

Synergism in mixtures of zwitterionic and ionic surfactants

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Abstract

We have studied the effect of the hydrocarbon length, electrical charge and the addition of inert electrolytes on the mixed aggregation process of alkyl ammonium propane sulfonate and the ionic surfactants, sodium dodecyl sulfate (SDS) and dodecyl trimethyl ammonium bromide (DTAB). Using conductivity and fluorescence probing, we determine the cmc of the mixed micelles and their variation with micelle composition. Results indicate that in the absence of electrolytes the cationic DTAB and the zwitterionic surfactants mix ideally. The binary mixtures of the anionic surfactant SDS and the zwitterionic DDPS present a non-ideal behavior with a weak interaction between the surfactants, as a result of the locations of the positive and negative charges on the zwitterionic surfactants, while no interactions are detected for TDPS + SDS and HDPS + SDS mixtures. The addition of inert electrolytes favors the interactions between the ionics and the zwitterionic surfactants, probably because more ionic surfactant can be accommodated in the micelles. Viscoelastic behavior is detected in mixed micelles of anionic–zwitterionic surfactants of equimolecular composition.

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1. Introduction

Surfactant mixtures are commonly used in practical applications because mixtures behave synergistically and provide more desirable properties than individual surfactants [1]. For example, in skin care applications synergism in a surfactant mixture decreases the total surfactant concentration and consequently reduces skin irritation [2]. Cleaning formulations often include anionic mixtures to maximize solubilization and non-ionic surfactants to maximize the water hardness tolerance [3]. In the case of mixtures containing zwitterionic surfactants, betaines are widely used as foam booster in commercial shampoos or in hair conditioners [4].

In previous works, mixtures of alkylbetaines and anionic surfactants have been studied and results reported shown strong synergistic effects of mixed solutions of SDS and C₁₂ betaine [5]. Rosen and Zhu found significant intermolecular attractions between anionic and betaines surfactants that were

explained by strong electrostatic attractions between these surfactant molecules [6]. Even though electrostatic interactions strongly contribute to synergism, in certain surfactant mixtures steric interactions between surfactant heads of different sizes as well as from packing surfactant hydrocarbon tails of different lengths are important sources of synergism [7,8]. Predictive theoretical models have been developed to describe the behavior of ionic/ionic or ionic/non-ionic surfactant mixtures [9–12], whereas mixtures containing zwitterionic surfactants have received poor attention. Notable exceptions are Nagarajan [9] and Shiloach and Blankshtein models [13,14], which introduce the effect of specific interactions on synergistic behavior.

We are interested to investigate the role of specific interactions on the synergism of mixtures of zwitterionic and ionic surfactants; therefore, we study the effect of the hydrocarbon chain length, the electrical charge and the addition of inert electrolytes on the synergism of binary mixtures of sulfobetaine and ionic surfactants. We choose alkyldimethyl ammonium propane sulfonate, sulfobetaines, because these zwitterionic surfactants are not sensitive to the pH value,

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remaining as real zwitterionic surfactant at any pH of aqueous solutions. The ionic surfactants are sodium dodecyl sulfate (SDS) and dodecyl trimethylammonium bromide (DTAB). We use electrical conductivity and pyrene fluorescence probing to study the surfactant interactions.

Finally, because mixtures of zwitterionic and ionic surfactants often exhibit interesting rheological behavior [15], we have also obtained the rheological properties of mixed micelles.

2. Experimental

2.1. Materials and sample preparation

The zwitterionic surfactants dodecyl (DDPS), tetradecyl (TDPS) and hexadecyl (HDPS) dimethyl ammonium propane sulfonate were from Fluka. These surfactants were purified by recrystallization in isopropanol [16]. The anionic surfactant sodium dodecyl sulfate from Merck and the cationic dodecyl trimethylammonium bromide (Sigma–Aldrich), were purified by recrystallization in ethanol. All the surfactants were recrystallized several times until obtain constancy in the surface tension value at a surfactant concentration close to the cmc. Pyrene was from Aldrich Chemika and sodium chloride, sodium bromide and methanol from Merck. Sodium chloride and sodium bromide were baked for several hours in a porcelain casserole at red heat to remove traces of organic compounds.

The surfactant solutions were prepared with water purified with a combination of RiOs and Milli-Q systems from Millipore. The conductivity of the water was lower than $0.2 \mu\text{S}/\text{cm}$.

Incorporation of pyrene into micelles was as follows: an appropriate volume solution of pyrene dissolved in methanol was poured into a volumetric flask and the solvent was evaporated. The solutions of pure surfactants or binary surfactant mixtures were added to the evaporated residue, and the solution was stirred until the fluorescence probe was solubilized. The pyrene concentration was kept constant at $1.5 \mu\text{M}$.

2.2. Steady-state fluorescence measurements

The emission spectra of pyrene incorporated to micelles were recorded with the LS-50B spectrofluorometer. The excitation wavelength was 320 nm and the excitation and emission slits were kept constant at values of 2.5/2.5 nm or 3/3 nm as a function of the fluorescence intensity.

2.3. Conductivity measurements

The electrical conductivity was measured with a conductometer model 727 from Metrohm operated at 2.4 kHz. A Metrohm Herisau conductivity cell, model AG 9101, was used. The cell constant, 0.847 cm^{-1} , was obtained by calibration with KCl solutions of known concentrations [17]. Because the correct determination of the cmc requires a large

number of experimental data, a conductometric titration was employed. During titration, solutions obtained by successive dilutions were allowed to equilibrate a few minutes until a stable measurement was obtained [18,19].

2.4. Rheological measurements

Rheological measurements have been carried out with an oscillating capillary viscosimeter (Vilastic Scientific Inc.). The magnitude of the complex viscosity, $|\eta^*|$, the storage modulus $G'(\omega)$ and the loss modulus $G''(\omega)$ are measured in the frequency range of 0.01–40 Hz at 25 °C. Here G' denotes the elastic response of the sample and G'' is the viscous part. In order to confirm rheological results, a Haake RS100 rheometer operating to 0.005–100 Hz was also used.

3. Results

3.1. Zwitterionic–ionic surfactant interaction

Fig. 1 shows the experimental conductivity values as a function of the total concentration, $[S]_t$, at several values of mole fraction, α_{SDS} , for aqueous solutions of the mixed micellar system TDPS + SDS. The total critical micellar concentration, cmc^* , is assigned with the break point and was calculated from the third derivative of the conductivity experimental data [20]. The inset in the Fig. 1 shows conductivity values versus the ionic surfactant concentration SDS. The slope below the cmc remains constant with the composition while the slopes above cmc increase in the binary mixtures as compared with that of pure SDS. The conductivity/total surfactant concentration curves for the mixed micellar systems DDPS + SDS and HDPS + SDS, present similar trends. The cmc^* values calculated from the break point of conductivity curves as a function of the mole fraction of the anionic surfactant SDS are represented in Fig. 2.

Fig. 3 shows the variation of the conductivity with the total surfactant concentration for binary mixtures of TDPS and DTAB. The inset in this figure shows conductivity values versus DTAB concentration. The slope below the cmc remains constant with the composition while the slopes above cmc increase in the binary mixtures as compared with that of pure DTAB. This behavior is the same to that observed in anionic–zwitterionic mixtures. A similar trend is observed for binary mixtures of DDPS + DTAB and HDPS + DTAB.

We obtain the cmc^* values of these mixed micelles from the break point of conductivity curves and their variation with the composition are also represented in Fig. 2.

3.2. Effects of the addition of electrolytes on the interactions between zwitterionic and ionic surfactants

To study the role of the electrostatic interactions on the synergism in zwitterionic–ionic surfactant mixtures, we have obtained the cmc^* of binary mixtures dissolved in saline

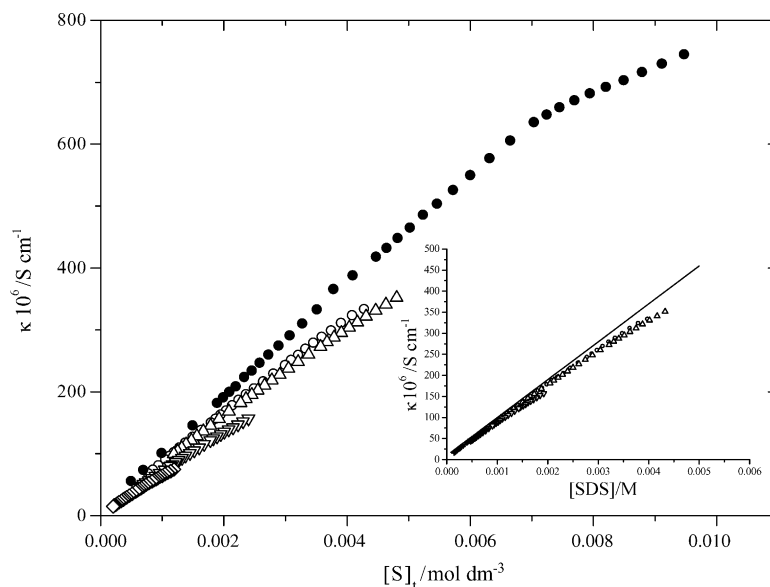


Fig. 1. Electrical conductivity values vs. total surfactant concentrations for mixtures of SDS and TDPS. Solid circles and solid line, $\alpha_{\text{SDS}} = 1$; open circles, $\alpha_{\text{SDS}} = 0.93$; open up triangles $\alpha_{\text{SDS}} = 0.90$; open down triangles, $\alpha_{\text{SDS}} = 0.80$; diamond, $\alpha_{\text{SDS}} = 0.70$. The inset contains the variation of conductivity with SDS concentration.

aqueous solutions of 0.1 M NaCl, anionic–zwitterionic and 0.1 M of NaBr for DTAB–zwitterionic solutions. In these systems, conductivity measurements are not indicated to determine the cmc because the conductivity of the aqueous saline solution is higher enough to detect accurately the break point of these curves. Therefore, we use fluorescence probing to obtain the cmc^* values.

Fluorescence probing has been widely used to obtain critical micelle concentrations, cmc, of micelles and to estimate and to evaluate the micropolarity of the hydrophobic core in micelles [21]. The pyrene fluorescence fine structure presents

five peaks. It is well established that the ratio between the intensities of the first (373 nm) and third (384 nm) vibration bands of the pyrene fluorescence spectrum, I_1/I_3 , is related to the polarity of the pyrene environment [22]. Low values of the I_1/I_3 ratio correspond to a non-polar environment. This ratio increases as the polarity of the medium rises [22]. For orientative purposes, the spectra of pyrene incorporated to mixed micelles of SDS and TDPS dissolved in 0.1 M NaCl containing total surfactant concentrations below and above the cmc^* are presented in Fig. 4. The results in Fig. 4 correspond to a composition of molar fraction 0.2 in SDS. As

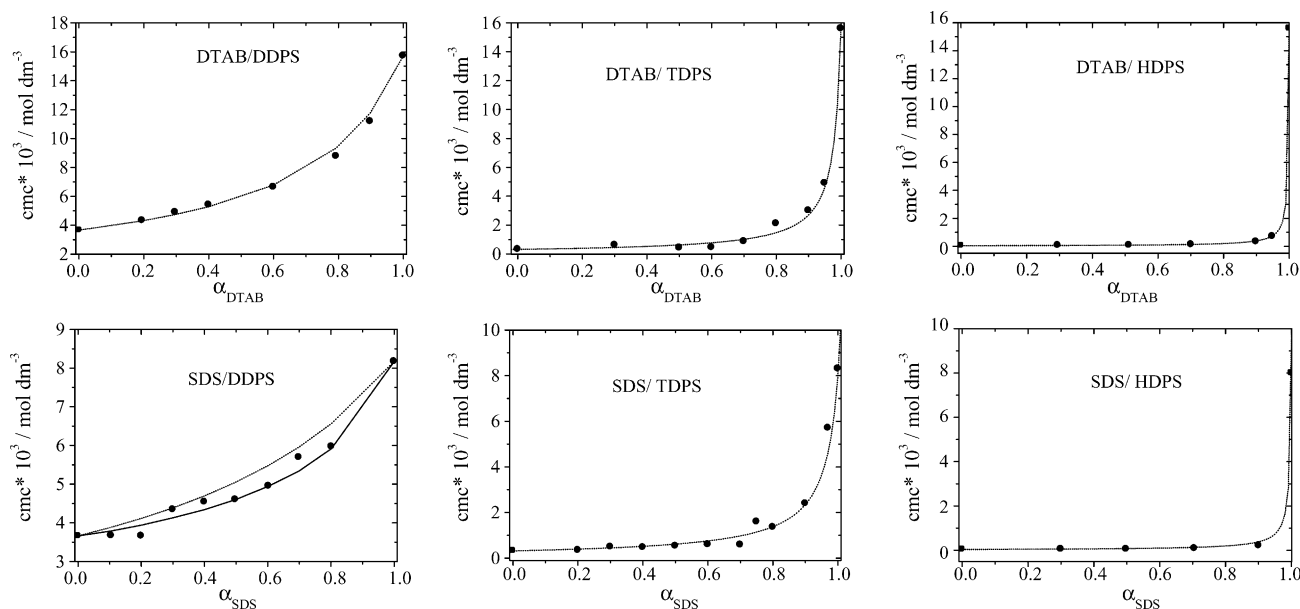


Fig. 2. Variation of the critical micelle concentration of mixed micelles, cmc^* , with the mole fraction of the ionic surfactants. Dotted line values calculated according to ideal mixed model and solid line values obtained from regular solution model, Eqs. (2)–(6) and β values in Table 2.

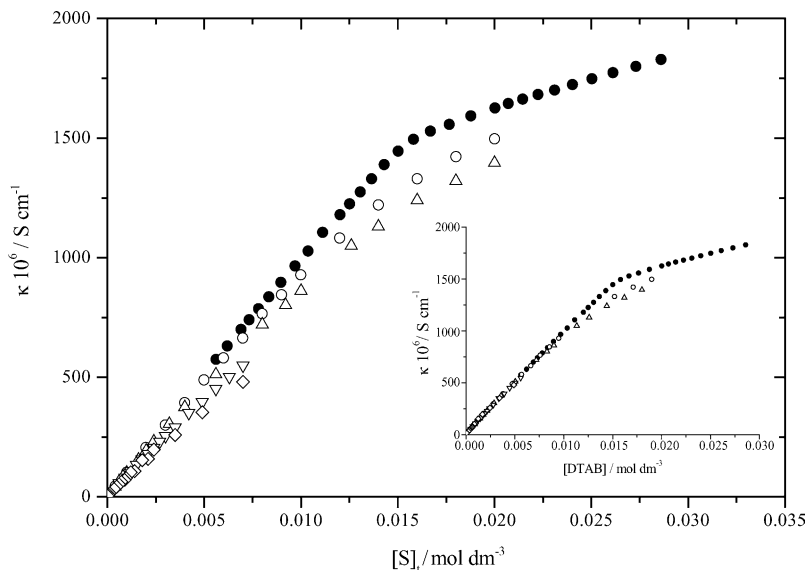


Fig. 3. Electrical conductivity vs. total surfactant concentration for mixed DTAB and zwitterionic surfactants solutions. Solid circles, $\alpha_{\text{DTAB}} = 1$; open circles, $\alpha_{\text{DTAB}} = 0.95$; open up triangles $\alpha_{\text{DTAB}} = 0.90$; open down triangles, $\alpha_{\text{DTAB}} = 0.80$; diamond, $\alpha_{\text{DTAB}} = 0.70$. The inset contains the variation of conductivity with DTAB concentration.

seen in the figure, the intensity of bands of the first and third vibronic peaks depends of the surfactant concentration.

Fig. 4 also shows a broad band centered on 470 nm ascribed to the pyrene excimer emission [23]. The intensity of this band also varies with the total surfactant concentration. It is well established that the pyrene excimer emission reflects important hydrophobic association, such as intra- or inter-chain hydrophobic associations between polymers or polymer–surfactant [24,25], therefore can be used to determine the cmc [26,27].

We have obtained the cmc* of the zwitterionic–ionic mixtures dissolved in aqueous saline solutions from both the plot

of the ratio between the first and third vibration bands of the pyrene emission, I_1/I_3 , and the ratio of the intensities of the excimer/monomer pyrene emission, I_E/I_M , where $I_M = I_1$. Fig. 5 presents the values corresponding to TDPS/SDS dissolved in 0.1 M NaCl and $\alpha_{\text{SDS}} = 0.2$. The variation of I_1/I_3 ratio with total surfactant concentration shows the typical sigmoid behavior characteristic of the micelle formation. Even though this is one of the most popular method to determinate the critical micelle concentration, there is not a unified criterion to obtain this value from this plot; however, in a recent paper a procedure based on objective criteria was developed [28]. According to that the pyrene I_1/I_3 plot can be adequately

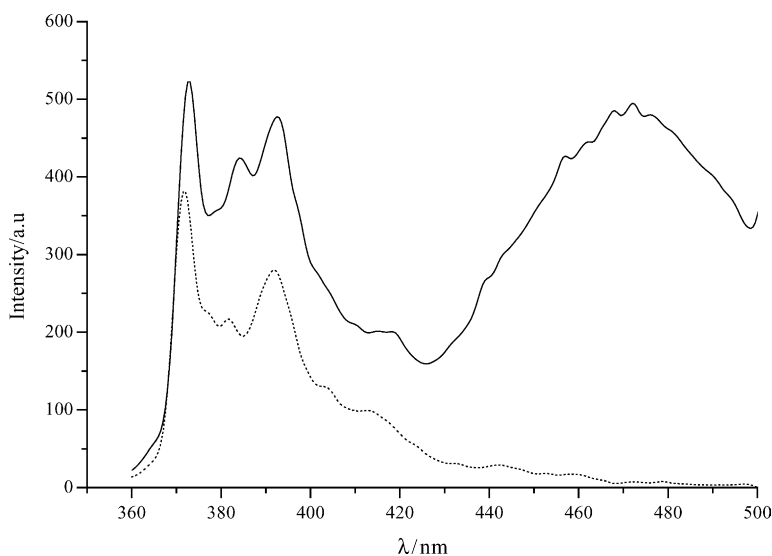


Fig. 4. Fluorescence spectra of pyrene dissolved in SDS/TDPS in NaCl 0.1 M, $\alpha_{\text{SDS}} = 0.20$ and different total surfactant concentrations. Dotted line, $[S]_t = 9 \times 10^{-5}$ M and solid line, $[S]_t = 1.8 \times 10^{-4}$ M.

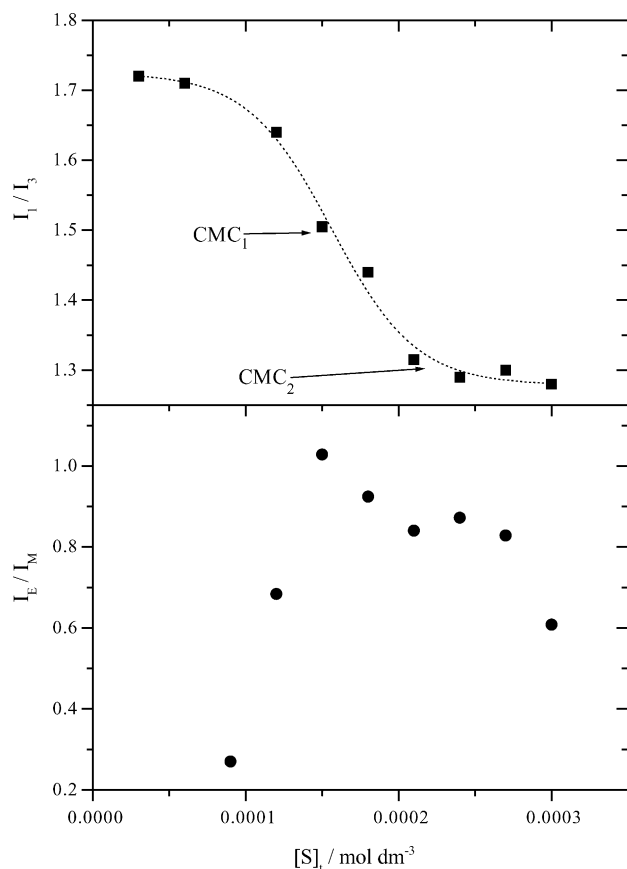


Fig. 5. I_1/I_3 and I_E/I_M , ratios as a function of the total surfactant concentration. The results correspond to solutions of SDS/TDPS in NaCl 0.1 M, $\alpha_{\text{SDS}} = 0.20$. The line is calculated according to Eq. (1) and parameters in Table 1, see text.

fitted to a decreasing sigmoid of the Boltzmann type given by:

$$y = \frac{A_1 - A_2}{1 + e^{([S]_t - x_0)/\Delta x}} + A_2 \quad (1)$$

where y is the pyrene I_1/I_3 ratio, x_0 the center of the sigmoid, A_1 and A_2 the upper and lower limits of the sigmoid, respectively, and Δx is related to the surfactant concentration range where the drastic change of y occurs. The authors show through numerous examples that the ratio, $x_0/\Delta x$, can be used to establish an objective criterion for choosing point corresponding to the cmc value. Thus, for $x_0/\Delta x$ ratios higher (typically >10), the cmc is calculated from the interception of the horizontal and steep parts of the curve, this point is

named cmc_2 in Fig. 5. In contrast for $x_0/\Delta x$, values smaller than 10, the cmc is the inflection point of the curve, cmc_1 .

To check the validity of this methodology, we obtain the cmc of pure zwitterionic surfactants. The pyrene I_1/I_3 versus surfactant concentration curves of the zwitterionic surfactants were fitted to Eq. (1) and the best parameters of the fitting processes are presented in Table 1. The values on Table 1 show two different behaviors: for the surfactant DDPS and HDPS, the $x_0/\Delta x$ ratios are smaller than 10, therefore the value of the cmc chosen was cmc_1 . In contrast for TDPS, $x_0/\Delta x > 10$, consequently the cmc value chose was cmc_2 . The values found using this criterion agree very well with literature values also presented in Table 1.

Fig. 5 also presents the I_E/I_M ratio as a function of the total surfactants concentration. As can be seen in the figure, below the cmc the probe pyrene is dissolved in the bulk and the concentration is too small to form excimer molecules. When the surfactant concentration increases, the migration of the fluorescent probe to a more hydrophobic domain favors excimer formation and the I_E/I_M ratio increases. Above the cmc, the number of micelles increases with the surfactant concentration and the fluorescent probe pyrene is distributed among these micelles, consequently the probability of finding two pyrene molecules in the same micelle decreases and the emission of the excimer also decreases [26]. The decay of the excimer emission depends of the probe concentration, in the experimental conditions used a sharply decrease is observed and the cmc can be determined as the maximum of the I_E/I_M curves. As can be seen in the Table 1, these values acceptably agree with those obtained from the I_1/I_3 ratio and with the literature values. Therefore, we use both I_1/I_3 and I_E/I_M ratios to determine the cmc^* of binary mixtures of the zwitterionic with SDS or DTAB in the presence of electrolytes. The values found in this work are represented as a function of the binary composition in Fig. 6.

In Fig. 7 are represented the saturation I_1/I_3 values, corresponding to mixed micelles of different compositions. Examination of the figure clearly shows two types of behavior, in mixtures of cationic DTAB and zwitterionic surfactants, the I_1/I_3 ratio is practically independent of the micelle composition and the value remains constant on that of pure zwitterionic micelles. In mixed micelles of the anionic SDS surfactant, the I_1/I_3 ratio decreases as the mole fraction of the SDS increases. In fact, the I_1/I_3 values indicate the degree of water penetration into micelles. In a micelle with compact head groups, the I_1/I_3 value is low indicating difficult

Table 1

Best fitting parameters of experimental I_1/I_3 results to Eq. (1) and cmc values for pure zwitterionic surfactants in water obtained by pyrene fluorescence measurements

Surfactant	$x_0/M (\times 10^4)$	$\Delta x/M (\times 10^4)$	$\text{cmc}_1/M (\times 10^4)$	$\text{cmc}_2/M (\times 10^4)$	$\text{cmc}_E/M (\times 10^4)$	$\text{cmc}_{\text{bib}}/M (\times 10^4)$
DDPS	25.3 ± 0.1	4.3 ± 0.4	25.3 ± 0.1	35.2	32	22 ^a
TDPS	2.78 ± 0.01	0.08 ± 0.01	2.78 ± 0.01	3.17	3	3.2 ^b
HDPS	0.38 ± 0.01	0.11 ± 0.02	0.38 ± 0.01	0.7	0.4	0.28 ^a

^a Data from Ref. [29].

^b Data from Ref. [16].

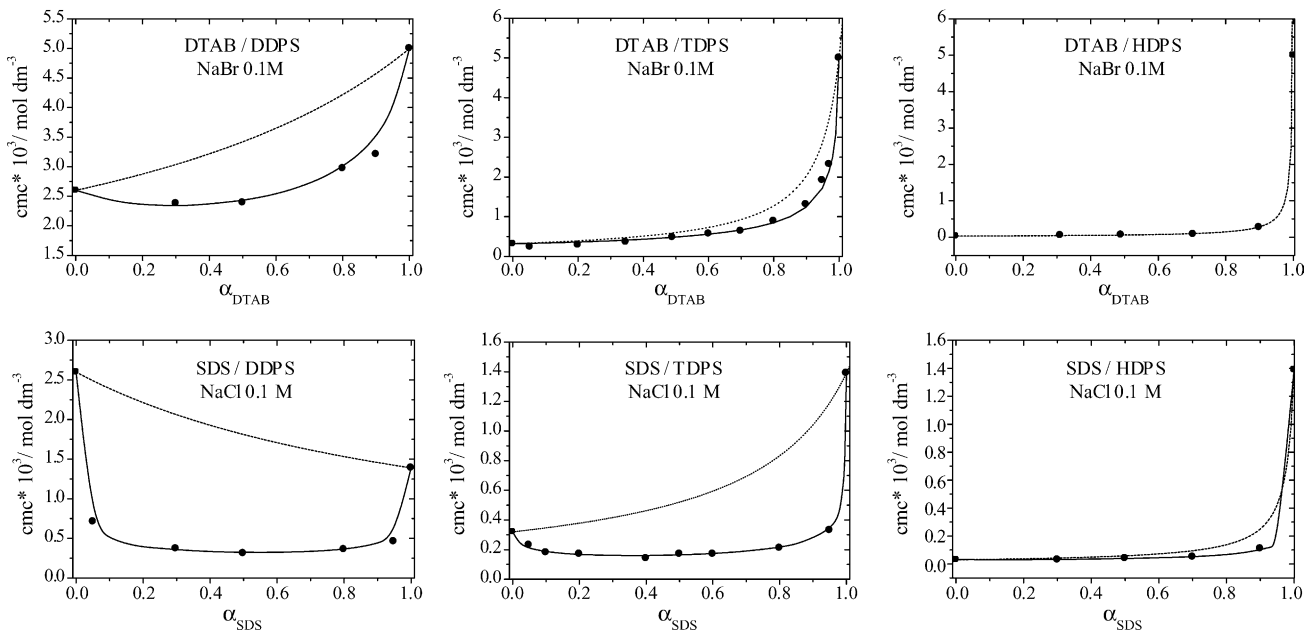


Fig. 6. Variation of the critical micelle concentration of mixed micelles dissolved in brine solutions, cmc^* , with the mole fraction of the ionic surfactants. Dotted line values calculated according to ideal mixed model and solid line values obtained from regular solution model, Eqs. (2)–(6) and β values in Table 2.

water penetration. Results found in this work seem to indicate that the anionic–zwitterionic mixed micelles became more compacted when the mole fraction of SDS increases. This fact can be the result of electrostatic interactions between the anionic SDS and the positive charge of the zwitterionic surfactants.

The I_E/I_M values for SDS mixed micelles increase with increasing the concentration of SDS and go through a maximum for compositions close to the equimolecular ratio. Because excimer formation depends on the viscosity of the solvent [23], the maximum on the excimer concentration could be due to the viscoelasticity of these solutions (see

below). In contrast, in the mixed micelles containing cationic DTAB, the I_E/I_M values remain constant in the value corresponding to pure zwitterionic micelles.

3.3. Rheological results

Fig. 8 represents rheological data obtained for binary mixtures composed by TDPS and SDS dissolved in 0.1 M NaCl. As seen in the figure, only binary mixtures with compositions close to the equimolecular ratio, $0.5 \geq \alpha_{SDS} \leq 0.6$, present viscoelasticity. Similar trend is observed in mixtures containing DDPS and HDPS dissolved in saline solution while no viscoelastic behavior was detected in these mixtures dissolved in water neither in the DTAB–zwitterionic mixed micelles studied in this work.

To study the origin of the viscoelastic behavior, we have also obtained the rheological properties of SDS–sulfobetaines of different total surfactant concentrations remaining the SDS mole fraction constant. Some of these results are represented in Fig. 8B. Results in the figure show that the viscoelastic behavior also depends of the total surfactant concentration. Thus, solutions of total surfactant concentration ranged from 4×10^{-4} M to 5.4×10^{-4} M present viscoelasticity, curves b–d in the Fig. 8B, while solutions of total surfactant concentrations of 6×10^{-4} M do not present viscoelasticity, curve a in the Fig. 8B. This fact can be explained if one considers that this mixture contains 3×10^{-4} M of TDPS, this surfactant concentration is just above to the cmc of brine TDPS solution, 2.7×10^{-4} M, consequently no viscoelastic TDPS micelles predominate in this mixture. Similar behavior was found for binary mixtures containing DDPS or HDPS as zwitterionic components.

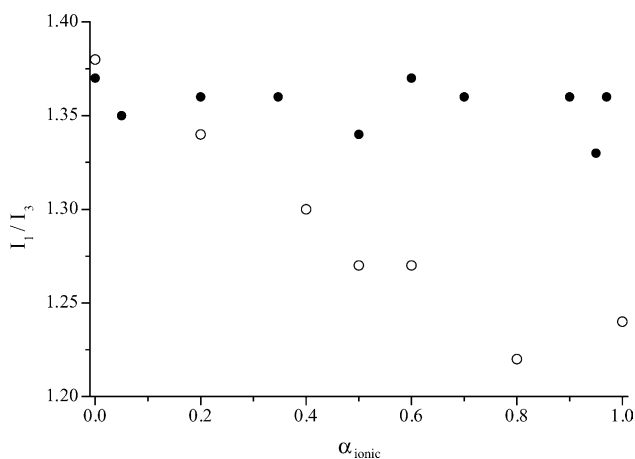


Fig. 7. I_1/I_3 saturation values for mixed micelles of ionic–zwitterionic surfactants dissolved in saline solutions as a function of the micelle composition. Solid circles, DTAB/TDPS in Na Br 0.1 M and open circles SDS/TDPS in NaCl 0.1 M.

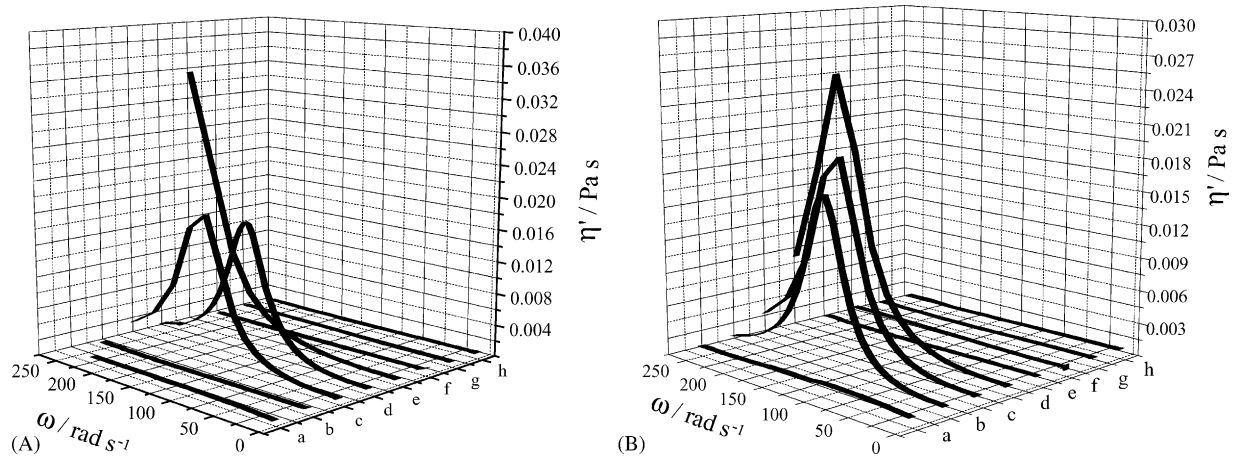


Fig. 8. (A) Viscosity values versus angular velocity of solutions containing a total surfactant concentration of 5.0×10^{-4} M and different composition of SDS/TDPS in NaCl 0.1 M: (a) $\alpha_{\text{SDS}} = 0.40$, (b) $\alpha_{\text{SDS}} = 0.45$, (c) $\alpha_{\text{SDS}} = 0.50$, (d) $\alpha_{\text{SDS}} = 0.55$, (e) $\alpha_{\text{SDS}} = 0.60$, (f) $\alpha_{\text{SDS}} = 0.65$, (g) $\alpha_{\text{SDS}} = 0.70$ and (h) $\alpha_{\text{SDS}} = 0.80$. (B) Viscosity values versus angular velocity of solutions containing a composition of SDS mole fraction of 0.5 and different total surfactant concentrations: (a) $[S]_t = 6.0 \times 10^{-4}$ M, (b) $[S]_t = 5.3 \times 10^{-4}$ M, (c) $[S]_t = 5.0 \times 10^{-4}$ M, (d) $[S]_t = 4.0 \times 10^{-4}$ M, (e) $[S]_t = 3.6 \times 10^{-4}$ M, (f) $[S]_t = 3.0 \times 10^{-4}$ M, (g) $[S]_t = 9 \times 10^{-5}$ M and (h) $[S]_t = 1 \times 10^{-5}$ M. Solutions are dissolved in 0.1 M of NaCl and TDPS as zwitterionic surfactant.

In order to confirm that the viscoelasticity is produced by mixed micelles, rheological measurements were also carried out in brine solutions of pure zwitterionic and in the pure DTAB and SDS surfactants. For comparative purposes, the surfactant concentration was the same than that in the viscoelastic mixed micelles. No viscoelastic behavior was detected in brine systems of pure surfactants.

4. Discussion

4.1. Interactions in mixed micelles

Molecular interactions between two surfactants in micelles are commonly measured by the so-called β parameter [30,31]. This parameter is conveniently calculated from critical micelle concentration data. Since the value of β is related to the free energy of mixing of the system, a negative value of β means that attractive interaction between two surfactants is stronger than attractive interaction of the two individual surfactants with themselves.

According to Rubing's non-ideal solution theory [30,31] after measuring the critical concentration of the aqueous mixed surfactants, cmc^* , and the cmc of individual surfactants, the value of the parameter β can be calculated from the following equations:

$$\frac{X_1^2 \ln[\text{cmc}_1 \alpha / \text{cmc}_1 X_1]}{[1 - X_1]^2 [\text{cmc}^* (1 - \alpha) / \text{cmc}_2 (1 - X_1)]} = 1 \quad (2)$$

$$\beta = \frac{\ln [\alpha \text{cmc}^* / X_1 \text{cmc}_1]}{(1 - X_1)^2} \quad (3)$$

where X_1 is the mole fraction of surfactant 1 in the total surfactant in mixed micelles, cmc_1 and cmc_2 the critical micelle concentrations in the aqueous phase of surfactants 1 and 2,

respectively, and α is the mole fraction of surfactant 1 in the total surfactant in aqueous solution. The surfactant 1 is the ionic component.

The total critical micelle concentration cmc^* is related with the cmc's of pure surfactants by:

$$\frac{1}{\text{cmc}^*} = \sum_1^2 \frac{\alpha_i}{f_i C_i} \quad (4)$$

In accordance with the theory of regular mixtures, the activity coefficients, f_i , are introducing by setting:

$$f_1 = \exp \frac{\beta}{RT} (1 - X_1)^2 \quad (5)$$

and

$$f_2 = \exp \frac{\beta}{RT} X_1^2 \quad (6)$$

When a surfactant and a co-surfactant mix ideally the parameter $\beta = 0$ and the activity coefficients are the unity, then Eq. (4) becomes [32]:

$$\frac{1}{\text{cmc}^*} = \sum_1^2 \frac{\alpha_i}{C_i} \quad (7)$$

We fit experimental cmc^* values to Eqs. (2)–(6) and the values of the parameter β are presented in Table 2. The cmc^* values calculated with the best values of the interaction parameter and for $\beta = 0$, ideal mixture, are represented along experimental data in Figs. 2 and 6 for aqueous binary mixtures and saline aqueous solutions, respectively.

Examination of the parameters in Table 2 shows that in aqueous solutions the cationic DTAB and the zwitterionic surfactants mix ideally. However, the addition of NaBr induces synergism. The binary mixtures of the anionic surfactant SDS and the zwitterionic DDPS present a non-ideal

Table 2
Interaction parameters found for ionic–zwitterionic mixtures

Mixtures	Solvent, β/RT		
	H ₂ O	NaCl 0.1 M	NaBr 0.1 M
SDS/DDPS	-0.39 ± 0.04	-7.1 ± 0.7	–
SDS/TDPS	0	-5.3 ± 0.2	–
SDS/HDPS	0	-4.4 ± 0.2	–
DTAB/DDPS	0	–	-1.5 ± 0.2
DTAB/TDPS	0	–	-2.0 ± 0.5
DTAB/HDPS	0	–	0

behavior with a weak interaction between the surfactants, while no interactions are detected for TDPS + SDS and HDPS + SDS mixtures. The addition of inert electrolytes favors the interactions between SDS and the zwitterionic surfactants. The interaction is reduced as the hydrocarbon length of the zwitterionic surfactant increases.

All these results show that in addition to electrostatic attractions, specific interactions seem to be responsible of the interaction between zwitterionic and ionic surfactants. Thus, the differences in the interactions between SDS with zwitterionic and DTAB can be interpreted by examining the location of the charged group [13]. On the zwitterionic sulfobetaines, the positive charge is close to the micelle core, therefore in an anionic/zwitterionic mixed micelle, the negative charge of the anionic surfactants is close to the positive charge on the dipole, while to achieve the closest proximity of opposite charges in the cationic/zwitterionic micelles, the tails of the cationic surfactants would have a protrude from the core moving the micellization process less favorable. In addition, in the anionic/zwitterionic mixed micelles the closest proximity is achieved when the hydrocarbon length is similar, consequently the strongest interaction is obtained in DDPS and SDS mixed micelles.

Finally, the effect the inert electrolytes can be due to a reduction of the electrostatic repulsion between the surfactant ions. This fact decreases the surface potential at the micellar interface [33] increasing the concentration of the ionic component in the mixed micelles.

4.2. Rheological properties of mixed micelles

Results obtained in this work show that the surfactant solutions containing mixed micelles of anionic and zwitterionic surfactants dissolved in 0.1 M NaCl, present viscoelastic behavior. If one takes into account that these systems correspond to mixtures with the strongest interaction parameter (see Table 2), the viscoelasticity would be due to the formation of worm-like micelles. These aggregates exhibit viscoelastic behavior and can be obtained in certain surfactant systems such cationic surfactants in the presence of added salt [34] or in cationic–anionic mixtures [35]. In these viscoelastic phases the zero-shear viscosity increases more than two orders of magnitude respect to the solvent viscosity [15]. The Cates and Candau model can be used to interpret the viscoelastic behavior [34]. This model considers two processes

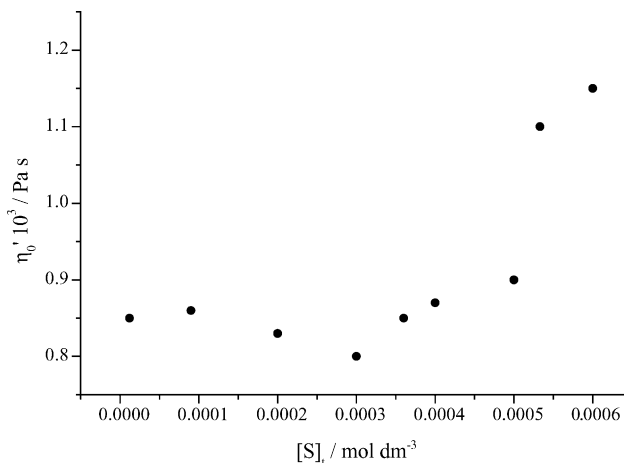


Fig. 9. Zero-shear viscosity values as a function of total surfactant concentration in mixtures of SDS/TDPS $\alpha_{\text{SDS}} = 0.50$ in NaCl 0.1 M.

of stress relaxation–reptation or reptile-like motion of the micelle along a tube and the reversible scission of micelles. These processes take place on two time scales, the reptation time, τ_{rep} and the breaking time τ_{b} . The viscoelastic behavior of such a system at low shear frequency often follows the Maxwell model with a single relaxation time $t_r = (\tau_{\text{rep}} \tau_{\text{b}})^{1/2}$ and plateau modulus, G_0 , described by [35]:

$$G' = \frac{G_0(\omega t_r)^2}{1 + (\omega t_r)^2} \quad (8)$$

$$G'' = \frac{G_0 \omega t_r}{1 + (\omega t_r)^2} \quad (9)$$

where G' is the storage modulus and G'' is the loss modulus.

Fig. 9 presents the zero-shear viscosity values as a function of the total surfactant concentration for a mixture of TDPS and SDS of mole fraction of SDS of 0.5. As can be seen in the figure, the viscosity weakly increases as the total concentration of surfactant. Even in the most concentrated solutions, the viscosity does not reach values corresponding to worm-like micelles [15]. On the other hand, experimental values of G' and G'' , obtained at different oscillatory shear frequencies, cannot be fitted to Eqs. (8) and (9). Fig. 10 presents the results for a mixture of TDPS/SDS of a composition $\alpha_{\text{SDS}} = 0.55$ and total surfactant concentration of 5×10^{-4} M. The data are presented under the form of Cole–Cole plot and clearly indicates deviations from Maxwell model. Similar behavior was found in all the anionic–zwitterionic mixtures with viscoelastic properties studied in this work.

Results in Figs. 8–10 indicate that the viscoelastic behavior appears a higher frequency and consequently smaller relaxation time than that corresponding to reptation of micelles in entangled aggregates. The existence of this faster relaxation process was supported by rheological measurements carried out in a wide frequency range. This process could be due to reorganization movements inside mixed micelles constituted by pairs of zwitterionic–anionic

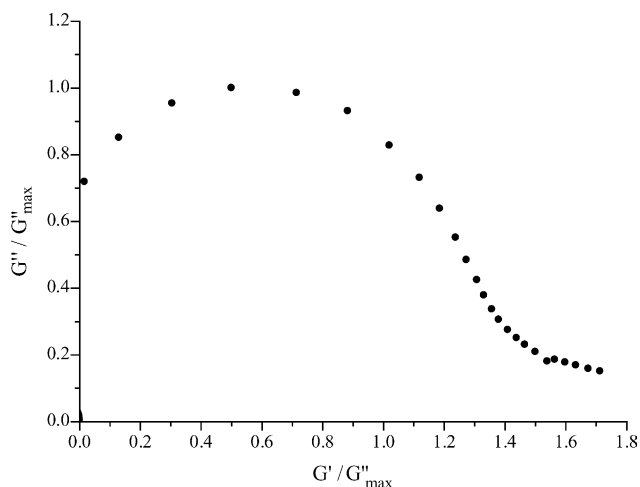


Fig. 10. Normalized Cole–Cole plot for SDS/TDPS dissolved in NaCl 0.1 M, 0.55 SDS mole fraction and 5.0×10^{-4} M of total surfactant concentration.

molecules. Therefore, it is only observed in brine solutions of mixed micelles of surfactant concentration close to the equimolecular composition and strong electrostatic attractions between the surfactant molecules.

5. Conclusions

The mixed aggregation process of alkyl ammonium propane sulfonate and the ionic surfactants, sodium dodecyl sulfate and dodecyl trimethyl ammonium bromide was studied by using conductivity and fluorescence probing. Results indicate that in the absence of electrolytes the cationic DTAB and the zwitterionic surfactants mix ideally. The binary mixtures of the anionic surfactant SDS and the zwitterionic DDPS present a non-ideal behavior with a weak interaction between the surfactants, while no interactions are detected for TDPS + SDS and HDPS + SDS mixtures. The different behavior is due to the location of charged groups in the zwitterionic surfactants. In these surfactants, the positive charge is located close to the micellar core, therefore opposite charges achieve the closest proximity in the anionic–zwitterionic micelles of similar hydrocarbon chain length.

The addition of inert electrolytes favors the interactions between the ionic and the zwitterionic surfactants. This fact is due to the reduction of the electrostatic repulsion between surfactant ions. In anionic–zwitterionic mixtures of brine solutions, the interaction is reduced as the hydrocarbon length of the zwitterionic surfactant increases.

For anionic–zwitterionic binary mixtures dissolved in NaCl, the solutions containing surfactant concentrations close to the equimolecular composition present viscoelastic behavior. This behavior cannot be interpreted according to the Maxwell model and could be due to a fast reorganization process into mixed micelles formed by pairs of anionic–zwitterionic surfactant molecules.

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