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ORIGINAL CONTRIBUTION

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Aqueous sodium oleate–sodium dehydrocholate mixtures at low concentration

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Abstract The aqueous mixed system sodium dehydrocholate (NaDHC)–sodium oleate (NaOL) was studied by several methods to determine the influence of the hydrophobic structure of both surfactants in the mixed micellization and the formation of the mixed monolayer adsorbed at the air–water interface. The molecular area at the critical micelle concentration in pure surfactant solutions suggests that the adsorbed oleate chain was folded to allow the double bond in the middle of the molecule to remain in contact with water, and that the NaDHC molecule was situated with its plane laying parallel to the water surface, allowing the three carbonyl groups in the hydrocarbon backbone to form hydrogen bonds with water. The interaction was repulsive at the surface, and in the mixed monolayer some molecules must move away the less hydrophilic groups from water (double bond of NaOL, carbonyl groups of NaDHC). The interaction in mixed micelles was strongly attractive, showing a preferential composition roughly equimolar. The hydrolysis in mixed micelles was augmented in comparison with pure surfactants systems, which could be explained by assuming the existence of a more hydrophobic mixed micelle core. The mixed micelle degree of ionization was below that of the pure micelles, thus indicating a high surface charge density.

Keywords Mixed micelles · Sodium oleate · Sodium dehydrocholate · Air–water monolayer composition

Introduction

Research on surfactant mixtures is of considerable interest for numerous technical applications, because surfactant mixtures enhance performance when compared to single surfactants. When mixing surfactants, not only the properties of components are 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 not well understood at a fundamental level. Surfactant mixtures for specific applications are often chosen on the basis of experience, empirical evidence, or trial-and-error research. To optimize the applications of surfactant mixtures, it is important to understand the interplay of forces that govern the phase behavior. The main work in this sense has been devoted to electrostatic interactions, while scarce attention has been directed at the steric ones, with the study being mainly focused on the hydrophobic group geometry.

There are theories that consider the influence of the surfactant structure on mixed micellization [1, 2,3]. To improve these theories it is necessary to have good knowledge of the factors affecting the formation of micelles and their structure.

Bile salts are natural surfactants mainly stored in the gall bladder. Their function is essentially the emulsification and transport of food fats and lipids. The physicochemical properties of bile salts are of interest because of their very important role in the metabolic process of absorption at intestinal level.

Bile salts are different from common surfactants, which in general have their polar head group attached to a flexible hydrocarbon chain. The bile salts consist of a steroid nucleus having two or three hydroxyl groups that are situated in the concave side (face or α side) of the steroid backbone. This side is hydrophilic, whereas the convex side (back or β side) is hydrophobic. Besides, the hydroxyl groups may form intermolecular links via hydrogen bonds. Attached at the C-24 position there is a short aliphatic chain ended by a carboxylate group that may or may not be conjugated with glycine or taurine. From the point of view of the surfactant physical chemistry, bile salts are far from being as studied as the more traditional structured surfactants. Their micellar behavior is considerably different from that of ordinary surfactants [4, 5,6]. This structure promotes the formation of unusual aggregates whose structure and properties are still controversial [7].

Dehydrocholic acid (HDHC) is a derivative of cholic acid by oxidation. Its sodium salt (NaDHC) has been scarcely studied. We previously investigated the aggregation of this surfactant in water [8,9].

Studies on mixed micelles formed with bile salts and common surfactants are very scarce. They are commonly devoted to mixtures with phospholipids and other double-chained surfactants, because of their biological interest. As examples, Pedersen et al. [10] studied lecithin–bile salts mixed systems, Marques et al. [11] studied the sodium taurodeoxycholate–didodecyldimethylammonium bromide aqueous system, and Hjelm et al. [12] studied complex systems formed by bile salt, fatty acid, and monoglycerides. Some work was devoted to bile salt–nonionic surfactants mixtures [13,14] and to bile salt–cationic surfactant mixtures [15]. In these studies a combination of interactions in the hydrophobic region of the mixed micelles and in the polar micelle–water interface occurs. This makes it difficult to determine the influence of the two kinds of interactions in the system's behavior. We studied an aqueous mixture of NaDHC and sodium oleate (NaOL). Since both surfactants have the same hydrophilic group, any difference concerning the ideal mixing behavior (both in micelles and the air–water adsorbed monolayer) must be attributed to structural interactions within the hydrophobic mixed micelle core.

Theory

Regular solution theory has been very widely used to model the thermodynamic nonidealities of mixed micelles; it has been shown to accurately model critical micelle concentration (cmc) values [16] and monomer–micelle equilibrium compositions [17] in surfactant systems exhibiting negative deviations from ideality. However, the theoretical validity of using regular solution theory to describe nonideal mixing in mixed surfactant micelles has been questioned [18]. 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 [19,20]. However, the pseudophase separation model and regular solution theory combination remains a very widely and convenient method for analyzing experimental data.

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

$$X_{\mathrm{i,M}} + X_{\mathrm{j,M}} = 1, \tag{1}$$

$$\alpha_{\mathrm{i}} + \alpha_{\mathrm{j}} = 1. \tag{2}$$

At the cmc [21]

$$\alpha_{\mathrm{i}}\gamma_{\mathrm{i,m}}\mathrm{cmc}_{\mathrm{i}} = X_{\mathrm{i,M}}\gamma_{\mathrm{i,M}}\mathrm{cmc}_{\mathrm{M}}, \tag{3}$$

where $\gamma_{\mathrm{i,m}}$ and $\gamma_{\mathrm{i,M}}$ are the activity coefficients of surfactant i in the intermicellar solution and in micelles, and $\mathrm{cmc}_{\mathrm{i}}$ and $\mathrm{cmc}_{\mathrm{M}}$ are the cmcs of pure surfactant i and the mixture. Each surfactant monomer form is assumed to be dilute enough to obey Henry's law, i.e., based on the infinite dilution standard state; surfactant monomer activity coefficients are unity [22]. In applying regular solution theory to mixed micelles, the micellar activity coefficients are given by [23]

$$\gamma_{\mathrm{i,M}} = \exp\left(\beta_{\mathrm{M}} X_{\mathrm{j,M}}^{2}\right), \tag{4}$$

where β_{M} is the dimensionless regular 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 [24, 25,26] and it often depends on the micelle composition [27,28], so an average value is commonly used. In spite of these limitations, β_{M} quantitatively captures the extent of nonideality 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 β_{M}, which is a measure of the degree of nonideality 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 the greater the probability of the existence of synergism between them [29]. 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 [30].

Typical values of β_M are 2.2 for lithium dodecyl sulfate–lithium perfluorooctanesulfonate [31], −2.6 in sodium dodecyl sulfate (SDS)–poly(oxyethylene)$_{23}$ dodecylether [32], −3.9 for SDS–poly(oxyethylene)$_4$ dedecylether [33], and −13.2 for sodium decyl sulfate–decyltrimethylammonium bromide [34].

β_M is related to the molecular interactions in the mixed micelle by [33]

$$\beta_M = N_A\left(W_{ii} + W_{jj} - 2W_{ij}\right), \tag{5}$$

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

β_M reflects the two main contributions to the free energy of mixed micellization. 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 electrostatic interactions between the charged hydrophilic groups of surfactants i and j [35]:

$$\beta_M = \beta_{M,core} + \beta_{M,elec}. \tag{6}$$

It is noteworthy that $\beta_{M,core}$ is typically zero for mixtures of two hydrocarbon-based (or fluorocarbon-based) surfactants [36,37], but is larger than zero for a binary mixture of hydrocarbon and fluorocarbon surfactants owing to the repulsive interactions in the micellar core [38, 39, 40,41].

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

$$\Delta\mu_{mix}^{excess} = \beta_M RT X_{i,M} X_{j,M}, \tag{7}$$

where R is the gas constant. Negative values of $\Delta\mu_{mix}^{excess}$ indicate attraction between the two components in the micelles, most of which may result from a decrease in the electrostatic energy of the micelles. $\Delta\mu_{mix}^{excess}$ 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 [42,43]. The $\Delta\mu_{mix}^{excess}$ value does not take into account the change in the degree of association of the counterion upon surfactant mixing [24, 25,26].

The value of β_M for the interactions in a mixed micelle was calculated from the equations [33]

$$F = \frac{\left(X_{i,M}\right)^2 \ln\left(\alpha_i \mathrm{cmc}_M / X_{i,M}\mathrm{cmc}_i\right)}{\left(1 - X_{i,M}\right)^2 \ln\left[(1-\alpha_i)\mathrm{cmc}_M / \left(1 - X_{i,M}\right)\mathrm{cmc}_j\right]} - 1 = 0 \tag{8}$$

and

$$\beta_M = \frac{\ln\left(\alpha_i \mathrm{cmc}_M / X_{i,M}\mathrm{cmc}_i\right)}{\left(1 - X_{i,M}\right)^2}. \tag{9}$$

Equation (8) is solved for $X_{i,M}$, which is then replaced in Eq. (9) to obtain β_M. Hoffmann and Pössnecker [18] have demonstrated by error expansion of Eq. (9) that the minimum error for β_M in a single determination is nearly 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 [42,44]

$$\mathrm{cmc}_M = \left(\frac{\alpha_i}{\gamma_{i,M}\mathrm{cmc}_i} + \frac{\alpha_j}{\gamma_{j,M}\mathrm{cmc}_j}\right)^{-1}. \tag{10}$$

In the ideal approximation, $\gamma_{i,M} = \gamma_{j,M} = 1$. This mainly occurs in mixtures of two homologous surfactants, such as sodium octyl sulfate and sodium hexadecyl sulfate [45].

The interfacial behavior of the mixed system can be treated by the extension of the pseudophase separation model for micelles, using a nonideal analog of Butler's equation [46,47], giving [48]

$$\pi^{mx} = \frac{RT}{A_i}\ln\left(\gamma_{i,M}X_{i,M}/\gamma_{i,S}X_{i,S}\right) + \pi_i, \tag{11}$$

in which A_i is the area per mole of pure surfactant i at the air–water interface [49], π^{mx} and π_i are the surface pressures at the cmc of the surfactant mixture and component i, respectively, and $\gamma_{i,S}$ and $X_{i,S}$ are the activity coefficient and mole fraction of component i in the surface adsorbed state, respectively. When this equation was derived, the assumption that A_i does not change in surfactant surface mixtures was made. The activity coefficients of the adsorbed monolayer are given by

$$\gamma_{i,S} = \exp\left(\beta_S X_{j,S}^2\right), \tag{12}$$

where β_S is a dimensionless parameter, interpreted as representing an excess free energy of mixing in the surfactant aggregate at the interface. Equations (11) and (12) together with the constraint that the surface mole fractions $X_{j,S}$ sum to unity and the measured values of π^{mx} and π_i give the basis for an iterative solution of the model, provided the micellar composition and activity coefficients were previously computed.

β_S can 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 interface; however, the significance of β_S as a proper measure of the magnitude of the excess free-energy changes in the adsorption phenomenon is very uncertain [48].

Some literature-reported β_S values are −3.7 [decyl dimethylphosphine oxide ($C_{10}PO$)–SDS in 1 mM aqueous Na_2CO_3], −3.0 [decyl methyl sulfoxide ($C_{10}NSO$)–SDS in 1 mM aqueous Na_2CO_3], −0.3 ($C_{10}PO$–$C_{10}NSO$ in 1 mM aqueous Na_2CO_3), −2.9 [tetraoxyethylene glycol monododecyl ether ($C_{10}E_4$)–SDS in 0.5 mM aqueous Na_2CO_3], −2.0 [$C_{10}E_4$–dodecyl dimethylamine oxide ($C_{12}AO$) in 0.5 mM aqueous Na_2CO_3], −7.2 ($C_{12}AO$–SDS in 0.5 mM aqueous Na_2CO_3), and −19.7 (sodium decyl sulfate–decyltrimethylammonium bromide in 0.05 M aqueous NaBr) [48], and between −40 and −31 in some catanionic systems [50] (although they were computed with an approach different from that employed here).

To compute the micellar degree of ionization, α, the equation proposed by Evans [51] was employed:

$$1000(\mathrm{d}\kappa/\mathrm{d}C)_2=\frac{(n-m)^2}{n^{4/3}}\left[1000(\mathrm{d}\kappa/\mathrm{d}C)_1-\lambda_X\right]+\alpha\lambda_X, \qquad (13)$$

where $(\mathrm{d}\kappa/\mathrm{d}C)_1$ and $(\mathrm{d}\kappa/\mathrm{d}C)_2$ 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 counterion ($\lambda_{Na^+}=50.9$ S cm^2 mol^{-1} [52]). Equation (13) is a quadratic function of α, because $(n-m)=n\alpha$. It is also dependent on n; however, this dependence is not strong and any reasonable value of n gives a good estimation of α [51]. We employed $n=100$, which is a common value for n in spherical micelles of surfactants having a C_{16} single chain [53,54].

Experimental

HDHC was from Dr. Theodor Schuchardt (Munich) and of analytical grade. A concentrated NaDHC aqueous solution was prepared by weighing a quantity of HDHC and by dissolution in an appropriate amount of concentrated NaOH solution. Then the solution was diluted to obtain the desired concentrations. Only double-distilled water was used. NaOL (Fluka, 98%) was used as purchased.

Conductivity measurements were made with an immersion cell and an automatic conductimeter, namely an Antares II from Instrumentalia. Surface tension was measured with a ring tensiometer (Krüss).

Two batteries of tubes having different surfactant concentration were used to perform dye solubilization experiments. Small Sudan III crystals were added to the tubes of one battery and small Sudan black B crystals to the other. The tubes were sealed and left for 1 week with periodic stirring. Then the tubes were centrifuged and the supernatant absorbance was measured with a Spectronic-20 UV–vis spectrophotometer at 600 nm (Sudan III) and 490 nm (Sudan black B).

The pH determinations were made with a millivoltmeter and CRIBABB pH meter and a Broade and James glass electrode. The same millivoltmeter was used with an Orion 8411 Ross Na^+ ion-selective electrode, an oleate ion-selective electrode and a dehydrocholate ion-selective electrode. All ion-selective electrodes were used against a saturated calomel electrode.

The dehydrocholate ion-selective electrode was made by gluing at one extreme of a PVC tube a membrane made with 300 mg PVC dissolved in 50 ml tetrahydrofuran (THF) plus 0.2 ml dibutyl phthalate (plasticizer) and 0.167 g $Pd(DHC)_2$. $Pd(DHC)_2$ was made by mixing the appropriate amounts of $PdCl_2$ and NaDHC aqueous solutions. The insoluble $Pd(DHC)_2$ salt was filtered and washed several times with double-distilled water and then left to dry. The crystals were powdered and suspended in previously mentioned solution. Then the PVC mixture was left in a Petri dish to let the THF evaporate, and the resulting membrane was cut and glued to the tube. The tube was filled with an aqueous solution of 0.01 mol dm^{-3} NaDHC plus 0.1 mol dm^{-3} KCl having a small amount of solid AgCl. An Ag/AgCl electrode made with a silver wire was placed into the tube, which was sealed with a rubber plug.

The oleate ion-selective electrode was constructed in a similar form to that of the dehydrocholate ion-selective electrode using barium oleate as an insoluble ion-exchange salt, and a solution of NaOL in the inner reference electrode.

All determinations were made at 25.0 °C.

Results

The surface tension, σ, is shown versus the concentration for the different mixtures in Fig. 1. Some curves were

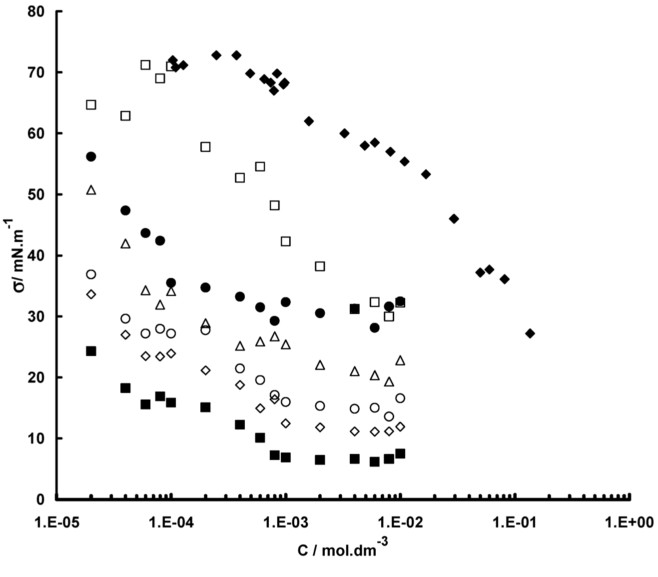

Fig. 1 Surface tension versus concentration for different sodium dehydrocholate (*NaDHC*)–sodium oleate (*NaOL*) mixtures. $\alpha_{NaDHC}=1$ (*closed diamonds*); $\alpha_{NaDHC}=0.85$ (*open squares*); $\alpha_{NaDHC}=0.7$ ($\sigma=5$ mN m^{-1}) (*triangles*); $\alpha_{NaDHC}=0.5$ ($\sigma=10$ mN m^{-1}) (*open circles*); $\alpha_{NaDHC}=0.3$ ($\sigma=15$ mN m^{-1}) (*open diamonds*); $\alpha_{NaDHC}=0.18$ (*closed circles*); $\alpha_{NaDHC}=0$ ($\sigma=20$ mN m^{-1}) (*closed squares*)

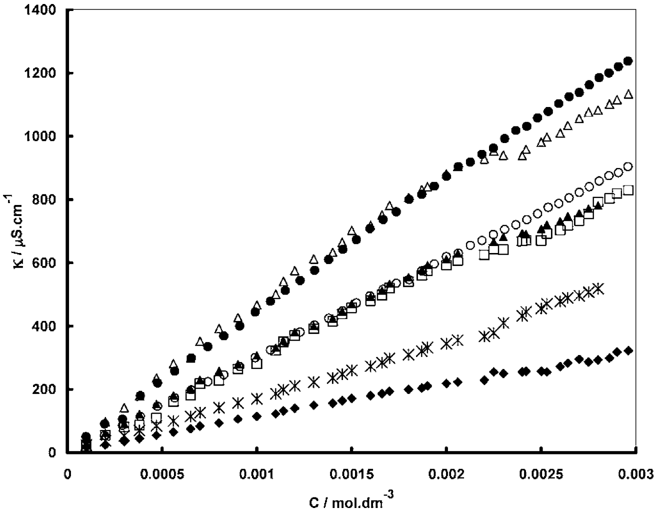

Fig. 2 Specific conductivity versus concentration for different NaDHC–NaOL mixtures. $\alpha_{NaDHC} = 1$ (stars); $\alpha_{NaDHC} = 0.85$ (*open squares*); $\alpha_{NaDHC} = 0.7$ (*closed triangles*); $\alpha_{NaDHC} = 0.5$ (*open triangles*); $\alpha_{NaDHC} = 0.3$ (*closed circles*); $\alpha_{NaDHC} = 0.18$ (*open circles*); $\alpha_{NaDHC} = 0$ (*diamonds*)

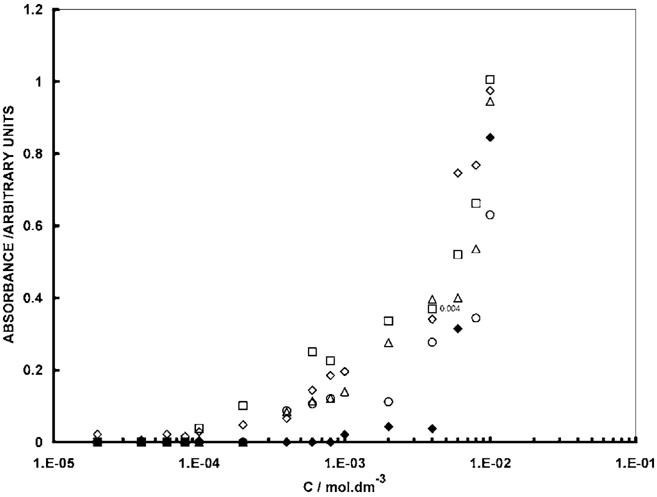

Fig. 4 Absorbance at 600 nm of solubilized Sudan III in micelles versus surfactant concentration. $\alpha_{NaDHC} = 1$ (*closed diamonds*); $\alpha_{NaDHC} = 0.7$ (*triangles*); $\alpha_{NaDHC} = 0.5$ (*circles*); $\alpha_{NaDHC} = 0.3$ (*open diamonds*); $\alpha_{NaDHC} = 0$ (*squares*)

shifted to avoid confusion. The specific conductivity, κ, is plotted in Fig. 2 as a function of the total concentration for each α_{NaDHC} value. The pH versus concentration curves for some different mixtures are depicted in Fig. 3. Some results of the Sudan III solubilization experiments are shown in Fig. 4. That of Sudan black B solubilization gave similar results.

An example of the responses of the three ion-selective electrodes to the mixture concentration is shown in Fig. 5. Changes at the cmc are readily visible. However, we found that the two surfactant ion-selective electrodes were sensitive to both surfactant ions (i.e., oleate is detected by the dehydrocholate ion-selective electrode and vice versa). In consequence, we did not use these data to determine the concentration of free surfactant ions.

Discussion

In order to obtain better cmc values from conductivity data, the $\Delta\kappa = \kappa - \kappa_{extrapolated}$ versus concentration method was used [55]. The $\kappa_{extrapolated}$ values were found by extrapolation of the pre-cmc specific conductivity data by fitting them to a least-squares straight line. This method magnifies the slope difference between pre- and post-cmc data. The results for three different α_{NaDHC} systems are shown in Fig. 6. The dependence of the cmc on the composition of the surfactant mixture is shown in

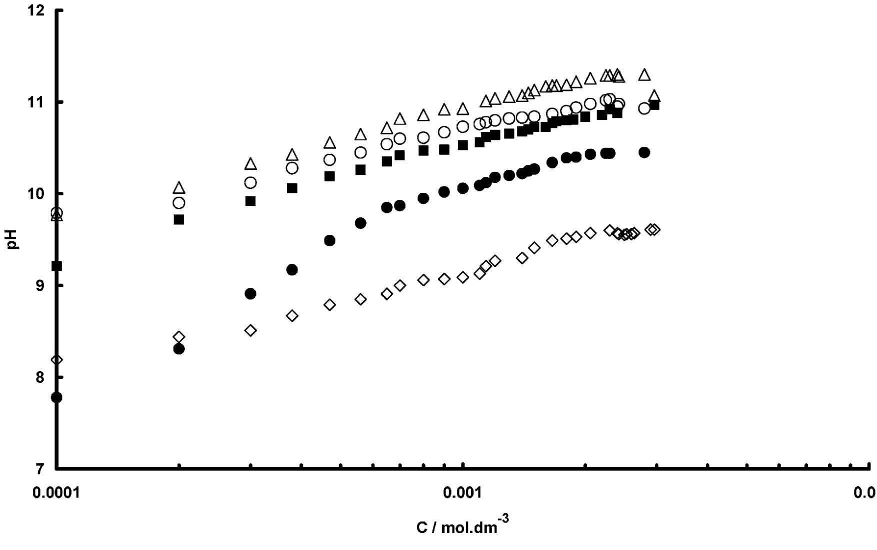

Fig. 3 pH versus concentration. $\alpha_{NaDHC} = 1$ (*closed circles*); $\alpha_{NaDHC} = 0.7$ (*open circles*); $\alpha_{NaDHC} = 0.5$ (*triangles*); $\alpha_{NaDHC} = 0.3$ (*squares*); $\alpha_{NaDHC} = 0$ (*diamonds*)

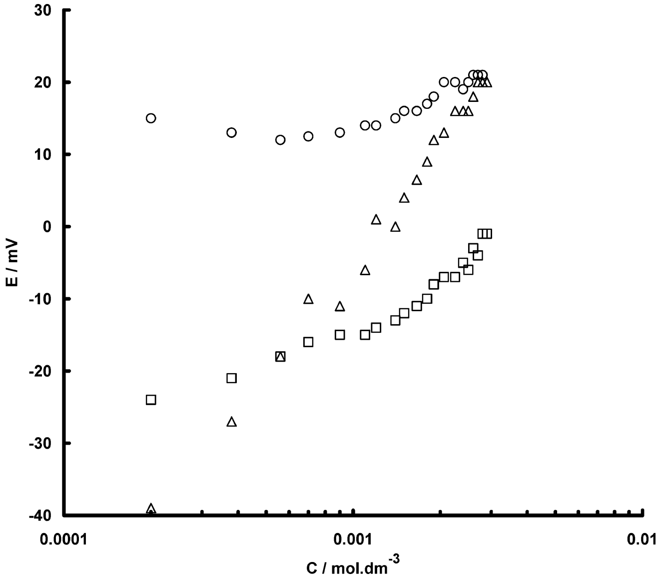

Fig. 5 Response of the ion-selective electrodes to surfactant concentration, $\alpha_{NaDHC} = 0.18$. Na^+ (*circles*), oleate (*diamonds*), and dehydrocholate (*squares*) ion-selective electrodes

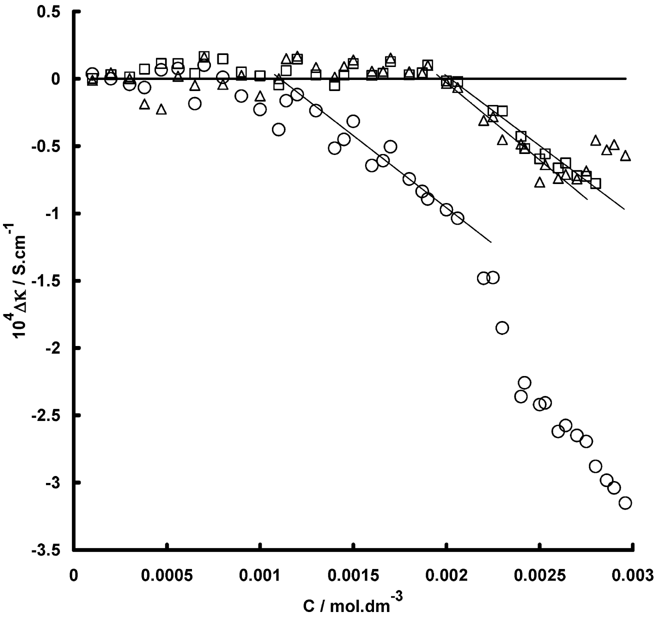

Fig. 6 $\Delta\kappa = \kappa - \kappa_{extrapolated}$ versus concentration for $\alpha_{NaDHC} = 0.3$ (*diamonds*), $\alpha_{NaDHC} = 0.5$ (*circles*), and $\alpha_{NaDHC} = 0.7$ (*triangles*)

Fig. 7. The ideal behavior was computed with Eq. (10) and is also plotted in Fig. 7. The cmc of NaOL was 0.6 mmol dm^{-3}, in agreement with literature values (0.66 mmol dm^{-3} [56], 0.6 mmol dm^{-3} [57]).

The composition of the micelles was computed with Eq. (8) and is plotted in Fig. 8 together with the composition of the mixed monolayer adsorbed at the air–solution interface. This latter magnitude was computed

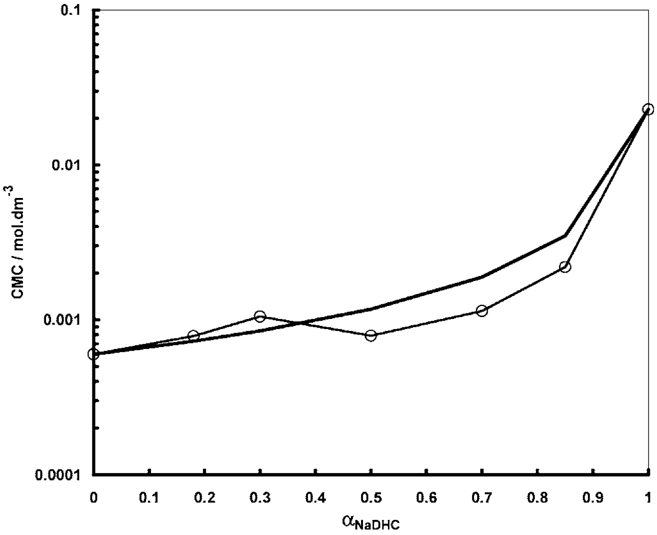

Fig. 7 Critical micelle concentration as a function of the mole fraction of NaDHC in the mixed surfactant system. The *solid line* shows the ideal behavior

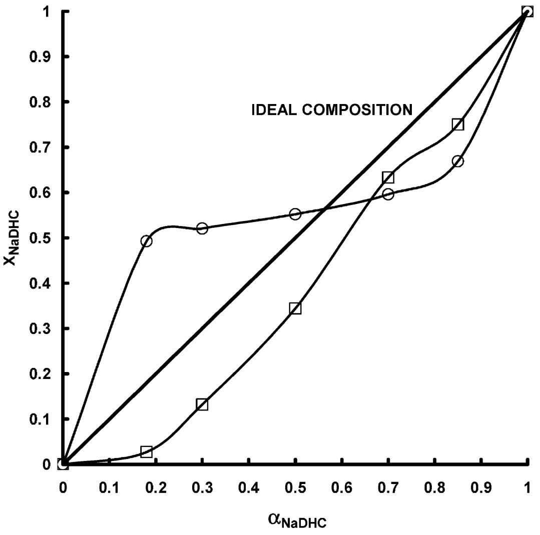

Fig. 8 Mole fraction of NaDHC in mixed micelles (*circles*) and in the mixed monolayer adsorbed at the air–solution interface (*squares*) versus composition of the surfactant mixture

by resorting to Eqs. (11) and (12). The area per molecule of pure surfactant was computed from the surface tension plots of pure NaOL and pure NaDHC solutions, using the Gibbs equation

$$\Gamma_i = \frac{1}{2RT} \frac{\partial \sigma}{\partial \ln C_i} \tag{14}$$

and the relationship $a_i = (\Gamma_i \ N_A)^{-1}$.

We found that the area per adsorbed molecule was $a_{NaOL} = 0.565$ nm^2, and that $a_{NaDHC} = 0.702$ nm^2. The

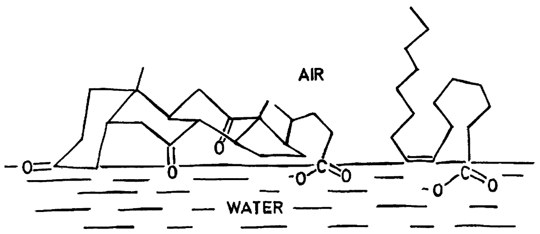

Fig. 9 Proposed accommodation of the NaOL and NaDHC molecules adsorbed at the air–water interface

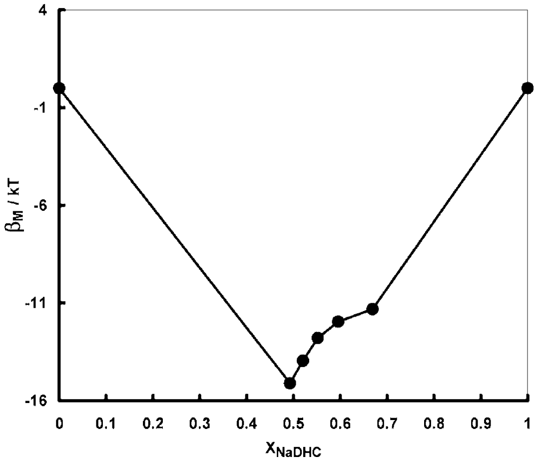

Fig. 10 Micellar interaction parameter, β_M, as a function of the micelle composition, $X_{NaDHC,M}$

value of a_{NaOL} is 2.76 times that of the transversal section of a saturated hydrocarbon chain (0.205 nm^2) [58]. This may be due to a chain folding which allows the double bond in the middle of the molecule to remain in contact with water (Fig. 9). It is well known that the π electrons of a double bond may form hydrogen bonds with water [59, 60, 61, 62, 63,64]. On the basis of the structure of the dehydrocholate ion, which may be roughly considered as a rectangular plate of 0.571-nm width and 1.286-nm length [65], the computed value of a_{NaDHC} was 0.735 nm^2. Therefore, the experimental value may be explained by an accommodation of the molecule with its plane lying parallel to the water surface. This situation allows the three carbonyl groups in the hydrocarbon backbone to form hydrogen bonds with water (Fig. 9). Some literature values of the limiting area at collapse pressure for bile salt monolayers are 1.08 nm^2 (cholic acid), 0.80 nm^2 (chenodeoxycholic acid), and 0.73 nm^2 (ursodeoxycholic acid) [66]. The similarity of the preceding areas with that of NaDHC suggested that the monolayer adsorbed at the air–water interface at the cmc was very compact. Other bile salts show less compact monolayers at the cmc, with an area per molecule of 1.48 nm^2 (sodium cholate) and 2.23 nm^2 (sodium deoxycholate) [67].

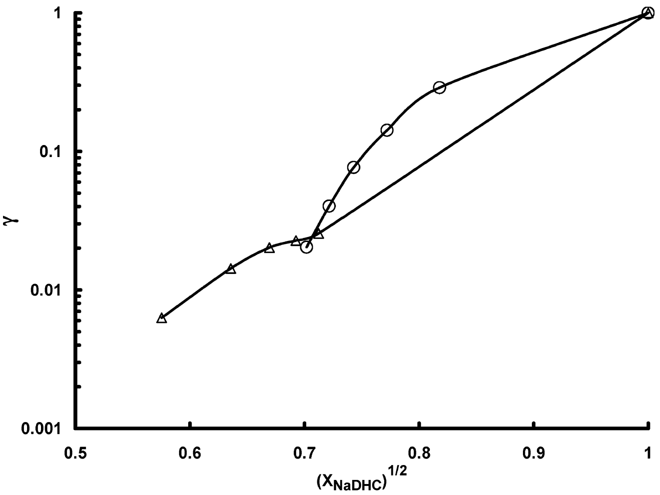

Fig. 11 Activity coefficient in micelles of NaOL (*triangles*) and NaDHC (*circles*) versus the square root of the micelle composition

Table 1 The degree of ionization of sodium oleate–sodium dehydrocholate mixed micelles

α_{NaDHC}	$X_{NaDHC,M}$	α
0	0	0.255
0.18	0.493	0.235
0.3	0.521	0.208
0.5	0.552	0.183
0.7	0.596	0.207
0.85	0.669	0.214
1	1	0.54

The β_M values are shown in Fig. 10 as a function of $X_{NaDHC,M}$, computed with Eq. (9). The activity coefficient of both surfactants in micelles is shown in Fig. 11 as a function of the square root of the micelle composition.

Since the hydrophilic groups of both surfactants are the same, we concluded that the negative values of β_M are associated with the hydrophobic core, i.e., $\beta_M \approx \beta_{M,core}$, in spite of the fact that both hydrophobic groups are hydrocarbons.

The degree of ionization of the micelles (α) was computed with Eq. (13). The dependence of α on the composition of the micelles and on the total mixture composition is shown in Table 1. The value for NaOL is in agreement with that in the literature ($\alpha = 0.393$ [56]). The value of α for NaDHC was taken from Ref. [9]. It may be seen that mixed micelles had degrees of ionization slightly smaller that those of pure NaOL micelles. This is consistent with a closely packed Stern layer. Pure NaDHC micelles are highly ionized [9]. A high α value is consistent with a low surface potential arising from a low surface charge density. This in turn may be due to the structure of the rigid hydrophobic backbone that hinders the formation of a compact hydrophobic core, even if a back-to-face aggregation structure is accepted.

But the inclusion of the flexible NaOL molecules evidently produces a tightly packed carboxylate layer having high electrostatic potential. This high potential in turn captures counterions.

Since α in mixed micelles was also smaller than that of the pure NaOL micelles, it may be concluded that the carboxylate groups arising from both surfactants must be in the same region of the micelles, probably the same as in pure NaDHC micelles. If the carboxylate groups were distributed on the complete surface of mixed micelles, the surface density of charge might be smaller than that of pure surfactant micelles, and α might be higher than that of pure surfactant micelles.

The degree of hydrolysis ($\beta = [HO^-]/\ c$) is shown versus the surfactant concentration in Fig. 12. It is evident that the mixed systems had degrees of ionization higher than those of the pure surfactant solutions. This means that there was an interaction between both surfactants that favored the elimination of the acid formed by hydrolysis from the aqueous medium. The formation of hydrogen bonds between the –COOH group of oleic acid (formed by hydrolysis) and the carbonyl groups of the dehydrocholate hydrophobic backbone may be the origin of this increased hydrolysis. Studies on the dissociation of micellced bile acids mixed with nonionic surfactants made by Tanaka et al. [13] suggest that the hydrocarbon micelle core is more hydrophobic in the mixed micelles than in the pure bile salt micelles. A more hydrophobic core can solubilize a larger amount of the acids formed by hydrolysis in comparison with pure NaDHC micelles. This phenomenon enhanced the hydrolysis by shifting the equilibrium toward the formation of more acid.

From Figs. 8, 9, 10, and 11, it is evident that the system has nonideal behavior. The β_M values ranged between−15.1 kT and −11.3 kT. These values are typical of strongly attractive interactions such as those in catanionic systems (−13.2 kT for sodium decyl sulfate–decyltrimethylammonium bromide [34], and about 17 kT for sodium cholate–hexadecylpyridynium chloride and sodium deoxycholate–hexadecylpyridynium [67]). Since the polar groups are the same, this strong interaction must be related to $\beta_{M,core}$. The intercalation of the flexible oleate chains among the rigid cholesteric structures must minimize the hydrocarbon–water interface in comparison with pure dehydrocholate and pure oleate micelles. The surface of the micelle that is not occupied by carboxylate groups is probably covered with the hydrophilic carbonyl groups of dehydrocholate and the double bounds of the oleate ions. The optimal coverage of the micelle surface by hydrophilic groups must occur at a given proportion of oleate to dehydrocholate. This proportion must be seen as a preferential composition of mixed micelles. This situation is easily seen in Fig. 8. From Fig. 10, the optimal composition seems to be $X_{NaDHC,M} \approx 0.5$, which corresponds to the minimum value of β_M.

The mixed monolayer at the air–water interface is monotonically richer in oleate than in dehydrocholate (Fig. 8), thus allowing the formation of a more compact adsorbed layer, which reduces the surface free-energy excess (i.e., the surface tension), as may be seen in Fig. 13. The maximum at $\alpha_{NaDHC} = 0.18$ may be due to

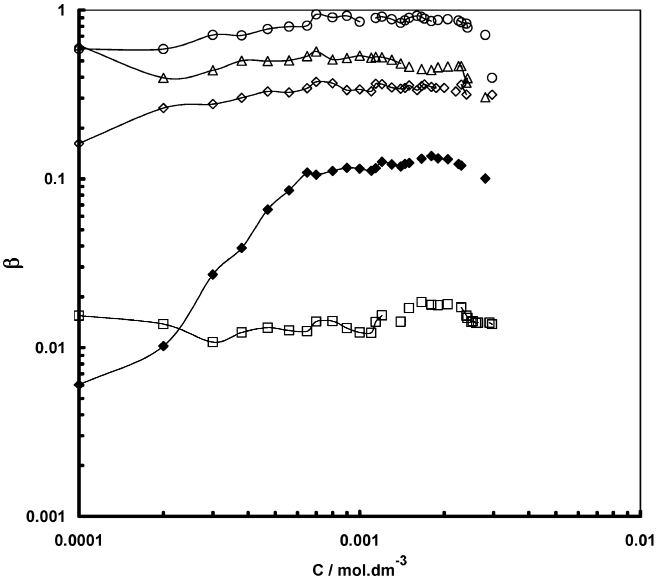

Fig. 12 Degree of hydrolysis versus total surfactant concentration of $\alpha_{NaDHC} = 1$ (*closed diamonds*), $\alpha_{NaDHC} = 0.7$ (*triangles*), $\alpha_{NaDHC} = 0.5$ (*circles*), $\alpha_{NaDHC} = 0.3$ (*open diamonds*), and $\alpha_{NaDHC} = 0$ (*squares*)

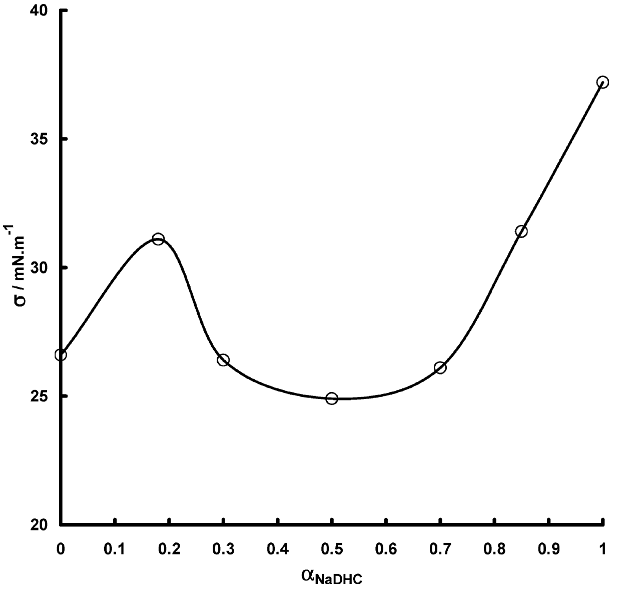

Fig. 13 Surface tension at the critical micelle concentration versus α_{NaDHC}

the inclusion of some NaDHC molecules because of the entropy of mixing. However, the attractive interaction between both surfactants in the micelles became repulsive in the adsorbed layer, reflecting the very different structure of both pseudophases. Similar behavior was observed at the air–water interface in mixtures of sodium cholate–hexadecylpyridynium chloride and sodium deoxycholate–hexadecylpyridynium [67]. The area per adsorbed molecule was obtained for each α_{NaDHC} value using Eq. (14) and is plotted in Fig. 14. The straight line was computed on the supposition that the values of a for both pure surfactants do not change in the mixed monolayer, with equation

$$a_{\mathrm{average}} = a_{\mathrm{NaDHC}} X_{\mathrm{NaDHC,S}} + a_{\mathrm{NaOL}} \left(1 - X_{\mathrm{NaDHC,S}}\right), \tag{15}$$

It may be seen that the first two mixtures richer in NaOL had experimental a_{average} values higher than the theoretical ones. This means that the monolayer was not compact. At $X_{\mathrm{NaDHC,S}} \approx 0.25$ a compact monolayer formed with NaOL and NaDHC molecules arranged as shown in Fig. 9 was formed. When $X_{\mathrm{NaDHC,S}}$ increased, a_{average} was smaller than the theoretical one. The only possibility is that a_{NaDHC} and a_{NaOL} did not remain constant. In particular, some of the oleate chains may be compelled to straighten, detaching the double bond from the water surface. As a result, a_{NaOL} had a value intermediate between 0.565 and 0.205 nm^2. At $X_{\mathrm{NaDHC,S}} = 0.5$, all NaOL molecules might be in this situation. The only explanation for the experimental a_{average} values for $X_{\mathrm{NaDHC,S}} > 0.5$ is that some of the adsorbed NaDHC molecules were also compelled to detach the carbonyl groups from water, and as a result, a_{NaDHC} had a value intermediate between 0.735 and 0.256 nm^2 (obtained from the dehydrocholate ion structure computed from the work of Sugihara and Tanaka [65]).

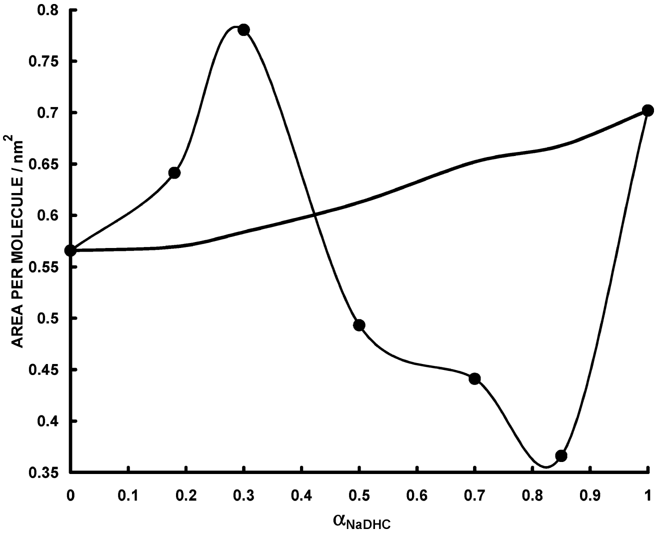

Fig. 14 Average area per molecule at the critical micelle concentration in the air–water interface versus α_{NaDHC}

Since the theory for mixed monolayers is based on the invariance of the A_i values, we concluded from the preceding discussion that the $X_{\mathrm{NaDHC,S}}$ values we found could also be criticized.

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