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ORIGINAL CONTRIBUTIONS

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Unusual volumetric and hydration behavior of the catanionic system sodium undecenoate: sodecyltrimethylammonium bromide

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Abstract Following the studies on the effect of double bonds in the surfactant hydrophobic tail on the formation of mixed surfactant aggregates, we studied the viscosity and density of the system Sodium 10-undecenoate (SUD)–decyltrimethylammonium bromide (DTAB)–water. We found that the partial molar volume (pmv) and intrinsic viscosity of both, micellised and unmicellised mixtures, are non-ideal, dependent on the mixture composition and related to structural changes in micelles. These phenomena are caused by the presence of the double bond at the distal extreme of the SUD molecule, which has some affinity with water by formation of hydrogen bonds. In particular, as far as we know, this is the first report on non-ideal behavior of the pmv in mixed micelles.

Keywords Mixed micelles · Partial molar volume · Micelle hydration · Sodium 10-undecenoate · Catanionic surfactant · Dodecyltrimethylammonium bromide

Introduction

Mixed surfactant systems find widespread use in many domestic and technical applications. Such surfactant mixtures are often preferable to single component systems since the solution properties may be tuned via the proportion of two suitable surfactants.

In spite of the importance of solubilisation and mixed micellisation, few studies have dealt with the volumetric properties of mixed-micellar or solubilised systems [1–5]. One of the volumetric properties of such solutions is expressed by the partial molar volume (pmv) that is a useful function to characterise solute-solvent interaction and may yield valuable information about the thermodynamics of mixed micelle formation. In mixed micelles pmv gives information on the surfactant-surfactant interactions in the hydrocarbon micelle core when applying the pseudophase model [6].

We have measured the densities of aqueous solutions that contain mixed micelles, and thereby examined the effect of mixing on the pvm in the micellar and the premicellar states. The mixed micellar system used in this study was sodium 10-undecenoate (SUD) and dodecyltrimethylammonium bromide (DTAB) in water. In this work we studied the effect of a double bond in the SUD hydrocarbon tail on the volumetric behaviour of mixing.

In the chemistry of colloids in aqueous solution or suspension, hydration plays an important role. Micelle hydration is information of interest to know the micelle structure. It can be obtained from viscosity data. In general micelle hydration is easily understood because micelles are more or less spherical, and its surface is a combination of charged groups, some counterions and some hydrocarbon surface exposed to water. However, we are studying a rather uncommon system, the aqueous SUD–DTAB catanionic system. Here the micelle surface contains carboxylate and trimethylammonium head groups, bromide and sodium counterions and the hydrocarbon surface is a combination of hydrophobic saturated hydrocarbons and hydrophilic double bonds, which can form hydrogen bonds with water.

The aqueous SUD–DTAB catanionic system was studied at low concentration in a previous work [7]. The system did not precipitate, even at 1:1 SUD:DTAB proportion, but showed the formation of a coacervate in a range of surfactant mixture composition. Micelles have a preferential composition of 0.37-mole fraction of SUD (X_{SUD}) [7]. This behavior is attributed to the presence of the double bound at the distal extreme of the SUD molecule, which can form hydrogen bonds with water. As a consequence, the vinyl groups ($\text{–CH}=\text{CH}_2$) are situated at the interface between the hydrocarbon micelle core and water, reducing the interfacial free energy. Structural computations demonstrated that the mentioned SUD proportion produces complete coverage of the micelle surface by the double bonds. The interaction between the surfactant components in the mixed micelle was non-ideal.

Experimental

Sodium 10-undecenoate was from Aldrich. DTAB was from Aldrich. Both surfactants were employed as received.

To prepare the different samples, the appropriate amount of both surfactants were 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 to prepare mixtures with mole fraction of SUD (without considering water) $\alpha_{\mathrm{SUD}}=0$ (pure DTAB solution), 0.1, 0.2, 0.3, 0.4, 0.7, 0.8, 0.9 and 1 (pure SUD solution). Since between $\alpha_{\mathrm{SUD}}=0.43$ and $\alpha_{\mathrm{SUD}}=0.67$ the system shows a two phase region [7], proportions included in this zone were not prepared. All initial solutions were prepared at concentrations well above the CMC's determined for each surfactant mixture [7].

To determine the density dependence on concentration, dilutions of the initial solutions were measured in a Becker'Sons chainomatic density balance having a precision of ± 0.00001 g cm^{-3}. Viscosity measurements were made with an automatic Ostwald viscometer, through titration with water of each concentrated solution. Water was used as a reference.

All determinations were made at 25.0 °C. When error limits were computed, the confidence level was 0.90.

The molecular mechanics modelling was performed in the Chem3D Ultra 5.0 Cambridge Soft package (1999). It includes an improvement of the Molecular Mechanics version 2 (MM2) software and the semi empirical Parameterized Method version 3 (PM3) method. MM2 was used to explore the steric energy of different conformations of the interacting molecules. Once the minimization of the steric energy was obtained, a PM3 calculation of the formation enthalpy was performed. The change of enthalpy and steric energy of interaction were calculated as the difference between the enthalpy or the steric energy of the product (Ethylene – water complex at the equilibrium distance) minus the enthalpy and the steric energy of reactants (ethylene and water at infinite distance).

Theory

Density

Density (δ) measurements as a function of the surfactant concentration C may be used to determine the pmv V_{pm} by [8]:

$$V_{\mathrm{pm}}=\frac{1}{\delta}\left[M-\frac{V\partial\delta}{\partial C}\right], \tag{1}$$

where M is the molar weight of the surfactant and V is the volume of the solution that contains 1,000 g of water:

$$V=\frac{1,000+MC}{\delta}. \tag{2}$$

In mixed surfactant systems, the average molar weight must be used:

$$M_{\mathrm{av}}=\alpha_{\mathrm{SUD}}M_{\mathrm{SUD}}-(1-\alpha_{\mathrm{SUD}})M_{\mathrm{DTAB}}. \tag{3}$$

By using Eq. 1 above the CMC and by extrapolation to the CMC, the micellised surfactant pmv at zero micelle concentration ($V^{\mathrm{o}}_{\mathrm{mp,M}}$) is found. The CMC for each α_{SUD} value was taken from reference [7].

By extrapolation to $C=0$ of V_{pm} computed with Eq. 1 below the CMC, the pmv of the unmicellised surfactant at infinite dilution ($V^{\mathrm{o}}_{\mathrm{mp,M}}$) is found.

Viscosity

The reduced specific viscosity of micelles is defined by [9]:

$$\frac{\eta_{\mathrm{sp}}}{C_{\mathrm{M}}}=\frac{\eta/\eta_0-1}{C_{\mathrm{M}}}, \tag{4}$$

where η and η_0 are the viscosity of the micellar solution and of the solvent. The concentration of the micellised surfactant C_{M}, in g cm^{-3}, is taken as:

$$C_{\mathrm{M}}=\frac{(C_{\mathrm{T}}-\mathrm{CMC})M}{1,000}, \tag{5}$$

where C_T is the total concentration and CMC the critical micelle concentration and M is the molecular weight of the surfactant.

By extrapolation to $C_M = 0$ the intrinsic viscosity $[\eta]$ may be obtained [10]:

$$[\eta] = vE(v_2 + w.v_1), \tag{6}$$

where v is the shape factor, $v_1$and v_2 are the specific volumes of the solvent (water) and the dry surfactant, and w is the grams of water per gram of surfactant ratio in micelles. E is the electroviscous effect correction.

Results and discussion

Density

Mixture behaviour below the CMC

Figure 1 shows the infinite dilution pmv ($V^o_{mp,M}$) of the unmicellised different mixtures as a function of α_{SUD}, the mole fraction of SUD in the surfactant mixture without considering water. The ideal pmv of the mixture having a given α_{SUD} value was computed by:

$$V^o_{mp,m,ideal} = \alpha_{SUD} \cdot V^o_{SUD} + (1 - \alpha_{SUD})V^o_{DTAB}, \tag{7}$$

where V^o_{SUD} and V^o_{DTAB} are the infinite dilution pmv of aqueous pure SUD and DTAB, respectively. It can be seen that the experimental pmv ($V_{mp,m}$) is less than the ideal value in the DTAB-rich region, whereas in the SUD-rich region on the other side of the two-phase region, the measured pmv ($V^o_{mp,M}$) is higher than the ideal one ($V^o_{mp,m,ideal}$).

By using the groups contributions to the pmv of Lepori and Gianni [11], the pmv of unmicellised SUD was computed as $V^o_{mp,m,SUD} = 165.8 \pm 3.7\ cm^3\ mol^{-1}$. Another computation was made by using the value $V^o_{mp,m,NaC10} = 149.5\ cm^3\ mol^{-1}$, for sodium decanoate and $V^o_{mp,m,NaC12} = 181.3\ cm^3\ mol^{-1}$, for sodium dodecanoate [12]. The pmv of sodium undecanoate was computed as the average of these experimental values, $V^o_{mp,m,NaC11} = 165.4\ cm^3\ mol^{-1}$, and that of SUD, by subtracting the group contributions of $-CH_2-$ ($15.93\ cm^3\ mol^{-1}$) and CH_3- ($21.44\ cm^3\ mol^{-1}$) and by adding that of $CH_2=$ ($18.82\ cm^3\ mol^{-1}$) and $=CH-$ ($13.29\ cm^3\ mol^{-1}$) [11]. The result was $V^o_{mp,m,SUD} = 160.14\ cm^3\ mol^{-1}$, The SUD pmv we found is $V^o_{mp,m,SUD} = 153 \pm 7\ cm^3\ mol^{-1}$. The slight difference may be explained in the light of the work of Gianni and Lepori [13], who found that the presence of two polar groups at the ends of a long hydrocarbon chain, irrespective of their nature and mutual separation, systematically produces a volume contraction with respect to the computed pmv. A partial overlapping of the solvation spheres of these hydrophilic centres has been invoked in order to explain these findings [14]. This hypothesis is in accordance with the average distance between the end groups of a straight chain molecule that, following statistical considerations, should be shorter than the distance corresponding to the completely extended chain. The molecular conformation of these compounds in water involves some coiling of the chain.

Gianni and Lepori [13] suggest that the long-chain α,ω-substituted molecules assume in aqueous phase a coiled conformation of Ω form, with the terminal groups on the same side, but their solvation spheres do not necessary overlap. Such a conformation would be more compact with respect to that of a linear monofunctional molecule and would accordingly have a lower pmv due to its easier packing in water.

In conclusion, the overlapping of hydration spheres and conformational changes are probably the two main factors that determine the sign and magnitude of the deviation from simple additivity rules for bifunctional compounds.

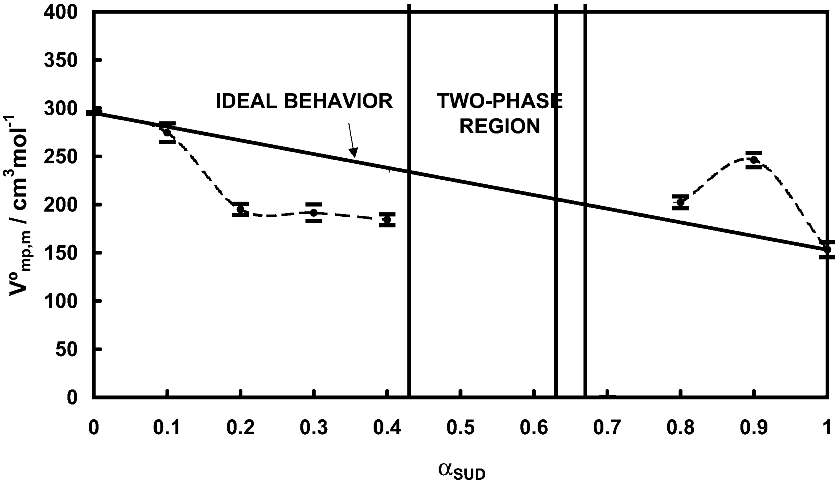

Fig. 1 The infinite dilution pmv ($V^o_{mp,m}$) of the unmicellised different mixtures as a function of the mixture composition α_{SUD}. The *vertical line* at $\alpha_{SUD} = 0.44$ indicates a sudden transition from the one-phase to two-phase region. The *two vertical lines* at the right-hand side of the two-phase region indicate the limits of the region in which a gradual transition occurs. *Lines* are eye guides

The value of DTAB pmv we found was 295.0 ± 0.8 cm^3 mol^{-1} that is similar to the literature values: 285.1 cm^3 mol^{-1} [15]; 295.5 cm^3 mol^{-1} [16]; 287.0 cm^3 mol^{-1} [17].

Effect of mixing the unmicellised surfactants

It is clear from Fig. 1 that there is a non-ideal interaction between unmicellised SUD and DTAB molecules, since the measured $V^{o}_{\mathrm{mp,m}}$ in the mixed systems is not ideal.

The effect is different in the low-SUD proportion side of Fig. 1 than on the high SUD proportion side. Below $\alpha_{\mathrm{SUD}} = 0.42$, the experimental average pmv is lower than the ideal one. The cause may be the inclusion of some DTA$^+$ ions in the Ω conformation of the UD$^-$ ions by formation of an ion pair at low concentration. This structure must be more compact than the two separate ions, giving a reduction in the average pmv. Above $\alpha_{\mathrm{SUD}} = 0.67$, the effect may be the opposite: the formation of an SUD-DTAB complex may affect the Ω conformation producing an increase in the pmv.

Effect of mixing on the micellar pmv

Figure 2 shows the micellised surfactant pmv at the mixture CMC, $V^{o}_{\mathrm{mp,M}}$, and the ideal value, $V^{o}_{\mathrm{mp,M,ideal}}$, computed by:

$$V^{o}_{\mathrm{mp,M,ideal}} = X_{\mathrm{SUD}} \cdot V^{o}_{\mathrm{SUD,M}} + (1 - X_{\mathrm{SUD}}) V^{o}_{\mathrm{DTAB,M}}, \qquad (8)$$

where $V^{o}_{\mathrm{SUD,M}}$ and $V^{o}_{\mathrm{DTAB,M}}$ are the pmv of micellised SUD and DTAB at the CMC of each pure surfactant, respectively, and X_{SUD} is the mole fraction of SUD in micelles (on a surfactant-only basis) at the CMC of the mixture, obtained from reference [7]. It can be seen that the experimental pmv ($V_{\mathrm{mp,M}}$) is higher than the ideal value in the DTAB-rich region where X_{SUD} is below 0.41, whereas in the SUD-rich region on the other side of the two-phase region ($X_{\mathrm{SUD}} > 0.67$), $V^{o}_{\mathrm{mp,M}} < V^{o}_{\mathrm{mp,M,ideal}}$. Figure 3 shows $V^{o}_{\mathrm{mp,M}}$ as a function of the micelle composition, X_{SUD}, which is a more significant representation than that as a function of α_{SUD}. The tendency is the same, showing that the behaviour is ideal when $X_{\mathrm{SUD}} = 0.41$.

In general, micelle formation is accompanied by an increase of $V_{\mathrm{mp,M}}$, when compared with $V_{\mathrm{mp,m}}$. [15]. As examples, for sodium decanoate $V^{o}_{\mathrm{mp,M}} = 160.8$ cm^3 mol^{-1} and $V^{o}_{\mathrm{mp,m}} = 149.5$ cm^3 mol^{-1}, for sodium dodecanoate, $V^{o}_{\mathrm{mp,M}} = 192.3$ cm^3 mol^{-1} and $V^{o}_{\mathrm{mp,m}} = 181.3$ cm^3 mol^{-1}, [12] or $V_{\mathrm{mp,M}} = 207.2$ cm^3 mol^{-1} and $V_{\mathrm{mp,m}} = 196.1$ cm^3 mol^{-1}, [18], for DTAB $V_{\mathrm{mp,M}} = 278.1$ cm^3 mol^{-1} and $V_{\mathrm{mp,m}} = 285.1$ cm^3 mol^{-1}, [15] or $V_{\mathrm{mp,M}} = 295.5$ cm^3 mol^{-1} and $V_{\mathrm{mp,m}} = 287.0$ cm^3 mol^{-1} [17].

It is clear from Figures 2 and 3 that the pmv was not additive in the micellar state. There is an excess pvm of mixing $\Delta V^{o}_{\mathrm{mp,M}}{}^{\mathrm{mix}} = V^{o}_{\mathrm{mp,M}}{}^{\mathrm{experimental}} - V^{o}_{\mathrm{mp,M}}{}^{\mathrm{ideal}}$. It is positive for $X_{\mathrm{SUD}} < 0.41$ and negative above this micelle composition.

In alkyltrimethylammonium bromides mixtures with hexaoxyethylene dodecyl ether or octaoxyethylene dodecyl ether, the change in pmv on micellisation with respect to the ideal value, $\Delta V^{o}_{\mathrm{mp,M}}{}^{\mathrm{mix}}$ was zero [4], although the enthalpy of mixing was not zero, and then, the mixing process is not ideal. Lopata et al [5] measured the volumetric behaviour of mixing in anionic/non-ionic, cationic / non-ionic and anionic/cationic mixed micelles at total surfactant concentrations much greater than the CMC. For all the mixed surfactant systems examined by

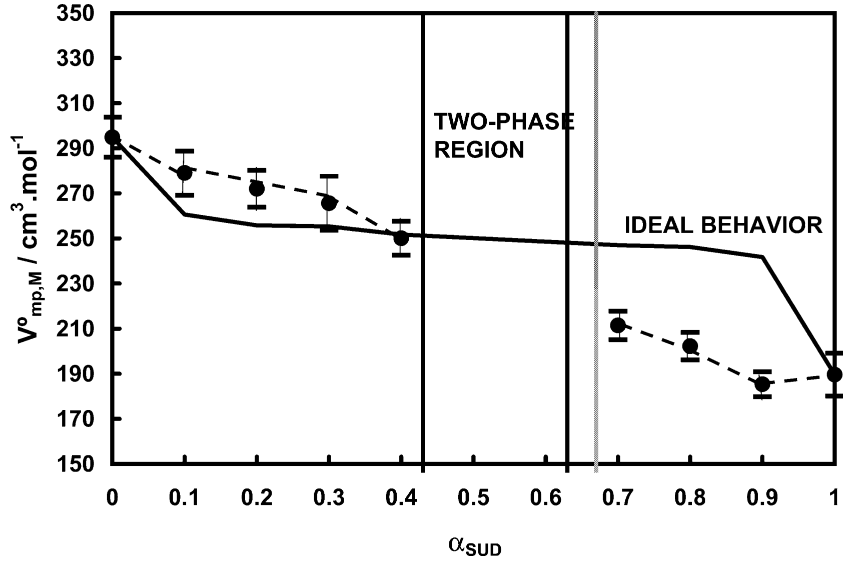

Fig. 2 The micellised surfactant pmv at the CMC, $V_{\mathrm{mp,M}}$, and the ideal value, $V^{o}_{\mathrm{mp,M,ideal}}$, as a function of the mixture composition α_{SUD}. *Vertical lines* have the same meaning as in Fig. 1. *Lines* are eye guides

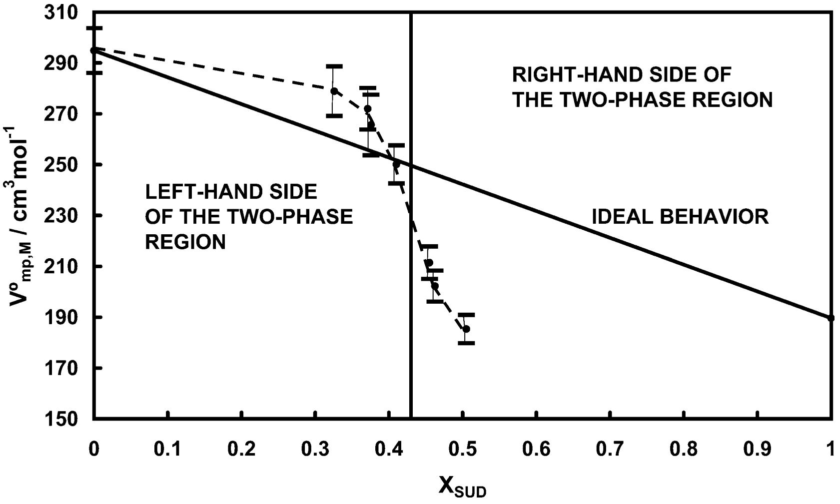

Fig. 3 The micellised surfactant pmv at the CMC, $V_{mp,M}$, and the ideal value, $V^o_{mp,M,ideal}$, as a function of the micelle composition X_{SUD}. *Lines* are eye guides

these authors, $\Delta V^o_{mp,M}{}^{mix} = 0$, even though the free energies, enthalpies and entropies of mixing at the onset of mixed micelle formation (as indicated by the mixture CMC) exhibited strong negative deviations from ideality [19]. However, a system exhibiting no volume change on mixing needs not conform to all the equations for ideal solution behaviour [20]. Furthermore, Lopata et al. [5] also found that by adding electrolyte the ideal volumetric mixing in the studied micelles did not change. The above results suggest that the electrostatic interactions do not significantly affect the molar volume of a mixed micelle. Therefore, the micelle hydrophobic core dominates the volumetric mixing in mixed micelles.

Lopata et al. [5] could not compare their results with the regular solution theory pseudophase separation modelling of the mixture critical micelle concentration data, because they worked at a surfactant concentration much higher than the CMC. We could compare our volumetric results at the CMC with the micelle composition obtained by the regular solution model.

Modern theories on the effect of molecular conformation changes on the pmv [21] could be a partial possible explanation of the volumetric changes on mixed micelle formation in the studied system. Hirata et al [21] found pmv changes of 10 cm^3 mol^{-1} by simply changing two conformational angles in the alanine tripeptide. When two surfactants having similar hydrocarbon tails coexist in mixed micelles, it is reasonable to suppose that the conformation of the tails in the mixed micelle core do not differ from that in the pure surfactant micelles, but when both surfactants have unlike tails, the conformation of both chains in the mixed micelle core could be very different from that in the pure surfactant micelles.

The pmv of ionic groups is less than that of a nonpolar group of similar volume, because of the polarizing effect of the charge on water with consequent volume contraction or shrinkage. The same effect is found in polar groups, the diminution being dependent on polarity as well as on the capability of hydrogen bonding [11]. Thus, changes that reduce the hydration of groups on micellisation will produce an increase in the pmv, and those that increase the hydration, a decrease in the pmv. The inclusion of water in the micellar structure because the hydrophilicity of the vinyl groups also may contribute to reduce the pmv (see below).

The above effects may explain the observed $\Delta V^o_{mp,M}{}^{mix}$ values found in this work. SUD in micelles having $X_{SUD} < 0.41$ may change its conformation and may partially dehydrate the terminal $CH_2{=}CH$– group causing an increase in the average $V_{mp,M}$ value. In micelles having $X_{SUD} > 0.41$ the conformational changes may cause a reduction of the average pmv by inclusion of DTA^+ ions into the loops formed by UD^- ions to maintain both the $-COO^-$ and $CH_2{=}CH$– groups in contact with water.

The interactions between SUD and DTAB in mixed micelles are not ideal [7]. However, since a system exhibiting no volume change on mixing need not conform to all the equations for ideal solution behaviour [20], this non-ideal behaviour of the pmv on mixing was not obviously predictable. As far as we known, this is the first surfactant mixture showing this behaviour.

Viscosity

The reduced specific viscosity $\eta_{r,sp} = (\eta/\eta_{CMC} - 1)/c_M$ was plotted versus the concentration of micellised surfactant in grams per cubic centimeter (c_M). Here η and η_{CMC} are the viscosity of the solution and that at the critical micelle concentration (CMC). By extrapolation of $\eta_{r,sp}$ to $c_M = 0$ the intrinsic viscosity $[\eta]$ was obtained. Figure 4 shows the $[\eta]$ values at the CMC versus α_{SUD}.

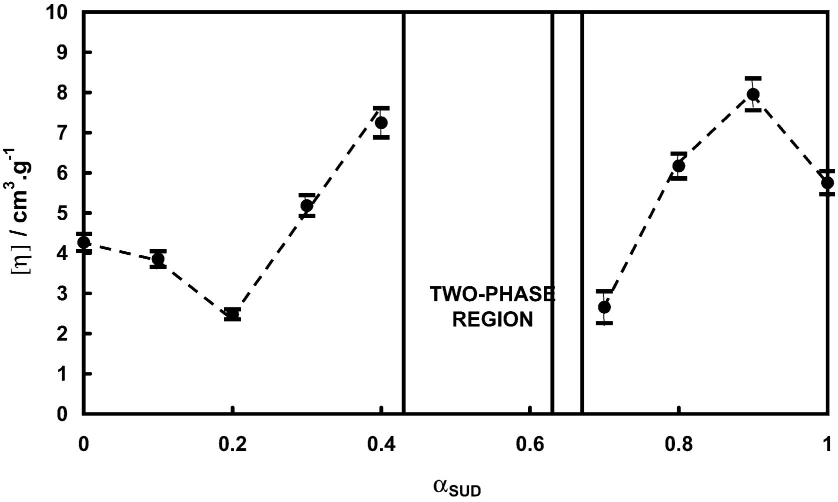

Fig. 4 The intrinsic viscosity [η] at the CMC versus α_{SUD}. *Vertical lines* have the same meaning as in Fig. 1. *Lines* are eye guides

Figure 5 shows the intrinsic viscosity as a function of the micelle composition X_{SUD}, which was obtained from literature [7].

To compute the micellised surfactant molecule hydration, Eq. 6 was employed. Since the relative viscosity at the CMC at all α_{SUD} values was small, spherical micelles were assumed. Then v was taken as 2.5, the value found by Einstein and verified for numerous spherical colloids [22]. To obtain the value of E, the charge of the micelle must be known. The values of the micelle ionization degree were determined in a previous work [7]. However, the true charge of the mixed micelles is not known, because part of the charge is neutralized by the opposite charged head groups, and part by the inclusion of counterions (Na^+ and/or Br^-) in the Stern layer of the micelles. This situation makes very uncertain the determination of E for the mixed micelles. Since for low surface potential micelles E is almost unity [23], we assumed this value. The value of v_2 was computed with:

$$v_2 = \frac{V^{\mathrm{o}}_{\mathrm{mp,m}}}{M_{\mathrm{mix}}}, \tag{9}$$

where $V^{\mathrm{o}}{}_{\mathrm{mp,M}}$ is the pmv of the micellised surfactant at the mixture CMC, and M_{mix} the average molecular weight of the mixed surfactant at the CMC, computed with:

$$M_{\mathrm{mix}} = X_{\mathrm{SUD}}M_{\mathrm{SUD}} + (1 - X_{\mathrm{SUD}})M_{\mathrm{DTAB}}. \tag{10}$$

The value of v_1 was taken as 0.81659 $cm^3\ g^{-1}$, computed from literature data [24]. With these data the values of w were computed for each α_{SUD} value. The hydration was then computed with $n_{\mathrm{hydr}} = w.M_{\mathrm{mix}}/M_{H_2O}, M_{H_2O}$ being the molar weight of water.

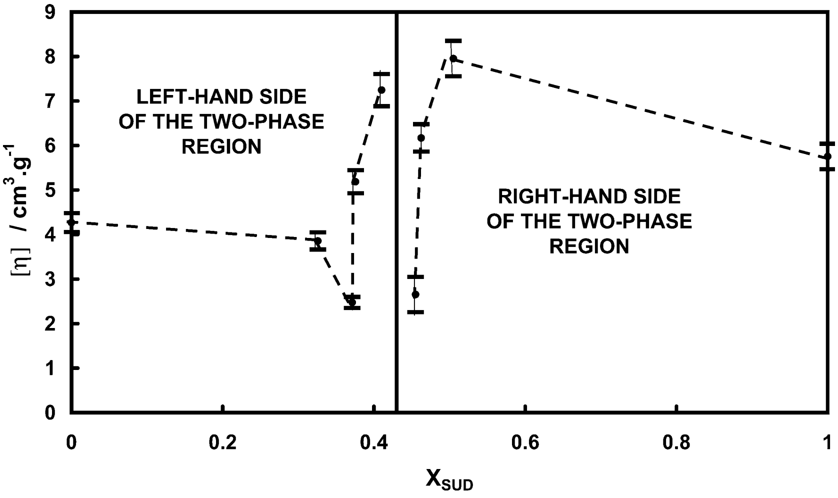

Fig. 5 The intrinsic viscosity as a function of the micelle composition X_{SUD}. *Lines* are eye guides

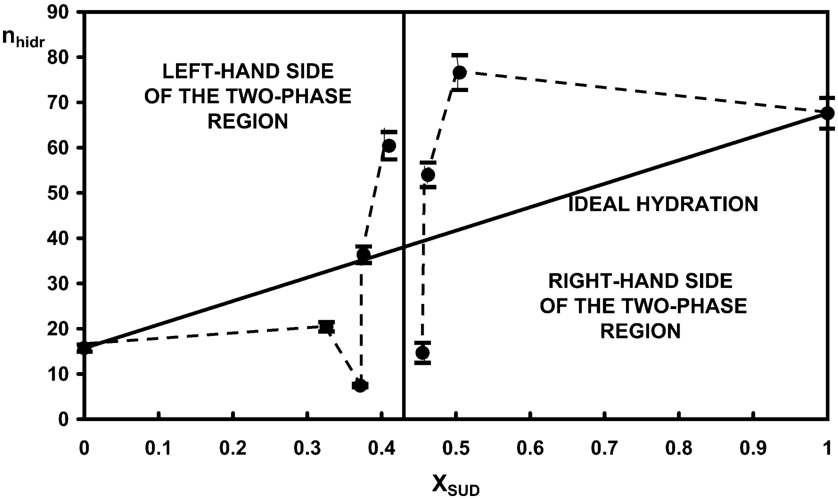

Fig. 6 The hydration of micelles (n_{hydr} = water molecules per surfactant molecule) represented as a function of X_{SUD}. *Lines* are eye guides

The n_{hydr} values are represented as a function of X_{SUD} in Fig. 6.

Hydration values for alkyltrimethylammonium bromides in literature range between 60 and 70 water molecules per surfactant molecule [25]. For dodecyltrimethylammonium hydroxide n_{hydr} is 39.2 ± 0.7 [26], the non-ionic surfactant Triton X-100 has 43 [27], while the hydration of micellised $C_{12}H_{25}NH_3^+$ ion is 1.60 water molecules per surfactant ion between 20 and 30 °C [28]. Since bromide ion has a hydration number of 2 ± 1 [29, 30], micellised dodecylammonium bromhydrate has $n_{hydr} \approx 3.6$. Thus, the hydration value found for micellised DTAB in this work, 15.7 ± 0.8 water molecules per surfactant ion is an intermediate value.

The hydration of sodium soaps was reported as about 10 [31, 32]. That of sodium dodecyl sulfate was reported as 6 [33], 8 [34] or 12 [35], but much larger values were suggested [36]. We found a higher value for pure sodium undecenoate micelles, 68 ± 3 water molecules per surfactant ion. Assuming that ten water molecules form the hydration of the sodium carboxylate group, the other 58 water molecules must appertain to the hydration of the hydrocarbon-water micelle interface, which probably is covered by the hydrophilic terminal $-CH=CH_2$ group.

Figure 6 shows that the behavior is different in the one-phase region at the right-hand side of the two-phase region than in the monophasic region at the left-hand side of the biphasic region. Micelles having lower SUD content show dehydration when compared with the ideal one. There is a minimum of hydration at $X_{SUD} = 0.37$, when the interaction parameter β shows a minimum and the micelle ionization degree (α) is maximum [7]. These facts suggest that when X_{SUD} is 0.37, the micelle compactness is maximal, with the opposite charged groups close each other. This situation must produce dehydration in both the polar head groups and the double bonds of SUD included in micelles. This also may explain the increase in the pmv of the mixed micelles in this region. When X_{SUD} increased, β increases and α decreases. The accumulation of the double bonds at the micelle hydrocarbon-water interface may explain the increase in hydration. The increase in β indicates that these micelles are less stable than that having $X_{SUD} = 0.37$. The capture of counterions indicates that the opposite polar head groups are far each other, retaining more water molecules among them.

Micelles in the right-hand monophasic side have almost the same α value but a large increase in β. This situation may be caused by an excess of double bonds over the ideal proportion ($X_{SUD} \approx 0.39$ [7]. Probably the compactness of micelles is reduced when X_{SUD} increases, causing an increase in hydration by inclusion of water among the ionic head groups that are separated by the hydrophilic $-CH=CH_2$ groups covering the hydrocarbon–water interface. Moreover, if there is water intrusion into de hydrocarbon core, as suggested by some authors [37–42], that intrusion would be facilitated by the inclusion of the double bonds in the hydrocarbon core of both the SUD micelles and in the mixed micelles. This inclusion of water in the micelle core may also contribute to the reduction in pmv.

One observation must be made about the absolute values of hydration. Since in the most general sense "hydration" involves the entire solute–solvent interaction, different experimental methods may be sensitive to different fractions of the total interaction. When hydration is defined in its generally accepted sense as the amount of water carried by a colloidal particle moving as a kinetic entity in solution, as in this work, the effects of hydration and shape factors cannot usually be disentangled unequivocally. The understanding of hydration from a structural point of view is made difficult by the many possible sources of hydration such as the presence of hydrated charged groups, hydrogen bonding, and mechanical entrapments of various kinds. Additionally, the specific volume of the micellised sur-

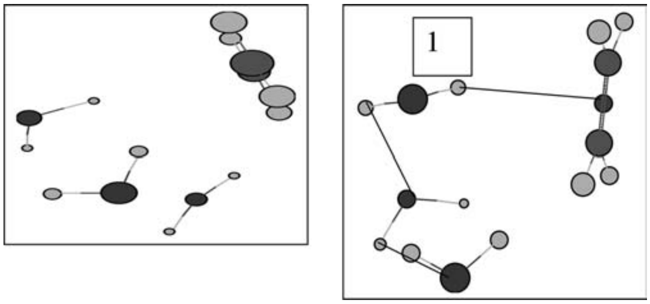

Fig. 7 The interaction between tree water molecules and one ethylene molecule in the gas phase. *Left* initial condition: the four isolated molecules, *right* the complex. The water molecule forming a hydrogen bond with the ethylene π-electrons is indicated as 1

factant used in the determination of the hydration from viscosity measurements (v_2) in Eq. 6 must strictly be that of the "dry" mixed surfactant molecule. As a consequence, the use of the pmv to compute v_2 (Eq. 9) leads to some uncertainty. Also, the assumption that the electroviscous effect $E=1$ introduced an additional uncertainty in the computations. Because of the above considerations, the absolute values of n_{hydr} here found must be considered as estimations. However, in view of the value obtained for DTAB, the error cannot be extremely large. The general trends here found are then plausible.

Ethylene–water interaction modelling

The computer modelling of the π-electrons–water interaction was performed by considering three water molecules and one ethylene molecule in the gas phase (See Fig. 7). Minimization of the steric energy gives a minimum distance of Water 1 molecule to the ethylene molecule centroid of 0.236 nm, which is only an approximation because the electronic interactions are very important in this case. This distance is near to that of the bridge-H bonding.

The enthalpy Δ H ° for the reaction:

$$3H_2O + CH_2 = CH_2 \rightarrow (H_2O)_2H_2O - - CH_2 = CH_2$$

was computed using the formation enthalpy for products and reactants, giving a negative interaction enthalpy in gas phase in the minimum −46.9 kJ mol^{-1}. The typical energy of hydrogen-bonds in liquid water lies in the 10–40 kJ mol^{-1} range [43]. The enthalpy of interaction of *n*-butane and water is −4.3 kJ mol^{-1}, obtained from its enthalpy of solubilisation in water, [ref. 43, page 130]

The PM3 semi-empirical minimization of the interaction of 3 water molecules plus that of ethylene gave a hydrogen bonding distance between the ethylene centroid and the water molecule labelled 1 of 0.249 nm. The distance for the H–O bonding between the water molecules in the $(H_2O)_3$ cluster were computed by the PM3 program falling in the range 0.2558–0.2528 nm, close to the common literature values (0.26–0.30 nm [44]]). Thus, the hydrogen bond between water molecule 1 and the ethylene centroid is shorter than that between two water molecules in the adjacent cluster. Figure 7 (right) shows the complex structure at the energy minimum.

Then, the simulation confirms an interaction between the aliphatic π-electrons and water that is stronger than that between a saturated hydrocarbon, and slightly stronger than the water–water hydrogen bond.

Concluding remarks

- Unlike the results obtained in literature for mixed micelles having the same kind of hydrocarbon chains, the aqueous SUD-DTAB mixture shows a non-ideal volume behavior of mixing.
- The complex behavior of hydration in SUD-DTAB mixed micelles is also non-ideal and reflects the complex structure and composition of the micelle surface.
- Computer simulation confirms an interaction between the aliphatic π-electrons and water which is stronger than that between a saturated hydrocarbon and water, and is slightly stronger than the water-water hydrogen bond.

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