Ionic Liquids: Solubility Parameters and Selectivities for Organic Solutes

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Ionic liquids (ILs) are innovative solvents for chemical processing. In this work, a database on activity coefficients of organic solutes at infinite dilution in ILs was collected from literature sources. The activity coefficients have been correlated by activity coefficient model for the regular solution and have been used to estimate the solubility parameter of ILs. The solubility parameters of ILs have been further correlated based on a concept of the group contribution method. Through the analysis of the database and the prediction results of selectivities, it was shown here that as compared with conventional organic solvents, higher selectivity can be achieved by using ILs as working solvents for separation of alkane/aromatic, aromatic/aromatic hydrocarbon mixtures via extraction or supported liquid membrane. © 2013 American Institute of Chemical Engineers *AIChE J*, 59: 3034–3041, 2013
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Introduction

The common organic solvents are remarkable similar in a relatively narrow liquidus region. This means that they are all relatively volatile and easily becoming emissions into the atmosphere at the process conditions. An estimated 20 million ton of volatile organic compounds (VOCs) is discharged into the atmosphere each year as a result of industrial processing operation.[1] These emissions have been linked to global climate change and human illness. It is the aim of chemical engineers to reduce the emissions of VOCs, its environmental impact, and to find a new class of "green" solvents. Room-temperature ionic liquids or simply "ionic liquids" (ILs) are low-melting point organic salts. They have unique properties such as negligible vapor pressure, high thermostability, wide liquidus range, and high ionic conductivity. The cations, substituents, and anions of ILs can be varied virtually at will to change their chemical and physical properties. Therefore, ILs can be designed to special task and have been applied as replacement for conventional toxic, flammable VOCs as reaction media in synthesis[2–5] and as solvents in the development of new separation processes.[1,6–8]

Toward a direction of developing an efficient and environmentally benign chemical process, many scientists have concentrated their research activities surrounding ILs and their application as green solvents, because not only ILs essentially do not evaporate, and so they cannot lead to fugitive emissions, but also they act much like good organic solvents, dissolving both polar and nonpolar species. An important example is the innovative application of ILs as working solvents in supported liquid membrane (SILM) for the separation gas mixtures[9] conducted by vapor pervaporization. As compared with the adsorption technology, the advantages of SILM are its low capital and operating cost, low energy requirements, easy scale-up, and long-term stability in continuous flow operation. In the SILM technology, an IL can be impregnated in the pore in polymer support or hollow fiber module, the capability of ILs to separate solutes mixtures depends on the selectivity of the solutes in ILs.

In the petrochemical industry, the separation of xylene isomers is of significant importance for production of chemicals such as terephthalic, phthalic, and isophthalic acids. Because of the close boiling points of these isomers, separation based on distillation is impractical; therefore, other processes based on crystallization or zeolitic adsorption have been developed, such as the most well-known industrial process developed by UOP.

The major driving force for selective separation of xylene isomer gas mixture by SILM is the solubility difference between these isomers in IL. Selectivity (S_{ij}) can be calculated from the ratio of solubilities of the two solutes in one solvent. We have experimental demonstrated that although these xylene isomers have close boiling points, their solubilities in an IL can be evidently different.[10] A separation factor, selectivity of the solutes at infinite dilution in an IL, can be calculated from the ratio of activity coefficients at infinite dilution (S_{ij}^{∞}, defined according to the equation: $S_{ij}^{\infty} = \gamma_{is}^{\infty}/\gamma_{js}^{\infty}$, where subscript s denotes solvent).

Activity coefficients at infinite dilution of different organic solutes in ILs can be determined with an IL as the stationary phase using gas–liquid chromatography (GLC).[11,12] In this work, we established a database of activity coefficient at infinite dilution of organic solutes in ILs from the open literatures. It is clear to find out from this database that how the change of cations and anions affects the γ_i^{∞} and S_{ij}^{∞} values.

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Based on the database, an activity coefficient model for regular solutions has been applied to correlate the experimental data and the obtained solubility parameters have been further correlated based on a concept of group contribution. Based on the activity coefficient model, S_{ij}^{∞} can be predicted. Through the analysis of S_{ij}^{∞} values and taking the advantage of ILs as designable solvents, we will discuss the possibility for the further application of ILs in SILM technology for xylene isomer separation.

Solubility Parameters of ILs

Classification of ILs and database

Activity coefficients at infinite dilution were determined by retention time method with an IL as the stationary phase using GLC. The values of γ_i^{∞} for a volatile solute in an involatile solvent were obtained by the equation proposed by Everett[11] and Cruickshank et al.[12] Retention in the column of GLC is a complex process involving gas–liquid partitioning with the bulk liquid phase, gas–liquid adsorption at the bulk liquid and structured liquid interfaces, and by adsorption at the gas–solid supports interface. The gas–liquid partition coefficient, K_L, can be determined based on the experimental retention data and following working equation

$$\frac{V_N^*}{V_L} = K_L + \frac{A_{GL}K_{GL} + A_{LS}K_{GLS}}{V_L} \tag{1}$$

For different solutes with same IL as solvent, a plot of V_N^*/V_L vs. $1/V_L$ will be a straight line and K_L can be obtained from the intercept at $1/V_L = 0$. When the slope of the line is smaller, then the contribution of partition for retention will be greater, and the contribution of interface adsorption for retention will be smaller. If the slope of a straight line is zero, then the retention of this solute in GLC is completely determined by the partition. If there is such an ideal state, the retention of solutes in the stationary phase completely determined by the gas–liquid partition, then the K_L can be expressed as $K_L = RT\rho_3/(P_i^0 M_3 \gamma_{i,3}^{\infty})$.

To correlate the activity coefficients with a wide range representation of organic solutes and ILs, we need to build a database. Cation and anion were separated and then numbered by an ID code, respectively. Results for 58 available ILs, from which 42 kinds of cations and 22 kinds of anions, were extracted, and they, as well as their abbreviations, chemical names, formulas, and molecular weights, are listed in Table 1. A database of activity coefficients of organic solutes at infinite dilution in ILs with the classification presented in Table 1 was collected from literature sources. There are more than 6000 experimental data points. The database is accessible in Table S1, Supporting Information. The experimental data of gas–liquid partition coefficient, K_L, were collected as Table S2, Supporting Information. From those data as listed in Table S2, Supporting Information, it can be seen that the K_L values of alkanes in some ILs are very small, although most of the polar solute shows large solubility in the ILs phase. Up to now, there are much more ILs in the literature for which the activity coefficients are measured. Reliable activity coefficient data should be obtained when the retention data is completely determined by the partition. However, most of the measurements did not measure the K_L values. The good idea is to compare obtained results of solubility parameters with the literature data.

Correlation of activity coefficients with Flory's equation

The temperature dependence of the activity coefficients at infinite dilution of a solute in an IL can be correlated by $\ln \gamma_i^{\infty} = a + b/T$. The plots of measured $\ln \gamma_i^{\infty}$ values vs. $1/T$ of different organic solutes in ILs were shown in our previous article,[13] in which a fairly good fitting to experimental data were obtained. The activity coefficients at infinite dilution of different solutes in a given solvent can be used to estimate solubility parameter of the solvents, when the solubility parameters of these solutes are known. These provide a basis for the correlation of the activity coefficients at infinite dilution of solutes in ILs. The activity coefficient model can be represented by a two-term equation in which the combinatorial term can be represented by the Kikic et al.[14] modification to Flory's equation, and the residual term is given by the regular solution theory

$$\ln \gamma_i^{\infty} = \ln \gamma_i^{\infty\mathrm{comb}} + \ln \gamma_i^{\infty\mathrm{res}} \tag{2}$$

$$\ln \gamma_i^{\infty\mathrm{comb}} = \ln (r_i/r_s)^{2/3} + 1 - (r_i/r_s)^{2/3} \tag{3}$$

$$\ln \gamma_i^{\infty\mathrm{res}} = (v_i/RT)(\delta_i - \delta_s)^2 \tag{4}$$

where r_i and r_s are the van der Waals volumes of solute and solvent, respectively; v_i is the solute molar volume; δ_i and δ_s are solubility parameters of solute and solvent, respectively. The temperature dependence of Eq. 2 agrees with the relation $\ln \gamma_i^{\infty} = a + b/T$. The solubility parameter of ILs can be correlated from the experimental γ^{∞} data. A residual function Y can be rearranged from Eq. 4 according to literature[15]

$$Y_i = -\frac{\ln \gamma_i^{\infty\mathrm{res}}}{v_i} + \frac{{\delta_i}^2}{RT} = \frac{2\delta_s}{RT}\delta_i - \frac{{\delta_s}^2}{RT} \tag{5}$$

This equation shows that there is a linear relation between Y_i and the solute solubility parameter δ_i for a given solvent and temperature T. The value of the solvent (i.e., IL) solubility parameter δ_s can be obtained from the slope of this line. The values of experimental γ^{∞} were taken from Table S1, Supporting Information, the values of ln $\gamma^{\infty\mathrm{comb}}$ were calculated by Eq. 3. In Eq. 2, with the $\ln \gamma_i^{\infty}$ known (by experimental data), the value of $\ln \gamma_i^{\infty\mathrm{res}}$ can be calculated according to Eq. 2, and finally the values of Y_i for different solutes in an IL were calculated according to Eq. 5. Information on v_i, δ_i, and r_i were obtained from the literature.[16,17] The van der Waals volumes of ILs were calculated by group contribution method.[18] The dependence between Y_i and δ_i ($\delta_i = \delta_{\mathrm{solute}}$) can, thus, be plotted for different solutes with a specified IL ([C$_{16}$MIM]BF$_4$]) and high accuracy of the linear correlation is displayed by the Figure 1 (more results are displayed in Figure 1S, Supporting Information, for different ILs). The temperature dependence of solubility parameters (δ_s) of IL calculated by this procedure was listed in Table S3, Supporting Information, and it can be seen that the temperature dependence of the solubility parameter is not obvious. An average value of solubility parameters obtained for an IL at different temperatures will be reasonable. The results of the solubility parameters obtained in this work, the van der Waals volumes and molar volumes of 26 ILs[18–25] are summarized in Table 2.

Group contribution of the solubility parameters

Carlisle et al.[26] estimated the solubility parameters of ILs based on a concept of group contribution method, which is

Table 1. Cations and Anions of the Ionic Liquids Included in the Data Base

ID	Abbreviation	Name	Formula	M (g mol^{-1})
Anions				
1	Cl	Chloride	Cl	35.45
2	Br	Bromide	Br	79.90
3	BF_4	Tetrafluoroborate	BF_4	86.80
4	PF_6	Hexafluorophosphate	PF_6	144.96
5	TfO	Trifluoromethanesulfonate	CF_3SO_3	149.07
6	NTf_2	Bis(trifluoromethylsulfonyl)imide	$C_2F_6S_2O_4N$	280.16
7	$MeSO_4$	Methylsulfate	CH_3SO_4	111.11
8	ESO_4	Ethylsulfate	$C_2H_5SO_4$	125.12
9	OSO_4	Octylsulfate	$C_8H_{17}SO_4$	209.28
10	$MASO_4$	Methoxyethylsulfate	$C_3H_8SO_5$	156.16
11	$EASO_4$	Ethoxyethylsulfate	$C_4H_{10}SO_5$	170.16
12	TOS	Tosylate	$C_7H_7SO_3$	171.20
13	$MDEGSO_4$	Diethyleneglycolmonomethylethersulfate	$C_5H_{11}O_6S$	199.20
14	$(CH_3)_2PO_4$	Dimethylphosphate	$C_2H_6PO_4$	125.04
15	$(C_2F_5)_3PF_3$	Tris(pentafluoroethyl) trifluorophosphate	$C_6F_{18}P$	445.01
16	NO_3	Nitrate	NO_3	62.00
17	$(CN)_2N$	Dicyanamide	C_2N_3	66.04
18	CF_3COO	Trifluoroacetate	$C_2F_3O_2$	113.02
19	SCN	Thiocyanate	SCN	58.08
20	$CoBr_4$	Tetrabromidocobaltate(ii)	$CoBr_4$	378.55
21	$FeCl_4$	Tetrachloridoferrate(iii)	$FeCl_4$	197.66
22	$(C_8H_{17})_2PO_2$	Bis-(2,4,4-trimethylpentyl)-phosphinate	$C_{16}H_{34}PO_2$	289.41
Cations				
31	C_1MIM	1-Methyl-3-methylimidazolium	$C_5H_9N_2$	97.14
32	C_2MIM	1-Ethyl-3-methylimidazolium	$C_6H_{11}N_2$	111.15
33	C_4MIM	1-Butyl-3-methylimidazolium	$C_8H_{15}N_2$	139.21
34	C_6MIM	1-Hexyl-3-methylimidazolium	$C_{10}H_{19}N_2$	167.27
35	C_8MIM	1-Octyl-3-methylimidazolium	$C_{12}H_{23}N_2$	195.33
36	$C_{10}MIM$	1-Decyl-3-methylimidazolium	$C_{14}H_{27}N_2$	223.38
37	$C_{16}MIM$	1-Hexadecyl-3-methylimidazolium	$C_{20}H_{39}N_2$	307.54
38	M_4B-py	4-Methyl-n-butylpyridinium	$C_{10}H_{16}N$	150.24
39	THTD-P	Trihexyl(tetradecyl)-phosphonium	$C_{32}H_{68}P$	483.86
40	$P_1M_{2,3}IM$	1-Propyl-2,3-dimethylimidazolium	$C_8H_{15}N_2$	139.22
41	HydEMIM	1-(2-Hydroxyethyl)-3-methylimidazolium	$C_6H_{11}N_2O$	127.16
42	BMPYR	1-Butyl-1-methyl-pyrrolidinium	$C_9H_{20}N$	142.25
43	HMPYR	1-Hexyl-1-methyl-pyrrolidinium	$C_{11}H_{24}N$	170.31
44	OMPYR	1-Octyl-1-methyl-pyrrolidinium	$C_{13}H_{28}N$	198.37
45	PPeMIM	1-Propenyl-3-methylimidazolium	$C_7H_{11}N_2$	123.18
46	PPeOIM	1-Propenyl-3-octylimidazolium	$C_{14}H_{25}N_2$	221.36
47	PPeDeIM	1-Propenyl-3-decylimidazolium	$C_{16}H_{29}N_2$	249.41
48	PPeDoIM	1-Propenyl-3-dodecylimidazolium	$C_{18}H_{33}N_2$	277.47
49	PBAMIM	1-Propyl boronicacid-3-methylimidazolium	$C_7H_{14}BO_2$	141.00
50	PBAOIM	1-Propyl boronicacid-3-octylimidazolium	$C_{14}H_{28}BO_2$	239.18
51	PBADeIM	1-Propyl boronicacid-3-decylimidazolium	$C_{16}H_{32}BO_2$	267.24
52	PBADoIM	1-Propyl boronicacid-3-dodecylimidazolium	$C_{18}H_{36}BO_2$	295.29
53	MAOOMIM	1-Methacryloyloxyhexyl-1-methylimidazolium	$C_{14}H_{23}O_2N_2$	251.39
54	AOOMIM	1-Acryloyloxypropyl-1-methylimidazolium	$C_9H_{13}O_3N_2$	197.21
55	TBMeP	Tributylmethylphosphonium	$C_{13}H_{30}P$	217.35
56	PY	Pyridinium	C_5H_6N	80.11
57	DMEIM	1,2-Dimethyl-3-ethyl-imidazolium	$C_7H_{16}N_2$	128.22
58	C_2PY	n-Ethylpyridinium	$C_7H_{10}N$	108.16
59	C_4PY	n-Butylpyridinium	$C_9H_{14}N$	136.21
60	C_5PY	n-Amylpyridinium	$C_{10}H_{16}N$	150.24
61	Me_3BuN	Trimethyl-butylammonium	$C_7H_{19}N$	117.23
62	Et_3S	Triethylsulphonium	$C_6H_{15}S$	119.25
63	$C_6H_{13}OCH_2MIM$	1-Hexyloxymethyl-3-methyl-imidazolium	$C_{11}H_{21}N_2O$	197.30
64	$(C_6H_{13}OCH_2)_2IM$	1,3-Dihexyloxymethylimidazolium	$C_{24}H_{33}N_2O_2$	381.53
65	$(OC_1)_2IM$	1,3-Dimethoxyimidazolium	$C_5H_9O_2N_2$	129.14
66	C_2OC_1MIM	1-(Methylethylether)-3-methylimidazolium	$C_7H_{13}N_2O$	141.19
67	C_2OHMIM	1-Ethanol-3-methylimidazolium	$C_6H_{11}N_2O$	127.16
68	C_3CNMIM	1-(3-Cyanopropyl)-3-methylimidazolium	$C_8H_{10}N_3$	148.19
69	OMA	Trioctylmethylammonium	$C_{25}H_{54}N$	368.70
70	BMPY	1-Butyl 4-methyl-pyridinium tosylate	$C_{10}H_{16}N$	150.23
71	P1,4,4,4	Tri-iso-butylmethylphosphonium	$C_{13}H_{30}P$	217.35
72	PMPIP	1-Propyl-1-methylpiperidinium	$C_8H_{18}N$	128.23

based on the idea that the total cohesive energy of a molecule is the sum of the individual cohesive energies (molar attraction constants) associated with each constituent group on the molecule. This method also assumes that molar attraction constants are considered constant regardless of the chemical nature of the molecule or of the surrounding chemical environment. The following expression can be used to calculate the solubility parameter δ_s of an IL

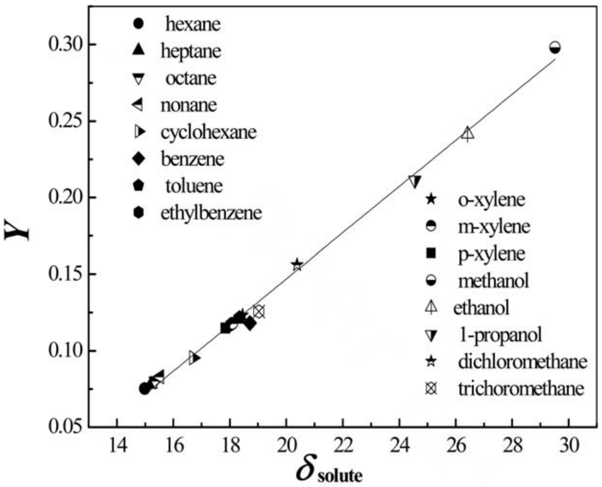

Figure 1. Residual function *Y* for [C_{16}MIM]BF_4] (Experimental data of activity coefficients at infinite dilution of [C_{16}MIM]BF_4] were taken from Ref. 18.) vs. solute solubility parameters δ_{solute} at 323.15 K.

$$\delta_s = \frac{\sum_j F_j}{v_s} \tag{6}$$

In Eq. 6, subscript s represents the solvent, *j* represents each substitute chemical group, *F* is the molar attraction constant of chemical group *j*, and v_s is the molar volume of the solvent. With the solubility parameters of the IL known, *F* can be obtained for the subgroup *j*. The classification of the structure of an IL is shown with 1-R_1-3-R_2-imidazolium tetrafluoroborate as example, as shown in Figure 2, in which the cationic imidazolium ring and tetrafluoroborate cation is defined together as one neutral group (ionic functional group, IFG), while the substitute R_1 and R_2 on the ring can be separated into methyl, methylene, and so forth. Molar attraction constants of several organic functional groups relevant to this study were taken from literature,[27] and some values were tabulated in Table S4, Supporting Information.

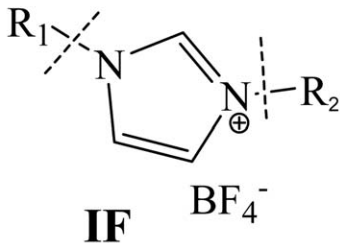

Figure 2. The classification of the structure of an IL.

Table 2. Solubility Parameters (δ_s) Obtained in this Work, the van der Waals Volumes (r_s), and Molar Volumes (v_s) of 26 Ionic Liquids

ILs	$10^6 r_s$ (m^3 mol^{-1})	$10^6 v_s$ (m^3 mol^{-1})	δ_s ($MPa^{1/2}$)
[MAOOMIM][Br]	170	362	25.83
[$PIM_{2,3}$IM][BF_4]	197	168	23.99
[C_2MIM][BF_4]	177	159	24.41
[C_4MIM][BF_4]	197	191	23.78
[C_6MIM][BF_4]	218	225	22.76
[C_8MIM][BF_4]	238	264	22.00
[C_{16}MIM][BF_4]	320	577	20.23
[HydEMIM][BF_4]	192	144	24.76
[C_4MIM][PF_6]	143	211	22.06
[C_6MIM][PF_6]	163	245	22.18
[C_8MIM][PF_6]	184	279	21.19
[C_1MIM][NTf_2]	154	244	24.71
[C_2MIM][NTf_2]	165	262	22.40
[C_4MIM][NTf_2]	186	297	23.46
[C_2PY][NTf_2]	167	261	22.71
[C_1MIM][$(CH_3)_2PO_4$]	120	179	25.08
[C_2MIM][ESO_4]	127	236	24.26
[C_1MIM][$MASO_4$]	140	195	25.03
[C_1MIM][$MeSO_4$]	115	159	31.15
[BMPYR][TfO]	149	233	22.83
[C_4MIM][TfO]	143	222	25.85
[C_4MIM][MDEGSO4]	194	284	24.80
[$C_6H_{13}OCH_2$MIM][NTf_2]	219	350	21.04
[$(C_6H_{13}OCH_2)_2$IM][NTf_2]	284	460	20.59
[Et_3S][NTf_2]	171	274	21.83
[C_4MIM][OSO_4]	218	328	22.83

The values for the IFG of ILs classified according to Figure 2 were estimated from the values of solubility parameter using group contribution method, and the results of the F_{IFG} values were summarized in Table 3. The F_{IFG} values calculated from ILs with different terminal alkyl substitutes are very consistent, suggesting the concept of the IFG for the ILs is reasonable.

Selectivities of ILs for Alkane/Aromatic and Aromatic/Aromatic Hydrocarbon Mixtures

A feature of ILs is that their physical properties can be tailored by judicious selection of cation, anion, and substitutes. Therefore, the γ_i^∞ value and selectivity can be controlled by the nature of the cation, anion, and substitutes. Figure 3A shows that both the activity coefficients at infinite dilution of 1-heptane and the selectivities of 1-heptane/toluene in ILs decrease with the increasing alkyl chain length on the cation. Figure 3B shows that the change of anions can affect activity coefficients at infinite dilution of 1-heptane in ILs, the order is $OSO_4 < NTf_2 < TfO < PF_6 < BF_4 < MDEGSO_4$. The change of anions affects selectivities of 1-heptane/toluene in ILs in a similar way, except highest selectivity is obtained from BF_4.

The selectivity at infinite dilution is important to select better entrainer for a given separation problem. Compared with conventional extractors, ILs show a higher selectivity for the separation problems such as the separation of alkanes

Table 3. Estimated Molar Attraction Constants of the Ionic Functional Group (IFG) by Group Contribution

ILs	F_{IFG} ($MPa^{1/2}$ cm^3 mol^{-1})
[IM][Br]	6068.46
[IM][BF_4]	3100.65
[IM][PF_6]	3381.58
[IM][NTf_2]	5378.46
[PY][NTf_2]	5353.57
[IM][$(CH_3)_2PO_4$]	3882.65
[IM][ESO_4]	4850.02
[IM][$MASO_4$]	4273.49
[IM][$MeSO_4$]	4345.99
[PYR][TfO]	3905.39
[IM][TfO]	4324.72
[IM][$MDEGSO_4$]	5629.20
[IM][Ntf_2]	4907.05
[IM][Ntf_2]	5379.25
[S][Ntf_2]	4262.82
[IM][OSO_4]	6074.24

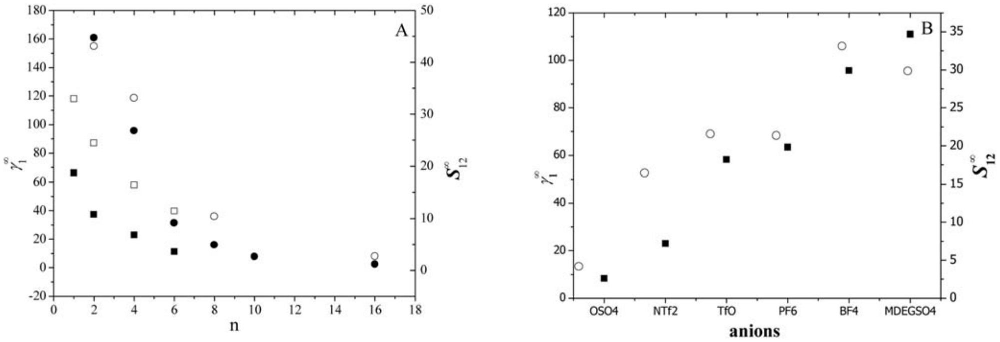

Figure 3. Activity coefficients at infinite dilution of 1-heptane and selectivities of 1-heptane/toluene in ILs.

(A) With carbon number *n* in alkyl chain C_n for cations. ■: γ^{∞}, [C_nMIM][$(CF_3SO_2)_2N$]; •: γ^{∞}, [C_nMIM][BF_4]; □: S_{12}^{∞}, [C_nMIM][$(CF_3SO_2)_2N$]; ○: S_{12}^{∞}, [C_nMIM][BF_4]; 1: heptane; and 2: toluene. (B) with different anions at 298.15 K (in which PF_6 at 313.15 K). ■: γ^{∞}; ○: S_{12}^{∞}; 1: heptane; and 2: toluene.

Table 4. Selectivities S_{12}^{∞} of Alkanes/Aromatic Hydrocarbon at Infinite Dilution for Ionic Liquids at $T = 323.15$ K

	S_{12}^{∞}					
IL	Benzene	Toluene	Ethylbenzene	*o*-Xylene	*m*-Xylene	*p*-Xylene
[PDMIM][BF_4][a]						
n-Pentane	38.58	22.52	10.80	15.34	11.80	12.49
n-Hexane	59.88	34.95	16.76	23.81	18.32	19.39
n-Heptane	98.56	57.52	27.58	39.19	30.15	31.91
n-Octane	152.13	88.79	42.57	60.48	46.53	49.26
n-Nonane	192.86	112.56	53.97	76.68	58.99	62.45
n-Decane	1212.94	707.91	339.43	482.24	371.01	392.74
Cyclohexane	26.67	15.57	7.46	10.60	8.16	8.64
Methylcyclohexane	43.00	25.10	12.03	17.10	13.15	13.92
2,2,4-Trimethylpentane	106.76	62.31	29.87	42.44	32.65	34.57
[HydEMIM][BF_4][a]						
n-Heptane	131.51	67.48	30.67	43.14	33.69	35.24
n-Octane	63.10	32.38	14.72	20.70	16.17	16.91
n-Nonane	63.99	32.84	14.93	20.99	16.39	17.15
Cyclohexane	53.65	27.53	12.52	17.60	13.75	14.38
Methylcyclohexane	46.32	23.77	10.80	15.20	11.87	12.41
2,2,4-Trimethyl-pentane	80.34	41.23	18.74	26.36	20.58	21.53
[BMIM][CF_3SO_3] [b]						
Cyclopentane	12.89	8.65	5.54	6.59	5.59	5.77
Cyclohexane	19.94	13.38	8.57	10.19	8.64	8.93
Cycloheptane	27.42	18.40	11.78	14.02	11.88	12.28
Cyclononane	38.87	26.08	16.70	19.87	16.84	17.41

[a] From database.
[b] From database (328.15 K).

from aromatics.[28] Selectivities (S_{12}^{∞}) of alkanes/aromatic hydrocarbon at infinite dilution for some ILs at $T = 323.15$ K were calculated from the database, and the results are listed in Table 4. According to Table 4, three ILs: [PDMIM][BF_4],[29] [HydEMIM][BF_4],[30] and [BMIM][CF_3SO_3][31] are found to have significant separation effect for those separation problems. From Table 4, it can be seen that the investigated ILs can be directly used as aromatic hydrocarbon extraction solvents from alkane/aromatic hydrocarbon mixtures. In which the selectivities S_{ij}^{∞} of [PDMIM][BF_4] (with three organic groups on the cation) are higher than other ILs (with only two organic groups on the cation). All the ILs listed in Table 4 show good separation ability as compared with the experimental selectivities of sulfolane.[32] The results of [PDMIM][BF_4] and [HydEMIM][BF_4] are much better than sulfolane. Figure 4A shows the selectivity at infinite dilution of cyclohexane /benzene system with different cations and anions. According to Figure 4A, the ILs with higher ability of separate cyclohexane/benzene system are in the area on the bottom of the figure, the highest selectivity appears in 41-3 ([HydEMIM][BF_4]).

In petrochemical industry, the development of production technology of terephthalic, phthalic, and isophthalic acids are mainly limited by the separation technology of xylene isomers. Up to now, the researches for the separation of *para*-xylene from its bulkier *meta*- and *ortho*-isomers by zeolite membranes via vapor permeation were successful,[33,34] and satisfactory permselectivities were obtained. However, from a point of view of petrochemical production, the results for the separation of *meta*-xylene from its *para*- and *ortho*-isomer mixtures were not success using same technique due to the limit by the kinetic diameter.[*]

In a SILM apparatus, the separation factor depends on the difference in solubilities of the isomers in IL, but not on the boiling points. Therefore, the isomer mixture can be theoretical separated by using SILM technology. Using the database and the group contribution activity coefficient model developed in this work, we can analyze the structure–property

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[*] Kinetic diameter *para*-xylene = 5.8 Å; kinetic diameter *meta*- and *ortho*-xylene = 6.8 Å (33).

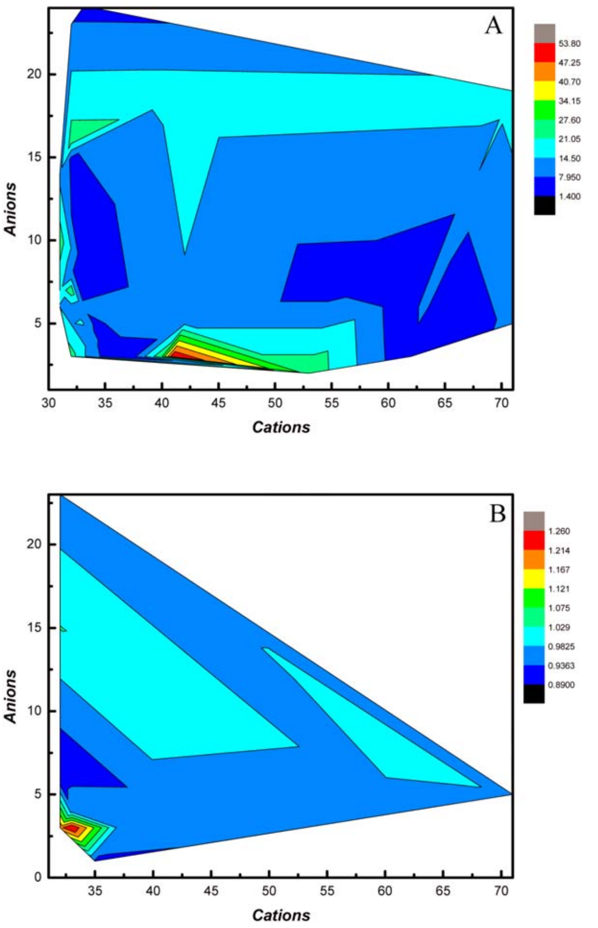

Figure 4. Selectivity at infinite dilution of hydrocarbon mixture with different cations and anions.

(A) cyclohexane/benzene and (B) *para*-xylene/*meta*-xylene. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

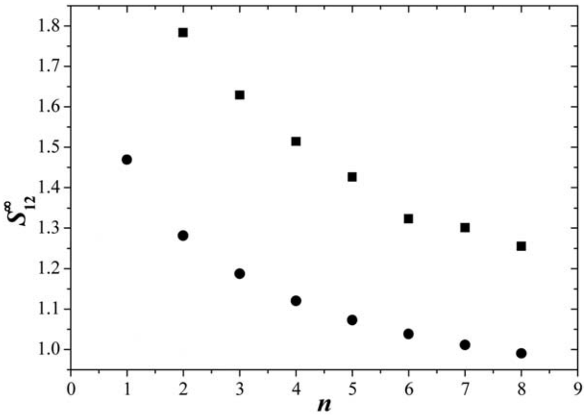

Figure 5. Selectivity at infinite dilution of *meta*-xylene/*ortho*-xylene binary mixture in ILs [MAOC$_n$-MIM]Br and [HydC$_n$MIM][BF4] with carbon number *n* in alkyl chain C$_n$ for cations.

■: [MAOC$_n$MIM]Br; •: [HydC$_n$MIM][BF$_4$]; 1: *m*-xylene; and 2: *o*-xylene.

relationship for ILs, especially for the effect of molecular structure on the selectivity of the xylene isomers in the IL.

Figure 4B shows the analysis for the selectivity from the experimental data of activity coefficients at infinite dilution of *para*-xylene/*meta*-xylene system with different cations and anions with the highest selectivity appears in 33-3 ([C$_4$MIM][BF$_4$]). Because the kinetic diameters of both *meta*- and *ortho*-xylene equal to 6.8 Å, it seems not possible to separate them with a zeolite membrane. Table 5 lists the selectivities S_{12}^{∞} of aromatic (1)/aromatic (2) hydrocarbon at infinite dilution for three ILs: [MAOOMIM]Br, [MAOOMIM][BF4], and [MAOOMIM][TfO]. From Table 5, it can be seen that the highest selectivity is obtained by using [MAOOMIM]Br to separate *meta*-xylene (1) and *ortho*-xylene (2), the result is $S_{12}^{\infty} = 1.323$. In addition, it can be seen from Table 5 that the selectivity in ILs can be changed by choice of anion, such as Br$^-$, [BF4]$^-$, and [TfO]$^-$. To explore the effect of carbon number in alkyl chain of cations on the selectivity, we calculated the activity coefficients based on the group contribution activity coefficient model, and the results are shown in Figure 5. From Figure 5, it can be seen that the selectivity of *meta*-xylene/*ortho*-xylene in ILs [MAOC$_n$MIM]Br and [HydC$_n$MIM][BF4] can both be increased with the reduction of carbon number in alkyl chain (the C$_n$ groups) of cations. When [MAOEMIM]Br is used to

Table 5. Selectivities S_{12}^{∞} of Aromatic (1)/Aromatic (2) Hydrocarbon at Infinite Dilution for Ionic Liquids

		(2)				
IL	(1)	Toluene	Ethylbenzene	*o*-Xylene	*m*-Xylene	*p*-Xylene[a]
[MAOOMIM]Br[b]	Toluene		0.422	0.613	0.461	0.460
	Ethylbenzene	2.370		1.447	1.089	0.847
	o-xylene	1.632	0.691		0.756	0.602
	m-xylene	2.170	0.918	1.323		0.816
	p-xylene[a]	2.172	1.181	1.662	1.225	
[MAOOMIM][BF$_4$][a]	Toluene		0.961	0.909	0.952	0.977
	Ethylbenzene	1.040		0.945	0.990	1.016
	o-xylene	1.101	1.058		1.047	1.075
	m-xylene	1.051	1.010	0.955		1.426
	p-xylene	1.024	0.798	0.930	0.974	
[MAOOMIM][TfO][c]	Toluene		0.960	0.928	0.953	0.965
	Ethylbenzene	1.041		0.966	0.993	1.005
	o-xylene	1.078	1.035		1.028	1.040
	m-xylene	1.049	1.007	0.973		1.354
	p-xylene	1.037	0.826	0.962	0.988	

[a] Predicted results at 323.15 K.
[b] From the database.
[c] Predicted results at 298.15 K.

replace [MAOOMIM]Br as solvent to separate *meta*-xylene (1) and *ortho*-xylene (2), the selectivity can be increased from 1.323 (experimental data) to 1.780 (predicted result).

Correlation of gas–liquid partition coefficient

The gas–liquid partition coefficient, K_L, for alkanes in different ILs listed in Table S2, Supporting Information, can be correlated with following linear equation

$$K_L = A + BC_n \tag{7}$$

where A and B are correlation coefficients, and C_n is the carbon number of the alkanes. The correlation results and experimental data are shown in Figure 6, and the results for correlation coefficients are listed in Table 6. From Figure 6, it can be seen that the gas–liquid partition coefficients increase with the increase of the carbon number of alkanes. Good fitting of Eq. 7 to the experimental data is obtained.

Conclusions

The activity coefficients at infinite dilution of organic solutes in ILs have been determined reliable by the retention time method using GLC by many researchers. These data are essential for both theoretical research and industrial application. The establishment of the database will definitely promote the research and application of ILs in the design of separation process. In this work, we find that as compared with conventional extractors, ILs show a higher selectivity for the separation problems such as the separation of alkanes from aromatics.

The activity coefficients can be represented by the regular solution theory. In this article, the activity coefficients at infinite dilution data of different organic solutes in a given solvent have been used to estimate the solubility parameter of ILs. The solubility parameters of ILs have been correlated based on a concept of group contribution. This article shows that based on the designable nature of ILs, there is a significant potential for exploiting how the variation of substitute, cation and anion influences the solubility of the xylene isomers in ILs. A traditional measurement method for the activity coefficient of solutes at infinite dilutions with an IL as the stationary phase using GLC and a classical thermodynamic model can be used to analyze this possibility. By a combination of ILs with supported liquid membrane technology, the restriction from thermodynamic and dynamic diameter can be eliminated. Further work is to measure more data under the direction of thermodynamic calculations, to study the restriction of mass transfer of the isomers in ILs from points of view of mass transfer, and environmental impact of the ILs. For a further work, a study of structure–property relationship may provide a direction for the design of the new ILs.

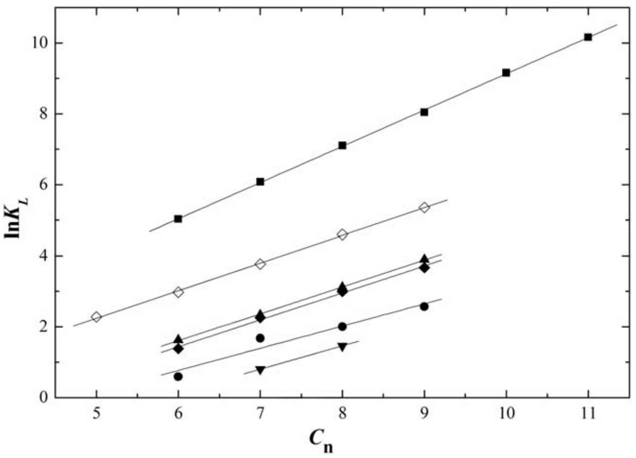

Figure 6. Plot of ln K_L vs. carbon number of normal alkanes in different ILs.

■, [P14,666][NTf_2] (298.15 K); •, [AOOMIM][Br] (313.15 K); ▲, [MAOOMIM][Br] (313.15 K); ▼, [EMIM][NO_3] (323.15 K); ◆, [HMIM][NO_3] (353.15 K); and ◇, [OMIM][NO_3] (323.15 K).

Table 6. Correlation Coefficients *A* and *B* of Gas–Liquid Partition Coefficient, K_L, with the Carbon Number of Alkanes

ILs	*A*	*B*
[P14,666][NTf_2]	−1.109	1.024
[AOOMIM][Br]	−2.993	0.627
[MAOOMIM][Br]	−2.946	0.759
[EMIM][NO_3]	−3.811	0.659
[HMIM][NO_3]	−2.993	0.760
[OMIM][NO_3]	−1.652	0.778

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