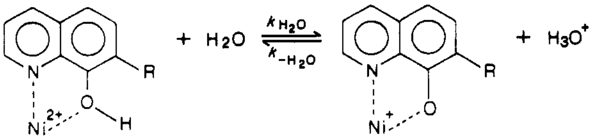
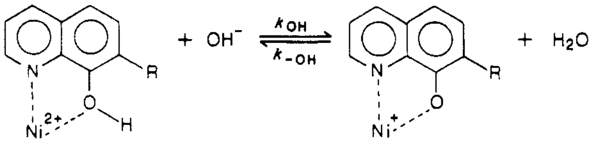
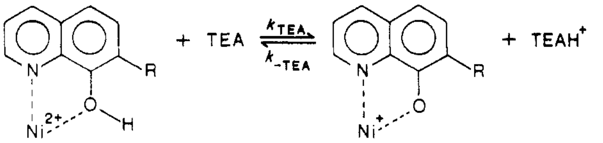

(28)


(29)


(30)

The expressions for k_3 and k_4 would be, respectively, in this case

$$k_3 = k_{H_2O} + k_{OH}[OH^-]_M + k_{TEA}[TEA]_M \tag{31}$$

$$k_4 = k_{-H_2O}[H^+]_M + k_{-OH} + k_{-TEA}[TEAH^+]_M \tag{32}$$

Proton removal by the hydroxylic ion (reaction 29) is very unlikely because of the electrostatic repulsions with the negatively charged surface of the micelles. It is admitted that water molecules can penetrate the micelles until the first CH_2 group after the polar head,[46] and it cannot be excluded that TEA behaves like a cosurfactant, which would facilitate its penetration. Reactions 28 and 30 appear thus to be quite plausible.

Equation 27 predicts that at low Ni^{2+} concentration ($k_1[Ni^{2+}] \ll k_2$) τ_{slow}^{-1} should vary linearly with $[Ni^{2+}]$, in agreement with Figure 5. It also predicts that at high Ni^{2+} concentration ($k_1[Ni^{2+}] \gg k_2$) τ_{slow}^{-1} should tend toward a constant value. This value should increase when the proton concentration increases. Although a plateau has only been attained at pH 8.5, there is no major disagreement between this prediction and the experimental results.

Conclusions

We have shown in this work that microemulsions can be employed to improve our understanding of the complicated reactions taking place in liquid–liquid extraction processes. Due to their transparency, they allow the use of methods generally limited to homogeneous kinetics, although providing information about heterogeneous kinetics. As the complexation step is often rate limiting in the extraction of metal ions, it is of major interest to have at our disposal this very convenient way of studying the influence of the nature of the components of the extraction medium, as well as the influence of potential additives.

Registry No. Ni, 7440-02-0; HQ, 148-24-3; 8-quinolinol, 29171-27-5.

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Nucleophilic Reactions in Zwitterionic Micelles of Amine Oxide or Betaine Sulfonate Surfactants

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Reactions of Cl^- and Br^- with methyl naphthalene-2-sulfonate (MeONs) are speeded by micelles of *N*-hexadecyl-*N*,*N*-dimethyl-3-ammonio-1-propanesulfonate (SB3-16), but reactions of OH^- and SO_3^{2-} are inhibited. Reactions of *o*-iodosobenzoate ion and its 5-octyloxy derivative and of F^- with *p*-nitrophenyl diphenyl phosphate (pNPDPP) are speeded by micelles of SB3-16 and less strongly by micelles of dodecyldimethylamine oxide. Comparison of these micellar effects with those of cationic micelles provides a qualitative estimate of the concentrations of the nucleophilic anions at the surface of micelles of SB3-16. For dephosphorylation by iodosobenzoate ions reactivity at the micellar surfaces is very similar in water and at the surfaces of cationic and zwitterionic micelles.

Ionic micelles in water concentrate counterions at their surface and repel co-ions due to Coulombic interactions. But non-Coulombic interactions are also important because hydrophilic, high charge density counterions are bound less strongly than polarizable, low charge density counterions. The concentration of reactants at micellar surfaces is the major source of enhancements of the rates of bimolecular reactions involving counterions, and examination of reaction rates and equilibria provides information on micelle–ion interactions.[1-5]

The specificity of counterion binding to micelles can be described in terms of a competition between ions. In one widely used treatment one for one competition is assumed and ion-exchange parameters are calculated as for binding to ion-exchange resins.[2-5] An alternative treatment uses a Langmuir equation without stipulating one for one exchange.[6,7] Other treatments involve calculation of Coulombic effects by solving the Poisson–Boltzmann equation, if necessary with inclusion of separate, non-Coulombic, interactions.[8,9]

There is kinetic and equilibrium evidence for the binding of both hydrophobic and hydrophilic co-ions to ionic micelles.[1-5,10] Many hydrophobic organic cations bind readily to cationic micelles because dispersive and hydrophobic attraction overcome the Coulombic repulsions. Hydrophilic anions, e.g., OH^-, are not completely excluded from anionic micelles if the solution is concentrated in electrolyte.[11] This partial binding is explained by

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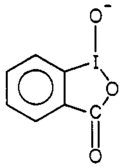
TABLE I: Second-Order Rate Constants in Water

	substrate	
nucleophile	pNPDPP[a]	MeONs[b]
OH^-	0.48[c]	85.0
F^-	0.1[c]	
Cl^-		1.47
Br^-		7.7
SO_3^{2-}		2350
IB^-	1.0	

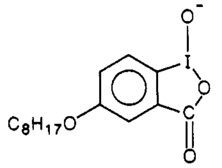
[a] Values of k_W (M^{-1} s^{-1}) at 25.0 °C. [b] Values of $10^5 k_W$ (M^{-1} s^{-1}).[8b,c] First-order rate constant in the absence of added nucleophile 1.2×10^{-5} s^{-1}. [c] Reference 6.

the ion-exchange model, and it is also understandable in terms of an electrostatic model, because electrolytes in solution sharply reduce the surface electrical potential of ionic colloids and, therefore, the repulsion of co-ions.[8,9,12]

We are interested in the use of rate effects as probes of ion binding to micelles and in the quantitative interpretation of these rate effects. Micelles of zwitterionic surfactants, e.g., betaines, sulfobetaines, or amine oxides, seem to bind OH^-, albeit weakly, although they are formally neutral.[13,14] Specific interactions should be relatively unimportant for very hydrophilic anions, e.g., OH^-, but they should be more important for polarizable or hydrophobic anions, and we examined their nucleophilic reactions. We used hydrophobic substrates that bind readily to micelles and both hydrophilic anions, e.g., OH^-, F^-, and SO_3^{2-}, and less hydrophilic anions, e.g., the *o*-iodosobenzoate ion (IB^-) and the 5-(octyloxy)-2-iodosobenzoate ion (OIB^-).



IB^-



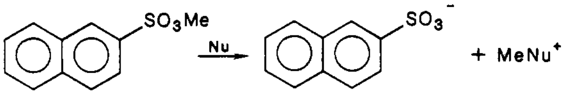
OIB^-

The reactions are as follows:

$$(PhO)_2POOC_6H_4NO_2\text{-}4 \xrightarrow{Nu} {}^-OC_6H_4NO_2\text{-}4 + (PhO)_2PO{\cdot}Nu^+$$

pNPDPP

$Nu = OH^-, F^-, IB^-, OIB^-$



MeONs

$Nu = OH^-, Cl^-, Br^-, SO_3^{2-}$

Dephosphorylation of pNPDPP and S_N2 reactions of MeONs have been investigated in the presence and absence of aqueous micelles,[6,8,15,16] and in some of the reactions micellar rate enhancements are due largely to an increased concentration of the nucleophile at the micellar surface. We examined the reactions in zwitterionic micelles of dodecyldimethylamine oxide (DDMAO) and the hexadecylsulfobetaine (SB3-16). Amine oxides are weakly nucleophilic and react with pNPDPP,[14] but the sulfonate residue of SB3-16 should be a very weak nucleophile in water.

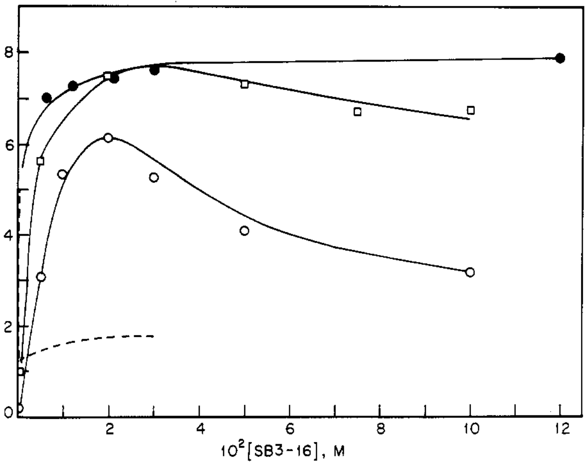


Figure 1. Dephosphorylation in zwitterionic micelles of SB3-16: ● and ○, 2×10^{-3} M IB^- and 0.03 M carbonate buffer at pH 9.0 and 8.0, respectively, $n = 2$; □, 10^{-2} M F^- at pH 8.0 and 0.03 M carbonate buffer, $n = 3$; broken line, reaction with 10^{-2} M OH^-, $n = 3$.[14]

TABLE II: Dephosphorylation by 5-(Octyloxy)-2-iodosobenzoate Ion[a]

10^3[SB3-16], M	1.6	3.4	7.6	13.6	19.6
$k\psi$, s^{-1}	0.092	0.268	0.174	0.105	0.076

[a] At 25.0 °C, 2.5×10^{-4} M OIB^-, pH 9.0, and 0.03 M carbonate buffer.

TABLE III: Dephosphorylation in Micellized DDMAO[a]

10^3 × [DDMAO], M	pH 7[b]	10^{-2} M OH^- [b]	10^{-2} M F^- [c]	2×10^{-3} M IB^- [d]	2.5×10^{-4} M OIB^- [d]
0		4.8	1.0	2.0	
0.5		4.54		(1.4)	
1.0		1.6		8.3 (3.0)	
2.0		2.1		17.0 (6.0)	
3.0				21.4 (8.3)	
5.0	1.2	2.41	2.01	23.0 (11.5)	
7.0					4.80
10.0	1.4	2.97	(1.88)	25.0 (12.2)	3.38
15.0	1.4		2.13 (2.15)	29.0	24.5
22.0	1.4		2.30 (2.30)	26.0 (15.1)	16.9
30.0		2.81			13.8
49.0					9.2
61.0					8.0

[a] Values of $10^3 k\psi$ (s^{-1}) at 25.0 °C. [b] Reference 14 and interpolated values where necessary. [c] At pH 8.0, 0.03 M carbonate buffer. Values in parentheses for 2×10^{-3} M carbonate buffer. [d] pH 9.0, 0.03 M carbonate buffer. Values in parentheses at pH 8.0.

$C_{12}H_{25}N^+Me_2O^-$ DDMAO

$C_{16}H_{33}N^+Me_2(CH_2)_3SO_3^-$ SB3-16

Iodosobenoate ions are very effective turnover catalysts of deacylation and dephosphorylation,[16,17] but we made all our experiments with the iodosobenzoate ion in large excess of pNPDPP.

Results

Second-order rate constants for reaction in water, k_W, are given in Table I. Most of the values are from the literature, but that for reaction of IB^- with pNPDPP was obtained by extrapolation of a plot of the first-order rate constants, $k\psi$, against the mole fraction of water (Experimental Section).

Micellar Reactions. First-order rate constants for dephosphorylation by F^- and IB in SB3-16 are depicted in Figure 1, and this figure includes data for reaction with OH^-. Rate constants for dephosphorylation by OIB^- in SB3-16 are in Table II, and

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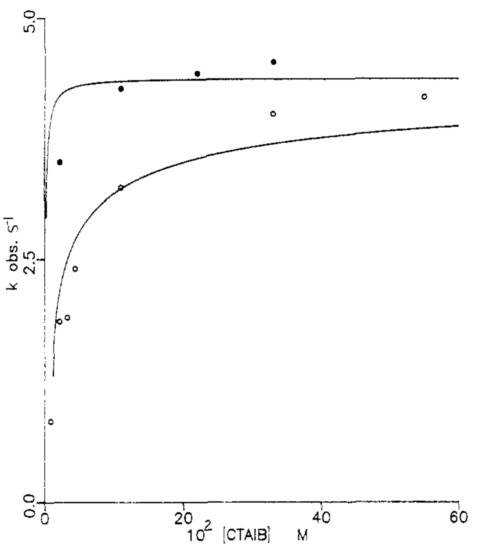


Figure 2. Dephosphorylation by micellized CTAIB: O, no added IB$^-$; ●, 0.05 M IB$^-$.

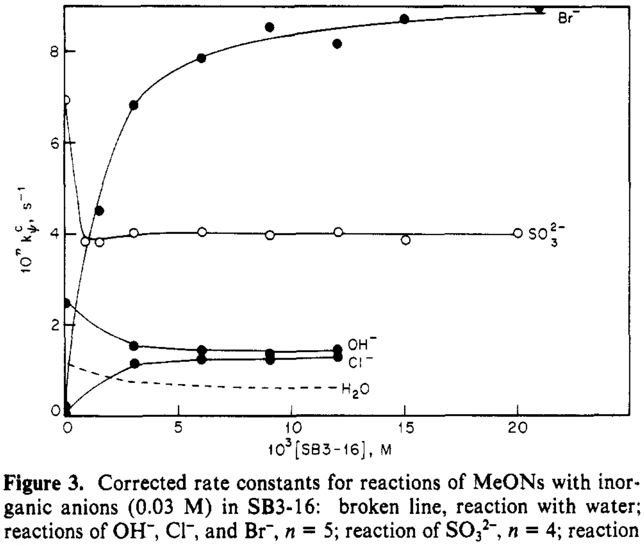


Figure 3. Corrected rate constants for reactions of MeONs with inorganic anions (0.03 M) in SB3-16: broken line, reaction with water; reactions of OH$^-$, Cl$^-$, and Br$^-$, $n = 5$; reaction of SO$_3^{2-}$, $n = 4$; reaction of H$_2$O, $n = 5$.

those for the reaction in DDMAO are in Table III. These results show that under the reaction conditions the iodosobenzoic acids are not fully deprotonated in zwitterionic micelles at pH 8.0. The reaction of pNPDPP with IB$^-$ was also followed in cetyltrimethylammonium 2-iodosobenzoate (CTAIB), so that the micellar counterion was also the reactive ion (Figure 2).

The first-order rate constants for the S$_N$2 reactions of MeONs in zwitterionic micelles of SB3-16 are shown in Figure 3, and this figure also illustrates the micellar effects upon the spontaneous, water-catalyzed hydrolysis. The rate constants, k_ψ^c, for the anionic reactions are corrected for the contribution of the spontaneous hydrolysis.[8b,c]

Discussion

Although zwitterionic micelles of SB3-16 and DDMAO are formally neutral, they do not completely suppress reactions of inorganic nucleophilic anions, e.g., OH$^-$, F$^-$, Cl$^-$, and SO$_3^{2-}$, although they inhibit some reactions (Figures 1 and 3; Table III). They speed reactions of F$^-$ and the iodosobenzoate ions with pNPDPP and of Br$^-$ and Cl$^-$ with MeONs in SB3-16 (Figures 1 and 3; Tables II and III). Qualitatively the micellar effects are related to the hydrophilicity of the anion, in that the more hydrophilic is the anion the less readily will it bind to a micelle. The situation is more complex for dephosphorylation by IB$^-$ in SB3-16, because reaction is faster at pH 9 than at pH 8 (Figure 1). This result shows that the zwitterionic micelles decrease deprotonation of the weak acid, probably by excluding OH$^-$, because deprotonation in cationic micelles can be related to the concentration of OH$^-$ at their surfaces.[2c]

Micelles of the betaine sulfonate (SB3-16) give larger rate enhancements than those of the amine oxide (DDMAO), as shown by comparing results for dephosphorylation by F$^-$ or by IB$^-$ (Figure 1; and Table III). The situation for reaction of OH$^-$ is complicated by reaction between the amine oxide and pNPDPP.[14]

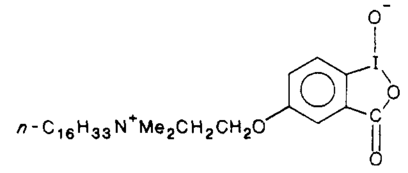
All the reactions discussed here have been followed in solutions of cationic micelles,[6,8,15-17] and although reaction conditions differ, qualitative inspection of the data shows that overall reactions are generally faster in cationic than in zwitterionic micelles. These differences could be due to several factors: (i) Reactivity could be higher in cationic than in zwitterionic micelles. (ii) Anionic reagents are bound more strongly by cationic than zwitterionic micelles.[18] (iii) For some nucleophiles deprotonation may be incomplete in zwitterionic micelles.

At the present time we cannot separate all these effects in the general case, but we can test explanations ii and iii by examining a nucleophilic anion that should bind strongly to both cationic and zwitterionic micelles at a pH such that it will be fully deprotonated.

The simplest system is the reaction of 5-(octyloxy)-2-iodosobenzoate ion (OIB$^-$) with pNPDPP. This hydrophobic nucleophile should bind very strongly to micelles, regardless of their charge, and we choose conditions under which it, and pNPDPP, should be quantitatively bound, i.e., with [surfactant] ~ 0.01 M. The observed first-order rate constant should depend upon the mole ratio of nucleophile to micellized surfactant [D$_n$] and the second-order rate constant at the micellar surface, k_M (s^{-1}) (eq 1).[2b,5,6] (If concentration is expressed as a mole ratio, it is dimensionless.)

$$k_\psi = k_M[\text{OIB}^-]/[\text{D}_n] \qquad (1)$$

For reaction of 2.5 × 10^{-4} M OIB$^-$ in 0.0196 M SB3-16 at pH 9.0, $k_\psi = 0.076$ s^{-1} (Table II) and therefore $k_M = 5.9$ s^{-1}. Moss and co-workers have investigated this reaction in CTACl,[16b] and we use their data under conditions in which both reactants should be fully micellar bound, i.e., at relatively high [CTACl], so that we can also neglect the concentration of monomeric CTACl. With 7.14 × 10^{-5} M OIB$^-$ in 0.002 M CTACl, $k_\psi \approx 0.18$ s^{-1}, and in 0.004 M CTACl, $k_\psi \approx 0.1$ s^{-1}.[16b] On the basis of these data $k_M \approx 5.5$ s^{-1}. Moss and co-workers also examined the reaction of pNPDPP with the functionalized hexadecyl derivative **1** comicellized with CTACl in a 1:5 ratio at pH 8.[16c] The rate constant became independent of [**1**] when substrate was fully bound, and then $k_\psi \approx 1.2$ s^{-1}. This value corresponds to $k_M \approx 6$ s^{-1}, as compared with ca. 5.5 s^{-1} for OIB$^-$. The nucleophilicities of **1** and OIB$^-$ should be very similar so our estimates of k_M agree for micellar and comicellar systems.



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The maximum value of k_ψ for reaction of pNPDPP in CTAIB is ca. 4.5 s^{-1} (Figure 2). Added iodosobenzoate ion slightly increases the reaction rate for fully bound reactants. This behavior is common to reactions of moderately hydrophobic anions.[2b,5b,8b,c] The approximate value of [IB$_M$]/[D$_n$] should be given by β, the fractional neutralization of the micelle, and generally $\beta \approx 0.7$, so that for CTAIB $k_M \approx 6$ s^{-1}. This value is very similar to those for reactions of the alkoxyiodosobenzoates,[16] suggesting that differences in electrolyte or buffer composition, or the presence of the alkoxy group, are not causing major problems. The value of k_M for reaction in CTACl is probably slightly low, because the

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(18) The hydrophobic substrates should bind strongly to micelles regardless of charge. At least 99% of pNPDPP and ca. 90% of MeONs should be micellar bound in 0.01 M SB3-16 by analogy with their binding to cationic micelles.[8,15]

iodosobenzoic acid is not fully deprotonated at pH 8.[16] It is difficult to estimate the extent of deprotonation, because it depends on the concentrations of surfactants and added electrolytes,[2-5] but under slightly different conditions the variations of k_ψ with pH were interpreted in terms of 80–85% deprotonation.[16b] On this basis $k_M \approx 7$ s^{-1} in CTACl. Therefore, to a first approximation the value of k_M is the same for various iodosobenzoates in both CTACl and SB3-16, despite differences in pH and buffer and salt composition and concentration.

The rate–surfactant profile for reaction in CTAIB (Figure 2) suggests that β is only approximately constant because k_ψ increases on addition of IB$^-$. An alternative model treats counterion binding in terms of eq 2,[6,7] where W and M denote aqueous and micellar pseudophases.

$$K_{IB}' = [IB_M^-]/[IB_W^-]([D_n] - [IB_M^-]) \qquad (2)$$

The binding of pNPDPP is written as[6]

$$K_s = [pNPDPP_M]/([pNPDPP_W][D_n]) \qquad (3)$$

with $K_s = 10^4$ M^{-1}. Equations 2 and 3 together with eq 1, applied to reaction of IB$^-$, give the calculated plots in Figure 2, based on K_{IB}', = 1500 M^{-1} and $k_M = 4.5$ s^{-1}. The differences between values of k_M calculated in different ways does not affect our qualitative comparisons of reactivity of IB$^-$ at micellar surfaces.

The second-order rate constants, k_M, cannot be compared directly with second-order constants, k_W (M^{-1} s^{-1}), in water because of the different concentration units. If we assume that the micellar reaction occurs in a region whose molar volume is 0.14 L,[2,5] we obtain k_2^m (M^{-1} s^{-1})

$$k_2^m = 0.14k_M \qquad (4)$$

and k_2^m and k_W can be compared directly. Other estimates of the molar volume of the reaction region range up to ca. 0.35 L.[2-5]

Second-order rate constants in water and at the micellar surface cannot be compared for reaction with OIB$^-$, because of its low solubility in water, but for reaction of IB$^-$ with pNPDPP, k_W = 1.0 M^{-1} s^{-1} at 25.0 °C (Table I) and this value is very similar to those of k_2^m for OIB$^-$ in CTACl and SB3-16 micelles, which are in the range 0.8–0.9 M^{-1} s^{-1}. This comparison is clouded by possible effects of the octyloxy group on the nucleophilicity of iodosobenzoates and uncertainties in the volume of the reactive region in the micelles, but as in other systems the micellar rate enhancements are due largely to concentration of reactants at the micellar surface.[2-9] Increasing the hydrophobicities of reagents often increases overall reaction rates in micelles, but this increase is due largely to increased incorporation in the micelles. Second-order rate constants at the micellar surface are relatively insensitive to changes in substrate hydrophobicity.

Dephosphorylation by IB$^-$ is slower in micelles of the amine oxide (Table III) than in those of the betaine sulfonate (SB3-16). The differences in rate could be due to decreased binding of the iodosobenzoate ion or to a decreased reactivity at the micellar surface. Both OIB$^-$ and pNPDPP should be fully micellar bound at high surfactant concentrations, and values of k_M are ca. 6 and 2 s^{-1} for reaction in micelles of SB3-16 and DDMAO, respectively, based on eq 1 and data in Tables II and III. There is a small difference in reactivity at the two micellar surfaces. For reaction of IB$^-$ the *overall* rate constant, k_ψ, SB3-16 is larger by a factor of ca. 2.5 than in DDMAO at similar concentrations (Figure 1; Table III), so that this difference could be ascribed to a difference in k_M rather than to ion binding. Reaction of F$^-$ with pNPDPP in 10^{-2} M surfactant is faster in SB3-16 than in DDMAO by a factor of ca. 4 (Figure 1; Table III), and, as for reaction of iodosobenzoate ions; the rate differences could be caused by a slightly lower rate constant in DDMAO micelles.

Binding of Hydrophilic Anions by Micellized SB3-16. Reactivities of the iodosobenzoate ions toward pNPDPP are very similar at the surfaces of cationic and zwitterionic micelles, and we analyze the effects of micelles of SB3-16 upon the other reactions in light of these conclusions. We restrict our discussion to the betaine sulfonate, SB3-16, because nucleophilic reactions of the amine oxide may complicate the analysis,[14] especially for reaction of OH$^-$ and F$^-$ with pNPDPP (Table III).

We apply two very simple models to this question of anion concentrations at the surfaces of sulfobetaine micelles. They both involve the assumption that second-order rate constants, k_2^m (M^{-1} s^{-1}), at the micellar surfaces will be very similar in cationic and zwitterionic micelles, for a given reaction, and that the rate of reaction will be governed by these rate constants and the reactant concentrations at the surface, as for reactions of pNPDPP with iodosobenzoate ions. For many bimolecular reactions, second-order rate constants at micellar and microemulsion surfaces are similar to those in water,[2-9] which supports our assumptions.

We consider first reactions of fully micellar bound MeONs with Cl$^-$ or Br$^-$. The first-order rate constant for the reactions in CTACl and CTABr are, respectively, 9.5 × 10^{-5} and 7 × 10^{-4} s^{-1}.[8b,c] These rate constants are larger than those in SB3-16 (Figure 3) by a factor of ca. 7. The micellar surfaces of cationic micelles are assumed to be saturated by counterions whose local concentration is ca. 4 M.[19] Therefore, the estimated local concentration of Cl$^-$ or Br$^-$ at the surface of micellized SB3-16 should be ca. 0.6 M, and considerably higher than that of 0.03 M in water. In these reactions the halide ions were in large excess over SB3-16 so that their incorporation in the micelle should not materially decrease their concentrations in water.

We can apply a similar treatment to the reaction of F$^-$ with pNPDPP in both SB3-16 (Figure 1) and cetyltrimethylammonium fluoride (CTAF). In CTAF + F$^-$ with fully bound pNPDPP, $k_\psi \approx 0.35$ s^{-1},[20] whereas its maximum value in 10^{-2} M F$^-$ and SB3-16 is ca. 7.5 × 10^{-3} s^{-1}, i.e., lower by a factor of ca. 40. Therefore, on the assumption that rate constants at the micellar surface are similar in micelles of CTA and SB3-16, the local concentration of F$^-$ at the surface of the sulfobetaine micelle will be ca. 0.1 M, as compared with 0.01 M in water.

These comparisons suggest that the hydrophilic F$^-$ binds less readily than Cl$^-$ or Br$^-$ to the sulfobetaine micelles but that local concentrations of halide ions *at the micellar surface* are higher than in water under our experimental conditions.

This simple treatment can also be applied to the reaction of OH$^-$ with pNPDPP. In CTAOH with fully bound pNPDPP, $k_\psi \approx 0.6$ s^{-1},[6] whereas it is 1.8 × 10^{-3} s^{-1} in micellized SB3-16 and 0.01 M OH$^-$; i.e., it is lower by a factor of ca. 330.[14] Therefore, if we assume that the concentration of OH$^-$ at the surface of a cationic micelle is ca. 4 M,[2a] our estimated value of its concentration at the surface of a SB3-16 micelle would be ca. 0.012 M; i.e., the predicted concentration is slightly higher than in water even though overall reaction is slower than in water by a factor of ca. 3. These qualitative conclusions suggest that betaine micelles can attract hydrophilic anions, although they are much less effective in this regard than cationic micelles.

The problem can be approached in a slightly different way. We calculated anion concentrations at the surfaces of cationic micelles by solving the Poisson–Boltzmann equation[5] and then calculated second-order rate constants, k_2^m, at the micellar surface in terms of the concentration of reactive ion, Nu, in a 2.4-Å shell at that surface. Therefore, if substrate is fully bound

$$k_\psi = k_2^m[Nu]_{2.4Å} \qquad (5)$$

If we assume that k_2^m will have the same value at the surface of a cationic and a zwitterionic micelle, we can calculate $[Nu]_{2.4Å}$ in the latter and compare it with the concentration in water. This comparison is illustrated in Table IV, where r is the ratio of anion concentrations in micelles to that in water. The results suggest that micelles of SB3-16 take up Cl$^-$ and Br$^-$, take up F$^-$ less readily, and have even less tendency to take up OH$^-$ and SO$_3^{2-}$. The estimated relative concentrations of OH$^-$ in water and at the surfaces of a micelle of SB3-16 are similar, based on reactions of either pNPDPP or MeONs. However, these estimates of the relative anion concentrations depend upon the assumed similarity

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(19) These estimates are based on the fractional micellar charge and the estimated volume of the Stern layer.[2a] Similar conclusions can be drawn from the solution of the Poisson–Boltzmann equation in spherical symmetry.[8,9]

(20) Bunton, C. A.; Frankson, J.; Romsted, L. S. *J. Phys. Chem.* **1980**, *84*, 2607.

TABLE IV: Estimated Ionic Concentrations in Sulfobetaine Micelles

reaction	$k\psi^{SB}$,[a] s^{-1}	k_2^m,[b] $M^{-1}\ s^{-1}$	$[Nu]_{2.4Å}$, M	$[Nu]_w$, M	r[c]
Br^- + MeONs	9×10^{-5}	1.4×10^{-4}	0.7	0.03	23
Cl^- + MeONs	1.3×10^{-5}	2.0×10^{-5}	0.7	0.03	23
OH^- + MeONs	1.5×10^{-5}	1.1×10^{-4}	0.13	0.03	4
SO_3^{2-} + MeONs	4.0×10^{-4}	8.0×10^{-3}	0.05	0.03	1.7
F^- + pNPDPP	7.0×10^{-3}	6.0×10^{-2}[e]	0.11	0.01	11
OH^- + pNPDPP	1.8×10^{-3}[d]	6.0×10^{-2}	0.03	0.01	3

[a] First-order rate constant for fully bound substrate in micellized SB3-16. [b] For reactions in CTA^+ micelles,[8b,c] unless specified. [c] Ratio of anionic concentration in the micelle to that in water. [d] Reference 14. [e] Based on a mass action like model.[6]

of values of k_2^m in cationic and zwitterionic micelles, as shown for reactions of iodosobenzoate ions. Polarizable and relatively hydrophobic anions bind to micelles by specific interactions, but Coulombic binding should be much more important in the binding of hydrophilic ions,[1-5,8,9] and locations of the ions at the surface may be different for cationic and zwitterionic micelles. In that event our assumptions regarding k_2^m will be least satisfactory for such hydrophilic anions as OH^- and SO_3^{2-}. Bimolecular reactions of hydrophilic anionic nucleophiles are slowed by hydroxylic solvents that strongly hydrogen bind to them. If the reaction site at the surface of a micelle of SB3-16 is close to the ammonium centers, the anion may lose some of its outer hydration shell because of the proximity of the trimethylene group and become more reactive. This partial dehydration would be less important for reaction at the surface of cationic micelle, because its head groups would be exposed to water.[2] On this hypothesis we may be underestimating the second-order rate constants at the surface of micelles of SB3-16 and therefore overestimating values of r (Table IV) although on the basis of other values of k_2^m and k_W[2-9] the overestimation should not be large.[21]

These results suggest that a pseudophase model can be applied, as a first approximation, to reactions in zwitterionic micelles, although they are less effective than cationic micelles in binding such hydrophilic ions as OH^- and SO_3^{2-} and the hydration shells may interact unfavorably with the trimethylene residue in the head group of SB3-16. Hydration is apparently less important in the binding of F^-, as compared with OH^-, and the sequence of the values of r (Table IV) is qualitatively reasonable even though the absolute values depend upon major simplifications. The similar values of r for reactions of OH^- with two substrates of different reactivities and hydrophobicities, as given by micellar binding constants, K_s, support this assumption.

Other kinetic evidence supports our conclusion that anions can bind to zwitterionic micelles. For example, specific interanionic competition for zwitterionic micelles implies micelle–anion interaction, although the specificity is less than with cationic micelles, based on kinetic salt effects.[14,23]

Most micellized functional surfactants react in their deprotonated, zwitterionic forms,[1-5] and interactions of inert anions with these and cationic micelles are qualitatively similar.[23] There is extensive physical evidence for binding of Br^- to cationic micelles,[1-5] and on the basis of evidence from NMR line widths the binding of Br^- to the micellized hydroxyethyl surfactant (**2**) is not eliminated when 1 M OH^- is added, even though deprotonation is then essentially complete:[24]

$$\underset{\mathbf{2}}{C_{16}H_{33}N^+Me_2CH_2CH_2OH} \xrightleftharpoons{OH^-} C_{16}H_{33}N^+Me_2CH_2CH_2O^-$$

TABLE V: Dephosphorylation by IB^- in the Absence of Surfactant[a]

% MeCN (w/w)	[IBA], M 0.01	0.02	0.03
10	7.2	14.5	21.0
15	6.2	12.8	17.8

[a] Values of $10^3k\psi$ (s^{-1}) at pH 7.0 in 10^{-2} M carbonate buffer.

The results of fluorescence quenching show that specific interactions play a major role in the binding of Br^- to cationic micelles.[25]

Aromatic solutes interact strongly with micellar cationic head groups,[1-3,26] which should help the binding of iodosobenzoate ions to zwitterionic micelles. Micelles of betaine surfactants bind the 6-nitrobenzisozazole-3-carboxylate ion and speed its decarboxylation.[27] This anion and IB^- are both polarizable, and not very hydrophilic, and should interact with the quaternary ammonium centers in zwitterionic micelles. Weakly hydrophilic polarizable anions such as Br^- should also interact readily with the quaternary ammonium groups in zwitterionic micelles because such anions can shed water molecules from the outer hydration layers, with a consequent increase of entropy. There are also Coulombic interactions because hydrophilic anions such as OH^- and F^- that bind Coulombically to cationic micelles also bind to zwitterionic micelles. This interaction was ascribed to a higher surface charge density at the cationic as compared with the anionic centers.[14]

The similarity of values of k_2^m for reactions of iodosobenzote ions in cationic and zwitterionic micellles is consistent with evidence that for many bimolecular, anionic reactions, $k_2^m \sim k_W$,[1-9] and would be unexpected if k_2^m was very sensitive to micellar charge. However, the situation is different for some spontaneous, water-catalyzed reactions where surface charge is important.[2b,5,28]

Experimental Section

Materials. The preparation and purification of the surfactants and reactants have been described.[8,14,16] 5-Octyl-2-iodosobenzoic acid was a gift from Dr. Durst, and cetyltrimethylammonium iodosobenzoate (CTAIB) was prepared, in solution, by neutralizing CTAOH[6] with 2-iodosobenzoic acid. Reaction solutions were made up in CO_2-free redistilled deionized water.

Kinetics. Reactions were followed spectrometrically as described elsewhere.[8,14] Formation of 4-nitrophenoxide ion was monitored at 400 nm, and the reactions of MeONs were followed at 326 nm. The iodosobenzoic acids were neutralized with equimolar NaOH, and where necessary 10^{-5} M H_2SO_4 was added to suppress reaction of MeONs with OH^-.[8b,c] The substrates were added as solutions in MeCN so that the surfactant solutions contained 0.1 vol % MeCN and 1×10^{-5} M substrate. Rate constants in the absence of surfactant for reaction with IB^- were obtained by extrapolation (Table V).

All the reactions were followed at 25.0 °C, and the first-order rate constants are in reciprocal seconds.

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Registry No. pNPDPP, 10359-36-1; IB^-, 84280-67-1; OIB^-, 117203-79-9; SB3-16, 2281-11-0; DDMAO, 1643-20-5; CTAIB, 117226-38-7; Cl^-, 16887-00-6; Br^-, 24959-67-9; OH^-, 14280-30-9; SO_3^{2-}, 14265-45-3; F^-, 16984-48-8; MeONs, 5138-53-4.

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(21) The concentration of monomeric surfactant, as given by the cmc, was neglected because values of the cmc of zwitterionic surfactants are much lower than those of otherwise similar ionic surfactants.[22]

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