Surface Light-Scattering at the Air−Liquid Interface: From Newtonian to Viscoelastic Polymer Solutions

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Received: November 12, 2004; In Final Form: January 17, 2005

The dynamics of the liquid−air interface of aqueous solutions of a tensioactive triblock copolymer (Pluronic F-68) has been studied using surface quasielastic light scattering over a broad range of concentrations and temperatures. Ancillary surface tension and bulk rheometry data have been obtained for the same system. The results show that the classical theoretical spectrum for monolayers on a Newtonian fluid can be applied only for concentrations below $4 \cdot 10^{-2}$ mM. For concentrations above $c = 14$ mM a clear peak centered at zero frequency appears in the spectrum. This feature is incompatible with the classical theoretical spectrum. The SQELS spectra have been described in terms of the theory of Wang and Huang [Wang, C. H.; Huang, Q. R. *J. Chem. Phys.* **1997**, *107*, 5898] considering that the loss modulus of the concentrated solutions shows the existence of two relaxation modes even at low frequencies. The theory is able to explain the existence of a peak centered at zero frequency in the spectra, and the theoretical spectra point out the existence of an elastic peak together with the capillary one. There is a reasonable agreement between the relaxation times and the product $G\tau$ obtained from the fits of the SQELS spectra to the theory of Wang and Huang and those obtained from bulk rheology.

Introduction

Surface quasielastic light scattering is a noninvasive technique suitable for characterization of fluid interfaces. In addition to be able to provide surface tension γ results, it also gives information about the dynamic elasticity ϵ and the dilational viscosity κ, most frequently in the frequency range 1 kHz $\leq \omega \leq$ 1 MHz.[1] To obtain the constitutive parameters of the interface, γ, $\epsilon(\omega)$, and $\kappa(\omega)$, it is necessary to fit the experimental spectra of scattered light to the theoretical spectrum derived from the hydrodynamic description of the interface. This procedure has been successfully used for fluid interfaces with and without monolayers, although anomalous viscosity results have been reported in some cases.[2]

However, the situation is somewhat different for interfaces of viscoelastic fluids. The behavior of surface waves of concentrated (viscoelastic) polymer solutions and gels is relevant for energy dissipation in lubricants by means of bulk-surface energy transfer and for explaining the anomalous turbulent flow through polymer gel-coated capillaries.[3] Harden et al.,[4] Wang and Huang,[5] Nakanishi and Kubota,[6] and Ahn et al.[7] have given detailed theoretical descriptions of the surface wave behavior as a function of γ, ϵ, and the viscoelastic behavior of the bulk solution, characterized by a zero frequency viscosity, a shear modulus amplitude G_0, and a relaxation time τ. In particular, refs 4−6 focus on the existence of crossovers from capillary waves to Rayleigh elastic waves or to overdamped waves as G_0 and ω (or the wavenumber q) were changed. Ahn et al.[7] presented a similar description of the surface wave behavior, although they claimed that in the low frequency range the character of the two coexisting waves is elastic, whereas one of them changes to capillary character at high frequencies (characteristic of the SQELS experiments). Even though there have been several attempts to test the theoretical predictions and the coexistence of two surface modes seems to be clearly demonstrated,[7−12] there still is some controversy about the physical nature of the coexistent surface waves.[7,13,14] This is in part due to the fact that some of the experiments have been carried out in systems that did not met all of the assumptions of the theory. For the sake of example, the system studied in ref 9 forms a viscoelastic monolayer,[15] whereas the theory of Harden et al.[4] strictly discards this possibility. Also, in refs 9 and 11, the authors fit the experimental spectra to a Lorentzian function plus a function that decreases monotonically with increasing frequency, instead of fitting them to a deconvolution of the theoretical spectrum plus the instrumental function. This procedure has been found to lead to large errors for polymer monolayers[16] and for polymer viscoelastic solutions.[10] Finally, the experimental study carried out by Huang et al.,[10] in order to test their theory for viscoelastic solutions with a viscoelastic monolayer,[4] did not consider any dilational viscoelasticity in the monolayer, which is the main difference between the theories of Harden et al.[4] and of Wang and Huang.[5] In summary, most of the experiments carried out so far cannot be considered adequate for testing the theory of capillary waves on viscoelastic polymer solutions with a strong preferential adsorption at the surface that originates a viscoelastic monolayer.

The purpose of this work is to carry out a detailed experimental study of the capillary-waves behavior of the free interface of a polymer solution for which the surface tension is strongly concentration dependent, thus presenting a marked preferential surface adsorption. The ability of the theory of Wang and Huang[5] to explain the results with a minimum of fitting parameters will be checked. We have selected to study the solutions of a surfactant copolymer: Pluronic F68. At low concentrations c the solutions show a Newtonian behavior,

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10.1021/jp044811r CCC: $30.25 © 2005 American Chemical Society
Published on Web 02/22/2005

whereas at higher concentrations, the solution presents viscoelastic behavior; finally at a concentration high enough ($c \approx$ 36 mM at 25 °C), the system shows a sol−gel transition.[17] In addition, for a given concentration, the increase of temperature T also induces the crossover from Newtonian to viscoelastic behavior. The experimental results will be compared with the predictions of the theory developed by Wang and Huang for solutions of surface active polymers,[5] in a concentration range in which the surface tension is concentration dependent and in which there is a viscoelastic polymer film adsorbed at the surface.[18]

Experimental Section

$PEO_{76}-PPO_{29}-PEO_{76}$ (also known as pluronic F68) was purchased from Aldrich (U.S.A.). Doubly distilled and deionized water from a MilliQ system (resistivity higher than 18 MΩ) was used. The solutions were prepared by weight on an analytical balance precise to ±0.01 mg. The precision of the weight fraction of polymer was better than ±0.0005.

In all of the experimental techniques, a Hart 2000 proportional controller was used, and the temperature was kept constant within ±0.01 °C. It was measured with a Pt-100 thermometer accurate to ±0.01 °C with respect to the IPTS-90. The surface light scattering technique was the same that was used in previous works.[19−21] Due to the presence of a viscoelastic peak centered at zero frequency in the concentrated solutions, special precautions were taken in the use of the low band electronic filter in order to optimize the signal-to-noise ratio of the spectra. Due to the slow adsorption kinetics of the low concentration solutions,[21] the measurements were carried out in a sealed cell, and long equilibration times (up to 48 h) were allowed. Each spectrum was the average of three measurements, and 20 000 accumulations were done in the spectrum analyzer for each measurement. The wavenumbers corresponding to each diffraction order were calibrated using the surface of water, dimethylether, and *n*-hexane. The viscosity of the low concentration solutions (c < 16.33 mM) were measured with an automatic Ubbelhode-type viscometer from Lauda (Germany). Three different capillary bores were used, and they were callibrated using standard silicone oils from Schott (Germany). A Bohlin-Vilastic VE-system (U.S.A.) rheometer was used for concentrated solutions (16.3 < c/mM < 37.1). The zero frequency viscosity was obtained with a precision of 0.5%, and good agreement was found between the two techniques for the viscosity range in which they overlaped. The densities of the samples were measured using a vibrating tube densimeter Anton Paar DMTA-DMA601T (Austria) with a precision of ±0.0002 g cm^{-3}. The surface tensions were measured with the plate method using a Krüus K-10 tensiometer.

Results

Bulk Rheology. As mentioned in the Introduction, the surface wave behavior of concentrated polymer solutions is strongly dependent on the rheological behavior of the subphase; thus, we briefly summarize the results obtained for the F68 solutions. The zero-frequency viscosity of the F-68 solutions has been measured as a function of concentration and of T. Below 4.1 × 10^{-2} mM the viscosity is essentially that of pure water. For c < 16.33 mM, the temperature dependence of η can be described by an Arrhenius dependence, with an activation energy very close to that of pure water. However, for more concentrated solutions the temperature dependence is nonmonotonic (see Figure 1) which reflects the competition between the usual Arrhenius behavior, and the development of entanglements, micelles, and, eventually, the gel phase at concentrations and temperatures high enough.

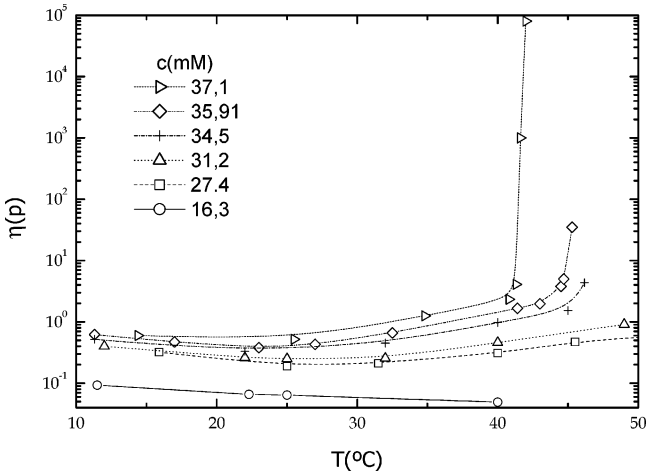

Figure 1. Temperature dependence of the zero-frequency shear viscosity for concentrated solutions. Notice that there is a minimum in the curves for $c \geq$ 27.4 mM.

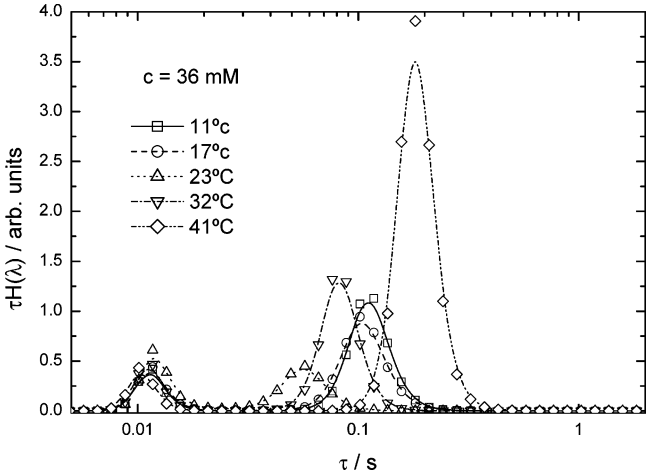

Figure 2. Relaxation spectra obtained from the components of the complex shear modulus using a regularization type algorithm.

Solutions with c < 31 mM behaved as Newtonian fluids for 10 ≤ T/°C ≤ 50 and in the frequency range of the rheometer. More concentrated solutions showed a viscoelastic response. It is important to remark that within the temperature and frequency ranges measured, the most concentrated solutions ($c \geq$ 10 mM) showed a two process relaxation. The relaxation spectra shown in Figure 2 were calculated from G' and G'' using an algorithm based on the regularization method[22] and show clearly the existence of two relaxation processes. The position of the long time relaxation peak (τ_1) follows closely the nonmonotonic temperature dependence of η, whereas for the short time relaxation peak, τ_2 is almost temperature independent. Moreover, τ_2 takes quite similar values for all of the samples studied. The last point has to be taken with care due to the upper frequency limit of the rheometer, which does not allow to completely define the high frequency relaxation mode. The results may be described very accurately by the sum of two Maxwell relaxation modes[23]

$$G^*(\omega) = G'(\omega) + iG''(\omega) = \sum_{j=1,2} \frac{G_{0,j}\omega\tau_j}{1 + i\omega\tau_i} \qquad (1)$$

The values of τ_j obtained from the fit to the G' and G'' results were coincident with those obtained from the relaxation spectra

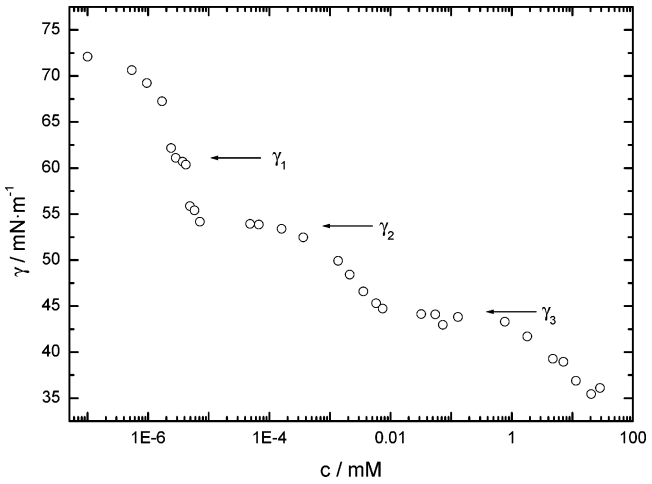

Figure 3. Surface tension of the pluronic F-68 solutions at 25 °C. The arrows mark the existence of surface phase transitions.

within their combined uncertainties. The existence of more than one Maxwell mode was already suggested by the analysis of the SQELS spectra in refs 8 and 10.

It must be remarked that the frequency range explored by the SQELS experiments (10−100 kHz) is rather different from that of the rheometer. In fact, the analysis of the SQELS spectra will point out that above $c = 15$ mM the pluronic solutions present a nonnegligible elasticity.

Surface Tension. Figure 3 shows the equilibrium surface tension results at 25 °C. In the $c <$ cmc region (the critical micelle concentration for F-68 at 25 °C is cmc $\approx$ 10 mM), the results show three concentration regions in which γ remains approximately constant. The short plateau at γ_1 has been found in other pluronic with different values of the block sizes,[24] in pure PEO,[25] and in PEO−PS copolymers (PS being polystyrene).[19] The plateau at γ_2 has been found also for other pluronics.[24] Finally, the plateau at γ_3 is present in solutions of PEO,[25] but it was not always present in other pluronic. The F68+water system presents an adsorbed monolayer even for highly diluted solutions ($c > 5 \times 10^{-6}$ mM), and γ continues to decrease with increasing c for concentrated (viscoelastic) solutions, as in the case of PEO solutions.[22] γ shows a linear decrease with increasing T, which is the usual behavior of polymer solutions.[26] The different plateaux in the γ vs c curves have been interpreted in terms of surface phase transitions in ref 18. Other authors relate the existence of the plateaux in adsorbed monolayers in terms of bulk phase transitions[27] or conformational changes.[15] Since the physical origin of the plateaux is not relevant for the test of the Wang-Huang theory,[5] we will not discuss it in this work.

Surface Light-Scattering (SQELS) Spectra. Figure 4a shows some of the SQELS spectra at 22 °C as a function of concentration for $q = 99.8$ cm^{-1}. The spectra shift to lower frequencies as the concentration is increased, which could be explained considering that the surface tension decreases. Also the width of the spectra increases with c. The most important feature of these results is that, for the two highest concentrations shown, the spectra are nonsymmetric and that a peak centered at $\omega = 0$ appears. Even though for the highest concentrations shown in the Figure the bulk solution scatters a noticeable amount of light, the $\omega = 0$ peak cannot be attributed to this fact. In effect, the intensity of the light scattered by the present solutions is lower than that of micellar solutions previously studied[28] and for which no peak centered at zero frequency was found. Moreover, notice that in Figure 4a this peak starts to

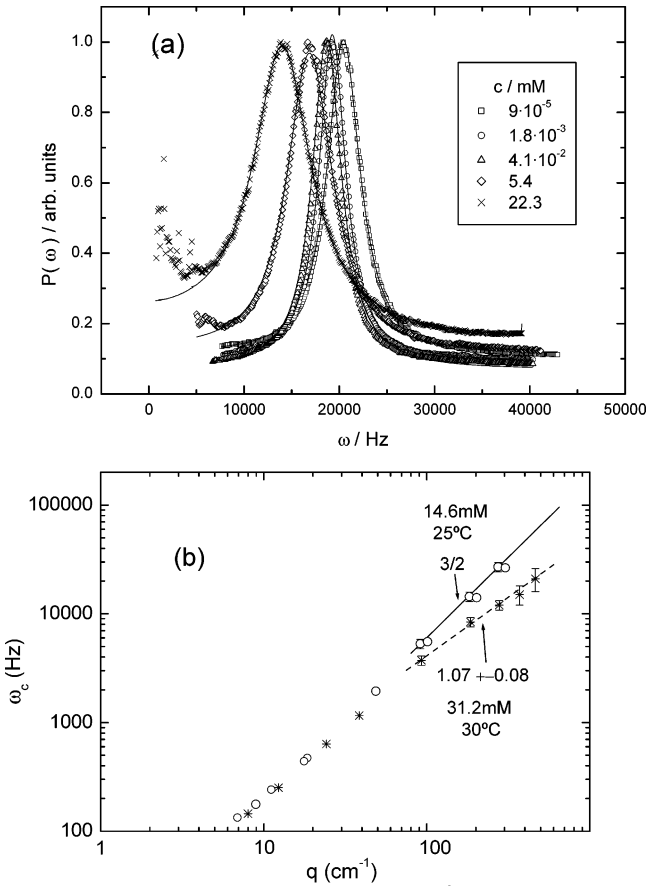

Figure 4. (a) SQELS spectra for the liquid−air interface of F-68 solutions as a function of concentration, at 22 °C and $q = 99.77$ cm^{-1}. The lines represent the best fit to the classical theoretical spectrum for a monolayer on the surface of a Newtonian subphase.[7] Notice that for the two most concentrated solutions there is a clear disagreement between theory and experiment in the low-frequency region. (b) Wave-vector dependence of the frequency of the maximum of the SQELS spectra for two concentrations. The values for $q <$ 99.77 cm^{-1} have been obtained by electrocapillary wave experiments. Notice that the slope changes from 3/2 to 1 in the high q range, whereas it remains equal to 3/2 in the low q range.

have a noticeable intensity at frequencies higher than 5 kHz, thus having a width much higher than the Rayleigh peak characteristic of viscous fluids make of large molecules.[29] As it will be discussed in the next section, the existence of the $\omega = 0$ peak is not compatible with the dispersion equation frequently used for the description of the dynamics of monolayers.

We have plotted the q dependence of the frequency of the maxima of the spectra ω_c for two concentrations in Figure 4b. As it can be observed, for solutions with $c \leq 14.6$ mM, the data can be represented by $\omega_c \sim q^{\xi}$ with $\xi = 3/2$, as it is usually found for the interface of simple fluids. However, for the highest concentration studied, $\xi = 1$, with intermediate values for intermediate concentrations. This change in ξ may be due to the effects of the viscoelasticity of the subphase[4,5] or simply to the increase of its viscosity.[1,8] The width at half-height (Γ) can be described by $\Gamma \sim q^2$ over the whole concentration range studied, with a prefactor that increases with c.

A significant result is that ω_c increases with T for $c = 14.6$ mM and for more concentrated solutions up to $c = 34$ mM (above that concentration the spectra were overdamped). To analyze this behavior, one has to consider the temperature dependence of η and of γ. Decreasing η and increasing γ would

lead to an increase of ω_{max}. As already said, for the pluronic solutions studied, γ decreases with increasing T. On the other hand η decreases with increasing T for the lowest concentrations, whereas it increases for $T > 25$ °C for $c > 27.4$ mM. Therefore, the increase of ω_{max} with T for the highest concentrations cannot be explained simply by the changes in η. Moreover, the shape of the spectra for this concentration range cannot be reproduced by the theoretical expression corresponding to a monolayer onto a viscous subphase. As it will be shown below, this behavior can be understood in terms of the increase of elasticity of the subphase as T increases.

Theoretical Background

In the quasielastic surface light scattering experiment, one measures the power spectrum $P_q(\omega)$ associated with the time correlation function of the q component of the surface roughness variable $\zeta_q(t)$

$$P_q(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-i\omega t}\langle\zeta_q(t)\zeta_q(0)\rangle\, dt \quad (2)$$

where the angular brackets denote the ensemble average over the surface variables, q is the amplitude of the scattering vector associated with the surface mode, and $\zeta_q(t)$ is related to $\zeta(x,t)$ by a one-dimensional Fourier transform with respect to x (the y direction is assumed to be uniform for simplicity)

$$\zeta_q(t) = \int \zeta(x,t)e^{iqx}\, dt \quad (3)$$

The thickness of the film adsorbed is assumed to be small compared to the wavelength of the thermal capillary waves.

For linear viscoelastic polymer solutions whose interfaces exhibit dilational response and preferential sorption of one of the components, the theory leads to[5]

$$P_q(\omega) = -\frac{2k_BT}{\omega}\mathrm{Im}\left[\frac{\tilde{\epsilon}q^2 + i\eta(\omega)\omega(q+m)}{D(q,\omega)}\right] \quad (4)$$

where Im indicates taking the imaginary part of the quantity on its right, $\tilde{\epsilon} = \epsilon(\omega) + i\kappa(\omega)$ is the complex elasticity of the monolayer, with $\epsilon(\omega)$ being the dynamic elasticity, and $\kappa(\omega)$ being the dilational viscosity. In eq 4, m is the capillary penetration length defined as

$$m^2 = q^2 + i\omega\frac{\rho}{\eta} \quad \text{with } Re(m) > 0 \quad (5)$$

ρ being the density. $D(q,\omega)$ is known as the dispersion equation and is given by

$$D(q,\omega) = [\eta(\omega)\omega(q-m)]^2 + [\tilde{\epsilon}(\omega)q^2 + i\tilde{\eta}(\omega)\omega(q+m)]\left[\gamma q^2 + i\eta(\omega)\omega(q+m) - \frac{\rho\omega^2}{q} + gq\right] = 0 \quad (6)$$

with $\tilde{\eta}(\omega)$ being the complex viscosity of the subphase, derived from eq 1. Although eqs 5 and 6 have been rewritten with respect to the form given in ref 5, both formulations are completely equivalent. When the subphase behaves as a Newtonian fluid, eqs 5 and 6 reduce to the well-known equations for viscoelastic monolayers on top of a fluid.[7]

Discussion

As already mentioned in the previous section, solutions with $c < 31$ mM show no bulk viscoelastic response in the frequency range $0.01 < \omega/\mathrm{Hz} < 100$. As a consequence one might expect

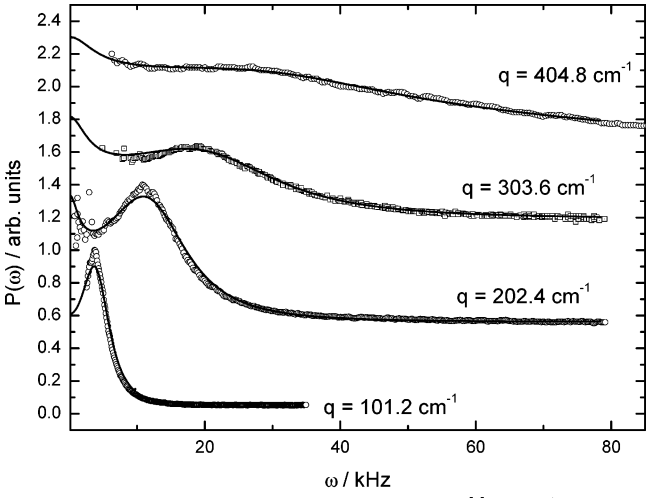

Figure 5. Comparison of the experimental SQELS spectra for $c = 24.7$ mM at 10 °C and for different values of q (symbols) with the predictions of the theory of Wang and Huang (lines).[11] Each of the spectra have been shifted 0.4 units in the $P_q(\omega)$ axis for the sake of clarity.

that the experimental data could be described with the theoretical spectrum (convoluted with the instrumental function) corresponding to a viscoelastic monolayer on the surface or a Newtonian fluid.[1,5] The results of the fits of the experimental spectra to such a model are shown in Figure 4a for different concentrations at 22 °C. It can be observed that the theory is able to describe accurately the experimental data up to $c \approx 4 \times 10^{-2}$ mM; however, for higher concentrations, there are clear deviations in the low-frequency range. In all of these calculations, the experimental surface tension and bulk viscosity have been used. For monolayers on Newtonian fluids, the theory does not predict any peak centered at $\omega = 0$, as seems apparent for the spectrum corresponding to $c = 22.3$ mM. Moreover, the theory predicts that, as the viscosity is increased, the spectra become more and more over-damped and that the q dependence of the frequency of the maximum of the spectrum ($\omega_{max} \sim q^{\xi}$) crosses over from $\xi = 3/2$ to 1. The spectra for the concentrated solutions ($10 \leq c/\mathrm{mM} \leq 34$) are not overdamped, although the change in the value of ξ is clear (see Figure 4b). However, it has to be notice that such a change is observed only for high q's corresponding to the SQELS experiments, whereas for the q's corresponding to electrocapillary wave experiments ξ remains equal to 3/2 for all of the concentrations. Dorshow and Turkevich[30] have shown that the crossover in ξ can be found in viscous fluids when $Y = \gamma\rho/4\eta^2 q$ changes from $Y > 1$ to $Y < 1$. This is indeed the case for the $c = 31.2$ mM solution shown in Figure 4b ($Y = 7.5$ for $q = 10$ cm^{-1} and $Y = 0.15$ for $q = 500$ cm^{-1}); therefore, one might be tempted to attribute the crossover of ξ to the change in the viscosity. However, the two following facts have to be considered: (a) The width at half-height (Γ) can be described by $\Gamma \sim q^2$ over the whole concentration range studied, with a prefactor that increases with c. Although this dependence is the same that the one obtained for low viscosity liquids (Stokes law), the viscosities calculated from the fits of the spectra to the theoretical expression characteristic of a monolayer onto a viscous subphase are very different from the experimental ones, while in ref 28 both sets of results were in agreement. (b) The analysis of the spectra for 31.2 mM in terms of the theoretical spectrum for interfaces of a pure viscous fluid with a monolayer is not able to reproduce the shape of the experimental spectra, which is similar to that of the spectra shown in Figure 5 for $c = 24.5$ mM. Therefore,

it seems reasonable to consider that the crossover of ξ is due to the viscoelastic character of the subphase. In any case, it must be stressed that, in general, the crossover behavior observed in Figure 4b is not sufficient to prove the existence of elastic waves in the surface.

The analysis of the dynamic elasticity and the dilational viscosity in the low concentration region (up to $c = 0.1$ mM) has been described in a recent work.[18] We will focus on the results for the higher concentration region $15 < c/\text{mM} < 32$; the spectra for higher concentrations were too broad to obtain conclusions from their fits to the theoretical equations. To use the single Maxwell mode theory [eqs 5 and 6] for the two bulk relaxation modes and considering the values of τ obtained above, we have assumed that at the frequencies of our SQELS measurements the fastest mode was already relaxed; thus, the effective viscosity of the bulk solution might be described by

$$\eta(\omega) = (\eta_0 + G_{0,2}\tau_2) + \frac{G_{0,1}\tau_1}{1 + i\omega\tau_1} \tag{7a}$$

An obvious constraint of eq 7b is that at zero frequency the experimental viscosity $\eta(0)$ must be given by

$$\eta(0) = \eta_0 + G_{0,2}\tau_2 + G_{0,1}\tau_1 \tag{7b}$$

To reduce the number of fitting parameters, we have taken ϵ and κ from the extrapolation of the values obtained in ref 18 at lower concentrations where no viscoelastic subphases were studied. Only $G_{0,1}$ and τ_1 were fitted to the experimental spectra. $(\eta_0 + G_{0,2}\tau_2)$ was determined from eq 7b using the experimental value of $\eta(0)$, obtained from the viscoelastic spectra, and the fitted $G_{0,1}$, and τ_1. The values of ϵ and κ used are affected by uncertainties as large as 15% for ϵ and 20% for κ. However, it must be taken into account that for the values of $\alpha = \epsilon/\kappa$ of the solutions studied ($\alpha \geq 0.25$) the influence of ϵ and κ on the shape of the SQELS spectra is lower than that of $G_{0,1}$ and τ_i.[5] Figure 5 shows the different fits obtained for $c = 25.7$ mM at 10 °C and for four different values of q; similar results were obtained for other concentrations. As it can be observed, the quality of the fits is reasonably good, and the theory is able to reproduce the trends of the frequency of the maximum and of the width of the spectra, as well as the existence of the zero-frequency peak. Neither the experimental spectra nor the theoretical spectra calculated from fitted parameters show some significant features predicted by the theory: in effect, the theory of Wuang and Huang[5] predicts the existence of a capillary and an elastic peak in the spectra (besides the zero-frequency peak).[4,5] A similar situation was found by Huang et al.[10] The existence of two separated capillary and elastic modes is strongly dependent on the values of γ, G_0, and τ, and for the present solutions, they overlap in a very broad single peak. In addition, it must be considered that the intensity of the capillary peak decreases with increasing α, being almost negligible for $\alpha = 0.5$.[5] The fact that $\alpha \geq 0.25$ for the concentrated solutions studied in this paper makes even more difficult to resolve the two peaks. For concentrations above 34 mM the spectra are overdamped.

Finally, Figure 6 shows the concentration dependence of the relaxation times and of $G_0\tau$ for the different solutions at 40 °C. It is clearly seen that the values of τ_1 and of $G_i\tau_i$ obtained from the fits of the SQELS spectra ($c \leq 31.2$ mM) smoothly extrapolate from those of the solutions studied with the rheometer ($c \geq 31.2$ mM). A good agreement for the G between the SQELS and the rheometer results was also reported by Huang et al.,[10] although they did not reported any τ values. The

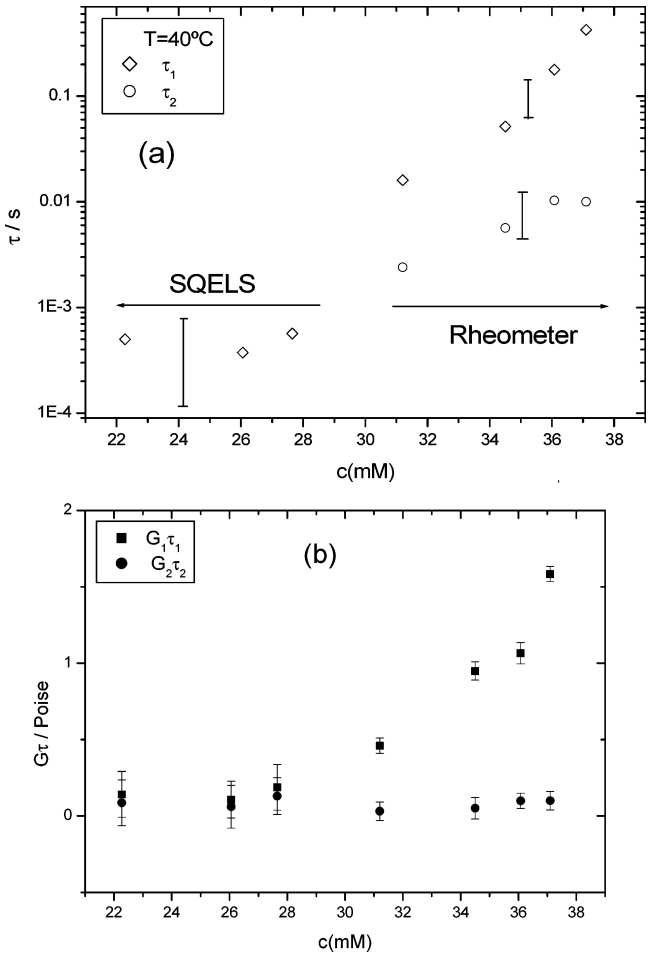

Figure 6. (a) Relaxation times for the two relaxation modes obtained from the loss modulus. The results for $c > 31.2$ mM were obtained from rheometry data, and those for $c \leq 31.2$ mM from the fits of the SQELS spectra. (b) Product $G_0\tau$ for the two relaxation modes. As in part a, the data for $c \geq 31.2$ mM were obtained with the rheometer and those for $c \leq 31.2$ mM with the SQELS technique.

agreement between both sets of data is very satisfactory if one takes into account that we have considered one of the viscoelastic modes fully relaxed and that the SQELS and bulk-rheology measurements were carried out in very different frequency ranges.

The values of τ and $G\tau$ obtained allow one to further discuss the crossover behavior shown in Figure 4b. In effect, the first point is that the crossover takes place in the same region in which $\omega\tau$ crosses over from <1 to >1. In addition, the region of the phase diagram in which the elastic waves can coexist with the capillary ones in a viscoelastic polymer solution has the following boundary values for the wavenumber: $q_- = (\gamma\tau^2/\rho)^{1/3}$ and $q_+ = (\gamma\rho/\eta_0^2)$, which for the $c = 31.2$ mM solution at 25 °C take the values 48 and 5979 cm^{-1}, respectively. On the other hand, the corresponding boundaries for the elastic modulus are given by $G_- = (\rho\gamma^2/\tau^2)^{1/3}$ and $G_+ = [\rho(\gamma/\eta_0)^2]$, which for this solution take the rather low values 0.2 and 23 kPa, respectively. As it can be observed in Figure 4b, the $\omega \sim q$ behavior is observed within the q_- and q_+ range; on the other hand, the total value of G' calculated from the fits is constant and close to 2.5 kPa at the frequencies of the SQELS experiments (10−100 kHz). This gives further support to the fact that for these solutions the crossover is due to the coexistence of capillary and elastic waves.

Conclusions

The solutions of Pluronic F-68 show a complex surface behavior. In addition, the shear modulus results point out that some elastic response exists above $c = 31.2$ mM, which is already well above the cmc (cm c$\approx$ 10 mM at 25 °C). At higher concentrations two different relaxation modes exist in the low-frequency range (0.01−100 Hz), at least at the highest temperatures studied.

The SQELS spectra can be described using the classical theoretical spectrum for a monolayer on a Newtonian fluid only for $c \leq 4 \times 10^{-2}$ mM, although above $c = 10^{-4}$ mM negative apparent dilational viscosities have to be used in the fits.[15] For $c \geq 5.4$ mM a peak centered at zero frequency appears in the SQELS spectrum; this feature is not compatible with the classical theoretical description. Above $c = 14.6$ mM the wavevector dependence of the frequency of the peak $\omega_c \sim q^{\xi}$ changes from $\xi = 3/2$ to $\xi = 1$ in the high q range characteristic of the SQELS experiments, whereas $\xi = 3/2$ remains valid in the low q range characteristic of electrocapillary wave experiments. Also, above $c = 14.6$ mM, the frequency of the peak for a given q increases with T, while the surface tension decreases. All of these features are characteristic of the behavior of surface waves on viscoelastic fluids.

The theory recently proposed by Wang and Huang[5] is able to fit the experimental spectra if the two relaxation behavior of the shear modulus of the subphase are taken into account. Both the relaxation time τ_i the product $G_i\tau_i$ ($i = 1$ and 2) of the two Maxwell modes obtained by fitting the SQELS spectra, and those obtained from the rheological measurements are in good agreement.

Acknowledgment. We thank MEC and CAM for financial support through grants: BQU2003-1556, MAT2003-1517, VEM2003-20574-CO3-03 and CAM07N/28/2002. We also thank Centro de Espectroscopía UCM for the use of their facilities. L.J.B. and M.E. thank MEC for PhD fellowships.

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