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Equation of State of Hydrogen-Bonded Polymer Solutions. Poly(propylene glycol) + *n*-Hexane and Poly(propylene glycol) + Ethanol

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ABSTRACT: We have measured the equation of state surface over the whole composition range for the mixtures poly(propylene glycol) + ethanol and poly(propylene glycol) + *n*-hexane up to 40 MPa. The excess volume for the system with ethanol is negative, decreasing in magnitude with increasing pressure. For the system with *n*-hexane, the excess volume becomes positive at high pressure and presents a complex shape with two changes in curvature along the composition axis. The $p-\rho-T$ data obey a superposition principle that makes it possible to build a master curve once the $p-\rho-T$ surface is known at a given pressure. The master curve depends on a single system-dependent parameter. The results have been analyzed with a lattice fluid model. The inclusion of hydrogen bond contributions in the model does not improve the prediction of the $p-\rho-T$ data for the system with *n*-hexane, while it makes a significant contribution in the system with ethanol, especially in ethanol-rich mixtures.

Introduction

Polymer solutions and blends exhibit very complex phase behavior, as a consequence of the combination of free volume and energetic contributions of the constituent components.[1] The frequent presence of a lower critical solution temperature in these systems is one of the key manifestations of the equilibrium between the above contributions.[2] Moreover, critical points and binodals often depend strongly on pressure and or the molar mass of the polymer.[3] In order to model the thermodynamics of these systems one needs an appropriate equation of state (EoS) applicable over a large range of densities.[4,5] In recent years different theoretical EoS's have been tested against extensive $p-\rho-T$ data of pure polymers,[6,7] and against vapor−liquid phase equilibria (VLE) and liquid−liquid phase equilibria (LLE) of polymer−solvent and blend systems.[4,8−10]

Hydrogen bonding has a considerable effect on the microscopic as well as the macroscopic properties of fluids and plays a fundamental role in the understanding and design of processes of biological and environmental importance. However, predicting thermodynamic properties and performing phase equilibria calculations for associating systems are challenging problems that have received considerable attention over the last 2 decades. Both activity coefficient models and EoS have been developed specifically for fluids that hydrogen bond. Donohue and Iconomou[11] and Ghonasgi et al.[12] have reviewed the basis of some of the most recent ones for associated fluids. More recently, Ghonasgi and Chapman[13] and Sear and Jackson[14] have discussed the important effects of the competition between intra- and intermolecular hydrogen bonds upon the thermodynamics of associated mixtures. Their main conclusions are in agreement with the experimental LLE studies of Gregg et al.,[15] and with $p-V-T$ data of Gee et al.[16] Moreover, Ghonasgi et al.[17] have discussed the importance of cyclic forms arising from association in the equation of state and phase equilibria of polymer systems.

As in the case of nonassociating systems, most of the theoretical models have been tested against computer simulation data and experimental phase equilibria data. Despite the fact that in many cases hydrogen bonding has been claimed to have important effects on the free volume, and therefore on the equation of state,[5,11,18,19] little systematic discussion exists on the ability of different theoretical approaches to describe $p-V-T$ data for associated polymer solutions.

Recently we have reported $p-V-T$ data for mixtures of poly(4-hydroxystyrene) (P4HS) mixed with either acetone,[20] tetrahydrofuran,[21] ethanol,[21] or [poly(vinylacetate + acetone)].[22] P4HS is known to self-associate through hydrogen bonds (both intra- and intermolecular) and also to associate with solvents or other polymers.[23,24] When the results were analyzed in terms of the Panayiotou−Sanchez model,[25] it was found that only when the second component was able to self-associate, e.g. ethanol, did the introduction of hydrogen bonds for the polymer component into the theory lead to significant improvements. Moreover, all the data followed a corresponding states correlation recently proposed.[26]

The effect of pressure on the phase behavior of hydrogen-bonding polymers has been found to be different in polar and nonpolar systems.[15] Moreover, pressure may induce inmiscibility in water−polymer systems by preventing the formation of hydrogen bonds.[27] Therefore, in order to test theoretical EoS's, it would be interesting to focus on a polymer soluble in solvents ranging from nonpolar hydrocarbons to self-associating molecules such as alcohol and water. Poly(propylene glycol) (PPG) is a good candidate, since at room temperature it is soluble in *n*-hexane, ethanol, and water.[28] For low molecular weights ($M_w < 1000$), PPG shows an UCST when mixed with *n*-alkanes, while with water it shows a LCST that is strongly affected both by pressure[27] or the presence of electrolytes.[28]

Despite the fact that PPG is miscible with poly(ethylene glycol) (PEG) at ambient conditions, the ternary system PEG + PPG + water displays a close-loop immiscibility gap.[29] Moreover, the triblock polymer PEG-*b*-PPG-*b*-PEG has been extensively studied in recent years and found to display very complex phase

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Table 1. Characteristics of the Fittings of the Experimental Data to Equation 1

x	$10^{-3}B_1$/kg m^{-3}	B_2/kg m^{-3} K^{-1}	10^3B_3/kg m^{-3} K^{-2}	$10B_4$	$10^{-3}B_5$/MPa	10^2B_6/K^{-1}	$\sigma(\rho)$/kg m^{-3}
$(1 - x)$ PPG400 + x n-Hexane							
0	1.2567	−0.8796	0.1104	0.6849	0.4869	0.5079	0.1
0.23651	1.2221	−0.8473	0.0392	0.9199	0.6877	0.5344	0.09
0.39687	1.2224	−1.0335	0.3294	0.8340	0.5956	0.5535	0.08
0.50500	1.1755	−0.8800	0.0596	0.8548	0.6248	0.5823	0.1
0.59756	1.1761	−1.0408	0.2920	0.8268	0.6595	0.6407	0.08
0.79920	1.1070	−1.0996	0.3329	0.8354	0.6682	0.7236	0.09
0.89964	1.0492	−1.1217	0.3522	0.8441	0.7779	0.8274	0.09
1	1.0358	−1.5870	1.0805	0.8521	0.9049	0.9540	0.1
$(1 - x)$−PPG400 + xEtOH							
0.13137	1.2685	−0.9746	0.2541	0.8076	0.6348	0.5292	0.1
0.22150	1.2604	−0.9412	0.1968	0.9170	0.6983	0.5157	0.09
0.41891	1.2397	−0.8740	0.0826	0.8069	0.6156	0.5330	0.1
0.51104	1.2254	−0.8274	0.0057	0.8176	0.6356	0.5429	0.08
0.60921	1.2124	−0.8069	−0.0363	0.7984	0.6242	0.5548	0.1
0.78808	1.2016	−0.9470	0.1687	0.8841	0.6622	0.5658	0.06
0.89978	1.1410	−0.8536	0.0056	0.8198	0.5837	0.5977	0.09
1	1.0371	−0.7983	−1.2641	0.8428	0.6103	0.7028	0.09

diagrams when mixed with water or with water + hydrocarbon, leading to the appearance of micellar and smectic phases.[30−32] Although some of the recent EoS's have been applied to systems containing copolymers,[33] the above systems still represent a extremely challenging case.

The purpose of the present work is to carry out a precise study of the $p-V-T$ surface mixtures formed by PPG + n-hexane and PPG + ethanol, over the whole composition range. The data is correlated in terms of the EoS developed by Panayiotou and Sanchez[25] and compared with those previously reported for P4HS + ethanol.[21] A similar study for aqueous systems of PPG, PPG + PEG, and the copolymer will be reported in a future work.

Experimental Section

The $p-\rho-T$ data have been measured using a modified Anton-Paar Model DMA 512 high-pressure vibrating tube densitometer, as in a previous work.[21] The densitometer was calibrated with eight pure substances according to the procedure described elsewhere.[34] It was also necessary to account for the dependence of the period of vibration upon the viscosity of the sample. We have followed the method of Ashcroft et al.,[35] using glycerol as reference. The precision in the measurements was ±0.01 MPa in p, ±0.5 mK in T, and $\pm 5 \times 10^{-7}$ in τ, the period of vibration, thus leading to an uncertainty in density of ±0.1 kg m^{-3} for the whole pressure range $0.1 \le p/\mathrm{MPa} \le 40.0$. The uncertainty in weight fraction was $\pm 2 \times 10^{-5}$.

n-Hexane ($n\mathrm{C}_6$) was purchased from Fluka (puriss quality), and ethanol was Carlo Erba (RPE quality). Both were dried over 0.4 nm molecular sieves and used without further purification. The purity of the substances used, estimated by GLC, was better than 99.9%. Their densities at 298.15 K and 0.1 MPa, in kg m^{-3}, were 654.966 and 785.112 respectively, in good agreement with literature values: 654.81 and 785.04 kg m^{-3}, respectively.[36] Also the surface tensions at 298.15 K, measured by the plate method (17.9 mN m^{-1} and 21.9 mN m^{-1}, respectively) were in good agreement with the values reported by Jasper.[37] Poly(propylene glycol) was obtained from Polysciences ($M_\mathrm{w} = 400$). Due to the influence of polydispersity on the phase equilibria of polymer−solvent systems,[38] and the proximity of the UCST for PPG + $n\mathrm{C}_6$,[28] we have used samples with $M_\mathrm{w}/M_\mathrm{n} < 1.5$ as determined by HPLC.

The preparation and manipulation of all solutions studied were carried out under a dry N_2 atmosphere.

Results

More than 500 $p-\rho-T$ experimental data points were obtained for each of the two mixtures over the intervals $298.15\ \mathrm{K} \le T/\mathrm{K} \le 328.15$, $0.1 \le p/\mathrm{MPa} \le 40.0$, and $0 \le x \le 1$, x being the mole fraction of the solvent. The results for 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

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

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

where B_i (i = 1−6) are constants independent of T and p. Table 1 summarizes the values of B_i for the different isopleths of the two mixtures, as well as the standard deviations of the fits which in general are within the experimental uncertainty. Figure 1 shows the influence of pressure for selected isopleths and isotherms. It also includes, for the sake of comparison, the data obtained by Gee et al.[16] for pure PPG. As can be observed, the agreement is quite good. As expected, the effect of pressure is larger as the concentration of solvent increases, reflecting the difference in free volume between polymer and solvent. The low M_w of PPG compared to that of P4HS ($M_\mathrm{w} \sim 30\,000$),[20,21] accounts for the fact that the differences between the isopleths $x = 0$ and $x = 1$ in Figure 1 are smaller than in the previous cases for P4HS + ethanol.[21] The fact that $n\mathrm{C}_6$ is more compressible than ethanol, leads to a larger influence of composition upon the compressibility of the PPG + $n\mathrm{C}_6$ mixture than in the PPG + ethanol.

Discussion

Using the parameters of Table 1, we have calculated the excess volumes for the two mixtures.

Figure 2 shows some of the results. In general, for a given temperature increasing the pressure tends to make V^E less negative in both systems. At a given pressure, the increase of temperature has almost no effect on V^E for the system PPG + ethanol, while the influence is noticeable for the system PPG + $n\mathrm{C}_6$, especially at low pressure where a 100% change in V^E ($x \sim 0.5$, p = 0.1 MPa) is found when T changes from 298.15 to 328.15 K. More striking is perhaps the shape of the V^E vs x curves for PPG + $n\mathrm{C}_6$, where two changes of curvature are apparent through the composition range. This behavior is absolutely unusual and is not related to the proximity of the UCST. In effect, as described by several authors,[39,40] near a critical point,

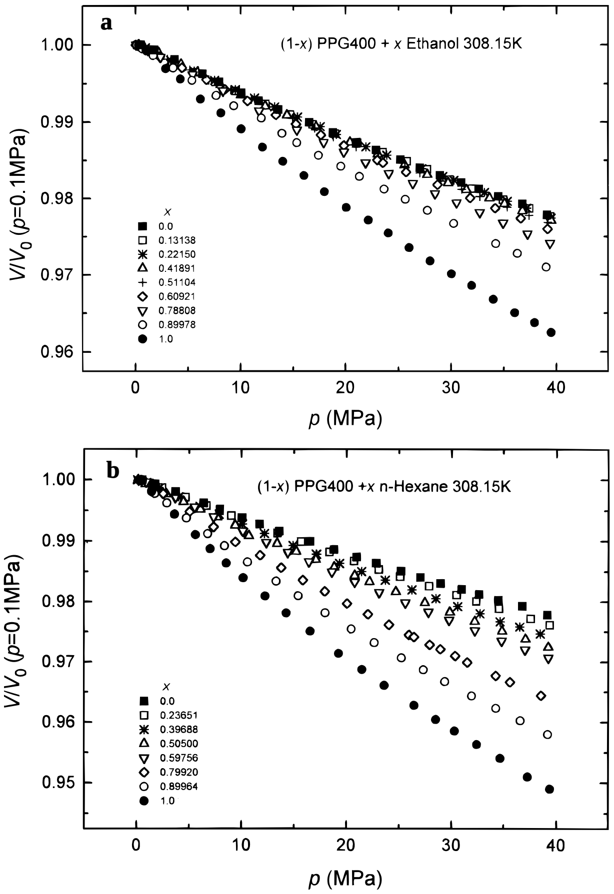

Figure 1. Pressure dependence of the molar volume at different compositions and 308.15 K: (a) (1 − *x*) PPG + *x* ethanol. (b) (1 − *x*) PPG + *x* *n*-hexane. *x* denotes mole fraction.

the V^E vs x curves present a flat region for compositions close to the critical one. This lends to an inflection point in the $(\partial V^E/\partial x)_T$ vs x curves at the critical composition. The results of Figure 2 indicate that the behavior of $(\partial V^E/\partial x)_T$ in the PPG + nC_6 system is much more complex for different temperatures and pressures.

Two changes in curvature have already been reported for C_p^E vs x curves in binary mixtures.[41] This behavior has been explained in terms of the divergence of C_p near a critical point.[42] However, no similar contribution exists in the molar volume. In any case, we have checked experimentally that even at 298.15 K and 40.0 MPa the system remained homogeneous. No data for other excess properties have been found in the literature for the PPG + nC_6 system.

Sanchez et al.[43] have shown that it should be possible to construct a master curve using the $p-\rho-T-x$ data of the following form:

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

where $\kappa_{T,0}$ is the isothermal compressibility at $p = 0.1$ MPa, and δ is a parameter characteristic of each system. Figure 3 shows that this is indeed the case for the two systems studied, with $\delta = 10.93$ for the system with nC_6 and $\delta = 11.19$ for the system with ethanol. These values compare well with $\delta = 11.70$ found for P4HS + tetrahydrofuran and $\delta = 11.44$ for P4HS + ethanol[21] and with $\delta = 10.09$ for P4HS + poly(vinylacetate).[20]

Equation 4 indicates that once the temperature dependence of ρ ($p = 0.1$ MPa) and $\kappa_{T,0}$ are known, the influence of p upon the volume can be characterized by δ. Figure 4 shows the residuals ($V_{exp} - V_{cal}$) for PPG + nC_6, with V_{cal} obtained from eq 4. As it can be observed, the magnitude of the residuals is similar to that obtained from eqs 1−3. The results for other temperatures, and for the PPG + ethanol system are similar and are also very close to the experimental uncertainty.

Using eqs 1−3 we have calculated the effect of pressure on the excess Gibbs energy and the excess enthalpy. Figure 5 shows the results for the two systems. While for the system PPG + ethanol increasing the pressure leads to a decrease in both G^E and H^E through the whole composition range, the situation is different for PPG + nC_6. In effect while H^E tends to

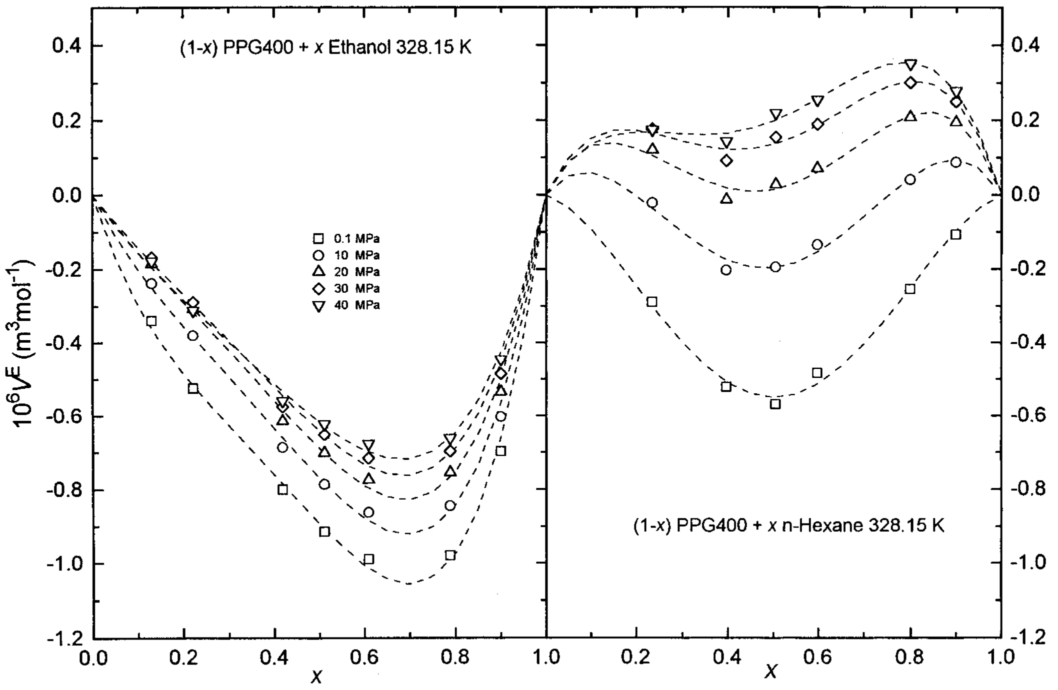

Figure 2. Excess volumes for the systems PPG + ethanol and PPG + *n*-hexane at 328.15 K and at different pressures. (1 − *x*) is the mole fraction of PPG. The curves are the fits of each isobar to a Redlich−Kister type equation.

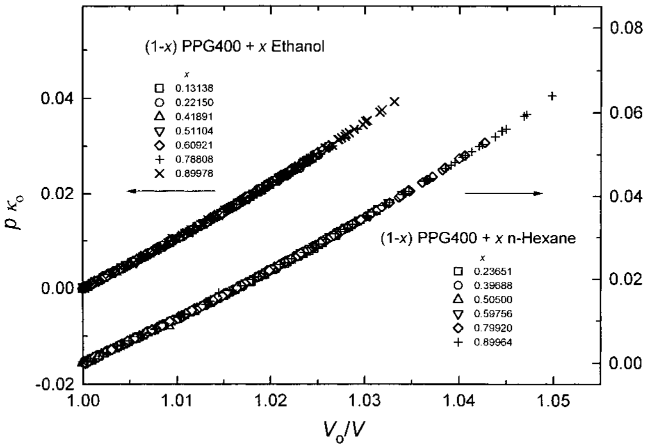

Figure 3. Sanchez's master curves for the $p-V-T$ data of the two binary systems at different composition (eq 4).

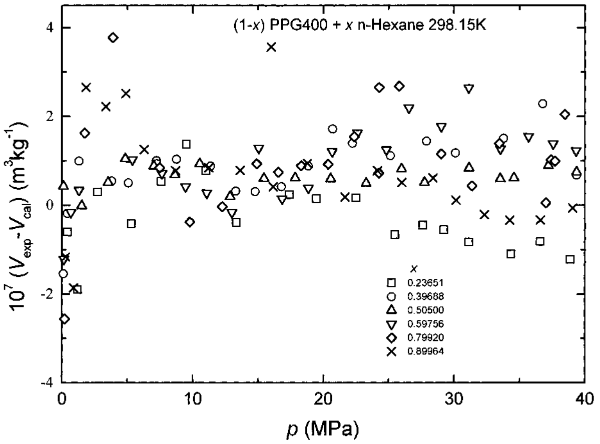

Figure 4. Residuals of the molar volume calculated using Sanchez's scaling equation (eq. 4) and experimental V data at $p = 0.1$ MPa. Notice that only one adjustable parameter $\delta = 10.93$ has been used and that the experimental precision of V is 1×10^{-7} m^3 kg^{-1}.

increase with pressure, G^E decreases from 0.1 to around 15 MPa, and then increases. The combined effect of p and x is not straightforward for the system with nC$_6$, since for a given p, ΔG^E and ΔH^E show minima or maxima for compositions around $x = 0.5$. For the system with ethanol, the change of ΔH^E with x is monotonous for any p, while a shallow minimum appears for ΔG^E at $x \sim 0.7$.

On the whole, the effect of pressure upon ΔG^E and ΔH^E for PPG + ethanol is similar to that previously found for P4HS + acetone,[20] P4HS + ethanol, or P4HS + tetrahydrofurane,[21] while the effect on PPG + nC$_6$ is rather different. Although speculative, a possible explanation might be the tendency of the PPG molecules to form cyclic, less polar structures in nC$_6$. As discussed by Ghonasgi et al.,[17] for a given molecular weight, cyclic forms tend to be more dense than linear ones; increasing density tends to decrease the importance of intra-molecular vs intermolecular hydrogen bonds.[12,13,17] The disruption of cyclic forms with increasing pressure (and thus density) would lead to a decrease of density, and hence to more positive excess volumes. The increase of more polar forms with increasing p would make the mixture more endothermic, leading to $(\partial \Delta H^E/\partial p)_x > 0$, as shown in Figure 5. The behavior of $(\partial \Delta G^E/\partial p)_x$ simply reflects the delicate balance between entropy and enthalpy effects.

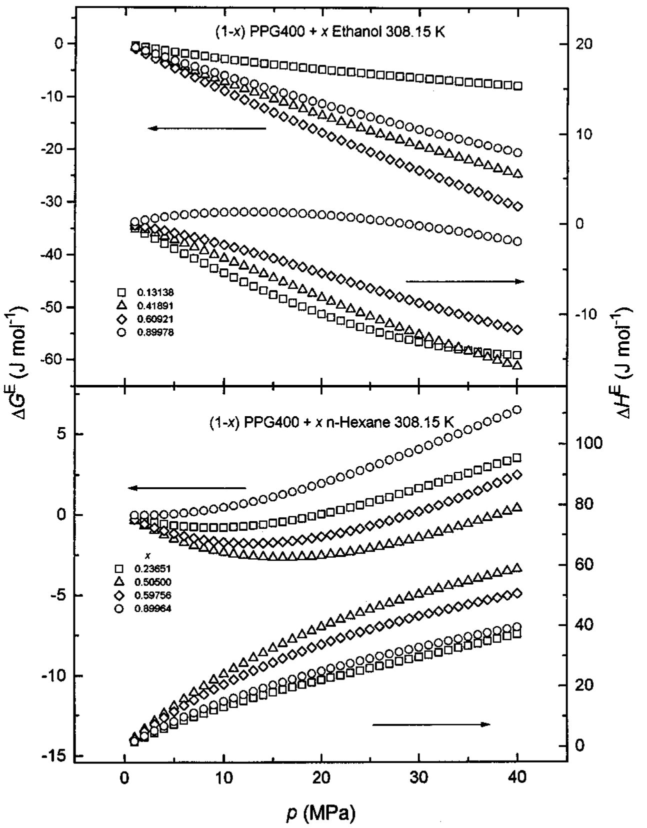

Figure 5. Pressure effect on the excess Gibbs energy (ΔG^E) and on the excess enthalpy (ΔH^E). for the systems PPG + ethanol and + n-hexane. $p = 0.1$ MPa has been taken as reference. $(1 - x)$ is the mole fraction of PPG.

Comparison with a Lattice–Fluid Model

The complete formulation for a lattice–fluid model incorporating hydrogen bonds has been given by Panayiotou and Sanchez.[25] We will only repeat here the equation of state and the equations that allow incorporation of hydrogen bonds into it.

The equation of state is

$$\tilde{\rho} + \tilde{\rho}^2 + \tilde{T}[\ln(1 - \tilde{\rho}) + \tilde{\rho}(1 - 1/\bar{r})] = 0 \qquad (5)$$

where the reduced variables are defined by $\tilde{p} = p/p^*$, $\tilde{T} = T/T^*$, and $\rho = \rho V^*$, p^*, V^*, and T^* 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

$$1/\bar{r} = 1/(r - \nu_H) \qquad (6)$$

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,[44] i.e., the average number of segments per molecule.

For the case of pure ethanol the equation that determines the fraction of hydrogen bonds is

$$r\nu_H = 1 - [[A_{11}(A_{11} + 4)]^{1/2} - A_{11}]/2 \qquad (7)$$

with

$$A_{11} = r/\tilde{\rho}\, \exp(G^\circ_{11}/RT) \qquad (8)$$

$$G^\circ_{11} = E^\circ_{11} - TS^\circ_{11} + pV^\circ_{11} \qquad (9)$$

Table 2. Pure Component Parameters Characteristic of Physical Interactions Obtained from $p-V-T$ Data, and Thermochemical Parameters of Each Type of Hydrogen Bond Interactions

	p^*/MPa	T^*/K	ρ^*/g cm^{-3}
PPG400	448.0	579.6	1.0884
a	449.3	571.1	1.0900
EtOH	349.8	642.0	0.8598
a	374.6	492.9	0.8898
n-Hexane	297.0	517.2	0.74703

	E^0/kJ mol^{-1}	S^0/J K^{-1} mol^{-1}	V^0/cm^3 mol^{-1}
OH−O (PPG−PPG)	−11.44	−29.22	−0.85
OH−OH (EtOH−EtOH)	−25.1	−26.5	−5.6

[a] Parameters for the case in which hydrogen bonds are considered in pure ethanol and PPG400.

E_{11}°, S_{11}°, V_{11}° being characteristic of the −OH···−OH hydrogen bonds in ethanol.

For pure PPG we have assumed that the molecule has $d = 2$ donor groups and $a = 7$ acceptor groups (changing a from 6 to 8 does not make any difference in the final results). The model leads to the following equations.

$$r\nu_H = [d + a - [A_{22}[A_{22} + 2(d + a)] + (d - a)^2]^{1/2} - A_{22}]/2 \quad (10)$$

where A_{22} is defined in a way similar to A_{11}.

For the binary mixture PPG + nC$_6$

$$r\nu_H = [(d + a)(1 - x) - [A_{22}[A_{22} + 2(d + a)(1 - x)] + [(d - a)(1 - x)]^2 - A_{22}]]/2 \quad (11)$$

while for the system PPG + ethanol the situation is similar to that described for P4HS + ethanol,[21] and one has to account for self- and cross-association in the pure components. This leads to a system of coupled equations

$$\nu_{ij}A_{ij} = r\left(\frac{N_d^{(i)}}{rN} - \sum_{k=i}^{n}\nu_{ik}\right)\left(\frac{N_a^{(j)}}{rN} - \sum_{k=1}^{m}\nu_{kj}\right) \quad (12)$$

with $N_d^{(1)} = N_a^{(1)} = 1$, $N_d^{(2)} = 2$, and $N_a^{(2)} = 7$. In eq 12, $y, j, m, n = 1, 2$ and the A_{ij} values are defined in a manner similar to A_{11} (notice that in general $A_{12} \neq A_{21}$).

Table 2 shows the pure component parameters used for characterizing both the physical and the hydrogen bond interactions. The binary parameter of the model ξ has been fitted in order to reproduce the composition dependence of the excess volume at $p = 0.1$ MPa. The calculations have been performed both with the full model and also with the lattice model without hydrogen bonds ($\nu_H = 0$). Figure 6 shows typical results. Both models reproduce the effect of pressure on the molar volume with almost the same precision. Similar conclusions are reached with respect to the V^E curves: the model does not reproduce the complex shape of the V^E curves, although the model with hydrogen bonds predicts a s-shape curve with $V^E < 0$ for $x < 0.8$, and $V^E > 0$ for $x > 0.8$. The situation is quite different for the system PPG + ethanol, where the inclusion of hydrogen bonds in the model leads to a significant improvement in the pressure dependence of V^E specially for solvent-rich mixtures. Moreover, when the hydrogen bond contributions are included in the model, the binary parameter ξ obtained is closer to unity, which means that in the bare lattice model the physical interactions are absorbing part of the effects of hydrogen bonds. These conclusions are similar to those previously reported for mixtures of P4HS[20,21] and lead to the conclusion that in aqueous systems the inclusion of hydrogen bonds in the model will play a fundamental role.

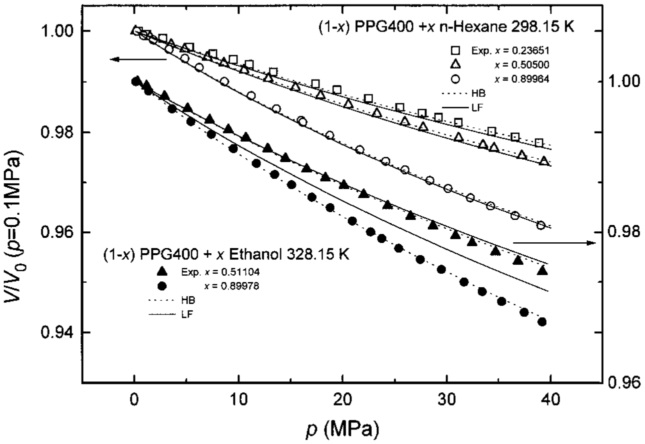

Figure 6. Pressure effect on the molar volume for two systems studied at 298.15 K and different compositions. Symbols are experimental data. Dashed lines are values calculated with the lattice−fluid model including hydrogen-bonds. Full lines are the predictions of the bare Lacombe−Sanchez lattice fluid without hydrogen bond contributions.

Conclusions

We have obtained extensive $p-\rho-T$ data for the systems PPG + nC$_6$ and PPG + ethanol. The excess volume curves of the mixture with nC$_6$ show a complex shape, with two changes in curvature through the whole composition range.

The $p-\rho-T$ data closely follow the corresponding state curve proposed by Sanchez et al.[26] The master curve calculated (characterized by a single system-dependent parameter) allows an accurate prediction of the pressure dependence of the density once data at one isobar are available. The analysis of the results in terms of a lattice fluid model indicates that for the description of $p-\rho-T$ surface the inclusion of hydrogen bond contributions are important only in the system with self-associating solvent, e.g., ethanol.

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