

# An Improved Prediction Result of Entropic-FV Model for Vapor–Liquid Equilibria of Solvent–Polymer Systems

Gede Wibawa, Shigeki Takishima, Yoshiyuki Sato, Hirokatsu Masuoka

Department of Chemical Engineering, Graduate School of Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima 739-8527, Japan

Received 25 March 2004; accepted 2 November 2004  
Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** In this work, entropic expressions of UNIFAC-FV and Entropic-FV models were evaluated by using an extensive database of infinite dilution vapor–liquid equilibrium (VLE) data of athermal systems containing polypropylene, polyethylene, and polyisobutylene. For the infinite dilution athermal systems, performance of the Entropic-FV model was better than that of the UNIFAC-FV model. Then, finite concentration VLE data of non-athermal systems that consisted of 16 polymers and 36 solvents containing a large variety of solvent–polymer systems ranging from nonpolar to polar substances were considered to optimized 46 pairs of

group interaction parameters of the Entropic-FV model. For systems containing polar solvents of three types of solvents studied, revised group interaction parameters gave significant improvements from 17.9 to 13.0% average absolute deviation (AAD) of solvent activities. For overall results, improvements were achieved from 15.1 to 12.4% AAD. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1145–1153, 2005

**Key words:** solubility; solution properties; thermodynamics; calculations; UNIFAC

## INTRODUCTION

With the rise in sophistication of polymer technology, polymeric materials were developed for many applications in aerospace, electronics, automotive, biomedical, and consumer industries. Polymerization often takes place in solvent and requires separation of remaining solvents and nonpolymerized monomers to meet product specifications as well as environmental, health, and safety regulations. To assess methods for these types of separations, vapor–liquid equilibrium (VLE) data and predictive models are required. In engineering applications, estimation techniques such as group contribution methods can save time and money because experimental data are frequently unavailable.<sup>1</sup>

Predictive models based on UNIFAC group contribution model<sup>2</sup> such as the UNIFAC-FV model of Oishi and Prausnitz<sup>3</sup> and the Entropic-FV model of Elbro et al.<sup>4</sup> were used over the years with good success for solvent–polymer systems. In both models, solvent activity is expressed as an addition of entropic and residual contributions. Entropic contribution accounts for combinatorial and free-volume effects between solvent and polymer in different ways that will be described later. Residual contribution accounts for the effect of enthalpy of mixing in which both models use

the residual contribution of UNIFAC model with group interaction parameters obtained from VLE data of low molecular weight substances. However, these models give somewhat larger errors of VLE for solvent–polymer systems than those for low molecular weight substance systems. Because the nature of intermolecular interactions of solvent–polymer systems may be different from that of low molecular weight substances, the authors revised the group interaction parameters of UNIFAC model by using a large variety of solvent–polymer systems based on the UNIFAC-FV model to improve the prediction results in the previous work.<sup>5</sup> The UNIFAC-FV model was chosen for the optimization of group interaction parameters because its entropic expression showed a good performance for systems that has no effect of enthalpy of mixing (athermal systems) comprising finite concentration VLE data of alkane and cycloalkane–polyisobutylene systems. On the other hand, Lindvig et al.<sup>6</sup> reported that the Entropic-FV model was more stable than the UNIFAC-FV model in the sense that no extreme deviations were observed for both infinite dilution and finite concentration non-athermal systems containing nonpolar, hydrogen-bonding solvents and water. Moreover, Kouskoumvekaki et al.<sup>7</sup> made an investigation of entropic expressions of the UNIFAC-FV and Entropic-FV models based on extensive database of athermal systems considering finite concentration and infinite dilution VLE data. The systems considered consist of polyisobutylene, polyethylene, and polypropylene. They reported that entropic expression (combinatorial and free-volume) of the Entropic-FV model

Correspondence to: S. Takishima (r736735@hiroshima-u.ac.jp).

performed better than that of UNIFAC-FV model for the athermal systems studied.

From the above two works, the entropic expression of the Entropic-FV model was confirmed to be stable for any polymers including athermal systems. The objective of this work was to improve the accuracy of the Entropic-FV model for the prediction of solvent activity in polymer solutions. Because evaluations of entropic expression of UNIFAC-FV and Entropic-FV based on different types of athermal systems yielded inconsistent results,<sup>5,7</sup> entropic expression of the UNIFAC-FV and Entropic-FV models were evaluated by using an extensive database of infinite dilution athermal systems in this work. Then, group interaction parameters of the Entropic-FV model were revised by using the latest finite concentration VLE data for solvent-polymer systems.

### DESCRIPTIONS UNIFAC-FV AND ENTROPIC-FV MODELS

The UNIFAC<sup>2</sup> model is based on a two-liquid lattice theory of liquid mixtures, which does not explicitly account for free volume caused by mixing. For mixtures of low or modest molecular weight substances, the free-volume effects make a small contribution, which is usually negligible in comparison with other contributions in the model. For most mixtures of solvents and polymers, however, because the polymer molecules are much more tightly packed than solvent molecules, free-volume effects are far from negligible. As observed by Oishi and Prausnitz,<sup>3</sup> predicted solvent activities in polymer solutions by the UNIFAC model tend to be lower than those observed experimentally. To apply the model to solvent-polymer systems, those authors modified the model by adding a free-volume term obtained from the Flory equation of state to the model. The modified UNIFAC model is called the UNIFAC Free-Volume (UNIFAC-FV) model. For a binary mixture, the activity of solvent is

$$\ln a_1 = \ln a_1^C + \ln a_1^R + \ln a_1^{FV} \quad (1)$$

where  $a_1$  is the solvent activity, superscripts C and R denote the combinatorial and residual terms, respectively, taken from original UNIFAC model, and superscript FV denotes the free-volume term. The combinatorial term of solvent activity,  $\ln a_1^C$ , is given by

$$\ln a_1^C = \ln \phi'_1 + \phi'_2 + \frac{z}{2} M_1 q'_1 \ln \frac{\theta'_1}{\phi'_1} - \frac{z}{2} M_1 q'_1 \left( 1 - \frac{\phi_1}{\theta'_1} \right) \quad (2)$$

where  $z$  is the coordination number set equal to 10,  $M$  is the molar mass, and subscripts 1 and 2 denote solvent and polymer, respectively. The composition

variables,  $\theta'$  and  $\phi'$ , are the surface area and the segment fractions, respectively, defined by

$$\theta'_i = \frac{q'_i w_i}{\sum_j q'_j w_j}; \quad \phi'_i = \frac{r'_i w_i}{\sum_j r'_j w_j} \quad (3)$$

where  $w$  is the mass fraction,  $r'$  is the van der Waals specific volume, and  $q'$  is the specific surface area of the molecule calculated from the sum of the van der Waals group volume,  $R_k$ , and surface area,  $Q_k$ , respectively,

$$r'_i = \frac{1}{M_i} \sum_k v_k^{(i)} R_k; \quad q'_i = \frac{1}{M_i} \sum_k v_k^{(i)} Q_k \quad (4)$$

where  $v_k^{(i)}$  is the number of groups of type  $k$  in molecule  $i$ . Group parameters  $R_k$  and  $Q_k$  are calculated by the method given by Bondi.<sup>8</sup>

The residual term of solvent activity,  $\ln a_1^R$ , is given by

$$\ln a_1^R = \sum_k v_k^{(1)} (\ln \Gamma_k - \ln \Gamma_k^{(1)}) \quad (5)$$

$$\ln \Gamma_k = Q_k \left[ 1 - \ln \left( \frac{\sum_m \theta'_m \psi_{mk}}{\sum_m \theta'_m \psi_{mm}} \right) - \sum_m \left( \frac{\theta'_m \psi_{km}}{\sum_m \theta'_m \psi_{mm}} \right) \right] \quad (6)$$

where  $\Gamma_k$  is the group residual activity,  $\Gamma_k^{(1)}$  is the group residual activity at a reference solution containing only of solvent molecules, and  $\theta'_m$  is the surface area fraction of group calculated in a manner similar to that for  $\theta'_i$ .

$$\theta'_m = \frac{Q_m W_m / M_m}{\sum_n Q_n W_n / M_n} \quad (7)$$

where  $W_m$  is the mass fraction of group  $m$  in the mixture. The group interaction parameter,  $\psi_{mn}$ , is given by

$$\psi_{mn} = \exp \left( \frac{a_{mn}}{T} \right) \quad (8)$$

where  $a_{mn}$  is the temperature-independent group interaction parameters evaluated from experimental VLE data of low molecular weight substances and  $T$  is the equilibrium temperature.

The free-volume term of solvent activity,  $\ln a_1^{FV}$ , is expressed by

$$\ln a_1^{FV} = 3c_1 \ln \left[ \frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}_M^{1/3} - 1} \right] - c_1 \left[ \left( \frac{\tilde{v}_1}{\tilde{v}_M} - 1 \right) \left( 1 - \frac{1}{\tilde{v}_1^{1/3}} \right)^{-1} \right] \quad (9)$$

The reduced volume of solvent,  $\tilde{v}_1$ , is given by

$$\tilde{v}_1 = \frac{v_1}{15.17br'_1} \quad (10)$$

where  $v_1$  is the specific volume. To simplify the calculation, the volume of liquid mixture was assumed to be additive. Then, the reduced volume for the mixture,  $\tilde{v}_M$ , is given by

$$\tilde{v}_M = \frac{v_1w_1 + v_2w_2}{15.17b(r'_1w_1 + r'_2w_2)} \quad (11)$$

The free-volume term contains two adjustable parameters ( $b$  and  $c_1$ ), where  $c_1$  is defined to be one-third the external degrees of freedom and set equal to 1.1, and  $b$  is a proportionality factor on the order to unity that was optimized. In that work, the authors used VLE data for 16 solvent-polymer systems and obtained a  $b$  value of 1.28.

The Entropic-FV model proposed by Elbro et al.<sup>4</sup> combines the combinatorial and free-volume effects that are both included in combinatorial-free-volume expression. For a binary mixture, the activity of solvent is

$$\ln a_1 = \ln a_1^{C+V} + \ln a_1^R \quad (12)$$

where the residual term of solvent activity,  $\ln a_1^R$ , is taken from the original UNIFAC model and superscript C+R denotes the combined term of combinatorial and free-volume contributions obtained from Flory-Huggins model with a free-volume fraction instead of volume fraction

$$\ln a_1^{C+V} = \ln \phi_1^{FV} + 1 - \frac{\phi_1^{FV}}{x_1} \quad (13)$$

The free volume fraction,  $\phi_1^{FV}$ , is given by

$$\phi_1^{FV} = \frac{w_1(v_1 - v_{w1})}{\sum_i w_i(v_i - v_{wi})} \quad (14)$$

where  $v_w$  is the van der Waals specific volume calculated by the method of Bondi.<sup>8</sup> In the original article,<sup>4</sup> the residual term of the UNIQUAC equation<sup>9</sup> was used for the residual term of the model and the molecular interaction parameters were determined from VLE data of low molecular weight systems. Kontogeorgis et al.<sup>10</sup> and Pappa et al.<sup>11</sup> evaluated this model for solvent-polymer systems by employing the UNIFAC residual term with its original group interaction parameters.

Both group contribution models considered here were obtained by accounting for the free-volume effect between solvent and polymer in different ways. Additionally, the models use the residual contribution of UNIFAC model with group interaction parameters

obtained from VLE data of low molecular weight substances. In our previous work,<sup>5</sup> revision of the parameters for the UNIFAC-FV model based on a large variety of VLE data for solvent-polymer systems could improve the prediction results.

#### PERFORMANCE OF ENTROPIC EXPRESSIONS OF UNIFAC-FV AND ENTROPIC-FV MODELS

Solvent-polymer systems in which the chemical structure of the solvent is similar to the repeating unit of the polymer can be expected to have interaction energies that are close to zero enthalpy of mixing. The systems in this category are called athermal systems and include systems such as solutions of hydrocarbons in polypropylene, polyethylene, and polyisobutylene. For these systems, it is apparent that the residual term of the UNIFAC-FV and Entropic-FV models do not contribute to the activity coefficient. Therefore, the entropic expressions of both models were evaluated against experimental data of the infinite dilution athermal systems determined from an inverse gas chromatographic method published elsewhere.<sup>12-23</sup> As reported by Lavoie and Guillet,<sup>24</sup> the relationship between solvent solubility in polymer and temperature exhibits surface adsorption at the experimental temperature lower than the glass transition temperature of the polymer for the case of amorphous polymers and lower than the melting temperature of the polymer in the case of crystalline polymer. This behavior was also investigated in our previous work.<sup>25</sup> Therefore, experimental data used in this work were selected carefully based on systems having an equilibrium temperature higher than the glass transition temperature for systems containing polyisobutylene and higher than the melting temperature of polymers for systems containing polypropylene and polyethylene.

The calculation of the free-volume contributions in the models above requires molar volumes for both solvent and polymer. If the experimental molar volumes are unavailable, then they will need to be estimated. For solvents, reliable molar volume estimation methods are available.<sup>26</sup> In this work, the HBT (Hankinson and Thomson<sup>27</sup>; Thomson et al.<sup>28</sup>) equation was used to calculate solvent molar volume. As shown in our previous work,<sup>5</sup> errors in polymer volume can have a large effect on activity calculations. For estimation of specific volume of polymers, the GCMCM model of Sato et al.<sup>29</sup> was shown to provide adequate estimations for a number of homopolymers, copolymers, and blended polymers. In this work, we adopted the GCMCM model for the estimation of polymer-specific volumes.

Prediction results of the UNIFAC-FV and Entropic-FV models for athermal infinite dilution VLE of solvent-polymer systems selected in this work are presented in Table I and are expressed as the average

**TABLE I**  
Average Absolute Deviation between Experimental and Predicted Solvent Activity Coefficient at Infinite Dilution Condition for Athermal Systems

Polymer <sup>a</sup>	Solvent	T [K]	N	AAD <sup>b</sup> (%)		Reference
				UNIFAC-FV	Entropic-FV	
PP	Pentane	448.2	1	14.4	50.9	12
	Hexane	448.2–498.2	3	26.6	27.1	12
	Heptane	448.2–523.2	4	25.0	17.8	12, 13
	Octane	448.2–523.2	4	22.7	8.8	12, 13
	Nonane	448.2–523.2	4	21.8	4.2	12, 13
	Decane	448.2–523.2	4	21.0	2.2	12, 13
	Dodecane	448.2–523.2	4	20.6	2.0	12
Overall for PP			24	21.7	16.1	
PE	Hexane	413.2–473.2	7	24.8	11.9	14, 15, 16
	Heptane	423.2–473.2	4	33.2	11.8	16, 17
	3-Methylhexane	418.3–425.8	3	20.2	6.5	18
	2-Methylheptane	418.3–425.8	3	24.4	6.4	18
	3-Methylheptane	418.3–425.8	2	25.7	8.7	18
	2,4-Dimethylhexane	418.3–425.8	9	18.3	14.1	18
	2,5-Dimethylhexane	418.3–425.8	3	27.5	2.4	18
	3,4-Dimethylhexane	418.3–425.8	3	20.6	4.6	18
	Octane	413.0–523.2	13	22.9	14.0	14, 15, 17, 18
	2,2,4-Trimethylpentane	418.3–425.8	3	25.8	11.0	18
	Nonane	408.2–448.2	6	8.1	27.5	17, 18
	Decane	418.3–448.2	9	7.5	26.8	17, 18, 19
	Dodecane	418.3–426.5	8	33.5	28.2	18, 19
	Overall for PE		73	22	5	13.4
PIB	Pentane	298.2–323.1	3	5.3	20.6	20, 21
	Cyclohexane	298.2–423.2	12	9.6	10.2	20, 21, 22, 23
	Hexane	298.2–423.2	10	10.5	13.0	20, 22, 23
	Heptane	298.2	1	9.4	22.0	20
	Octane	298.2	1	9.4	19.6	20
Overall for PIB			27	8.8	17.1	
Overall			124	19.6	14.9	

<sup>a</sup> PP = polypropylene; PE = polyethylene; PIB = polyisobutylene.

<sup>b</sup> AAD (%) =  $(100/N) \sum |\Omega_{1,\text{calcd}}^\infty - \Omega_{1,\text{exp}}^\infty| / \Omega_{1,\text{exp}}^\infty$ .

absolute deviation (AAD) between experimental and predicted solvent activity coefficients at infinite dilution condition ( $\Omega^\infty$ ). As the overall results, the performance of the Entropic-FV model was found to be better than the UNIFAC-FV model. This result agrees with those of Kouskoumvekaki et al.<sup>7</sup> However, for systems containing polyisobutylene, the UNIFAC-FV model had smaller AAD than the Entropic-FV model. This result agrees with our previous work using finite concentration VLE data.<sup>5</sup> Good performance of the UNIFAC-FV model for athermal systems containing polyisobutylene was also shown by Kontogeorgis et al.<sup>10</sup> Because the experimental uncertainty of infinite dilution data are often large and available reliable experimental data for athermal systems are limited, it is not easy to conclude whether the Entropic-FV model has better entropic expression at this point.

#### REVISED GROUP INTERACTION PARAMETERS FOR ENTROPIC-FV MODEL

In this work, group interaction parameters for the Entropic-FV model were revised by using a total of

142 of the latest VLE data for solvent–polymer systems at finite concentrations and at various temperatures. The data used were for 16 polymers and 36 solvents collected from polymer data collections of Wen et al.<sup>30</sup> and other literature.<sup>31–37</sup> All database were split up into three groups containing (1) alkane and cycloalkane, (2) aromatic, and (3) polar solvents, and each group had 32, 37, and 73 systems, respectively. The data sources, equilibrium temperature range, and numbers of data points were listed in Table II.

The group interaction parameters were optimized by using the following objective function,  $F$ , to be minimized

$$F = \sum_N \left( \frac{a_{1,\text{calcd}} - a_{1,\text{exp}}}{a_{1,\text{exp}}} \right)^2 \quad (15)$$

where  $N$  is the number of data points and subscripts calcd and exp denote the calculated and the experimental values, respectively. In optimization of group parameters, the original UNIFAC group interaction parameters of Hansen et al.<sup>38</sup> determined from the



**TABLE II**  
**Improvement of Prediction Results Obtained Using Group Contribution Models with Original and Revised Group Interaction Parameters (expressed as average absolute deviation of solvent activities)**

Polymer <sup>a</sup>	Solvent	T [K]	N	AAD <sup>b</sup> (%)				Reference, page
				UNIFAC-FV		Entropic-FV		
				(ori) <sup>c</sup>	(rev) <sup>c</sup>	(ori) <sup>c</sup>	(rev) <sup>c</sup>	
PI	Octane	293.2–353.2	32	33.5	28.5	26.3	4.2	[36]
PI	Cyclopentane	293.2–353.2	9	43.4	40.9	37.5	27.0	[36]
PI	Cyclohexane	293.2–353.2	31	24.4	20.9	17.8	3.2	[36]
PI	Cyclohexane	296.65	6	9.5	4.1	4.3	15.9	[32]
PIB	Propane	308.2	4	5.3	5.3	22.0	22.0	[30]
PIB(24)	Pentane	298.2	10	7.1	7.1	7.1	7.1	[30]
PIB(48)	Pentane	298.2	10	3.1	3.1	9.1	9.1	[30]
PIB	Pentane	298.2–308.2	30	13.9	13.9	18.7	18.7	[30]
PIB	Hexane	298.2–338.2	24	5.5	5.5	3.9	3.9	[30]
PIB	Octane	293.2–353.2	24	7.3	7.3	10.2	10.2	[36]
PIB	Octane	298.15	5	2.3	2.3	2.1	2.1	[30]
PIB	Isopentane	298.2–319.7	24	10.1	10.1	22.9	22.9	[30]
PIB	2-Methyl, propane	298.2–319.7	20	11.1	11.1	24.6	24.6	[30]
PIB	2,2-Dimethyl propane	298.2–319.7	10	18.2	18.2	28.8	28.8	[30]
PIB	Cyclopentane	293.2–353.2	15	6.9	6.9	7.4	7.4	[36]
PIB	Cyclohexane	293.2–353.2	26	6.3	6.3	7.2	7.2	[36]
PBMA	Octane	293.2–353.2	37	4.1	4.1	7.9	8.4	[36]
PBMA	Cyclopentane	293.2–353.2	33	9.6	9.6	13.1	13.5	[36]
PBMA	Cyclohexane	293.2–353.2	34	5.5	5.5	6.8	6.8	[36]
PVAc	Octane	313.2–353.2	30	34.1	34.1	33.7	34.1	[36]
PVAc	Cyclopentane	313.2–353.2	28	26.0	26.0	26.9	26.7	[36]
PVAc	Cyclohexane	313.2–353.2	26	13.2	13.2	21.1	19.4	[36]
PS	Nonane	423.2	7	10.8	10.8	29.4	30.1	[34]
PS	Cyclohexane	303.2–338.2	24	3.0	3.0	4.0	3.3	[30], 365,369,371
PDMS	Hexane	303	8	0.4	11.2	3.1	3.1	[30], 52
PDMS	Heptane	298.2–313.2	34	12.6	2.0	8.5	8.5	[30],65–67
PDMS	Octane	298.2–313.2	27	7.6	4.3	1.8	1.8	[30], 77–78
PDMS	Nonane	293.2–323.2	19	0.2	0.4	0.1	0.1	[30], 90–91
PDMS	2,2,4-Trimethyl Pentane	298.2–313.2	29	15.7	8.6	10.2	10.2	[30], 85–86
PBD	Hexane	296.7	4	10.7	0.4	16.3	3.8	[32]
PBD	Nonane	353.2–403.2	33	14.7	14.9	36.1	31.5	[30], 11–13
PBD	Cyclohexane	296.7	4	12.9	5.7	6.7	9.7	[32]
Overall for alkane and cycloalkane solvents				12.1	10.8	14.9	13.3	
PI	Benzene	293.2–353.2	25	13.5	18.3	12.5	29.9	[36]
PI	Benzene	283.2–353.2	29	32.6	37.7	35.2	45.7	[30], 252–257
PI	Toluene	293.2–353.2	27	21.7	7.7	17.8	15.7	[36]
PI	Toluene	296.7	4	5.0	18.9	3.8	17.5	[32]
PI	Ethyl benzene	293.2–353.2	27	15.2	10.0	13.5	16.5	[36]
PI	<i>p</i> -Xylene	293.2–353.2	32	22.5	24.3	19.9	25.8	[36]
PIB	Benzene	293.2–353.2	18	5.8	5.8	6.9	6.3	[36]
PIB	Benzene	296.7	29	3.0	3.0	3.6	2.6	[30], 205–207
PIB	Toluene	293.2–353.2	23	10.4	10.4	10.2	8.8	[36]
PIB	Ethyl benzene	293.2–353.2	20	13.3	13.3	11.5	10.7	[36]
PIB	<i>p</i> -Xylene	293.2–353.2	25	14.6	14.6	12.9	7.7	[36]
PBMA	Benzene	293.2–353.2	25	8.1	8.1	8.6	9.3	[36]
PBMA	Toluene	293.2–353.2	32	8.7	8.7	9.3	6.9	[36]
PBMA	Ethyl benzene	293.2–353.2	27	7.9	7.9	9.0	7.9	[36]
PBMA	<i>p</i> -Xylene	293.2–353.2	31	11.0	11.0	11.8	6.4	[36]
PVAc	Benzene	313.2–353.2	18	15.5	15.5	10.2	10.0	[36]
PVAc	Toluene	313.2–353.2	24	20.2	20.2	15.9	20.9	[36]
PVAc	Ethyl benzene	313.2–353.2	27	13.7	13.7	12.6	13.5	[36]
PVAc	<i>p</i> -Xylene	313.2–353.2	22	16.1	16.1	14.8	22.8	[36]
PS	Benzene	303.2–333.2	23	5.4	5.4	3.4	3.6	[30], 334–336 [30],
PS	Toluene	298.2–338.2	36	3.9	3.9	2.8	2.4	393,398,400,402
PS	Ethyl benzene	283.2–333.2	14	1.0	1.0	0.9	0.9	[30], 416–418

TABLE II Continued

Polymer <sup>a</sup>	Solvent	T [K]	N	AAD <sup>b</sup> (%)				Reference, page
				UNIFAC-FV		Entropic-FV		
				(ori) <sup>c</sup>	(rev) <sup>c</sup>	(ori) <sup>c</sup>	(rev) <sup>c</sup>	
PS	<i>p</i> -Xylene	403.2–448.2	22	15.6	15.6	8.0	2.9	[31]
PS	<i>m</i> -Xylene	403.2–448.2	22	16.3	16.3	8.8	2.9	[31]
PPO	Benzene	320.4–247.9	38	7.0	0.3	5.0	1.2	[30], 303–306
PMMA	Toluene	321.7	8	6.7	6.7	10.4	7.4	[30], 259
PEO	Benzene	318.9–343.2	18	1.96	7.6	1.03	2.66	[30],
PDMS	Benzene	298.2	33	6.2	3.8	3.8	2.4	133,135,136
PDMS	Toluene	298.2–313.2	23	1.5	3.6	4.6	1.8	[30], 30,33
PCS	Toluene	294.2	6	15.2	0.6	14.1	20.7	[30], 63–64
PBD	Benzene	296.7	5	14.0	7.5	21.3	13.3	[30], 15
PBD	Ethyl benzene	353.2–403.2	35	18.2	7.8	9.7	10.6	[32]
P $\alpha$ MS	$\alpha$ -Methyl styrene	338.2	9	3.3	1.5	1.1	1.0	[30], 8,9
P $\alpha$ MS	Isopropyl benzene	338.2	8	6.0	6.0	4.0	1.9	[30], 267
PH	Toluene	303.2	21	9.0	9.0	5.8	4.4	[30], 268
PDD	Toluene	303.2	20	15.9	15.9	11.8	9.9	[30], 172
PD	Toluene	303.2	17	6.3	6.3	3.2	4.9	[30], 95
Overall for aromatic solvents				11.1	10.4	9.7	10.3	[30], 16
PI	Dichloromethane	296.65	5	2.5	0.6	13.8	0.8	[32]
PI	Chloroform	296.65	6	22.2	2.5	32.4	3.8	[32]
PI	Tetrachloromethane	296.65	7	1.9	0.2	6.1	0.1	[32]
PI	Methanol	293.2–353.2	35	43.6	20.5	46.0	17.4	[37]
PI	Ethanol	293.2–353.2	40	44.0	10.8	23.9	18.3	[37]
PI	Propanol	293.2–353.2	34	21.1	24.6	28.8	26.7	[37]
PI	2-Propanol	293.2–353.2	39	15.8	25.5	24.3	20.2	[37]
PI	Butanol	293.2–353.2	38	41.8	4.8	12.5	29.9	[37]
PI	2-Butanol	293.2–353.2	37	25.7	17.6	22.0	29.6	[37]
PI	2-Methyl,1-propanol	293.2–353.2	30	30.1	13.1	24.0	21.3	[37]
PI	Acetone	293.2–353.2	38	13.6	19.2	19.5	15.2	[37]
PI	Acetone	273.2–298.2	9	24.9	7.6	19.5	16.2	[30], 246–247
PI	Methyl ethyl ketone	293.2–353.2	26	10.7	16.3	15.1	15.9	[37]
PI	Methyl ethyl ketone	298.2–318.2	18	9.3	5.7	6.4	1.6	[30], 248–249
PI	Methyl acetate	293.2–353.2	31	11.1	11.2	12.0	13.8	[37]
PI	Propyl acetate	293.2–353.2	30	11.7	7.0	9.1	8.8	[37]
PIB	Chloroform	293.2–353.2	5	15.8	0.3	8.9	6.4	[33]
PIB	Methanol	293.2–353.2	32	63.6	17.4	38.7	24.0	[37]
PIB	Ethanol	293.2–353.2	34	16.3	16.3	34.6	28.2	[37]
PIB	Propanol	293.2–353.2	31	20.0	20.0	16.8	19.7	[37]
PIB	2-Propanol	293.2–353.2	39	18.8	18.8	22.2	21.7	[37]
PIB	Butanol	293.2–353.2	39	16.5	16.5	19.5	18.1	[37]
PIB	2-Butanol	293.2–353.2	37	27.4	27.4	23.5	29.0	[37]
PIB	2-Methyl,1-propanol	293.2–353.2	35	19.1	19.1	21.7	22.3	[37]
PIB	Acetone	293.2–353.2	39	23.3	10.6	17.3	18.3	[37]
PIB	Methyl ethyl ketone	293.2–353.2	26	22.9	11.8	19.4	20.2	[37]
PIB	Methyl acetate	293.2–353.2	37	7.0	7.0	9.0	10.8	[37]
PIB	Propyl acetate	293.2–353.2	38	6.6	6.6	4.2	5.5	[37]
PBMA	Methanol	293.2–353.2	33	37.5	33.7	30.1	12.1	[37]
PBMA	Ethanol	293.2–353.2	32	18.0	18.1	29.9	30.1	[37]
PBMA	Propanol	293.2–353.2	27	14.3	15.7	17.8	18.8	[37]
PBMA	2-Propanol	293.2–353.2	39	10.5	13.3	13.5	14.2	[37]
PBMA	Butanol	293.2–353.2	39	9.3	11.3	10.9	11.4	[37]
PBMA	2-Butanol	293.2–353.2	36	17.3	13.8	16.5	17.1	[37]
PBMA	2-Methyl,1-propanol	293.2–353.2	34	16.9	9.3	13.8	14.3	[37]
PBMA	Acetone	293.2–353.2	28	16.8	12.3	18.4	17.4	[37]
PBMA	Methyl ethyl ketone	293.2–353.2	22	10.1	7.5	12.5	10.5	[37]
PBMA	Methyl acetate	293.2–353.2	37	1.9	1.9	3.8	6.3	[37]
PBMA	Propyl acetate	293.2–353.2	38	4.4	4.4	4.7	5.0	[37]
PVAc	Methanol	313.2–353.2	29	17.4	20.7	18.1	8.3	[37]
PVAc	Ethanol	313.2–353.2	24	43.0	6.4	9.6	10.6	[37]
PVAc	Propanol	313.2–353.2	20	33.5	8.7	11.6	11.3	[37]
PVAc	2-Propanol	313.2–353.2	28	21.1	13.9	11.3	11.2	[37]
PVAc	Butanol	313.2–353.2	28	26.1	9.3	10.8	9.4	[37]

TABLE II Continued

Polymer <sup>a</sup>	Solvent	T [K]	N	AAD <sup>b</sup> (%)				Reference, page
				UNIFAC-FV		Entropic-FV		
				(ori) <sup>c</sup>	(rev) <sup>c</sup>	(ori) <sup>c</sup>	(rev) <sup>c</sup>	
PVAc	2-Butanol	313.2–353.2	23	38.0	16.1	27.4	24.5	[37]
PVAc	2-Methyl,1-propanol	313.2–353.2	23	42.8	10.9	16.1	15.1	[37]
PVAc	Acetone	313.2–353.2	20	6.5	3.7	11.2	7.0	[37]
PVAc	Methyl ethyl ketone	313.2–353.2	15	5.6	4.2	8.4	7.3	[37]
PVAc	Methyl acetate	313.2–353.2	20	3.7	3.7	2.9	5.1	[37]
PVAc	Propyl acetate	313.2–353.2	24	7.5	7.5	6.3	6.6	[37]
PS	Chloroform	298.2–323.2	23	3.0	2.2	8.1	2.7	[30], 310,314
PS	Tetrachloro methane	293.2	14	22.8	1.4	8.7	1.0	[30], 309
PS	Acetone	298.2–323.2	15	9.3	10.9	17.9	6.7	[30], 316–317
PS	Methyl ethyl ketone	321.7–343.2	38	2.7	4.1	11.9	2.8	[30], 319,322,323
PS	Propyl acetate	298.2–343.2	19	2.2	2.2	18.0	16.6	[30], 329,330
PS	Dipropyl ether	293.2	10	17.9	27.9	33.6	40.3	[30], 392
PS	Diethyl ketone	293.2	22	27.4	20.4	39.2	17.0	[30], 327–328
PS	Buthyl acetate	283.2–363.2	43	1.8	1.8	2.0	2.3	[30], 387,391
PS	Buthyl acetate	293.2	9	20.2	20.2	37.7	34.3	[30], 386
PPO	Methanol	248.2–298.2	80	5.4	3.8	5.1	6.7	[30], 283–302
PPO	Water	303.2–323.2	12	77.6	19.9	43.8	21.1	[30], 307–308
PMMA	Methyl ethyl ketone	321.7	8	6.9	6.6	8.0	10.4	[30], 258
PEO	Chloroform	298.2	11	34.4	34.2	33.4	37.1	[30], 126
PEO	Water	293.1–338.2	58	97.6	8.0	20.7	5.8	[30], 145–149
PE	Chlorobenzene	403.2–413.2	13	9.31	1.63	18.48	2.49	[35]
PDMS	Dichloromethane	303	8	50.9	0.1	51.1	1.2	[30], 18
PDMS	Chloroform	303	8	47.5	0.9	46.7	0.3	[30], 17
PDMS	Methyl ethyl ketone	303.2–323.2	15	0.6	0.5	1.1	0.4	[30], 19–24
PDMS	Methyl ethyl ketone	303.15	18	2.5	0.4	6.4	0.4	[30], 25–27
PDMS	4-Methyl pentanone	293.2–308.2	11	6.5	6.8	3.0	2.1	[30], 46,47
PDMS	2,6-Dimethyl,4-heptanone	308.2	6	0.2	0.2	0.4	0.4	[30], 89
PBD	Dichloromethane	296.7	5	13.0	0.2	17.6	0.4	[32]
PBD	Chloroform	273.2–298.2	11	12.9	6.6	18.1	0.2	[30], 4,5
Overall for polar solvents				20.0	10.8	17.9	13.0	
Overall				15.9	10.7	15.1	12.4	

<sup>a</sup> PI = polyisoprene; PIB = polyisobutylene; PBMA = poly(*n*-butyl methacrylate); PVAc = poly(vinyl acetate); PE = polyethylene; PH = polyheptene-1; PD = polydecene-1; PDD = polydodecene-1; PS = polystyrene; PαMS = poly(α-methyl styrene); PBD = polybutadiene; PEO = poly(ethylene oxide); PPO = poly(propylene oxide); PMMA = poly(methyl methacrylate); PCS = poly(4-chloro styrene); PDMS = poly(dimethyl siloxane).

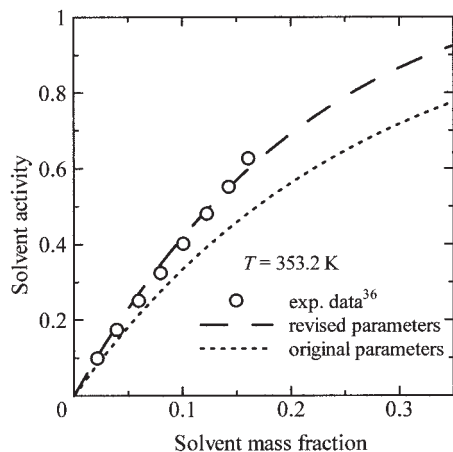
<sup>b</sup> AAD (%) =  $(100/N) \sum |a_{j,calcd} - a_{j,exp}| / a_{j,exp}$ .

<sup>c</sup> (ori) original group interaction parameters; (rev) revised group interaction parameters obtained in this work for Entropic-FV model and revised group interaction parameters obtained in the previous work<sup>5</sup> for UNIFAC-FV model.

TABLE III  
Group Interaction Parameters,  $a_{mn}$  [K] Obtained in this Work for the Entropic-FV Model

Main group	1	2	3	4	5	6	7	9	11	13	22	23	24	25	43	
CH <sub>3</sub> , CH <sub>2</sub> , CH, C	1	0.00	870.79	160.99	-92.10	1011.44	776.59	—	619.79	251.40	251.50 <sup>a</sup>	5.22	429.54	104.31 <sup>a</sup>	303.06	252.70 <sup>a</sup>
CH <sub>2</sub> =, CH, CH=CH	2	-298.73	0.00	38.81 <sup>a</sup>	387.08	723.26	452.31	—	369.38	247.55	—	-209.86	-176.46	-60.68	—	—
ACH, AC	3	-85.62	3.45 <sup>a</sup>	0.00	-235.83	—	—	—	334.22	5.99 <sup>a</sup>	-197.13	—	-227.82	38.43	538.20	123.25
ACCH <sub>3</sub> , ACCH <sub>2</sub> , ACCH	4	230.75	1304.31	2005.57	0.00	—	—	—	335.17	5688.00 <sup>a</sup>	213.10 <sup>a</sup>	—	-12.14	37.49	0.00	355.50 <sup>a</sup>
OH	5	143.35	220.50	—	—	0.00	—	—	—	27.89	—	—	—	—	—	—
CH <sub>3</sub> OH	6	-113.60	241.49	—	—	—	0.00	—	—	-10.72 <sup>a</sup>	349.03	—	—	—	—	—
H <sub>2</sub> O	7	—	—	—	—	—	—	0.00	—	—	-92.02	—	—	—	—	—
CH <sub>3</sub> CO, CH <sub>2</sub> CO	9	-139.78	-0.84	-61.40	-287.86	—	—	—	0.00	-95.18	—	—	—	—	—	260.98
CH <sub>3</sub> COO, CH <sub>2</sub> COO	11	90.14	109.64	85.84 <sup>a</sup>	-170.00 <sup>a</sup>	285.33	249.60 <sup>a</sup>	—	145.01	0.00	—	—	—	—	—	—
CH <sub>2</sub> O	13	83.36 <sup>a</sup>	—	478.88	65.69 <sup>a</sup>	—	-396.71	256.50	—	—	0.00	—	-154.30 <sup>a</sup>	—	—	—
CH <sub>2</sub> Cl <sub>2</sub>	22	255.82	169.42	—	—	—	—	—	—	—	0.00	—	—	—	—	192.75
CHCl <sub>3</sub>	23	-218.37	239.55	374.07	33.61	—	—	—	—	—	-20.93 <sup>a</sup>	—	0.00	—	—	829.47
CCl <sub>4</sub>	24	-78.45 <sup>a</sup>	89.05	33.46	-259.92	—	—	—	—	—	—	—	—	0.00	—	—
ACCl	25	-227.43	—	-237.70	0.00	—	—	—	—	—	—	—	—	—	0.00	—
SiO	43	110.20 <sup>a</sup>	—	367.10	221.80 <sup>a</sup>	—	—	—	137.31	—	—	-77.81	56.00	—	—	0.00

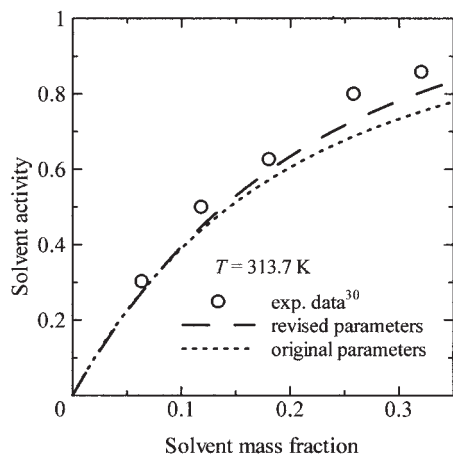
<sup>a</sup> The value obtained in this work is the same value as the original one.



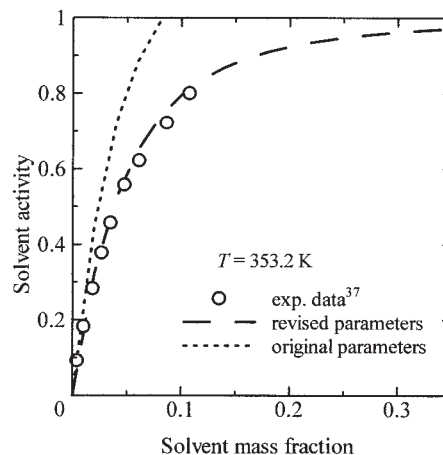
**Figure 1** Experimental and predicted activities by the Entropic-FV model with original and revised group interaction parameters for cyclohexane-polyisoprene system.

VLE data of low molecular weight substances were used as initial values whenever possible. A total 46 pairs of group interaction parameters obtained in this work is presented in Table III, wherein 10 pairs of the parameters were found to have the same values as original UNIFAC parameters.

Table II also shows AAD between experimental and calculated solvent activities by the Entropic-FV model with original and revised group interaction parameters obtained in this work. This table also presents the results of the UNIFAC-FV model using original and revised group interaction parameters reported previously.<sup>5</sup> The overall AAD were calculated by assigning the same weight to each system. For systems containing aromatic solvents, both models with original group interaction parameters gave the best prediction results. Errors were highest for systems containing polar solvents wherein the residual term of the En-



**Figure 2** Experimental and predicted activities by the Entropic-FV model with original and revised group interaction parameters for toluene-poly(methyl methacrylate) system.



**Figure 3** Experimental and predicted activities by Entropic-FV model with original and revised group interaction parameters for methanol-poly(*n*-butyl methacrylate) system.

tropic-FV model are often overestimates of solvent activities. Revised group interaction parameters for the Entropic-FV model obtained in this work gave insignificant improvements for systems containing aromatic solvents because the results with the original parameters have achieved the error in the limit of experimental uncertainties. The highest improvements were achieved for systems containing polar solvents from 17.9 to 13.0% AAD. In the overall results, the improvements of AAD were achieved from 15.1 to 12.4%. Figures 1–3 present three examples of plots of the solvent activities versus solvent mass fraction calculated from the original and revised parameter sets for each type of solvent. From the figures, it can be seen that the greatest improvements were for the systems containing polar solvents. As shown in Table III, the improvements of the Entropic-FV model were lower than those of UNIFAC-FV model with revised parameters obtained in the previous work.<sup>5</sup> The improvement of Entropic-FV with the revised parameters, however, must be considered comparable to those of the UNIFAC-FV model with revised parameters, considering uncertainties of experimental VLE data for solvent-polymer systems.

## CONCLUSION

UNIFAC group interaction parameters were revised for the Entropic-FV model based on VLE data of solvent-polymer systems over a wide concentration range. Significant improvements were achieved by the Entropic-FV model with revised parameters from 17.9 to 13.0% AAD for systems containing polar solvents and from 15.1 to 12.4% AAD for all system studied. These results were comparable to those of the UNI-



FAC-FV model with revised parameters obtained in the previous work.<sup>5</sup>

## References

1. Chen, C. C.; Mathias, P. M. *AIChE J* 2002, 48, 194.
2. Fredenslund, A.; Jones, R. L.; Prausnitz, J. M. *AIChE J* 1975, 21, 1085.
3. Oishi, T.; Prausnitz, J. M. *Ind Eng Chem Process Des Dev* 1978, 17, 333.
4. Elbro, H. S.; Fredenslund, A.; Rasmussen, P. *Macromolecules* 1990, 23, 4707.
5. Wibawa, G.; Takishima, S.; Sato, Y.; Masuoka, H. *Fluid Phase Equilib* 2002, 202, 367.
6. Lindvig, T.; Hestkjaer, L. L.; Hansen, A. F.; Michelsen, M. L.; Kontogeorgis, G. M. *Fluid Phase Equilib* 2002, 194–197, 663.
7. Kouskoumvekaki, I. A.; Michelsen, M. L.; Kontogeorgis, G. M. *Fluid Phase Equilib* 2002, 202, 325.
8. Bondi, A. *Physical Properties of Crystals, Liquids and Glasses*; John Wiley & Sons: New York, 1968.
9. Abrams, D. S.; Prausnitz, J. M. *AIChE J* 1975, 21, 116.
10. Kontogeorgis, G. M.; Fredenslund, A.; Tassios, D. P. *Ind Eng Chem Res* 1993, 32, 362.
11. Pappa, G. D.; Voutsas, E. C.; Tassios, D. P. *Ind Eng Chem Res* 1999, 38, 4975.
12. Ohzono, M.; Iwai, Y.; Arai, Y. *Kagaku Kogaku Ronbunshu* 1984, 10, 536.
13. Munk, P.; Hattam, P.; Du, Q.; Abdel-Azim, A. A. *J Appl Polym Sci, Appl Polym Symp* 1990, 45, 289.
14. Varsano, J. L.; Gilbert, S. G. *J Pharm Sci* 1973, 62, 87.
15. Maloney, D. P.; Prausnitz, J. M. *AIChE J* 1976, 22, 74.
16. Ferreira, N. M. S.; Nobrega, R.; D'Avila, S. G. *Rev Brasil Tecnol* 1979, 10, 55.
17. Tseng, H. -S.; Lloyd, D. R.; Ward, T. C. *J Appl Polym Sci* 1985, 30, 1815.
18. Schreiber, H. P.; Tewari, Y. B.; Patterson, D. *J Polym Sci, Polym Phys Ed* 1973, 11, 15.
19. Braun, J. -M.; Cutajar, M.; Guillet, J. E.; Schreiber, H. P.; Patterson, D. *Macromolecules* 1977, 10, 864.
20. Price, G. J.; Guillet, J. E.; Purnell, J. H. *J Chromatogr* 1986, 369, 273.
21. Oener, M.; Dincer, S. *Polymer* 1987, 28, 279.
22. Newman, R. D.; Prausnitz, J. M. *AIChE J* 1974, 20, 206.
23. Lichtenthaler, R. N.; Liu, D. D.; Prausnitz, J. M. *Macromolecules* 1974, 7, 565.
24. Lavoie A.; Guillet, J. E. *Macromolecules* 1969, 2, 443.
25. Takishima, S.; Wibawa, G.; Sato, Y.; Masuoka, H. *Fluid Phase Equilib* 2003, 211, 241.
26. Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *The Properties of Gases and Liquids*, 5th ed; McGraw-Hill: New York, 2001, pp. 4.33–4.46, 8.78–8.93.
27. Hankinson, R. W.; Thomson, G. H. *AIChE J* 1979, 25, 653.
28. Thomson, G. H.; Brobst, K. R.; Hankinson, R. W. *AIChE J* 1982, 28, 671.
29. Sato, Y.; Hashiguchi, H.; Takishima, S.; Masuoka, H. *Fluid Phase Equilib* 1998, 144, 427.
30. Wen, H.; Elbro, H. S.; Alessi, P. *Polymer Solution Data Collection, Part 1: Vapor-Liquid Equilibrium*; DECHEMA Chemistry Data Series, Frankfurt am Main, Germany, 1992.
31. Bonner, D. C.; Prausnitz, J. M. *J Polym Sci, Polym Phys Ed* 1974, 12, 51.
32. Saeki, S.; Holste, J. C.; Bonner, D. C. *J Polym Sci, Polym, Phys Ed* 1982, 20, 793.
33. Saeki, S.; Holste, J. C.; Bonner, D. C. *J Polym Sci, Polym Phys Ed* 1982, 20, 805.
34. Iwai Y.; Arai, Y. *J Chem Eng Jpn* 1989, 22, 155.
35. Wohlfarth, Ch. *Plaste Kautschuk* 1993, 40, 272.
36. Wibawa, G.; Takahashi, M.; Sato, Y.; Takishima, S.; Masuoka, H. *J Chem Eng Data* 2002, 47, 518.
37. Wibawa, G.; Hatano, R.; Sato, Y.; Takishima, S.; Masuoka, H. *J Chem Eng Data* 2002, 47, 1022.
38. Hansen, H. K.; Rasmussen, P.; Fredenslund, A.; Schiller, M.; Gmehling, J. M. *Ind Eng Chem Res* 1991, 30, 2352.