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# UNIFAC Model for Ionic Liquids

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This work focuses on the extension of group parameters of the UNIFAC model to systems with ionic liquids. The new group parameters for ionic liquids were obtained by means of correlating the activity coefficients of solutes at infinite dilution in ionic liquids at different temperatures. The group parameters for 12 main groups and 24 subgroups were added into the current UNIFAC parameter matrix. It was verified that the new group parameters can be used not only for predicting the vapor–liquid equilibria of the systems with ionic liquids at finite concentration, but also for screening the suitable ionic liquids in separation processes. Since there have been only a limited number of functional groups for ionic liquids included in the UNIFAC model, the future development of this predictive model will still require much more accurate experimental data.

## 1. Introduction

In recent years, room temperature ionic liquids have attracted considerable attention for their potential as “designer solvents”. Due to their negligible vapor pressure and electrolyte properties, they can be applied as replacements for conventional toxic, flammable, and volatile organic solvents and become very interesting entrainers in separation processes (e.g., extractive distillation, liquid–liquid extraction, absorption).<sup>1–9</sup> However, typical ionic liquids are composed of a large organic cation and an anion. This means that many kinds of ionic liquids are able to be constructed from one ionic liquid by adjusting the length, position, and number of alkyl chain on the organic cation. A large number of possible ionic liquids are of little use for separation science if no “predictive thermodynamic models” for the tailor-making of ionic liquids for specific separation tasks are provided.

The term “predictive thermodynamic models” means the types of models that phase equilibria can be described as, provided that molecular structures or physical properties of pure components in the mixture are known.<sup>10–12</sup> The predictive thermodynamic models are very important in separation processes as screening tools to find out the best suited ionic liquid rapidly to reduce the amount of experimental work. By far there are the following approaches for predicting phase equilibria for the systems with ionic liquids: the COSMO-RS model,<sup>13–15</sup> the quantitative structure–property relationship (QSPR) method,<sup>16</sup> the regular solution model,<sup>17–21</sup> and the UNIFAC model.<sup>22–31</sup> The COSMO-RS model is a novel and efficient method for the priori prediction of thermophysical data. It is based on quantum chemistry and uses only atom-specific parameters, which can be used to predict the thermodynamic properties of solvent–ionic liquid systems. However, its calculation program is very complicated and cannot be found in the open literature. The COSMO-RS model is used to the best advantage only by its developers, their colleagues, and subscribers. On the other hand, for the QSPR method, it is possible to construct a quantitative relationship between molecular structures and thermodynamic properties by some descriptors. However, this method is difficult to reduce to practice in chemical engineering and thus is not popular. The regular solution model can predict only gas solubility with the atomic molar volume of imidazolium-based

ionic liquids, and in this model the group contribution methods are used to calculate the solubility parameters from molecular structure. Also, the COSMO-RS model, the regular solution model, and the QSPR method cannot be incorporated into such famous simulation programs as ASPEN PLUS and PROII.

As we know, the original<sup>22–27</sup> and modified<sup>28–31</sup> UNIFAC models are widely used as predictive thermodynamic models, which even have been applied to predict the phase equilibria of systems with ionic liquids. However, the main groups of ionic liquids involved are imidazolium and BTI (bis(trifluoromethylsulfonyl)imide), as reported by Kato and Gmehling.<sup>15</sup> Therefore, the goal of this work is to extend the group parameters of ionic liquids in the current UNIFAC parameter matrix based on the experimental data of activity coefficients of solutes at infinite dilution in ionic liquids at different temperatures. The original UNIFAC model was adopted in this work because in most cases the experimental data only at a limited series of temperatures are available from the literature, but in the modified UNIFAC model the temperature-dependent interaction parameters are needed.

## 2. Extension of the Group Parameter Matrix

**2.1. UNIFAC Model.** The original UNIFAC model that combines the functional group concept with a model for activity coefficients based on an extension of the quasi-chemical theory of liquid mixtures (UNIQUAC) was proposed by Fredenslund et al. in 1975.<sup>32</sup> This model can be applied at infinite dilution and finite concentrations and was the most widely used before several revisions and extensions were developed. The activity coefficient is expressed as a function of composition and temperature. The model has a combinatorial contribution to the activity coefficient, i.e.,  $\ln \gamma_i^C$ , essentially due to differences in size and shape of the molecules, and a residual contribution, i.e.,  $\ln \gamma_i^R$ , essentially due to energetic interactions.

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (1)$$

### 2.1.1. Combinatorial Part.

$$\ln \gamma_i^C = 1 - V_i + \ln V_i - 5q_i \left( 1 - \frac{V_i}{F_i} + \ln \left( \frac{V_i}{F_i} \right) \right) \quad (2)$$

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$$F_i = \frac{q_i}{\sum_j q_j x_j}; \quad V_i = \frac{r_i}{\sum_j r_j x_j} \quad (3)$$

The pure component parameters  $r_i$  and  $q_i$  are, respectively, relative to molecular van der Waals volumes and molecular surface areas. They are calculated as the sum of the group volume and group area parameters,  $R_k$  and  $Q_k$ :

$$r_i = \sum_k v_k^{(i)} R_k; \quad q_i = \sum_k v_k^{(i)} Q_k \quad (4)$$

where  $v_k^{(i)}$ , always an integer, is the number of groups of type  $k$  in molecule  $i$ . The group parameters  $R_k$  and  $Q_k$  (see Table 1) are normally obtained from van der Waals group volumes and surface areas,  $V_k$  and  $A_k$ , given by Bondi:

$$R_k = \frac{V_k}{15.17}; \quad Q_k = \frac{A_k}{2.5 \times 10^9} \quad (5)$$

### 2.1.2. Residual Part.

$$\ln \gamma_i^R = \sum_k v_k^{(i)} [\ln \Gamma_k - \ln \Gamma_k^{(i)}] \quad (6)$$

$\Gamma_k$  is the group residual activity coefficient, and  $\Gamma_k^{(i)}$  is the residual activity coefficient of group  $k$  in a reference solution containing only molecules of type  $i$ .

$$\ln \Gamma_k = Q_k \left[ 1 - \ln \left( \sum_m \theta_m \psi_{mk} \right) - \sum_m \left( \theta_m \psi_{km} / \sum_n \theta_n \psi_{nm} \right) \right] \quad (7)$$

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n}; \quad X_m = \frac{\sum_i v_m^{(i)} x_i}{\sum_i \sum_k v_k^{(i)} x_i} \quad (8)$$

$X_m$  is the fraction of group  $m$  in the mixture. The group interaction parameter  $\psi_{nm}$  is defined by

$$\psi_{nm} = \exp[-(a_{nm}/T)] \quad (9)$$

The parameter  $a_{nm}$  (see Table 2) characterizes the interaction between groups  $n$  and  $m$ . For each group–group interaction, there are two parameters:  $a_{nm} \neq a_{mn}$ .

Equations 7 and 8 also hold for  $\ln \Gamma_k^{(i)}$ , except that the group composition variable,  $\theta_k$ , is now the group fraction of group  $k$  in pure fluid  $i$ . In pure fluid,  $\ln \Gamma_k = \ln \Gamma_k^{(i)}$ , which means that, as  $x_i \rightarrow 1$ ,  $\gamma_i^R \rightarrow 1$ .  $\gamma_i^R$  must be close to unity because as  $x_i \rightarrow 1$ ,  $\gamma_i^C \rightarrow 1$  and  $\gamma_i \rightarrow 1$ . Therefore, the group parameters ( $R_k$ ,  $Q_k$ ,  $a_{nm}$ , and  $a_{mn}$ ) should be given beforehand to solve the above equations.

**2.2. Group Parameters.** In the original UNIFAC model ionic liquids are required to decompose into groups. In this work we would decompose ionic liquids in the same manner as proposed by Kim et al.<sup>33</sup> For example, the ionic liquid [BMIM][BF<sub>4</sub>] is composed of one CH<sub>3</sub> group, three CH<sub>2</sub> groups, and one [MIM][BF<sub>4</sub>] group. The reason is that the ionic pair has strong electrostatic interaction and thus it is better to treat the skeletons of the cation and the anion as a whole. On the other hand, the [MIM] (methylimidazolium)-based cations are probably the common cations. Therefore, the main group [MIM][BF<sub>4</sub>] has two subgroups, i.e., [MIM][BF<sub>4</sub>] and [IM][BF<sub>4</sub>]. This also holds for other groups of ionic liquids.

**Table 1. Group Parameters of Volume  $R_k$  and Surface Area  $Q_k$**

	main group	subgroup	$R_k$	$Q_k$
1	CH <sub>2</sub>	CH <sub>3</sub>	0.9011	0.8480
		CH <sub>2</sub>	0.6744	0.5400
		CH	0.4469	0.2280
		C	0.2195	0.0000
2	CH=CH	CH <sub>2</sub> =CH	1.3454	1.1760
		CH=CH	1.1167	0.8670
		CH <sub>2</sub> =C	1.1173	0.9880
		CH=C	0.8886	0.6760
3	ACH	ACH	0.5313	0.4000
		AC	0.3652	0.1200
4	ACCH <sub>2</sub>	ACCH <sub>3</sub>	1.2663	0.9680
		ACCH <sub>2</sub>	1.0396	0.6600
		ACCH	0.8121	0.3480
5	OH	OH	1.0000	1.2000
6	CH <sub>3</sub> OH	CH <sub>3</sub> OH	1.4311	1.4320
7	H <sub>2</sub> O	H <sub>2</sub> O	0.9200	1.4000
9	CH <sub>2</sub> CO	CH <sub>3</sub> CO	1.6724	1.4880
		CH <sub>2</sub> CO	1.4457	1.1800
11	CCOO	CH <sub>3</sub> COO	1.9031	1.7280
		CH <sub>2</sub> COO	1.6764	1.4200
13	CH <sub>2</sub> O	CH <sub>3</sub> O	1.1450	1.0880
		CH <sub>2</sub> O	0.9183	0.7800
		CHO	0.6908	0.4680
		THF	0.9183	1.1000
14	[MIM][BTI]	[MIM][BTI]	8.3145	7.3920
		[IM][BTI]	7.4134	6.5440
15	[MIM][DMP]	[MIM][DMP]	6.2609	4.9960
		[IM][DMP]	5.3598	4.1480
16	[PY][BTI]	[MPY][BTI]	6.7248	5.5793
		[PY][BTI]	5.8237	4.7313
17	[MIM][CH <sub>3</sub> SO <sub>4</sub> ]	[MIM][CH <sub>3</sub> SO <sub>4</sub> ]	3.7481	3.0714
		[IM][CH <sub>3</sub> SO <sub>4</sub> ]	2.8470	2.2234
18	[MIM][CH <sub>3</sub> OC <sub>2</sub> H <sub>4</sub> SO <sub>4</sub> ]	[MIM][CH <sub>3</sub> OC <sub>2</sub> H <sub>4</sub> SO <sub>4</sub> ]	4.7144	3.8444
		[IM][CH <sub>3</sub> OC <sub>2</sub> H <sub>4</sub> SO <sub>4</sub> ]	3.8133	2.9964
19	[PY][C <sub>2</sub> H <sub>5</sub> OC <sub>2</sub> H <sub>4</sub> SO <sub>4</sub> ]	[MPY][C <sub>2</sub> H <sub>5</sub> OC <sub>2</sub> H <sub>4</sub> SO <sub>4</sub> ]	6.6784	5.6699
		[PY][C <sub>2</sub> H <sub>5</sub> OC <sub>2</sub> H <sub>4</sub> SO <sub>4</sub> ]	5.7773	4.8219
20	[MIM][BF <sub>4</sub> ]	[MIM][BF <sub>4</sub> ]	6.5669	4.0050
		[IM][BF <sub>4</sub> ]	5.6658	3.1570
21	[MIM][Cl]	[MIM][Cl]	5.7073	4.9741
		[IM][Cl]	4.8062	4.1261
22	[MIM][CF <sub>3</sub> SO <sub>3</sub> ]	[MIM][CF <sub>3</sub> SO <sub>3</sub> ]	9.5357	5.0500
		[IM][CF <sub>3</sub> SO <sub>3</sub> ]	8.6346	4.2020
23	[MIM][PF <sub>6</sub> ]	[MIM][PF <sub>6</sub> ]	7.6909	4.6930
		[IM][PF <sub>6</sub> ]	6.7898	3.8450
24	[MIM][SCN]	[MIM][SCN]	6.6175	3.4169
		[IM][SCN]	5.7164	2.5689
25	[MPY][BF <sub>4</sub> ]	[MPY][BF <sub>4</sub> ]	6.8846	4.1040
		[PY][BF <sub>4</sub> ]	5.9835	3.2560

For some ionic liquids, the van der Waals parameters,  $r_i$  and  $q_i$ , can be found from the literature.<sup>34</sup> For other ionic liquids, a correlation as proposed by Domańska and Mazurowska<sup>35</sup> was used:

$$r_i = 0.029281 V_m; \quad q_i = \frac{(z-2)r_i}{z} + \frac{2(1-l_i)}{z} \quad (10)$$

where  $V_m$  is the molar volume of ionic liquids at 298.15 K,  $z$  is the coordination number, and  $l_i$  is the bulk factor. In terms of eqs 4 and 10, the group parameters of volume  $R_k$  and surface area  $Q_k$  of subgroups for ionic liquids were then derived. Up to 12 main groups for ionic liquids were concerned: [MIM][BTI] (methylimidazolium bis(trifluoromethylsulfonyl)imide); [MIM]-[DMP] (methylimidazolium dimethylphosphate); [PY][BTI] (pyridinium bis(trifluoromethylsulfonyl)imide); [MIM][CH<sub>3</sub>SO<sub>4</sub>] (methylimidazolium methylsulfate); [MIM][CH<sub>3</sub>OC<sub>2</sub>H<sub>4</sub>SO<sub>4</sub>] (methylimidazolium methoxyethylsulfate); [PY][C<sub>2</sub>H<sub>5</sub>OC<sub>2</sub>H<sub>4</sub>SO<sub>4</sub>] (pyridinium ethoxyethylsulfate); [MIM][BF<sub>4</sub>] (methylimidazolium tetrafluoroborate); [MIM][Cl] (methylimidazolium chloride); [MIM][CF<sub>3</sub>SO<sub>3</sub>] (methylimidazolium trifluoromethanesulfonate); [MIM][PF<sub>6</sub>] (methylimidazolium hexafluorophosphate);

**Table 2. Fitted Group Interaction Parameters for the UNIFAC Model Not Previously Available ( $a_{mn} \neq a_{nm}$ )**

<i>m</i>	<i>n</i>	$a_{mn}$	$a_{nm}$
1	14	400.89	145.80
2	14	799.84	-61.17
3	14	602.87	-163.26
4	14	593.40	-113.12
5	14	-200.71	506.67
6	14	4.39	301.20
7	14	-60.36	392.88
9	14	-200.52	164.22
13	14	-322.56	869.53
1	15	965.96	180.41
2	15	9364.24	79.37
3	15	1152.16	-47.21
4	15	1150.56	34.26
5	15	9.67	-746.52
7	15	6617.00	-1154.30
9	15	-289.27	745.16
13	15	6618.56	459.26
1	16	327.30	301.96
2	16	-88.94	556.21
3	16	998.04	-131.54
4	16	-139.79	644.47
5	16	14.23	116.91
6	16	4.61	229.11
7	16	32.15	263.20
9	16	-6.48	-117.24
13	16	-188.71	159.94
1	17	575.45	473.80
2	17	341.76	619.61
3	17	172.62	394.65
4	17	270.59	533.21
5	17	13.83	-570.26
6	17	-265.34	-66.51
1	18	2270.95	319.59
2	18	130.41	425.72
3	18	394.05	112.31
4	18	162.43	461.02
9	18	-0.317	154.91
1	19	0.022	333.41
2	19	0.069	108.70
3	19	562.49	-76.63
4	19	-0.053	201.82
9	19	-333.61	712.87
1	20	1108.51	588.74
2	20	431.16	563.42
3	20	1494.39	85.64
4	20	55.96	1834.88
5	20	-13.77	131.24
6	20	-74.10	388.76
7	20	242.88	-408.00
9	20	1322.44	-164.14
11	20	32.09	112.17
1	21	2093.97	1129.01
2	21	476.86	581.65
3	21	418.17	526.13
4	21	4213.32	310.80
1	22	405.39	284.37
2	22	-27.05	420.33
3	22	808.06	-39.56
4	22	-104.48	467.44
5	22	34.90	-305.24
6	22	54.43	-17.30
7	22	40.42	-335.22
13	22	-6.34	-117.44
1	23	692.26	401.54
2	23	148.61	467.80
3	23	1133.18	-25.13
5	23	-8.04	117.31
6	23	155.65	254.95
9	23	1316.40	-343.20
1	24	620.77	445.48
2	24	187.47	386.53
3	24	1141.38	57.74
4	24	84.32	344.73
5	24	32.30	-469.50
6	24	-16.28	-68.29
7	24	21.98	-659.24
1	25	1030.93	613.31
2	25	701.60	842.95
3	25	1262.75	62.65
4	25	446.89	375.31
5	25	3.55	-99.51
6	25	-17.97	212.08
9	25	133.94	-77.58
11	25	192.07	-22.50
13	25	2.20	165.84

[MIM][SCN] (methylimidazolium thiocyanate); [MPY][BF<sub>4</sub>] (methylpyridinium tetrafluoroborate). Their subgroup parameters of volume  $R_k$  and surface area  $Q_k$  are listed in Table 1.

A large number of experimental data of activity coefficients of solutes at infinite dilution in ionic liquids at different temperatures have been systematically collected from the literature published in recent years.<sup>36–66</sup> The group binary interaction parameters,  $a_{nm}$  and  $a_{mn}$ , were obtained by means of correlating these experimental data. The following objective function (OF) minimized was adopted:

$$\text{OF} = \min \sum_i^N \left| \gamma_i^{\text{exp}} - \gamma_i^{\text{cal}} \right| \quad (11)$$

where  $\gamma_i^\infty$  is the activity coefficient of the solute at infinite dilution and  $N$  is the number of data points. Calculations were performed in the temperature range 293.15–368.15 K. The Marquardt method as in Press et al.<sup>67</sup> was used to fit the parameters  $a_{nm}$  and  $a_{mn}$ . The global minimum of OF was found until the maximum iteration deviations of  $a_{nm}$  and  $a_{mn}$  were less than 0.001.

The fitting procedure was done in a sequential fashion in order to decrease the number of fitted parameters in the OF: alkanes, cycloalkanes, alkenes, cycloalkenes, aromatics, alcohols, ethers, ketones, esters, etc. That is, the parameters for groups CH<sub>3</sub> and CH<sub>2</sub> were first regressed using only alkane and cycloalkane data, then the parameters for groups CH<sub>2</sub>=CH and CH=CH were regressed using alkene and cycloalkene data. These values were then used in conjunction with data for aromatics to obtain the ACH group parameters, and so forth. However, it should be mentioned that the UNIFAC group parameters ( $R_k$ ,  $Q_k$ ,  $a_{nm}$ , and  $a_{mn}$ ) and group number between the solute groups have not been changed in this work and we still use the values presented in the literature.<sup>22–27</sup>

In this way, many new group parameters were derived, and the group binary interaction parameters,  $a_{nm}$  and  $a_{mn}$ , are listed in Table 2. The current UNIFAC parameter matrix is also illustrated in Figure 1, where the new 12 main groups are added.

### 3. Results and Discussion

Although the UNIFAC group parameters are derived from the solute–ionic liquid binary systems at infinite dilution, they are also applicable for predicting the activity coefficients of the solutes in multicomponent systems even including mixed ionic liquids, and the vapor–liquid equilibria of the systems with ionic liquids at finite concentration. Of course, as a predictive thermodynamic model, the UNIFAC model can also be used for screening out the suitable ionic liquid in some separation processes (e.g., extractive distillation, liquid–liquid extraction, absorption) where ionic liquid serves as entrainer.<sup>68,69</sup>

**3.1. Prediction of Activity Coefficients at Infinite Dilution in Mixed Ionic Liquids.** The  $\gamma_i^\infty$  values for *n*-hexane in the ionic liquids [EMIM][BTI], [BMIM][BTI], and their mixture (50:50 weight fraction of [EMIM][BTI] and [BMIM][BTI]) are shown as a function of the inverse temperature in Figure 2. It can be seen that the experimental data almost lie on the lines obtained by the UNIFAC model, which means that the calculated results by the UNIFAC are accurate for multicomponent systems even including mixed ionic liquids. Moreover, the  $\gamma_i^\infty$  values in the mixed ionic liquids are between those in the pure ionic liquids [EMIM][BTI] and [BMIM][BTI], and exhibit a similar linear temperature dependency as in the pure ionic liquids. The  $\gamma_i^\infty$  values become larger with decreasing temperature and average alkyl chain length on cation.

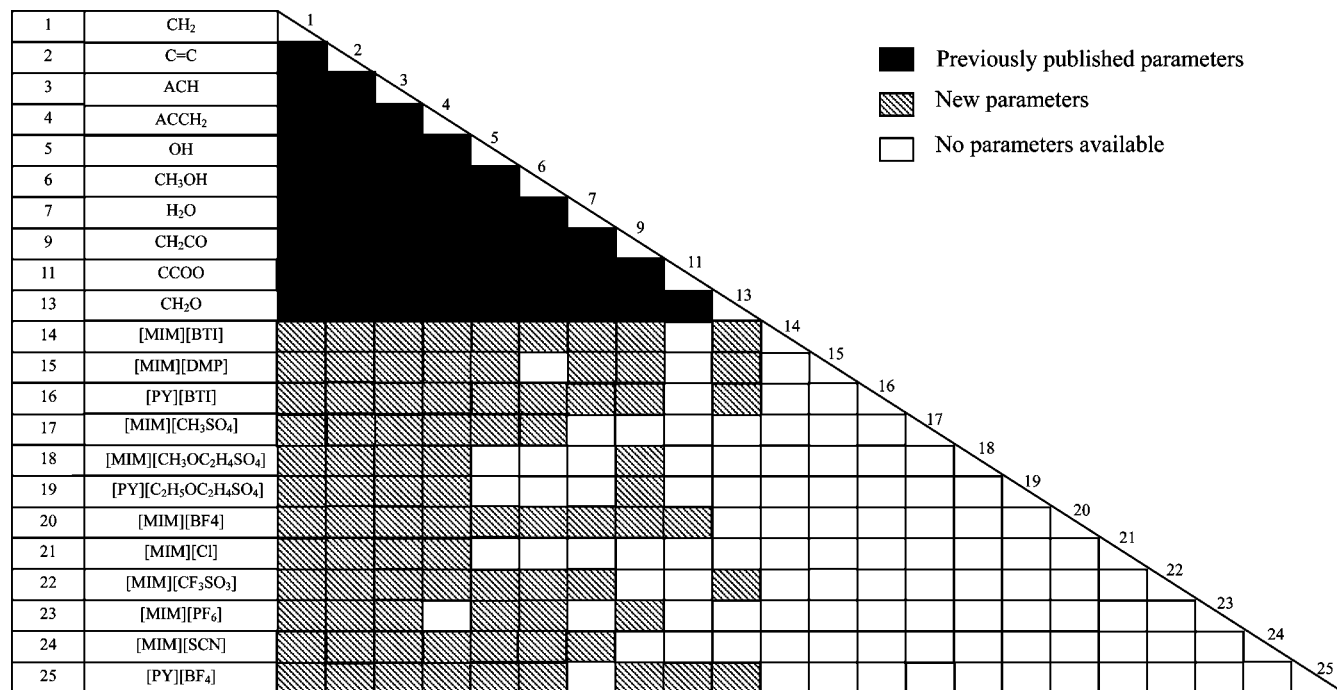
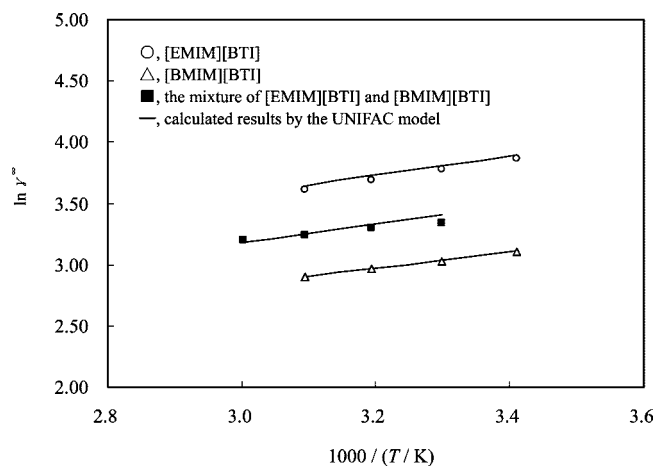
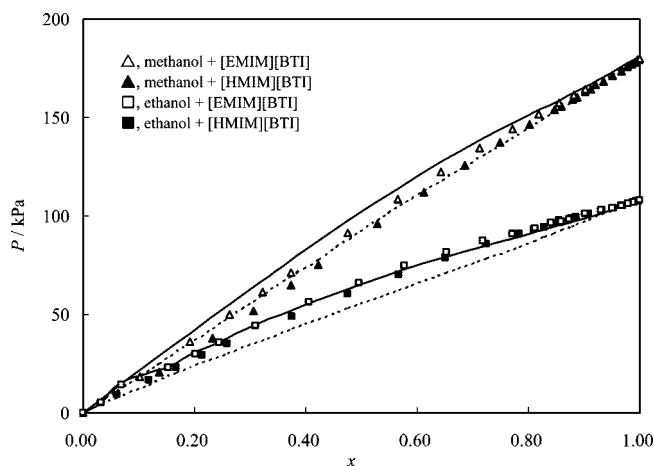


Figure 1. Current UNIFAC parameter matrix.

Figure 2. Activity coefficients at infinite dilution of *n*-hexane in the ionic liquids [EMIM][BTI], [BMIM][BTI], and their mixture (50:50 weight fraction of [EMIM][BTI] and [BMIM][BTI]) in the temperature range 303–343 K.

**3.2. Prediction of Vapor–Liquid Equilibria of Systems with Ionic Liquids at Finite Concentration.** The  $P$  (pressure)– $x$  (mole fraction in the liquid phase) curves of methanol and ethanol with [EMIM][BTI] and [HMIM][BTI] at  $T = 353$  K are shown in Figure 3. The experimental data fall close to the lines obtained by the UNIFAC model. The average relative deviations (ARDs) of vapor pressures for methanol/[EMIM][BTI], ethanol/[EMIM][BTI], methanol/[HMIM][BTI], and ethanol/[HMIM][BTI] are 5.43%, 3.77%, 1.81%, and 6.37%, respectively.

For nonpolar solute–ionic liquid systems, the  $P$ – $x$  curves of cyclohexane and cyclohexene with [HMIM][BTI] at  $T = 353$  K are shown in Figure 4. Unlike polar solute–ionic liquid systems, at low and high concentrations, the experimental data almost lie on the lines obtained by the UNIFAC model, but at middle concentration, the relative deviations between the experimental and calculated results seem to be a little large. The reason is that homogeneous behavior in the liquid phase is

Figure 3. Vapor–liquid equilibria for methanol and ethanol with the ionic liquids [EMIM][BTI] and [HMIM][BTI] at  $T = 353$  K. The solid and dashed lines represent the calculated results by the UNIFAC model for methanol/ethanol + [EMIM][BTI] and methanol/ethanol + [HMIM][BTI], respectively.

observed for polar solute–ionic liquid systems, while a miscibility gap can be found at middle concentration for nonpolar solute–ionic liquid systems. This indicates that the UNIFAC model may be not so accurate when a liquid–liquid demixing takes place.

**3.3. Screening of Suitable Ionic Liquid as Entrainer in Separation Processes.** The separation of aliphatic from aromatic hydrocarbons by extractive distillation or liquid–liquid extraction is investigated because it is commonly encountered in industry. It is assumed that *n*-hexane (1)/benzene (2) and cyclohexane (1)/benzene (2) are taken on as representative of aliphatics and aromatics since their separation mechanisms are consistent.

The selectivities and capacities at infinite dilution provide a useful index for the selection of suitable entrainers, which are defined as



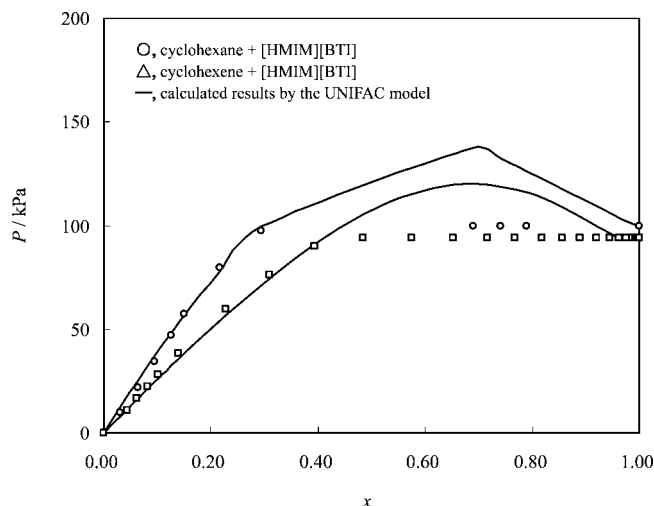
$$S_{12}^{\infty} = \frac{\gamma_1^{\infty}}{\gamma_2^{\infty}} \quad (12)$$

$$k_2^{\infty} = \frac{1}{\gamma_2^{\infty}} \quad (13)$$

Table 3 lists the experimental and calculated selectivities  $S_{12}^{\infty}$  and capacities  $k_2^{\infty}$  at infinite dilution for 18 ionic liquids at  $T = 298.15$  K. Figures 5 and 6 show the comparison of experimental selectivities at infinite dilution of *n*-hexane to benzene and cyclohexane to benzene with the calculated results by the UNIFAC model in decreasing order, respectively. It is evident that the sequences of experimental and calculated selectivities coincide well with each other.

It is evident that a long alkyl chain length on the cation is unfavorable for increasing the selectivities since the selectivities are in the order [EMIM][BTI] > [BMIM][BTI] > [HMIM][BTI] > [OMIM][BTI] and [EMIM][BF<sub>4</sub>] > [BMIM][BF<sub>4</sub>] > [HMIM][BF<sub>4</sub>] > [OMIM][BF<sub>4</sub>]. For the same cation, the selectivities are in the order [OMIM][BF<sub>4</sub>] > [OMIM][BTI] > [OMIM][Cl], [MMIM][CH<sub>3</sub>OC<sub>2</sub>H<sub>4</sub>SO<sub>4</sub>] > [MMIM][CH<sub>3</sub>SO<sub>4</sub>]. Therefore, the favorable anions are those where sterical shielding effect around their charge centers exists, e.g., [BTI]<sup>−</sup>, [PF<sub>6</sub>]<sup>−</sup>, [CF<sub>3</sub>SO<sub>3</sub>]<sup>−</sup>, and [BF<sub>4</sub>]<sup>−</sup>. On the contrary, the unfavorable anions are those where sterical shielding effect around their charge centers does not exist, e.g., [Cl]<sup>−</sup> and [CH<sub>3</sub>SO<sub>4</sub>]<sup>−</sup>. Therefore, the suitable ionic liquids for the separation of aliphatic from aromatic hydrocarbons are of small molecular volume and sterical shielding effect around the anion charge center.

Figure 7 shows the comparison of experimental capacities of benzene with the calculated results by the UNIFAC model in decreasing order, and both agree very well. However, it was found that the capacities of benzene are often small for ionic liquids with high selectivities. For instances, the capacities are in the order [EMIM][BTI] < [BMIM][BTI] < [HMIM][BTI] < [OMIM][BTI] and [EMIM][BF<sub>4</sub>] < [BMIM][BF<sub>4</sub>] < [HMIM][BF<sub>4</sub>] < [OMIM][BF<sub>4</sub>], which means that a long alkyl chain length on the cation is unfavorable for increasing the selectivities, but is favorable for increasing the capacities. Therefore, care should be taken to consider the demixing effects at finite concentration in separation processes.

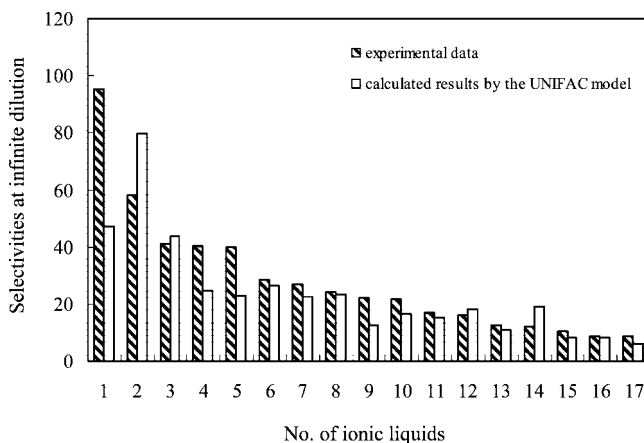


**Figure 4.** Vapor-liquid equilibria for cyclohexane and cyclohexene with [HMIM][BTI] at  $T = 353$  K.

**Table 3.** Selectivities  $S_{12}^{\infty}$  and Capacities  $k_2^{\infty}$  at Infinite Dilution for Ionic Liquids Investigated in This Work at  $T = 298.15$  K

ionic liquid	$S_{12}^{\infty}$				$k_2^{\infty}$	
	<i>n</i> -hexane (1)/benzene (2)		cyclohexane (1)/benzene (2)		benzene	
	expt	calcd	expt	calcd	expt	calcd
[OMIM][Cl] <sup>a</sup>	8.64	6.16	5.28	3.78	0.50	0.51
[EMIM][BTI] <sup>b</sup>	24.47 <sup>i</sup>	23.41	13.76 <sup>i</sup>	13.58	0.84 <sup>i</sup>	0.88
[BMIM][BTI] <sup>b</sup>	16.70 <sup>i</sup>	15.24	10.16 <sup>i</sup>	9.59	1.14 <sup>i</sup>	1.15
[HMIM][BTI] <sup>c</sup>	12.36	10.91	8.16	7.27	1.48	1.40
[OMIM][BTI] <sup>d</sup>	8.76 <sup>i</sup>	8.39	5.92 <sup>i</sup>	5.83	1.59 <sup>i</sup>	1.63
[MMIM][DMP] <sup>e</sup>	—	—	13.96 <sup>i</sup>	12.57	0.28 <sup>i</sup>	0.28
[EPY][BTI] <sup>e</sup>	28.66 <sup>i</sup>	26.45	15.68 <sup>i</sup>	14.24	0.81 <sup>i</sup>	0.81
[MMIM][CH <sub>3</sub> SO <sub>4</sub> ] <sup>e</sup>	15.93 <sup>i</sup>	17.98	19.74 <sup>i</sup>	8.35	0.13 <sup>i</sup>	0.14
[MMIM][CH <sub>3</sub> OC <sub>2</sub> H <sub>4</sub> SO <sub>4</sub> ] <sup>e</sup>	41.19 <sup>i</sup>	43.54	26.51 <sup>i</sup>	18.29	0.21 <sup>i</sup>	0.22
[PY][C <sub>2</sub> H <sub>5</sub> OC <sub>2</sub> H <sub>4</sub> SO <sub>4</sub> ] <sup>e</sup>	12.14 <sup>i</sup>	19.10	9.70 <sup>i</sup>	9.40	0.26 <sup>i</sup>	0.26
[EMIM][BF <sub>4</sub> ] <sup>f</sup>	58.11 <sup>i</sup>	79.75	23.29 <sup>i</sup>	25.14	0.42 <sup>i</sup>	0.36
[BMIM][BF <sub>4</sub> ] <sup>f</sup>	40.36 <sup>i</sup>	24.63	19.58 <sup>i</sup>	10.07	0.42 <sup>m</sup>	0.55
[HMIM][BF <sub>4</sub> ] <sup>f</sup>	22.12 <sup>i</sup>	12.56	11.75 <sup>i</sup>	5.96	0.62 <sup>i</sup>	0.71
[OMIM][BF <sub>4</sub> ] <sup>g</sup>	10.42	8.13	6.77	4.26	0.84	0.85
[BMIM][CF <sub>3</sub> SO <sub>3</sub> ] <sup>h</sup>	26.84	22.54	13.29	8.32	0.65	0.65
[HMIM][PF <sub>6</sub> ] <sup>i</sup>	21.84	16.26	12.28	7.60	0.97	0.97
[EMIM][SCN] <sup>j</sup>	95.34	47.25	33.21	14.12	0.29	0.29
[BMPY][BF <sub>4</sub> ] <sup>k</sup>	39.74 <sup>i</sup>	22.91	19.78 <sup>i</sup>	9.22	0.61 <sup>i</sup>	0.61

<sup>a</sup> Reference 36. <sup>b</sup> Reference 37. <sup>c</sup> Reference 38. <sup>d</sup> Reference 15. <sup>e</sup> Reference 39. <sup>f</sup> Reference 40. <sup>g</sup> Reference 41. <sup>h</sup> Reference 42. <sup>i</sup> Reference 43. <sup>j</sup> Reference 44. <sup>k</sup> Reference 45. <sup>l</sup> Extrapolated values.

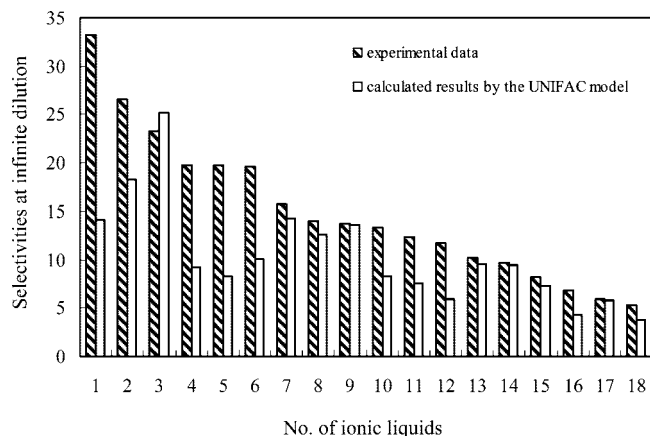


**Figure 5.** Selectivities of *n*-hexane to benzene at infinite dilution for 17 ionic liquids at  $T = 298.15$  K. The corresponding type of ionic liquids (1–17) is as follows: 1, [EMIM][SCN]; 2, [EMIM][BF<sub>4</sub>]; 3, [MMIM][CH<sub>3</sub>OC<sub>2</sub>H<sub>4</sub>SO<sub>4</sub>]; 4, [BMIM][BF<sub>4</sub>]; 5, [BMPY][BF<sub>4</sub>]; 6, [EPY][BTI]; 7, [BMIM][CF<sub>3</sub>SO<sub>3</sub>]; 8, [EMIM][BTI]; 9, [HMIM][BF<sub>4</sub>]; 10, [HMIM][PF<sub>6</sub>]; 11, [BMIM][BTI]; 12, [MMIM][CH<sub>3</sub>SO<sub>4</sub>]; 13, [HMIM][BTI]; 14, [PY][C<sub>2</sub>H<sub>5</sub>OC<sub>2</sub>H<sub>4</sub>SO<sub>4</sub>]; 15, [OMIM][BF<sub>4</sub>]; 16, [OMIM][BTI]; 17, [OMIM][Cl].

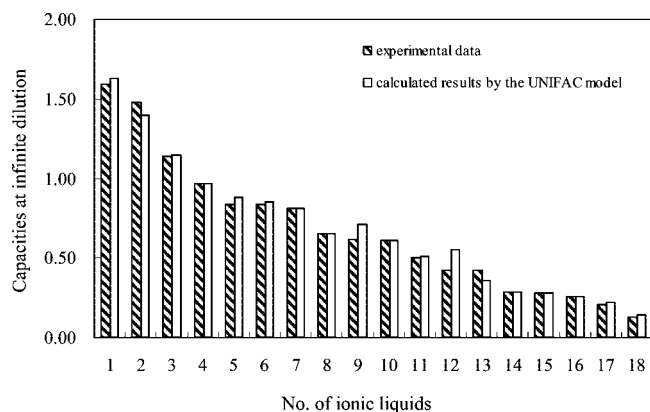
#### 4. Conclusions

Predictive molecular thermodynamic models are very necessary in separation processes because we should identify the relation between the molecular structures of the entrainers and separation performance to rapidly screen out the suitable entrainers and thus reduce the amount of experimental work.<sup>70</sup> The main advantage of the UNIFAC model over other predictive molecular thermodynamic models (e.g., COSMO-RS model and QSPR method) is that its formulation is simple and can be directly incorporated into such famous simulation programs as ASPEN PLUS and PROII. Thus, it is easy to go a step further to simulate and optimize the whole separation processes with ionic liquids.

Up to now, the group parameters for 12 main groups and 24 subgroups have been added into the current UNIFAC parameter matrix by means of correlating the activity coefficients of solutes at infinite dilution in ionic liquids at different temperatures. They



**Figure 6.** Selectivities of cyclohexane to benzene at infinite dilution for 18 ionic liquids at  $T = 298.15$  K. The corresponding type of ionic liquids (1–18) is as follows: 1, [EMIM][SCN]; 2, [MMIM][CH<sub>3</sub>OC<sub>2</sub>H<sub>4</sub>SO<sub>4</sub>]; 3, [EMIM][BF<sub>4</sub>]; 4, [BMPY][BF<sub>4</sub>]; 5, [MMIM][CH<sub>3</sub>SO<sub>4</sub>]; 6, [BMIM][BF<sub>4</sub>]; 7, [EPY][BTI]; 8, [MMIM][DMP]; 9, [EMIM][BTI]; 10, [BMIM][CF<sub>3</sub>SO<sub>3</sub>]; 11, [HMIM][PF<sub>6</sub>]; 12, [HMIM][BF<sub>4</sub>]; 13, [BMIM][BTI]; 14, [PY][C<sub>2</sub>H<sub>5</sub>OC<sub>2</sub>H<sub>4</sub>SO<sub>4</sub>]; 15, [HMIM][BTI]; 16, [OMIM][BF<sub>4</sub>]; 17, [OMIM][BTI]; 18, [OMIM][Cl].



**Figure 7.** Capacities of benzene at infinite dilution for 18 ionic liquids at  $T = 298.15$  K. The corresponding type of ionic liquids (1–18) is as follows: 1, [OMIM][BTI]; 2, [HMIM][BTI]; 3, [BMIM][BTI]; 4, [HMIM][PF<sub>6</sub>]; 5, [OMIM][BF<sub>4</sub>]; 6, [EMIM][BTI]; 7, [EPY][BTI]; 8, [BMIM][CF<sub>3</sub>SO<sub>3</sub>]; 9, [HMIM][BF<sub>4</sub>]; 10, [BMPY][BF<sub>4</sub>]; 11, [OMIM][Cl]; 12, [BMIM][BF<sub>4</sub>]; 13, [EMIM][BF<sub>4</sub>]; 14, [EMIM][SCN]; 15, [MMIM][DMP]; 16, [PY][C<sub>2</sub>H<sub>5</sub>OC<sub>2</sub>H<sub>4</sub>SO<sub>4</sub>]; 17, [MMIM][CH<sub>3</sub>OC<sub>2</sub>H<sub>4</sub>SO<sub>4</sub>]; 18, [MMIM][CH<sub>3</sub>SO<sub>4</sub>].

can be used for predicting the vapor–liquid equilibria of the systems with ionic liquids at finite concentration, and screening the suitable ionic liquids in separation processes. However, it was found that, for nonpolar solute–ionic liquid systems, the calculated results may be not so satisfactory because in this case a liquid–liquid demixing takes place.

There have been only a limited number of functional groups for ionic liquids included in the UNIFAC model. The future development of this predictive model will still require much more accurate experimental data to fill the gap since ionic liquids as green and potential environmentally friendly entrainers are very attractive in separation processes.

## Acknowledgment

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