K. Both EELS and TDS results show the absence of CO adsorption after the Rh/Al_2O_3 layer is heated to 1100 K. Assuming the detection limit of both EELS and TDS techniques for CO adsorption to be approximately 1% of a monolayer and that the CO is adsorbed on identical Rh hemispheres' surfaces exposing a total surface area equivalent to ~1% of the original Rh monolayer, the average radius of the Rh hemispheres would be ~500 Å. However, if this Rh aggregation process were to occur on the surface of the Al_2O_3 substrate, we estimate that the intensity of the Rh (302 eV) Auger feature would be at most 6% of that measured on the original dispersed Rh layer deposited at 120 K. This predicted loss of Rh Auger intensity is due to the self-screening of the Rh Auger signal from inside of the hemispheres by the outer layers of the hemispheres. This is clearly not the case since 10 separate Auger measurements on Rh/Al_2O_3 layers with $d_{Al_2O_3}$ of 6-55 Å indicate that the intensity of the Rh (302 eV) Auger feature upon heating to 1100 K is about 70-85% of that measured initially at 120 K.

While we can clearly rule out the aggregation of Rh into large particles, the increase in the Mo Auger signal above ~700 K suggests that the Mo is less well screened after heating. This may be due to some tendency of the Rh or the Al_2O_3 to coalesce on heating. The tendency for Rh to coalesce has been observed in transmission electron microscopy work on model Rh/Al_2O_3 catalysts.[11]

2. Model B: Reaction of Rh with Al_2O_3. The physical and chemical measurements employed in this work are not especially sensitive to a chemical reaction between Rh and Al_2O_3 at elevated temperatures. The major experimental observation was that no significant change in the energy or line shape of the Rh Auger line occurred during this study. Studies made on Al^0-rich Al_2O_3[16] indicate that effects identical with those reported here are also observed in the nonstoichiometric aluminum oxide. Thus, excess Al^0 in Al_2O_3 is not likely to be the cause of the deactivation of Rh. Conversely, since excess oxygen is unlikely to be present in Al^0-rich Al_2O_3, the involvement of unreacted oxygen in stoichiometric Al_2O_3 may also be ruled out as an explanation for the Rh deactivation upon heating. The reaction of Rh with Al_2O_3 to form rhodium aluminate cannot be ruled out, except that extensive discussions and searches of the literature have not revealed any evidence that a rhodium aluminate exists.[27]

3. Model C: Diffusion of Rh into Al_2O_3. Finally, the extensive loss of CO chemisorption combined with the small fractional decrease in Auger intensity of the deposited Rh following heating suggests that most of the Rh remains in the sampling region of Auger spectroscopy, i.e., within a depth of 10-20 Å in the Al_2O_3 surface. Penetration or diffusion of Rh into the near surface region of the Al_2O_3 (or alternatively migration of Al_2O_3 onto the surface of Rh particles) would be expected to poison the Rh for CO chemisorption, while permitting the Rh to remain near the Al_2O_3 surface. The fact that there is no correlation of the fractional decrease in Rh Auger intensity (upon heating to 1100 K) with the thickness of the Al_2O_3 film strongly supports the idea that Rh remains in the near surface region of the Al_2O_3. If Rh diffusion throughout the Al_2O_3 were occurring, a larger fractional decrease in intensity would be expected on the thick Al_2O_3 film, and this is not observed over a 10-fold thickness range for the Al_2O_3. This model is also consistent with observations on high surface area Rh/Al_2O_3, where Rh reactivity is lost at high temperatures.[11-13]

C. Hydrogen Activation Experiments. In the Introduction the partial reactivation of rhodium via high-temperature reduction in hydrogen is described.[8,10-13] In an attempt to restore the CO adsorption capability of a preheated Rh/Al_2O_3 model catalyst, hydrogen from the doser was directed onto the Rh/Al_2O_3 interface while it was held at 1100 K. A flux of 1.1×10^{15} H_2 cm^{-2} s^{-1} was maintained for 600 s. After terminating the H_2 flow and then cooling, it was found by EELS that CO could not be readsorbed at 150 K. This observation, along with the absence of a change in the Auger line shape, supports our view that rhodium is not undergoing oxidation from the support or from residual oxygen. This behavior is also consistent with the difficulty in reactivating supported Rh/Al_2O_3 catalysts.[8,10-13]

IV. Conclusions

In summary, our results indicate that, upon heating a Rh/Al_2O_3 model catalyst to 1100 K, Rh loses its capability to chemisorb CO. We conclude that diffusion of rhodium into the Al_2O_3 near surface region or diffusion of an Al_2O_3 film onto the Rh film surface under vacuum conditions is likely to be the cause of this effect. This observation provides useful information for the understanding of the structural properties and catalytic reactivity of rhodium-alumina catalysts.

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Registry No. Rh, 7440-16-6; CO, 630-08-0.

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Micellar Effects upon Rates of S_N2 Reactions of Chloride Ion. 1. Effects of Variations in the Hydrophobic Tails

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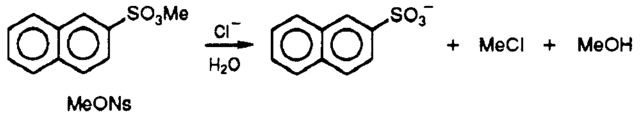
Interactions of $^{35}Cl^-$ with trimethylammonium surfactants increase with increasing length of the hydrophobic alkyl group on the basis of NMR line widths. The dependence of line width upon [surfactant] and [NaCl] can be fitted by a Langmuir isotherm, and for alkyl = C_8H_{17}-$C_{18}H_{37}$ the binding parameters, K'_{Cl}, agree reasonably well with those estimated kinetically from rate constants of the reaction of Cl^- with methyl naphthalene-2-sulfonate. The second-order rate constants for reaction in the micellar pseudophase decrease modestly with decreasing length of the alkyl group and are similar to those in water. For $C_8H_{17}NMe_3Cl$ there appear to be interactions of Cl^- with both micelles and monomeric surfactant, or small clusters of it. This nonmicellar interaction is also kinetically significant with $C_6H_{13}NMe_3Cl$ and Me_4NCl, but interactions with substrate and Cl^- are weak.

Aqueous micelles speed bimolecular reactions by bringing reactants together or inhibit them by keeping reactants apart.[2] The rate enhancements can be treated quantitatively by estimating reactant concentrations at the micellar surface,[3] and calculated

SCHEME I



MeONs

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 quantitatively 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^-, N_3^-, CN^- and H_3O^+ have been examined in solutions of reactive ion surfactants.

The micellar fractional ionic dissociation, α, is often little affected by the nature or the concentration of the counterion. The micellar surface appears to be saturated with counterions, and the fractional coverage $\beta = 1 - \alpha$ is constant.[3b-d] If β is a measure of counterion concentration at the surface and is constant, the reaction rate 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 cetyltrimethylammonium surfactants, provided that the counterion binds strongly to the micelle, e.g., for the reaction of Br^-, Cl^-, and CN^-[3c,e,4a,c] where α is low. However, for very hydrophilic anions such as OH^-, F^-, and HCO_2^- 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 isotherm, 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] An alternative approach is to measure α directly, for example, by conductivity.[5c,10]

Anionic reactions in micellized reactive-ion surfactants had been examined in cetyltrimethylammonium surfactants,[4-7] and we have examined reactions of Cl^- and Br^- in cetyltrialkylammonium chlorides or bromides.[11] The reactivity increases with increasing bulk of the head group in the sequence $Me_3N^+ < Et_3N^+ < n\text{-}Pr_3N^+ < n\text{-}Bu_3N^+$ although the affinity of the micelles for halide ion decreases in this sequence. This result was related to the disruption of the hydration of Br^- at the micellar surface and to interaction of the naphthalene π-system with cationic nitrogen.[11]

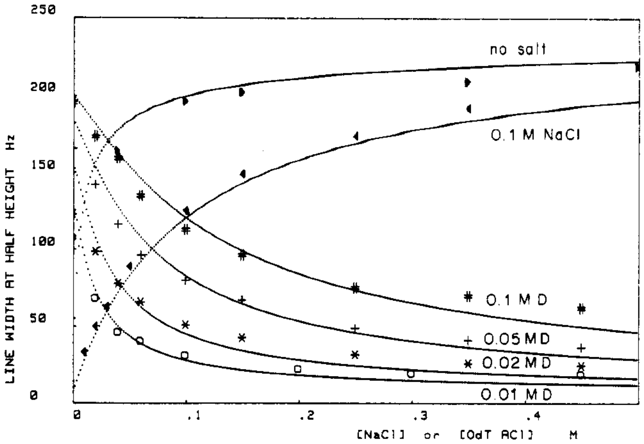


Figure 1. Dependence of the ^{35}Cl NMR line width on [NaCl] at constant [OdTACl] and on [OdTACl] at constant [NaCl].

High-field NMR spectroscopy is a useful method for relating micellar effects on reactivity to colloidal structure. Micellar incorporation of Br^- markedly increases the NMR spectral width of ^{79}Br, due to disruption of ionic hydration.[12]

We have examined the reaction of methyl naphthalene-2-sulfonate (MeONs) with Cl^- and H_2O in alkyltrimethylammonium chlorides (alkyl = methyl (TMACl), hexyl (HeTACl), octyl (OcTACl), decyl (DeTACl), dodecyl (DoTACl), tetradecyl (TeTACl), hexadecyl (CTACl) and octadecyl (OdTACl)) (Scheme I). Reaction with water can be followed in sulfate or methanesulfonate surfactants. These reactions are mechanistically simple, with no interionic competition. We also measured line widths of the NMR resonances of ^{35}Cl and correlated them with the kinetic results.

Results

^{35}Cl Relaxations. For the atoms with spin quantum numbers $I = {}^3/_2$, e.g., ^{35}Cl, the dominant relaxation mechanism in solution involves interaction of the nuclear electric quadrupole moment with fluctuating electric field gradients at the nucleus. Under conditions of extreme narrowing, the longitudinal T_1 and transverse T_2 relaxation times are equal and the line width B, which is proportional to the reciprocal relaxation time $1/T_2$, can be written[13-16]

$$B = Kq^2\tau_c \qquad (1)$$

where K is a constant for a given nucleus, q is the mean-square electric field gradient at the nucleus, and τ_c is the correlation time characteristic of the random molecular motions that produce the fluctuating field gradient. Thus line-width measurement yields the product $q^2\tau_c$. These quantities depend on the bonding properties of the ions, including solvation and the microdynamic properties of the system. Although the separation of these parameters is difficult, comparison of data for different systems is informative. The assumption of extreme narrowing is applicable when the motion is rapid enough to give $\omega_0 \ll 1$, where ω_0 is the Larmor frequency, and holds for the relaxation of ^{35}Cl in al-

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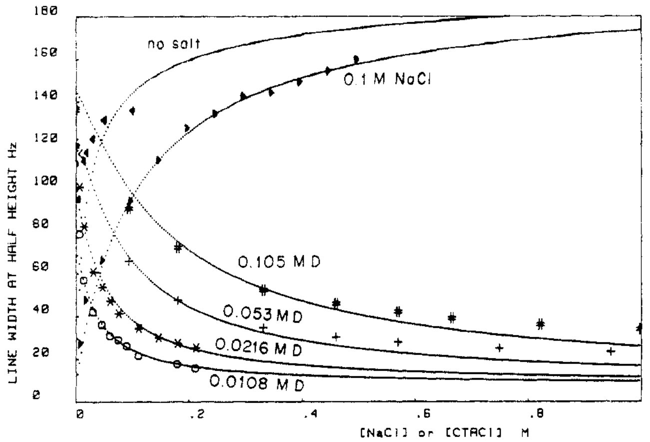

Figure 2. Dependence of the ^{35}Cl NMR line width on [NaCl] at constant [CTACl] and on [CTACl] at constant [NaCl].

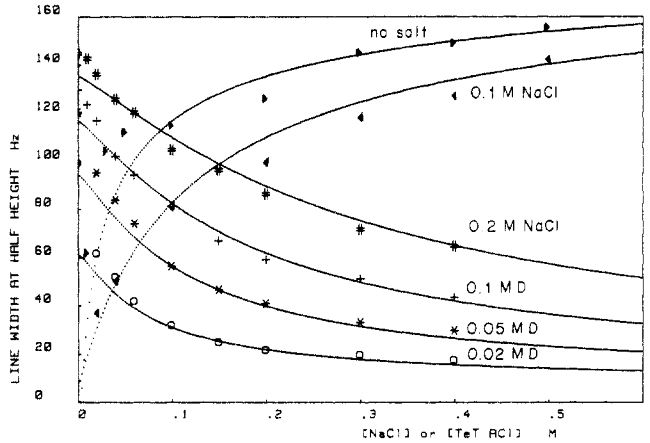

Figure 3. Dependence of the ^{35}Cl NMR line width on [NaCl] at constant [TetACl] and on [TeTACl] at constant [NaCl].

kyltrialkylammonium chlorides.[14,15] We assume that it is also true for all aqueous alkyltrialkylammonium chlorides.

If a quadrupolar nucleus, e.g., ^{35}Cl, is located at different kinds of sites in solution, the resulting line shape depends on relative concentrations at the various sites, their characteristic values of q and τ_c, and the rate of exchange among the sites. When the residence time of the anion in different sites is much shorter than the relaxation time, the line width is given by the sum of line width at each site multiplied by the mole fraction of the atom at this site.[13-16] In the pseudophase model of micelles,[17] two types of sites of Cl^- are considered. One corresponds to a free ion (designated by subscript W), solvated by water in the bulk solvent and interacting with other free ions, largely those from added salts, because monomeric surfactant cation is in low concentration. The other site is the micellar surface (designated by subscript M). Exchange between these sites is much faster than the relaxation of ^{35}Cl,[16] as shown for aqueous alkyltrimethylammonium halide surfactants. No quadrupolar splitting was observed in these experiments.

In these conditions the line width can be written

$$B = p_W B_W + p_M B_M \tag{2}$$

where p denotes the molar fraction and B the line width in water and micelles with the appropriate subscripts W and M. The line width in water B_W has been taken as 8 Hz corresponding to $1/T_2 = 25\ s^{-1}$,[16] although data fits are insensitive to small changes in this value.

We measured the line broadening of ^{35}Cl in H_2O solution containing 20 vol % D_2O in variable [alkyltrimethylammonium chloride] and [NaCl] using a GE-300 NMR spectrometer at 25

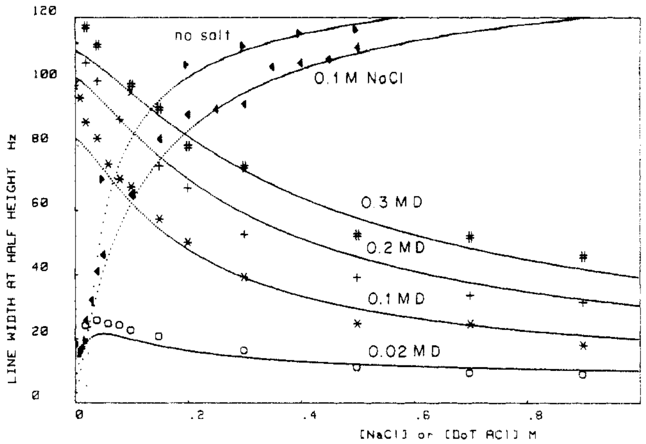

Figure 4. Dependence of the ^{35}Cl NMR line width on [NaCl] at constant [DoTACl] and on [DoTACl] at constant [NaCl].

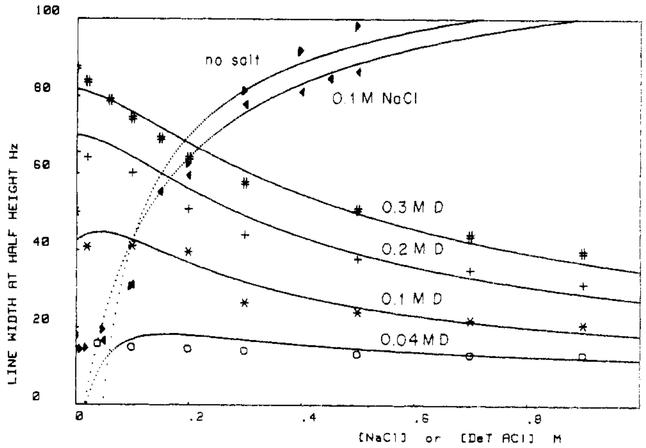

Figure 5. Dependence of ^{35}Cl NMR line width on [NaCl] at constant [DeTaCl] and on [DeTACl] at constant [NaCl].

°C. The experimental line widths are large in absence of added salt but decrease rapidly with increasing [NaCl]. They increase with surfactant concentration at constant [NaCl] (Figures 1–5).

We could not fit these data to a pseudophase model with constant fractional ionization, α, and we calculated the concentration of Cl^- at the micellar site [Cl^-_W] by using a Langmuir isotherm:[12,18]

$$K'_{Cl} = [Cl_M^-]/([D_T] - cmc - [Cl_M^-])[Cl_W^-] \tag{3}$$

where cmc is the critical micellar concentration and the quantities in squared brackets are molarities written in terms of total solution volume. Subscripts T, M, and W denote total surfactant (detergent), D, and that in micellar and aqueous pseudophases respectively.

The line width B can be fitted using eqs 2–5:

$$p_W = [Cl_W^-]/[Cl_T^-] \tag{4}$$

$$p_M = [Cl_M^-]/[Cl_T^-] \tag{5}$$

and optimizing values of B_M and K'_{Cl}. Figures 1–5 show the experimental line widths of the ^{35}Cl resonances and the calculated plots based on values of B_M and K'_{Cl} (Table I).

The fits are reasonable for the longer chain surfactants but not for OcTACl, which has a very high cmc, even with added NaCl (Table II). Counterion NMR line widths often depend on [surfactant] even below the cmc, probably because the halide ions interact with the cations even with no micelle formation.[15c] For various quaternary ammonium bromides line widths of the ^{79}Br NMR resonance increase rapidly with increasing length of the alkyl groups and salt concentration.[14a] The bromide ions are

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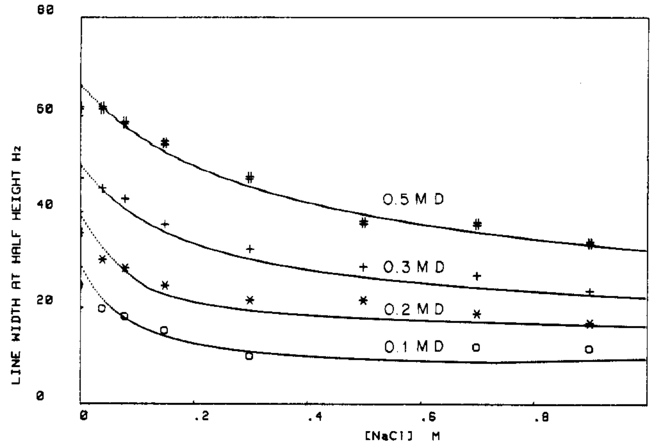


Figure 6. Dependence of the ^{35}Cl NMR line width on [NaCl] at constant [OcTACl].

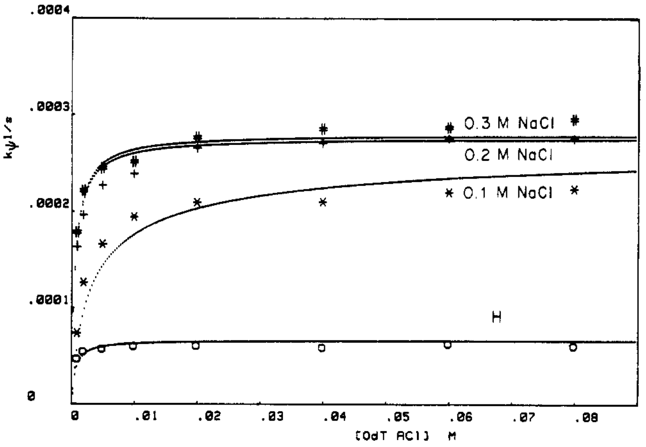


Figure 7. Dependence of $k\psi$ for reaction of MeONs with Cl^- on [OdTACl] and [NaCl] and of hydrolysis on $[OdTA(SO_4)_{1/2}]$ (H).

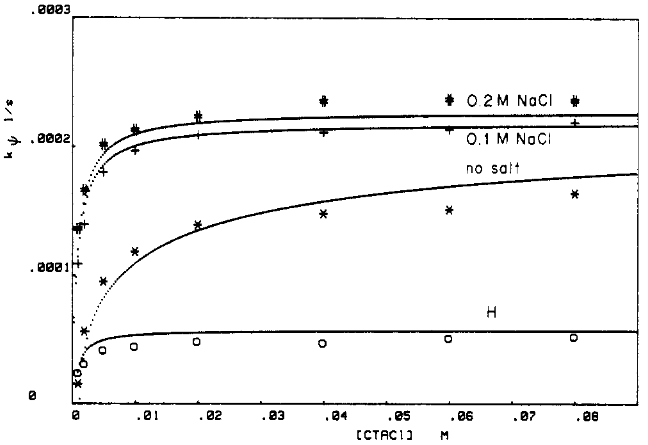


Figure 8. Dependence of $k\psi$ for reaction of MeONs with Cl^- on [CTACl] and [NaCl] and of hydrolysis on $[CTA(SO_4)_{1/2}]$ (H).

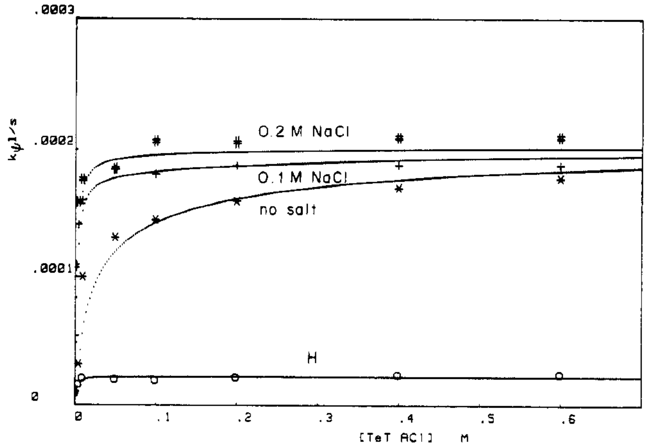


Figure 9. Dependence of $k\psi$ for reaction of MeONs with Cl^- on [TeTACl] and [NaCl] and of hydrolysis on $[TeTA(MeSO_3)]$ (H).

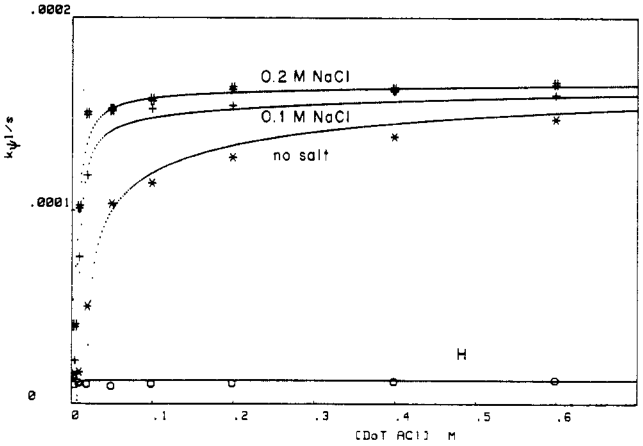


Figure 10. Dependence of $k\psi$ for reaction of MeONs with Cl^- on [DoTACl] and [NaCl] and of hydrolysis on $[DoTA(SO_4)_{1/2}]$ (H).

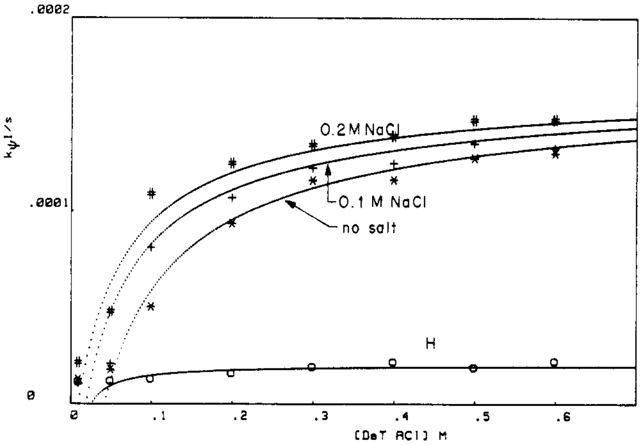


Figure 11. Dependence of $k\psi$ for reaction of MeONs with Cl^- on [DeTACl] and [NaCl] and of hydrolysis on $[DeTA(MeSO_3)]$ (H).

probably rapidly exchanging between two sites, corresponding to Br^- in the water lattice and as ion pairs in a clathratelike water lattice.[14a] Alternatively the nonpolar groups of the ammonium ions exert a structure making effect on the water lattice, and some of the anions are incorporated into this modified water structure in the vicinity of the cations.

We therefore considered a simplified model with Cl^- moving rapidly between three sites: nonmicellized OcTACl, micelles and bulk water. The concentration of nonmicellized surfactant is taken as the cmc at the corresponding [NaCl]. There is an interaction between Cl^- and nonmicellized ammonium ion to form an ion pair with an equilibrium constant, K'_{ip}:

$$K'_{ip} = [Cl_{ip}^-]/([Cl_T^-] - [Cl_{ip}^-] - [Cl_M^-])(\mathrm{cmc} - [Cl_{ip}^-]) \quad (6)$$

where $[Cl^-_{ip}]$ is the concentration of ion pairs.

The line width is now

$$B = p_W B_W + p_M B_M + p_{ip} B_{ip} \quad (7)$$

where p denotes the mole fraction at the three sites. Fitting this equation as above gave the parameters for OcTACl (Table I). Ion pairing was neglected for the longer chain surfactants that have low cmc (Table II).

Figure 6 shows the experimental values of line width and the calculated plots based on the values in Table I for OcTACl.

Kinetics. First-order rate constants of reaction of Cl^- with MeONs, $k\psi$, increase with increasing surfactant concentration and reach limiting values. These limiting values increase with the length of the alkyl group and on addition of Cl^- (Figures 7–11).

TABLE I: Fitting Parameters for Reactions of MeONs and for ^{35}Cl NMR Line Widths in Alkyltrimethylammonium Surfactants ($RNMe_3Cl$)[a]

	kinetics					NMR	
R	K_s, M^{-1}	K'_{Cl}, M^{-1}	$10^5 k_M$, s^{-1}	$10^5 k_2^m$,[b] M^{-1} s^{-1}	k_M°,[c] s^{-1}	K'_{Cl}, M^{-1}	B_M,[d] Hz
$C_{18}H_{37}$	1537	268	21.8	3.1	6.7	250	243
$C_{16}H_{33}$	1093	74.2	18.2	2.6	5.8	77.0	204
$C_{14}H_{29}$	556	40.0	19.7	2.7	2.4	41.0	191
$C_{12}H_{25}$	310	42.0	16.7	2.3	1.3	44.0	148
$C_{10}H_{21}$	154	22.9	16.1	2.3	2.0	21.8	132
C_8H_{17}	0.65	0.66	6.4	1.0	2.2	1.6	129[h]
	0.34[e]	0.66[f]	9.4[g]			0.37[f]	104[i]
C_6H_{13}	0.005[e]	0.0005[f]	10.0[g]				
CH_3	0.0044[e]	0.0004[f]	10.9[g]				

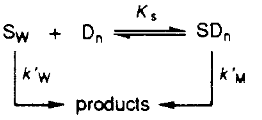
[a] At 25.0 °C, in water. [b] In the absence of micelles $k_w = 1.5 \times 10^{-5}$ M^{-1} s^{-1}. [c] In the absence of micelles $k^\circ_w = 1.2 \times 10^{-5}$ s^{-1}. [d] Line width at half-height. [e] Binding constant K_s^{ip} of MeONs. [f] Ion pair association constant, K'_{ip}. [g] k'_{ip}, s^{-1}, for reaction in ion pairs. [h] Lit. 120 Hz.[13c] [i] In ion pairs.

TABLE II: Critical Micellar Concentrations[a]

	X				
R	Cl		Cl + [NaCl][b]	$(SO_4)_{1/2}$	$MeSO_3$
$C_{18}H_{37}$	0.3	0.4[c]	0.025 [0.05]	0.24	
$C_{16}H_{33}$	1.3	1.3–1.5[c]	0.66 [0.005]	0.54	1.45
			0.30 [0.01]		
			0.15 [0.04]		
			0.10 [0.05]		
$C_{14}H_{29}$	4.1	4.5[c]	2.39 [0.02][c]	1.5[c]	4.90
			1.36 [0.04][c]		
			1.02 [0.01][c]		
$C_{12}H_{25}$	20	18–21[c]	15.91 [0.02][c]	9.3–16[c]	22.6
			11.7 [0.04][c]		
			7.2 [0.1][c]		
$C_{10}H_{21}$	50	61–65[c]	44.7 [0.1]	50.3[c]	63.1
			8.13 [0.5]		
			3.55 [1.0]		
C_8H_{17}	245	250[d]	209 [0.1]		93.3
			120 [0.5]		
			84.1 [1.0]		

[a] In water at 25 °C in mM. [b] In the presence of NaCl at the indicated [NaCl], in square brackets. [c] Reference 25. [d] Reference 15c.

SCHEME II



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 surfactant concentrations for the shorter alkyl groups and added Cl^- speeds reaction, so that it appears that the micelles are not saturated with Cl^-.

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).[2,19]

In Scheme II substrate in water (S_W) is in equilibrium with bound substrate (SD_n). The binding constant is written in terms of 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

$$k'_\psi = (k'_W + k'_M K_S[D_n])/(1 + K_S[D_n]) \tag{8}$$

The first-order rate constants can be written in terms of second-order rate constants, k_W and k_M, with the appropriate units of concentration, and for k_M we define concentration of halide ion, Cl^-, in the micelle, as a mole ratio.[3c,e,4]

$$k'_W = k_W[Cl^-] \tag{9}$$

$$k'_M = k_M[Cl^-_M]/[D_n] \tag{10}$$

The value of $[Cl^-_M]$ was assumed to follow[5-7,18]

$$K'_{Cl^-} = [Cl_M^-]/[Cl_W^-]([D_n] - [Cl_M^-]) \tag{11}$$

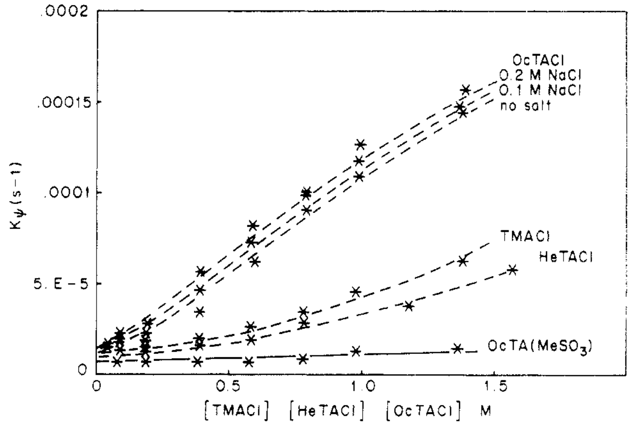


Figure 12. Dependence of $k\psi$ for reaction of MeONs with Cl^- on [TMACl], [HeTACl], and [OcTACl] and [NaCl] and of hydrolysis on [OcTA($MeSO_3$)].

Equation 11 has been used to describe the interaction of various anions with cationic micelles, and we used it with eqs 8–10 to fit variations of $k\psi$ with $[D_n]$ and $[Cl^-]$. Equations akin to 11 but applied to mixtures of reactive and inert anions have been used to describe interionic competition in micellar-assisted reactions.[7]

The hydrolysis was followed by the disappearance of MeONs in sulfate or methanesulfonate surfactants. The first-order rate constant for hydrolysis is given by

$$k_\psi = (k^\circ_W + k^\circ_M K_S[D_n])/(1 + K_S[D_n]) \tag{12}$$

with $k^\circ_W = 1.2 \times 10^{-5}$ s^{-1} for the nonmicellar hydrolysis. The binding constant, K_S, the Langmuir constant K'_{Cl}, and the rate constant k°_M and k_M for reactions of H_2O and Cl^-, respectively, in the micellar pseudophase were obtained by the simultaneous fitting of the experimental first-order rate constants of hydrolysis and attack of Cl^- (Figures 7–11) and are given in Table I with $k_W = 1.5 \times 10^{-5}$ M^{-1} s^{-1} for reaction of Cl^- in water.[11] The kinetic data in CTACl are slightly different from those reported earlier (by <10% in k_M) because of a small difference in the numerical treatment that corrects for the contribution of reactions in the aqueous pseudophase.[11]

The fits of kinetic data are satisfactory for surfactants with alkyl groups $C_{12}H_{25}$ or longer. The fit for DeTACl is reasonably good, but limiting rates are not reached in OcTACl or shorter chain length compounds. We noted NMR evidence for ion pairing and association with substrate will speed the nucleophilic reaction. We assume that reaction can also take place in complexes of ion pairs and substrate. If association of these ion pairs with the substrate has the equilibrium constant K_S^{ip}, then the observed rate constant is

$$k_\psi = (k'_W + k'_{ip} K_S^{ip}[D_{ip}])/(1 + K_S^{ip}[D_{ip}]) \tag{13}$$

for reaction of substrate in water and in ion pairs (D_{ip}) and k'_{ip} is the first-order rate constant in the ion pairs; cf. eq 8. Therefore we have three reaction sites in solutions of OcTACl, in bulk water, in ion pairs and in micelles, and we combined eqs 8, 12, and 13

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with the mass balance relation to fit the kinetic date (Figure 12 and Table I).

On the basis of overall rate data short-chain tetralkylammonium chlorides ion pair rather than micellize, as shown by the $^{35}Cl^-$ NMR line width (see above). These ion pairs should associate with MeONs and speed its reactions with Cl^-. We therefore investigated nucleophilic substitution in solutions of HeTACl and TMACl. The first-order rate constants of these reactions are similar and increase faster than first order with concentration of ammonium chloride salt (Figure 12). They can be fitted with a model similar to that discussed above, considering only reactions in bulk water and in ion pairs. NMR evidence on OcTACl (Table I) supports the hypothesis that ion pairing rather than an ionic strength effect is kinetically important. The calculated parameters are in Table I.

This evidence for rate enhancements by ion pairs or similar clusters is consistent with existing evidence that tri-*n*-octylammonium ions interact with hydrophobic or anionic reagents and promote their reactions in aqueous media. In some cases these rate enhancements are similar to or larger than those by aqueous micelles.[20]

Discussion

Micellar Binding of Cl^-. The lengths of the alkyl groups affect micellar interactions with Cl^- and consequently its reaction with MeONs. The Langmuir constants, K'_{Cl}, obtained from kinetic fits are similar to those obtained from NMR data and decrease with decreasing length of the alkyl group, corresponding to an increase of micellar dissociation of Cl^-. This decrease should be related to the headgroup spacing at the micellar surface. A decrease in the length of the alkyl group decreases the aggregation number. Micellar radius should approximately follow the length of the alkyl group, and aggregation numbers are in the range 100–115 for CTACl and ca. 60 for DoTACl.[21,22] There is also a decrease in micellar stability as shown by the change in cmc (Table II).

The line width corresponding to the presence of Cl^- at a micellar site decreases with decreasing length of the alkyl group (Table I), suggesting that there is less interaction between the solvation shell of the anion and the hydrophobic residue of the micelle.[2,4] It appears that in cationic micelles with shorter alkyl groups the solvated anions penetrate the surface less. This change in interaction is consistent with the dependence of the Langmuir parameters, K'_{Cl} (eq 3), upon chain length (Table I). There is no big difference between B_M and B_{ip} for OcTACl, which implies that Cl^- is situated near the methyl groups in the ion pair and does not interact with the long alkyl group.

Micellar Rate Constants. The pseudophase description of micellar rate effects involves the implicit assumption that micelles provide a discrete reaction environment, and on this basis we compare rate constants in this environment with those in water.

There is a problem in selecting the appropriate concentration units of 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

$$k_2^m = k_M V_M \qquad (14)$$

where V_M is the molar volume of the reactive region at the micellar surface, and we take $V_M = 0.14\ M^{-1}$, 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^m are given in Table I. The value for the reaction of MeONs with Cl^- in CTACl is very similar to that of $k_2^m = 0.2 \times 10^{-4}\ M^{-1}\ s^{-1}$ calculated by solving the Poisson–Boltzmann equation.[8b] Rate constants k_2^m increase in going from OcTACl, where the value is approximately equal to that in water, to OdTACl.

The factors involved in this increase appear to be electrophilic interaction of the ammonium headgroup and the forming naphthalene-2-sulfonate ion and disruption of the hydration shell of the halide ion. This second factor is probably the more important, because reactions of nucleophilic anions are strongly inhibited by anionic solvation, and disruption of this solvation is a major part of the energy barrier to reaction.[23] Therefore even a small change in hydration of the anion will have a large effect on the reaction rate. This conclusion is supported by a parallel between decrease of the ^{35}Cl NMR line width, indicative of a decrease of the perturbation of the hydration shell of Cl^-, and the rate constants (Table I). There is a similar effect upon the rate constant of the reaction of water in the micellar pseudophase, k°_M, which is probably due to a change in water structure at the micellar surface with increase of the length of the alkyl group.

The rate constants for reaction of Cl^- with MeONs associated with ammonium ion pairs are similar for OcTACl, HeTACl, and TMACl (Table I), as expected if interactions at the cationic headgroups lead to similar effects upon the hydration shell of Cl^-.

Binding Constants. The binding constants, K_S, decrease rapidly with decreasing length of the alkyl group and substrate associates weakly with ion pairs. This decrease can be related to a decrease in the space available to accommodate substrate at the surface of the micelles or other assemblies. We note that K'_{ip} decreases very sharply in going from OcTACl to HeTACl and TMACl (Table I). These differences suggest that what we call "ion pairing" involves not monomeric ammonium ions but small clusters of them. To that extent the assumed dependence of binding parameters upon ammonium ion concentration will only be an approximation, but this uncertainty does not change the qualitative picture.

Conclusions

The hypothesis that micelles speed bimolecular reactions only by bringing the reactants together and that second-order rate constants at the surface of micelles equal those in water is an oversimplification. The reactivity of Cl^- depends on its hydration shell, which is determined by the degree of penetration of the anions between the cationic headgroups of the surfactants and perturbations due to interaction with hydrophobic alkyl groups.

The fractional dissociation of micelles is also affected by anionic penetration between headgroups. When the alkyl group is short and the surface area per headgroup decreases, the fractional dissociation, α, increases and becomes dependent on the anion concentration, especially for hydrophilic counterions, where K'_{Cl} decreases sharply with decreasing chain length. One of the original assumptions of the pseudophase model is that α is constant and independent of the nature and concentration of counterions.[3b–e] This assumption is reasonably satisfactory for low concentrations of moderately hydrophilic anions, e.g., Cl^- or Br^-, but it fails for very hydrophilic anions[3b,e,5,6] and with increasing concentrations of moderately hydrophilic anions.[11,12] It is then necessary to use treatments that do not demand constancy of α, based, for example, on eq 11 or its equivalent or on quantitative estimates of Coulombic and specific ion–micelle interactions.[8,9]

The values of k_2^m/k_W suggest that these S_N2 reactions of halide ions are modestly catalyzed by cationic micelles, although for many anionic reactions $k_2^m < k_W$.[3] In this context "catalysis" is a phenomenon distinct from rate enhancement due to an increase in reactant concentration at the micellar surface.[3] This conclusion

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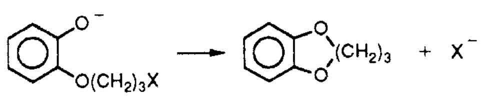
is supported by micellar rate enhancements of cyclization of **1**,



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which is mechanistically an intramolecular S_N2 reaction. With X = Br rate constants in CTACl or CTABr are larger than that in water by a factor of 1.8, but this factor increases to 29 for reaction of X = I in $C_{16}H_{33}NBu_3Br$.[24]

There is a marked difference between the results for micellar reactions of MeONs with Cl^- and Br^-. The Langmuir parameters for micellar binding of Cl^-, derived kinetically and by NMR line widths, are very similar (Table I), but for Br^- the kinetic values are considerably larger than those from NMR line width.[11,12] This difference suggested that NMR line widths sensed largely Br^- that was very close to a cationic headgroup and the kinetics sensed not only these ions but also those that are less tightly bound to the micellar surface. This question will be discussed more fully on related work on the effect of headgroup size on interactions of Cl^- with cationic micelles.[11b]

Experimental Section

Materials. Preparation and purification of MeONs and CTACl have been described.[8b] The other surfactants were obtained by heating alkyl chloride (0.3 mol) with aqueous 4 M trimethylamine (0.5 mol) in 150 mL of EtOH at reflux, generally for 3–4 h. After solvent evaporation, the surfactants were recrystallized two or three times from EtOAc with a small amount of EtOH. The sulfate surfactants were obtained from the corresponding chlorides by treatment with stoichiometric Ag_2SO_4 in EtOH and recrystallization from EtOAc with a small amount of EtOH. The methanesulfonates were obtained from the chlorides by ion exchange using Dowex cationic resin MSA-1 in the methanesulfonate form and purification as above.

Critical Micelle Concentrations. Values of the cmc were determined by surface tension measurements and agreed with available literature data.[25] There were no minima in the surface tension plots.

Kinetics. Reactions were followed spectrophotometrically at 326 nm. MeONs was added in 20 μL 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}), for reaction in CTACl agreed with earlier values.[8b,10]

NMR Spectroscopy. The ^{35}Cl line widths were measured on a GE-300MHz FT-NMR spectrometer at 29.445 MHz by using a one-pulse sequence. Typical settings for FT parameters were flip angle 30–45°, delay 1 s, and spectral width 4 kHz. The memory block for storage of the FID with 4K and the resolution was better than 1 Hz. The line width at half-height was calculated by using the Lorenzian fit subroutine. For exponential multiplication a line broadening of 1 Hz was used. The aqueous surfactant or NaCl solution contained 20 vol % D_2O as lock. At this concentration the deuterium isotopic effect is negligible. The simulations were unaffected by a 2-fold variation in the line width in water.

Calculations. The fit of experimental data has been made using a modified program designed initially for fitting of kinetic data.[26]

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Micellar Effects upon Rates of S_N2 Reactions of Chloride Ion. 2. Effects of Cationic Headgroups

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Observed first-order rate constants for reaction of methyl naphthalene-2-sulfonate with Cl^- in micelles of cetyltrialkylammonium chlorides ($C_{16}H_{33}NR_3Cl$, R = Me, Et, *n*-Pr, *n*-Bu, *n*-Pe) increase monotonically with increasing concentrations of surfactant and Cl^- and tend to limiting values. These variations can be fitted to a model that describes micelle–ion interactions in terms of Langmuir isotherms. The binding parameters, K'_{Cl}, decrease with increasing headgroup bulk, but second-order rate constants at the surface increase. The value of K'_{Cl} is higher with a quinuclidinium as compared with a N^+R_3 headgroup, but the second-order rate constant is similar to that for R = Et. Values of K'_{Cl} are high with hydroxyethyl head groups N^+R_3 = $N^+Me_2CH_2CH_2OH$ or $N^+(CH_2CH_2OH)_3$, but these groups decrease second-order rate constants. Values of K'_{Cl} estimated from ^{35}Cl NMR line widths agree with the kinetic values except with the $N^+(CH_2CH_2OH)_3$ headgroup for which the kinetic values are much higher. The effect of headgroup bulk upon the spontaneous reaction with water was examined by using sulfate as the surfactant counterion. Trends in reactivity are very similar for reactions of H_2O and Cl^-.

The hypothesis that micelles speed bimolecular reactions merely by bringing reactants together and that calculated second-order rate constants at micellar surfaces are very similar[2] is an oversimplification. Reactivities of counterions depend on their solvation shell, which may be perturbed by interaction with the micelle.[3,4]

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