J. Phys. Chem. 1993, 97, 10236–10244

Effect of Head-Group Size on Micellization and Phase Behavior in Quaternary Ammonium Surfactant Systems

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Received: April 13, 1993; In Final Form: July 12, 1993[●]

The micellization and phase equilibria in aqueous solutions of cationic quaternary ammonium bromide surfactants of the type alkyltrimethyl-, -ethyl-, -propy-, -butyl-, and -pentylammonium bromide have been investigated as a function of alkyl chain length, electrolyte concentration, and temperature. A large isotropic (micellar) phase is observed in triethyl- and tripropylammonium surfactants, which demixes into two conjugate phases on warming in the case of the alkyltributylammonium bromides. Liquid–liquid phase separation is also observed for tetradecyltripentylammonium bromide. Critical micelle concentrations are found to decrease with increasing hydrophobicity of the surfactant ion, but the free energy of micellization of tetradecyltributylammonium bromide is the same as that of tetradecyltrimethylammonium bromide over a range of temperatures. Some evidence is found for the formation of premicellar aggregates in tributylammonium surfactants at elevated temperatures, consistent with significant polydispersity and changing monomer concentrations observed previously. The results are discussed in terms of the hydrophobic and electrostatic contributions to the free energy of micellization, and some inferences are drawn regarding the nature of the interactions which give rise to phase separation.

Introduction

Lower consolute behavior, or spontaneous demixing of a micellar solution into dilute and concentrated conjugate phases on warming, has recently been reported for binary mixtures consisting of a certain ionic surfactant and water.[1,2] Prior to this, the only ionic surfactant systems known to exhibit lower consolute behavior all contained high concentrations of added electrolyte.[3,4] These micelles are all reported to be rodlike, or even flexible "worms", under the electrolyte conditions where they demix. While there have been only a limited number of investigations of such ternary systems, the electrolyte was always presumed necessary to suppress electrostatic repulsions between charged micelles thereby allowing an attractive interaction to dominate the behavior. The nature of this attractive potential is unknown. However, the existence of attractive intermicellar potential is well documented in the behavior of certain nonionic surfactants and also of some uncharged polymers in aqueous solution which also display lower consolute temperatures.[5–10]

The cationic surfactant dodecyltributylammonium bromide differs from the above case in that it phase separates without addition of electrolyte, and its micelles remain spherical or near spherical throughout its region of stability.[1] This work explores in further detail the parameters which govern the phase equilibria and particularly the lower consolute behavior of aqueous quaternary ammonium surfactant solutions. Head-group size, alkyl chain length, and electrolyte concentration and type are varied, and the effect on solution structure is examined. In addition, the micellization of quaternary ammonium surfactants with varying head-group size is examined to determine whether any of the effects causing the anomalous phase behavior are manifested in more dilute solution. The aim is to elucidate the mechanism of the microscopic attractive potential which causes macroscopic demixing. We begin by briefly reviewing what is known about micellar systems with lower consolute boundaries and recapitulating the important features of the interactions which underly this effect.

Lower Consolute Curves in Aqueous Surfactant Solutions. Lower consolute behavior in surfactant solutions is well documented in two situations: nonionic surfactants, either poly(oxyethylene)alkyl ethers or alkyldimethylamine oxides in water,[10–12] and cationic surfactants in concentrated electrolyte solutions.[3,4] The nonionic poly(oxyethylene) systems have been investigated in far greater detail than the ionics, but both classes exhibit several common features.

Scattering investigations manifest a strong low-angle component in both kinds of solution exhibiting lower consolute temperatures.[9] Historically this was ascribed to micelle growth with increasing temperature but is now widely associated with attractions between micelles. The existence of attractive interactions between poly(oxyethylene)alkyl ethers at elevated temperatures has been demonstrated convincingly by Claesson *et al.*[13] who directly observed the interaction between adsorbed surfactant films on mica. Changes in the hydration of the hydrophilic ethylene oxide moieties of nonionic surfactants with temperature is widely viewed as the cause of phase separation. This sits well with a general description of lower consolute behavior in which demixing arises from thermal dissociation of A–B dimers into immiscible phases concentrated in A and B.[14] In this model A and B do not mix ordinarily but do combine to form a dimer at low temperatures which is miscible with A and B in all proportions. This is one interpretation of the unique thermodynamics of lower consolute systems, that enthalpy (which necessarily opposes mixing in these systems) must dominate configurational entropy considerations, which always favor the formation of a mixed solution. Below a lower consolute boundary the system cannot be an ideal or regular solution—something exceptional is going on in the mixing process.

More recently, Lindman[15] has advanced a model based on conformational changes in the poly(oxyethylene) chain with changing temperature, from which a change in the dipole moment of the hydrophilic chain arises. This in turn leads to a decrease in the polarity or hydrophilicity of the surfactant and hence to phase separation. This approach differs from the direct H-bond approach associated with hydration models. Rather it presents a change in the nature of the solute molecule with temperature, giving rise to a changed A–B interaction.

All of these models for the microscopic, intermolecular interactions will be manifested in a scattering experiment as an *effective* attractive potential between micelles as the phase

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[●] Abstract published in *Advance ACS Abstracts*, September 1, 1993.

0022-3654/93/2097-10236$04.00/0

boundary is approached. Both nonionic surfactant–water and cationic surfactant–electrolyte solution phase boundaries typically have critical points in the vicinity of 1 wt % surfactant.[3-5] Kjellander[6,7] has argued persuasively that attractions between spherical micelles cannot give rise to the low observed critical concentrations but are a consequence of attractions between anisotropic micelles. He also showed that micelle growth alone is insufficient to cause phase separation. As ionic surfactants are also known to form long, cylindrical or wormlike micelles in concentrated electrolyte solution, this general description of the phase separation is entirely appropriate.

There has been much debate as to the effect of micelle growth near lower consolute boundaries, particularly for nonionic surfactants, and there is certainly evidence for the presence of anisotropic micelles near the critical point in many systems. Opinions as to the shape of nonionic micelles vary however from oblate spheroids,[16] to cylinders with varying degrees of flexibility.[5,17]

In ternary systems, cationic surfactant + water + electrolyte, experimental evidence favors long, cylindrical micelles. Such micelles are known to exist for many ionic surfactants at moderate salt concentrations and to grow with increasing ionic strength. Their phase equilibria are quite specific to the added anion,[3,4] prompting the notion that there is a separate adsorption effect which governs the electrostatic interactions between micelles.

In ionic surfactant–electrolyte solutions little is known about the attractive potential. Porte[3,4] has suggested an analogy with the (Flory–Huggins) phase separation of polymers in a poor solvent, based largely on the wormlike structure of ionic micelles at high ionic strength. It is not easy to envisage how this causes lower consolute behavior, unless "solvent quality" decreases as temperature rises. As with nonionic micelles, demixing must arise from changes in the relative magnitudes of solute–solvent and solvent–solvent interactions. The Flory–Huggins model of a constant interaction potential which competes with configurational entropy to cause phase separation on cooling therefore does not apply. Introduction of such a label to the phase separation does not in fact help us here, instead it deflects attention from the true issue of what mechanism gives rise to the attractions between ionic micelles in solution.

A New Class: Binary Ionic Surfactant–Water Mixtures. The cationic surfactant dodecyltributylammonium bromide, $C_{12}NBu_3Br$, has a lower consolute boundary with a critical point at 46 wt % and 58 °C in water (48 °C in D_2O).[1] The large head group of this surfactant makes it very unlikely to form anything but spherical micelles, unlike the systems mentioned above, so that shape and interaction effects can be distinguished. Small angle neutron scattering spectra show clear evidence of an attractive interaction potential between micelles in solution which increases with increasing temperature as the critical point is approached. A similar attractive component was also noted in the static and dynamic light scattering of solutions of the octyl analogue, C_8NBu_3Br, although phase separation in this solution was not reported.[18] The micelle aggregation numbers of both of these species are consistent with those of small, nearly spherical micelles at all concentrations and temperatures studied, consistent with expectations based on surfactant packing considerations.

To our knowledge there are no reports in the literature of phase separation in aqueous micellar solutions of trimethyl-, triethyl-, or tripropylammonium head groups with increasing temperature, although only the alkyltrimethylammonium salts have been examined in detail. (The sole case in which an anionic surfactant solution has been observed to phase separate with increasing temperature is that of tetrabutylammonium tetradecylsulfate, the behavior of which was recently detailed.[19,20] The critical concentration and temperature for this system appears to be above 80 wt % surfactant and approximately 10 °C (from Figure 5 of ref 19).)

The high critical concentration observed for the $C_{12}NBu_3Br$–water system is vastly different from those previously observed in micellar solutions. The strange behavior of $C_{12}NBu_3Br$ has been explained by the weakly cooperative nature of micellization in this system, leading to a monomer concentration which continues to increase above its critical micelle concentrations (cmc).[1,2] As the monomer surfactant concentration mounts it screens the electrostatic interaction, acting as a background electrolyte. When this reduces the Debye length to something of the order of molecular dimensions, attractive effects can dominate solution behavior and induce liquid–liquid immiscibility. This satisfactorily explains the location of the critical point at high surfactant content and also the stability of the dilute conjugate solution at a relatively concentrated 10 wt % surfactant in the phase-separated system. This is to be compared with surfactant concentrations in the dilute conjugate phase of nonionic systems, which are usually below the cmc of the surfactant (10^{-4}–10^{-2} M).

In this investigation we will examine the effect of head-group structure, alkyl tail, ionic strength, and temperature on the micellization and consolute behavior of cationic surfactant–water mixtures. Some similarities between surfactant + water and surfactant + concentrated electrolyte systems are noted and their consequences explored.

Experimental Section

Materials. Quaternary ammonium bromide surfactants were prepared by reaction of a 1-bromoalkane with the appropriate trialkylamine. The starting compounds 1-bromodecane (Fluka), 1-bromododecane (Aldrich), 1-bromotetradecane (Fluka), 1-bromohexadecane (Aldrich), triethylamine (Ajax), tri-*n*-propylamine (BDH), and tri-*n*-butylamine (Aldrich) were all AR grade and were used without further purification. All results reported for octyltrialkylammonium salts are taken from ref 18.

Potassium bromide and potassium chloride (Merck) were AR grade and were used as received.

Surfactant Preparation. Surfactants were prepared using a common synthesis for quaternary ammonium surfactants. Stoichiometric amounts of the reactants, the appropriate 1-bromoalkane, and trialkylamine were refluxed for approximately 24 h in acetonitrile. A total reactant to solvent ratio of around 1:2.2 was used. After reflux a yellow two-phase mixture remained. This mixture was rotary evaporated to remove the acetonitrile and then freeze dried to produce a solid. The solid product was then recrystallized from dry ether (dried over sodium) 1–3 times until all of the impurity had been removed. The pure product was then freeze dried to remove water. Since many of the products were hygroscopic, they were handled under nitrogen and stored under vacuum following freeze drying.

Tetradecyltripentylammonium bromide ($C_{14}NPe_3Br$) proved to be very easy to produce by this method. It gave, after purification, around 40% yield. The smaller head groups, however, were less cooperative and yielded less of the pure product.

Tetradecyltributylammonium chloride was prepared from the bromide salt in methanol/water (1:5 v/v) solution by ion exchange using Amberlite IRA-400 (Cl) resin. The methanol/water solution was employed to avoid the presence of micelles which would inhibit ion exchange. The eluant was then rotary evaporated to produce a yellow solid, indicating some decomposition of the product. This was subsequently recrystallized twice from dry ether to yield the pure chloride salt.

The purity of these surfactants was checked by proton NMR, taken on a Bruker AC200F FT-NMR in dichloromethane-d_2. Comparison of the surfactant spectra with that of the starting products showed neither residual reactants nor water remained at a detectable level, estimated as 1% or less.

Critical Micelle Concentrations (cmc's). Critical micelle concentrations were determined by bromide ion selective electrode, from the change in the fluorescence spectrum of pyrene accompanying micellization,[21] by surface tension, or by conductivity.

Fluorescence emission spectra of pyrene-containing solutions were recorded on a Perkin-Elmer LS-50 spectrofluorometer under excitation at 275 nm. The intensities of the first and third vibronic bands were measured, and their ratio was used as a sensitive probe of the average environment (aqueous or micellar) of the pyrene.

The surface tensiometer used consisted of a platinum du Nouy ring suspended by wire from a Mettler analytical balance above a glass sample dish connected to a stepper motor. The du Nouy ring was rinsed with methanol and then flame dried between measurements. The ring was immersed in the test solution and then slowly raised through the interface until a maximum apparent mass was measured. The method described by Huh and Mason[22] was then employed to calculate the surface tension. A water-jacketed sample beaker was used to control the sample temperature.

A Wayne Kerr Autobalance Universal Bridge B642 was used to determine surfactant solution conductivities. Conductivity measurements were facilitated by placing the sample container in a thermostated water bath. A temperature variance of no greater than 1 °C was observed throughout a run.

Light scattering experiments on $C_{14}NPe_3Br$ solutions were preformed by Mr. Jean-Pierre Dalbiez at the Centre d'Etudes Nucléaires de Saclay, France. Two temperatures, 20 and 60 °C, were studied, using an argon-ion laser (Spectra Physics SP 165 Model) and a K7025 Malvern digital correlator. The samples were centrifuged at 6000 RPM for 5 min. One set of samples was filtered with a Millex-GS Millipore 0.22-μm system before centrifuging, while the other set were left unfiltered. The experimental method used was similar to that described by Drifford *et al.*[18]

Micellar Surface Potentials. Previous work has established that a prototropic moiety at an interface has a pK_a which depends on the electrostatic potential of the interface.[23] The probe used in this study was 4-heptadecyl-7-hydroxycoumarin. The coumarin dye is amphiphilic, having a charged head group in its basic form and a long hydrophobic tail. NMR studies have shown that the average residence for the prototropic moiety is in the plane of the surfactant head groups in a micelle.[24] This dye has been well characterized in micellar systems.[23,25] The basic form of the coumarin is fluorescent around 446 nm when excited by light of 366 nm. The fluorescent intensity is thus proportional to the amount of unprotonated dye at the interface.

If α is the fraction of unprotonated dye, then

$$\alpha = \frac{I - I_{HX}}{I_X - I_{HX}} \tag{1}$$

where I is the intensity measured at a certain pH, I_{HX} is the fluorescence of the fully protonated dye (minimum), and I_{X^-} is the (maximum) fluorescence of the conjugate base. By using the Henderson–Hasselbach equation,[23]

$$\begin{aligned} pK_a &= pH - \log_{10}\left(\frac{[X^-]}{[HX]}\right) \\ &= pH - \log_{10}\left(\frac{\alpha}{1-\alpha}\right) \end{aligned} \tag{2}$$

a plot of $\log\{\alpha/(1-\alpha)\}$ against pH allows the pK_a to be determined. Comparison of pK_a values in neutral and charged micelles is then used to determine the micelle surface potential, ψ_0, using

$$pK_a = pK_a^0 - \frac{F\psi_0}{RT} \tag{3}$$

where p$K_a{}^0$ is the pK_a of the indicator solubilized in uncharged micelles. In this work octa(ethylene glycol)-*n*-dodecyl ether was used as the neutral reference.

TABLE I: Critical Micelle Concentrations (mol dm^{-3}) of Quaternary Ammonium Surfactants Determined by Several Methods

	head group (m)			
tail length (n)	methyl (1)	ethyl (2)	propyl (3)	butyl (4)
8	0.34^a	0.28^a	0.22^a	0.15^a
10	$6.5 \times 10^{-2\,b}$			
12	$1.44 \times 10^{-2\,b}$	$1.4 \times 10^{-2\,b}$		$4.8 \times 10^{-3\,c}$
		$1.36 \times 10^{-2\,e}$		
14	$3.6 \times 10^{-3\,d}$	$3.2 \times 10^{-3\,b}$	$2.1 \times 10^{-3\,b}$	$1.5 \times 10^{-3\,e}$
	$3.7 \times 10^{-3\,e}$	$2.6 \times 10^{-3\,a}$	$2.1 \times 10^{-3\,h}$	$1.3 \times 10^{-3\,f}$
		$3.0 \times 10^{-3\,e}$		$1.2 \times 10^{-3\,e}$
16	$9.0 \times 10^{-4\,a}$	$7.3 \times 10^{-4\,e}$	$4.6 \times 10^{-4\,e}$	$2.7 \times 10^{-4\,f}$
			$5.7 \times 10^{-4\,h}$	$2.0 \times 10^{-4\,g}$
				$2.7 \times 10^{-4\,e}$

[a] By bromide ion selective electrode, from ref 21. [b] By conductivity, from ref 24. [c] By conductivity, from ref 1. [d] By bromide ion selective electrode, from ref 24. [e] By conductivity, this work. [f] By pyrene fluorescence, this work. [g] By bromide ion selective electrode, this work. [h] By surface tension, ref 23.

A Perkin-Elmer LS-50 Luminescence Spectrophotometer was employed to record fluorescence spectra. A Radiometer Ionmeter pH meter was used to measure pH with a standard calomel electrode providing a reference. The outer chamber was filled with tetraethylammonium chloride and the inner chamber of the reference electrode filled with saturated KCl solution. This system was calibrated using two Radiometer buffer solutions, bracketing the pH values used to carry out the titration.

Phase Equilibria. Phase boundaries were detected by visual observation of the clouding of the isotropic solution phase on warming. Temperatures were oscillated slowly through the phase boundary until reproducible.

Results

Several trends are evident in the micellization and phase behavior of quaternary ammonium surfactants with head-group sizes between trimethyl and tributyl, as described below. However, the properties of tetradecyltripentylammonium bromide were anomalous, and this compound is discussed in a separate section at the end of this paper. The effect of head-group size on the dilute solution behavior—critical micelle concentrations, micelle surface potential, the counterion binding—are presented first, after which the phase equilibria are discussed.

Micellization. Critical micelle concentrations (cmc's) at 20 °C for a set of $C_nH_{2n+1}N(C_mH_{2m+1})_3Br$ surfactants are listed in Table I for surfactants with n = 8, 10, 12, 14, and 16 and m = 1–4. Data obtained in this investigation using a number of techniques is shown together with results from the literature,[1,18,26,27] and good agreement is obtained for most systems.

It is evident from Table I that, for a given surfactant head group, the cmc decreases with increasing length of the alkyl tail, as is usually observed. In addition, as the size of the head group increases for a particular tail length, the cmc also decreases. The conventional interpretation of the chain-length dependence of the cmc is in terms of the hydrophobic part of the free energy of micellization, *i.e.*, the change in free energy due to the transfer of a CH_2 moiety from water into the hydrocarbonlike environment of the micelle core. Mukerjee[28] first showed that it was necessary in this interpretation to account for the contribution of the counterion to the micellization process. This is briefly recapitulated below.

Within the mass-action model of micellization, a micelle is conventionally regarded as a kinetic unit composed of N surfactant ions and C counterions. Micelle formation is then described by the following equilibrium

$$N\mathrm{RNR'}_3{}^+ + C\mathrm{Br}^- \rightleftharpoons \mathrm{micelle}^{(N-C)+} \tag{4}$$

TABLE II: Fractional Counterion Association Values for $C_nN(C_m)_3Br$ Micelles in Aqueous Solution, Determined by Conductivity Unless Otherwise Noted

	head group			
alkyl chain	methyl	ethyl	propyl	butyl
octyl	0.65[a]	0.60[a]	0.56[a]	
dodecyl	0.77	0.70		0.61
tetradecyl	0.74, 0.60	0.65	0.54, 0.60	0.54
hexadecyl	0.84	0.65	0.66	0.67

[a] Bromide ion selective electrode, ref 18.

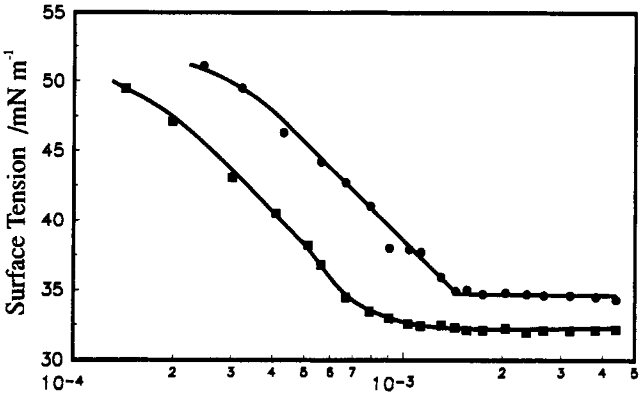

Figure 1. Surface tension versus log concentration of $C_{14}NBu_3Br$ at (●) 22 and (■) 65 °C.

The cmc is related to the free energy of micellization via

$$\Delta G_{\text{mic}}{}^{\circ} = (1 + \beta)RT\ln(\text{cmc}) \qquad (5)$$

where $\beta = C/N$ is the fraction of bound counterions per micellized surfactant monomer.

This model can also be used to obtain β, using the relationship

$$\ln(\text{cmc}) \simeq \frac{\Delta G_{\text{mic}}{}^{\circ}}{RT} - \beta\ln(\text{cmc} + c_{\text{salt}}) \qquad (6)$$

provided the dependence of the cmc on the concentration of added electrolyte, c_{salt}, is known. An alternative route to obtaining β is from conductivity results, although this method neglects the mobility of the charged micelles. We have used both methods in this work with reasonable agreement, and β values obtained for all of the surfactants used are listed in Table II. As the head-group size of the surfactant increases and the surface charge density of the micelle decreases, the degree of counterion condensation also decreases.

Surface tension results, shown in Figure 1, yield a molecular cross-sectional area for $C_{14}NBu_3Br$ at the air–solution interface of 88 Å^2/molecule at 22 °C. This value is somewhat smaller than the area/molecule of 120 ± 15 Å^2 previously determined in $C_{12}NBu_3Br$ micelles from small-angle scattering, possibly due to the different packing of the tributylammonium groups around a spherical micelle. Nevertheless both values are substantially larger than is typically reported for ionic surfactants (approximately 65 Å^2/molecule) and indicate a steric contribution to the molecular areas and a decrease in the micelle surface charge density.

This is also supported by measured micelle surface potentials for surfactants of differing head-group size. Surface potentials determined from titration of micelle-bound 4-heptadecyl-7-hydroxycoumarin and derived surface charge densities[29] for 0.050 M surfactant solutions are listed in Table III. The result of 138 mV for $C_{16}NMe_3Br$ agrees well with the literature,[23] and increasing head-group size decreases the magnitude of the surface potential and surface charge density. Note that the calculated surface charge density does not correspond to the surface density of head groups. This is because the probe titration result includes the effect of any adsorbed counterions.

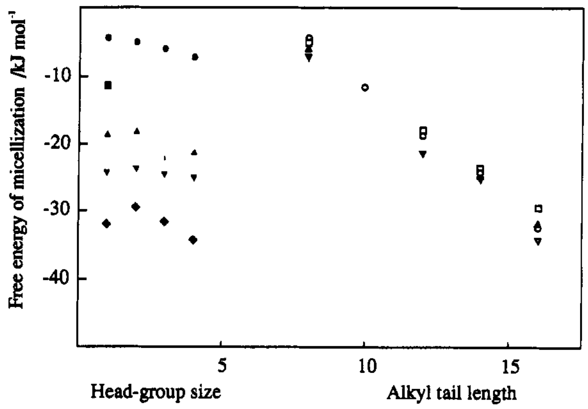

Figure 2. Variation of the standard free energy of micellization, $\Delta G_{\text{mic}}{}^{\circ}$, of quaternary ammonium surfactants with alkyl tail length, and head-group size for trialkylammonium moieties. Head-group size effects: ●, octyl; ■, decyl; ▲, dodecyl; ▼, tetradecyl; ◆, hexadecyl chains. Chain length effects: ○ trimethylammonium; □, triethylammonium; △, tripropylammonium; ▽, tributylammonium head group sizes.

TABLE III: Dependence of Micelle Surface Potential on Head-Group Size

surfactant	surface potential/ ±5 mV	surface charge density/ μC m^{-2}
$C_{16}NMe_3Br$	138	0.23
$C_{16}NEt_3Br$	124	0.19
$C_{16}NPr_3Br$	115	0.15
$C_{14}NBu_3Br$	89	0.12

The free energy of micellization may be regarded as consisting of hydrophobic, interfacial tension, and electrical contributions. A reductionist approach is then to write $\Delta G_{\text{mic}}{}^{\circ}$ as

$$\Delta G_{\text{mic}}{}^{\circ} = g_{\text{hp,tail}} + g_{\text{hp,head}} + N\gamma a_0 + g_{\text{elec}} \qquad (7)$$

where γ is the micelle–solution interfacial tension, a_0 the area per molecule, and N the aggregation number; the various g terms describe the free energy of transferring a hydrophobic moiety of the tail or head group from water into the micelle and the free energy of generating the electrical double layer surrounding the micelle.

The fractional contribution per CH_2 group in the hydrophobic tail to the free energy of micellization thus may be obtained for a fixed head-group size from eq 6 by equating it with eq 4. The appropriate plot is shown in Figure 2. From this we have calculated an incremental free energy change of micellization of 3.18 ± 0.11 kJ (moles of CH_2)$^{-1}$ in good agreement with other determinations.[30] This value is independent of the size of the head group. As we have only used alkyl chains of eight or more carbons, the initial and final environments of the methylenes should be only marginally affected by the state of the micelle surface, and independence of head group type is unsurprising.

Of more interest to the present study is the variation of the cmc, or rather $\Delta G_{\text{mic}}{}^{\circ}$, with the length of the alkyl arms about the charged nitrogen. It has previously been established that the area occupied per surfactant at the micelle–solution interface increases as the head-group chain length increases,[26] and it is clear from Table II that the degree of counterion binding also varies considerably. The contribution of CH_2 groups in the head-group region to $\Delta G_{\text{mic}}{}^{\circ}$ may be obtained from the variation of the cmc with head-group size, again including the effect of fractional ionization. The results of this are also shown in Figure 2. Here, however, no simple linear relationship is apparent. Although the cmc decreases with increasing head-group size, this is offset by decreasing β. The net effect of additional CH_2 groups around the nitrogen is far smaller than that of addition to the tail. For the trimethyl-, triethyl, and tripropylammonium head groups the

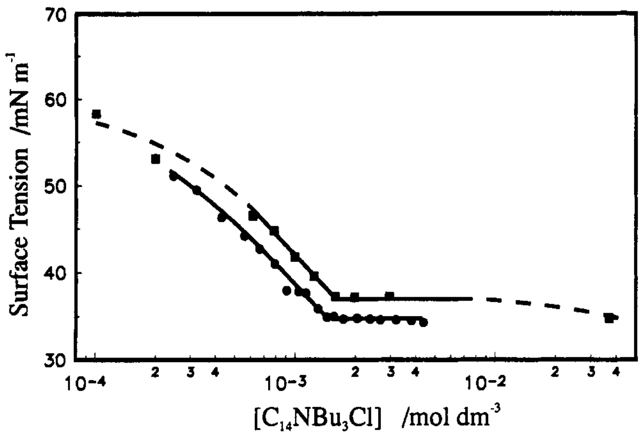

Figure 3. Surface tension versus log concentration of $C_{14}NBu_3Cl$ (■). Also shown for comparison is $C_{14}NBu_3Br$ (●).

$\Delta G_{mic}°$ are all the same within experimental uncertainty, and it is only in the tributyl case that a significant depression of $\Delta G_{mic}°$ occurs. (The same has been observed for the series of alkyldodecyldimethylammonium bromides.[26] The cmc changes with head-group size, but $\Delta G_{mic}°$ is independent of the length of the alkyl group up to around C_4.)

It is clear from Figure 2 that the effect of additional methylenes in the head-group region is nothing like that in the core of the micelle. In this situation the interfacial free energy of the micelle is affected through steric interactions between neighboring head groups, a change in the micellar surface charge density, and also by changes to the packing of the alkyl tails. The "hydrophobic" component arising from dehydration of alkyl groups, which should favor micellization, is lost among the interfacial effects for methyl through propyl arms and only shows itself with butyl groups. The free energy change upon going from *tri*propyl to *tri*butyl is approximately 3 kJ mol^{-1}. This is much less per CH_2 than for transfer to the micelle core, but its closeness to the alkyl chain value raises the possibility that *one* of the butyl moieties may bury itself partially into the micelle core. Molecular models confirm that butyl groups are just large enough to allow this conformation.

The micellization of tetradecyltributylammonium chloride is close to that expected from results for trimethylammonium salts.[31,32] Room temperature critical micelle concentrations were measured by both conductivity and surface tensiometry. The surface tension curve is shown in Figure 3, and the results summarized in Table IV. Values of the cmc determined by the two methods agree well for the bromide salt, and although there is some discrepancy for the chloride, the agreement is reasonable. Notice that the areas per molecule and degrees of counterion binding are essentially equal for the two salts. The equal molecular areas arise from the steric effect of the butyl groups surrounding the charged nitrogen center. These force the head groups to sit further apart than they would if electrostatic interaction were dominant, as is the case in most ionic surfactants. As a result, the equilibrium head-group area is independent of counterion type, and we would anticipate that micelle aggregation numbers would also be independent of the counterion. There may still be a discrimination in counterion binding between chloride and bromide; however, it is at the limit of resolution of the measurement and is certainly less than has been reported for alkyltrimethylammonium salts. These have β values of 0.61 and 0.77 for chloride and bromide, respectively.[32,33] One would expect that specificity in counterion binding arises from intimate contact between the micelle surface and counterions, whereas the measured β includes some ions from the diffuse layer which remain electrokinetically associated with the micelle. As the surface charge density is lowered, the concentration of counterions at the interface is similarly lowered and hence the opportunity for a discriminating interaction reduced, leading to a greater contribution of the diffuse layer charge to the overall measured β.

In all of this alkyltrimethyl-, -triethyl-, and -tripropylammonium surfactants all display similar behavior, typical of ionic micelles. The alkyltributylammonium bromides deviate slightly from expectation, probably due to the bulkiness and hydrophobicity of the head group. Nothing is so far evident in the room temperature behavior which could lead to phase separation on warming.

It was noted in ref 1 that the cmc of $C_{12}NBu_3Br$ was not as abrupt as usual for ionic surfactants, and it was suggested that micellization of this species is a gradual process. This was based on the difficulty in locating the cmc using molar ionic conductivity and also on the increasing monomer concentrations above the cmc. Here we have used the fluorescence spectrum of pyrene in $C_{14}NBu_3Br$ solutions to determine the cmc, as it is sensitive to the presence of premicellar aggregates. The ratio of the intensities of the first and third vibronic bands[21] for $C_{14}NBu_3Br$ solutions are shown in Figure 4 as a function of concentration of surfactant. The result for $C_{14}NBu_3Br$ shows a gradual change over at least one decade of concentration below the cmc. This is in stark contrast to normal behavior, *e.g.*, for $C_{16}NMe_3Br$, which has almost the same cmc but exhibits an abrupt spectral change.[21] We interpret the behavior of $C_{14}NBu_3Br$ as indicating premicellar aggregates below the cmc, also providing further evidence for a gradual process of micellization. This experiment alone is always ambiguous, subject as it is to the criticism that hydrophobic additives can change the aggregation pattern of a solution. The existence of premicellar aggregates is not apparent from room temperature surface tension results and can only be detected from conductivity when many data points are collected close to the cmc.[1] However, taken in concert with the earlier conductivity evidence for gradual aggregation of $C_{12}NBu_3Br$ and the increase in monomer concentration of $C_{12}NBu_3Br$ above the cmc, the result is more persuasive.

Temperature Effects. If tributylammonium surfactants indeed display gradual aggregation, then the thermodynamics of that aggregation process might be expected to differ from more typical ionic surfactants. Surface tension and conductivity measurements at elevated temperatures have been used to probe the thermodynamics of self-assembly of $C_{14}NBu_3Br$. Critical micelle concentrations and bound counterion fractions β as a function of temperature determined from conductivity are listed in Table V. As temperature is increased, the cmc from conductivity increases and the degree of counterion binding decreases, much as do more typical cationic surfactants.[34] Indeed the free energy of micellization calculated from these results mimics the behavior of tetradecyltrimethylammonium bromide over the range of temperatures examined, as shown in Figure 5. We can therefore reasonably expect that the enthalpies and entropies of micellization are also similar for the two surfactants over this temperature range. No premicellar aggregation is evident in these results, and, above the cmc, the usual thermodynamics appear to be an adequate description of the micellar solution.

Close inspection of the surface tension results at elevated temperature provides further evidence for an anomalous aggregation process in this system. The surface tension of $C_{14}NBu_3Br$ solutions as a function of concentration is shown in Figure 1 at both 22 and 65 °C. At the higher temperature there is no abrupt cmc where it would be expected from conductivity results. Instead, at much lower concentrations there is a gradual transition between two linear regions in the surface tension versus log(concentration) plot. Above 1.2×10^{-3} mol dm^{-3} the surface tension is independent of surfactant concentration, as would be expected for a micellar solution, and below 7×10^{-4} mol dm^{-3}, the surface tension varies linearly with log(concentration), indicating a monomeric surfactant solution. In this concentration region the molecular area per molecule is 85 Å^2, well within experimental uncertainty of the room temperature value.

TABLE IV: Comparison of the Micellization Properties of Tetradecyltributylammonium Chloride and Bromide

surfactant	cmc/mol dm^{-3}		area per molecule/Å^2	degree of counterion binding, β
	surface tension (T/°C)	conductivity (T/°C)		
$C_{14}NBu_3Br$	1.44 × 10^{-3} (22)	1.36 × 10^{-3} (25)	88 ± 6	0.58
$C_{14}NBu_3Cl$	1.58 × 10^{-3} (19)	2.04 × 10^{-3} (17)	85 ± 6	0.54

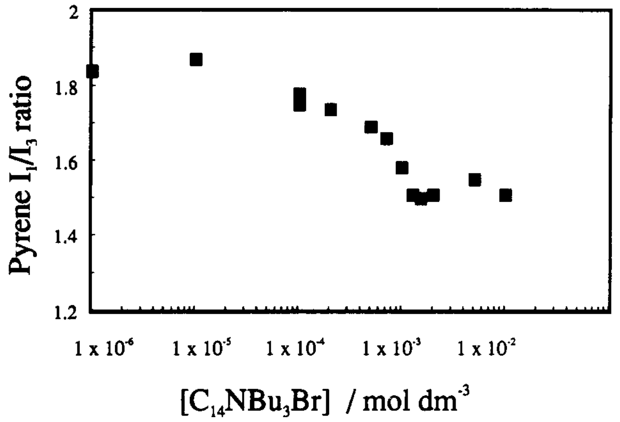

Figure 4. Ratio of the intensities of the first and third vibronic bands of pyrene fluorescence as a function of surfactant concentration for $C_{14}NBu_3Br$.

TABLE V: Micellization Parameters for $C_{14}NBu_3Br$ as a Function of Temperature

temp/°C	cmc/10^{-3} mol dm^{-3}		degree of counterion binding, β
	conductivity	surface tension	
22		1.44	
25	1.36		0.58
40	1.36		0.54
55	1.53		0.49
65	1.63	0.80 ± 0.20^a	0.47
79	2.17		0.42

^{a} Estimated from the change in slope of the surface tension curve; see Figure 1.

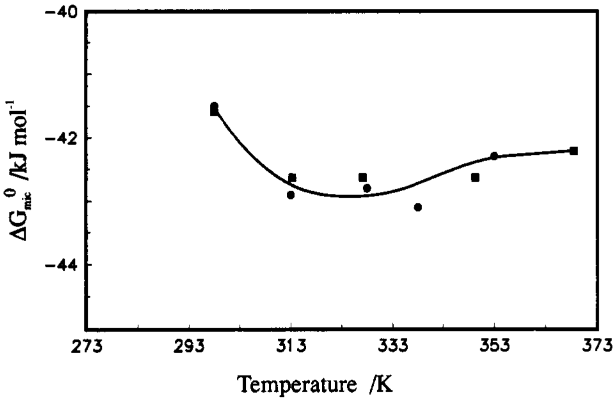

Figure 5. Standard free energy of micellization, $\Delta G_{mic}°$, from conductivity data versus temperature for $C_{14}NBu_3Br$ (●) and $C_{14}NMe_3Br$ (■). The solid line is a guide for the eye only.

This behavior is consistent with formation of premicellar aggregates. Presuming that only the monomeric surfactant is surface active, then the decreasing slope of the γ–log concentration curve reflects a gradual decrease in the fraction of the surfactant present as monomer. Eventually the monomer concentration becomes constant (on this scale), at which point the aggregates have grown to become micelles. Surface tension is highly sensitive to the formation of non-surface-active aggregates, which may only cause slight changes in solution conductivity.

Consolute Behavior. It has previously been established that binary mixtures of $C_{12}NBu_3Br$ and water undergo phase separation upon warming into dilute micellar and concentrated phases.[1] Indications from previous work are that C_8NBu_3Br solutions behave in a like manner, based on their light scattering behavior in dilute solution.[18] Nevertheless there are no reports of such a miscibility gap for other cationic systems, save in the presence of high concentrations of salt. We have therefore undertaken a survey of the phase behavior of this class of surfactants.

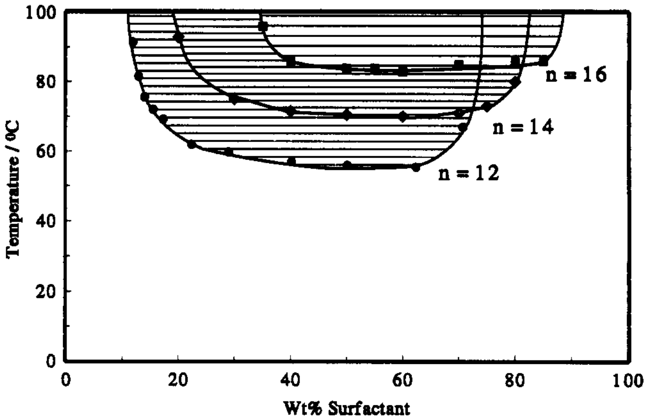

Figure 6. Partial binary phase diagrams for alkyltributylammonium bromide–water mixtures showing a two-phase region for 12 (●), 14 (◆), and 16 (■) carbon alkyl chains. Horizontal hatching represents isothermal tie lines through a two-phase region.

Most immediately noticeable is that none of the trimethyl, triethyl, and tripropyl salts examined undergo phase separation on warming up to at least 100 °C. There is a qualitative change in the surfactant behavior when a tributyl head group is included, and in each case phase separation not only occurred at a high surfactant weight fraction but also with increasing temperature and increasing concentration of the critical composition as the length of the alkyl tail increased from 12 to 16. The consolute boundaries for these three butyl surfactants are shown in Figure 6.

Phenomenologically, phase separation may be pictured as a conventional coagulation process involving the micelles. The micelles interact via repulsive electrostatic and as yet undetermined attractive interactions which increase with increasing temperature. The attractive interactions are presumably shorter range than electrostatics, at least in dilute solution. Changing solution conditions (temperature, concentration, ionic strength) alters the balance between attraction and repulsion, and if the repulsion is diminished then the barrier to coagulation is lowered.

The dilute conjugate solution of demixed $C_{12}NBu_3Br$ is known to be a micellar solution. Accepting this to be the case for all of these systems, the low-concentration phase boundary corresponds to the greatest ionic strength which can still prevent the intermicellar attraction from coagulating the micellar dispersion. It is also known that monomer concentrations continue to rise above the cmc in $C_{12}NBu_3Br$ solutions[1,2] and that the monomer concentrations are essentially independent of temperature. Thus the ionic strength is determined in these mixtures by the monomer surfactant concentration; we expect it to be lower at any particular total surfactant concentration for the surfactant with the lower cmc. This agrees with the observation that the maximum concentration of the dilute conjugate phase increases with increasing alkyl chain length (Figure 6). Greater total concentrations of surfactant are needed to realize the same ionic strengths and hence to adequately screen the intermicellar electrostatic repulsions. Surfactant concentrations at the more dilute phase boundaries of the n = 12, 14, and 16 tributylammonium bromide solutions should therefore correspond to approximately the same

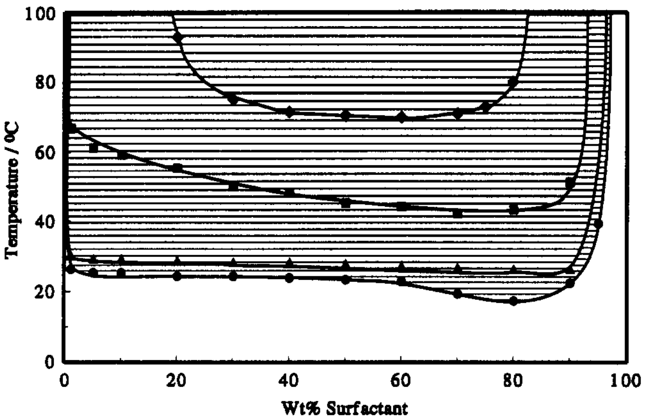

Figure 7. Partial pseudobinary phase diagrams for $C_{14}NBu_3Br$–electrolyte (KBr) mixtures showing the effect of increasing KBr concentration. Horizontal hatching represents isothermal tie lines through a two-phase region. (◆) no KBr; (■) 0.01 M KBr; (▲) 0.05 M KBr; (●) 0.1 M KBr.

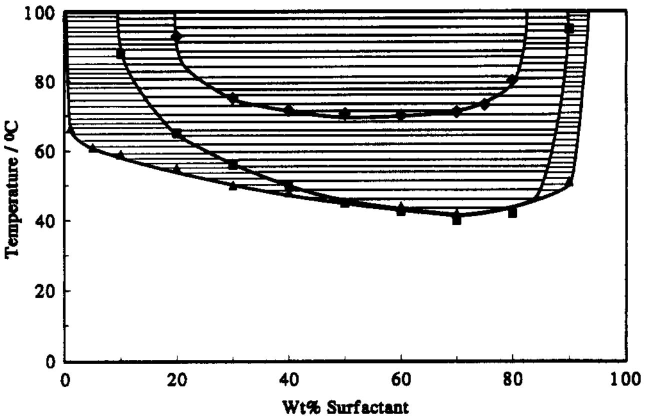

Figure 8. Partial pseudobinary phase diagram for $C_{14}NBu_3Br$–electrolyte solution mixtures comparing (■) 0.01 M KCl with (▲) 0.01 M KBr. The two-phase body with no added electrolyte is also shown (◆). Horizontal hatching represents isothermal tie lines through a two-phase region.

monomer concentrations. The same argument might equally be applied to the position of the critical composition, which also moves to higher surfactant concentration with increasing alkyl chain length.

The concentrated conjugate solution is also enriched in surfactant as the alkyl chain length increases. Little is known at present about the structure of the concentrated phase formed on demixing, although the small-angle scattering pattern is at least consistent with a concentrated micellar solution in a broth of concentrated surfactant monomers.[1]

Figure 7 shows the effect of added electrolyte, KBr, on the consolute boundary of $C_{14}NBu_3Br$ solutions. The most striking qualitative observation is that electrolyte destabilizes the dilute conjugate phase to below 1 wt % surfactant. This is consistent with the conclusion that electrostatic repulsions between micelles in the absence of added salt stabilize the relatively concentrated micellar solution in equilibrium with a concentrated conjugate phase. High concentration of added electrolyte screens the electrostatic repulsions so that only a much more dilute phase may be stabilized. We have not attempted to determine whether either phase is enriched in the electrolyte but assume that it may be viewed as a pseudobinary separation. This has been found to be the case in other ionic surfactant/electrolyte solution systems undergoing demixing.

Again the phase boundary of the concentrated conjugate solution moves to higher surfactant concentration as electrolyte concentration increases. We know nothing about the monomer concentration in these systems. However, the cmc should decrease with increased electrolyte concentration and the monomer concentration at any point would consequently be lower, probably much lower at the electrolyte concentrations used here. We therefore expect the coagulated phase to be effectively screened by KBr, leading to a greater concentration of aggregated surfactant as the ionic strength is increased.

The phase equilibria of $C_{14}NBu_3Cl$ was also examined and no evidence for phase separation observed. An important role for the counterion in the demixing mechanism is therefore indicated. This is supported by the observed phase equilibria for $C_{14}NBu_3Br$ in the presence of 0.01 M KCl and KBr, shown in Figure 8. Chloride ion is much less effective at lowering and broadening the two-phase region than is bromide. The differences are most striking at low concentrations, where chloride ion is in excess over bromide. Here the phase boundaries differ significantly, and solutions which have phase separated in the presence of KBr remain stable in KCl solution. The dilute conjugate solution of $C_{14}NBu_3Br$/0.01 M KCl is around 10 wt % surfactant, whereas that for $C_{14}NBu_3Br$/0.01 M KBr is at less than 1 wt %. At these compositions the chloride will have at least partly displaced bromide from the micelle surface. At higher surfactant concentrations the phase boundaries are similar for KBr and KCl. Here, at 50–90 wt % surfactant, bromide ion will be in excess and hence dominate the phase behavior. Interestingly the concentrated conjugate phases also differ in composition for the two salts. Bromide is expected to bind more strongly than chloride to the micelle surface, so the concentrated solution phase boundary should be dominated by the bromide behavior. This anomaly may be due to some difference in concentrations of the two ions in the two phases.

The critical temperature, T_c, is observed to increase with increasing alkyl chain length in these systems (Figure 6). This trend is the reverse of that observed for nonionic surfactants. For exampe, for C_nEO_6 the observed cloud points decrease from 74 to 37 upon increasing n from 8 to 16.[35] As electrolyte is added, T_c also decreases quite substantially. As the monomer concentration is independent of temperature,[1] this effect cannot be due to changes in the electrostatic repulsion between the micelles but must be due to the mechanism for attraction between the micelles which engenders phase separation. The observation of increasing monomer concentration above the cmc for $C_{12}NBu_3Br$ solutions[1] explains why phase separation can occur in binary ionic solutions but skirts the issue of what drives the attractive interaction.

Discussion

It is clear from this study and also from previous work that electrolyte plays an important role in the phase equilibria of aqueous surfactant solutions.[1-4] As stated above, the most obvious effect arises due to screening of the electrostatic repulsions between the micelles, and this is reflected in the compositions of the dilute conjugate solutions along the phase boundary. We have also demonstrated that the phase equilibria are sensitive to the nature of the counterion and its modulation of the electrostatic surface potential through specific binding to the micelle surface. This is indicated by the differing phase boundaries of $C_{14}NBu_3Br$ in the presence of KCl and KBr.

Porte[3,4] has reported that the phase boundaries of $C_{16}NMe_3Br$ and hexadecylpyridinium bromide + concentrated electrolyte systems are sensitive to counterion type, although no details are available. Imae *et al.*[11,12] also note a dependence of the phase boundaries of alkyldimethylammonium halides on the nature of the halide ion. This is attributed to the salting-out power of the ion and explains the intermicellar attraction as being a consequence of the breaking of $RNH\cdots OH_2$ hydrogen bonds. This is an appealing explanation and suggests some commonality with nonionic poly(oxyethylene) and amine oxide micellar systems, much along the lines of the A–B dimer model developed by Goldstein.[14]

Lower consolute behavior must arise from an increase in the effective attractive interaction between surfactant molecules with increasing temperature, as is amply displayed in small-angle scattering spectra.[1] Models developed to describe how such interactions arise may be broadly subdivided into three classes;[15] those based on surfactant–surfactant interactions,[15] those based on water–surfactant interactions,[10-12,14] and those based on water–water interactions.[6,7] Surfactant–surfactant interactions which increase in magnitude with increasing temperature have been postulated for poly(ethylene oxide) surfactants on the basis of a change in the dipole moment of the –OCCO– group with chain unfolding which accompanies warming.[15] Examination of the conformation of butyl groups in $C_{12}NBu_3Br$ has revealed instead a moderate decrease in chain extension on warming.[36] In this system such changes in this relatively small head group will lead to negligible change in the intermicellar interactions in any case. Chain coiling suggests instead a hydrophobic interaction in which the butyl group minimizes contact with water.

As noted previously the possibilities for direct surfactant–water interactions in this system are limited. There is no possibility for H-bonding to quaternary ammonium surfactants. Hence the present work and that of Porte[3,4] seem to preclude a demixing mechanism based on surfactant–water interactions, setting them apart from other clouding surfactant systems. This leads us to conclude that the temperature dependence of water–water interactions must underlie the observed demixing.

Around a hydrophobic group like tributylammonium, water molecules take on a highly ordered, clathrate-like structure. Although there is no ordering via direct hydrogen bonds to the charged center, water molecules in the solvents sheath H-bond to each other more effectively than in the bulk, lowering their configurational entropy. This is known from the solution chemistry of tetrabutylammonium hydroxide.[37] We propose that this leads to the formation of a lower consolute boundary as follows. As temperature is increased the entropy cost of ordering water around micelles becomes untenable. Two phases are then produced. In one, there is a dilute micellar solution satisfying electrostatic repulsions and containing mainly bulk water. The other phase is a concentrated surfactant broth. In both phases intimate water–surfactant contact is much reduced.

It is noteworthy that such an attraction between hydrophobic solutes was recently observed in computer simulations.[38] In that study free energy versus separation was decomposed into enthalpy and entropy and the attraction unequivocally assigned to the entropy of ordered water around the solute molecules.

These conclusions regarding the attractive potential are somewhat speculative at this stage. However, the lack of potential H-bonds between surfactant and water does offer the opportunity to discriminate between demixing mechanisms, which is contentious in nonionic systems, particularly. They suggest future investigative routes which may be instructive. If the H-bond network structure of water does strongly influence the behavior of these systems, then the high concentrations at which demixing occurs should make it amenable to thermodynamic or spectroscopic examination.[39] We are currently examining the water network structure in aqueous $C_{12}NBu_3Br$ solutions by Raman spectroscopy by analysis of vibrations arising from collective proton motions.[40] The possibility of demixing of alkyltributylammonium surfactants in other solvents may yield further information.

Phase Behavior of Tetradecyltripentylammonium Bromide ($C_{14}NPe_3Br$)

Unlike smaller head-group homologues, $C_{14}NPe_3Br$ crystallizes easily after synthesis and shows no significant hygroscopicity. Figure 9 shows a phase diagram of $C_{14}NPe_3Br$ solutions, including directly observed and inferred phase boundaries. Because of the long equilibration times we have not determined some of the phase boundaries with any great accuracy.

$C_{14}NPe_3Br$ forms metastable dilute solutions (2.5–5 × 10^{-4} M) at room temperature which precipitate after more than one week. Above this concentration precipitation occurs more rapidly. Conductivity of the metastable solutions shows $C_{14}NPe_3Br$ to behave like a micelle-forming surfactant, with a characteristic break in conductivity at around 0.5 mM. The position of this break is independent of temperature up to 60 °C. Light-scattering measurements did not support the existence of micelles at room temperature, pointing instead to larger scattering units which we conclude to be solid surfactant precipitating from a metastable micellar solution. These crystals could be observed visually after several days.

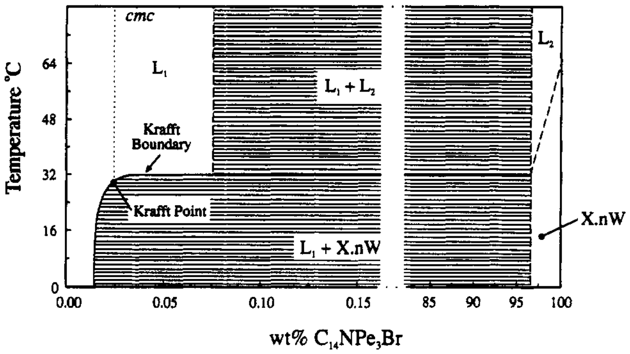

Figure 9. Partial phase diagram for $C_{14}NPe_3Br$–water mixtures. — denotes a measured phase boundary and – – – an inferred boundary. ··· indicates the locus of cmc's. L denotes isotropic liquid phases, X a crystal, and X·*n*W a hydrated crystal. Horizontal hatching represents isothermal tie lines through a two-phase region.

Surface tension measurements on metastable $C_{14}NPe_3Br$ solutions also showed a break at 5 × 10^{-4} M, suggesting a metastable micellar phase above this concentration. The molecular area derived from surface tension is 110 Å^2, indicating even greater steric effects in this system.

Above 35 °C $C_{14}NPe_3Br$ forms stable micellar solutions up to approximately 0.07 wt %. The cmc from conductivity is approximately 5 × 10^{-4} M and is almost independent of temperature. Samples between 10 and 90 wt % surfactant consisted of solid (hydrated crystal) dispersed in water below 35 °C and formed two liquid phases at higher temperatures. The composition of the concentrated conjugate phase was not determined but was estimated from phase volumes to be greater than 95 wt % surfactant. The liquid cannot be pure $C_{14}NPe_3Br$ because it exists below the melting point of the pure solid, 63 °C.

The micellization and phase behavior of tetradecyltripentylammonium bromide has much in common with the tributyl system, including the existence of a liquid–liquid miscibility gap. However the similarities are masked by the intrusion of a solid hydrated crystal phase (or phases) at temperatures above the lower liquid–liquid critical point. Certainly the tripentylammonium salt has a lower critical temperature than its tributylammonium homologue, and the concentrations of the conjugate solutions differ by more than in the tributylammonium case. The dilute conjugate solution is still above its cmc and is therefore also an electrostatically stabilized micellar solution. Due to the intervention of the hydrated crystal phase, measurement of the monomer concentration in tetradecyltripentylammonium bromide solutions was not possible. However, the position of the dilute conjugate solution phase boundary suggests that screening of electrostatic repulsion is unnecessary to allow demixing to proceed in this system. Hence we conclude that the intermicellar attractions are stronger in tripentyl than in tributyl systems.

Conclusions

Quaternary ammonium bromide surfactants are found to undergo liquid–liquid demixing in aqueous solution only when the head group is a tributyl- or tripentylammonium. With other head groups, liquid crystalline or isotropic micellar phases remain favored. Phase separation in alkyltributylammonium systems is facilitated by a gradual micellization process which produces high monomer concentrations in the micellar solutions. Due to the intervention of a crystalline phase for the tripentylammonium salt, monomer concentrations below the two-phase body could not be determined. However, based on the position of the dilute conjugate solution phase boundary, it is likely that the attractive interaction between the micelles is strong enough in this case that attenuation of the repulsion by electrolyte is unnecessary for phase separation to proceed.

A mechanism for the molecular interactions leading to demixing on warming of alkyltributylammonium bromide surfactants has been proposed. Unlike many other systems exhibiting similar demixing phenomena, there are no strong water–surfactant interactions which could cause demixing on warming, necessitating a mechanism based on water structuring around surfactant monomers and/or micelles. The apparent intermicellar attraction is postulated to be driven by the entropy cost of hydrophobically hydrating the micelle surface, which becomes more and more unfavorable as the temperature is raised, leading eventually to demixing in order to reduce the area of contact between surfactant and water. This mechanism may also be important in the phase equilibria of more common cationic surfactants in the presence of high electrolyte concentrations.

Acknowledgment. This work was supported in its initial stages by a University of Sydney URG Special Projects Grant and subsequently by the Australian Research Council. Many of the phase equilibria were determined by Ms. M. Guzman, whose contribution is gratefully acknowledged. We also thank Mr. Jean-Pierre Dalbiez of the CEN de Saclay for the light-scattering experiments on $C_{14}NPe_3Br$.

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