Carbon Dioxide Solubility in the Homologous 1-Alkyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide Family[†]

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The high-pressure phase behavior of the binary system CO_2 + 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide was determined experimentally by a synthetic method. Bubble points were measured for mixtures of various carbon dioxide concentrations within a temperature and pressure range of (310 to 450) K and (0.5 to 14) MPa, respectively. The results were compared with solubility data obtained by three other research laboratories using different phase equilibria measuring techniques, and good agreement was observed in every case. The effect of the cation alkyl chain length was also investigated by comparing CO_2 solubility in four homologous members of the 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide family in which the alkyl was either ethyl, butyl, hexyl, or octyl. It was shown that CO_2 solubility increases almost linearly with increasing alkyl chain length.

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1. Introduction

Ionic liquids (ILs) are receiving increasing attention by researchers throughout the world. Mixtures of CO_2 and imidazolium-based ILs, in particular, are interesting for a variety of applications, partly because CO_2 has shown remarkable solubilities in these ILs. Mixtures of CO_2 + ILs have been used for a range of homogeneously catalyzed reactions. Supercritical CO_2 can be used as an environmentally benign solvent to extract organic products or contaminants from ILs.[1,2] It has also been shown that CO_2 can be used to separate organic liquids and water from ILs by inducing a liquid−liquid split.[3,4] Due to the remarkable solubility of CO_2 in imidazolium-based ILs,[5−20] there is an emerging interest in applying ILs for gas separations.[21] It is obvious that a fundamental understanding of the phase behavior of CO_2 with ILs is important for all these applications and for future developments. Although most published solubility data are at low pressures, high-pressure data of carbon dioxide solubility in ionic liquids are also gradually becoming available. Abbreviations of ILs for the discussion that follows are given in Table 1, and the molecular structures of these ILs are given by Andersen and co-workers.[16]

Table 1. Symbols Used for Various Anions and Cations of Some Ionic Liquids

cation	abbreviation
1-ethyl-3-methylimidazolium	[emim]
1-butyl-3-methylimidazolium	[bmim]
1-hexyl-3-methylimidazolium	[hmim]
1-octyl-3-methylimidazolium	[omim]
anions	**abbreviation**
hexafluorophosphate	[PF_6]
tetrafluoroborate	[BF_4]
bis(trifluoromethylsulfonyl)imide	[Tf_2N]
dicyanamide	[DCA]
trifluoromethanesulfonate	[TfO]
(trifluoromethylsulfonyl)methide	[methide]
nitrate	[NO_3]

Anthony et al.[6] studied the solubilities of some gases in [bmim][PF_6] at (283, 298, and 323) K by means of a gravimetric microbalance. Perez-Salado Kamps et al.[22] also reported the solubility of carbon dioxide in [bmim][PF_6] for temperatures from (293 to 393) K and pressures up to about 9.7 MPa. Husson-Borg et al.[15] studied the solubilities of carbon dioxide in [bmim][BF_4] at temperatures between (303 and 343) K and at pressures close to atmospheric. Shariati and Peters,[23,24] Costantini et al.,[25] and Kroon et al.[26] studied the high-pressure phase behavior of binary mixtures consisting of carbon dioxide and imidazolium-based ionic liquids (1-alkyl-3-methylimidazolium tetrafluoroborate and 1-alkyl-3-methylimidazolium hexafluorophosphate) over a wide range of solute concentrations and at pressures up to about 100 MPa. Blanchard et al.[27] and Aki et al.[28] obtained the solubility of CO_2 up to 333 K in various ionic liquids of [DCA], [NO_3], [BF_4], [PF_6], [TfO], [Tf_2N], and [methide] but having the [bmim] cation in common. Camper et al.[12] reported low-pressure gas solubilities and Henry's constants of carbon dioxide in a number of different ionic liquids under both dry and water-saturated conditions at 303.15 K. The imidazolium-based ionic liquids used in their study were [bmim][PF_6], [emim][Tf_2N], [emim][TfO], and [emim][DCA].

The following experimental studies were conducted on the ionic liquid family [Tf_2N]. Kim et al.[29] presented CO_2 solubilities in the ionic liquid [emim][Tf_2N] at low pressures (below 1 MPa). Schilderman et al.[30] used a synthetic method to measure carbon dioxide solubilities in [emim][Tf_2N] up to much higher pressures of 15 MPa. Anthony et al.[7] studied gas solubilities (CO_2, O_2, N_2O, C_2H_4, and C_2H_6) in [bmim][Tf_2N] up to pressures of about 1.5 MPa. Lee and Outcalt[31] increased the pressure range of carbon dioxide in [bmim][Tf_2N] to about 5 MPa using an equilibrium apparatus equipped with a cylindrical

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Table 2. Experimentally Measured Solubility Data (Bubble-Point Curves) for Carbon Dioxide (1) in [bmim][Tf$_2$N] (2)

x_1	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa
0.0847	313.55	0.422	323.08	0.488	332.73	0.558
	342.43	0.648	352.13	0.723	361.82	0.813
	371.50	0.903	381.17	1.003	390.67	1.098
	400.58	1.198	410.32	1.303	420.12	1.408
	429.98	1.503	439.54	1.603	449.29	1.703
0.1886	313.60	1.002	323.08	1.172	332.74	1.357
	342.42	1.552	352.11	1.757	361.76	1.972
	371.43	2.202	380.99	2.433	390.86	2.668
	400.64	2.912	410.37	3.158	420.16	3.398
	429.89	3.648	439.64	3.888	449.38	4.133
0.2926	313.58	1.724	323.08	2.024	332.75	2.350
	342.55	2.700	352.10	3.105	361.77	3.500
	371.56	3.900	381.22	4.304	390.88	4.729
	400.62	5.150	410.37	5.600	420.21	6.035
	429.87	6.475	439.60	6.900	449.36	7.325
0.3818	313.50	2.473	323.08	2.938	332.77	3.423
	342.47	3.943	352.12	4.497	361.86	5.082
	371.50	5.682	381.25	6.303	390.91	6.943
	400.63	7.593	410.52	8.248	420.12	8.933
	429.86	9.548	439.65	10.198	449.41	10.833
0.4866	313.57	3.799	332.76	5.289	342.53	6.137
	352.10	7.197	371.46	9.172	390.87	11.273
	410.37	13.473	415.25	14.023		
0.5257	314.65	4.448	323.15	5.174	332.79	6.099
	342.45	7.074	352.11	8.124	361.76	9.250
	371.43	10.425	381.11	11.625	390.95	12.874
	400.59	14.099				
0.5852	313.65	5.483	323.13	6.588	332.73	7.828
	342.43	9.213	352.11	10.713	361.93	12.304
	371.59	13.959	313.65	5.527		

view cell. Aki and co-workers[28] obtained CO_2 solubilities in the [bmim], [hmim], and [omim] ionic liquids of [Tf$_2$N] up to 333 K and 14 MPa using a stoichiometric method. For the ionic liquid [hmim][Tf$_2$N], Costa Gomes[32] measured carbon dioxide solubilities at atmospheric pressure, while Kim et al.[29] presented CO_2 solubilities in [hmim][Tf$_2$N] at slightly higher pressures up to 1 MPa. Shiflett and Yokozeki[33] presented data obtained using a gravimetric microbalance for the same binary system, but up to pressures of about 2 MPa. The measured pressures of this system were further increased to about 10 MPa by Kumelan et al.[34] using a high-pressure view cell.

Although the solubility of CO_2 has previously been measured in [bmim][Tf$_2$N] by other investigators as mentioned above, the temperature range was limited to temperatures up to 340 K. As part of a broader project to investigate the feasibility of using ionic liquids for gas separations,[35] this study extends the solubility data of CO_2 in [bmim][Tf$_2$N] to much higher temperatures than currently available. The obtained results are compared to those in the literature where available.

2. Experimental Section

The Cailletet apparatus used for performing the phase behavior experiments operates according to the synthetic method. A mixture of gas + ionic liquid is injected into a mass transfer−closed pyrex equilibrium cell in the shape of a tube. In this way, the overall composition of the mixture remains the same throughout successive measurements through incremental temperature steps. At any single set temperature, the pressure on the sample is increased until the disappearance of the last bubble of gas is observed visually. The experimental setup and measuring procedure is explained extensively elsewhere.[36,37] Carbon dioxide was supplied by Messer-Griesheim with a purity of 99.995 %. The ionic liquid [bmim][Tf$_2$N] was purchased from Fluka with an initial purity of over 98 %. This ionic liquid was further purified by drying with molecular sieves for several days under vacuum. The accuracies of measurements were within 0.03 % of the reading for pressure, 0.02 K for temperature, and 0.001 for molar fraction.

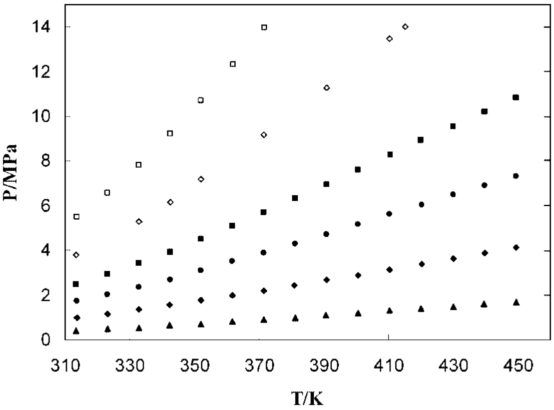

Figure 1. Experimentally measured solubility data (bubble points) for six different isopleths of the binary system CO_2 + [bmim][Tf$_2$N] with the following molar percentages of CO_2: ▲, 8.5 %; ♦, 18.9 %; ●, 29.3 %; ■, 38.2 %; ◇, 48.7 %; □,58.5 %.

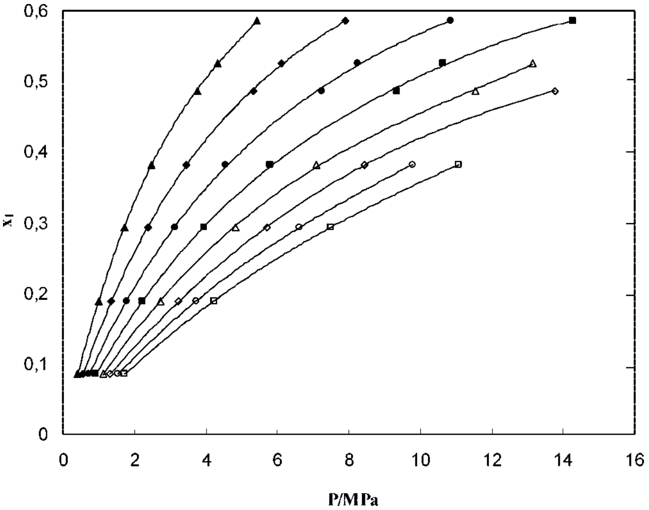

Figure 2. Interpolated solubility curves at eight different temperatures for the binary system CO_2 (1) + [bmim][Tf$_2$N] (2): ▲, 313.15 K; ♦, 333.15 K; ●, 353.15 K; ■, 373.15 K; Δ, 393.15 K; ◇, 413.15 K; ○, 433.15 K; □, 453.15 K. The curves are polynomial fits to the data for easier visual interpretation.

3. Results

Experimentally measured bubble points, indicative of the upper limit of gas solubility for the system CO_2 + [bmim][Tf$_2$N], are presented in Table 2 and shown graphically in Figure 1 in the temperature and pressure range of (313 to 450) K and (0.5 to 14.0) MPa, respectively. The data were reproducible to within 0.005 MPa by repeating a point two or three times, even after keeping the sample at temperatures of about 450 K for at least 10 h. This shows that no reactions nor thermal degradation occur for mixtures of CO_2 and [bmim][Tf$_2$N] within the experimental operating conditions (up to 450 K). It is seen that as temperature rises increasingly higher pressures are necessary to dissolve a fixed amount of CO_2 in the ionic liquid. The interpolation of this data with polynomial functions onto a more descriptive pressure−composition diagram is given in Table 3 and Figure 2. This figure emphasizes the strong functionality of solubility on temperature and pressure, especially at higher gas concentrations where pressures start to approach a diverging behavior with

Table 3. Interpolated Isothermal Solubility Curves for CO_2 (1) in [bmim][Tf_2N] (2)

T/K	313.15	333.15	353.15	373.15	393.15	413.15	433.15	453.15
x_1	P/MPa	P/MPa	P/MPa	P/MPa	P/MPa	P/MPa	P/MPa	P/MPa
0.0847	0.420	0.564	0.734	0.922	1.123	1.331	1.539	1.741
0.1886	0.994	1.363	1.783	2.241	2.725	3.225	3.729	4.224
0.2926	1.723	2.379	3.132	3.957	4.829	5.724	6.617	7.483
0.3818	2.467	3.437	4.557	5.789	7.094	8.435	9.774	11.073
0.4866	3.758	5.339	7.234	9.341	11.558	13.782		
0.5257	4.331	6.119	8.254	10.632	13.151			
0.5852	5.437	7.907	10.849	14.261				

gas concentrations. This diverging region should be avoided in the vast majority of operations, as it would result in excessive compressor energy loss with little gain in gas solubility. The curvature of the isotherms on this plot indicates the nonideality of the system, and hence the extent of errors that will arise by extending the linear Henry's law to inapplicable regions of high gas solubility. Figure 2 also shows the remarkable mole fraction solubility of CO_2 in [bmim][Tf_2N], going up to 60 % within the range of temperatures and pressures measured in this work. Figures 3a and 3b compare CO_2 solubility with two other ionic liquids having the same cation as [bmim][Tf_2N], but with different anions ([BF_4] and [PF_6]).[24,26] Comparing these experimental data further confirms the excellence of the selected ionic liquid for high CO_2 solubility, showing solution capacities for CO_2 to be typically 1.5 times higher in [Tf_2N] ionic liquids than in the other two most commonly investigated ionic liquid families.

The data measured in this work are compared in Figure 4 to those of the same binary system measured by other research laboratories, namely, the data of Aki et al.[28] at 313 K using a stoichiometric phase equilibrium apparatus, the data of Anthony et al.[7] at 323 K measured by gravimetric microbalances, and the data of Lee and Outcalt[31] at 340 K based on a saturation method at constant volume. In contrast to some other known ionic liquids,[20] the solubility of carbon dioxide in imidazoleum−[Tf_2N] ionic liquids is not greatly affected by water impurities. The ionic liquid samples tested in ours and two of the other laboratories[7,31] were dried prior to use, but the undried samples of Aki and co-workers[28] also showed no systematic differences to the dried samples, although their data had more scattering. Such closely matching ionic liquid solubility data measured with differing experimental techniques can assist in alleviating the ongoing discussion among ionic liquid researchers who debate whether the common data discrepancies are due to impurities or chemical stabilities of the ILs or to systematic measurement errors.[33]

The effect of the cation alkyl chain length on CO_2 solvation capacity of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide is shown in Figure 5 at 313 K for the cases where the alkyl side chain is ethyl, butyl, hexyl, and octyl. It is evident that the size of the alkyl side chain of the cation does indeed affect solubility; however, the effect is not as pronounced as the substitution of the anion. Figure 5 suggests that the gas solubility increases with increasing alkyl chain. The crossover of the [hmim][Tf_2N] and [omim][Tf_2N] curves at lower pressures is most probably a result of experimental errors and not a systematic behavior, especially by considering that both of these curves were experimentally determined by Aki et al.,[28] whose data were already shown in Figure 4 to have some scattering. Aki and co-workers[28] explained the increase in gas solubility with increasing alkyl chain based on the decreasing densities of imidazolium-based ILs with increasing alkyl chain length. The greater free volume in ILs with longer alkyl chains allows for more CO_2 to dissolve. As seen in Figure 5, the differences in CO_2 solubility at fixed temperatures are more distinct at higher pressures. Although not shown, similar trends are observed at other temperatures from the data of this study. There may exist an almost linear relationship between the alkyl chain length and the solubility of CO_2 in such ILs. We had observed this previously[38] in the 1-alkyl-3-methylimidazolium hexafluorophosphate family of ionic liquids. It is also shown here for the bis(trifluoromethylsulfonyl)imide family in Figure 6. The observed scattering of the data is most probably due to experimental errors. The varying degrees of impurities of the various 1-alkyl-3-

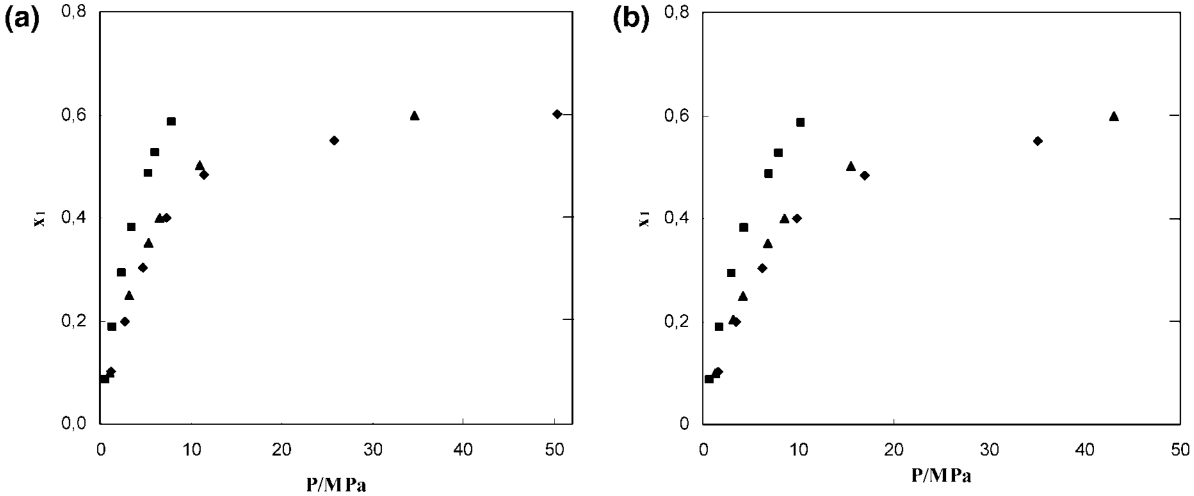

Figure 3. Comparison of CO_2 (1) solubility in several ionic liquids with varying anions but having the same cations at (a) 333.15 K and (b) 350.00 K: ■, [bmim][Tf_2N], this work; ▲, [bmim][PF_6], Shariati et al.;[24] ♦, [bmim][BF_4], Kroon et al.[26]

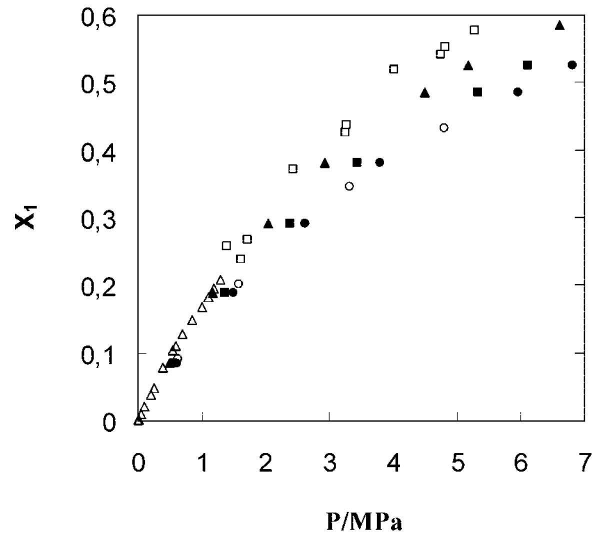

Figure 4. Comparison of the measured solubility data of this work on CO_2 (1) + [bmim][Tf_2N] (2) with literature data: ■, 313.15 K, this work; □, 313.15 K, Aki et al.;[28] ▲, 323.15 K, this work; Δ, 323.15 K, Anthony et al.;[7] ●, 340.00 K, this work; ○, 339.97 K, Lee and Outcalt.[31]

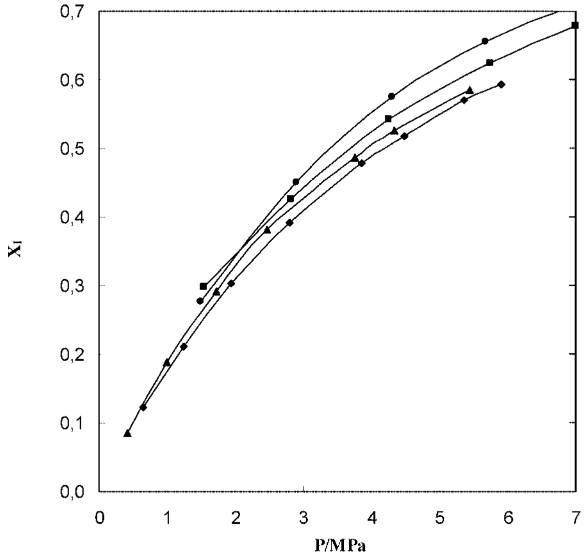

Figure 5. Comparison of the effect of the cation alkyl-chain length on CO_2 (1) solubility at 313.15 K in: ♦, [emim][Tf_2N], Schilderman et al.;[30] ▲, [bmim][Tf_2N], this work; ■, [hmim][Tf_2N], Aki et al.;[28] ●, [omim][Tf_2N], Aki et al.[28]

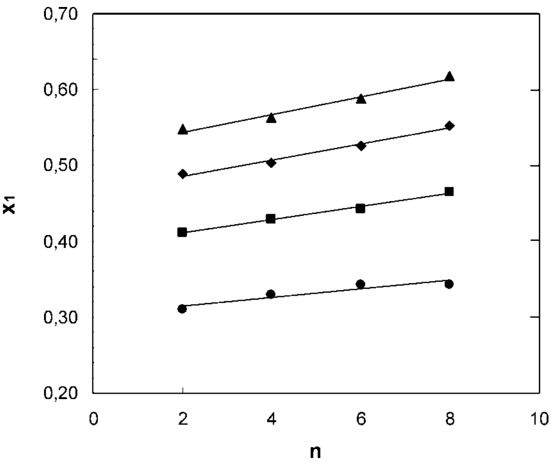

Figure 6. Effect of alkyl chain length on the solubility of CO_2 (1) in the 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide family at 313.15 K and various pressures: ●, 2 MPa; ■, 3 MPa; ♦, 4 MPa; ▲, 5 MPa. Data taken from this work, Schilderman et al.,[30] and Aki et al.[28]

methylimidazolium bis(trifluoromethylsulfonyl)imide samples used in the experiments is of significant importance. Data scattering may also be partly explained by taking into account that the data were obtained in two different laboratories, using different equipment.

4. Conclusions

Reproducible CO_2 solubility data in [bmim][Tf_2N] have been measured within a temperature and pressure range of of (310 to 450) K and (0.5 to14) MPa, respectively. The results show that there is a remarkable capacity for [bmim][Tf_2N] to dissolve carbon dioxide gas, up to 60 %. This is higher than the CO_2 solubility in the commonly investigated ionic liquids with [BF_4] and [PF_6] anions. It is seen that the CO_2 solubility in [bmim][Tf_2N] has a nonideal behavior and depends strongly on temperature and pressure.

A comparison of CO_2 solubility data in various members of the 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide family (namely, ethyl, butyl, hexyl, and octyl, as the alkyl side chain) has shown that there is a linear relationship between CO_2 solubility and alkyl chain length.

Literature Cited

(1) Blanchard, L. A.; Brennecke, J. F. Recovery of Organic Products from Ionic Liquids using Supercritical Carbon Dioxide. *Ind. Eng. Chem. Res.* **2001**, *40*, 287–292.
(2) Scovazzo, P.; Visser, A. E.; Davis, J. H.; Rogers, R. D.; Koval, C. A.; Dubois, D. L.; Noble, R. D. Supported Ionic Liquid Membranes and Facilitated Ionic Liquid Membranes. *ACS Symp. Ser.* **2002**, *818*, 69–87.
(3) Scurto, A. M.; Aki, S. N. V. K.; Brennecke, J. F. CO_2 as a Separation Switch for Ionic Liquid/Organic Mixtures. *J. Am. Chem. Soc.* **2002**, *124*, 10276–10277.
(4) Scurto, A. M.; Aki, S. N. V. K.; Brennecke, J. F. Carbon Dioxide Induced Separation of Ionic Liquids and Water. *Chem. Commun.* **2003**, 572–573.
(5) Bates, E. D.; Mayton, R. D.; Ntai, I.; Davis, J. H. CO_2 Capture by a Task-Specific Ionic Liquid. *J. Am. Chem. Soc.* **2002**, *124*, 926–927.
(6) Anthony, J. L.; Maginn, E. J.; Brennecke, J. F. Solubilities and Thermodynamic Properties of Gases in the Ionic Liquid 1-n-butyl-3-methylimidazolium hexafluorophosphate. *J. Phys. Chem. B* **2002**, *106*, 7315–7320.
(7) Anthony, J. L.; Anderson, J. L.; Maginn, E. J.; Brennecke, J. F. Anion Effects on Gas Solubility in Ionic Liquids. *J. Phys. Chem. B* **2005**, *109*, 6366–6374.
(8) Baltus, R. E.; Culbertson, B. H.; Dai, S.; Luo, H. M.; DePaoli, D. W. 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.
(9) Baltus, R. E.; Counce, R. M.; Culbertson, B. H.; Luo, H. M.; DePaoli, D. W.; Dai, S.; Duckworth, D. C. Examination of the Potential of Ionic Liquids for Gas Separations. *Sep. Sci. Technol.* **2005**, *40*, 525–541.
(10) Cadena, C.; Anthony, J. L.; Shah, J. K.; Morrow, T. I.; Brennecke, J. F.; Maginn, E. J. Why is CO_2 so Soluble in Imidazolium-Based Ionic Liquids. *J. Am. Chem. Soc.* **2004**, *126*, 5300–5308.
(11) Cammarata, L.; Kazarian, S. G.; Salter, P. A.; Welton, T. Molecular States of Water in Room Temperature Ionic Liquids. *Phys. Chem. Chem. Phys.* **2001**, 5192–5200.
(12) Camper, D.; Scovazzo, P.; Koval, C.; Noble, R. Gas Solubilities in Room-Temperature Ionic Liquids. *Ind. Eng. Chem. Res.* **2004**, *43*, 3049–3054.
(13) Costa Gomes, M. F.; Padua, A. A. H. Gas−Liquid Interactions in Solution. *Pure Appl. Chem.* **2005**, *77*, 653–665.
(14) Hert, D. G.; Anderson, J. L.; Aki, S.; Brennecke, J. F. Enhancement of Oxygen and Methane Solubility in 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide using Carbon Dioxide. *Chem. Commun.* **2005**, 2603–2605.
(15) Husson-Borg, P.; Majer, V.; Gomes, M. F. C. 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.

(16) Andersen, J. L.; Dixon, J. K.; Brennecke, J. F. 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.

(17) Muldoon, M. J.; Aki, S. N. V. K.; Anderson, J. L.; Dixon, J. K.; Brennecke, J. F. Improving Carbon Dioxide Solubility in Ionic Liquids. *J. Phys. Chem. B* **2007**, *111*, 9001–9009.

(18) Scovazzo, P.; Camper, D.; Kieft, J.; Poshusta, J.; Koval, C.; Noble, R. Regular Solution Theory and CO2 Gas Solubility in ionic Liquids. *Ind. Eng. Chem. Res.* **2004**, *43*, 6855–6860.

(19) Shiflett, M. B.; 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.

(20) Shariati, A.; Gutkowski, K.; Peters, C. J. Comparison of the Phase Behavior of Some Selected Binary Systems with Ionic Liquids. *AIChE J.* **2005**, *51*, 1532–1540.

(21) Scovazzo, P.; Kieft, J.; Finan, D. A.; Koval, C.; Dubois, D.; Noble, R. Gas Separations using Non-hexafluorophosphate [PF_6](-) Anion Supported Ionic Liquid Membranes. *J. Membr. Sci.* **2004**, *238*, 57–63.

(22) Kamps, A.; Tuma, D.; Xia, J.; Maurer, G. Solubility of CO_2 in the Ionic Liquid [bmim][PF_6]. *J. Chem. Eng. Data* **2003**, *48*, 746–749.

(23) Shariati, A.; Peters, C. J. High-Pressure Phase Behavior of Systems with Ionic Liquids: Measurements and Modeling of the Binary System Fluoroform+1-ethyl-3-methylimidazolium hexafluorophosphate. *J. Supercrit. Fluids* **2003**, *25*, 109–117.

(24) Shariati, A.; Peters, C. J. High-pressure phase Behavior of Systems with Ionic Liquids: Part V. The Binary System Carbon Dioxide+1-butyl-3-methylimidazolium tetrafluoroborate. *J. Supercrit. Fluids* **2005**, *34*, 173–176.

(25) Costantini, M.; Toussaint; V. A.; Shariati, A.; Peters, C. J.; Kikic, I. High-Pressure Phase Behavior of Systems with Ionic Liquids: Part IV. Binary System Carbon Dioxide+1-Hexyl-3-methylimidazolium tetrafluoroborate. *J. Chem. Eng. Data* **2005**, *50*, 52–55.

(26) Kroon, M.; Shariati, A.; Costantini, M.; van Spronsen, J.; Witkamp, G.-J.; Sheldon, R. A.; Peters, C. High-Pressure Phase Behavior of Systems with Ionic Liquids: Part V. The binary System Carbon Dioxide+1-Butyl-3-methylimidazolium Tetrafluoroborate. *J. Chem. Eng. Data* **2005**, *50*, 173–176.

(27) Blanchard, L. A.; Gu, Z.; Brennecke, J. F. High-Pressure Phase Behavior of Ionic Liquid/CO_2 Systems. *J. Phys. Chem. B* **2001**, *105*, 2437–2444.

(28) Aki, S. N. V. K.; Mellein, B. R.; Saurer, E. M.; Brennecke, J. F. High-Pressure Phase Behavior of Carbon Dioxide with Imidazolium-Based Ionic Liquids. *J. Phys. Chem. B* **2004**, *108*, 20355–20365.

(29) Kim, Y. S.; Choi, W. Y.; Jang, J. H.; Yoo, K. P.; Lee, C. S. Solubility Measurement and Prediction of Carbon Dioxide in Ionic Liquids. *Fluid Phase Equilib.* **2005**, 439–455.

(30) Schilderman, A. M.; Raeissi, S.; Peters, C. J. Solubility of Carbon Dioxide in the Ionic Liquid 1-Ethyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide. *Fluid Phase Equilib.* **2007**, *260* (1), 19–22.

(31) Lee, B. C.; Outcalt, S. L. Solubilities of Gases in the Ionic Liquid 1-n-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. *J. Chem. Eng. Data* **2006**, *51* (3), 892–897.

(32) Costa Gomes, M. F. 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 and 343 K. *J. Chem. Eng. Data* **2007**, *52*, 472–475.

(33) Shiflett, M. B.; Yokozeki, A. Solubility of CO_2 in Room Temperature Ionic Liquid [hmim][Tf_2N]. *J. Phys. Chem. B* **2007**, *111*, 2070–2074.

(34) Kumelan, J.; Kamps, A. P. S.; Tuma, D.; Maurer, G. Solubility of CO_2 in the Ionic Liquid [hmim][Tf_2N]. *J. Chem. Thermodyn.* **2006**, *38*, 1396–1401.

(35) Florusse, L.; Raeissi, S.; Peters, C. J. High Pressure Phase Behaviour of Ethane with 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. *J. Chem. Eng. Data* **2008**, *53*, 1283–1285.

(36) Raeissi, S.; Peters, C. J. Experimental Determination of High-Pressure Phase Equilibria of the Ternary System Carbon Dioxide plus Limonene plus Linalool. *J. Supercrit. Fluids* **2005**, *35*, 10–17.

(37) Raeissi, S.; Peters, C. J. Bubble Point Pressures of the Binary System Carbon Dioxide + Linalool. *J. Supercrit. Fluids* **2001**, *20*, 221–228.

(38) Shariati, A.; Raeissi, S.; Peters, C. J. CO_2 Solubility in Alkylimidazolium-Based Ionic Liquids. In *Developments and Applications in Solubility*; Letcher, T. M., Ed.; The Royal Society of Chemistry: Cambridge, UK, 2007.

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