30-45°; delay, 1.5 s; the resolution was better than 3 Hz. The memory block for the storage of the FID was 64K. The signals of HDO and CHCl₃ were used as standards in D₂O and CDCl₃ solutions, respectively, for the proton spectra. The signals of CDCl₃ and added CD₃OD were used as standards for the ¹³C spectra. The optimizations of $B_{\rm M}$ and $K'_{\rm NMR}$ values were based on the Powell minimization subroutine, and a program was written for an HP-300 microcomputer.

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Registry No. MeONs, 5138-53-4; "ONs, 16023-36-2; Br", 24959-67-9; cetyltrimethylammonium bromide, 57-09-0; cetyltriethylammonium bromide, 13316-70-6; cetyltripropylammonium bromide, 25268-61-5; cetyltributylammonium bromide, 6439-67-4.

Micellar Enhancements of Rates of S_N2 Reactions of Halide Ions. The Effect of **Headgroup Size**

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Observed first-order rate constants for reaction of methyl naphthalene-2-sulfonate with Cl⁻ or Br⁻ in micelles of cetyltrialkylammonium halide ($C_{16}H_{33}NR_3X$, R = Me, Et, *n*-Pr, *n*-Bu, X = Cl, Br) increase monotonically with increasing surfactant and halide ion concentrations and tend to limiting values. The variation of rate constants with concentrations of surfactant and halide ions can be fitted to an equation that accounts for the distribution of both reactants between water and micelles. Fractional micellar ionization, α , increases, i.e., the affinity of the micelles for the halide ion decreases, with increasing bulk of the N-alkyl groups, but the second-order rate constants at the micellar surface and the overall rate constants increase. The rate effects of the micelles of the bromide ion surfactants can be understood in terms of NMR evidence on the micellar binding of the reactants and their location at the micellar surface. The reactivity increase with increasing headgroup bulk is related to the disruption of the hydration of Br⁻ and to the electrostatic interaction of the naphthalene π -system with cationic nitrogen.

Aqueous micelles speed bimolecular reactions by bringing reactants together or inhibit them by keeping reactants apart.² The enhancements can be treated quantitatively by estimating reactant concentrations at the micellar surface,³ and calculated second-order rate constants at that surface are generally similar to those in water.

Ionic micelles attract counterions Coulombically, but specific forces are also important, and reactive and inert counterions compete for the micellar surface. This competition is described quantiatively by equations of varying complexity, but it can be eliminated by making the counterion the reactant, in the absence of other counterions.⁴⁻⁶ Reactions of OH⁻, F⁻, Cl⁻, Br⁻, N₃⁻, CN⁻, and H₃O⁺ have been examined in solutions of reactive ion surfactants.

The fractional ionic dissociation, α , of micelles is often little affected by the nature or the concentration of the counterion. In other words, the micellar surface appears to be saturated with counterions, and the fractional coverage $\beta = 1 - \alpha$, is constant.^{3b-d}



If β is constant, the rate of a reaction should increase as substrate is taken up by the micelles, but once substrate is fully bound the rate should be independent of added surfactant or counterion. This prediction is reasonably satisfactory for reactions in micelles of alkyltrimethylammonium surfactants, provided that the counterion binds strongly to the micelle, e.g., for the reaction of Br⁻, Cl⁻, and CN^{-.3c,e,4a,c} However, for very hydrophilic anions such as OH⁻, F, and HCO₂⁻ reaction rates increase with increasing concentrations of surfactant or reactive ion even when the substrate is fully bound.^{4b,5,6} This kinetic behavior can be fitted to a simple equation of the Langmuir form, which describes the distribution of the ion between water and micelles,^{4b,7} or the concentration of the hydrophilic ion at the micellar surface can be calculated by solving the Poisson-Boltzmann equation.^{8,9}

Reactions of anions in micellized reactive-ion surfactants had been examined only in trimethylammonium surfactants,⁴⁻⁶ but we have now examined reactions in cetyltrialkylammonium chlorides or bromides (alkyl = Me (CTAX), Et (CTEAX), n-Pr (CTPAX), and n-Bu (CTBAX); X = Cl, Br). The substrate is methyl naphthalene-2-sulfonate (MeONs) and this reaction was chosen because it is mechanistically simple, with no interionic

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Figure 1. Fit to first-order rate constants of reaction of MeONs with Cl^{-} in presence of CTACl and indicated concentrations of NaCl (A denotes fitting with $K'_{Cl} = 80 \text{ M}^{-1}$ and B with $K'_{Cl} = 130 \text{ M}^{-1}$).



Figure 2. Fit of first-order rate constants of reaction of MeONs with Cl⁻ in presence of CTEACl and indicated concentrations of NaCl.

competition and MeONs reacts readily with halide ions (Scheme I).^{8b,c}

These reactions have been examined in cetyltrimethylammonium chloride and bromide (CTACl, CTABr), and firstorder rate constants followed the distribution of substrate between water and micelles. They increased modestly with added Cl⁻ and less so with added Br⁻,^{8b,c} as expected if β is approximately constant.^{3c,e}

There is little information on the effect on micellar structure of variation of the trialkylammonium moiety. Anacker reports that aggregation numbers of $C_{10}H_{21}NR_3$ (R = Et, *n*-Pr, *n*-Bu) are similar, but solubilizing power increases in going from the triethyl to tributyl surfactant.¹⁰ The value of $\alpha = 0.48$ for tetradecyltributylammonium bromide, from conductivity, is much larger than that ($\alpha \approx 0.22$) for the trimethylammonium derivative, so that the bulky alkyl groups are reducing the attraction of the micelles for Br^{-10,11a} In contrast with the Anacker's report on decyl surfactants, the aggregation numbers for micelles of the tetradecyl surfactants decrease with increasing bulk of the headgroup.^{11b}

We have prepared cetyltrialkylammonium chlorides and bromides (alkyl = Me, Et, *n*-Pr, *n*-Bu, *n*-Pe), measured α conductimetrically, and studied their effect on halide ion reactions with MeONs. The tri-*n*-pentylammonium bromide is only sparingly water-soluble, similar to tetradecyltri-*n*-pentylammonium bromide,¹¹ and we did not examine it in detail. The accompanying paper gives NMR evidence on the interactions of the reactants with micellized surfactant,¹² and we use this evidence to elucidate



Figure 3. Fit of first-order rate constants of reaction of MeONs with Cl⁻ in presence of CTPACl and indicated concentrations of NaCl.



Figure 4. Fit of first-order rate constants of reaction of MeONs with Cl⁻ in presence of CTBACl and indicated concentrations of NaCl.



Figure 5. Fit of first-order rate constants of reaction of MeONs with Br^- in presence of CTABr and indicated concentrations of NaBr.

the factors that control the micellar reactions.

Results

Kinetics. First-order rate constants of reaction with halide ion, k_{ψ} , with respect to substrate, increase with increasing surfactant concentration and reach limiting values. These limiting values increase in the sequence Me < Et < n-Pr < n-Bu and on addition of halide ion (Figures 1-8). This behavior is similar to that found for reactions in other reactive-ion micelles,^{4.6} except that the limiting rate constants are reached at relatively high concentrations of the tripropyl and tributyl surfactants, and added halide ion

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TABLE I: Fitting Parameters for Reaction of MeONs with Halide Ions^a

alkyl	CI			Br ⁻				
	$\overline{K'_{\text{Cl}}}, \text{ M}^{-1}$	$10^4 k_{\rm M}, {\rm s}^{-1}$	$10^4 k_2^{\rm m}$, M ⁻¹ s ⁻¹	K'_{Br}, M^{-1}	$K_{\rm NMR}$, ^b M ⁻¹	$10^4 k_{\rm M}, {\rm s}^{-1}$	$10^4 k_2^{\text{m}}, \text{ M}^{-1} \text{ s}^{-1}$	$k_{\rm M}^{\rm Br}/k_{\rm M}^{\rm Cl}$
Me	80°	1.62	0.23	475	14.7	9.6	1.34	5.6
Et	70	2.76	0.39	350	20.7	14.0	2.00	5.2
n-Pr	45	3.20	0.45	290	15.0	18.1	2.53	5.6
n-Bu	45	3.44	0.48	155	4.8	25.1	3.51	7.3

^a With $K_S = 10^3$ M⁻¹ and $k_W = 0.15 \times 10^{-4}$ and 0.76×10^{-4} M⁻¹ s⁻¹ for Cl⁻ and Br⁻, respectively. ^bReference 12. ^cA better fit for low surfactant concentrations has been obtained with $K'_{Cl} = 130$ M⁻¹ (Figure 1).



Figure 6. Fit of first-order rate constants of reaction of MeONs with Brin presence of CTEABr and indicated concentrations of NaBr.

SCHEME II



speeds reaction, so that it appears that the micelles are not saturated with halide ions.

The rate-surfactant profiles can be treated in terms of the pseudophase model in which water and micelles are regarded as distinct reaction media (Scheme II).^{2,13}

In Scheme II substrate in water (S_W) is in equilibrium with bound substrate (SD_n) . The binding constant is written in terms of the micellized surfactant (D_n) , and k'_W and k'_M are first-order rate constants for reaction in aqueous and micellar pseudophases. The first-order rate constant for overall reaction is given by

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

The first-order rate constants can be written in terms of second-order rate constants, $k_{\rm W}$ and $k_{\rm M}$, with the appropriate units of concentration, and for $k_{\rm M}$ we define concentration of halide ion, X⁻, in the micelle, as a mole ratio:^{3c,e,4}

$$k'_{\rm W} = k_{\rm W}[{\rm X}_{\rm W}^{-}] \tag{2}$$

$$k'_{\rm M} = k_{\rm M} [{\rm X}_{\rm M}^{-}] / [{\rm D}_n] \tag{3}$$

The value of $[X_M^-]$ was assumed to follow eq 4.⁵⁻⁷

$$K'_{\mathbf{X}} = \frac{[\mathbf{X}_{\mathbf{M}}^{-}]}{[\mathbf{X}_{\mathbf{W}}^{-}]([\mathbf{D}_{n}] - [\mathbf{X}_{\mathbf{M}}^{-}])}$$
(4)

Equation 4 has been used to describe the interaction of various anions with cationic micelles, and we used it with eq 1-3 to fit variations of k_{ψ} with $[D_n]$ and $[Cl^-]$ or $[Br^-]$. Equations akin to eq 4 but applied to mixtures of reactive and inert anions have been used to describe interionic competition in micellar-assisted reactions.⁷





Figure 7. Fit of first-order rate constants of reaction of MeONs with Brin presence of CTPABr and indicated concentrations of NaBr.



Figure 8. Fit of first-order rate constants of reaction of MeONs with Brin presence of CTBABr and indicated concentrations of NaBr.

Methyl naphthalene-2-sulfonate binds readily to cationic micelles, and we take $K_{\rm S} = 1000 \ {\rm M}^{-1}$ as in earlier work.^{8b,c} The fits of the rate data are shown in Figures 1–8, and the rate and equilibrium parameters are in Table I. The concentrations of monomeric surfactant in the absence of added salt were assumed to be slightly lower (by 25%) than the values of the cmc in water (Experimental Section) to allow for substrate-induced micellization,¹⁴ and micellized surfactant is indicated by subscript M. The fits are not very sensitive to these assumed values.

Values of $k_{\rm M}$ are also not very sensitive to the values of $K'_{\rm X}$. Our values of $K'_{\rm X}$ are lower than those used earlier,^{4,7} but the plots in Figure 1 show that $K'_{\rm X}$ can be varied without markedly changing the fit or values of $k_{\rm M}$ (Table I). The model based on eq 4 is an oversimplification in that is difficult to simulate the data for both low and high surfactant concentrations with the same parameters. The fits are poorer for reaction with Cl⁻ because here reaction with water makes a significant contribution to the overall rate, and for all the surfactants we correct for it, using the rate

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TABLE II: Fractional Ionic Dissociation^a

		Cl-	Br ⁻		
alkyl	α^{b}	ac	α^{b}	ac	
Me	0.38	0.25-0.26 (80-60)	$\sim 0.2^{d}$	·	
Et	0.53	0.31-0.35 (70-40)	0.38	0.24-0.26 (80-50)	
n-Pr	0.80	0.42-0.47 (50-30)	0.49	0.29-0.34 (70-40)	
n-Bu	0.83	0.43-0.50 (40-20)	0.66	0.48-0.52 (50-30)	

^a In water at 25 °C. ^b From ratio of slopes of conductivity plots below and above the cmc. ^c From Evans' equation,¹⁶ calculated for the range of aggregation numbers in parentheses. ^d Mean value from var-ious methods of determination.^{3b,c,11a,15}

in cetyltrimethylammonium sulfate in the absence of added nucleophile, based on first-order rate constants of $k'_{\rm W} = 1.2 \times 10^{-5}$ s⁻¹ and $k'_{\rm M} = 4.4 \times 10^{-5} \, {\rm s}^{-1}$ for the reaction of water in the aqueous and micellar pseudophases, respectively.8b We therefore neglect possible headgroup size and anion effects upon the reaction of MeONs with water in the micelles.

Determination of α by Conductivity. Zana has estimated α for tetradecyltrialkylammonium bromides conductimetrically from the ratio of slopes of a plot of conductance against surfactant concentrations below and above the critical micelle concentration, cmc.^{11a} His values for triethyl ($\alpha = 0.35$), tripropyl ($\alpha = 0.42$), and tributyl ($\alpha = 0.48$) surfactants are larger than those of 0.2–0.3 typically found for alkyltrimethylammonium bromides.^{10,11,15} This method treats the micelle as a large macroion whose contribution to the net conductivity is the same as that of the number of surfactant monomers that are equivalent in charge, and Evans¹⁶ described a method that takes into account the differential contribution of macroions and free ions and gives lower values. Our experimental values of α calculated by both methods are in Table II. The difference in values from the two methods are relatively small when α is small, i.e., when the micelle is not highly charged. But with increasing α and increasing micellar charge, the contribution of the micelles to conductivity increases, and the Evans' equation attempts to solve this problem in terms of estimated mobilities of macroions based on the application of Stokes' law and the micellar aggregation number, N, which was assumed to be directly related to the hydrodynamic radius. Micellar hydrodynamic radii measured by dynamic light scattering^{15b} are larger than those chosen by Evans,¹⁶ so his treatment probably underestimates α , whereas the alternative method^{11a} overestimates it.

Discussion

Micellar Binding of Halide Ion. The concentration of reactive counterions at the micellar surface is a significant source of the rate enhancements in bimolecular ionic reactions, and the fractional ionic coverage, β , can be regarded as a measure of this concentration.^{3c,4a,c} Alternatively this concentration can be estimated in terms of a Langmuir relation, e.g., eq 4,5-7 and it has also been calculated by solving the Poisson-Boltzmann equation.^{8,9}

Another possible approach is to estimate the concentration of micellar-bound Br⁻ by fitting the variation of its line width with concentration of added Br⁻ to a Langmuir relation similar to that applied in kinetics (eq 4).¹² But these values, K'_{NMR} , are much lower than those estimated kinetically (Table I). In addition estimated concentrations of bound Br- from either kinetic or NMR experiments tend to be lower than those given by conductimetric obtained values of $\beta = 1 - \alpha$ (Tables I and II). Concentrations of bound Cl⁻, estimated kinetically, are also lower than those given by α (Tables I and II).

These differences show that there are various ways of defining counterion concentration at a micellar surface, and it is understandable that different experimental methods give different results. Conductivity senses the counterions that move freely in the solution, provided that the contribution of the micelles to the overall conductivity is accounted for correctly. The determination





of $\beta = 1 - \alpha$, or rather of the fractional micellar charge, by scattering methods involves analysis of the Coulombic contributions to micellar interactions.¹⁵ On the other hand, chemical reactivity senses those reactive ions that can readily interact with micellar-bound substrate, and ⁷⁹Br NMR spectra sense only bromide ions whose hydration shell is disrupted by interaction with the micellar head groups.^{12,17} The region sampled by the various experimental probes is largest for conductimetric or other transport determinations of α and probably smallest for the NMR line-width measurements.

An additional problem with the kinetic and NMR estimates of bound Br⁻ is that they are based on two state models and therefore will give misleading results if the micellar structure, in particular, changes with changing concentrations of surfactant, electrolyte, or solute. There is strong growth of CTABr micelles on addition of Br-, with formation of rodlike micelles and an increase in viscosity,¹⁸ but qualitatively there is no evidence for growth of other bromides; cf. ref 12. Differences between binding constants due to growth are to be expected for CTABr but not for the other bromides.

Regardless of the method used to estimate micellar binding of the halide ion, it decreases with increasing bulk of the N-alkyl headgroups.¹² If the region at the micellar surface was a structureless continuum, its lower dielectric constant for micelles with bulkier headgroups should increase electrostatic binding of counterion, but unfavorable interactions of the hydrated halide ions with alkyl groups decrease binding. This conclusions is consistent with extensive evidence for specific, non-Coulombic, micelle-counterion interactions. $^{4,3b-e,7-9}$

Micellar Binding of the Substrate and Site of Reaction. Changes in the ¹H and ¹³C chemical shifts of substrate and sulfonate ion on their incorporation in the micelle show that they both locate at the micellar surface.^{12,19} With increase of the size

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of the micellar headgroups the aromatic solutes move closer to the quaternary ammonium ion center.¹² Interaction of these quaternary ammonium headgroups and the aromatic π -system should increase the reactivity of MeONs because the naphthalene-2-sulfonate ion will became a better leaving group. The methyl group of MeONs is not buried in the micellar interior, on the basis of its ¹H chemical shift, which is insensitive to incorporation in micelles.¹²

The transition state for an $S_N 2$ reaction is a trigonal bipyramid,²⁰ and a plausible description of its interaction with a micellar surface is shown in Scheme III, based on our NMR evidence on the average locations of reactants and product.¹² The sulfonate ester and the sulfonate ion have similar locations in the micelles, and the naphthalene ring appears to insert radially into the micellar surface, so that the methyl group at the reaction center and attacking halide ion will be at the micelle-water interface, adjacent to the micellar surface. Water is assumed to penetrate to the first one or two methylenes of the cetyl group, and the region between the two dashed lines corresponds approximately to the micellar Stern layer. The dimensions of reactions in Scheme III are approximately to scale, but as we have no evidence regarding the bond lengths in the transition state they are shown as 50% longer than the corresponding covalent bonds.

Rate Constants in the Micelle. The pseudophase description of micellar rate effects involves the implicit assumption that micelles provide a discrete reaction environment, and on this basis we attempt to compare rate constants in this environment with those in water. This comparison will be misleading for multistep reactions if micelles change the rate-limiting step or a preequilibrium,²¹ but this should not be a problem for S_N2 reactions.

There is a problem in selecting the appropriate concentration units in second-order rate constants, which in homogeneous solvents are typically expressed as $M^{-1} s^{-1}$, and cannot be compared directly with k_M , where concentration is written as a mole ratio. Second-order rate constants in micellar phase with same dimensions, k_2^m , $M^{-1} s^{-1}$, are given by

$$k_2^{\rm m} = k_{\rm M} V_{\rm M} \tag{5}$$

where $V_{\rm M}$ is the molar volume of the reactive region at the micellar surface, and we take $V_{\rm M} = 0.14 \text{ L} \text{ mol}^{-1}$, on the basis of earlier estimates.^{3c,e,4} Other estimates are generally higher and vary by a factor of ca. 2.5.^{3a,d}

Our values of $k_2^{\rm m}$ are given in Table I. The values for the reaction of MeONs with Cl⁻ and Br⁻ in CTACl and CTABr respectively are very similar to values of $k_2^{\rm m} = 0.2 \times 10^{-4}$ and 1.4×10^{-4} M⁻¹ s⁻¹ calculated for the same reactions by solving the Poisson-Boltzmann equation.^{8b,c} Both sets of values depend on the *average* concentration of halide ion at the micellar surface, although our NMR, kinetic, and conductrimetric data suggest that there is a nonuniform distribution of counterions.¹²

Our values of $k_2^{\rm m}$ are based on a constant $V_{\rm M} = 0.14 \, {\rm L} \, {\rm mol}^{-1}$, and to the extent that it may increase with increasing bulk of the alkyl group we underestimate the rate enhancement in going from the N-methyl to N-butyl surfactants. However, our NMR evidence for "folding-back" of the larger alkyl groups suggests that $V_{\rm M}$ does not change markedly.¹² Overall rate constants increase in going from CTA⁺ to CTBA⁺ (Figures 1–8) despite decreased binding of halide ion, so uncertainties in values of $V_{\rm M}$ do not invalidate qualitative conclusions regarding reactivities at the micellar surfaces.

All values of k_2^m are larger than k_w and increase with the increasing bulk of the N-alkyl headgroups. The two factors involved in this increase appear to be electrophilic interaction of the ammonium headgroup and the forming naphthalene-2-sulfonate ion and the disruption of the hydration shell of the halide ion. This second factor is probably more important, because reactions of nucleophilic anions are strongly inhibited by anionic solvation, and disruption of this solvation is major part of the

energy barrier to reaction.²² Therefore even a small change in hydration of the anion will have a large effect on the reaction rate. However, this medium effect of the micelles is not all important, because the relative values of $k_2^{\rm m}$ for reaction of Br⁻ and Cl⁻ $(k_{\rm M}^{\rm Br}/k_{\rm M}^{\rm Cl})$, Table I) are similar to the relative second-order rate constants in water $k_{\rm W}^{\rm 8b,c}$ $(k_{\rm W}^{\rm Br}/k_{\rm W}^{\rm Cl} = 5.1)$. If reaction were occurring in a nonaqueous environment, Cl⁻ would be more reactive than Br⁻.²³ This observation is consistent with the NMR evidence that the methyl groups are in an aqueous environment.¹²

The values of $k_2^{\rm m}/k_{\rm W}$ suggest that these S_N2 reaction of halide ions are modestly catalyzed by cationic micelles, although for most anionic reactions values of $k_2^{\rm m}$ are smaller than $k_{\rm W}$.³ In this context "catalysis" is a phenomenon distinct from rate enhancement due to an increase in reactant concentration at the micellar surface.³

We discuss micellar rate effects in terms of a pseudophase model that attempts to factor out the contributions of the transfer free energies of the reactants between water and micelles and the activation free energies in the micellar pseudophase. Hall has developed a transition-state model that predicts that if α is large, limiting rate constants will be reached only at relatively high concentrations of surfactant and nucleophile ion.²⁴ Our rate data for reaction in micelles with bulky headgroups fit this prediction, although we believe that the pseudophase model is useful in relating the rate and NMR effects.¹²

Experimental Section

Materials. Preparation and purification of MeONs, CTACl, and CTABr have been described.^{8b,c} The other surfactants were prepared from the 1-hexadecane halide (0.1 mol) and the appropriate trialkylamine (0.12 mol, alkyl = Et, n-Pr, n-Bu, n-Pe) by heating them under reflux in absolute EtOH for 1-3 days for the bromides and 5-30 days for the chlorides, depending upon the reactivities of amines. These decrease considerably with increase of the bulk of the alkyl groups. The bromide surfactants were recrystallized three or four times from EtOAc, because the NMR spectra showed that small amounts of tetralkylammonium bromide (alkyl = Et, n-Pr, n-Bu, n-Pe) were formed by alkylation of the amine by the surfactant. These impurities disappeared after several recrystallizations, and if high-purity material was not needed, the yield could be increased by precipitating the surfactant with pentane from EtOAc. The chlorides could not be recrystallized from EtOAc except by addition of pentane, and on the basis of their 500-MHz NMR spectra, they contained traces (<1%) for CTEACl and CTPACl and (<3%) for CTBACl of tetralkylammonium chloride.

The water solubility of the surfactants increases markedly as the size of the alkyl group increases from Me to *n*-Bu. For example, we could obtain up to 70% of CTBABr in water, and 0.1 M aqueous solutions with up to 0.7 M NaBr show no obvious increase in viscosity, so that rodlike micelles did not form. Further addition of NaBr gave a separation into two liquid phases of low viscosity, and their miscibility decreased with an increase in temperature. The chlorides are very soluble in water and are hygroscopic, and CTBACl appears to be miscible with water in all proportions.

Cetyltripentylammonium bromide is sparingly water soluble, but is solubility increases with temperature. Its solubility behavior is similar to that of tetradecyltripentylammonium bromide.¹¹ There is a break in plots of conductivity against [CTPeABr] at 1.8×10^{-4} M which corresponds to a cmc, and on the basis of ratios of slopes of the conductivity plots the micelles or other assemblies have $\alpha \simeq 0.8$.

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TABLE III: Critical Micelle Concentrations^a

	C	21-	Br-		
alkyl	cmc, ^b mM	cmc, ^c mM	cmc, ^b mM	cmc, ^c mM	
Me	1.36	1.30 ^d		0.89 ^d	
Et	1.20	1.20	0.79	0.81	
n-Pr	0.65	0.66	0.53	0.56	
<i>n</i> -Bu	0.52		0.27	0.24	

"In water at 25 °C. "Conductimetric values. "Surface tension values. ^dReference 14.

The effect of N-alkyl groups on solubility and micelle shape parallels their contribution to the stability of the micelles. By "folding-back" the groups Et to n-Bu fill the space between headgroups at the micellar surface and therefore increase the stability of micelles.

Critical Micelle Concentrations. Values of the cmc in absence of added electrolyte were determined conductimetrically at 25 °C or determined by variations in surface tension. There were no minima in plots of surface tension against log concentration, and our values of cmc agreed with literature values where available¹⁴ (Table II). The cmc decreases with increasing size of the N-alkyl groups and is larger for the chlorides than bromides. These differences are consistent with differences in anion binding.

Fractional Ionization. Values of α were determined conductimetrically from the ratio of slopes of plots of specific conductance against surfactant, concentration below and above the cmc,¹¹ or by use of Evans equation¹⁶ (Table III).

Kinetics. Reactions were followed spectrophotometrically at 326 nm. MeONs was added in 20 μ L of MeCN to 3 mL of reaction solution at 25 °C, so that [MeONs] = 10^{-4} M. The first-order rate constants, k_{ψ} (s⁻¹), the reaction in CTACl and CTABr with no added salt agree with earlier values.^{8b,c} Rate constants k_{ψ}^{c} are corrected for the contribution of the spontaneous reaction with H₂O.

Note Added in Proof. The value of the cmc of CTPeABr has been confirmed by surface tension.

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Registry No. CTACl, 112-02-7; CTEACl, 13287-79-1; CTPACl, 110214-22-7; CTBACl, 6439-71-0; CTABr, 57-09-0; CTEABr, 13316-70-6; CTPABr, 25268-61-5; CTBABr, 117942-60-6; MeONs, 5138-53-4; Cl⁻, 16887-00-6; Br⁻, 24959-67-9.

Origin of the Apparent Breakdown of the Pseudophase Ion-Exchange Model for Micellar **Catalysis with Reactive Counterion Surfactants**

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One of the more important failures of the pseudophase ion-exchange (PPIE) model for micellar catalysis has been its inability to reproduce kinetic data for reactions in surfactants with highly hydrophilic counterions such as hexadecyltrimethylammonium hydroxide ((CTA)OH) and fluoride ((CTA)F). In the present work, it is shown that this apparent failure is due not to fundamental flaws in the model itself but to the inadequacy of the commonly employed assumption that the degree of micellar dissociation (α) is constant under all conditions. Thus, kinetic data in both (CTA)OH and (CTA)F are quantitatively simulated by PPIE when the appropriate surfactant concentration dependent values of α , determined by conductivity, are employed for these two detergents.

Introduction

Over the last several decades, there has been a steady increase in the number of studies dealing with the effects of micelles, synthetic and natural vesicles, monolayers, microemulsions, and polyelectrolytes on a wide variety of ground- and excited-state reactions and equilibria.^{1,2} These experimental studies have, in turn, stimulated parallel attempts to develop semiquantitative models or formalisms capable of describing and, eventually, predicting the observed effects.

For ionic micellar solutions, the best model currently available is the pseudophase ion-exchange (PPIE) formalism, which is capable of describing and predicting most ionic micellar effects on reaction rates and equilibria over a wide range of experimental conditions (pH, detergent and added salt concentrations, etc.) from a single set of parameters.³⁻⁵ Advances in our understanding of

the various modes of substrate binding to ionic micelles have permitted application of this model to a broad spectrum of quite diverse types of bimolecular reactions in both cationic and anionic micellar solutions. For virtually all of these reactions, the dominant factor responsible for the observed micellar effects on the reaction rate is the substantial change in the local concentrations of the reactive species that results from the binding of these to the micelle surface.

The fact that the PPIE model judiciously ignores all details of micelle structure, treating the micelles as if they were a bulklike pseudophase, has permitted application and extension of the basic concepts of PPIE to various other types of aqueous ionic interfaces, including synthetic vesicles,^{6,7} reversed micelles,⁸ and microemulsions.9,10

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