

ARTICLES

Effect of the Addition of Polyelectrolytes on Monolayers of Carboxybetaines

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We have studied the effect of the addition of sodium poly(styrene sulfonate) polymers on the properties of monolayers formed by the adsorption of two carboxybetaines with different number of separation methylenes between their charged groups. Fluorescence and surface tension measurements indicate that above the critical aggregation concentration a surfactant–polymer complex of electrostatic origin is formed in bulk. The complexes have a negative charge that is repelled by the negative charge of the surfactant adsorbed at the interface; consequently, the monolayer seems to be exclusively formed by surfactant carboxybetaines. The high-frequency surface viscoelasticity of the monolayers was studied by surface dynamic light-scattering measurements. The behavior of the dilational elasticity and viscosity is explained by relaxation involving molecular reorientation within the adsorbed layer.

Introduction

The mixtures of surfactants and polymers are extensively used in a wide range of cosmetic, industrial, and technological applications. In applications such as hair shampoos or conditioners, paints, or drug delivery systems, the polymer is added as a viscosity modifier or as an emulsifier or a foaming agent. In the recent years, there was an important growth in studies of polymer–surfactant mixtures, see refs 1 and 2 for reviews;^{1,2} however, the surface properties of polymer–surfactant mixtures have been less studied and consequently are less understood. In particular, the weakly interacting nonionic polymer–ionic surfactant mixtures have been studied by surface tension measurements and more recently using neutron reflectivity measurements.^{3–6} Results showed the difficulties to relate bulk with surface behaviors. In the case of more interacting systems such as polyelectrolyte–oppositely charged surfactants mixtures, the existence of attractive interactions in bulk and at the surface give a great variety of behaviors as a function of surfactant concentration. Thus, poly(styrene sulfonate) PSS and (C_n TAB) mixtures are the example of surface polymer–surfactant complexes more energetically favorable than complexes in bulk. These surface complexes can form monolayers at low surfactant concentrations^{5,7} and also different surface structures such as multilayers^{8–10} or even microgels^{11,12} at high surfactant concentrations. In contrast, in mixtures with cationic polymer and anionic surfactants^{13–16} surface tension and neutron reflectivity measurements show the existence of a cooperative adsorption of surfactant and polymer molecules at the interface and its subsequent desorption at intermediate surfactant concentration, attributed to the competition of the formation of bulk surfactant–polymer complexes.¹³

All these results seem to indicate the necessity of investigate systematically the factors that determine whether a system will form complex structures at the interface. In this context, zwitterionic surfactants such as carboxybetaines provide an excellent opportunity to study the effect of the charge on the structure and properties of mixed polymer–surfactant monolayers, because the hydrophilic polar heads carry both a negative and positive charge. In addition, betaines are widely used as boosters because stabilize foams against the antifoaming action of the oil droplets contained in commercial hair conditioners or shampoos.¹⁷ Moreover these surfactants reduce the irritation action of the surfactants on the eye and skin;¹⁸ therefore they are preferred to ionic surfactants, which have more adverse effects. In these applications zwitterionic surfactants are often mixed with polymers; however, there is little information about mixed monolayers containing polyelectrolytes and zwitterionic surfactants.

The present work is an attempt to contribute to the understanding the role of the electrical charge on the properties of mixed polymer surfactant monolayers; therefore we have studied the equilibrium and dynamic properties of monolayers formed by sodium PSS molecules and zwitterionic surfactants of different dipole strength. Carboxybetaines with different distances between the charged groups and two molecular weights of sodium PSS at 70 and 1000 kDa were chosen. The remaining sections of the paper are organized as follows: the next section contains experimental details and description of methodologies and techniques. In the following section, results and discussion, we use the equilibrium surface tension and fluorescence probing to obtain the critical aggregation concentration (cac) of mixed polymer surfactant aggregates. The polymer–surfactant isotherms along to dynamic surface tension of mixtures allow us to study the existence of surface interaction between betaines and PSS polymers. This section also contains the rheological properties of surfactant/polymers films, studied by surface

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quasielastic light scattering, SQLS. Finally, the main conclusions are presented.

Experimental

Chemicals. The surfactants *N-N*-dimethyl-*N*-dodecyl-*N*-propane ammonium carboxylate and *N-N*-dimethyl-*N*-dodecyl-*N*-pentane ammonium carboxylate, C3 and C5 hereafter, contain different numbers of methylene groups between their charged groups. The carboxybetaines are synthesized according to a method previously described in the literature.^{19,20}

PSS fractions were used as received from Aldrich. The molecular weights provided by the manufacturer are 70 (PSSk70) and 1000 kDa (PSSk1000). We have used dilute polymer concentrations in order to avoid the adsorption of PSS.²¹ The fluorescent probe, pyrene-1-carboxyaldehyde (PyCHO, $M_r = 230.97$), was high-performance liquid chromatography grade, from Fluka. All the materials are stored at vacuum and out of the scope of light, to avoid their hydration and photo-degradation.

The water was purified with a combination of RIOs and Milli-Q systems from Millipore. This water was also employed to prepare the solutions and to clean the glassware.

The polymer solutions were prepared by direct weight and then dissolved in a surfactant solution of a given concentration. Incorporation of PyCHO into micelles was as follows: an appropriate volume solution of PyCHO, dissolved in methanol, was poured into a volumetric flask, and the solvent was evaporated. The solutions of pure surfactants or polymer-surfactant mixtures were added to the evaporated residue, and the solution was stirred until the fluorescence probe was solubilized. The fluorescent probe concentration was kept constant at 1.5 μM .

Surface Tension Measurements. The measurements of the equilibrium surface tension were carried out with a drop tensiometer model TVT-1 from Lauda²² using the standard method. The best conditions to ensure the correct determination of the equilibrium surface tension values have been chosen using criteria published elsewhere.^{20,23} 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 model MPT-2 from Lauda.²⁴

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, respectively.

SQLS Experiments. We have used a homemade setup, which has been described in detail elsewhere.²⁵ The spectrometer has been calibrated using the air/liquid interface of liquids such as ethanol, ethyl ether, and water, and the wave vectors used in the range $100 < q \text{ (cm}^{-1}\text{)} < 500$ were obtained by a calibration with the air/water interface.

Since measurements are carried out in soluble monolayers, the surface pressure was continuously measured by means of a Pt Wilhelmy plate attached to an electrobalance until the equilibrium value was reached, and then the SQLS experiment was performed. Even though the adsorption of pure surfactant and mixtures is relatively faster as will be seen below, times ranging from 1 to 3 h were allowed to guarantee the monolayer equilibration. The experiments were carried out at 25 °C.

The calculation of the elasticity ϵ and the dilational viscosity κ from the SQLS spectra were done by a nonlinear fitting²⁶ to the convolution of the theoretical spectrum $P(\omega)$ with the experimental instrumental function²⁷

$$P(\omega) = -\frac{k_B T}{\pi\omega} \text{Im} \left(\frac{i\omega\eta(q+m) + \tilde{\epsilon}q^2}{D(\omega)} \right) \quad (1)$$

with

$$D(\omega) \equiv [\tilde{\epsilon}q^2 + i\omega\eta(q+m)][\gamma q^2 + i\omega\eta(q+m) + g\rho - \omega^2\rho/q] - [i\omega\eta(q-m)^2] = 0 \quad (2)$$

where η and ρ are the viscosity and the density of the subphase, respectively. The capillary penetration length m is given by: $m^2 = q^2 + i\omega\rho/\eta$ for $\text{Re}(m) > 0$.

Steady-State Fluorescence Measurements. The emission spectra of PyCHO incorporated to polymer-surfactant micelles were recorded with the LS-50B spectrofluorometer from Perkin-Elmer. The excitation wavelength was 400 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. All spectra were recorded at 25 °C.

Results and Discussion

Surfactant-Polymer Mixtures in Bulk. The zwitterionic surfactants used in this work form soluble monolayers at the air-water interface (Gibbs monolayers). In this kind of monolayer, the adsorbed molecules at the interface are in dynamic equilibrium with the molecules in solution, therefore to give a correct interpretation of the processes taking place at the interface it is necessary to know the aggregation state of the surfactant-polymer mixture. With this objective in mind we studied the interaction between carboxybetaines and the polyelectrolyte PSS by determining the critical micelle concentration (cmc) in the absence and presence of polymer. Two different techniques, bulk and interfacial, are used to determine the cmc values, fluorescence probing, and surface tension measurements. Comparison between the critical concentration values obtained by these two procedures provides additional information about complexes formation in bulk or at the surface or simultaneously in both surface and solution.

Fluorescence probing have been widely used to determine the cmc of micelles, in this work we choose PyCHO because the fluorescence of this probe strongly depends on solvent polarity, with a λ_{max} , which has a linear variation with the solvent dielectric constant.²⁸ Thus, when the probe is dissolved in water, at a surfactant concentration below the cmc, the fluorescence maximum is centered around 470 nm, whereas above the cmc the maximum position is blue-shifted, indicating that the probe is displaced to a more hydrophobic environment, the micellar interface.^{29,30}

For comparative purposes Figure 1 shows the results obtained for fluorescence and surface tension measurements. The figure also presents the results corresponding to pure surfactant solutions. In the absence of polyelectrolyte, the λ_{max} curve presents the expected behavior for a pure micellar system, and the cmc estimated from the break point in the resulting curve is in excellent agreement with the one obtained by surface tension.²⁰ In systems containing PSS and surfactant molecules, the curves show two break points, corresponding to the classical behavior of strongly interacting polymer-surfactant mixtures initially described by Jones³¹ with two break points at surfactant concentrations corresponding to the onset of micellar aggregation on the polymer,³² cac, and to the concentration at which free micelles form, cmc. The cac values found for different polymer concentrations are practically independent of both polymer concentration and molecular weight. In contrast, the cmc linearly increases with the polymer concentration. Taking

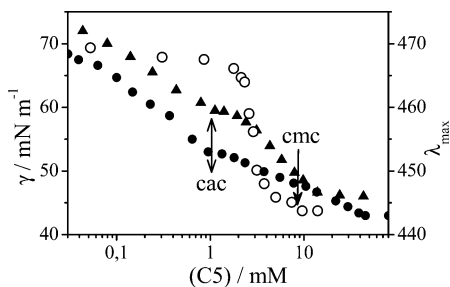


Figure 1. Variation of the position of the fluorescence maximum of PyCHO with the surfactant concentration for: (open circles) C5 surfactant and (circles) mixtures of C5 with 0.1% of PSSk1000. The figure also shows surfactant concentration dependence of the surface tension for the surfactant C5 (triangles). The results were obtained at 25 °C.

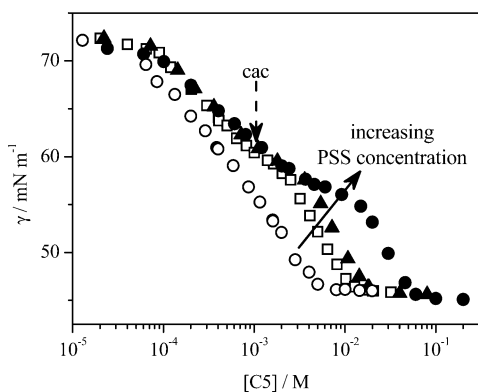


Figure 2. Adsorption isotherms for C5 surfactant at different polymer concentrations: (open circles) without polymer, (squares) with 0.1% PSSk70, (triangles) with 0.2% PSS, and (circles) with 1.0% PSSk70. All the results were obtained at 25 °C.

into account that the cmc corresponds to the polymer saturation and to the formation of pure surfactant micelles in bulk, from the cmc dependence on polymer concentration, it is possible to obtain the surfactant molecules/polymer repeat unit ratio;³³ the value found for these mixtures is close to 1.

It is important to notice that the cac and cmc values obtained for both fluorescence and equilibrium surface tension measurements are the same within the experimental error. This fact seems to indicate that the surface tension isotherms do not detect any additional process at the interface, such as the formation of surfactant–polymer complexes at the air–water interface. This behavior is observed in all mixtures studied in this work.

Surfactant–Polymer Mixtures Adsorbed at the Air–Water Interface. We also analyze the polymer concentration dependence of the equilibrium surface tension values. Figure 2 shows the surface tension isotherms for the betaine C5 without and with different PSSk70 concentrations. Similar behavior was found for the rest of mixtures. As it can be seen in the figure, the equilibrium surface tension increases on increasing PSS concentration. This tendency is more pronounced at surfactant concentrations higher than cac and was elsewhere observed in mixtures of PSS with the sulfobetaine dodecyl dimethyl propane sulfonate.³⁴

The behavior observed in our systems is opposite than the most usually found in the literature for polyelectrolytes and surfactants with opposite charge, in which the equilibrium surface tension decreases as the polymer concentration increases.^{9,11,12,35} In our systems one could interpret this opposite behavior by considering that, if the polymer and the zwitterionic surfactant strongly interact in bulk, the complexes in solution decrease the free surfactant monomer and consequently the

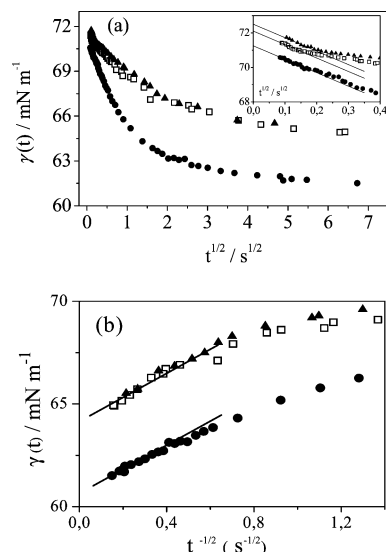


Figure 3. Dynamic surface tensions of with 2.01×10^{-4} M C5 against (a) the square root of time and (b) the inverse square root of time for solutions containing: (circles) no polymer, (squares) with 0.1% PSSk70, and (triangles) with 0.1% PSSk1000. The lines are calculated according to the diffusion-controlled adsorption model using the parameters obtained elsewhere; see text.

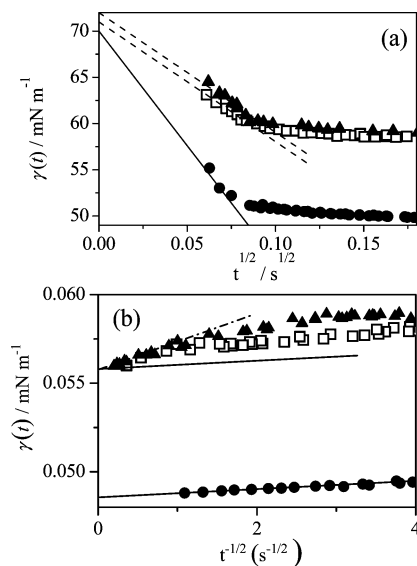


Figure 4. Variation of the dynamic surface tension with the square root of time for solutions of C5 3.041×10^{-3} M: (circles) without polymer, (squares) with 0.1% PSSk70, and (triangles) with 0.1% PSSk1000. The solid lines are calculated according to the eqs 3a and 3b and parameters obtained in a previous work; see text. Dotted lines are only a guide to the eyes.

surface tension increases. In this hypothesis neither the polymer nor the polymer–surfactant molecules adsorb at the interface. Another interpretation could be that the equilibrium surface tension is not reached because the adsorption of free PSS or the surfactant–PSS complexes is very slow.²¹ In order to check this point we have obtained the dynamic surface tension of the surfactant solutions without and with polymers. To illustrate these results, Figures 3 shows the dynamic surface tension values of the C5 surfactant solution without polymer and with 0.1% of PSSk70 and 0.1% of PSSk100, respectively. The surfactant concentration was kept constant in a value below the cac. In addition, Figure 4 shows the dynamic surface tension curves of C5 without and with 0.1% of PSSk70 and 0.1% of PSSk1000, respectively. In the latter the surfactant concentration ($3.041 \times$

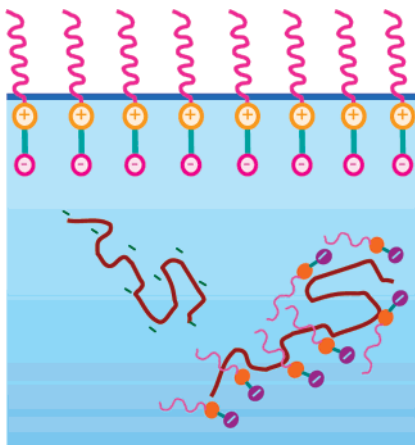


Figure 5. Possible structure of a monolayer formed in mixed solutions containing carboxybetaines and PSS. The zwitterionic monolayer structure has been proposed by Mulqueen (ref 35).

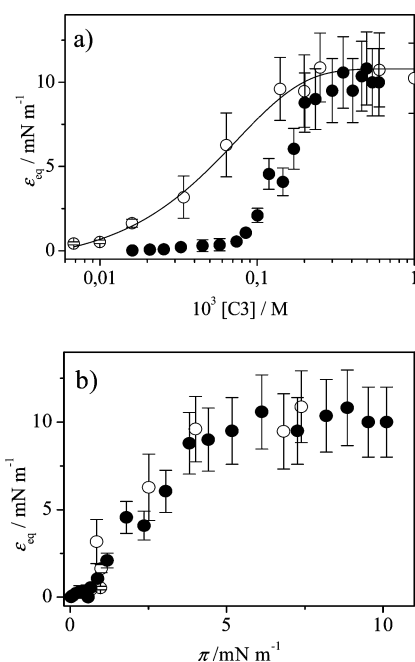


Figure 6. (a) Variation of the equilibrium Gibbs elasticity with surfactant concentration for the carboxybetaine C3: (open circles) without PSS and (circles) with 0.1% PSSk70. The line is a help to the eye. (b) Variation of the equilibrium elasticity with surface pressure for C3 betaine: (open circles) without polymer and (circles) with 0.1% PSSk70. All the results were obtained at 25 °C.

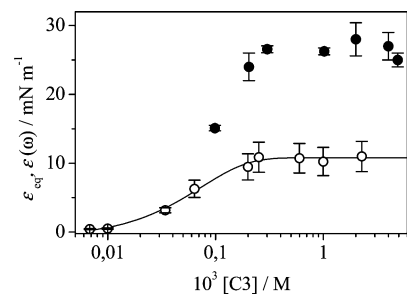


Figure 7. Comparison between the equilibrium (open circles) and dynamic elasticity values (circles) for C3. The line is only a guide to the eyes.

10^{-3} M) remains constant in a value above the cac. The results in figures were obtained using both the maximum bubble pressure tensiometer and the drop tensiometer. The dynamic surface tension values at $t \rightarrow \infty$, equilibrium surface tension,

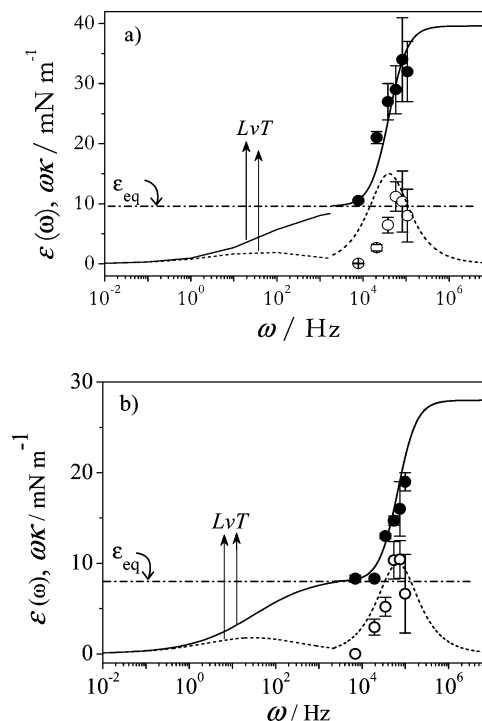


Figure 8. Frequency dependence of both the dynamic elasticity (circles) and viscosity values (open circles) for: (a) C3 (0.2 mM) and (b) mixtures of C3 (0.2 mM) with 0.1% PSSk1000. Gray lines are calculated using the Lucassen model, eqs 4 and 5, and the black lines correspond to values calculated from the Maxwell model, eqs 6 and 7, with parameters presented in the Table 1. The elasticity values are always represented by solid lines, while the viscosity values correspond to the dashed lines.

obtained by both are in excellent agreement. The equilibrium surface tension values also agree with the values found with the Pt Wilhelmy plate used in SQLS measurements. This fact allows us to confirm that the monolayers are equilibrated within the adsorption times available with these tensiometers. On the other hand, the surface tension at $t \approx 0$, surface tension of the aqueous polymer solutions, weakly increases with the polymer concentration and with the polymer molecular weight. This is due to the free Na^+ concentration left by PSS molecules.²¹

To interpret the dynamic results we consider that the kinetics of adsorption of carboxybetaines is a diffusion-controlled process.²⁰ According to this model the Ward and Tordai equation was obtained to relate the excess surface concentration with time; however because this equation cannot be solved analytically the asymptotic solutions have to be employed at long and at short times.³⁶ For zwitterionic surfactants these equations are

$$\gamma(t)_{t \rightarrow 0} = \gamma_0 - 2CRT \sqrt{Dt/\pi} \quad (3a)$$

$$\gamma(t)_{t \rightarrow \infty} = \gamma_{\text{eq}} - RT \frac{\Gamma^2}{C} \sqrt{\pi/4Dt} \quad (3b)$$

In the equations Γ represents the maximum excess surface concentration and γ_0 and γ_{eq} are the equilibrium surface tension of solvent and solution, respectively. D is the diffusion coefficient of the surfactant monomer, and C is the bulk surfactant concentration. From eqs 3a and 3b and the Γ and D values obtained for pure carboxybetaines,²⁰ we calculate the $\gamma(t)$ values considering that in the mixtures with PSS the only adsorbed specie is the surfactant monomer. The values are represented in Figures 3 and 4 as solid lines. As can be seen in the Figure 3, when the surfactant concentration is below the

TABLE 1: Parameter Values Estimated from the LvT Model, Eqs 2 and 3, and Parameters Obtained by Fitting of the Experimental Data to Maxwell Model, Eqs 4 and 5

system	LvT		Maxwell			
	ω_D/Hz	$\epsilon_{\infty}/\text{mN m}^{-1}$	$\epsilon_0/\text{mN m}^{-1}$	$\epsilon_{\infty}/\text{mN m}^{-1}$	$\tau/\mu\text{s}$	$\epsilon_{\text{eq}}/\text{mN m}^{-1}$
C3	25 ± 4	9.5 ± 0.4	9.6 ± 0.6	30 ± 2	19 ± 6	9 ± 2
C3–0.1% PSSk70	9 ± 3	7.8 ± 0.2	8.2 ± 0.4	39 ± 8	10 ± 5	8 ± 2
C3–0.1% PSSk1000	15 ± 6	8.0 ± 0.4	8.1 ± 0.3	22 ± 5	15 ± 8	9 ± 1
C5	22 ± 8	10.2 ± 0.4	10.4 ± 0.5	40 ± 9	22 ± 7	9 ± 1
C5–0.1% PSSk70	17 ± 6	7.3 ± 0.4	7.1 ± 0.2	25 ± 6	21 ± 9	8 ± 1
C5–0.1% PSSk1000	22 ± 6	9.1 ± 0.3	9.3 ± 0.6	36 ± 8	12 ± 8	8 ± 2

cac, the experimental $\gamma(t)$ values at long and short times agree very well with the calculated ones. This fact indicates that below the cac there are no surfactant–polymer complex molecules in bulk; consequently the monolayer is exclusively formed by the monomer surfactant molecules. In addition the adsorption process is a diffusion-controlled process.

Parts a and b of Figure 4 show the linear dependence of $\gamma(t)$ with $t^{1/2}$ and with $t^{-1/2}$ predicted by eqs 3a and 3b. This indicates that, at surfactant concentration above the cac, the adsorption is also controlled by diffusion. However, the experimental and calculated $\gamma(t)$ values are in disagreement when the solution contains mixtures of polymer and surfactant molecules. In these cases the slopes corresponding at the short times asymptotic solution are lower in mixtures than in the pure surfactant solution. Simultaneously, the slopes corresponding to the long times asymptotic solution are higher in the mixtures than in pure surfactant solutions. All these facts are compatible with the decrease of free monomer surfactant molecules due to the formation of a no surface-active surfactant–polymer complex in bulk.

The fluorescence and surface tension results seem to indicate that the interface of mixtures of carboxybetaines and PSS polymers is exclusively formed by surfactant molecules. This fact can be explained attending at the nature of zwitterionic surfactant monolayers. According to the model proposed by Mulqueen,³⁷ the monolayer of zwitterionic surfactant such as carboxybetaines lead their negative charged group toward to the inner of solution, Figure 5; consequently, because the polymer molecules and polymer–surfactant complexes are negatively charged, they are strongly repelled by the surfactant monolayer and remain dissolved.

Surface tension measurements are often no sensitive to changes in the monolayer structure. However the rheological properties of monolayers detect surface association or reorganization processes that cannot be studied by surface tension measurements.^{38,39} On the other hand, the knowledge of the surface rheology plays an important role from the point of view of applications since the viscoelasticity is a key factor in emulsion and foam stabilization.^{39–41} Therefore, we decide to study the surface rheology of these monolayers using SQLS. We choose SQLS to study the rheology of soluble monolayers because the frequencies used in the technique are very high and the diffusional exchange with bulk it is expected to be fully relaxed.⁴²

Surface Rheology. Previously, to obtain the dynamic rheological properties of monolayers, we have obtained the equilibrium Gibbs elasticity from the isotherms:³⁸ $\epsilon_{\text{eq}} = -\partial \gamma / \partial \ln \Gamma$. Such values of the equilibrium elasticity correspond to a state of the adsorption layer in which both, the diffusive exchange with bulk and the structural rearrangement within monolayer are relaxed.

Figure 6a presents the ϵ_{eq} values obtained for C3 surfactant without polymer and with 0.1% of PSSk70, similar results are obtained with the rest of mixtures.

As can be seen in Figure 6a, the equilibrium elasticity increases as the surfactant concentration increases and reaches a constant value at a surfactant concentration smaller than the cmc of pure surfactant. This fact was observed for monolayers of pure surfactants, and it seems to indicate that the monolayer saturates at surfactant concentrations below the cmc.^{43,44}

On the other hand the equilibrium elasticity values of mixtures are always smaller than the values for pure surfactant monolayers; this is consistent with the formation of a complex in bulk responsible of the decrease of surfactant available to adsorption in monolayer. Accordingly, it is preferred to compare the equilibrium elasticity of similar states without and with polymer; therefore we represent in Figure 6b the elasticity ϵ_{eq} vs surface pressure in systems with and without polymer. The figure shows that the equilibrium elasticity of the monolayers formed from the adsorption of pure surfactant solution and from the polymer–surfactant mixtures are in excellent agreement for states of the same surface pressure. This confirms that the monolayers formed in solutions with PSS and carboxybetaines are exclusively formed with surfactant molecules.

We have calculated the dilational frequency for the constitutive parameters (γ , ϵ , and κ) that best fit the experimental SQLS spectra,^{26,45} eqs 1 and 2. The dilational elasticity of monolayers is higher than the equilibrium elasticity in all systems studied in the work. These differences are indicative of viscoelastic monolayers.³⁸ To illustrate the behavior in Figure 7 are represented both the equilibrium and dilational elasticity values for pure C3 betaine at different surfactant concentrations; the dynamic values are obtained at a wave vector $q = 268.8 \text{ cm}^{-1}$. Despite the fact that the dilational viscosity values at this frequency are noisy, there is no doubt that they are much smaller than the dilational elasticity, $\omega\kappa = 1.5 \pm 0.5 \text{ mN/m}$, which means that the monolayers are essentially elastic films.

The frequency dependence of the dilational elasticity points out the existence of, at least, a fast relaxation process in the monolayer. To obtain information of the origin of this process, we study the variation of dilational elasticity and viscosity with the frequency using SQLS. Figure 8 shows the frequency dependence of both dilational elasticity and viscosity for monolayers of pure C3 surfactant, Figure 8a, and for the C3 carboxybetaine with 0.1% PSSk1000 monolayer. Similar behavior is observed for the rests of systems studied.

In soluble monolayers the frequency dependence of the elasticity has been well described by the diffusive control model of Lucassen–van den Tempel⁴⁶ (LvT). This model considers that surface viscoelasticity is due to the interchange of surfactant monomers between the interface and the bulk, which leads to the following equations for the dilational viscoelasticity, $\epsilon = \epsilon(\omega) + i\omega\kappa$

$$\epsilon(\omega) = \epsilon_{\infty} \frac{1 + \Omega}{1 + 2\Omega + 2\Omega^2} \quad (4)$$

$$\omega\kappa = \epsilon_{\infty} \frac{\Omega}{1 + 2\Omega + 2\Omega^2} \quad (5)$$

with $\Omega = \sqrt{\omega_D/\omega}$ where $\omega_D = D/2(\partial C/\partial \Gamma)^2$ and $\epsilon_{\infty} = \Gamma(\partial \pi/\partial \Gamma)$.

In these equations, ϵ_{∞} is the elasticity at high-frequency limit; Γ , is the surface excess concentration; π , the surface pressure; ω_D , the frequency of diffusion process; D , the diffusion coefficient; and C , the bulk surfactant concentration.

However, its predictions for both $\epsilon(\omega)$ and $\omega\kappa$ do not coincide with the experimental data. The gray lines in Figure 8 represent the $\epsilon(\omega)$ and $\omega\kappa$ values calculated from eqs 4 and 5 using the diffusion coefficients obtained previously²⁰ and the Langmuir equation to calculate²⁰ ϵ_0 and $\partial C/\partial \Gamma$. As can be seen in the figure, this model does not interpret properly the experimental results, because the frequency employed in dynamic surface light scattering is much higher than ω_D ; consequently to study the diffusion process by rheological techniques it would be necessary to have experimental data in the intermediate frequency region (10 Hz–1 kHz).

We fit our experimental results to the Maxwell rheological model.⁴⁷ According to the model, the frequency dependence of the dilational elasticity and viscosity is given by

$$\epsilon(\omega) = \epsilon_0 + \epsilon_{\infty} \frac{(\omega\tau)^2}{1 + (\omega\tau)^2} \quad (6)$$

$$\omega\kappa = \epsilon_{\infty} \frac{\omega\tau}{1 + (\omega\tau)^2} \quad (7)$$

In these equations, ϵ_0 represents the equilibrium elasticity value; ϵ_{∞} , is the amplitude of relaxation and τ its characteristic time.

In Figure 8, the elasticity and viscosity at different frequencies calculated with eqs 6 and 7 and the parameters of Table 1, obtained from the fit of the experimental data to eqs 6 and 7, are also represented. Comparison of experimental and calculated values demonstrates that the frequency dependence is consistent with the Maxwell rheological model. A similar tendency is followed by the rest of studied systems.

The parameters obtained from the fit procedure are collected in Table 1. The table also contains the parameters corresponding to the LvT predictions. From the values presented in Table 1 and in the Figure 8 one can see that the ϵ_{∞} and ϵ_0 values and the equilibrium elasticity are the same, within experimental error. This seems to indicate no additional process in the range of frequency between 1 and 10 kHz.

On the other hand, neither the relaxation time nor the ϵ_{∞} Maxwell parameters changes with polymer addition. This fact confirms that the monolayers formed from the adsorption of betaine–PSS mixtures are exclusively formed by surfactant molecules.

Finally, the value of relaxation time ($\tau \approx 10 \mu\text{s}$) is in the order of magnitude to that related to the molecular reorientation⁴² observed elsewhere in surfactant monolayers.^{48,49}

Conclusions

Florescence probing and surface tension measurements show strong interactions between carboxybetaine surfactants and PSS polymer resulting in the formation of the complexes in bulk. The complex (1:1) is the electrostatic origin and determines the properties of the monolayers adsorbed at the interface air–water. Thus the complex formation in bulk decreases the free surfactant concentration and consequently decreases the surface concentration of surfactant. Dynamic surface tension measurements and

the rheological properties of monolayers formed by the adsorption of molecules from the bulk to the interface demonstrate that neither the polymer nor the polymer–surfactant complex molecules are adsorbed at the interface. To the best of our knowledge, this is the first report of this behavior, and it can be explained by considering the structure of monolayers of zwitterionic surfactants.

Finally, the behavior of the dilational elasticity and viscosity can be explained by relaxation probably involving molecular reorientation within the adsorbed layer, with a relaxation time of 10 μs .

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