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Polymer 41 (2000) 7407–7414

polymer

Equation of state of a blend of water-soluble polymers: poly(propylene glycol) + poly(ethylene glycol)

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Received 26 September 1999; received in revised form 15 December 1999; accepted 21 January 2000

Abstract

We have measured the equation of state surface of the blend poly(propylene glycol) (PPG) + poly(ethylene glycol) (PEG) over the whole composition range up to 40 MPa. The excess volume of the blend is negative, except for PPG-rich mixtures, and becomes more positive with increase in pressure or temperature. The *P–V–T* data can be described very accurately in terms of a corresponding-states principle that depends on a single system-dependent parameter. Moreover, the effect of pressure on the volume has been found to be the same as that of a chemically dissimilar blend, and slightly different from that of a triblock copolymer with the same relative content of PEG and PPG. The results have been analysed in terms of a lattice-fluid model. Although it is not possible to reproduce the asymmetry of the excess volume curves, the model accounts for the pressure dependence of the volume. No significant differences are found between predictions of the bare lattice-model and the model with hydrogen-bond interactions. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Equation of state; Polymer blends; Lattice-fluid corresponding states

1. Introduction

In the integration of polymer production, processing and material development the thermodynamics of polymer systems plays a key role [1]. In general, the more advanced the performance of the final polymer material, the more complex its phase behaviour turns out to be; e.g. the mechanical properties of polymer blends, block copolymers and composites are rather dependent on phase relationships and morphology [2]. Polymer solutions and blends exhibit complex phase behaviour [3]. The blending and compounding of polymers reveal emphatically the sensitivity towards phase separation, which, depending on application purposes, may well or not have to be avoided.

In many production routes, and also during the processing, polymer systems have to undergo pressure, thus compressibility and thermal expansivity are necessary over wide ranges of pressure and temperature. Moreover, critical points and binodals depend strongly on pressure, thus making it necessary to have precise equations of state (EoS). Despite the importance of locating the phase boundaries of polymer mixtures, the prediction of the phase behaviour of such systems is a non-trivial problem. In general, their phase behaviour tends to be explained in terms of a delicate balance between the combinatorial, free-volume and energetic contributions of the constituent components [4]. The situation is further complicated when the system contains components that can associate (e.g. through hydrogen bonding) [5], the aqueous mixtures representing an extreme case of enormous technological importance [6].

In recent years different theoretical EoS's have been tested against extensive *P–V–T* data of pure polymers [7,8], and against vapour–liquid phase equilibrium (VLE) and liquid–liquid phase equilibrium (LLE) of polymer solvent and blend systems [8–10]. Donohue and Iconomou [11], and Sear and Jackson [12] have reviewed the basis of some of the theoretical models that can be applied to mixtures with complex interactions. Rudolf and Cantow [13], and Dormidontova and ten Brinke [14] have addressed the theoretical description of polymer blends and mixtures of polymers and oligomers. Although equation of state effects have been claimed to be very important for the correct description of the phase behaviour of polymer systems, little systematic work has been devoted to test the ability of current theoretical models to predict the EoS of polymer blends.

We have recently studied the *P–V–T* surface for mixtures of poly(propylene glycol) (PPG) with several solvents ranging from non-polar hydrocarbons to water [15,16]. The results point out that the pressure dependence predicted by a recent lattice-fluid model is not completely satisfactory for several thermodynamic properties [17]. The phase

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PII: S0032-3861(00)00087-2

Table 1
Characteristics of the fitting of the experimental data to Eq. (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})
0	1.2567	−0.8796	0.1104	0.6848	0.4869	0.5079	0.1
0.13477	1.2467	−0.7737	−0.0442	0.8133	0.6074	0.4979	0.09
0.28390	1.2444	−0.6836	−0.2037	0.8403	0.8395	0.5793	0.1
0.39598	1.2257	−0.5116	−0.4591	0.8876	0.5820	0.4335	0.1
0.60723	1.2798	−0.7195	−0.1221	0.8689	0.5832	0.4132	0.1
0.80381	1.2888	−0.6133	−0.2763	0.7598	0.5532	0.4133	0.1
0.88454	1.3305	−0.7873	0.0043	0.9985	0.6971	0.3730	0.1
1	1.3723	−0.8781	0.1257	0.8763	0.5832	0.3336	0.1

behaviour of a related system, poly(ethylene glycol) (PEG) + water has been extensively studied in recent years. Although it has been found that pressure has a strong influence on the thermodynamics of this system [18], most of the theoretical studies have been done with rigid lattice models [19,20]. From the structural point of view PPG and PEG are not very different: ether groups and two hydroxyl groups at both extremes of the chains, which give them the possibility of both inter- and intra-chain hydrogen bonds. However, when mixed they show phase separation at low temperatures [21,22]. Moreover, the ternary system PPG + PEG + water shows a loop of immiscibility at temperatures at which the three binary mixtures are miscible (for low molecular weights of the polymers). Again, the theoretical predictions are based on rigid lattice models [23]. Understanding these systems is mandatory if one wants to explain the very complex behaviour of the triblock copolymers known as pluronics (PEG–PPG–PEG) systems, which when mixed with water lead to the formation of micelles due to the small difference in hydrophobicity of the PPG and PEG segments [24], and to gels at high concentrations [25]. In addition, when mixed with water and a hydrocarbon very complex phase diagrams appear, which contain not only micellar phases, but also several liquid-crystal phases [26].

In the present work we present an experimental study of the P–V–T surface for the blend PPG + PEG between $298 < T(\mathrm{K}) < 328$ and $0.1 < P(\mathrm{MPa}) < 40$, and over the whole composition range. The results will be compared with those of a triblock copolymer, and with those of a blend previously studied which has a rather different chemical nature. Finally, the predictions of a lattice-fluid model will be compared with the experimental results.

2. Experimental

The P–V–T data have been obtained using a modified Anton-Paar (model DMA 512) high-pressure vibrating tube densitometer. The experimental set-up has been described in a previous work [27]. The densitometer was

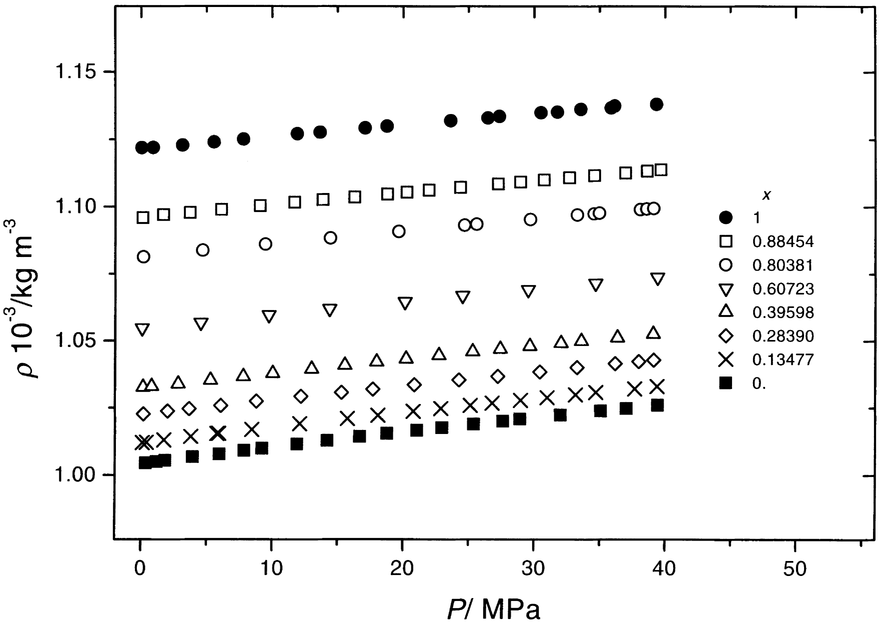

Fig. 1. Effect of pressure on the density of PPG + PEG at 298.15 K for different mole fractions of PEG, x, as indicated in the figure.

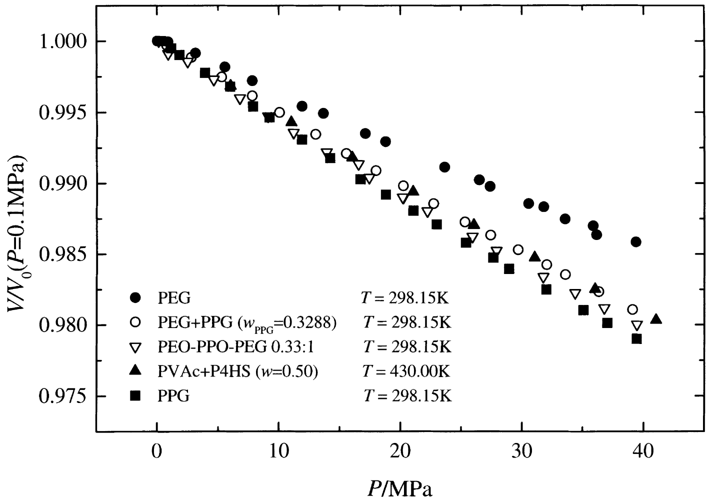

Fig. 2. Comparison of the effect of pressure on the reduced volume of the pure polymers studied in this work and of two polymer blends. Notice that in spite of the big chemical nature and of the difference in *T* between the two blends their data lay on the same curve.

calibrated with eight pure substances according to a procedure described elsewhere [28]. To account for the influence of the viscosity of the sample, we have followed the method of Ashcroft et al. using glycerol as the reference [29]. The precision of the measurements were ± 0.01 MPa in P, ± 0.5 mK in T, and $\pm 5 \times 10^{-7}$ s in τ, the period of vibration. This led to an uncertainty of ± 0.1 kg m^{-3} for the density (ρ) over the whole pressure range $0.1 < P(\mathrm{MPa}) < 40.0$. The samples were prepared by weight in a balance with a precision of ± 0.01 mg. The uncertainty in the weight fraction was $\pm 2 \times 10^{-5}$. Some measurements at 0.1 bar were carried out in a more precise DMA 601 densitometer for comparison.

The polymers PPG, PEG and the triblock copolymer PEG–PPG–PEG were obtained from Polysciences (Germany). The average molecular weights M_w and the polydispersity indices M_w/M_n as measured by gel permeation chromatography using tetrahydrofuran as solvent were: 400 and <1.5 for PPG, 200 and <1.4 for PEG. The copolymer has two identical PEG blocks. Its overall M_w was 3400 and the ratio PEG/PPG was 0.33:1. The preparation and manipulation of all the samples was carried out under a dry N_2 atmosphere. Since the polymers are liquids at room temperature the blends were prepared by mixing under stirring for 4 days at 20°C.

3. Results

Around 20 P–V experimental data points were obtained for each of the compositions at each temperature over the intervals $0.1 \leq P(\mathrm{MPa}) \leq 40.0$, $298.15 \leq T(\mathrm{K}) \leq 328.15$ and $0 \leq x \leq 1$, x being the mole fraction of PEG. Thus the equation of state of the PPG + PEG blend has been sampled over more than 600 experimental points. The

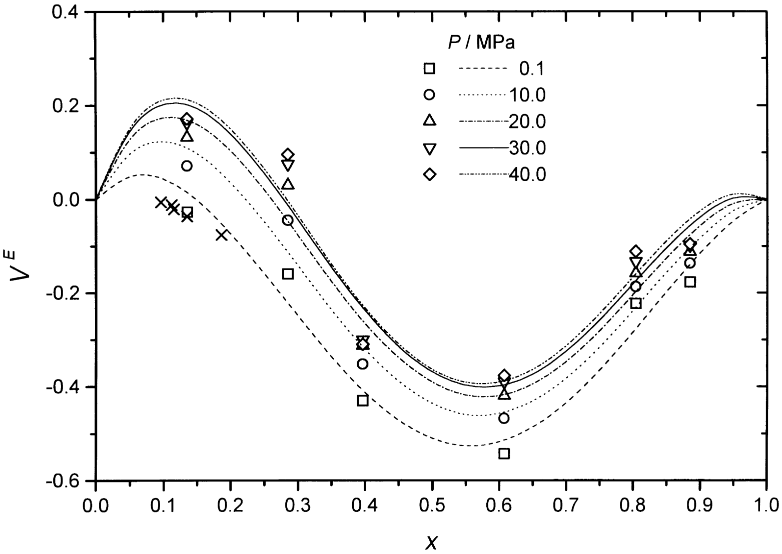

Fig. 3. Pressure and composition dependence of the excess volume of the PPG + PEG blend at 298.15 K. The curves are fits to the Redlich–Kister equation.

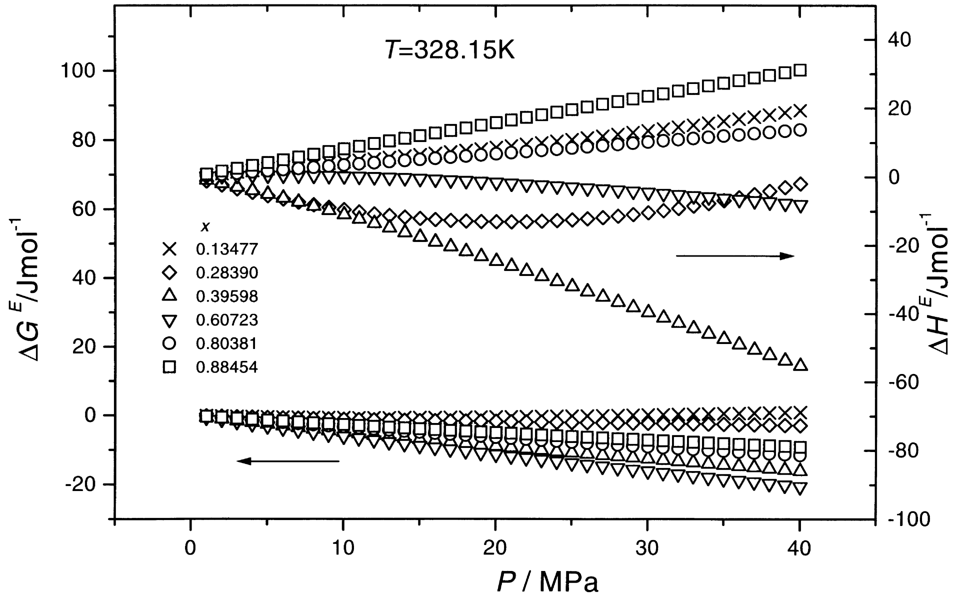

Fig. 4. Pressure effect on the excess Gibbs energy (ΔG^{E}) and on the excess enthalpy (ΔH^{E}) for the PPG + PEG blend at 328.15 K. Similar results are found at other temperatures. $P = 0.1$ MPa has been taken as the reference. x is the mole fraction of PEG.

results for each composition were fitted to a generalised Tait equation of the form:

$$\rho = \frac{\rho_0}{1 - B_4 \ln\left(\dfrac{B + P}{B + P_0}\right)} \quad (1)$$

where

$$\rho_0 = B_1 + B_2 T + B_3 T^2 \quad (2)$$

$$B = B_5 \exp(-B_6 T) \quad (3)$$

where the B_i ($i = 1$–6) are constants that are independent of T and P. Table 1 shows the values of B_i that best fit the experimental results. In general, the standard deviations of the fits are within the experimental uncertainty. Fig. 1 shows the density results for selected isopleths at 298.15 K. Similar results are found for the other temperatures. The agreement of the present results with those of Dee et al. [30] for pure PPG and PEG is excellent. Fig. 2 shows the influence of the pressure on the reduced volume for the pure components, for one of the composition (weight fraction of

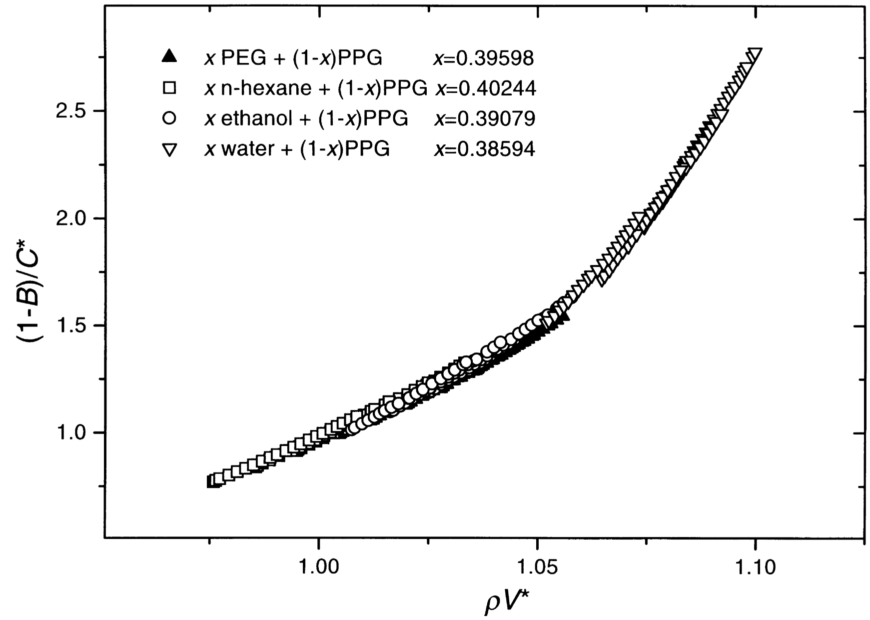

Fig. 5. Universal curve for the bulk modulus B according to the model of Huang and O'Connell [32] for different mixtures containing PPG (mole fraction of PPG approximately equal to 0.6) in the temperature interval 298.15–328.15 K. The data for the systems PPG + n-hexane, and + ethanol were taken from Ref. [15], and those for PPG + water were taken from Ref. [16].

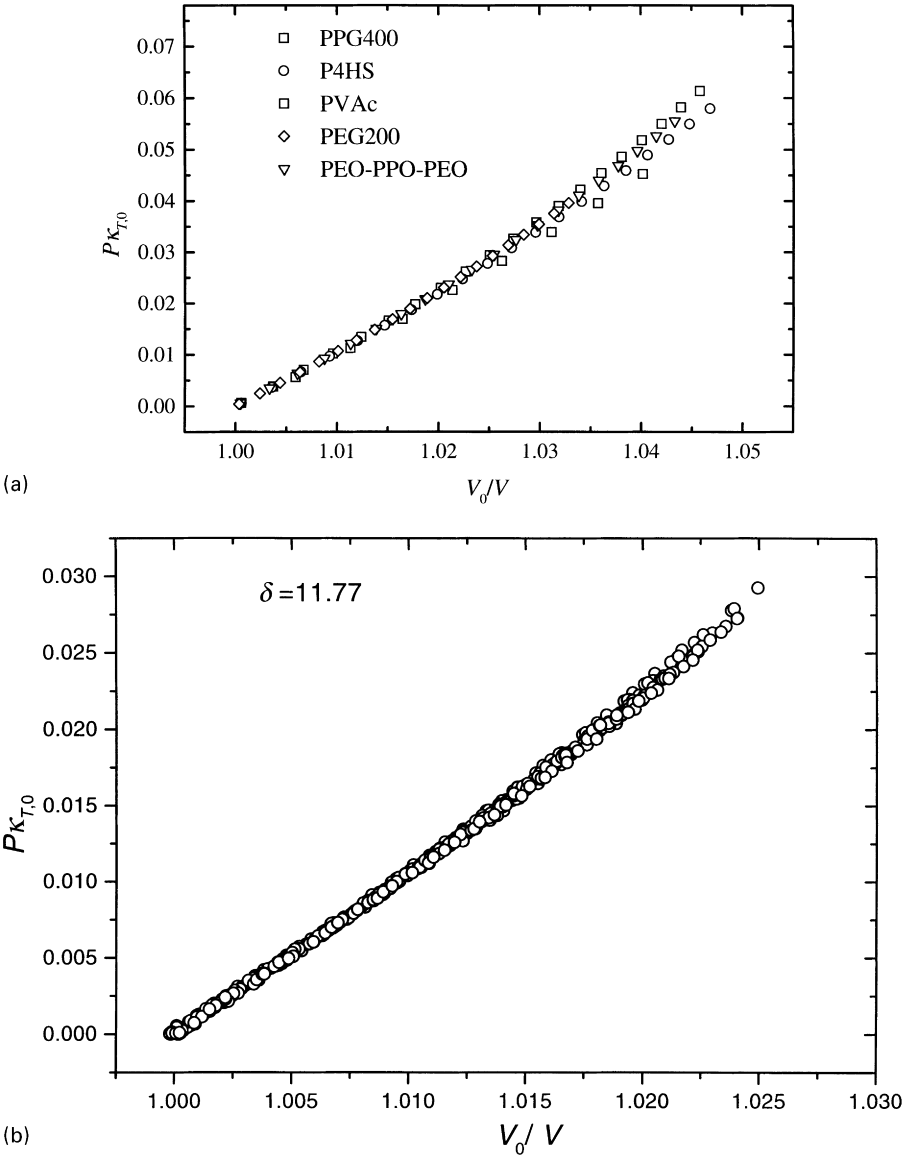

Fig. 6. (a) Corresponding-states function according to Sanchez et al. [33] for several pure polymers the data for P4HS and PVAc were taken from Ref. [31]. (b) The same for the PPG + PEG blend between 298.15 and 328.15 K and 0.1–40 MPa. PEG200: poly(ethylene glycol) $M_w = 200$; PEG400: poly(ethylene glycol) $M_w = 400$; PVAc: poly(vinylacetate); P4HS: poly(4-hydroxystyrene); PEO–PPO–PEO: poly(ethylene glycol)-*b*-poly(propylene glycol)-*b*-poly(ethylene glycol).

PEG $w \cong 0.33$), for the triblock copolymer with weight fraction of PEG 0.33, and for a blend of poly(4-hydroxystyrene) + poly(vinylacetate) (P4HS + PVAc) previously reported [31]. As it can be observed, the effect of pressure is larger for PPG than for PEG. Despite the big difference in chemical composition the data of the two blends lie on the same curve; however, for a given value of *P* and *T*, the PEG + PPG mixture has a slightly higher density than the copolymer, which may be explained in terms of the connectivity of the segments in the copolymer.

The excess volume V^E is a rather sensitive variable, and it can be calculated only if very precise density data are obtained. Fig. 3 shows the results for selected pressures at 298.15 K. These curves represent the best fit to a Redlich–Kister equation. Negative values over most of the composition range seem reasonable for systems that may form hydrogen bonds between the terminal hydroxyl groups and the ether groups. The effect of pressure is to make V^E less negative, leading to positive values for the blends with low PEG content. In order to confirm the shape of the curves for low values of *x*, more precise density data were obtained with a low-pressure densitometer (0.1 MPa). As it can be observed the agreement with the values obtained with the high-pressure apparatus is excellent. This strong asymmetry is similar to that found previously for the PPG + *n*-hexane system [15]. The magnitude of V^E is similar to that of the PPG + ethanol mixture [15]. The effect of temperature on V^E is small, and

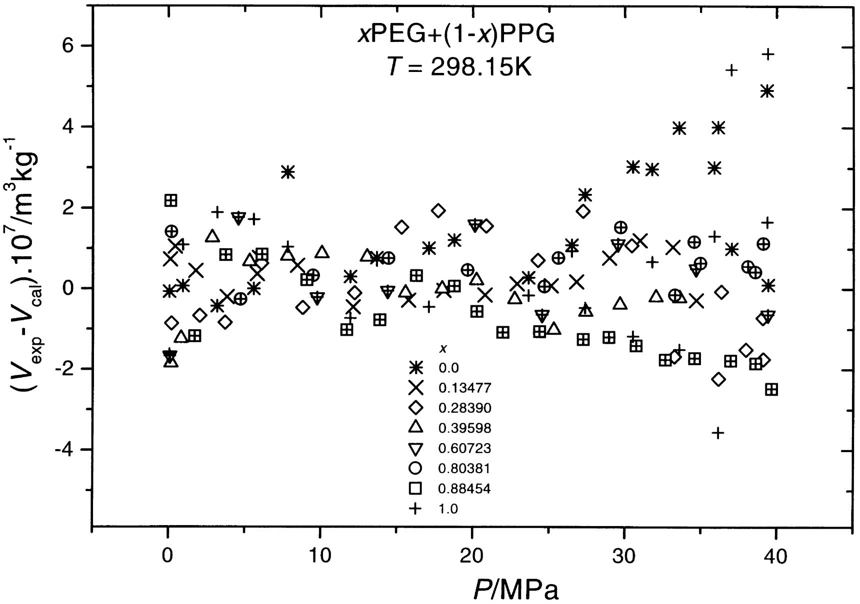

Fig. 7. Residuals of the molar volume calculated using Sanchez's scaling equation (Eq. (7)) and experimental V data. Notice that only one adjustable parameter $\delta = 11.77$ has been used and that the experimental precision of V is 1×10^{-7} m^3 kg^{-1}.

$(\partial V^{\mathrm{E}}/\partial T)_{P,x} > 0$, which is compatible with the fact that increasing T is unfavourable for hydrogen bonding.

The P–V–T results also allow one to calculate the dependence of the excess enthalpy H^{E} and excess Gibbs energy G^{E} on pressure:

$$\left(\frac{\partial H^{\mathrm{E}}}{\partial P}\right)_T = V^{\mathrm{E}} - T\left(\frac{\partial V^{\mathrm{E}}}{\partial T}\right)_P \tag{4}$$

$$\left(\frac{\partial G^{\mathrm{E}}}{\partial P}\right)_T = V^{\mathrm{E}} \tag{5}$$

Fig. 4 shows the results for the blend. Increasing the pressure decreases G^{E} thus making the mixing process more favourable, especially in the mid-concentration range. However, H^{E} increases with P for blends in the mid-concentration range, while the opposite is found for blends rich in either PPG or PEG. While the results for ΔG^{E} are qualitatively similar to those of the PPG + ethanol or + water systems [15,16], in the latter cases increasing P leads to a decrease in H^{E} through the whole concentration range. In contrast, for the system PPG + n-hexane [15], increasing P leads to increase in both G^{E} and in H^{E}.

4. Corresponding-states correlations

In previous works [15,16] it has been found that polymer–solvent systems follow quite closely the corresponding-states laws of Huang and O'Connell [32] and of Sanchez et al. [33]. According to Huang and O'Connell:

$$\frac{1-B}{C^*} = \sum_{i=0}^{3}\sum_{j=0}^{2} a_{ij}(\tilde{\rho})^i(\tilde{\tau})^j \tag{6}$$

with $\tilde{\rho} = \rho V^*$, $\tilde{\tau} = T/T^*$. The terms C^*, V^*, and T^* are integrals of the direct correlation function, and B is the bulk modulus $B = (\rho k_{\mathrm{B}} T \kappa_T)^{-1}$. The terms a_{ij} are universal constants [32]. Fig. 5 shows the results found for different systems containing a similar mole fraction of PPG (approximately $x = 0.40$) at four different temperatures. As it can be observed the correlation is acceptable.

Sanchez et al. [33] proposed that it should be possible to plot a master curve of the form

$$P\kappa_{T,0} = \frac{\rho^{\delta} - 1}{\delta} \tag{7}$$

where $\kappa_{T,0}$ is the isothermal compressibility at $P = 0.1$ MPa and δ is a parameter characteristic of each mixture. Fig. 6a shows the results of the correlation for different polymers, and Fig. 6b shows the correlation for the PPG + PEG blend with $\delta = 11.77$. It is worth noting that δ is relatively insensitive to the chemical nature of the system (e.g. $\delta = 10.93$ for the PPG + n-hexane system). Eq. (7) indicates that once the temperature dependence of ρ at $P = 0.1$ MPa and $\kappa_{T,0}$ are known, the influence of P upon the volume can be characterised by δ. Fig. 7 shows the residuals ($V_{\mathrm{exp}} - V_{\mathrm{calc}}$) for the system PPG + PEG at 298.15 K obtained from Eq. (7). It must be remarked that the experimental uncertainty in V is of the order of 1×10^{-7} m^3 mol^{-1}. Since similar results were found for polymer–solvent systems, Eq. (7) can clearly be used as a predictive tool for the effect of pressure on the density once ρ at $P = 0.1$ MPa and $\kappa_{T,0}$ are known.

5. Comparison with the lattice-fluid model

Panayiotou and Sanchez [17] have proposed a lattice-fluid model that incorporates specific interactions such as

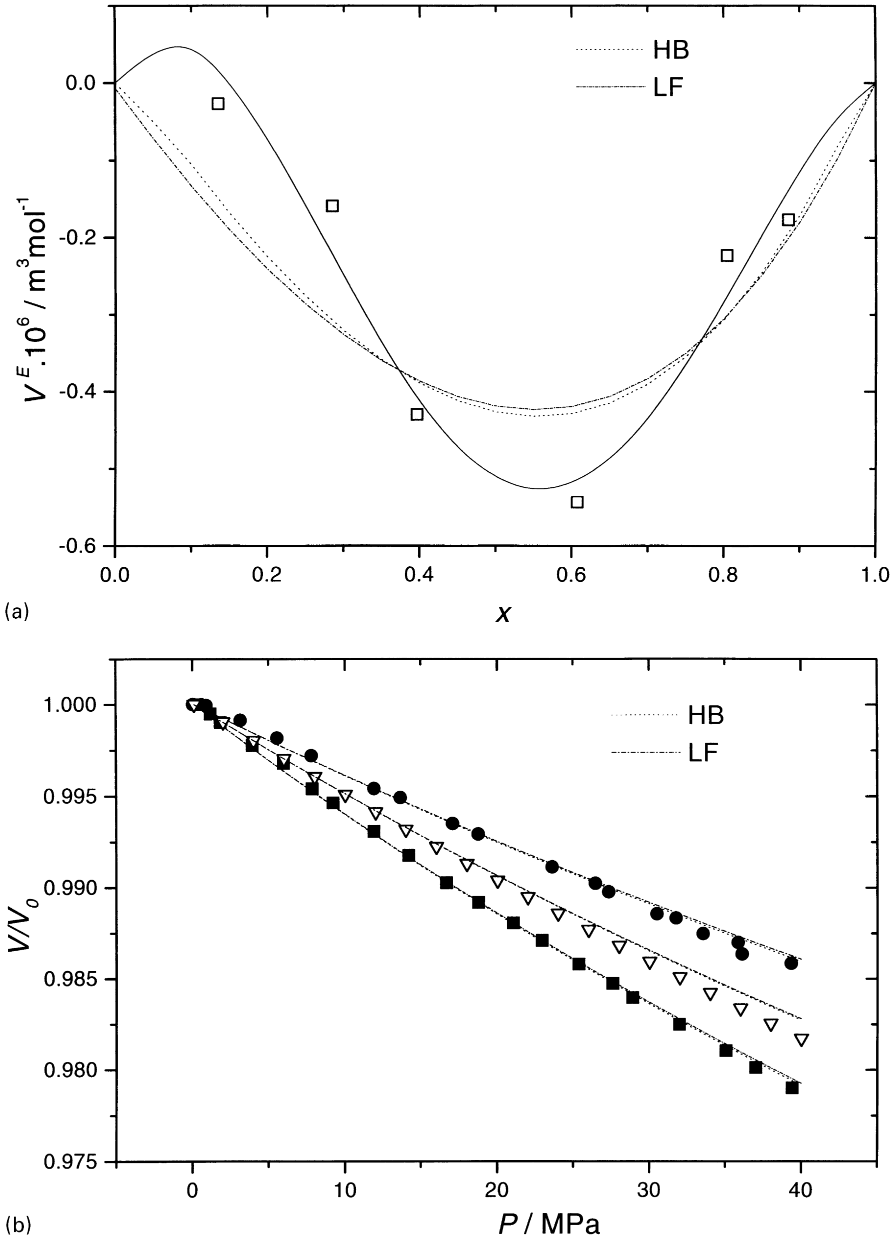

Fig. 8. (a) Comparison between the experimental V^E data at 298.15 K and $P = 0.1$ MPa and those predicted by the lattice-fluid model with and without hydrogen bond contributions. Similar results are found at other pressures and temperatures. (b) Comparison between the experimental and predicted effect of pressure on the reduced volume. Notice that the difference between the models with and without hydrogen bonds is negligible.

hydrogen bonds. We will give here only the EoS and the equations that allow one to account for such interactions. The EoS is

$$\tilde{P} + \tilde{\rho}^2 + \tilde{T}[\ln(1 - \tilde{\rho}) + \tilde{\rho}(1 - 1/\tilde{r})] = 0 \qquad (8)$$

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 size of the molecules and the van der Waals type interactions between them. The average number of segments per molecule $\bar{r}$ is defined by

$$1/\bar{r} = 1/r - \nu_H \qquad (9)$$

where ν_H is the fraction of hydrogen bonds in the system and r has the same meaning as that in the original lattice-fluid model of Lacombe and Sanchez [34], i.e. the average number of segments per molecule.

For pure PPG and PEG we have assumed that the molecules have $d = 2$ donor groups and $a = 7$ and $a = 5$ acceptor groups, respectively. The model leads to the following equation:

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

with $A_{ij} = r/\tilde{\rho}\exp(G^0_{ij}/RT)$, and $G^0_{ij} = E^0_{ij} - TS^0_{ij} + PV^0_{ij}$, where the energy, entropy and volume are characteristics of the i–j specific interaction (either –OH···OH–, or –OH···–C–O–C–). We have used for these parameters the same values as given in Ref. [15].

For the blend PPG + PEG it is necessary to account for self and cross-association, which leads to a system of coupled equations.

$$\nu_{ij}A_{ij} = r\left(\frac{N_d^{(i)}}{rN} - \sum_{k=i}^{n} \nu_{ik}\right)\left(\frac{N_a^{(j)}}{rN} - \sum_{k=j}^{m} \nu_{kj}\right) \quad (11)$$

The binary parameter of the model ξ has been fitted in order to reproduce the composition dependence of $V^E(P = 0.1\ \text{MPa})$. The calculations have been performed both with the full model, and also with the lattice model without specific interactions ($\nu_H = 0$). For both models a binary parameter $\xi > 1$ is necessary. Fig. 8a shows that none of the models reproduce the asymmetry of the experimental V^E curves, although they reproduce reasonably well the pressure dependence of the reduced volume, with no significant differences between both models (see Fig. 8b). Similar results were obtained at other temperatures.

In order to obtain a spinodal curve in the same temperature range as the experimental phase separation range, a binary parameter $\xi < 1$ has been found to be necessary, thus leading to poor predictions for V^E.

6. Conclusions

The equation of state surface of the PPG + PEG blend has been extensively mapped up to 40 MPa. At a given temperature and 0.1 MPa, the excess volume of the mixture is rather asymmetrical, being negative except for the PPG-rich blends. $(\partial V^E/\partial T)_{x,P}$ and $(\partial V^E/\partial P)_{x,T}$ are positive. Increasing the pressure decreases G^E at all blend compositions, while the effect on H^E is more complex: while H^E decreases in the mid concentration range, the opposite is found at the extremes of the concentration range.

The experimental results can be described very accurately with a corresponding-state model that uses a single fitting parameter. Moreover, such a parameter turns out to be system dependent to a very little extent. As a consequence, the pressure dependence of the density of the system can be calculated from density and compressibility data at ambient pressure.

The lattice-fluid model of Panayiotou and Sanchez [17] has been used to describe the results. The model is not able to account for the asymmetry of the excess volume curves, although it describes quite well the pressure dependence of the density. However, using the binary parameter that best fits the V^E data is not possible to predict the liquid–liquid equilibrium found for the PPG + PEG blend. No significant differences have been found between the model with and without hydrogen bond interactions.

Acknowledgements

This work was supported in part by DGICYT under grant PB95-0379, and DGES under grant PB96-609.

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