Structure of Micellar Head-Groups and the Hydrolysis of Phenyl Chloroformate − The Role of Perchlorate Ion

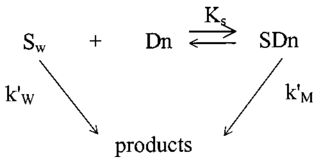
Lucia Brinchi,[a] Pietro Di Profio,[a] Francesca Micheli,[a] Raimondo Germani,[a]
Gianfranco Savelli,*[a] and Clifford A. Bunton[b]

Keywords: Cations / Colloids / Hydrolyses / Micelles / Perchlorate

Spontaneous hydrolysis of phenyl chloroformate is inhibited by micelles, but inhibition by SDS (n-$C_{12}H_{25}OSO_3Na$) micelles is much greater than inhibition by cationic or sulfobetaine micelles (n-$C_{16}H_{33}NR_3X$: CTAX, CTEAX, CTBAX, R = Me, Et, Bu, respectively, X = Cl, Br, OMs; n-$C_{14}H_{29}N^+R_2(CH_2)_3SO_3^-$: SB3-14, SBP3-14, R = Me, Pr, respectively, and n-$C_{14}H_{29}N^+Me_2(CH_2)_nSO_3^-$: SB4-14, SB5-14, n = 4 and 5, respectively). − Inhibition by cationic micelles increases with increasing head-group bulk and affinity of the counterion for cationic micelles, while addition of $NaClO_4$ to sulfobetaines inhibits reaction strongly. Values of k_{obs} relative to reactivity in water, for cationic micelles, are 0.64 (CTACl) and 0.32 (CTBABr); sulfobetaines behave similarly, but the corresponding values for SDS and sulfobetaine/ClO_4^- mixtures are ca. 0.06. These head-group and counterion effects indicate that depletion of water in the interfacial region complements the charge effect in controlling reactivity in micelles.

Introduction

Aqueous micelles and similar association colloids affect reaction rates and equilibria by placing reactants in environments different from that of bulk solvent.[1] The pseudophase model treats overall rates as the sum of those in water and those in micelles, and allows quantitative treatment of variation of rate constants with concentrations of reactants, surfactants or other amphiphiles, and, in some systems, inert electrolytes. Implicit in this model is the assumption that the interfacial reaction region behaves as though it provides a uniform environment, the properties of which are comparable with those of bulk solvents. Reactant transfer is an equilibrium process that is much faster than most thermal reactions, and Scheme 1 describes micellar rate effects.



Scheme 1

Substrate S is distributed between water and micelles, denoted by subscripts W and M, with an association constant, K_S, with respect to micellized surfactant (detergent) Dn. ([Dn] is total concentration minus the critical micelle concentration (cmc), which is assumed to be the concentration of monomeric surfactant). For spontaneous reactions, the observed first-order rate constant, k_{obs}, is given by the association constant of the substrate and its first-order rate constants in water and micelles: k'_W and k'_M, respectively.

Bimolecular reactions with an added second reagent are generally followed under first-order conditions, by using excess reagent. In such cases, k'_W and k'_M are functions of local concentrations of the second reagent in water and micelles; in favorable cases they can be measured experimentally, but often have to be calculated by using a variety of theoretical treatments.

The first-order rate constant, k_{obs}, with respect to S is given by:

$$k_{obs} = (k'_W + k'_M \cdot K_S[Dn])/(1 + K_S[Dn]) \quad (1)$$

For reactions with a second reagent, k'_W and k'_M are related to local second-order rate constants and are functions of local concentrations of this reagent; of a nucleophile in water and micelles, for example. This raises conceptual and practical problems regarding estimation or direct determination of local concentrations in micelles.[1,2] It is therefore much easier to arrive at conclusions regarding micellar rate effects by examining spontaneous reactions rather than those involving an added reagent. However, for both spontaneous reactions and those involving an added reactant, micelles typically behave qualitatively as reaction media that are somewhat less polar than water, and the use of spectral probes indicates that micellar polarities, as given by E_T, for example, are similar to those of mixtures of water and solvents such as EtOH, dioxane, or MeCN.[3,4]

We are interested in the effects of changes in the sizes of cationic head-groups and the nature of counterions on the properties of interfacial regions of cationic, anionic, and zwitterionic micelles. The surfactants of interest are: cetyl

---

[a] Dipartimento di Chimica, Università di Perugia,
Via Elce di Sotto, no. 8, 06123 Perugia, Italy
Fax: (internat.) +39−075/5855538
E-mail: savelli@unipg.it
[b] Department of Chemistry and Biochemistry,
University of California, Santa Barbara, CA 93106, USA

Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/eurjoc or from the author.

1434−193X/01/0306−1115 $ 17.50+.50/0

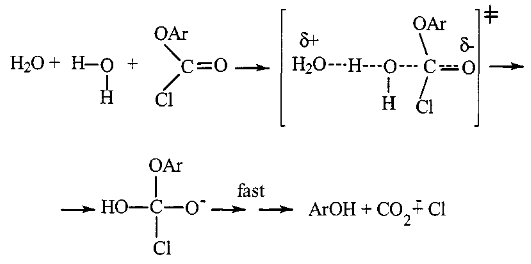
trialkylammonium chloride, bromide, and mesylate (n-$C_{16}H_{33}NR_3X$: CTAX, CTEAX, CTBAX, R = Me, Et, Bu, X = Cl, Br, OMs, respectively); sodium dodecylsulfate (n-$C_{12}H_{25}OSO_3Na$, SDS); and a number of sulfobetaines [n-$C_{14}H_{29}N^+R_2(CH_2)_3SO_3^-$: SB3-14, SBP3-14, R = Me, Pr, respectively, and n-$C_{14}H_{29}N^+Me_2(CH_2)_nSO_3^-$: SB4-14, SB5-14, n = 4 and 5, respectively].

Estimations exist of second-order rate constants of reactions of anionic nucleophiles in these cationic and zwitterionic micelles.[1] Within the uncertainties and assumptions of the treatments, the micellar rate constants, relative to those in water, are qualitatively consistent with independent estimates of interfacial polarities[3,4] and treatments of kinetic solvent effects.[5] This state of affairs also applies to micellar effects on spontaneous reactions − S_N1 and S_N2 hydrolyses at alkyl centers, for example, or water-catalyzed deacylations[1d,6,7] − for which only substrate transfer has to be considered. Micelles inhibit most hydrolyses at alkyl or acyl centers, with the exception of acyl chlorides possessing strongly electron-withdrawing substituents.[7a,8]

Rate constants of these spontaneous hydrolyses typically decrease on addition of organic solvents to water, especially for S_N1 hydrolyses of nonionic substrates,[5] and micellar inhibitions are qualitatively consistent with the interfacial region being less polar and "less aqueous" than water.[3,4,6] The high electrolyte content of ionic interfacial regions may also inhibit hydrolyses, and there is a micellar charge effect related to reaction mechanism.[7,8] When bond-making by water is important, such as in S_N2 hydrolyses and deacylations of carboxylic anhydrides, reactions in the micellar pseudophase are faster in cationic or zwitterionic sulfobetaines than in anionic micelles. As bond-breaking becomes more important, however, as in S_N1 hydrolyses, for example, reactions are faster in anionic micelles than in their cationic or sulfobetaine counterparts, although most reactions are slower in micelles than in water. These generalizations apply regardless of substrate hydrophobicity or relative reactivities in water and micelles. Most experiments with cationic micelles have involved trimethylammonium surfactants, but inhibition of the spontaneous S_N2 hydrolysis of methyl naphthalene-2-sulfonate increases slightly with increasing bulk of the cationic head-group,[7c] which should reduce the polarity and water content of the interfacial region.[2c,9,10]

Our intention was to examine other spontaneous hydrolyses in micelles with different head-groups and counterions. We needed a substrate that would not react with halide ions,[7c] and used phenyl chloroformate (**1**), hydrolysis of which can be followed by spectrophotometric means in water and aqueous surfactants. Alternative substrates such as benzoic anhydride react slowly, and some aroyl chlorides too rapidly, for convenient work.[7a]

The hydrolysis of **1** is well studied and is assumed to involve rate-limiting formation of a tetrahedral intermediate with general base catalysis by a second water molecule[11,12] (Scheme 2). Negative charge is shown as localized on carbonyl oxygen and positive charge on water. The relative importance of bond-making and bond-breaking in haloformate solvolyses depends on substrate structure and the reaction medium; the evidence is summarized concisely by Kevill and D'Souza.[12]



Scheme 2

In water-catalyzed deacylations, such as that of a chloroformate in micelles, positive charge on the nucleophilic water molecule is dispersed into other water molecules, and negative charge is dispersed into the organic moiety situated close to the micellar head-groups. Therefore, reactivity in the micellar pseudophase should be related to the availability of water in the interfacial region, and also to interactions with ionic head-groups in the transition state, relative to the initial state.

Results and Discussion

Effects of Cationic Micelles

Inhibition by cationic micelles is shown in Figure 1 and in Table S1 of the Supplementary Materials, and increases significantly with increasing head-group bulk. Hydrolyses were followed in the presence of dilute acid ($1 \cdot 10^{-3}$M $MeSO_3H$), which suppresses reaction with OH^-. Inhibition also increases as the affinity of the counterion for CTA^+ increases, and so k_{obs} decreases in the sequence $Cl^- > OMs^- > Br^-$ for univalent ions. Some limited data exist for reaction in micelles of $(CTA)_2SO_4$, which (in terms of $[CTA^+]$) is very similar to CTABr in its rate effects,[7a] since Br^- and SO_4^{2-} have high affinities for cationic micelles.[14]

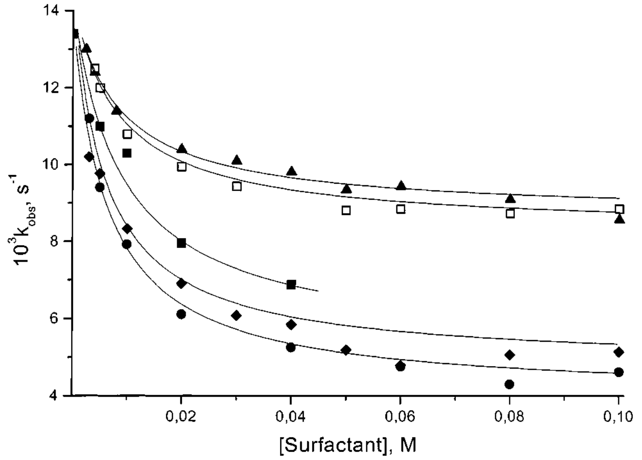


Figure 1. Reaction of **1** in cationic surfactants, CTABr (full square), CTEABr (full rhombus), CTBABr (full circle), CTAOMs (hollow square), CTACl (full triangle). Lines are from fitting to Equation (1).

Equation (1) describes inhibition by the cationic micelles and the lines in Figure 1 are simulated by using Equation (1) with the fitting parameters in Table 1.

Table 1. Fitting parameters for the micellar reaction of **1**[a]

Surfactant	10^3 k_M, s^{-1} [a]
CTACl	8.6
CTAOMs	8.3
CTABr	5.2
CTEABr	4.8
CTBABr	4.0
SB3-14	8.3
SBP3-14	6.5
SB4-14	ca. 7[b]
SB5-14	< 11[b]
SDS	1.00[b]

[a] At 25.0 °C, $MeSO_3H$ or HBr 10^{-3} M, $k_W=13.4\cdot10^{-3}$, s^{-1}; K_S = 100 M^{-1} for CTACl, CTAOMs, CTABr, and SDS, and 150 M^{-1} for the other surfactants. – [b] See text.

Effects of Sulfobetaine Micelles

Sulfobetaine micelles behave similarly to cationic micelles in inhibiting hydrolysis (Figure 1 and Figure 2 and Table S2 of the Supplementary Materials). An increase in the tether length has little effect on inhibition, but SB4-14 and SB5-14 are only sparingly soluble in water and could not be used at concentrations higher than 0.015 M. Inhibition by SB3-14 and SBP3-14 fits Equation (1), and variations of k_{obs} with concentrations of these surfactants are simulated with the parameters in Table 1.

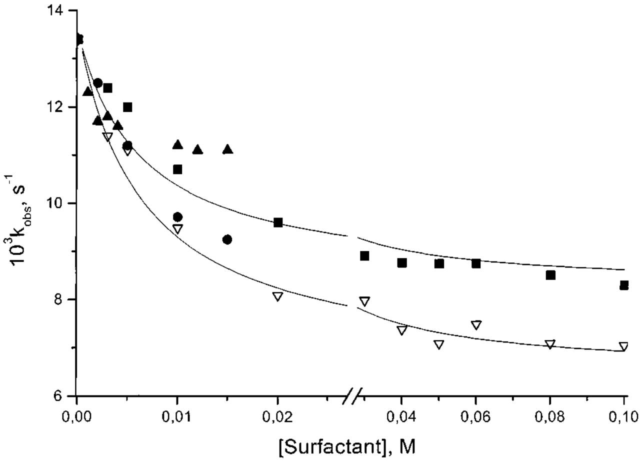


Figure 2. Reaction of **1** in sulfobetaine surfactants, SB3-14 (full square), SBP3-14 (▽), SB4-14 (full circle), SB5-14 (full triangle). Lines are from fitting to Equation (1).

Hydrolysis in sulfobetaine micelles is further inhibited by addition of $NaClO_4$ (Figure 3 and Table 2, and Table S4 of the Supplementary Materials), which interacts strongly with micelles of SB3-14 and displaces water from the interfacial region.[13] These experiments were performed using 0.05 M surfactant, where reaction is largely in the micellar pseudophase (Figure 2), and the solubilities of SB4-14 and SB5-14 are sharply increased by $NaClO_4$. Pairing of ionic centers should lessen the solubilities of these sulfobetaines in water, but this should decrease on addition of ClO_4^-, which pairs with the cationic center. The significance of these observations is considered later in relation to SDS kinetic effects.

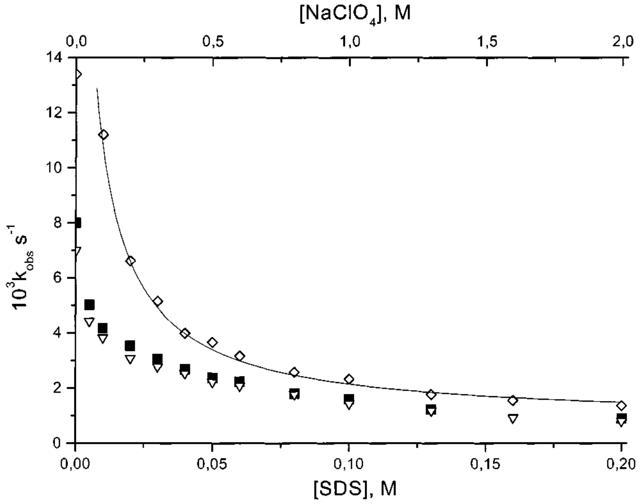


Figure 3. Reaction of **1** in SDS (rhombus) refers to the lower axis, line is from fitting to Equation (1). Reaction in [sulfobetaine] 0.05 M with added $NaClO_4$, SB3-14 (full square), SBP3-14 (triangle), refers to the upper axis.

Table 2. Effect of $NaClO_4$ upon the reaction of **1** in sulfobetaine micelles of SB4-14 and SB5-14

[$NaClO_4$], M	SB4-14[a]	SB5-14[a]
–	ca 9.0[b]	< 11[b]
0.05	5.42	5.06
0.6	2.13	2.19
1.0	1.67	1.62
2.0	0.85	0.85

[a] Values of 10^3 k_{obs}, s^{-1}, at 25.0°C, [$MeSO_3H$] = $1\cdot10^{-3}$ M, and 0.05 M surfactant. – [b] Approximate values, see text.

Inhibition by SDS

Anionic micelles of SDS strongly inhibit hydrolysis of **1** (Figure 3, and Table S3 of the Supplementary Materials), in agreement with earlier evidence on this and other spontaneous hydrolyses.[7,8] Very dilute SDS does not sharply decrease k_{obs} because the cmc in water[15] is ca. $8\cdot10^{-3}$ M, although it will be somewhat decreased by the substrate and added acid. Monomeric or premicellar SDS apparently has little effect on the rate of hydrolysis. The decrease in k_{obs} with [SDS] fits Equation (1) and the line in Figure 3 is derived from simulation using the values of K_S and k'_M given in Table 1. However, limitations exist for quantitative treatment of rate data based on the pseudophase model when substrates are not very hydrophobic, such as with $K_S \approx 10^2$ M^{-1} and $k'_W >> k'_M$. Reasonable fits can be obtained with various combinations of K_S and k'_M; the following sets of values which give acceptable fits (within 5% limits), for example, are in the range of K_S = 80 M^{-1}, k'_M $=0.6\cdot10^{-3}$ s^{-1} and K_S =100 M^{-1}, k'_M $=1.0\cdot10^{-3}$ s^{-1}. We cannot determine K_S directly, because of hydrolysis, and therefore have to accept these uncertainties in k'_M. However, these values of K_S are typical of organic solutes with a phenoxy group.[16]

Even in relatively concentrated SDS there is a minor reaction in the aqueous pseudophase, affecting values of k_{obs}, and its contribution is dependent on the value of K_S. There is also a more fundamental limitation in the quantitative validity of the pseudophase treatment [Equation (1)], involving the assumption that the rate and equilibrium constants are independent of [surfactant]. Surfactants have relatively high molecular weights (for SDS, for example, $M_W = 288$), and 0.2 M surfactant may affect the properties of bulk water. This problem is less acute for reactions of hydrophobic substrates that are fully bound in dilute surfactant, or micelle-accelerated reactions, in which there is little contribution from reaction in the aqueous pseudophase.

Menger and Portnoy[17] showed how a linearized form of Equation (1) could be used to estimate values of K_S and k'_M, by, in effect, extrapolating the data to infinite [surfactant], but this form is not useful for estimating k'_M when it is much less than k'_W.

Rate-surfactant Profiles

Variations of k_{obs} with [surfactant] fit the pseudophase treatment, and the fitting parameters obtained by using Equation (1) are given in Table 1, except for reactions in the sparingly soluble sulfobetaines SB4-14 and SB5-14. In the limited range of concentration that could be examined (Figure 2), SB4-14 and SBP3-14 gave similar values of k_{obs} and we assume that they should give similar values of k'_M, but for reaction in SB5-14 we can only conclude that k'_M is less than $11 \cdot 10^{-3}$ s^{-1}. The value of k'_M for hydrolysis in the hexadecyl surfactant, SB3−16,[8a] is $6 \cdot 10^{-3}$ s^{-1} and is similar to that in SB3-14 (Table 1).

Effects of Micellar Structure

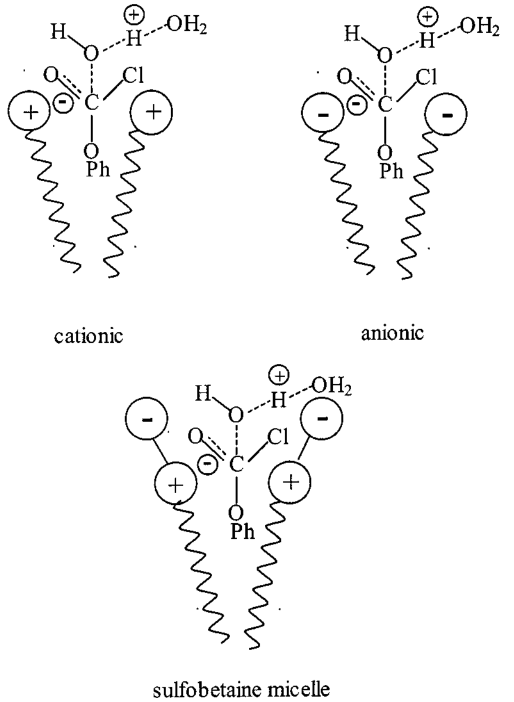
Hydrolysis is inhibited by micelles, regardless of surfactant structure or charge. This agrees with earlier data on this reaction, and extensive evidence from other micelle-mediated deacylations.[6−8a] Inhibition is understandable, in that these reactions are inhibited by decreases in solvent polarity and water content, and these are less in micellar interfacial regions than they are in water.[3,4]

Values of k'_M in cationic micelles decrease with increasing head-group bulk (Figure 1 and Table 1) as, but to a lesser extent, in the S_N2 hydrolysis of methyl naphthalene-2-sulfonate.[7c] Cationic and sulfobetaine micelles have very similar effects upon values of k'_M for S_N2 and other spontaneous hydrolyses,[7c,8a,18] indicating that their interfacial regions behave similarly as reaction media. This conclusion is consistent with other evidence from, for example, nonsolvolytic bimolecular[13,19] and E1cB[20] reactions involving nucleophilic or basic anions. However, reactions of nucleophilic anions are slower in sulfobetaine micelles than in cationic micelles, because of the higher affinity of the latter for anions. However, provided that transfer equilibria are taken into account, second-order rate constants in the micellar pseudophase are similar for cationic and sulfobetaine micelles.[13][19b] Although sulfobetaine micelles have no net charge, the positive charge density at the cationic surface is higher than the negative charge density at the sulfonate surface, which accounts for their interaction with anions of high charge density, such as OH^- and F^-.[18,21] They also interact specifically with anions of low charge density,[13] and interactions with ClO_4^- are discussed later. Many cationic micelles have low fractional charge α, i.e., the head-groups are largely neutralized by anions,[1c−1g] and sulfobetaine micelles behave, in many respects, like cationic micelles with $\alpha \rightarrow 0$.

Effects of head-group bulk on hydrolysis of **1** are due to decreases in polarity and water content of the interfacial region when methyl is replaced by larger alkyl groups such as butyl, and this conclusion is consistent with estimates of the water contents of these regions.[2c] We can explain some aspects of the relationship between k'_M and head-group structure in terms of changes in polarities of the interfacial regions, but the strong inhibition of hydrolysis of **1** and other spontaneous bimolecular hydrolyses by anionic micelles of SDS shows that charge cannot be neglected. The surface of an SDS micelle should be "water-rich" and water activity in this region is not much lower than that of bulk water;[22] in addition, hydrogen bonding to the sulfate ion should increase the nucleophilicity of bound water.[23]

The charge effect of micelles on spontaneous hydrolyses appears to be related to charge asymmetry in the interfacial region and contrasting charge distributions in the transition states of spontaneous bimolecular hydrolyses, viz-a-viz S_N1 hydrolyses.[7,8a] In the transition state for hydrolysis of **1**[11,12] or a similar acyl compound (Scheme 2), negative charge builds up on the organic moiety and interacts unfavorably with the anionic head-group of an SDS micelle, as compared with a cationic head-group. Conversely, in an S_N1 reaction, positive charge at the alkyl center in the transition state interacts unfavorably with a cationic head-group.[7,8a] Therefore, in analyzing kinetic micellar effects on spontaneous hydrolyses, we have to consider not only polarity and water content, but also surface charge distributions at micellar surfaces, which depend on interactions between counteranions and head-groups. The charge interactions in chloroformate hydrolysis, with one water molecule acting as a nucleophile and the other as a general base,[12] are illustrated in a simplified form in Scheme 3, in which counterions are eliminated for clarity, charges are shown as fully developed in the transition states, and the reaction center is depicted as adjacent to the micellar head-groups.

Substituents change the relative extents of bond-making and bond-breaking in hydrolyses where water is the nucleophile, and this affects relative reactivities in water and micelles, and the charge effect. For example, hydrolyses of 4-nitrophenyl chloroformate and nitrobenzoyl chlorides are accelerated by cationic and sulfobetaine micelles, although hydrolyses of the parent compounds are inhibited by micelles.[8] Relative rate constants of hydrolyses of 4-substituted benzenesulfonyl chlorides in water and in micelles are sensitive to electronic effects, and electron-withdrawing groups strongly promote reactivity in cationic micelles over that in anionic ones, even though the molecularity of the reaction does not change.[18]



Scheme 3

Effects of Anions

The fractional micellar charge, α, of cationic micelles increases − i.e., the affinity for anions decreases − as the charge density of monoanions is increased, but decreases on going from monoanions to dianions.[1a,1c−1g,14,24] Values of k'_M for a series of anions in CTA^+ micelles correlate with values of α, in the sequence $Cl^- > OMs^- > Br^- \approx (SO_4^{2-})_{0.5}$. Values of k'_M in $(CTA)_2SO_4$ are based on $[CTA^+]$.[7a] The large difference between values of k'_M in cationic and anionic micelles (Table 1) indicates that charge neutralization of cationic head-groups reduces k'_M. However, consideration of the effects of $NaClO_4$ upon values of k'_M in sulfobetaine micelles (Figure 3 and Table 2) indicates that micellar charge is not the only factor responsible for the rate effects.

Physical evidence (NMR spectroscopy and conductivity data) shows that ClO_4^- binds readily to micelles of SB3-14, which therefore become anion-like;[7c,13] this, by analogy with the behavior of SDS micelles (Figure 3), should inhibit reaction. However, reaction in mixtures of sulfobetaines and $NaClO_4$ is, with high $[NaClO_4]$, slightly slower than in high [SDS] with largely micelle-bound substrate (Figure 3). Hydrolysis of methyl naphthalene-2-sulfonate is slower in SB3-14 and $NaClO_4$ than in high [SDS], which shows that the rate decrease is due not only to development of anionic character in micelles of SB3-14, but also to displacement of water from the interfacial region by ClO_4^-.[7c] Interfacial regions of betaine micelles are very open[25] and accessible to water, which can be displaced by ClO_4^- or other anions of low charge density.

This evidence that incorporation of ClO_4^- into sulfobetaine micelles inhibits S_N2 and water-catalyzed hydrolyses, by partially displacing water and by exerting a charge effect, has a bearing on reactivities in cationic micelles. Dediazotization trapping shows that Br^-, which has a high affinity for cationic micellar head-groups, displaces water from the interfacial region.[2c] The sequence of values of k'_M: CTACl > CTAOMs > CTABr (Table 1) is due to decreases in both the cationic character and the water content of the micellar interfacial region. It is difficult to separate these factors for spontaneous bimolecular hydrolyses, but S_N1 hydrolyses are consistently faster in anionic micelles than in cationic ones, although both inhibit reaction. Both S_N1 and S_N2 hydrolyses are accelerated by increases in water contents of mixed solvents,[5] and therefore differences in the behavior of cationic and anionic micelles in these reactions are related to charge asymmetries at the micellar surfaces, which are more important than changes in local water content.

As a counterpoint to the specificity of micellar effects upon spontaneous deacylations and S_N2/S_N1 hydrolyses, we note that spontaneous decarboxylations[26] and cyclizations[10,26] of anionic substrates are accelerated by cationic and zwitterionic betaine micelles (these substrates have little affinity for anionic micelles, which complicates analysis of their rate effects). These reactions are accelerated by decreases in solvent polarity and water content, because localized negative charge in the initial state is dispersed into an organic moiety in the transition state.[27] The factors that influence micellar effects upon these reactions are similar to those that affect rates of spontaneous hydrolyses in aqueous micelles, and it is reasonable to draw analogies between micellar interfacial regions and bulk solvents as reaction media. These analogies extend to bimolecular reactions, such as of basic or nucleophilic anions, but here allowance has to be made for anion transfer equilibria between water and micelles.

Experimental Section

Materials: Surfactants were materials used earlier as described;[7,9,13] compound **1** was obtained from ACROS. Reactions were carried out in redistilled, deionized, CO_2-free water.

Kinetics: Hydrolysis was followed spectrophotometrically at 25.0 °C in Shimadzu UV-160A or HP 8452 spectrometers at 270 nm, with $2 \cdot 10^{-4}$ M **1**. We added 10^{-3} M $MeSO_3H$ or HBr to suppress any reaction with base, and in water we obtained the same values of k_{obs} with $MeSO_3H$ and HBr (HBr was always used with the bromide ion surfactants, Supporting Material). The substrate was added in MeCN and the final solutions contained 1 vol% MeCN.

First-order rate constants k_{obs} (s^{-1}) were calculated from the integrated first-order rate equation, with absorbances measured at complete reaction; values in water and micelles agreed with earlier data,[7a,11,12] although slightly different conditions were used. In simulating the micellar rate data we used the following values of cmc (mM): CTACl, CTAOMs, 1.4; CTABr, 0.8; CTEABr, 0.7; SB3-14, SBP3-14, 0.3; and SDS, 70. Surfactant concentrations were so much greater than the cmc that their values did not affect simulations.

Acknowledgments

Support of this work by the Consiglio Nazionale delle Ricerche, Rome, by the Ministero dell'Università e della Ricerca Scientifica, Rome, and by the Fulbright Commission for a grant to L. B. is gratefully acknowledged.

---

[1] [1a] J. H. Fendler, *Membrane Mimetic Chemistry*, Wiley Interscience, New York, **1982**. – [1b] K. Martinek, A. K. Yatsimirski, A. V. Levashov, I. V. Berezin, in: *Micellization, Solubilization and Microemulsions*, (Ed.: K. L. Mittal), Plenum Press, New York, **1977**, vol. 2. p. 489. – [1c] L. S. Romsted, in: *Surfactants in Solution* (Eds.: K. L. Mittal, B. Lindman), Plenum Press, New York, **1984**, Vol. 2, p. 1015. – [1d] C.A. Bunton, G. Savelli, *Adv. Phys. Org. Chem.* **1986**, *22*, 213–309. – [1e] C. A. Bunton, F. Nome, L. S. Romsted, F. H. Quina, *Acc. Chem. Res.* **1991**, *24*, 357–363. – [1f] L. S. Romsted, C. A. Bunton, J. Yao, *Curr. Opin. Colloid Interface Sci.* **1997**, *2*, 622–628. – [1g] G. Savelli, R. Germani, L. Brinchi, in: *Reactions and Synthesis in Surfactant Systems* (Ed.: J. Texter), M. Dekker, New York, in press.

[2] [2a] A. Chaudhuri, L. S. Romsted, *J. Am. Chem. Soc.* **1991**, *113*, 5052–5053. – [2b] J. H. Yao, L. S. Romsted, *J. Am. Chem. Soc.* **1994**, *116*, 11779–11786. – [2c] V. Soldi, J. Keiper, L. S. Romsted, I. M. Cuccovia, H. Chaimovich, *Langmuir* **2000**, *16*, 59–71.

[3] [3a] K. A. Zachariasse, N. Y. Phuc, C. Kozankiewicz, *J. Phys. Chem.* **1981**, *85*, 2676–2683. – [3b] C. Ramachandran, R. A. Pyter, R. Mukerjee, *J. Phys. Chem.* **1982**, *86*, 3198–3205.

[4] L. P. Novaki, O. A. El Seoud, *Phys. Chem. Chem. Phys.* **1999**, *1*, 1957–1964.

[5] C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, 2nd edn., Cornell University Press, Ithaca, New York, **1969**, chap. 7.

[6] [6a] F. M. Menger, H. Yoshinaga, K. S. Venkatasubban, A. R. Das, *J. Org. Chem.* **1981**, *46*, 415–419. – [6b] N. Fadnavis, J. B. F. N. Engberts, *J. Am. Chem. Soc.* **1984**, *106*, 2636–2640. – [6c] N. J. Buurma, A. M. Herranz, J. B. F. N. Engberts, *J. Chem. Soc., Perkin Trans. 2* **1999**, 113–119.

[7] [7a] H. Al-Lohedan, C. A. Bunton, M. M. Mhala, *J. Am. Chem. Soc.* **1982**, *104*, 6654–6660. – [7b] C. A. Bunton, S. Ljunggren, *J. Chem. Soc., Perkin Trans. 2* **1984**, 355–261. – [7c] L. Brinchi, P. Di Profio, R. Germani, G. Savelli, N. Spreti, C. A. Bunton, *J. Chem. Soc., Perkin Trans. 2* **1998**, 361–364. – [7d] C. A. Bunton, N. D. Gillitt, M. M. Mhala, J. R. Moffatt, A. K. Yatsimirsky, *Langmuir*, **2000**, *16*, 8595–8603.

[8] [8a] C. A. Bunton, in: *Nucleophilicity* (Eds.: J. M. Harris, S. P. McManus), Adv. Chem. Ser., No. 215, American Society, Washington, D. C., **1987**, ch. 29. – [8b] S. Possidonio, F. Siviero, O. A. El Seoud, *J. Phys. Org. Chem.* **1999**, *12*, 325–332.

[9] [9a] P. Di Profio, R. Germani, G. Savelli, G. Cerichelli, N. Spreti, C. A. Bunton, *J. Chem. Soc., Perkin Trans. 2* **1996**, 1505–1509. – [9b] F. Del Rosso, A. Bartoletti, P. Di Profio, R. Germani, G. Savelli, A. Blaskò, C. A. Bunton, *J. Chem. Soc., Perkin Trans. 2* **1995**, 673–678.

[10] G. Cerichelli, L. Luchetti, G. Mancini, M. N. Muzzioli, R. Germani, P. P. Ponti, N. Spreti, G. Savelli, C. A. Bunton, *J. Chem. Soc., Perkin Trans. 2* **1989**, 1081–1805.

[11] [11a] A. Queen, *Can. J. Chem.* **1967**, *45*, 1619–1629. – [11b] A. R. Butler, I. H. Robertson, R. Bacaloglu, *J. Chem. Soc., Perkin Trans. 2* **1974**, 1733–1736. – [11c] D. N. Kevill, in: *The Chemistry of Acyl Halides*, (Ed., S. Patai), Interscience, New York, **1972**, ch. 12.

[12] D. N. Kevill, M. J. D'Souza, *J. Chem. Soc., Perkin Trans. 2* **1997**, 1721–1724.

[13] P. Di Profio, R. Germani, G. Savelli, G. Cerichelli, M. Chiarini, G. Mancini, C. A. Bunton, N. D. Gillitt, *Langmuir* **1998**, *14*, 2662–2669.

[14] [14a] E. Lissi, E. B. Abuin, L. Sepulveda, F. H. Quina, *J. Phys. Chem.* **1984**, *88*, 81–85. – [14b] G. Biresaw, D. C. Mc Kenzie, C. A. Bunton, D. F. Nicoli, *J. Phys. Chem.* **1985**, *89*, 5144–5146.

[15] P. Mukerjee, K. L. Mysels, *Critical Micelle Concentrations of Aqueous Surfactant Systems*, National Bureau of Standards, Washington, D. C. **1970**.

[16] [16a] L. Sepulveda, E. Lissi, F. H. Quina, *Adv. Colloid Interface Sci.* **1986**, *25*, 1–57. – [16b] F. H. Quina, E. O. Alonso, *J. Phys. Chem.* **1995**, *99*, 1178–11714. – [16c] H. Abraham, H. S. Chadha, J. P. Dixon, C. Rafols, C. Treiner, *J. Chem. Soc., Perkin Trans. 2* **1995**, 887–894. – [16d] H. Abraham, H. S. Chadha, J. P. Dixon, C. Rafols, C. Treiner, *J. Chem. Soc., Perkin Trans. 2* **1997**, 19–24.

[17] F. M. Menger, C. E. Portnoy, *J. Am. Chem. Soc.* **1967**, *89*, 4698–4703.

[18] C. A. Bunton, M. M. Mhala, J. R. Moffatt, *J. Org. Chem.* **1985**, *50*, 4921–4924.

[19] [19a] C. A. Bunton, M. M. Mhala, J. R. Moffatt, *J. Org. Chem.* **1987**, *52*, 3832–3835. – [19b] C. A. Bunton, M. M. Mhala, J. R. Moffatt, *J. Phys. Chem.* **1989**, *93*, 854–585.

[20] V. R. Correia, I. M. Cuccovia, M. Stelmo, H. Chaimovich, *J. Am. Chem. Soc.* **1992**, *114*, 2144–2146.

[21] M. da Silva Baptista, I. Cuccovia, H. Chaimovich, M. J. Politi, W. F. Reed, *J. Phys. Chem.* **1992**, *96*, 6442–6449.

[22] A. Angeli, R. Cipiciani, R. Germani, G. Savelli, G. Cerichelli, C. A. Bunton, *J. Colloid Interface Sci.* **1988**, *121*, 42–48.

[23] M. C. R. Symons, *Acc. Chem. Res.* **1981**, *14*, 179–187.

[24] J. D. Morgan, D. H. Napper, G. G. Warr, *J. Phys. Chem.* **1995**, *99*, 9458–9465.

[25] [25a] Y. Chevalier, P. Le Perchec, *J. Phys. Chem.* **1990**, *94*, 1768–1774. – [25b] Y. Chevalier, N. Kamenka, M. Chorro, R. Zana, *Langmuir* **1996**, *12*, 3225–3232.

[26] [26a] G. Cerichelli, G. Mancini, L. Luchetti, G. Savelli, C. A. Bunton, *J. Phys. Org. Chem.* **1991**, *4*, 71–76. – [26b] G. Cerichelli, L. Luchetti, G. Mancini, G. Savelli, C. A. Bunton, *Langmuir* **1996**, *12*, 2348–2352.

[27] [27a] D. S. Paul, K. G. Kemp, *J. Am. Chem. Soc.* **1975**, *97*, 7305–7312. – [27b] L. Mandolini, *Adv. Phys. Org. Chem.* **1986**, *22*, 1–111.

Received July 25, 2000
[O00378]