

# Equilibrium Behavior and Dilational Rheology of Polyelectrolyte/Insoluble Surfactant Adsorption Films: Didodecyldimethylammonium Bromide and Sodium Poly(styrenesulfonate)

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The surface pressure of monolayers of an insoluble surfactant, didodecyldimethylammonium bromide (DODAB), has been measured onto subphases with different concentrations of poly(styrenesulfonate) (PSS) and at different temperatures. The presence of PSS in the subphase shifts the surface-pressure ( $\Pi$ ) curves to larger areas per DODAB molecule,  $A$ , and shifts the surface phase transition to higher  $\Pi$ 's. The presence of PSS chains decreases the surface electric potential; the decrease is higher than expected from the formation of a double layer between the DODAB molecules and the PSS segments. Increasing the temperature shifts the surface-pressure curves to higher areas and also increases the values of  $\Pi$  of the surface phase transition. The effect of the PSS chains on the  $\Pi$  versus  $A$  curves is contrary to the one induced by the presence of inert electrolytes in the subphase. The behavior is consistent with the existence of a dense layer of PSS segments beneath the DODAB monolayer at low PSS concentrations,  $c$ . Two PSS layers exist at higher concentrations, a dense layer immediately below the DODAB and a less-dense layer, below the first one, that protrudes deep into the subphase. The surface-pressure relaxation curves have been found to be bimodal through the whole range of surface pressures and at all the values of polymer concentration studied. These results point out that the adsorption layers behave mainly as elastic bodies, with zero-frequency elasticity,  $\epsilon(\omega = 0)$ , which agrees with the equilibrium compressibility modulus. The increase [ $\epsilon(\omega = 1) - \epsilon(\omega = 0)$ ] has been found to be independent of both polymer concentration and molecular weight. The zero-frequency-dilational viscosity,  $\kappa(\omega = 0)$ , strongly increases with  $\Pi$  in the two-dimensional condensed-liquid region. The surface viscosity strongly decreases with increasing frequency; the decreasing rate is higher than the one found for the monolayers of nonionic insoluble polymers.  $\kappa(\omega = 0)$  has also been found to be independent of both polymer concentration and molecular weight. These results seem to indicate that it is the film formed by the DODAB molecules and the first dense polymer layer that determines the surface viscoelastic moduli of this system.

## Introduction

The adsorption characteristics of charged polymers are the determinants that control processes such as flocculation, colloid stabilization, or fabrication of multilayer films and coating, as well as tune the specific properties of many products that rely on the stability of suspensions and emulsions and on the ability to change the surface properties by adsorption.<sup>1</sup> In general, the applications are based either on attaching charged chains to a solid surface or on locating them at a liquid/liquid or liquid/air interface. Monolayers of insoluble amphiphiles at the air/water interface are suitable model systems to study interfaces. They allow one to study the interaction of soluble polyelectrolytes with oppositely charged surfaces. The adsorption of polyelectrolytes on such model surfaces results in changes to the monolayer structure and properties.

The surface-tension isotherms are different for aqueous solutions of nonionic polymers and synthetic polyelectrolytes. While in the former case the surface tension deviates from the

value of pure water even at concentrations less than 0.0001 wt %, the surface tension of polyelectrolyte solutions begins to decrease only at relatively high concentrations when the ionic strength is high enough and the lateral repulsion of charged groups is screened to a great extent.<sup>2–4</sup>

Neutron and X-ray reflectivity studies on poly(styrene-sulfonate) (PSS) solutions, concentrated enough to be surface-active, have pointed out that the segment profile is rather sensitive to the polymer concentration and to the ionic strength of the solution. In the case of dilute solutions, the polymer forms a dense surface layer in which the PSS segments lie at the air/liquid surface with the low-surface-energy backbone exposed to the air and the sulfonate groups are submerged into the liquid in such a way that the counterions lie about 1.2 nm deep.<sup>9</sup> The discontinuity of the dielectric constant induces an enhanced Coulomb interaction that increases counterion condensation.<sup>5</sup> As the polymer concentration is increased (or the concentration of an inert electrolyte is increased), the segment profile becomes the bilayer type with a second layer of a much lower segment concentration that extends well into the subphase. This type of profile is at odds with the predictions of the self-consistent theory.<sup>6</sup> The data also point out that there is no correlation

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between the surface tension,  $\gamma$ , and the surface concentration,  $\Gamma$ , of the polymer.<sup>7</sup>

In the case of polyelectrolytes adsorbed on a surface of opposite charge, the adsorbed layers can be thin with the chains lying flat on the surface or they can be more fluffy with the chains forming loops and dangling ends between adsorption trains in a "pseudo-brush" configuration. Which conformation is favored depends mostly on the charge fraction of the polymer and the surface charge of the substrate.<sup>8</sup> A two-layer profile has been used to fit the X-ray reflectivity data for the PSS chains adsorbed on an insoluble monolayer of didodecylmethylammonium bromide (DODAB) in the presence of an inert electrolyte. A high monomer density layer is located immediately beneath the DODAB monolayer, and a second less-dense layer is located below the previous layer, which extends toward the bulk. It must be remarked that there is a high degree of charge overcompensation in the first layer (1.2–6 monomers/DODAB molecule).<sup>9</sup> A complex, gel-like, interfacial structure has been also proposed by Noskov et al. for polyelectrolyte/soluble surfactant adsorption films at high concentrations when polymer aggregates are present in the bulk solution.<sup>10</sup>

Another peculiarity of adsorbed polyelectrolyte films is a very slow adsorption kinetics.<sup>8,11,12</sup> This is frequently explained in terms of electrostatic and steric barriers.

It must be remarked that both the reflectivity and the adsorption-kinetics experiments have been carried out at relatively high polyelectrolyte concentrations, where the polyelectrolyte is already surface-active. At very low polymer concentrations, PSS does not adsorb at the air–water surface, except for very low molecular weights.<sup>3</sup> Of course, the situation is different when the polymer is mixed with a soluble surfactant of opposite charge<sup>10</sup> or when the surface is covered with a monolayer of insoluble surfactant of opposite charge.<sup>9</sup> The presence of a monolayer of positively charged surfactants attracts the PSS chains to the surface even at very low polymer concentrations. Ahrens et al.<sup>9</sup> have studied X-ray reflectometry of the DODAB + PSS system at relatively high polymer concentrations and variable salt concentrations; the experiments were carried out at a fixed temperature of 293 K. In this work, we carry out a detailed study of the equilibrium and rheology of the DODAB + PSS films in the low-PSS concentration range, where no adsorption of PSS takes place in the absence of DODAB. Two molecular weights of PSS are studied. The experiments will be carried out at four different temperatures over the whole  $\Gamma$  range and for different PSS concentrations.

## Experimental Section

The DODAB was purchased from Aldrich (Germany) and recrystallized three times from acetone. Two PSS samples of molecular weights  $M_w = 70$  and 1000 kDa, respectively, were purchased from Aldrich (Germany). The PSS samples were dialyzed against pure water, although no significant differences were found with respect to the samples used as received. The KCl and NaBr were purchased from Aldrich (Germany) and were extensively dried under a vacuum prior to use. Deionized water from a Milli-Q system was used. The solutions were prepared by weight on an analytical balance that was precise to  $\pm 0.01$  mg. The surface tension of the PSS solutions was measured with a pendant-drop tensiometer with axisymmetric drop-shape analysis. The drops were formed in a closed-thermostated chamber, and the measurements were carried out over a period of 4 days. This experiment showed that the surface tension remained equal to the value of pure water and that no PSS adsorption takes place for the concentrations studied.

Two computer-controlled Langmuir balances were used to study the surface-pressure ( $\Pi$ ) curves versus the surface-concentration ( $\Gamma$ ) curves: a KSV mini-trough (Finland) and a BAM-750 trough from Nima (U.K.). The surface pressure was measured with a Pt plate connected to the microbalances. The temperature control of the subphase in the troughs was carried out by flowing thermostated water through jackets at the bottom of the troughs. The temperature near the surface was measured with a calibrated Pt-100 sensor. To confirm the stability of the monolayer, two different forms for preparing the monolayers were used. In the first one, the surface concentration was changed by subsequent additions of the DODAB solution (1 mg/mL in chloroform) on the liquid/air interface. The surface pressure was continuously monitored, and the equilibrium value was taken when the surface pressure ( $\Pi$ ) had remained constant for at least 10 min. In the second way, the monolayers were symmetrically compressed by moving two barriers under computer control after the spreading of the surfactant solution. The maximum barrier speed was 10 mm/min. The  $\Pi$  measurements were reproducible to  $\pm 0.05$  mN·m<sup>-1</sup>.

The surface electric potential  $\Delta V$  was measured simultaneously with the point-by-point  $\Pi$  measurements. A Kelvin probe from Trek, Inc. (U.K.), located approximately 2 mm above the aqueous surface, was used. The reference gold electrode was placed in the subphase. The surface-potential measurements were reproducible to  $\pm 20$  mV and are referenced to the value of  $\Delta V$  of the air/water interface.

The relaxation experiments were performed on the Langmuir trough by the step-compression method.<sup>13</sup> The barriers were moved after the desired surface concentration had been reached and the equilibrium value of  $\Pi$  had been obtained. In these experiments, the area change,  $\Delta A$ , was kept below 5% of the total area to ensure that the system remained in the linear regime. The time necessary to make the compression was slightly less than 2 s. Readings of  $\Pi$  at constant intervals of 1 s each were taken until the equilibrium- $\Pi$  value corresponding to the final area was reached. A relaxation curve was accepted only if the initial and final values of  $\Pi$  for a given compression were in agreement with the corresponding equilibrium  $\Pi$  versus  $\Gamma$  curve.

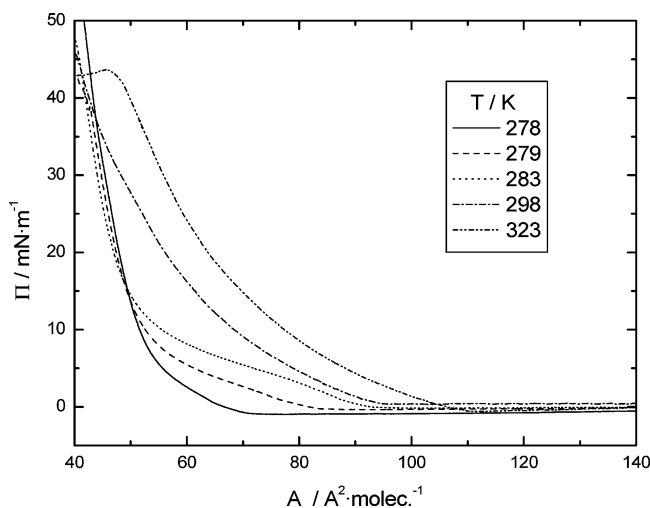
The Brewster angle microscopy (BAM) images were taken using an EP-3 imaging ellipsometer (Nanofilm, Germany) and a Nima trough.

All the solutions were made by weight using an analytical balance that was precise to  $\pm 0.01$  mg.

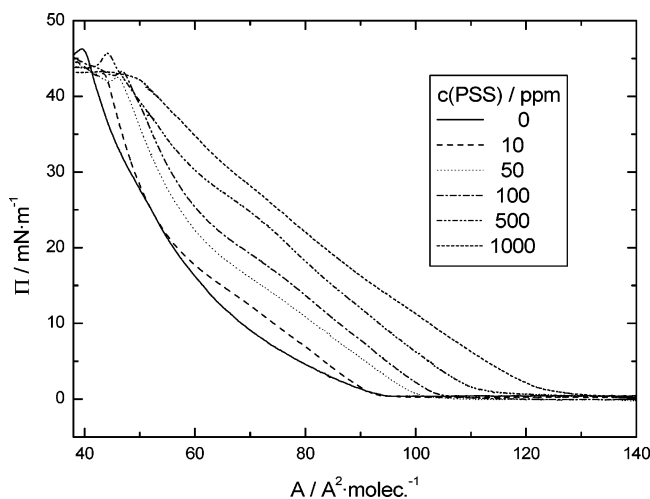
## Results

**Equilibrium Measurements.** Figure 1 shows the  $\Pi$  versus  $A$  curves for the monolayers of DODAB on pure water at different temperatures. The isotherms measured by the point-by-point method agree within the experimental error with those done by continuous compression. No differences were found for the isotherms measured by continuous compression at velocities in the 5–20 mm/min range. The hysteresis found on compression and expansion was below 1 mN·m<sup>-1</sup>, in agreement with the results of Ahrens et al.,<sup>9</sup> of Taylor et al.,<sup>14</sup> and of Kahn et al.<sup>15</sup> The increase in  $T$  reduces the size of the first-order transition and lowers the value of  $\Pi$  at the transition. At the lowest temperature, the isotherm is of the compressed type. The effect of  $T$  is qualitatively similar to that found in other monolayers that show phase transitions<sup>16</sup> and is similar to that reported by Taylor et al.<sup>14</sup> Moreover, decreasing  $T$  has a qualitative effect similar to that of adding salt to the subphase.<sup>9</sup>

Figure 2 shows the effect of adding PSS to the subphase at 298 K. It can be observed that the presence of polymer chains

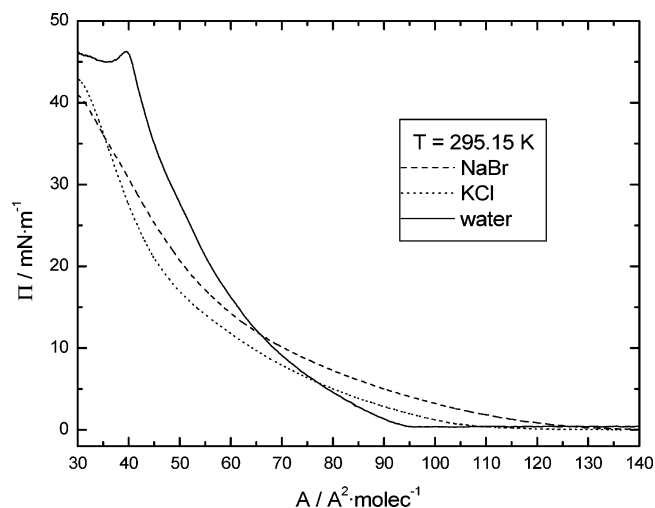


**Figure 1.** Surface-pressure curves for DODAB on pure water at different temperatures.

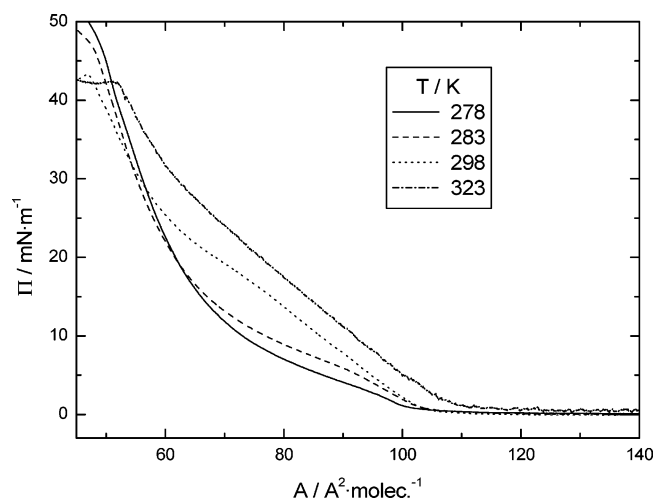


**Figure 2.** Effect of the concentration of PSS ( $M_w = 70$  kDa) on the  $\Pi$  vs  $A$  isotherms at 298 K.

increases the pressure at which the phase transition is observed and makes the isotherm more expanded. The effect of the polymer concentration in Figure 2 is also qualitatively similar to that reported by Noskov et al. for the adsorption layers of PSS and dodecyltrimethylammonium bromide.<sup>10</sup> It must be remarked that, for the polyelectrolyte concentration range studied, the PSS does not show any surface activity. It is important to demonstrate that the effect of the PSS on the  $\Pi$  versus  $A$  curves of DODAB is not due to the mere change of ionic strength of the subphase caused by the polyelectrolyte. Because a concentration of 1000 ppm is equivalent to a 0.4 mM concentration of sodium sulfonate groups, we have compared the  $\Pi$  versus  $A$  curves of DODAB on water and on subphases of 1 mM KCl or 1 mM NaBr at 298 K. Figure 3 clearly shows that the presence of NaBr shifts the isotherm to lower areas and that KCl has an even more pronounced effect. This behavior is the same as that already found by Taylor et al.<sup>14</sup> for dioctadecyldimethylammonium chloride (DODAC) and that reported by Ahrens et al.<sup>9</sup> for DODAB. In both cases, the shift toward lower areas increased with salt concentration. It must be taken into account that the actual concentration of free ions in high-molecular-weight polyelectrolytes (as well as in micelles) is lower than the nominal concentration of ionizable groups; hence, the actual value of the ionic strength of the PSS solution is lower than that of the 1 mM KCl solutions. Therefore,



**Figure 3.** Isotherms of DODAB on pure water and on 1 mM solutions of NaBr and KCl.

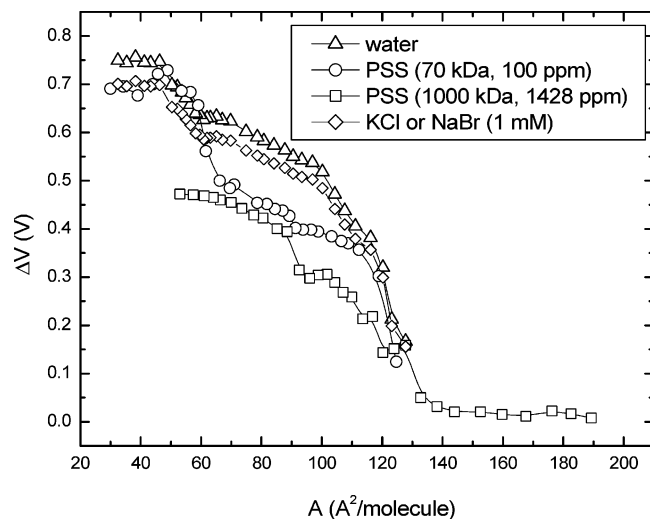


**Figure 4.** Effect of temperature on the isotherms of DODAB on PSS (70 kDa,  $c = 100$  ppm).

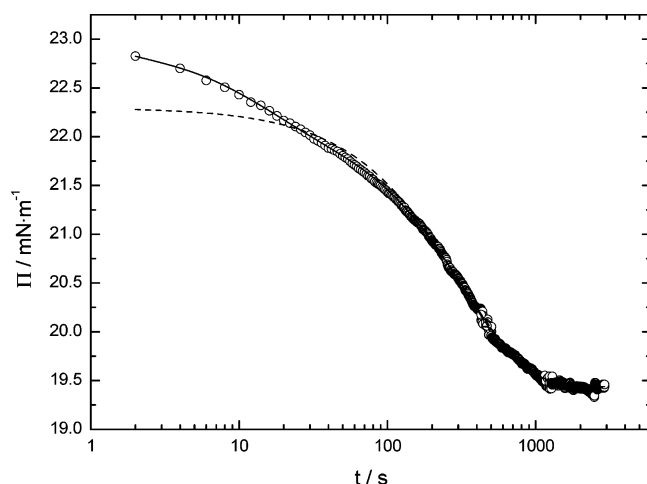
it must be concluded that the effect of PSS on the  $\Pi$  versus  $A$  isotherms of DODAB arises from the formation of complexes between DODAB molecules and the PSS chains that strongly modify the structure of the surface layer.

Figure 4 shows the effect of  $T$  on the surface layer corresponding to a polymer concentration of  $c = 100$  ppm of PSS ( $M_w = 70$  kDa). Similar effects were found for other concentrations of PSS. Increasing the molecular weight of PSS shifts the isotherm to higher areas for the same molar concentration of polymer, although it shifts the isotherms toward lower areas per DODAB molecule for the same segment concentration in the subphase.

Figure 5 shows the surface potential for the DODAB monolayer on pure water and on solutions of equal molar concentration of two PSS's with different molecular weights. The first point to notice is that  $\Delta V$  starts to increase at values of  $A$  for which  $\Pi \approx 0$ . Increasing the monomer density in the subphase reduces the surface potential with respect to the value of the DODAB monolayer on pure water, already, for very large values of area for which the surface pressure remains equal to that of the water surface. This behavior is consistent with the formation of a polymer–DODAB complex at the surface, which, at least for high polymer concentrations, leads to a charge overcompensation.<sup>9</sup>



**Figure 5.** Surface-potential curves for DODAB monolayers at 298 K on different subphases.



**Figure 6.** Relaxation curve after a step compression for DODAB monolayers at 298 K on a subphase of PSS (70 kDa,  $c = 100$  ppm). The dashed line corresponds to the best fit to a single-exponential decay, and the continuous line corresponds to the fit obtained considering two relaxation modes. The initial surface pressure corresponds to  $11.78 \text{ mN} \cdot \text{m}^{-1}$ .

The decrease of  $\Delta V$  in the presence of PSS is slightly larger than when the monolayer is formed on 1 mM solutions of KCl or NaBr (there is no difference in  $\Delta V$  between the two salts within our experimental precision). The value of  $\Delta V$  found for the condensed monolayer ( $A \approx 40 \text{ Å}^2 \cdot \text{molecule}^{-1}$ ) is close to that reported by Taylor et al.<sup>14</sup> for DODAC on KCl solutions.

**Rheology.** Figure 6 shows a typical relaxation curve after a step compression. Similar results were obtained for other  $\Gamma$ 's and other subphases (i.e., different molecular weights of PSS and polymer concentrations). The relaxation experiments have been carried out only at 298 K. It is clearly observed that the relaxation curves obtained in all the experiments cannot be described by a single-exponential decay. The relaxation spectra<sup>13</sup> point out that at least two dynamic processes are present in the DODAB–PSS surface layers. There are no relaxation experiments in the literature for comparable systems, and the limited frequency range of the oscillatory barrier results of Noskov et al.<sup>10</sup> for PSS + a soluble cationic surfactant do not allow the authors to discuss the existence of more than one relaxation.

It has to be stressed that no relaxation experiments can be carried out either on the DODAB monolayer on water or on the DODAB monolayer on salty solutions. In these cases, the

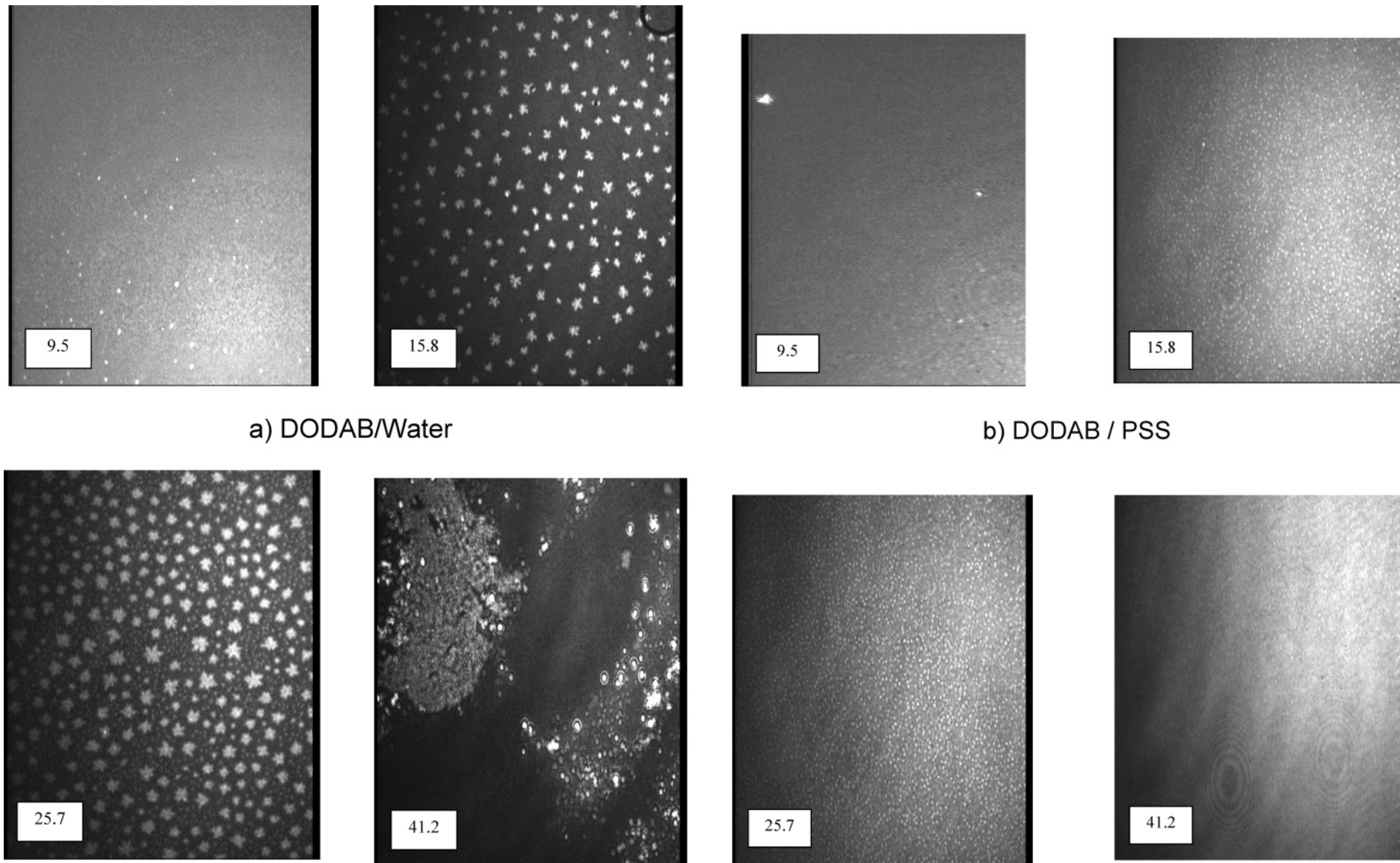
relaxation takes place in periods of time that are too short to be measured by the Wilhelmy plate technique. Therefore, any frequency-dependent viscoelastic modulus observed is due to the interaction between the DODAB molecules and the PSS chains.

## Discussion

**Equilibrium Properties.** DODAC and DODAB monolayers have been extensively studied in the literature, both as a function of the temperature and as a function of the salt concentration.<sup>14,15,17</sup> The surface pressure versus area curves present a liquid-expanded to liquid-condensed phase transition which is clearly visible above 295 K. The X-ray reflectivity data show that, in the condensed phase, the hydrophobic chains of the DODAB molecules form an angle of  $45^\circ$  with the normal to the surface. A thickness of about  $12 \text{ Å}$  is obtained in the region of  $60 \text{ Å}^2$  per molecule, which leads Ahrens et al. to suggest that, in the condensed phase, the DODAB molecules have a staggered-headgroup conformation with interweaved counterions.<sup>9</sup> However, the ellipsometric thickness of the monolayer increases in a continuous way from 12 to  $21 \text{ Å}$  as the area per molecule decreases from 120 to  $60 \text{ Å}^2$  without any significant change at the phase transition region.<sup>15</sup> These values differ significantly from those obtained using X-ray reflectivity. The surface-potential values (Figure 5) point out a strong increase between 140 and  $100 \text{ Å}^2$ , where the surface pressure remains null within the experimental uncertainty (see Figure 1). Between 100 and  $60 \text{ Å}^2$ ,  $\Delta V$  slightly increases, and finally there is a sharp increase up to the collapse of the monolayer. This behavior is qualitatively similar to the one described by Ahuja et al. for DODAC.<sup>17</sup> A simple calculation of the double-layer potential at  $60 \text{ Å}^2$  using the Gouy–Chapman model leads to a value of about 400 mV, which is smaller than the experimental value; similar conclusions were reached by Taylor et al. for DODAC.<sup>14</sup> However, the interpretation of the  $\Delta V$  decrease in the presence of an inert electrolyte in the subphase has to be taken with care as a result of the morphology of the surface film. In effect, Figure 7 shows Brewster angle images for the DODAB monolayer on water (similar images were on 1 mM KCl and 1 mM NaBr solutions). It can be observed that the monolayer is not homogeneous, even for values of  $\Pi$  well below the surface phase transition. Similar results were reported by Cuvillier et al.,<sup>18</sup> although they did not experience the change of shape of the aggregates from circular below the surface phase transition to starlike at higher surface pressures.

The effect of PSS on the DODAB monolayers is shown in Figure 2 for concentrations of polyelectrolyte ranging from 100 to 1000 ppm. In this concentration range, the PSS is not surface-active. Moreover, for the range of temperatures and concentrations studied in this work, the subphase remains below the overlapping concentration.<sup>19</sup> The presence of polymer chains in the subphase shifts the isotherms toward larger effective areas per DODAB molecule and makes the expanded-liquid to condensed-liquid transition more marked. This behavior is qualitatively similar to that which was reported by Ahrens et al.<sup>9</sup> Using X-ray reflectivity data, these authors have proposed that, at low polymer concentrations, the DODAB–PSS monolayer was formed by a thin layer of PSS (ca.  $10 \text{ Å}$  thick) below the DODAB monolayer. For large values of effective area per DODAB molecule the number of PSS monomers per DODAB molecule may be as high as six, thus, the charge overcompensation being rather large. The monomer coverage of this PSS layer is almost independent of  $\Pi$  for a given polymer concentration, with about  $44 \text{ Å}^2/\text{monomer}$ , although below  $60 \text{ Å}^2$ , the monomer





**Figure 7.** (a) BAM images of the DODAB monolayer on water for four different states. The surface pressure is indicated in each figure. (b) BAM images of the DODAB monolayer on a subphase of PSS (70 kDa,  $c = 100$  ppm). Notice that the inhomogeneities exist even for surface pressures below that of the phase transition.

density increases slightly. On compression, the constant negative chain charge of the PSS monolayer is progressively neutralized by DODAB instead of by the monovalent counterions. For high DODAB concentrations, the charge overcompensation rises to about 1.2. Beneath this first PSS layer there is a second more diffuse polymer layer. The thickness of this second layer decreases as the effective area per DODAB molecule increases. Ahrens et al.<sup>9</sup> argue that the hydrophobic forces are the reason for the constant PSS coverage in the layer immediately below the DODAB molecules. The increase of DODAB concentration increases the repulsion between the hydrophobic tails of the surfactant, thus, increasing  $\Pi$ . It must be pointed out that the behavior reported by Engelkin and Menzel<sup>11</sup> is different from that found in this work and in ref 9. In effect, these authors found that the presence of a small concentration of PSS produces a shift of the  $\Pi$  versus  $A$  curve toward lower effective areas per DODAB molecule, while the presence of carboxymethyl cellulose produces a shift in the opposite direction. Engelkin and Menzel explain the different behavior assuming that the chains of both polyelectrolytes have rather different distances between charges. This interpretation is not compatible with the existence of the layer of constant monomer density and the fact that PSS is a relatively flexible polyelectrolyte. Surprisingly, the increase of PSS concentration leads, in ref 11, to a shift of the  $\Pi$  versus  $A$  curves toward higher values of area as is found in the present work. This behavior may be explained in terms of the increase of the second diffuse polymer layer of PSS beneath the DODAB layer. Neutron and X-ray reflectivity lead to similar conclusions for the adsorption of PSS at the air/water interface at high PSS concentration.<sup>7</sup> It must be remarked that the effect of the PSS on the  $\Pi$  versus area curves found in this work and in ref 9 is different from that found for nonpolymeric polyanions such as polyoxametalates,<sup>15</sup> which provoke a condensation of the DODAB monolayer. It is also different from the effect found for soluble surfactants in which the ratio of the surfactant and polyelectrolyte concentrations plays a major role.<sup>10</sup>

It has already been mentioned that the effect of the PSS chains on the  $\Pi$  versus  $A$  curves cannot be attributed to the change in the ionic strength of the subphase because the presence of an inert electrolyte has the opposite effect. It must be remarked here that PSS has also a more intense effect on the surface phase transition. In effect, for 1 mM salt, it is almost undetectable at 298 K, while for a PSS subphase (70 kDa, 100 ppm) it can be clearly observed.

The effect of  $T$  on the PSS + DODAB layer is similar to that found for DODAB monolayers on water: increasing  $T$  makes the monolayer more expanded and makes the expanded-liquid to condensed-liquid phase transition less marked.

Theories predict a slight charge overcompensation when the polyelectrolyte is adsorbed on a wall of opposite charge. Figure 5 shows that there is an important change in  $\Delta V$  when the DODAB monolayer is on a PSS solution ( $M_w = 70$  kDa,  $c = 100$  ppm, 298 K). The decrease is larger when the molecular weight is increased while maintaining the same molar concentration, which would reflect a more important role of the second diffuse polymer layer beneath the DODAB monolayer. While the theoretical predictions suggest a change of  $\Delta(\Delta V) \approx k_B T/e \approx 30$  mV, Figure 5 shows that the change is much larger in the 100–60 Å<sup>2</sup> effective area per DODAB molecule range. For a homogeneous monolayer  $\Delta V$  is related to the component of the dipole moment of the molecules perpendicular to the surface. Thus, one might be tempted to conclude that the formation of complexes between the DODAB molecules and the PSS chains

is more effective in modifying the structure of the DODAB monolayer than the presence of ions from an inert salt. However, such a comparison is not straightforward because of the change of the morphology of the surface film. Figure 7 shows the BAM images of the monolayer on a subphase with PSS (70 kDa, 100 ppm). As it can be observed, the surface film still shows inhomogeneities even for surface pressures below that of the surface phase transition, although they are smaller than for the water subphase.

**Viscoelastic Properties.** In a relaxation experiment, the stress is defined as  $\sigma = (\Pi(t) - \Pi_\infty)/(\Pi_0 - \Pi_\infty)$ , and the strain is defined as  $s = \Delta A/A_0$ , where  $\Delta A$  is the area change and  $A_0$  is the initial value of the area available to the monolayer.  $\Pi_\infty$  and  $\Pi_0$  are the equilibrium surface pressures at the end and at the beginning of the relaxation experiments, respectively. Loglio et al.<sup>20</sup> showed that for a system not too far from equilibrium and when nonlinear processes are not present, the complex elasticity modulus can be written as

$$\epsilon^*(\omega) \equiv \epsilon(\omega) + i\omega\kappa(\omega) = \frac{\mathcal{T}[-\Delta\Pi]}{\mathcal{T}[\Delta A/A_0]} = \frac{\mathcal{T}[-d\Delta\Pi/dt]}{\mathcal{T}[d \ln A/dt]} \quad (1)$$

where  $\mathcal{T}(x)$  is the Fourier transform of  $x$ ,  $\epsilon(\omega)$  is the elasticity modulus, and  $\omega\kappa(\omega)$  is the loss modulus, where  $\kappa(\omega)$  is the dilational viscosity. For a fast change of area, one can write

$$\mathcal{T}[\Delta A/A_0] = i\omega(\Delta A/A_0) \equiv i\omega\theta \quad (2)$$

which leads to

$$\epsilon^*(\omega) = i\omega/\theta \int_0^\infty -\Delta\Pi \exp[-i\omega t] dt \quad (3)$$

It is difficult to know a priori how to model  $\Delta\Pi(t)$ ; thus, we have calculated the relaxation spectrum as described by Monroy et al.<sup>13</sup> The results point out the existence of two relaxation modes; thus, we have fitted all our relaxation curves (Figure 6) by

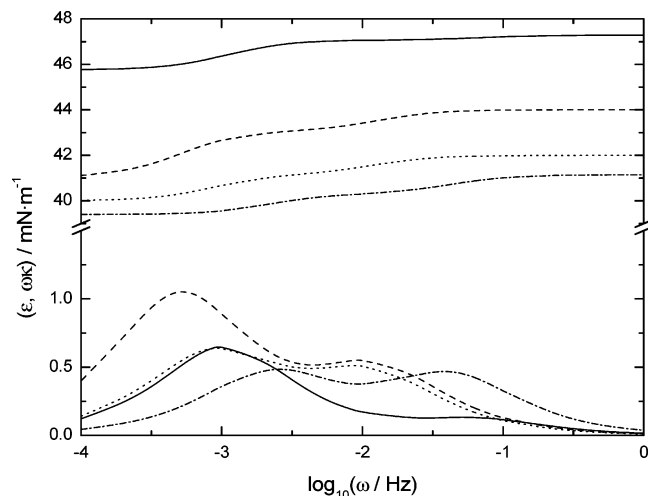
$$\frac{\Pi(t) - \Pi_\infty}{\Pi_0 - \Pi_\infty} = A_0 \exp(-t/\tau_1) + A_1 \exp(-t/\tau_2) \quad (4)$$

which after substitution in eq 3 results in

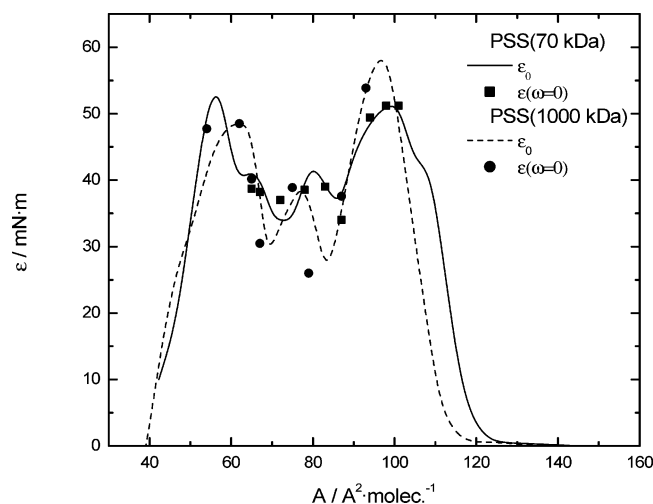
$$\theta\epsilon^*(\omega) = \sum_{i=1}^2 \epsilon_i^0 \frac{i\omega\tau_i}{1 + i\omega\tau_i} \quad (5)$$

that is, the elasticity modulus can be expressed as the sum of two Maxwell modes. Figure 8 shows the frequency dependence of the elasticity and of the loss modulus for some relaxation experiments on the PSS (70 kDa, 100 ppm) subphase. Similar results were obtained for other concentrations and for  $M_w = 1000$  kDa. As it can be observed,  $\epsilon \gg \omega\kappa$  through the whole frequency range, which means that the monolayers are essentially elastic films; this behavior is similar to that found by Noskov et al.<sup>10</sup> in their study of the adsorbed films of PSS and a soluble surfactant.

In Figure 9 we compare the equilibrium compressibility modulus  $\epsilon_0 = -(\partial\Pi/\partial \ln A)_T$  and the zero-frequency value of the elasticity modulus  $\epsilon(\omega = 0)$ ; both sets of results coincide within the experimental uncertainty. Also, there is no difference between the results for the two samples of PSS even though, for the higher molecular weight, the concentration is 1428 ppm. The finite value of  $\epsilon(\omega = 0)$  is characteristic of insoluble monolayers, while for soluble ones  $\epsilon(\omega = 0) = 0$ . Figure 10



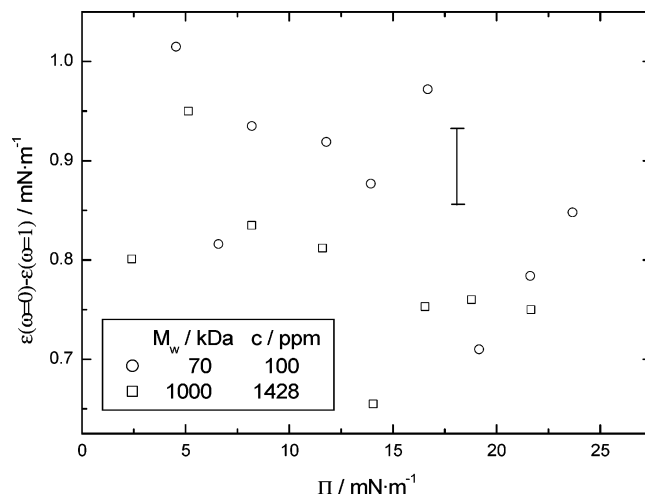
**Figure 8.** Elastic ( $\epsilon$ ) and loss moduli ( $\omega\kappa$ ) for the surface layer of DODAB + PSS (70 kDa,  $c = 100$  ppm, 298 K). The curves correspond to different initial states marked by the initial value of  $\Pi$ : from bottom to top in the  $\epsilon$  curves,  $\Pi_0$  ( $\text{mN}\cdot\text{m}^{-1}$ ) = 4.53, 21.62, 19.16, and 11.78, respectively. The loss modulus curves have been drawn with the same type of lines as the elasticity ones.



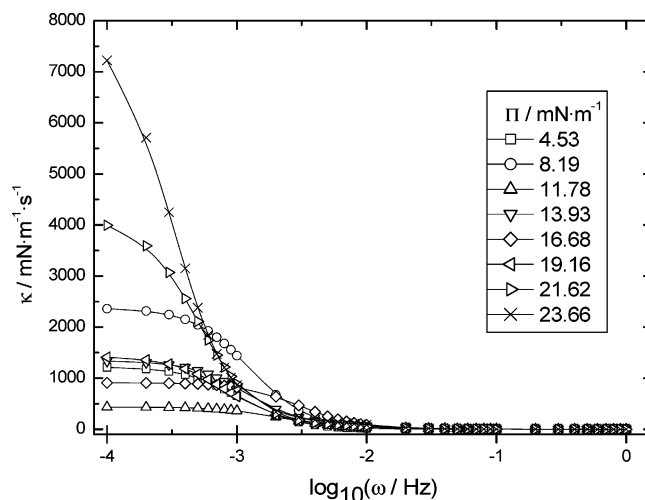
**Figure 9.** Comparison of the equilibrium compressibility modulus obtained from the equilibrium  $\Pi$  vs  $A$  curves for DODAB + PSS (70 kDa,  $c = 100$  ppm, 298 K) and for DODAB + PSS (1000 kDa,  $c = 1428$  ppm, 298 K; symbols), and the values corresponding to the zero frequency obtained from the relaxation experiments (curves).

shows the difference in the elasticity modulus between the high-frequency limit ( $\omega = 1$  Hz) of the experiments and the zero-frequency value for two different systems. Again, it can be observed that, within the scattering of the data, neither the molecular weight of PSS nor its concentration has important effects on the elasticity. This might indicate that it is only the film formed by the DODAB molecules and the first dense layer of the PSS segments (i.e., the part of the surface layer where the complexes are formed) which essentially determine the elasticity modulus.

Figure 11 shows the frequency dependence of the dilational viscosity for monolayers of DODAB + PSS (70 kDa,  $c = 100$  ppm, 298 K) at different values of  $\Pi$ . As it can be observed, the viscosity decreases strongly as  $\omega$  increases; in the decreasing range  $\kappa \sim \omega^a$  with  $a \approx -1.5 \pm 0.1$  for all the polymer concentrations and for the two molecular weights. This frequency dependence is stronger than the one previously found for monolayers of insoluble polymers<sup>13,21</sup> and may simply reflect the more complex structure of the surface layer. Figure 12 shows

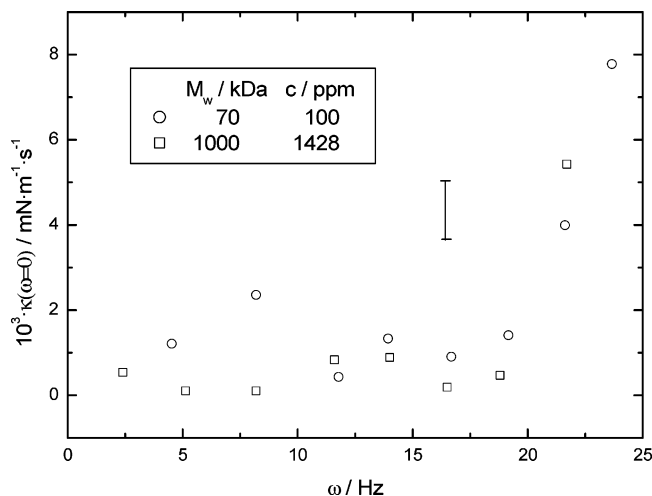


**Figure 10.** Surface-pressure difference between the high-frequency limit of the elasticity modulus obtained from the relaxation curves,  $\epsilon(\omega = 1 \text{ Hz})$ , and the corresponding zero-frequency limit for two monolayers.



**Figure 11.** Frequency dependence of the dilational viscosity for monolayers of DODAB + PSS (70 kDa,  $c = 100$  ppm, 298 K) at different values of the surface pressure. Similar results were obtained for other PSS concentrations.

that the zero-frequency-dilational viscosity increases with the surface pressure and, hence, with the DODAB surface concentration. The increase takes place at values of  $\Pi$  higher than those corresponding to the surface phase transition. This behavior is consistent with the increase of order of the DODAB molecules and with the increase of the number of DODAB–PSS complexes.<sup>9</sup> It might seem surprising that the viscosity of DODAB + PSS (1000 kDa,  $c = 1428$  ppm, 298 K) is not higher than that of the sample of PSS (70 kDa, 100 ppm) through the whole  $\Pi$  range studied. However, this is again consistent with the idea that the viscoelastic moduli are determined mainly by the DODAB monolayer and the first dense layer of PSS. It must be stressed that  $\omega\kappa \approx 0$  for the DODAB monolayer on pure water. These results together with those of  $\epsilon$  point out that the mechanical properties of the PSS + DODAB films are strongly affected by the PSS chains. In a study of the adsorption complexes of PSS and a soluble surfactant, Noskov et al.<sup>10</sup> concluded that the viscoelastic moduli of the adsorption layers were essentially a result of the PSS chains, the DODAB molecule playing the role of a charged wall that keeps the PSS molecules in the surface. The strong increase of  $\kappa$  after the surface phase transition points out that the change of the



**Figure 12.** Zero-frequency limit of the dilational viscosity for two of the monolayers studied. Notice that, within the experimental scattering, there is no effect of the molecular weight or the polyelectrolyte concentration.

structure of the DODAB plays a role, although it might also reflect an increase of the charge density of the surface.

It is not clear why the dynamics of this system is bimodal. The inhomogeneous character of the surface layer (see Figure 7) might explain this behavior by assuming that the fast mode corresponds to the dynamics of the adsorption layer and that of the slow mode is associated with the dynamics of the inhomogeneities. The assignment of the slow and fast modes would be consistent with the fact that, for high PSS concentrations, the amplitude of the slow mode increases with  $\Pi$ , while the one of the fast mode decreases. The existence of inhomogeneities would also explain the fact that the analysis of the surface light-scattering spectra (results not shown) leads to apparent negative dilational viscosities for the present adsorption layers.<sup>22</sup> However, the X-ray reflectance experiments of Ahrens et al.<sup>9</sup> do not give any hint on the existence of such inhomogeneities at high surface pressures. In addition, the inhomogeneities exist for the DODAB monolayers on water and on KCl and NaBr subphases, while no relaxation mode is observed for the time interval at which the relaxations are observed in the DODAB/PSS system. Another possibility is to consider that one of the relaxation modes is associated to the dynamics of the monolayer, while the slow mode is associated to the PSS loops and tails of the second less-dense layer. In any case, the present experiments do not allow us to make any specific assignment of the two dynamic modes.

## Conclusions

The presence of PSS in the subphase leads to an expansion of the DODAB monolayer and makes the surface phase transition of the monolayer more intense. An increase in temperature also produces an expansion of the monolayer. The surface-potential data show that the PSS chains produce a charge compensation through the formation of DODAB/PSS complexes. These equilibrium results are consistent with the picture of the interface suggested by Ahrens et al.<sup>9</sup> in which, beneath the DODAB monolayer, there is a high-density polymer layer

and also a second low-density polymer layer which extends deeper into the solution.

Bimodal relaxation curves have been obtained through the whole range of PSS concentrations studied and at most of the surface pressures. The adsorption layers behave as essentially elastic bodies through the whole frequency range. The zero-frequency limit of the elastic modulus agrees with the value corresponding to the equilibrium compressibility obtained from the surface-pressure curves. The dilational viscosity decreases as  $\kappa \sim \omega^{-1.5 \pm 0.1}$ , which is a stronger decay than usually found for monolayers of insoluble neutral polymers.<sup>13,19</sup> The zero-frequency limit of  $\kappa$  shows a marked increase with the surface pressure of the monolayer above the surface phase transition of the surface layer. It has been found that neither the molecular weight nor the PSS concentration of the subphase has noticeable effects on the viscoelastic moduli of the DODAB/PSS system.

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