Liquid−Liquid Phase Equilibrium in Polymer−Solvent Systems: Correlation and Prediction of the Polymer Molecular Weight and the Pressure Effect

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A G^E model is used for the correlation and prediction of partial miscibility in polymer solutions that exhibit both upper critical solution temperature and lower critical solution temperature as well as hourglass-type phase separation in some cases. The model employs a combinatorial/free-volume term and the residual term of UNIQUAC, for which interaction parameters between the solvent molecule and the repeating unit (segment) of the polymer are determined. The obtained parameters are then used to predict the effect of the polymer molecular weight on the solvent/polymer partial miscibility. The model is also successfully applied in the prediction of the pressure effect on mutual solubility by incorporating it through the free volumes of the components. Finally the prediction of excess properties using the proposed model is investigated.

1. Introduction

Knowledge of phase equilibria in polymer solutions is essential for the design of various processes such as polymerization, devolatization, or drying. In particular, liquid−liquid equilibria (LLE) information is essential for polymerization processes where polymers are produced in one or two liquid phases and unreacted monomers, solvents, and additives must be separated.[1] In recent years extensive work is done in the correlation and prediction of LLE in polymer solutions. The proposed models can be classified in the following main categories:

(i) Modifications/extensions of the Flory−Huggins model (Koningsveld and Staverman,[2] Bae et al.,[3] and Enders and de Loos[4]).

(ii) Free-volume theories capable of describing the lower critical solution temperature (Flory[5] and Patterson and Delmas[6]).

(iii) Models based on the lattice-fluid theory (Sanchez and Lacombe,[7,8] Kleintjens and Koningsveld,[9] Panagiotou and Vera,[10] and High and Danner[11,12]).

(iv) Local composition models (Heil and Prausnitz,[13] Brandani,[14] Vera,[15] and Chen[16]).

(v) UNIFAC-based models that include the free-volume effects (Iwai et al.[17] and Kontogeorgis et al.[18]).

UNIFAC-based models have been shown to be quite successful in vapor−liquid equilibria (VLE) predictions in polymer/solvent systems[19−22] and, moreover, to be capable of predicting at least qualitatively all types of phase splits in polymer solutions.[18] In this study the free-volume/combinatorial term proposed by Elbro et al.[19] is combined with the UNIQUAC residual term[23] considering, however, interactions between the solvent molecule and the polymer segment (repeating unit). The proposed model, referred to as the free volume (FV)/UNIQUAC, can be thus used for prediction purposes. A similar approach was used by Bogdanic and the late

Vidal[24] for the prediction of the polymer molecular weight (MW) effect on partial miscibility for various polymer solutions, the majority of which exhibit only an upper critical solution temperature (UCST) or a lower critical solution temperature (LCST) phase split.

In the present study the FV/UNIQUAC model is applied to systems that exhibit both UCST and LCST as well as an hourglass phase split in some cases. It is also applied in the prediction of the pressure effect on LLE by incorporating pressure-dependent molar volumes for the solvent and the polymer.

2. The Model

The model employs the combinatorial term proposed by Elbro et al.[19] and the residual term of UNIQUAC.[23] The combinatorial expression is similar to the Flory−Huggins one, but free-volume fractions are used instead of volume fractions. Thus, both combinatorial and free-volume effects are included in a single combinatorial/FV term:

$$\ln \gamma_i^{\text{comb−fv}} = \ln \frac{\varphi_i^{\text{fv}}}{x_i} + 1 - \frac{\varphi_i^{\text{fv}}}{x_i} \qquad (1)$$

where x_i is the mole fraction of component i and φ_i^{fv} is the fraction of free volumes:

$$\varphi_i^{\text{fv}} = \frac{x_i V_i^{\text{fv}}}{\sum_i x_i V_i^{\text{fv}}} \qquad (2)$$

the free volume (V_i^{fv}), which is accessible to other molecules volume, is assumed to be equal to

$$V_i^{\text{fv}} = V_i - V_i^{\text{w}} \qquad (3)$$

where V_i is the molar volume of component i and V_i^{w} is the van der Waals volume as calculated by the method of Bondi.[25]

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Note that eq 1 allows for variation of the activity coefficients with pressure by introducing in eq 3 the variation of the molar volumes with pressure. This, of course, implies the existence of an excess volume of mixing and requires relaxation of the assumption of V^E = 0 made by Elbro et al.[19] in the theoretical development of eq 1.

For the application of the model, every system was assumed to be a mixture of two groups: the solvent molecule and the polymer repeating unit. The systems examined in this study exhibit both UCST and LCST and in some cases hourglass phase split too, and hence the temperature range of the experimental data is very wide, more than 150 K in most cases. For this reason linearly temperature-dependent solvent/segment interaction parameters of the following form were calculated:

$$\alpha_{mn} = \alpha_{mn}^0 + \alpha_{mn}^1 (T - 298.15) \tag{4}$$

For the estimation of the parameters, the following objective function (OF) was minimized:

$$OF = \sum_{n\,\exp} \sum_i [\ln(x_i^I \gamma_i^I) - \ln(x_i^{II} \gamma_i^{II})] \tag{5}$$

where x_i^I and x_i^{II} are respectively the mole fractions of component i in the liquid phases I and II and γ_i^I and γ_i^{II} are the corresponding activity coefficients.

Logarithms were used because the polymer and solvent activity coefficients differ by several orders of magnitude.

3. Estimation of the Molar Volumes of the Components

The combinatorial term of Elbro et al.[19] used in this study is very sensitive to the accuracy of the molar volumes used for the components. This was demonstrated in a previous study on VLE prediction in polymer solutions,[22] where it was shown that an error introduced to the molar volume of one of the components leads to a double or even triple error in the calculated activity coefficient. It is, thus, necessary to use accurate volumes for both polymer and solvent with respect to temperature and pressure in order to make a reliable evaluation of the performance of the model.

In this study, polymer molar volumes were obtained by using the T- and P-dependent Tait correlation with the parameters available in the publication by Rodgers.[26] To account for the pressure effect on solvent molar volumes, modifications of the Peng–Robinson (PR) equation of state (EoS) were used. For the nonpolar solvents (e.g., methylcyclohexane), the so-called t–mPR EoS[27] was used (see Appendix 1), while for polar solvents, for which t–mPR gives poor saturated liquid volume predictions, the a, b, and m parameters of the PR EoS were fitted to vapor pressures and saturated liquid molar volume experimental data taken from DIPPR as proposed by Kontogeorgis et al.[28] The obtained a, b, and m parameters of the EoS are presented in Table 1.

4. Pressure Effect on LLE in Polymer Solutions

The effect of pressure on the miscibility in liquid mixtures is associated with the volume change on mixing (or the excess volume of mixing, V^E) at fixed

Table 1. PR Parameters for the Polar Solvents

solvent	T range (K)	a (bar·L²/mol)	b (L/mol)	m	ΔP^a (%)	ΔV^b (%)
acetone	254−468	15.9136	0.0619	0.7715	0.39	0.96
diethyl ether	210−350	18.6056	0.0836	0.8625	1.79	0.41
tert-butyl acetate	240−447	29.9782	0.1148	0.9269	0.69	0.77
ethyl formate	229−452^c	16.6131	0.1067	0.8036	0.79	0.85

^{a} ΔP % is the average absolute percent deviation in vapor pressure ΔP % = average$|(P^{s,calc} - P^{s,exp})/P^{s,exp}| \times 100$. ^{b} ΔV % is the average absolute percent deviation in saturated liquid molar volumes ΔV % = average$|(V^{calc} - V^{exp})/V^{exp}| \times 100$. ^{c} Parameters for t-PR EoS.

temperature and composition. If V^E is positive, then the solubility decreases with increasing pressure, while for negative V^E, the solubility increases with increasing pressure.[29]

The UCST phase separation is mainly connected with differences in intermolecular forces between the solvent and the polymer. Experimentally it has been found that pressure may lower or raise the UCST, corresponding to negative and positive values of V^E.[30] A parabolic-like pressure dependence of the UCST with a minimum is also reported for a few polymer solutions.[31,32] On the other hand, the LCST is mainly attributed to the differences in the free volumes of the polymer and the solvent[33] or, in other words, to the fact that the solvent is more expanded than the polymer especially as the critical temperature of the solvent is approached. The polymer is less compressible than the solvent, and hence raising the pressure decreases the free-volume difference and lowers the tendency toward partial miscibility at constant temperature, thus raising the LCST.[30,34] As experiments show, the pressure effect is more pronounced on the LCST than on the UCST. There are, however, systems where the LCST phase separation is due to strong interactions between the solvent and the polymer molecules like hydrogen bonding,[35] such as, for example, the system poly(ethylene glycol) (PEG)/water for which the LCST is almost constant for 1−50 atm.[36]

4.1. Results of the Pressure Effect on LLE. The systems examined in this study, the type of phase separation they exhibit, and the temperature range of the available experimental data are listed in Table 2. The polymer polydispersity index (M_w/M_n) is also listed in the same table. As shown, all data used correspond to practically monodispersed polymers, thus avoiding to incorporate the polydispersity effect in the model. The EoS used for the calculation of the solvent molar volume for each system and the obtained solvent/segment interaction parameters are shown in Table 3. For these systems the model yields negative excess volumes, and consequently it predicts increasing miscibility with pressure.

System PS(20400)/Acetone (Where PS = Polystyrene). Though this system is partially miscible for all temperatures at atmospheric pressure (hourglass behavior), raising the pressure results in the appearance of a complete miscibility region at intermediate temperatures (UCST and LCST behavior). Experimental data at atmospheric pressure were used to calculate the necessary interaction parameters, and then predictions were made for higher pressures. Results are presented in Figure 1. A very satisfactory correlation is obtained and, moreover, the pressure effect predictions are remarkably accurate, with deviations of less than 5 K for the UCST and LCST even at the highest pressure of 100 bar.

Table 2. Experimental LLE Data for Polymer/Solvent Systems at Various Pressures

system	M_w/M_n	pressure (bar)	LLE type	T range (K)	data used for
PS(20400)/acetone[30]	<1.06	0	hourglass	284.2−413.3	correlation
		20	UCST, LCST	288.1−407.7	prediction
		50	UCST, LCST	283.4−427.8	prediction
		100	UCST, LCST	276.1−455.0	prediction
PS(20400)/diethyl ether[37]	<1.06	0	UCST, LCST	226.2−317.2	correlation
		10	UCST, LCST	224.5−323.5	prediction
		20	UCST, LCST	223.1−329.7	prediction
		30	UCST, LCST	220.8−335.5	prediction
		40	UCST, LCST	219.4−341.9	prediction
PS(17500)/methyl cyclohexane [31]	<1.06	1	only UCST available	296.7−297.7	correlation
		100	only UCST available	295.0−296.0	prediction
		200	only UCST available	294.0−294.9	prediction
		400	only UCST available	293.2−294.0	prediction
		700	only UCST available	293.5−294.1	-
		800	only UCST available	293.7−294.4	-

Table 3. Solvent (1)/Segment (2) Interaction Parameters for the FV/UNIQUAC Model

system	solvent molar volumes from	a_{12}^0 (K)	a_{12}^1	a_{21}^0 (K)	a_{21}^1
PS(20400)/acetone	PR[a]	−73.222	−0.1186	202.897	−0.1034
PS(20400)/diethyl ether	PR[a]	−87.600	−0.3817	173.225	0.6105
PS(17500)/methylcyclohexane	$t-m$PR	−74.995	−3.0862	153.785	4.9753
		−66.648[b]	−1.1454[b]	137.397[b]	0.9001[b]

[a] With fitted a, b, and m (Table 1). [b] Correlation of all data together.
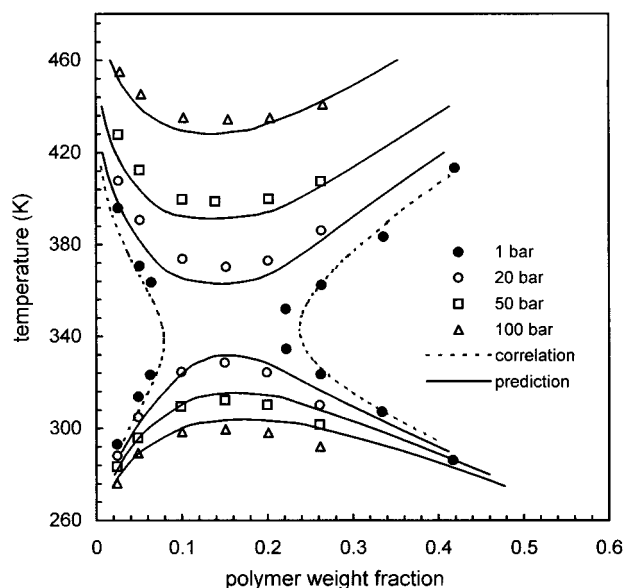
Figure 1. Correlation and prediction results of the pressure effect on LLE for the system PS(20400)/acetone.
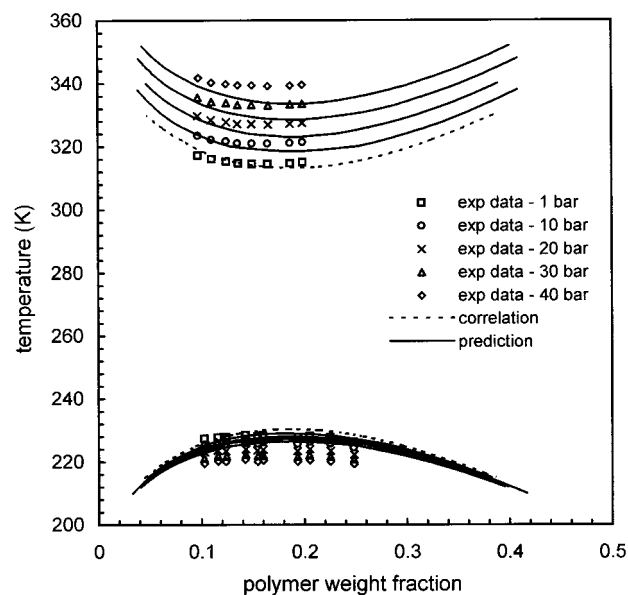
Figure 2. Correlation and prediction results of the pressure effect on LLE for the system PS(20400)/diethyl ether.

System PS(20400)/Diethyl Ether. Correlation and prediction results are shown in Figure 2. Also for this system, a very good correlation is obtained at atmospheric pressure. The model correctly predicts the stronger effect of pressure on the LCST than on the UCST, though in both cases this effect is slightly underestimated, at most by 5 K.

System PS(17500)/Methylcyclohexane. Vanhee et al.[31] reported UCST data for the system PS(17500)/methylcyclohexane as a function of pressure. They found a minimum in the cloud-point isopleth, close to 500 bar, which indicates that increasing the pressure up to 500 bar favors the miscibility while a further increase reduces the miscibility. In this study we correlated the experimental data for atmospheric pressure and predicted the pressure effect for pressures up to 400 bar (Figure 3) again with very satisfactory results. The model overpredicts the pressure effect by about 2 K at

the highest pressure of 400 bar, but this is mainly due to the narrow temperature range of the data used for correlation (approximately 1 K) which results in a strong, and consequently very sensitive to the data used, dependency of the interaction parameters on temperature. This is supported by the results presented in Figure 4, where it is shown that the model can correlate with a very good accuracy the data for all pressures, up to 400 bar, together. For higher pressures, the model cannot predict the unfavorable effect of pressure on the miscibility.

4.2. Prediction of the Pressure Effect with an EoS. Harismiadis et al.[38] have shown that the van der Waals (vdW) EoS with the vdW one-fluid mixing rules coupled with the Berthelot combining rule for the cross energy parameter and the arithmetic mean for the cross covolume parameter cannot predict the pressure effect on the UCST in polymer solutions. Kalospiros and
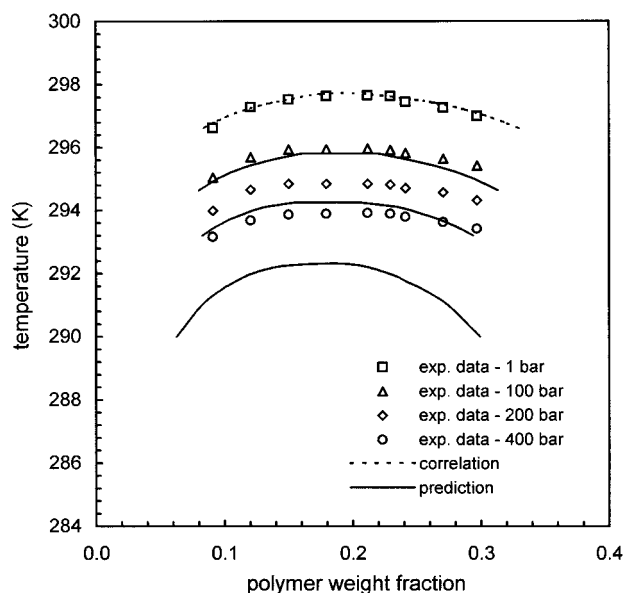
Figure 3. Correlation and prediction results of the pressure effect on LLE for the system PS(17500)/methylcyclohexane.
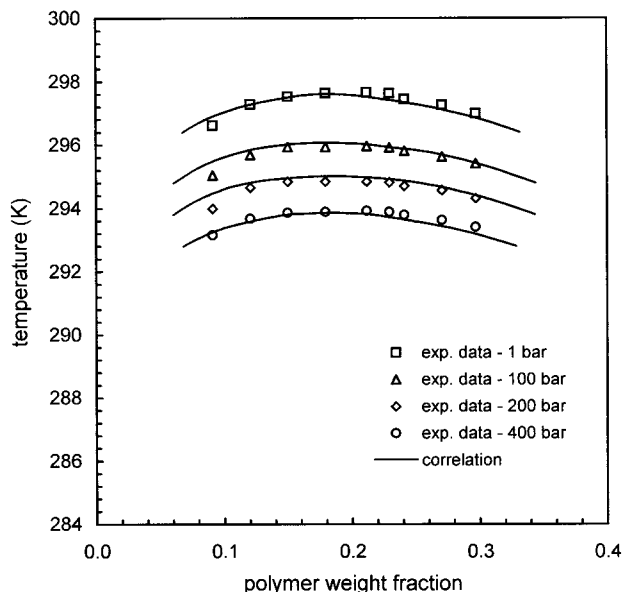

Figure 4. Correlation of all sets of experimental LLE data for the system PS(17500)/methylcyclohexane.

Tassios[39] have developed an EoS/G^E model that incorporates the pressure effect on the vapor- and liquid-phase fugacities. The model was derived by equating the excess Gibbs free energy obtained by a free volume/UNIFAC model (Entropic-FV[20]) with that obtained by the t−mPR EoS at zero pressure. The EoS was appropriately modified to describe the volumetric behavior of the pure polymer. Application of the derived EoS/G^E model to several polymer solutions provided excellent correlation and satisfactory VLE prediction.

This EoS/G^E model was applied here in the prediction of the pressure effect on LLE for the system PS(20400)/diethyl ether for comparison purposes. Results are presented in Figure 5. As shown, the correlation for atmospheric pressure is excellent. However, the model fails to predict the solubility decrease with increasing pressure for the UCST and, moreover, though it gives the correct trend for the LCST, a negligible pressure effect is predicted.
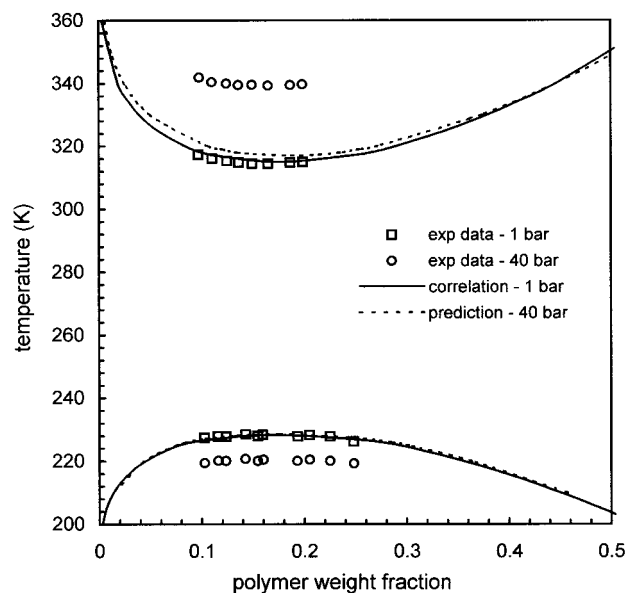

Figure 5. Performance of the EoS/G^E model proposed by Kalospiros and Tassios[39] in the prediction of the pressure effect on LLE for the system PS(20400)/diethyl ether.

5. Polymer MW Effect on LLE

In polymer solutions the tendency toward limited miscibility rises with the polymer MW. Thus, with an increase of the polymer MW, the UCST is raised and the LCST is lowered, shrinking the temperature region of complete miscibility. In some systems the UCST and LCST limited-miscibility regions merge to give an hourglass shape.

In this study we have used the FV/UNIQUAC model to predict the effect of the polymer MW on LLE. Considering the aforementioned effect of pressure on LLE, especially for LCST, all calculations were carried out assuming that the system is under the solvent vapor pressure.

The systems examined and the type of LLE they exhibit are shown in Table 4, while the obtained segment/solvent interaction parameters are listed in Table 5. For all PS systems examined, the polymer is practically monodispersed, while for poly(butadiene) (PBD), only M_v was available in the corresponding data source. In each case, we have selected for correlation the MW for which enough data were available. However, this choice has no impact on the quality of the prediction.

PS/Ethyl Formate. Using MW = 37 000 for the correlation, satisfactory predictions are obtained for both high and lower MWs as shown in Figure 6a. For comparison purposes, results using P = 1 atm are presented in Figure 6b. Notice the improvement obtained by incorporating the pressure effect which is more pronounced, as expected, at the higher solvent reduced temperatures (T_r).

PS/Methycyclohexane. For this system, increasing the polymer MW raises the UCST and lowers LCST up to limiting values, so that no hourglass shape immiscibility region is observed for very high polymer MWs. As is demonstrated in Figure 7a,b, excellent correlation is obtained for MW = 400 000, while the predictions for the rest of the MWs are also are very satisfactory, with UCST and LCST deviations of about 5 K for the lowest MW.

Table 4. Experimental LLE Data for Polymer/Solvent Systems for Various Polymer MWs

system	M_w	M_w/M_n	LLE type	T range (K)	data used for
PS/ethyl formate[40]	4000	<1.10	UCST, LCST	242.7−483.0	prediction
	10 000	<1.06	UCST, LCST	272.0−452.6	prediction
	20 000	<1.06	UCST, LCST	293.3−432.1	prediction
	37 000	<1.06	UCST, LCST	308.4−416.9	correlation
	97 000	<1.06	hourglass	333.9−413.8	prediction
PS/methylcyclohexane[41]	37 000	<1.06	UCST, LCST	307.0−520.1	prediction
	97 200	<1.06	UCST, LCST	321.1−507.4	prediction
	200 000	<1.06	UCST, LCST	326.6−501.0	prediction
	400 000	<1.06	UCST, LCST	331.4−495.8	correlation
	670 000	<1.10	UCST, LCST	333.9−493.1	prediction
PBD/2,2,4-trimethylpentane[42]	44 500	M_v	UCST, LCST	302.3−448.6	prediction
	65 000	M_v	UCST, LCST	316.3−424.9	prediction
	104 000	M_v	UCST, LCST	321.9−407.9	correlation
	135 000	M_v	hourglass	300.7−435.0	prediction
PS/*tert*-butyl acetate[43]	100 000	<1.06	UCST, LCST	240.6−438.7	prediction
	233 000	<1.06	UCST, LCST	260.3−413.1	prediction
	600 000	<1.10	UCST, LCST	270.5−398.1	correlation
PS/acetone[44]	4800	<1.06	UCST, LCST	210.5−471.2	prediction
	10 300	<1.06	UCST, LCST	256.5−427.9	prediction
	19 800	<1.06	hourglass	298.3−394.1	prediction

Table 5. Solvent (1)/Segment (2) Interaction Parameters for the FV/UNIQUAC Model

system	solvent molar volumes from	incorporation of the pressure effect	a_{12}^0 (K)	a_{12}^1	a_{21}^0 (K)	a_{21}^1
PS/ethyl formate	t-PR^a	no	−67.038	0.4270	180.315	0.4398
		yes	−65.955	−0.5251	177.664	0.6794
PS/methylcyclohexane	t−mPR	yes	−82.370	−0.3768	171.327	0.3873
PBD/2,2,4-trimethylpentane	t−mPR	yes	−74.666	−0.3634	127.642	0.4812
PS/*tert*-butyl acetate	PR^a	no	−65.128	−0.3149	122.799	0.4221

^{a} With fitted a, b, and m (Table 1).

PBD/2,2,4-Trimethylpentane. As shown in Figure 8, satisfactory correlation and predictions are obtained. Regarding the largest MW, the model predicts qualitatively the hourglass partial miscibility region: it gives excellent results in the solvent-rich phase but lower polymer concentrations in the polymer-rich phase.

PS/*tert*-Butyl Acetate. The results shown in Figure 9 correspond to correlation for the higher MW and prediction for the lower two. The MW effect for the lower MW is underestimated by about 10 K for the UCST and 15 K for the LCST.

PS/Acetone. Prediction results presented in Figure 10 were obtained with interaction parameters estimated from the correlation for PS(20400)/acetone at 1 bar (Table 3 and Figure 1). The performance of the model is quite satisfactory with the exception of the UCST for the lowest MW.

6. Excess Properties Predicted with the FV/UNIQUAC Model

6.1. Variation of the Activity Coefficients with Concentration. The thermodynamic condition for phase instability of a binary liquid mixture is given by the expression

$$\left(\frac{\partial^2 \Delta G^{mix}}{\partial x_i^2}\right)_{T,P} < 0 \qquad (6)$$

where ΔG^{mix} is the Gibbs energy change of mixing and x_i is the concentration of component i on a mole fraction basis.

For a binary mixture, eq 6 leads, after application of some simple algebra, to the following expression for the variation of the activity coefficient with concentration:

$$\left(\frac{\partial \ln \gamma_i}{\partial x_i}\right)_{T,P} < -\frac{1}{x_i} \qquad i = 1, 2 \qquad (7)$$

Equation 7 indicates that a necessary condition for phase instability is that $\ln \gamma_i$ should decrease with increasing concentration. Polymer activity coefficients calculated by the FV/UNIQUAC model, especially at the polymer dilute region, are much lower than unity, i.e., their logarithms are negative, and taking into account that for $x_{pol} = 1$ $\ln \gamma_{pol} = 0$, it follows that for partial miscibility the polymer activity coefficient exhibits a minimum with concentration. Of course, the solvent activity coefficient exhibits a maximum at the same concentration. The existence of these extremes is a necessary but not sufficient criterion for phase split, and consequently they may also be present in completely miscible polymer/solvent systems. An example is presented in Figure 11a,b for the system PS(10300)/acetone, where the predicted logarithms of the polymer and the solvent activity coefficient respectively are plotted vs polymer concentration for three temperatures: one lower than the UCST, one higher than the LCST, and one that corresponds to the intermediate complete miscibility region. As shown, the behavior is similar for all three cases; i.e., all three plots exhibit minima.

Polymer solutions are not the only systems where such an unusual behavior is observed. Shealy and Sandler[46] demonstrated that in aqueous solutions of polar nonelectrolytes (like butanol, ethyl acetate, etc.) ordering (clustering) of solute molecules leads to extremes in the dependency of the activity coefficients on concentration: a maximum for the solute and a minimum for the solvent (water). In polymer solutions we
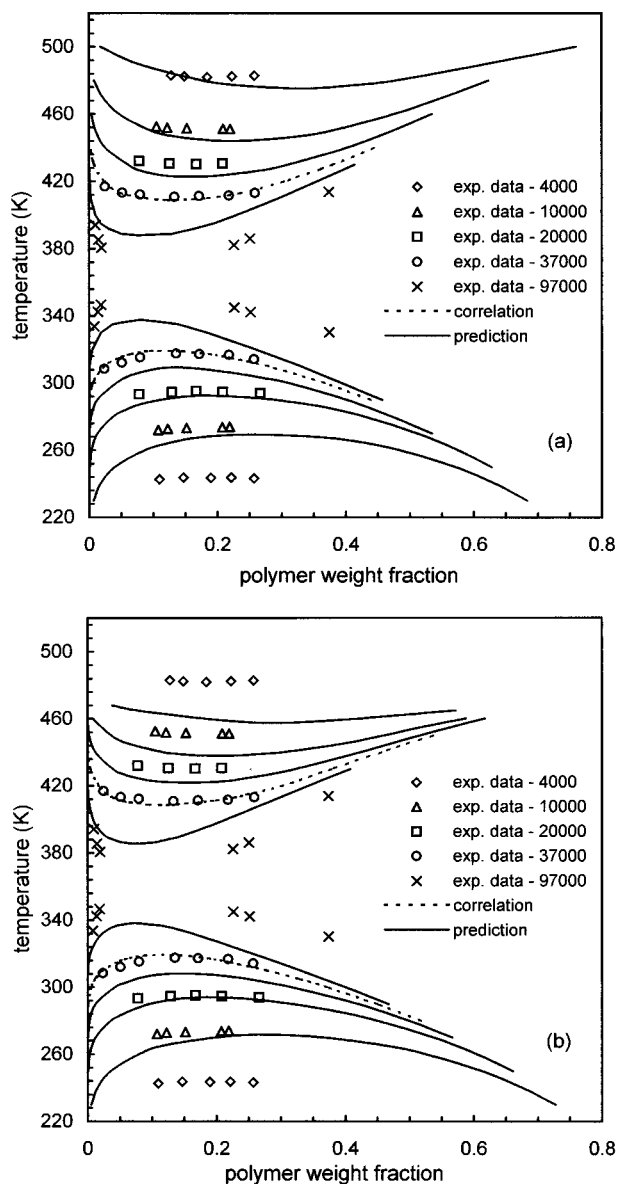
Figure 6. Correlation and prediction results of the MW effect on LLE for the system PS/ethyl formate assuming that experimental pressure equals (a) the solvent vapor pressure at high temperatures and (b) 1 bar for all temperatures. The numbers in the caption denote polymer MW.

Figure 7. Correlation and prediction results of the MW effect on LLE for the system PS/methylcyclohexane: (a) LCST; (b) UCST. The numbers in the caption denote polymer MW.

have the opposite case: solvent ordering around polymer molecules as demonstrated by the combinatorial model of Saeki[47] supported by the entropy of mixing data of Eisinger and Flory.[48−50] Thus, in this case, we have a maximum for the solvent and a minimum for the polymer.

6.2. Variation of the Activity Coefficients with Temperature. Close inspection of Figure 11a,b suggests that the polymer and solvent activity coefficients exhibit extremes with temperature at constant composition. This should, of course, be expected from a model that successfully captures simultaneously UCST and LCST. Thus, in the UCST region where polymer solubility increases with temperature, the corresponding activity coefficients should decrease, while in the LCST region where polymer solubility decreases with temperature, the corresponding activity coefficients should increase and, consequently, the activity coefficients should present a minimum with temperature. This is clearly shown in Figure 12 for the PS(10300)/acetone
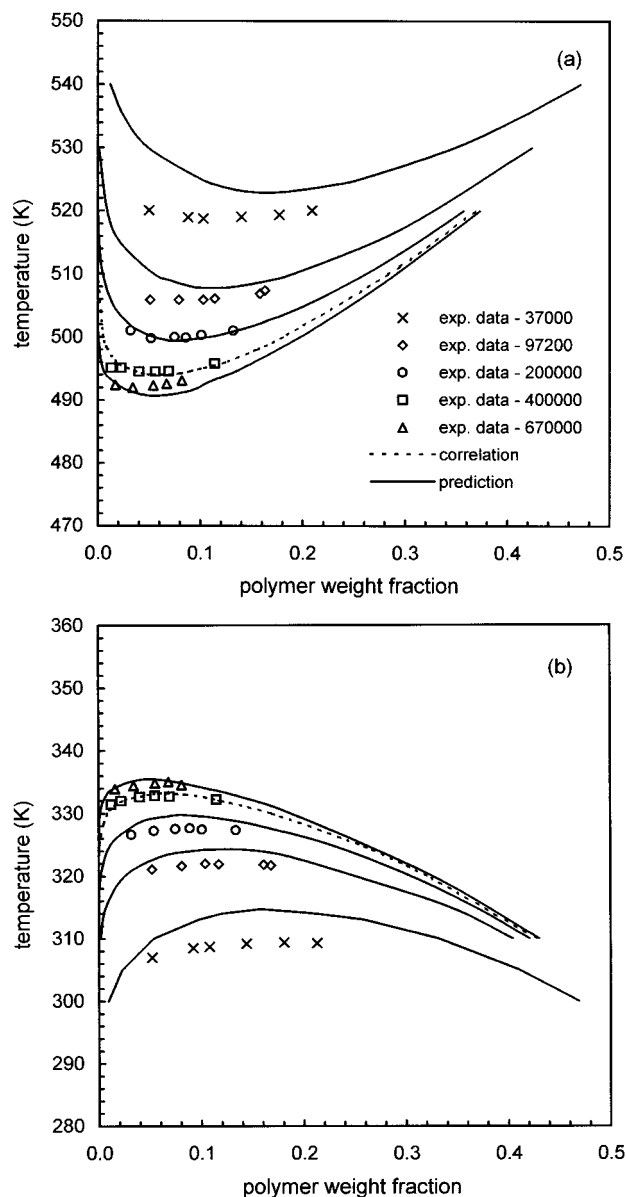
mixture for three different polymer compositions, and similar behavior is observed for the solvent activity coefficients.

6.3. Prediction of Excess Molar Volumes. As mentioned in section 4, if V^E at fixed temperature and composition is positive, then the solubility decreases with pressure and the opposite holds for negative V^E. It is expected that the FV/UNIQUAC model, which successfully predicts the effect of pressure on solubility in polymer/solvent systems (section 4.1) should give, at least, the correct sign for the V^E of the mixture. An example is shown in Figure 13a for the PS/diethyl ether system. It must be noted that although for the derivation of the combinatorial term of Elbro et al.[19] the additive mixing rule for the mixture volume was assumed, i.e., $V = \sum x_i V_i$ or $V^E = 0$, the incorporation of the pressure effect on volume gives excess molar volumes different than zero.

Figure 13b presents V^E predictions for the PS/diethyl ether system with the EoS/G^E model presented in section 4.2. The failure of the EoS/G^E model to predict
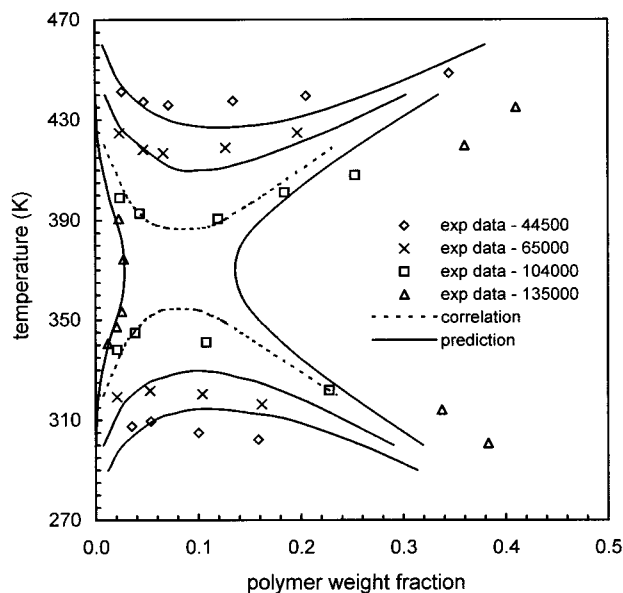
Figure 8. Correlation and prediction results of the MW effect on LLE for the system PBD/2,2,4-trimethylpentane. The numbers in the caption denote polymer MW.
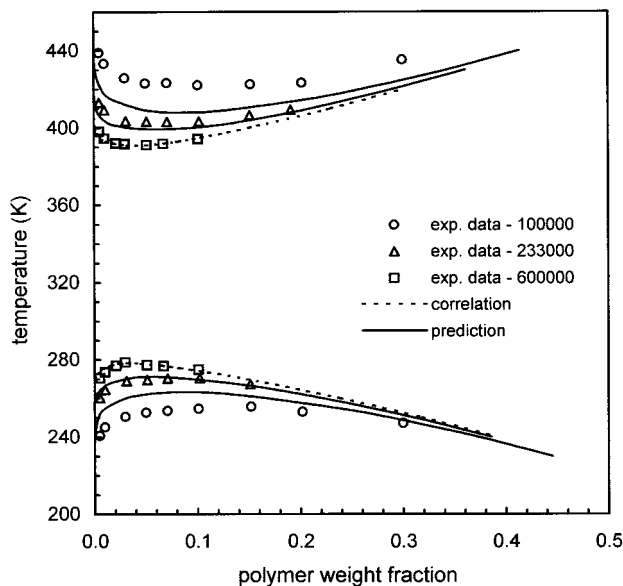

Figure 10. Prediction results of the MW effect on LLE for the system PS/acetone. The numbers in the caption denote polymer MW.

Figure 9. Correlation and prediction results of the MW effect on LLE for the system PS/*tert*-butyl acetate: (a) LCST; (b) UCST. The numbers in the caption denote polymer MW.

correctly the effect of pressure on solubility (Figure 5) is attributed to the wrong prediction of the V^E sign.

In a strict sense the obtained V^E could be incorporated in the volume of the mixture in order to obtain a new value for V^E until convergence is reached. This leads to small changes in V^E, which is in agreement with the observations of Elbro et al.[19] that inclusion of V^E in eq 1 has a negligible effect on the obtained results.

6.4. Enthalpic and Entropic Contributions. Liquid–liquid phase separation in polymer/solvent systems occurs through a competition between the enthalpy and the entropy of mixing.

At low temperatures with an UCST, enthalpic effects arising from attractive forces are more important than the entropic ones, while at high temperatures with an LCST, where attractive forces weaken, entropic effects arising from increased free-volume differences predominate. This is supported by the results of Figure 14,
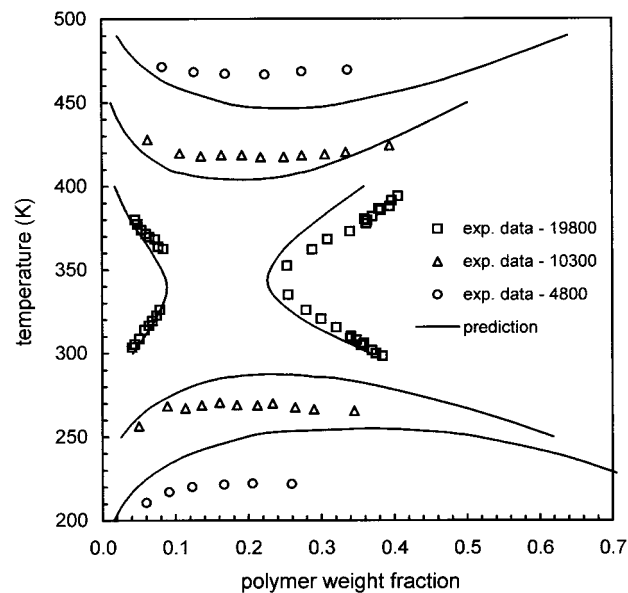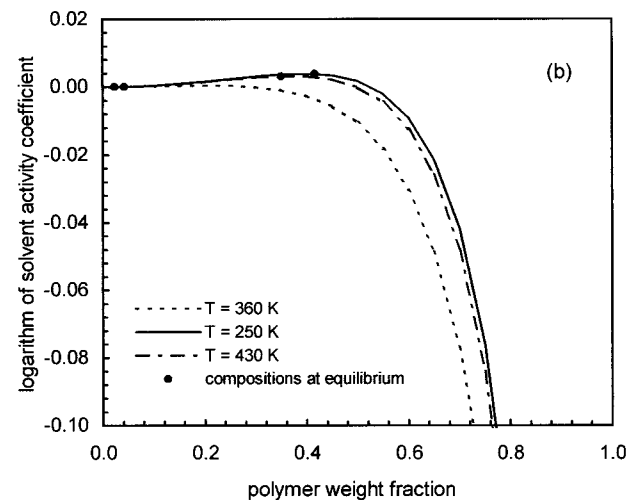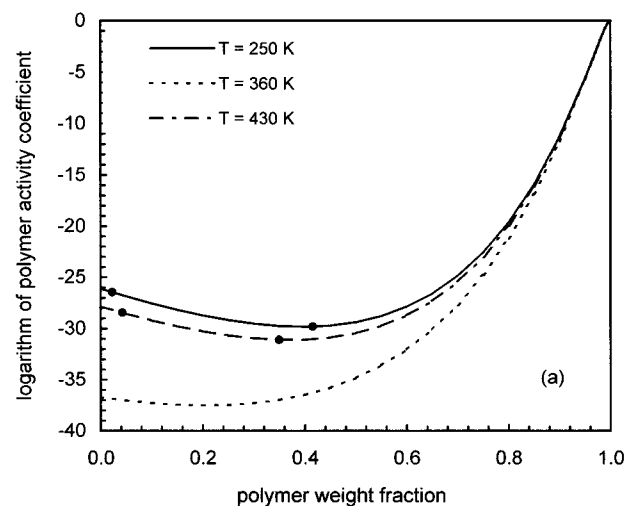

Figure 11. Variation of (a) the polymer and (b) the solvent activity coefficients with composition for PS(10300)/acetone. Interaction parameters: $a_{12}^0 = 127.205$ K, $a_{12}^1 = 0.121\ 08$, $a_{21}^0 = -41.05$ K, $a_{21}^1 = -0.159$.
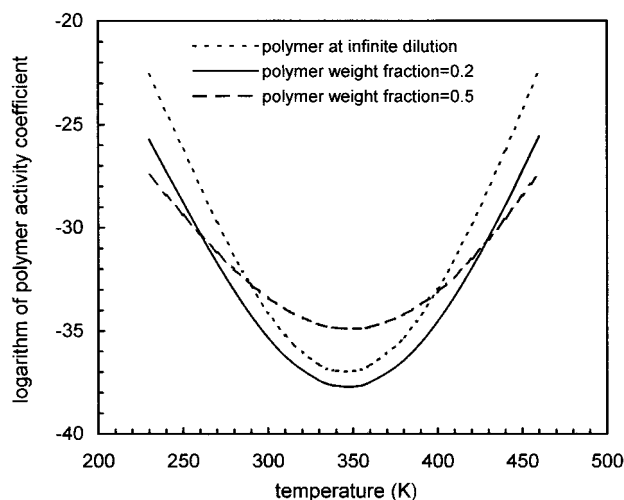
Figure 12. Variation of the polymer activity with temperature for PS(10300)/acetone. Interaction parameters: $a_{12}^0 = 127.205$ K, $a_{12}^1 = 0.121\ 08$, $a_{21}^0 = -41.05$ K, $a_{21}^1 = -0.159$.
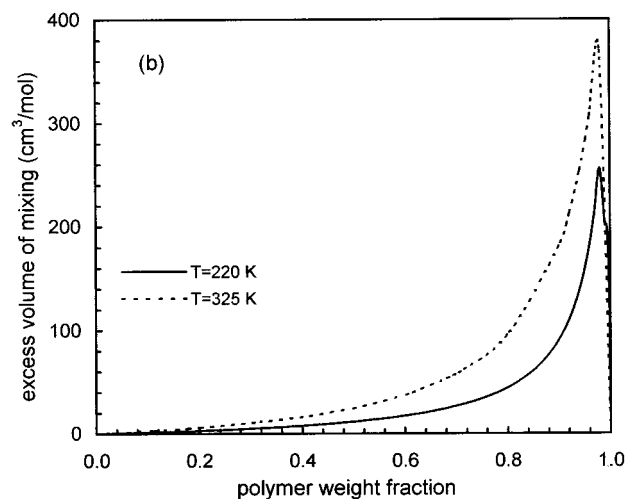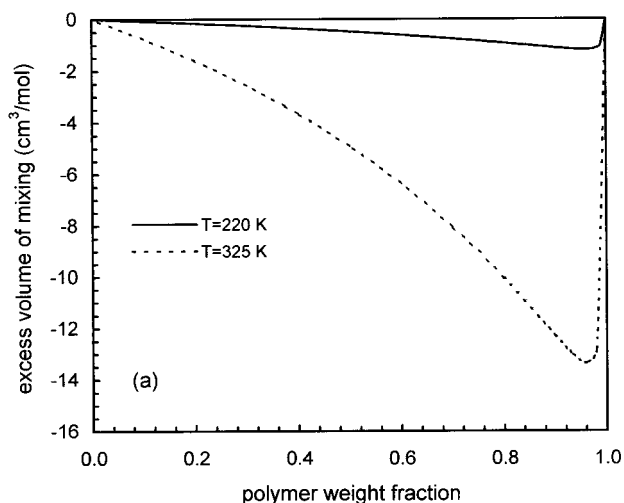

Figure 14. Variation of the excess enthalpy, excess entropy, and excess Gibbs free energy with temperature as predicted with the FV/UNIQUAC model for PS(10300)/acetone. Interaction parameters: $a_{12}^0 = 127.205$ K, $a_{12}^1 = 0.121\ 08$, $a_{21}^0 = -41.05$ K, $a_{21}^1 = -0.159$.

Figure 13. Excess molar volumes of the mixture for PS(10300)/diethyl ether with (a) the FV/UNIQUAC model and (b) the EoS/G^E model of Kalospiros and Tassios.[39]

Figure 15. Contribution of the combinatorial/free volume and the residual part to the excess enthalpy of the mixture as predicted with the FV/UNIQUAC model for PS(10300)/acetone. Interaction parameters: $a_{12}^0 = 127.205$ K, $a_{12}^1 = 0.12108$, $a_{21}^0 = -41.05$ K, $a_{21}^1 = -0.159$.

which presents the variation of H^E, S^E, and the resulting G^E with temperature predicted by the FV/UNIQUAC model for the PS(10300)/acetone system. It is shown that at low temperatures the liquid–liquid phase separ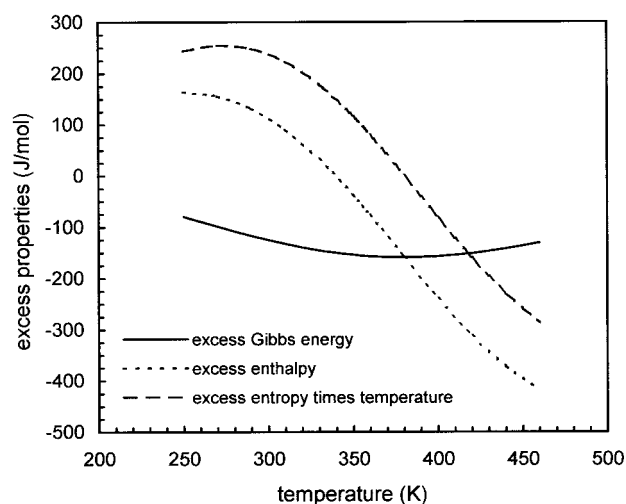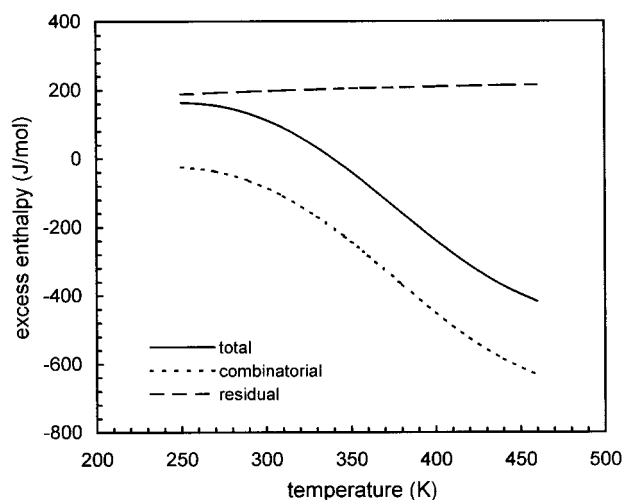ation is not favored by the positive S^E values and the phenomenon is motivated by the positive H^E values. On the other hand, at high temperatures H^E becomes negative and the phenomenon is motivated by the negative S^E values.

An interesting feature of the FV/UNIQUAC model is that, unlike the classical UNIFAC models, its combinatorial/free-volume part (eq 1) predicts a contribution to H^E because it involves the temperature effect on volume. Furthermore, this contribution is very significant, as suggested by the results of Figure 15 for the PS(10300)/acetone system. In the absence of combined G^E and H^E data for polymer/solvent systems, we decided to apply the model in the prediction of H^E data calculated through molecular simulation[45] for mixtures containing a monomer and its 20-mer. These mixtures are assumed as nearly athermal and, consequently, only the combinatorial/free-volume term of the model has been considered. Calculations have been performed considering that the monomer corresponds to n-hexane and the 20-mer to n-C_{134}, so that the ratio of their van der Waals volumes is equal to 20, which is a reasonable assump-
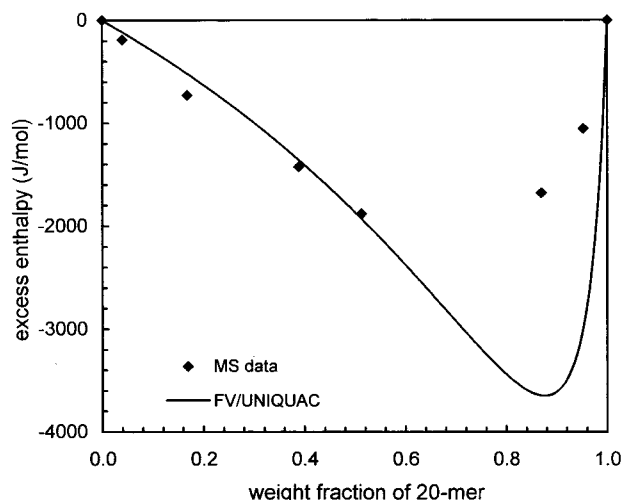
Figure 16. Prediction of the excess enthalpy of a monomer/20-mer mixture with the free-volume/combinatorial term of the FV/UNIQUAC model in comparison with data calculated with molecular simulation.[45]

tion.[51] The results are presented in Figure 16 and indicate that satisfactory H^E values are predicted by the combinatorial/free-volume term of the FV/UNIQUAC model. It must be noted that application of the classical UNIFAC models gives zero H^E for these types of systems.

7. Conclusions

A FV/UNIQUAC model with solvent/polymer segment interaction parameters is applied in the correlation/prediction of the polymer molecular weight and pressure effect on the LLE in polymer/solvent mixtures. The model accounts for the pressure effect on LLE because it incorporates pressure-dependent molar volumes in the free-volume term.

Successful predictions are obtained for pressures up to 400 bar using interaction parameters evaluated at atmospheric pressure. Prediction of the molecular weight effect on polymer/solvent LLE, by using interaction parameters evaluated for one molecular weight, yields satisfactory results. Incorporation of the pressure effect in this case becomes important when the change in the polymer MW shifts the two-phase region to temperatures near the critical point of the solvent.

Finally the prediction of the excess properties in polymer/solvent mixtures with the proposed model is investigated. It is found that the model correctly predicts the extrema in the activity coefficients of both polymer and solvent, which are required by LLE thermodynamics. An explanation for this behavior is given through solvent clustering around the polymer molecules. The model also provides a reasonable prediction of excess properties (enthalpy and entropy) including a surprisingly large contribution from the free-volume term.

Appendix: $t-m$PR EoS

$$P = \frac{RT}{V + t - b} - \frac{a}{(V + t)^2 + 2b(V + t) - b^2}$$

$$a = 0.457235\frac{(RT_c)^2}{P_c}\alpha(T_R)$$

$$b = 0.077796\frac{RT_c}{P_c}$$

$$\alpha(T_R) = [1 + m(1 - \sqrt{T_r})]^2$$

$$t = t_0 + (t_c - t_0)\exp(\beta|1 - \sqrt{T_r}|)$$

Expressions for parameters m, t_0, β, and t_c as functions of ω are given by Magoulas and Tassios (1990).[27]

$$m = 0.384401 + 1.52276\omega - 0.213808\omega^2 + 0.03461\omega^3 - 0.001976\omega^4$$

$$t_0 = \frac{RT_c}{P_c}(-0.014471 + 0.067498\omega - 0.084852\omega^2 + 0.067298\omega^3 - 0.017366\omega^4)$$

$$\beta = -10.2447 - 28.6312\omega$$

$$t_c = \frac{RT_c}{P_c}(0.3074 - z_c),$$

$$\text{with } z_c = 0.289 - 0.0701\omega - 0.0207\omega^2$$

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