Colloid Polym Sci (2002) 280: 1045–1052
DOI 10.1007/s00396-002-0731-y

ORIGINAL CONTRIBUTION

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Aggregation of the aqueous dodecyltrimethylammonium bromide–didodecyldimethylammonium bromide system at low concentration

Received: 8 September 2001
Accepted: 27 April 2002

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Abstract The dodecyltrimethylammonium bromide (DTAB)–didodecyldimethylammonium bromide (DDAB)–water system was studied to elucidate whether the mixed surfactant aggregates are mainly micelles or vesicles, and whether the surfactant–surfactant interaction is ideal or not. The regular solution theory of mixed micelles and the Israelachvili–Mitchell–Ninham (IMN) packing parameter of the aggregated mixture were used. The interaction between dissimilar surfactant species was found to be non-ideal, with a positive value of the regular solution theory interaction parameter. The steric hindrance interaction parameter of Huang and Somasundaran theory indicated that the introduction of DTAB into DDAB layers was favoured at very low DTAB content, but became highly unfavourable when the proportion of DTAB increased. The aggregates were systematically much richer in DDAB than the solution of interaggregates. The IMN values systematically were compatible with flat surfaces, i.e., lamellar liquid crystals and vesicles. The results may be explained by a different composition of the inner and outer monolayers in the bilayer structure of the vesicles.

Keywords Mixed surfactants · Vesicles · Packing parameter · Cationic surfactants

Introduction

Micelle formation of surfactant mixtures is of considerable interest from both fundamental and practical points of view. Surfactants used in practical applications are often mixtures of homologous compounds or are contaminated by impurities. In addition, mixed microstructures of two or more components are important in biological systems such as cell membranes. Much of the work reported in the biochemical literature has focused on mixed microstructures of monoalkyl surfactants and phospholipids [1, 2, 3]. Mixed aqueous dispersions of lipids and surfactants have been considered as potential tools for membrane research and protein reconstitution. The initial compositions of lipid–surfactant mixtures and the changes in the local compositions of the mixtures during surfactant removal are very important for the production of stable lamellar structures in the formation of vesicles and in protein reconstitution processes [4, 5, 6, 7, 8, 9]. Mixed microstructures such as micelles [10], vesicles and liposomes [11, 12, 13, 14] are important to medical applications such as drug delivery. Liposomes and vesicles are employed as bioreactors [15].

Although both hydrocarbon tail length and headgroup effects have been extensively studied for surfactant mixtures, little work has been devoted to monoalkyl/dialkyl surfactant mixtures, in which the volume occupied by the hydrocarbon tails is the parameter which is varied through compositional changes. Most of the work concerning monoalkyl/dialkyl surfactant mixtures has appeared in the biochemical literature [1, 2, 3, 16], where the effects of monoalkyl surfactants on phospholipid bilayers have been extensively reported. These effects include fluidification of bilayers [1], breakdown of cell membranes [3, 16], and suppression of the immune response in animals [17].

Monolayer curvature is determined by several factors, including geometric constraints, repulsive forces between neighbouring headgroups, and the chain-packing of hydrocarbon tails [18]. Manipulating the monolayer composition modifies the factors determining curvature and aggregate size, so aggregate composition can be efficiently and systematically changed. As shown by simple packing arguments, changes in average geometric parameters per surfactant molecule, such as headgroup area, tail length, or tail volume, significantly modify the geometry of the surfactant aggregate [18, 19]. It may be supposed that altering the didodecyldimethylammonium bromide (DDAB)–dodecyltrimethylammonium bromide (DTAB) mixing ratio provides a means for studying structural changes induced by changes in the average tail volume per molecule, since headgroup areas and tail lengths are nearly equivalent for DTAB and DDAB. This leads to the assumption of ideal mixing. However, the data in the literature are contradictory: ideal behaviour was reported for DDAB–DTAB mixtures [20], whereas nonideal behaviour was reported for DDAB–dodecyltrimethylammonium chloride (DTAC) mixtures [21].

Since in some cases the substitution of one counterion by another produces dramatic changes in the structure of surfactant aggregates, such as the substitution of chloride or bromide by hydroxide ions in twin-tailed surfactants do [22, 23], we explored the possibility that chloride ion produced this discrepancy. The selectivity of cetyltrimethylammonium halide micelles toward two different counterions, here Cl^- and Br^-, is defined by an ion-exchange constant, $K_{Br/Cl} = [Br_m][Cl_w]/[Br_w][Cl_m]$, in which m and w denote micelle and water, respectively. This constant ranges from 2.7 to 6 [23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34] and implies that bromide ion adsorbs preferentially to the micelle surface. This means that in DDAB–DTAC mixtures, the surfaces of the aggregates preferentially bond bromide ions, releasing the chloride ones to water for both spherical and rodlike micelles, and for hexagonal mesophases [27]. The properties of cetyltrimethylammonium chloride (CTAC) and cetyltrimethylammonium bromide (CTAB) micelles are very similar: the critical micelle concentrations (cmc) are $\mathrm{cmc}_{CTAC} = 1.2$ mM and $\mathrm{cmc}_{CTAB} = 0.9$ mM, the micelle degrees of ionisation are $\alpha_{CTAC} = 0.29$ and $\alpha_{\ CTAB} =\ 0.3$, [24], and the micelle surface potentials are $\Psi 0_{CTAC} = 150$ mV and $\Psi 0_{CTAB} = 140–156$ mV [28]. The properties of dioctadecyldimethylammonium chloride (DODAC) and dioctadecyldimethylammonium bromide (DODAB) are also very similar. Their zeta potentials are $\zeta_{DODAC} = 54$ mV and $\zeta_{DODAB} = 58$ mV and the *Z*-average diameter of the vesicles are $D_{DODAC} = 321$ nm and $D_{DODAB} = 345$ nm. The molecular areas at the air–water interface are also similar: $A_{DODAC} = 0.52\ \mathrm{nm}^2$ and $A_{DODAB} = 0.54\ \mathrm{nm}^2$ [29]. All these data suggest that the partial substitution of bromide ions by chloride ones cannot explain the difference among the DDAB–DTAB and DDAB–DTAC systems.

In this work we studied the low-concentration behaviour of aqueous DDAB–DTAB mixtures in order to determine whether the behaviour is ideal or not, and whether micelles or vesicles are the predominant structures.

Theory

The mixed micelle theory

Regular solution theory has been very widely used to model the thermodynamic nonidealities of mixed micelles and mixed monolayers [35]. It has been shown to accurately model cmc values [30] and monomer–micelle equilibrium compositions [31] in surfactant systems exhibiting negative deviations from ideality. However, it must be pointed out that the theoretical validity of using regular solution theory to describe nonideal mixing in mixed-surfactant micelles has been questioned [32]. Although the theory assumes that the excess entropy of mixing is zero, it has been demonstrated that in some surfactant mixtures this assumption is not true [33, 34]. However, the pseudophase separation model and regular solution theory combination remains as a very widely used and convenient method for analysing experimental data. Since this treatment includes the pseudophase separation model, it is applicable to any aggregation microstructure and not only for micelles. It has been successfully employed to modelling the mixed monolayer at the air–water interface [35] and in mixed micelles in which one of the components do not form micelles but saturate water [36]. In consequence, it may even be employed if the structure of the aggregates changes with the proportion of components, provided these microstructures may be considered as pseudophases.

A mixture of two different surfactants 1 and 2 form aggregates with composition $X_{1,M}$ and $X_{2,M}$, in equilibrium with solution monomers of composition α_1 and α_2. These mole fractions are on a surfactant-only basis, so $X_{1,M} + X_{2,M} = 1$ and $\alpha_1 + \alpha_2 = 1$.

At the cmc

$$\alpha_i \gamma_{i,m} \mathrm{cmc}_i = X_{i,M} \gamma_{i,M} \mathrm{cmc}_M, \qquad (1)$$

where $\gamma_{i,m}$ and $\gamma_{i,M}$ are the activity coefficients of surfactant *i* in the intermicellar solution and in micelles, and cmc_i and cmc_M are the cmcs of pure surfactant *i* and that of the mixture. In general it is supposed that $\gamma_{i,m} \approx 1$ and the nonideality is considered accumulated in the $\gamma_{i,M}$ value.

In the regular solution theory of mixed aggregates [37, 38], β_M is the dimensionless interaction parameter (in kT units, k being 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 [39, 40, 41] and it often depends on the composition of the aggregates [42, 43], 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 the strength of the interaction between two surfactants are measured by the value 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 larger the probability of the existence of synergism between them [44]. Repulsive interactions yield a positive β_M value and the possibility of antagonism, whereas $\beta_M = 0$ indicates an ideal mixture, typically for mixtures of two hydrocarbon-based (or fluorocarbon-based) surfactants [45]. Positive β_M values occur in mixtures of fluorocarbon–hydrocarbon surfactants owing to the repulsive interactions in the micelle core [46, 47, 48, 49, 50].

Typical values of β_M are 2.2 for lithium dodecyl sulfate–lithium perfluorooctanesulfonate [51], –2.6 for sodium dodecyl sulfate (SDS)–poly(oxyethylene)$_{23}$ dodecylether [52], –3.9 for SDS–poly(oxyethylene)$_4$ dodecylether [53], and 13.2 for sodium decyl sulfate–decyltrimethylammonium bromide [54].

β_M reflects the two main contributions to the Gibbs free energy of mixed micellisation. These are a free-energy contribution associated with the interactions between the hydrophobic groups of surfactants 1 and 2 in the micelle core, $\beta_{M,\mathrm{core}}$, and an electrostatic contribution, $\beta_{M,\mathrm{elec}}$, associated with electrostatic interactions between the charged hydrophilic groups of surfactants 1 and 2 [55]:

$$\beta_M = \beta_{M,\mathrm{core}} + \beta_{M,\mathrm{elec}}. \tag{2}$$

The electrostatic contribution, $\beta_{M,\mathrm{elec}}$, gives negative deviations from ideality when strong electrostatic interactions between headgroups are present, such as in mixtures of anionic and cationic surfactants. Negative values of $\beta_{M,\mathrm{elec}}$ may also be found in mixtures where there are no specific interactions between the headgroups (e.g., ionic/nonionic mixtures). In such cases, the nonionic surfactants simply reduce the free energy of micellisation by screening the ionic charges from one another. Generally the deviation from ideality is much smaller than in the case where specific attractions between the surfactant components exist.

When the interaction parameter is dependent on the value of X, the activity coefficients for each surfactant species in aggregates are given by [56]

$$\gamma_{1,M} = \exp\left[\beta_M X_{1,M}\left(1 - X_{1,M}\right)^2 + X_{1,M}\left(1 - X_{1,M}\right)^2 \mathrm{d}\beta_M X_{1,M}/\mathrm{d}X_{1,M}\right] \tag{3}$$

and

$$\gamma_{2,M} = \exp\left[\beta_M X_{1,M} \mathrm{X}_{1,M}^2 - X_{1,M}^2\left(1 - X_{1,M}\right)\mathrm{d}\beta_M X_{1,M}/\mathrm{d}X_{1,M}\right]. \tag{4}$$

A theory developed by Huang and Somasundaran [57] relates the activity coefficients with a packing constraint parameter, P^*, which describes the nonrandom mixing of components in mixed aggregates. This parameter indicates the packing constraints of one of the components in aggregates which are rich in the other component. These relationships are

$$\ln\gamma_{1,M} = \beta_M X_{1,M}\left(1 - X_{1,M}\right)\left[1 - X_{1,M}/f(\alpha)\mathrm{P}^*\right] + \beta_M\left(1 - X_{1,M}\right) \times \left[1 - 2X_{1,M} - 2X_{1,M}\Big/f(\alpha)P^* + 3X_{1,M}^2\Big/f(\alpha)P^*\right] \tag{5}$$

and

$$\ln\gamma_{2,M} = \beta_M X_{1,M}\left(1 - X_{1,M}\right)\left[1 - X_{1,M}/f(\alpha)P^*\right] + \beta_M\left(1 - X_{1,M}\right) \times \left[1 - 2X_{1,M} - 2X_{1,M}/f(\alpha)P^* + 3X_{1,M}^2\Big/f(\alpha)P^*\right], \tag{6}$$

in which $f(\alpha) = \alpha$ for $\alpha > 0.5$ and $f(\alpha) = 1 - \alpha$ for $\alpha \leq 0.5$. Component 1 is the more surface-active. The packing constraint changes with any change in the overall surfactant mixing ratio. When the overall mixing ratio approaches zero or unity, the packing ability in mixed micelles will be better than that when the ratio is about 0.5 (1:1 mixture). For the same total concentration of the binary mixture, the possibility for surfactants 1 and 2 to be in contact with each other will be a maximum when the overall mixing ratio is 0.5, and the packing constraint will then become more significant [57].

The excess chemical potential of mixing is given by [57]

$$\Delta\mu_{\mathrm{mix}}^{\mathrm{excess}} = RT\beta_M X_{1,M}\left(1 - X_{1,M}\right)\left[1 - \mathrm{X}_{1,M}/f(\alpha)P^*\right], \tag{7}$$

in which R is the gas constant. Negative values of $\Delta\mu_{\mathrm{mix}}^{\mathrm{excess}}$ indicate the attraction between the two components in the micelles, most of which may result from a decrease in the electrostatic energy of the micelles. $\Delta\mu_{\mathrm{mix}}^{\mathrm{excess}}$ is the difference between the partial molar free energy of the mixed micelles and that calculated according to the ideal behaviour, as a function of the mixture composition. The energy is expected to strongly depend on the surface charge density of the micelles and the ionic strength, and less on the size and shape of the micelles [58, 59]. The $\Delta\mu_{\mathrm{mix}}^{\mathrm{excess}}$ value does not take into account the change in the degree of association of the counterion upon surfactant mixing [39, 40, 41].

The value of β_M for the interactions in a mixed micelle was calculated with the method given by Rubingh [53].

The Israelachvili–Mitchell–Ninham packing parameter

The size and the shape of surfactant aggregates are to a large extent determined by geometrical constraints based on the packing of amphiphiles into closed aggregates giving rise to a given curvature of the interfaces [60]. Israelachvili et al. [19] developed a simple packing parameter, the Israelachvili–Mitchell–Ninham (IMN) number, $\mathrm{IMN} = v/al$, which allows the prediction of an aggregate structure with three parameters: the effective headgroup area, a, and the hydrocarbon chain volume, v, and length, l. When $\mathrm{IMN} \leq 1/3$, spherical micelles are favoured. For $1/3 < \mathrm{IMN} < 1/2$, disks, ellipsoids, and rod-shaped micelles are formed. When $1/2 < \mathrm{IMN} \leq 1$, vesicles and lamellae form, while for $\mathrm{IMN} > 1$, inverted structures are found. Jansson et al. [61] suggested that the size and the shape of mixed surfactant aggregates are largely determined by geometrical constraints based on the size and the shape of the component molecules. This geometrical influence may be assumed in the effective IMN number of the surfactant mixture in the aggregate, $\mathrm{IMN}_{\mathrm{eff,mix}}$.

Evans et al. [18] predicted the IMN value achieved by mixing DDAB with DTAB by linear combination of the packing parameters of the two individual surfactants, i.e.:

$$\mathrm{IMN}_{\mathrm{eff,mix}} = (v/al)_{\mathrm{eff,mix}} = \mathrm{IMN}_{\mathrm{DDAB}}\alpha_{\mathrm{DDAB}} + \mathrm{IMN}_{\mathrm{DTAB}}\alpha_{\mathrm{DTAB}}. \qquad (8)$$

It is evident that this equation is accurate only if the composition of the aggregates ($X_{i,\mathrm{M}}$ values) is the same as that of the total surfactant mixture (α_i values), i.e., in ideal surfactant mixtures. If this is not the case, the α_i values in Eq. (8) must be exchanged by the appropriate $X_{i,\mathrm{M}}$ ones.

The packing parameters of the two individual surfactants were taken from the literature [62]. For DTAB, $l = 1.668$ nm, $a = 0.63$ nm^2, $v = 0.3519$ nm^3, $\mathrm{IMN}_{\mathrm{DTAB}} = 0.335$; for DDAB, $l = 1.668$ nm, $a = 0.68$ nm^2, $v = 0.7037$ nm^3, $\mathrm{IMN}_{\mathrm{DDAB}} = 0.620$.

Experimental

DTAB and DDAB were acquired from Sigma and were of analytical grade. Doubly distilled water was used. For each surfactant mixture composition, a concentrated aqueous solution (total concentration of 0.2 moldm^{-3}) was prepared by weighing the appropriate amount of each surfactant. The dry surfactants were put into a volumetric flask and then water was added to the desired volume. No sonication was employed. Mixtures with total mole fractions of DDAB (without taking into account water) of 1, 0.875, 0.75, 0.625, 0.5, 0.375, 0.25, 0.125, and 0 were prepared. Then the working solutions were made by dilution of the concentrated one.

A drop of dilute solution of rhodamine 6G was added to tubes with solutions of different surfactant concentration and the critical aggregation concentration (cac) was determined by the changes in fluorescence and colour.

Conductivity measurements were made with an immersion cell and an automatic conductimeter, namely an Antares II from Instrumentalia.

Sealed tubes with Sudan III and solutions of different surfactant concentration were left for 1 week in a thermostatted bath, with periodic stirring. Then the tubes were centrifuged and the supernatant absorbance was measured with a Spectronic-20 UV–vis spectrophotometer at 600 nm. The turbidity of samples of different surfactant mixtures without solubilised dye was also measured at 400 nm as a function of concentration in the same spectrophotometer.

All determinations were made at 25.0 °C.

Mean values and variances were computed by the minimum variance linear unbiased method [63] and the Student t function was employed to compute the error intervals. The confidence level was 0.90. The errors of the derived data were computed with the error expansion method.

Results

The measured DTAB cmc was 0.0155 ± 0.0009 moldm^{-3}, in good agreement with literature values (0.0114 moldm^{-3} [64], 0.0118 moldm^{-3} [65], 0.0147 moldm^{-3} [66], 0.019 moldm^{-3} [67], 0.015 moldm^{-3} [68]).

The measured critical vesicle concentration of pure DDAB was $5.3\times10^{-5} \pm 3.3\times10^{-5}$ moldm^{-3}, in agreement with the literature values, $(3–5)\times10^{-5}$ moldm^{-3} [20, 69, 70] and $(1.4–1.8)\times10^{-5}$ moldm^{-3} [71, 72].

The cac of aqueous DDAB–DTAB mixtures is shown in Fig. 1. The curve shows the expected behaviour of the system if it were an ideal mixture [58, 73]. The points are average values from cac data determined using conductivity, Sudan III solubilisation, rhodamine 6G, and turbidity.

The turbidity curves determined without any added dye show that all the mixtures between $\alpha_{\mathrm{DDAB}} = 1$ and 0.875 sharply increased their absorbance at the cac. Only pure DTAB solutions did not show a turbidity increase; an example is shown in Fig. 2. Three representative curves of differential conductivity ($\Lambda_d = 1{,}000\,d\kappa/dc$ versus c, in which κ is the specific conductivity) are shown in Fig. 3.

The mole fraction of DDAB in the aggregates is shown in Fig. 4 versus that in the total mixture. The straight line is the ideal behaviour. β_M is shown against the mole fraction of DDAB in the mixture and in the aggregate in Fig. 5. The activity coefficients are shown in Fig. 6 and the packing constraint parameter, P^*, is shown in Fig. 7. The excess free energy of mixed micellisation is shown in Fig. 8.

In Fig. 9, the IMN number of the mixtures in the aggegates, obtained by use of the composition of the

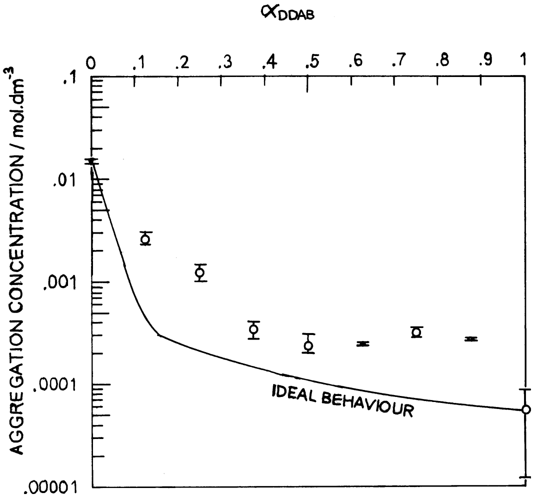

Fig. 1. Critical aggregation concentration of didodecyldimethylammonium bromide (*DDAB*)–dodecyltrimethylammonium bromide (*DTAB*) aqueous mixtures as a function of the surfactant mixture total composition. The *solid line* represents the ideal behaviour

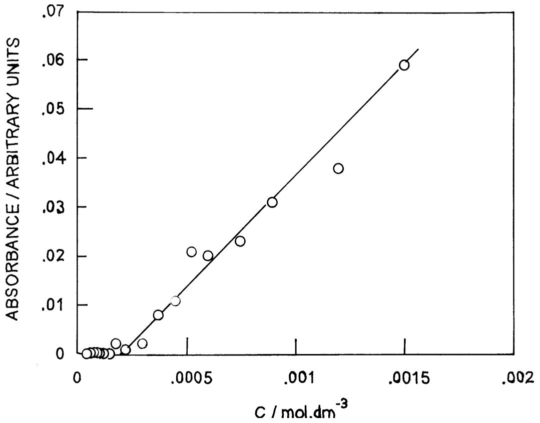

Fig. 2. Turbidity without dye addition versus concentration, $\alpha_{DDAB} = 0.5$

aggregates, is shown versus α_{DDAB}. The solid line depicts the ideal behaviour and the dashed lines the limit between lamellar and cylindrical aggregates (upper line) and between cylindrical and spherical aggregates (lower line).

Discussion

Figure 2 shows that the aggregates formed in DDAB–DTAB mixtures are vesicles and not micelles. Since DDAB vesicle and liposome suspensions are turbid, whereas DTAB micellar solutions are optically transparent [74], turbidity is a simple, sensitive, and convenient method to detect the aggregation of vesicles [75]. Vesicles formed spontaneously, without sonication. This phenomenon was also observed in pure DDAB–water systems [76]. Pure DTAB forms spherical micelles in

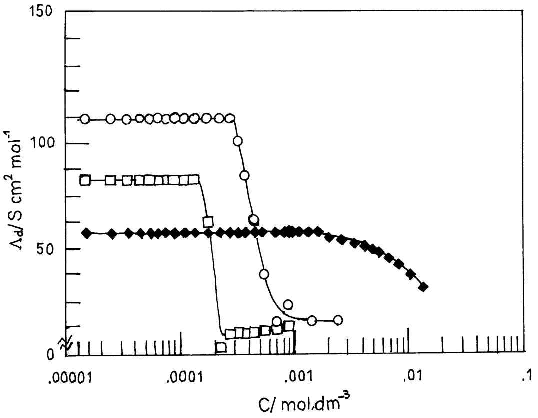

Fig. 3. Differential conductivity, $\Lambda_d = 1{,}000 d\kappa/dc$, versus c for mixtures with $\alpha_{DDAB} = 0.75$ (*circles*); $\alpha_{DDAB} = 0.50$ (*squares*), and $\alpha_{DDAB} = 0.25$ (*diamonds*)

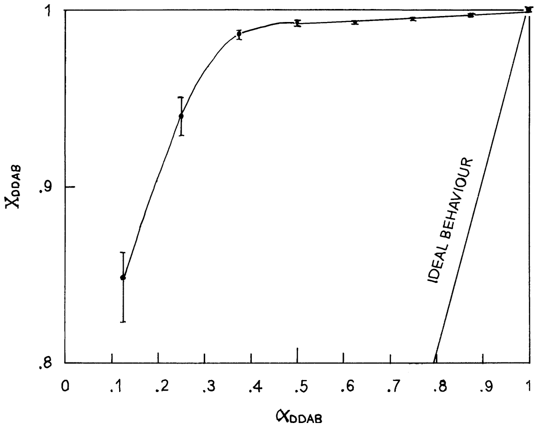

Fig. 4. Aggregate composition versus α_{DDAB}. The *straight line* corresponds to ideal behaviour

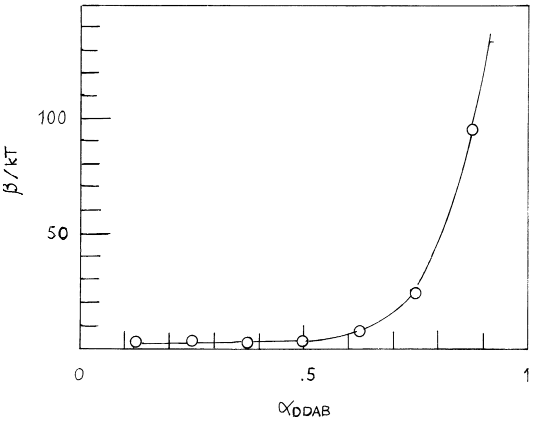

Fig. 5. Interaction parameter as a function of the surfactant mixture total composition

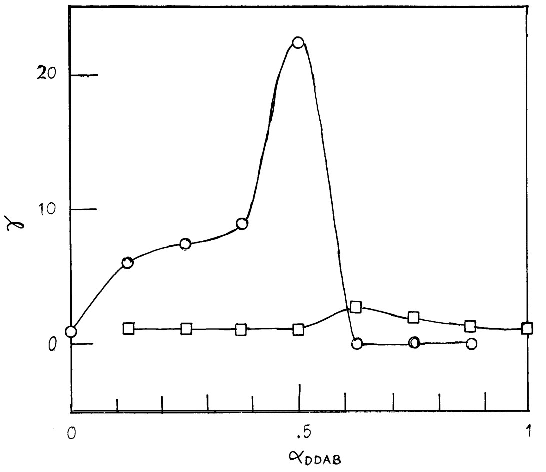

Fig. 6. Activity coefficient in the aggregates versus surfactant mixture total composition: $\gamma_{\mathrm{DDAB,M}}$ (*squares*); $\gamma_{\mathrm{DTAB,M}}$ (*circles*)

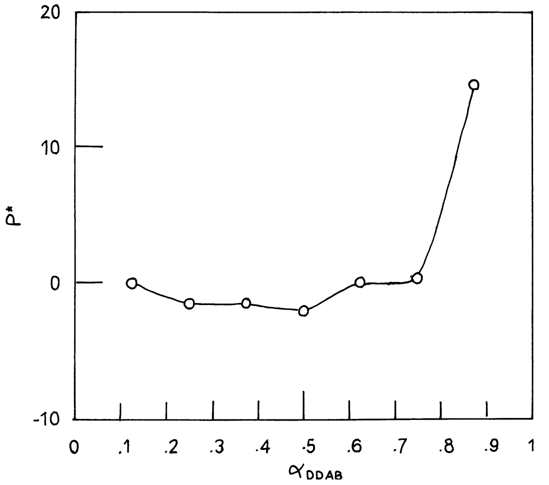

Fig. 7. Packing hindrance parameter, *P**, for the inclusion of DTAB in DDAB aggregates versus α_{DDAB}

water [77,78], whereas pure DDAB forms bilayers and vesicles in water [79, 80]. Figure 2 shows that at $\alpha \geq 0.5$, the formation of aggregates gives a dramatic decrease in the differential conductivity (Λ_d), which is consistent with the behaviour of the pure DDAB–water system [79]. The sample with 25% DDAB shows a gradual decrease in Λ_d, which means that the aggregates changed gradually in size. The same behaviour was found in the pure DDAB–water system, when small unilamellar vesicles gradually increased in size and became larger multilamellar liposomes [79]. The value of Λ_d at the plateau after the cac is interpreted as the molar conductivity of the aggregates, Λ^{agg}, including the diffuse ionic double layer [81, 82]. For $\alpha \geq 0.5$, $\Lambda^{\mathrm{agg}} \approx 28$–$30\ \mathrm{Scm^2mol^{-1}}$, the same value obtained in the pure DDAB–water system for vesicles [79].

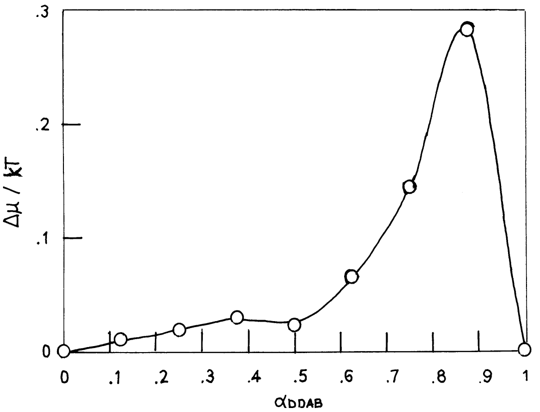

Fig. 8. Excess free energy of mixing in the DDAB–DTAB aggregates versus α_{DDAB}

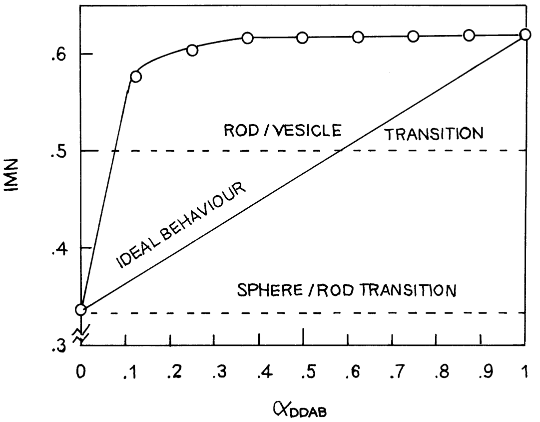

Fig. 9. Israelachvili–Mitchell–Ninham (*IMN*) parameter for the aggregated surfactant mixture versus α_{DDAB}. The *straight line* corresponds to ideal behaviour

In the derivation of the thermodynamics of mixed-micelle formation, the structure of the aggregates is not defined, and the pseudophase aggregation model is adopted, though usually micelles are supposed to form [34]. As a consequence, the model is also applicable to the formation of other aggregates. This is why we use the expression "cac" instead of cmc in this discussion.

Figure 1 shows the measured cac values with their error, and the ideal cac. It can be seen that the mixture behaviour was not ideal. The aggregates are richer in DDAB than the whole solution mixture (Fig. 4). It was surprising that β_M was positive (Fig. 5). The interaction approaches ideality at $\alpha_{\mathrm{DDAB}} \leq 0.5$, but β_M did not become zero. The low α_{DDAB} value of β_M was 2.80 ± 0.53.

Figure 6 shows the activity coefficients of both surfactants in the aggregates. That of DDAB is almost constant, with an average value of $\gamma_{\mathrm{DDAB,M}} = 1.51 \pm 0.10$ between $\alpha_{\mathrm{DDAB}} = 0.375$ and 0.875.

Figure 7 shows the dependence of P^* on α_{DDAB}. It was computed by Eqs. (6) and (7), to obtain the packing constraints in the inclusion of DTAB in DDAB aggregates. It can be seen that there is a change at $\alpha_{\mathrm{DDAB}} = 0.5$. According to Huang and Somasundaran [57], the smaller P^* is, the more difficult the mixing of surfactants in aggregates is, owing to packing constraints. It can be seen in Fig. 7 that for $\alpha_{\mathrm{DDAB}} = 0.875$, $P^* = 14.6$; thus, favouring the inclusion of DTAB molecules in the DDAB layer, but there is a rapid decrease in P^* with α_{DDAB}, giving negative values at $\alpha_{\mathrm{DDAB}} \leq 0.5$. This behaviour suggests that there is an optimal proportion of DTAB in the mixed aggregate, and exceeding this optimal proportion, the inclusion of more DTAB molecules is sterically not favourable.

The excess free energy of mixing was then always positive with a change in its tendency at $\alpha_{\mathrm{DDAB}} \approx 0.45$ (Fig. 8) The change in the $\Delta\mu_{\mathrm{mix}}^{\mathrm{excess}}$ dependence on α_{DDAB} suggests that there are changes in the interaction between the two surfactant molecules in the aggregates, which depend on which surfactant is in the largest proportion.

A glance at Figs. 3, 4, 5, 6, 7, and 8 suggests that some structural change occurs at $\alpha_{\mathrm{DDAB}} = 0.5$–$0.4$ which affects the kind of interaction between both surfactants and the size and the structure of the aggregates.

With the composition of the aggregates, we computed the IMN value for the aggregated surfactant mixture (Fig. 9). All the values fell in the region in which flat interfaces are favoured (i.e., lamellar liquid crystals, liposomes, and vesicles). This confirms the conclusion obtained from turbidity and conductivity measurements.

Our conclusion is that in DDAB–DTAB aqueous solution the surfactant–surfactant interaction is not ideal and vesicles form in almost all proportions of DDAB to DTAB. This is in agreement with Viseu et al. [21], who studied DDAB–DTAC aqueous mixtures and found vesicles even at a DTAC proportion as high as $\alpha_{\mathrm{DTAC}} = 0.95$.

However, Weers and Scheuing [20] studied DDAB–DTAB mixtures and they found micelles and ideal mixing behaviour. They suggested that as DDAB is added to DTAB micellar solutions, spherical micelles undergo a transition from spheres to disks to rods as a function of composition.

At first sight, the assumption of ideal mixing in DDAB–DTAB mixtures seems reasonable, because of the similarity of the hydrophobic tails and hydrophilic headgroups. Ideal mixing implies that any composition-dependent differences in packing within the headgroup region are not significant enough to alter the free energy of micellisation appreciably. However, it is evident that the addition of DDAB molecules to DTAB micelles sterically alters the packing of the hydrophobic tail region. This situation must affect the excess free energy of aggregation, and this alteration must be different in the DDAB-rich side than in the DTAB-rich side of the composition range. This difference can be seen in Figs. 6, 7, and 8.

The preceding discussion leads us to conclude that steric hindrances are probably the cause of the nonideality in the DDAB–DTAB interaction. Since the steric factor is probably negligible when the regular solution theory of mixed aggregation is used in micelles, it was not taken into account in the formulation of the interaction parameter; however, in dealing with more complex structures, steric constraints may become important. The concept of sterically stabilized vesicles and liposomes, caused by asymmetric bilayers with nonzero spontaneous curvature, which may originate from differences in internal and external monolayers, is known [83].

Viseu et al. [21] proposed that the main factor which ruled the appearance of vesicles in the DDAB–DTAC–water system was the difference in the spontaneous curvature (or IMN packing parameter) of the two surfactants. They said that an asymmetric bilayer with adequate inner and outer curvatures may be reached spontaneously when DDAB is the main (even exclusive) component of the inner layer, but it is mixed with DTAC in the outer layer. Pure DDAB also forms vesicles, so the addition of DTAC (or DTAB) should favour vesicle formation. Vesicles form at a concentration much lower than micelles and capture the adequate proportion of DTAB molecules to form the outer monolayer with an appropriate curvature. On the basis of the data between $\alpha_{\mathrm{DTAB}} = 0.5$ and 1 in Fig. 4, the appropriate composition to obtain spontaneous vesicles seems to be $X_{\mathrm{DDAB}} = 0.994 \pm 0.003$. By assuming that half of the aggregated DDAB molecules are in the inner monolayer of a vesicle, this means that the mole fraction of DTAB molecules in the outer monolayer is about $X_{\mathrm{DTAB,out}} = 0.012 \pm 0.003$, and the packing parameter of the mixture in the outer monolayer is $\mathrm{IMN} = 0.617 \pm 0.006$.

Since DTAB is much more water-soluble than DDAB, the excess of unaggregated DTAB molecules remains in monomer form until its own concentration reaches the DTAB cmc when the total concentration is raised. This situation may explain the presence of globular micelles together with vesicles in DDAB–DTAC systems [21]; however, in our own systems, the DTAB's own cmc was not attained.

Acknowledgement This work was financed by a grant from the Universidad Nacional del Sur.

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