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ORIGINAL CONTRIBUTION

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Dodecyltrimethylammonium bromide–disodium dodecanephosphonate mixed micelles

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Abstract The aqueous catanionic system dodecyltrimethylammonium bromide (DTAB)–disodium-dodecanephosphonate (DSDP) was studied by potentiometry, conductivity, surface tension, spectrometry and dye solubilization. No precipitation of neutral salts was found in the entire range of compositions studied. Up to four transitions were detected. The first transition, at about 0.001 mol dm^{-3}, was probably related to a state change in the adsorption monolayer at the air/water interface. The second, at about 0.0065 mol dm^{-3}, was probably related to the formation of ion pairs. The third transition was the critical micelle concentration which was analyzed with the pseudophase separation model and regular solution theory. The interaction between DTAB and DSDP molecules in micelles was weaker than in other cationic–anionic surfactant mixed micelles. Large, probably rodlike, micelles formed at the fourth transition at higher surfactant concentration. No vesicles or lamellar liquid crystals were detected. The adsorbed monolayer at the air/water interface was also studied by means of regular solution theory. It was much richer in DTAB than the micelles and the intermicellar solution. The interaction between DTAB and DSDP molecules at the air/water interface was very low. The results were explained on the basis of steric factors.

Key words Mixed micelles · Catanionic surfactant · Dodecyltrimethylammonium bromide · Disodium dodecanephosphonate · Monolayer composition

Introduction

Research on surfactant mixtures is of considerable interest for numerous technical applications, because surfactant mixtures enhance performance when compared to single surfactants. When mixing surfactants, not only the properties of components are combined, but in many cases new properties are found, such as in cationic–anionic surfactant mixtures. These properties are of both fundamental and commercial interest, since surfactants used in industrial applications (e.g. detergents, tertiary oil recovery, drug carrier systems, flotation) are often mixtures. In spite of their widespread use, surfactant mixtures are not well understood at a fundamental level. Surfactant mixtures for specific applications are often chosen based on experience, empirical evidence, or trial and error research. To optimize the applications of surfactant mixtures, it is important to understand the interplay of forces that govern the phase behavior. The main work in this sense has been devoted to electrostatic interactions, while scarce attention has been directed at the steric ones, with the focus being main on the hydrophobic group geometry.

Aqueous systems containing mixtures of oppositely charged surfactants have recently attracted the attention of numerous investigators. The catanionic system dodecyltrimethylammonium hydroxide (DTAOH)–

dodecanephosphonic acid (DPA) was studied in aqueous solution, and showed very particular behavior [1–3]. The interaction among headgroups changed in nature over the composition range. This interaction was governed mainly by the changes in the hydrogen-bonded structure of the micellar phosphonic acid headgroup layer at the micelles' surface.

In this study, we investigated the nature of molecular interactions of disodium dodecanephosphonate (DSDP) and dodecyltrimethylammonium bromide (DTAB) aqueous mixtures ranging from $Y_{\mathrm{DTAB}} = 1$ to $Y_{\mathrm{DTAB}} = 0$, Y_{DTAB} being the mole fraction of DTAB in the surfactant mixture, and Y_{DSDP} that of the acid ($Y_{\mathrm{DTAB}} + Y_{\mathrm{DSDP}} = 1$). The goal was the elimination of the effect of the hydrogen-bonded structure among -PO_3H_2 groups which was responsible for the peculiar behavior of the DTAOH–DPA system, to reveal the nature of the interaction among the fully ionized -PO_3^{2-} and -$N(CH_3)_3^+$ headgroups.

Theory

Regular solution theory has been very widely used to model the thermodynamic nonidealities of mixed micelles; it has been shown to accurately model critical micelle concentration (cmc) values [4] and monomer–micelle equilibrium compositions [5] in surfactant systems exhibiting negative deviations from ideality. However, the theoretical validity of using regular solution theory to describe nonideal mixing in mixed surfactant micelles has been questioned [6]. Although this theory assumes that the excess entropy of mixing is zero, it has been demonstrated that in some surfactant mixtures this assumption is not true [7, 8]. However, the pseudophase separation model and regular solution theory combination remains a very widely used and convenient method for analyzing experimental data.

A mixture of two different surfactants, 1 and 2, form micelles with composition $X_{1,\mathrm{M}}$ and $X_{2,\mathrm{M}}$ in equilibrium with solution monomers of composition α_1 and α_2. These mole fractions are on a surfactant-only basis, so

$$X_{1,\mathrm{M}} + X_{2,\mathrm{M}} = 1 \tag{1}$$

$$\alpha_1 + \alpha_2 = 1 \tag{2}$$

At the cmc [9]

$$\alpha_1 \gamma_{1,\mathrm{m}} \mathrm{cmc}_1 = X_{1,\mathrm{M}} \gamma_{1,\mathrm{M}} \mathrm{cmc}_\mathrm{M} \tag{3}$$

$$\alpha_2 \gamma_{2,\mathrm{m}} \mathrm{cmc}_2 = X_{2,\mathrm{M}} \gamma_{2,\mathrm{M}} \mathrm{cmc}_\mathrm{M} \ , \tag{4}$$

where $\gamma_{i,\mathrm{m}}$ and $\gamma_{i,\mathrm{M}}$ are the activity coefficients of surfactant i in the intermicellar solution and in micelles, and cmc_1, cmc_2 and cmc_M are the cmcs of pure surfactant 1, 2 and the mixture. Each surfactant monomeric form is assumed to be dilute enough to obey Henry's law, i.e., based on the infinite dilution standard state, surfactant monomer activity coefficients are unity [1]. In applying regular solution theory to mixed micelles, the micellar activity coefficients are given by [10]

$$\gamma_{1,\mathrm{M}} = \exp(\beta_\mathrm{M} X_{2,\mathrm{M}}^2) \tag{5}$$

$$\gamma_{2,\mathrm{M}} = \exp(\beta_\mathrm{M} X_{1,\mathrm{M}}^2) \ , \tag{6}$$

where β_M is the dimensionless regular solution theory interaction parameter (in kT units), k is the Boltzmann constant and T the absolute temperature. Theoretically, β_M is independent of both temperature and the composition of the micelle; however, in practice β_M is temperature-dependent [11–13] and it often depends on the micelle composition [14, 15], so an average value is commonly used. In spite of these limitations, the β_M parameter quantitatively captures the extent of nonideality in a single number that can be easily compared among different pairs of surfactants. The nature and strength of the interaction between two surfactants are measured by the value of the β_M parameter, which is a measure of the degree of nonideality of the interaction in a mixed micelle. The larger the negative value of β_M, the stronger the attractive interaction between the two different surfactant molecules, and the greater the probability of the existence of synergism between them [16]. Repulsive interactions yield a positive β_M value and the possibility of antagonism, whereas $\beta_\mathrm{M} = 0$ indicates an ideal mixture. Positive β_M values occur in mixtures of fluorocarbon–hydrocarbon surfactants [17].

Typical values of β_M are +2.2 for lithium dodecylsulfate–lithium perfluorooctanesulfonate [18], −2.6 in sodium dodecyl sulfate (SDS)–poly (oxyethylene) (23) dodecylether [19], −3.9 for the system SDS–poly (oxyethylene) (4) dodecylether [20] and −13.2 for sodium decylsulfate (SDeS)–decyltrimethylammonium bromide (DeTAB) [21].

The parameter β_M is related to the molecular interactions in the mixed micelle by [20]

$$\beta_\mathrm{M} = N_\mathrm{A}(W_{11} + W_{22} - 2W_{12}) \ , \tag{7}$$

where W_{11} and W_{22} are the energies of interaction between molecules in the pure micelle and W_{12} is the interaction between the two species in the mixed micelle. N_A is the Avogadro number.

The parameter β_M reflects the two main contributions to the Gibbs free energy of mixed micellization. These are a free-energy contribution associated with the interactions between the hydrophobic groups of surfactants 1 and 2 in the micelle core, $\beta_{\mathrm{M,core}}$, and an electrostatic contribution, $\beta_{\mathrm{M,elec}}$, associated with electrostatic interactions between the charged hydrophilic groups of surfactants 1 and 2 [22]:

$$\beta_\mathrm{M} = \beta_{\mathrm{M,core}} + \beta_{\mathrm{M,elec}} \ . \tag{8}$$

It is noteworthy that $\beta_{M,core}$ is typically zero for mixtures of two hydrocarbon-based (or fluorocarbon-based) surfactants [23, 24], but is larger than zero for a binary mixture of hydrocarbon and fluorocarbon surfactants due to the repulsive interactions in the micellar core [25–28].

It can be demonstrated using regular solution theory that the chemical potential of a mixing is given by

$$\Delta\mu_{mix}^{excess} = \beta_M RTX_{1,M}X_{2,M} \ , \tag{9}$$

in which R is the gas constant. Negative values of $\Delta\mu_{mix}^{excess}$ indicate attraction between the two components in the micelles, most of which may result from a decrease in the electrostatic energy of the micelles. $\Delta\mu_{mix}^{excess}$ is the difference between the partial molar free energy of the mixed micelles and that calculated according to the ideal behavior, as a function of the mixture composition. This energy is expected to depend more on the surface charge density of micelles and the ionic strength, and less on the size and shape of the micelles [29, 30]. The $\Delta\mu_{mix}^{excess}$ value does not take into account the change in the degree of association of the counterion upon surfactant mixing [11–13].

The value of the parameter β_M for the interactions in a mixed micelle was calculated from the equations [20]

$$\frac{(X_1)^2\ln(\alpha_1\mathrm{cmc_M}/X_1\mathrm{cmc_1})}{(1-X_1)^2\ln[(1-\alpha_1)\mathrm{cmc_M}/(1-X_1)\mathrm{cmc_2}]} - 1 = 0 \tag{10}$$

and

$$\beta_M = \frac{\ln(\alpha_1\mathrm{cmc_M}/X_1\mathrm{cmc_1})}{(1-X_1)^2} \ . \tag{11}$$

Equation (10) is solved for X_1, which is then replaced in Eq. (11) to obtain β_M. Hoffmann and Pössnecker [6] have demonstrated by error expansion of Eq. (11) that the minimum error for β_M in a single determination is nearly 0.1 kT. The error strongly increases when one component in the micelle dominates.

The $\mathrm{cmc_M}$ value can be calculated as a function of the composition using the expression

$$\mathrm{cmc_M} = \left[\frac{\alpha_1}{\gamma_{1,M}\mathrm{cmc_1}} + \frac{\alpha_2}{\gamma_{2,M}\mathrm{cmc_2}}\right]^{-1} \ . \tag{12}$$

In the ideal approximation, $\gamma_{1,M} = \gamma_{2,M} = 1$, then Eq. (12) reduces to [29, 31]

$$\mathrm{cmc_M} = \left[\frac{\alpha_1}{\mathrm{cmc_1}} + \frac{\alpha_2}{\mathrm{cmc_2}}\right]^{-1} \ . \tag{13}$$

This occurs mainly in mixtures of two homologous surfactants, such as sodium octyl sulfate and sodium hexadecyl sulfate [32].

The interfacial behavior of the mixed system can be treated by the extension of the pseudophase separation model for micelles, using a nonideal analog of Butler's equation [33, 34], giving [35]

$$\pi = \frac{RT}{A_i}\ln(\gamma_{i,M}X_{i,M}/\gamma_{S,i}X_{S,i}) + \pi_i^{mx} \ , \tag{14}$$

in which A_i is the area per mole of pure surfactant i at the interface [36], π and π_i^{mx} are the surface pressure at the cmc of the surfactant mixture and the component i, respectively; $\gamma_{S,i}$ and $X_{S,i}$ are the activity coefficient and mole fraction of component i in the surface adsorbed state, respectively. When this equation was derived, the assumption that A_i does not change in surfactant surface mixtures was made. The activity coefficients of the adsorbed monolayer are given by

$$\gamma_{S,1} = \exp(\beta_S X_{S,2}^2) \tag{15}$$

$$\gamma_{S,2} = \exp(\beta_S X_{S,1}^2) \ , \tag{16}$$

where β_S is a dimensionless parameter, interpreted as representing an excess free energy of mixing in the surfactant aggregate at the interface. Equations (14)–(16) together with the constraint that the surface mole fractions, $X_{S,i}$, sum to unity, and the measured values of π_i^{mx} and A_i, give the basis for the iterative solution of the model, provided the micellar composition and activity coefficients were previously computed.

β_S can be viewed as empirically accounting for the free-energy changes that occur in forming the mixed surfactant aggregate, including those due to any counterion effects, changes in molar areas on mixing and residual solvent effects at the interface; however, the significance of β_S as a proper measure of the magnitude of the excess free-energy changes involved in the adsorption phenomenon is very uncertain [35].

Some literature-reported β_S values are −3.7 [decyl dimethylphosphine oxide (C_{10}PO)–SDS in aqueous Na_2CO_3, 1 mM]; −3.0 [decyl methyl sulfoxide (C_{10}MSO)–SDS in aqueous Na_2CO_3, 1 mM]; −0.3 (C_{10}PO–C_{10}MSO in aqueous Na_2CO_3, 1 mM); −2.9 [tetraoxyethylene glycol monododecyl ether ($C_{10}E_4$)–SDS in aqueous Na_2CO_3, 0.5 mM]; −2.0 [$C_{10}E_4$–dodecyl dimethylamine oxide (C_{12}AO) in aqueous Na_2CO_3, 0.5 mM]; −7.2 (C_{12}AO–SDS in aqueous Na_2CO_3, 0.5 mM) and −19.7 [SDeS–DeTAB in 0.05 M NaBr] [35], and between −40 and −31 in some catanionic systems [37] (although they were computed with an approach different from that employed here).

Experimental

DTAB (Aldrich) was used as received. The synthesis of *n*-dodecanephosphonic acid and the preparation of the disodium salt were described elsewhere [38, 39]. Solutions with Y_{DTAB} = 0, 0.2, 0.4, 0.6, 0.8 and 1 were studied. The maximum concentration studied was 0.04 mol dm^{-3} in mixtures, and 2.2 mol dm^{-3} in pure surfactant solutions. Double-distilled water was used.

A combined pH meter and millivoltmeter was employed to obtain potentiometric data. pH measurements were made with an Orion glass electrode. The free dodecyltrimethylammonium ion (DTA^+) concentration was measured with a DTA^+ ion-selective electrode. Details of its construction and use were published elsewhere [40]. The free dodecanephosphonate ion (DP^{2-}) concentration was measured with a DP^- ion-selective electrode, whose construction and use were described in previous papers [38, 41]. Br^- determinations were made with an Orion Br^- ion-selective electrode, and Na^+ determinations with a Metrohom EA 109 Na^+ ion-selective electrode. All ion-selective determinations were made versus the saturated calomel electrode. Details of the treatment of potentiometric data may be found in the literature [38, 41].

Conductivity measurements were performed with an immersion cell and an automatic conductimeter, namely an Antares II (Instrumentalia).

Sealed tubes with Sudan III and solutions of different surfactant concentration were left for 1 week in a thermostated bath, with periodic stirring. Then the tubes were centrifuged and the supernatant absorbance was measured with a Spectronic-20 UV-vis spectrophotometer at 600 nm. The turbidity of samples of different surfactant mixtures without solubilized dye was also measured at 400 nm as a function of concentration in the same spectrophotometer.

The surface-tension measurements were performed with a Du Noüy (Krüss) tensiometer.

All determinations were made at 25.0 °C.

Mean values and variances were computed by the minimum variance linear unbiased method [42] and the Student *t* function was employed to compute the error intervals. The confidence level was 0.9. The errors of the derived data were computed with the error expansion method.

Results

No precipitation of neutral salts was found in the entire range of compositions studied, which is not the common behavior for this kind of surfactant mixtures; however, this behavior has been detected in other systems such as aqueous cetyltrimethylammonium bromide–sodium heptylsulfate [43] and aqueous dodecyltrimethylammonium chloride–sodium decanoate [44].

All mixtures of surfactants show up to four transition concentrations, which were detectable by several methods. The solubilization of Sudan III by the system with $Y_{DTAB} = 0.4$ is shown in Fig. 1. Figure 2 shows the surface tension versus log c_T (total concentration) curve for the $Y_{DTAB} = 0.8$ mixture. Although the decrease in σ above the cmc is not common, it has been observed in other mixed-surfactant systems [30] and was interpreted as a change in micelle composition associated with increasing total concentration. Figure 3 shows the differential conductivity versus c_T for the $Y_{DTAB} = 0.8$ mixture, computed as

$$\Lambda_d = 1000\, d\kappa/dc_T \ . \tag{17}$$

All determinations of turbidity gave horizontal lines within experimental error.

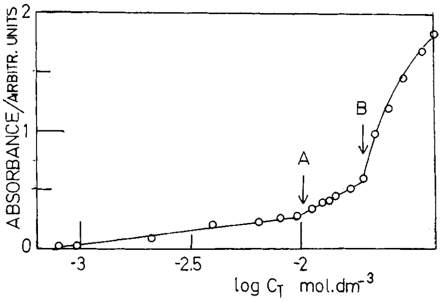

Fig. 1 Solubilization of Sudan III by the dodecyltrimethylammonium bromide (*DTAB*)–disodium dodecanephosphonate (*DSDP*) system. Mole fraction of DTAB (Y_{DTAB}) = 0.4. *A*: critical micelle concentration (*cmc*); *B*: change in micelle structure

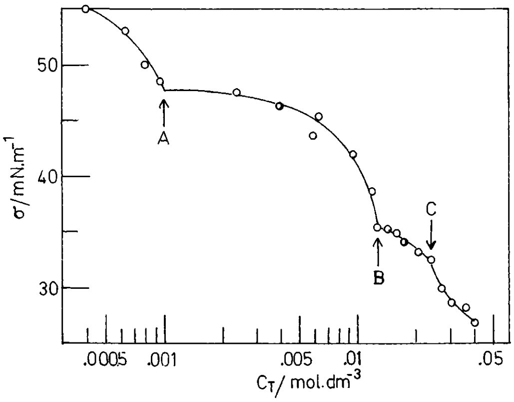

Fig. 2 Surface tension versus the logarithm of the total concentration. Y_{DTAB} = 0.8. *A*: change in surface state; *B*: cmc; *C*: change in micelle structure

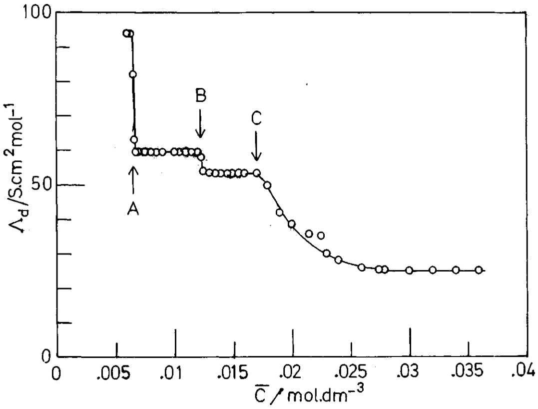

Fig. 3 Differential conductivity versus the total concentration. Y_{DTAB} = 0.8. *A*: ion-pair formation; *B*: cmc; *C*: change in micelle structure

Potentiometric determinations show that samples with $Y_{DTAB} = 0.4$ and 0.6 did not capture counterions in the micelle Stern layer, but micelles with $Y_{DTAB} = 0$, 0.2, 0.8 and 1 did. When there was an excess of DTAB, mainly bromide ions were included in the micelle surface. If DSDP was in excess, mainly sodium counterions were captured by micelles; however, the opposite counterion was also captured, although in a lower proportion. This was not the case in DTAB–SDS aqueous solutions, in which only the counterion belonging to the predominant surfactant was captured by micelles [45]. In the case of $Y_{\mathrm{DTAB}} = 0.8$, the precision of the potentiometric measurements led to the construction of Fig. 4, in which the concentration of the different species versus total concentration is plotted. The micelle ionization could not be computed from these data, because pH measurements indicated that DSDP underwent enhanced hydrolysis at the cmc; thus, it was not possible to determine the amount of hydrolyzed decanephosphonate in micelles, which affects their net charge.

The cmc and the concentration at which the micelle structure changed (see Discussion) are shown in Fig. 5.

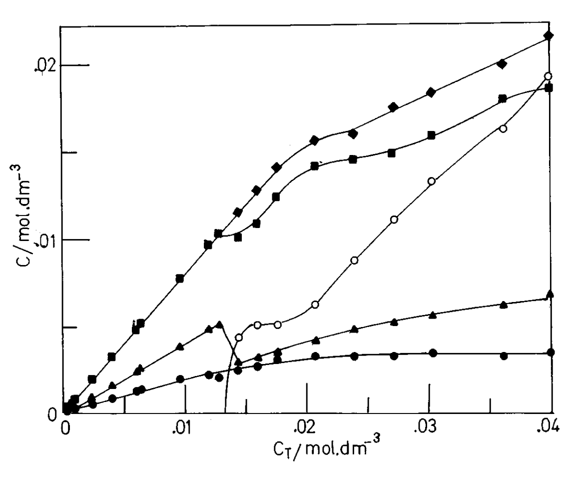

Fig. 4 Concentration of the different species in solution versus the total concentration. $Y_{\mathrm{DTAB}} = 0.8$. ▲: free Na^+; ◆: free Br^-; ●: free DP^{2-}; ■: free DTA^+; ○: micellized surfactant

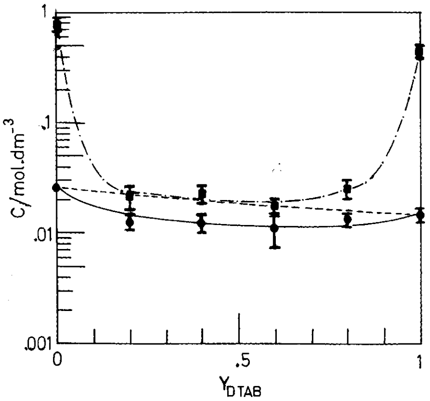

Fig. 5 Aggregation transitions in the DTAB–DSDP system versus Y_{DTAB}. ●: cmc; ■: change in micelle structure; ——: computed cmc with $\beta_M = -2.0$; - - - - - : cmc computed with ideal mixing theory; –. –. –: drawn to guide the eye

The first transition (not shown in Fig. 5) was at about 0.001 mol dm^{-3} in all mixtures, while the second was at about 0.0065 mol dm^{-3}.

The surface tension at the cmc is shown in Fig. 6 for different mixture compositions.

Discussion

The first transition

This transition was detected by surface-tension experiments. It may be related to a state change in the adsorbed layer, as was found in decyltrimethylammonium bromide–SDeS mixed systems [46], in which this transition corresponds to the surface gaseous state to surface expanded liquid state transition. This phenomenon has also been found in pure surfactant solutions [47].

The second transition

The transition at 0.0065 mol dm^{-3} was not associated with micelle formation. It may be related to the formation of ion pairs, because there was a reduction in the conductivity of the solutions above this point. The formation of dimers might increase the conductivity [48]. It may be seen in Fig. 3 that the transition was sharp and led to a reduction of about 36% in the total molar conductivity. Following the interpretation of the differential conductivity Λ_d given in Ref. [49], the value of Λ_d may be interpreted as the molar conductivity of the ion pairs. Formation of ion pairs was found in other cationic–anionic surfactant systems [50–52]. The possibility of formation of larger submicelles in catanionic systems has also been proposed [53].

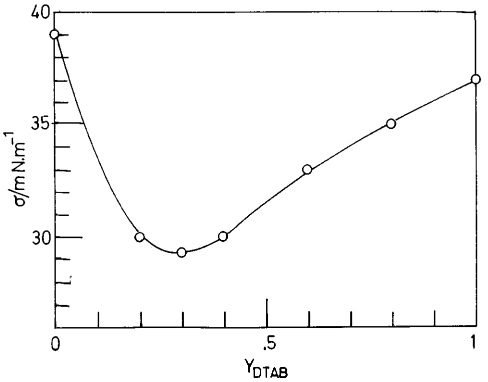

Fig. 6 Surface tension at the cmc versus Y_{DTAB}. *Line* drawn to guide the eye

The third transition (cmc)

All experiments indicated that this transition is at the cmc. In view of the interpretation of the fourth transition (see later) it may be concluded that the micelles formed are isometric or globular. Other mixed systems form globular micelles at the cmc, for example, aqueous lithium dodecyl sulfate–dodecyldimethylammoniumpropanesulfonate [54].

The mean value of β_M was −1.66 ± 0.05 in kT units. The dependence of this interaction parameter on Y_{DTAB} is shown in Fig. 7. It may be seen that there is a slight dependence on the mixture composition. The unexpectedly low value of β_M was similar to that in ionic–nonionic surfactant mixtures. The β_M value in cationic–anionic surfactant mixtures is in general much higher (about −20) [37]; however, Swanson-Vethamuthu et al. [55] found $\beta_M = -2.7$ in cetyltrimethylammonium bromide (CTAB)–sodium deoxycholate aqueous mixtures, and −4.0 in CTAB–sodium cholate aqueous mixtures.

The small β_M values may be due to steric factors in micelle formation. Increased bulkiness in the hydrophilic groups may reduce the interaction between oppositely charged groups and give rise to smaller micelles [56, 57].

The composition of the micelles at the cmc is plotted in Fig. 8 versus Y_{DTAB}. Between $Y_{DTAB} = 0.5$ and 1, there was not a significant difference between the total composition and the micelle composition. For $Y_{DTAB} < 0.5$, there was an excess of DTAB in the micelles. Since both hydrocarbon tails are equal, according to Eq. (8) $\beta_M = \beta_{M,elec}$, and hence is only due to the electrostatic interaction between the -N(CH$_3$)$_3^+$ and -PO$_3^{2-}$ groups.

The micellar activity coefficient of DTAB and DSDP versus the square root of X_{DTAB} is shown in Fig. 9.

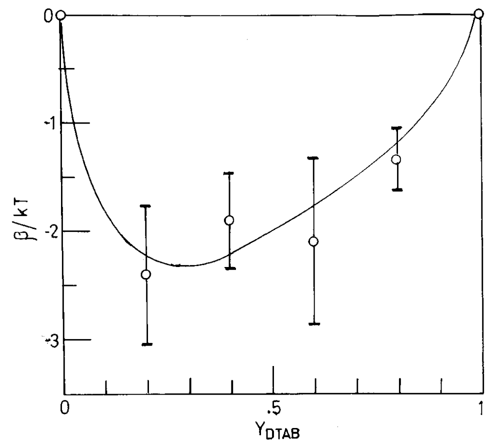

Fig. 7 Dependence of the micellar interaction parameter β_M on Y_{DTAB}. *Line* drawn to guide the eye

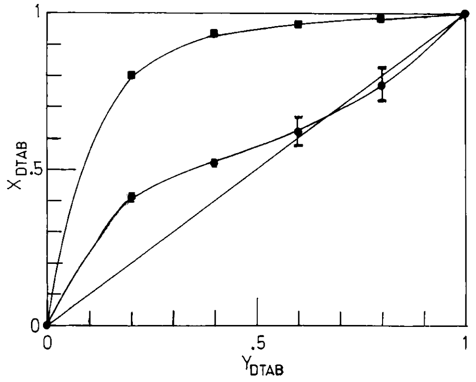

Fig. 8 Micelle composition ($X_{M,DTAB}$) at the cmc (●) and composition of the air/solution interface adsorbed monolayer at the cmc ($X_{S,DTAB}$) (■) as a function of Y_{DTAB}. The *straight line* indicates $X_{M,DTAB} = X_{S,DTAB} = Y_{DTAB}$. *Lines* were drawn to guide the eye

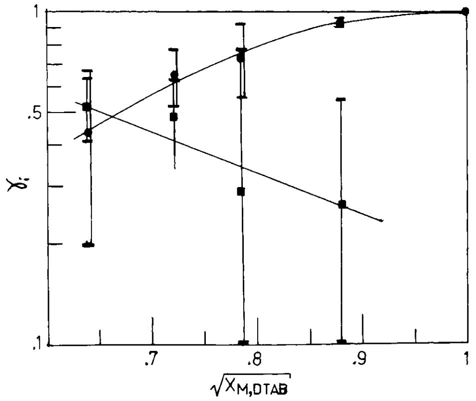

Fig. 9 Micellar activity coefficient of DTAB (●) and DSDP (■) versus the square root of X_{DTAB}

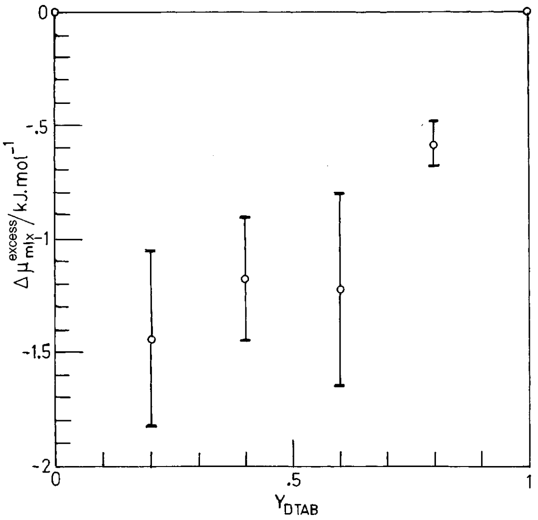

Fig. 10 The excess chemical potential of mixing in micelles, $\Delta\mu_{mix}^{excess}$ versus Y_{DTAB}

The $\Delta\mu_{\mathrm{mix}}^{\mathrm{excess}}$ values are shown versus Y_{DTAB} in Fig. 10. It can be seen that there is an increase in the (negative) value of the change in chemical potential with the increase in Y_{DSDP}. The curve is not symmetrical, and it may be interpreted as a nonsymmetrical interaction between -PO_3^{2-} and $\text{-N(CH}_3)_3^+$ headgroups in the micelles. The mixture of a few -PO_3^{2-} groups with a lot of $\text{-N(CH}_3)_3^+$ groups was more ideal than the mixture of a few $\text{-N(CH}_3)_3^+$ groups with a lot of -PO_3^{2-} groups. A glance at Figs. 7–9 leads to the same conclusion.

The behavior of the DTAB–DSDP system is more classical than that of the DTAOH–DPA system, but there were some peculiar characteristics: the interaction between the $\text{-N(CH}_3)_3^+$ and the -PO_3^{2-} groups was not symmetrical, and the interaction is more similar to that between ionic and nonionic headgroups than that between anionic and cationic groups.

The fourth transition

The transition at higher concentration was associated with a change in micelle shape. The turbidity did not change at this concentration. This means that no liquid crystals or vesicles were formed at this point.

The transition was gradual, as can be seen in Fig. 3. This gradual transition might reflect the gradual increase in size from spheres to increasingly longer rod-shaped micelles. The solubility power increased at this point, as seen in Fig. 1, which is a well-known characteristic of rodlike micelles. Rodlike micelles were found in other cationic–anionic mixed-surfactant systems [44, 51, 58–60].

Cationic–anionic surfactant mixtures generally yield vesicles when the total concentration is raised [61–66]. In some cases, rodlike micelles are precursors of vesicles [68, 69]. This is a result of strong attractive interaction between oppositely charged headgroups which creates a mixed-surfactant architecture similar to a double-chain catanionic surfactant, which is compatible with a planar water/aggregate interface.

The bulky structure of the hydrated phosphonate and trimethylammonium headgroups together with the relatively small electrostatic interaction probably favored the formation of curved water/aggregate interfaces, which generated rodlike micelles (see later).

The adsorbed layer at the air/water interface

Figure 6 shows the surface tension at the cmc. It can be seen that the aggregation of DTAB to DSDP gave rise to a sharp decrease in σ_{cmc}, whereas the addition of DSDP to DTAB produced a slower decrease. This behavior also supports the interpretation of an asymmetrical interaction between polar headgroups. The minimum σ was found at $Y_{\mathrm{DTAB}} \approx 0.66$, which corresponds to the formation of a neutral $\mathrm{DTA_2DP}$ salt, which was soluble and did not precipitate. It may also be seen that the surface synergism in the mixtures is very low. The decrease in surface tension was not as strong as in other cationic–anionic surfactant mixtures. In these systems, generally the cmc of the mixture decreases considerably and the region of single dispersion for the mixture is appreciably reduced [69–73].

The molar area of DSDP at the cmc was $A_2 = 4.91 \times 10^9\ \mathrm{cm^2\ mol^{-1}}$ ($\mathrm{d}\sigma/\mathrm{d}\ln c|_{\mathrm{cmc}} = -15.15\ \mathrm{mN\ m^{-1}}$, $\Gamma_{\mathrm{cmc}} = 2.04 \times 10^{10}\ \mathrm{mol\ cm^{-2}}$), and for DTAB, $A_1 = 1.47 \times 10^9\ \mathrm{cm^2\ mol^{-1}}$ [74]. The composition of the surface layer was plotted in Fig. 8 versus Y_{DTAB}. It may be seen that the surface composition is monotonically richer in DTAB than in DSDP. This situation may be related to the higher hydrophilicity of the latter. Neutron reflectivity experiments on adsorbed nonionic surfactant mixtures have shown that the more hydrophobic surfactant preferentially adsorbs at all surfactant concentrations [75, 76]. Other work has also shown the same result in cationic–anionic surfactant mixtures [77]; however, other systems show different behavior. In the DeTAB–SDeS system an equimolecular mixture of SDeS and DeTAB exists in the adsorbed film at almost all compositions irrespective of the bulk composition in the solution [78]. The DTAB–SDS system shows the same behavior [69].

The value of β_{S} was negative, which indicates a synergistic interaction. The computed absolute values were very low, between -8.3×10^{-10} ($Y_{\mathrm{DTAB}} = 0.2$) and -1.87×10^{-10} ($Y_{\mathrm{DTAB}} = 0.8$) in kT units. Moreover, this value was not constant, but was a linear function Y_{DTAB}, giving the relationship $\beta_{\mathrm{S}} = 1 \times 10^{-9} \times Y_{\mathrm{DTAB}} - 1 \times 10^{-9}$, with a correlation coefficient $r = 0.9979$. This small value indicates a very weak attraction. In general β_{S} values are larger than β_{M} in the same system [37]. The very low β_{S} values in this system may be due to the almost total expulsion of DSDP molecules from the surface. This situation increased the mutual distances among DTAB and DSDP molecules at the surface and weakened the surface electrostatic interactions.

The volume of the micellized phosphonate headgroup is $43.22 \pm 0.96\ \mathrm{cm^3\ mol^{-1}}$ [79]; that of the trimethylammonium headgroup is $70.6 \pm 3.4\ \mathrm{cm^3\ mol^{-1}}$ [80]. The area occupied by each headgroup at the micelle surface may be computed from these data, giving $a_{\mathrm{DSDP}} = 0.209 \pm 0.005\ \mathrm{nm^2}$ and $a_{\mathrm{DTAB}} = 0.29 \pm 0.01\ \mathrm{nm^2}$, respectively. Using the hard-disk model for the adsorbed state [81] and the supposition that the state of the headgroups is the same in the micelles and the adsorbed monolayer, the surface covered by 1 mol of each pure surfactant may be computed as $A_{\mathrm{DSDP}} = (1.26 \pm 0.03) \times 10^9\ \mathrm{cm^2\ mol^{-1}}$ and $A_{\mathrm{DTAB}} = (1.75 \pm$

0.06) × 10^9 cm^2 mol^{-1}. The values of A_i computed using $d\sigma/d \ln c|_{cmc}$ and the Gibbs equation gave $a_{D\text{-}SDP} = 0.815$ nm^2 and $a_{DTAB} = 0.244$ nm^2. The area per water molecule is 0.097 nm^2 [82–86]. The comparison between both a_i values for the same surfactant gave 6.2 water molecules per phosphonate group and none for the trimethylammonium headgroup.

These computations may explain why DTAB was preferentially adsorbed at the air/water surface in DTAB–DSDP mixtures. Because of the small a_{DTAB} value, the hydrocarbon chains may be close enough to each other to form a compact monolayer, whereas those of DSDP are too far from each other, giving a poorer cohesion of the interfacial layer. The electrostatic interaction was low because of the distance between the bulky hydrated phosphonate and the trimethylammonium groups, and it did not compensate the loss of the van der Waals energy of interaction among the hydrocarbon tails when they were pushed away from each other by the intrusion of the DSDP molecules at the adsorbed monolayer.

The mixed-micelle behavior may also be explained in view of these results. The more hydrophobic DTAB was preferentially solubilized in micelles, but because of the bulkiness of both the trimethylammonium and hydrated phosphonate groups the electrostatic interaction was lower than in other cationic–anionic surfactant mixtures. This bulkiness may also explain the formation of rodlike micelles instead of vesicles or lamellar mesophases.

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