



Effect of the concentration and composition on the size and shape of micelles of sodium oleate–cetyltrimethylammonium bromide mixtures

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ABSTRACT

The dependence of the aggregation number (N_{agg}) on composition and concentration of sodium oleate–cetyltrimethylammonium bromide mixed micelles as revealed by cyclic voltammetry experiments shows a complex relationship with the total concentration and the composition of surfactant mixtures. This behavior is related to the evolution with composition of the HLB values and with the composition and the excess free energy of mixed micellization, and is explained by the inclusion of the double bonds of oleate chains in the micellar Stern layers. The increase in size probably leads to a reduction of the micelle surface available for the polar headgroups, causing a reduction in the proportion of double bonds in the hydrocarbon–water interface and a change in the mixed micelle composition. Therefore, the generally held supposition that the composition of mixed micelles does not change with concentration seems rather unrealistic.

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1. Introduction

Research on surfactant mixtures is of considerable interest for numerous technical applications, because the use of surfactant mixtures enhances the performance of many applications when compared to the use of single surfactants. When mixing surfactants, specially the oppositely charged ones, new properties may appear. Aqueous mixtures of anionic and cationic surfactants exhibit many unique properties that arise from strong electrostatic interactions between the oppositely charged headgroups. These systems have attracted the attention of numerous investigators [1–6]. It is important to have a general understanding of the mechanism of the interactions between the surfactants in mixed systems and of the factors that influence various features of the phase equilibrium. There are theories that consider the influence of the structure of the micelle polar layer and the electrostatic effects on micellization [7] and mixed micellization [8–10]. To improve these theories it is necessary to have a good knowledge of the factors affecting the formation of micelles and their structure.

In order to study the evolution of the mixed micelles size and shape, the system formed by sodium oleate (NaOL) and cetyltrimethylammonium bromide (CTAB) was selected because their mixtures do not precipitate even in the 1:1 proportion [11]. Thus, mixtures having all proportions could be investigated.

The determination of the self-diffusion coefficient of the micelles by electrochemical methods was employed to compute their aggregation number in many works. Polarographic techniques were used via the redox behavior of associated electroactive probes [12–19]. An alternative method is the employ of cyclic voltammetry [20,21]. Both methods are based on the measurement of the diffusion current intensity caused by the electroactivity of a probe attached to micelles so that its diffusion coefficient is that of the micelles. These studies assume that the presence of a small number of these probes per micelle will not affect its size and shape [16]. Polarographic and voltammetric techniques give the micelle's self-diffusion coefficient, which are amenable to interpretation in terms of micelle size and shape.

2. Experimental

Tri-distilled water was used and the measurements were run twice. Cetyltrimethylammonium bromide (CTAB) and sodium oleate (NaOL) were both Fluka. Both chemicals were of analytical grade and used as received.

Concentrated samples were prepared by weighing the appropriate amount of each surfactant and then adding water to obtain the desired concentration. Mixtures having $\alpha_{CTAB} = 0$ (pure NaOL), 0.33, 0.5 and 0.67 were prepared, with α_{CTAB} being the mole fraction of CTAB in the mixture without considering the solvent. Solutions above the critical micelle concentration (CMC), obtained from El Kadi et al. [11] were prepared by dilution of the concentrated one. The explored fixed concentrations were $C = 0.01, 0.005,$

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0.003, 0.0008, 0.0006, 0.0005 and 0.0004 M. Cd^{+2} was used as probe by adding to each solution an amount equal to half the micellized NaOL content (NaOL_M), in order to ensure that each micelle has not more than one electroactive probe. This was computed by $\text{NaOL}_M = (C - \text{CMC})(1 - \alpha_{\text{CTAB}})/200$ (assuming an aggregation number of about 200). No additional supporting electrolyte was added because the high liberation of counterions from the cationic micelles provides enough conductivity. Moreover, the addition of such electrolytes will change the micelle size and shape.

Before use, the electrodes were washed carefully with fourfold quartz-distilled water, polished using an alumina powder (0.3 μm), and washed again as described above. All aqueous solutions were prepared with fourfold quartz-distilled water and purged with N_2 prior to every experience. Electrochemical studies were based on the analysis of cyclic voltammetric (CV) measurements. A conventional three-electrode electrochemical cell was used for all the experiments. The working electrode was a glassy carbon (GC) disk with an area of 0.07 cm^2 . A Pt wire was used as counter electrode and a saturated calomel electrode (SCE) inside a Luggin capillary was used as reference electrode. All potentials stated here are referred to the SCE unless stated otherwise. The measurements were carried out with a computer controlled EG&G Princeton Applied Research Model 273A potentiostat–galvanostat. In the electrochemical measurements, the scan rates were varied between 200 and 1000 mV/s.

In CV the peak current i_p (μA) for a redox-active reversible system at 25 °C is given by the following equation:

$$i_p = (2.687 \times 10^5) n^{3/2} A D_m^{1/2} C v^{1/2} \quad (1)$$

where n is the number of electrons involved in oxidation or reduction, A is the area of the electrode (cm^2), D_m is the diffusion coefficient of the kinetic unit carrying the electroactive probe, i.e., the micelles ($\text{cm}^2 \text{s}^{-1}$), C is the concentration of the electroactive probe in the solution (mol cm^{-3}) and v is the sweep rate (V s^{-1}). From the slope of i_p vs. $v^{1/2}$ plot, the D_m values of various micelle concentrations were obtained at various probe concentrations.

3. Theory

To determine the aggregation number of micelles (N_{agg}) the micelle self-diffusion coefficient (D_M) obtained from voltammetry measurements was used (Table 1). The equivalent sphere hydrodynamic radius R_{eq} (i.e., the radius of a spherical micelle having the same D_M value) was obtained from the Einstein–Stokes equation:

$$D_M = RT/6\pi\eta R_{\text{eq}} \quad (2)$$

where R and T are the gas constant and the absolute temperature, and η is the viscosity of the medium, taken as water.

To compute the intermicellar interaction, we used the method developed by Corti and Degiorgio [22], which considers a hard-core repulsion, a screened Coulomb repulsion and a London – van der Waals attraction. This gives

$$D_M = D_{M,0}[1 + k_D(C - \text{CMC})] \quad (3)$$

and

$$k_D = [0.5 + 2(1 + x)^2(1 + 4x) + (15/8)(1 + x)^{-1}]V_M \quad (4)$$

where $D_{M,0}$ is the diffusion coefficient corrected to eliminate the interaction between micelles, $x \approx \kappa^{-1}/R_{\text{eq}}, \kappa^{-1}$ being the Debye length and V_M is the partial specific volume of the micelles. To compute, we used the first CMC as the ionic strength. In order to calculate the value of V_M , the volume of the equivalent surfactant molecule (V_s) was calculated with:

$$V_s = V_{\text{CTAB}}\alpha_{\text{CTAB}} + V_{\text{NaOL}}\alpha_{\text{NaOL}} \quad (5)$$

where the volumes of the components (V_{CTAB} and V_{NaOL}) were computed from the partial molar volumes of components PMV_{CTAB} and PMV_{NaOL} in micellar state. The partial molar volume of CTAB is $\text{PMV}_{\text{CTAB}} = 365.4 \text{ cm}^3/\text{mol}$ [23], which by subtraction of the Br-PMV (29.2 cm^3/mol [24]) gives $\text{PMV}_{\text{CTA}^+} = 336.2 \text{ cm}^3/\text{mol}$. For the oleate ion, the partial molar volume was estimated as 315.0 cm^3/mol with the group contributions to the partial molar volume method developed by Gianni and Lepori [25,26], and taking into account that on micellization the PMV increases in 8% above that of unmicellized surfactant molecules [23,27]. With these data the volumes of the micellized molecules were computed as $V_{\text{CTAB}} = 0.5076 \text{ nm}^3$ and $V_{\text{NaOL}} = 0.4756 \text{ nm}^3$.

The partial specific volume of micelles was computed as $V_M = V_s/M_s$, M_s being the equivalent surfactant molecular weight:

$$M_s = M_{\text{CTAB}}\alpha_{\text{CTAB}} + M_{\text{NaOL}}\alpha_{\text{NaOL}} \quad (6)$$

Using Eq. (2) with the values of the diffusion coefficient obtained from the diffusion current (D_M) the uncorrected equivalent hydrodynamic radius was obtained (R_{eq}). Then R_{eq} was used to determine k_D and the value of $D_{M,0}$ was computed. Then, using Eq. (2), the corrected equivalent hydrodynamic radius of micelles ($R_{\text{eq},0}$) was computed.

The values of $R_{\text{eq},0}$ were then compared with the length of a fully extended surfactant molecule l_s . If $l_s \geq R_{\text{eq},0}$ micelles were supposed as being spherical, otherwise they were considered as rod-like. Then the volume of spherical micelles (V_{sp}) was computed using the $R_{\text{eq},0}$ value. To obtain the dimensions of the rod-like micelles the following equation was used [28]:

$$R_{\text{eq},0} = L/(2\sigma - 0.19 - 8.42/\sigma + 12/\sigma^2) \quad (7)$$

where L is the length, r the radius of the cylinder, and $\sigma = \ln(L/r)$. This equation was solved numerically by taking $r = l_s$. Then, the volume of the rod-like micelle was computed as [29]:

$$V_{\text{rod}} = 4\pi l_s^3/3 + 2\pi l_s^2(L - 2l_s) \quad (8)$$

where

$$l_s = l_{\text{CTA}} + \alpha_{\text{CTAB}} + l_{\text{OL}} - \alpha_{\text{NaOL}} \quad (9)$$

Here the length of each surfactant molecule was computed by [29]:

$$l_i \text{ (nm)} = 0.13n_c + 0.1704 + 2r_{\text{ph}} \quad (10)$$

where n_c is the number of carbon atoms in the chain, and r_{ph} is the radius of the hydrated polar headgroup obtained from its contribution to the PMV. For both micellized headgroups $\text{PMV}_{\text{N(CH}_3)_3^+} = 70.6 \pm 3.4 \text{ cm}^3/\text{mol}$ [30], and $\text{PMV}_{\text{COO}^-} = 20.63 \text{ cm}^3/\text{mol}$ [25,26].

To obtain the aggregation number, the volume of the micelles was divided by that of the equivalent surfactant molecule V_s .

4. Results

Fig. 1 shows as an example the voltammograms of one sample (pure NaOL).

Fig. 2 shows a i_p vs. $v^{1/2}$ plot of one of the systems as an example, the other being similar. Plots are straight lines indicating that the process is diffusion-controlled, and thus, Eqs. (1)–(3) are applicable.

Fig. 3 shows the dependence of $D_{M,0}$ on concentration and composition of the surfactants mixtures.

Fig. 4 depicts the evolution of the main dimension L of the micelles (i.e., the radius of the spherical micelles or the length of the rod-like ones) as determined from $D_{M,0}$. The upper limit for stiff rod-like micelles is $L = 100 \text{ nm}$ [31] corresponding to $N_{\text{agg}} \approx 4600$ [17]. The limit for non-entangled micelles is $L = 125 \text{ nm}$. This indicates that micelles at the highest concentrations are flexible and

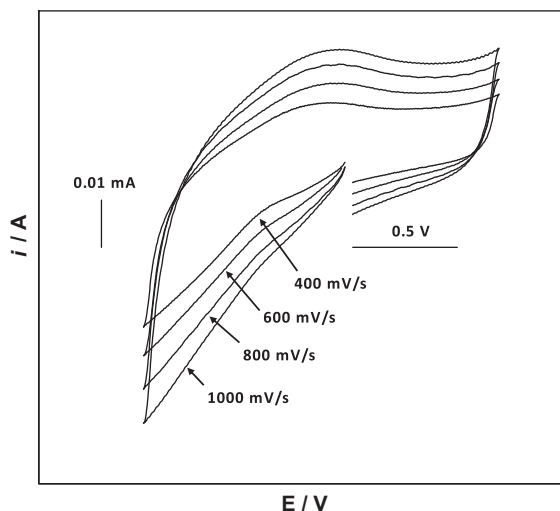


Fig. 1. Voltammograms for $\alpha_{\text{CTAB}} = 0$ (pure NaOL), $C = 6 \times 10^{-4}$ M and different values of v .

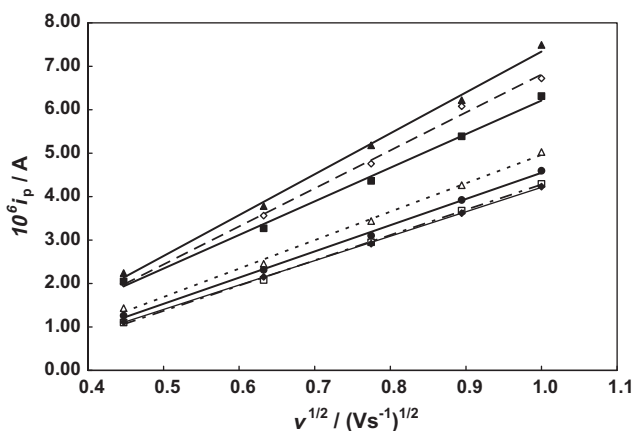


Fig. 2. i_p vs. $v^{1/2}$ Plot for the system with $\alpha_{\text{CTAB}} = 0.667$ at different concentrations: \blacktriangle : 0.02 M; \diamond : 0.005 M; \blacksquare : 0.002 M; \triangle : 0.0008 M; \bullet : 0.0006 M; \square : 0.0005 M; \blacklozenge : 0.0004 M.

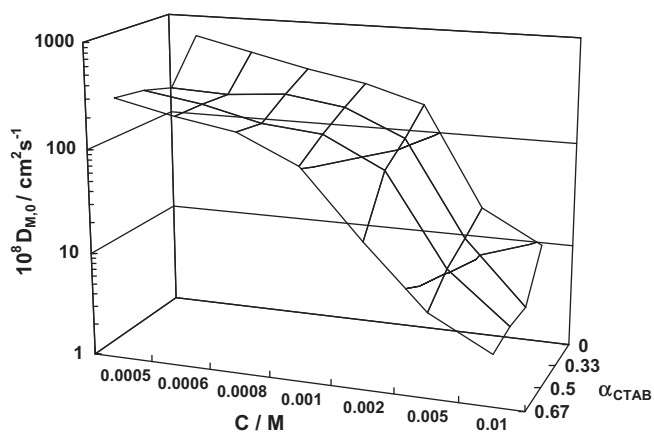


Fig. 3. The values of $D_{M,0}$ as a function of concentration and α_{CTAB} .

entangled, so the N_{agg} values at these concentrations may be unrealistic. These limits are indicated in Fig. 4.

The determination of the aggregation number (N_{agg}) gave the data presented in Table 1.

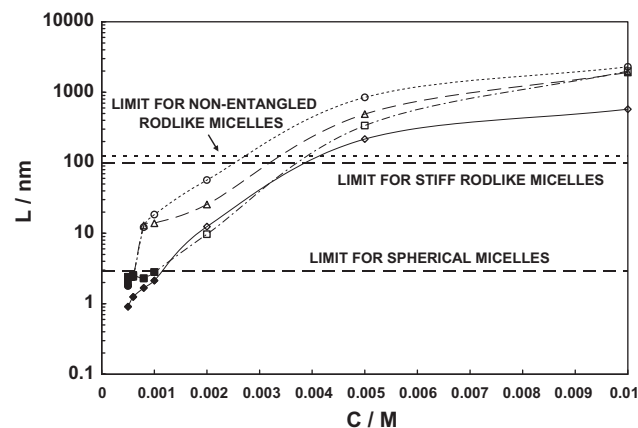


Fig. 4. The largest dimension of micelles L as a function of concentration and $\alpha_{\text{CTAB}} = 0$ (\diamond , \blacklozenge), 0.33 (\square , \blacksquare), 0.5 (\triangle , \blacktriangle) and 0.667 (\circ , \bullet). Open symbols represent rodlike micelles, while closed symbols correspond to spherical ones.

In this table the values of N_{agg} for pure CTAB micelles were obtained from literature [32–35]. Values for higher concentrations were also obtained from literature [36–39], which followed the same tendency of the data represented in Table 1 and Refs. [32–35].

There is few data on NaOL aggregation number available in literature. Mahieu et al. [40] found that NaOL in D_2O form rod-like micelles at 5×10^{-3} M, which is in partial agreement with our data (Table 1). For KOL, $N_{\text{agg}} = 103$ (25 °C) [41].

The representation of the dependence of N_{agg} on both α_{CTAB} and C is shown in Fig. 5 for a better overall insight.

A better comprehension of these dependences may be seen with cutting the surface at different α_{CTAB} and at different C values (Figs. 6 and 7).

The dependence of N_{agg} as a function of C for $\alpha_{\text{CTAB}} = 1$ (i.e., pure CTAB, Fig. 6) corresponds to the expected behavior with the increase of the aggregation number with concentration, showing a smooth evolution. The behavior of the surfactant mixtures shows a sudden change in the N_{agg} vs. C increase at $C \approx 0.003$ mol dm^{-3} , being more steeper than at lower concentrations. However, the absolute values of N_{agg} at $C > 0.004$ M are only of relative confidence since they correspond to systems in which micelles entangle.

When N_{agg} is represented as a function of α_{CTAB} at different fixed concentrations, one or two maxima can be seen (Fig. 6). We have found in literature a similar behavior in mixtures of tetradecyltrimethylammonium bromide (TTAB) and the gemini surfactants 1,5 bis(N-tetradecylN,N-dimethyl ammonium) butane (or pentane or hexane) dibromide (16-s-16) with spacers s having 4, 5 and 6 methylene groups [42]. The same behavior is shown by mixtures of the two gemini surfactants 16-s-16 and 14-s-14 [43]. The mixed system decyltrimethylammonium bromide (DTAB) cetyltrimethylammonium bromide (CTAB) [44] also gives a dependence of the aggregation number with the composition of the mixture, showing an almost ideal behavior at low DTAB content and a strong nonideality and a very large maximum at high DTAB content in the surfactant mixture. It must be reminded that all these N_{agg} measurements were made with the pyrene fluorescence method at twice the CMC. Then, its dependence on the composition of the system is not at a constant concentration and represents a curved cut in the $N_{\text{agg}}(\alpha, C)$ surface. Thus, it is not directly comparable with our results, but it may be used as an indicative of a tendency.

For mixtures of CTAB and tetradecyltrimethylammonium bromide with Triton X-100 or Pluronic F68, Rahajan et al. [45] found by cyclic voltammetry a dependence of the micellar diffusion coef-

Table 1
Aggregation number of CTAB–NaOL mixtures as a function of the composition of the surfactant mixture and the concentration. Data for $\alpha_{\text{CTAB}} = 1$ were obtained from literature.

	C/M						
α_{CTAB}	0.01	0.005	0.003	0.0008	0.0006	0.0005	0.0004
0	6.59×10^4	2.45×10^4	991	92	44.6	18	7.2
0.33	2.52×10^5	4.22×10^4	745	226	125	173	143.2
0.5	2.52×10^5	6.45×10^4	2.88×10^3	1.33×10^3	1.20×10^3	153	81.8
0.67	3.04×10^5	1.25×10^5	2.03×10^4	1.94×10^3	1.11×10^3	148	62
1	17,033	15,035	14,035	9532	8534		

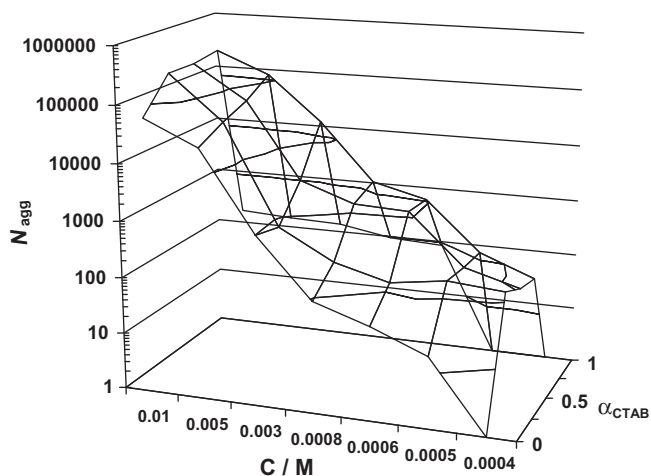


Fig. 5. The dependence of N_{agg} on both α_{CTAB} and C .

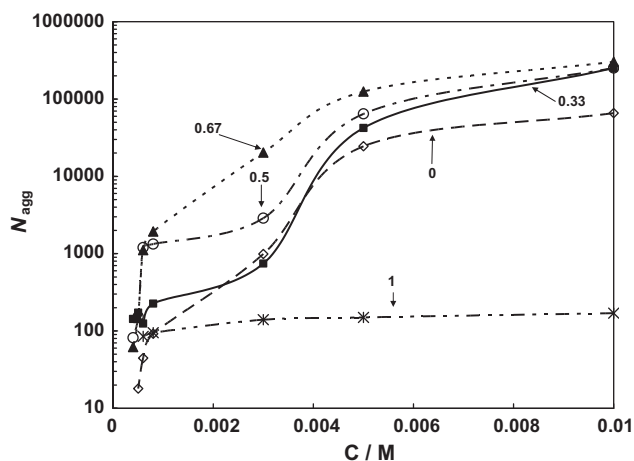


Fig. 6. N_{agg} as a function of the concentration for different surfactant mixture compositions. Numbers on the plot are α_{CTAB} values.

cient on the mixture composition with maxima and minima. Catanionic mixtures of CTAB and sodium cumene sulfonate (NaCS) [38] show a strong increase in N_{agg} when the proportion on NaCS is increased from $\alpha_{\text{NaCS}} = 0$ ($N_{\text{agg}} = 156 \pm 14$) up to 0.015 ($N_{\text{agg}} = 506 \pm 83$), at a total concentration of about 100 mM. Mixtures of the gemini surfactant dimethylene-1,2-bis(dodecyl-dimethylammonium bromide (12-2-12) with the non-ionic hexaethyleneglycol monododecylether at different temperatures show a maximum in the aggregation number at about $\alpha_{12-2-12} = 0.5$ [46]. Mixtures of CTAB–sodium butyl benzene sulfonate at constant total concentration also show a maximum in N_{agg} when the composition is changed [47]. Mixtures of SDS and C_{12}E_6 also show a maximum in the aggregation number when α_{SDS} is increased [48]. NMR self diffusion studies of CTAB and Triton X-100 mixtures show a mini-

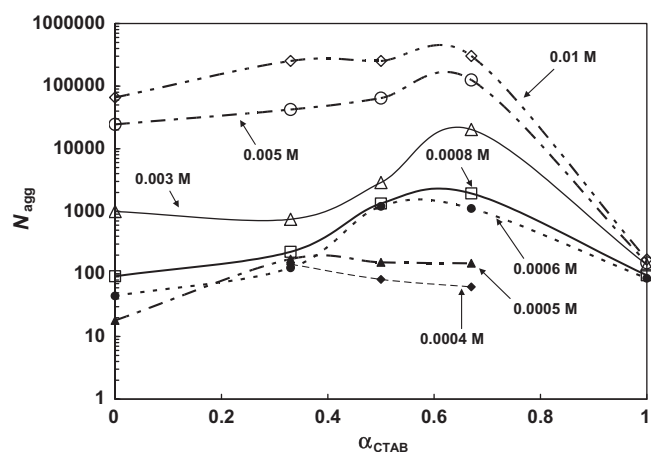


Fig. 7. N_{agg} as a function of the surfactant mixture composition for different concentrations.

um in the micellar self-diffusion coefficient at $\alpha_{\text{CTAB}} \approx 0.7$ when measured at $C = 10$ CMC [49]. The micellar aggregation number of the mixtures of DDAB and amitriptyline hydrochloride at twice the CMC, were measured by Rodríguez et al. by pyrene fluorescence [50], showing a maximum in the N_{agg} vs. α_{DTAB} plot at about $\alpha_{\text{DTAB}} \approx 0.7$. Both components are cationic. Then, several mixed systems show a N_{agg} vs. mixture composition behavior similar to that detected in aqueous NaOL–CTAB mixtures.

The formation of large elongated micelles was detected in other catanionic systems. Bergström and Pedersen [51] found that mixtures of SDS and DTAB produce elongated tablet-shaped micelles and flexible ribbon-like ones with a thousand Å in length, 3.2 nm in thickness and about 6 nm in width are observed close to the surfactant composition where a transition to lamellar sheets is seen. In the NaOL–CTAB system, the lamellar structure needed to form ribbon-like micelles is impeded by the inclusion of the double bonds of a NaOL chain among the polar headgroups, which produces a curvature favoring the formation of spherical or rod-like structures [11,52–54]. The inclusion of non-ionic heads between the ionic ones in mixtures of ionic and non-ionic micelles reduces the electrostatic repulsion between the charged groups, thus facilitating the formation of larger micelles. The inclusion of the double bonds of the oleate chains in the micelle Stern layer also produces the same effect. This inclusion occurs because the π -electrons may form hydrogen bonds with water molecules.

The only literature work we have found studying the aggregation of a mixed system as a function of both the composition and concentration (aqueous sodium dodecyl sulfate (SDS) – sodium octanoate) was one made by Leaist and MacEwan [55]. Their results are not directly comparable with ours, but the micelles have a maximum when α_{SDS} is changed.

Generally, the micellar mixing non-idealities result from the electrostatic and steric interactions between the surfactant hydrophilic heads and from the packing of the surfactant hydrophobic tails of unequal lengths in the micellar core. [49]. These non-

idealities also affect the critical micelle concentration and other values related as the hydrophile–lipophile balance (HLB). In a previous paper [56] we have measured the HLB values of NaOL–CTAB mixtures and obtained the data plotted in Fig. 8.

The HLB of the NaOL–CTAB mixtures is not ideal and reveals some correlation with the aggregation numbers determined in the same systems. The HLB values were determined at a total concentration of the mixture of 0.01 mol dm^{-3} , in which there is a similar dependence of N_{agg} on α_{CTAB} (Fig. 7). Moreover, the excess free energy of micellization at the critical micelle concentration (1st CMC) and the second critical concentration (i.e., that at which the micelle structure changes, 2nd CMC), shown in Fig. 9 [56] also show some correlation with the evolution of the aggregation numbers at commensurable concentrations, and the effect of changing the concentration on the micellization thermodynamics (and hence, on the aggregation behavior).

In particular, there are two minima in the HLB and the ΔG^{excess} at the two sides of $\alpha_{\text{CTAB}} = 0.5$, which correspond to maxima in the N_{agg} vs. α_{CTAB} plot. Moreover, the ΔG^{excess} minimum in the low α_{CTAB} values side is smaller than that in the high α_{CTAB} values, corresponding to low (left) and high (right) N_{agg} maxima in Fig. 7. At $\alpha_{\text{CTAB}} = 0.5$ there is a maximum in the HLB curve (Fig. 8), which corresponds to a small minimum in N_{agg} at the same total concentration ($C = 0.01 \text{ M}$). For lower concentrations the evolution of N_{agg} is similar to that of ΔG^{excess} at twice the CMC. It may be concluded that the evolution of the aggregation number with the composition of the mixture agrees (between the logical differences arising from diverse techniques and dissimilar concentrations used in the dif-

ferent experiments) with that of HLB and the excess free energy of mixed micellization.

The evolution of N_{agg} with C for the mixtures is more similar to that of pure NaOL micelles than that of pure CTAB ones (Fig. 7). Then, this behavior must be related to the principal difference between NaOL and CTAB: the presence of a double bond in the oleate chain. It is well-known that π -electrons of double bonds interact with water via hydrogen bonds [57–62]. This means that the double bonds locate (almost in part) at the hydrocarbon–water interface of micelles, between the polar headgroups, thus reducing the interfacial free energy in about $13\text{--}16 \text{ mJ/m}^2$ when compared with that of a saturated hydrocarbon–water interface [63,64]. Then, this inclusion produces a curvature which impedes the formation of planar surfaces and favors the formation of spherical and rod-like micelles. When rod-like micelles grow, the micelle surface per surfactant molecule headgroup (S_{ph}) is reduced [65]. At some value of S_{ph} the extra reduction of the interfacial free energy furnished by the inclusion of the double bonds may be unnecessary because the reduction in the hydrophobic surface exposed to water is low. Then, either the double bonds of some oleate tails submerge into the hydrocarbon micelle core, or more CTAB molecules are included in the micelle. This increases the proximity between carboxylate and trimethylammonium groups in the Stern layer and favors the increase in aggregates size. In both cases, the composition of micelles is changed with concentration. This in turn leads to the conclusion that the generally held supposition that the composition of mixed micelles does not change with concentration seems rather unrealistic. However, the error may be not excessive if the difference between the CMC and the experimental concentration is not too great.

5. Concluding remarks

The dependence of the aggregation number (N_{agg}) of sodium oleate (NaOL)–cetyltrimethylammonium bromide (CTAB) mixed micelles as revealed by cyclic voltammetry experiments shows a complex relationship with the total concentration and the composition of the mixtures. N_{agg} increases when the total concentration (C) increases, but mixed micelles behave more similar to those composed by pure NaOL, rather than those of pure CTAB. The evolution of N_{agg} with the composition (α_{CTAB}) at different C values shows a maximum and minimum. This behavior is related to the evolution with composition of the HLB values and the excess free energy of mixed micellization, and it is explained by the inclusion of the double bonds of the oleate chains in the micelle Stern layer. The increase in size probably leads to a reduction of the micelle surface available for the polar headgroups, causing a reduction in the proportion of double bonds in the hydrocarbon–water interface and a change in the mixed micelle composition. When the largest dimension of micelles (L), derived from the diffusion coefficient of micelles is analyzed as a function of C for different α_{CTAB} values, it was found that for the two higher concentrations used, micelles entangle and then the values of L and N_{agg} at these concentrations may incur into some degree of error.

As a consequence of the above findings, it may be also concluded that the generally held supposition that the composition of mixed micelles does not change with concentration seems rather unrealistic.

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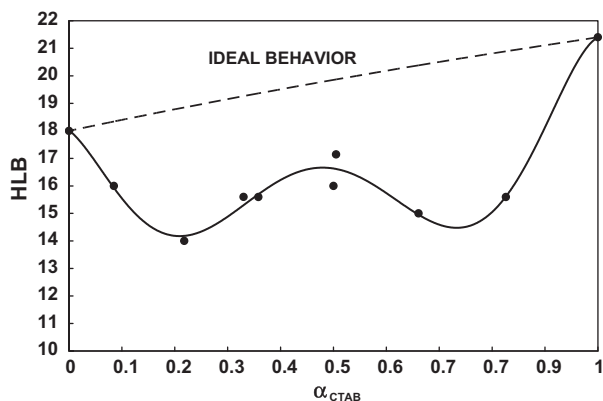


Fig. 8. Hydrophile–lipophile balance (HLB) for NaOL–CTAB mixtures as a function of the mole fraction of CTAB (α_{CTAB}) [57].

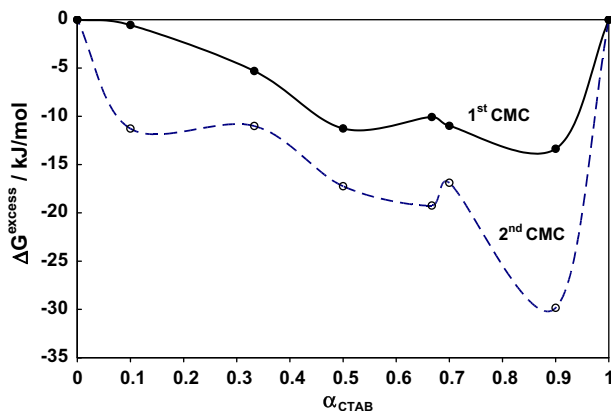


Fig. 9. Excess free energy of micellization for the CTAB–NaOL mixed system at the first and second CMC [57].

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcis.2010.07.040.

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