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Temperature and Concentration Effects on the Equilibrium and Dynamic Behavior of a Langmuir Monolayer: From Fluid to Gel-like Behavior

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The equilibrium isotherms of monolayers of poly(4-hydroxystyrene) on the air/water interface have been studied in the 5−60 °C range. The results indicate that the interface is a poor solvent for the monolayers over the whole tempeaure range. For surface pressures within the semidilute regime, the plot of the area occupied by the polymer coils versus temperature at constant surface pressure shows a sharp change of slope near 30 °C. Also, the surface excess entropy shows a similar change of slope at the same temperature. The surface shear viscosity can be described by a power law of the surface concentration. Within the semidilute regime, the exponent of the power law changes. The temperature dependence of the viscosity points out a change from independent particle to collective dynamics.

Introduction

Polymer Langmuir films are good examples of quasi-two-dimensional (quasi-2D) soft-matter systems. They are relevant to important practical processes such as film deposition, lubrication, and emulsion and foam stability,[1−3] or in mimicking systems of biological relevance such as transmembrane transport[4] or breathing.[5]

The equilibrium properties of Langmuir monolayers of insoluble noncharged polymers have received significant attention in the last two decades.[6] It has been shown that the overall behavior can be described within the framework of 2D polymer solution theory.[6−8] For intermediate values of the surface concentration, Γ, the behavior of the surface pressure, $\Pi = \gamma_0 - \gamma$ (where γ is the surface tension of the air/water interface covered by a monolayer of surface concentration Γ and γ_0 is the value corresponding to the bare interface) depends on the Flory critical exponent ν that describes the molecular weight dependence of the radius of gyration: $R_g \sim M^\nu$. This is a fundamental result of the scaling theory of polymer solutions.[7−9] For polymers adsorbed at an interface, the value of ν depends on whether the interface is a good or a poor solvent for the polymer coils.[6] However, scaling theory of polymer solutions is based upon the existence of entanglements between polymer chains. The existence of entanglements in polymer quasi-2D systems is still a matter of strong controversy.[10,11]

The availability of experimental techniques have allowed researchers to obtain many interesting results on the dynamics of Langmuir monolayers in the past few years.[6,10,12−16] Even though interfacial rheology has been found to be very important for processes of industrial interest,[1−3] many questions remain still open in this field: (a) The physical mechanism underlying the dynamics of polymer chains at interfaces has not been clarified yet. Several mechanisms have been proposed (reptation, amoeba-like, overcraft, etc.), but the available experimental results are not conclusive.[10,11,17−19] (b) Also, some monolayers have been found to form soft glasslike structures in the high concentration regime. However, the existence of a glass transition in these quasi-2D systems has not been clearly demonstrated,[20,21] and the nature of the soft glasslike phases has not been elucidated.

In previous papers, we have studied the equilibrium isotherm (Π versus Γ curve) for monolayers of poly(4-hydroxystyrene) (P4HS) onto acidic water, and it was found that the water/air interface is a poor solvent (almost Θ solvent) for the polymers at 25 °C. Also, the dilational rheology of these monolayers was studied.[21,22] Under poor solvent conditions, it is assumed that the polymer coils form collapsed pancakes at the interface. At low surface concentrations (Γ), the coils do not contact each other; above the so-called overlapping concentration (Γ^*), they start to overlap, and the monolayer crosses over from the dilute to the semidilute regime.[6−8] The transition that takes place at Γ^* has been described as a percolation transition of deformable soft particles, in which the rheology is essentially governed by the free area of the monolayer.[23] At a concentration $\Gamma^{**} > \Gamma^*$, the monolayer enters the concentrated regime where it forms a continuous film. In the percolated state, the relaxation time corresponding to cooperative rearrangements of the coil's distribution follows an

(1) Langevin, D. *Adv. Colloid Interface Sci.* **2000**, *82*, 209.
(2) Valentini, J. E.; Chandler, J. T.; Jianj, Q.; Chiew, Y. C.; Fina, L. J. *Ind. Eng. Chem. Res.* **1996**, *35*, 434.
(3) Dickinson, E. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 1657.
(4) Heim, M.; Jansen, S. *Nature* **1997**, *388*, 526.
(5) Herold, R.; Dewitz, R.; Schuren, S.; Pison, U. In *Drops and Bubbles in Interfacial Research*; Mobius, D., Miller, R., Eds.; Elsevier: Amsterdam, 1998.
(6) Esker, A. R.; Kim, Ch.; Yu, H. *Adv. Polym. Sci.* **2007**, *209*, 59.
(7) Vilanove, R.; Poupinet, D.; Rondelez, F. *Macromolecules* **1988**, *21*, 2880.
(8) Monroy, F.; Ortega, F.; Rubio, R. G. *J. Phys. Chem. B* **1999**, *103*, 2061.
(9) Monroy, F.; Hilles, H. M.; Ortega, F.; Rubio, R. G. *Phys. Rev. Lett.* **2003**, *91*, 268302.
(10) Sukhishvili, S. A.; Chen, Y.; Muller, J. D.; Gratton, E.; Schweizer, K. S.; Granick, S. *Macromolecules* **2002**, *35*, 1776.
(11) Wang, X.; Foltz, V. J. *J. Chem. Phys.* **2004**, *121*, 8158.
(12) *Light Scattering by Liquid Surfaces and Complementary Techniques*; Langevin, D., Ed.; Marcel Dekker: New York, 1992.
(13) Liggieri, L.; Ferrari, M.; Mondelli, D.; Ravera, F. *Faraday Discuss.* **2005**, *129*, 125.

(14) Noskov, B. A.; Akentiev, A. V.; Bilibin, A.Yu.; Zorin, I. M.; Miller, R. *Adv. Colloid Interf. Sci* **2003**, *104*, 245.
(15) Cicuta, P.; Hopkinson, I. *Phys. Rev. E* **2002**, *65*, 041404.
(16) Ding, J.; Warriner, H. E.; Zasadzinski, J. A. *Langmuir* **2002**, *18*, 2800.
(17) Kumaki, J.; Kawauchi, T.; Yashima, E. *Macromolecules* **2006**, *39*, 1209.
(18) Luap, C.; Goedel, W. A. *Macromolecules* **2001**, *34*, 1343.
(19) Gavranovic, G. T.; Deutsch, J. M.; Fuller, G. *Macromolecules* **2005**, *38*, 6672.
(20) Cicuta, P.; Stancik, E. J.; Fuller, G. G. *Phys. Rev. Lett.* **2003**, *90*, 136101.
(21) Hilles, H. M.; Ortega, F.; Rubio, R. G.; Monroy, F. *Phys. Rev. Lett.* **2004**, *92*, 255503.
(22) Monroy, F.; Rivillon, S.; Ortega, F.; Rubio, R. G. *J. Chem. Phys.* **2001**, *115*, 530.
(23) Monroy, F.; Ortega, F.; Rubio, R. G.; Ritacco, H.; Langevin, D. *Phys. Rev. Lett.* **2005**, *95*, 056103.

exponential dependence on the interfacial energy stored as a consequence of the lateral compression, and thus higher compression would lead to a faster relaxation.[23]

The relaxation experiments pointed out that the monolayer had a crossover from single molecule to a collective dynamics as Γ was increased at constant temperature, or as T was decreased at constant Γ (for Γ values well in the semidilute regime).[21] The relaxation results were interpreted in terms of the transition from sol to soft-glass states.[20,21] This was a challenging result because a lot of debate exists about the influence of the thickness of polymer films on the glass transition,[24−26] and Langmuir monolayers are the thinnest possible films. It was reported that when the interaction between the solid substrate and the polymer is small, or for unsupported polymer films, the glass transition temperature, T_g, decreases with the film thickness. However, for strong solid−polymer interactions, T_g may increase as the thickness is reduced.[27] Quite recently, Kremer's group have pointed out that many of the effects reported might arise from an incomplete aging of the ultrathin samples.[28] This problem would not affect Langmuir monolayers onto an aqueous subphase. Moreover, because the monolayer thickness may become smaller than the radius of gyration of the polymer coils, the existence of the dynamic heterogeneity typical of the glass transition might be pointed out more easily,[29] and the corresponding decrease of T_g should be larger.[24−26] Rheological experiments have been the most frequently used to study the glass transition in polymer materials.[30] For any system undergoing a fluid to glass transition, one may expect an important increase of the shear viscosity and of the real part of the elastic modulus. It must be stressed that an increase of the shear viscosity alone is not indicative of a glass transition, since it is also found in the sol−gel transition in polymer systems.[31] Another mark of the existence of a glass transition is the change of the temperature dependence of the shear viscosity from an Arrhenius to a non-Arrhenius behavior.[30] In the proximity of the T_g, the viscosity is usually described by the Vogel−Fulcher−Tamman equation: $\ln(\eta/\eta_0) = A/T - T_0$, where A and T_0 are system dependent parameters.[32]

In order to obtain some further information about this change of behavior, in this paper, we have studied the monolayer of P4HS onto water over the 5−60 °C range. From the equilibrium results, we have concluded that the plot of the area per molecule versus the temperature at constant Π shows a clear break. This is similar to the break found in bulk systems when the molar volume is plotted against the temperature near the glass transition temperature.[33] The temperature at which the transition takes place is close to 30 °C, far below the value for the glass transition of bulk P4HS: 115 °C.

In the dilute regime, the surface shear viscosity was found to follow an Arrhenius behavior over the whole temperature regime. However, for higher densities, two different regimes can be clearly
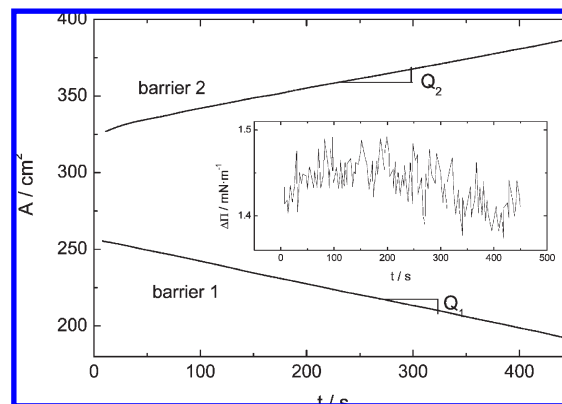
(24) Forrest, J. A.; Mattson, J. *J. Chem. Phys.* **2000**, *61*, R53.

(25) Kabori, K.; Tanaka, K.; Nagamura, T.; Takahara, A.; Kajiyama, T. *Macromolecules* **2005**, *38*, 9735.

(26) Kremer, F.; Huwe, A.; Schonhals, A.; Rózanski, S. A. In *Broadband Dielectric Spectroscopy*; Kremer, F., Schonhals, A., Eds.; Springer: Berlin, 2002.

(27) Zheng, W.; Simon, S. L. *J. Chem. Phys.* **2007**, *127*, 194501.

(28) Serghei, A.; Huth, H.; Schick, C.; Kremer, F. *Macromolecules* **2008**, *41*, 3636.

(29) Donth, E.; Hempel, E.; Schick, C. *J. Phys.: Condens. Matter* **2000**, *12*, L281.

(30) Riande, E.; Díaz-Calleja, R.; Prolongo, M. G.; Masegosa, R.; Salom, C. *Polymer Viscoelasticity. Stress and Strain in Practice*; Marcel Dekker: New York, 2000.

(31) Larson, R. G. *The Structure and Rheology of Complex Fluids*; Oxford University Press: Oxford, 1999.

(32) Sanchis, A.; Prolongo, M. G.; Masegosa, R. M.; Rubio, R. G. *Macromolecules* **1995**, *28*, 2693.

(33) Elliot, S. R. *Physics of Amorphous Materials*, 2nd ed.; Longman: Essex, 1990.

Figure 1. Typical steady-flow diagram on a canal viscometry experiment ($T = 38$ °C and $\Pi = 4$ mN·m^{-1}). The inset shows the time dependence of the difference of the surface pressure at both sides of the canal. Notice that the uncertainty of $\Delta\Pi$ is ± 0.1 mN·m^{-1}.

distinguished: at high temperatures, a low value of the activation energy ($E_A \sim 2RT$) is found, whereas a value $E_A \sim 83RT$ is observed below 30 °C. This is again a clear indication of a crossover from a regular fluid to a fluid with a highly correlated dynamics.

Experimental Section

Poly(4-hydroxystyrene) was purchased from Polysciences (Germany). The molecular weight was $M_w = 10\,000$ g·mol^{-1} with a polydispersity index of 2. We have checked by UV and ^{13}C NMR that no significant amounts of P4HS hydroxyl groups had been converted to the quinine form. The polymer was dissolved in a mixture of tetrahydrofuran and benzene (5:1) in order to improve the spreading of the solution on the free surface of water. Poly(vinyl stearate) (PVS) was purchased from Aldrich. The molecular weight was $M_w = 50\,000$ g·mol^{-1} with a polydispersity index of 1.7. The polymer was dissolved in chloroform (Riedel de Haen, Chromasolv quality). The benzene and tetrahydrofuran used were of RPE quality and were purchased from Carlo Erba (Italy). The total polymer concentration of the spreading solutions was close to 1 mg·mL^{-1}. Before spreading the polymer solutions, the surface tensions of water and the spreading solvents were measured by the Wilhelmy plate method in order to be sure that they did not have significant amounts of surface-active impurities. The water used was from a Milli-Q-RG unit, with a resistivity higher than 18 MΩ cm. The pH of the aqueous subphase was adjusted to pH = 2.0.

The monolayers were formed on a modified Nima 702 Langmuir trough (Coventry, U.K.). The trough is half-divided in two compartments interconnected through a narrow canal ($w = 2$ mm width, $L = 20$ mm length). The independent motion of each barrier allows one to maintain a constant Π gradient under which a steady-flow is established. The instrument is similar to the one described by Sachetti et al.[34] For given canal dimensions, the surface shear viscosity, η_{sh}, is calculated as

$$\eta_{sh} = \frac{\Delta\Pi w^3}{12LQ} - \frac{w\eta_w}{\pi} \qquad (1)$$

where $\Delta\Pi$ is the surface pressure gradient across the canal and $Q = dA/dt$, the steady flow rate measured at stationary conditions, that is, constant Q ($A = 1/\Gamma$ is the area per molecule, and η_w is the shear viscosity of the subphase). The last term of eq 1 is the correction due to the hydrodynamic coupling between the monolayer and the subphase liquid which usually is lower than 1%. In all the experiments, we have kept $\Delta\Pi \leq 1-2$ mN·m^{-1}. Figure 1 shows a typical example of a canal viscosimetry experiment. It is

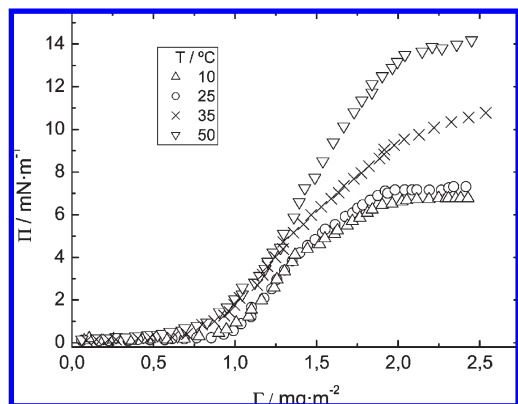(34) Sachetti, M.; Yu, H.; Zografi, G. *Langmuir* **1993**, *9*, 2168.

Figure 2. Temperature dependence of the Π versus area curves for monolayers of P4HS onto an aqueous subphase (pH = 2.0).

very important to remark that for an experiment to be valid, $\Delta\Pi$ must remain constant within the experimental uncertainty. For each temperature, the whole range of concentrations from the dilute to the concentrate regime were measured; the temperature range of the experiments was 5−60 °C. Special care was taken to minimize the evaporation and to keep the subphase level constant. The same trough was used for measuring the equilibrium Π versus Γ isotherms for which the canal was removed and the motion of the two barriers was synchronized. In studying the temperature dependence of Π, one must take into account the temperature dependence of γ_0.

Independent measurements of η have been carried out using a particle tracking technique. Polystyrene latex microparticles with diameters ranging from 0.5 to 5 μm have been spread on the P4HS monolayers, and their Brownian motion has been followed by video microscopy obtaining the diffusion coefficient (D) from the trajectories of the particles.[35] The technique has been described in a previous paper.[36] We have recently demonstrated that the ratio D/D_0 (with D_0 being the diffusion coefficient on the bare interface) obtained by particle tracking, together with Danov's hydrodynamic calculations, leads to values of η_{sh} that compare well with those obtained by macroscopic conventional rheometry.[37]

Results

Equilibrium Properties. Figure 2 shows the equilibrium Π versus area curves for the monolayer at different temperatures. The behavior of the present monolayers in the semidilute regime can be discussed in terms of the critical exponent ν that characterizes the molecular weight (M_w) dependence of the radius of gyration.[22] The average value $\nu = 0.54 \pm 0.07$ over the 10−60 °C range indicates that the water/air interface is a poor (near Θ) solvent condition.[6]

Interfacial Shear Viscosity. Figure 3 shows a representative set of the η_{sh} results obtained as a function of Π and at three different temperatures. For the sake of clarity, only three different temperatures are shown. The agreement of the results obtained by canal viscosimetry and by particle tracking is satisfactory. In all the cases, power-like $\eta_{sh} \sim \Pi^{\alpha}$ is observed. At the highest temperatures, $\alpha \approx 1$ over the whole surface pressure range. However, at low temperatures, α crosses over from a value not too far from unity to values of the order of 7−10. Such a behavior is shown by Figure 4 together with the temperature dependence of the surface pressure (Π_0) at which the change in α is found. It can be observed that Π_0 shows a break at $T \approx 30$ °C.

(35) Waigh, T. A. *Rep. Prog. Phys.* **2005**, *68*, 685.
(36) Cicuta, P.; Donald, A. M. *Soft Matter* **2007**, *3*, 1449.
(37) Bonales, L. J.; Ritacco, H.; Rubio, J. E. F.; Rubio, R. G.; Monroy, F.; Ortega, F. *Open J. Phys. Chem.* **2007**, *1*, 25.
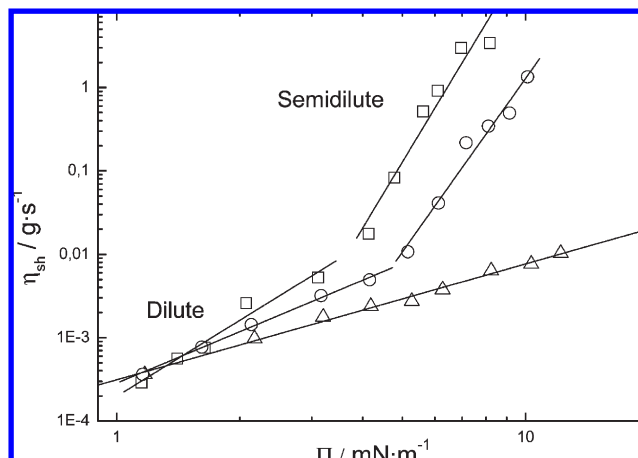
Figure 3. Surface pressure dependence of the surface shear viscosity of the P4HS monolayer at different temperatures: ($\square$) 16.0 °C, ($\bigcirc$) 31.8 °C, and ($\triangle$) 41.0 °C.
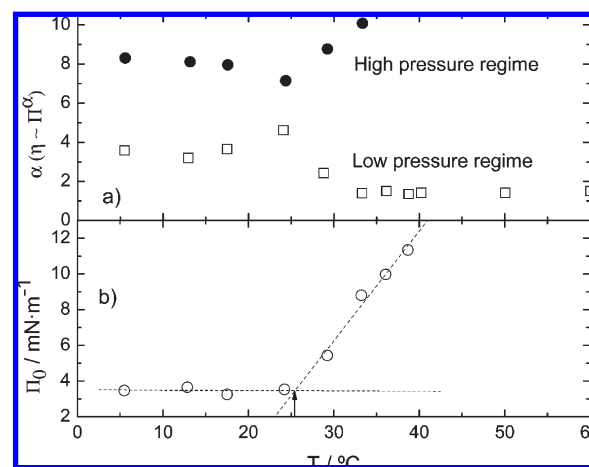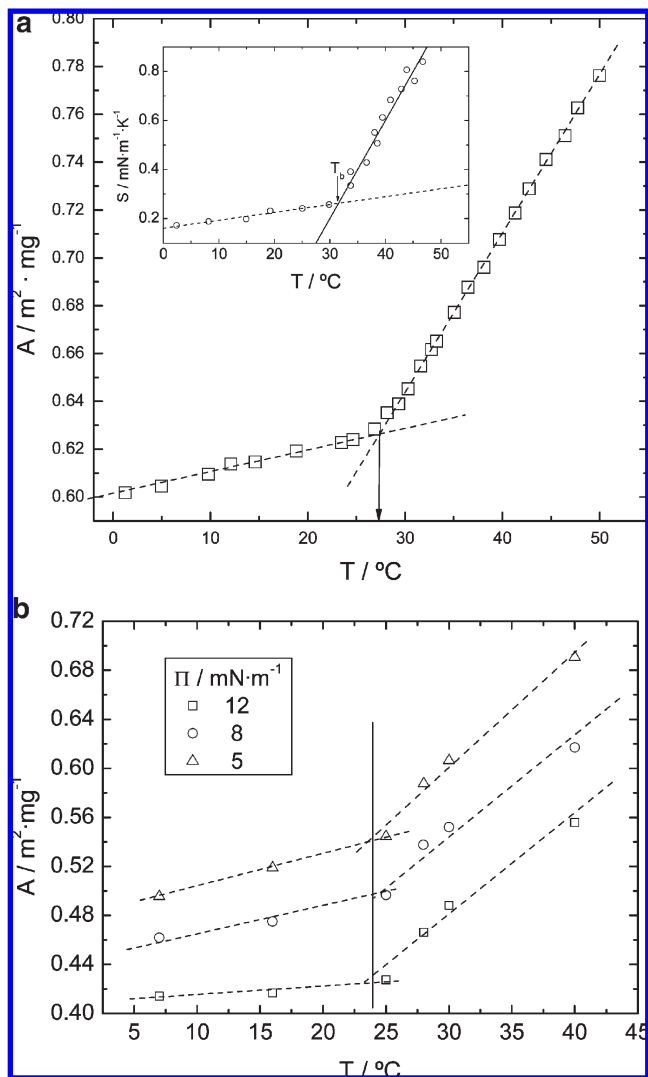

Figure 4. (a) Temperature dependence of the power-law exponent $\eta \sim \Pi^{\alpha}$. (b)Temperature dependence of the pressure at which the shear viscosity shows a break in a η versus Π plot (see Figure 3).

Discussion

Figure 5a shows the temperature dependence of the area per molecule at $\Pi = 6$ mN·m^{-1}; similar plots were found for other Π values. The sharp change in the slope of the plot resembles the one found in bulk systems when the molar volume is plotted versus T at constant pressure and the break point identifies the fluid-to-glass transition. In the present case, the temperature of the breaks is $T_b \approx 28$ °C. Similar results have also been found for another polymer, poly(vinyl stearate), for which the interface is also a poor solvent (see Figure 5b). No clear dependence of T_b on Π (or Γ) has been observed for any of the two polymers.

The value estimated for T_b is rather close to the one previously reported from the temperature dependence of the coupling parameter calculated from dilational relaxation experiments on the P4HS monolayer.[21] Such a change of behavior was interpreted as a crossover from fluid (independent particle) to glass-like (collective) dynamics.

Besides a change of isobaric expansivity of the monolayer, it is possible to calculate the surface entropy change as T is decreased

$$S = S_0 + \left(\frac{d\Pi}{dT}\right)_A \tag{2}$$

where $S_0 = 0.15$ mN·m^{-1}·K^{-1} is the surface entropy of the bare aqueous surface. The inset of Figure 5a shows that the plot of

Figure 5. (a) Isobaric cooling of a Langmuir film of P4HS at $\Pi = 6 \, mN \cdot m^{-1}$. Similar values of T_b were obtained for other values of Π within the semidilute regime. The inset shows the temperature dependence of the surface entropy, eq 2, at the same value of Π. (b) Isobaric cooling of a Langmuir monolayer of poly(octadecyl acrylate) at different values of Π. Within the experimental precision, it is not possible to discuss any density dependence of T_b.

S versus T also shows a break at $T \approx 30 \, °C$. The behavior observed in the inset of Figure 5a suggests that there should be a slowing down in the dynamics of the system associated with the decrease in the number of configurations that the system is able to sample as it approaches the crossover temperature T_b. Also, the temperature dependence of relaxation time, τ, characteristic of the polymer coil dynamics should show a significant change around T_b. One might expect that such an effect should be apparent in the experimental results of the shear viscosity.

Figure 4 shows that, at high temperature, the exponent α of the power-law behavior of the shear viscosity is close to unity. In principle, this might suggest that the shear rheology of the system is controlled by the free area. The free-area model has been shown to describe correctly η_{sh} for Langmuir films of polymers and surfactants[34,38] and predicts

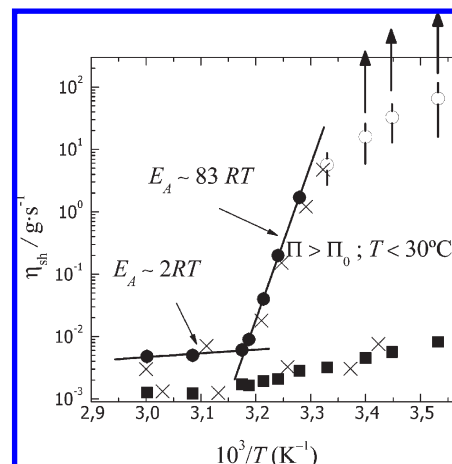$$\ln \eta_{sh} = \ln \eta_{sh}^0 + \frac{E_A}{RT} \frac{A_0}{A - A_0} \qquad (3)$$

Figure 6. Temperature dependence of the shear viscosity of a monolayer of P4HS. Circles correspond to $\Pi = 8 \, mN \cdot m^{-1}$, that is, above the overlapping concentration, and squares correspond to $\Pi = 2 \, mN \cdot m^{-1}$. The data were obtained by canal viscosimetry (squares and circles) and by particle tracking experiments (crosses).

where A_0 is the area obtained from the extrapolation to $\Pi = 0$ of the linear behavior of Π versus A in the semidilute regime. The present results cannot be correlated with eq 3 even at the highest temperatures measured. As the temperature is decreased at low Π values, the exponent α increases from unity to values in the 7–10 range. This implies a high cooperativity of the dynamics of the system: increasing Π less than a decade leads to an increase of 4 orders of magnitude in η_{sh}. This cannot be explained in terms of a decrease of the available free area, but by a strong increase of the cooperativity of the dynamics characteristic of the fluid to soft glass transition.

Figure 6 shows a rather typical plot of a system undergoing a fluid to glass transition. It can be observed that for low densities ($\Pi = 2 \, mN \cdot m^{-1}$) the viscosity follows a typical Arrhenius behavior. However, as the density of the monolayer is increased above the overlapping concentration (e.g., $\Pi = 8 \, mN \cdot m^{-1}$), there is a clear change in the slope of the plot. The apparent activation energy for the concentrated monolayer changes from $E_A = 2RT$ at high temperatures to $E_A = 83RT$ below $T = 40 \, °C$. Below 25 °C, measuring η_{sh} by both the canal and the particle tracking techniques becomes rather difficult due to the high value of the shear viscosity (points marked with an arrow in Figure 6). The temperature range for which measurements have been possible in our Langmuir trough is rather limited for $T > T_b$, thus making it very difficult to detect any curvature in the $\ln \eta_{sh}$ versus $1/T$ plot indicative of a transition from Arrhenius to Vogel–Fulcher–Tamman behavior as mentioned in the Introduction.[39,40]

It must be remarked that Figure 6 points out clearly that density plays a significant role in the existence of a fluid to glass-like transition. Below a certain value of Π, no break is observed in the monolayer ($T = 0 \, °C$ is the lower boundary for the measurements!). This is in agreement with the conclusions obtained from the studies of the effect of pressure on the dynamics of bulk systems,[41] and also from the classical work of Pusey and van Megen on the glass transition of colloidal suspensions.[38] Unfortunately, the precision of the data does not allow us to make a detailed discussion of the density dependence of T_b.

(38) Pusey, P. N.; van Megen, W. *Phys. Rev. Lett.* **1987**, *59*, 2083.

(39) Ngai, K. L. *Eur. Phys. J. E* **2002**, *8*, 225.
(40) Luengo, G.; Ortega, F.; Rubio, R. G.; Rey, A.; Prolongo, M. G.; Masegosa, R. M. *J. Chem. Phys.* **1994**, *100*, 3258.
(41) Roland, C. M.; Hensel-Bielowka, S.; Paluch, M.; Casalini, R. *Rep. Prog. Phys.* **2005**, *68*, 1405.
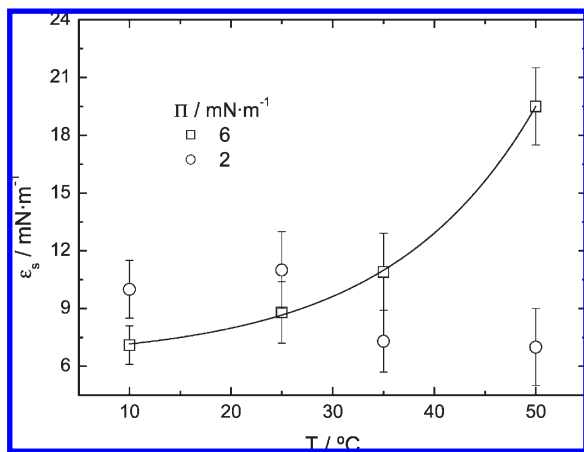
Figure 7. Temperature dependence of the equilibrium elasticity for the P4HS monolayers at two different surface pressures.

Even though one might be tempted to conclude that both the equilibrium and the dynamic results discussed indicate that the monolayers of P4HS have a glass transition in the proximity of 30 °C,[42] the behavior of the equilibrium elasticity ε_s does not seem to be compatible with such a conclusion. The values of ε_s have been calculated from the data in Figure 2 through $\varepsilon_s = \Gamma(\partial\Pi/\partial\Gamma)_T$. As shown in Figure 7, the results lead to elasticity values that increase with temperature for dense monolayers where the viscosity is found to increase strongly as T is decreased $[(\partial\varepsilon_s/\partial\Gamma)_\Pi > 0$ for $\Pi > 6$ mN·m$^{-1}]$. On the contrary, for low density monolayers $[\Pi < 3$ mN·m$^{-1}]$, where a single Arrhenius behavior is found for the viscosity, the elasticity slightly increases as the temperature is decreased below 30 °C. Contrary to what has

(42) López-Díaz, D.; Velázquez, M. M. *Eur. Phys. J. E* **2008**, *26*, 417.
(43) Freer, E. M.; Yim, K. S.; Fuller, G. G.; Radke, C. J. *J. Phys. Chem. B* **2004**, *108*, 3835.

been discussed for the shear viscosity (Figures 3 and 6), the results of the elasticity for $\Pi > 3$ mN·m^{-1} are not compatible with the existence of a glass transition.[23,40]

Power-law dependences of the shear viscosity on concentration have been described in percolating systems[23] and in the sol−percolating gel transition.[29] This might explain the increase of η_{sh} shown in Figure 3 and its power-law dependence on the surface pressure, because in the semidilute regime the following power-law has been found to hold $\Pi \sim \Gamma^y$, where $y = 2\nu/(2\nu - 1)$.[6] Therefore, the present results indicate that the soft-glass state suggested by Freer et al.[43] may just be a quasi-two-dimensional gel.

Conclusions

The Π versus A isotherms for the P4HS monolayers lead to a break in the A versus T plots at constant Π which is consistent with a glass transition close to 30 °C. Similar conclusions are reached at when the excess surface entropy data are analyzed.

The surface shear viscosity shows an Arrhenius behavior at low surface densities over the whole temperature range 5−60 °C. However, a change from single-molecule-like (low activation energy) to cooperative dynamics is also observed near 30 °C for denser monolayers. The temperature dependence of the equilibrium elasticity for the high surface pressure range does not seem to be compatible with the existence of a glass state at low temperatures. The results may be interpreted as the transition from a fluid to a quasi-2D gel.