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Extension of the UNIFAC Model for Ionic Liquids

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S Supporting Information

ABSTRACT: The UNIFAC model has recently become very popular for ionic liquids (ILs) because of its applicability for prediction of thermodynamic properties. This work is a continuation of our studies on the extension of group parameters of the UNIFAC model to systems with ILs. The new IL groups for 33 main groups and 53 subgroups were added into the current UNIFAC parameter matrix. The parameters of group surface area and volume for ILs were obtained by the COSMO calculation, while the group binary interaction parameters, a_{nm} and a_{mn} , were obtained by means of correlating the activity coefficients of solutes at infinite dilution in ILs at different temperatures exhaustively collected from literature by the end of 2011. The predicted results of UNIFAC model are more accurate than those of the COSMO-RS model so that it can be used for identifying the general relationship between molecular structure of ILs and separation performance for the separation of liquid mixtures with ILs.

1. INTRODUCTION

Ionic liquids (ILs) usually consist of a large organic cation and a small inorganic polyatomic anion, and have gained popular attention in recent years due to their unique thermophysical properties, such as salt effect, liquid state around room temperature, extremely low vapor pressure, indefinite recycling potential by simple flash distillation or stripping, specific solvent abilities, nonflammability, and thermal and chemical stabilities. Much work has been carried out on the application of ILs for the separation of liquid mixtures, such as extractive distillation, liquid–liquid extraction, liquid-phase microextraction, and supported liquid membranes.^{1–14} Among others, selection of a suitable IL plays an important role in ensuring an effective and economical design of separation process.

Because a large number of ILs can be constructed from the combination of cations and anions, it is no sense to choose the best one for a given system through experiments. In this case, predictive molecular thermodynamic models, which mean that thermodynamic properties such as activity coefficient, selectivity, phase equilibria, and so on can be derived provided that molecular structures or physical properties of pure components in the mixture are known, are necessary as a theoretical tool for shortening the screening time and reducing the amount of experimental work. For this purpose, the COSMO-RS (conductor-like screening model for real solvents) and UNIFAC (universal quasichemical functional-group activity coefficients) models can be used for evaluating the ILs as separating agents. The COSMO-RS model is a novel method for predicting thermodynamic properties of pure and mixed liquids on the basis of unimolecular quantum chemical calculations for the respective individual molecules.^{15–26} As an a priori prediction method, it requires molecular structure as the only information and is independent of experimental data. Some researchers have used COSMO-RS model to predict the activity coefficients at infinite dilution γ_i^∞ of solutes in ILs, and found that for the methylimidazolium-based ILs, the mean relative deviations between experimental data and predicted results are up to 79.4% for VLE (vapor–liquid equilibria) and

more than 100% for γ_i^∞ of alkanes, alkenes, cycloalkenes, and alcohols.²⁷ Thus, it seems that significant deviations occur when using the COSMO-RS model. On the other hand, the UNIFAC model is a classical thermodynamic model and widely used in separation science because its formulation is simple and can be directly incorporated into such famous simulation programs as ASPEN PLUS, PROII, and ChemCAD to establish equilibrium stage (EQ) and nonequilibrium stage (NEQ) models for design and simulation.^{28–30} However, in the current UNIFAC parameter matrix for ILs as reported by Lei et al.,²⁸ Santiago et al.,^{31,32} Alevizou et al.,³³ Kato and Gmehling,²⁷ and Nebig and Gmehling,^{34–36} the cations involved in total are imidazolium (IM), pyridinium (PY), and pyrrolidinium (PYR), while the anions are bis(trifluoromethylsulfonyl)imide (Tf₂N), trifluoromethanesulfonate (CF₃SO₃), tetrafluoroborate (BF₄), hexafluorophosphate (PF₆), methylsulfate (CH₃SO₄), methoxyethylsulfate (CH₃OC₂H₄SO₄), ethoxyethylsulfate (C₂H₅OC₂H₄SO₄), dimethylphosphate (DMP), chloride (Cl), and thiocyanate (SCN). Evidently, the number of these ions is not adequate to meet the increasing requirement for development and challenge of ILs in the community of chemical engineering.

Therefore, the focus of this work is to extend the group parameters of UNIFAC model to establish the more complete UNIFAC parameter matrix since there have been only a limited number of functional groups for ILs included in the current UNIFAC model.²⁸ On this basis, the UNIFAC model is used for identifying the general relationship between molecular structure of ILs and separation performance (i.e., selectivity and capacity), which requires the close integration of theoretically predictive models and experiments. The meaning of abbreviations for anions and cations of ILs throughout this article is given in the Supporting Information (SI).

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2. EXTENSION OF THE UNIFAC GROUP PARAMETER MATRIX

2.1. Model Description. 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 1975.³⁷ This model can be applied at infinite dilution and finite concentration, and has still been the most widely used even after several versions of this model have been developed. The activity coefficient is expressed as functions 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, that is, $\ln \gamma_i^R$, essentially due to energetic interactions.

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

2.2. Decomposition of IL Groups. To apply the UNIFAC model, the pure IL must be decomposed into separate functional groups. There are three approaches for the choice of UNIFAC functional groups:

- (i) The IL is divided into one cation group and one anion group.^{31,32} This will require a large number of parameters for different ILs. This approach does not reflect the influence of structural variation of substituents on the cations (or anions) on the separation performance.
- (ii) The IL is divided into several groups with the imidazolium ring as a functional group.^{33–36} Although the structural variations of cations, anions, and substituents are considered in this approach, it requires a large number of experimental data to correlate the group interaction parameters. Therefore, only a few functional groups for ILs have been included due to a limited number of experimental data available from the literature.
- (iii) The IL is also divided into several groups, but the skeletons of cation and anion are treated as a whole since the ionic pair has a strong electrostatic interaction.^{28–30} For example, $[\text{BMIM}]^+[\text{BF}_4]^-$ is composed of one CH_3 group, three CH_2 groups, and one $[\text{MIM}][\text{BF}_4]$ group. The main group $[\text{MIM}][\text{BF}_4]$ has two subgroups, i.e. $[\text{MIM}][\text{BF}_4]$ and $[\text{IM}][\text{BF}_4]$, whose group volume and surface area parameters are derived by the addition of those of $[\text{MIM}]$ (or $[\text{IM}]$) and $[\text{BF}_4]$. In this work, we adopted this decomposition because ILs are required to decompose into electrically neutral groups so as to avoid additional terms accounting for long electrostatic contributions.

2.3. Group Surface Area and Volume for ILs. The combinatorial part $\ln \gamma_i^C$ contains the group parameters R_k and Q_k , and is derived by

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

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

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

where $v_k^{(i)}$, always an integer, is the number of groups of type k in molecule i , and R_k and Q_k can be obtained from the COSMO calculation. The modern COSMO-RS model can not only calculate the thermodynamic properties, but can also provide the parameters of group surface area and volume for ILs for the UNIFAC model.^{38,39} Since one group (or molecule) has a charge distribution and thus possess an electric field, it will polarize the embedding medium which will result in another electric field, given by a charge distribution on the surface of the group shaped cavity. This charge distribution is generated by the COSMO quantum mechanical calculation, in which the surface of the group shaped cavity will be called group surface, and the corresponding volume will be called group volume. The concept of solvent accessible surface introduced by Delley⁴⁰ was used for modeling the cavity by continuous variation of all properties as a function of geometry. Therefore, in principle, all of the group surface area and volume parameters for ILs can be obtained virtually by the COSMO calculation, which will greatly promote the development of UNIFAC model.

In this work, the molecular geometry for cations and anions was optimized at the ADF (Amsterdam Density Functional) software,⁴¹ which is a Fortran program for calculations on atoms and molecules (in gas phase or solution), the underlying theory being the Kohn–Sham approach to Density Functional Theory (DFT). ADF input was used to create the initial structure of all species. The following settings were adopted: the Generalized Gradient Approximation and Becke Perdew exchange correlation functional (GGA: BP), use of the scalar relativistic ZORA Hamiltonian, a TZP (triple- ζ valence potential) small core basis set, and an integration accuracy of 6. For more detail, please see <http://www.scm.com/Doc/Doc2010/CRS/CRS/page18.html>.

The group parameters for volume R_k and surface area Q_k in the UNIFAC model are calculated by

$$R_k = \frac{V \times N_A}{V_{\text{VW}}}, \quad Q_k = \frac{A \times N_A}{A_{\text{VW}}} \quad (5)$$

where V and A are group volume and surface area obtained from the COSMO calculation, respectively; V_{VW} ($15.17 \text{ cm}^3 \cdot \text{mol}^{-1}$) and A_{VW} ($2.5 \times 10^9 \text{ cm}^2 \cdot \text{mol}^{-1}$) are standard segment volume and surface area as suggested by Bondi,⁴² respectively; and N_A is the Avogadro's number ($6.023 \times 10^{23} \text{ mol}^{-1}$).

2.4. Group Interaction Parameters. The group binary interaction parameters contained in $\ln \gamma_i^R$, a_{nm} and a_{mn} , were obtained by means of correlating the activity coefficients of solutes at infinite dilution in ILs exhaustively collected from literature by the end of 2011 in the temperature range of 293–368 K.^{43–122} The kinds of ILs, molecular solutes, number of data points, experimental method, and temperature range are provided in detail in the SI. The following objective function (OF) minimized was adopted:

$$\text{OF} = \min \sum_i^N |\gamma_i^{\infty, \text{exp}} - \gamma_i^{\infty, \text{cal}}| \quad (6)$$

where $\ln \gamma_i^{\infty}$ is activity coefficient of solute at infinite dilution and N is the number of data points. The Marquardt method as in Press et al.¹²³ 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

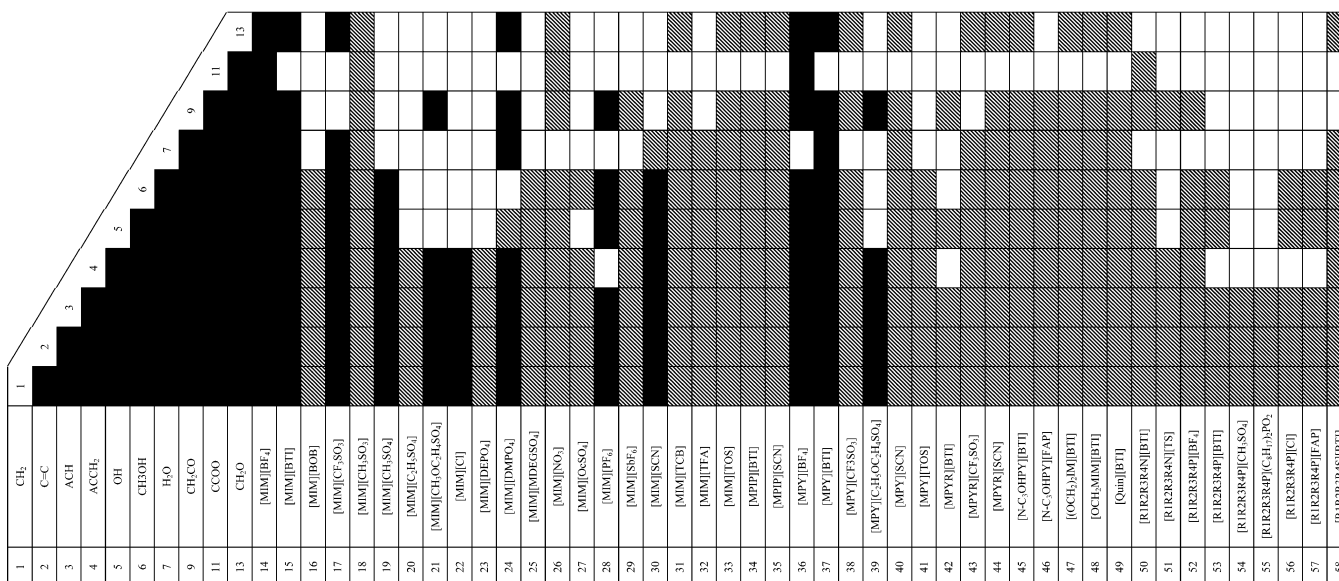
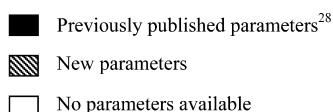


Figure 1. Current UNIFAC parameter matrix.

fitting procedure was done in a similar way as our previous publication.²⁸

Thus, the new group parameters for 33 main groups and 53 subgroups for ILs were derived and are listed in the SI. The current UNIFAC parameter matrix is illustrated in Figure 1, where 45 main groups and 77 subgroups for ILs are included in conjunction with the previous functional groups for ILs in a similar fashion. Strictly speaking, the UNIFAC model for ILs discussed in this work should be called “ γ^∞ -based UNIFAC model”.¹²⁴

2.5. Selectivity and Capacity at Infinite Dilution. The selectivity and capacity at infinite dilution provide a useful assessment for the selection of suitable ILs, which are defined as

$$S_{ij}^\infty = \gamma_i^\infty / \gamma_j^\infty \quad (7)$$

$$k_i^\infty = 1 / \gamma_i^\infty \quad (8)$$

It is noted that all comparison between the literature and predicted results was done at 298.15 K. If it happens that the literature data at 298.15 K is missing since the experimental temperature cannot be kept exactly at this temperature, it was deduced from those at other temperatures using a linear regression:

$$\ln \gamma_i^\infty = a/T + b \quad (9)$$

where a and b are constants. However, another problem may arise in that the literature data from some sources differ greatly for activity coefficients at infinite dilution under the same operating conditions. The difference is probably caused by different experimental methods, and/or input thermophysical data of solutes, sometimes more than 140%.^{52,53} It is known that measuring activity coefficients at infinite dilution with gas–liquid chromatography method may give some inaccuracy. In this case all literature data are present, and we can use the UNIFAC model to judge the accuracy of different data sources.

3. RESULTS AND DISCUSSION

In this work, we decide to discuss the UNIFAC model on identifying the general relationship between molecular structure of ILs and separation performance for the separation of liquid mixtures with ILs by the combination of UNIFAC model and experimental data coming from the literatures.

Separation of aromatics and nonaromatics is a specific problem in the field of hydrocarbon processing, and the systems of hexane/benzene, heptane/benzene, and cyclohexane/benzene are taken on as the representatives of nonpolar systems. On the other hand, ethanol and water are taken on as the representative of polar systems since anhydrous ethanol is used not only as a chemical reagent and organic solvent but also as the raw material of many important chemical products and intermediates. For these systems, an additional solvent (namely separating agent) is normally required to add into the mixture to alter the selectivity of the components to be separated.

3.1. Separation of Nonpolar System. The curves, as shown in SI Figures S1–S3, exhibit the similar trend since the separation mechanism between aromatics and nonaromatics is consistent based on the different mobility of electron cloud of C–C (no double bond) and ACH (conjugated double bond) and thus different interaction between separating agent and the components to be separated. The previous findings that the ILs with small molecular volume (i.e., short alkyl chain length), unbranched group, and sterical shielding effect around anion charge center are favorable for increasing selectivity but decreasing capacity are also confirmed. Among all the ILs investigated in this work, the IL [CPMIM]⁺[N(CN)₂][−] possesses the highest selectivity, [P_{6,6,6,14}]⁺[(C₈H₁₇)₂PO₂][−] having the lowest selectivity. As shown in Figure S4, the trend of capacity is generally opposite to selectivity. But the IL [P_{6,6,6,14}]⁺[(C₂F₅)₃PF][−] possesses the highest capacity, [MMIM]⁺[CH₃SO₄][−] having the lowest capacity. This means that the IL with the highest selectivity does not always possess the lowest capacity. A majority of ILs have better selectivity and

capacity for the separation of nonpolar system than the conventional NMP (*N*-methyl-pyrrolidone) and sulfolane.^{125,126} Among others, it seems that $[\text{CPMIM}]^+[\text{N}(\text{CN})_2]^-$ is the most potential IL with the highest selectivity and enough capacity comparable to sulfolane.

As a whole, the predicted results by the UNIFAC model and the voluminous experimental data exhibit a similar trend regarding separation performance. But for some ILs, the experimental data points come from more than one data source, and those that apparently deviate away from the trendline and are marked with black circle should be identified as skeptical. For example, the selectivity for $[\text{MMIM}]^+[\text{TF}_2\text{N}]^-$ should be higher than that for $[\text{EMIM}]^+[\text{TF}_2\text{N}]^-$, but it is not always true for some experimental data (see Figure S1). Anyway, the predicted results by the UNIFAC model are quantitatively consistent with the experimental data, and the comparison of selectivity and capacity at infinite dilution is summarized in Table 1.

Table 1. Comparison of Selectivity and Capacity at Infinite Dilution Between Experimental Data and UNIFAC Results at $T = 298.15\text{ K}$

components to be separated	kinds of ILs	no. of data points	ARDs (%)
selectivity at infinite dilution			
<i>n</i> -hexane–benzene	59	73	22.72
<i>n</i> -heptane–benzene	51	65	15.37
cyclohexane–benzene	59	75	28.68
ethanol–water	17	20	11.26
capacity at infinite dilution			
benzene	63	81	10.34
water	17	19	53.09

3.1.1. Cation Type. The influence of imidazolium, pyrrolidinium, pyridinium, isoquinolinium, tetra-alkylammonium, and tetra-alkylphosphonium-based cations with the same $[\text{TF}_2\text{N}]^-$ anion on the selectivity and capacity is shown in Figure 2. The selectivity is in the order of $[\text{N}_{1,1,1,4}]^+ > [\text{BMIM}]^+ \approx [\text{BMPY}]^+ \approx [\text{BMPYR}]^+ > [\text{C}_4\text{iQuin}]^+ > [\text{C}_8\text{iQuin}]^+ > [\text{N}_{1,8,8,8}]^+ \approx [\text{P}_{6,6,6,14}]^+$, while the order of capacity is reversed. It was found that there is almost no difference of both selectivity and capacity among $[\text{BMIM}]^+$, $[\text{BMPY}]^+$, and $[\text{BMPYR}]^+$ with the same alkyl substituent. Among others, changing the alkyl chain length from $[\text{N}_{1,8,8,8}]^+$ to $[\text{N}_{1,4,4,4}]^+$ leads to increasing selectivity and decreasing capacity as expected due to the decreasing molecular volume of IL and the increasing activity coefficient of benzene. It is also noted that the selectivity for $[\text{P}_{6,6,6,14}]^+$ is only slightly higher than that for $[\text{N}_{1,8,8,8}]^+$, both of which have the almost same number of carbon atoms on the cation, indicating that the effect of central P or N atom of the cation on selectivity and capacity is actually not predominant. The reason why the selectivity for $[\text{C}_4\text{iQuin}]^+$ is slightly lower than that of $[\text{BMIM}]^+$, $[\text{BMPY}]^+$, and $[\text{BMPYR}]^+$ with the same branched group is attributed to its larger molecular volume brought on by two benzene rings. In addition, it seems that the UNIFAC model gives better prediction for imidazolium-based cations than for other cation types. Moreover, since a lot of imidazolium-based ILs are much easier to available from chemical markets at lower prices, it is actually more feasible to tailor them by judicious combination of cations, anions, and substituents than other types of ILs.

3.1.2. Hydroxylation on the Cation. The influence of adding a OH group to the alkyl chain of pyridinium-based

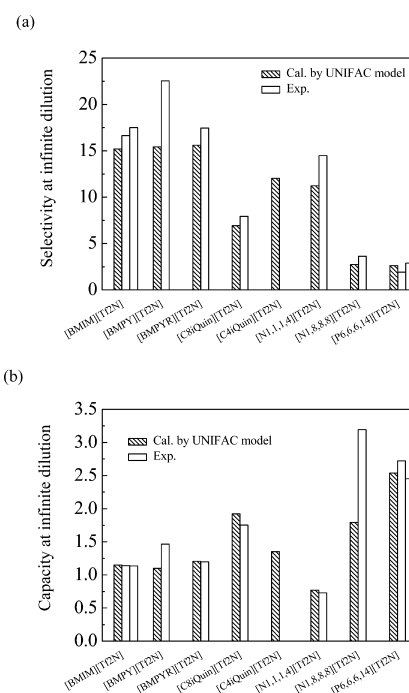


Figure 2. Selectivity of *n*-hexane to benzene (a) and capacity of benzene (b) at infinite dilution for the ILs $[\text{BMIM}]^+[\text{TF}_2\text{N}]^-$ (exp.^{78,83}), $[\text{BMPY}]^+[\text{TF}_2\text{N}]^-$ (exp.⁵¹), $[\text{BMPYR}]^+[\text{TF}_2\text{N}]^-$ (exp.²⁷), $[\text{C}_8\text{iQuin}]^+[\text{TF}_2\text{N}]^-$ (exp.¹¹²), $[\text{N}_{1,1,1,4}]^+[\text{TF}_2\text{N}]^-$ (exp.⁴⁸), $[\text{N}_{1,8,8,8}]^+[\text{TF}_2\text{N}]^-$ (exp.⁴⁷), and $[\text{P}_{6,6,6,14}]^+[\text{TF}_2\text{N}]^-$ (exp.^{16,90}) at $T = 298.15\text{ K}$.

cation with the same $[\text{TF}_2\text{N}]^-$ anion on the selectivity and capacity is shown in Figure 3. The selectivity is in the order of

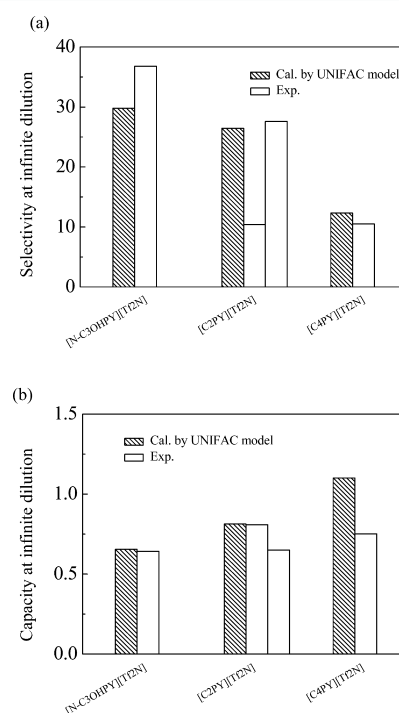


Figure 3. Selectivity of *n*-hexane to benzene (a) and capacity of benzene (b) at infinite dilution for the ILs $[\text{N}-\text{C}_3\text{OHPPY}]^+[\text{TF}_2\text{N}]^-$ (exp.¹¹⁶), $[\text{C}_2\text{PY}]^+[\text{TF}_2\text{N}]^-$ (exp.^{52,53}), and $[\text{C}_4\text{PY}]^+[\text{TF}_2\text{N}]^-$ (exp.⁵²) at $T = 298.15\text{ K}$.

$[n\text{-C}_3\text{OHPY}]^+ > [\text{C}_2\text{PY}]^+ > [\text{C}_4\text{PY}]^+$, indicating that hydroxylation on the cation does increase the selectivity because for the analogous cation $[\text{C}_3\text{PY}]^+$, it should take the following order: $[\text{C}_2\text{PY}]^+ > [\text{C}_3\text{PY}]^+ > [\text{C}_4\text{PY}]^+$.

The capacity is in the order of $[n\text{-C}_3\text{OHPY}]^+ < [\text{C}_2\text{PY}]^+ < [\text{C}_4\text{PY}]^+$. For the analogous cation $[\text{C}_3\text{PY}]^+$, it should take the following order: $[\text{C}_2\text{PY}]^+ < [\text{C}_3\text{PY}]^+ < [\text{C}_4\text{PY}]^+$. Therefore, hydroxylation on the cation can increase selectivity but decrease capacity.

3.1.3. Alkyl, Benzyl, and Alkoxy Substitutions on the Anion. The influence of alkyl, benzyl, and alkoxy groups on sulfate-based anion with the same $[\text{BMIM}]^+$ cation on the selectivity and capacity is shown in Figure 4. The selectivity is

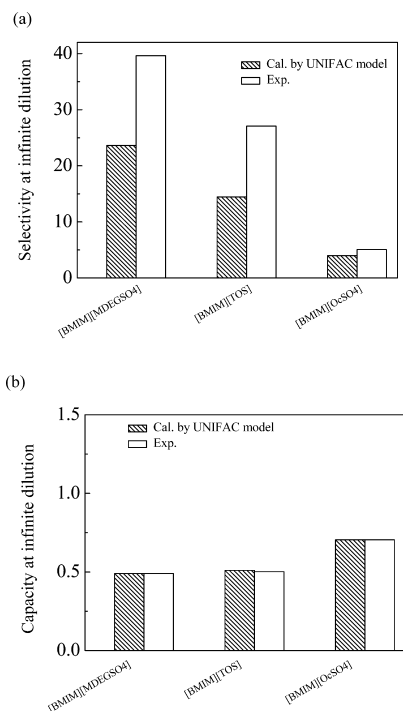


Figure 4. Selectivity of *n*-hexane to benzene (a) and capacity of benzene (b) at infinite dilution for the ILs $[\text{BMIM}]^+[\text{MDEGSO}_4]^-$ (exp.¹⁰¹), $[\text{BMIM}]^+[\text{TOS}]^-$ (exp.⁹⁶), and $[\text{BMIM}]^+[\text{OcSO}_4]^-$ (exp.¹⁰⁰) at $T = 298.15$ K.

in the order of $[\text{BMIM}]^+[\text{MDEGSO}_4]^- > [\text{BMIM}]^+[\text{TOS}]^- > [\text{BMIM}]^+[\text{OcSO}_4]^-$ from alkoxy, benzyl, to alkyl substitutions in series. That is to say, adding a strong polar group substitution on the anion is favorable for increasing selectivity as a result of the enhanced interaction between anion and benzene ring in aromatics. Meanwhile, their capacities have comparable values probably caused by the almost same number of carbon atoms on the anion. Therefore, it is advisable to tailor ILs by substituting with strong polar groups on the anion for the separation of nonpolar systems.

3.1.4. Fluorination on the Anion. For imidazolium-based ILs, the anions containing fluorine atoms, e.g. $[\text{Tf}_2\text{N}]^-$ and $[\text{BF}_4]^-$, are very common. The influence of fluorination on the anion with the same $[\text{BMIM}]^+$ cation on the selectivity and capacity is shown in Figure 5. It can be seen that selectivity is in the order of $[\text{BMIM}]^+[\text{BF}_4]^- > [\text{BMIM}]^+[\text{CF}_3\text{SO}_3]^- > [\text{BMIM}]^+[\text{Tf}_2\text{N}]^- \approx [\text{MMIM}]^+[\text{CH}_3\text{SO}_4]^-$, while capacity is in the order of $[\text{MMIM}]^+[\text{CH}_3\text{SO}_4]^- < [\text{BMIM}]^+[\text{BF}_4]^- < [\text{BMIM}]^+[\text{CF}_3\text{SO}_3]^- < [\text{BMIM}]^+[\text{Tf}_2\text{N}]^-$.

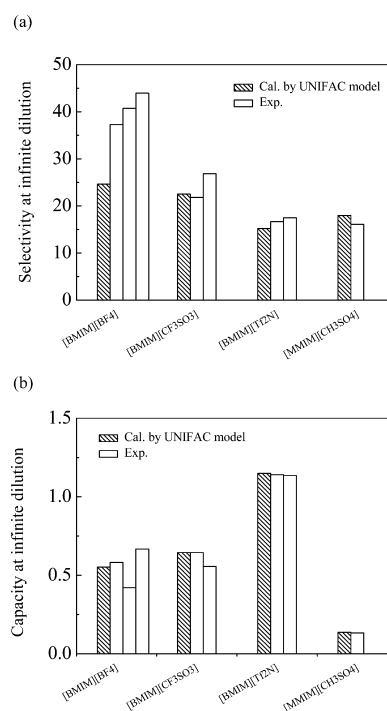


Figure 5. Selectivity of *n*-hexane to benzene (a) and capacity of benzene (b) at infinite dilution for the ILs $[\text{BMIM}]^+[\text{BF}_4]^-$ (exp.^{71,73,119}), $[\text{BMIM}]^+[\text{CF}_3\text{SO}_3]^-$ (exp.^{65,66}), $[\text{BMIM}]^+[\text{Tf}_2\text{N}]^-$ (exp.^{78,83}), and $[\text{MMIM}]^+[\text{CH}_3\text{SO}_4]^-$ (exp.⁵³) at $T = 298.15$ K.

For the analogous IL $[\text{MMIM}]^+[\text{CH}_3\text{SO}_4]^-$, fluorination on the anion leads to increasing both selectivity and capacity. But this increase is not proportional to the number of fluorine atoms as expected. On the contrary, the selectivity for $[\text{BF}_4]^-$ is roughly twice as high as that for $[\text{Tf}_2\text{N}]^-$. But the capacity for $[\text{BF}_4]^-$ and $[\text{CF}_3\text{SO}_3]^-$ is much smaller than for $[\text{Tf}_2\text{N}]^-$, indicating that the affinity between $[\text{Tf}_2\text{N}]^-$ and nonpolar components is stronger due to more fluorine atoms introduced into the anion.

3.2. Separation of Polar System. SI Figures S5 and S6 show the results predicted by the UNIFAC model and the experimental data exhaustively collected from literature for the separation of ethanol and water, all exhibiting the similar trend with ARDs 10.35% for selectivity and 42.23% for capacity due to the possible experimental errors arising from very small activity coefficients at high capacity. Among all the ILs investigated in this work, the IL $[\text{EMIM}]^+[\text{SCN}]^-$ possesses the highest selectivity, $[\text{BMIM}]^+[\text{TOS}]^-$ having the highest capacity. The IL $[\text{C}_8\text{iQuin}]^+[\text{Tf}_2\text{N}]^-$ possesses both the lowest selectivity and the lowest capacity. A majority of ILs have better selectivity and capacity for the separation of polar system than the conventional EG (ethylene glycol).¹²⁷ Among others, it seems that $[\text{EMIM}]^+[\text{SCN}]^-$ is the most potential IL with the highest selectivity and enough capacity comparable to EG.

Similarly, the previous findings that the ILs with small molecular volume (i.e., short alkyl chain length), unbranched group, and no sterical shielding effect around anion charge center are favorable for increasing both selectivity and capacity for the separation of polar systems are also confirmed. But herein we would like to consider some new structure–property relations.

3.2.1. Cation Type. The influence of imidazolium, pyrrolidinium, pyridinium, isoquinolinium, tetra-alkylammo-

nium, and tetra-alkylphosphonium-based cations with the same $[\text{CF}_3\text{SO}_3]^-$ anion on the selectivity and capacity is shown in Figure 6. Like the separation of nonpolar systems, there is almost no difference of both selectivity and capacity among $[\text{BMIM}]^+$, $[\text{BMPY}]^+$, and $[\text{BMPYR}]^+$ with the same alkyl substituent.

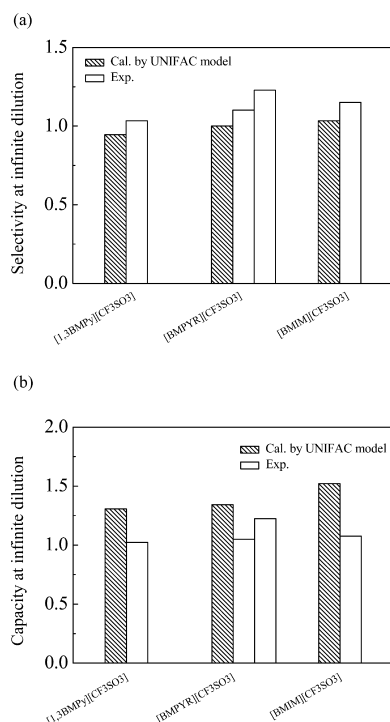


Figure 6. Selectivity of ethanol to water (a) and capacity of water (b) at infinite dilution for the ILs $[\text{1,3BMPY}][\text{CF}_3\text{SO}_3]^-$ (exp.⁹⁴), $[\text{BMPYR}][\text{CF}_3\text{SO}_3]^-$ (exp.^{50,118}), and $[\text{BMIM}][\text{CF}_3\text{SO}_3]^-$ (exp.⁶⁵) at $T = 298.15$ K.

3.2.2. Hydroxylation on the Cations. The influence of adding a OH group to the alkyl chain of pyridinium-based cation with the same $[\text{Tf}_2\text{N}]^-$ anion on the selectivity and capacity is shown in Figure 7. Both selectivity and capacity are in the order of $[\text{n-C}_3\text{OHPY}]^+ > [\text{C}_2\text{PY}]^+$, indicating that hydroxylation on the cation does increase both selectivity and capacity because for the analogous cation $[\text{C}_3\text{PY}]^+$, it should take the following order: $[\text{C}_2\text{PY}]^+ > [\text{C}_3\text{PY}]^+$.

4. CONCLUSION

Since a large number of possible ILs are of little use for separation science, it is very important for us to establish the predictive molecular thermodynamic models. In this work, the new IL groups for 33 main groups and 53 subgroups were added into the current UNIFAC parameter matrix so that it will become a universal and reliable predictive model. The predicted results by the UNIFAC model are quantitatively consistent with the experimental data, more accurate than the COSMO-RS model. Besides, the UNIFAC model for ILs has been applied for identifying the structure–property relation. Besides the alkyl chain length and branched group on the imidazolium-based cation, and sterical shielding effect on the anion investigated in previous study, new structure factors such as cation type, hydroxylation on the cation, substitutions (alkyl, benzyl, and alkoxy) on the anion, and fluorination on the anion were considered, and some new structure–property relations

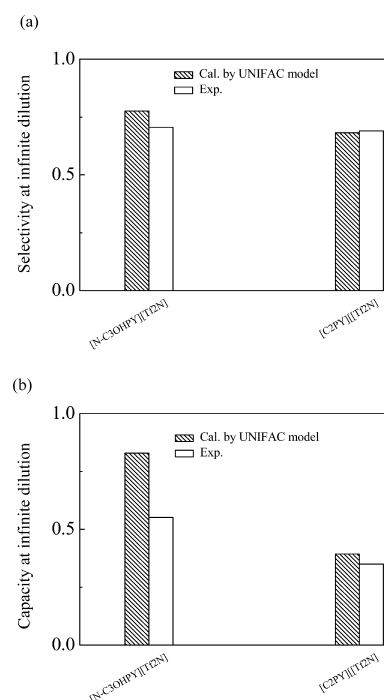


Figure 7. Selectivity of ethanol to water (a) and capacity of water (b) at infinite dilution for the ILs $[\text{N-C}_3\text{OHPY}][\text{Tf}_2\text{N}]^-$ (exp.¹¹⁶), and $[\text{C}_2\text{PY}][\text{Tf}_2\text{N}]^-$ (exp.⁵³) at $T = 298.15$ K.

for the separation of liquid mixtures with ILs were derived by the combination of UNIFAC model and experimental data coming from the references.

It should be noted that in the current UNIFAC parameter matrix for ILs, gas molecules (e.g., CO_2 , SO_2 , CO , H_2 , etc.) have not yet been included, and would be considered in future work so as to meet various requirements put forward by chemical engineers over a broad range of separation science.

■ ASSOCIATED CONTENT

Supporting Information

Abbreviations and full names for IL anions and cations, their chemical structures, new UNIFAC group parameters, Figures S1–S6, activity coefficients of solutes at infinite dilution in ILs exhaustively collected from literature including the kinds of ILs, molecular solutes, number of data points, experimental method, and temperature range. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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