

Vapor–Liquid Equilibria for Polymer Solutions Through a Group-Contribution Method: Chain-Length Dependence

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ABSTRACT: A new group-contribution model based on the modified double-lattice theory considering chain-length dependence of the universal parameters was developed and applied to describe the vapor–liquid equilibria of polymer solutions. The proposed model includes the combinatorial energy contribution that is responsible for the revised Flory–Huggins entropy of mixing, the van der Waals energy contribution from dispersion and polar

forces, and the specific energy contribution from hydrogen bonding. The quantitative description according to the proposed model was in good agreement with experimentally observed solvent activities of polymer solutions. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2634–2640, 2008

Key words: chain; lattices; lattice models; modification

INTRODUCTION

For engineering purposes, it is often necessary to estimate phase behaviors for binary polymer systems where only fragmentary data, or no data at all, are available. For vapor–liquid equilibria, such estimates can be made with a group-contribution method.¹

Since activity coefficient calculation with group contributions was suggested by Langmuir,² the most widely used and best known group-contribution method is UNIFAC.³ The acronym UNIFAC denotes the universal quasi-chemical activity coefficient (UNIQUAC)⁴ functional group activity coefficient. The UNIFAC correlation is based on a semiempirical model for liquid polymer solutions called UNIQUAC. When compared with the experimental data, however, the UNIFAC equation shows deviations too large to satisfactorily explain the polymer solutions.

Oishi and Prausnitz⁵ modified the UNIFAC model by providing a free-volume contribution to consider the compressibility and the change in density upon isothermal mixing suggested by the Prigogine–Flory–Patterson theory for polymer solutions.

Later, many modifications of the UNIFAC model were reported by Holten-Andersen and coworkers,^{6,7} Chen et al.,⁸ Elbro et al.,⁹ Kontogeorgis et al.,¹⁰ and Bogdanic et al.¹¹

Those methods were based on the UNIFAC correlation, which is often successful for estimating the phase equilibria in mixtures containing ordinary (nonpolymer) liquids.

The fundamental basis for existing group-contribution methods for polymer solutions is the lattice theory of Flory¹² and Huggins.¹³ To pursue a formal exact solution to the lattice model with advanced statistical and mathematical methods, Freed and Bawendi^{14,15} developed a lattice-cluster theory for polymer–solvent systems. This theory provides an exact mathematical solution for the Flory–Huggins model.

Hu et al.¹⁶ proposed a new theory called the *double-lattice model*, which is based on Freed's lattice-cluster theory. In this theory, ordinary polymer solutions are described by the primary lattice, and a secondary lattice is mentioned as a perturbation to account for the orientation effect of hydrogen bonding. Oh and Bae¹⁷ reported a modified double-lattice model and provided an exact mathematical form for the secondary lattice of the double lattice. Chang and Bae¹⁸ introduced new universal parameters to

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consider chain-length dependence in the primary lattice.

Hu et al.¹⁹ presented a group-contribution method, including a revised Flory–Huggins entropy, a series expression for excess internal energy, and a double-lattice model, to account for specific interactions.

In this article, we propose a group-contribution model that can be used to describe the solvent activities of polymer solutions. The proposed model is based on a modified double-lattice model and considers the chain-length dependence of universal parameters, wherein the Helmholtz function of mixing includes the revised Flory–Huggins entropy contribution, the van der Waals energy contribution, and the specific energy contribution.

MODEL DEVELOPMENT

Modified double-lattice model

Primary lattice

Oh and Bae¹⁷ proposed a new Helmholtz energy of mixing as the form of Flory–Huggins theory.^{12,13} This expression is given by

$$\Delta A/N_r kT = (\phi_1/r_1) \ln \phi_1 + (\phi_2/r_2) \ln \phi_2 + \chi_{OB} \phi_1 \phi_2 \quad (1)$$

where ΔA is the Helmholtz energy of mixing difference, N_r is the total number of lattice sites, T is the absolute temperature, and k is the Boltzmann's constant. ϕ_i is volume fraction of component i , and r_i is the number of segments per molecule i . χ_{OB} is a new interaction parameter defined by

$$\chi_{OB} = C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1} \right)^2 + \left(2 + \frac{1}{r_2} \right) \tilde{\varepsilon} - \left(\frac{1}{r_2} - \frac{1}{r_1} + C_\gamma \tilde{\varepsilon} \right) \tilde{\varepsilon} \phi_2 + C_\gamma \tilde{\varepsilon}^2 \phi_2^2 \quad (2)$$

where the parameters C_β and C_γ are universal constants and $\tilde{\varepsilon}$ is a reduced interaction parameter given by

$$\tilde{\varepsilon} = \varepsilon/kT = (\varepsilon_{11} + \varepsilon_{22} - 2\varepsilon_{12})/kT \quad (3)$$

where ε is interchange energy, and ε_{11} , ε_{22} , and ε_{12} are for the corresponding nearest-neighbor segment–segment interactions.

Universal constants¹⁷

C_β and C_γ are not adjustable parameters and are determined by comparison with Madden et al.'s²⁰ Monte-Carlo simulation data ($r_1 = 1$ and $r_2 = 100$). The best fitting values of C_β and C_γ are 0.1415 and 1.7985, respectively.

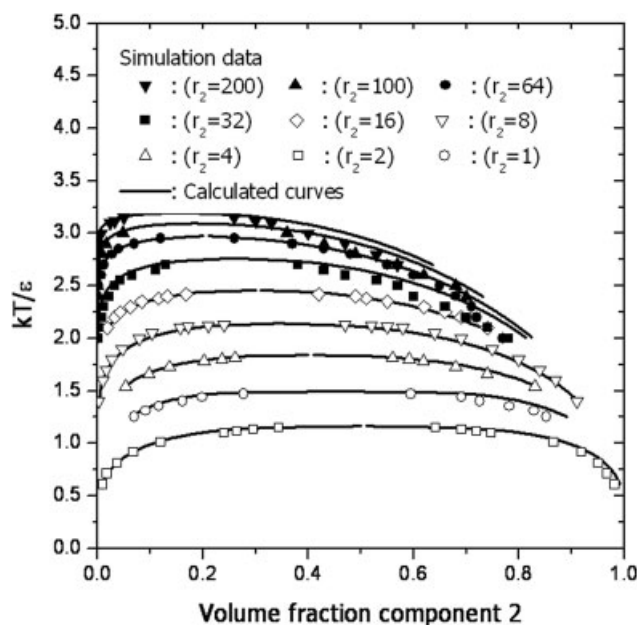


Figure 1 Phase diagram of lattice-polymer systems with chain lengths $r^2 = 1$ –200. The solid lines show data calculated with a primary lattice.

Chain-length dependence term

In a previous study, Chang and Bae¹⁸ proposed a chain-length dependence term of the universal parameters C_β and C_γ for the modified double-lattice model.

Figure 1 shows the configurational bias vaporization method simulation results by Hu et al.²¹ for various chain lengths of component 2. The solid lines are the best fit given by the proposed primary lattice.

Figure 2 represents the chain-length dependence of C_β and C_γ . The parameters appear to be asymptotic values with respect to r_2 . The following equations are suggested for the r -mer dependence of C_β and C_γ :

$$C_\beta = 0.1080 + \frac{1.0647}{1.9907 + (r_2 - 1)} \quad (4)$$

$$C_\gamma = 1.1529 + \frac{1.1035}{0.0738 + (r_2 - 1)} \quad (5)$$

Equations (4) and (5) can be applied for large r_2 values. For $r_2 > 100$, C_β and C_γ are very weakly dependent on r_2 , according to Figure 2.

Secondary lattice

In Freed's theory,^{14,15} the solution of the Helmholtz energy of mixing for the Ising model is given by

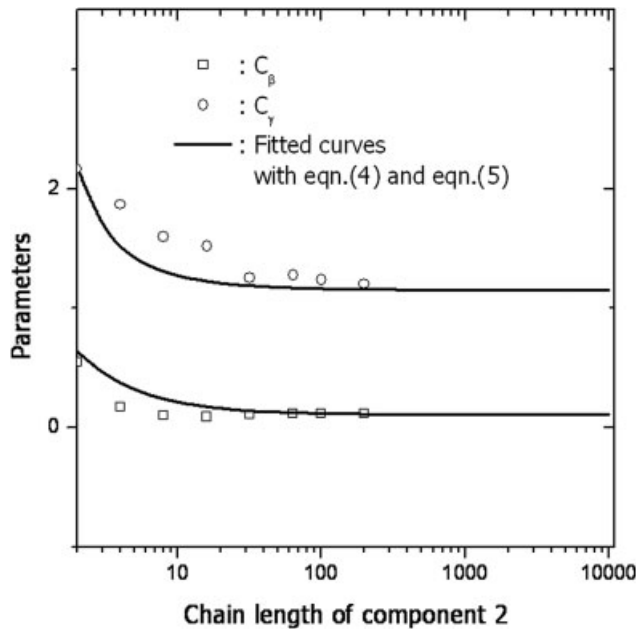


Figure 2 Dependence of C_β and C_γ on r -mer chain length. Data shown with squares and circles were calculated by a primary lattice from the simulation results and represent C_β and C_γ , respectively. The solid lines show data calculated by eqs. (4) and (5).

$$\Delta A/N_r kT = x_1 \ln x_1 + x_2 \ln x_2 + z\tilde{\varepsilon}x_1x_2/2 - z\tilde{\varepsilon}^2x_1^2x_2^2/4 + \dots \quad (6)$$

where z is the coordination number and x_i is the molar fraction of component i .

To obtain an analytical expression for the secondary lattice, we defined a new Helmholtz energy of mixing as the fractional form to improve the mathematical approximation defect by revising eq. (6). The expression is given by

$$\frac{\Delta A_{\text{sec},ij}}{N_{ij}kT} = \frac{2}{z} \left[\eta \ln \eta + (1 - \eta) \ln(1 - \eta) + \frac{zC_\alpha \delta \tilde{\varepsilon}_{ij} (1 - \eta) \eta}{1 + C_\alpha \delta \tilde{\varepsilon}_{ij} (1 - \eta) \eta} \right] \quad (7)$$

where $\Delta A_{\text{sec},ij}$ is the Helmholtz energy of mixing of the secondary lattice for the i - j segment-segment pair, N_{ij} is the number of i - j pairs, η is the surface fraction permitting oriented interactions, and $\delta \tilde{\varepsilon}_{ij}$ is the reduced energy parameter contributed by the oriented interactions. For simplicity, η is arbitrarily set to 0.3 as Hu et al.¹⁶ suggested. C_α is a universal constant. C_α also is not an adjustable parameter and is determined by comparison with Panagiotopoulos et al.'s²² Gibbs-Ensemble Monte-Carlo simulation data of the Ising lattice. The best fitting value of C_α is 0.4880.

Incorporation of the secondary lattice into the primary lattice

To account for the oriented interaction, the secondary lattice contribution is a perturbation to the primary lattice. To incorporate a secondary lattice, we replace ε_{ij} with $\varepsilon_{ij} - \Delta A_{\text{sec},ij}/N_{ij}$ in eq. (3). Following the definition of $\tilde{\varepsilon}$ in eq. (3); if oriented interaction occurs in the i - j segment-segment pairs, we replace $\tilde{\varepsilon}$ with $\varepsilon/kT + 2\Delta A_{\text{sec},ij}/N_{ij}kT$ in eq. (3). If oriented interaction occurs in the i - i segment-segment pairs, $\tilde{\varepsilon}$ is replaced by $\varepsilon/kT - \Delta A_{\text{sec},ii}/N_{ii}kT$.

Correlating equations

To calculate the binary coexistence curve, we need a chemical potential for components 1 and 2. They are given by

$$\begin{aligned} \frac{\Delta \mu_1}{kT} = & \ln(1 - \phi_2) - r_1 \left(\frac{1}{r_2} - \frac{1}{r_1} \right) \phi_2 + r_1 \left[C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1} \right)^2 \right. \\ & + \left. \left(\left(\frac{1}{r_2} - \frac{1}{r_1} \right) + C_\gamma \tilde{\varepsilon} \right) \tilde{\varepsilon} + \left(2 + \frac{1}{r_2} \right) \tilde{\varepsilon} \right] \phi_2^2 \\ & - 2r_1 \left[\left(\left(\frac{1}{r_2} - \frac{1}{r_1} \right) + C_\gamma \tilde{\varepsilon} \right) \tilde{\varepsilon} + C_\gamma \tilde{\varepsilon}^2 \right] \phi_2^3 + 3r_1 C_\gamma \tilde{\varepsilon}^2 \phi_2^4 \quad (8) \end{aligned}$$

$$\begin{aligned} \frac{\Delta \mu_2}{kT} = & \ln \phi_2 + r_2 \left[\left(\frac{1}{r_2} - \frac{1}{r_1} \right) + C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1} \right)^2 + \left(2 + \frac{1}{r_2} \right) \tilde{\varepsilon} \right] \\ & - r_2 \left[\left(\frac{1}{r_2} - \frac{1}{r_1} \right) + 2 \left(\left(\frac{1}{r_2} - \frac{1}{r_1} \right) + C_\gamma \tilde{\varepsilon} \right) \tilde{\varepsilon} \right. \\ & + 2C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1} \right)^2 + 2 \left(2 + \frac{1}{r_2} \right) \tilde{\varepsilon} \left. \right] \phi_2 + r_2 \left[4 \left(\left(\frac{1}{r_2} - \frac{1}{r_1} \right) \right. \right. \\ & + \left. \left. C_\gamma \tilde{\varepsilon} \right) \tilde{\varepsilon} + \left(2 + \frac{1}{r_2} \right) \tilde{\varepsilon} + C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1} \right)^2 + 3C_\gamma \tilde{\varepsilon}^2 \right] \phi_2^2 \\ & - r_2 \left[6C_\gamma \tilde{\varepsilon}^2 + 2 \left(\left(\frac{1}{r_2} - \frac{1}{r_1} \right) + C_\gamma \tilde{\varepsilon} \right) \tilde{\varepsilon} \right] \phi_2^3 + 3r_2 C_\gamma \tilde{\varepsilon}^2 \phi_2^4 \quad (9) \end{aligned}$$

where $\Delta \mu_i$ is the chemical potential difference of component i .

Group contribution

van der Waals energy contribution

The energy parameter ε_{ij}^* in eq. (10) is due to van der Waals forces (dispersion and polar forces). For a pure component i , ε_{ii}^* can be estimated with the square of the pure-component van der Waals solubility parameter of Hansen (δ_{vdw} ; Barton),²³ which is the sum of a dispersion contribution (δ_d) and a polar contribution (δ_p ; $\delta_{vdw}^2 = \delta_d^2 + \delta_p^2$)

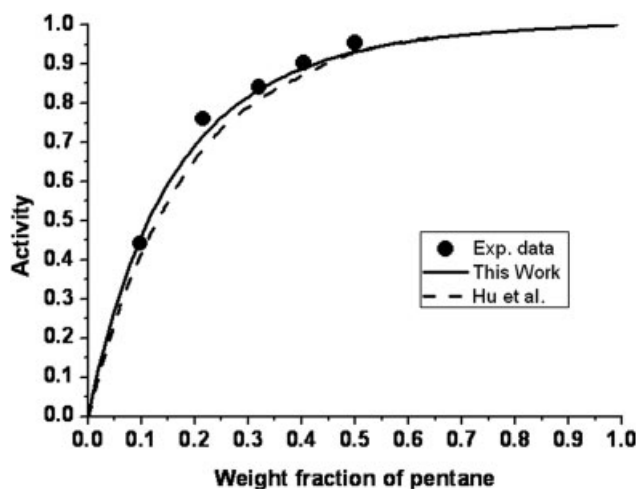


Figure 3 Solvent activities for the polyisobutylene ($M_w = 1170$)/pentane system at 298.15 K. The dark circles show experimental data by Wen et al.²⁴

$$\delta_{vdw,i}^2 = \frac{3N_A \epsilon_{ii}^* r_i}{V_{mi}} \quad (10)$$

where N_A is the Avogadro's number and where V_{mi} is the molar volume of component i , and δ_{vdw}^2 and V_{mi} are at 25°C. For a pure component, the effect of temperature on the cross-interaction van der Waals energy parameter (ϵ_{ij}^*) is given by

$$\epsilon_{ii}^* = \frac{\epsilon_{ii}^+}{V_{mi}} \quad (11)$$

where V_{mi} depends on temperature. The temperature-independent parameter (ϵ_{ii}^+) can be estimated by

$$\epsilon_{ii}^+ = \frac{\delta_{vdw}^2 V_{mi}^2(25^\circ\text{C})}{3N_A r_i} \quad (12)$$

ϵ_{ij}^* is estimated by the geometric mean of the corresponding pure-component parameters:

$$\epsilon_{ij}^* = \sqrt{\epsilon_{ii}^* \epsilon_{jj}^*} \quad (13)$$

TABLE I
Group-Interaction Parameters

Solvent		Polymer		
		CH ₃	CH ₂	C
CH ₃	g_{mn} (1)	81.56	-71.794	1956.6
	g_{mn} (2)	—	-669.52	—
	g_{mn} (3)	—	2439.9	-8909.2
CH ₂	g_{mn} (1)	—	663.25	-2115.6
	g_{mn} (2)	—	-1088.48	—
	g_{mn} (3)	1614.5	—	-9250

These data were taken from Hu et al.¹⁹

Specific energy contribution

The pure-component parameters ($\delta\tilde{\epsilon}_{ii}$ and $\delta\tilde{\epsilon}_{jj}$) are calculated from Hansen's hydrogen-bonding solubility parameter (δ_h). It is related to the additional specific energy ($\Delta U_{sec,ii}$) by

$$\Delta U_{sec,ii}(25^\circ\text{C}) = -\delta_h^2 V_{mi}(25^\circ\text{C}) \quad (14)$$

For the temperature dependence of $\Delta U_{sec,ii}$, we assume

$$\Delta U_{sec,ii} = \frac{\Delta U_{sec,ii}^+}{V_{mi}} \quad (15)$$

where $\Delta U_{sec,ii}^+$ (additional specific energy) is independent of temperature. From eqs. (14) and (15), we get

$$\Delta U_{sec,ii(T)} = -\frac{\delta_h^2 V_{mi}^2(25^\circ\text{C})}{V_{mi}(T)} \quad (16)$$

For a pure component i , when eq. (7) is inserted into the thermodynamic relation $[\frac{\partial(\Delta A/T)}{\partial(1/T)}] = \Delta U$, where ΔU is the internal energy difference and we have

$$\frac{\Delta U_{sec,ii}}{k} = \frac{N_i r_i z C_\alpha (1 - \eta) \eta (\frac{\delta\tilde{\epsilon}_{ii}}{k})}{[1 + C_\alpha \frac{\delta\tilde{\epsilon}_{ii}}{kT} (1 - \eta) \eta]^2} \quad (17)$$

The cross-specific energy parameter ($\delta\tilde{\epsilon}_{ij}$) is calculated from pair-interaction-group parameters

TABLE II
Group-Interaction Parameters: g_{mn} (K)

Solvent	Polymer					
	CH ₃	CH ₂	CH	C	C ₆ H ₅	O
CH ₃	534.03	-2946.4	671.98	3293.99	926.04	
CH ₂	-741.82	2134.29		-3337.73		
C ₆ H ₅		438.89	-2546.93		-313.97	-2337.03
H		-1377.27				-9861.6
OH		-2283.28				-1076.68

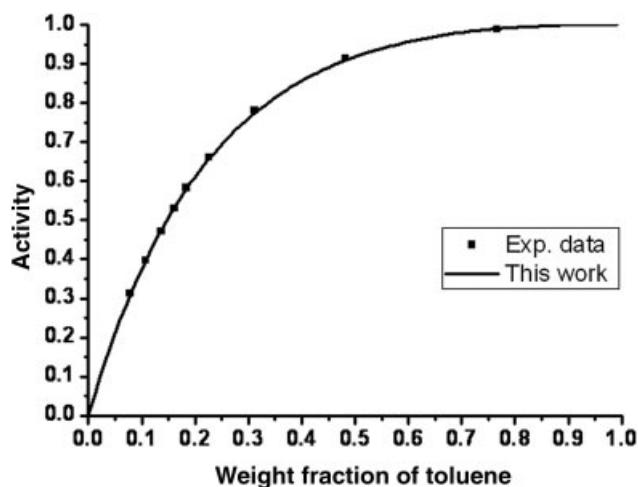


Figure 4 Solvent activities for the polystyrene ($M_w = 10,920$)/toluene system at 321.65 K. The dark circles show experimental data by Wen et al.²⁴

$$\frac{\delta\epsilon_{ij}}{k} = \sum_{m=1}^{N_s} \sum_{n=1}^{N_p} \phi_m \phi_n g_{mn} \quad (18)$$

where N_s and N_p are the number of groups in the solvents and polymers, respectively; ϕ_m and ϕ_n are the volume fractions of group m in a solvent and that of group n in a polymer, respectively; and g_{mn} is the pair-interaction parameters between group m in a solvent and group n in a polymer. To improve the accuracy of prediction, we assume that a functional group in a polymer is different from that in a solvent.

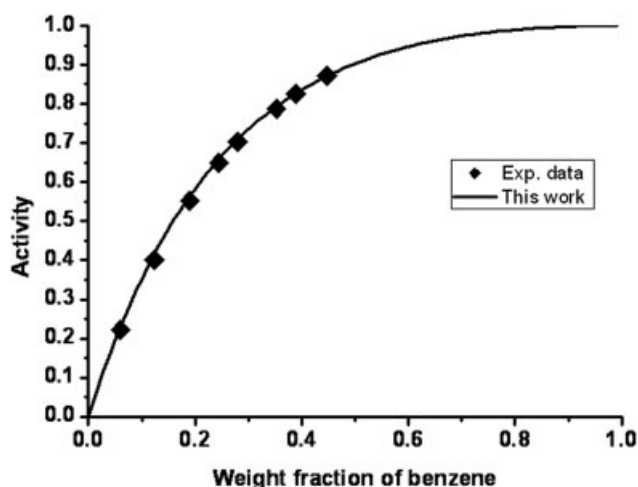


Figure 5 Solvent activities for the PEO ($M_w = 100,000$)/benzene system at 343.15 K. The dark circles show experimental data by Wen et al.²⁴

RESULTS AND DISCUSSION

In this article, we have proposed a new group-contribution model to describe the Vapor-liquid equilibria for a variety of polymer-solvent systems. The new model uses the secondary lattice concept to take into account an oriented interaction. The advantage of this model follows from its simplicity. In this study, most parameters were calculated from pure-component properties, either from experimental data or from published estimation methods. To establish the group-contribution method, the most significant factor was the determination of the cross-pair interaction between the polymer and solvent segments.

Figure 3 shows a comparison of the activities of a polyisobutylene [weight-average molecular weight (M_w) = 1170]/pentane system at 298.15 K calculated by Hu et al.¹⁹ with those of this study. The solid line indicates data from this study, and the dashed line indicates data from Hu et al.¹⁹ The dark circles represent experimental data reported by Wen et al.²⁴ Both models gave fairly good agreement with experimental results. However, Hu et al.'s model needed 18 group parameters, and the proposed model required only 6 parameters. The calculated group parameters from Hu et al.'s model are listed in Table I, and all parameters from this study are listed in Table II.

The solid line indicates data from this study. Dark circles represent experimental data reported by Wen et al.²⁴ With molar volumes at different temperatures selected for the pure component i , ϵ_{ii}^* , ϵ_{jj}^* , ϵ_{ij}^* , $\delta\epsilon_{ii}$, and $\delta\epsilon_{jj}$ are calculated. The pair-interaction energy parameter values were $g_{\text{CH}_3-\text{CH}_3} = 534.03$ K, $g_{\text{CH}_2-\text{CH}_3} = -2946.4$ K, $g_{\text{C}-\text{CH}_3} = 3293.99$ K, $g_{\text{CH}_3-\text{CH}_2} = -741.82$ K, $g_{\text{CH}_2-\text{CH}_2} = 2134.29$ K, and $g_{\text{C}-\text{CH}_2} = -3337.73$ K. With molar volumes at different

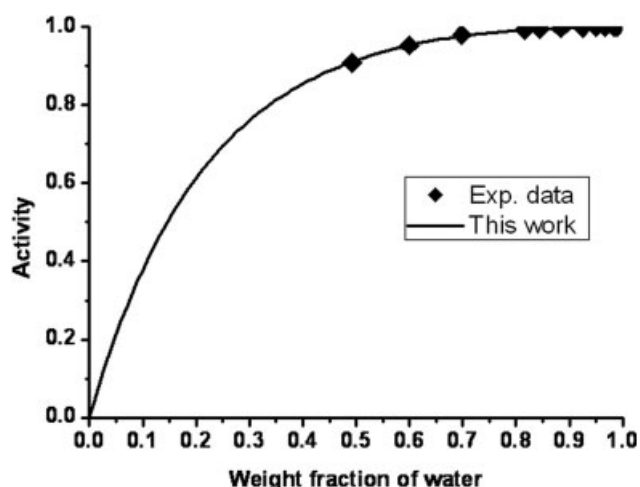


Figure 6 Solvent activities for the PEO ($M_w = 1460$)/water system at 273.15 K. The dark circles show experimental data by Wen et al.²⁴

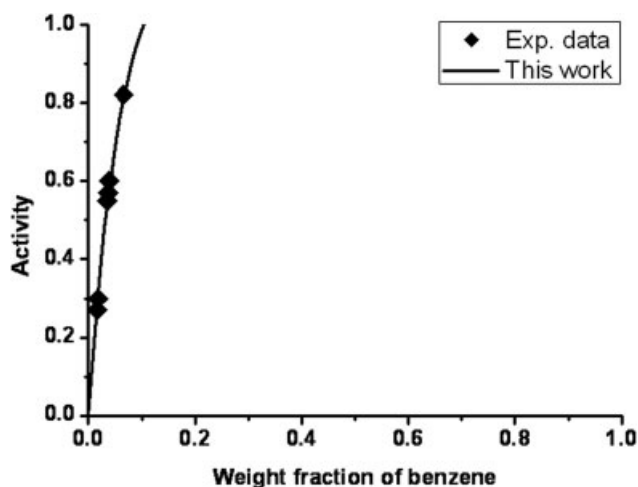


Figure 7 Solvent activities for the polyethylene ($M_w = 80,000$)/benzene system at 273.15 K. The dark circles show experimental data by Wen et al.²⁴

temperatures selected for the pure component i , $\delta\epsilon_{ii}$ was calculated from eq. (17). The pair-interaction energy parameter values were obtained by the fitting of the experimental data at 298.15 K.

Figure 4 shows the described solvent activities of polystyrene [molecular weight (MW) = 10,920]/toluene systems at 321.65 K. The solid line represents data calculated in this study. Dark circles represent experimental data reported by Wen et al.²⁴ The pair-interaction energy parameter values were $g_{\text{CH}_2-\text{CH}_3} = -2946.4$ K, $g_{\text{CH}-\text{CH}_3} = 671.98$ K, $g_{\text{C}_6\text{H}_5-\text{CH}_3} = 926.04$ K, $g_{\text{CH}_2-\text{C}_6\text{H}_5} = 438.89$ K, $g_{\text{CH}-\text{C}_6\text{H}_5} = -2546.93$ K, and $g_{\text{C}_6\text{H}_5-\text{C}_6\text{H}_5} = -313.97$ K. As shown in Figure 4, the calculated curve agreed very well with the experimental data.

Figure 5 shows the described solvent activities of a poly(ethylene oxide) (PEO; MW = 100,000)/benzene system at 343.15 K. The solid line represents data predicted by this study. Dark circles represent experimental data reported by Wen et al.²⁴ The pair-interaction energy parameter values were $g_{\text{CH}_2-\text{C}_6\text{H}_5} = 438.89$ K, $g_{\text{O}-\text{C}_6\text{H}_5} = -2337.03$ K, $g_{\text{CH}_2-\text{H}} = -1377.27$ K, and $g_{\text{O}-\text{H}} = -9861.6$ K.

Figure 6 shows the predicted solvent activities of a PEO (MW = 1460)/water system at 273.15 K. The solid line shows data calculated in this study. Open circles represent experimental data reported by Wen et al.²⁴ The pair-interaction energy parameter values were $g_{\text{CH}_2-\text{H}} = -1377.27$ K, $g_{\text{O}-\text{H}} = -9861.6$ K, $g_{\text{CH}_2-\text{OH}} = -2283.28$ K, and $g_{\text{O}-\text{OH}} = -1076.68$ K. In this case, agreement with the experimental data showed slight deviation compared with other results. The proposed model does not consider the various polydispersities of chain molecules. Particularly, PEO has a high polydispersity number ($M_w/\text{number-average molecular weight} = 1.6$); this model implicitly

assumes that all of the polymers are monodisperse. It is likely that this deficiency was responsible for the observed discrepancy between the proposed model and the experimental data.

Figure 7 shows the described solvent activities of a polyethylene (MW = 80,000)/benzene system at 273.15 K. The solid line represents predicted by this study. This result was predicted with only previously obtained pair-interaction energy parameters. Open circles represent experimental data reported by Wen et al.²⁴ The pair-interaction energy parameter values were $g_{\text{CH}_2-\text{C}_6\text{H}_5} = 769.864$ K and $g_{\text{CH}_2-\text{H}} = -5776.11$ K. These parameters were not obtained by the fitting of experimental data.

CONCLUSIONS

We proposed a group-contribution model based on a modified double-lattice theory that includes the chain-length dependence of universal parameters. The proposed model has a simplified and improved expression for the Helmholtz energy of mixing for polymer-solvent systems, which includes the combinatorial entropy contribution, the van der Waals energy contribution, and the specific energy contribution. We presented several solvent activities for various binary polymer-solvent systems to compare the calculated results with experimental data. The proposed model gave very good agreement with the experimental data. However, the list of group-interaction parameters was not sufficient. More experimental data are required.

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