

## Group Contribution Method for Group Contribution Method for Estimation of Vapor Liquid Equilibria in Polymer Solutions

Suk Yung Oh and Young Chan Bae\*

Division of Chemical Engineering and Molecular Thermodynamics Lab., Hanyang University, Seoul 133-791, Korea

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**Abstract:** This study introduces a specified group-contribution method for predicting the phase equilibria in polymer solutions. The method is based on a modified double lattice model developed previously. The proposed model includes a combinatorial energy contribution that is responsible for the revised Flory-Huggins entropy of mixing, the van der Waals energy contribution from dispersion, a polar force and specific energy contribution. Using the group-interaction parameters obtained from data reduction, the solvent activities for a large variety of mixtures of polymers and solvents over a wide range of temperatures can be predicted with good accuracy. This method is simple but provides improved predictions compared to those of the other group contribution methods.

**Keywords:** modified double lattice model, group contribution method, vapor liquid equilibria, solvent activity.

### Introduction

Problems related to the thermodynamics of polymer solutions and blends can be encountered in a broad range of industrial processes. Nevertheless, data for evaluating the thermodynamic behavior of these systems are very scarce. Therefore, a method for extrapolating the more abundant information available for mixtures of low molar mass compounds into the area of mixtures with polymers is an attractive option. The basic purpose of group-contribution methods is to utilize existing phase equilibrium data to predict the phase behaviors of systems for which no data are available.

The most well-known and convenient model, UNIFAC was developed by Fredenslund *et al.*<sup>1</sup> It is based on Guggenheim's quasi-chemical theory and contains two parts: a combinatorial part, due to differences in the size and shape of the molecules in the mixture, and a residual part, due to energy interactions. UNIFAC has been successfully used for the design of industrial application areas. However, when compared with experimental data, the UNIFAC model shows some deficiencies.

The UNIFAC model was extended to polymer solutions by Oishi and Prausnitz.<sup>2</sup> The modified UNIFAC model by providing a free-volume correction, as suggested by Flory's EOS theory, can estimate VLE for polymer solutions. Later, several variations of the UNIFAC model were developed by Voutsas and Tassios,<sup>3</sup> Mollmann and Gmehling,<sup>4</sup> Zhang *et*

*al.*,<sup>5</sup> Magnussen *et al.*,<sup>6</sup> Gupta and Danner<sup>7</sup> and Hooper *et al.*<sup>8</sup>

Gmehling *et al.*<sup>9-12</sup> developed a group-contribution EOS model, based on the Soave-Redlich-Kwong EOS and predicted gas-solubility and VLE at various pressures.

Holten-Anderson *et al.*<sup>13</sup> gave another extension, based on perturbed-hard-chain theory, and obtained the free-volume contribution from EOS. In addition, the equation has a free-volume term from the correct ideal gas limit and an attractive term, that takes into account both random intermolecular orientations and favored intermolecular configurations.

Fei Chen *et al.*<sup>14</sup> presented a group contribution extension of a slightly modified form of the Flory equation. The equation is similar to, but simpler than, the Holten-Andersen model.

Elbro *et al.*<sup>15</sup> proposed to include free volume contributions to solvent activities in polymer solutions using a generalized van der Waals partition function.

At present all of the published group contribution models provide good estimates of solvent activities for those polymer/solvent systems where the polymer is readily soluble and where both components are nonpolar or weakly polar. If strong oriented interactions from hydrogen bonding or other specific forces exist in the system, modifications with specific interactions are often required. Recently, Hu *et al.*<sup>16</sup> presented a new group contribution method, that contains a revised Flory-Huggins entropy and a series expression for excess internal energy, as well as a double lattice model to account for oriented interactions. They included parameters for cross specific interaction

\*Corresponding Author. E-mail: ycbae@hanyang.ac.kr

energy from hydrogen bonding between the polymer and solvent segments.

In this study, we propose a group contribution model that can be used to predict the solvent activities of polymer solutions. The proposed model is based on a modified double lattice model where 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.** The framework of the lattice model starts with a simple cubic lattice (coordination number  $z=6$ ) containing  $N_r$  sites. For systems (two different polymer chains, polymer/solvent systems *etc.*) that interact strongly, they must be in the correct orientation to each other, *i.e.* a specific interaction. Ordinary polymer solutions are described by the primary lattice, while a secondary lattice is introduced as a perturbation to account for oriented interactions.

**Primary Lattice:** The general form of the Helmholtz energy of mixing, based on Freed's theory,<sup>17-19</sup> can be expressed as follows:

$$\frac{\Delta A}{N_r kT} = \left(\frac{\phi_1}{r_1}\right) \ln \phi_1 + \left(\frac{\phi_2}{r_2}\right) \ln \phi_2 + \sum_m \sum_n a_{mn} \phi_1^m \phi_2^n \quad (1)$$

where  $N_r$  is the total number of lattice sites (coordination number  $z=6$ ),  $k$  is the Boltzmann constant,  $r_i$  is the chain length and  $\phi_i$  is the volume fraction of component  $i$ . The subscripts 1 and 2 refer to the solvent and polymer, respectively.  $a_{mn}$  is a function of the  $z$ ,  $r_1$  and  $r_2$ , and energy parameters. To obtain an analytically simple expression for the Helmholtz energy of mixing for the primary lattice, Oh *et al.*<sup>21</sup> modified Hu *et al.*<sup>20</sup>'s expressions for  $a_{mn}$  in the form of the Flory-Huggins theory. This expression is

$$\frac{\Delta A}{N_r kT} = \left(\frac{\phi_1}{r_1}\right) \ln \phi_1 + \left(\frac{\phi_2}{r_2}\right) \ln \phi_2 + \chi_{OB} \phi_1 \phi_2 \quad (2)$$

$\chi_{OB}$  is a new interaction parameter defined by

$$\chi_{OB} = C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1}\right)^2 + \left(2 + \frac{1}{r_2}\right) \tilde{\varepsilon} - \left(\frac{1}{r_2} - \frac{1}{r_1} + C_\gamma \tilde{\varepsilon}\right) \tilde{\varepsilon} \phi_2 + C_\gamma \tilde{\varepsilon}^2 \phi_2^2 \quad (3)$$

where  $C_\beta$  and  $C_\gamma$  are universal constants. These constants are obtained through fitting to the simulation data.<sup>22</sup> The best-fit values of  $C_\beta$  and  $C_\gamma$  are 0.1415 and 1.7986, respectively.

$\tilde{\varepsilon}$  is a reduced interaction energy parameter given by

$$\tilde{\varepsilon} = \frac{\varepsilon}{kT} = \frac{\varepsilon_{11} + \varepsilon_{22} - 2\varepsilon_{12}}{kT} \quad (4)$$

where  $\varepsilon_{11}$ ,  $\varepsilon_{22}$  and  $\varepsilon_{12}$  are for the corresponding nearest neighbor segment-segment interactions. In the lattice model, the chain length ( $r_i$ ) is usually used for the fitting parameter, but in this work, to keep reasonability and to remove the fitting parameter, we use a simple calculation method as follows:

$$r_i = \frac{V_{mi(vdW)}}{10.23 \text{ cm}^3/\text{mol}} \quad (5)$$

where the constant 10.23 cm<sup>3</sup>/mol is the molar *vdW* volume of a CH<sub>2</sub> group from van Krevelen<sup>23</sup> and  $V_{mi(vdW)}$  is the molar *vdW* volume of component  $i$ . In our model, the group-contribution concept is considered in order to calculate the chain length contrary to that of the existing modified double lattice model.

**Secondary Lattice:** To improve the mathematical approximation defect and to reduce the number of parameters, a new Helmholtz energy of mixing as the fractional form is defined.<sup>21</sup> The expression is given by

$$\frac{\Delta A_{sec,ij}}{N_{ij} kT} = \frac{2}{z} \left[ \eta \ln \eta + (1-\eta) \ln(1-\eta) + \frac{z C_\alpha \delta \tilde{\varepsilon}_{ij} (1-\eta) \eta}{1 + C_\alpha \delta \tilde{\varepsilon}_{ij} (1-\eta) \eta} \right] \quad (6)$$

where  $\Delta A_{sec,ij}$  is the Helmholtz energy of mixing of the secondary lattice for  $i$ - $j$  segment-segment pairs and  $N_{ij}$  is the number of  $i$ - $j$  pairs,  $\delta \tilde{\varepsilon}$  is the reduced energy parameter contributed by the oriented interactions and  $\eta$  is the surface fraction permitting oriented interactions. For simplicity, we arbitrarily set  $\eta$  to 0.3 as suggested by Hu *et al.*<sup>20</sup>  $C_\alpha$  is a universal constant that is determined by comparing with the Gibbs-ensemble Monte Carlo simulation data of the Ising lattice from Panagiotopolus *et al.*<sup>24</sup> The best-fit value of  $C_\alpha$  is 0.4881.

**Incorporation of Secondary Lattice Into Primary Lattice:** To incorporate a secondary lattice, we replace  $\varepsilon_{ij}$  by  $\varepsilon_{ij} - \Delta A_{sec,ij}/N_{ij}$  in eq. (4). If oriented interaction occurs in the  $i$ - $j$  segment - segment pairs, we replace  $\tilde{\varepsilon}$  by  $\varepsilon/kT + 2\Delta A_{sec,ij}/N_{ij}kT$  in eq. (4). If oriented interaction occurs in the  $i$ - $i$  segment - segment pairs, we replace  $\tilde{\varepsilon}$  by  $\varepsilon/kT - \Delta A_{sec,ii}/N_{ii}kT$ . In this study, we assume the oriented interaction occurs in the  $i$ - $i$ ,  $j$ - $j$ , and  $i$ - $j$  segment-segment pairs. We replace  $\tilde{\varepsilon}$  by

$$\varepsilon_{12} = (\varepsilon_{11}^* + \varepsilon_{22}^* - 2\varepsilon_{12}^*) + \left( -\frac{\Delta A_{sec,11}}{N_{11}} - \frac{\Delta A_{sec,22}}{N_{22}} + \frac{2\Delta A_{sec,12}}{N_{12}} \right) \quad (7)$$

where  $\varepsilon_{11}^*$ ,  $\varepsilon_{22}^*$ , and  $\varepsilon_{12}^*$  are the van der Waals energy interaction parameters and  $\Delta A_{sec,11}$ ,  $\Delta A_{sec,22}$  and  $\Delta A_{sec,12}$  are the additional Helmholtz functions for the corresponding secondary lattice. Eq. (7) then becomes

$$\tilde{\varepsilon} = \frac{\varepsilon_{11}^* + \varepsilon_{22}^* - 2\varepsilon_{12}^*}{kT} - 2C_\alpha(1-\eta)\eta$$

$$\left[ \frac{\frac{\delta\varepsilon_{11}}{kT}}{1 + C_\alpha \frac{\delta\varepsilon_{11}}{kT}(1-\eta)\eta} + \frac{\frac{\delta\varepsilon_{22}}{kT}}{1 + C_\alpha \frac{\delta\varepsilon_{22}}{kT}(1-\eta)\eta} - \frac{2\frac{\delta\varepsilon_{12}}{kT}}{1 + C_\alpha \frac{\delta\varepsilon_{12}}{kT}(1-\eta)\eta} \right]$$
(8)

In a binary mixture, the activity of solvent 1 in polymer 2 is

$$\ln a_1 = \ln \phi_1 - r_1 \left( \frac{1}{r_2} - \frac{1}{r_1} \right) \phi_2 +$$

$$r_1 \left[ C_\beta \left( \frac{1}{r_2} - \frac{1}{r_1} \right)^2 + \left( \frac{1}{r_2} - \frac{1}{r_1} + C_\gamma \tilde{\varepsilon} \right) \tilde{\varepsilon} + \left( 2 + \frac{1}{r_2} \right) \tilde{\varepsilon}^2 \right] \phi_2^2$$

$$- 2r_1 \left[ \left( \frac{1}{r_2} - \frac{1}{r_1} + C_\gamma \tilde{\varepsilon} \right) \tilde{\varepsilon} + C_\gamma \tilde{\varepsilon}^2 \right] \phi_2^3 + 3r_1 C_\gamma \tilde{\varepsilon}^2 \phi_2^4$$
(9)

**Van der Waals Energy Contribution.** The energy parameter  $\varepsilon_{ij}^*$  in eq. (7) is due to van der Waals forces (dispersion and polar forces). For the pure component  $i$ ,  $\varepsilon_{ii}^*$  can be estimated using the square of the pure-component van der Waals solubility parameter of Hansen (Barton),<sup>25</sup> which is the sum of the dispersion contribution and a polar contribution:  $\delta_{vdw}^2 = \delta_d^2 + \delta_p^2$ .

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

where  $N_A$  is the Avogadro number and where  $\delta_{vdw}^2$  and  $V_{mi}$  are at 25 °C. For a pure component, the effect of temperature on  $\varepsilon_{ii}^*$  is given by:

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

where  $V_{mi}$  depends on temperature. The temperature -independent parameter  $\varepsilon_{ii}^+$  can be estimated by

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

The cross interaction van der Waals energy parameter  $\varepsilon_{ij}^*$  is estimated by the geometric mean of the corresponding pure-component parameters:

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

**Specific Energy Contribution.** The Hilderbrand parameters are calculated by using group molar volumes.<sup>23</sup> This method requires knowledge of chemical structure, without the molar volume (or density), but it is applicable only at 25 °C.

$$\delta = -\left(\frac{U}{V}\right)^{1/2} = -\left(\frac{\sum_z U}{\sum_z V}\right)^{1/2} \quad (14)$$

Hansen and Beerbower have assumed that hydrogen bonding cohesive energy is additive, leading to

$$\delta_h = \left(\sum_z -\frac{U_h}{V}\right)^{1/2} \quad (15)$$

In this study, to obtain the pure-component parameter  $\delta\varepsilon_{ij}$ , we use Hansen's hydrogen-bonding solubility parameter,  $\delta_h$ . It is related to the additional specific energy  $\Delta U_{sec,ii}$  by

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

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

$$\Delta U_{sec,ii} = \frac{\Delta U_{sec,ii}^+}{V_{mi}} \quad (17)$$

where  $\Delta U_{sec,ii}^+$  is independent of temperature. From eqs. (16) and (17), we get

$$\Delta U_{sec,ii}(T) = -\frac{\delta_h^2 V_{mi}^2(25^\circ\text{C})}{V_{mi}(T)} \quad (18)$$

for the pure component  $i$ , upon inserting eq. (6) into the thermodynamic relation  $[\partial(\Delta A/T)/\partial(1/T)] = \Delta U$ , we have

$$\frac{\Delta U_{sec,ii}}{k} = \frac{N_i r_i z C_\alpha (1-\eta) \eta \left(\frac{\delta\varepsilon_{ii}}{k}\right)}{\left[1 + C_\alpha \frac{\delta\varepsilon_{ii}}{kT}(1-\eta)\eta\right]^2} \quad (19)$$

The cross specific energy parameter  $\delta\varepsilon_{ij}$  is calculated from pair-interaction group parameters

$$\frac{\delta\varepsilon_{ij}}{k} = \sum_{m=1}^{N_s} \sum_{n=1}^{N_p} \phi_m \phi_n g_{mn} \quad (20)$$

where  $N_s$  and  $N_p$  are the number of groups in solvents and polymers, respectively.  $\phi_m$  and  $\phi_n$  are volume fractions of group  $m$  in a solvent and that of group  $n$  in a polymer, respectively;  $g_{mn}$  are 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 of a solvent. In this study, they are estimated by fitting experimental vapor-liquid equilibria data of polymer solutions.<sup>26</sup>

Using the parameter  $g_{mn}$ , this double lattice-based group contribution model can predict VLE of polymer solutions without adjustable parameters. It means the proposed model

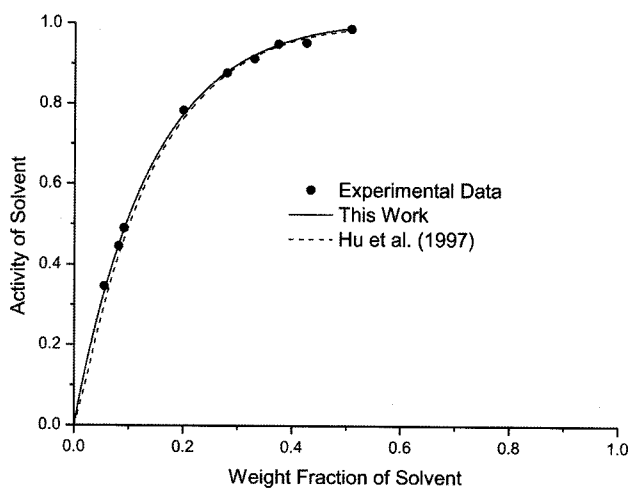
can predict the phase equilibrium of systems which have no experimental data.

## Results and Discussion

The proposed model contains two basic assumptions. Firstly, various flexibilities of the polymer chain are neglected. All polymers have the same flexibility and solvent molecules are considered to be monomers where the concept of flexibility does not apply. Secondly, the energy parameters and the size parameters are independent of volume change of mixing and free volume, that is, incompressible. The advantage of this model is taking into account oriented interactions as well as its simplicity.

Figure 1 shows a comparison with activities of a polystyrene ( $M_w=1.03 \times 10^4$ )/2-butanone system at 321.65 K calculated by Hu *et al.*<sup>16</sup> with that of this work. The solid line indicates this work and the dashed line is from Hu *et al.*<sup>16</sup> Dark circles are experimental data reported by Wen *et al.*<sup>26</sup> Both models give fairly good agreement with experimental results. However, Hu *et al.*'s Model<sup>16</sup> needs 27 model parameters and the proposed model requires only 9 parameters. All parameters are listed in Table I.

To establish the group-contribution method, the most significant role is to determine the cross pair interaction between polymer and solvent segments. To determine the group interaction parameters, we correlate the experimental VLE data. Table II shows results and comparison for the absolute average deviation (AAD) and mean deviation (Mean Dev.) of calculated solvent activities of all systems among Hu *et al.*'s,<sup>16</sup> UNIQUAC<sup>27</sup> and this work. All the models give fairly good agreement with experimental results. However, the number of parameters needed in this work is one third less than that of Hu *et al.*'s, and this work is somewhat more universal than the



**Figure 1.** Calculated and experimental activities of 2-butanone in polystyrene ( $M_w=1.03 \times 10^4$ ) at 321.65 K.

**Table I. Group Interaction Parameters of PS ( $M_w=1.03 \times 10^4$ )/2-Butanone System at 321.65 K ( $g_{mn(1)}/K$ ,  $10^{-3} g_{mn(2)}/K^2$ ,  $10^{-6} g_{mn(3)}/K^3$ ,  $g_{mn}/K$ )**

Solvent		Polymer		
		C <sub>6</sub> H <sub>5</sub>	CH	CH <sub>2</sub>
Hu <i>et al.</i> (1997)				
CO	$g_{mn(1)}$	-777.25	13783	3597.8
	$g_{mn(2)}$	2862.4	0.0	-6210.6
	$g_{mn(3)}$	-33.85	-47784	-1058.6
CH <sub>2</sub>	$g_{mn(1)}$	225.34	1693.2	663.25
	$g_{mn(2)}$	0.0	-1243.6	-1088.4
	$g_{mn(3)}$	0.0	-6338.7	0.0
CH <sub>3</sub>	$g_{mn(1)}$	2033.3	-4121.4	-71.794
	$g_{mn(2)}$	-2216.7	0.0	-669.52
	$g_{mn(3)}$	-622.36	12983	2439.3
Proposed Model				
CO	$g_{mn}$	334.67	3543.5	-306.30
CH <sub>2</sub>	$g_{mn}$	1088.9	9884.7	122.56
CH <sub>3</sub>	$g_{mn}$	776.17	994.07	791.78

UNIQUAC in the sense that the parameters of this work are constant while those of the UNIQUAC vary according to systems.

The group interaction parameters are listed in Table III. All experimental data used in the correlation are available elsewhere.<sup>26</sup>

Figure 2 and Figure 3 show solvent activities of a polystyrene ( $M_w=2.0 \times 10^4$ ,  $M_w=5.0 \times 10^5$ )/benzene system at 293.15 K. Good results are shown for different  $M_w$  of polymers. Figure 4 and Figure 5 represent solvent activities of a polydimethylsiloxane ( $M_w=5,921$ )/benzene system at 298.15 K and 313.15 K. In this system, the polymer-solvent oriented interactions are similar to those of solvent-solvent oriented interactions. Therefore, the solvent activity hardly depends on temperature. Calculated values again agree well with experimental results. Figure 6 shows predicted solvent activities of a polydimethylsiloxane ( $M_n=958$ ,  $M_w=1,418$ )/n-octane system at 298.15 K. In this case, agreement with experimental data shows a slight deviation compared with other results. The proposed model does not consider the various polydispersities of chain molecules. In particular, this system has a high polydispersity number ( $M_w/M_n=1.48$ ), this model implicitly assumes that all the polymers are monodisperse. It is likely that this deficiency is responsible for the observed discrepancy between the proposed model and the experimental data.

Predicted solvent activities for four polymer-solvent systems compared with UNIFAC1 and UNIFAC with

**Table II. Calculations of Solvent Activities for Polymer Solutions**

System	T(K)	AAD(%)		Mean Dev.	
		Hu <i>et al.</i> (1997)	This work	UNIQUAC	This work
PE/benzene	273.15	2.67	3.09	0.0065	0.0168
PE/n-hexane	273.15	1.27	2.08	0.0038	0.0083
	303.15		3.02		0.0098
PE(8.e4)/n-pentane	298.15		11.28		0.0067
PE(8.e4)/benzene	298.15		4.71		0.0253
PE/2-methyl-1-propene	265.15		0.69		0.0021
	273.15		1.83		0.0028
	303.15		0.74		0.0013
PBD/trichloro methane	273.15		0.23		0.0014
	298.15		0.33	0.0014	0.0008
PBD/benzene	300.05	0.36	0.28		0.0017
PBD(2.5e5)/ethyl benzene	353.15		6.09	0.0152	0.0196
	373.15		2.98	0.0067	0.0077
	403.15	3.20	1.49	0.0030	0.0029
PBD(2.5e5)/n-nonane	353.15		7.66	0.0379	0.0221
	373.15		6.76	0.0194	0.0182
	403.15	3.26	3.45	0.0071	0.0118
Polydecene-1/toluene	303.15		2.82	0.0074	0.0066
PDMS(8.9e4)/trichloromethane	303.00		0.54	0.0002	0.0008
PDMS(8.9e4)/dichloromethane	303.00		0.08	0.0001	0.0001
PDMS(4.6e3)/2-butanone	303.15	1.45	1.54		0.0142
PDMS(1.6e4)/2-butanone	303.15	1.55	1.45		0.0136
PDMS(4.0e4)/ 2-butanone	303.15	1.85	1.82		0.0168
PDMS(5.5e4)/ 2-butanone	303.15		1.43		0.0134
PDMS(6.1e4)/ 2-butanone	303.15		2.00		0.0183
PDMS(2.2e5)/ 2-butanone	303.15		1.57		0.0147
PDMS(8.0e4)/ 2-butanone	293.15	0.34	0.09		0.0009
	308.15		0.07		0.0007
	323.15		0.09		0.0009
PDMS(8.9e4)/n-pentane	303.04		7.97	0.0034	0.0045
PDMS(1540)/benzene	298.15	2.98	1.30	0.0012	0.0086
	313.15		3.50	7.61	0.0150
PDMS(4170)/benzene	298.15	2.03	1.42	0.0076	0.0104
	313.15		2.75	3.02	0.0095
PDMS(6650)/benzene	303.00	1.41	2.55	0.0074	0.0084
PDMS(1.57e4)/benzene	303.00	0.88	0.12	0.0002	0.0003
PDMS(2.6e4)/benzene	303.00	1.17	0.16	0.0002	0.0003
PDMS(8.9e4)/benzene	303.00		5.42	0.0028	0.0033
PDMS(8.9e4)/cyclohexane	303.00		6.76	0.0031	0.0038
PDMS(1.22e5)/cyclohexane	293.15	0.12	0.00		0.0000
PDMS(8.e4)/4-me-2-pentanone	293.15	0.96	0.04		0.0004
	308.15		0.36	0.04	
PDMS(3350)/n-hexane	303.00	4.06	0.17	0.0002	0.0004
PDMS(6650)/n-hexane	303.00		0.21	0.0001	0.0004

Table II. (continued)

System	T(K)	AAD(%)		Mean Dev.	
		Hu <i>et al.</i> (1997)	This work	UNIQUAC	This work
PDMS(1.57e4)/n-hexane	303.00		0.18	0.0001	0.0003
PDMS(2.6e4)/n-hexane	303.00		0.29	0.0003	0.0004
PDMS(8.9e4)/n-hexane	303.00	1.62	0.12	0.0002	0.0002
PDMS(665)/hexamethyl disiloxane	298.15		1.38	0.0078	0.0076
PDMS(1418)/hexamethyl disiloxane	298.15		0.79	0.0036	0.0054
PDMS(1540)/toluene	298.15	2.32	1.84	0.0012	0.0092
	313.15	2.27	1.00	0.0031	0.0040
PDMS(4170)/toluene	298.15	1.25	0.81	0.0013	0.0054
	313.15	1.89	1.18	0.0049	0.0044
PDMS(1540)/n-heptane	298.15	0.76	0.68	0.0015	0.0038
	313.15	2.42	0.76	0.0033	0.0023
PDMS(1540)/n-octane	298.15	0.60	0.31	0.0007	0.0017
	313.15	4.54	1.57	0.0036	0.0048
PDMS(4170)/n-octane	298.15	1.42	0.97	0.0033	0.0050
	313.15	1.31	1.46	0.0077	0.0061
Polydodecene-1/toluene	303.15	1.61	7.05	0.0159	0.0248
PEO(335)/benzene	297.75	0.51	0.10	0.0001	0.0010
	307.75		0.10	0.0001	0.0010
PEO(4150)/benzene	307.75		0.01	0.0001	0.0001
PEO(5700)/benzene	318.95	0.94	0.34		0.0030
	343.15	2.03	0.89	0.0013	0.0044
PEO(6.e5)/benzene	323.45	1.43	0.30		0.0026
	343.15	2.82	0.86	0.0007	0.0052
PEO(4.e6)/benzene	348.25	2.46	0.57		0.0019
	361.25		0.23		0.0003
	375.15	1.56	3.85	0.0027	0.0072
	398.55		0.57		0.0004
	423.55		2.04		0.0010
PEO(218)/water	293.10		5.39	0.0244	0.0185
PEO(335)/water	297.75		0.22	0.0012	0.0021
	307.75		0.15	0.0011	0.0015
PEO(1460)/water	307.75		0.05	0.0004	0.0005
PEO(5000)/water	338.15		12.59	0.0316	0.0677
Nylon-6,6/water	296.15		6.48		0.0237
Nylon-6,10/water	296.15		2.19		0.0138
PIB(1.e6)/n-butane	298.15		1.27	0.0036	0.0034
PIB(1.e6)/2-me-propane	298.15	4.73	1.17	0.0037	0.0046
	308.15	1.83	0.52	0.0011	0.0009
	319.65	3.68	3.45	0.0051	0.0058
PIB(1.e6)/2-me-butane	298.15	4.93	2.83	0.0047	0.0048
	308.15	1.66	0.68	0.0017	0.0014
	319.65	3.41	1.79		0.0016
PIB(1170)/n-pentane	298.15	1.28	2.04	0.0124	0.0140
	308.15	0.94	1.54	0.0093	0.0106

Table II. (continued)

System	T(K)	AAD(%)		Mean Dev.	
		Hu <i>et al.</i> (1997)	This work	UNIQUAC	This work
PIB(1170)/n-pentane	318.15	0.92	1.29		0.0087
	328.15	0.83	1.00		0.0067
PIB(1350)/n-pentane	298.15	3.17	0.27	0.0008	0.0015
PIB(2700)/n-pentane	298.15	1.98	1.66	0.0013	0.0092
PIB(2.25e6)/n-pentane	298.15	1.28	0.36	0.0027	0.0035
	308.15	2.92	0.35		0.0033
	313.15	0.58	0.10	0.0002	0.0010
	318.15	2.89	0.34		0.0032
	328.15	2.95	0.29		0.0028
PIB(4.5e4)/benzene	298.15	2.39	1.42	0.0097	0.0109
	313.15	2.73	2.94	0.0180	0.0160
	338.15	3.80	1.80	0.0132	0.0091
PIB(1.e5)/cyclohexane	298.15	1.44	1.34	0.0103	0.0090
	313.15	0.70	0.56	0.0045	0.0044
	338.15	2.87	1.81	0.0128	0.0132
PIB(5.e4)/cyclohexane	298.15		1.48	0.0052	0.0080
	311.15		3.50	0.0078	0.0115
	338.15		2.39	0.0076	0.0070
PIB(5.e4)/toluene	298.15		11.78	0.0176	0.0504
	313.15	5.56	9.04	0.0093	0.0292
	338.15	4.68	13.21	0.0376	0.0306
PIB(5.e4)/ethyl benzene	298.15	9.17	9.02	0.0097	0.0409
	313.15	9.76	9.61	0.0122	0.0282
	338.15		8.02	0.0212	0.0183
PIB(4.e4)/n-octane	298.15	1.79	0.11		0.0011
PIP/2-butanone	298.15	9.13	8.49	0.0050	0.0482
	318.15	8.26	6.65	0.0051	0.0344
PIP(4.e4)/ethyl acetate	298.15	5.16	6.16	0.0075	0.0240
	323.15	3.56	2.40		0.0094
PIP/benzene	283.15		0.17		0.0012
	298.15	0.45	0.50	0.0026	0.0028
	313.15	0.44	0.07		0.0004
PMMA(1.98e4)/2-butanone	321.65		3.49	0.0220	0.0113
PMMA(1.98e4)/toluene	321.65	4.98	2.98	0.0102	0.0190
PMS(1.e5)/toluene	294.15		0.47	0.0015	0.0042
PMS(1.7e4)/isopropyl benzene	338.19	1.09	1.14	0.0053	0.0090
PP(1.5e4)/tetrachloro methane	298.15		5.65	0.0056	0.0253
PP(2.05e5)/tetrachloro methane	298.15		8.14	0.0106	0.0440
	298.15		24.21		0.0871
PP(2.5e4)/3-pentanone	308.15		23.45		0.0786
	298.15				
PPO(150)/methanol	248.15	0.54	0.43		0.0040
	263.15	0.55	0.26		0.0024
	273.15	0.65	0.19		0.0017
	288.15		0.19		0.0017

Table II. (continued)

System	T(K)	AAD(%)		Mean Dev.	
		Hu <i>et al.</i> (1997)	This work	UNIQUAC	This work
PPO(150)/methanol	298.15	0.15	0.17		0.0015
PPO(1120)/methanol	248.15		0.38		0.0037
	263.15	1.90	0.40		0.0038
	298.15	2.06	0.34		0.0033
PPO(1955)/methanol	248.15		0.39		0.0038
	273.15		0.31		0.0031
	298.15		0.27		0.0026
PPO(3350)/methanol	298.15		0.18		0.0018
PPO(5.e5)/benzene	320.35	1.94	1.01	0.0005	0.0068
	333.35	2.24	0.77	0.0002	0.0058
	343.05	4.89	1.03	0.0002	0.0050
	347.85	3.86	1.13	0.0005	0.0065
PPO(400)/water	303.15		14.58	0.0104	0.0839
	323.15		15.06	0.0093	0.0884
PS(5.e5)/tetrachloro methane	293.15		0.95	0.0063	0.0064
PS(5.e5)/nitromethane	293.15		2.99	0.0157	0.0249
PS(1.57e4)/2-propanone	298.15		3.48	0.0017	0.0246
	323.15		3.63	0.0038	0.0276
	333.15		0.00		0.0000
PS(1.03e4)/2-butanone	321.65	1.27	1.16	0.0066	0.0071
PS(2.9e5)/2-butanone	298.15	2.16	3.69	0.0256	0.0208
	343.15	4.32	2.91	0.0081	0.0191
PS(9.72e4)/2-butanone	283.15	1.45	0.09		0.0009
	323.15	0.60	0.08		0.0008
PS(800)/benzene	298.15	2.78	0.45	0.0019	0.0027
PS(2.e4)/benzene	293.15	4.74	4.50	0.0174	0.0213
PS(6.3e4)/benzene	288.15	2.12	2.30	0.0110	0.0173
	303.15	2.10	1.99	0.0090	0.0147
	318.15	2.96	0.57	0.0045	0.0043
	333.15	2.73	0.39	0.0031	0.0032
PS(5.e5)/benzene	293.15		5.26	0.0278	0.0217
PS(9.e5)/benzene	288.15	2.86	2.20	0.0126	0.0177
	303.15	2.42	2.35	0.0103	0.0176
	318.15	1.21	0.62	0.0028	0.0053
	333.15	1.64	0.83	0.0030	0.0067
PS(4.9e4)/cyclohexane	290.55		0.01	0.0001	0.0000
	298.35		0.00	0.0001	0.0000
	308.15		0.02	0.0000	0.0002
	338.15		0.04	0.0000	0.0004
PS(1.54e5)/cyclohexane	298.15		0.00	0.0000	0.0000
	303.15	1.12	1.05	0.0006	0.0100
	318.15	0.98	0.89	0.0002	0.0084
	338.15	3.80	0.82	0.0003	0.0076
PS(1.03e4)/toluene	321.65	0.86	0.54	0.0027	0.0028



Table II. (continued)

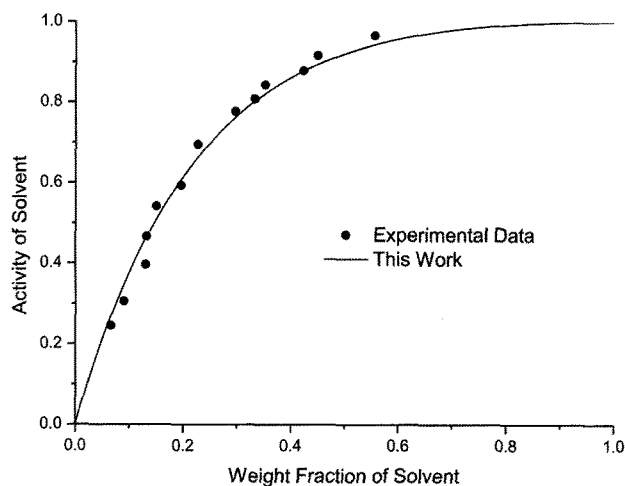
System	T(K)	AAD(%)		Mean Dev.	
		Hu <i>et al.</i> (1997)	This work	UNIQUAC	This work
PS(1.54e5)/toluene	298.15	2.80	0.01	0.0001	0.0001
	318.15	1.03	0.01	0.0000	0.0001
	338.15	0.41	0.00	0.0000	0.0000
PS(2.9e5)/toluene	298.15	1.39	7.40	0.0391	0.0126
	333.15		0.63		0.0034
	353.15		0.37		0.0032
PS(9.72e4)/ethyl benzene	283.15	0.78	0.23		0.0023
	308.15		0.04		0.0004
	333.15		0.03		0.0003
PS(5.37e4)/n-nonane	403.15	5.30	4.30		0.0176
	423.15	2.73	1.68	0.0057	0.0053
	448.15		1.23		0.0024
PS(2.9e5)/propyl acetate	298.15	1.60	1.36	0.0108	0.0068
	343.15	2.41	0.99	0.0074	0.0045
PVAc(1.7e5)/2-propanone	303.15		5.94		0.0089
	323.15		0.58		0.0011
PVAc(1.7e5)/2-propanol	303.15		6.60		0.0257
	323.15		4.82		0.0075
PVAc(1.7e5)/isopropylamine	313.15		1.19		0.0047
PVAc(4.8e4)/benzene	303.15	3.23	3.00	0.0045	0.0164
PVAc(1.43e5)/benzene	303.15	2.35	7.07	0.0555	0.0251
PVAc/water	313.15		20.30		0.0960
Pheptane(2.24e5)/toluene	303.15	1.71	4.62	0.0053	0.0087
PVC(3.96e4)/tetrachloromethane	338.15		0.45	0.0035	0.0024
PVC(3.4e4)/toluene	316.35	5.62	6.91	0.0042	0.0382
PVC(3.4e4)/dibutyl ether	315.35		7.18	0.0153	0.0419
PVME(1.4e4)/trichloromethane	298.15		0.72	0.0029	0.0024
PVME(1.4e4)/benzene	298.15	1.02	0.36	0.0014	0.0018

Note:  $AAD(\%) = \frac{1}{n} \times \sum |(a_{cal} - a_{exp}) / a_{exp}| \times 100$ ,  $Mean\ Dev. = \frac{1}{n} \times \sum (a_{cal} - a_{exp})$ .

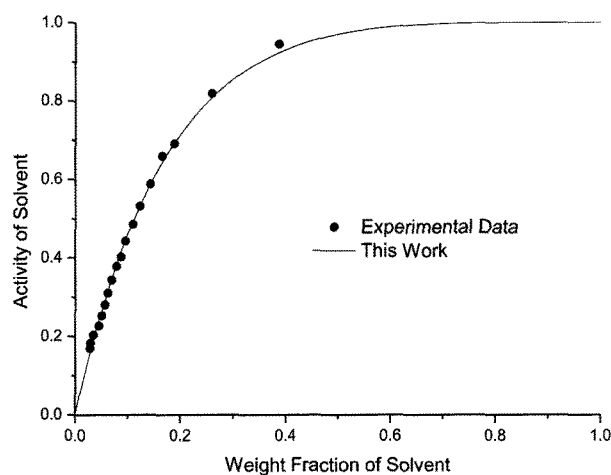
 Table III. Group Interaction Parameters ( $g_{mn}/K$ )

Solvent	Polymer											
	2	4	5	6	8	9	10	11	12	13	14	16
1	-24992	3307.0		3797.9	27080	105.33	-3221.7	6641.3	-10227	3499.4	2958.5	
2	-16431		-4086.9	-5728.8		126.52	219.64	153.24			177.86	
3	45592	28637				196.43	7869.7	294.38	17922			
4	139.38					153.13	180.25	207.00	191.77			
5	1800.4		-161.08	-527.64		9124.7	-295.55	-332.16		240.74	-562.07	
6	-1504.2			-1811.4				449.12				
7						-446.67	-4649.1				954.30	
8	110.25		7575.0			-82838	20493	30143	123.89		5376.9	
9	5064.2			7232.4	10663	111.19	5873.6	136.24	256.59	-2414.5		7232.4
10	-642.76		-17.530	-3219.8	-3786.4	9884.7	122.56	-142.55	202.17	9739.2	1088.9	
11	105.51		477.84	389.12	2230.9	994.07	791.78	575.36	372.62	-2635.4	776.17	209.79
12	50.787			223.46	133.01	3543.5	-306.30	303.20	216.42		334.67	
14	2220.8		2575.6	1158.1	4843.8	3157.0	721.56	-818.41	332.40	-2033.6	-585.32	442.79
15	758.73			464.74	1824.7	-23592	-2885.8	-51.560			1649.4	
17	1054.5											

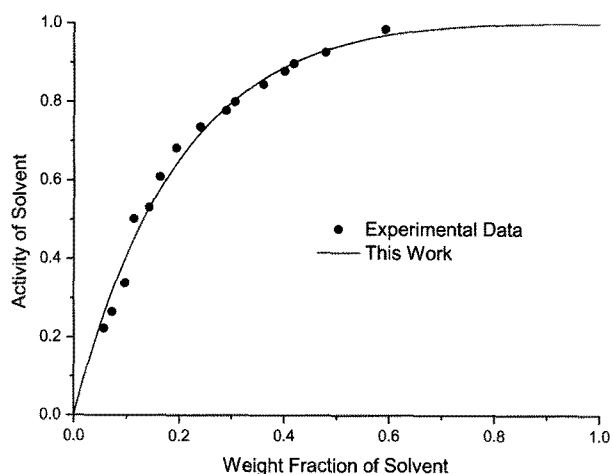
(1)H, (2)O, (3)OH, (4)NH, (5)Cl, (6)Si, (7)NO<sub>2</sub>, (8)C, (9)CH, (10)CH<sub>2</sub>, (11)CH<sub>3</sub>, (12)CO, (13)CH=CH, (14)C<sub>6</sub>H<sub>5</sub>, (15)C<sub>6</sub>H<sub>11</sub>, (16)C<sub>6</sub>H<sub>4</sub>, (17)CH=C(CH).



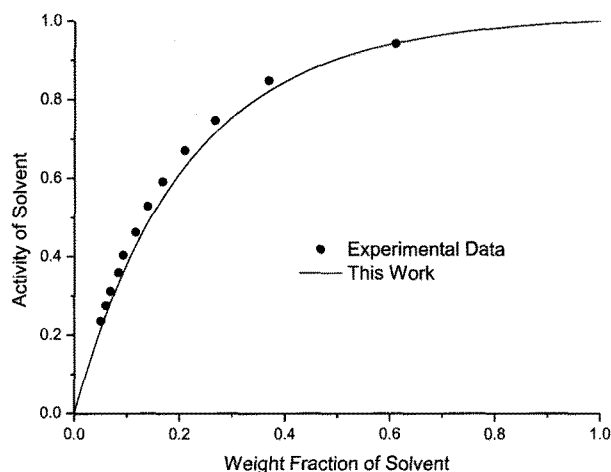
**Figure 2.** Calculated and experimental activities of benzene in polystyrene ( $M_w=2.0 \times 10^4$ ) at 293.15 K.



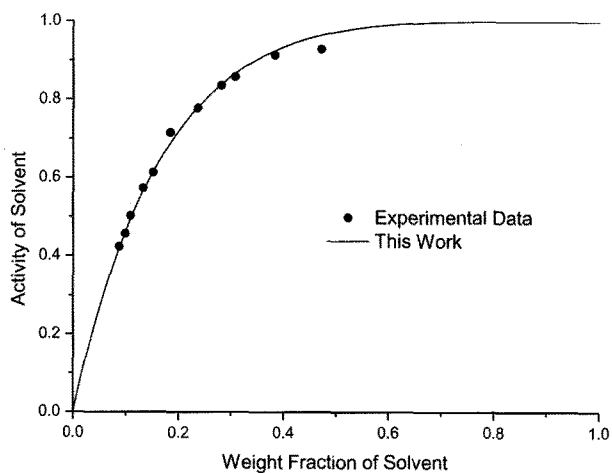
**Figure 5.** Calculated and experimental activities of benzene in polydimethylsiloxane ( $M_w=5,921$ ) at 313.15 K.



**Figure 3.** Calculated and experimental activities of benzene in polystyrene ( $M_w=5.0 \times 10^5$ ) at 293.15 K.



**Figure 6.** Calculated and experimental activities of n-octane in polydimethylsiloxane ( $M_n=958$ ,  $M_w=1,418$ ) at 298.15 K.



**Figure 4.** Calculated and experimental activities of benzene in polydimethylsiloxane ( $M_w=5,921$ ) at 298.15 K.

free volume correction<sup>2</sup> are given in Tables IV, V and Figures 7, 8. In all cases the activity calculated from UNIFAC and UNIFAC with free volume correction are low. The proposed model always raises the solvent's activity. Similar results are shown in Figures 9 and 10. Our results are more accurate than those of Elbro *et al.*<sup>15</sup> The results indicate that taking into account an oriented interaction provides a substantial improvement in the predicted activities.

Figures 11-13 show predicted and experimental solvent activities in polystyrene, polyisobutylene and polypropyleneoxide. In these figures, the computed activities from the proposed model, the GC-Flory model<sup>28</sup> and the Holtz-Anderson model<sup>13</sup> are indicated by the solid, dotted and dashed lines, respectively. For all three systems, the predictions of solvent activities using the proposed model are satisfactory and as good as or often better than those

**Table IV. Comparison of Calculated and Experimental Activities for Cyclohexane(1) in Polyisobutylene(2) at 298.15K ( $M_n(2)=40,000$ )**

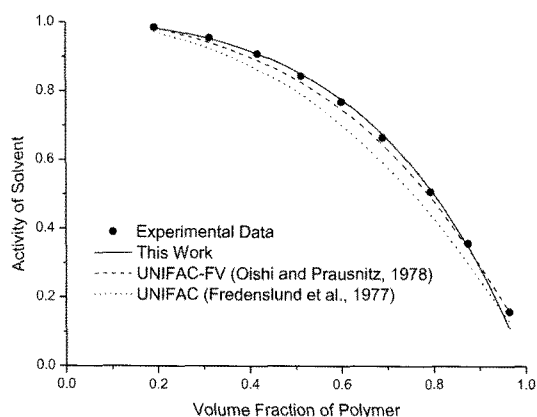
Vol%(2)	Exp. *100	UNIFAC *100	(Dev.%)	UNIFAC-FV *100	(Dev.%)	This Work *100	(Dev.%)
39.0	96.0	87.7	(8.65)	93.2	(2.92)	95.7	(0.31)
55.9	87.6	73.2	(16.44)	83.7	(4.45)	87.6	(0.00)
66.0	78.4	61.1	(22.07)	74.6	(4.85)	78.7	(0.38)
78.4	61.0	42.6	(30.16)	57.5	(5.74)	61.3	(0.49)
85.2	46.3	30.9	(33.26)	44.4	(4.10)	47.3	(2.16)

Note:  $Dev.\% = |(a_{cal} - a_{exp}) / a_{exp}| \times 100$ .

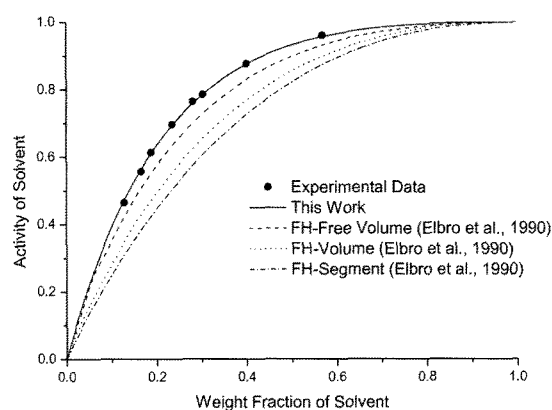
**Table V. Comparison of Calculated and Experimental Activities for Propyl Acetate(1) in Polystyrene(2) at 298.15 K ( $M_n(2)=290,000$ )**

Vol% (2)	Exp. *100	UNIFAC *100	(Dev.%)	UNIFAC-FV *100	(Dev.%)	This Work *100	(Dev.%)
44.5	99.0	92.5	(6.57)	99.6	(0.61)	99.0	(0.00)
54.5	95.0	85.8	(9.68)	96.3	(1.37)	96.0	(1.05)
62.2	90.6	78.2	(13.69)	91.4	(0.88)	91.9	(1.43)
66.7	88.0	72.7	(17.39)	87.2	(0.91)	88.3	(0.34)
75.6	76.3	58.9	(22.80)	75.3	(1.31)	77.6	(1.70)
83.1	61.8	44.2	(28.48)	60.0	(2.91)	63.3	(2.43)

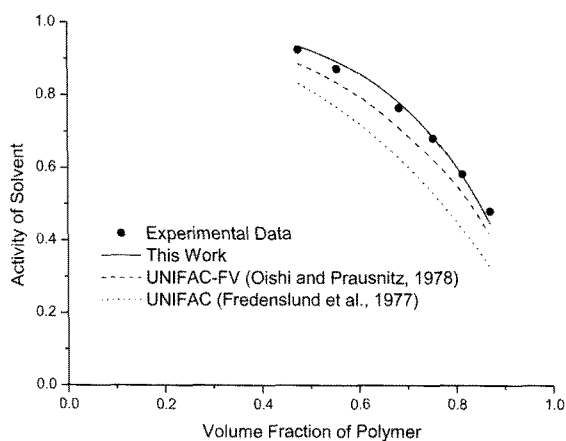
Note:  $Dev.\% = |(a_{cal} - a_{exp}) / a_{exp}| \times 100$ .



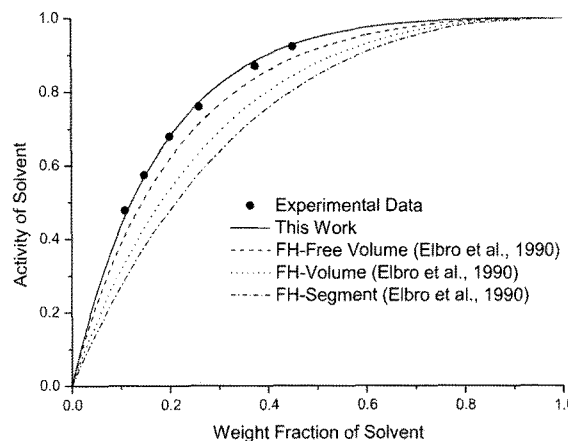
**Figure 7.** Calculated and experimental activities of benzene in polyethyleneoxide ( $M_n=5.7 \times 10^3$ ) at 343.15 K.



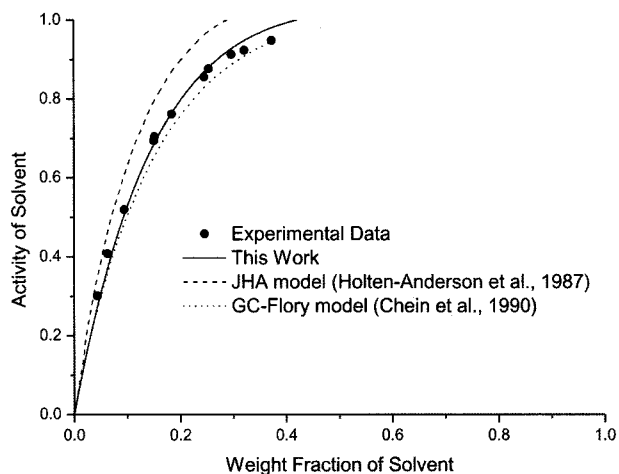
**Figure 9.** Calculated and experimental activities of cyclohexane in polyisobutylene ( $M_n=4.0 \times 10^4$ ) at 298.15 K.



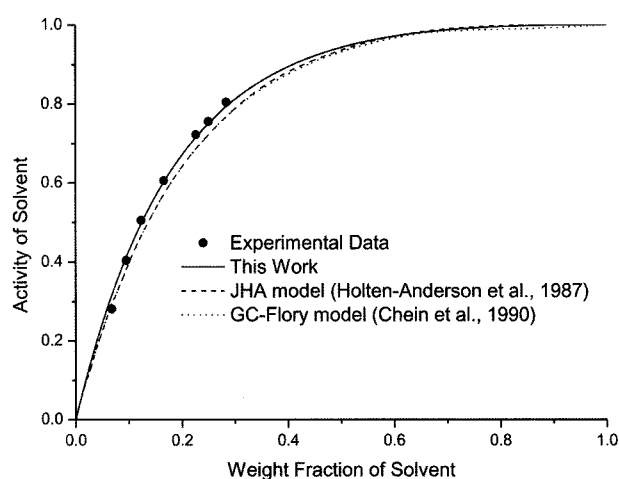
**Figure 8.** Calculated and experimental activities of ethyl acetate in polyvinylacetate ( $M_n=1.1 \times 10^5$ ) at 303.15 K.



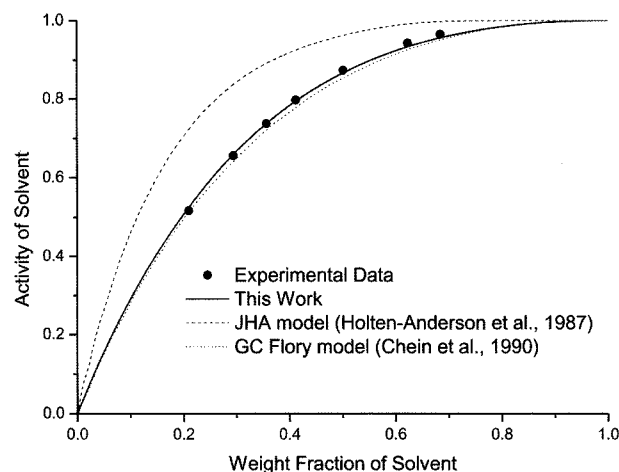
**Figure 10.** Calculated and experimental activities of ethyl acetate in polyvinylacetate ( $M_n=1.1 \times 10^5$ ) at 303.15 K.



**Figure 11.** Calculated and experimental activities of benzene in polyisobutylene ( $M_w=4.0 \times 10^4$ ) at 298.15 K.



**Figure 12.** Calculated and experimental activities of n-hexane in polyisobutylene ( $M_w=5.0 \times 10^4$ ) at 338.15 K.



**Figure 13.** Calculated and experimental activities of benzene in polypropyleneoxide ( $M_w=1.5 \times 10^6$ ) at 333.35 K.

resulting from the GC-Flory model and the Holten-Anderson model.

## Conclusions

A specified group-contribution method based on a modified double lattice model for the prediction of vapor liquid equilibria is developed and present new group interaction parameter tables. Nevertheless, we introduce several assumptions for simplicity, and the model substantially improves the ability to describe phase equilibria in very different types of mixtures in a consistent and semi-quantitative manner.

The results obtained with the proposed model are often better than those of other published models. This is because the model can account for specific oriented interactions by incorporating a double lattice.

However, the list of group interaction parameters is not plentiful. More experimental data are required to improve and extend the method to a larger variety of systems.

The application of the model to liquid liquid equilibria and to polymer mutual compatibility predictions will be illustrated in a subsequent contribution.

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