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Estimation of EOS interaction parameters from scattering and predictions of phase diagram from them

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The interaction energy parameter (X_{12}), and the interaction entropy parameter (Q_{12}) of the Flory's equation-of-state theory were determined from the Flory–Huggins interaction parameter, χ, which was measured from scattering data for the miscible blend systems, polystyrene (PS)/poly(vinyl methyl ether) (PVME) and deuterated polystyrene (dPS)/PVME blends. The phase diagram of the polymer mixture was predicted from the values of X_{12} and Q_{12}. The spinodal curve predicted from theory showed a similar shape to the experimental one although the lower critical solution temperature from theory is ca. 10–70°C higher than the experimental values. It was found that a small difference in the χ values leads to a large shift of spinodal curve. On the other hand, the parameters X_{12} and Q_{12} were determined by fitting the EOS theory to experimental data, and then the parameter χ was calculated from the best-fit values of X_{12} and Q_{12}. The parameter χ calculated from theory showed a composition dependency which was in good agreement with those obtained from the neutron scattering measurements. Copyright © 1996 Elsevier Science Ltd.

(Keywords: phase behaviour; interaction energy parameter; interaction entropy parameter)

INTRODUCTION

The thermodynamic properties of polymer mixtures have very often been interpreted with the Flory's equation-of-state theory[1-3]. This theory has proved quite successful in explaining many thermodynamic properties, such as the lower critical solution temperature (*LCST*) behaviour, the volume change of mixing, and the heat of mixing, that the Flory–Huggins theory has failed to explain[4,5].

The determination of the equation-of-state interaction parameters, X_{12} and Q_{12} is a prerequisite for the prediction of the thermodynamic quantities of polymer mixtures from the equation-of-state theory. There are several ways to determine X_{12}, for instance, by fitting the theoretical values of the thermodynamic quantity to the experimental data of the mixtures such as the heat of mixing[6], liquid–liquid phase separation[6,7], and chemical potential measured by the solvent vapour sorption technique[4] or melting point depression[8].

Recently, small-angle neutron scattering (SANS) has been one of the most powerful methods for obtaining the composition dependent χ-parameter, because of the high contrast between labelled and unlabelled species. Zimm analyses have been extended to apply to concentration polymer–polymer mixtures[9-12], where the concentration dependence of the χ-parameter becomes apparent[13]. The scattering theories for polymer mixtures have been derived on the concept of the Flory–Huggins theory.

The Flory–Huggins interaction parameter can be directly related to the equation-of-state theory. Therefore, the interaction energy parameter, X_{12}, and interaction entropy parameter, Q_{12}, in the EOS theory can be determined from the experimental values of χ. In this report, we determined the values of X_{12} and Q_{12} for binary mixtures of polystyrene (PS) poly(vinylmethylether) (PVME) and deuterated polystyrene (dPS)/PVME from the χ values obtained from scattering data and then predicted spinodal curves from the equation-of-state (EOS) theory, which were compared with experimental data. In addition, the effect of the substitution of deuterium for hydrogen on the phase behaviour will be discussed in terms of the EOS interaction parameters.

THEORETICAL BACKGROUND

According to Flory *et al.*[1], the reduced equation-of-state derived from the partition function is given at zero pressure by

$$\frac{1}{\tilde{v}\tilde{T}} = \frac{\tilde{v}^{1/3}}{(\tilde{v}^{1/3} - 1)} \tag{1}$$

where $\tilde{v}$ and $\tilde{T}$ are the reduced volume and temperatures, respectively. The hard-core volume per segment, v^*, the characteristic pressure, p^*, and the characteristic temperature, T^*, can be calculated from the measurements of the thermal expansion coefficient, α, the specific volume, v, and the thermal pressure coefficient,

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γ. The relations are given by

$$\tilde{v} = v/v^* = [1 + \alpha T/3(1+\alpha T)]^3 \tag{2}$$

$$\tilde{T} = T/T^* = (\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3} \tag{3}$$

$$p^* = \gamma T \tilde{v}^2 \tag{4}$$

The application of this theory to mixtures of $N_1 r_1$-mers and $N_2 r_2$-mers is based on the mean-field approximation. An interaction energy parameter X_{12} is introduced, which arises from considering the difference in interaction energy between like and unlike segmental pairs. The equation-of-state for a two-component mixture has a form identical with that for the pure component if the following mixing rules are made

$$p^* = \phi_1 p_1^* + \phi_2 p_2^* - \phi_1 \theta_2 X_{12} \tag{5}$$

$$1/T^* = (\phi_1 p_1^*/T_1^* + \phi_2 p_2^*/T_2^*)/p^* \tag{6}$$

$$\theta_2 = s\phi_2/(\phi_1 + s\phi_2) \tag{7}$$

where ϕ_1 and ϕ_2 denote the segment fractions of components 1 and 2, respectively, and θ_2 is the surface fraction of component 2. In equation (7), s is defined as s_2/s_1, the ratio of surface area per unit core volume which can be estimated by a group contribution method[15]. In a region sufficiently far away from the critical point, it is reasonable to assume that a polymer blend follows the mean-field approximation. In this concept the Gibbs free energy of mixing, ΔG_m, is given by

$$\frac{\Delta G_m}{RT} = \frac{\phi_1}{V_1}\ln\phi_1 + \frac{\phi_2}{V_2}\ln\phi_2 + \phi_1\phi_2\chi \tag{8}$$

where V_1 and V_2 are the molecular volumes of polymers 1 and 2, respectively, and R is the gas constant.

In the equation-of-state theory, the chemical potential of component 1 in a mixture is given by:

$$\begin{aligned}\Delta\mu_1/RT = {} & \ln\phi_1 + (1 - r_1/r_2)\phi_2 + \frac{p_1^* V_1^*}{RT} \\ & \times \left\{ 3T_1 \ln\left(\frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}^{1/3} - 1}\right) + \left(\frac{1}{\tilde{v}_1} - \frac{1}{\tilde{v}}\right)\right\} \\ & + \frac{V_1^* X_{12}\theta_2^2}{\tilde{v}RT}\end{aligned} \tag{9}$$

where V_1^* and $\tilde{v}_1$ are the molar core volume and the reduced volume of component 1, respectively. When the expression for the chemical potential of component 1 in the equation-of-state theory is compared with the first derivative of equation (8) with respect to component 1, the Flory–Huggins interaction parameter, χ, is expressed as:

$$\begin{aligned}\chi = {} & \frac{p_1^* V_1^*}{RT\phi_2^2}\left\{3T \ln\frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}^{1/3} - 1} + \left(\frac{1}{\tilde{v}_1} - \frac{1}{\tilde{v}}\right)\right\} \\ & + \frac{(X_{12} - TQ_{12}\tilde{v})\theta_2^2}{RT\tilde{v}\phi_2^2}\end{aligned} \tag{10}$$

Examination of equation (10) reveals that the Flory–Huggins interaction parameter, χ, is divided into two terms, namely an interaction contribution which is the second term in equation (10), and an entropic contribution, which is the first term in equation (10). The latter is a segmental entropy and is supposed to be related to the free volume of the blend. Therefore, the χ parameter is expressed as the sum of two contributions from free volume and interaction:

$$\chi = \chi_{\text{free vol.}} + \chi_{\text{interact}} \tag{11}$$

where $\chi_{\text{free vol.}}$ represents the effect of the free volume change upon mixing, and χ_{interact} is due to the non-equivalence of the contacts between like and unlike molecules. Comparing equation (10) with equation (11) yields

$$\chi_{\text{free vol.}} = \frac{p_1^* V_1^*}{RT\phi_2^*}\left\{3\tilde{T}_1 \ln\frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}^{1/3} - 1} + \left(\frac{1}{\tilde{v}_1} - \frac{1}{\tilde{v}}\right)\right\} \tag{12}$$

and

$$\chi_{\text{interact}} = \frac{\theta_2^2}{RT\tilde{v}\phi_2^2}(X_{12} - TQ_{12}\tilde{v}) \tag{13}$$

Since the χ parameter is determined from neutron scattering experiment and the value of $\chi_{\text{free vol.}}$ can be also calculated if characteristic parameters are known, the difference between χ and χ_{interact} is estimated. The difference, $\chi - \chi_{\text{free vol.}}$, which corresponds to χ_{interact}, is expressed as:

$$\chi - \chi_{\text{free vol.}} = \frac{\theta_2^2}{R\phi_2^2}\frac{X_{12} - TQ_{12}\tilde{v}}{T\tilde{v}} \tag{14}$$

A plot of this difference against $(T\tilde{v})^{-1}$ should give straight lines. Thus the values of X_{12} and Q_{12} can be determined from the slope and the ordinate intercept, respectively. It seems that the reduced volume of mixing, $\tilde{v}$, is a function of X_{12} as known from equations (3), (5) and (6). Therefore, in order to determine X_{12} and Q_{12} from the plot of $\chi - \chi_{\text{free vol.}}$ *versus* $(T\tilde{v})^{-1}$, the value of $\tilde{v}$ should be determined independently. In this study, the value of $\tilde{v}$ was calculated by following the procedure proposed by Flory *et al.*[22]. Summarizing the procedure, the reduced volume per segment $\tilde{v}^{\circ}$ is expressed as equation (15) if no volume change occurs upon mixing:

$$\tilde{v}^{\circ} = \phi_1\tilde{v}_1 + \phi_2\tilde{v}_2 \tag{15}$$

where $\tilde{v}_1$ and $\tilde{v}_2$ are the reduced volume of components 1 and 2, respectively. $\tilde{T}^{\circ}$ corresponding to $\tilde{v}^{\circ}$ can be calculated by equation (1). Given $\tilde{T}_1$ and $\tilde{T}_2$, the reduced temperature of mixture, $\tilde{T}$, is written as equation (16):

$$\tilde{T} = \phi_1\tilde{T}_1 + \phi_2\tilde{T}_2 \tag{16}$$

Then the excess reduced volume $\tilde{v}^{E}$ is expressed as

$$\begin{aligned}\tilde{v}^{E} = \tilde{v} - \tilde{v}^{\circ} & = \left(\frac{\partial\tilde{v}}{\partial\tilde{T}}\right)(\tilde{T} - \tilde{T}^{\circ}) \\ & = 3\tilde{v}^{7/3}(4 - 3\tilde{v}^{\circ\,1/3})^{-1}(\tilde{T} - \tilde{T}^{\circ})\end{aligned} \tag{17}$$

From equation (17), the value of $\tilde{v}$ can be calculated if the value of $\tilde{v}^{\circ}$ is known.

RESULTS AND DISCUSSION

Determination of X_{12} and Q_{12} (ref. 18)

The PS/PVME blends were chosen for model systems. For SANS experiments, deuterium should be substituted for hydrogen in one component of the polymer blend. It is assumed that this type of substitution does not affect the thermodynamic interaction between components. In other words, for mixtures of PS (H) or dPS (D) with PVME (B), the interaction parameters χ_{HB} and χ_{DB} are assumed to be equal and χ_{HD} is assumed to be zero. The validity of the assumption of $\chi_{HB} = \chi_{DB}$ has been demonstrated through the observation of a zero second virial coefficient by SANS studies[17,23]. Therefore, it can be assumed that χ from scattering experiments for dPS/PVME blends is equal to χ for PS/PVME blends. The EOS interaction parameters for both dPS/PVME and PS/PVME blends can be estimated from the χ obtained from scattering experiments for dPS/PVME blends[14]. To determine the X_{12} and Q_{12}, as mentioned above, the exact values of characteristic parameters for dPS, PS and PVME are required. The characteristic parameters of pure component are taken from literature[19,20] and listed in *Table 1*. The parameter s in equation (7) was determined by Bondi's group contribution method[15] and the value was 0.83.

Figure 1 is plots of $\chi - \chi_{\text{free vol.}}$ *versus* the reciprocal of $T\tilde{\nu}$ for dPS/PVME and PS/PVME blends. As shown in *Figure 1*, straight lines are obtained. The values of X_{12} and Q_{12} were determined from slopes and intercepts of the lines, respectively and listed in *Table 2*. The values of X_{12} and Q_{12} are somewhat dependent upon the composition. These results are not consistent with the concept of Flory's equation-of-state theory, since the theory assumes that X_{12} and Q_{12} do not depend on the composition. This inconsistency may indicate that Flory's assumption in the theory is not valid and/or the determination of χ from scattering data gives an error. At present, it is not possible to further investigate the reasons for the inconsistency.

Simulation of the spinodal

The spinodal condition is given by

$$\frac{\partial}{\partial\phi_2}\left(\frac{\Delta\mu_1}{RT}\right) = 0 \tag{18}$$

When the spinodal condition is applied to equation (9), one obtains

$$\frac{V_1^*}{RT}\left(p_1^* D\left(\frac{1}{\tilde{\nu}^2} + \tilde{p}_1\right) + X_{12}\left(\frac{2\theta_2^2\theta_1}{\tilde{\nu}\phi_1\phi_2}\right) - X_{12}D\left(\frac{\theta_2}{\tilde{\nu}}\right)^2\right)$$
$$= \left[\frac{1}{\phi_1} - \left(1 - \frac{r_1}{r_2}\right)\right] + \frac{p_1^*}{T_1^*}\frac{D}{\tilde{\nu} - \tilde{\nu}^{2/3}}\frac{V_1^*}{R}\frac{2\theta_2^2\theta_1}{\phi_1\phi_2}\frac{V_1^*}{R}Q_{12} \tag{19}$$

where $D = \partial\tilde{\nu}/\partial\phi_2 = -\partial\tilde{\nu}/\partial\phi_1$,

$$\frac{\partial\tilde{\nu}}{\partial\phi_2} = \left\{\frac{\partial\tilde{p}}{\partial\phi_2} - \frac{\partial\tilde{T}}{\partial\phi_2}\left(\frac{\tilde{p}}{\tilde{T}} + \frac{1}{\tilde{T}\tilde{\nu}^2}\right)\right\}\Big/ \times \left\{\frac{2}{\tilde{\nu}^3} - \frac{\tilde{T}}{3\tilde{\nu}^{5/3}}\frac{3\tilde{\nu}^{1/3} - 2}{(\tilde{\nu}^{1/3} - 1)^2}\right\} \tag{20}$$

$$\frac{\partial p}{\partial\phi_2} = p/[p^{*2}(p_1^* - p_2^* - \theta_2 X_{12}(1 - \theta_1/\phi_2))] \tag{21}$$

$$\frac{\partial\tilde{T}}{\partial\phi_2} = \frac{\tilde{T}}{\tilde{p}}\left(\frac{\partial\tilde{p}}{\partial\phi_2}\right) + \frac{p_1^*\tilde{T}_2 - p_2^*\tilde{T}_1}{p^*} \tag{22}$$

Table 1 Characteristic parameters for pure polymers

Polymer	p^* (J cm^{-3})	T^* (K)	ν^* (cm^3 g^{-1})
PVME[a]	483	7051	0.8173
PS[a]	506	7948	0.8205
dPS[b]	425.7	10235	0.7999

[a] From ref. 19
[b] From ref. 20

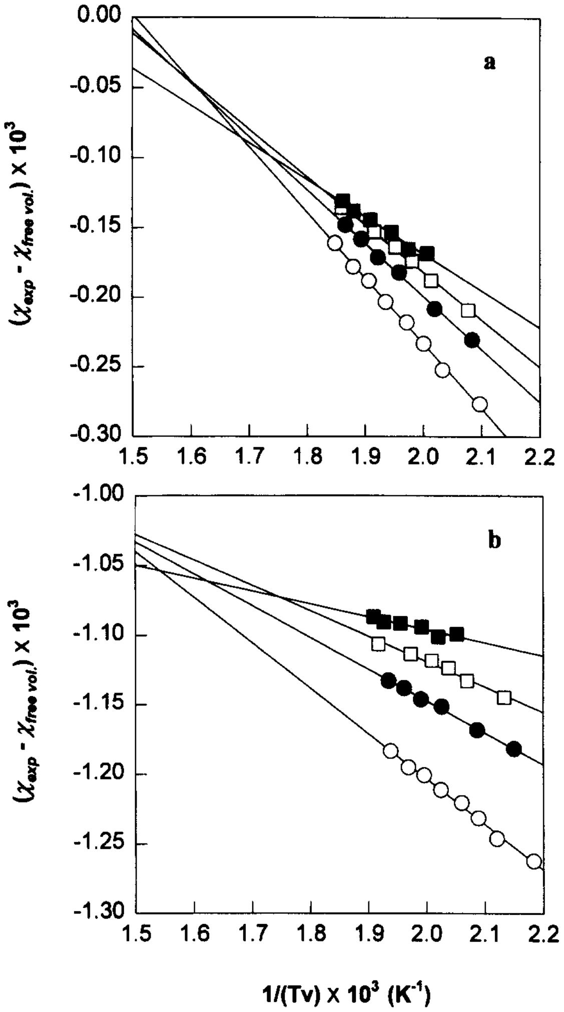

Figure 1 Plots of $\chi_{\text{exp}} - \chi_{\text{free vol.}}$ vs. $(T\tilde{\nu})^{-1}$ for (a) PS/PVME and (b) dPS/PVME blends: ○, 80; ●, 60; □, 50; ■, 40 vol% of dPS

Table 2 Contact interaction parameters and entropy interaction parameters for PS/PVME and dPS/PVME blends

Polymer blend	ϕ_{PS} or ϕ_{dPS}	X_{12} (J cm^{-3})	Q_{12} (J cm^{-3} K^{-1})
PS/PVME	0.8	−6.9	−0.010
	0.6	−5.9	−0.009
	0.5	−5.5	−0.008
	0.4	−4.4	−0.006
dPS/PVME	0.8	−4.8	0.008
	0.6	−3.6	0.011
	0.5	−2.9	0.012
	0.4	−1.6	0.015

The parameter Q_{12} is considered to represent the non-combinatorial entropy due to interaction between unlike segments. The Q_{12} has usually been treated as an adjustable parameter when there was a discrepancy

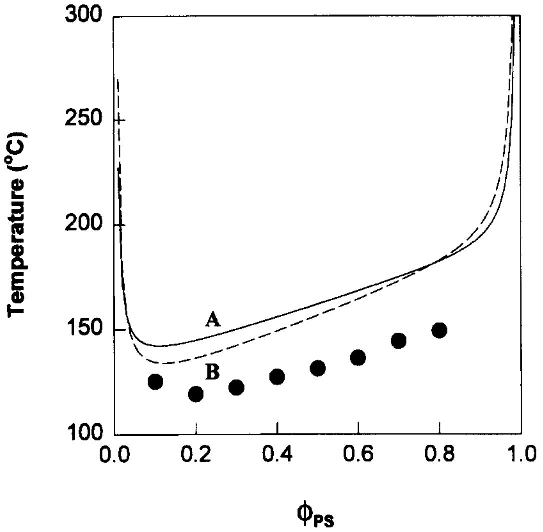

Figure 2 Simulated spinodal curves of PS/PVME blends: (A) $X_{12} = -6.9$, $Q_{12} = -0.01$; (B) $X_{12} = -4.4$, $Q_{12} = -0.006$

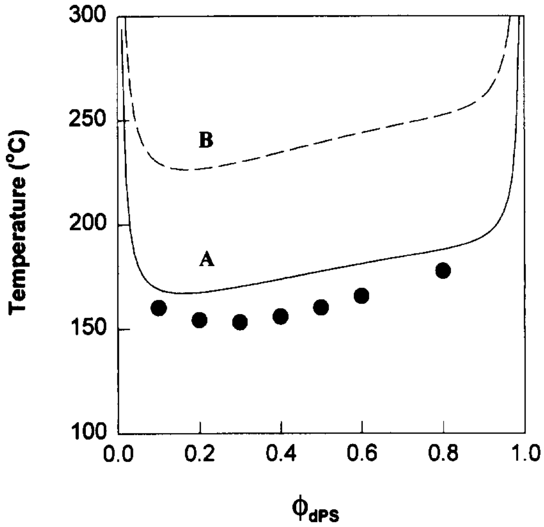

Figure 3 Simulated spinodal curves of dPS/PVME blends: (A) $X_{12} = -4.8$, $Q_{12} = 0.008$; (B) $X_{12} = -1.5$, $Q_{12} = 0.015$

between the theoretical curve and experimental data. In this study, however, the Q_{12} is not adjustable, since the Q_{12} was determined by following the scheme mentioned above.

Figures 2 and *3* are plots of simulated spinodal curves for PS/PVME blends and for dPS/PVME blends, respectively. Patterson[16] suggested that one can estimate the contribution of equation-of-state on the thermodynamic properties from the following equation:

$$\tau = 1 - \frac{T_1^*}{T_2^*} \qquad (23)$$

In equation (23), τ reflects the difference in free volume between the components. Thus, it is expected that the equation-of-state effect becomes more dominant as the value of τ increases. Since the value of τ for dPS/PVME blends ($\simeq 0.1$) is higher than that of PS/PVME blends ($\simeq 0.01$), the effect of equation-of-state for dPS/PVME blends is larger than that of PS/PVME blends. *Figure 2* shows a comparison of experimental data with simulation results of the spinodal when two sets of X_{12} and Q_{12} in *Table 2* were used. The experimental data in the figure were taken from the experimental work of Halary *et al.*[21] for PS/PVME blends. The discrepancy between the simulated sinodal curves and the experimental points was about 15–20°C, and the variation of spinodal line with change of X_{12} and Q_{12} was not large. In *Figure 3*, however, the spinodal line of dPS/PVME blends located at higher temperature than that of PS/PVME blends and varied dramatically with the change of interaction entropy parameters. Generally, the spinodal curve moves downward as the X_{12} value increases or the Q_{12} value decreases, since the overall interaction corresponding to $(X_{12} - TQ_{12}\tilde{v})$ becomes greater. For PS/PVME blends, the spinodal curve moves downward with increasing both the X_{12} and Q_{12}. This implies that the effect of X_{12} on the spinodal curve predominates over that of Q_{12}, which means that the contribution of equation-of-state on phase behaviour is not large in PS/PVME blends. However, the spinodal curve of dPS/PVME blends moves upward with increasing X_{12} and Q_{12}, implying that the effect of Q_{12} on the spinodal line is more dominant than that of X_{12}, which indicates that the substitution of deuterium for hydrogen affects the free volume of the blend system and thus the contribution of non-combinatorial entropy increases remarkably. Yang *et al.*[17] reported that the *LCST* of PS/PVME blends increased by approximately 40°C when the normal PS was replaced by the deuterated PS. The increase in *LCST* may arise from the change of free volume in the segmental region due to the substitution of deuterium for hydrogen. As shown in *Figure 3*, the spinodal curves, which were simulated by using the EOS interaction parameters estimated at higher composition of dPS, showed comparatively good agreement with the experimental observation. The positive value of Q_{12} for dPS blends means that dPS/PVME blends are more miscible than PS/PVME blends which have negative Q_{12} value.

It has been predicted that the *LCST* of dPS/PVME is higher than that of PS/PVME, although both systems have the same χ value. This is because the same χ value may yield different sets of X_{12} and Q_{12}. The different set of X_{12} and Q_{12} at a constant value of χ would give the different spinodal curve because the effects of X_{12} and Q_{12} on the spinodal curve are different from each other as mentioned above.

It seems that the substitution of deuterium increases the interaction with PVME and decreases the unfavourable equation-of-state term. However, the effect of the free volume change on the phase behaviour is more dominant than that of interaction. Therefore the substitution of deuterium shifts the miscibility boundary to a higher temperature region.

χ-*parameter analysis*

Figure 5 shows the simulated spinodal curves of dPS/PVME blends. When the values of $X_{12} = -4.5\,\mathrm{J\,cm^{-3}}$ and $Q_{12} = 0.008\,\mathrm{J\,cm^{-3}\,K^{-1}}$ were used, the spinodal curve showed the best-fit with experimental data. It is noteworthy that the small variation of Q_{12} gives a large change of *LCST*. This suggests that the free volume change due to the substitution of deuterium greatly affects the phase behaviour. On the other hand, the χ

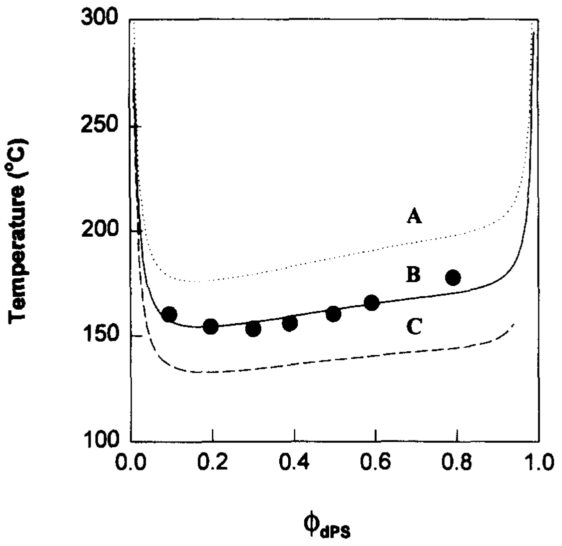

Figure 4 Simulated spinodal curves of dPS/PVME blends with X_{12} kept at $-4.5\,\mathrm{J\,cm^{-3}}$: (A) $Q_{12} = 0.009$; (B) $Q_{12} = 0.008$; (C) $Q_{12} = 0.007$

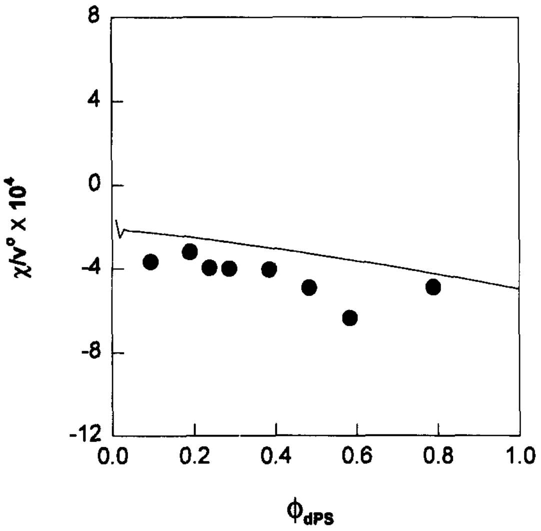

Figure 5 Interaction parameter χ as a function of composition for dPS/PVME blends. The solid line is calculated from equation (10) with $X_{12} = -4.5\,\mathrm{J\,cm^{-3}}$ and $Q_{12} = 0.008\,\mathrm{J\,cm^{-3}\,K^{-1}}$

parameters were calculated by equation (10) using the best-fit equation-of-state parameters. *Figure 5* shows a comparison of the calculated χ parameters with experimentally determined ones. The experimental χ values were determined at room temperature by means of the SANS technique[14]. The calculated values are in good agreement with the experimental χ values obtained from scattering measurements. The calculated values also predict the composition dependence of χ parameters.

CONCLUSIONS

The phase diagrams for dPS/PVME and PS/PVME blends were predicted by the equation-of-state theory with X_{12} and Q_{12} extracted from the Flory–Huggins interaction parameters which were measured by scattering experiment. In the case of dPS/PVME blends, the spinodal curve moves very sensitively with a small variation of Q_{12}. It was found that the non-combinatorial entropy affects the phase behaviour more dominantly than the interaction itself. The calculated χ parameters from the equation-of-state theory are in good agreement with experimental χ when the best-fit value of X_{12} and Q_{12} are used, and the composition dependence of χ could be properly predicted. Although the χ parameters of dPS/PVME and PS/PVME blends are the same, the substitution of deuterium for hydrogen affects the free volume change which causes a dramatic change of the phase boundary.

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