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- (5) S. R. Morrison, *J. Vac. Sci. Technol.*, **7**, 84 (1970).
- (6) R. Memming, *Proc.—Electrochem. Soc.*, **77**, 38 (1977).
- (7) T. Kobayashi, H. Yoneyama, and H. Tamura, *Chem. Lett.*, 457 (1979).
- (8) M. J. Madou, F. Cardon, and W. P. Gomes, *J. Electrochem. Soc.*, **124**, 1623 (1977).
- (9) K. Nakatani, S. Matsudaira, and H. Tsubomura, *J. Electrochem. Soc.*, **125**, 406 (1978).
- (10) M. S. Wrighton and A. J. Bard, *J. Am. Chem. Soc.*, in press. We thank Professor Wrighton for a preprint of this work.
- (11) M. S. Wrighton, J. M. Bolts, A. B. Bocarsley, M. C. Palazzoto, and E. G. Walton, *J. Vac. Sci. Technol.*, **15**, 1429 (1978).
- (12) R. Memming and F. Möllers, *Ber. Bunsenges. Phys. Chem.*, **76**, 609 (1972).
- (13) S. R. Morrison, "The Chemical Physics of Surfaces", Plenum, New York, 1977.

Self-Diffusion and NMR Studies of Chloride and Bromide Ion Binding in Aqueous Hexadecyltrimethylammonium Salt Solutions

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A combination of tracer self-diffusion and NMR techniques was used to study mixed solutions of hexadecyltrimethylammonium chloride ($C_{16}TAC$) and bromide ($C_{16}TAB$). The degree of counterion association with the micelles, (β_x), and the relative strength of counterion binding was obtained from ^{35}Cl and ^{82}Br self-diffusion studies. A slight increase in β_{Br} occurs at the transition from spherical to rodlike $C_{16}TAB$ micelles and is markedly greater than β_{Cl} of $C_{16}TAC$ solutions at all concentrations. For $C_{16}TAC/C_{16}TAB$ mixtures there is a pronouncedly preferential binding of Br^- ions for both spherical and rodlike micelles. For pure $C_{16}TAC$ or $C_{16}TAB$ solutions there is a marked increase in ^{35}Cl or ^{81}Br quadrupole relaxation on the formation of rods. For mixtures the quadrupole relaxation rate of $^{81}Br^-$ is strongly influenced by the presence of rodlike micelles while that of $^{35}Cl^-$ is not. This can be interpreted either as the presence of two binding sites in the micelles with preferential Br^- binding close to the head groups or as a coexistence of spheres and rods and a preferential binding of Br^- to rods. For hexagonal liquid crystals of $C_{16}TAC/C_{16}TAB$ mixtures, ^{35}Cl quadrupole splittings demonstrate a preferential binding of Br^- ions.

Introduction

There is a considerable body of evidence to demonstrate that the hexadecyltrimethylammonium bromide ($C_{16}TAB$) forms rod micelles at high concentrations, while hexadecyltrimethylammonium chloride ($C_{16}TAC$) forms only spherical micelles. Early reports were based on X-ray data,² but more recent studies have involved the use of NMR techniques.³⁻⁶ Of particular interest were studies of the counterion NMR which showed a dramatic increase in line width of the ^{81}Br resonance on formation of rod micelles; this was taken to indicate an enhancement of counterion binding.^{3,6} No change in ^{35}Cl line widths was observed in $C_{16}TAC$ solutions as expected, since rod micelles do not form in this system at room temperature. Even in $C_{16}TAB/C_{16}TAC$ mixtures, where an increase in ^{81}Br line widths indicated the formation of rod micelles, no change in the ^{35}Cl line widths occurred. This was interpreted to suggest that such mixtures contain both spherical and cylindrical micelles, with the Cl^- ions being mainly associated with spherical micelles while Br^- ions are bound to cylindrical micelles. The occurrence of this very specific type of counterion binding is not consistent with elementary electrostatic theory, where the ions would be expected to mix almost ideally and to bind similarly to both types of micelles. For this reason it was decided to further investigate the ion binding in hexadecyltrimethylammonium salts.

The measurement of ion self-diffusion coefficients in surfactant solutions is a well-established technique for the estimation of the fraction of ions bound to micelles.⁷⁻⁹ We report here self-diffusion coefficients for mixtures of $C_{16}TAC$ and $C_{16}TAB$ and obtain a measure of counterion binding from this alternative technique to NMR. In ad-

dition we sought to obtain ^{35}Cl NMR line widths for $C_{16}TAC$ in rod micelles. In $C_{16}TAB$ solutions it is known that low temperatures or addition of aromatic solubilizers favor the formation of rod micelles.^{3,10,11} We discovered that $C_{16}TAC$ forms rod micelles on addition of α -methylnaphthalene, or at low temperature (278 K), and counterion NMR line widths are reported for these systems. Furthermore, the hexagonal phase consists of aligned rod micelles, and both $C_{16}TAB$ and $C_{16}TAC$ form hexagonal phase as the first liquid crystal phase. It is now well established that, for ions having spin quantum number $I > 1/2$ and present in hexagonal or lamellar liquid crystal phases, the NMR spectrum is split into $2I + 1$ resonances; in favorable cases the magnitude of the frequency difference between adjacent resonances (the quadrupole splitting, Δ) can be related to the fraction of ions bound at the interface.¹²⁻¹⁵ Thus NMR studies in hexagonal-phase samples prepared from $C_{16}TAB/C_{16}TAC$ mixtures could enable information about ion binding to be obtained from quadrupole splittings (Δ) as well as give more details of line-width behavior.

Bromide ion self-diffusion in $C_{16}TAB$ solution¹⁶ gave a much smaller change at the sphere-to-rod transition than the change in ^{81}Br relaxation³ which cannot, therefore, reflect solely a change in the number of bound counterions. During the course of the study, Smith¹⁷ published similar values of Br^- self-diffusion coefficients for $C_{16}TAB$ solutions and concluded that no dramatic increase in counterion binding occurred on formation of rod micelles. Our results are in agreement with this conclusion and indicate that the interpretation of the NMR quadrupole relaxation is more complex than was previously thought. On the other hand, counterion quadrupole splittings often reliably

report on the degree of counterion binding.

Experimental Section

Materials. C_{16} TAB was purchased from Th. Schuchardt, München, West Germany. C_{16} TAC was prepared by transferring C_{16} TAB to the hydroxide form on a Dowex 21 K ion exchanger (British Drug Houses). The C_{16} TAOH was immediately neutralized with HCl to pH 4–5. The solution was lyophilized and C_{16} TAC was recrystallized from acetone. The samples were prepared by weighing appropriate amounts of C_{16} TA salts and doubly distilled water.

The radioactive labels used in the self-diffusion studies were ^{82}Br -enriched sodium bromide (specific activity 0.6 mCi/mg), ^{22}Na -enriched sodium chloride (specific activity > 100 mCi/mg) from C.E.A., Département des Radioéléments, Gif-sur-Yvette, France, ^{36}Cl -enriched sodium chloride (specific activity 7 $\mu\text{Ci}/\text{mg}$) from Amersham Radiochemical Center, Buckinghamshire, U.K., and ^{14}C -enriched decanol (specific activity 14 mCi/mmol) from I.C.N., Chemical and Radioisotope Division, Irvine, CA.

Self-Diffusion Measurements. The measurements of self-diffusion coefficients were performed by using the open-ended capillary-tube method essentially as described previously.⁷ Radioactive labeling was employed by using the isotopes ^{14}C for decanol, ^{22}Na for sodium ions, ^{36}Cl for chloride counterions, and ^{82}Br for bromide counterions. ^{14}C , ^{36}Cl , and ^{82}Br are β emitters, and radioactivity measurements were then performed by transferring the capillary contents into a liquid scintillator solution (Instagel Packard). ^{22}Na , which is a γ emitter, could be measured directly in the capillaries. ^{82}Br has a half-life of 35 h, making it necessary to take into account the decrease in radioactivity during the course of the diffusion (~ 48 h for the counterions and ~ 150 h for decanol). The reported self-diffusion coefficients have an estimated error of 2% and are averages of four to eight separate measurements. All diffusion measurements were performed at 306 ± 0.1 K.

NMR Measurements. ^{35}Cl quadrupole relaxation (obtained from NMR line widths) studies were performed on a modified Varian XL-100-15 pulsed spectrometer working in the Fourier transform mode using an external lock. A variable temperature control unit was used to control the temperature of the precooled (methanol/solid carbon dioxide) N_2 gas flow in which the sample was situated in the NMR probe. The temperature of the sample (12-mm i.d.) was determined by using a mercury thermometer before and after running each experiment. Transverse relaxation rates, T_2^{-1} ($=\pi\Delta\nu_{1/2}$), were obtained from the line width at half-height ($\Delta\nu_{1/2}$) of the resonance signal. ^{35}Cl quadrupole splittings and ^{81}Br quadrupole relaxation were studied at 25.0 MHz on a home-built Fourier transform spectrometer equipped with an Oxford Instruments 6-T wide-bore superconducting magnet. The temperature of the sample was held constant at 301 ± 1 K by a stream of dry thermostated N_2 gas. Quadrupole splittings were measured as the distance between adjacent peaks in the spectra. ^1H NMR spectra were obtained on a Jeol MH-100 spectrometer.

Results and Discussion

Self-Diffusion Measurements. Self-diffusion coefficients were measured for Cl^- , Br^- , Na^+ , and decanol in C_{16} TAB, C_{16} TAC, and their mixtures at three total surfactant concentrations, ~ 5 , ~ 10 , and $\sim 15\%$. Small concentrations of sodium chloride or sodium bromide together with decanol were added to the solutions for the following reasons: (i) The measurements on decanol enable the

micelle self-diffusion coefficient to be measured since decanol will partition almost completely into the micelles. This value is required for estimates of β (see below). (ii) The diffusion measurements on sodium ions provide a check on the magnitude of possible changes associated with increasing surfactant composition that are additional to ion binding. This will include micelle excluded volume effects.

The surfactant concentrations chosen are those where C_{16} TAB alone is known to form spherical micelles ($\sim 5\%$), rod micelles (15%), and the transition region (10%).^{3,6} The presence of electrolyte and uncharged amphiphiles such as decanol does promote the formation of rod micelles in other systems, and would be expected to do so here.^{18,19} However, the effects will be small, since even at 5% surfactant the "free" electrolyte concentration is $> 10^{-2}$ M due to counterions plus free monomers, and this is far larger than the concentration of added electrolyte. Also, the highest concentration of added decanol in the micelles is at least an order of magnitude lower than the surfactant concentration. That its effect is small is seen by comparison of measured diffusion coefficients at 5% surfactant with those from other systems.

The degree of counterion association (binding) to micelles (β_X) for species X is calculated as follows. (An alternative definition of β has been used in previous papers.)^{7,8} The measured diffusion coefficient (D_X) is an average of the diffusion of free and micellar-bound species, i.e.

$$D_X = P_f D_{X,f} + P_b D_{X,b} \quad (1)$$

(where subscripts f and b refer to free and micelle-bound states, and P is the population fraction of a particular state). It is easy to show that

$$\beta_X = \frac{C_{X,b}}{C_X} = \frac{D_{X,f} - D_X}{D_{X,f} - D_{X,b}} \quad (2)$$

(The total concentration and micelle-bound concentration of species X are C_X and $C_{X,b}$ respectively.)

Experimental values of the various diffusion coefficients are listed in Tables I–III together with values of β_X calculated from eq 2. The value of $D_{X,b}$ was taken equal to D of decanol measured for the particular solution. Measured values of diffusion coefficients for free ions were the following: $D_{\text{Na}} = 1.51 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (NaCl solution); $D_{\text{Cl}} = 2.28 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (NaCl solution); $D_{\text{Br}} = 2.25 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (NaBr solution).

The results in Tables I–III for Br^- diffusion in C_{16} TAB solutions are in general agreement with previous results^{16,17} apart from the values at 15% concentration. Here our value is similar to that obtained previously¹⁶ but is $\sim 10\%$ lower than the value of Smith.¹⁷ His suggestion¹⁷ that this discrepancy is due to the effect of high solution viscosity on our measurements is not consistent with the observation of a much larger Cl^- diffusion coefficient in a solution having almost the same composition (Table III).

Before discussing the magnitudes of the β_X values, it is worthwhile to indicate some difficulties with this technique for the determination of absolute values. First, we have ignored the effects of micelle excluded volume. The values of D_{Na} decrease by up to $\sim 25\%$ at 15% surfactant concentration. (Comparable effects in co-ion diffusion have been observed for several other systems.) This presumably is because they are excluded from the micelle core and, additionally, from a significant region adjacent to the positively charged surfactant head groups. The effect will be smaller for the counterions but will still be significant and will result in smaller values of $D_{X,f}$. An effect of 15%

TABLE I: Self-Diffusion Coefficients (D) and Degree of Counterion Association (β) for C_{16} TAB/ C_{16} TAC Mixtures (ca. 5% Concentration, 306 K)

% C_{16} TAC	[C_{16} TAC], mol kg ⁻¹	% C_{16} TAB	[C_{16} TAB], mol kg ⁻¹	$10^{-5}D_{Cl}$, cm ² s ⁻¹	β_{Cl}	$10^{-5}D_{Br}$, cm ² s ⁻¹	β_{Br}	$10^{-5}D_{decanol}$, cm ² s ⁻¹	$10^{-5}D_{Na}$, cm ² s ⁻¹	η , cP
4.75	0.156	0	0	0.942	0.617			0.11		
4.74	0.155	0	0			0.447	0.839	0.101	1.346	1.090
3.21	0.105	1.49	0.043	0.994	0.580			0.061	1.38	1.091
3.40	0.112	1.46	0.041			0.486	0.806			1.11
2.54	0.0835	2.44	0.0705	1.004	0.595			0.135	1.334	1.09
2.42	0.0775	2.42	0.0698			0.520	0.818			
1.94	0.0638	2.93	0.0846	1.105	0.530			0.065	1.40	1.163
2.03	0.0674	3.58	0.104			0.545	0.780			
1.30	0.0428	3.62	0.104	1.003	0.574			0.058	1.28	1.057
1.42	0.0450	3.50	0.101			0.573	0.765	0.065		1.092
0	0	4.89	0.141	1.233	0.473					
0	0	3.6	0.102			0.655	0.730			
0	0	6.8	0.2			0.630	0.741			

TABLE II: Self-Diffusion Coefficients (D) and Degree of Counterion Association (β) for C_{16} TAC/ C_{16} TAB Mixtures (ca. 10% Concentration, 306 K)

% C_{16} TAC	[C_{16} TAC], mol kg ⁻¹	% C_{16} TAB	[C_{16} TAB], mol kg ⁻¹	$10^{-5}D_{Cl}$, cm ² s ⁻¹	β_{Cl}	$10^{-5}D_{Br}$, cm ² s ⁻¹	β_{Br}	$10^{-5}D_{decanol}$, cm ² s ⁻¹	$10^{-5}D_{Na}$, cm ² s ⁻¹	η , cP
9.60	0.332	0	0	1.014	0.566					
12.34	0.440	0	0			0.480	0.803	0.045	1.26	1.858
7.63	0.263	1.18	0.0523	1.014	0.568			0.052	1.29	1.55
7.95	0.276	1.99	0.0605			0.495	0.798			
5.72	0.201	5.51	0.170	1.032	0.561			0.056	1.23	1.52
4.84	0.167	4.84	0.147			0.542	0.778	0.044		
4.81	0.166	5.45	0.166							
3.84	0.134	5.92	0.180	1.072	0.542					
3.84	0.133	5.75	0.1745			0.605	0.748		1.31	1.38
2.55	0.0886	7.31	0.222	1.113	0.521					
2.45	0.0849	7.34	0.223			0.603	0.746	0.042	1.203	1.575
0	0	9.78	0.297	1.219	0.475			0.045		
0	0	8.60	0.258							1.76
0	0	9.866	0.300			0.615	0.741			

TABLE III: Self-Diffusion Coefficients (D) and Degree of Counterion Association (β) for C_{16} TAC/ C_{16} TAB Mixtures (ca. 15% Concentration, 306 K)

% C_{16} TAC	[C_{16} TAC], mol kg ⁻¹	% C_{16} TAB	[C_{16} TAB], mol kg ⁻¹	$10^{-5}D_{Cl}$, cm ² s ⁻¹	β_{Cl}	$10^{-5}D_{Br}$, cm ² s ⁻¹	β_{Br}	$10^{-5}D_{decanol}$, cm ² s ⁻¹	$10^{-5}D_{Na}$, cm ² s ⁻¹	η , cP
13.35	0.481	0	0							1.98
14.97	0.55	0	0	0.997	0.573					
14.7	0.538	0	0			0.498	0.792	0.0392	1.18	2.204
14.99	0.551	0	0					0.0403		
11.72	0.432	3.44	0.111	1.011	0.568					
11.27	0.397	4.08	0.132			0.528	0.781	0.0457	1.16	2.307
11.18	0.393	5.36	0.175					0.035		
7.03	0.257	7.53	0.242	1.078	0.533				1.13	
9.18	0.351	9.18	0.308			0.555	0.761			2.704
7.65	0.288	9.29	0.307					0.024		
5.79	9.212	8.95	0.288	1.048	0.551					
5.13	0.186	8.60	0.273			0.591	0.752	0.0429	1.17	2.06
3.56	0.131	11.25	0.362	1.068	0.535				1.12	
3.41	0.125	11.21	0.360			0.622	0.728			2.853
3.48	0.130	12.94	0.425					0.015		3.57
1.70	0.0625	13.23	0.427	1.114	0.516					6.71
1.76	0.0643	12.78	0.410			0.614	0.734	0.0313	1.12	
1.69	0.0625	13.84	0.449					0.011		
0	0	14.48	0.465	1.027	0.554				1.029	8.78
0	0	12.89	0.462			0.554	0.760			
0	0	13.09	0.471					0.017		

(which seems to be a reasonable upper limit) would reduce β_X values of 0.8 and 0.6 to 0.76 and 0.53, respectively.

A more serious criticism concerns the assumption that $D_{X,b}$ is equal to the micelle (decanol) diffusion coefficient. If the lifetime of an ion in the bound state (τ_b) is long, compared to the time for a surfactant ion/counterion complex to diffuse around the micelle, then the assumption is valid. If the bound ion exchanges between adjacent "binding sites" rapidly, but still remains associated with

the micelle for a long time compared with the time taken for an ion to diffuse around the micelle surface, then the assumption is also valid. However, if the τ_b is short, and the bound ion moves rapidly across the micelle surface, compared to the rate of the diffusion of the micelle, then the assumption is not valid. The result will be $D_{X,b} > D_{decanol}$ and values of β_X will be too low.

The lifetime of a surfactant molecule in a micelle is $\sim 10^{-6}$ s or larger, depending on chain length.⁹ It is likely

that the lifetime of a counterion would be much shorter than this because the association is far weaker. If $\tau_b \sim 10^{-8}$ s, with $D_{\text{decanol}} = 5 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ the micelle moves ~ 17 Å in this time. However, if the ion diffuses over the surface with a higher diffusion coefficient, it will move a proportionally larger distance. With a lateral diffusion coefficient of $D_{x,b} = 2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, the distance is 34 Å, which is less than half the circumference of a spherical C_{16}TAB micelle. The actual distance moved by the ion will be a combination of both diffusion processes, and neglecting the effect of ion diffusion at the surface of the micelle obviously will result in values of β_x that are too low.

The results in Tables I–III show that $\beta_{\text{Cl}} < \beta_{\text{Br}}$ at all surfactant concentrations, indicating that Br^- ions bind more strongly to the micelles than Cl^- ions in both rod-shaped and spherical micelles. The decrease in both β values with increasing proportions of C_{16}TAB is in agreement with this. In solutions containing a high proportion of C_{16}TAC , a larger proportion of Br^- ions will be bound than in solutions containing a high proportion of C_{16}TAB . Again, for β_{Cl} since addition of Br^- ions displaces Cl^- ions, the value decreases with increasing C_{16}TAB content at constant total surfactant concentration. The β_{Cl} values are generally smaller at the three overall surfactant concentrations, indicating that the degree of counterion association is not related to micelle shape. (That rod micelles do form at high surfactant concentrations is shown by the increase in viscosity and reduction in D_{decanol} values.) This conclusion is in agreement with that of Smith.¹⁷ Thus measurements on counterion diffusion can give no information about micelle size distributions in $\text{C}_{16}\text{TAC}/\text{C}_{16}\text{TAB}$ mixtures.

Other estimates of β_x for C_{16}TAC and C_{16}TAB solutions are those of Price and Hall using a novel electrochemical method.²⁰ The method involves measurements of counterion and co-ion electrode potentials in surfactant/electrolyte solutions and uses theoretical equations analogous to the Donnan equation describing the equilibrium between a polyelectrolyte and salt across a semipermeable membrane. These authors obtain values of β_{Cl} and β_{Br} of ~ 0.78 and ~ 0.84 , respectively. The values of β_{Br} show no change at the rod/sphere transition in micelle shape. The electrochemical technique measures the excess concentration of ions associated with the micelle at all distances from the micelle, and some of these ions will have diffusion coefficients almost the same as those of free ions. Nevertheless these electrochemical measurements give results that are in agreement with our general conclusions. This agrees with the theoretical results of Gunnarsson et al.²¹ based on solutions of the Poisson–Boltzmann equation giving closely the same β values for transport and thermodynamic measurements.

NMR Measurements. Theory. The factors that determine line widths of Cl and Br resonances for surfactant systems have been discussed in detail previously.^{3,6,12} The line widths obtained from first-derivative spectra ($\Delta\nu_d$) or from absorption spectra ($\Delta\nu_{1/2}$) are related to the transverse relaxation rate (T_2^{-1}) by eq 3.

$$T_2^{-1} = \pi\Delta\nu_d 3^{1/2} = \pi\Delta\nu_{1/2} \quad (3)$$

The relaxation rate is dependent on (a) the distribution of counterions over different environments, (b) the time-dependent field gradients that the nuclei experience, and (c) the rate of change of the field gradients. Thus we may write eq 4, where P_i is the fraction of counterions in site

$$T_2^{-1} = K \sum_i P_i (\partial^2 V / \partial Z^2)_i^2 \tau_{ci} \quad (4)$$

i, $(\partial^2 V / \partial Z^2)_i$ is the field gradient characterizing this site,

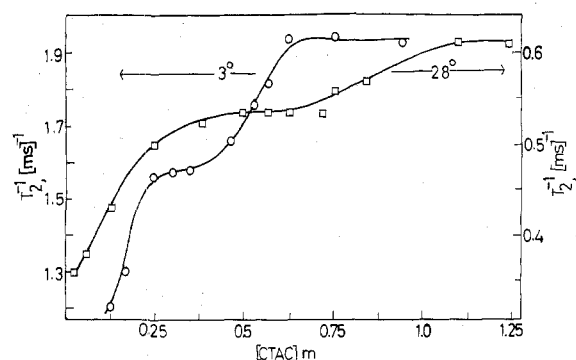


Figure 1. ^{35}Cl quadrupole relaxation rates (T_2^{-1} in ms^{-1}) of C_{16}TAC solutions as a function of the C_{16}TAC molality (m) at 28 (\square) and 3 $^\circ\text{C}$ (\circ).

and τ_{ci} is the correlation time of the field gradient time variation. The constant K is given by nuclear properties and is known for the nuclei considered here.²²

For proton NMR in micellar solutions, there are a number of different factors that determine the line width, and the theory can be complex.^{5,23–25} For the purpose of this study, we require only the fact that the sharp resonances observed for spherical micelles ($\Delta\nu_{1/2} < 5$ Hz) become broad on the formation of rod-shaped micelles ($\Delta\nu_{1/2} > 10$ Hz).^{5,24,25} This is because one correlation time determining proton relaxation is much larger for rod-shaped than for spherical micelles, since only part of the dipole–dipole interaction is averaged by motions (aggregate rotation or monomer lateral diffusion) around the cylinder axis for rod micelles.

Quadrupole splittings for ions in lyotropic liquid crystals have been discussed in detail elsewhere,^{12–15} and only a brief description will be given here. The splittings arise from a fast exchange between ions within ~ 1 – 3 Å of the micelle surface and those further distant from the surface. Ions at the surface have a splitting of magnitude $\Delta = \Delta_b$; those in the bulk have $\Delta = 0$. Thus if Δ_b is independent of variables such as composition of the micelle, then changes in Δ can be used to monitor changes in the surface concentration of ions, i.e.

$$\Delta = P_b \Delta_b$$

where P_b is the fraction of ions at the surface.

NMR Results. In previous reports,^{3,6} concerned with concentrations up to ca. 0.5 m , it has been shown that ^{35}Cl line widths (or T_2^{-1} values) are almost invariant (above 0.25 m) in C_{16}TAC solutions and $\text{C}_{16}\text{TAC}/\text{C}_{16}\text{TAB}$ mixtures while the ^{81}Br line widths show sharp increases on formation of rod micelles. (Below 0.25 m an increase in both ^{81}Br and ^{35}Cl line widths is observed which is related to a rearrangement of micelle-bound counterions just after micelles are first formed.) Figure 1 shows ^{35}Cl line widths as a function of C_{16}TAC concentration at 3 and 28 $^\circ\text{C}$. At 28 $^\circ\text{C}$ the micelles are spherical up to high concentration. However, at 3 $^\circ\text{C}$ the line widths start to increase at a much lower concentration (ca. 0.4 m) demonstrating an appreciable formation of rodlike micelles at low temperatures. This is confirmed by observations of marked viscosity increases and marked line broadenings in ^1H NMR spectra for C_{16}TAC solutions at low temperatures; however, even at 3 $^\circ\text{C}$ these effects are much smaller than for C_{16}TAB at ca. 30 $^\circ\text{C}$.

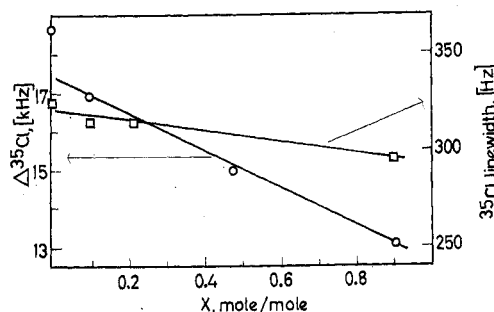
The effects of an additive in promoting rod micelle formation is shown in Table IV. The increase in proton line widths is clear evidence for the formation of rod micelles above 1.4% α -methylnaphthalene, and this is accompanied by an increase of $\sim 20\%$ in the ^{35}Cl line widths.

TABLE IV: Line Widths (Hz) of C₁₆TAC/ α -Methylnaphthalene (MeN) Solutions^a

C ₁₆ TAC, %	MeN, %	$\Delta\nu_{1/2}$ of ³⁵ Cl, Hz	$\Delta\nu_{1/2}$ of ¹ H(CH ₂) ₂ , ^b Hz	$\Delta\nu_{1/2}$ of ¹ H(NMe ₃) ₃ , ^c Hz
13.74	0	204	6.0	2.0
13.58	1.4	256	10.0	4.5
13.41	2.8	259	84	37
13.24	4.2	242	80	40
13.07	5.6	239	54	7.5

^a In D₂O, at ~35 °C (ambient probe temperature).^b Main alkyl chain resonance. ^c N-trimethyl resonance.TABLE V: ⁸¹Br Line Widths (kHz) in C₁₆TAB/Benzene Solutions^a

C ₁₆ TAB, %	benzene, %	⁸¹ Br line width, kHz
15.0	0	15.1
15.0	0.59	13.3
14.95	1.96	12.9
14.95	2.01	11.8
14.0	2.47	11.8

^a All solutions had high viscosity, indicating the presence of rod-shaped micelles.Figure 2. ³⁵Cl quadrupole splittings ($\Delta\nu$ in kHz) and ³⁵Cl line widths (in Hz) for the hexagonal phase of the C₁₆TAC-C₁₆TAB-H₂O system as a function of the molar ratio of Cl⁻ to Br⁻ at 28 °C. All samples contained 55% total surfactant and 45% water. (O) quadrupole splittings; (□) line width.

That the subsequent decrease may be real is shown by the behavior of the ⁸¹Br line widths in C₁₆TAB/benzene (Table V). Here the 50% increase in line widths over those of spherical micelles is decreased to 25%, although the high viscosity of solutions at all levels of benzene is an obvious indication that rod micelles are present.

Finally, we have measured ³⁵Cl line widths and quadrupole splittings for the hexagonal phase as a function of C₁₆TAB/C₁₆TAC composition (Figure 2). The line widths show almost no change, but the splittings show a definite decrease as the Br⁻ content is increased. In line with the theoretical expectation given above, we anticipate that the ³⁵Cl splittings will decrease if the proportion of Cl⁻ ions at the aggregate surface is reduced. This observation agrees with the conclusion from the self-diffusion measurements that Br⁻ ions bind preferentially to Cl⁻ ions.

It is more difficult to relate the observed line widths to ion binding. Since no change in the fraction of bound ions occurs at the rod/sphere transition, the change in line width is due either to an increase in the field gradient for the bound ions or to an increase in τ_{ci} , the correlation time for the time variation of the field gradient. In practice it is likely that the largest contribution to $\Delta\nu_{1/2}$ is given by a rather small fraction of ions close to the head groups. The slight changes in head-group geometry caused by the sphere/rod transition could result in changes in both

($\partial^2V/\partial Z^2$)_i and τ_{ci} . The changes in $\Delta\nu_{1/2}$ for Cl⁻ are smaller than those for Br⁻ because a smaller fraction of Cl⁻ ions are bound in this state than Br⁻ ions. The effect of aromatic solubilizates (Tables IV and V) is to displace some of these "tightly-bound" ions. The previously reported results for C₁₆TAB/C₁₆TAC mixtures are consistent with a picture where Cl⁻ and Br⁻ ions are bound to all micelles in the system, with a proportionally larger fraction of Br⁻ ions occupying the sites giving the larger contribution to $\Delta\nu_{1/2}$. This would result in the ³⁵Cl line widths being unaffected by the presence of rod micelles in 1:1 C₁₆TAC/C₁₆TAB mixtures.

Since there are only marginal energy differences between spherical and rod-shaped micelles, one can also imagine a situation with a considerable coexistence of the two types of micelles⁶ (or perhaps better a very broad micelle size distribution involving a considerable fraction of micelles with aggregation numbers of the order of 100). There would then be a preferential binding of bromide ions to both types of micelles (cf. the self-diffusion results) and also a preference of Br⁻ ions for binding to rods rather than spheres. An appreciable preference for binding to rods would result in β_{Br} values larger than those observed. Thus, in view of the small concentration dependence of β_{Br} for C₁₆TAB solutions and the high concentration for the sphere-to-rod transition, such a marked preference does not seem probable. However, it appears that the results are consistent also with a model involving a broad distribution of micelle size where spherical and rodlike micelles coexist and with a preferential binding of Br⁻ ions to the latter. It is not possible at present to choose reliably between the two models; this should best involve direct studies of micelle size distribution which is not straightforward.

Very recently, Almgren and co-workers reported fluorescence data for pyrene solubilized in C₁₆TAB/C₁₆TAC mixtures.²⁶ The fluorescence decays were fitted by a double exponential, with two different lifetimes and a varying intensity for the two curves. The two lifetimes were attributed to bromide-ion-rich rod micelles (short lifetime) and chloride-ion-rich spherical micelles (long lifetime). The lifetimes were of the order of $\sim 1 \times 10^{-7}$ – 2×10^{-7} s and differed at most by a factor of 2. In addition, the varying intensity of the two curves was attributed to the preferential solubilization of pyrene in rod micelles. This explanation is consistent with the second of our models above. However, the experimental results do deviate significantly from those calculated by assuming the presence of two types of micelles with invariant compositions. In addition the fit of the experimental data to a double exponential may not be a unique description; a distribution of lifetimes corresponding to a distribution of micelle compositions could be relevant, especially since the two lifetimes are not very different. Further fluorescence experiments, for example, with addition of NaCl or NaBr to surfactant solutions, might be helpful for distinguishing between the two possibilities.

Conclusions

Self-diffusion measurements on Cl⁻ and Br⁻ ions in C₁₆TAB/C₁₆TAC mixtures enable β_X values to be estimated, and these show that no dramatic change in ion binding occurs at the sphere/rod micelle shape transition. Bromide ions bind preferentially to chloride ions in both spherical and rod micelles. NMR measurements on chloride and bromide ions are consistent both with a single micellar species having both Cl⁻ and Br⁻ ions in the bound counterions being in a slightly more tightly bound state, and with an alternative model involving the coexistence

of spherical and rodlike micelles and a small specificity of Br^- for binding to the rods.

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References and Notes

- (1) (a) Faculté des Sciences, Montpellier; (b) Physical Chemistry 1, Lund; (c) Physical Chemistry 2, Lund; (d) Unilever Research, Port Sunlight.
- (2) F. Reiss-Husson and V. Luzzati, *J. Phys. Chem.*, **68**, 3504 (1964).
- (3) G. Lindblom, B. Lindman, and L. Mandell, *J. Colloid Interface Sci.*, **42**, 400 (1973).
- (4) U. Henriksson, L. Ödberg, J. C. Eriksson, and L. Westman, *J. Phys. Chem.*, **81**, 76 (1977).
- (5) J. Ulmius and H. Wennerström, *J. Magn. Reson.*, **28**, 309 (1977).
- (6) J. Ulmius, B. Lindman, G. Lindblom, and T. Drakenberg, *J. Colloid Interface Sci.*, **65**, 88 (1978).
- (7) B. Lindman and B. Brun, *J. Colloid Interface Sci.*, **42**, 388 (1973).
- (8) N. Kamenka, B. Brun, and B. Lindman, *Proc.—Int. Congr. Surf. Act. Subst.*, 7th, 1976, Sect. B, Part II, p 1019.
- (9) H. Wennerström and B. Lindman, *Phys. Rep.*, **52**, 1 (1979), and references therein.
- (10) J. C. Eriksson and G. Gillberg, *Acta Chem. Scand.*, **20**, 2019 (1966).
- (11) R. M. Bain and A. J. Hyde, *Symp. Faraday Soc.*, **5**, 145 (1971).
- (12) H. Wennerström, G. Lindblom, and B. Lindman, *Chem. Scr.*, **6**, 97 (1974).
- (13) G. Lindblom, B. Lindman, and G. J. T. Tiddy, *J. Am. Chem. Soc.*, **100**, 2299 (1978).
- (14) G. J. T. Tiddy, G. Lindblom, and B. Lindman, *J. Chem. Soc., Faraday Trans. 1*, **74**, 1290 (1978).
- (15) H. Wennerström, G. Lindblom, B. Lindman, and G. J. T. Tiddy, *J. Chem. Soc., Faraday Trans. 1*, **75**, 663 (1979).
- (16) N. Kamenka, H. Fabre, M. Chorro, and B. Lindman, *J. Chim. Phys.*, **74**, 510 (1977).
- (17) D. H. Smith, *J. Colloid Interface Sci.*, **68**, 70 (1979).
- (18) N. A. Mazer, G. B. Benedek, and M. C. Carey, *J. Phys. Chem.*, **80**, 1075 (1976).
- (19) D. E. Clarke and D. G. Hall, *Colloid Polym. Sci.*, **252**, 153 (1974).
- (20) T. J. Price and D. G. Hall, to be submitted.
- (21) G. Gunnarsson, B. Jönsson, and H. Wennerström, to be submitted.
- (22) B. Lindman and S. Forsén, "Chlorine, Bromine and Iodine N.M.R.", Springer-Verlag, Heidelberg, 1976.
- (23) H. Wennerström, *Chem. Phys. Lett.*, **18**, 41 (1973).
- (24) J. Ulmius and H. Wennerström, *J. Magn. Reson.*, **23**, 431 (1966).
- (25) E. J. Staples and G. J. T. Tiddy, *J. Chem. Soc., Faraday Trans. 1*, **74**, 2530 (1978).
- (26) M. Almgren, J. E. Löfroth, and R. Rydholm, *Chem. Phys. Lett.*, **63**, 265 (1979).

Cupric Ion-Selective Electrode and Inorganic Cationic Complexes of Copper

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The response of the solid-state, cupric ion-specific electrode toward some inorganic copper complexes was investigated by using E vs. pH titration curves. Different Nernst slopes were obtained depending on the assumptions made concerning the identity of the species being sensed by the electrode. Correspondence between slopes based on different assumptions and the theoretical slope and experimental slopes was used as a criterion for determining the species being sensed by the electrode. In this way it is shown that the electrode very probably responds not only to Cu^{2+} but also to CuOH^+ , $\text{Cu}_2(\text{OH})_2^{2+}$, and CuHCO_3^+ . At pH 8.3 and 9.0, cupric ion activities measured with this electrode would be determined too high by a factor of 10 and 40, respectively, relative to the calculated cupric ion activities, if no allowance were made for this lack of specificity.

Introduction

In aqueous systems that are free from interfering ions the solid-state cupric ion electrode is generally considered to respond specifically to the cupric ion activity. Because in simple acidic aqueous systems (i.e., distilled water solutions) the experimental slope of the Nernst equation for such an electrode has been found to be the same as the theoretical slope for a doubly charged ion, this type of electrode has therefore been used with increasing confidence over a wide pH range for the measurement of the cupric ion activity or the "free" cupric ion concentration in such diverse areas as kinetic studies, toxicity studies, and the determination of stability constants of copper complexes. For solutions more complex than copper in distilled water, such as natural waters, for example, the slope of the Nernst equation may be quite different from the theoretical slope, which has led to doubts about the specificity of the electrode.^{1,2}

In an aqueous solution of copper (in equilibrium with the atmosphere) there are a number of inorganic complexes of copper that will be formed unavoidably to a greater or lesser extent depending on the pH of the solution: Cu^{2+} , CuOH^+ , $\text{Cu}_2(\text{OH})_2^{2+}$, $\text{Cu}(\text{OH})_2^0$, $\text{Cu}(\text{CO}_3)_2^{2-}$, etc. If in addition some chelating agents such as EDTA, humic acids, etc., are present, the corresponding chelates with copper will be formed, but these chelates are known not to be

sensed by the ion-selective electrode³⁻⁵ and are not of interest in this investigation. Of the inorganic complexes that may be present in "distilled water solutions" of copper, only Cu^{2+} is generally assumed to be sensed by the cupric ion-selective electrode, but this has never been demonstrated conclusively in basic solutions where such complexes occur. Certainly, nothing can be proved in this regard by calibrating the electrode in the usual way of successively increasing the total copper concentration under otherwise fixed conditions, since an increase in the concentration of total copper causes an increase in the concentration of the various species in direct proportion to the total increase. On the other hand, if one maintains the total copper concentration constant and changes the pH, the influence of the copper species on the Nernstian slope is allowed to manifest itself.

The purpose of this investigation was to determine the Nernstian slope in three different ways and, from a comparison of these slopes with the theoretical slope, to deduce whether the solid-state, copper-selective electrode responds only to cupric ion or also to other inorganic cationic complexes of copper. To this end the following scheme and rationale was employed: (1) to establish first of all whether the electrode behaved normally under the conditions of the experiment by determining the slope from purely experimental data and without assuming the identity of the