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ORIGINAL CONTRIBUTION

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Monolayers of hydrogen-bonded polymer blends at the air–water interface: poly(vinylacetate)+poly (4-hydroxystyrene)

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Abstract The surface pressure (Π) vs surface concentration (Γ_s) curves of the hydrogen-bonded polymer blend poly(vinylacetate) + poly(4-hydroxystyrene) (PVAc + P4HS) have been measured at 25 °C onto a water subphase at pH = 2.0. While PVAc forms extended monolayers, and the free surface of water is found to be a good solvent for it, P4HS forms compressed monolayers, and the surface is a near Θ-type solvent for it. PVAc and P4HS form miscible non-ideal monolayers until near the collapse pressure through the whole concentration range. The composition dependence of the Π–Γ_s curves is rather complex. Contrary to what might be expected, the addition of PVAc to the blend does not reduce the rigidity of the monolayer until its weight fraction is larger than 0.5. The compressibility data of the P4HS-rich monolayers suggest the existence of a second maximum at high surface coverages, a result already observed in some polysiloxanes.

Key words Monolayers – polymer blends – hydrogen bonds – poly (4-hydroxystyrene) – poly(vinylacetate)

Introduction

There exist many studies of mixed polymer films spread at the water–air interface. Gabrielli et al. [1], Kawaguchi [2], and Gaines [3] have reviewed recent results concerning the general reasons for compatibility of two polymers or a polymer plus a low molecular weight compound in the monolayers. Understanding the behavior of this kind of systems is important both from the applicative and biological points of view, since they can throw light on the behavior of biological and synthetic membranes, as well as on the structure of films deposited by the Langmuir–Blodgett technique [4].

One of the main conclusions reached at by Gabrielli and coworkers [1] is that the compatibility of mixed polymers spread at the water–air interface strongly depends on the interfacial orientation of the polymer chains. In general, the components that show compatibility have the same interfacial orientation, and the incompatible ones have a different orientation. However, the work of Kawaguchi and Nishida [5] seems to indicate that, besides orientational conditions, the thermodynamic interaction between the two polymers plays a fundamental role.

Hydrogen bonds play a key role in the bulk phase diagram of polymer blends [6] and of block copolymers, in which morphological changes may take place when the surface concentration is varied [7]. Although the existence of hydrogen bond interactions facilitates the miscibility of polymer blends, strong concentration fluctuations may still exist in this type of blends, leading to heterogeneities at the level tens of nanometers [8]. This type of microheterogeneities might have noticeable effects in the behavior of monolayers of polymer blends.

In recent years the bulk behavior of blends formed by poly(4-hydroxystyrene) (P4HS) and poly(vinylacetate) (PVAc) or polyacrylates has been characterized [9, 10]. While the blends with PVAc and poly(methylacrylate) were found to be homogeneous at the level of a few nanometers, the blend with poly(methylmethacrylate) was found to present heterogeneities at levels of the order of 30 nm [8]. In all these systems hydrogen bonds between the hydroxyl groups of P4HS and the carbonyl groups of the second component were revealed by FT-IR [11], hence the existence of strong exothermic interactions does not guarantee complete miscibility at the microscopic level in 3D systems. It might be of interest to check whether these effects are also found in monolayers.

From the technological point of view, P4HS has been used extensively in electronic and photographic applications [12, 13], however, because of its high glass-transition temperature and poor mechanical properties it is difficult to process it [9]. This might have important negative consequences in order to prepare thin films of P4HS by the Langmuir–Bodgett technique. The bulk mechanical properties of the blend can be strongly improved upon mixing with other polymers, e.g. PVAc or poly(acrylates), [9, 14] thus mixed monolayers might help in preparing thin films.

The purpose of this paper is to carry out a detailed study of the equilibrium properties of the monolayers of one of the above-mentioned blends for which miscibility in 3D has been confirmed at the nm scale: P4HS + PVAc.

PVAc monolayers have been extensively studied [5, 15], and found to be of the expanded type. As far as we know, monolayers of P4HS have not been reported yet. As it will be shown, P4HS forms condensed-type monolayers at the air–water interface. In addition, it will also be shown that the surface is a good solvent for PVAc, while it is a near Θ solvent for P4HS. Hence, mixed monolayers of PVAc + P4HS are adequate in order to explore a broad range of monolayer behavior: from expanded to condensed type, and from good to bad solvent conditions. If may also be of interest in order to understand the rheological behavior of polymer films, since the transverse and dilational viscosities have been found to have rather different relative weights in expanded and compressed monolayers [16].

Materials and methods

Experimental setup

A commercially available Teflon Langmuir trough (KSV Instrument model 3000 with a minitrough, Finland) with a computerized control was used. A Pt-Wilhelmy balance was used as a surface pressure (Π) sensor. Polyoxymethylene (Delrin) barriers were used. The whole setup was enclosed in a box through which a small flow of filtered N_2 (0.1 μm filter) was maintained. A Petry cell with subphase was placed inside the box in order to keep the humidity at the saturation value corresponding to the measuring temperature. The temperature control of water in the trough was carried out by passing thermostatted water into the jacket at the bottom of the trough. The temperature near the surface was measured with a calibrated Pt-100 sensor. The temperature of the box was maintained constant within ± 0.1 °C at the same temperature of the measurements.

The spreading solution was slowly applied by a microsyringe onto the surface with completely open barriers. The surface concentration (Γ_s) was changed by subsequent additions of the polymer solution. Times ranging from 15 to 50 min were allowed for solvent evaporation. The surface pressure was continuously monitored, and the equilibrium value was taken only when Π remained constant for at least 20 min. The surface of the subphase was swept with the barriers and cleaned until the expected surface tension was obtained. In order to ensure that the spreading solvent did not add significant impurities, blank experiments with the solvent were done before each experiment. In order to ensure that equilibrium states were measured, the Π vs. Γ_s curves of PVAc and P4HS were also recorded by moving the Delrin barriers. Neither significant differences with the addition method nor appreciable hysterisis were found for low speed of the barriers (4–30 $mm^2 s^{-1}$).

Each reading of the surface pressure was determined with ± 10 μN/m, although the repetitivity under small cyclic changes of the position of the barriers was around ± 30 μN/m. The stability of the temperature was better than ± 0.05 °C.

Materials

The polymers, purchased from Polysciences (Germany), were the same used in previous works [9, 10, 13]. For PVAc $M_w = 90\,000$, and for P4HS $M_w = 10\,000$. In both cases, the polydispersity indices were approximately 2. We checked by UV and ^{13}C-NMR that no significant amount of the hydroxyl groups of P4HS had reacted to the quinone form. Before preparing the spreading solutions, the polymers were dissolved in tetrahydrofurane (THF) and filtered through 0.5 μm Teflon membranes. As spreading solvent a mixture of benzene + THF (5:1) has been used. The total polymer concentration in the spreading solution was close to 10^{-3} M. The solvents were purchased from Carlo Erba (RPE quality). Before preparing the polymer solutions, the surface tensions of the solvents were measured by the plate method in order to be sure that they did not have significant amounts of surface active impurities. Good agreement was found between the values measured and those reported by Jasper [17]. We used deionized water from a MilliQ-RG system, its resistivity was always higher than 18 MΩ, and its surface tension at 25 °C was (72.12 ± 0.08) mN m^{-1}.

Results and discussion

Pure polymers

PVAc

Yoo and Yu [18] have presented an extensive study of monolayers of PVAc in the 15–30 °C range, and on water subphase with pH = 7.0. Vilanove et al. [15] have carried out a detailed study of the dilute region of the monolayer, and concluded that the water-air interface is a good solvent for this polymer.

For the sake of comparison, Fig. 1a shows the Π–Γ_s curve at 25 °C reported in ref. [18] and our results of pH = 7.0. The agreement is rather satisfactory. It also shows the isotherm for pH = 2.0 obtained in this work. The effect of the pH is very small, only a small increase of the collapse pressure at pH = 2.0 being noticeable. Figure 1b shows the isotherms obtained between 25 and 1 °C for pH = 2.0. As it can be observed the overall effects of lowering T is the same than decreasing pH. For $\Gamma_s < 10^{-7}$ g cm^2 $(\partial\Pi/\partial T)_\Gamma < 0$, while at higher concentrations it is positive. This behavior is similar to that found by Yoo and Yu between 15 and 30 °C [18]. This leads to surface entropies and enthalpies that are positive at low concentrations, and negative at high ones.

Following standard procedures [19], we have calculated the limit areas A_0 from the Π–Γ_s curves. Figure 2a shows the values obtained, together with those reported in ref. [18] for pH = 7.0. It becomes evident that the effect of pH increases as T is decreased. Despite this fact, the quality of the interface as solvent of PVAc remains unchanged as revealed by the behavior of the critical exponent v, defined by

$$\Pi \approx \Gamma_s^y , \tag{1}$$

where $y = 2v/(2v - 1)$. This scaling law is valid in the so-called semidilute regime [15], that for the PVAc isotherms is limited to values of $\Pi < 20\,\mathrm{mN\,m^{-1}}$ and $0.2 < \Gamma_s(10^{-7}\,\mathrm{g\,cm^{-2}}) < 1.3$. Figure 2b shows that the critical exponents v does not change either with T or with pH. Figure 2b also includes the value of v reported by Vilanove et al. for pH = 7.0 [15]. Despite the uncertainty of our values, they are compatible with the value $v = 0.77$ derived from Renormalization Group for good solvent conditions [20]. Figure 2c shows the overlap concentration Γ^* that marks the transition between dilute and semidilute concentrations (where the polymer coils start to overlap) on subphase with pH = 2. As it can be observed, Γ^* increases with T, which indicates that the polymer coils are more expanded at high temperatures. The value of Γ^* at 25 °C and pH = 7.0 ($0.24 \times 10^{-7}\,\mathrm{g\,cm^{-2}}$) is higher than that of pH = 2.0 ($0.18 \times 10^{-7}\,\mathrm{g\,cm^{-2}}$).

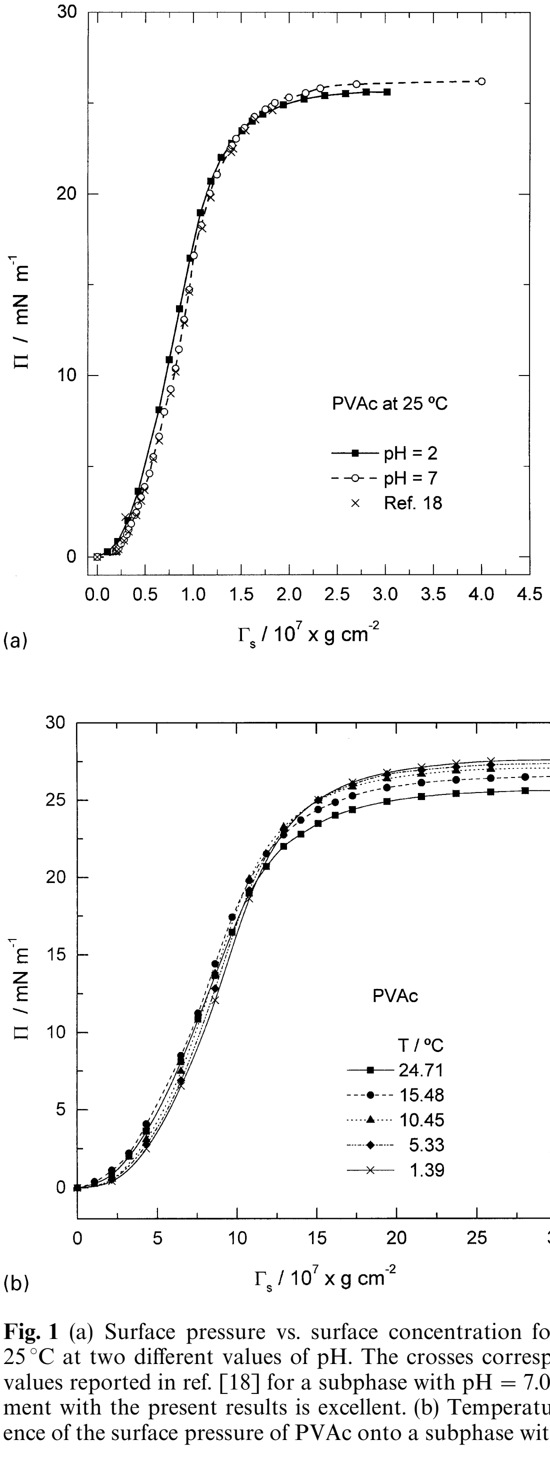

Fig. 1 (a) Surface pressure vs. surface concentration for PVAc at 25 °C at two different values of pH. The crosses correspond to the values reported in ref. [18] for a subphase with pH = 7.0, the agreement with the present results is excellent. (b) Temperature dependence of the surface pressure of PVAc onto a subphase with pH = 2.0

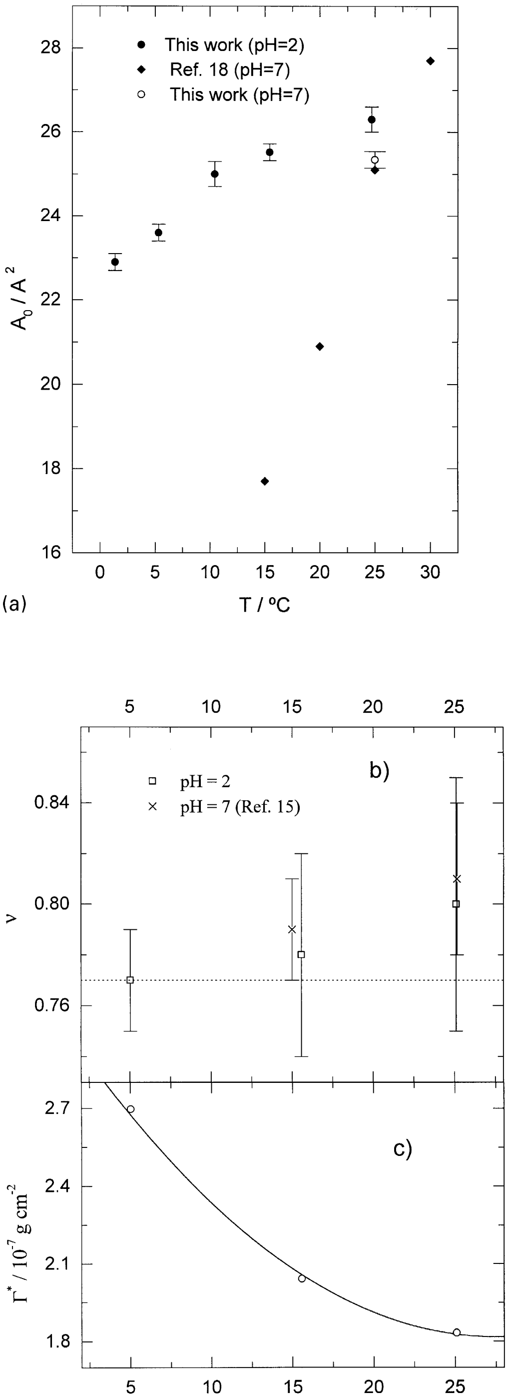

Fig. 2 (a) Limit area for the PVAc monolayer as a function of the temperature, and at two values of pH. (b) Critical exponent of the hydrodynamic radius for the PVAc monolayer at three temperatures and two values of pH. The dashed line represents the Renormalization Group prediction for good solvent conditions. (c) Overlapping concentration for the PVAc monolayer onto aqueous subphase with pH = 2.0

P4HS

Figure 3 shows the Π–Γ_s curves at 25 °C and pH = 7.0 and 2.0. The inset shows a log–log scale to illustrate the degree of fulfilment of the scaling laws in the different regimes (dilute, semidilute, concentrate). The first aspect to point out is that, contrary to PVAc, the isotherms are of the condensed type. On the other hand, the effect of pH is opposite to that found in PVAc in the same range of Π's. In the present case the acid subphase avoids the ionization of the phenol groups, thus reducing the effect of coulombic repulsions.

From the intermediate-Γ_s regime of the isotherm with pH = 2.0, we have estimated the critical exponent ν and the overlap concentration Γ^*, and found the following values: 0.58 ± 0.06 and $0.8\,\mathrm{mg\,m^{-2}}$, respectively. The value of ν is close to the theoretical value for a polymer chain in a Θ solvent: 0.505, and very close to the value found in ref. [15] for a sample of atactic poly(methylmethacrylate) (PMMA) of similar molecular weight.

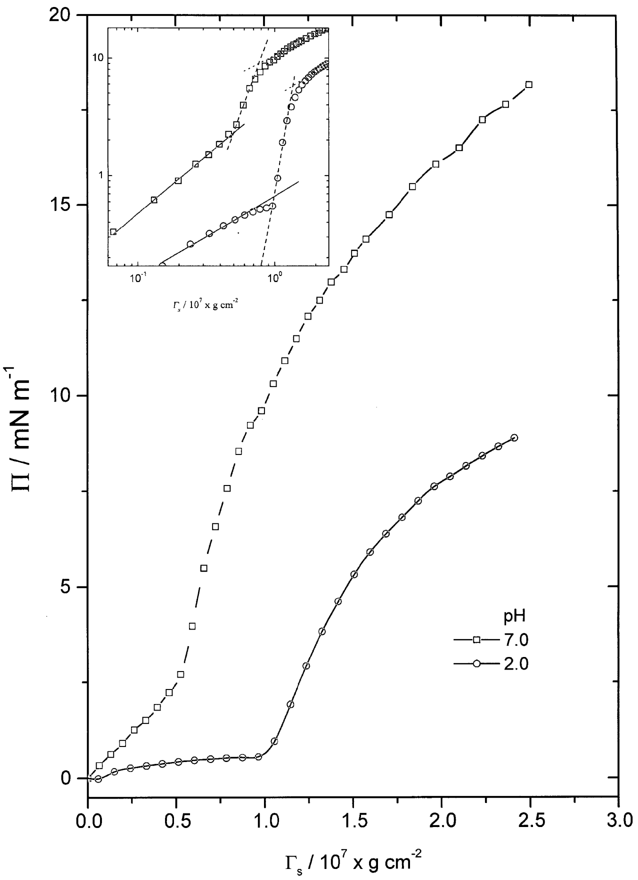

Fig. 3 Surface pressure vs. surface concentration for the P4HS monolayer at 25 °C and at two values of pH

The high value of Γ^* is equivalent to a hydrodynamic radius of the overlapping chains $R_g = 2.6$ nm, very similar to that of the sample of PMMA, $R_g = 2.5$ nm [15], and much smaller than the corresponding value of PVAc, $R_g = 16.4$ nm. For the isotherm at pH = 7.0 the values obtained were $\Gamma^* = 0.5 \times 10^{-7}$ g cm^{-2}, and $\nu = 0.6 \pm 0.1$, which again indicates that the quality of the interface as solvent does not depend on pH, and that the chains tend to be more extended on the surface at the higher pH. This conclusion is also drawn from the values of the limit areas A_0 that are: 20.1 ± 0.1Å^2/monomer for pH = 2 and 37.8 ± 0.1Å^2/monomer for pH = 7.0. This might be qualitatively explained by considering that at high pH there is a higher density of ionized phenoxide groups that exclude more volume than the non-ionized phenol groups due to electrostatic interactions.

Blends

Figure 4 shows the Π–Γ_s curves for the PVAc + P4HS blend at 25 °C and pH = 2.0 over the whole concentration range. It also includes the isotherms corresponding to the two pure polymers. It can be observed that it is not possible to reach a high-Π plateau for any of the blends. It also shows the dramatic effect of P4HS on the monolayer behaviour: the blend with 50% of PVAc presents a Π–Γ_s curve quite similar to that of pure P4HS. Blends richer in P4HS show more compressed isotherms, with a maximum for the blend 0.25 PVAc + 0.75 P4HS. Figure 5 shows the ν exponent as a function of the weight fraction of PVAc, w. Within the estimated uncertainty, one can observe that the surface presents a smooth change from good to near-Θ solvent character as w is decreased. This is accompanied by a decrease of the limit area, which passes through a shallow minimum for the blend with $w = 0.30$ (see Fig. 4).

Since no collapse pressure is reached, the miscibility of the blends must be discussed in terms of the composition dependence of surface areas at constant Π [1, 2]. Figure 6a shows the excess areas, A^E, for different values of Π:

$$A^E(\Pi) = A^M(\Pi) - x_1 A^1(\Pi) - x_2 A^2(\Pi)\,, \qquad (2)$$

where $A^i(\Pi)$ is the area of component i or of the mixture at surface pressure Π, and x_i is the mole fraction of component i. The curves are fits to a Redlich–Kister-type equation [21].

$$A^E/x_1x_2 = \sum_0^n a_i(x_1 - x_2)^{i-1}\,, \qquad (3)$$

where the a_i's are adjustable parameters, and for the present data the maximum value of n has been 3.

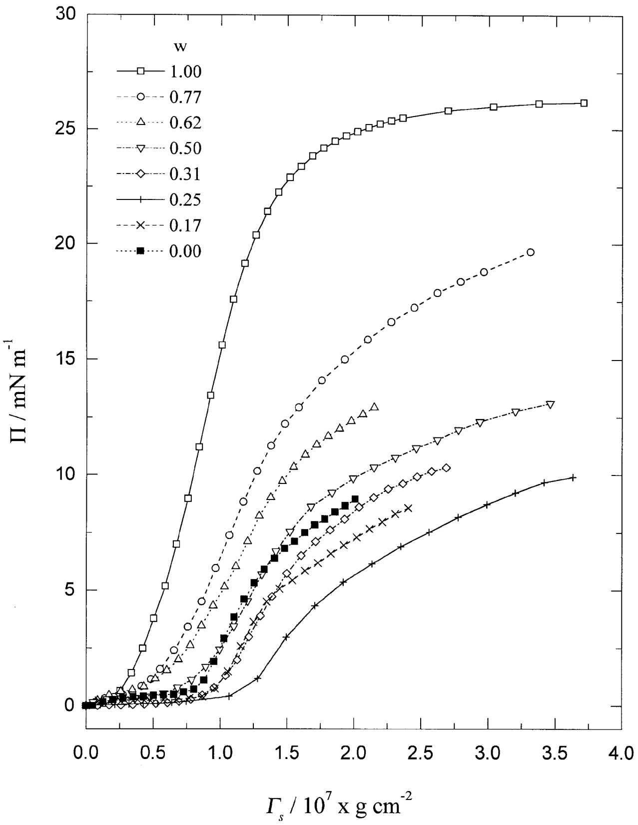

Fig. 4 25 °C isotherms for the w PVAc + (1 − w) P4HS blends onto aqueous subphase with pH = 2.0, w represents the weight fraction of PVAc

It can be observed that A^E is negative through the whole Π range that can be studied. The minimum area is found for the near equimolar blend, and decreases with Π. These results indicate that the blends are miscible, which, as in the case of the bulk blend [11], can be explained in terms of strong hydrogen bonds built between the carboxyl groups of PVAc and the hydroxyl groups of P4HS. These interactions might favour a closer packing than the corresponding to each polymer separately.

Besides A^E, the excess Gibbs energy provides an important information about the stability of the mixed monolayers. It can be calculated through

$$\Delta G^E(\Pi) = \int_0^{\Pi} A^E(\Pi)\,\mathrm{d}\Pi\,. \qquad (4)$$

As observed in Fig. 6b, the values of ΔG^E are strongly negative, and quite symmetrical around the equimolar mixture. Contrary to the A^E results, the minima of the ΔG^E vs. x_1 curves decreases with increasing Π.

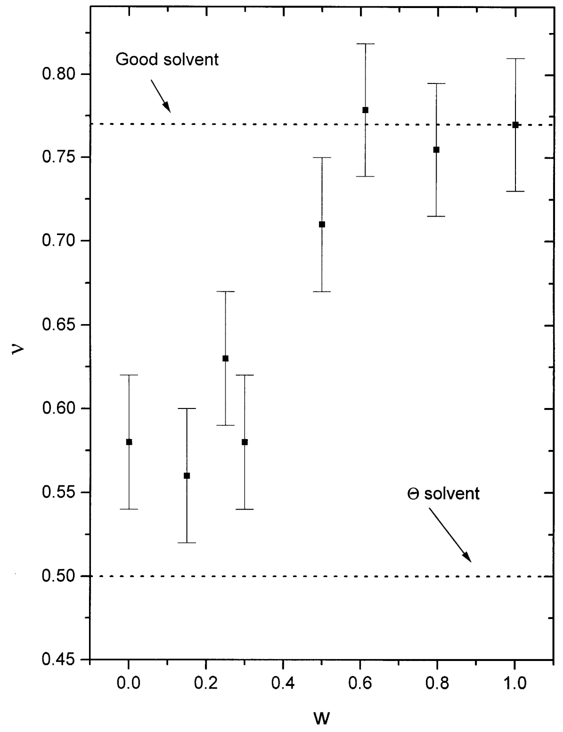

Fig. 5 Composition dependence of the critical exponent of the hydrodynamic radius ν for the w PVAc + (1 − w) P4HS blend. The two dashed lines denote the predicted values for interfaces acting as good or as Θ-solvents

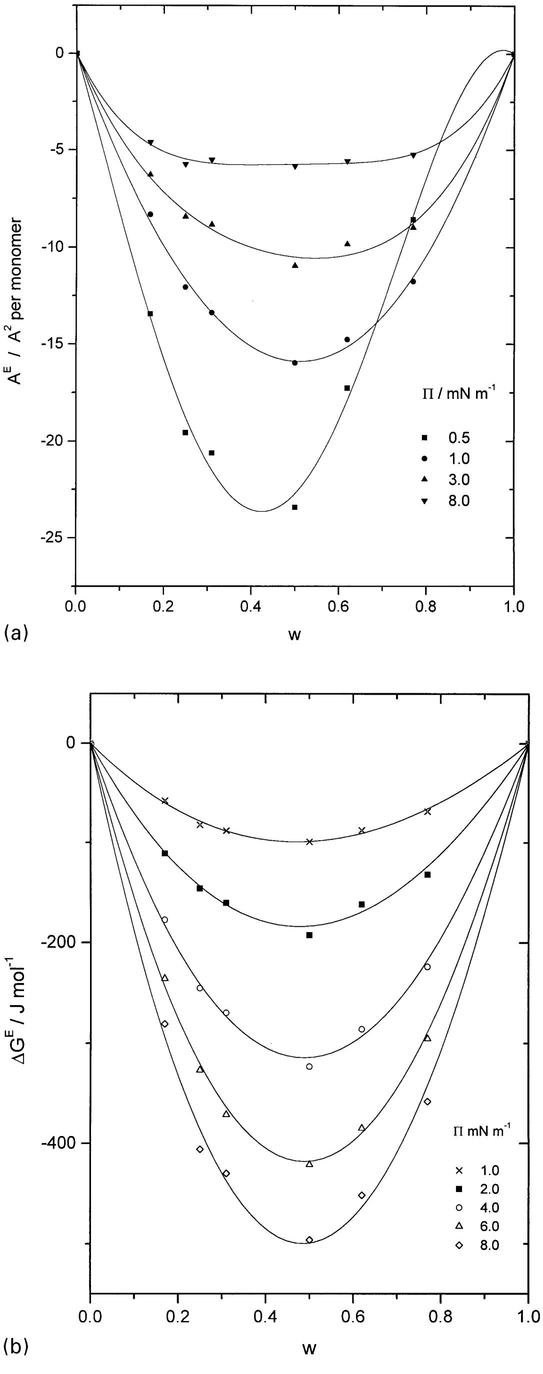

Fig. 6 (a) Excess area for the w PVAc + (1 − w) P4HS blend at 25 °C onto aqueous subphase with pH = 2.0. The curves correspond to different values of the surface pressure. (b) Excess Gibbs energy for the w PVAc + (1 − w) P4HS monolayers at 25 °C and pH = 2.0 as a function of the surface pressure

Compressibility

The static compressibility factor of the monolayer ε

$$\varepsilon = -A\left(\frac{\partial \Pi}{\partial A}\right)_T \tag{5}$$

can be calculated from the Π–Γ_s curves. We have used a five-point spline method to estimate the derivative. Figure 7 shows the results at 25 °C. We do not show the temperature dependence of ε for PVAc since it is rather small: for the 1 and 25 °C isotherms, the difference is only slightly larger than the uncertainty in ε. The values for PVAc agree with the values given by Yoo and Yu [18]. It must be noticed that most of the increase of ε (from aprox. 1–25 mN m^{-1}) corresponds to the semidilute regime. The same can be said for pure P4HS, however, in this case, the behavior in the concentrate regime is quite different: above 1.5×10^{-7} g cm^{-2} ε increases again. Similar complex behavior of ε have been described by Garrett and Zisman [22], for poly(phenylsiloxane), and by Runge and Yu [23] for poly(dimethylsiloxane) (PDMS) + PVAc. In the case of PDMS the existence of two maxima in the ε vs. Γ_s curves is associated to the presence of two collapse pressures, which have been related to the existence of conformational and/or packing transitions as the monolayer is compressed. Several maxima can also be deduced from the Π–Γ_s curves of

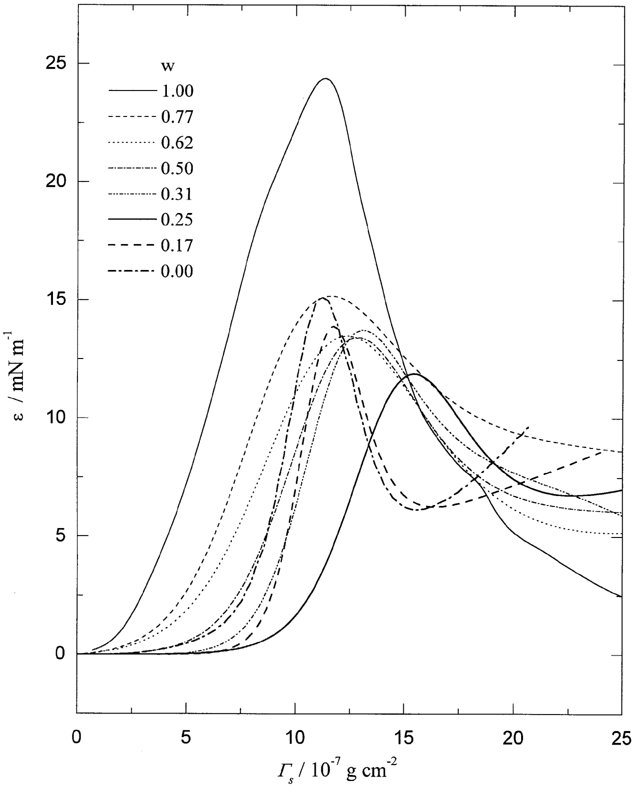

Fig. 7 Elasticity coefficient of the w PVAc + (1 − w) P4HS monolayer at 25 °C and pH = 2.0. The curves correspond to the weight fractions of PVAc indicated in the figure. Notice the increase of ε at high surface concentrations for the P4HS-rich blends

some triblock copolymers, [24] and have been associated to the solubilization of one of the blocks. The present results for P4HS do not allow one to associate the details of the ε vs. Γ curve to any physical mechanism of the P4HS monolayer. The composition dependence of the compressibility modulus indicates that the addition of small amounts of PVAc of P4HS does not reduce in a significant way the rigidity of the monolayer, until PVAc contents larger than 80% in weight fraction are reached. Moreover, for compositions below 25%, the addition of PVAc makes the monolayer more rigid.

The surface composition at which the maximum in ε appears, Γ_M, shows a small change except for blends with PVAc content below 30%. The increase of the rigidity of the monolayer may be qualitatively explained in terms of the existence of strong hydrogen bonds between PVAc and P4HS.

Conclusions

PVAc monolayers over pH = 2.0 water subphase forms extended monolayers between 1 and 25 °C, and the surface is found to be a good solvent for the polymer. These results are similar to those reported in the literature over pH = 7.0 water subphase. However, P4HS forms compressed monolayers, and no plateau region in Π is observed at high surface concentrations.

The composition dependence of the Π–Γ_s curves is complex. As PVAc is added to P4HS the monolayers become more compressed until the weight fraction of PVAc reaches the value $w = 0.25$. Beyond that value, the monolayers become more expanded until $w = 0.50$. where the shape of the Π–Γ_s curve is almost the same than for pure P4HS, though larger values of Π can be reached.

Analysis of the semidilute region of the monolayers in terms of scaling laws indicate that the aqueous–air interface is a good solvent for PVAc-rich monolayers, while a near Θ solvent for monolayers rich in P4HS.

The compressibility data of the P4HS-rich monolayers suggest the existence of a second maximum at high surface concentrations. This behavior is similar to the one reported in the literature for some polysiloxanes. However, the present data do not allow one to suggest a physical interpretation of the second maximum.

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References

1. Gabrielli G, Puggelli M, Baglioni P (1982) J Coll Interface Sci 86:485
2. Kawaguchi M (1993) Prog Polym Sci 18:341
3. Gaines Jr GL (1991) Langmuir 7:834
4. Roberts G (ed) (1990) Langmuir–Blodgett Films. Plenum Press, New York
5. Kawaguchi M, Nishida R (1990) Langmuir 6:492
6. Olabisi O, Robeson LI, Shaw MT (1990) Polymer–Polymer Miscibility. Academic Press, New York
7. Gonçalves da Silva AM, Filipe EJM, d'Oliveira JMR, Martinho JMG (1996) Langmuir 12:6547
8. Zhang X, Takegoshi K, Hikichi K (1991) Macromolecules 24:5756
9. Luengo G, Ortega F, Rubio RG, Rey A, Prolongo MG, Masegosa RM (1994) J Chem Phys 100:3258
10. Prolongo MG, Salom C, Masegosa RM, Moreno S, Rubio RG (1997) Polymer 38:5097
11. Sanchis A, Prolongo MG, Rubio RG, Masegosa RM (1995) Polymer J 27:10
12. Hiraoku H, Welsh LW (1983) Proc Electrochem Soc 83:171
13. Fujiwara H, Takahashi A (1973) Yuki Gosei Kagaku 35:877
14. Sanchis A, Prolongo MG, Masegosa RM, Rubio RG (1995) Macromolecules 28:2693
15. Vilanove R, Poupinet D, Rondelez F (1988) Macromolecules 21:2880

16. Kawaguchi M, Sauer BB, Yu H (1989) Macromolecules 22:1735
17. Jasper JJ (1972) J Phys Chem Ref Data 1:841
18. Yoo KM, Yu H (1989) Macromolecules 22:4019
19. Gaines HE Jr (1966) Insoluble Monolayers at Liquid–Gas Interface. Interscience, New York
20. Fleer GJ, Cohen-Stuart MA, Scheutjens JMHM, Cosgrove T, Vincent B (1993) Polymers at Interfaces. Chapman & Hall, London
21. Prausnitz JM, Lichtenthaler RN, Gomes de Azevedo E (1986) Molecular Thermodynamics of Fluid-Phase Equilibria, 2nd ed. Prentice-Hall, Englewood Cliffs, NJ
22. Garrett WD, Zisman WA (1969) J Chem Phys 74:1796
23. Runge FE, Yu H (1993) Langmuir 9:3191
24. Myrvold R, Hansen FK, Balinov B (1996) Colloids Surfaces 117:27