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High-Pressure Phase Behavior of Ethane with 1-Hexyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide

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The solubility of ethane gas has been measured in 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide within a temperature and pressure range of (290 to 370) K and (0.4 to 13) MPa. The results have shown high ethane solubility in this ionic liquid, but lower than the corresponding solubilities of carbon dioxide in the same ionic liquid. For example, the solubility of ethane at 313 K and 4 MPa is in the range of 0.3 mol fraction while that of CO_2 is in the range of 0.5 mol fraction. The gas solubilities increase with pressure and decrease with temperature. The pressure−temperature relationship is seen to be linear for any particular isopleth. However, the pressure−composition solubility isotherms show a highly curved behavior in which the solubility increases considerably with pressure up to a certain ethane concentration, above which further pressure increase has little effect on the ethane solubility.

Introduction

As ionic liquids (ILs) are gaining ground in various applications as green solvents, the thorough understanding of their fundamental thermodynamic properties is becoming essential. For example, a clear understanding of gas solubilities in ILs is important since many of the reactions studied in ILs, such as hydrogenations, hydroformylations, and oxidations, involve the reaction of gases in the IL solutions.[1–3] If the gas has a low solubility in the IL, the mass transfer of the gas into the IL phase will likely be the rate-limiting factor. These limitations could affect the ability of ILs to realistically compete with conventional solvents and may require that efforts be made to increase the interfacial area and/or to use high-pressure operations to reach the necessary concentrations of gas in the IL.[4] In addition to its importance in reactions, understanding gas solubilities in ILs is required for assessing the feasibility of using ILs to separate gas mixtures, either as conventional absorbers or as supported-liquid membrane systems.[5–12] This would provide a particular advantage over conventional organic solvents because the insignificant vapor pressures of ILs will minimize contamination of the gas stream by the IL and increase the supported liquid-membrane life. Understanding the solubility of compressed gases and supercritical fluids in ILs is also required for assessing the feasibility of separating species from an IL mixture. It has been shown that supercritical carbon dioxide can successfully be used to extract a wide variety of solutes from an IL without any contamination to the CO_2 phase by the IL.[13,14] Theoretically, other compressed gases, such as ethene and ethane, could also be used in IL extraction systems and will therefore require an understanding of their phase behavior with ILs.[4] Finally, an investigation of gas solubilities in ILs can be used to extract information about specific chemical and molecular interactions between the gas and the IL, such as hydrogen bonding and dipole–dipole, dipole–induced dipole, and dispersion forces. These simple probes can provide valuable information on the underlying solvent behavior of ILs.[4]

The above-mentioned necessities have prompted investigations in this field by various research groups resulting in the gradual growth of the ionic liquid–gas soulibility databank. One of the ionic liquid families which is the subject of investigation for various industrial applications due to its particular properties such as high thermal stability, relatively low viscosity, water stability, and very high solvation capacity for gases such as CO_2, SO_2, and N_2O is 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. For example, Aki et al.,[15] Anthony et al.,[16] Kim et al.,[17] Kumelan et al.,[18] Schilderman et al.,[19] Raeissi and Peters,[12,20] Lee and Outcalt,[21] Shiflett and Yokozeki,[22] and Costa Gomes[23] have investigated the solubilities in this ionic liquid family of various gases such as CO_2, O_2, H_2, N_2O, CH_4, C_2H_6, C_3H_6, C_4H_{10}, C_2H_4, and C_3H_6. Among the systems of interest is the binary system of ethane + 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([hmim][Tf_2N]). The only solubility information available on this system is the recent study of Costa Gomes.[23] She used an isochoric saturation technique to obtain Henry's law constants at various temperatures. But her experimental investigation was limited to only low pressures close to atmospheric. In the present study, we have obtained solubility data of ethane in [hmim][Tf_2N] at various temperatures up to pressures as high as 13 MPa.

Experimental

Experiments are carried out in a Cailletet apparatus, which allows the measurement of phase equilibrium according to the synthetic method within temperatures and pressures up to 450 K and 15 MPa, respectively. At any desired temperature, the pressure is increased for a sample of constant overall composi-

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Table 1. Experimentally Measured Mole Fraction x (Bubble-Point Curves) for Ethane in [hmim][Tf_2N]

x	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa
0.0501	298.17	0.388	308.19	0.443	318.15	0.493
	323.14	0.528	328.25	0.558	330.71	0.568
	338.19	0.618	348.21	0.683	358.20	0.748
	368.23	0.818				
0.0995	293.37	0.738	303.33	0.853	313.39	0.973
	323.36	1.093	330.87	1.193	333.39	1.223
	338.37	1.288	348.34	1.423	358.40	1.558
	368.39	1.708				
0.2005	293.17	1.648	300.65	1.853	308.22	2.078
	315.63	2.303	315.73	2.303	323.21	2.513
	323.22	2.513	330.76	2.748	338.23	2.998
	345.70	3.238	345.73	3.228	353.17	3.478
	353.21	3.478	360.69	3.718	360.70	3.708
	368.27	3.963				
0.2662	293.19	2.253	300.68	2.553	308.14	2.853
	315.65	3.213	323.19	3.573	323.20	3.573
	330.65	3.933	338.20	4.313	345.72	4.693
	353.18	5.093	360.68	5.453	368.26	5.833
0.3306	293.33	3.031	300.81	3.496	308.40	3.991
	315.88	4.501	323.38	5.066	330.90	5.631
	338.37	6.210	345.89	6.810	353.30	7.415
	360.83	8.015	368.40	8.611		
0.3678	293.37	3.562	300.81	4.172	308.39	4.853
	315.81	5.608	323.37	6.412	330.90	7.243
	338.36	8.083	345.85	8.893	353.39	9.683
	360.85	10.433				
0.4016	293.30	7.000	300.83	7.755	308.38	8.506
	315.92	9.236	323.41	9.981	330.88	10.736
	338.31	11.491	338.31	11.501	345.93	12.280
	353.32	13.066	353.36	13.070		

tion until the dissolution of the last bubble of gas in the ionic liquid is observed visually. Details of the experimental apparatus and procedure are given elsewhere.[20,24] Ethane was purchased from Messer-Griesheim with a volume fraction purity of 0.9995. As part of IUPAC project 2002-005-1-100, the [hmim][Tf_2N] ionic liquid sample was synthesized by the group of Prof. J. F. Brennecke at the University of Notre Dame, Indiana, and dried at the National Institute of Standards and Technology in Boulder. The minimum stated mole fraction purity was 0.995 as found by ^1H and ^{19}F NMR spectroscopy. The sample was further dried under vacuum for two days. The accuracies of the measurements were within 0.02 K for temperature, 0.003 MPa for pressure, and 0.001 for molar fraction.

Results

The experimentally measured solubility curves in the form of bubble points are presented in Table 1 for seven different mixtures of constant overall composition for the binary system C_2H_6 and [hmim][Tf_2N]. The data are also shown graphically in Figure 1 as isopleths. The solubility of ethane increases with increasing pressure and decreasing temperature. The pressure−temperature relationship is shown to be more or less linear (Figure 1) within the range of experimental data measured in this work. This figure also shows that temperature effects are much higher at higher molar concentrations of ethane. This means that when already large amounts of ethane are dissolved in [hmim][Tf_2N] it is possible to notably decrease the necessary solution pressure by decreasing the temperature. This is not the case when only small amounts of ethane have been dissolved.

Table 2 and Figure 2 present the data interpolated into isotherms as functions of pressure and composition. The results indicate the high solubility of ethane in the selected ionic liquid; for example, mole fractions of ethane up to about 0.30 can be dissolved in [hmim][Tf_2N] at 298 K and 3 MPa. This mole fraction can be increased up to about 0.4 by increasing the pressure up to 6 MPa at the same temperature. Such high gas solubilities enable process applications such as, for example, homogeneous reactions involving ethane with the ionic liquid acting as a solvent. Although the observed ethane solubilities are quite high, they are still not as large as the well-known solubilities of carbon dioxide.[15] This is shown, for example, at 313 K, in Figure 3. Figures 2 and 3 also illustrate the particular shape of the solubility curve, increasing gently in pressure with

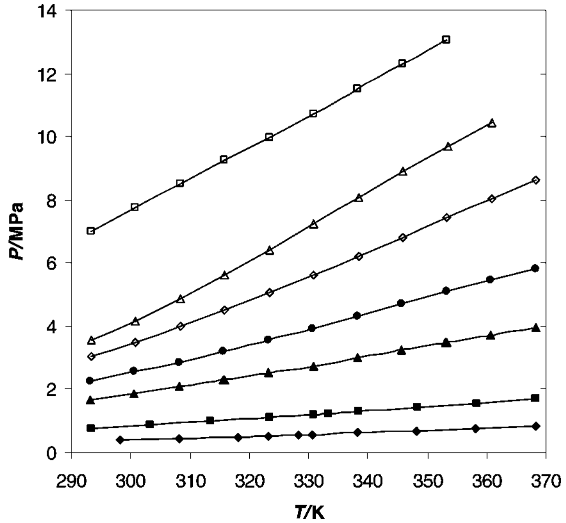

Figure 1. Experimentally measured pressure−temperature points (bubble points) of C_2H_6 in [hmim][Tf_2N] with the following varying mole fractions of C_2H_6: ◆, $x = 0.0501$; ■, $x = 0.0995$; ▲, $x = 0.2005$; ●, $x = 0.2662$; ◇, $x = 0.3306$; △, $x = 0.3678$; □, $x = 0.4016$.

Table 2. Interpolated Isothermal Mole Fraction x for Ethane in [hmim][Tf_2N]

x	T = 298.15 K	T = 313.15 K	T = 333.15 K	T = 353.15 K
mole fraction C_2H_6	P/MPa	P/MPa	P/MPa	P/MPa
0.0501	0.388	0.469	0.586	0.714
0.0995	0.793	0.969	1.22	1.489
0.2005	1.786	2.219	2.832	3.472
0.2662	2.445	3.092	4.061	5.079
0.3306	3.323	4.316	5.806	7.396
0.3678	3.936	5.333	7.496	9.662
0.4016	7.486	8.969	10.965	13.048

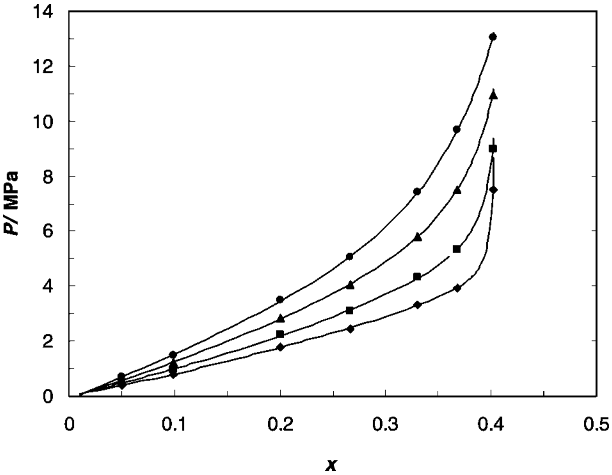

Figure 2. Mole fraction of ethane, x, as a function of pressure in [hmim][Tf_2N] at the following temperatures: ◆, T = 298.15 K; ■, T = 313.15 K; ▲, T = 333.15 K; ●, T = 353.15 K.

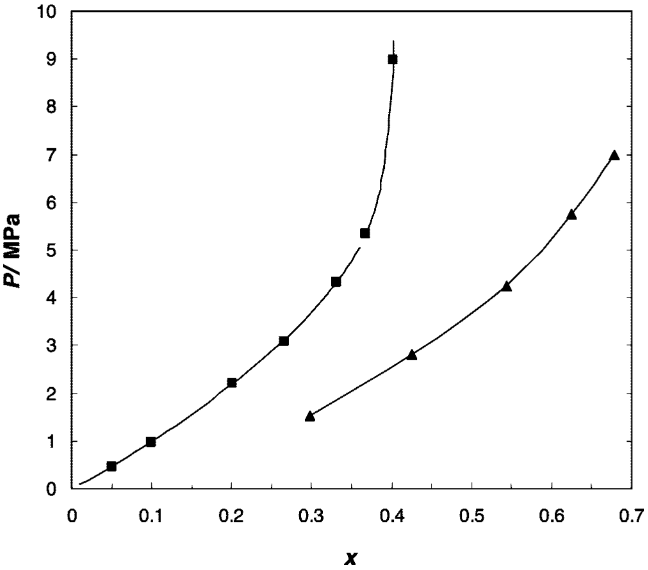

Figure 3. Comparison of mole fraction, x, of C_2H_6 to that of CO_2 in [hmim][Tf_2N] at 313 K. ■, C_2H_6; ▲, CO_2. The solubility curve of ethane is from this work, and that of CO_2 is taken from Aki et al.[15]

Table 3. Henry's Law Constants for C_2H_6 in [hmim][Tf_2N]

T/K	H/MPa
298.15	7.9243
313.15	9.6624
333.15	12.1471
353.15	14.8206

ethane concentration up to a certain concentration, above which increases in pressure have little effect on increasing solubility. This "double-sloped" behavior had previously been observed for some carbon dioxide + ionic liquid systems (for example, refs 15, 25, and 26).

Table 3 presents the calculated Henry's law constants for solutions of ethane dissolved in [hmim][Tf_2N]. In this system, Henry's law is applicable up to ethane mole fractions of about 0.1. The results presented for four different temperatures show that the Henry's law constant increases with temperature.

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Literature Cited

(1) Welton, T. Review: Ionic Liquids in Catalysis. *Chem. Rev.* **1999**, *99*, 2071–2083.
(2) Wasserscheid, P.; Keim, W. Ionic liquids - New "Solutions" for Transition Metal Catalysis. *Angew. Chem., Int. Ed.* **2000**, *39*, 3773–3789.
(3) Joglekar, H. G.; Rahman, I.; Kulkarni, B. D. The Path Ahead for Ionic Liquids. *Chem. Eng. Technol.* **2007**, *30*, 819–828.
(4) 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.
(5) Brennecke, J. F.; Maginn, E. J. Ionic Liquids: Innovative Fluids for Chemical Processing. *AIChE J.* **2001**, *47*, 2384–2389.
(6) Scovazzo, P.; Camper, D.; Kieft, J.; Poshusta, J.; Koval, C.; Noble, R. Regular Solution Theory and CO_2 Gas Solubility in Ionic Liquids. *Ind. Eng. Chem. Res.* **2004**, *43*, 6855–6860.
(7) 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.
(8) Anderson, J. L.; Dixon, J. K.; Maginn, E. J.; Brennecke, J. F. Measurement of SO_2 Solubility in Ionic Liquids. *J. Phys. Chem. B* **2006**, *110*, 15059–15062.
(9) Jiang, Y. Y.; Zhou, Z.; Jiao, Z.; Li, L.; Wu, Y. T.; Zhang, Z. B. SO_2 Gas Separation Using Supported Ionic Liquid Membranes. *J. Phys. Chem. B* **2007**, *111*, 5058–5061.
(10) Gan, Q.; Rooney, D.; Xue, M.; Thompson, G.; Zou, Y. An Experimental Study of Gas Transport and Separation Properties of Ionic Liquids Supported on Nanofilteration Membranes. *J. Membr. Sci.* **2006**, *280*, 948–956.
(11) Yokozeki, A.; Shiflett, M. B. Hydrogen Purification Using Room-Temperature Ionic Liquids. *Appl. Energy* **2007**, *84*, 351–361.
(12) Raeissi, S.; Peters, C. J. A Potential Ionic Liquid for CO_2-Separating Gas Membranes: Selection and Gas Solubility Studies, manuscript in preparation.
(13) Blanchard, L. A.; Hancu, D.; Beckman, E. J.; Brennecke, J. F. Green Processing Using Ionic Liquids and CO_2. *Nature* **1999**, *399*, 28–29.
(14) Blanchard, L. A.; Brennecke, J. F. Recovery of Organic Products from Ionic Liquids Using Supercritical Carbon Dioxide. *Ind. Eng. Chem. Res.* **2001**, *40*, 2550–2550.
(15) 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.
(16) Anthony, J. L.; Anderson, J. L.; Maginn, E. J.; Brennecke, J. F. Anion Effects on Gas Solubilities in Ionic Liquids. *J. Phys. Chem. B* **2005**, *109*, 6366–6374.
(17) 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**, *228–229*, 439–445.
(18) 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.
(19) 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*, 19–22.
(20) Raeissi, S.; Peters, C. J. Carbon Dioxide Solubility in the Homologous 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide Family, manuscript in preparation.
(21) 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*, 892–897.
(22) 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.
(23) 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.
(24) Raeissi, S.; Peters, C. J. Bubble-Point Pressures of the Binary System Carbon Dioxide Plus Linalool. *J. Supercrit. Fluid* **2001**, *20*, 221–228.
(25) Shariati, A.; Peters, C. J. High-Pressure Behavior of Systems with Ionic Liquids: II. The Binary System Carbon Dioxide + 1-ethyl-3-methylimidazolium hexafluorophosphate. *J. Supercrit. Fluids* **2004**, *29*, 43–48.
(26) Shariati, A.; Raeissi, S.; Peters, C. J. In *Developments and Applications in Solubility*; Letcher, T. M., Ed.; The Royal Society of Chemistry: Cambridge, U.K., 2007; pp 131–152.

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