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ORIGINAL CONTRIBUTION

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The aggregation of aqueous dodecylphosphonic acid in dodecyltrimethylammonium hydroxide mixtures

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Abstract The aggregation of aqueous dodecylphosphonic acid (DPA) and dodecyltrimethylammonium hydroxide (DTAOH) mixtures was studied by several methods. The behavior of DPA-rich mixtures is close to that of pure DPA. This is probably due to the preservation of the hydrogen-bonded structure of the micellar headgroup layer. The behavior is almost ideal. Between $y_{DPA} = 0.5$ and 0.33 (y_{DPA} being the mole fraction of DPA in the surfactant mixture), the hydrogen-bonded structure of the micellar headgroup layer is destroyed. A sort of "micellar azeotrope" is formed, and the maximum of non-ideal interaction between the two surfactants is attained at $y_{DPA} = 0.4$. For $y_{DPA} < 0.33$ the system behaves as a common mixture of a cationic surfactant and a non-ionic one (DPA.2LTA). There is a phenomenon of counterion "condensation" on aggregates at concentrations over the CMC.

Key words Dodecanephosphonic acid – dodecyltrimethylammonium hydroxide – mixed micelles – critical micelle concentration – aggregation

Introduction

Anionic–cationic surfactant mixtures are of interest in pharmacy [1], analytical chemistry [1–4] wastewater treatment [5], chemical kinetics [6], textile wetting and detergency [7]. It is of significant interest to understand the interactions in mixed micelles containing both anionic and cationic surfactants [8]. These interactions include those among surfactant headgroups, between headgroups and counterions and between the charged surface and surrounding medium with its diffuse double layer. The presence of oppositely charged headgroups in the micelle/solution interface causes a high degree of charge neutralization and permits the mixed micelles to attain a large size [9]. In the equimolar concentration region, in most mixtures a slow precipitation of insoluble salts occurs [10].

Mixed surfactant systems show synergistic effects relative to the properties of their individual surfactant components. The synergism increases with the degree of charge difference and it is maximal in anionic–cationic mixtures [11].

Understanding of the physical mechanisms involved in the formation of mixed micelles and the modeling of this process are areas of great theoretical and practical interest [12].

In this study, we investigated the nature of molecular interactions of dodecylphosphonic acid (DPA) and dodecyltrimethylammonium hydroxide (DTAOH) in mixtures ranging from $y_A = 1$ to $y_A = 0$, y_A being the mole fraction of acid in surfactant mixture, and y_B that of base ($y_A + y_B = 1$).

Theory

One model commonly used to describe micelle formation is the pseudophase separation model [13] which considers the micelles as a thermodynamic phase in equilibrium with the monomer. By treating the monomer and micelle as pseudophases, the CMC of a mixture of similarly structured ionic surfactants [13, 14] or nonionic surfactants [13, 16, 17] can be predicted reasonably well by assuming that ideal solution theory is obeyed in the micellar phase. However, the CMC of ionic/nonionic and anionic/cationic (catanionic) surfactant mixtures can be much less than that predicted by ideal solution theory [12, 17]. This indicates that mixed-micelle formation between these dissimilar surfactants is enhanced, relative to that between surfactants of similar structure [12].

Regular solution theory has been very widely used to model the thermodynamic nonidealities of mixed micelles; it has been shown to accurately model CMC values [17–31] and monomer-micelle equilibrium compositions [24] in surfactant systems exhibiting negative deviations from ideality.

The most important mechanistic reason for the nonideality of the ionic/nonionic micelles is believed to be the reduction of the repulsion between the ionic head groups due to the insertion of the nonionic hydrophilic groups between the charged groups [17, 20–23, 26, 32, 33]. For catanionic micelles, this reduction is due to the mutual neutralization of charges between positively and negatively charged groups.

A mixture of two different surfactants 1 and 2 form micelles with composition X_1 and X_2, in equilibrium with solution of monomers of composition α_1 and α_2. These mole fractions are on a surfactant-only basis, so that:

$$X_1 + X_2 = 1 \tag{1}$$

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

At the CMC [23]:

$$\alpha_1 \gamma_{1,\mathrm{m}} \mathrm{CMC}_1 = X_1 \gamma_{1,\mathrm{M}} \mathrm{CMC}_\mathrm{M} \tag{3}$$

$$\alpha_2 \gamma_{2,\mathrm{m}} \mathrm{CMC}_2 = X_2 \gamma_{2,\mathrm{M}} \mathrm{CMC}_\mathrm{M} \,, \tag{4}$$

where $\gamma_{1,\mathrm{m}}$ and $\gamma_{1,\mathrm{M}}$ are the activity coefficients of surfactant i in the intermicellar solution and in micelles. CMC_1, CMC_2 and CMC_M are the CMC of pure surfactant 1 and 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. It is common to take $\gamma_1 \approx \gamma_2 \approx 1$ in dilute solutions. In view of the agreement between experimentally and computed CMC's, the implication is that the deviation of the ideality caused by the neglected nonideality in the intermicellar solution is either small or successfully included in the micellar activity coefficients. In applying regular solution theory to mixed micelles, the micellar activity coefficients are given by [34]:

$$\gamma_{1,\mathrm{m}} = \exp(\beta X_2^2/kT) \tag{5}$$

$$\gamma_{2,\mathrm{m}} = \exp(\beta X_1^2/kT) \,, \tag{6}$$

where β is the regular solution theory interaction parameter, k is the Boltzmann constant and T is the absolute temperature. Theoretically, β is independent of both temperature and the composition of the micelle. However, in practice β is temperature dependent [35–37] and it often depends on the micelle composition, so that an average value is commonly used [35]. In addition, β is very sensitive to the CMC value so that for a given system a different series of CMC's can allow β values differing by even more than 100% [35, 38].

The nature and strength of the interaction between two surfactants are measured by the value of the β parameter, which is a measure of the degree of non-ideality of the interaction in a mixed micelle. The larger the negative value of the β parameter, the stronger the attractive interaction between the two different surfactant molecules, and the greater is the probability of the existence of synergism between them [39]. Repulsive interactions yield a positive β value and the possibility of antagonism, whereas $\beta = 0$ indicates an ideal mixture. Positive β values occur in mixtures of fluorocarbon–hydrocarbon surfactants [40, 41].

The parameter β is related to the molecular interactions in the mixed micelle by [24]:

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

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 Avogadro's number.

The parameter β reflects two main contributions to the free energy of mixed micellization. There is a free-energy contribution associated with interactions between the hydrophobic groups of surfactants 1 and 2 in the micelle core, β_core, and an electrostatic contribution β_elec, associated with electrostatic interactions between the charged hydrophilic groups of surfactants 1 and 2 [42]:

$$\beta \approx \beta_\mathrm{core} + \beta_\mathrm{elec} \,. \tag{8}$$

It is noteworthy that β_core is typically equal to zero for mixtures of two hydrocarbon based (or fluorocarbon based) surfactants [43], but is greater than zero for a binary mixture of hydrocarbon and fluorocarbon surfactants due to repulsive interactions in the micellar core [44].

It can be demonstrated within the regular solution context that the free energy excess of mixing is given by

$$\Delta G_{\mathrm{ex}} = \beta RTX_1(1 - X_1)\,. \tag{9}$$

Negative values of ΔG_{ex} indicate the attraction between the two components of the micelles, most of which may result from a decrease in the electrostatic energy of the micelles. This energy is expected to depend much on the surface charge density of micelles and the ionic strength, and little on the size and shape of micelles [45].

By assuming β to be temperature dependent [36] the following equations can be written for the excess of enthalpy ΔH_{ex} and the excess of entropy ΔS_{ex} [36]:

$$\Delta H_{\mathrm{ex}} = -X_1(1 - X_1)RT^2\frac{\partial\beta}{\partial T} \tag{10}$$

$$\Delta S_{\mathrm{ex}} = -X_1(1 - X_1)R\left(\beta + T\frac{\partial\beta}{\partial T}\right). \tag{11}$$

According to Hey and MacTaggart [37], the excess properties derived from the regular solution theory do not take into account the change in the degree of association of the counter ions upon surfactant mixing. The above excess properties are the difference between the partial molar properties of the mixed micelles and those calculated according to the ideal behavior, as a function of the mixture composition.

The value of the parameter β for the interaction in a mixed micelle was calculated from the equations [24]:

$$F = \frac{(X_1)^2\ln(\alpha_1\,\mathrm{CMC_M}/X_1\,\mathrm{CMC_1})}{(1 - X_1)^2\ln[(1-\alpha_1)\mathrm{CMC_M}/(1 - X_1)\mathrm{CMC_2}]} = 1 \tag{12}$$

$$\beta = \frac{\ln(\alpha_1\,\mathrm{CMC_M}/X_1\,\mathrm{CMC_1})}{(1 - X_1)^2}\,. \tag{13}$$

Equation (10) is solved for X_1, which is then substituted in Eq. (11) to obtain β. Sarmoria et al. [42] have attempted to calculate the β values in common surfactants from the structural groupings in the molecule and from thermodynamic considerations.

Hoffmann and Pössnecker [41] have demonstrated by error expansion of Eq. (11) that the minimum error for β in a single determination is nearly 0.1 kT. The error is strongly increasing when one component in the micelle dominates.

The $\mathrm{CMC_M}$ value can be calculated as a function of the composition by the expression:

$$\mathrm{CMC_M} = \left[\frac{\alpha_1}{\gamma_{1,\mathrm{M}}\mathrm{CMC_1}} + \frac{\alpha_2}{\gamma_{2,\mathrm{M}}\mathrm{CMC_1}}\right]^{-1}. \tag{14}$$

In the ideal approximation, $\gamma_{1,\mathrm{M}} = \gamma_{1,\mathrm{M}} = 1$, then Eq. (12) reduces to [46, 47]:

$$\mathrm{CMC_M} = \left[\frac{\alpha_1}{\mathrm{CMC_1}} + \frac{\alpha_2}{\mathrm{CMC_1}}\right]^{-1}. \tag{15}$$

This occurs mainly in mixtures of two homologous surfactants, such as sodium octyl sulfate and sodium hexadecyl sulfate [48].

The relationships for monomer concentrations valid above the CMC can be developed from the relation: [24]

$$X_1 = \frac{\alpha_1}{C}\,\frac{C - C_1}{- C_1 - C_2}\,, \tag{16}$$

where C, C_1 and C_2 are the total concentration of surfactant 1 and 2, and the concentrations of monomeric surfactants 1 and 2. By substituting C_1 and C_2 from Eqs. (3) and (4) the resulting quadratic expression in X_1 can be solved to yield [24]:

$$X_1 = \frac{-(C - \Delta) + \sqrt{(C - \Delta)^2 + 4\alpha C\Delta}}{2\Delta} \tag{17}$$

where $\Delta = \gamma_{1,\mathrm{M}}\,\mathrm{CMC_1} - \gamma_{2,\mathrm{M}}\,\mathrm{CMC_2}$.

The monomer concentrations of the different components of a surfactant mixture, even above the $\mathrm{CMC_M}$ are not constant, but depend on the total surfactant concentration. This fact is a direct consequence of the phase separation model and has been outlined in the literature [17, 29, 31, 41, 47].

Experimental

Dodecanephosphonic acid (DPA) was synthesized by the Kossolapoff method [49]. Details of the preparation and purification are published elsewhere [50].

Dodecyltrimethylammonium hydroxide was prepared by pouring a concentrated solution of dodecyltrimethylammonium bromide (Aldrich, [1119–94–4]) through an ion-exchange column filled with Amberlite IRA −900 (OH) [51]. Much care was taken to avoid CO_2 contamination.

Glass electrode measurements

OH^- determinations were made with an Orion glass electrode and pH-meter.

Conductivity measurements

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

Dye solubilization measurements

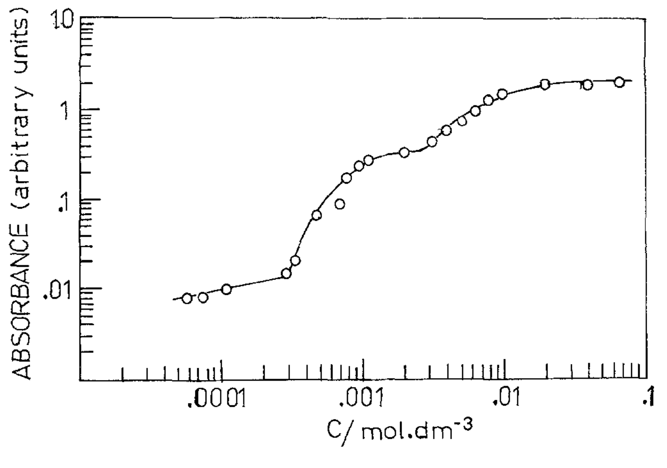
Sealed tubes with Sudan III or Sudan Black B and surfactant mixture solutions of different concentration were left for 1 week in a constant temperature bath, with periodic stirring. Then the tubes were centrifuged and the supernatant absorbance was measured with a Hewlett-Packard Diode Array HP84 52A spectrophotometer at 488 nm (Sudan III) or 600 nm (Sudan Black B).

Sudan Black was employed in DTAOH-rich systems, because Sudan III has a phenol group which has acidic character and increases its water solubility in alkaline solutions. The dielectric constant in the micro-environment of the micelles was studied by the dependence of the position of the ~600 nm maximum (λ_{max}) on the solvent dielectric constant [52 and references therein].

Results

The concentration of aggregation of surfactant ions was determined with a combination of conductivity, pH and dye solubilization.

Fig. 1 Sudan Black solubilization by aqueous solutions of DPA-DTAOH mixture with $y_{DPA} = 0.28$. Absorbance in arbitrary units. Concentrations in mol·dm^{-3}



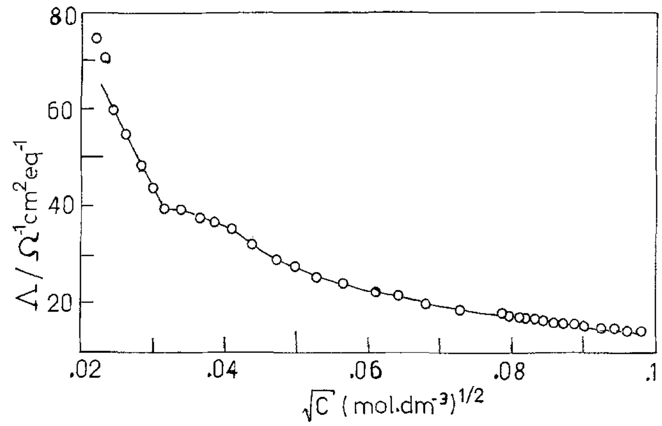


Fig. 2 Equivalent conductivity, Λ, of aqueous solutions of DPA-DTAOH mixtures with $y_{DPA} = 0.6$

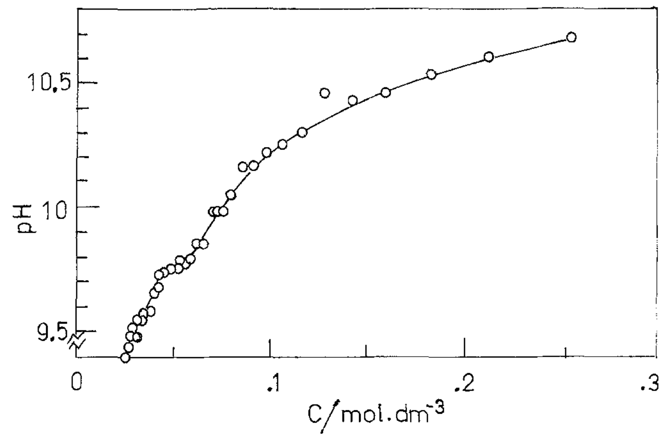


Fig. 3 pH of aqueous solutions of DPA-DTAOH mixtures with $y_{DPA} = 0.2$

Figure 1 shows the curve of Sudan Black solubilization by solutions of mixture with $y_{DPA} = 0.28$, showing two changes, one of them at 2.7×10^{-4} mol · dm^{-3} corresponding to the first formation of aggregates, and the other at 2.1×10^{-3} mol·dm^{-3}, in which aggregates change in nature. Other mixtures showed similar curves.

Figure 2 shows the equivalent conductivity of solutions of mixtures with $y_{DPA} = 0.6$.

We have determined the concentration of "counterion condensation" by a combination of conductivity and pH measurements.

Figure 3 shows the pH vs. concentration curve for solutions of mixtures with $y_{DPA} = 0.2$.

Figure 4 shows the critical aggregation points of the different mixtures of surfactants (CMC), the concentration at which aggregates change in nature, and the concentration at which counterions joint the aggregates. The dashed curve corresponds to ideal behavior.

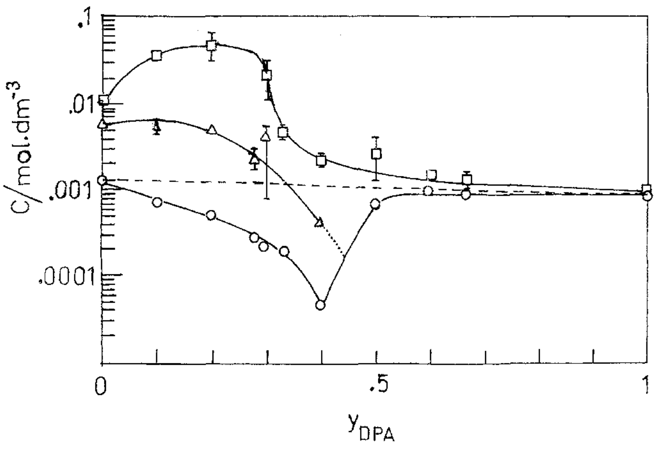


Fig. 4 Critical aggregation concentrations of aqueous DPA-DTAOH mixtures as a function of y_{DPA}. ○: aggregation of surfactant ions. △: change in structure of aggregates, □: counter ion aggregation, ----: ideal aggregation. Vertical lines indicate 90% probability errors

Discussion

DPA is a weak acid with $pK_1 = 3.98$ and $pK_2 = 8.42$ [53]. LTAOH is a stronger base, with $pK_b = 2.89$ [51]. Thus, the DPA-rich mixtures have a slight degree of ionization, whereas the DTAOH-rich mixtures have a higher degree of ionization.

We have selected two surfactants with the same chain length, to make $\beta_{core} = 0$, and with almost the same volume of the polar heads, to avoid steric effects in the replacement of one type of molecule by the other in the micelle structure [54]. The partial molar volume of the micellized phosphonic group is 45.5 ± 4.7 cm^3 mol^{-1} [55] and that of trimethyammonium is 63.6 ± 7.1 cm^{3}mol^{-1} [56], as computed from partial molar volume measurements. The electrostatic attraction between negative and positive groups possibly reduces the slight difference in volume.

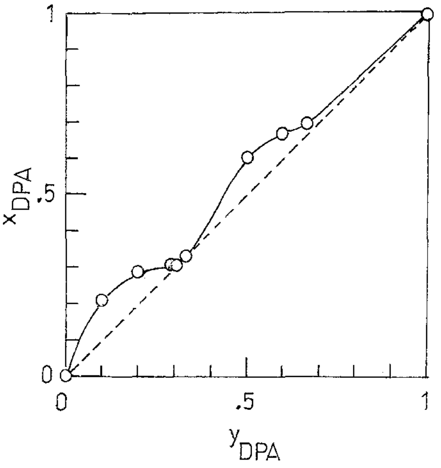
As in pure DTAOH, the aggregation of surfactant ions and counter ions occurs at different concentrations [57a]. This may be due to the high hydrophilicity of the hydroxile ion. On the other hand, DTAOH micelles have high degree of ionization at low micelle concentrations [57]. Mixed micelles of Brij-35 – Tetradecyltrimethylammonium bromide [58] and of Brij-35 – Hexadecyltrimethylammonium bromide [59] show the same phenomenon. This also occurs in pure alkyltrimethylammonium bromides and its mixtures with non-ionic surfactants [60]. It was interpreted in terms of a critical ionic composition needed to form the Stern layer in mixed micelles [59], or to counterion "condensation" on the micelle surface, in terms of the theory of polyelectrolytes [61].

The dye solubilization experiments showed that some change in the aggregate structure occurs between the first aggregation of monomers and the "counterion condensation". This phenomenon changes the solubilization power of the aggregates. It also can be detected in some cases with methods which are sensitive to changes in the monomer concentration, e.g., conductivity, and can be misunderstood as the formation of a second kind of micelle, especially when the component with the higher CMC has the highest mole fraction, as Hoffmann and Pössnecker reported [41]. The dielectric constant (ε) of the microenvironment of solubilized Sudan Black indicates that over this curve micelles are larger and possibly of different shape than below it. With $y_{DPA} = 0.1$ and $C = 3.84 \times 10^{-3}$ M, we found $\varepsilon = 39$, whereas at $C = 7.96 \times 10^{-3}$ M, $\varepsilon = 21$. This indicates that the dye molecule (which is not charged in the experimental conditions) sank deeper in the micelle hydrocarbon core in the more concentrated system. This is possible if the micelles are larger than in the diluted system.

As in some other systems [41], the CMC vs. y_{DPA} curve cannot be described by one constant parameter β.

Three zones may be seen in Fig. 4: Between $y_{DPA} = 1$ and 0.5, (Zone I) the CMC is almost constant and equal to the CMC of DPA. At $y_{DPA} = 0.5$, the first ionization of DPA is completely neutralized by DTA$^+$ ions. Between $y_{DPA} = 0.5$ and 0.33, the second DPA ionization is neutralized by DTAOH. Below $y_{DPA} = 0.33$, there is an excess of DTAOH. The application of Eq. (12) to these three different parts, leads to the values of X_{DPA} (mole fraction of DPA in the micelle) shown in Fig. 5. By application of Eq. (13), the β values (in kT units) were obtained and plotted in Fig. 6. Figure 7 shows the ΔG_{ex}, ΔH_{ex} and ΔS_{ex} values obtained by Eqs. (9), (10) and (11). To compute the last two

Fig. 5 Mole fraction x_{DPA} in DPA-DTAOH mixed micelles at the concentration of aggregation of surfactant ions vs. y_{DPA}



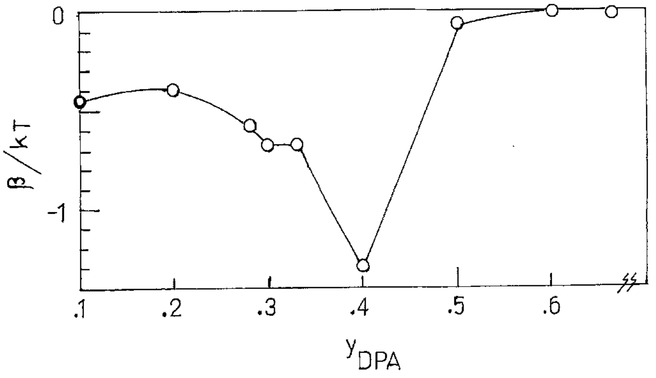


Fig. 6 β values (in kT units) vs. y_{DPA}

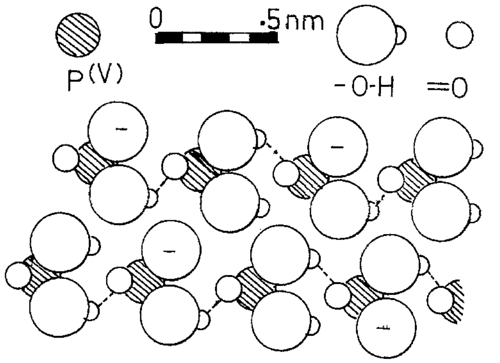


Fig. 8 Probable hydrogen-bonded structure of the surface of DPA micelles

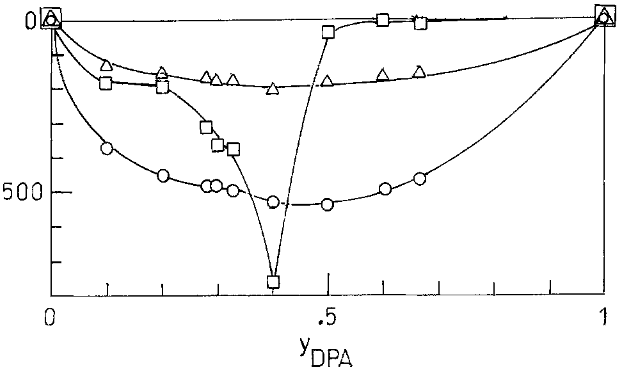


Fig. 7 Excess thermodynamic quantities in DPA-LTAOH mixed micelles vs. y_{DPA} □: ΔG_{ex} ($J \cdot mol^{-1}$), ○: $\Delta H_{ex} \times 10^{-1}$ ($J \cdot mol^{-1}$), △: $\Delta S_{ex} \times 10$ ($J \cdot mol^{-1} K^{-1}$)

thermodynamic quantities, we assumed $\partial\beta/\partial T = 0.03\ K^{-1}$ [35].

Between $y_{DPA} = 1$ and 0.5, the interaction seems to be almost ideal ($\Delta G_{ex} \approx 0$, $\beta \approx 0$). The CMC is that of pure DPA. Micelles of pure DPA probably have the polar head groups bound by hydrogen bonds, as occurs in the lamellar mesophase which exists at concentrations slightly above the CMC [62]. Therefore, the DPA micelle surface probably has the structure of Fig. 8, with some OH groups ionized and some non-ionized, owing to the pK_1 value. The size and shape of $-PO_3H_2$ and $-N(CH_3)_{3^+}$ groups are similar, so the intercalation of DTA^+ ions in the polar layer of DPA micelles only slightly alters the area per polar head. In the zone considered, this intercalation does not significantly disturb the hydrogen bonds between adjacent phosphonic groups. Each phosphonic group can bond only with another two adjacent ones, so the replacement of the other non-hydrogen-bonded adjacent phosphonic groups by trimethylammonium groups does not alter their structure very much. The hydrogen-bonded structure is maintained by the non-ionized P–OH groups.

The β value in this zone ($\beta = (-0.050 \pm 0.081)kT$) indicates that the type of interaction between DPA and DTA^+ ions is weak and does not change greatly with y_{DPA}.

On the other hand, the "dilution" of the phosphonic groups on the micelle surface by the trimethylammonium groups lead to the reduction of the surface charge density and less retention of the counterions [63], allowing a separation between the concentration of aggregation of surfactant ions and that of counterions. In this case, the aggregation of counterions is the difference between the H^+ ions retained by the phosphonic groups in the micelles because the first ionization equilibrium and the extra-counterions retained close the micelle surface by changing the surface potential. This is equivalent to a reduction in the first ionization constant.

Between $y_{DPA} = 0.5$ and 0.33 (Zone II), the second P-OH group of DPA is neutralized by the added DTAOH. Now, the hydrogen-bonded structure is destroyed. The interaction constant and ΔG_{ex} values indicate a sudden withdrawal from ideality. β reaches a value comparable to that of some mixtures of ionic and non-ionic surfactants ($\beta = -1.40\, kT$ for SDS–C_9-Φ-E_{10} mixtures [64], $\beta = -1.30\, kT$ for $C_{16}(C_5H_5N)Cl$–C_9-Φ-E_{10} mixtures [64], $\beta = -1.44\, kT$ for C_{14}TMAC–$C_{10}E_5$ mixtures [42]). The continuous change in β indicates that the nature of the interactions between the two components changes continuously.

The minimum value of ΔG_{ex} at $y_{DPA} = 0.4$ indicates a minimum in the electrostatic repulsion. This may mean that at this composition, micelles are almost uncharged and behave as non-ionic species.

Between $y_{dpa} = 0.33$ and 0, i.e., in the region of excess of DTAOH (Zone III), β shows an almost constant value: $(-0.55 \pm 0.14)kT$, similar to that of the C_{16}TMAC–$C_{12}E_6$ system: $-0.92\, kT$ [65] and the hexadecylpyridinium chloride–hexadecyltrimethylammonium chloride system: − 0.21 [64]. This indicates that the type of interaction between components does not change in nature with composition, and may indicate that the DPA. 2DTA units act as a non-ionic diluent of the DTA^+ ions in the micelle. The dependence of ΔG_{ex} on y_{DPA} in this zone is as expected in common mixtures of surfactants [45].

Figure 5 shows that except between $y_{DPA} = 0.4$ and 0.33, the composition of micelles at the CMC is systematically rich in DPA molecules. This may be explained because this component is the less water soluble, and is a common situation in non-ideal micelles. The "micellar azeotrope" between $y_{DPA} = 0.4$ and 0.33 indicates that some sort of stable compound is formed, giving the same surfactant composition in micelles and intermicellar solution.

The excess entropy (Fig. 7) has an average value of $\Delta S_{ex} = -16.9 \pm 1.2$ J/K·mol. The negative value may indicates that mixed micelles are more ordered than single component ones, because of the electrostatic polar head interaction, leading to a non-random arrangement of polar heads. Random arrangements are expected for mixtures in which there is no difference in affinity between unlike molecules and molecules which are alike. As Osborne-Lee et al. pointed out [66], the attraction between unlike molecules tends to favor arrangements with a greater number of contacts between unlike molecules than would occur for random mixing. Because the arrangements increasing the number of unlike contacts are only a fraction of the total possible arrangements, the entropy in such mixed micelles is, then, less than that for micelles which result from random mixing.

Due to the negative value of ΔS_{ex}, the stability of mixed micelles is mainly an enthalpic effect. The dependence of ΔH_{ex} with y_{DPA} is similar to that found in other systems [35, 65]. Experimental values in the literature were well fitted by the regular solution theory [35].

Figure 9 shows the composition of micelles at the concentration at which counter ions join the micellar surface. The situation has been reversed: except for $y_{DPA} < 0.2$, in which the composition is ideal, micelles are richer in LTA^+ ions. The effective charge per micellized molecule in the "naked" micelle in Zone III, computed as $\alpha = X_{LTA} - 2X_{DPA}$, is shown in Fig. 10. It is higher at the concentration at which the counter ions "condense".

It must be pointed out that regular solution theory has been subjected to much criticism and that the values of the thermodynamic parameters obtained by this theory must be seen as having a doubtful interpretation [43]. However, we believe that the general trends may be a useful indication of the various phenomena occurring in the system, even though there may be some doubt about the numerical values.

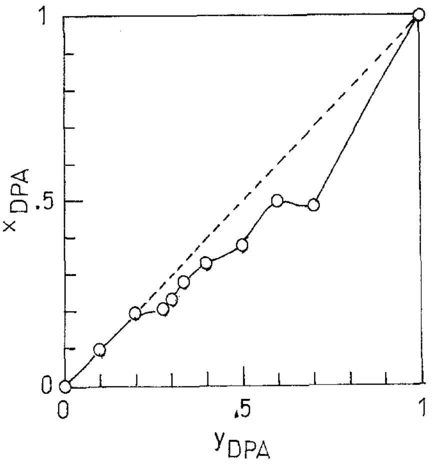


Fig. 9 Mole fraction of DPA in DPA-DTAOH mixed micelles at the concentration of aggregation of counterions, vs. y_{DPA}

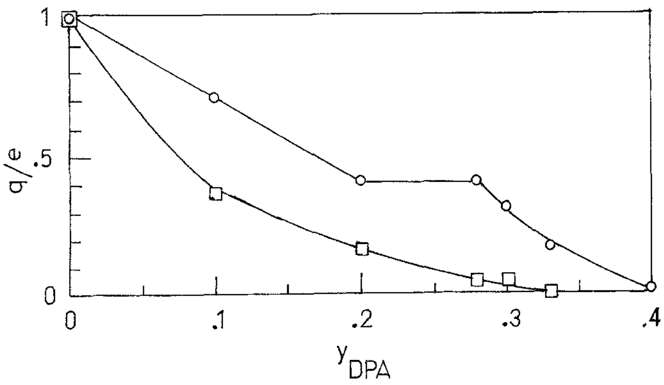


Fig. 10 Effective charge per micellized molecule in DPA-DTAOH mixed micelles vs. y_{DPA}. □: at the aggregation of surfactant molecules, ○: at the aggregation of counter ions

Conclusions

Three different behaviors are shown by dodecane-phosphonic acid – dodecyltrimethylammonium hydroxide mixed micelles, depending on the mixed surfactant composition. Between $y_{DPA} = 1$ and 0.5, the CMC is almost constant and equal to that of DPA. This is probably due to the preservation of the hydrogen-bonded structure of the micellar headgroup layer. The behavior is almost ideal.

Between $y_{DPA} = 0.5$ and 0.33, the hydrogen-bonded structure of the micellar headgroup layer is destroyed. A sort of "micellar azeotrope" is formed, and the maximum value of nonideal interaction between the two surfactants is attained at $y_{DPA} = 0.4$.

Between $y_{DPA} = 0.33$ and 0, the system behaves as a common mixture of a cationic surfactant and a non-ionic one (DPA.2DTA).

The mixed micelle formation in this system is mainly an enthalpy-driven phenomenon.

There is a phenomenon of counter ion "condensation" on aggregates at concentrations over the CMC.

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