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ORIGINAL CONTRIBUTION

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Critical behavior and interfacial tension of mixtures of propylene glycol and ethylene glycol oligomers

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Abstract This investigation presents an analysis of the critical behavior of mixtures of oligomers of propylene glycol, PG_{17}, and ethylene glycol, EG_n, with $n = 3, 4, 5, 6.4, 8.7, 12.1$ and 22.1. The critical coordinates, ϕ_c and T_c were determined from the phase diagrams. The critical compositions compare very well with the Huggins–Flory predictions. The interaction parameter χ_{12} is around one for EG_3, EG_4 and EG_5 and it increases up to two for the higher oligomers. The break in the interaction parameter also corresponds to a minimum in the critical temperature. The phase diagrams and the interfacial tension were used to get the critical exponents β and μ, respectively. The data were analysed with two approaches. First, from the temperature dependence of the length of the tie-lines and of the interfacial tension up to the upper critical solution temperature, UCST. Second, with the data at 30 °C using the critical temperature of the systems as the variable. The first method led to $\langle\beta\rangle = 0.39 \pm 0.05$ in good agreement with the result of the second method, $\langle\beta\rangle = 0.37 \pm 0.04$. The exponents for the interfacial tension, μ, determined with the first method for PG_{17} with $EG_{6.4}$, $EG_{8.7}$ and $EG_{12.1}$ are $\mu = 1.66 \pm 0.11$, 1.46 ± 0.25 and 1.73 ± 0.18, respectively. The second method led to $\langle\mu\rangle = 1.17 \pm 0.14$. The critical exponents are compared to mean field and Ising-3D predictions.

Key words Critical exponent – interfacial tension – phase diagram – polymer mixtures

Introduction

In a previous investigation [1], we determined the interfacial tension between an oligomer of propylene glycol, PG_{17}, and three ethylene glycol oligomers, $EG_{6.4}$, $EG_{8.7}$ and $EG_{12.1}$, at 30 °C through the analysis of Rayleigh instabilities caused by an abrupt change of the angular speed of spinning drops. In this study, we investigate the critical behavior of the interfacial tension in the partly miscible mixtures of PG_{17} with oligomers of ethylene glycol, EG_n with $n = 2, 3, 4, 5, 6.4, 8.7, 12.1$ and 22.1.

The interfacial tension between polymers and its temperature dependence are key parameters for the processing of polymer blends and alloys [2]. For many immiscible blends, the critical temperature is much higher than the processing temperature and the interfacial tension can be expressed as a linear function of temperature [3]. This is no longer true for systems that exhibit partial miscibility such as the mixtures of PG_{17} with EG_n. The phase diagram of these systems is characterized by an upper critical solution temperature, UCST, and a critical composition, ϕ_C. The critical composition and the interaction parameter, χ_{12}, between PG_{17} and EG_n may be evaluated [2] from the second and third derivatives of the Huggins and Flory free energy of mixing of the systems.

$$\chi_{1,2} = (2 \cdot \phi_{1,c}^2)^{-1} \tag{1}$$

$$\phi_{1,C} = (1 - \phi_{1,c}) \cdot (V_2/V_1)^{1/2} , \tag{2}$$

where ϕ_i and V_i are the volume fraction and molar volume of component i and the subscripts 1 and 2 refer to EG_n and PG_{17}, respectively.

As the temperature of the system is raised to its upper critical solution temperature, the difference between the density of the coexisting phases, $\Delta\rho$, and the interfacial tension, γ, vanish with a critical exponent β and μ, respectively.

$$\Delta\rho = \Delta\rho_0 \cdot \varepsilon^{\beta} \tag{3}$$

$$\gamma = \gamma_0 \cdot \varepsilon^{\mu} , \tag{4}$$

where $\varepsilon = [T_c - T]/T_c$ and the subscript 0 refers to constants characteristic of the system. In this investigation, the critical exponents μ and β are determined in two ways. First, the exponents are obtained for individual systems by varying the reduced temperature, ε, through the experimental temperature, T. In the second approach, the exponents are obtained from the many systems at a constant temperature using T_c to vary ε. The latter approach should give the same exponents provided that the constant, $\Delta\rho_0$ and γ_0, are the same for the seven systems.

The exponents β and μ are universal but their estimates depend on the model used for the calculation. In the mean field approach, $\beta = 0.5$ and $\mu = 3 \cdot \beta$ while the Ising-3D predicts $\beta = 0.312$ and $\mu = 4 \cdot \beta$. Ising-3D usually applies to mixtures of small molecules. However, it is not clear which theory applies to polymer mixtures and polymer solutions. There are few reports of critical exponents in polymer mixtures [4–7] and they correspond either to mean field [4, 5] or they stand between [6, 7] mean field and Ising-3D predictions.

On the other hand, there are many reports of critical exponents in polymer solutions, in particular for polystyrene in methyl cyclohexane [8–11]. The ratio $\mu/\beta = 3.85$, reported [8] for polystyrene molecular weights in the range 17.5 to 175 kg·mol^{-1}, is close to the Ising-3D predictions as is the reported [11] value of $\mu = 1.248$ for polystyrene molecular weights in the range 9 to 1260 kg·mol^{-1}. The values of the exponent β reported [8–10] for these systems is in the range 0.34 to 0.39, between the mean field and the Ising-3D predictions.

In this investigation, we will compare the experimental critical exponents of the partly miscible mixtures of PG_{17} and EG_n with the mean field and Ising-3D predictions.

Experimental

Chemicals

The molecular weight, density and refractive index of the oligomers used in this investigation are reported in Table 1. Polypropylene glycol with an average molecular weight of 1000 g·mol^{-1} (Aldrich Chemicals Company inc.), PG_{17}, and the ethylene glycol oligomers (American Chemicals Ltd) were used as received. EG_3, EG_4 and EG_5 were received as tri, tetra and penta ethylene glycol with a purity > 99%, while $EG_{6.4}$, $EG_{8.7}$, $EG_{12.1}$ and $EG_{22.1}$ were received as polyethylene glycol with an average molecular weight of 300, 400, 550 and 1000 g·mol^{-1}.

Phase diagram

The liquid-liquid phase diagrams of PG_{17} with the oligomers of ethylene glycol were determined with the cloud point technique using a photoresistive cell (EG&G

Table 1 Density, ρ, and refractive index, n, of PG_{17} and EG_n and the critical composition, ϕ_c, temperature, T_c, and interaction parameter, χ_{12}, of their mixtures

Oligo.	$M_W^{(1)}$ g/mol	ρ^{30} kg/m^3	n^{30}	$n_L^{30(2)}$	$\phi_{EGn,c}^{(3)}$	$T_c^{(3)}$ °C	$\chi_{12}^{(3)}$
PG_{17}	⟨1000⟩	997.52	1.4463				
EG_3	150	1116.49	1.4534	1.4525	0.68	83	1.08
EG_4	194	1096.52	1.4565	1.4554	0.73	53	0.93
EG_5	238		1.4587	1.4574	0.68	51	1.10
$EG_{6.4}$	⟨300⟩	1118.82	1.4607	1.4583	0.67	52	1.13
$EG_{8.7}$	⟨400⟩	1118.85	1.4632	1.4605	0.62	49	1.30
$EG_{12.1}$	⟨550⟩	1119.97	1.4651	1.4613	0.56	61	1.62
$EG_{22.1}$	⟨1000⟩	solid	solid	solid	0.50	86	1.99

(1) ⟨⟩ refers to average values of molecular weight.
(2) Refractive index of the lower phase, rich in EG_n, in equilibrium with PG_{17} used for the correction of the diameter of the spinning drops.
(3) From the phase diagram of PG_{17} with EG_n.

Vactec) to monitor the opacity, $Op = (I_0 - I)/I_0$ of the samples. This technique has proven useful for the determination of the phase diagram of aqueous solutions of Pluronic [12] copolymers. Typically, 2 ml of the mixture is heated until it becomes a clear solution. The sample is then cooled slowly while the opacity and the temperature of the mixture are monitored. The cooling rate of the samples was between 2 and 4 °C$\cdot$min^{-1} except for the systems with EG_3 and $EG_{22.1}$ where it could reach 12 °C$\cdot$min^{-1} in the vicinity of the critical point.

The cloud point temperature, T_{CP}, was defined as the sharp increase of the opacity vs temperature curves. Because phase separation is a kinetic process, the temperatures reported in this investigation are certainly lower than the actual binodal temperatures. However, some tests as a function of the cooling rate of the mixtures indicated no significant effects on T_{CP} within the experimental reproducibility over three measurements, i.e., ± 1 °C.

The critical coordinates of the systems, T_C and ϕ_C, and the length of the tie lines, $|\phi_1^a - \phi_1^b|$ were determined graphically.

Interfacial tension

The interfacial tension was determined with the spinning drop technique. The details of the apparatus and methodology are described elsewhere [13]. To ensure composition equilibrium in the mixtures, the samples were equilibrated at the experimental temperature and vigorously shaken into a fine dispersion. The dispersion was then allowed to separate into two phases. The mixture was dispersed and allowed to settle a second time after which the compositions of the phases were assumed to be at equilibrium.

A drop of the upper phase, rich in PG_{17}, was introduced in a glass tube, $ID = 2$ mm, containing the lower phase, rich in EG_n. The tube was then rotated at an angular speed, ω, until the dimensions of the spinning drop were constant. In all cases, the elongated drops had a length at least four times their diameter, $2 \cdot r$, and the cylindrical approximation derived by Vonnegut was used to evaluate the ratio between the interfacial tension, γ, and the density difference of the coexisting phases, $\Delta\rho$.

$$\gamma/\Delta\rho = \omega^2 \cdot r^3/4 \qquad (5)$$

At each temperature, the equilibrium radius of the spinning drop, corrected for the index of refraction of the phase rich in EG_n (see Table 1), was determined to be between 3000 and 8000 rpm and the ratio $\gamma/\Delta\rho$ was obtained as the slope of ω^2 vs $4/r^3$. The linearity of the plot indicated that the interfacial tension of the systems studied was constant over the range of angular speed investigated.

The density of PG_{17} and EG_n and the density of the coexisting phases of the mixtures of PG_{17} with $EG_{6.4}$, $EG_{8.7}$ and $EG_{12.1}$ were determined with a vibrating tube densimeter (Sodev 03-D[14]) calibrated with nitrogen and water at 30 °C.

Results and discussion

This section is divided in three parts. First, the critical coordinates and the interactions deduced from the experimental phase diagrams are presented. Second, the critical exponents β and μ are determined for individual systems with T as the variable. Finally, the critical exponents are determined collectively at 30 °C using T_c as the variable.

Critical coordinates and interactions

The phase diagrams of the mixtures of PG_{17} and EG_n are characterized by an upper critical solution temperature, UCST. The results for EG_3, EG_4 and EG_5 are shown in Fig. 1a while those for the oligomers with an average degree of polymerisation, $EG_{6.4}$, $EG_{8.7}$, $EG_{12.1}$ and $EG_{22.1}$, are shown in Fig. 1b. The UCST was interpolated and the critical compositions, in weight fraction, were converted in volume fractions using the densities. The critical coordinates, T_c and ϕ_c, are reported in Table 1.

As shown in Fig. 2, the experimental critical compositions, ϕ_c, are in very good agreement with the Huggins–Flory theory, Eq. (2). Equation (1) was used to calculate the Huggins–Flory interaction parameter and the results are plotted in Fig. 3a and reported in Table 1. The interaction parameter decreases linearly from $\chi_{12} = 2$ to $\chi_{12} = 1$ up to a ratio of $V_{PG17}/V_{EGn} = 4$. At higher values, it remains almost constant to a value of one.

From melting point depression, Shilov et al. [15] also report values around 2 for the mixtures of $EG_{22.1}$ and PG_{17}. From the enthalpy of mixing of Cooper and Booth [16], one gets $\chi_{12} = 2.76$ for $PG_{12.6} + EG_{13.2}$ at 30 °C while Friday et al [17] report $\chi_{12} = 2.20$ for $PG_{17} + EG_{13.2}$ also at 30 °C. These values are higher than $\chi_{12} = 1.6$ that we calculate for $PG_{17} + EG_{12.1}$ around 50 °C. The difference may be attributed to the decrease of the interaction parameter with temperature or to enthalpic contributions included in the enthalpy measurements but not in the Huggins–Flory parameter as described in Eq. (1).

As mentioned above, χ_{12} shows a change of slope around $V_{PG17}/V_{EGn} = 4$. That break could indicate a change in the type of interactions between PG_{17} and EG_n. For instance, the interaction parameter is the lowest for the lower oligomers, indicating that tri, tetra and penta

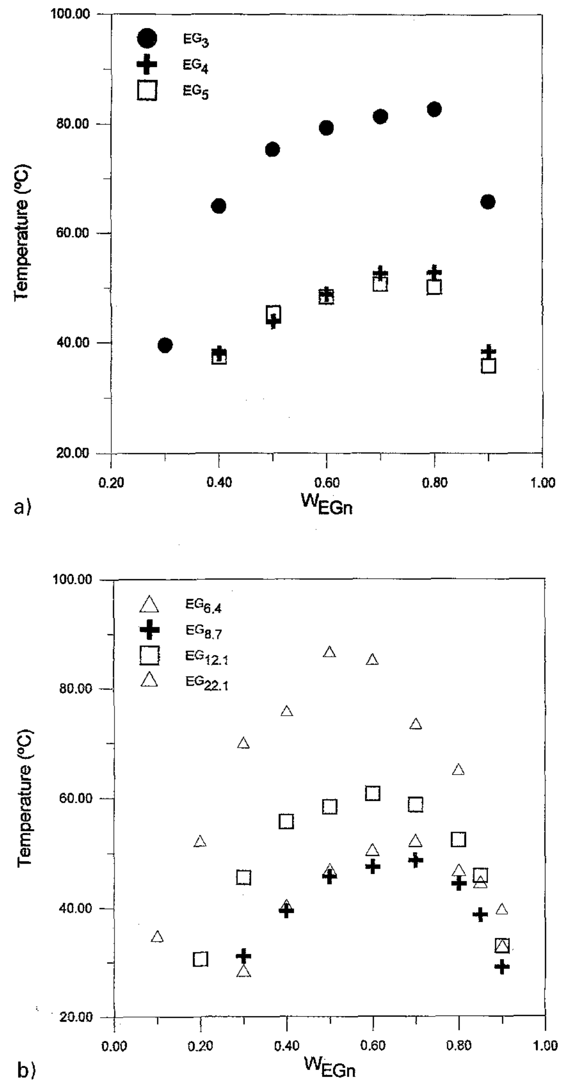

Fig. 1 Phase diagram of PG_{17} with a) EG_3, EG_4 and EG_5 and b) $EG_{6.4}$, $EG_{8.7}$, $EG_{12.1}$ and $EG_{22.1}$. Data were obtained with the cloud point technique as the temperature is decreased into the two phases region

ethylene glycol molecules interact more with themselves through hydrogen bonding than with the molecules of PG_{17}. The self hydrogen bonding ability decreases as the size of the oligomer increases so that the higher oligomers are left with the usual polymer-polymer interactions with the PG_{17} molecules. This change could thus be seen as the passage from polymer-polymer interactions, for the higher oligomers, to polymer-solvent interactions, for the lower oligomers.

This change in the type of interactions could also explain the peculiar trend of the UCST which goes through a minimum around $V_{PG17}/V_{EGn} = 4$ as shown in Fig. 3b. The decrease of the UCST with the reciprocal of

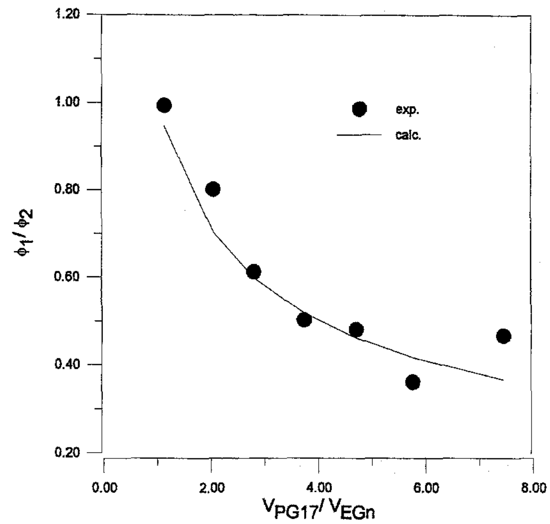

Fig. 2 Comparison of the experimental critical composition, $\phi_{1,c}$, with the Huggins–Flory predictions for PG_{17} and EG_n

the molar volume of EG_n is consistent with polymer mixtures. However, the trend is reversed for the lower oligomers, probably an indication that the self hydrogen bonding contribution has become dominant for the lower oligomers.

Critical exponents μ and β with T as the variable

The exponent β is linked to the density of the coexisting phases. The density of each phase may be evaluated from the density of the pure components and the appropriate concentration scale.

$$\rho^{U} = \rho_{PG17} + c^{U}_{EGn} \cdot (\rho_{EGn} - \rho_{PG17}) \tag{6a}$$

$$\rho^{L} = \rho_{PG17} + c^{L}_{EGn} \cdot (\rho_{EGn} - \rho_{PG17}) \tag{6b}$$

$$\Delta\rho = |\rho^{U} - \rho^{L}| = |c^{U}_{EGn} - c^{L}_{EGn}| \cdot (\rho_{EGn} - \rho_{PG17}) , \tag{6c}$$

where c represents the appropriate composition scale that linearizes the density of the mixture. Once the scale is known, one can correlate the difference between the density of the coexisting phases, $\Delta\rho$, to the length of the tie-lines, $|c^{U}_{EGn} - c^{L}_{EGn}|$. Replacing $\Delta\rho$ of Eq. (6c) with the right side of Eq. (3) leads to another expression to get the exponent β from the phase diagram.

$$|c^{U}_{EGn} - c^{L}_{EGn}| = (\Delta\rho_0/(\rho_{EGn} - \rho_{PG17})) \cdot \varepsilon^{\beta} . \tag{7}$$

We measured the density of the coexisting phases of the mixtures of PG_{17} with $EG_{6.4}$, $EG_{8.7}$ and $EG_{12.1}$ at 30 °C

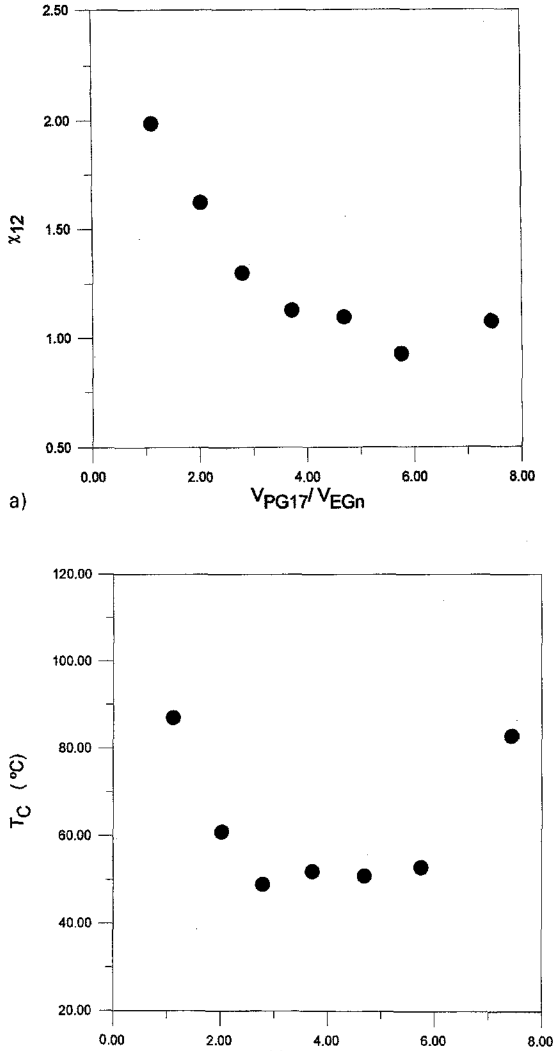

Fig. 3 Comparison of a) experimental Huggins–Flory interaction parameter, χ_{12}, and b) experimental upper critical solution temperature for the mixtures of PG_{17} with EG_n

and we calculated the values of c^U and c^L for the three systems according to Eqs. (6a) and (6b). The results are reported in Table 2 and they are compared with the weight and volume fractions deduced from the phase diagrams. It turns out that these two scales both describe fairly well the composition dependence of the density. Other groups [17] also reported a volume fraction dependence of the density of similar mixtures so that the length of the tie-lines was expressed in volume fraction, i.e., $|c^U_{EGn} - c^L_{EGn}| = |\phi^U_{EGn} - \phi^L_{EGn}|$.

The values of β obtained for the seven systems are reported in Table 3. The average value over the seven systems is $\langle 0.39 \rangle \pm 0.05$ and the standard deviation is concordant with the uncertainty attached to the individual exponents. The value of $\beta = 0.39 \pm 0.05$ is in good agreement with the values reported either for polymer mixtures [6] or polymer-solvent systems [8,9], $\beta = 0.34$–0.39, and it falls between the Ising-3D, $\beta = 0.312$, and the mean field, $\beta = 0.5$, predictions. Although our values stand closer to Ising-3D than mean field predictions, it is thus difficult to discriminate between the two theories.

One could have expected a cross over [10] of the critical exponent from Ising-3D to mean field as the ethylene glycol oligomers evolve from solvent-like to polymer-like. However, there is no definite trend of β with the size of EG_n. This supports the universality of the critical exponent, at least for systems experiencing the same type of interactions as seems to be the case in this investigation.

As described in Eq. (4), the critical exponent μ is obtained from the temperature dependence of the interfacial tension. However, Eq. (5) tells us that the interfacial tension determined with the spinning drop technique also requires the knowledge of the density of the coexisting phases. The alternative is to measure the temperature dependence of the ratio of the interfacial tension to the density difference between the coexisting phases, $\gamma/\Delta\rho$, which, using Eqs. (3) and (4), leads to the composite exponent $(\mu - \beta)$.

$$\gamma/\Delta\rho = (\gamma/\Delta\rho)_0 \varepsilon^{(\mu-\beta)} \,. \tag{8}$$

Using the experimental values of β and $(\mu - \beta)$, one can evaluate the critical exponent of the interfacial tension, μ.

Figure 4 shows the temperature dependence of the ratio $\gamma/\Delta\rho$ for the mixtures of PG_{17} with $EG_{6.4}$, $EG_{8.7}$ and $EG_{12.1}$. The composite exponents, $(\mu - \beta)$, calculated with Eq. (8) are reported in Table 3. The experimental values of

Table 2 Comparison between experimental, w and ϕ, and calculated, c_{EGn}, concentrations of the coexisting phases of the mixtures of PG_{17} with EG_n at 30 °C

EG_n	$\rho^{U(1)}$ kg/m^3	$c^{U(2)}_{EGn}$	$w^{(3)}$	$\phi^{(3)}$	$\rho^{L(1)}$ kg/m^3	$c^{L(2)}_{EGn}$	$w^{(3)}$	$\phi^{(3)}$
$EG_{6.4}$	1032.16	0.29	0.30	0.28	1101.62	0.86	0.90	0.89
$EG_{8.7}$	1033.50	0.30	0.30	0.28	1097.62	0.82	0.90	0.89
$EG_{12.1}$	1027.03	0.24	0.20	0.18	1102.21	0.85	0.90	0.89

(1) Experimental densities of the upper, U, and lower, L, phases of the systems $EG_n + PG_{17}$.
(2) Concentration calculated with (6a) and (6b).
(3) Experimental concentration of EG_n in the coexisting phases expressed in weight, w, and volume, ϕ, fraction.

Table 3 Summary of the critical exponents of PG_{17} with EG_n

EG_n	$\gamma/\Delta\rho^{(1)}$ $10^6 m^3/s^2$	β	$(\mu-\beta)$	$(\gamma/\Delta\rho)_0$ $10^6 m^3/s^2$
EG_3	5.149	0.33		
EG_4	2.607	0.43		
EG_5	2.891	0.38		
$EG_{6.4}$	2.741	0.43	1.23 ± 0.06	4.36 ± 0.07
$EG_{8.7}$	2.386	0.34	1.12 ± 0.25	4.11 ± 0.08
$EG_{12.1}$	3.734	0.38	1.35 ± 0.13	4.53 ± 0.18
$EG_{22.1}$	solid	0.48		
$Coll^2$		0.37 ± 0.04	0.81 ± 0.10	

$^{(1)}$ Experimental values at 30 °C.
$^{(2)}$ Result obtained collectively at $T = 30$ °C using T_c as the variable.

$(\mu - \beta)$ are all significantly higher than the Ising-3D and mean field theories, $(\mu - \beta) = 0.936$ and 1.0. Using the values of β from the phase diagrams one gets $\mu = 1.66 \pm 0.11$, 1.46 ± 0.25 and 1.73 ± 0.18 for $EG_{6.4}$, $EG_{8.7}$ and $EG_{12.1}$, respectively. Our values are also higher than the range reported [8, 11] for polystyrene in methylcyclohexane, $\mu = 1.30 - 1.51$. They are also higher than the model predictions but closer to the mean field value of 1.5.

Critical exponents μ and β with T_c as the variable.

The reduced temperature, $\varepsilon = |T_c - T|/T_c$, in Eqs. (3), (4) and (8) is always calculated with respect to the critical temperature of a given system. However, ε can also change from one system to another at a given experimental temperature. This provides a new method for the determination of the critical exponents. Assuming that the value of $(\gamma/\Delta\rho)_0$ is the same for systems that experience the same type of interactions, one can use Eq. (8) to get the composite exponent from data obtained at one temperature with many systems having different critical temperatures. The values of $(\gamma/\Delta\rho)_0$ for the three systems investigated are reported in Table 3 and they agree within experimental uncertainty. So, we assumed that it was constant for all the systems investigated. Figure 5 shows the plot of the ratio $\gamma/\Delta\rho$ as a function of the reduced temperature, $\varepsilon = |T_c - 303|/T_c$, at 30 °C for the systems investigated. The plot is fairly linear, but now the composite exponent, $(\mu - \beta) = 0.81 \pm 0.10$, is lower than both the mean field and Ising-3D predictions.

The same approach can be used to get the critical exponent β from the tie-lines of the phases diagrams at 30 °C. Figure 6 shows the plot of the length of the

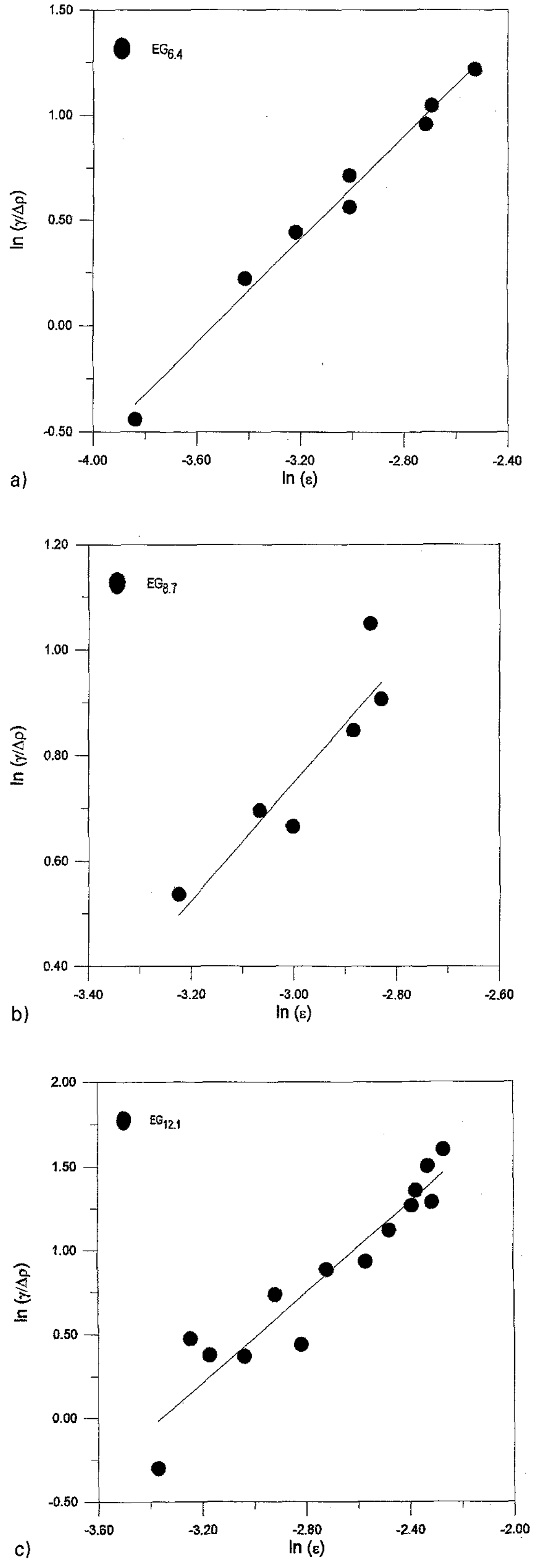

Fig. 4 Log-Log plot of $(\gamma/\Delta\rho)$ vs $|T_c - T|/T_c$ for PG_{17} with a) $EG_{6.4}$, b) $EG_{8.7}$, and c) $EG_{12.1}$

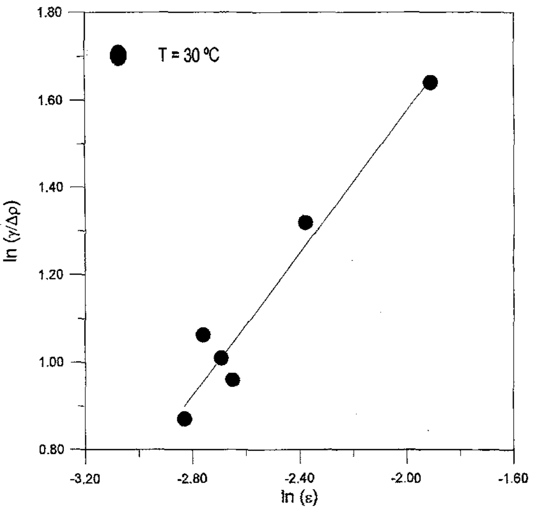

Fig. 5 Log-Log plot of $(\gamma/\Delta\rho)$ at 30 °C vs $|T_c - 303|/T_c$ for the systems EG_n with PG_{17}. In this case, ε varies with the critical temperature of the system

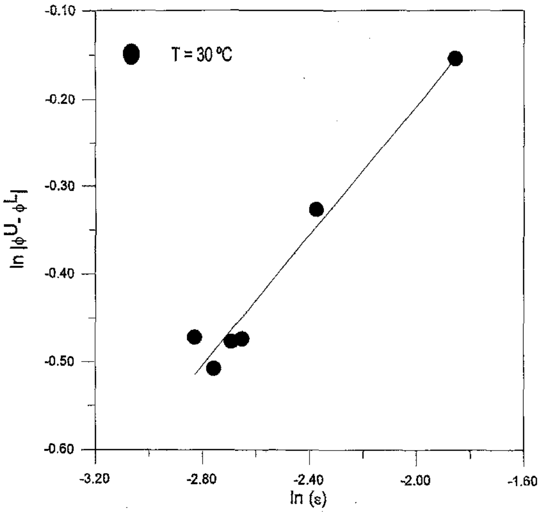

Fig. 6 Log-Log plot of the length of the tie-lines at 30 °C vs $|T_c - 303|/T_c$ for the systems EG_n with PG_{17}. In this case, ε varies with the critical temperature of the system

tie-lines as a function of the reduced temperature, $\varepsilon = |T_c - 303|/T_c$. At 30 °C, we did not have sufficient data for EG_3 and the data for $EG_{8.7}$ was rejected. This gave a slope of $\langle\beta\rangle = 0.37 \pm 0.04$, in fair agreement with $\langle\beta\rangle = 0.39 \pm 0.05$ obtained from the temperature dependence of the length of the tie-lines of the phase diagrams.

Using $\langle\beta\rangle = 0.37 \pm 0.04$ and $\langle\mu - \beta\rangle = 0.81 \pm 0.10$, one gets $\langle\mu\rangle = 1.18 \pm 0.14$. This time, all the values are close to the Ising-3D estimates. Nevertheless, the method shows some potential for the determination of critical exponents of polymer mixtures having the same type of interactions. This approach could be useful for the investigation of systems where it is difficult to get the temperature dependence of the physico-chemical properties.

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