Appendix

The fundamental quantities calculated by the PSS model are the surfaces and the volumes, from which all the other quantities are calculated. We report eqs 2 and 3 which calculate the surface areas S and volumes V per unit cell:

$$\frac{S}{R^2} = 2\pi Z (1-g)^2 \left[2 - n \left(\frac{f-c}{1+f} \right) \right] + 2\pi Z n (f+g) \left[(1+f) \times \sin \cos^{-1} \left(\frac{1+c}{1+f} \right) \left(\frac{\pi}{2} - \cos^{-1} \left(\frac{1+c}{1+f} \right) \right) - (f+g) \left(\frac{1+c}{1+f} \right) \right]$$
(2)
$$\frac{V}{R^3} = \frac{\pi}{3} Z (1-g)^3 \left[4 - n \left(\frac{f-c}{1+f} \right)^2 \frac{2f+c+3}{1+f} \right] + \pi Z n (f+g) \left(\frac{1}{3} [3(f+g)^2 + (f+g)(2h+H) + hH + h^2 + H^2] \left(\frac{1+c}{1+f} \right) - (f+g) [h+f+g] \left(\frac{\pi}{2} - \cos^{-1} \left(\frac{1+c}{1+f} \right) \right) \right]$$
(3)

with

$$h = (1 + f) \sin \cos^{-1} \left(\frac{1 + c}{1 + f} \right) - (f + g)$$

and

$$H = (1 - g) \sin \cos^{-1} \left(\frac{1 + c}{1 + f} \right)$$

R is given by eq 1, *f* and *c* are defined in the text, *Z* is the number of spheres in the unit cell, *n* is the coordination number of the spheres, and g = d/R with $d = 0, d_2, d_3, ...$ where $d_2, d_3, ...$ are the thicknesses by means of which different parallel surfaces, necessary for the description of a multilayer (monolayers included), are created. Five different parallel surfaces are necessary for a bilayer (normal or reversed): one for the interface and four for defining $V_{chains}, v/al$, etc. In eqs 2 and 3 the areas and volumes of the half-necks are considered, since each neck belongs to a couple of spheres.

When (double) neck overlapping occurs, the areas and volumes given by eqs 2 and 3 have to be supplemented with the necessary

correction terms. The correction terms to surfaces are $S_{\rm corr} = -2S_{AB} + S'_{AB}$ where $2S_{AB}$ are the areas of those parts of the surfaces of necks A and B that are hidden by the overlapping and have to be neglected. These portions of surfaces form a sort of concave-convex "tent". S'_{AB} are the areas of the portions of spherical surfaces that underlie the "tents". The correction terms for volumes are $V_{\rm corr} = -V_{AB} + 2V'_{AB}$ where V_{AB} are the portions of the volumes that are in common to neck A and neck B (because of the overlapping) and V'_{AB} the volumes of the spherical segments that are in common to the same necks. The correction terms are as many as the parallel surfaces and underlying volumes considered. Each correction term has to be multiplied by 0.5Znm, where m is the number of next-neighbor necks to each neck upon the sphere. The calculations of the correction terms involve surface and volume integrals which are written in cylindrical coordinates and computed numerically.

When two necks widely overlap, the overlapping involves about the whole height of both necks and not only their bases. This happens for high f and c values which may be necessary in describing some structures (see Figure 4). The corresponding correction terms which involve a great number of surface and volume integrals and which are very complicated because of the biconical C_{xy} symmetry of the (isolated) necks were calculated.

The (double) overlapping occurs when the angle at the center of the sphere θ , which subtends the arc of the maximum overlap on the sphere, changes sign. It is easy to show that $\theta = 2\alpha_0 - \beta$, where α_0 is the angle (at the center of the sphere) between the principal axis of symmetry of a neck and the point of tangence of this neck to the sphere and β the angle at the center of the sphere between the two principal symmetry axes of the two nearest-neighbor necks. β depends on the symmetry of the unit cell.

The nearest-neighbor assumption which underlies eq 1 can be abandoned for a different assumption which considers a different number of necks allowed around each sphere (i.e., n has to be redefined for each symmetry). In such a case only eq 1 has to be modified. The new assumption can be intentionally designed to obtain particular topologies and symmetries otherwise out of reach by the PSS model as described here.

Micellar Head-Group Size and Anion Nucleophilicity in S_N2 Reactions

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Rates of reaction of OH⁻ with methyl naphthalene-2-sulfonate (MeONs) in aqueous cationic surfactants ($C_{16}H_{33}NR_3OH$, R = Me, Et, *n*-Pr, *n*-Bu, and cetylquinuclidinium hydroxide) increase with increasing surfactant and hydroxide ion concentrations. The variations of rate constants can be fitted to an equation that describes the distribution of both reactants between water and micelles in terms of Langmuir isotherms. The Langmuir coefficients for OH⁻ decrease in the head-group sequence Me₃N > quinuclidinium > Et₃N > Pr₃N > Bu₃N. The second-order rate constants at the micellar surfaces are not very sensitive to the bulk of the head group, although they increase at high added OH⁻. Rate constants for attack of water on micellar-bound substrate increase with increasing bulk of the head group.

Rate effects of aqueous colloidal self-assemblies, e.g., micelles, microemulsion droplets, and synthetic vesicles, are generally ex-

plained in terms of pseudophase models.²⁻⁴ Reaction occurs in water or at colloidal surfaces that are treated as distinct reaction

media. The overall reaction rate is the sum of rates in each pseudophase, and the first-order rate constant, k_{ψ} , in aqueous micelles is given by

$$k_{\psi} = \frac{k_{W}' + k_{M}' K_{\rm s}[{\rm D}_{\rm n}]}{1 + K_{\rm s}[{\rm D}_{\rm n}]} \tag{1}$$

where $k_{W'}$ and $k_{M'}$ are first-order rate constants in aqueous and micellar pseudophases, respectively, and K_s is the binding constant of the substrate to micellized surfactant, D_n.

Equation 1 fits data for spontaneous reactions and for micellar-inhibited reactions where $k_{M}' \approx 0$. However, for nonspontaneous micellar-assisted reactions k_{W}' and k_{M}' depend on the concentration of the second reagent in each pseudophase. The distribution of organic nucleophiles, for example, between water and micelles can often be measured directly.^{3a,5} The problem is more difficult for hydrophilic ions, unless their distribution can be estimated electrochemically⁶ or spectrometrically,⁷ and a variety of quantitative treatments have been developed to attack this problem.

In many systems both reactive and inert counterions are present and compete for the micellar surface.^{3b-d,4,8} This competition can be described by equations similar to those applied to binding to ion-exchange resins or by equations that include both Coulombic and specific micelle-ion interactions. The competition is eliminated when reactive ion is the surfactant counterion,^{9,10} and the simplest hypothesis is that ionic concentration at the micellar surface is directly related to $\beta = 1 - \alpha$, where α is the fractional micellar charge. Values of β are not very sensitive to surfactant and electrolyte concentrations and are ca. 0.7 for aqueous cationic micelles that have moderately hydrophilic counterions, e.g., Br-. Ionic concentrations at micellar surfaces should then be approximately constant and independent of added anion.^{3c,4b} This hypothesis predicts that rate constants for reaction with a substrate bound to CTABr ($C_{16}H_{33}NMe_3Br$), for example, should be unaffected by added Br^{-11} However, rate constants increase, although slowly, on addition of Br^{-12} Reactions of other moderately hydrophilic ions give similar rate dependence on surfactant and ion concentrations.^{3b,c,9b} The situation is much worse for reactions of very hydrophilic anions, e.g., OH⁻ or F⁻, where rate constants increase sharply with increasing concentrations of reactive ion 9a,c,13,14 The hypothesis of a constant β is completely

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inadequate for these systems and other approaches are needed.

Various groups have postulated that concentrations of OH⁻ at the surface of a CTAOH micelle increase with increasing [OH⁻] or [CTAOH].^{3c,4b,9c,10} Neves et al. calculated values of α for CTAOH and CTAF from slopes of plots of conductivity against [surfactant] above and below the critical micelle concentration, cmc.¹⁵ For "well-behaved" surfactants, e.g., CTACl and CTABr, these plots are linear with an abrupt change of slope in the region of the cmc 12,15,16 $\,$ With CTAOH and CTAF they are curved with no sharp break, and with CTAOH plots become less curved at high surfactant, especially with added NaOH.9c,15

This curvature is strongly indicative of a variation of α , but determination of α (or β) from the ratio of slopes of conductivity against [surfactant] above and below the cmc has problems. Above the cmc conductivity is due largely to free counterion and the macroionic micelle, and there is a problem in estimating the contribution of the micelle to overall conductivity, especially when α is high, i.e., the micelle is highly charged. Evans' equation attempts to solve this problem, but it includes the micellar aggregation number¹⁷ which is not known with certainty for CTAOH and may well vary with concentration. Generally values of α calculated from the ratio of slopes are higher than those from use of Evans' equation,¹² although they are useful in illustrating trends in α due to changes in solvent or surfactant structure.^{12,15,16} The possible presence of submicellar species also complicates estimation of α from conductivities. Values of the cmc of hydroxide ion surfactants, measured by surface tension, are lower than those from conductivity (Experimental Section and ref 9c), possibly because submicellar species are contributing to conductivity but differ from monomer in their surface activity.

However, Neves et al. used their conductivity data to calculate α for CTAOH and CTAF from the ratio of slopes and stated that they could fit micellar effects upon elimination in up to 0.035 M CTAOH, and upon dephosphorylation in up to 0.2 M CTAF, on the assumption that concentrations of OH- and F- at micellar surfaces are directly related to conductimetric values of $\beta = 1$ $-\alpha$.¹⁵ We understand from Professor Nome¹⁸ that the actual fitting procedure used to relate conductimetric values of α to overall reaction rates in CTAOH and CTAF was not that described in ref 15. Values of α were measured conductimetrically only up to ca. 5×10^{-3} and 8×10^{-3} M for CTAF and CTAOH, respectively. Values at higher concentrations were calculated by using an equilibrium equation that described variations of α for surfactant concentrations between ca. 3×10^{-3} M and the highest concentrations shown in Figures 3 and 4 of ref 15. These values, obtained by extrapolation, were then used to fit rate data at surfactant concentrations higher than those used in the conductivity experiments.

We do not know of a direct experimental method for determination of concentrations of OH⁻ or F⁻ (or of β) at the relatively high concentrations of CTAOH and CTAF that have been examined kinetically. Two theoretical treatments have been used to estimate ionic concentrations at micellar surfaces. The first involves solution of the Poisson-Boltzmann equation (PBE).^{19,20} This method is reasonably satisfactory, at least for dilute ionic solutions, but as applied to reactions in CTAOH and similar surfactants, it involves the assumption that the micelle grows on addition of OH^{-.19a,20} The second treatment assumes that ionic distribution between water and micelles follows a Langmuir form, eq 2, 9c,10,12,14,21 where $[X^-w]$ and $[X^-M]$ are molarities of X^- in

$$K_{X'} = \frac{[X^{-}_{M}]}{[X^{-}_{W}]([D_{n}] - [X^{-}_{M}])}$$
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TABLE I: Micellar Effects upon the Spontaneous Reaction with Water^a

10 ³ [D].	surfactant					
M	CTAX	CTEAX	CTPAX	CTBAX	CQX	
1	2.45	2.94	2.55	3.06	3.42	
2	3.16	3.54	3.58	4.44	4.71	
5	4.25	4.81	6.39	8.33	5.78	
10	4.53	5.00	7.38	9.61	6.21	
20	4.92	5.54	8.45	9.66	6.74	
40	4.81	6.18	8.95	10.2	6.87	
60	5.19	6.22	9.81	11.3	7.00	
80	5.32	6.63	9.80	11.2	7.39	

^a Values of $10^5 k_{\psi}^{\circ}$ at 25.0 °C, X = (SO₄)_{0.5}; in water $k_{\psi} = 1.2 \times 10^{-5} \text{ s}^{-1}$.

aqueous and micellar pseudophases in terms of total solution volume.

Values of K_x are low for hydrophilic ions, e.g., OH⁻, so that their concentrations at micellar surfaces should increase sharply with added anion. However, $K_{x'}$ should be larger for less hydrophilic anions, e.g., Br⁻, and their concentrations at micellar surfaces should be less sensitive to changes in concentrations of surfactant or counterion. Equation 2 can be applied to a variety of ionic reactions, and it is convenient to write the first-order rate constants in eq 1 as^{3c,4}

$$k_{\mathbf{W}'} = k_{\mathbf{W}}[\mathbf{X}_{\mathbf{W}}] \tag{3}$$

$$k_{\mathbf{M}'} = k_{\mathbf{M}}[\mathbf{X}_{\mathbf{M}}] / [\mathbf{D}_{\mathbf{n}}]$$
⁽⁴⁾

with ionic concentration in the micellar pseudophase written as a mole ratio.

This treatment has been applied to reactions of several hydrophilic anions, e.g., OH⁻, F⁻, and HCO₂⁻; with larger values of $K_{\mathbf{x}'}$, to reactions of less hydrophilic anions;^{11,12} and also to reactions in mixtures of reactive and inert anions;^{21,22} We apply it here to reaction of OH⁻ with methyl naphthalene-2-sulfonate ion (MeONs):



Reactions of MeONs with Cl⁻ and Br⁻ have been followed in solutions of cetyltrialkylammonium chlorides and bromides (alkyl = Me(CTAX), Et(CTEAX), *n*-Pr(CTPAX), *n*-Bu(CTBAX); X = Cl, Br). Overall first-order rate constants increase with increasing bulk of the surfactant head group, even though ionic concentrations at the micellar surface, as given by β or K_X' , decrease.¹² The bulkier head groups are therefore increasing the nucleophilicity of the halide ions. This increase is due, at least in part, to a decrease in hydration of the halide ions at the micellar surface, and changes in their NMR line widths confirm this explanation.^{12,23}

Ions such as OH^- are very strongly hydrated, so they may behave differently to CI^- or Br^- in cationic micelles. We also examined reaction in cetylquinuclidinium hydroxide (CQOH).



This surfactant head group is relatively bulky but it has a rigid structure, unlike those of the trialkylammonium surfactants.

Reactions were followed with and without added OH⁻, and we corrected the overall rate constants for the contribution of the

TABLE II: Rate and Binding Constants for Spontaneous Hydrolysis of $MeONs^{\alpha}$

surfactant	$K_{\rm s}, {\rm M}^{-1}$	10 ⁵ k _M °, s ⁻¹	
CTAX	1090	5.8	
CTEAX	1000	6.4	
CTPAX	1000	9.0	
CTBAX	1000	11.0	
COX	1000	7.0	

^aAt 25.0 °C, $k_w^\circ = 1.2 \times 10^{-5} \text{ s}^{-1}$.



Figure 1. Reaction in CTAOH: O. With 0.05, 0.1, and 0.5 M total OH⁻: Δ , \Box , \diamond , respectively.



Figure 2. Reaction in CTEAOH: O. With 0.1 and 0.5 M total OH⁻: \Box , \diamond , respectively.

spontaneous reaction with water.12

Results

Spontaneous Reaction. Micellar effects upon reaction of water with MeONs were examined by using sulfate as counterion (Table I). Reaction is speeded by cationic micelles and rate constants increase smoothly with [surfactant] and become constant with fully bound substrate, following eq 5:^{3,4,24}

$$k_{\psi}^{\circ} = \frac{k_{\mathrm{W}}^{\circ} + k_{\mathrm{M}}^{\circ} K_{\mathrm{s}}[\mathrm{D}_{\mathrm{n}}]}{1 + K_{\mathrm{s}}[\mathrm{D}_{\mathrm{n}}]}$$
(5)

where $[D_n]$ is total surfactant concentration, less that of monomeric surfactant, which is assumed to be given by the cmc. Superscript ° denotes the spontaneous reaction.

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Figure 3. Reaction in CTPAOH: O. With 0.1, 0.5, and 1.0 M total OH⁻: \Box , \diamond , \times , respectively.



Figure 4. Reaction in CTBAOH: O. With 0.5 and 1.0 M total OH⁻: \diamond , +, respectively.

Values of $k_{\rm M}^{\circ}$ and $K_{\rm s}$ are in Table II. Rate increases by cationic micelles of these S_N2 reactions of water had been observed earlier.²⁵

Reaction with Hydroxide Ion. The variations of k_{ψ} with surfactant concentration are given in Figures 1-5 in the absence and presence of added OH⁻. Values of k_{ψ} are given by

$$k_{\psi}^{c} = k\psi - k_{\psi}^{o} \tag{6}$$

on the assumption that reaction with water will not be very sensitive to the nature of the counterion. The correction is small except in dilute surfactant.

Rate constants in the absence of added OH⁻ do not reach limiting values, even at high [surfactant], as found for other reactions in CTAOH.^{9c,14} Overall rate constants, at a given [OH⁻], decrease with increasing bulk of the trialkylammonium groups, although they increase for reactions of MeONs with Cl⁻ and Br⁻¹² (Figures 1–5 and Table III). Despite its bulk the quinuclidinium head group does not disfavor reaction.

Table IV illustrates the magnitude of micellar rate enhancements by comparing rate constants of reaction in the absence and presence of CTAOH (0.05 M). Comparisons were based on the total concentration of OH⁻ in solution $[OH^-_T]$. The micellar rate



Figure 5. Reaction in CQOH: O. With 0.5 M total OH⁻: \diamond .

 TABLE III: Fitting Parameters for Reaction of MeONs with Hydroxide Ion^a

surfactant	[OH ⁻ _T], ^b M	10⁴cmc, M	$10^{3}k_{\rm M},$ s ⁻¹	$10^4 k_2^{\rm m}, M^{-1} {\rm s}^{-1}$
CTAOH		7	1.95	2.8
CTAOH	0.05	3	2.0	2.9
СТАОН	0.1	1	2.0	2.9
СТАОН	0.5	0	2.8	4.0
CTEAOH		6	1.85	2.6
CTEAOH	0.1	1	1.8	2.6
CTEAOH	0.5	0	2.5	3.6
СТРАОН		5	1.5	2.1
СТРАОН	0.1	2	1.5	2.1
СТРАОН	0.5	0	2.2	3.1
СТРАОН	1.0	0	3.0	4.3
СТВАОН		2	1.8	2.6
СТВАОН	0.5	0	2.1	3.0
СТВАОН	1.0	0	2.9	4.1
сдон		6	2.3	3.3
сдон	0.5	0	3.3	4.7

 ${}^{a}K_{s}$ as in Table II, $K_{OH}' = 55$, 45, 25, 12, and 50 for CTAOH, CTEAOH, CTPAOH, CTBAOH, and CQOH, respectively, and for reaction of OH⁻ $k_{W} = 8.3 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1.19b}$ b Concentration of CTAOH + added OH⁻, when unspecified OH⁻ was derived solely from CTAOH.

TABLE IV: First-Order Rate Constants of Overall Reaction with Hydroxide Ion^a

surfactant	[OH ⁻ _T], M	$10^4 k_{\psi}, \mathrm{s}^{-1}$	k _{rel} ^b	
 CTAOH	0.05	11	27	
СТАОН	0.5	26	6.3	
CTEAOH	0.05	8.9	21	
CTEAOH	0.5	24	5.8	
СТРАОН	0.05	6.9	17	
СТРАОН	0.5	21	5.0	
СТВАОН	0.05	6.0	14	
СТВАОН	0.5	18	4.3	
СООН	0.05	13	31	
CQOH	0.5	32	7.7	

 a In 0.05 M surfactant. b Relative to values in 0.05 or 0.5 M NaOH in water.

enhancements decrease with increasing $[OH_T]$ as is generally found for overall rates of bimolecular reactions in micellar solutions.²⁻⁴

The rate data were fitted to eqs 1–4 with the parameters shown in Table III. The value of $K_{OH}' = 55 \text{ M}^{-1}$ for CTAOH had been used in earlier simulations, and we assumed that it applied to reaction of MeONs.^{9c,10} The fits are reasonably good in view of the simplicity of the model, although rate constants at high [OH⁻] are underpredicted with a constant k_M , in agreement with observations on eliminations in cationic surfactants.¹⁴ The fitting

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TABLE V: Critical Micelle Concentrations⁴

head group	cmc, mM	head group	cmc, mM
Me ₃ N ^b Et.N	0.76 (≈1.1) 0.63	<i>n</i> -Pr ₃ N	0.46 (≈1) 0.22
Et₃N	0.63	n-Bu ₃ N	0.22

^a From surface tension measurement. Values in parentheses correspond approximately to breaks in the conductivity plots. ^bReported values were 0.86 and 1-2 mM from surface tension and conductivity.^{9c}

at high $[OH^-]$ is not very sensitive to values of K_{OH}' and K_s , and the shapes of the plots suggest that values of k_M in the trialkylammonium surfactants increase at high $[OH^-]$. Kinetic data for reactions of MeONs in CTACl and CTABr were fitted at constant k_M , but salt concentrations were limited to 0.2 M for Cl⁻ and 0.1 M for Br^{-.12}

Rate constants in dilute surfactant with no added OH⁻ were also underpredicted by eqs 1-4, and there appears to be an additional reaction path with [surfactant] < 6×10^{-3} M (Figures 1-5). The deviations are largest in dilute CTPAOH and CTB-AOH. These anomalies did not appear in dephosphorylation, aromatic nucleophilic substitution, or elimination in CTAOH.^{9c,14} Elimination, in particular, was well studied with [CTAOH] < 6×10^{-3} M, so deviations would not have been missed because of paucity of data.¹⁴

These deviations are probably due to the presence of submicellar species that are kinetically effective but are not included in pseudophase treatments such as eqs 1–5. Addition of OH⁻ should stabilize micelles relative to submicelles, and the kinetics fit eqs 1–4 with added NaOH. Substrate structure may also affect formation of submicelles, especially if surfactant is not in large excess over substrate, as in some of our experiments in dilute surfactant. We used ca. 10⁻⁴ M substrate, so as to have reasonable absorbance changes in the course of the reaction. In other reactions studied to date in CTAOH [substrate] was <10⁻⁵ M because absorbance changes during reaction were large.^{9c,14} However, striking deviations from the predicted rate–surfactant profiles for nucleophilic reactions of dinitroarenes and N-alkyl-2-bromopyridinium ions in dilute cetyltrialkylammonium chloride and bromide were ascribed to reactions in submicellar aggregates.²⁶

The naphthalene residue of MeONs could interact with surfactant cations and stabilize small clusters of them, and if OHis attracted to the clusters, reaction rates should be higher than predicted by a micellar model (eqs 1-5). The rate increases above predicted values are largest with surfactants that have the less hydrophilic head groups, which is consistent with interactions of substrate with surfactant monomers or *n*-mers. These small assemblies should be converted into micelles with increasing [surfactant].²⁶ This explanation is consistent with differences in the cmc determined conductimetrically and by surface tension (Table V).

Discussion

Values of $k_{\rm M}$ are not very sensitive to changes in surfactant head group and without added OH⁻ range from $1.5 \times 10^{-3} \text{ s}^{-1}$ in CTPAOH to $2.3 \times 10^{-3} \text{ s}^{-1}$ in CQOH (Table III). Addition of small amounts of OH⁻ does not affect $k_{\rm M}$, although values increase at high [OH⁻]. Some of these differences may be due to the approximations in eqs 1-5. The results are consistent with the qualitative generalization that concentration of reactants at the surface of a micelle or similar colloidal particle is a significant source of rate enhancements of bimolecular reactions.^{3-5,8} However, comparison of micellar effects upon reactions of MeONs with H₂O, OH⁻, and halide ions suggests that there are differences in behavior that can be related to structures of the reactants and micellar surfaces, and therefore to the locations of the sites of reaction. In water OH⁻ is a better nucleophile than Cl⁻ or Br⁻, and the second-order rate constants are respectively 8.3×10^{-4} , 0.15×10^{-4} , and $0.76 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ at 25.0 °C.^{4b} However, in dilute surfactant the overall reaction with Br- is faster than with

TABLE VI: Comparison of Rate Constants in Micelles^a

surfactant	OH-	Cl ^{-b}	Br ^{-b}	
CTAX	10.5 (2.0)	0.8 (0.18)	7.0 (0.96)	
CTEAX	8.3 (1.9)	1.5 (0.25)	10 (1.4)	
CTPAX	6.1 (1.5)	1.7 (0.25)	13 (1.8)	
CTBAX	5.0 (1.8)	1.8 (0.26)	16 (2.5)	
CQX	12.5 (2.3)	2.2 (0.32)		

^a Values of $10^4 k_{\psi}^{c} \text{ s}^{-1}$ for 0.05 M surfactant; values for Cl⁻ and Br⁻ are interpolated from ref 12. ^b Values in parentheses are $10^3 k_{\text{M}}$, s⁻¹ (Table II and refs 12 and 23b).

OH⁻, except for CTAOH and CTABr, but Cl⁻ is always less reactive than OH⁻ or Br⁻. This difference is due in part to the higher concentration of Br⁻, as compared with OH⁻ at the micellar surface, as shown by values of $K_X'^{4b,9c,12}$ or α^{3c} (Table VI). The trend is even more striking if we consider values of k_M . They change little with surfactant structure for reaction of OH⁻ but increase with increasing head-group size, modestly for reaction of Cl⁻, and more strongly for reaction of Br⁻, so that $k_M(Br) > k_M(OH)$ for reaction in CTPAX and CTBAX (Table VI). This is one of those rare situations in which micelles generate an inversion of a reactivity sequence for anionic nucleophiles reacting with a common substrate. There are clear differences between the behaviors in cationic micelles of a very strongly hydrophilic anion, OH⁻, a moderately hydrophilic ion, Cl⁻, and a weakly hydrophilic ion, Br⁻.

A major problem in analyzing medium effects upon nonspontaneous bimolecular reactions is that of defining the appropriate concentration units, because second-order rate constants have the dimensions of reciprocal time and reciprocal concentration. There is no such problem with spontaneous reactions, which may be bimolecular, water-catalyzed, hydrolyses,²⁵ or intramolecular nucleophilic displacements, or heterolyses.^{3c,d,4}

It is simplest to consider first the S_N^2 reaction of water with MeONs where the rate constant for reaction in the micellar pseudophase increases by a factor of almost 2 in going from CTA⁺ to CTBA⁺ (Table II). The methyl group of MeONs is located, on the average, in a water-rich region at the micellar surface²³ and away from the ammonium ion, and increasing hydrophobicity of the *N*-alkyl groups increases the reaction rate, probably by slightly perturbing the hydrogen bonding of adjacent water molecules and increasing their reactivity.¹²

A guide to medium effects upon bimolecular reactions of anions at micellar surfaces is provided by cyclization of 1.



For this reaction rate enhancements range from factors of 1.8 for Y = Br in CTABr to 7.2 and 29 for Y = Br and I, respectively, in CTBABr.²⁷ These differences are probably due to decreased hydration of the oxide function in the initial state and interactions of the leaving halide ions with quaternary ammonium head groups. This cyclization is mechanistically equivalent to an S_N^2 reaction, and although there are no concentration effects, micellar rate enhancements are larger than for many bimolecular reactions (Table IV and refs 2–4).

Micellar enhancements of unimolecular decarboxylations are by factors of 10^2-10^3 , because charge is delocalized in the transition state from a carboxylate residue into a π -system that in-

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teracts with cationic head groups²⁸ and reaction rate is very solvent dependent.²⁹ These general arguments suggest that second-order rate constants at micellar surfaces may differ considerably from those in water, depending upon the nature of the reaction.

The different micellar effects upon reactions of MeONs with OH⁻ and Cl⁻ or Br⁻, which lead to inversions of reactivities (Table VI), are probably due to differences in hydration of the nucleophilic anions. Hydroxide ion interacts so strongly with water that its hydration should be little perturbed by cationic micelles, regardless of the head group, but hydration of Br⁻ and Cl⁻ is decreased when they interact with the micellar surface, with consequent increase in their nucleophilicities. These conclusions are based on data fitting in terms of the Langmuir isotherm (2), but similar conclusions are drawn if we compare k_{ψ} at high [surfactant] and [OH⁻] where the rate constants tend toward limiting values (Figures 1-5 and Table VI). Although eq 2 fits the data reasonably well, it is an empirical approach because micelle-ion interactions depend upon Coulombic and ion-specific interactions and the properties of the micelle-water interface. However, alternative treatments have their limitations; for example, kinetic data can be fitted by solving the PBE,^{19,20} but to date only with spherical micelles and dilute electrolyte. The experimental approach of estimating β conductimetrically also has limitations. The report of Neves et al. that rates of elimination in CTAOH and dephosphorylation in CTAF can be related directly to their values of $\beta = 1 - \alpha$ depends upon extrapolation of α from conductimetric data in dilute surfactant,^{15,18} and it is difficult to test the validity of the extrapolation. The failure of the assumption of a constant β was recognized some years ago, $3^{c,4,9c,10}$ and the best treatment remains in doubt. It is premature to believe that estimation of α solves the problem, if only because values assigned to α appear to depend upon the method of estimation, ^{3c,30} and rate increase on addition of a hydrophilic reactive anion, e.g., OH- or F-, to CTAOH or CTAF are sometimes too large to be related to changes in α within the normal limits.^{9,14} The pseudophase treatment that relates rates in micellar pseudophases to values of β is reasonably satisfactory in limiting cases of low concentrations of moderately hydrophilic reactive anions, but it is at best a first approximation that breaks down outside these limits.

The pseudophase models in their simplest form write aqueous and micellar pseudophases as distinct regions. This description is unrealistic because counterion concentrations decrease smoothly with distance from the micellar surface, toward the concentration in bulk solvent at the cell wall. The description of counterion concentrations as following a step function, as used in the ionexchange and similar descriptions (eqs 1-5 and refs 2-5 and 8-15), is least satisfactory at high concentrations of hydrophilic counterions; cf. ref 14. However, if anions, e.g., Br-, have strong specific affinities for cationic micellar head groups, pseudophase models such as the ion-exchange treatment, or eqs 2-4, seem to be reasonably satisfactory.

Second-order rate constants can be defined unambiguously by writing reactant concentration as a mole ratio, but these constants $k_{\rm M}$, s⁻¹ (eq 4), cannot be compared directly with those in water, $k_{\rm W}$, M⁻¹ s⁻¹ (eq 3), unless a molar volume, $V_{\rm M}$, is assigned to the reactive region at the micellar surface. If we take $V_{\rm M} = 0.14 \text{ M}^{-1}$, the second-order rate constant k_2^{m} , M^{-1} s⁻¹, is given by^{3c,4}

$$k_2^{\rm m} = 0.14k_{\rm M}$$
 (7)

and these values can be compared with $k_{\rm W}$. The values of $V_{\rm M}$ should be similar for reactions of OH⁻, Cl⁻, and Br⁻ with MeONs in the various surfactants, so that we can compare values of $k_2^{\rm m}/k_{\rm W}$ on this basis. These results are consistent with the hypothesis that the reaction center is in a water-rich region, because values of $k_2^{\rm m}/k_{\rm W}$ for reaction of OH⁻ are in the range 0.3–0.55, whereas $k_2^{\text{m}}/k_{\text{W}} \approx 0.1$, or less, for reactions of OH⁻ with hydrophobic esters whose reaction center will be more deeply in the micellar surface.^{3c,d,4b,8,9c,19} The corresponding values of $k_2^{\text{m}}/k_{\text{W}}$ for reactions of Cl⁻ and Br⁻ with MeONs are ca. 1.4 and 1.8, respectively, in CTAX and ca. 2.8 and 5.4 in CTBAX. These values of k_2^{m} are calculated with a constant V_{M} , and if it increases with head-group bulk, k_2^{m} will correspondingly increase.

Tentatively we suggest that effects of head-group bulk on anion reactivity at a micellar surface can be rationalized on the assumption that, with ions that are very hydrophilic, and interact largely Coulombically, second-order rate constants, $k_{\rm M}$, will not be very sensitive to head-group bulk. However, bulky head groups will speed reactions of anions that bind specifically to micellar surfaces.

Experimental Section

Materials. The preparations of MeONs and the surfctants in their bromide form have been described.¹² The surfactants in the hydroxide form were prepared from the sulfates^{9c} or by use of Amberlite IRA-400 resin. The resin was purified by slurrying it with distilled H_2O followed by filtration (four times), then slurrying it with MeOH, and finally washing it with distilled H₂O. Solutions of the hydroxide forms of the surfactants were centrifuged to remove resin particles and were tested for adventitious anions. These operations were carried out under N_2 .

Critical Micelle Concentrations. Values of the cmc were determined from plots of surface tension against log [surfactant].³¹ There were no minima in these plots and measurements were made under N_2 .

We also examined variations of conductivity with concentration for two of the surfactants, but there were no clean breaks, corresponding to the cmc, between linear plots. Instead we saw a smooth variation of slope with [surfactant] with indications of breaks approximately at the concentrations given in Table V. This behavior is similar to that observed earlier with CTAOH.^{9c,15} In the absence of added OH⁻ there may be a polydisperse population of submicellar species that contribute to conductivity, and influence the surface tension, so that the two methods appear to give different values of the cmc.

Kinetics. Reactions were followed at 25.0 °C in an HP diode array spectrometer with 6×10^{-5} - 10^{-4} M MeONs at 327 nm.¹² In experiments with added OH⁻ [surfactant] was varied and total concentration of OH⁻, [OH⁻_T], was constant. Solutions were made up under N₂, and the first-order rate constants, k_{ψ} , are in reciprocal seconds. The computer simulations based on eqs 1-4 give reasonable fits to the rate-surfactant profiles. We used constant values of K_{OH} for a given surfactant and allowed values of k_{M} to increase with added OH⁻. The data could be fitted reasonably well with combinations of changes in the values of these parameters within limits of ca. 15%. This situation is typical of fits of rate-surfactant profiles based on a variety of models.^{2c,d,4}

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