Polymer Solutions with Specific Interactions: Equation of State for Poly(4-hydroxystyrene) + Acetone

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ABSTRACT: We have obtained the p–V–T surface of the mixture acetone + poly(4-hydroxystyrene) over the intervals $298 \le T/\mathrm{K} \le 328$, $0 \le p/\mathrm{MPa} \le 40$, and $0.45 \le w \le 0.97$, w being the weight fraction of acetone. The results obey a p–T–w superposition principle, making it possible to build a master curve when the pressure and the density are reduced with the isothermal compressibility and the density is at a reference pressure, respectively. The master curve depends on a single system-dependent parameter, which takes similar values for quite different mixtures. The master curve allows us to describe the pressure dependence of the density within experimental uncertainty. The bulk modulus of the system can be described quite accurately using a correlation inspired by a perturbation theory which assumes a spherical reference system. The data have been analyzed with two versions of a lattice–fluid model. One of the versions includes, in an approximated way, the existence of hydrogen bonds, both in the polymer and between the polymer and the solvent. However, almost no difference is found between the predictive ability of the two versions, at least for the p–V–T–w surface.

Introduction

Our understanding of the thermodynamics of polymer solutions is important in many processes of technological interest.[1] The study of polymer blends has attracted much attention toward polymer systems in which they are strong specific interactions, since their existence seems to be the main reason for the miscibility of a majority of polymer pairs.[2,4]

In polymer systems, the chain character of the components associated by hydrogen bonds leads to association complexes that are three-dimensional in character. Since the hydrogen bonds are formed and disrupted continuously, the system is in a sense a dynamic physical network. The existence of this network introduces strong difficulties in the theoretical description of these systems. In effect, two hypotheses are frequently assumed in the development of the theoretical models most frequently used to describe the thermodynamic properties of polymer mixtures: (i) the intermolecular potential has an isotropic character, and (ii) the distribution of the molecules in the mixture is random. Both assumptions are clearly inadequate for systems in which hydrogen bonds play a significant role.

An important attempt toward establishing a theoretical framework for such systems is that of Coleman and Painter's group[5] which is a semiempirical extension of Flory's rigid-lattice approach of consecutive linear association.[6] Equation of state (EoS) effects in polymer solutions have been recognized for years, especially in their ability to predict lower critical solution temperatures.[1,3] There have been comparisons of the performance of the most frequently used EoSs,[7–10] leading to the conclusion that, at least in the range of moderate pressures (0–50 MPa), the differences among them are very small in describing p–V–T surfaces,[7,10] although there might be differences in predicting other properties.

Recently, Panayiotou and Sanchez[11] have presented a general EoS theory of hydrogen bonding which is valid for linearly associated systems as well as for hydrogen bonded networks. In the case of nonassociated systems the model reduces to the lattice–fluid theory of fluids.[12,13]

A basic premise of the theory is the division of the intermolecular interactions into physical (van der Waals) and chemical (hydrogen bonds), leading to two separable factors in the partition function. There are also two groups of parameters that have to be known in order to apply the theory: three per pure component, p^*, T^*, and ρ^* or r, which already existed in the original lattice-fluid theory[12,13] and three others, $E°$, $V°$, and $S°$, characteristic of each hydrogen bond interaction. This means that a rigorous test of the theory occurs through the comparison of the theoretical predictions for thermodynamic properties of systems for which both the pure component physical parameters and those of the hydrogen bond interactions are already known.

In a recent paper vapor–liquid equilibrium data for poly(4-hydroxystyrene) + poly(vinylacetate) + acetone (P4HS + PVAc + Ac) and p–V–T data for P4HS and a 50:50 P4HS + PVAc blend have been presented.[14] It was found that the Panayiotou and Sanchez model[11] gave a quantitative description of the vapor–liquid equilibrium data, strongly improving the description given by the Lacombe and Sanchez model.[12,13] However, the improvement was not so evident for the p–V–T surface of the blend. Moreover, the parameters corresponding to the –OH···–CO– hydrogen bond were fitted to the experimental data. Therefore, an additional independent set of data seems to be convenient for a rigorous test of the theory. In this paper we present extensive p–V–T data for the Ac + P4HS system. These, and the previous p–V–T results,[14] will also be used to test a recently proposed p–w–T superposition principle, with w being the weight fraction of one polymer.[15,16]

The rest of this paper is organized as follows: the experimental details are given in the next section. In a subsequent section the results are presented and discussed; the final section compares the experimental data with theoretical predictions.

Experimental Section

The p–ρ–T data have been measured with a high-pressure vibrating tube densimeter. The whole apparatus has been described in detail in a previous work.[17] The strain gauge pressure transducers were calibrated against a dead weight gauge, and the

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Table 1. Characteristic of the Fitting of the Experimental Data to Eq 1

w	B_1/g cm^{-3}	10^2B_2/cm^3 K^{-1}	10^6B_3/g cm^{-3} K^{-1}	$10B_4$	$10^{-3}B_5$/MPa	10^2B_6/K^{-1}	$10^4\sigma(\rho)$/g cm^{-3}
0.967 48	1.0956	−0.0893	−0.3587	0.9135	1.1777	0.9254	0.9104
0.936 84	1.1691	−0.1296	0.2703	0.9088	1.2046	0.9286	1.6515
0.922 48	1.4034	−0.2787	2.6940	0.9229	1.3020	0.9381	0.9446
0.879 47	1.1693	−0.1165	0.0589	0.9070	1.1966	0.8991	0.7320
0.774 89	1.3852	−0.2382	2.1434	0.8065	0.9405	0.8180	1.2757
0.738 91	1.2048	−0.1133	0.1551	0.8809	1.1722	0.8319	0.9022
0.684 43	1.4138	−0.2402	2.3193	0.8738	0.9886	0.7526	0.7537
0.622 53	1.3365	−0.1746	1.2688	0.8034	0.8702	0.7081	1.1390
0.491 11	2.2944	−0.7797	11.6134	0.5368	0.5368	0.3779	2.0431

calibration was checked after the experiments on each substance were completed; this allowed the pressure to be known within ±0.01 MPa. The temperature of the U-tube was kept constant within ±0.5 mK and monitored with a thermistor placed beside the vibrating tube. The temperature was measured with a quartz thermometer placed in the water bath whose calibration was checked weekly against a Ga melting point standard. The temperature of the whole apparatus (except the electronics) was kept constant to ±0.01 K of that of the sample.

In addition to the calibration procedure described elsewhere,[18] it was necessary to account for the dependence of the period of vibration upon the viscosity of the sample. Ashcroft et al.[19] have discussed such a dependence for a low-pressure vibrating tube densimeter; we have followed a similar procedure to cover the viscosity range of our samples. The calibration curve was tested after the experiments on each pure substance were carried out. No hysteresis was found within $\pm 5 \times 10^{-7}$ in τ, the period of vibration, when measuring at low pressure after the vibrating tube was subjected to a high pressure. Under the conditions described, ρ can be obtained within $\pm 10^{-4}$ g cm^{-3} for the $0.1 \leq p/\mathrm{MPa} \leq 40.0$ range.

Acetone was purchased from Carlo Erba (RPE quality) and was used without further purification, except for being kept over 0.4-nm molecular sieves; its density $\rho = 0.785\,29$ g cm^{-3} agrees with the literature, 0.785 08 g cm^{-3}.[20] P4HS was obtained from Polyscience (M_w = 30 000). HPLC experiments on dioxane revealed a polydispersity $M_w/M_n \approx 2$.

Results and Discussion

Over 800 p–ρ–T–w experimental data have been obtained over the intervals $298 \leq T/\mathrm{K} \leq 328$, $0 \leq p/\mathrm{MPa} \leq 40$, and $0.45 \leq w \leq 0.97$, w being the weight fraction of acetone. The results at each composition were fitted to a generalized Tait equation of the form

$$\rho = \rho_0/[1 - B_4 \ln[(B + p)/(B + p_0)]] \qquad (1)$$

where

$$\rho_0 = B_1 + B_2T + B_3T^2 \qquad (2)$$

and

$$B = B_5 \exp(-B_6T) \qquad (3)$$

B_i (i = 1–6) being independent of T and p. Table 1 collects the values of B_i for the different isopleths and the corresponding standard deviations. Figure 1 shows the effect of pressure upon the molar volume at some of the temperatures and compositions. As expected, the effect of pressure is larger as the concentration of solvent increases, reflecting the difference in free volume between Ac and P4HS.

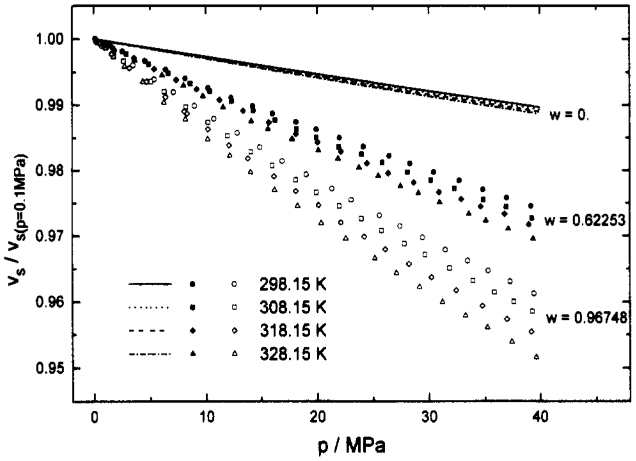

Figure 1. Pressure dependence of the specific volume for wAc + $(1 - w)$P4HS mixtures at different temperatures and compositions.

Sanchez et al.[15,16] have proposed that by choosing adequate variables, it was possible to merge the p–V–T–w data of polymer mixtures into a singlet curve; Figure 2A shows that the results of the Ac + P4HS system confirm this p–w–T superposition principle. Furthermore, Sanchez et al.[15,16] have suggested that

$$p\kappa_{T,0} = (\rho^{\delta} - 1)/\delta \qquad (4)$$

where δ is a parameter characteristic of the system; as can be observed in Figure 2A, eq 4 describes quite accurately the present results with $\delta = 10.32$. Figure 2B shows similar results for pure P4HS and a 50:50 P4HS + PVAc blend,[14] for which the best value of δ was 10.09. It is remarkable that the same curve is obtained for different substances such as P4HS and PVAc. This suggests that once knowing the behavior of V_0 and $\kappa_{T,0}$ as a function of temperature, it should be possible to generate the whole p–ρ–T surface from low-pressure data and the pressure dependence of other thermophysical data. In order to test this point we have compared such a prediction with the fits obtained with eqs 1–3; Figure 3 shows the residuals obtained which are almost within experimental uncertainty and that are quite comparable with the residuals obtained with the Tait equation.

A similar p–w–T superposition principle is found when combining Pruzan's equation[21] for the isobaric thermal expansion coefficient, α_p, and Furth's model[22] for describing the spinodal. Pruzan's equation reads

$$\alpha_p = A(p^* - p)^{\gamma} \qquad (5)$$

where A depends on T for one pure component (and on w for mixtures), p^* is the pseudospinodal pressure, and $\gamma \sim 0.5$. Furth's model allows the calculation of p^* from σ, the surface tension, through

$$p^* = p_0 - 1.32[\sigma(p_0)]^{3/2}(RT)^{-1/2} \qquad (6)$$

with p_0 being the orthobaric pressure. The validity of this model was tested for simple fluids[23,24] and more recently for a wider variety of liquids.[25] Of course, due to the presence of the pressure p^* in eq 5, this approach is limited to $T < T_c$.

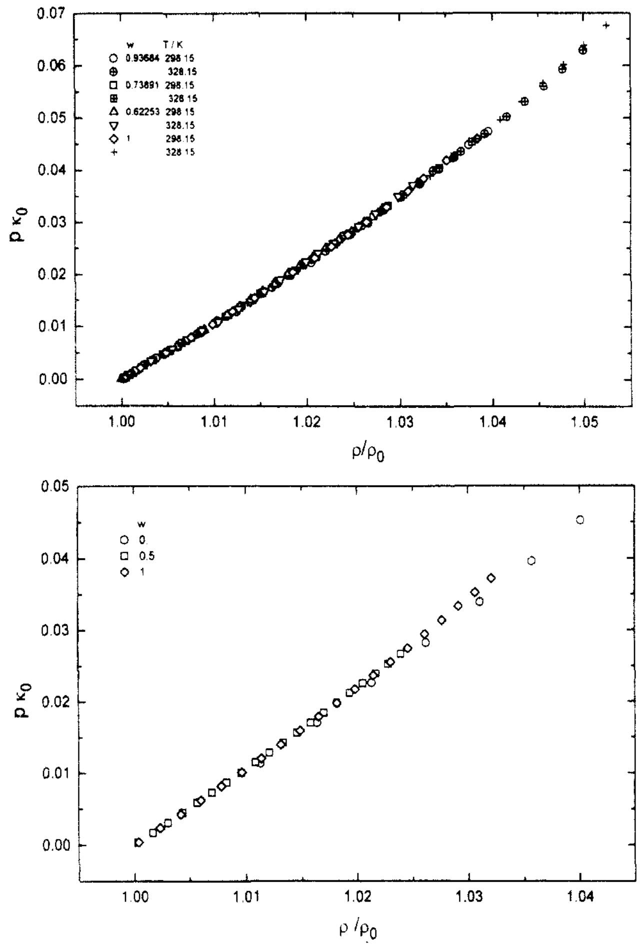

Figure 2. Test of the p–T–w superposition principle as defined by eq 4: (A, top) wAc + (1 − w)P4HS; (B, bottom)wP4HS + (1 − w)PVAc.

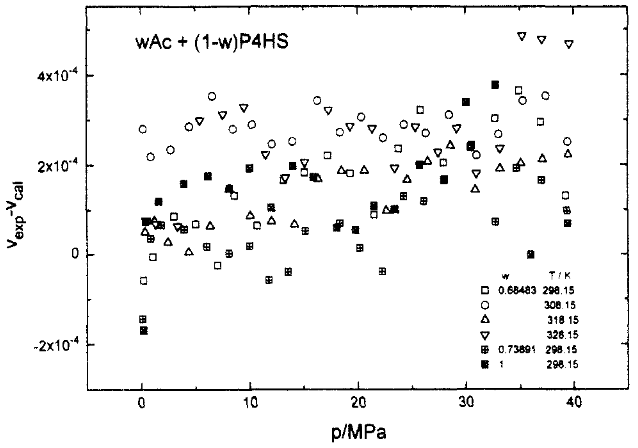

Figure 3. Difference between the experimental values of the specific volume and the values calculated from eq 4 when the temperature dependence of the density and the compressibility at 0.1 MPa are given by eq 1. Notice that only one parameter δ is needed to describe the pressure dependence. The experimental uncertainty in V is 2×10^{-4} cm^3 g^{-1}.

Even though for the present pressure range the T_g of P4HS is above 420 K,[14] we have calculated the excess volume from eqs 1–3 by assuming for P4HS the density given by the extended Tait equation valid for the liquid range ($T > T_g$).[14] This is a somewhat arbitrary approximation based on the fact that small amounts of acetone strongly reduce the T_g of the system below the temperature range studied in this paper. Figure 4 shows the effect of pressure upon V^E for two of the compositions. It can be observed that, as expected for strongly interacting systems, $VE < 0$; also $(\partial V^E/\partial p) > 0$, which can be explained

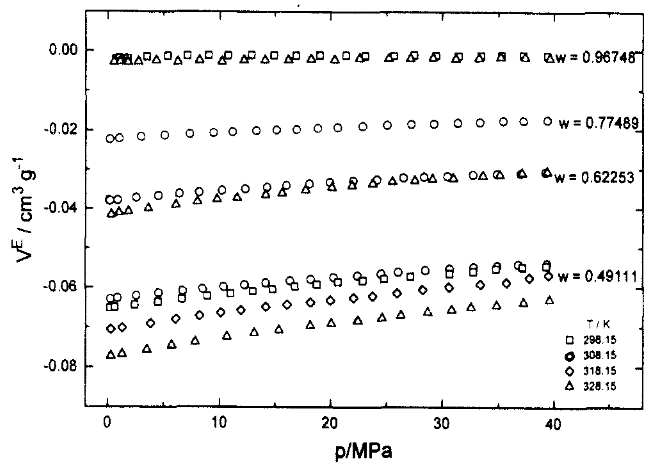

Figure 4. Pressure dependence of the excess volume for the wAc + (1 − w)P4HS system.

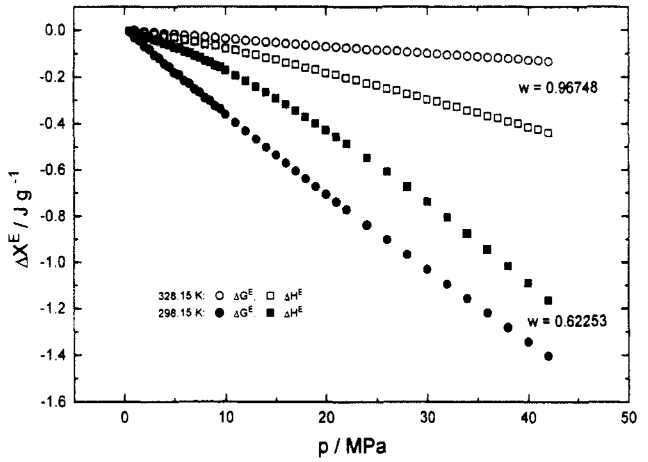

Figure 5. Effect of pressure upon G^E and H^E for wAc + (1 − w)P4HS. ΔG^E and ΔH^E are given by eqs 7 and 8, respectively.

by considering that hydrogen bonds have a marked directional character which leads the system to keep open structures that tend to be prevented at higher pressures.

From eqs 1–3 we have also calculated the effect of pressure on the excess enthalpy, H^E, and excess Gibbs energy, G^E, of the system, according to

$$(\partial H^E/\partial p)_p = V^E - T(\partial V^E/\partial T)_p \tag{7}$$

$$(\partial G^E/\partial p)_T = V^E \tag{8}$$

the results of which are shown in Figure 5 for two compositions.

Comparison with Theory

Bulk Modulus. For simple fluids, using Pople's expansion for the intermolecular potential and a reference system characterized by the angular average of the full intermolecular potential

$$U^\circ(r) = \langle U(r_1,w_1,w_2) \rangle_{w_1 w_2} \tag{9}$$

where w_i denotes the orientation of molecule i and $\langle\ \rangle$ indicates a canonical average, Gubbins and O'Connell[26] have shown that the bulk modulus B follows

$$B \equiv (\rho k_B T \kappa_T)^{-1} = (\rho k_B T \mathring{\kappa}_T)^{-1}(1 + \rho k_B T \mathring{\kappa}_T G_\kappa) \tag{10}$$

k_B being the Boltzmann constant and $\mathring{\kappa}_T$ the isothermal compressibility of the reference system. G_κ involves integrals over the anisotropic part of the intermolecular

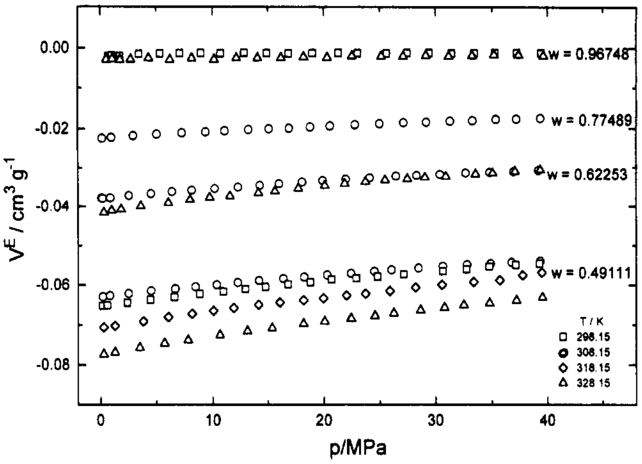

Figure 6. Test of the universal correlation proposed by Huang and O'Connell[27] for the bulk modulus of the mixture.

potential and the center pair correlation function of the reference system. For a wide variety of anisotropic contributions to the potential $G_\kappa \approx 1$, and therefore

$$B \approx \rho k_B T\kappa_T^{\circ} = f_\kappa^{\circ}(\rho\sigma^3, k_B T/\epsilon) \tag{11A}$$

where ϵ and σ are the parameters of a (n,m) Mie-like potential. Furthermore, f_κ° was found to show a very weak temperature dependence for wide density intervals $\rho > 2\rho_c$, ρ_c being the critical density, hence

$$\rho k_B T\kappa_T \approx f_\kappa^{\circ}(\rho\sigma^3) \tag{11B}$$

Equation 11B expresses a law of corresponding states since the different fluids may be described by the same reference potential, i.e., the same f_κ°.

In spite of the theoretical limitations of the framework from which eq 10 is derived, eq 11B was found to be valid for quite complex fluids and mixtures.[27,28] Huang and O'Connell[27] have proposed a correlation based on the above results. The full volumetric properties might be predicted by a combination of such a model and an accurate correlation for saturation densities

$$\frac{1-B}{C^*} = \sum_{i=0}^{3}\sum_{j=0}^{2} a_{ij}(\tilde{\rho})^i(\tilde{\tau})^j \tag{12}$$

with $\tilde{\rho} = \rho V^*$ and $\tilde{\tau} = T/T^*$. C^*, V^*, and T^* are the integrals of the direct correlation function, i.e., $(1 - B)$, the inverse density, and the temperature at the crossover point of the different isotherms $(1 - B)$ vs V. The a_{ij}'s are universal constants given by Huang and O'Connell.[27]

For binary mixtures

$$F^*(=T^*,C^*) = x_1F^*_1 + x_2F^*_2 \tag{13A}$$

$$V^* = x^2_1V^*_1 + x^2_2V^*_2 + 2x_1x_2V^*_{12}(1-\kappa_{12}) \tag{13B}$$

$$V^*_{12} = [(V^{*\,1/3}_1 + V^{*\,1/3}_2)/2]^3 \tag{13C}$$

where the x_i's are mole fractions and κ_{12} is a binary adjustable parameter.

The experimental data have been fitted to eq 12; Figure 6 shows that eq 12 is able to describe quite correctly the present results, although for the higher polymer concentrations κ_{12} seems to present some concentration dependence. This result is somewhat striking since eq 11, and hence eq 2, was obtained on the basis of a simple spherical reference system.

Table 2. Pure Component Parameters Characteristic of the Physical Interactions Obtained from p–ρ–T Data and Thermochemical Parameters of Each Type of Hydrogen Bond Interaction of the System

	p^*/MPa	T^*/K	ρ^*/g cm^{-3}
P4HS	454.7	768.4	1.244
acetone	526.14	482.4	0.916
	E°/ kJ mol^{-1}	S°/ J K^{-1} mol^{-1}	V°/ cm^3 mol^{-1}
OH–OH (P4HS–P4HS)	−21.8	−26.5	0.0
OH–carbonyl (P4HS–acetone)	−21.65	−12.9	0.0

Lattice–Fluid Model. The general theory for hydrogen bonded systems was given in the original paper by Panayiotou and Sanchez[11] and will not be repeated here, but we will give just the final equation of state for a system formed by a polymer (component 2) with d_2 proton-donor groups, and a_2 proton-acceptor groups and a solvent with a_1 proton-acceptor groups.

The equation of state reads

$$\tilde{p} + \tilde{\rho}^2 + \tilde{T}[\ln(1-\tilde{\rho}) + \tilde{\rho}(1-1/\bar{r})] = 0 \tag{14}$$

where the reduced variables are defined by $\tilde{p} = p/p^*$, $\tilde{T} = T/T^*$, and $\tilde{\rho} = \rho V^*$, p^*, T^*, and V^* being substance dependent parameters that define the van der Waals-type interactions between molecules. The average number of segments per molecule, $\bar{r}$, is defined by

$$1/\bar{r} = 1/r - \nu_H \tag{15}$$

where ν_H is the fraction of hydrogen bonds in the system and r has the same meaning as in the original lattice–fluid model of Lacombe and Sanchez.[12,13]

For the self-associated P4HS homopolymer

$$r\nu_H = 1 - [[A(A+4)]^{1/2} - A]/2 \tag{16}$$

with

$$A = r/\tilde{\rho}\exp(G^\circ_{22}/RT) \tag{17A}$$

and

$$G^\circ_{22} = E^\circ_{22} - TS^\circ_{22} + pV^\circ_{22} \tag{17B}$$

E°_{22}, S°_{22}, and V°_{22} being characteristic of the –OH···–OH hydrogen bonds in the P4HS homopolymer.

For the binary mixture Ac(1) + P4HS(2)

$$r\nu_H = [x_1 + ax_2 + A[(x_1 + ax_2 + A)^2 - 4ax_1x_2]^{1/2}]/2 \tag{18}$$

where A has the same form as given in eq 17B and a is the number of proton-acceptor groups per polymer molecule. Table 2 shows the pure component parameters used for characterizing both the van der Waals-like and the hydrogen bond interactions. Figures 7 and 8 show the predictions of the model both with hydrogen bonds, $\bar{r}$ given by eq 15, and without them ($\bar{r} = r$); the binary parameters were $\xi = 1.10 \pm 0.01$ and $\xi = 1.14 \pm 0.01$, respectively. It can be observed that the theoretical predictions do not describe well enought the influence of pressure on the density; it must be stressed that similar results were obtained with other free volume models when no pressure or temperature dependence of p^*, T^*, and ρ^* was considered. On the other hand, the composition dependence of V^E at $p = 0.1$ MPa is relatively well described (the binary parameters, ξ, were obtained from low-pressure data).

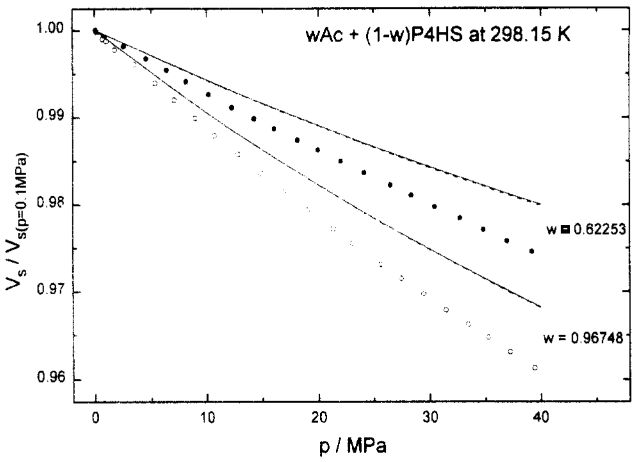

Figure 7. Predictions of the lattice–fluid model for the effect of pressures on the relative specific volume: (continuous line) without hydrogen bonds; (dashed lined) with hydrogen bonds.

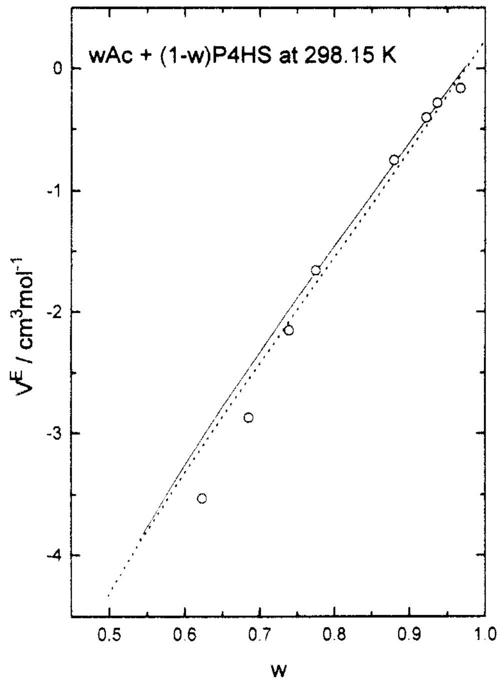

Figure 8. Predictions of the lattice–fluid model for V^E at 0.1 MPa: (continuous line) without hydrogen bonds; (dashed line) with hydrogen bonds.

Finally, almost no difference is observed between the two models in the prediction of volumetric properties, which contrasts with the improvement obtained in the prediction of the vapor–liquid equilibrium for Ac + P4HS and P4HS + PVAc + Ac when hydrogen bonds are considered.[14]

Conclusions

The p–ρ–T–w surface has been measured for the Ac + P4HS system in the $298.15 \leq T/\mathrm{K} \leq 328.15$ and $0.1 \leq p/\mathrm{MPa} \leq 40.0$ range. The results confirm the p–T–w superposition principle recently proposed by Sanchez et al.[15,16] The data have allowed the calculation of the pressure dependence of excess functions.

The calculated bulk modulus has been analyzed in terms of a universal correlation arising from quite drastic assumptions in a perturbation theory suitable for simple polar fluids.

Finally, the results have been compared with the predictions of a lattice–fluid model, with and without taking into account hydrogen bond interactions. It is found that, although it is possible to describe the composition dependence of V^E, the model does not describe correctly the pressure effect on the density. No noticeable difference is found between the two versions of the model.

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Supplementary Material Available: Table of experimental data for wAc + $(1 - w)$P4HS (4 pages). Ordering information is given on any current masthead page.

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