ELSEVIER

Polymer 43 (2002) 6627–6634

polymer

www.elsevier.com/locate/polymer

Vapor–liquid equilibria and liquid–liquid equilibria calculations of binary polymer solutions

Bong Ho Chang, Young Chan Bae*

Division of Chemical Engineering, Molecular Thermodynamics Laboratory, Hanyang University, Sungdong Gu Hengdang Dong 17, Seoul 133-791, South Korea

Received 9 June 2002; received in revised form 23 August 2002; accepted 23 August 2002

Abstract

We investigate vapor–liquid equilibria (VLE) for polymer/solvent systems using the same model binary parameters obtained from liquid–liquid equilibria (LLE) calculations. For the systems affected by free-volume differences between molecules, the VLE calculation results are corrected by Elbro et al.'s conceptual expression. In addition, we present the semi-quantitative description of contribution to VLE by oriented interaction. Our proposed model is directly applicable to VLE of binary polymer solution systems for various temperature ranges as well as for LLE calculations. © 2002 Published by Elsevier Science Ltd.

Keywords: Vapor–liquid equilibria; Oriented interaction; Free-volume differences

---

1. Introduction

Phase behavior of polymer solutions play major roles in polymer processing and applications, since many polymers are produced in solution. Therefore, the final polymer product contains some residual solvents. The physical properties of polymers are affected by the amount and type of solvent. A technical problem is to remove the residual solvents. The removal of solvents is particularly important for polymeric materials used in the food and pharmaceutical industry.

In the description of the phase equilibria for polymer solutions, the Flory–Huggins lattice theory [1–5] developed in the early 1940s has been used extensively. Much work has been reported both for vapor–liquid equilibria (VLE) and liquid–liquid equilibria (LLE) of polymer solution systems though not typically in the same publications. We cannot give a complete review here, but outline the particularly relevant literature in this area. Freed and co-workers [6–13] developed a lattice field theory (or lattice cluster theory) for polymer/solvent systems to pursue a formal 'exact' solution to the lattice model using advanced statistical–mechanical methods. To consider the oriented interactions, Hu et al. [14,15] proposed double-lattice model based on Freed's lattice field theory and assumed that the secondary lattice is independent of the primary lattice. They considered the secondary lattice as a perturbation term about the primary lattice. To account for compressibility and density changes upon isothermal mixing, Sanchez and Lacombe [16] and Kleintjens and Koningsveld [17,18] derived different forms of a lattice-fluid model based on Flory–Huggins lattice theory. Sanchez and Balazs [19] used a lattice-fluid equation of state to include specific interactions such as hydrogen bonding. In their model, a quantitative description of the spinodal phase diagram, as well as a semi-quantitative description of the composition and temperature dependence of the χ interaction parameter, is possible. A modified lattice-fluid model by Panayiotou and Sanchez [20,21] is based on the original random-mixing Flory–Huggins theory to account for strong interactions between polymer and solvent. Qian et al. [22] described upper and lower critical solution temperatures (UCST and LCST) with the LCST lying above the UCST, closed loop, and hourglass shapes using a generalized Flory–Huggins theory with the temperature and concentration dependence of χ for polymer solutions and alloys.

Those works mentioned earlier had focused on describing LLE of polymer containing systems. There is also extensive literature on VLE though these studies generally do not simultaneously consider LLE or compare the theories for the two simulation classes. Simplifying Qian's model,

---

* Corresponding author. Tel.: +82-2-2290-0529; fax: +82-2-2296-6280. *E-mail address:* ycbae@hanyang.ac.kr (Y.C. Bae).

0032-3861/02/$ - see front matter © 2002 Published by Elsevier Science Ltd.
PII: S0032-3861(02)00605-5

Bae et al. [23] reported an extended Flory–Huggins equation to represent VLE and LLE for phase behaviors of binary polymer solutions. However, this model is a semi-empirical model.

In this study, we propose a new Helmholtz energy of mixing expression, which is extended to predict solvent activities using the same adjustable binary parameters obtained from LLE calculations for various binary polymer solution systems showing partially miscible phase behavior.

2. Model development

In this section, we derive the Helmholtz energy of mixing to describe the phase behaviors of ordinary polymer solutions. To take the oriented interaction into account, the secondary lattice concept [14,15], which is a perturbation to a fixed reference system (i.e. the Helmholtz energy of mixing for the ordinary polymer solutions), is introduced. Finally, solvent activity equation for VLE description is derived from the Helmholtz energy of mixing.

2.1. Internal and Helmholtz energies of mixing

The energy of mixing related to the number of nearest-neighbor pairs is given by

$$\frac{\Delta_{\text{mix}}U}{N_{\text{r}}\varepsilon} = \frac{1}{2}\frac{N_{12}}{N_{\text{r}}} \tag{1}$$

where N_{12} and N_{r} are the total number of 1–2 pair contacts and total lattice sites, respectively, and ε is the interchange energy defined by Eq. (2)

$$\varepsilon = \varepsilon_{11} + \varepsilon_{22} - 2\varepsilon_{12} \tag{2}$$

where ε_{ij} is the i–j nearest-neighbor interaction energy. The Helmholtz energy of mixing ($\Delta_{\text{mix}}A$) is obtained by integrating the Gibbs–Helmholtz equation using the Guggenheim's athermal entropy of mixing [24] as a boundary condition:

$$\frac{\Delta_{\text{mix}}A}{N_{\text{r}}kT} = \left(\frac{\Delta_{\text{mix}}A}{N_{\text{r}}kT}\right)_{1/\tilde{T}=0} + \int_0^{1/\tilde{T}} \frac{\Delta_{\text{mix}}U}{N_{\text{r}}\varepsilon}\, d\left(\frac{1}{\tilde{T}}\right) \tag{3}$$

$$\left(\frac{\Delta_{\text{mix}}A}{N_{\text{r}}kT}\right)_{1/\tilde{T}=0} = \frac{\phi_1}{r_1}\ln\phi_1 + \frac{\phi_2}{r_2}\ln\phi_2 + \frac{z}{2} \times\left[\phi_1\frac{q_1}{r_1}\ln\frac{\theta_1}{\phi_1} + \phi_2\frac{q_2}{r_2}\ln\frac{\theta_2}{\phi_2}\right] \tag{4}$$

A dimensionless temperature is defined by $\tilde{T} = kT/\varepsilon(\tilde{\varepsilon}^{-1})$, where T is an absolute temperature and k is a Boltzmann's constant. r_i, ϕ_i and θ_i are the relative molar volume, volume fraction and surface fraction of component i, respectively. ϕ_i and θ_i are defined by Eqs. (5) and (6), respectively

$$\phi_i = \frac{N_i r_i}{N_1 r_1 + N_2 r_2} \tag{5}$$

$$\theta_i = \frac{N_i q_i}{N_1 q_1 + N_2 q_2} \tag{6}$$

where q_i is the surface area parameter as defined by

$$z q_i = r_i(z-2) + 2 \tag{7}$$

where z is the lattice coordination number. A simple cubic lattice is used in this study ($z = 6$).

The mathematical form to correlate energy of mixing with Monte-Carlo simulation data [24], which give the values of N_{12} taking nonrandom mixing into account, is given by

$$\frac{2\Delta_{\text{mix}}U}{N_{\text{r}}\varepsilon} = \phi_1\phi_2\left[\frac{B'}{1 - A'(\phi_2 - \phi_1)}\right] \tag{8}$$

where

$$A' = a_0 + a_1[\exp(\tilde{\varepsilon}) - 1] \tag{9}$$

$$B' = b_0 + b_1[\exp(\tilde{\varepsilon}) - 1] \tag{10}$$

Parameters, a_0, a_1, b_0 and b_1 depend on the polymer chain lengths. The following equations are obtained from Monte-Carlo simulations

$$a_0 = 0.00012 + \frac{0.22999(r_2 - 1)}{1 + 1.37129(r_2 - 1)} \tag{11}$$

$$a_1 = -0.01717 + \frac{0.02160(r_2 - 1)}{1 + 0.09642(r_2 - 1)} \tag{12}$$

$$b_0 = 5.79880 - \frac{1.45604(r_2 - 1)}{1 + 1.83417(r_2 - 1)} \tag{13}$$

$$b_1 = -1.42112 - \frac{0.16059(r_2 - 1)}{1 - 1.34296(r_2 - 1)} \tag{14}$$

The determining procedures for Eqs. (11)–(14) are described elsewhere [25].

A simple lattice model expression for $\Delta_{\text{mix}}A$ is given by Eq. (15) from Eqs. (3) and (8).

$$\frac{\Delta_{\text{mix}}A}{N_{\text{r}}kT} = \left(\frac{\Delta_{\text{mix}}A}{N_{\text{r}}kT}\right)_{1/\tilde{T}=0} + \frac{1}{2}\phi_1\phi_2 \times\left[C\tilde{\varepsilon} - \frac{B}{a_1(2\phi_2 - 1)}\ln\left\{1 - \frac{a_1(2\phi_2 - 1)}{1 - a_0(2\phi_2 - 1)}\{\exp(\tilde{\varepsilon}) - 1\}\right\}\right] \tag{15}$$

where

$$B = \frac{(a_1 b_0 - a_0 b_1)(2\phi_2 - 1) + b_1}{1 + (a_1 - a_0)(2\phi_2 - 1)}; \quad C = \frac{b_0 - b_1}{1 + (a_1 - a_0)(2\phi_2 - 1)} \tag{16}$$

2.2. Oriented interaction term

In Freed's theory [6–13], $\Delta_{\text{mix}}A$ of two monomers is

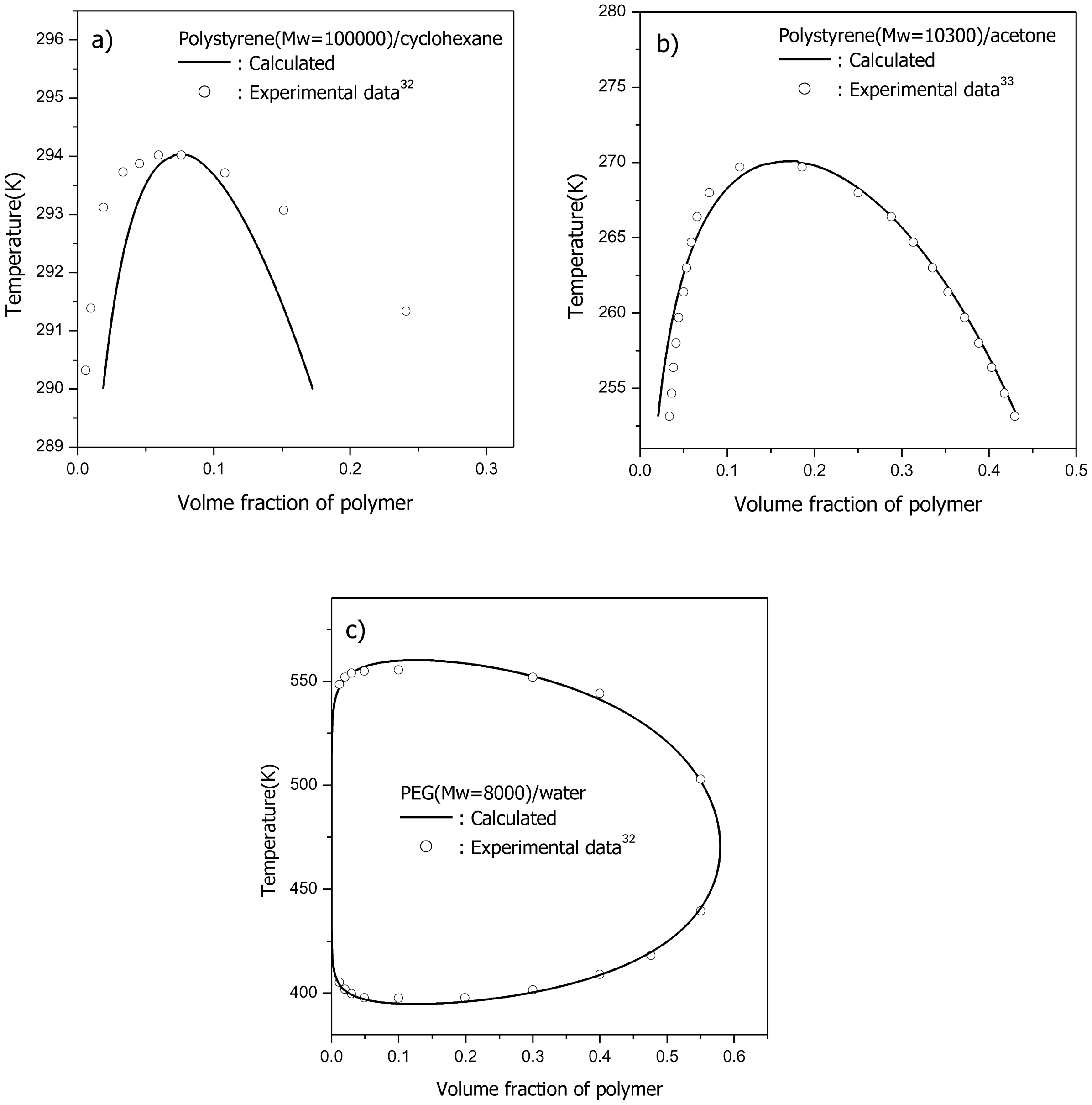

Fig. 1. The coexistence curve for the polymer solution systems given in Table 1.

given by

$$\Delta A_{\mathrm{mix}}/N_{\mathrm{r}}kT = x_1 \ln x_1 + x_2 \ln x_2 + z\tilde{\varepsilon}x_1x_2/2 - z\tilde{\varepsilon}^2x_1^2x_2^2/4 + \cdots \qquad (17)$$

where z is the coordination number and x_i is the mole fraction of the component i. To obtain an analytical expression of the secondary lattice, Oh and Bae [26] defined a new expression for $\Delta_{\mathrm{mix}}A$, replacing x by η and $\tilde{\varepsilon}$ by $\delta\tilde{\varepsilon}$ in Eq. (17). Their expression is given by

$$\frac{\Delta A_{\mathrm{sec},ij}}{N_{ij}kT} = \frac{2}{z}\left[\eta \ln \eta + (1-\eta)\ln(1-\eta) + \frac{zC_\alpha\delta\tilde{\varepsilon}_{ij}(1-\eta)\eta}{1+C_\alpha\delta\tilde{\varepsilon}_{ij}(1-\eta)\eta}\right] \qquad (18)$$

where $\Delta A_{\mathrm{sec},ij}$ is the Helmholtz energy of mixing for the secondary lattice for an i–j segment–segment pair and N_{ij} is the number of i–j pairs. η is the surface fraction permitting oriented interactions. In general, η is different for different components. The calculation results are not sensitive to η. For simplicity, we arbitrarily set η to 0.3 following Hu et al. [14,15] within a reasonable range from 0.3 to 0.5. C_α is a universal constant equal to 0.4881. $\delta\tilde{\varepsilon}_{ij}(\delta\varepsilon_{ij}/kT)$ is the reduced energy parameter contributed by the oriented interactions of i–j pairs such as hydrogen bonding, donor–acceptor electron transfer or dipole–dipole interaction except London dispersion force. If the secondary lattice is regarded as an independent one, $\delta\varepsilon_{ij}$ is separated into two parts [2] for the system with strongly oriented interactions between two components

$$\delta\varepsilon_{ij} = \delta\varepsilon_{ij}^{\mathrm{H}} - \delta\varepsilon_{ij}^{\mathrm{S}} T \tag{19}$$

where $\delta\varepsilon_{ij}^{\mathrm{H}}$ and $\delta\varepsilon_{ij}^{\mathrm{S}}$ are enthalpic and entropic energy contributions for the oriented interactions, respectively. Two parameters represent the enthalpic disadvantage, $\delta\varepsilon_{ij}^{\mathrm{H}}$, and the entropic advantage, $\delta\varepsilon_{ij}^{\mathrm{S}}$, for $\delta\varepsilon_{ij}$ when system temperature increases. To incorporate a secondary lattice with $\Delta_{\mathrm{mix}}A$ in Eq. (15), ε_{ij} is replaced by $\varepsilon_{ij} - \Delta A_{\mathrm{sec},ij}/N_{ij}$. Following the definition of $\tilde{\varepsilon}$ in Eqs. (2) and (3), if an oriented interaction occurs in an i–j segment–segment pair, we replace $\tilde{\varepsilon}$ in Eq. (15) by $\varepsilon/kT + 2\Delta A_{\mathrm{sec},ij}/N_{ij}kT$. If oriented interaction occurs in an i–i segment–segment pair, $\tilde{\varepsilon}$ is replaced by $\varepsilon/kT - \Delta A_{\mathrm{sec},ii}/N_{ii}kT$.

2.3. Solvent activity

If the solvent of a binary polymer solution is designated as component 1, the solvent activity can be derived from Eq. (15):

$$\begin{aligned}\ln a_1 &= \left(\frac{\Delta_{\mathrm{mix}}\mu}{N_{\mathrm{r}}kT}\right)\\ &= \ln\phi_1 + \left(1 - \frac{r_1}{r_2}\right)\phi_2 + \frac{z}{2}\\ &\quad\times\left[q_1 \ln\frac{\theta_1}{\phi_1} + (\theta_1 - \phi_2)q_1 + \frac{r_1\phi_2}{r_2\phi_1}(\phi_1 - \theta_1)q_2\right]\\ &\quad + r_1\phi_2^2 I + r_1\phi_2^2\phi_1\left(\frac{\partial I}{\partial\phi_1}\right)\end{aligned} \tag{20}$$

$$\begin{aligned}I &= \tfrac{1}{2}\phi_1\phi_2\\ &\times\left[C\tilde{\varepsilon} - \frac{B}{a_1(2\phi_2 - 1)}\ln\left\{1 - \frac{a_1(2\phi_2 - 1)}{1 - a_0(2\phi_2 - 1)}\{\exp(\tilde{\varepsilon}) - 1\}\right\}\right]\end{aligned}$$

In our proposed model, we assumed that the volume change upon mixing and free-volume change are both negligible. However, for some polymer solution systems, the entropy of mixing is significantly affected by the free-volume change. To take the effect of free-volume change into account for these systems, the first term of Eq. (20) is replaced by Elbro et al.'s conceptual expression [27], which was derived from a van der Waals free-volume type of expression [28]. We rewrite Eq. (20) as follows

$$\begin{aligned}\ln a_1^{\mathrm{FV}} &= \left(\frac{\Delta_{\mathrm{mix}}\mu}{N_{\mathrm{r}}kT}\right)\\ &= \ln\phi_1^{\mathrm{FV}} + \left(1 - \frac{V_{\mathrm{m1}}^{\mathrm{FV}}}{V_{\mathrm{m2}}^{\mathrm{FV}}}\right)\phi_2^{\mathrm{FV}} + \frac{z}{2}\\ &\quad\times\left[q_1 \ln\frac{\theta_1}{\phi_1} + (\theta_1 - \phi_2)q_1 + \frac{r_1\phi_2}{r_2\phi_1}(\phi_1 - \theta_1)q_2\right]\\ &\quad + r_1\phi_2^2 I + r_1\phi_2^2\phi_1\left(\frac{\partial I}{\partial\phi_1}\right)\end{aligned} \tag{21}$$

where ϕ_i^{FV} is the free-volume fraction of component i, which is defined by

$$\phi_i^{\mathrm{FV}} = \frac{N_i V_{\mathrm{m}i}^{\mathrm{FV}}}{\sum_i N_i V_{\mathrm{m}i}^{\mathrm{FV}}} \tag{22}$$

$$V_{\mathrm{m}i}^{\mathrm{FV}} = V_{\mathrm{m}i} - V_{\mathrm{m}i(\mathrm{vdW})} \tag{23}$$

where $V_{\mathrm{m}i}$ and $V_{\mathrm{m}i(\mathrm{vdW})}$ are the molar volume and the van der Waals volume of component i, respectively. $V_{\mathrm{m}i}$ is a function of temperature; however, $V_{\mathrm{m}i(\mathrm{vdW})}$ is a constant. $V_{\mathrm{m}i}$ and $V_{\mathrm{m}i(\mathrm{vdW})}$ are estimated by the Van Krevelen group contribution method [29]. The molar volume of solvents is estimated by the modified Racett equation [30] for accuracy.

3. Results and discussion

In LLE calculations, it is necessary to use experimental data to obtain the energy parameters, ε/k, $\delta\varepsilon_{ij}^{\mathrm{H}}/k$, $\delta\varepsilon_{ij}^{\mathrm{S}}/k$ and the size parameter, r_2 with $r_1 = 1$. For systems showing an ordinary UCST phase behavior, ε/k and r_2 are adjusted. For systems showing a UCST phase behavior with the weakly oriented interaction, ε/k, $\delta\varepsilon_{ij}^{\mathrm{H}}/k$ and r_2 are needed. For a miscibility loop due to the strongly oriented interaction, ε/k, $\delta\varepsilon_{ij}^{\mathrm{H}}/k$, $\delta\varepsilon_{ij}^{\mathrm{S}}/k$ and r_2 are needed.

We chose polystyrene (PS, $M_{\mathrm{w}} = 100\,000$)/cyclohexane, PS ($M_{\mathrm{w}} = 10\,300$)/acetone and poly(ethylene glycol) (PEG, $M_{\mathrm{w}} = 8000$)/water for our model systems.

Fig. 1 shows phase diagrams of the aforementioned systems. The calculated curve agrees very well with experimental data; however, the PS/cyclohexane system shows fairly large deviations. It is likely that PS has bulky functional groups and cyclohexane is a bulky solvent, while we assume that polymer chain is freely flexible independent

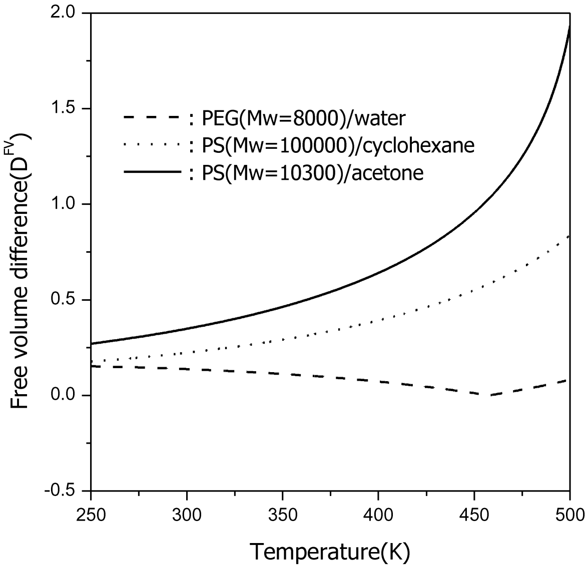

Fig. 2. The free-volume difference (D^{FV}) for the polymer solution systems given in Table 1. The three lines are calculated by Eq. (24).

of solvent structure. That is, the structural hindrance between polymer chains and solvent molecules is neglected and the entropic contribution is overestimated. The model adjustable parameter values are given in Table 1.

In VLE calculations, no additional parameters are needed. The same adjustable parameters obtained from an LLE calculation can be used. The free-volume effects are estimated hypothetically by

$$D_{\mathrm{FV}} = \left| \frac{V_{\mathrm{m1}}^{\mathrm{FV}}}{V_{\mathrm{m1(vdW)}}} - \frac{V_{\mathrm{m2}}^{\mathrm{FV}}}{V_{\mathrm{m2(vdW)}}} \right| \tag{24}$$

Calculation results are shown in Fig. 2. The free-volume effect plays a considerable role in PS/cyclohexane and PS/acetone systems on the VLE measurement temperature range (300–350 K). Aqueous polymer solutions such as PEG/water systems have comparatively similar free-volume differences, and consequently free-volume corrections are not necessary for these systems [31].

Fig. 3 shows measured and predicted solvent activities of the PS ($M_{\mathrm{w}} = 100\,000$)/cyclohexane system. Results using Eqs. (20) and (21) are both shown at two different temperatures. The same adjustable model parameters given in Table 1 are used. For these systems, the results calculated by Eq. (20) tend to underestimate the activity across the whole concentration region due to the underestimated energy of the LLE calculation. However, using Eq. (21) tends to overestimate in the higher solvent concentration region. Overestimating the free-volume difference between polymer and solvent (Eqs. (22) and (23)) causes an underestimation of the calculated entropy (Eq. (21)).

Fig. 4 shows results for the PS ($M_{\mathrm{w}} = 5700$)/acetone

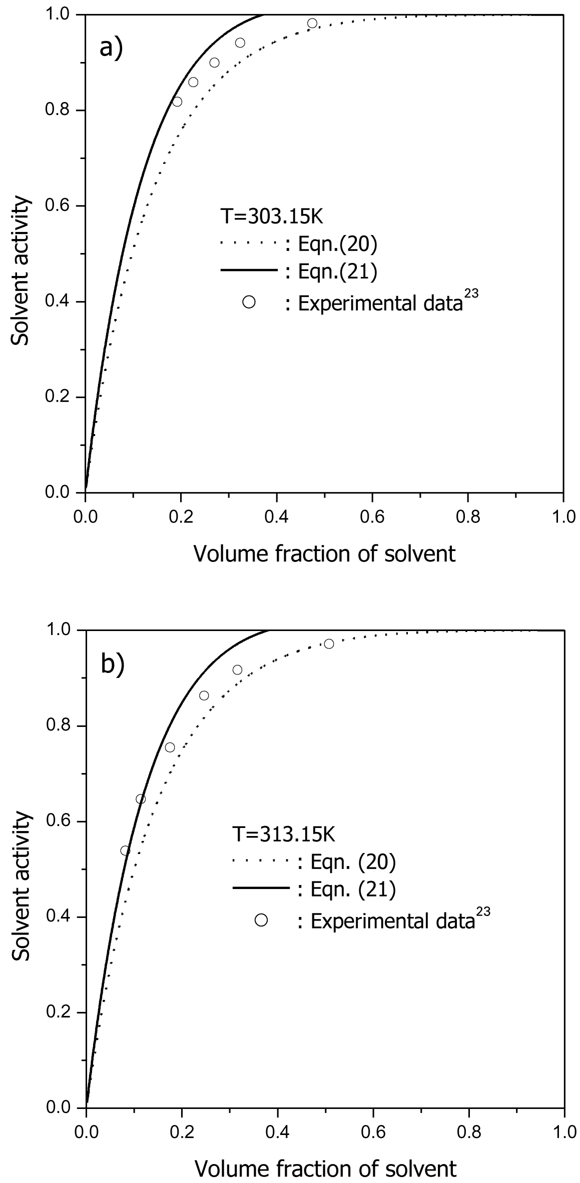

Fig. 3. Solvent activities for PS ($M_{\mathrm{w}} = 100\,000$)/cyclohexane at (a) 303.15 and (b) 313.15 K.

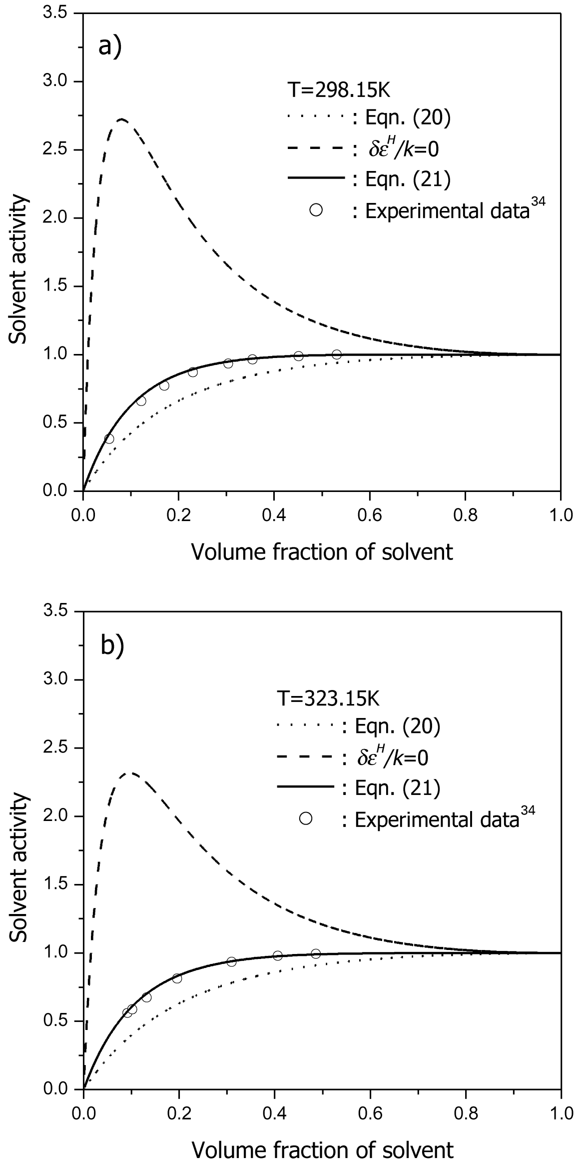

Fig. 4. Solvent activities for PS ($M_{\mathrm{w}} = 15\,700$)/acetone at (a) 298.15 and (b) 323.15 K.

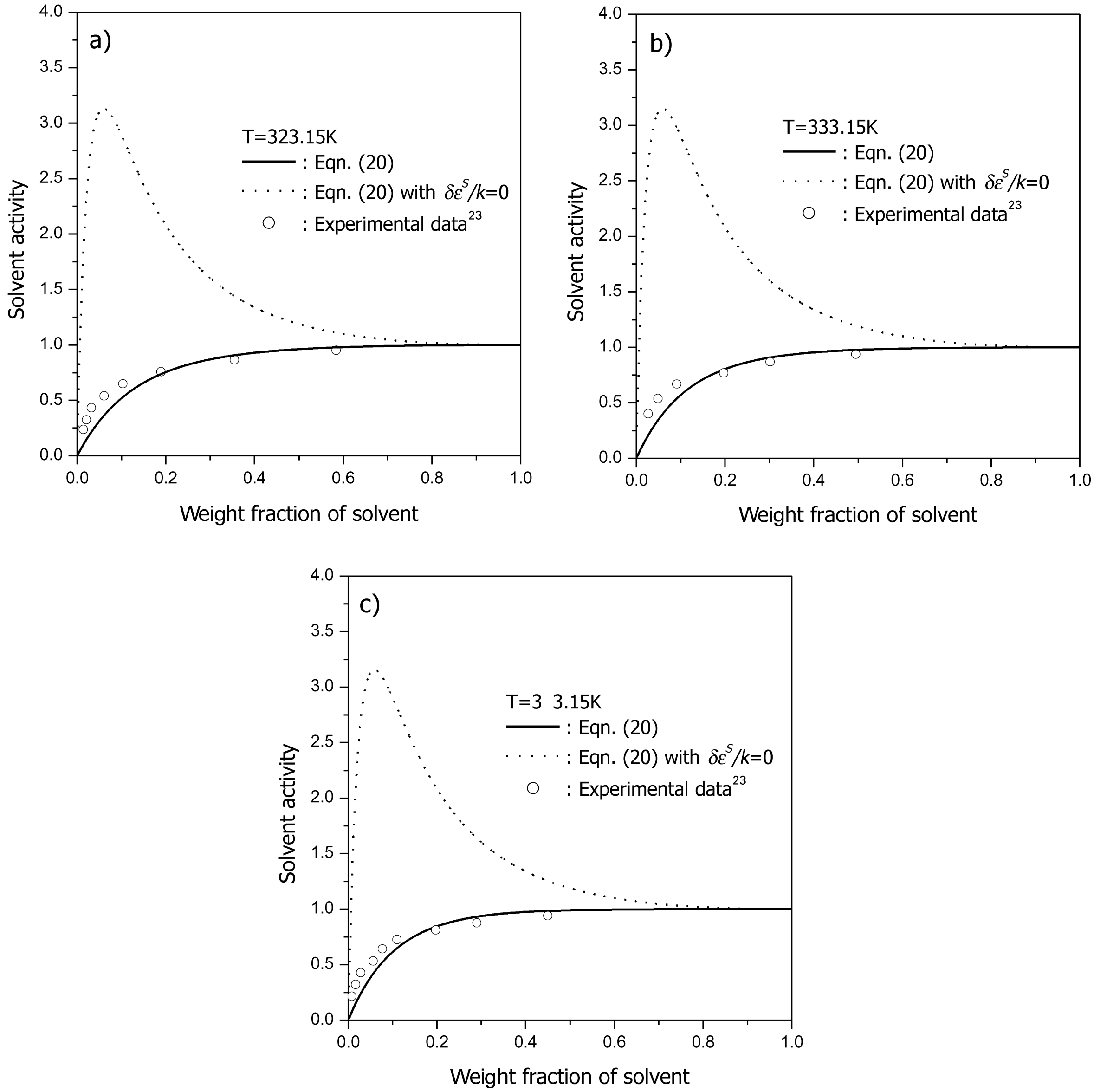

Fig. 5. Solvent activities for PEG ($M_w = 8000$)/water at (a) 323.15, (b) 333.15, and (c) 343.15 K.

system. For this system, we assume that the energy parameter, ε/k, is independent of the polymer molecular weights. The same adjustable parameters, ε/k and $\delta\varepsilon_{ij}^{\mathrm{H}}/k$, given in Table 1 are used and r_2 is calculated by

$$r_2 = \frac{v_2 \mathrm{Mw}_2}{v_1 \mathrm{Mw}_1} \tag{25}$$

where v_1, v_2, Mw_1 and Mw_2 are the specific volumes of solvent and polymer and the molecular weight of solvent and polymer, respectively. In this case the dominant contribution of the energy change dependence upon temperature is ε/k. Therefore, the total energy diminishes with VLE measurement temperature. The results calculated by Eq. (20), without the oriented interaction correction

Table 1
The values of the adjustable model parameters

System	M_w of polymer	Ref.	Parameter			
			ε/k (K)	$\delta\varepsilon_{ij}^{\mathrm{H}}/k$ (K)	$\delta\varepsilon_{ij}^{\mathrm{S}}/k$ (K)	r_2
PS/cyclohexane	100 000	30	76.702	–	–	619.13
PS/acetone	10 300	31	512.308	−609.24	–	94.661
PEG/water	8000	30	1291.861	− 1346.269	0.956	308.38

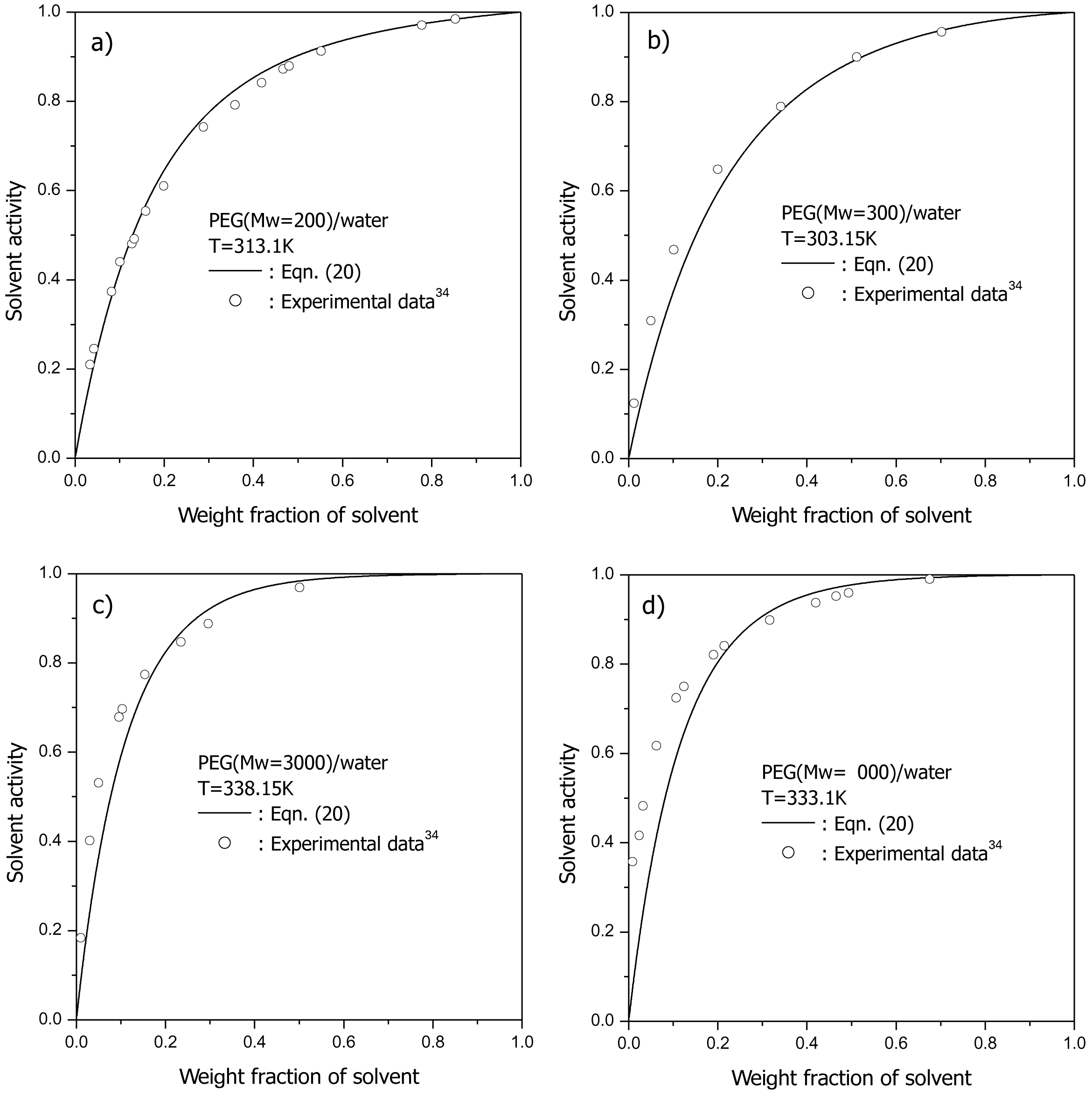

Fig. 6. Solvent activities for PEG/water at various M_w of PEG and temperatures.

($\delta\varepsilon_{ij}^{H}/k = 0$, dashed line), exhibit phase instability. The results calculated by Eq. (21) agree remarkably well with experimental data.

Fig. 5 shows the experimented and predicted solvent activities of the PEG ($M_w = 8000$)/water system. In this system, the free-volume effect is neglected. The same adjustable parameters given in Table 1 are used. The results setting $\delta\varepsilon_{ij}^{S}/k = 0$ (dashed lines) also show the phase instability. Calculated values agree fairly well with experimental data. In the lower concentration region, there are some deviations. In this case, 2 $\Delta A_{\mathrm{sec},ij}/N_{ij}kT$ dominates the energy change with temperature; therefore, the total energy increases with temperature.

Fig. 6 shows activities of the PEG/water system at various molecular weight of PEG. The same adjustable parameters, ε/k, $\delta\varepsilon_{ij}^{H}/k$ and $\delta\varepsilon_{ij}^{S}/k$ given in Table 1 are used and r_2s are calculated. Analogous results are shown to those in Fig. 3.

4. Conclusion

We propose a new Helmholtz energy of mixing equation to describe both LLE and VLE using the same model adjustable binary parameters. For simplicity, we introduce several assumptions. In our model, the relative flexibility of the polymer chains is not considered. Polymers and solvent molecules are considered to be monomers where the concept of flexibility does not apply. We also assume that the parameters, ε/k, $\delta\varepsilon_{ij}^{H}/k$, $\delta\varepsilon_{ij}^{S}/k$ and r_2 are independent of the free-volume difference. It is likely that these assumptions are basically responsible for the discrepancy between the proposed model and experimental results. Nevertheless, our model describes remarkably well the phase equilibria of various polymer solutions over the entire concentration and for various temperatures.

Acknowledgements

This paper was supported by the International Cooperation in Korea Science and Engineering Foundation, 2001 (No. 20016-301-03-2).

References

[1] Flory PJ. J Chem Phys 1942;10:51.
[2] Flory PJ. Principles of polymer chemistry. Ithaca: Cornell University Press; 1953.
[3] Flory PJ. J Am Chem Soc 1965;87:1833.
[4] Flory PJ. Discuss Faraday Soc 1970;49:7.
[5] Huggins ML. J Phys Chem 1942;46:151.
[6] Freed KF. J Phys A: Math Gen 1985;18:871.
[7] Pesci AI, Freed KF. J Chem Phys 1989;90:2017.
[8] Dudowicz J, Freed KF. Macromolecules 1990;23:1519.
[9] Madden WG, Pesci AI, Freed KF. Macromolecules 1990;23:1181.
[10] Dudowicz J, Freed KF. Macromolecules 1991;24:5076.
[11] Dudowicz J, Freed KF. Macromolecules 1991;24:5096.
[12] Dudowicz J, Freed KF. Macromolecules 1991;24:5112.
[13] Dudowicz J, Freed KF. Theor Chim Acta 1992;82:357.
[14] Hu Y, Lambert SM, Soane DS, Prausnitz JM. Macromolecules 1991;24:4356.
[15] Hu Y, Liu H, Soane DS, Prausnitz JM. Fluid Phase Equilib 1991;67:65.
[16] Sanchez IC, Lacombe RH. J Phys Chem 1976;21:2568.
[17] Kleintjens LA, Koningsveld R. Colloid Polym Sci 1980;258:711.
[18] Kleintjens LA, Koningsveld R. Sep Sci Technol 1982;17:215.
[19] Sanchez IC, Balazs AC. Macromolecules 1989;22:2325.
[20] Panayiotou C, Sanchez IC. J Chem Phys 1991;95:1009.
[21] Panayiotou C, Sanchez IC. Macromolecules 1991;24:6231.
[22] Qian C, Mumby SJ, Eichinger BE. Macromolecules 1991;24:1655.
[23] Bae YC, Shim JJ, Soane DS, Prausnitz JM. J Appl Polym Sci 1993;47:1193.
[24] Lambert SM, Soane DS, Prausnitz JM. Fluid Phase Equilib 1993;83:59.
[25] Chang BH, Bae YC. Polymer 1998;39:1735.
[26] Oh JS, Bae YC. Polymer 1998;39:1149.
[27] Elbro HS, Fredenslund Aa, Rasmussen P. Macromolecules 1990;23:4707.
[28] Sandler SI. Fluid Phase Equilib 1985;19:233.
[29] van Krevelen DW. Properties of polymers, 3rd ed. Amsterdam: Elsevier; 1990.
[30] Spencer CF, Danner RP. J Chem Engng Data 1972;17:236.
[31] Rasmussen D, Rasmussen P. Chem Engng Process 1989;85:50.