

Surface properties of mixed monolayers of sulfobetaines and ionic surfactants

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Abstract

To study the influence of the head group in the properties of the mixed monolayers adsorbed at the air–water interface, the surface tension and surface potential of binary mixtures of surfactant have been determined as a function of the surfactant composition. Experiments were carried out with anionic–zwitterionic sodium dodecyl sulfate and dodecyl dimethyl ammoniopropene sulfonate (SDS/DDPS), and cationic–zwitterionic dodecyl trimethylammonium bromide and dodecyl dimethyl ammoniopropene sulfonate (DTAB/DDPS), and dodecyl trimethylammonium bromide and tetradecyl dimethyl ammoniopropene sulfonate (DTAB/TDPS). It was shown that mixed monolayers of cationic–zwitterionic surfactant exhibit small negative deviations of ideal behavior, whereas for SDS/DDPS monolayers show strong negative deviation from the ideality. Deviations of ideal behavior are interpreted by regular solution theory. The surface potential values agree very well with the concentration of the ionic component at the interface. The dynamic surface tension values show that the adsorption kinetics on the interface is a diffusion-controlled process. In monolayers with significant deviation of the ideal behavior, anionic–zwitterionic, there is some evidence of intermolecular attractions after diffusion of both surfactants at the interface.

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1. Introduction

The properties of the liquid films that build disperse colloidal systems such as foams or emulsions are closely related to the adsorption layers on the fluid interfaces. Quantitative knowledge of the surfactant adsorption allows one to estimate the influence of surfactant interactions or the electric double layer structure on the stability of these colloidal systems. The proper description of the adsorption layers properties requires appropriated adsorption isotherms. The adsorption of surfactants has been extensively studied [1–5] and several isotherms have been developed to interpret the adsorption of pure and mixed surfactants at the air–liquid interface (see Refs. [4–6]). A great number of these works study pure nonionic and ionic surfactants or

their binary mixtures, while monolayers containing zwitterionic surfactants have received minor attention.

On the basis of results in the literature it was observed that the mixed adsorbed films of homologous surfactants mix ideally and that the assumption of the ideal mixing of such surfactants in micelles is helpful for prediction of their surface equilibrium properties [7,8]. However, mixed monolayers of dissimilar surfactants show a nonideal behavior described by a regular solution theory [9]. Modification of the general Frumkin model has also been used to interpret the adsorption of several mixtures of ionic–nonionic surfactants [10]. Recently, a two-component version of the van der Waals model, which accounts for the binding of counterions, was developed [11,12]. However, this model involved nine parameters whose values have to be obtained from the fit of the experimental surface tension isotherms, with the consequent indetermination in the parameters found from fitting process.

On the other hand, to interpret the behavior of several systems in which monolayers play an important role, it is also

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necessary to obtain the dynamic properties of monolayers. This is because several technological processes use surfactant solutions under no equilibrium conditions. In these applications the dynamic surface tension is an important property, which allows obtaining kinetic information of the surfactant adsorption at the interface.

Betaines are widely used as boosters because they stabilize foams against the antifoaming action of the oil droplets contained in commercial hair conditioners or shampoos [13]. Moreover, these surfactants reduce the irritation action of the surfactants on the eye and skin [14]. In a previous work [15], we studied the interaction of alkyldimethyl ammoniopropane sulfonate, sulfobetaines, with sodium dodecyl sulfate (SDS) and dodecyl trimethylammonium bromide (DTAB) in micelles, and the effect of inert electrolytes in the interaction. Results showed that in aqueous solutions the cationic DTAB and the zwitterionic surfactants mix ideally. However, the addition of NaBr induces synergism. Binary mixtures of the anionic surfactant SDS and the zwitterionic dodecyl dimethyl ammoniopropane sulfonate, DDPS, present a nonideal behavior with a weak interaction between the surfactants, while no interactions are detected for tetradecyl or hexadecyl dimethyl ammoniopropane sulfonate mixed with SDS. The addition of inert electrolytes favors the interactions except in the SDS + HDPS mixed micelles, which mix ideally, even in the presence of NaCl 0.1 M.

The aim of the present work is to analyze the role of both the charge and hydrocarbon chain on the properties of mixed monolayers formed by binary mixtures of dodecyl or tetradecyl dimethyl ammoniopropane sulfonate, sulfobetaines, and the ionic surfactants sodium dodecyl sulfate (SDS) and dodecyl trimethylammonium bromide (DTAB). The remaining sections of the paper are organized as follows: Section 2 contains experimental details and description of methodologies and techniques. In Section 3, the equilibrium surface tension and potential of different mixtures and their interpretations in terms of regular solution theory are presented. This section also contains the results of dynamic surface tension and their interpretation. Finally, Section 4 is conclusions.

2. Experimental

2.1. Materials

The zwitterionic surfactants dodecyl dimethyl ammonium propane sulfonate (DDPS) and tetradecyl dimethyl ammonium propane sulfonate (TDPS) were from Fluka. These surfactants were purified by recrystallization in isopropanol [16]. The anionic surfactant sodium dodecyl sulfate (SDS) from Merck and the cationic dodecyl trimethylammonium bromide (DTAB) from Sigma–Aldrich were purified by recrystallization in ethanol. All the surfactants were recrystallized several times and their purity is controlled by HPLC–mass spectrometry. The purity of surfactants is 99.9 and 99.5% for SDS.

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 $\mu\text{S}/\text{cm}$.

2.2. Surface tension measurements

The measurements of the equilibrium surface tension were carried out with a drop tensiometer Model TVT 1 from Lauda [17]. The inner radius of the steel capillary was 1.345 mm, and the employed syringe was of 5 ml. The measurements of the dynamic surface tension in the range time below 10 s were carried out with a maximum bubble pressure tensiometer MPT2, from Lauda [18].

It is well known that the purity of surfactant sample is the prerequisite for the correct interpretation of the surface results. In the case of SDS surfactant *n*-dodecanol from the surfactant synthesis is the most frequent contaminant and one of hardest to remove. The interference of *n*-dodecanol trace is due to the higher surface activity of this alcohol. Therefore to choose the experimental conditions to obtain the equilibrium surface tension of solutions containing SDS, the dynamic surface tension, $\gamma(t)$, of SDS aqueous solutions were obtained. Fig. 1 shows the dynamic surface tension of 2 mM SDS solution, using maximum bubble pressure tensiometer and pendant drop

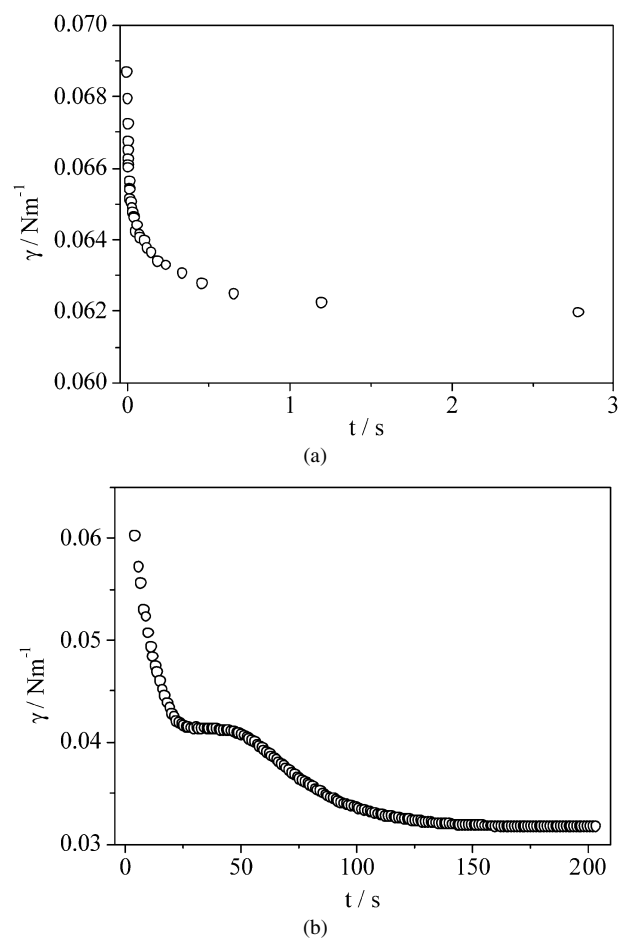


Fig. 1. Dynamic surface tension decay curves of sodium dodecyl sulfate. Short times (a) have been obtained to maximum pressure tensiometer and long times (b) to pendant drop tensiometer.

tensiometer developed by Cabrerizo et al. [19]. We use different kinds of tensiometers to obtain the dynamic curves for times ranging from milliseconds to hours. As can be seen in the figure the dynamic surface curve presents two plateaus, one at 62.2 mN/m and the second one at 41 mN/m. We ascribed the first one to the equilibrium surface tension of SDS because the surface tension value in the plateau is the same to that corresponding to the surface-chemical pure SDS solution [20]. After the plateau the dynamic surface tension decreases due to the dodecanol co-adsorption. The second plateau corresponds to a first-order phase transition [20]. After this phase transition dodecanol domains surrounded by a homogeneous fluid-like phase are formed as visualized by BAM [20]. In pure SDS the phase transition was not observed. At the end of the adsorption kinetics the *n*-dodecanol domains coalesce and form a condensed phase. From the results one can obtain the equilibrium surface tension of SDS without interferences of the dodecanol co-adsorption by obtaining drops of ages in the time corresponding to the adsorption of pure SDS, $t \leq 3$ s.

To obtain the equilibrium surface tension we used the TVT-1 drop tensiometer with the so-called standard mode. It consists of a two-step process: first, a drop with a certain volume is quickly formed at the capillary. This volume must be smaller than the critical volume according to the actual interfacial tension at the drop surface and at first the drop will remain at the tip of the capillary. After that, drop volume is increased more slowly to minimize hydrodynamic effects until it becomes large enough to detach. In order to reach the equilibrium surface tension the standard method permits to select the dosing rate. Thus, to ensure that the solutions do not show long time dependence, slow surfactant adsorption, we have obtained the dynamic surface tension of the dilute surfactant solutions. The dosing rate at which the surface tension agrees with the dynamic surface tension at long times, equilibrium surface tension, was used for the measurements with the standard mode. In our systems the dosing rate employed was 0.07 s/ μ l, except for solutions of TDPS, slow adsorption, in which the dosing rate was 1.5 s/ μ l. In addition, to ensure no interferences due to dodecanol co-adsorption the optimal dosing rate was 0.07 s/ μ l. Results determined with in this experimental condition for SDS solutions, Fig. 2b, are in excellent agreement with those corresponding to monolayers of surface-chemical pure SDS solutions (see Refs. [20,21]). Consequently, it was not possible to determine the equilibrium surface tension of mixtures with TDPS and SDS with the drop method because using the adequate dosing rate to reach the equilibrium for TDPS solutions, interferences due to dodecanol adsorption become important.

In the case of maximum bubble pressure tensiometer (MPT2), air is blown into a surfactant solution, to obtain bubbles. If the system volume is much larger than the bubble one the dynamic surface tension can be determined in the millisecond range taking into account the variation of the bubble pressure with the flow rate of air. So, we work in all cases with a volume of 10 ml. The diameter of the capillary was 0.15 mm.

All measurements were carried out at 25.0 °C. Temperature in tensiometers was controlled by means of thermostat/cryostat RM 6 and thermostat/cryostat Ecoline RE 104 from Lauda.

2.3. Surface potential measurements

The surface potential ΔV was measured in a Teflon Langmuir minitrough (KSV, Finland). A Kelvin probe SPOT1 from KSV located at ≈ 2 mm above the aqueous surface was used. SPOT1-KSV is based on the non-contact vibrating plate capacitor method with the reference electrode placed in the subphase. The surface potential measurements were reproducible to ± 20 mV. The temperature control of water in the trough was carried out by passing thermostated water into the jacket at the bottom of the trough. The temperature near the surface was measured with a calibrated sensor from KSV and was maintained at 25.0 °C. Since measurements are carried out in soluble monolayers, the surface pressure was simultaneously measured until reaches the equilibrium value. Then the surface potential was measured taken the clean water subphase as reference. The measurements were repeated at least three times and the average of these values was calculated.

3. Results and discussion

3.1. Equilibrium surface tension

Figs. 2a and 2b show the equilibrium surface tensions for binary mixtures of dodecyl dimethyl ammonium propane sulfonate (DDPS) with the cationic dodecyl trimethylammonium bromide (DTAB) and sodium dodecyl sulfate (SDS), respectively. Each isotherm is obtained at a fixed composition and varying the total surfactant concentration. Surface tension values decrease rapidly when increasing the total surfactant concentration before reaching a plateau region. The cmc is estimated from the break point in the resulting curve. In this way, cmc's values (not shown here) are in excellent agreement with data obtained previously by fluorescence probing and electrical conductivity [15].

The insert in the figures shows surface tension values vs concentration of the most active surfactant, i.e., zwitterionic surfactant DDPS. From figures one can see that the surface tension at the same zwitterionic concentration for mixtures is lower than that for pure DDPS. This fact suggests better surface properties of mixtures than of DDPS pure surfactant. The effect is more accused in mixtures with the anionic surfactant SDS.

The equilibrium surface tension values of solutions with tetradecyl dimethyl ammonium propane sulfonate, TDPS and the cationic dodecyl trimethylammonium bromide, DTAB are presented in Fig. 2c. The isotherms correspond to different bulk composition of surfactants. The insert shows clearly that all data except those for mixtures with 0.95 mole fraction of DTAB fall in a single curve corresponding to the isotherm of the zwitterionic surfactant. This fact indicates the TDPS is responsible for the surface properties of these mixtures because is the most surface active component with a great difference on superficial activity respect to DTAB surfactant. This behavior was observed elsewhere in mixtures of DTAC with the double-tailed surfactant didodecyl dimethylammonium bromide (DDAB) [22]. In this case the most active component is DDAB, which governs the properties of the monolayer.

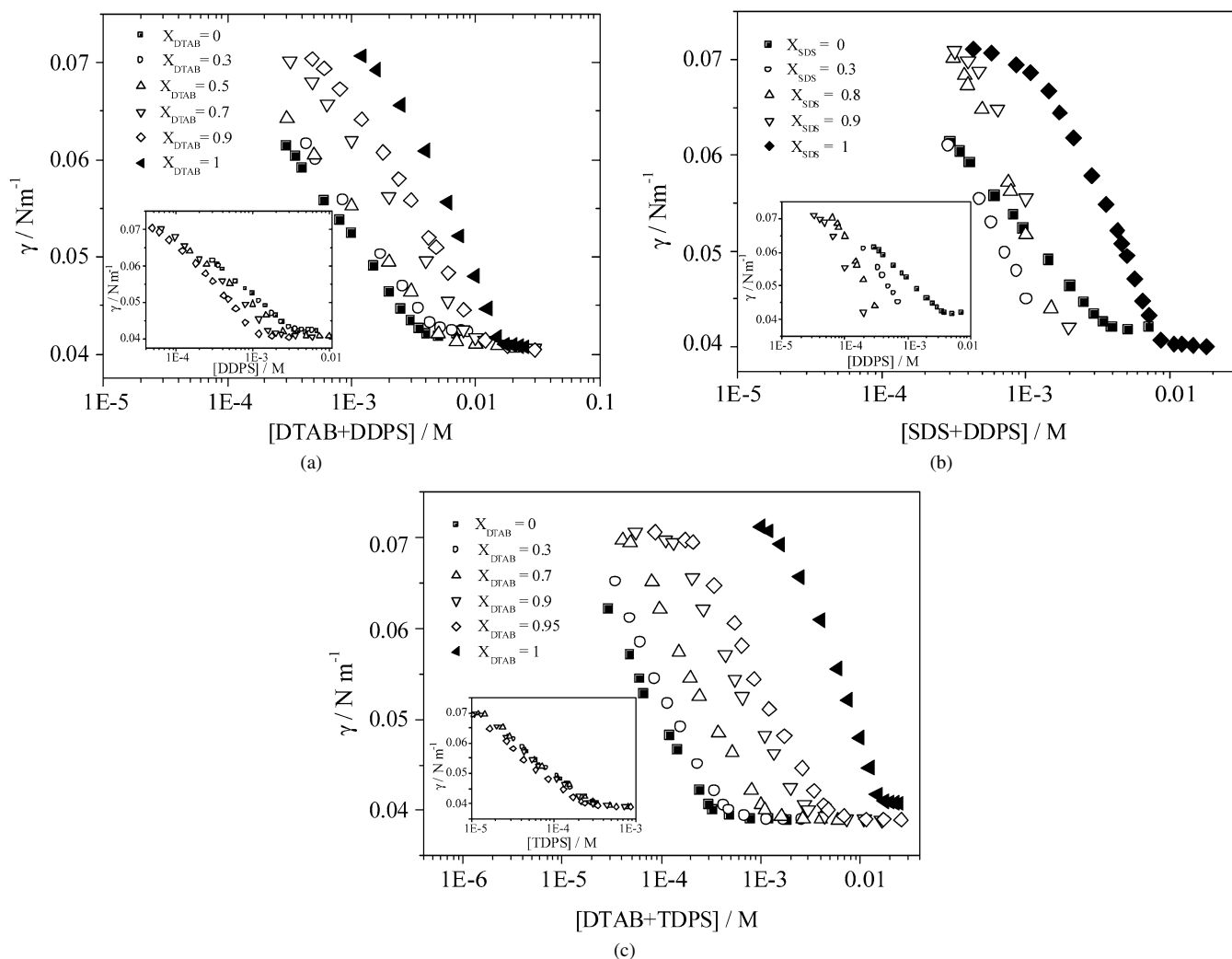


Fig. 2. Surface tension vs total surfactants concentration plots for different mixed compositions.

3.2. Composition of mixed adsorbed monolayers

It is well known that surface composition in mixed adsorbed films differs from pure monolayers and from bulk composition. In order to calculate the composition of mixed monolayers, equations resulting of the Rubing [23] model for mixed micelles and extended by Rosen [24] to mixed monolayers have been applied. According to this model, at a specific surface tension value the mole fraction of the surfactant 1, ionic component, in the total surfactant in the monolayer, X_1^S , is calculated by the following equations:

$$\frac{(X_1^S)^2 \ln(C_1/C_1^0 X_1^S)}{(1 - X_1^S)^2 \ln[C_2/C_2^0 (1 - X_1^S)]} = 1, \tag{1}$$

$$\frac{1}{C} = \frac{X_1^S}{C_1^0 f_1^S} + \frac{1 - X_1^S}{C_2^0 f_2^S}, \tag{2}$$

where C_1^0 , C_2^0 , and C are the molar concentration in the solution phase of surfactants 1 and 2 and their mixture, respectively, at the molar fraction of the component 1, X_1 required to produce a given surface tension value. Here f_i^S represents the activity coefficient of the individual surfactant in the mixed monolayer

and C_1 and C_2 are the molar concentration of components 1 and 2 for each mixture in solution.

Using the regular solution theory the activity coefficients are given by

$$f_i^S = \exp \left| \frac{\beta}{RT} (1 - X_i^S)^2 \right| \tag{3}$$

and

$$\beta = \frac{\ln(C_1/C_1^0 X_1^S)}{(1 - X_1^S)^2}, \tag{4}$$

where β is the molecular interaction parameter for mixed monolayers. Since the value of β is related to the free energy of mixing of the system, a negative value of β means that attractive interactions between the two surfactants adsorbed at the interface are stronger than attractive interactions of the two individual surfactants with themselves [23,24].

In order to solve the above set of equations, we use the experimental values of C_1^0 , C_2^0 , and C for different composition in bulk, ranging from $X_{\text{ionic}} = 0.20$ – 0.95 , at fixed surface tension values. The iterative resolution of these equations conduces to the unknown parameters X_1^S and β . In some mixed micelles one

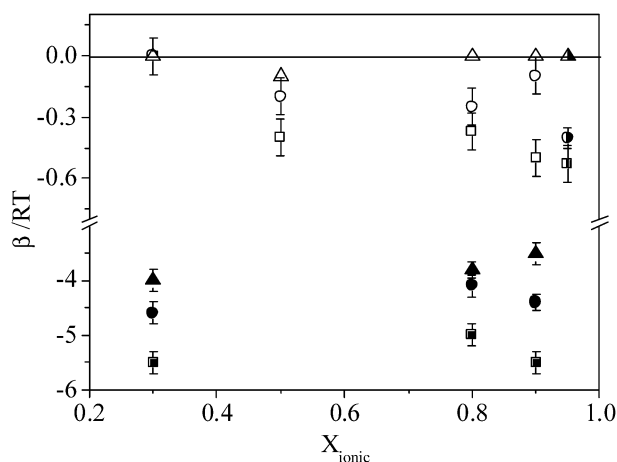


Fig. 3. Variation of β interaction parameter with the composition for the following surface tensions: squares: $\gamma = 45 \text{ mN m}^{-1}$, circles: $\gamma = 50 \text{ mN m}^{-1}$, and triangles: $\gamma = 55 \text{ mN m}^{-1}$. Solid symbols represent values for mixtures of SDS and DDPS; open symbols for DTAB/DDPS, and half-solid symbols for DTAB/TDPS.

Table 1
Interaction parameters β/RT found for ionic–zwitterionic monolayers

Mixtures	Surface tension		
	$\gamma = 55 \text{ mN m}^{-1}$	$\gamma = 50 \text{ mN m}^{-1}$	$\gamma = 45 \text{ mN m}^{-1}$
DTAB/DDPS	0	-0.20 ± 0.05	-0.32 ± 0.07
DTAB/TDPS	0	-0.40 ± 0.06^a	-0.53 ± 0.09^a
SDS/DDPS	-3.80 ± 0.05	-4.40 ± 0.04	-5.33 ± 0.04

^a The β values have only been obtained for $X_{\text{DTAB}} = 0.95$, see text.

different β value for each composition was obtained [25–28], therefore we have calculated the interaction parameters for different compositions and results are represented in Fig. 3. As can be seen in the figure the parameter β remains constant with composition at a given surface tension for SDS/DDPS and DTAB/DDPS mixtures, and then we obtain the average value by iterative resolution of all results corresponding to different composition at each surface tension value. These values are collected in Table 1.

On the other hand, results presented in Fig. 2c for TDPS and DTAB indicate that these monolayers are practically formed by the zwitterionic component and consequently it is not possible to talk about mixed monolayers except in monolayers containing $X_{\text{DTAB}} = 0.95$. In this mixed monolayer the β parameters, in RT units, calculated for monolayers of surface tension 50 and 45 mN/m are -0.4 and -0.53 , respectively, and the monolayer composition is practically equimolecular. These values seem to indicate that when DTAB molecules are adsorbed at the interface small deviations of ideal behavior are detected.

Examination of β parameters in Table 1 shows that at the air–water interface the cationic DTAB and the zwitterionic surfactants present a practically ideal behavior with a small β parameter. In addition the β parameter decreases, increases in absolute value, as the chain length of the zwitterionic surfactant increases. The value of β becomes more negative in anionic–zwitterionic mixed monolayers. Finally, β increases (more neg-

ative) in compressed monolayers, low surface tension, in all systems studied in this work.

As commented above, negative β values are commonly described as indicating of attractive interactions between surfactants [23,24]. However, in recent works [29,30], the synergistic effects are explained as due mainly to entropic free energy contributions of counterions in the diffused layer outside the micelle charged surface. In addition, the Mulqueen’s theoretical model [31] for mixed ionic–zwitterionic monolayers considers this monolayer as a two-dimensional charged layer with a Stern layer where steric repulsions exclude the surfactant counterions present in the diffuse region [32]. The Stern layer is considered as the distance that the longest surfactant head extends into the aqueous region plus the radius of the counterions of the ionic component [31]. According to these models, the counterions excluded from the Stern layer can contribute to the increase of the entropy decreasing the β parameter, more negative values. One hopes that when the monolayer packing increases, i.e., monolayers with higher surface pressure, the counterions excluded also increase. Consequently, the entropic effects rises and the β values become more negative (see Table 1).

The resolution of Eqs. (1)–(4) allows to obtain the monolayer phase diagram, expressed as mole fraction of the “ i ” component in the total surfactant in the monolayer, X_i^S vs mole fraction of the “ i ” component in bulk. In Fig. 4 the symbols along the solid lines are calculated by applying Eqs. (1)–(4) and using the β values of Table 1. The simulated curves satisfy the experimental results.

3.3. Surface potential measurements

Fig. 5 shows the surface potential of monolayers formed by pure zwitterionic and cationic surfactant and binary mixed monolayers with the cationic DTAB surfactant and the zwitterionic DPPS and TDPS surfactants. It was not possible to obtain the surface potential in monolayers with SDS because to obtain the surface potential it is necessary that the monolayer reaches the equilibrium. In this time the co-adsorption of dodecanol is sufficiently important to gives significant changes on the monolayer surface potential. For comparative purposes the surface composition of monolayers is also represented in figures. Results correspond to monolayers of surface tension 45 mN m^{-1} .

As one can see in figures the surface potential of mixed monolayer is always positive as expected of the head group of the cationic surfactant. In addition the monolayers of the pure zwitterionic components have also positive surface potential. This fact was also observed in zwitterionic insoluble monolayers [33], and is due to the contribution of the tail group moments [34,35].

In mixed monolayers the surface potential increases as the cationic surfactant adsorbed at the air–liquid interface increases. The trend of variation of surface potential with composition in bulk is in excellent agreement with that of mole fraction of the cationic component on monolayers calculated using the Rubing model. This fact confirms the validity of the Rubing model to estimate the composition of mixed monolayers.

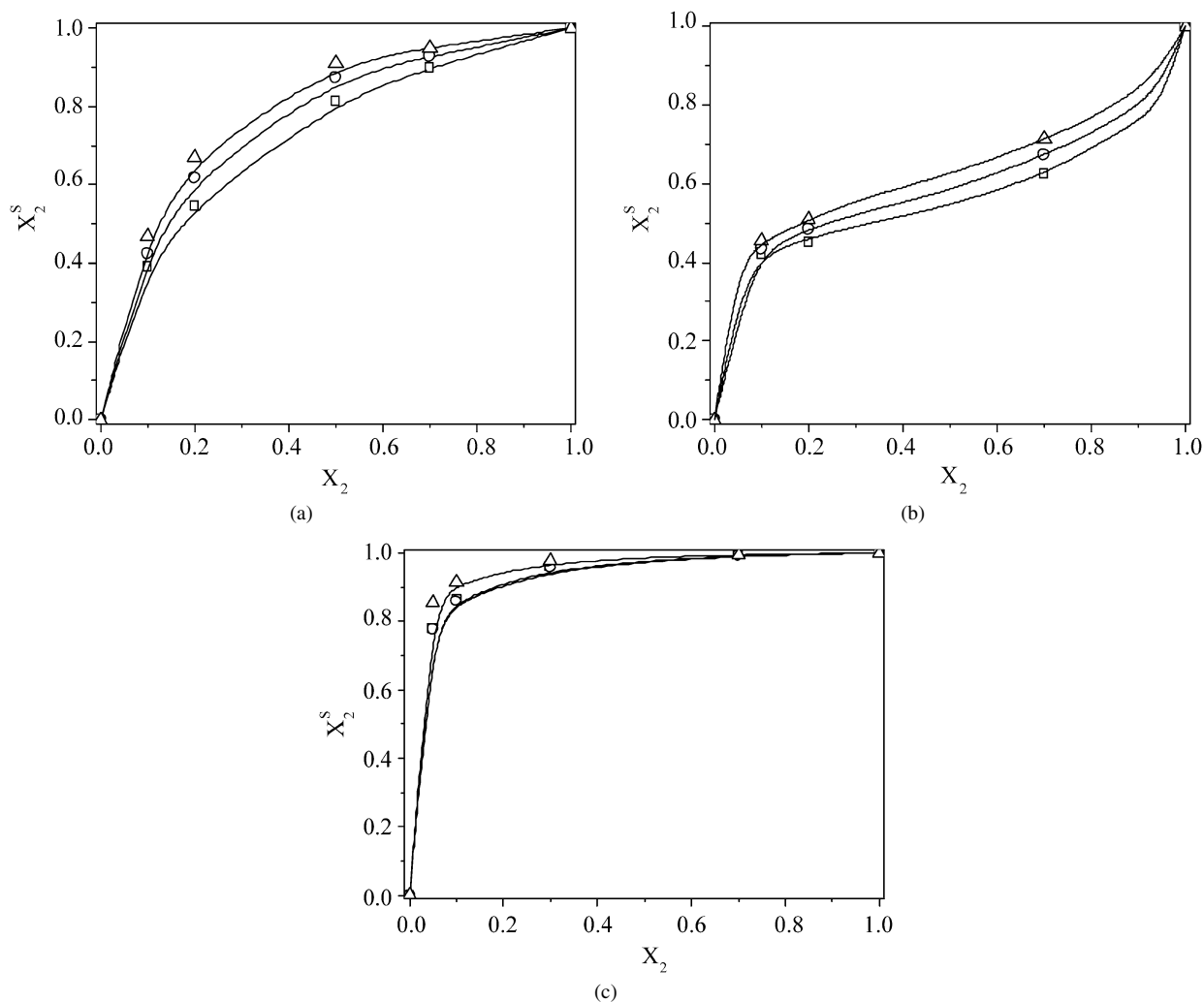


Fig. 4. Surface mole fraction values vs mole fraction in bulk solution for ionic–zwitterionic mixtures at different surface tension: (a) DTAB/DDPS, (b) SDS/DDPS, and (c) DTAB/TDPS. Squares: $\gamma = 45$ mN m⁻¹, circles: $\gamma = 50$ mN m⁻¹, and triangles: $\gamma = 55$ mN m⁻¹.

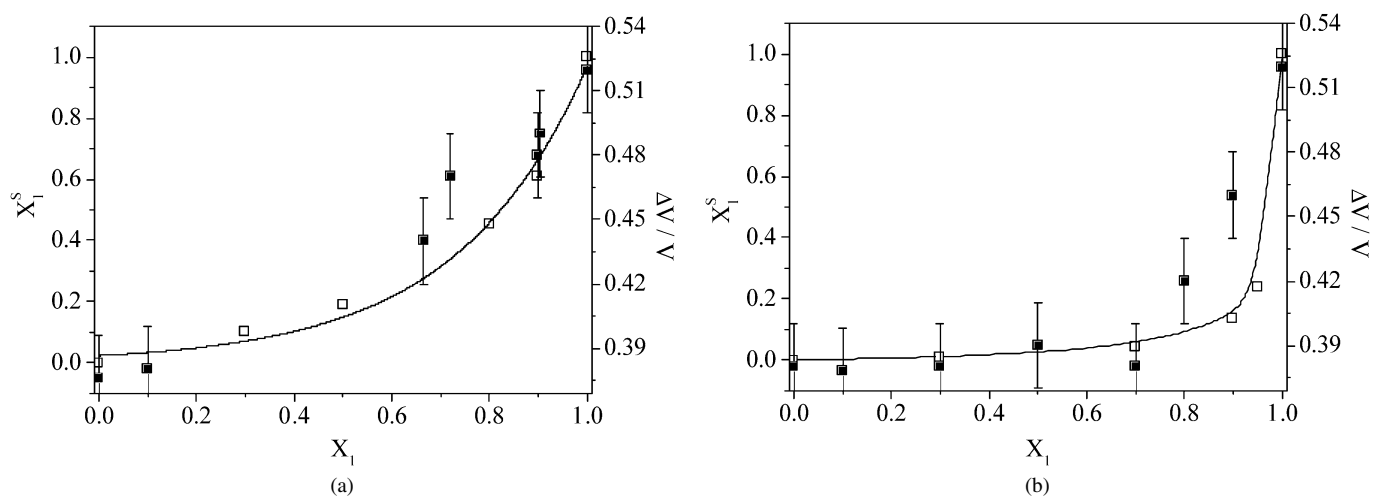


Fig. 5. Variation of both, surface mole fraction of the ionic component (open squares) and surface potential (solid squares) with bulk composition for: (a) DTAB/DDPS and (b) DTAB/TDPS.

3.4. Dynamic surface tension measurements

Experimental and theoretical studies of the adsorption kinetic of surfactant mixtures on the liquid interfaces have been

discussed in several works (see, for example, Refs. [36–40]). In these studies no specific interactions between the molecules adsorbed at the interfaces are considered. Therefore, we are interested to study the effect of surface interactions on

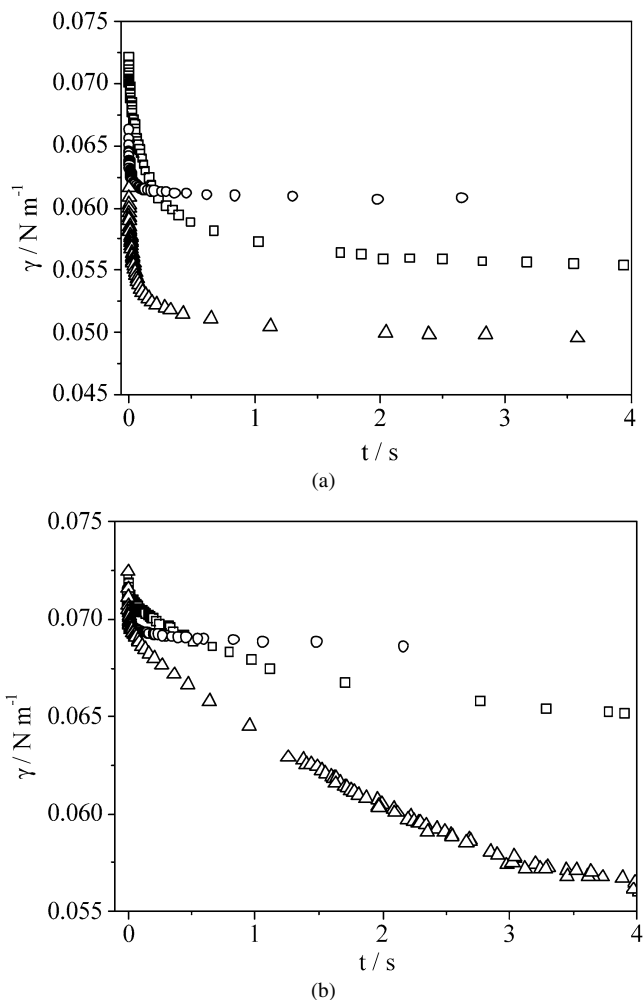


Fig. 6. Dynamic surface tension curves for pure surfactants. (□) DDPS, (○) ionic components, and (△) binary mixtures. Surfactant concentrations are indicated in text. (a) DTAB/DDPS and (b) SDS/DDPS.

the adsorption kinetics of surfactants at the air–water interface, and then we obtain the dynamic surface tension of solutions corresponding to mixed monolayers with and without interactions. Fig. 6a presents dynamic surface tension values of DTAB/DDPS solutions with $X_{\text{DTAB}} = 0.85$ and total surfactant concentration of 4.85×10^{-3} M, $\gamma_{\text{eq}} = 50$ mN m $^{-1}$. The monolayer compositions calculated according the Rubing model is $X_{\text{DTAB}}^{\text{S}} = 0.5$. This monolayer exhibits a practically ideal behavior with a small β parameter of $-0.2RT$. For comparative purpose the dynamic surface tension values of pure DTAB ($C = 3.6 \times 10^{-3}$ M) and pure DDPS ($C = 6.4 \times 10^{-4}$ M) are also presented. In Fig. 6b dynamic surface tension results of SDS/DDPS mixtures with $X_{\text{SDS}} = 0.8$ and total surfactant concentration of 1×10^{-3} M ($\gamma_{\text{eq}} = 50$ mN m $^{-1}$) and $X_{\text{SDS}}^{\text{S}} = 0.5$ are represented. This monolayer exhibits a significant non ideal behavior with $\beta/RT = -4.4$. The dynamic surface tension values of pure components (SDS = 8.0×10^{-4} M and DDPS = 2.4×10^{-4} M) are also represented.

The main model to analyze the dynamic surface tension curves considers dynamic adsorption at the interface as a diffusion-controlled process [41] and it relates the excess surface concentration and the time by the following equation:

$$\Gamma(t) = 2C \left(\frac{Dt}{\pi} \right)^{1/2} - 2 \left(\frac{D}{\pi} \right)^{1/2} \int_0^{t^{1/2}} C_s(t - \tau) d\tau^{1/2}, \quad (5)$$

where D denotes the diffusion coefficient, $\Gamma(t)$ and C_s the surface and subsurface concentrations, which are related to time, and C is the bulk surfactant concentration.

This equation cannot be solved analytically and therefore, asymptotic solutions have to be employed at long and at short times [36]. Using the Henry law isotherm to transform surface concentration into the corresponding surface tension values the asymptotic solutions are given by

$$\gamma(t)_{t \rightarrow 0} = \gamma_0 - 2CRT \left[\frac{Dt}{\pi} \right]^{1/2} \quad (6)$$

and

$$\gamma(t)_{t \rightarrow \infty} = \gamma_{\text{eq}} - \frac{RT\Gamma^2}{C} \left[\frac{\pi}{4Dt} \right]^{-1/2}, \quad (7)$$

where Γ represents the maximum excess surface concentration, and γ_0 and γ_{eq} are the equilibrium surface tension of solvent and solution, respectively. According to these equations the graphic representation of the dynamic surface tension, $\gamma(t)$, is linear with $t^{1/2}$ and $t^{-1/2}$, for short and long times, respectively. The results of these mixtures are plotted in Fig. 7. Theoretical straight lines are calculated according to Eq. (6), short times asymptotic solution, and Eq. (7), long times approximation. The diffusion coefficients and Γ used are obtained from Refs. [36,42,43]: $D_{\text{SDS}} = 3.0 \times 10^{-10}$ m 2 s $^{-1}$, $D_{\text{DDPS}} = 1.77 \times 10^{-10}$ m 2 s $^{-1}$, and $\Gamma_{\text{DDPS}} = 3.8 \times 10^{-6}$ mol m $^{-2}$; and $D_{\text{DTAB}} = 4.6 \times 10^{-10}$ m 2 s $^{-1}$, $\Gamma_{\text{DTAB}} = 3.77 \times 10^{-6}$ mol m $^{-2}$.

Fig. 7a clearly shows that experimental and theoretical values agree very well at short times. In mixtures the ionic surfactants are adsorbed faster than the zwitterionic surfactant DDPS. Taking into account that the diffusion coefficient values for these surfactants are similar, this fact can be due to concentration effect, because in these mixtures ionic surfactants have greater concentration than the zwitterionic one. This behavior was confirmed from results of dynamic surface tension for mixtures with $X_{\text{ionic}} = 0.3$ (not shown here). In these mixtures DDPS is the most concentrated surfactant in solution and is adsorbed faster than the ionic ones.

Fig. 7b shows the results of DTAB/DDPS at long times. As in Fig. 7a experimental and theoretical values acceptably agree. This fact indicates that the adsorption of these surfactants is also diffusion-controlled. Similar behavior was observed in mixtures with $X_{\text{ionic}} = 0.3$. The dynamic surface tension of SDS/DDPS mixtures (Fig. 7c) shows a sharp decreasing after surfactants diffusion at the interface. This decrease of surface tension cannot be ascribed to dodecanol adsorption because the adsorption of alcohol in mixtures is observed at longer times. Therefore it was attributed to the existence of intermolecular attractions after adsorption of the anionic and zwitterionic surfactants. We have confirmed this behavior in SDS/DDPS mixtures of $X_{\text{SDS}} = 0.8$ and total surfactant concentration 2×10^{-3} and 8×10^{-4} M. The equilibrium surface tension values of these mixtures are 45 and 55 mN m $^{-1}$, respectively. The dynamic surface tension results seem to indicate that anionic–zwitterionic

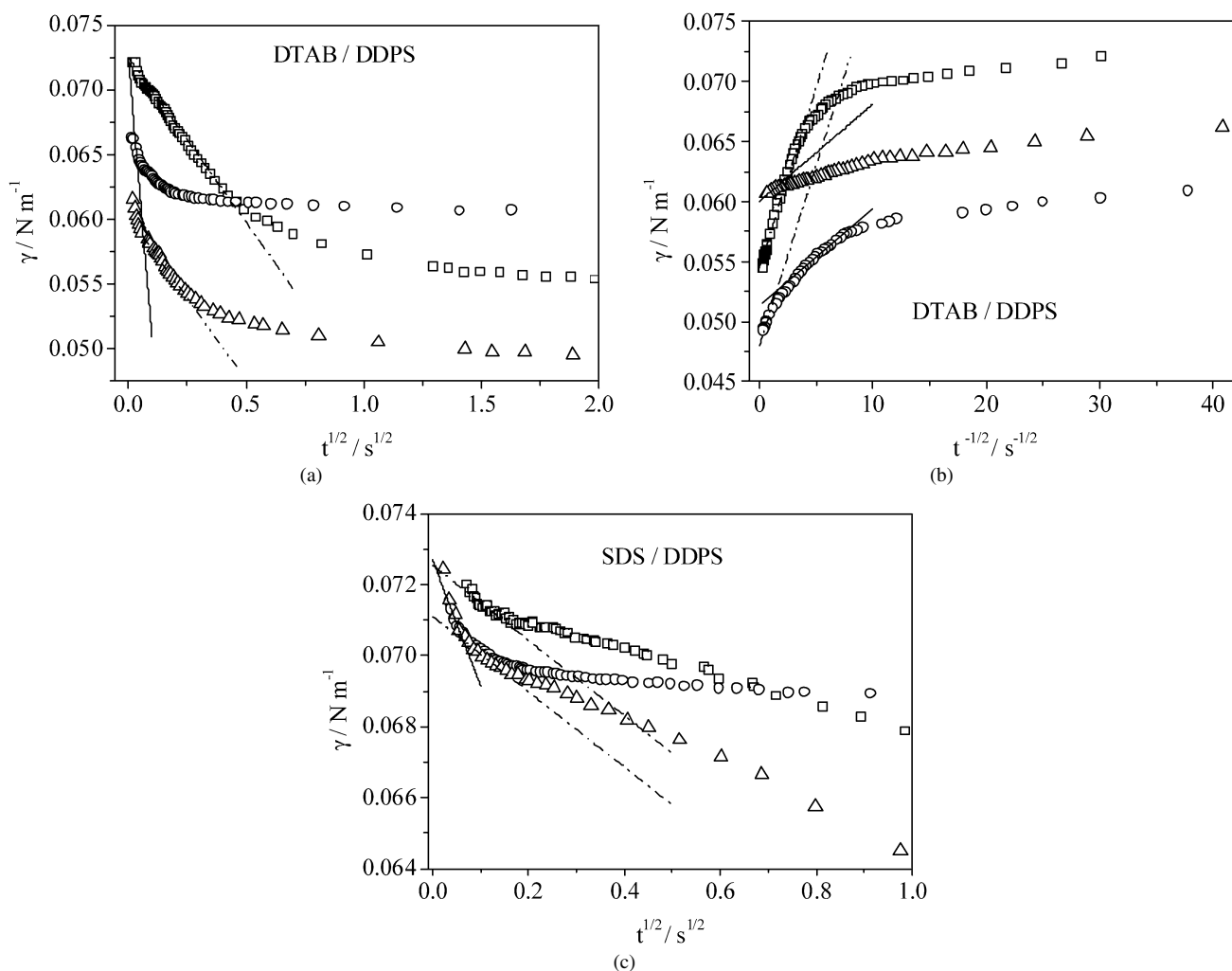


Fig. 7. Variation of the dynamic surface tension vs $t^{1/2}$ for: (□) DDPS, (○) ionic components, and (Δ) binary mixtures of (a) DTAB/DDPS and (c) SDS/DDPS. Part (b) presents dynamic surface tension vs $t^{-1/2}$ for: (□) DDPS, (Δ) DTAB, and (○) DTAB/DDPS mixture. Simulated lines are calculated according to Eqs. (6) and (7) for short and long approximations, respectively, and correspond to ionic components (solid lines) and zwitterionic DDPS (dash-dot lines), see text.

monolayers exhibit attractive interactions between the surfactants adsorbed at the interface. The attractive interactions give a quick adsorption of surfactants at long times and are consistent with the greater (negative) value of β obtained from the equilibrium surface tensions values.

4. Conclusions

The equilibrium surface tensions values of different mixtures are interpreted by means of regular solution theory (RST). Negative values of β parameter were obtained for both zwitterionic–cationic and zwitterionic–anionic mixed monolayers. The β values become more negatives for the most compressed monolayers and for anionic–zwitterionic mixtures. Differences between the β values are qualitatively analyzed in terms of entropic free energy contributions related with ionic surfactant counterions [29,30].

Using regular solution theory the composition of mixed monolayers was obtained. Surface potential of mixed monolayers was also determined and their values are related with the adsorption of the ionic surfactant at the interface. Values of

surface potential are in excellent agreement with the mole fraction of the ionic component on the interface calculated from the RST. This fact confirms the validity of this model to obtain the composition of mixed monolayers.

Dynamic surface tension measurements show that in cationic–zwitterionic monolayers, small $|\beta|$, the most concentrated component adsorbs faster and the kinetics process is diffusion-controlled. The dynamic results evidence attractive interactions between the anionic and zwitterionic surfactants, these interactions seem to be responsible of the sharp decreasing of the surface tension in these mixed monolayers.

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