Screening of Ionic Liquids to Capture CO_2 by COSMO-RS and Experiments

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*A screening method is proposed for the molecular design of ionic liquids (ILs) to capture carbon dioxide (CO_2), which can reduce efficiently the necessary experimental efforts. The COSMO-RS method is implemented to predict the Henry's law constants of CO_2 in 408 ILs with various combinations of cations and anions. It is found by the screening that the ILs with the anion tris(pentafluoroethyl)trifluorophosphate ([FEP]) show improved capability to capture CO_2, compared with other ILs reported in literature. Then, three [FEP]-based ILs are chosen to perform the solubility measurements by the intelligent gravimetric analyzer (IGA 003, Hiden Analytical), with cations of 1-hexyl-3-methylimidazolium ([hmim]), 1-butyl-1-methylpyrrolidinium ([bmpyrr]), and S-ethyl-*N,N,N′,N′*-tetramethylthiouronium ([ETT]) at 283.2, 298.2, and 323.2 K, up to the pressure of 1.8 MPa. The experimental data show that the solubility of CO_2 in [hmim][FEP] is about 15% higher than that in 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([hmim][Tf_2N]), which is in fair agreement with the screening results, indicating the method proposed in this work is reliable.* © 2008 American Institute of Chemical Engineers *AIChE J,* 54: 2717–2728, 2008

Keywords: ionic liquid, COSMO-RS, solubility, carbon dioxide, screening

Introduction

As is well known, carbon dioxide (CO_2) is a serious greenhouse gas, resulting in the global warming problem. On the other hand, it is also an important carbon source for the synthesis of many chemicals. Therefore, the capture of CO_2 for its emission control and utilization is a significant research topic in recent years. However, current technologies for the capture of CO_2 mainly consist of adsorption by aqueous amines, which induce a certain amount of water into gas stream and the loss of solvent.[1]

Ionic liquids (ILs) are a kind of novel solvents composed of cations and anions. Because of their unique properties, such as negligible vapor pressure, adjustable solvation behavior, thermal stability, and a broad range of liquid temperatures, the applications have been expanding in various fields.[2]

A lot of studies were focused on CO_2-ILs systems. For example, Brennecke and coworkers[3–8] carried out a series of researches on separation processes for the systems of CO_2 and ILs. The solubilities of CO_2 in various ILs[8–27] were reported, as well as their phase behaviors at high pressures.[28–32]

Although experimental data on ILs are dramatically accumulated in recent years, predictive models are always useful in the design of chemical engineering processes. Both the equation of states[33–35] and activity coefficient models[36] is presented for CO_2-ILs systems. However, the parameters in these models must be correlated by using experimental data. Hence, their estimation depends largely on the database used.

The so-called ab initio calculations based on quantum chemistry are completely predictive, which, however, suffer from expensive calculation cost. Atomic-scale simulations, such as molecular dynamics, are used successfully to predict

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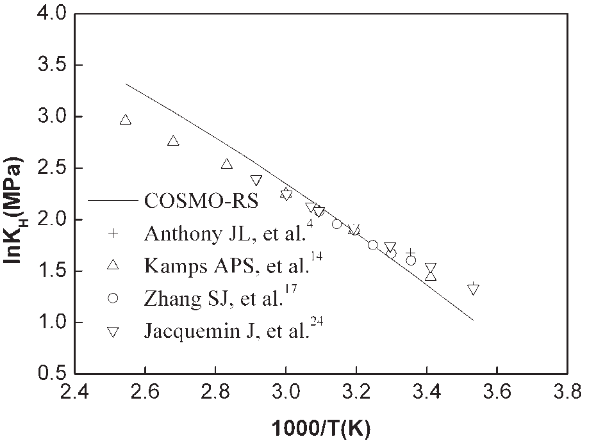


Figure 1. Comparison of the Henry's law constants of CO_2 in [bmim][PF_6].

lot of properties and behaviors of complex systems, but the accuracy of the results depends on the force fields used.[37–41] In addition, reliable evaluation of the free energies in molecular simulation is still a difficult task until now.[42]

The conductor-like screening model for real solvents (COSMO-RS) developed by Klamt et al.[43] provides an alternative approach to predict the thermodynamic properties of fluids[44] for various systems, including ILs,[45–47] such as solubilities,[48] activity coefficients,[45,49] and phase equilibria.[50,51] It requires only quantum calculations of single molecules or ions, irrespective of any experimental data of the systems of interest. However, it is worth mentioning that some functional groups, such as amine, are still incapable of reliable prediction by the COSMO-RS method.[43]

It is noted that we have recently developed a refined force field for imidazolium ILs[38,52] and carried out molecular simulations on mixtures[53] and gas solubilities.[54] However, it is difficult to explore wide range combinations of cations and anions by molecular simulations to find a "good" solvent for absorption of CO_2 because of the unbearable computational cost.

In this work, we use COSMO-RS to predict the Henry's law constants of 408 kinds of ILs with different combinations of cations and anions first. By screening of the results, the combinations with one of the anions, tris(pentafluoroethyl)trifluorophosphate ([FEP]), show the better capabilities to absorb CO_2. Therefore, the solubilities of CO_2 in the three ILs with [FEP] are measured by using the intelligent gravimetric analyzer (IGA 003, Hiden Analytical).

The article is organized as follows. First, calculations of the Henry's law constants of CO_2 in various ILs are carried out to validate the COSMO-RS method. Second, wide range combinations of cations and anions are explored by the prediction method to find the most efficient solvent to absorb CO_2. Then, the experimental results are reported. Finally, conclusion remarks are addressed.

Validation of COSMO-RS Method

As mentioned earlier, COSMO-RS has been used to predict thermophysical properties in various systems.[44–48,51] However, to our best knowledge, seldom results are reported about its prediction performance on CO_2 solubilities in ILs. Thus, it is necessary to validate the method with available experimental data.

As is suggested,[45] ILs are treated as equimolar mixtures of cation and anion in COSMO calculations. Therefore, the distinct COSMO files were generated for cations and anions using the BP functional[55] with TZVP basis set[56] using the TURBOMOLE program package.[57] Note that in our calculations, the typical CPU time to generate the COSMO file for a new ion is about several hours, depending on the numbers of electrons and atoms of the ion. For example, it needs about 7 h for [FEP] on a 1.3G Intel Itanium CPU. All COSMO-RS calculations were implemented with the COSMOtherm[58] program, which offers an efficient performance of the COSMO-RS method. In addition, the latest parameterization method BP_TZVP_C21_0104[58] was adapted in this work.

The calculated Henry's law constants of CO_2 in [bmim][PF_6] and [bmim][BF_4], covering the temperature range of 277–357 K, are compared with corresponding experimental data in Figures 1 and 2. As is seen in the figures, although the line's slope appears to deviate from the literature data, the predicted Henry's law constants around ambient temperature agree perfectly well with the experimental data. Consequently, the COSMO-RS method can be used as a tool to screen candidates from a variety of ILs for the capture of CO_2 at ambient temperature.

Hunting the Ionic Liquids to Absorb CO_2 by Solubility Prediction

The ILs can be designed by combining different cations and anions. In this work, 24 cations and 17 anions are chosen to combine 408 solvents, which cover most of the reported ILs and some of their derivatives. Their structures and abbreviations are listed in Table 1.

The cations include imidazolium (with alkyl, fluoroalkyl, and alkyloxyalkyl substituted), pyridinium, pyrrolidinium, guanidinium, isouranium, and phosphonium. The anions include tetrafluoroborate, hexafluorophosphate, lactate, sulfo-

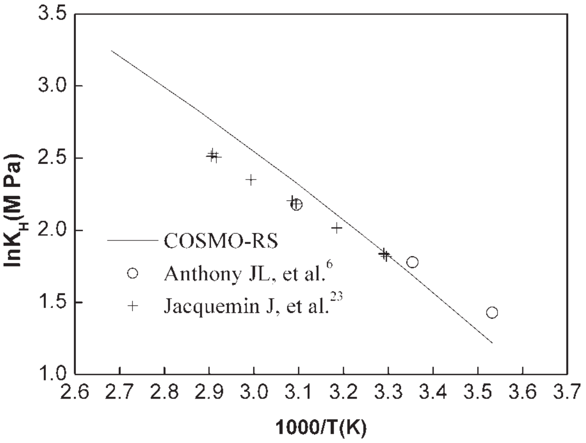


Figure 2. Comparison of the Henry's law constants of CO_2 in [bmim][BF_4].

nate, sulfate, and tris(perfluoroalkyl)trifluorophosphate ([FAP]). Note that some of the cations and anions are reported very recently, such as guanidinium[17] and [FEP].[59]

The Henry's law constants of CO_2 in 408 ILs are predicted by the COSMO-RS method at 298.15 K, given in Table 2. For clarity, a contour plot of 196 ILs is shown in Figure 3.

As is well known, the higher Henry's law constant means the lower solubility. It can be found that the ILs with anion [FEP] and cations *S*-ethyl-*N*,*N*,*N*′,*N*′-tetramethylisouronium ([ETT]), *O*-ethyl-*N*,*N*,*N*′,*N*′-tetramethylisouronium ([ETU]), and *N*,*N*,*N*′,*N*′,*N*″-pentamethyl-*N*″-ethylguanidinium ([PEG]) can capture more CO_2. For example, with the same cation

Table 1. List of Cations and Anions in this Work

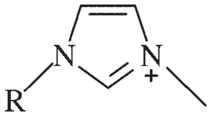
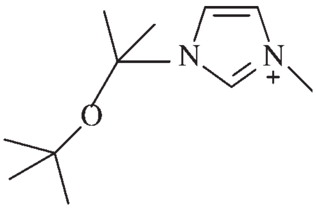
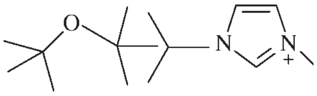
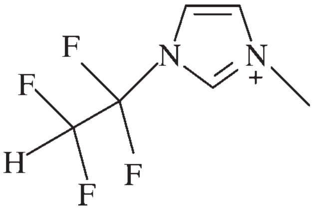
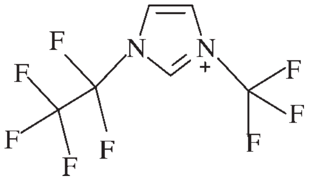
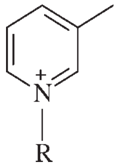
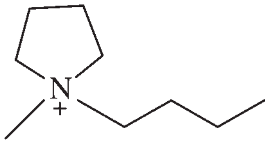
Formal Name	Abbreviation	MW	Structure
1,3-Dimethylimidazolium; R=CH_3 1-Ethyl-3-methylimidazolium; R=C_2H_5 1-Butyl-3-methylimidazolium; R=C_4H_9 1-Pentyl-3-methylimidazolium; R=C_5H_{11} 1-Hexyl-3-methylimidazolium; R=C_6H_{13}	[dmim]+ [emim]+ [bmim]+ [pmim]+ [hmim]+	97.14 111.17 139.22 153.24 167.27	
1-Methoxymethyl-3-methylimidazolium	[C_2Omim]+	127.16	
1-(2-Methoxyethyl)-3-methylimidazolium	[C_3Omim]+	153.2	
1-(1,1,2,2-Tetrafluoroethyl)-3-methylimidazolium	[TFEmim]+	183.13	
1-Pentafluoroethyl-3-trifluoromethylimidazolium	[FEFmim]+	255.09	
1-*N*-Butyl-3-methylpyridinium; R=C_4H_9 1-*N*-hexyl-3-methylpyridinium; R=C_5H_{11}	[bmpy]+ [hmpy]+	150.24 164.27	
1-Butyl-1-methylpyrrolidinium	[bmpyrr]+	142.26	

Table 1. (*Continued*)

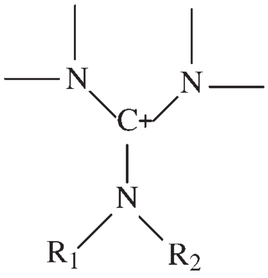
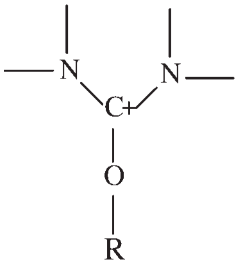
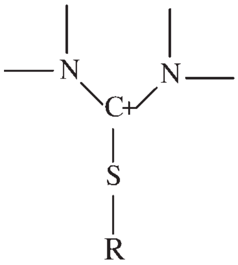
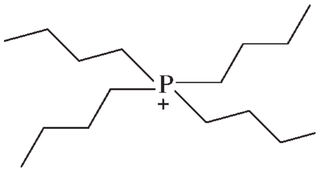
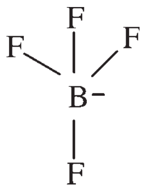
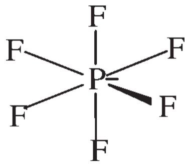
Formal Name	Abbreviation	MW	Structure
1,1,3,3-Tetramethylguanidinium; R_1=H, R_2=H	[TMG]+	116.18	
Hexamethylguanidinium; R_1=CH_3, R_2=CH_3	[HMG]+	144.24	
N,*N*,*N*′,*N*′,*N*″-Pentamethyl-*N*″-ethylguanidinium; R_1=CH_3, R_2=C_2H_5	[PEG]+	158.26	
N,*N*,*N*′,*N*′,*N*″-Pentamethyl-*N*″-propylguanidinium; R_1=CH_3,R_2=C_3H_7	[PPrG]+	172.29	
N,*N*,*N*′,*N*′-Tetramethyl-*N*″,*N*″-diethylguanidinium; R_1=C_2H_5, R_2=C_2H_5	[TDEG]+	172.29	
N,*N*,*N*′,*N*′-Tetramethyl-*N*″,*N*″-dipropylguanidinium; R_1=C_3H_7, R_2=C_3H_7	[TDPrG]+	200.34	
O-Ethyl-*N*,*N*,*N*′,*N*′-tetramethylisouronium; R=C_2H_5	[ETU]+	145.22	
O-Benzyl-*N*,*N*,*N*′,*N*′-tetramethylisouronium; R=$C_6H_5CH_2$	[BTU]+	207.29	
S-Ethyl-*N*,*N*,*N*′,*N*′-tetramethylisothiouronium; R=C_2H_5	[ETT]+	161.29	
S-Propyl-*N*,*N*,*N*′,*N*′-tetramethylisothiouronium; R=C_3H_7	[PrTT]+	175.32	
S-Phenyl-*N*,*N*,*N*′,N′-tetramethylisothiouronium; R=C_6H_5	[PhTT]+	209.33	
Tetrabutylphosphonium	$[P(C_4)_4]$+	259.43	
Tetrafluoroborate	$[BF_4]$−	86.8	
Hexafluorophosphate	$[PF_6]$−	144.96	

Table 1. (*Continued*)

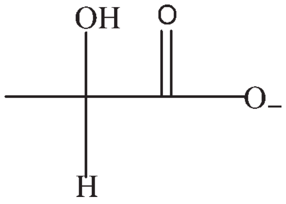
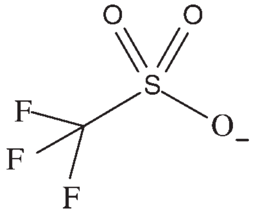
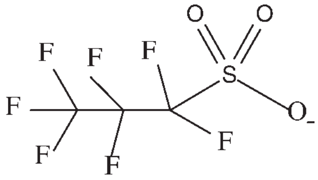
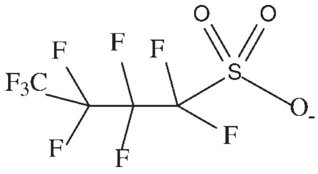
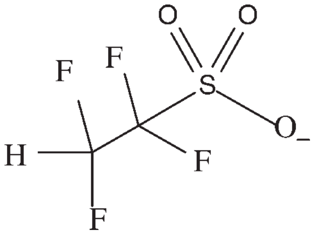
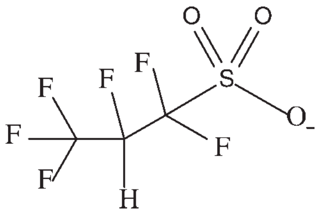
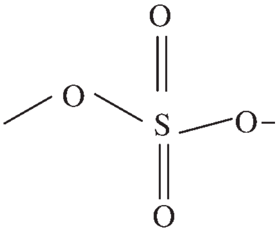
Formal Name	Abbreviation	MW	Structure
Lactate	[L]−	89.07	
Trifluoromethylsulfonate	[TfO]−	149.07	
Heptafluoropropylsulfonat	[HfO]−	249.09	
Nonafluorobutylsulfonate	[NfO]−	299.09	
1,1,2,2-Tetrafluoroethanesulfonate	[TFES]−	181.09	
1,1,2,3,3,3-Hexafluoropanesulfonate	[HFPS]−	231.09	
Methyl sulfate	[$MeSO_4$]−	111.1	

Table 1. (*Continued*)

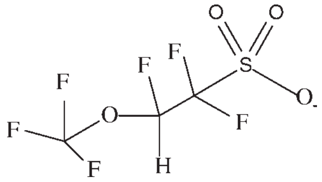
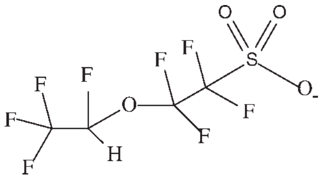
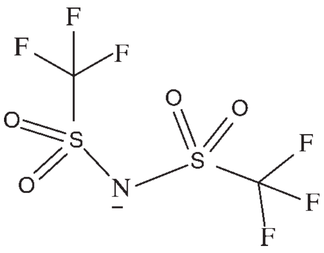
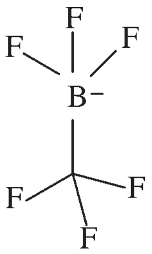
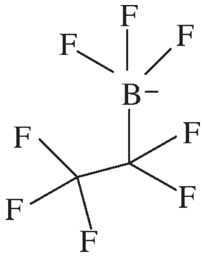
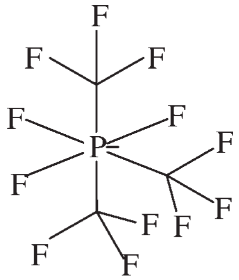
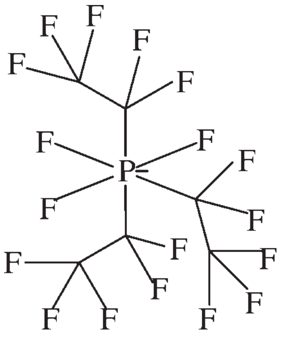
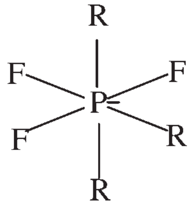
Formal Name	Abbreviation	MW	Structure
1,1,2-trifluoro-2-(Trifluoromethoxy)ethanesulfonate	[TTES]−	247.09	
2-(1,2,2,2-Tetrafluorothoxy)-1,1,2,2-tetrafluoroethanesulfonate	[FS]−	297.1	
Bis(trifluoromethylsulfonyl)imide	[Tf$_2$N]−	280.14	
Trifluoromethyltrifluoroborate	[FMB]−	136.8	
Pentafluoroethyltrifluoroborate	[FEB]−	186.82	
Tris(trifluoromethyl)trifluorophosphate	[FMP]−	294.99	

Table 1. (***Continued***)

Formal Name	Abbreviation	MW	Structure
Tris(pentafluoroethyl)trifluorophosphate	[FEP]−	445.01	
Tris(heptafluoropropyl)trifluorophosphate; R=C_3F_7	[FPrP]−	595.03	

1-hexyl-3-methylimidazolium ([hmim]), the Henry's law constants are 3.7, 3.4, and 2.0 MPa for anions hexafluorophosphate ([PF_6]), bis(trifluoromethylsulfonyl)imide ([Tf_2N]) and [FEP], respectively, in which the solubility of CO_2 in [hmim][FEP] is about two times higher than that in [hmim][PF_6].

The predicted results indicate that the solubility generally increases with the number of carbon atoms in alkyls, no matter where they are located. However, the substitutes have little effect when the Henry's law constant is as low as 2.0 MPa, which reaches the lowest limit in physical adsorption. For example, the solubilities in [FEP] and tris(hepta-

Table 2. The Henry's Law Constants (MPa) of CO_2 in 408 Ionic Liquids Predicted by COSMO-RS at 298.15 K

	Anion																
Cation	BF_4	PF_6	L	TfO	HfO	NfO	TFES	HFPS	$MeSO_4$	TTES	FS	Tf_2N	FMB	FEB	FMP	FEP	FPrP
dmim	6.4	8.6	6.0	7.0	5.1	4.5	7.7	5.9	7.2	5.6	4.6	4.9	5.4	5.3	3.0	2.3	2.1
Emim	5.9	6.0	6.1	5.8	4.4	3.9	5.5	5.0	5.9	4.8	4.0	4.2	5.4	4.2	2.7	2.2	2.1
Bmim	5.4	4.4	6.2	5.0	3.9	3.5	4.2	4.3	5.0	4.2	3.6	3.7	5.6	3.5	2.4	2.0	2.0
pmim	5.1	4.0	6.1	4.7	3.7	3.4	3.8	4.1	4.7	4.0	3.4	3.5	5.5	3.2	2.3	2.0	2.0
hmim	4.8	3.7	6.0	4.5	3.6	3.3	3.6	3.9	4.5	3.8	3.3	3.4	5.3	3.1	2.3	2.0	2.0
C_2Omim	8.4	8.3	7.6	7.6	5.3	4.7	7.4	6.1	7.5	5.8	4.7	5.0	7.1	5.3	3.1	2.4	2.2
C_3Omim	6.5	6.1	6.7	6.0	4.5	4.1	5.6	5.1	6.0	4.9	4.1	4.3	6.1	4.4	2.9	2.3	2.2
TFEmim	11.3	7.5	8.4	8.4	5.9	5.2	6.8	6.6	8.0	6.3	5.1	5.1	9.0	5.2	3.0	2.3	2.2
FEFmim	8.5	6.1	7.0	7.1	5.6	5.1	5.9	6.1	6.9	5.9	5.0	4.9	7.0	5.0	3.2	2.6	2.5
bmpy	4.2	3.6	5.2	4.1	3.4	3.1	3.5	3.7	4.2	3.6	3.2	3.3	4.5	3.0	2.3	2.0	2.0
hmpy	3.9	3.2	5.1	3.8	3.2	3.0	3.1	3.5	3.9	3.4	3.0	3.1	4.4	2.8	2.2	2.0	2.0
bmpyrr	3.9	3.6	4.7	3.7	3.0	2.8	3.4	3.4	3.9	3.3	2.9	3.1	4.0	2.9	2.2	1.9	1.9
TMG	4.2	4.3	4.6	4.4	3.6	3.4	4.2	4.1	4.6	4.0	3.5	3.8	4.0	3.5	2.4	2.0	2.0
HMG	2.1	2.5	2.5	2.5	2.3	2.2	2.5	2.5	2.7	2.5	2.4	2.6	2.2	2.3	2.1	1.9	1.9
PEG	2.2	2.4	2.5	2.4	2.3	2.2	2.4	2.5	2.6	2.5	2.3	2.5	2.3	2.2	2.1	1.9	1.9
PPrG	2.2	2.4	2.6	2.5	2.2	2.2	2.3	2.5	2.6	2.5	2.3	2.5	2.4	2.2	2.0	1.9	1.9
TDEG	2.2	2.4	2.6	2.4	2.2	2.2	2.3	2.4	2.6	2.4	2.3	2.5	2.3	2.2	2.0	1.9	1.9
TDPrG	2.3	2.3	2.7	2.4	2.2	2.1	2.3	2.4	2.6	2.4	2.2	2.4	2.5	2.1	2.0	1.9	1.9
ETU	2.7	3.1	3.1	3.0	2.7	2.5	3.0	2.9	3.2	2.9	2.7	2.9	2.7	2.7	2.3	2.0	2.0
BTU	3.8	3.7	4.0	3.7	3.1	2.9	3.5	3.4	3.8	3.3	2.9	3.2	3.7	3.0	24.9	2.1	2.0
ETT	2.0	2.3	2.4	2.3	2.1	2.0	2.2	2.3	2.4	2.3	2.2	2.3	2.1	2.0	1.8	1.7	1.7
PrTT	2.1	2.2	2.5	2.3	2.1	2.0	2.1	2.3	2.4	2.3	2.1	2.3	2.2	2.0	1.8	1.7	1.7
PhTT	2.3	2.4	2.6	2.5	2.2	2.1	2.3	2.4	2.6	2.4	2.2	2.4	2.4	2.1	1.9	1.7	1.7
$P(C_4)_4$	2.5	2.3	3.3	2.6	2.4	2.3	2.3	2.5	2.7	2.5	2.4	2.5	2.9	2.2	2.0	2.0	2.0

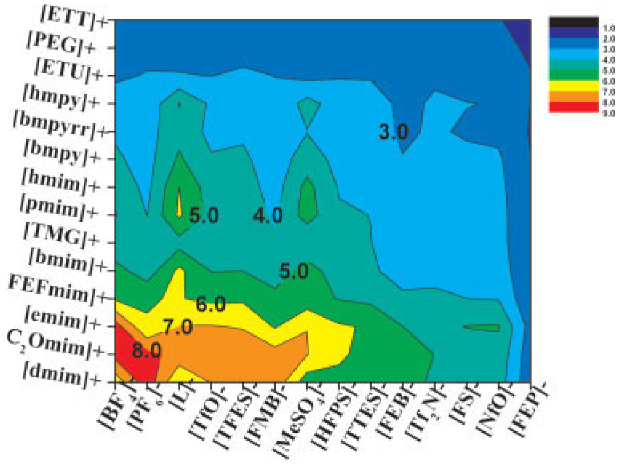


Figure 3. Henry's law constants of CO_2 in 196 ionic liquids predicted by COSMO-RS method at 298.15 K.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

fluoropropyl)trifluorophosphate ([FPrP]) ILs are almost the same, although more carbons are included in the latter anion. In addition, the effect of the counter-ion is also very limited with regard to the "high-solubility" ions, such as [FEP] and [ETT].

The introduction of electron withdrawn element, such as O and F, in the side chain of imidazolium, will decrease the solubility of CO_2 in ILs, which can be found by comparing the results of 1-ethyl-3-methylimidazolium ([emim]) and 1-(1,1,2,2-tetrafluoroethyl)-3-methylimidazolium ([TFEmim]).

In summary, anion [FEP] and cations [ETT], [ETU], and [PEG] are selected as promising candidates in CO_2 capture by screening from 408 ILs in terms of the COSMO-RS method in this work.

Experiment

In fact, the screening of ILs for the capture of CO_2 by the COSMO-RS method is a preliminary stage for the determination of the most effective ILs. In any case, experimental measurements of the solubility data for the systems screened in this work are essential.

As is described earlier, the ILs with anion [FEP] and cations [ETT], [ETU], and [PEG] can dissolve more CO_2. However, some of their combinations are actually solid at room temperature. For example, the melting point of [ETU][FEP] is 304 K. Thus, three ILs with [FEP] are chosen to carry out additional experimental measurements of CO_2 solubilities by the apparatus of the IGA 003. As a result, our experimental measurements were focused on the ILs, consisting of the cations of 1-hexyl-3-methylimidazolium ([hmim]), 1-butyl-1-methylpyrrolidinium ([bmpyrr]), and S-ethyl-*N*,*N*,*N*′,*N*′-tetramethylthiouronium ([ETT]).

Materials

All the samples of ILs are obtained from Merck KGaA, including [hmim][FEP], [bmpyrr][FEP], and [ETT][FEP]. In all the samples, both the water and halide contents are less than 100 ppm (mg/kg). The CO_2 is supplied by Beijing AP BeiFen Gases Industry Company Limited with the purity of 99.99%.

Apparatus and measurements

The details of IGA 003 can be found in Ref. 10. The procedures in the measurements are as follows:

All the measurements were performed in the static mode in this work. About 60–70 mg of IL samples were loaded into the sample container. After the reactor was sealed carefully, the samples were heated to 348.2 K under vacuum to outgas water and other impurities for 48–72 h. Once the weight was stabilized for at least 1 h within the accuracy of ±0.5 μg, the sample dry mass was recorded, then three isotherms were measured at 283.2 K, 298.2 K, and 323.2 K, respectively. The temperature was controlled by a water jacket with the fluctuation within 0.2 K. Once the temperature was achieved and stable, the admittance and exhaust valves would automatically open and close to adjust the pressure to the preset values in accuracy within ±0.4 to 0.6 kPa. Fourteen isobars up to 1.8 MPa were measured for each isotherm. The samples were maintained at each pressure for a minimum of 1 h with a maximum timeout of 3 h to reach equilibrium, where the weight fluctuation was within ±1 μg.

The gas solubilities in ILs were decided by measuring the equilibrium mass uptake at a given pressure and temperature. The effect of volume expansion on the buoyancy correction is ignored because of the high solubility of CO_2 in the ILs and the small expansion of the ILs at low pressure, as is pointed out in Ref. 8.

The uncertainty of solubility comes from not only the accuracy of the mass measurement, but also the fluctuation of temperature and pressure. It is difficult to carry out a mathematical estimation of the uncertainty. However, it can be determined by repeating experiments on the same system. In this work, we repeated the measurements of CO_2/[hmim][FEP] at 298.2 K by several times and found that the uncertainty is less than 0.006 molar fraction.

It should be noted here that ILs were believed to be nonvolatile in early studies. It seems true at the atmosphere pressure. However, Earle et al.[60] have reported very recently that many ILs can be distilled at low pressure without decomposition. In this work, we also found the sample would be evaporated under vacuum (as low as 10^{-9} MPa) at higher temperatures. For example, it is observed that the weight of [ETT][FEP] would decrease continually at 373.2 K under vacuum, with a rate of 7.6 μg/h. To avoid the weight loss in outgas, we recommend 348.2 K as a safe temperature for outgas in the absorption experiments in ILs.

Results and Discussion

The solubilities of CO_2 in [hmim][FEP], [bmpyrr][FEP], and [ETT][FEP] were measured up to the pressure of 1.8 MPa at three temperatures: 283.5 K, 298.6 K, and 323.3 K. The data are presented in Tables 3–5. It is noted that the solubility of CO_2 in [hmim][FEP] is in excellent agreement with the data reported by Brennecke's group very recently,[8] which proves that our experimental measurements are reliable.

Table 3. Solubility of CO_2 in [hmim][FEP] at Different Pressures and Temperatures

P (MPa)	Mole Fraction	P (MPa)	Mole Fraction	P (MPa)	Mole Fraction
T = 283.5 K		T = 298.6 K		T = 323.2 K	
0.0297	0.016	0.0297	0.016	0.0297	0.012
0.0501	0.027	0.0501	0.024	0.0501	0.017
0.0701	0.037	0.0701	0.031	0.0700	0.022
0.1000	0.051	0.0998	0.041	0.0998	0.028
0.1998	0.102	0.1999	0.081	0.2000	0.055
0.3000	0.148	0.3000	0.116	0.2999	0.082
0.3997	0.188	0.3999	0.148	0.3999	0.107
0.5997	0.258	0.5998	0.202	0.5997	0.143
0.7997	0.316	0.7997	0.251	0.7997	0.178
1.0000	0.367	0.9997	0.294	0.9998	0.213
1.1999	0.413	1.2000	0.333	1.1997	0.248
1.3997	0.453	1.3999	0.364	1.3999	0.273
1.5996	0.487	1.5996	0.396	1.5998	0.293
1.7998	0.517	1.7996	0.420	1.7998	0.321

Table 5. Solubility of CO_2 in [ETT][FEP] at Different Pressures and Temperatures

P (MPa)	Mole Fraction	P (MPa)	Mole Fraction	P (MPa)	Mole Fraction
T = 283.2 K		T = 298.5 K		T = 323.5 K	
0.00477	9 E-4	0.00489	2 E-4	0.00482	0.000
0.0298	0.013	0.0299	0.009	0.0298	0.006
0.0501	0.023	0.0499	0.016	0.0499	0.011
0.0701	0.032	0.0700	0.023	0.0700	0.015
0.1000	0.045	0.0999	0.033	0.1000	0.020
0.2000	0.092	0.1999	0.068	0.1999	0.052
0.2998	0.137	0.3000	0.102	0.2998	0.077
0.4000	0.175	0.3998	0.133	0.3997	0.098
0.6000	0.238	0.5997	0.181	0.5997	0.132
0.8000	0.297	0.7997	0.229	0.7998	0.167
0.9997	0.348	0.9999	0.270	0.9999	0.195
1.1997	0.391	1.1998	0.305	1.1997	0.225
1.3998	0.434	1.3997	0.343	1.3996	0.247
1.7997	0.497	1.7997	0.397	1.7996	0.295

Henry's law constants

The solubility of a gas in a solvent can be described by the Henry's law, which is defined in the molar fraction scale as

$$K_{H,x} = \lim_{x_1 \to 0} \frac{\hat{f}_1^{\,l}(T,P,x_1)}{x_1} \tag{1}$$

or, as an alternative, in the molality scale,

$$K_{H,m} = \lim_{m_1 \to 0} \frac{\hat{f}_1^{\,l}(T,P,m_1)}{m_1/m^\circ} \tag{2}$$

where $K_{H,x}$ and $K_{H,m}$ are the Henry's law constants of the gas in the liquid in the molar fraction and molality scale, respectively. The subscription 1 denotes the gas, and $\hat{f}_1^{\,1}$ is its fugacity in the solution, where m_1 is the molality of CO_2 in the solution and m° is the standard molality, i.e., 1 mol kg^{-1}. One can reasonably assume that there is not any IL in the equilibrium gas phase. Thus, we get

$$K_{H,x} = \lim_{x_1 \to 0} \frac{f_i^{g}(T,P)}{x_1} \tag{3}$$

Or,

$$K_{H,m} = \lim_{m_1 \to 0} \frac{f_1^{g}(T,P)}{m_1/m^\circ} \tag{4}$$

where $\hat{f}_1^{\,g}$ is the fugacity of the pure gas at T and P in the equilibrium gas phase, which can be easily calculated by a conventional equation of state with good accuracy.

The relationship between the fugacity and molality (f-m) is shown in Figure 4. Thus the Henry's law constant is calculated by the linear slope of f-m at low pressures.

According to the definition of molar fraction and molality, the relationship between $K_{H,x}$ and $K_{H,m}$ can be easily deduced,

$$K_{H,x} = \frac{K_{H,m}}{M_2/m^\circ} \tag{5}$$

where M_2 is the molar mass of the solvent.

Table 4. Solubility of CO_2 in [bmpyrr][FEP] at Different Pressures and Temperatures

P (MPa)	Mole Fraction	P (MPa)	Mole Fraction	P (MPa)	Mole Fraction
T = 283.5 K		T = 298.6 K		T = 323.3 K	
0.0297	0.013	0.0297	0.009	0.0297	0.007
0.0500	0.023	0.0500	0.017	0.0501	0.012
0.0701	0.033	0.0700	0.024	0.0701	0.017
0.1000	0.046	0.0994	0.033	0.1000	0.022
0.2000	0.094	0.1999	0.068	0.2000	0.046
0.3000	0.137	0.3000	0.104	0.2999	0.074
0.3997	0.175	0.3998	0.133	0.3997	0.095
0.5998	0.243	0.5999	0.188	0.5998	0.136
0.7998	0.301	0.7998	0.232	0.7997	0.162
0.9997	0.350	0.9999	0.273	0.9999	0.193
1.1998	0.394	1.1997	0.311	1.1998	0.223
1.4000	0.433	1.3997	0.344	1.3997	0.252
1.5996	0.467	1.5996	0.374	1.5997	0.275
1.8001	0.498	1.7999	0.401	1.7996	0.293

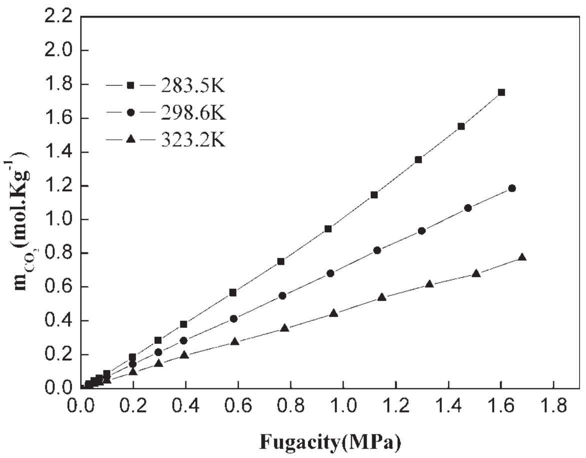


Figure 4. The solubility in molality scale of CO_2 in [hmim][FEP] as a function of gas fugacity at different temperatures.

Table 6. The Henry's Law Constants (MPa) in Mole Fraction Scale of CO_2 in [FEP]-based Ionic Liquids with Various Cations by Experiments

	283.5 K	298.6 K	323.3 K
[hmim][FEP]	1.85	2.37	3.66
[bmpyrr][FEP]	2.03	2.85	4.45
[ETT][FEP]	2.08	2.94	4.84

The Henry's law constants of CO_2 in the three ILs, [hmim][FEP], [bmpyrr][FEP], and [ETT][FEP], are listed in Table 6. The Henry's law constant of 2.37 MPa in [hmim][FEP] is comparable with 2.52 MPa, which is reported in literature.[8]

Effect of anions on CO_2 solubility

With the same cation [hmim], the Henry's law constants of CO_2 in [hmim][FEP] and [hmim][Tf_2N] are 2.37 and 3.16 MPa[8] at 298.15 K, respectively. As a comparison, the values for [bmim][Tf_2N], [bmim][PF_6], and [bmim][BF_4] are 3.30, 5.34, and 5.90 MPa.[6] Thus, the solubility of CO_2 in ILs with the four anions has a sequence of [FEP] > [Tf_2N] > [PF_6] > [BF_4], which is consistent with the above conclusion in the screening procedure by the COSMO-RS calculations.

The solubilities of CO_2 in [hmim][FEP], [hmim][Tf_2N], and [hmim][PF_6] at 298.15 K changing with pressure are demonstrated in Figure 5. The anion effect of ILs can be shown more clearly that [FEP]-based IL has the best capability to dissolve CO_2. For example, the solubilities in [hmim][FEP], [hmim][Tf_2N], and [hmim][PF_6] are 0.251, 0.213, and 0.146 at 0.8 MPa, respectively, as shown in Figure 5, indicating [hmim][FEP] can absorb more than 15 and 70% higher CO_2, compared with [hmim][Tf_2N] and [hmim][PF_6], respectively.

Brennecke's group[6] discussed in detail the anion effect on solubility of CO_2 in ILs. They concluded that the fluoroalkyl groups in anion improve the CO_2 solubilities, which is confirmed in their recent studies.[8] Because one [FEP] anion contains three C_2F_5 groups, it is expected ILs with [FEP] can absorb more CO_2. In addition, [FEP] possesses some other advantages, such as very low uptake of water compared with other ILs, high stability towards hydrolysis and low viscosity.[59] Therefore, the [FEP]-based IL is not only promising in capturing CO_2, but also one type of hydrophobic solvent in many other applications.

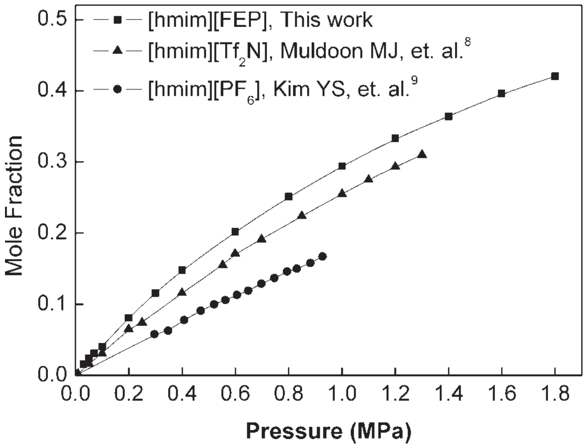


Figure 5. Effect of the anions on the solubility of CO_2 in [hmim]-based ionic liquids at 298.2 K.

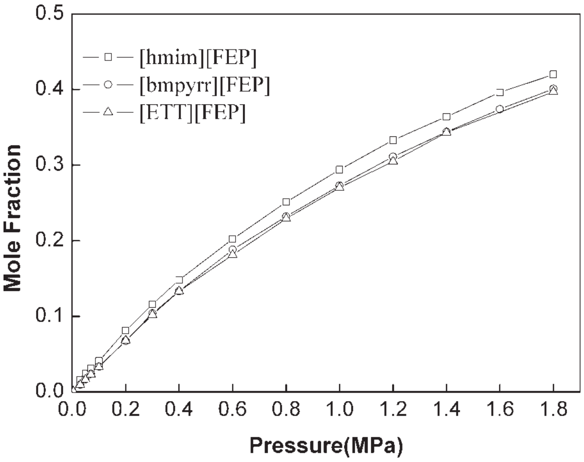


Figure 6. Effect of the cations on the solubility of CO_2 in [FEP]-based ionic liquids at 298.6 K.

Effect of cations on CO_2 solubility

The Henry's law constants in three [FEP]-based ILs with different cations are listed in Table 6. As is expected, the cations have much smaller influence on the solubility of CO_2 in ILs. For example, the Henry's law constants at 298.6 K are 2.37, 2.85, and 2.94 MPa in [ETT][FEP], [bmpyrr][FEP], and [hmim][FEP], respectively. Figure 6 shows isotherms for the three ILs at 298.6 K. As is shown, the solubility of CO_2 increases in the following order: [ETT] < [bmpyrr] < [hmim]. Similar trends are observed at 283.6 K and 323.3 K.

Temperature dependent gas solubility

In this work, all the CO_2 solubilities decrease with the increase of temperature, indicating the negative solvation enthalpy. The values of enthalpy and entropy to dissolve a gas in solvent can be estimated as follows,[6]

$$\frac{\Delta h_{\mathrm{sol}}}{R} = \frac{\partial \ln K_{\mathrm{H},x}}{\partial(1/T)} \tag{6}$$

$$\frac{\Delta s_{\mathrm{sol}}}{R} = -\frac{\partial \ln K_{\mathrm{H},x}}{\partial(\ln T)} \tag{7}$$

The estimated solvation enthalpy and entropy for CO_2 in [hmim][FEP] are -13.0 kJ mol^{-1} and -43.1 J mol^{-1} K^{-1}, respectively. It is comparable with the previous values of CO_2 in [bmim][PF_6] reported in the literature,[6] -14.3 kJ mol^{-1} and -47.6 J mol^{-1} K^{-1}.

Conclusions

A screening method is proposed successfully in this work for the molecular design of ILs to capture CO_2, which is based on the prediction of the Henry's law constant by using the COSMO-RS method without any specific parameter adjustment. The method would be a valuable approach to reduce efficiently the necessary experimental efforts for the measurements of gas solubility in ILs.

Four hundred and eight kinds of ILs, with 24 cations and 17 anions, are screened to find promising candidates in CO_2 capture, by using the COSMO-RS method. The screening results show that more CO_2 can be absorbed in ILs with [FEP] anion. It is also shown that a value of 0.2 MPa seems the lowest limit of the Henry's law constant of CO_2 in ILs at 298 K in physical absorption.

To confirm the screening results, three [FEP]-based ILs are chosen to perform the experimental measurements, with cations of 1-hexyl-3-methylimidazolium ([hmim]), 1-butyl-1-methylpyrrolidinium ([bmpyrr]), and *S*-ethyl-*N*,*N*,*N′*,*N′*-tetramethylthiouronium ([ETT]). The solubilities of CO_2 in the three ILs are measured by the IGA 003 at 283.2 K, 298.2 K, and 323.2K with the pressure range 0–1.8 MPa. To our best knowledge, the solubility data of CO_2 in the latter two ILs, i.e., [bmpyrr][FEP] and [ETT][FEP], have not been reported in the literature.

The experimental data indicate that the CO_2 solubility is improved in [FEP]-based ILs. For example, the solubility in [hmim][FEP] is about 15% higher, compared with the other promising CO_2-capture IL, 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([hmim][Tf_2N]). It is also found that the cation has limited influence on the solubility of CO_2 in the [FEP]-based ILs.

In conclusion, the [FEP]-based ILs are recommended here as the most promising candidates for the capture of CO_2 at ambient temperature.

It is noticed that the mechanism of CO_2 dissolved in ILs can be explored by molecular simulation. Therefore, molecular dynamics will be carried out in our future work to understand the good performance of CO_2 absorption in the [FEP]-based ILs.

Acknowledgments

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Literature Cited

1. Zhang SJ, Chen YH, Li FW, Lu XM, Dai WB, Mori R. Fixation and conversion of CO_2 using ionic liquids. *Catal Today*. 2006; 115:61–69.
2. Freemantle M. New frontiers for ionic liquids. *Chem Eng News*. 2007;85:23–26.
3. Blanchard LA, Gu ZY, Brennecke JF. High-pressure phase behavior of ionic liquid/CO_2 systems. *J Phys Chem B*. 2001;105:2437–2444.
4. Anthony JL, Maginn EJ, Brennecke JF. Solubilities and thermodynamic properties of gases in the ionic liquid 1-n-butyl-3-methylimidazolium hexafluorophosphate. *J Phys Chem B*. 2002;106:7315–7320.
5. Cadena C, Anthony JL, Shah JK, Morrow TI, Brennecke JF, Maginn EJ. Why is CO_2 so soluble in imidazolium-based ionic liquids? *J Am Chem Soc*. 2004;126:5300–85308.
6. Anthony JL, Anderson JL, Maginn EJ, Brennecke JF. Anion effects on gas solubility in ionic liquids. *J Phys Chem B*. 2005;109:6366–6374.
7. Anderson JL, Dixon JK, Brennecke JF. Solubility of CO_2,CH_4, C_2H_6, C_2H_4, O_2, and N_2 in 1-hexyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide: comparison to other ionic liquids. *Acc Chem Res*. 2007;40:1208–1216.
8. Muldoon MJ, Aki S, Anderson JL, Dixon JK, Brennecke JF. Improving carbon dioxide solubility in ionic liquids. *J Phys Chem B*. 2007;111:9001–9009.
9. Kim YS, Choi WY, Jang JH, Yoo KP, Lee CS. Solubility measurement and prediction of carbon dioxide in ionic liquids. *Fluid Phase Equilib*. 2005;228:439–445.
10. Shiflett MB, Yokozeki A. Solubilities and diffusivities of carbon dioxide in ionic liquids: [bmim][PF_6] and [bmim][BF_4]. *Ind Eng Chem Res*. 2005;44:4453–4464.
11. Shiflett MB, Yokozeki A. Solubility of CO_2 in room temperature ionic liquid [hmim][Tf_2N]. *J Phys Chem B*. 2007;111:2070–2074.
12. Ferguson L, Scovazzo P. Solubility, diffusivity, and permeability of gases in phosphonium-based room temperature ionic liquids: data and correlations. *Ind Eng Chem Res*. 2007;46:1369–1374.
13. Hou Y, Baltus RE. Experimental measurement of the solubility and diffusivity of CO_2 in room-temperature ionic liquids using a transient thin-liquid-film method. *Ind Eng Chem Res*. 2007;46:8166–8175.
14. Kamps APS, Tuma D, Xia JZ, Maurer G. Solubility of CO_2 in the ionic liquid [bmim][PF_6]. *J Chem Eng Data*. 2003;48:746–749.
15. Camper D, Becker C, Koval C, Noble R. Diffusion and solubility measurements in room temperature ionic liquids. *Ind Eng Chem Res*. 2006;45:445–450.
16. Kumelan J, Kamps APS, Tuma D, Maurer G. Solubility of CO_2 in the ionic liquid [hmim][Tf_2N]. *J Chem Thermodyn*. 2006;38:1396–1401.
17. Zhang SJ, Yuan XL, Chen YH, Zhang XP. Solubilities of CO_2 in 1-butyl-3-methylimidazolium hexafluorophosphate and 1,1,3,3-tetramethylguanidium lactate at elevated pressures. *J Chem Eng Data*. 2005;50:1582–1585.
18. Zhang SJ, Chen YH, Ren RXF, Zhang YQ, Zhang JM, Zhan XP. Solubility of CO_2 in sulfonate ionic liquids at high pressure. *J Chem Eng Data*. 2005;50:230–233.
19. Yuan XL, Zhang SJ, Chen YH, Lu XM, Dai W, Mori R. Solubilities of gases in 1,1,3,3-tetramethylguanidium lactate at elevated pressures. *J Chem Eng Data*. 2006;51:645–647.
20. Gomes MFC. Low-pressure solubility and thermodynamics of solvation of carbon dioxide, ethane, and hydrogen in 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide between temperatures of 283 K and 343 K. *J Chem Eng Data*. 2007;52:472–475.
21. Husson-Borg P, Majer V, Gomes MFC. Solubilities of oxygen and carbon dioxide in butyl methyl imidazolium tetrafluoroborate as a function of temperature and at pressures close to atmospheric pressure. *J Chem Eng Data*. 2003;48:480–485.
22. Kumelan J, Kamps APS, Tuma D, Maurer G. Solubility of CO_2 in the ionic liquids [bmim][CH_3SO_4] and [bmim][PF_6]. *J Chem Eng Data*. 2006;51:1802–1807.
23. Jacquemin J, Gomes MFC, Husson P, Majer V. Solubility of carbon dioxide, ethane, methane, oxygen, nitrogen, hydrogen, argon, and carbon monoxide in 1-butyl-3-methylimidazolium tetrafluoroborate between temperatures 283 K and 343 K and at pressures close to atmospheric. *J Chem Thermodyn*. 2006;38:490–502.
24. Jacquemin J, Husson P, Majer V, Gomes MFC. Low-pressure solubilities and thermodynamics of solvation of eight gases in 1-butyl-3-methylimidazolium hexafluorophosphate. *Fluid Phase Equilib*. 2006; 240:87–95.
25. Lee BC, Outcalt SL. Solubilities of gases in the ionic liquid 1-n-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. *J Chem Eng Data*. 2006;51:892–897.
26. Zhang J, Zhang QH, Qiao BT, Deng YQ. Solubilities of the gaseous and liquid solutes and their thermodynamics of solubilization in the novel room-temperature ionic liquids at infinite dilution by gas chromatography. *J Chem Eng Data*. 2007;52:2277–2283.
27. Baltus RE, Culbertson BH, Dai S. Luo HM, DePaoli DW. Low-pressure solubility of carbon dioxide in room-temperature ionic liquids measured with a quartz crystal microbalance. *J Phys Chem B*. 2004; 108:721–727.
28. Aki S, Mellein BR, Saurer EM, Brennecke JF. High-pressure phase behavior of carbon dioxide with imidazolium-based ionic liquids. *J Phys Chem B*. 2004;108:20355–20365.
29. Liu ZM, Wu WZ, Han BX, Dong ZX, Zhao GY, Wang JQ, Jiang T, Yang GY. Study on the phase behaviors, viscosities, and thermodynamic properties of CO_2/[C_4mim][PF_6]/methanol system at elevated pressures. *Chem-Eur J*. 2003;9:3897–3903.
30. Schilderman AM, Raeissi S, Peters CJ. Solubility of carbon dioxide in the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. *Fluid Phase Equilib*. 2007;260:19–22.

31. Shariati A, Peters CJ. High-pressure phase equilibria of systems with ionic liquids. *J Supercrit Fluids*. 2005;34:171–176.
32. Zhang ZF, Wu WZ, Wang B, Chen JW, Shen D, Han BX. High-pressure phase behavior of CO_2/acetone/ionic liquid system. *J Supercrit Fluids*. 2007;40:1–6.
33. Kroon MC, Karakatsani EK, Economou IG, Witkamp GJ, Peters CJ. Modeling of the carbon dioxide solubility in imidazolium-based ionic liquids with the tPC-PSAFT equation of state. *J Phys Chem B*. 2006;110:9262–9269.
34. Wang TF, Peng CJ, Liu HL, Hu Y. Description of the pVT behavior of ionic liquids and the solubility of gases in ionic liquids using an equation of state. *Fluid Phase Equilib*. 2006;250:150–157.
35. Andreu JS, Vega LF. Capturing the solubility Behavior of CO_2 in ionic liquids by a simple model. *J Phys Chem C*. 2007;111:16028–16034.
36. Heintz A. Recent developments in thermodynamics and thermophysics of non-aqueous mixtures containing ionic liquids. A review. *J Chem Thermodyn*. 2005;37:525–535.
37. Morrow TI, Maginn EJ. Molecular dynamics study of the ionic liquid 1-n-butyl-3-methylimidazolium hexafluorophosphate. *J Phys Chem B*. 2002;106:12807–12813.
38. Liu ZP, Huang SP, Wang WC. A refined force field for molecular simulation of imidazolium-based ionic liquids. *J Phys Chem B*. 2004; 108:12978–12989.
39. de Andrade J, Boes ES, Stassen H. Computational study of room temperature molten salts composed by 1-alkyl-3-methylimidazolium cations-force-field proposal and validation. *J Phys Chem B*. 2002; 106:13344–13351.
40. Canongia Lopes JN, Deschamps J, Padua AAH. Modeling ionic liquids using a systematic all-atom force field. *J Phys Chem B*. 2004; 108:2038–2047.
41. Youngs TGA, Del Popolo MG, Kohanoff J. Development of complex classical force fields through force matching to ab initio data: application to a room-temperature ionic liquid. *J Phys Chem B*. 2006;110:5697–5707.
42. Lu ND, Kofke DA. Accuracy of free-energy perturbation calculations in molecular simulation. II. Heuristics. *J Chem Phys*. 2001; 115:6866–6875.
43. Klamt A, Jonas V, Burger T, Lohrenz JCW. Refinement and parametrization of COSMO-RS. *J Phys Chem A*. 1998;102:5074–5085.
44. Eckert F, Klamt A. Fast solvent screening via quantum chemistry: COSMO-RS approach. *AIChE J*. 2002;48:369–385.
45. Diedenhofen M, Eckert F, Klamt A. Prediction of infinite dilution activity coefficients of organic compounds in ionic liquids using COSMO-RS. *J Chem Eng Data*. 2003;48:475–479.
46. Kato R, Gmehling J. Systems with ionic liquids: measurement of VLE and gamma(infinity) data and prediction of their thermodynamic behavior using original UNIFAC, mod. UNIFAC(Do) and COSMO-RS(O1). *J Chem Thermodyn*. 2005;37:603–619.
47. Jork C, Kristen C, Pieraccini D, Stark A, Chiappe C, Beste YA, Arlt W. Tailor-made ionic liquids. *J Chem Thermodyn*. 2005;37:537–558.
48. Klamt A. Prediction of the mutual solubilities of hydrocarbons and water with COSMO-RS. *Fluid Phase Equilib*. 2003;206:223–235.
49. Banerjee T, Khanna A. Infinite dilution activity coefficients for trihexyltetradecyl phosphonium ionic liquids: measurements and COSMO-RS prediction. *J Chem Eng Data*. 2006;51:2170–2177.
50. Banerjee T, Singh MK, Khanna A. Prediction of binary VLE for imidazolium based ionic liquid systems using COSMO-RS. *Ind Eng Chem Res*. 2006;45:3207–3219.
51. Spuhl O, Arlt W. COSMO-RS predictions in chemical engineering - A study of the applicability to binary VLE. *Ind Eng Chem Res*. 2004;43:852–861.
52. Liu ZP, Wu XP, Wang WC. A novel united-atom force field for imidazolium-based ionic liquids. *Phys Chem Chem Phys*. 2006;8:1096–1104.
53. Wu XP, Liu ZP, Huang SP, Wang WC. Molecular dynamics simulation of room-temperature ionic liquid mixture of [bmim][BF4] and acetonitrile by a refined force field. *Phys Chem Chem Phys*. 2005;7:2771–2779.
54. Wu XP, Liu ZP, Wang WC. Molecular dynamics simulation of gas solubility in room temperature ionic liquids. *Acta Phys-Chim Sin*. 2005;21:1138–1142.
55. Becke AD. Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys Rev A*. 1988;38:3098–3100.
56. Schäfer A, Huber C, Ahlrichs R. Fully optimized contracted Gaussian basis sets of triple-ξ valence quality for atoms Li to Kr. *J Chem Phys*. 1994;100:5829–5835.
57. Ahlrichs R, Bar M, Haser M, Horn H, Kolmel C. Electronic structure calculations on workstation computers: the program system TURBOMOLE. *Chem Phys Lett*. 1989;162:165–169.
58. Eckert F, Klamt A. *COSMOtherm Users Manua: Version C2.1 Release 01.04*. Germany, Leverkusen: COSMOlogic GmbH & Co KG, 2004.
59. Ignat'ev NV, Welz-Biermann U, Kucheryna A, Bissky G. Willner H. New ionic liquids with tris(perfluoroalkyl)trifluorophosphate (FAP) anions. *J Fluor Chem*. 2005;126:1150–1159.
60. Earle MJ, Esperanca J, Gilea MA, Lopes JNC, Rebelo LPN, Magee JW, Seddon KR, Widegren JA. The distillation and volatility of ionic liquids. *Nature*. 2006;439:831–834.

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