylations or S_N2 hydrolyses, indicating that the micellar interfacial region is 'water-rich'.[1,5] There could also be effects due to the high ionic concentration in this region, as well as its slightly lower polarity relative to water.[1,6,7] This region is electrically asymmetric in ionic and zwitterionic micelles, which may affect hydrolyses in which local charges are developed in the transition state, and inhibition of spontaneous hydrolyses is larger in anionic than in cationic micelles.[5c,7] Inhibition is larger for S_N1 than for spontaneous, bimolecular hydrolyses and then the more effective inhibitors are cationic, rather than anionic, micelles.[5a,d,8] These different charge effects can be rationalized in terms of interactions of the micellar head groups with local charges in the transition states of uni- and bi-molecular hydrolyses at acyl or alkyl centers. Similar interactions with head groups are apparently important in anionic decarboxylations[9] and dephosphorylations[10] and E1cB reactions[11] in ionic and zwitterionic micelles.

Although charge affects rates of spontaneous hydrolyses at micellar surfaces there is limited evidence regarding effects of head group size or structure.[10] Engberts and co-workers found that micelles and other association colloids modestly inhibit spontaneous hydrolyses of acyltriazoles and the extent of inhibition is sensitive to colloid structure.[5b,c] Spontaneous hydrolyses of benzenesulfonyl chlorides are micellar inhibited and inhibition is greater for anionic than for cationic micelles, but zwitterionic sulfobetaine and cationic micelles behave similarly.[12] Similar micellar charge effects are seen in spontaneous hydrolyses of carboxylic anhydrides and acyl chlorides.[5d,8a]

In the present work we examine micellar effects on the spontaneous (S_N2) hydrolysis of methyl naphthalene-2-sulfonate (MeONs), Scheme 1.



Scheme 1

This reaction is a mechanistically simple, concerted displacement, whereas hydrolyses of acyl derivatives may be concerted or step-wise,[13] and the hydrophobic substrate binds strongly to micelles. As a result we obtain limiting values of the rate constants in relatively dilute surfactant so that changes due to micellar growth are unimportant. We used cationic, anionic and zwitterionic surfactants and varied the head group structures. The amine oxides are useful because protonation converts them from zwitterions, which are nucleophilic,[14] into cations, and protonation in dilute acid is well established.[15] Surfactants used in this work are cetyltrimethylammonium methanesulfonate (CTAOMs) n-$C_{16}H_{33}N^+Me_3MeSO_3^-$; cetyltripropylammonium methanesulfonate (CTPAOMs) n-$C_{16}H_{33}N^+Pr_3MeSO_3^-$; sodium dodecyl sulfate (SDS) $C_{12}H_{25}OSO_3Na$; 3-(*N*,*N*-dimethylmyristylammonio)propanesulfonate (SB3-14) n-$C_{14}H_{29}N^+$-$Me_2(CH_2)_3SO_3^-$; 3-(*N*,*N*-dibutylmyristylammonio)propanesulfonate (SBBu3-14) n-$C_{14}H_{29}N^+Bu_2(CH_2)_3SO_3^-$; 1,1-dimethylmyristylamine oxide (DMMAO) n-$C_{14}H_{29}N^+Me_2O^-$; 1,1-dipropylmyristylamine oxide (DPMAO) n-$C_{14}H_{29}N^+Pr_2O^-$.†

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† Cetyl = hexadecyl, myristyl = tetradecyl.

Table 1 Rate constants of the spontaneous hydrolysis of MeONs in cationic surfactants

	CTAOMs	CTPAOMs
[Surfactant]/10^{-3} mol dm^{-3}	$k_{obs}/10^{-6}$ s^{-1}	$k_{obs}/10^{-6}$ s^{-1}
0	12.3	12.3
3	9.30	8.04
5	8.83	7.58
10	7.82	7.27
30	7.35	
50	7.34	6.90
100	7.32	6.96

Table 2 Rate constants of the spontaneous hydrolysis of MeONs in sulfobetaine surfactants

	SB3-14	SBBu3-14
[Surfactant]/10^{-3} mol dm^{-3}	$k_{obs}/10^{-6}$ s^{-1}	$k_{obs}/10^{-6}$ s^{-1}
0	12.3	12.3
1	9.15	
3	8.12	8.50
5		8.07
8	7.19	
10	7.09	7.69
30	6.89	7.70
50	7.17	7.75
100	7.11	

Table 3 Rate constants of the spontaneous hydrolysis of MeONs in amine oxide surfactants

[Surfactant]/10^{-3} mol dm^{-3}	DMMAO		DPMAO
	$k_{obs}/10^{-6}$ s$^{-1\,a}$	$k_{obs}/10^{-6}$ s$^{-1\,b}$	$k_{obs}/10^{-6}$ s$^{-1\,a}$
0	13.4	13.3	13.4
2	9.74	9.03	9.08
6			7.42
7	7.97	7.61	
10	7.64	7.20	7.12
12			7.04
18			7.07
21	6.96	6.90	
31			7.06
35	7.47	6.72	

[a] In 0.05 mol dm^{-3} $MeSO_3H$. [b] In 0.1 mol dm^{-3} $MeSO_3H$.

Table 4 Rate constants of the spontaneous hydrolysis of MeONs in SDS

[SDS]/10^{-3} mol dm^{-3}	$k_{obs}/10^{-6}$ s^{-1}
0	12.5
10	7.43
20	3.54
30	3.10
50	2.85
70	2.93
100	2.69

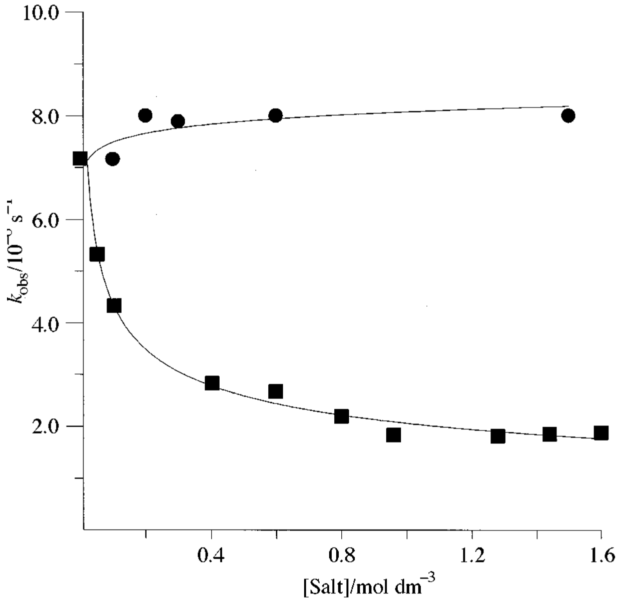

Fig. 1 Rate constants of the spontaneous hydrolysis of MeONs in 0.05 mol dm^{-3} SB3-14 with addition of $MeSO_3Na$ (●) and $NaClO_4$ (■)

The counterion in the cationic surfactants was mesylate rather than halide ion to limit nucleophilic participation,[2] as in solutions of HBr and DMMAO or DPMAO,[16] and therefore we used $MeSO_3H$ to protonate the amine oxides.

Results and discussion

Micellar kinetics

Micelles and water are treated as distinct reaction media, *i.e.*, as pseudophases,[1] and the observed first-order rate constant, k_{obs}, is given by eqn. (1):

$$k_{obs} = \frac{k'_W + k'_M K_S[D_n]}{1 + K_S[D_n]} \qquad (1)$$

Substrate, S, is rapidly partitioned between water and micelles, designated by subscripts W and M respectively, with a binding constant, K_S, with respect to micellized surfactant (detergent), D_n, whose concentration is the total less that of the monomer, *i.e.*, the critical micelle concentration, c.m.c., under the kinetic conditions.[17]

The value of K_S of MeONs in cationic micelles[2,3] is *ca.* 10^3 dm^3 mol^{-1} and this hydrophobic substrate probably promotes micellization, so that, except in dilute surfactant, MeONs is fully micellar bound and $k'_M \approx k_{obs}$. We observed limiting rate constants in the range 0.03–0.1 mol dm^{-3} surfactant, consistent with quantitative substrate binding (Tables 1–4). The electrolyte concentration was varied by addition of $MeSO_3Na$ or $MeSO_3H$ and $NaClO_4$ with SB3-14, and the hydrolysis rate in water is almost unaffected by up to 1 mol dm^{-3} electrolyte. Rate data with added $MeSO_3Na$ and $MeSO_3H$ are available as supplementary material and in Fig. 1.‡ Added ClO_4^- binds very strongly to sulfobetaine micelles as shown by ^{35}Cl NMR spectroscopy and strong inhibition of the reaction of Br$^-$ with MeONs.[16] It therefore converts a zwitterionic into an anionic micelle, which should affect rates of spontaneous hydrolyses.

Values of k'_M are given in Table 5 and variations of k_{obs} with [surfactant] are given in Tables 1–4. Values of k'_M were obtained by fitting rate data to eqn. (1) as described.[1,2]

Effect of micellar charge

The spontaneous hydrolysis of methyl benzenesulfonate is inhibited by both CTAOMs and SDS and values relative to reaction in water, k_{rel}, are 0.70 and 0.40 respectively.[5d,18] Values of k_{rel} for reaction of MeONs in surfactants (Table 5) are similar to, but slightly lower than, those for reaction of methyl benzenesulfonate, despite differences in hydrophobicities of these substrates (for the benzenesulfonate[18] K_S = 50–70 dm^3 mol^{-1}). Both substrates reside in a similar region of the micelle

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‡ This material has been deposited in the Supplementary Publications Scheme (SUPPL NO. 57320, 3 pp.) For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, available *via* the RSC Web pages (http://www.rsc.org/authors).

Table 5 Rate constants of the spontaneous hydrolyses in the micellar pseudophase[a]

Surfactant[b]	$k'_M/10^{-6}\ s^{-1}$
CTAOMs	7.33 (0.59)
CTAOMs + $MeSO_3Na$[b]	7.23 (0.58)
CTPAOMs	6.93 (0.55)
CTPAOMs + $MeSO_3Na$[b]	7.01 (0.56)
SB3-14	7.03 (0.56)
SB3-14 + $MeSO_3Na$[b]	7.94 (0.64)
SB3-14 + $MeSO_3H$[b]	7.27 (0.58)
SB3-14 + $NaClO_4$[c]	1.85 (0.15)
SBBu3-14	7.73 (0.62)
SBBu3-14 + $MeSO_3Na$[b]	7.40 (0.59)
$DMMAOH^+$ + $MeSO_3H$[d]	7.22 (0.58)
$DMMAOH^+$ + $MeSO_3H$[b]	6.81 (0.54)
$DPMAOH^+$ + $MeSO_3H$[d]	7.06 (0.56)
SDS	2.81 (0.22)

[a] At 25.0 °C, with $k'_W = 1.25 \times 10^{-5}\ s^{-1}$. Values in parentheses are relative rate constants in micelles and water, k_{rel}. [b] 0.1 mol dm^{-3} $MeSO_3Na$ or $MeSO_3H$. [c] 1–1.6 mol dm^{-3} $NaClO_4$ (Fig. 1). [d] 0.05 mol dm^{-3} $MeSO_3H$.

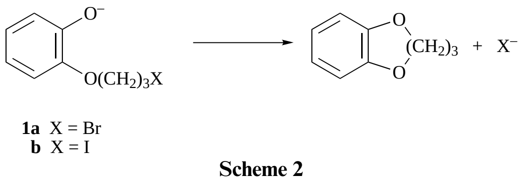
which, based on NMR data with MeONs, is the micelle–water interface adjacent to the ionic head groups.[19] However, increased penetration of the more hydrophobic substrate, MeONs, should partially shield it from water molecules.[19]

Zwitterionic and cationic micelles, including protonated amine oxides, behave differently from anionic micelles (Table 5). Neutral amine oxides can increase k_{obs} by nucleophilic displacement on MeONs[14] and we discuss these reactions elsewhere. The values of k'_M in Table 5 do not seem to be related to the hydrogen bonding of water to anionic or zwitterionic head groups. Hydrogen bond donation to sulfate or sulfonate residues might activate water as a nucleophile,[20] but this effect does not explain our results, because reactions are slower in anionic than in cationic micelles, and water at the micellar surface is apparently not deactivated by hydrogen-bonding to protonated amine oxides (Table 5). However, analyses of micelle–solute interactions in terms of linear solvation free energy relationships indicate the importance of hydrogen bonding,[7] and the specificity of micelle–ion interactions[1] is related to the ease of partial ionic dehydration.[21]

Effect of head group structure

The insensitivity of k'_M to head group bulk and structure (Table 5) was unexpected because of the observed acceleration in spontaneous anionic decarboxylations and dephosphorylations in cationic and sulfobetaine micelles with increasing head group bulk.[9b,10]

Cyclization of the phenolic derivatives, **1**, (Scheme 2) is also



1a X = Br
b X = I

Scheme 2

accelerated by an increase in head group bulk,[4] as are S_N2 reactions of Cl^- and Br^- with MeONs.[2] However, an increase in the bulk of cationic head groups slightly decreases second-order rate constants for reactions of OH^- at micellar surfaces.[3] Bulky alkyl groups at the ammonium ion center may partially exclude water molecules from the micellar surface and decrease its polarity and hydrogen bonding of interfacial water to anions. The absence of such an acceleration of reactions of OH^- is understandable because this ion has a high affinity for water and its hydration should be unaffected by an increase in head group bulk. The Hughes–Ingold rules predict that S_N2 solvolyses should be inhibited by a decrease in water content or polarity of the solvent.[22] Extension of these rules to micellar surfaces is satisfactory for a number of reactions[1d,5] and we therefore expected that polarity and availability of water at micellar surfaces, and therefore rate constants, would be affected by bulky alkyl groups.

Similarities in kinetic behaviours of quaternary ammonium and sulfobetaine micelles are understandable. The charge in ionic micelles is extensively neutralized by counterions[1] and if the trimethylene tether in our sulfobetaine surfactants is extended[23] the sulfonate residue should not strongly perturb the environment of the quaternary ammonium ion. As noted earlier protonated amine oxides are cationic surfactants, but although they can strongly hydrogen-bond to water they appear to have no special effect on its reactivity towards MeONs (Table 5).

$$R'R_2N^+{-}O^- \overset{H^+}{\rightleftharpoons} R'R_2N^+{-}OH$$

The nature of the reaction region

Rate enhancements of nonsolvolytic bimolecular reactions at micellar surfaces are fitted quantitatively by models that take into account the high concentration of reagents in the interfacial region, which is often identified as the Stern layer, a few Angstroms thick, where counterions are concentrated.[1] Based on other kinetic evidence, the properties of this region as a reaction medium should depend on the head group structure, *cf.*, refs. 2–5, 8–10, in contrast to the apparent insensitivity of our spontaneous S_N2 hydrolyses (Table 5). The hydrophobic naphthalene group of MeONs will orient itself towards the quaternary ammonium ions and the attached alkyl tails,[19,24] but the methylsulfonate residue can extend into a more aqueous region (the question of the 'wetness' of the micellar surface and the extent of water–hydrocarbon contact has been discussed in terms of various micellar models[1,5a,7,25]). In the transition state negative charge should build up on the naphthalenesulfonate residue and interact unfavorably with anionic head groups in SDS micelles, consistent with the difference in k_{rel} for these and the cationic or zwitterionic micelles. (Table 1 and refs. 5*d*, 8, 11). Inhibitions are similar with cationic and zwitterionic micelles, which have similar charge asymmetry in the interfacial region. There is no indication that changes in the average location of a substrate in the micellar interfacial region, as related to its hydrophobicity, have a major effect on the rate of spontaneous hydrolysis.

The role of perchlorate ion

The hydrolysis rate of MeONs in SB3-14 is almost unaffected by the addition of up to 1.5 mol dm^{-3} $MeSO_3Na$ (with a slight increase), but we observe a large effect upon addition of $NaClO_4$ (Fig. 1). As noted, perchlorate ion interacts strongly with sulfobetaine micelles,[16] and in effect, $C1O_4^-$ converts a zwitterionic sulfobetaine into an anionic micelle. This generation of head group charge inhibits the spontaneous hydrolysis of MeONs (Table 5 and Fig. 1). However, the inhibition by $NaClO_4$ is higher than expected for an anionic micelle, with $k_{rel} = 0.15$ as compared with 0.22 in SDS. It is difficult to explain inhibition by $C1O_4^-$ solely in terms of micellar charge because micellized SB3-14 + $C1O_4^-$ should not be more 'anionic' than SDS. Chevalier and co-workers have suggested that the interfacial region of betaine micelles can be very open,[23,26] which allows water molecules to penetrate these regions. However, $C1O_4^-$ interacts with the ammonium centers, based on changes in the ^{14}N NMR spectrum,[16] and it will then expel water from this region and thus inhibit spontaneous, bimolecular hydrolyses (Table 5). The insolubility of cationic surfactants + $C1O_4^-$ prevents our examining this system.

Conclusions

Our evidence regarding effects of cationic, betaine sulfonate and anionic micelles on a spontaneous S_N2 hydrolysis fits the generalization that cationic and betaine micelles behave similarly as reaction media.[9b,10,11] Rate enhancements of reactions of anionic reagents are generally lower with betaine sulfonate than with cationic micelles but these differences are due to relatively weak binding of anions to betaine micelles, and not to reactivities at micellar surfaces.[27] We can explain rate effects on a variety of spontaneous reactions in terms of a lower polarity and water availability in the interfacial region, relative to bulk water,[6,7,23] together with electrical asymmetry in this region, which generates the differences between cationic and anionic micelles.[5d]

The E1cB reaction of the carbanion of a fluorenyl carboxylic ester also illustrates the role of charge asymmetry at micellar surfaces. In this reaction negative charge is dispersed out of the hydrophobic fluorenyl group in the ketene-like transition state. Rate effects are small, but reaction is inhibited by cationic and betaine micelles and accelerated by anionic and phospholipid-derived micelles.[11]

We note that micellar effects on rates of spontaneous reactions may be very large, as in decarboxylations,[9] or small as in these S_N2 hydrolyses or the E1cB reaction.[11] They are qualitatively understandable in terms of a simple model of the micelle–water interface and evidence on its hydration and polarity.[6,7] These considerations should also apply to reactions in other association colloids, *e.g.*, microemulsions and vesicles.[1,5c] However, changes in the properties of the interfacial region, induced, for example, by changes in the head group structure, can induce modest rate effects depending on reaction mechanism.

Experimental

Materials

Preparation and purification of MeONs and the surfactants have been described.[2,10] Critical micelle concentrations (c.m.c./mmol dm^{-3}) of the zwitterionic surfactants were: SB3-14, 0.29; SBBu3-14, 0.11; DMMAO, 0.14; DPMAO, 0.05. They were measured by surface tension and there were no minima in the relevant plots.[1a] Reactions were carried out in redistilled, deionized water.

Kinetics

Reactions were followed at 25.0 °C in a Shimadzu UV-160 A or an HP 8452 spectrophotometer by following decreasing absorbance at 326 nm with 10^{-4} mol dm^{-3} MeONs, as described.[2] The slower reactions could not be followed to 10 half-lives and k_{obs} was then calculated by a nonlinear, least-squares fitting of the variation of absorbance with time to a first-order rate equation. For the faster reactions values of k_{obs} from this method and those based on an infinity absorbance agreed. Values of k_{obs} over a range of [surfactant] are in Tables 1–4 and supplementary material. Addition of $MeSO_3H$ to solutions of the sulfobetaines had little effect on k_{obs} showing that there is no reaction with OH^-.

Reactions in solutions of amine oxides were followed in excess $MeSO_3H$ where protonation is quantitative.[15] The electrolyte concentration was varied, in the absence of surfactants, by addition of $MeSO_3H$, $MeSO_3Na$ and $NaClO_4$; the hydrolysis rate in water is almost unaffected by added salt. In 0.05–0.1 mol dm^{-3} $MeSO_3H$ $k_{obs} = 1.33 \pm 0.01 \times 10^{-5}$ s^{-1}; in 0.1–1 mol dm^{-3} $MeSO_3Na$ $k_{obs} = 1.25 \pm 0.07 \times 10^{-5}$ s^{-1}; in $NaClO_4$ 0.1–1 mol dm^{-3} $k_{obs} = 1.14 \pm 0.40 \times 10^{-5}$ s^{-1}.

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