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The aqueous cationic system sodium undecenoate-dodecyltrimethylammonium bromide at low concentration

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Abstract The aqueous sodium undecenoate (SUD)–dodecyltrimethylammonium bromide (DTAB) cationic system was studied at low concentration. The system did not precipitate, even at a 1:1 SUD:DTAB proportion, but showed the formation of a coacervate in a range of surfactant mixture compositions. Micelles have a preferential composition of 0.37 mole fraction of SUD. This behavior is attributed to the presence of the double bond at the distal extreme of the SUD molecule, which can form hydrogen bonds

with water. Consequently, the $-\text{CH}=\text{CH}_2$ group is situated at the interface between the hydrocarbon micelle core and water, reducing the interfacial free energy. Structural computations demonstrate that the mentioned SUD proportion produces complete coverage of the micelle surface by the double bonds.

Keywords Sodium undecenoate · Dodecyltrimethylammonium bromide · Cationic surfactant · Critical micelle concentration · Coacervation

Introduction

Research on surfactant mixtures is of considerable interest for numerous technical applications, because surfactant mixtures are known to enhance performance as compared to single surfactants. When mixing surfactants, in particular surfactants of opposite charge, not only are the properties of each component combined, but in many cases new properties are found. 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 fundamentally not that well understood. It is therefore important to have a basic understanding of the mechanisms of interaction between surfactants in mixed systems and of the factors influencing various features of the phase equilibrium. Surfactant mixtures for specific applications are often chosen based on experience, empirical evidence, or a trial and error approach. To optimize the applications

of surfactant mixtures, it is important to understand the interplay of forces that govern the phase behavior. The main focus in this sense has been on electrostatic interactions, while little attention has been directed at the steric interaction level with the main study focused on the geometry of the hydrophobic group.

Aqueous mixtures of anionic and cationic surfactants exhibit many unique properties that arise from the strongly electrostatic interactions between the oppositely charged head groups and have therefore attracted the attention of numerous investigators [1, 2, 3, 4, 5, 6].

Present theories take into account the influence that the structure of the micelle polar layer and electrostatic effects have on micellisation [7] and mixed micellisation [8, 9, 10]. However, in order to improve on these theories it is necessary to have the knowledge needed to understand the factors affecting the formation of micelles and their structure.

In general, those cationic-anionic surfactant mixtures under study are composed of strong electrolytes such as alkyltrimethylammonium halides and alkaline salts of

alkylsulfonic acids. It is interesting to investigate the effect that mixed micellisation has on hydrolysis, for instance, when one of the components chosen is a salt of a weak acid or a weak base. With this aim in mind we explored the dodecyltrimethylammonium bromide (DTAB) –sodium undecenoate (SUD) aqueous mixed system. Both components have relatively large critical micelle concentrations (*CMC*). This allows the use of many different methods in order to study the aggregation. Few investigations on mixed systems including soaps exist. Scowen and Leja [11] and Oakenfull and Fenwick [12] studied mixtures of soaps and alkyltrimethylammonium halides of the same chain length, but not with the aim to study the effect that mixed micellisation has on hydrolysis of the soap whereas Edlund et al. [13] studied the system dodecyltrimethylammonium chloride –sodium octanoate.

Theory

Classical solution theory has been widely used to model the thermodynamic non-idealities of mixed micelles. Solution theory has also shown to accurately model critical micelle concentration (*CMC*) values [14] and monomer-micelle equilibrium compositions [15] in surfactant systems exhibiting negative deviations from ideality. However, the combination of the separation model and classical solution theory to describe non-ideal mixing in mixed surfactant micelles has been questioned [16]. 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 [17, 18]. However, the pseudophase separation model and classical solution theory combination remains a very widely used and convenient method for analyzing experimental data.

A mixture of two different surfactants, *i* and *j*, form micelles with composition $X_{i,M}$ and $X_{j,M}$ in equilibrium with solution monomers of composition α_i and α_j . The mole fractions are on surfactant-only basis, so

$$X_{i,M} + X_{j,M} = 1 \quad (1)$$

$$\alpha_i + \alpha_j = 1 \quad (2)$$

At the *cmc* [19]:

$$\alpha_i \gamma_{i,m} cmc_i = X_{i,M} \gamma_{i,M} cmc_M \quad (3)$$

where $\gamma_{i,m}$ and $\gamma_{i,M}$ are the activity coefficients of surfactant *i* in the intermicellar solution as well as in micelles. cmc_i and cmc_M are the critical micellar concentration of the pure surfactant *i* as well as in the mixture. Each monomeric form of the surfactant 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 expressed as unity [20]. Applying classical solution theory to mixed micelles the micellar activity coefficients are given by [21]:

$$\gamma_{i,M} = \exp(\beta_M X_{j,M}^2) \quad (4)$$

where β_M is the dimensionless classical 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 [22, 23, 24] and often depends on the micelle composition [25, 26], so that an average value is commonly used. In spite of these limitations the β_M parameter quantitatively captures the extent of non-ideality 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 non-ideality 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 therefore the greater the probability of the existence of synergism between them [27]. Repulsive interactions yield a positive β_M value and the possibility of antagonism, whereas $\beta_M = 0$ indicates an ideal mixture. Positive β_M values occur in mixtures of fluorocarbon –hydrocarbon surfactants [28].

Typical values of β_M are +2.2 for lithium dodecylsulfate –lithium perfluorooctanesulfonate [29], –2.6 in sodium dodecyl sulfate (SDS) –poly (oxyethylene)₂₃ dodecylether [30], –3.9 for the system SDS –poly (oxyethylene)₄ dedecylether [31] and –13.2 for sodium decylsulfate –decyltrimethylammonium bromide [32].

The parameter β_M is related to the molecular interactions in the mixed micelle by [31]:

$$\beta_M = N_A (W_{ii} + W_{jj} - 2W_{ij}) \quad (5)$$

where W_{ii} and W_{ij} are the energies of interaction between molecules in the pure micelle and that between the two species in the mixed micelle. N_A represents Avogadro's number.

The parameter β_M reflects the two main contributions to the free energy of mixed micellisation. There is a free-energy contribution associated with the interactions between the hydrophobic groups of surfactants *i* and *j* in the micelle core, $\beta_{M,core}$, and also an electrostatic contribution, $\beta_{M,elec}$, associated with the electrostatic interactions between the charged hydrophilic groups of the surfactants *i* and *j* [33]:

$$\beta_M = \beta_{M,core} + \beta_{M,elec} \quad (6)$$

It is worth noting that $\beta_{M,core}$ is typically zero for mixtures of two hydrocarbon-based (or fluorocarbon-based) surfactants [34, 35], but is larger than zero for a

binary mixture of hydrocarbon and fluorocarbon surfactants due to the repulsive interactions in the micellar core [36, 37, 38, 39].

It can be demonstrated using classical solution theory that the excess chemical potential of mixing is given by:

$$\Delta\mu_{\text{mix}}^{\text{excess}} = \beta_{\text{M}}RTX_{i,\text{M}}X_{j,\text{M}} \quad (7)$$

where R is the gas constant. Negative values of $\Delta\mu_{\text{mix}}^{\text{excess}}$ indicate attraction between the two components in the micelles most of which may result from a decrease in the electrostatic energy of the micelles. $\Delta\mu_{\text{mix}}^{\text{excess}}$ 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 micelles [40, 41]. The $\Delta\mu_{\text{mix}}^{\text{excess}}$ value does not take into account the change in the degree of association of the counter ion upon surfactant mixing [22, 23, 24].

The value of the parameter β_{M} for the interactions in a mixed micelle was calculated from the equation [31]:

$$F = \frac{(X_{i,\text{M}})^2 \ln(\alpha_i \text{cmc}_{\text{M}}/X_{i,\text{M}} \text{cmc}_i)}{(1 - X_{i,\text{M}})^2 \ln[(1 - \alpha_i) \text{cmc}_{\text{M}}/(1 - X_{i,\text{M}}) \text{cmc}_j]} - 1 = 0 \quad (8)$$

and

$$\beta_{\text{M}} = \frac{\ln(\alpha_i \text{cmc}_{\text{M}}/X_{i,\text{M}} \text{cmc}_i)}{(1 - X_{i,\text{M}})^2} \quad (9)$$

Equation 8 is solved for $X_{i,\text{M}}$, which is then substituted into equation 9 to obtain β_{M} . Hoffmann and Pössnecker [16] have shown that by using the error expansion of equation 9 the minimum error for β_{M} in a single determination is almost $0.1 kT$. The error strongly increases when one component in the micelle dominates.

The cmc_{M} value can be calculated as a function of the composition using the expression [40, 42]:

$$\text{cmc}_{\text{M}} = \left[\frac{\alpha_i}{\gamma_{i,\text{M}} \text{cmc}_j} + \frac{\alpha_j}{\gamma_{j,\text{M}} \text{cmc}_i} \right]^{-1} \quad (10)$$

In the ideal approximation, $\gamma_{i,\text{M}} = \gamma_{j,\text{M}} = 1$. This mainly occurs in mixtures of two homologous surfactants, such as sodium octyl sulfate and sodium hexadecyl sulfate [43].

To compute the micellar ionisation degree α the equation proposed by Evans [44] was employed:

$$1000(d\kappa/dC)_2 = \frac{(n - m)^2}{n^{4/3}} [1000(d\kappa/dC)_1 - \lambda_{\text{X}}] + \alpha\lambda_{\text{X}} \quad (11)$$

where $(d\kappa/dC)_1$ and $(d\kappa/dC)_2$ are the slopes of the specific conductivity curves before and after the CMC , n is the aggregation number, m the number of counterions attached to the micelle, and λ_{X} is the equivalent conductivity of the counter ion. Equation 11 is a quadratic function of α because $(n - m) = nx$. It is also dependent on n . However, this dependence is not strong and any reasonable value of n gives a good estimation of α [44]. We selected $n = 61$, which is the value for DTAB [45]. Filipovic-Vincekovic [46] found that non-equimolecular micelles in catanionic systems are significantly smaller than the equimolecular ones. Since all the micelles studied here are not equimolecular (even if $\alpha_{\text{CTAB}} = 0.5$, vide infra), the use this constant value of n does not significantly affect the estimated value of α .

In the estimation of α for surfactant mixtures, we employed average counter ion conductivity:

$$\Lambda_{\text{X}} = \alpha_{\text{CTAB}}\lambda_{\text{Br}^-} + (1 - \alpha_{\text{CTAB}})\lambda_{\text{Na}^+} \quad (12)$$

where $\lambda_{\text{Br}^-} = 77.4$ and $\lambda_{\text{Na}^+} = 50.9 \text{ S cm}^2 \text{ mol}^{-1}$ [47]. The degree of ionization thus obtained are shown in Table 1.

The value of α for pure DTAB micelles ($\alpha = 0.24$) is in agreement with the values found in the literature ($\alpha = 0.19$ [48]) and reflects the hydrophobicity of the bromide ion [49] and its high polarizability, which favors its adsorption at the micelle surface [50]. The α value for SUD is similar to the values for other sodium soaps (sodium dodecanoate: $\alpha = 0.36$ [51]).

The degree of ionization of SUD micelles was also computed giving $\alpha = 0.518$. Values found in the literature are $\alpha = 0.392 \pm 0.007$, [52] from ion-selective electrode measurements. Using vapor pressure osmometry, Larrabee and Sprague [53] found $\alpha = 0.27$ at 37°C , and Vikingstad et al [54] reported a value of $\alpha = 0.28 \pm 0.02$ at 25°C from emf experiments. This higher value of α reflects the higher hydrophilicity of Na^+ ions, and the probable low charge density at the SUD micelle surface, caused by the inclusion of the double bonds among the carboxylate groups.

Table 1 Ionization degree of DTAB-SUD mixed micelles

α_{SUD}	α
0	0.239
0.1	0.517
0.2	0.743
0.3	0.621
0.4	0.552
0.5	-
0.6	-
0.7	0.491
0.8	0.485
0.9	0.488
1	0.518

Experimental

Sodium undecenoate (SUD) was purchased from Aldrich. Dodecyltrimethylammonium bromide (DTAB, Aldrich) was used as received.

In order to prepare the different samples, the appropriate amount of each surfactant was weighed and dissolved in double-distilled water to produce two concentrated solutions. Then the appropriate volume of each solution was poured into a volumetric flask in order to prepare mixtures with mole fraction of SUD (without considering water) $\alpha_{\text{SUD}}=0$ (pure DTAB solution), 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1 (pure SUD solution). Using the SUD and DTAB critical micelle concentrations (CMC) from literature, all solutions were prepared at concentrations above the CMC predicted by the regular solution theory of mixed micelles for each proportion.

Conductivity measurements were made with an immersion cell and an automatic conductivity meter namely an Antares II from Instrumentalia. The CMC was determined using the representation of $\Delta\kappa = \kappa - \kappa_{\text{extrapol}}$ as a function of the total concentration (not shown), where κ_{extrapol} is the extrapolated specific conductivity from the specific conductivity under the CMC value. This representation shows a well-defined break in the dependency of the conductivity with the concentration and improves the determination of the CMC, especially when plots of κ vs C do not show a well-defined change in slope.

Two batteries of tubes having different mixture concentration were used to perform dye solubilisation experiments. Small Sudan III crystals were added to the tubes of one battery, and small Sudan Black B crystals to the other. Both dyes were used because Sudan III has a phenol group and is slightly soluble in basic solutions such as those having an excess of SUD. Then Sudan III was employed in solutions having $\alpha_{\text{SUD}} \leq 0.5$ and Sudan Black B (which is insoluble in basic solutions) in solutions having $\alpha_{\text{SUD}} > 0.5$. The tubes were sealed and periodically stirred for one week. Then the contents of the tubes were centrifuged and the supernatant absorbance was measured using a Spectronic-20 UV-Vis spectrophotometer at $\lambda = 600$ nm (Sudan III) and $\lambda = 490$ nm (Sudan Black B).

The system revealed phase separation at α_{SUD} values of about 0.5. Two mutually immiscible liquid phases were observed (coacervation). In order to determine the boundaries of the domain of existence of the coacervate solutions of DTAB were titrated with SUD solutions and after each addition the absorbance (A) was measured with a Spectronic-20 UV-Vis spectrophotometer. This enabled us to determine the α_{SUD} value at which the absorbance rises and that at which absorbance decreases.

Changes in color and fluorescence in Rhodamine 6G were detected by sight by adding a drop of dilute Rhodamine 6G solution to tubes with surfactant solution at different concentration in order to detect micelle formation [55, 56, 57, 58].

In order to determine the composition of the coexisting phases within the two-phase region aliquots of both phases were extracted and weighed. Thereafter the samples were dried and weighed to determine the amount of water. The dry surfactant mixture was re-dissolved in double-distilled water and titrated against hydrochloric acid using conductivity to determine the equivalent point. This allowed quantification of the amount of SUD in the mixture. The amount of DTAB was computed from the total weight of the dry surfactant mixture.

All determinations were made at 25.0 °C.

Results

Figure 1 shows the determination of the limits of existence of the coacervate. When α_{SUD} was increased, the

coacervate suddenly appeared at $\alpha_{\text{SUD}}=0.44$ and disappeared in a more gradual form between $\alpha_{\text{SUD}}=0.57$ and $\alpha_{\text{SUD}}=0.63$.

Figure 2 shows the CMC values of the solutions having different α_{SUD} values and the two-phase region of existence of the coacervate. The full line shows the CMC of ideal mixing, computed with equation 10. The SUD CMC was $0.12 \text{ mol}\cdot\text{dm}^{-3}$, in agreement with the literature values: $\text{CMC}=0.117 \pm 0.007 \text{ mol}\cdot\text{dm}^{-3}$ [52], and $0.117 \text{ mol}\cdot\text{dm}^{-3}$ [59]. The DTAB CMC was $0.0152 \text{ mol}\cdot\text{dm}^{-3}$. Some literature values are $0.015 \text{ mol}\cdot\text{dm}^{-3}$ [60] and $0.0155 \text{ mol}\cdot\text{dm}^{-3}$ [61, 62].

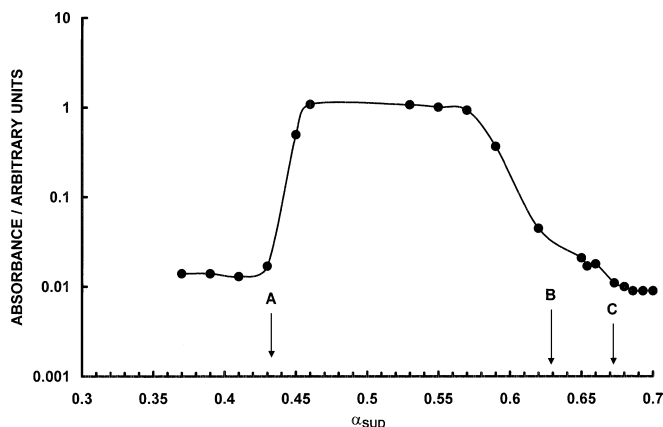


Fig. 1 Determination of the limits of existence of the coacervate region

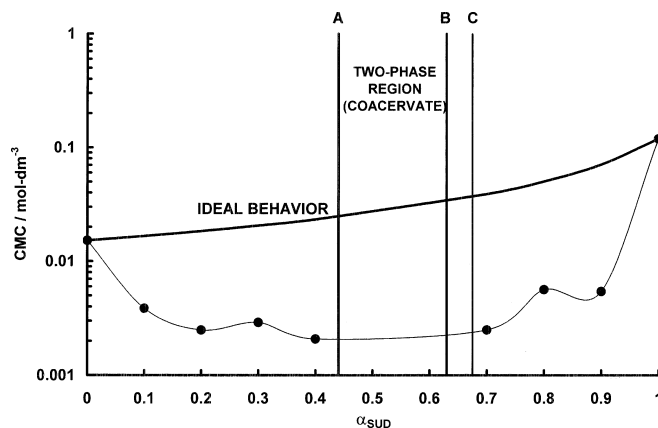


Fig. 2 Critical micelle concentration vs the total composition of the surfactant mixtures. The line shows the expected CMC if the mixture were ideal. The vertical lines indicate the limits of existence of coacervate. The right-hand limit of existence of the two-phase region was less defined. The line at $\alpha_{\text{SUD}}=0.675$ indicates the complete elimination of the coacervate

Discussion

The samples having $\alpha_{\text{SUD}}=0.5$ and 0.65 separated into two immiscible liquid phases. For $\alpha_{\text{SUD}}=0.5$, the upper phase had density $\delta_{\text{u.p.}}=0.9136 \text{ g cm}^{-3}$, total concentration $C_{\text{u.p.}}=0.517 \text{ mol dm}^{-3}$ and $\alpha_{\text{SUD,u.p.}}=0.67$, whereas the bottom phase had $\delta_{\text{b.p.}}=1.0326 \text{ g cm}^{-3}$, $C_{\text{b.p.}}=0.0214 \text{ mol dm}^{-3}$ and $\alpha_{\text{SUD,b.p.}}=0.04$. For $\alpha_{\text{SUD}}=0.65$, $\delta_{\text{u.p.}}=0.9683 \text{ g cm}^{-3}$, total concentration $C_{\text{u.p.}}=0.287 \text{ mol dm}^{-3}$ and $\alpha_{\text{SUD,u.p.}}=0.76$; $\delta_{\text{b.p.}}=1.0394 \text{ g.cm}^{-3}$, $C_{\text{b.p.}}=0.00887 \text{ mol dm}^{-3}$ and $\alpha_{\text{SUD,b.p.}}=0.042$.

Using equation 8 the mixed micelle composition X_{SUD} was computed and represented in Figure 3. It may be seen that there is a preferential composition, lying between 0.33 and 0.47 . Only at very high SUD proportion ($\alpha_{\text{SUD}}=0.9$) did the micelles have $X_{\text{SUD}}=0.505$. When $\alpha_{\text{SUD}}=0.42$, micelles have the same composition as the total surfactant mixture. No precipitation was observed, even when $\alpha_{\text{SUD}}=0.5$ or $X_{\text{SUD}}=0.5$.

Figure 4 shows the interaction parameter β computed with equation 9 vs the micelle composition. It can be seen that the minimum value is $X_{\text{SUD}}=0.372$, with $\beta=6.15$ (in kT units). Another characteristic of this figure is that the dependence of β with X_{SUD} is asymmetric. The interaction between SUD and DTAB is increasingly favourable when X_{SUD} is increased from 0 to about 0.4 , and then becomes suddenly unfavourable when $X_{\text{SUD}}\geq 0.47$. The β values in cationic systems are generally higher (in absolute value) than that of the minimum in this system (e.g. -13.2 for sodium dodecylsulfate–decyltrimethylammonium bromide [32] or about -20 [63]).

The β value at $X_{\text{SUD}}\geq 0.47$ is close to that of ionic-nonionic surfactant mixtures ($+2.2$ for lithium dodecyl-

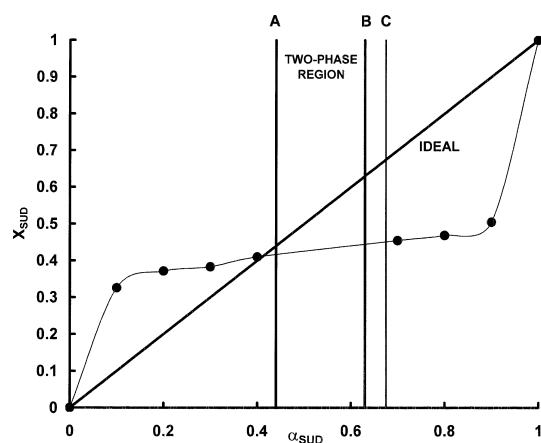


Fig. 3 Composition of the mixed micelles as a function of the total surfactant mixture. The vertical bars show the limits of the two-phase region. The solid line shows the composition of ideal mixed micelles

sulfate–lithium perfluorooctanesulfonate [29], -2.6 in sodium dodecyl sulfate (SDS)–poly (oxyethylene)₂₃ dodecylether [30], -3.9 for the system SDS–poly (oxyethylene)₄ dedecylether [31]). However, small β_{M} values were found for some particular anionic–cationic surfactant aqueous mixtures, as CTAB–sodium deoxycholate ($\beta=-2.7$ [64]), CTAB–sodium cholate ($\beta=-4.0$ [53]), and dodecyltrimethylammonium bromide–disodium dodecanephosphonate ($\beta=-1.66$ [65]). All of these systems have some structural characteristics that are different to the most commonly studied cationic-anionic mixtures.

The excess free energy of mixed micellisation showed the same dependence on the micelle composition as β .

Figure 5 shows the value of the micelle ionisation degree as a function of X_{SUD} . It may be seen that there is a maximum at $X_{\text{SUD}}=0.37$ ($\alpha_{\text{SUD}}=0.2$) with $\alpha=0.74$. Since equation 11 detects the unmicellised counter-ions, this is not the fraction of charge per micellised surfactant, except for the pure surfactant micelles. As a consequence, the electric surface potential of micelles having $X_{\text{SUD}}=0.37$ must be the minimum and only capture 26% of the counter-ions.

It is evident that there is a preferential composition of about $X_{\text{SUD}}=0.37$. Figure 4 shows, that the addition of more SUD molecules to the mixed micelle when $X_{\text{SUD}}<0.37$, increases the micelle stability whereas this addition when $X_{\text{SUD}}>0.37$ produces a sudden decrease in micelle stability. The different behavior of the system below and above this limit is also reflected in Fig. 1. The transition between micellar solution and the two-phase system is very sharp in the low α_{SUD} (and then, low X_{SUD}) side of the system, and gradual in the high α_{SUD} (and then, high X_{SUD}) side. Going out from the coacervate region, micelles with $X_{\text{SUD}}\approx 0.37$ form very easily, whereas those with $X_{\text{SUD}}>0.37$ are less stable and coexist with the coacervate in an extensive range of α_{SUD} values.

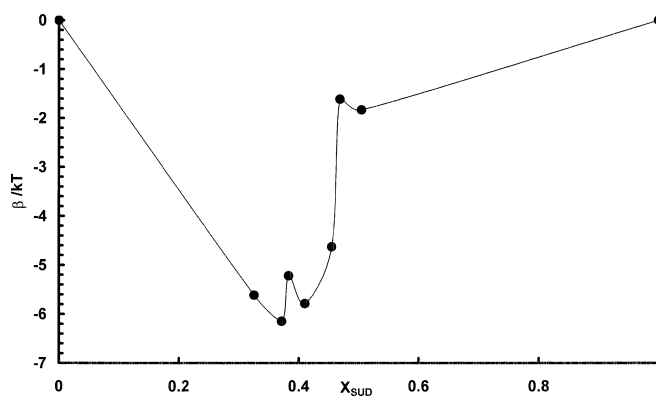


Fig. 4 The interaction parameter β vs the composition of the mixed micelles

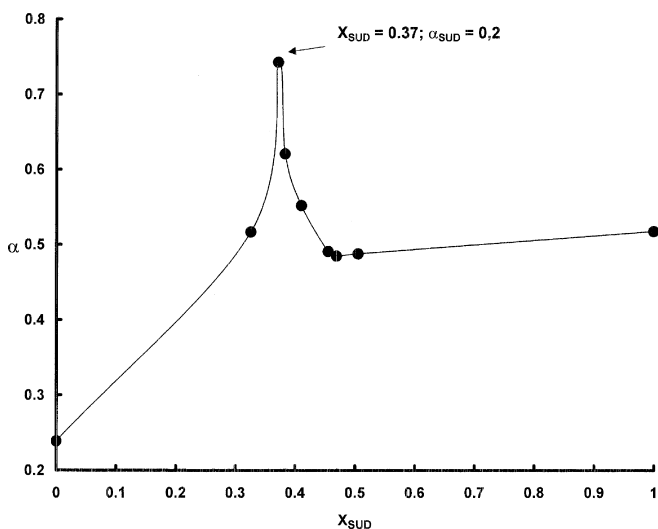


Fig. 5 The micelle ionisation degree as a function of micelle composition

A previous study on the catanionic system sodium oleate (SOL)–hexadecyltrimethylammonium bromide (HTAB) also showed a preferential composition of mixed micelles with $X_{SOL} = 0.25$, [66].

This behavior is attributed to the presence of the double bond in the distal extreme of the SUD hydrocarbon chain, whose π electrons have some affinity with water and can form hydrogen bonds with it [67, 68, 69, 70, 71, 72]. The double bond has the tendency to remain at the micelle surface, explaining the difference between the structure of SUD micelles and those of DTAB. The DTAB chains have a tendency to avoid contact with water. It is impossible to make a spherical or cylindrical micelle of DTAB or SUD with a surface completely covered by hydrophilic groups: a certain fraction of the surface consists of hydrocarbon exposed to water. Since the hydrocarbon chains are in liquid-like state [73], some of them are folded and part of the chain is in contact with water [74, 75, 76, 77, 78, 79, 80, 81]. Then, the substitution of the fully saturated DTA^+ chains in micelles by UD^- ions having a double bond with water affinity must diminish the interfacial Gibbs' free energy of micelles. This diminution is of the order of 13–16 mJ/m² with respect to a saturated hydrocarbon-water interface [82, 83]. All the DTA^+ chains can remain in the hydrophobic core interior, whereas all the UD^- double bonds could remain in contact with water.

The energetic situation of DTA^+ ions in mixed micelles having about 37% of UD^- will be more favorable than in other proportions, which may explain the minimum of β and $\Delta\mu_{mix}^{excess}$. However, the energetic situation of the UD^- ions is not considerably affected by the mixed micellisation, provided that all (or almost all) of them have their double bond at the micelle surface.

β may 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 micelle interface. However, the significance of β as an appropriate measure of the magnitude of the excess free-energy changes in the aggregation phenomenon is very uncertain [84].

This effect may be the reason for the systematic excess of DTAB in micelles in comparison with the intermicellar solution. To verify this theory, a model micelle having $n=60$ and $X_{SUD}=0.37$ was studied. Using the contribution of the groups to the partial molar volume in aqueous solution given by Lepori and Gianni [85], the partial molar volume of the DTA^+ ion may be estimated in 262 cm³mol⁻¹, and that of the DU^- one, in 172 cm³mol⁻¹. Then the volumes of the DTA^+ and DU^- ions were estimated to be 0.435 nm³ and 0.286 nm³, respectively. The volume of the hydrocarbon core of the model micelle was then estimated to be 17.9 nm³ and its radius 1.62 nm. The area of the hydrocarbon micelle core was 33.04 nm², whereas the area per micellised molecule was 0.551 nm². However, a fraction of the micelle surface is occupied by the polar head groups. If these groups are presumed to be spherical, the radius for $(-N(CH_3)_3^+)$ is 0.302 nm and for $(-COO^-)$ is 0.172 nm [85]. Both head groups are hydrated in micelles [81, 86, 87]. The area per water molecule is 0.097 nm² [88, 89, 90, 91, 92, 93]. Presuming that there is a monomolecular water layer around the polar head groups, the areas occupied by them are 0.571 nm² for $(-N(CH_3)_3^+)$ and 0.276 nm² for $(-COO^-)$. The weighted average area per micellised head group is $0.63 \times 0.751 + 0.37 \times 0.276 = 0.462$ nm². Consequently, the area of the hydrocarbon micelle core in contact with water per micellised surfactant ion may be estimated to be 0.0975 nm².

If the terminal double bond is situated at the surface, for geometrical reasons it must include the adjacent methylene group (Fig. 6). Using the group contributions to the partial molar volume given by Lepori and Gianni [85] and the bond lengths and angles, the area occupied by the $-CH_2-CH=CH_2$ group may be estimated (Fig. 6) to be 0.25 nm². This value gives a proportion of 0.39 $-CH_2-CH=CH_2$ groups per micellised surfactant molecule. Taking into account the approximations made, the agreement is very good. Therefore, the mixed micelle should have the structure as shown in Fig. 7.

In the surfactant mixtures, one Na^+ and one Br^- ion in solution is available for each dodecyltrimethylammonium undecenoate ($DTA.UD$) pair in the micelle. Besides, in systems in which one surfactant (SUD or DTAB) is in excess, there are free counter-ions coming from the ionization of the non-paired surfactant molecules in the micelles. Since the degree of ionisation is not unity within any proportion, some

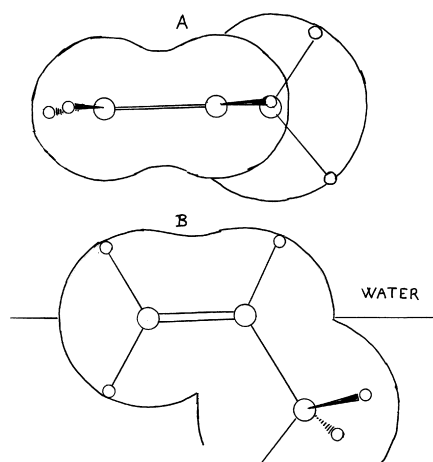


Fig. 6 The structure of the terminal $-\text{CH}_2-\text{CH}=\text{CH}_2$ group at the micelle surface. **A** top view, **B** lateral view

counter-ions are attached to the Stern layer, even in the 1:1 mixed micelles.

The radius of the model micelle is 2.21 nm (taking into account the size of the predominant head group, i.e. $\text{N}^+(\text{CH}_3)_3$, and a layer of water molecules of head groups' hydration). The micelle is composed of 18 UD^- and 42 DTA^+ ions, 18 of these are neutralised by the micellised UD^- ions. This implies that only 24 positive charges are distributed at the micelle surface to produce the potential that captures some counter-ions. The resulting electrical potential at the surface of this micelle without attached counter-ions (and supposing homogeneous charge distribution at the surface) was computed to be 81 mV. This is similar to the ζ potential obtained for micelles of similar size with attached counter-ions, namely 80.9 mV for micelles of sodium dodecylsulfate in $0.03 \text{ mol}\cdot\text{dm}^{-3}$ NaCl [94], 75 mV for dodecyltrimethylammonium chloride [95] and 78–87 mV for dodecyltrimethylammonium hydroxide [96]. Since ζ is the external potential after the capture of the counter-ions at the micelle Stern layer, it can be concluded that in this micelle model, the driving force to capture the counter-ions is not the electrostatic potential but the specific adsorptive forces derived from the polarizability of the bromide ion [50]. The inclusion of the double bonds in the micelle surface may also be the explanation for the high value of α in pure SUD micelles: the separation of the carboxylate groups reduces the surface potential and the capacity for capturing the counter-ions.

The inclusion of the $-\text{CH}_2-\text{CH}=\text{CH}_2$ group in the Stern layer can also favor the formation of spherical micelles at low concentration. This inclusion gives an appropriate curvature and some hydrophilicity to the

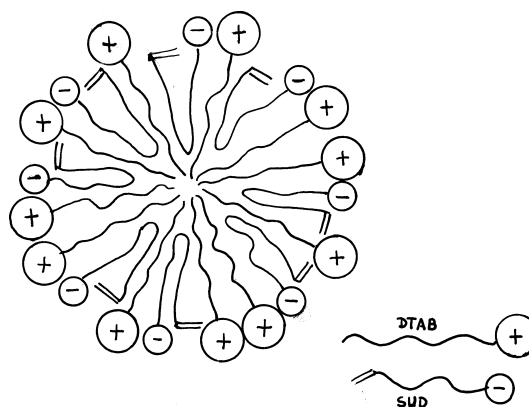


Fig. 7 The proposed structure of a SUD—DTAB mixed micelle

micelle-water interface, which favors the spherical shape rather than cylindrical or planar structures. The folding of the undecenoate chain to expose the double bond to water causes a hydrocarbon crowding at the proximity of the surface. There is a loop of the portion of the chain between the carboxylate and the $-\text{CH}_2-\text{CH}=\text{CH}_2$ groups, both anchored at the surface. Then, this system may be considered similar to a mixture of a long-chained surfactant (DTAB) with a surfactant having a bulky, short hydrophobic group (SUD). In this case, Edlund et al. [13] explained this behavior on the basis of geometrical effects caused by the different values of n_C . The critical packing parameter of the mixture $CPP = v/al$, where v is the alkyl chain volume, a is the polar head area and l is the alkyl chain length [97]. According to Edlund et al. [13], the inclusion of the shortest surfactant molecule in the longest surfactant micelle gives rise to a reduction of the effective CPP of the surfactant mixture, by augmentation of a , whereas l remains constant and v increases slightly. A $CPP < 1/3$ value is compatible with the formation of spherical micelles. Increasing the surfactant mixture concentration produces a reduction of the value of a , caused by the reduction of the electrostatic repulsion between the charged head groups in excess in non-equimolecular micelles, and the possible change in the micelle composition (The values of X_1 given by the mixed micelles theory are valid at the CMC). This leads to an increase of CPP . If $1/3 < CPP < 1/2$, the surface curvature of aggregates is compatible with cylindrical micelles. This situation may be extrapolated to the DTAB-SUD mixture.

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References

1. Filipovic-Vincekovic N, Bujan M, Dragecic D, Nekić N (1995) *Colloid Polym Sci* 273:182
2. Amante JC, Scamehorn JF, Harwell JH (1991) *J Colloid Interface Sci* 144:243
3. Jockela P, Jönson B, Wennerström H (1985) *Progr Colloid Polym Sci* 70:17
4. Boglioni P (1987) In: Mittal KL, Bothorel P (eds) *Surfactants in Solution*, vol 4. Plenum, New York, pp 393–404
5. Herrington KL, Kaler EW, Miller DD, Zasadzinski JA, Chiruvolu S (1993) *J Phys Chem* 97:13792
6. Matsuki H, Aratono M, Kaneshina S, Motomura K (1997) *J Colloid Interface Sci* 191:120
7. Halle B, Landgren M, Jönsson B (1988) *J Phys (Paris)*, 49:1235
8. Szliefer I, Ben-Shaul A, Gelbart WM (1967) *J Phys Chem* 88:7094
9. Maeda H (1995) *J Colloid Interface Sci* 172:98
10. Nishikido N (1993) In Ogino K, Abe M, (eds) *Mixed Surfactant Systems*, cap 2. Dekker, New York pp 32–43
11. Scowen RV, Leja S (1967) *Can J Chem* 45:2821
12. Oakenfull DG, Fenwick DE (1973) *Aust J Chem* 26:2649
13. Edlund H, Sadaghiani A, Khan A (1997) *Langmuir* 13:4953
14. Barzykin AV, Almgren M (1996) *Langmuir* 12:4672
15. Eriksson JC, Ljunggren S, Enriksson U (1985) *J Chem Soc Faraday Trans 2* 81:833
16. Hoffmann H, Pössnecker G (1994) *Langmuir* 10:381
17. Forster T, von Rybinski W, Schwugere MJ (1990) *Tenside Surfactants Deterg* 27:254
18. Osborne-Lee IW, Schechter RS (1986) In: Scamehorn JF (ed) *Phenomena in Mixed Surfactant Systems*, ACS Symposium Series 311, American Chemical Society, Washington DC pp 30
19. Scamehorn JF, Schechter RS, Wade WH (1982) *J Dispersion Sci Technol* 3:261
20. Minardi RM, Schulz PC, Vuano B (1996) *Colloid Polym Sci* 274:669
21. Balzhiser RE, Samuels MR, Eliassen JD (1972) *Chemical Engineering Thermodynamics*. Prentice Hall, Englewood Cliffs, pp 225
22. Crisantino R, De Lissi R, Miloto S (1994) *J Solution Chem* 23:639
23. Hey MJ, Mac Taggart JW, (1985) *J Chem Soc Faraday Trans 1* 81:207
24. Rosen MJ, Zhao F (1983) *J Colloid Interface Sci* 95:443
25. Treiner C, Amar Khodja A, Fromon M (1987) *Langmuir* 3:729
26. Shiloach A, Blankschtein D (1998) *Langmuir* 14:1618, and references therein
27. Rosen MJ, Gao T, Nakatsuji Y, Masuyama A (1994) *Colloids Surf A* 88:1
28. Mukerjee P, Yang A (1976) *J Phys Chem* 89:1388
29. Miyagishi JH, Ishibai Y, Asakawa T, Nishida M (1985) *J Colloid Interface Sci* 103:164
30. Treiner C, Vaution C, Miralles E, Puisieux F (1985) *Colloids Surf* 14:285
31. Rubingh DN (1979) In: Mittal KL (ed) *Solution Chemistry of Surfactants*, vol 1, Plenum, New York pp 337
32. Holland PM, Rubingh DN (1983) *J Phys Chem* 87:1984
33. Sarmoria C, Puvvada S, Blankschtein D (1992) *Langmuir* 8:2690
34. Scamehorn JF (1986) In: Scamehorn JF (ed) *Phenomena in Mixed Surfactant Systems*. ACS Symposium Series 311, American Chemical Society, Washington DC pp 177
35. Ghogomu M, Bourouka M, Dellacherie J, Balesdent D, Dirand M (1997) *Termochim Acta* 306:69
36. Mukerjee P, Handa T (1981) *J Phys Chem* 85:2298
37. Handa T, Mukerjee P (1981) *J Phys Chem* 85:3916
38. Clapperton RM, Ottewill RH, Ingram BT (1994) *Langmuir* 10:51
39. Burkitt SJ, Ingram BR, Ottewill RH (1988) *Progr Colloid Polym Sci* 76:247
40. Lange H, Beck KH (1973) *Kolloid Z u Z Polym* 251:424
41. Funasaki N, Hada S (1979) *J Phys Chem* 83:2471
42. Clint J (1975) *J Chem Soc* 71:1327
43. Cheng C-H (1994) *J Chin Chem Soc* 42:33
44. Evans HC (1956) *J Chem Soc Pt 1*:579
45. Anacker EW, Rush RM, Johnson JS (1964) *J Phys Chem* 68:81
46. Filipovic-Vincekovic N, (1986) *Radioanalyt Nucl Chem* 99:89
47. *Handbook of Chemistry and Physics* (1975–1976) CRS, Cleveland, 56th edn
48. Anacker EW, Ghose HM, (1963) *J Phys Chem* 67:1713
49. Morini MA, Schulz PC, Puig JE (1996) *Colloid Polym Sci* 274:662
50. Schulz PC, Gschaider de Ferreira ME, Pedroni V (1993) *Latin American Applied Research* 23:237
51. Shishido S (1951) *Bull Chem Soc Japan* 24:41
52. Rodríguez JL, Schulz PC, Puig JE (1999) *Colloid Polym Sci* 277:1072
53. Larrabee C, Sprague E (1986) *J Colloid Interface Sci* 114:256
54. Vikingstad E, Skauge A, Hoiland H (1978) *J Colloid Interface Sci* 66:240
55. Corrin ML, Harkins WD (1947) *J Chem Soc* 68:679
56. Sheppard SE (1942) *Rev Mod Phys* 14:303
57. Kortüm G (1936) *Z Physik Chem B33*:1–B34:255
58. Lewschin WL (1934) *Acta Physicochim URSS* 1:685
59. Sprange ED, Ducker DC, Larrabee CE (1983) *J Colloid Interface Sci* 92:416
60. Katsu T (1991) *Colloids Surf* 60:199
61. Causi S, de Lisi R, Milioto S, Tirona N (1991) *J Phys Chem* 95:5664
62. Ingram T, Jones MN (1969) *Trans Faraday Soc* 65:297
63. Liu I, Rosen MJ (1996) *J Colloid Interface Sci* 179:454
64. Swanson-Vethamuthu M, Almgren M, Ansson P, Zheo J (1996) *Langmuir* 12:2186
65. Schulz PC, Minardi RM, Vuano B (1999) *Colloid Polym Sci* 277:837
66. El-Kadi N, Martins F, Clausse D, Schulz PC (2003) *Colloid Polym Sci* 281:353
67. Furutaka S, Ikawa S-I (1998) *J Phys Chem* 108:1347
68. Furutaka S, Ikawa S-I (1998) *J Chem Phys* 108:5159
69. Goldman M, Crisler RO (1958) *J Org Chem* 23:751
70. Oki M, Iwamura H (1960) *Bull Chem Soc Jpn* 33:717
71. Rablen PR, Lockman JW, Jorgensen WL (1998) *J Phys Chem A* 102:3782
72. Atwood JL (1991) *Nature* 349:683
73. Stigter D (1967) *J Colloid Interface Sci* 23:379
74. Clifford J, Pethica BA (1965) *Trans Faraday Soc* 61:182
75. Clifford J (1965) *Trans Faraday Soc* 61:1276
76. Stigter D (1974) *J Phys Chem* 78:2480
77. Muller M, Pellerin JM, Chen WW (1972) *J Phys Chem* 76:3012
78. Drakenberg T, Lindman B (1973) *J Colloid Interface Sci* 44:184
79. Walker T (1973) *J Colloid Interface Sci* 45:372
80. Griffith GH, Dehlinger PH, Van SP (1974) *J Membrane Biol* 15:159
81. Ekwall P, Mandell L, Solyom P (1971) *J Colloid Interface Sci* 35:519
82. Fowkes FM (1987) *J Adhes Sci Technol* 1:7
83. Fowkes FM (1963) *J Phys Chem* 67:2538
84. Holland PM (1986) *Colloids Surf* 19:171
85. Lepori L, Gianni P (2000) *J Solutn Chem* 29:405
86. Solyom P, Ekwall P (1969) *Chimie Physique Appliquée, Treatments Agents de Surface, CR Congrès Internationale des Detergents 5th 1968* 2:1041

-
87. McBain JW, Kawakami J, Lucz HP (1933) *J Am Chem Soc* 55:2762–2763
88. Fowkes FM (1962) *J Phys Chem* 66:385
89. Joos P (1967) *Bull Chem Soc Belg* 76:591
90. Rodakiewicz-Nowak J (1982) *J Colloid Interface Sci* 85:586
91. Rodakiewicz-Nowak J (1982) *J Colloid Interface Sci* 84:532
92. Rodakiewicz-Nowak J (1983) *Colloids Surfaces* 6:143
93. Luchasen-Reynders EH (1976) *Progr. Surf Membr Sci* 10:253
94. Stigter D, Mysels KJ (1955) *J Phys Chem* 59:45
95. Hoyer HW, Marmo A (1961) *J Phys Chem* 65:1807
96. Morini MA, Schulz PC (1997) *Colloid Polym Sci* 275:802
97. Mitchell DJ, Ninham BW (1980) *J Chem Soc Faraday Trans 2* 77:776