ORIGINAL CONTRIBUTION

The low concentration aggregation of sodium oleate–sodium linoleate aqueous mixtures

**Maria B. Sierra · José L. Rodríguez ·
Rosanna M. Minardi · Marcela A. Morini ·
Emilio Aicart · Elena Junquera · Pablo C. Schulz**

Abstract Sodium oleate (NaOL, $C_{18}H_{33}O_2Na$)–sodium linoleate (NaLin, $C_{18}H_{31}O_2Na$) mixtures were studied in the micellar and in the air/water interface states at 298.15 K. Three aggregation steps were found: a premicellar aggregation, the critical micelle concentration (CMC), and a structural change of micelles. Micelles, both at the CMC and at the structural change concentration, are richer in oleate than the overall mixture composition. Micelles are strongly non-ideal and the interaction is repulsive. The non-ideal behavior and the dependence of the micelle ionization degree with micelle composition are explained on the basis of the interaction of the π electrons of the surfactants' chains with water at the hydrocarbon/water micellar interface. The air/solution adsorbed monolayer is also non-ideal, but the interaction is attractive and there is a preferential composition with a mole fraction of sodium oleate of about 0.7. The surface pseudophase behaves as if oleate were the solvent and linoleate a strongly soluble solute. This behavior and the dependence of the average area per adsorbed molecule were explained on the basis of the interaction of the double bonds with water. At the air/solution interface, the linoleate molecule area was similar to that of a heterogemini surfactant having a spacer with seven carbon atoms.

Keywords Sodium oleate · Sodium linoleate ·
Soap mixtures · Mixed micelles · Mixed monolayer ·
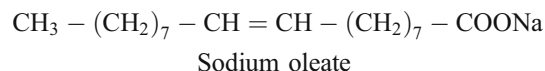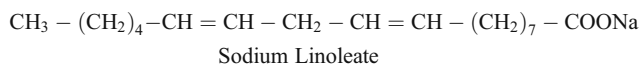Water/double bonds interaction

Introduction

In previous papers on mixed micelles, we have found that the presence of double bonds in the hydrocarbon chain of one of the surfactants leads to an interaction which does not follow the presumptions of the theory of mixed micelles [1–6]. Cationic–anionic mixtures do not precipitate, even at a 1:1 proportion, and micelles have a preferential proportion which is not that of 1:1, but produces the complete substitution of the micelle-saturated hydrocarbon/water interface by an unsaturated hydrocarbon/water one [2–4]. The presence of a double bond also gives an unusual non-ideal behavior of the partial molar volume of mixed micelles, which indicates that the effect is originated in the hydrocarbon micelle core [5]. Computer simulation supports the explanation that the interaction between the π-electrons of the double bond and water produces a reduction in energy which is responsible for this behavior [5, 6]. In an anionic–anionic mixture (sodium undecenoato–sodium dodecanoate), we also have found a behavior which is in agreement with this interaction [7]. To extend this study, we have explored here a mixture of two surfactants, one with a double bond in the middle of its chain, sodium oleate, and the other with two double bonds in the chain,

M. B. Sierra (✉) · J. L. Rodríguez · R. M. Minardi ·
M. A. Morini · P. C. Schulz
Departamento de Química e INQUISUR,
Universidad Nacional del Sur,
Bahía Blanca, Argentina
e-mail: mbsierra@uns.edu.ar

E. Aicart · E. Junquera
Departamento de Química Física I, Facultad de Ciencias
Químicas, Universidad Complutense de Madrid,
28040 Madrid, Spain

sodium linoleate, both having the same polar head group and chain length:

$$CH_3 - (CH_2)_4 - CH = CH - CH_2 - CH = CH - (CH_2)_7 - COONa$$
$$\text{Sodium Linoleate}$$

$$CH_3 - (CH_2)_7 - CH = CH - (CH_2)_7 - COONa$$
$$\text{Sodium oleate}$$

Conductivity, dye solubilization, pH, and surface tension experiments have permitted to analyze the behavior of the system in both the bulk and the air/solution adsorbed monolayer. These techniques allowed for the determination, in the whole range of composition, of the mixed critical micelle concentration (CMC), the micelle ionization degree (α), and a structural change of the micelles together with the composition of the micellar phase and the monolayer. The obtained results have been found in agreement with the theoretical models also used herein.

Experimental

Sodium oleate (NaOL) and linoleic acid were >99% from Aldrich and used as received. Sodium linoleate (NaLin) was prepared by neutralization of linoleic acid with NaOH. Aqueous NaOL–NaLin mixtures were prepared at concentrations of about five times the CMC computed assuming ideal behavior for each mixture. The proportions were α_{NaOL}=0 (pure NaLin solution), 0.2, 0.4, 0.5, 0.65, 0.8, and 1 (pure NaOL solutions), where α_{NaOL} is the mole fraction of NaOL in the mixture of surfactants, without considering the solvent. Only double distilled water was used.

Conductivity data were collected at 298.15 K (±1 mK) with an automatic conductivity meter Antares II from Instrumentalia with an immersion cell calibrated with a KCl standard solution as usual, thermostatized at 298.15 K, by titration of water with concentrated solution of each surfactant mixture. To analyze the conductivity data, the excess specific conductivity $\Delta\kappa$ was also employed, which is defined as $\Delta\kappa = \kappa_{measured} - \kappa_{extrapolated}$ in which $\kappa_{extrapolated}$ is the specific conductivity extrapolated from the very low concentration-specific conductivity vs. concentration using a least squares fitting straight line. The values of $\Delta\kappa$ are plotted against the total concentration. This representation was proposed by Miura and Kodama [8] to magnify the conductivity changes especially when the breaks are poorly defined. In some cases, up to three breaks were found. To unequivocally determine which of them was the CMC, three auxiliary methods were

employed: dye solubilization, surface tension, and pH measurements.

Dye solubilization experiments were performed by a battery of tubes having different concentrations of each α_{NaOL} system. Small Sudan III crystals were added to the tubes which were sealed and left a week with periodic stirring. Then, the solutions were centrifuged and the supernatant absorbance measured with a Spectronic-21 UV–Vis spectrophotometer at λ=600 nm.

Surface tension (σ) measurements were made on the same solutions as in the Sudan III solubilization experiments using a Du Noüy (Krüss) tensiometer thermostated to 298.15 K.

The pH determinations were made with a millivoltmeter and pH meter CRIBABB and a Broade and James glass electrode using the same procedure as the conductivity measurements.

Mean values and variances were computed by the minimum variance linear unbiased method [9], and the Student's t function was employed to compute the error intervals. Confidence level was 0.90. Errors of derived data were computed with the error expansion method.

Theory

Regular solution theory has been very widely used to model the thermodynamic non-idealities of mixed micelles; it has been shown to accurately model CMC values [10] and monomer–micelle equilibrium compositions [11] in surfactant systems exhibiting negative deviations from ideality. However, it must be pointed out that the theoretical validity of using regular solution theory to describing non-ideal mixing in mixed surfactant micelles has been questioned [12]. 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 [1, 13]. However, the pseudophase separation model and regular solution theory combination remains as a very widely used and convenient method for analyzing experimental data. Details of the method were done elsewhere [14, 31]. Briefly, an equation relating the mixture CMC, the CMC of pure surfactants, the mole fraction of each surfactant in the total mixture (without considering water), e.g., α_{NaOL} for sodium oleate, and the mole fraction of one component in micelles without considering the solvent, e.g., X_{OL} for oleate, is numerically solved to obtain X_{OL} (Eq. 1). Then, the interaction parameter β_M (in $k_B T$ units, k_B being the Boltzmann constant and T the absolute temperature) is obtained from Eq. 2. The minimum error for β_M in a single determination is nearly 0.1k_BT [11]. From the values of β_M and X_{OL}, the activity coefficient of each surfactant (e.g., f_{OL}

for oleate) in the mixed micelle may be obtained from Eq. 3.

$$F = \frac{(X_1)^2 \ln(\alpha_1 CMC_M / X_1 CMC_1)}{(1 - X_1)^2 \ln[(1 - \alpha_1) CMC_M / (1 - X_1) CMC_2]} - 1 = 0 \qquad (1)$$

$$\beta_M = \frac{\ln(\alpha_1 CMC_M / X_1 CMC_1)}{(1 - X_1)^2} \qquad (2)$$

$$f_1 = \exp(\beta_M X_2{}^2) \qquad (3)$$

Theoretically, β_M is independent on both temperature and composition of the micelle. However, in practice, β_M is temperature-dependent [15–17] and often depends on the micelle composition (18, 19] and references therein), so an average value is commonly used. The nature and strength of the interaction between two surfactants are measured by the value of the β_M parameter which informs about the degree of non-ideality of the interaction in a mixed micelle through a single number that can be easily compared among different pairs of surfactants. The larger the negative value of β_M, the stronger the attractive interaction between the two different surfactant molecules and the greater is the probability of the existence of synergism between them [20]. 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 [21].

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

$$\beta_M = \beta_{M,core} + \beta_{M,elec} \qquad (4)$$

It is noteworthy that $\beta_{M,core}$ is typically considered equal to zero for mixtures of two hydrocarbon-based (or fluorocarbon-based) surfactants [23, 24]. However, recently, it was stated that this assumption is not true if the two chains are of different length and depends on the difference in number of carbon atoms, Δn_C [25], and the interaction is attractive (i.e., $\beta_{M,core}$ is negative if $\Delta n_C \neq 0$). The $\beta_{M,core}$ value is typically positive for a binary mixture of hydrocarbon and fluorocarbon surfactants due to the repulsive interactions in the micellar core [26–29].

The micelle ionization degree (α) was determined with the equation [30]:

$$\alpha \approx [(dK)_M / dC] / [(dK)_m / dC] \qquad (5)$$

where $d\kappa/dC$ is the slope of the specific conductivity dependence on the total concentration, the subscripts M and m meaning the micellar and monomer regions. This equation is based on the assumption that micelle contribution to conductivity is negligible, an assumption that is not strictly true.

The composition of the monolayer adsorbed at the air/solution interface was determined with a procedure proposed by Rosen and Hua [31]. The following equation is numerically solved for $X_{i,}^S$, the mole fraction of component i at the monolayer, without considering the solvent:

$$F = \frac{X_i^{S2} \ln(\alpha_i C_{ij} / X_i^S C_i)}{(1 - X_i^S)^2 \ln[(1 - \alpha_i) C_{ij} / (1 - X_i^S) C_j]} - 1 = 0 \qquad (6)$$

where C_i, C_j and C_{ij} are the molar concentrations of the pure components i and j and their mixture at a given α_i value, respectively, needed to produce a fixed value of the surface tension, e.g., 40 mN m^{-1}. The interaction parameter in the adsorbed monolayer in $k_B T$ units is given by:

$$\beta_S = \frac{\ln(\alpha_i C_{ij} / X_i^S C_j)}{(1 - X_i^S)^2} \qquad (7)$$

and the activity coefficient of each component in the monolayer is computed as:

$$\gamma_i^S = \exp(\beta_S X_j^{S2}). \qquad (8)$$

Results and discussion

Micellization

Conductivity plots (as $\Delta\kappa$ vs. total concentration, not shown) display three breaks. This leads to the need to determine which of these breaks is the CMC and to determine the meaning of the other critical concentrations. Accordingly, the surface tension and Sudan III solubilization experiments were performed.

Figure 1 shows the surface tension as a function of the logarithm of concentration for the system having $\alpha_{NaOL} = 0.65$ where two breaks may be seen. The second one is probably due to the CMC. Similar behavior was seen in the other compositions. This behavior was general, and the surface tension above the CMC continued decreasing with increasing total concentration. This means that the micelle structure changes with concentration. This phenomenon occurs in some mixed systems, e.g., aqueous solutions of
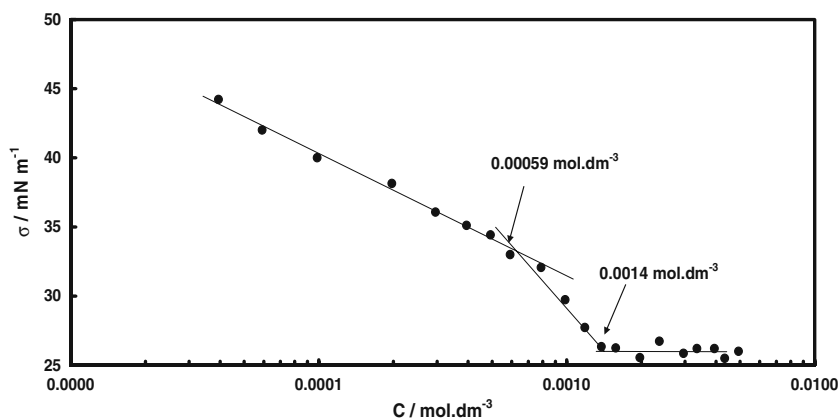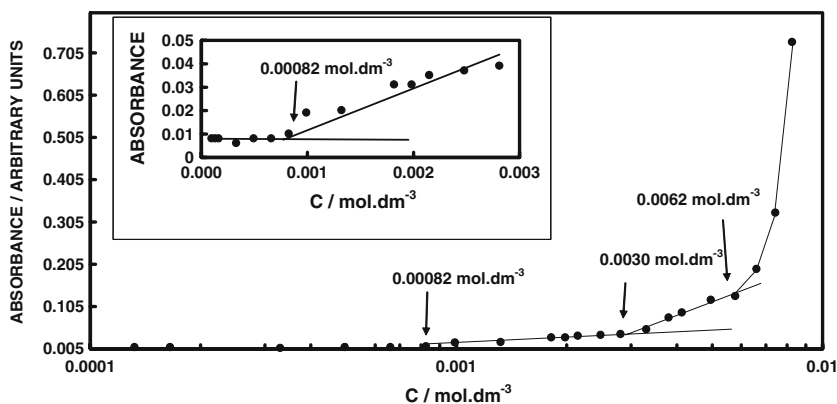
n-decyl methyl sulfoxyde (DeMS)–heptaoxyethylene n-dodecyl ether, but not in others such as DeMS–hexadecyl-trimethylammonium bromide [32]. In some other systems, the surface tension increases above the CMC [33].

The Sudan III solubilization experiments gave dependencies of the supernatant absorbance on the surfactant concentration with three breaks (except for pure NaOL where two breaks appeared). Figure 2 shows as an example the plot given by the mixed system having $\alpha_{NaOL}=0.2$. In compositions showing three breaks, the first corresponds to the formation of premicelles, the second to the CMC, and the third to a structural change in micelles. This may be the formation of cylindrical or disk-like micelles because these structures have one or two infinite curvature radii. This reduces the Laplace pressure in comparison with a sphere, and consequently, their capacity to solubilize large hydrophobic molecules such as Sudan III increases. This causes the sudden increase in the absorbance [34, 35]. Dye solubilization may induce micelle formation at concentrations below the CMC, so this technique was used to interpret the results of the other techniques. However, we have found that the influence of Sudan III in the CMC values was negligible.

Figure 3 shows the hydrolysis degree $\beta=[OH^-]/C$, where C is the total concentration (obtained from pH measurements), for the system having $\alpha_{NaOL}=0.2$, where two

breaks may be seen; the first corresponds to the CMC and the second to a structural change in micelles. The hydrolysis constant, $K_h=[OH^-]^2/(C-[OH^-])$, as a function of the total concentration was also represented (figure not shown) and also showed three breaks.

Figure 4 shows the different transitions as a function of the composition of the surfactant mixtures. The CMC was determined by conductivity, dye solubilization, pH, and surface tension. It may be seen that the CMC is not ideal and there is a premicellar association and a change in micelle structure. The CMC_{NaOL} was 0.0004 mol dm^{-3}, having the same order as that in the literature values (≈ 0.0006 mol dm^{-3}) [2, 36, 37]. However, it seems that literature CMC values correspond to an intermediate value between the CMC and the concentration corresponding to the micelle structure change which was determined here as 0.0026 mol dm^{-3}. The CMC_{NaLin} here found was 0.0020 mol dm^{-3}, in good agreement with the literature (0.0018 mol.dm^{-3}) [38].

Figure 5 shows the micelle composition at the CMC as a function of the total composition of the mixture, obtained with the method described in the above theoretical section. Micelles are monotonically richer in NaOL than the total composition ($X_{OL} > \alpha_{NaOL}$). Figure 6 shows the same data at the concentration at which a structural change occurs in micelles. In this case, at predominant concentration of both

Fig. 2 Absorbance of the supernatant vs. total concentration of the surfactant mixture in the system with $\alpha_{NaOL}=0.2$. The *inset* is an amplification of the first break region

Fig. 3 Hydrolysis degree ($\beta = [OH^-]/C$) as a function of the total concentration of surfactant for the system having $\alpha_{NaOL}=0.2$
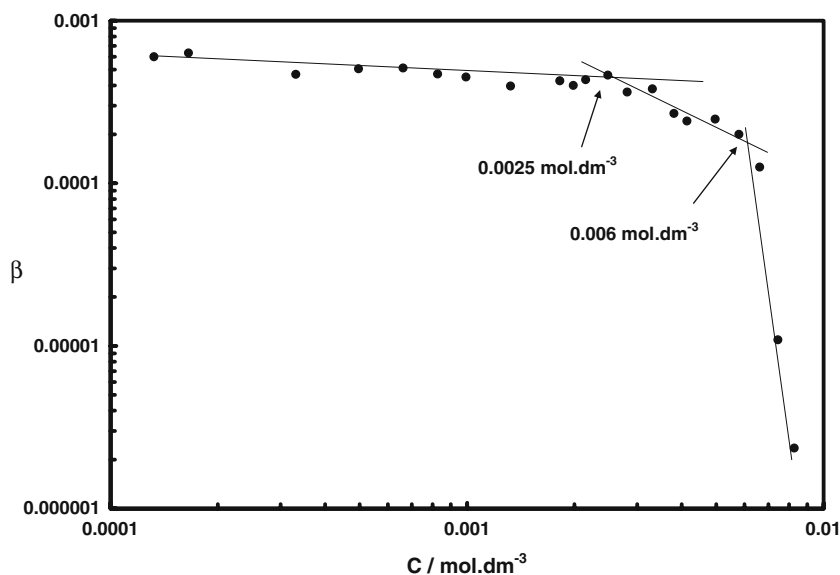
surfactants, the micelle composition is closer to the ideal one. Except for $\alpha_{NaOL}=0.2$, micelles remain richer in NaOL than the total composition. Both at the CMC and the structural change concentration, micelles are strongly non-ideal.

The dependence of the interaction parameter β_M on the micelle composition at the CMC is shown in Fig. 7. It may be seen that between $X_{OL}=0$ and $X_{OL}\approx0.45$, the interaction is slightly repulsive, but the repulsion between both components rises when the proportion of NaOL in the mixed micelle increases, and at $X_{OL}\approx0.8$, β_M strongly increases up to a maximum when $X_{OL}\approx0.89$, with $\beta_M=4.9$. Positive values of β_M are characteristic of mixtures of perfluorocarbon–hydrocarbon surfactants, but not of mixtures of two hydrocarbon-based surfactants and still less for mixtures of hydrocarbon surfactants having the same polar head group and the same chain length. As examples, $\beta_M=2.2$ for lithium dodecylsulfate–lithium perfluorooctanoate [39], $\beta_M=-0.685\pm0.072$ for $C_{11}COOK$–$C_{13}COOK$ mixtures [40], and $\beta_M=-1.26\pm0.11$ for C_7COOK–$C_{10}COOK$ mixtures [41].

Figure 8 shows the micelle ionization degree (α) at the CMC as a function of micelle composition. The system behaves non-ideally, although the current theory predicts an ideal one. The non-ideality may be caused by the interaction between water molecules and the π-electrons of the double bonds via hydrogen bonds [6]. The ionization degree behavior is in agreement with the NaOL content in micelles. Since the –CH=CH– group is smaller than the –CH=CH–CH$_2$–CH=CH– one, the inclusion of the first group in the hydrocarbon/water interface of micelles causes a lesser separation between carboxylate groups than that of the

Fig. 4 The different aggregation transitions vs. the surfactant mixture composition. *Curves* are eye guides
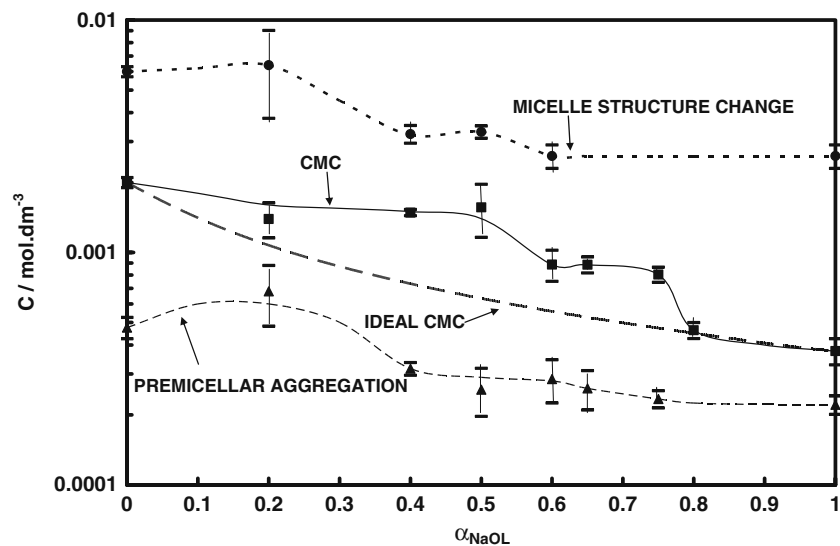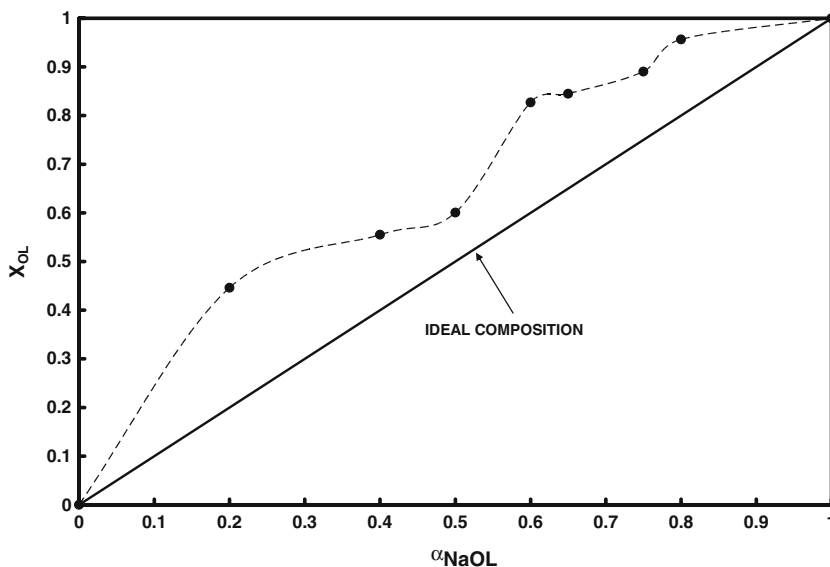
Fig. 5 Micelle composition at the CMC as a function of the total composition of the surfactant mixture. *Curve* is an eye guide

linoleate unsaturated chain. This feature increases the surface charge density and consequently the capture of counterions, thus decreasing α.

In conclusion, the mixture of both unsaturated soaps, which, following the assumptions of the current theory of mixed micelles, must be almost ideal (because both surfactants have same chain lengths and polar head groups) is strongly non-ideal. As expected, micelles are richer in the more hydrophobic component (NaOL), but surprisingly, the interaction is repulsive. This interaction is small in micelles predominantly formed by NaLin, but the positive value of β_M strongly increases when NaOL predominates. In mixtures of saturated homologous, the interaction is attractive and increases with increasing difference in chain length [25]. The repulsive interaction may be caused by the

competence between the unsaturated groups for loci in contact with water at the micelle surface. The presence of the –CH=CH–CH$_2$–CH=CH– groups in micelles rich in NaOL may force the –CH=CH– groups of the latter to submerge inside the hydrocarbon micelle core, which means that some hydrogen bonds with water are eliminated and then the excess micellization free energy will increase.

The air/solution interface

The composition of the monolayer adsorbed at the air/ solution interface was determined with the Rosen and Hua procedure [31], taking the surface tension $\sigma = 35$ mN m^{-1} as reference for the concentrations used in computations because all systems reached that value, which is close to

Fig. 6 Micelle composition at the concentration of micelle structural change as a function of the total composition of the surfactant mixture. *Curve* is an eye guide
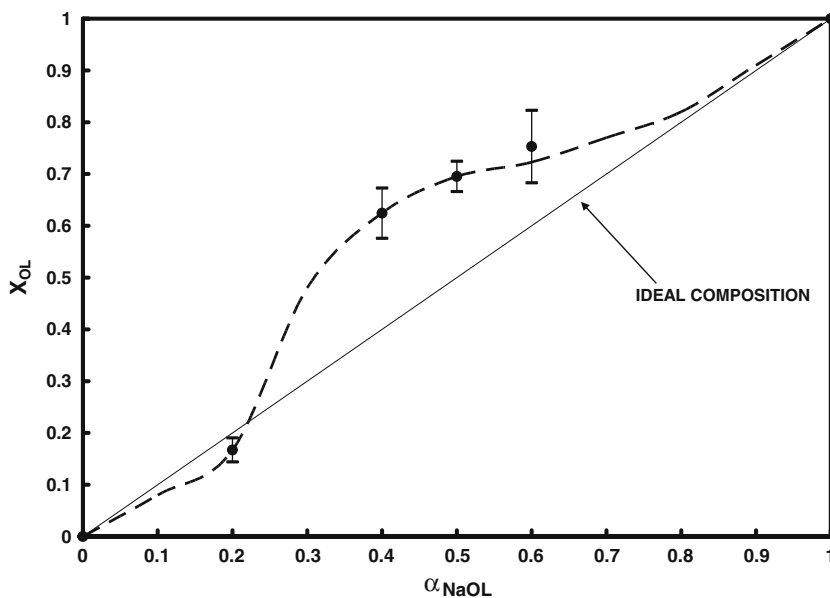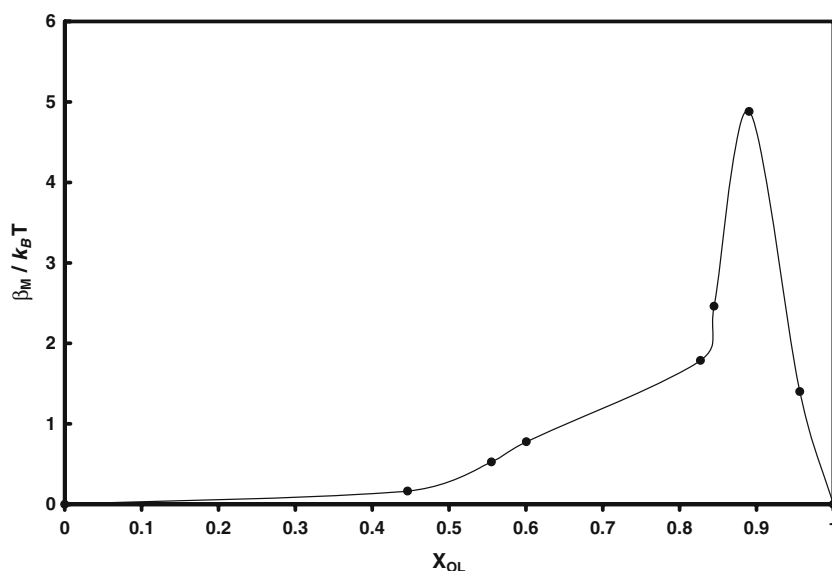
Fig. 7 Dependence of the interaction parameter β on the micelle composition at the CMC. The *line* is an eye guide

Figure 12 depicts the area per adsorbed molecule (a_0) at the air/water interface just below the CMC, computed from the surface excess Γ obtained with the Gibbs adsorption isotherm, and $a_0 = 10^{18}/\Gamma N_A$ nm^2 per molecule, where N_A is the Avogadro's number. The ideal behavior may be represented by [36]:

$$a_0 = X_1 a_{0,1} + X_2 a_{0,2} \qquad (6)$$

where $a_{0,1}$ and $a_{0,2}$ are the areas per adsorbed molecule in the solutions of pure components 1 and 2. This equation supposes that both areas do not change with the mixed surfactant composition. Values of $a_{0,NaLin} = 1.15$ nm^2 and $a_{0,NaOL} = 0.60$ nm^2 have been obtained. The value for NaOL is in very good agreement to that we obtained in a previous work [36]. The value of $a_{0,NaOL}$ is around 3 times the cross-section of a saturated hydrocarbon chain (0.205 nm^2) [42]. This fact may be attributed to a folding of the chain which puts the double bond in contact with water, together with

that obtained at the CMC. Figure 9 shows the monolayer composition below the CMC. When $\sigma = 35$ mN m^{-1}, the surface is systematically richer in NaOL than in NaLin in comparison with the total surfactant composition, owing to the higher hydrophobicity of the first. A preferential composition of $X_{OL}^s \approx 0.7$ is observed, i.e., a composition which is maintained along a large range of system composition. The interaction is non-ideal, but it is attractive. As it can be seen in Fig. 10, the interaction parameter at the monolayer (β_S) is monotonically negative with a minimum at $X_{OL}^s \approx 0.72$, in agreement with the preferential composition. Figure 11 shows the activity coefficients of both components in the mixed monolayer. The activity coefficient for linoleate suddenly drops at $X_{OL} > 0.65$. This indicates that its solubility at the surface rises when the oleate content increases. The value of f_{OL} reaches a minimum at $X_{OL} \approx 0.75$, which indicates that the mutual attraction is a maximum at this monolayer composition.

Fig. 8 Micelle ionization degree at the CMC as a function of micelle composition. *Line* is a fitting curve
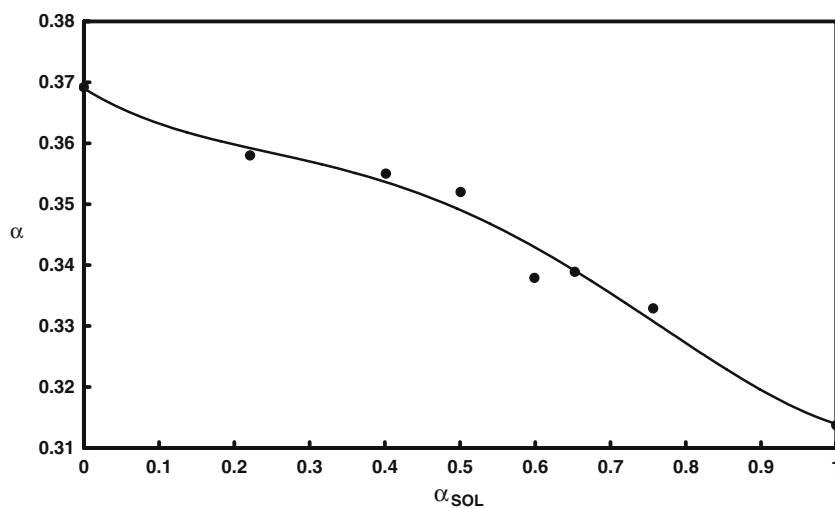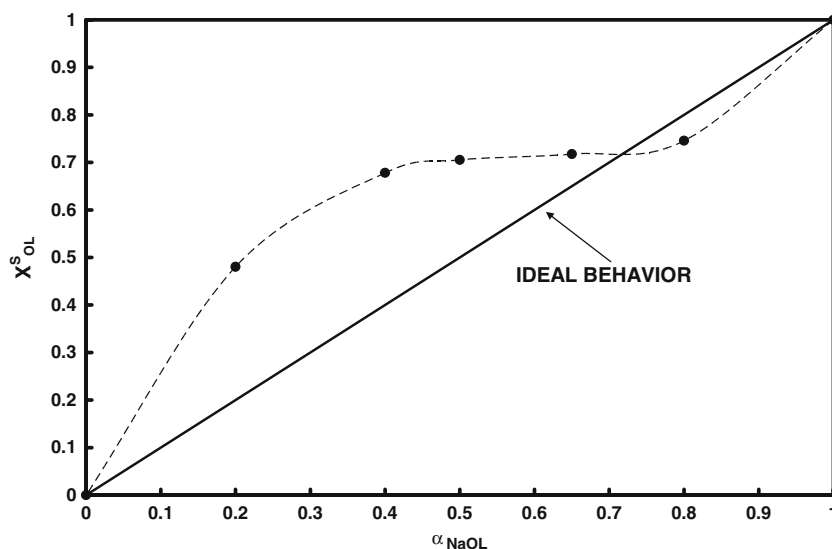
Fig. 9 Monolayer composition at the air/solution interface as a function of the surfactant mixture composition. The *line* is an eye guide

the carboxylate group. The value for NaLin seems too large even for soluble surfactant monolayers with only one chain. As an example, for saturated soaps, $a_0=0.45$ nm² for sodium dodecanoate, a soluble surfactant, and 0.234 nm² for potassium octadecanoate, a scarcely soluble one [43]. Kanicky et al. [44] found that a_0 for saturated soaps depend on the pH of the aqueous solution, between 0.567 nm² (pH=7.50) and 0.769 nm² (pH=8.50). However, other single-tailed surfactants show larger molecular areas, especially nonionic ones [45–47]. The value of $a_{0,NaLin}$ here found is similar to that found in systems having gemini surfactants. As an example, in the system C_8H_{17}–$N(CH_3)_2$–C_8H_{17}–$N(CH_3)_2$–C_8H_{17}–SDS, $a_0=1.04$ nm²/molecule [48]. For gemini surfactants of the same kind with chains having 12 carbon atoms and a spacer of six methylene groups, $a_0=$ 0.95 nm², and with a spacer of ten carbon atoms, $a_0=$ 1.47 nm² [49]. Then, the value of $a_{0,NaLin}=1.15$ nm² is

close to that corresponding to a spacer with seven methylene groups. Li et al. [50] results also agree with this conclusion. Thus, the NaLin behavior at the air/water interface is similar to that of a gemini surfactant having two different hydrophilic groups (–COONa and –CH=CH–CH₂–CH=CH–) and a spacer with seven methylene groups, similar to the heterogemini surfactants reported by Alami et al. [51]. Both hydrophilic groups must remain in contact with water, while the spacer may be curved forming a loop in the gas side of the interface [49]. In a previous work [36], we determined that the NaOL molecule is located at the air/water surface with the chain folded, causing both the carboxylate and the –CH=CH– groups to be contact with water. In practice, this works as a molecule having two polar head groups, a short hydrocarbon chain, and a spacer. The large value of $a_{0,NaLin}$ is probably caused by the necessity of place the central –CH=CH–CH₂–CH=CH–

Fig. 10 The interaction parameter in the adsorbed monolayer at the air/solution interface vs. the total surfactant mixture composition. The *curve* is an eye guide
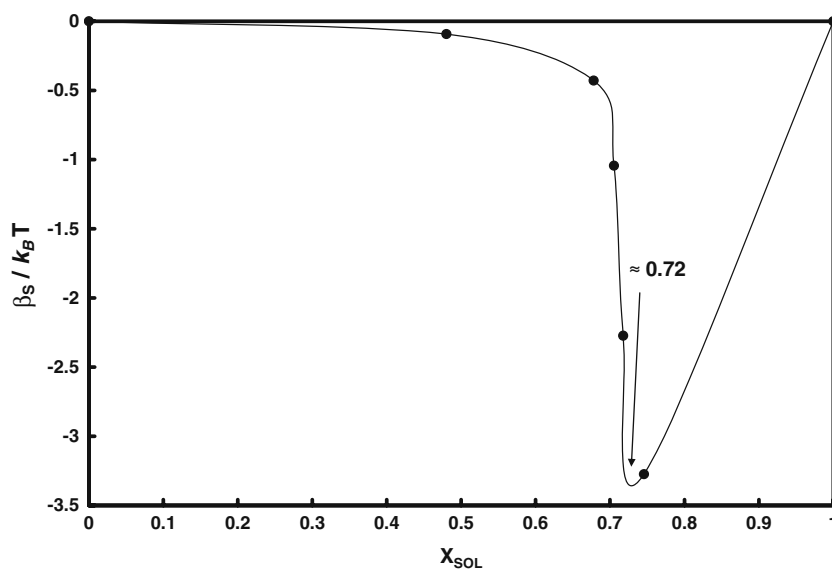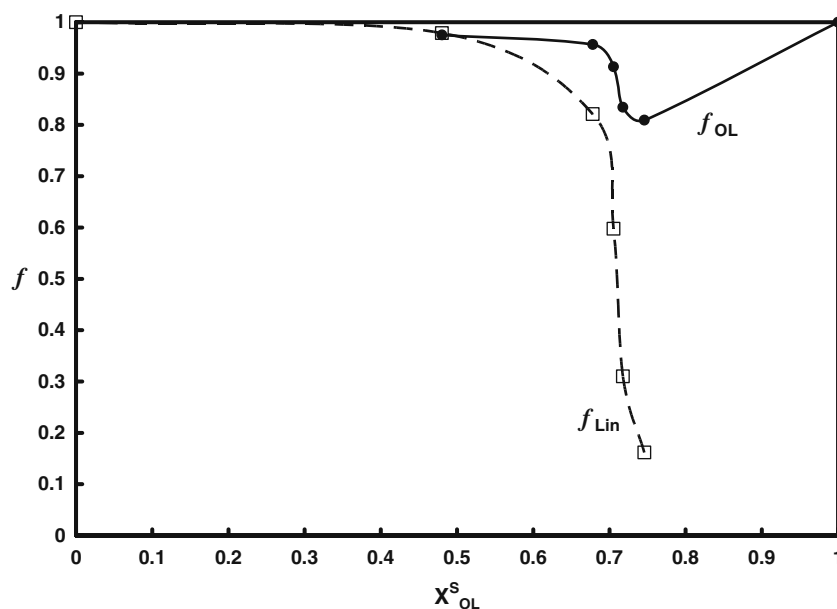
Fig. 11 Activity coefficient of both surfactants at the air/water interface as a function of the mixed monolayer composition. *Lines* are eye guides


group horizontal at the interface. Moreover, this situation reduces the cohesion to the hydrophobic chains layer acting as a spacer between them, thus reducing the van der Waals interactions.

Figure 12 shows a non-ideal behavior of the surface, with a reduction of the mixture a_0 with respect to the ideal value up to $X_{OL}^s \approx 0.71$, followed by a rapid increase above the ideal a_0 at higher X_{OL}^s values. A glance at Fig. 9 shows that $X_{OL}^s \approx 0.71$ is a preferential monolayer composition. Due to the higher hydrophobicity and the smaller distance between the saturated residues in the NaOL chain, the inclusion of this soap in the monolayer may compel the NaLin chain to crowd and eventually to retire the –CH=CH–CH$_2$–CH=CH– group from the contact with water, just as detected with the –CH=CH– of oleate in

NaOL–sodium dehydrocholate mixed monolayers [36]. Notice that at the minimum, $a_0=0.40$ nm^2 about the area occupied by a saturated soap molecule in a soluble surfactant monolayer. This may mean that the molecules of both components maintain their polar head groups in contact with water, but their double bonds in the air phase without any contact with water as they were saturated soaps. As it can be seen in Fig. 10, the interaction is attractive in all compositions, but it reaches a maximum at $X_{OL}^s \approx 0.71$. This can explain the contraction of a_0. Once X_{OL}^s exceeds the preferential value, the surface has a slight excess of NaLin and a_0 rises, which may be caused by a return of the double bonds/water contact. Then, NaLin may extend the hydrocarbon loop between the carboxylate and the –CH=CH–CH$_2$–CH=CH– groups, thus reducing the

Fig. 12 Area per adsorbed molecule at the air/water interface just below the CMC as a function of the mixed monolayer composition compared with the ideal behavior. The *dotted curve* is an eye guide
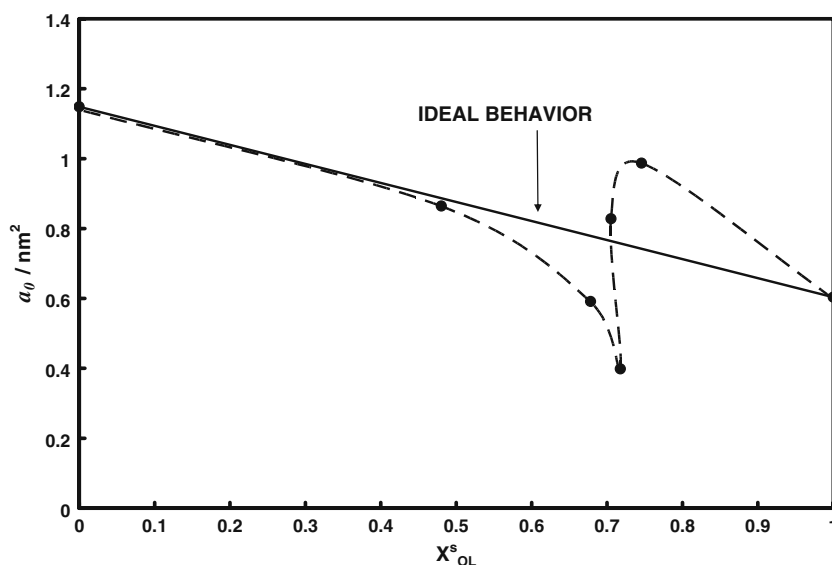
monolayer compactness because of the higher affinity with water of the –CH=CH–CH$_2$–CH=CH– group than the –CH=CH– one.

Figure 11 shows that NaLin is the more affected component by the inclusion in the monolayer; its activity coefficient monotonically decreases, while that of NaOL has a minimum at $X_{OL}^s \approx 0.71$. Then, the attraction to the surface increases monotonically with X_{OL}^s for NaLin, but for NaOL, the attraction increases up to $X_{OL}^s \approx 0.71$ and then diminishes. It is possible that at $X_{OL}^s \approx 0.71$, the proportion between components is optimal to compensate the loss of π-water energy via the π–π interaction between the unsaturated groups belonging to the oleate and linoleate chains.

Conclusions

The aggregation of NaOL and NaLin mixtures occurred in a gradual way; first, a type of premicellar aggregates appeared followed by the formation of true micelles, which in turn change their structure forming micelles with higher solubilizing capacity, probably cylinders or disks. As expected, micelles are richer in the more hydrophobic component NaOL, but the interaction is repulsive. This repulsion is relatively low in micelles richer in NaLin, but grows faster NaOL when predominates in the micelle composition.

The micellization behavior was not ideal, although the commonly accepted theory predicts an ideal one (the length of both components differs only in a methylene group). Non-ideality is caused by the interaction through hydrogen bonds between water and π-electrons of the double bonds.

Contrary to micellar pseudophase, below the CMC, the air solution adsorbed layer has a preferential composition of $X_{OL}^S = 0.7$. The interaction is still non-ideal, but here, it is attractive; the surface interaction parameter (βs) is monotonically negative, showing a minimum in $X_{OL}^S \approx 0.72$, which is coherent with the preferential composition. The surface is also systematically richer in sodium oleate than linoleate when compared with the system total composition, reflecting the higher hydrophobicity of the first component.

This study showed that the complex interaction between components in mixed micelles and mixed air solution monolayer is affected by the presence of double bonds in the hydrocarbon chains and its interactions with water.

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