JOURNAL OF CHEMICAL & ENGINEERING DATA

ARTICLE

pubs.acs.org/jced

Hydrogen Solubilities in the IUPAC Ionic Liquid 1-Hexyl-3-methylimidazolium Bis(Trifluoromethylsulfonyl)Imide

S. Raeissi,*[,†] L. J. Florusse,[‡] and C. J. Peters[§,∥]

[†]School of Chemical and Petroleum Engineering, Shiraz University, Shiraz 71345, Iran

[‡]Department of Chemical Technology, Faculty of Science and Technology, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

[§]Laboratory of Process Equipment, Department of Process and Energy, Faculty of Mechanical, Maritime, and Materials Engineering, Delft University of Technology, Leeghwaterstraat 44, 2628 CA Delft, The Netherlands

[∥]Chemical Engineering Department, The Petroleum Institute, P.O. Box 2533, Abu Dhabi, United Arab Emirates

ABSTRACT: Because of some disagreements among published data on the solubilities of gases in ionic liquids, an IUPAC project to establish recommended values for some properties and suggest suitable measurement methods was initiated. As part of this large project, this study focused on the solubility of hydrogen gas in the ionic liquid 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. High-pressure gas solubilities were measured at various temperatures up to 370 K and pressures up to 12 MPa. The results showed very good agreement between the data measured in this laboratory and those of two other laboratories where the hydrogen solubilities in the same IUPAC sample were measured using differing experimental setups.

1. INTRODUCTION

There is an ongoing discussion about the quality of some of the data available in the open literature.[1] Among the many reasons for differences in recently published experimental data, the question of purity and stability of the investigated samples of ionic liquids are the most serious.[1] This problem prompted the establishment of an IUPAC task group aimed at organizing a systematic study of the thermodynamic and thermophysical properties of typical ionic liquids.[1−9] This study is part of IUPAC Project 2002-005-1-100 (Thermodynamics of Ionic Liquids, Ionic Liquid Mixtures, and the Development of Standardized Systems).[9] The task was to determine the solubility of hydrogen in the ionic liquid 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, commonly abbreviated as [hmim][Tf_2N]. The molecular structure of this ionic liquid is presented in Figure 1.

Ionic liquids containing the bis(trifluoromethylsulfonyl)imide anion were reported first by Koch et al.[10] and shortly after by Bonhôte et al.[11] Since then, this family of ionic liquids has proven particularly popular for a range of applications because of its particular properties.[12] Ionic liquids with the bis(trifluoromethylsulfonyl)imide anion have been shown to have substantially lower melting points and higher fluidities than those containing almost any other ionic-liquid anion.[12] In addition, they are generally hydrophobic and are characteristically extremely stable, both thermally and electrochemically, making them attractive for a range of applications such as high-temperature reactions[12] and gas separations.[13]

2. EXPERIMENTAL SECTION

Binary phase behavior experiments were carried out using a piece of equipment called the Cailletet apparatus. This apparatus has been explained in detail elsewhere.[14,15] Therefore, only a brief overview will be given here. This device allows the measurement of phase equilibrium according to the synthetic method at 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 composition until the dissolution of the last bubble of gas in the ionic liquid is observed visually.

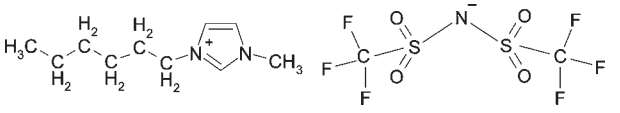

Figure 1. Molecular structure of 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide.

The IUPAC sample ionic liquid [hmim][Tf_2N] was provided by the group of Prof. J. F. Brennecke at the University of Notre Dame (Notre Dame, Indiana) and dried at the National Institute of Standards and Technology (Boulder, CO). The synthesis of this ionic liquid and the purification procedure have been described previously.[8] This sample had a water mass fraction on the order of 1×10^{-5} and a minimum purity of 0.995 in mole fraction, as indicated by ^{1}H and ^{19}F NMR spectroscopy. Within our own lab, the sample was further dried with molecular sieves under vacuum for 2 days. Hydrogen was purchased from Fluka with a purity of 99.9990 %.

The uncertainties in the measurements were within 0.03 % of the reading for pressure, 0.02 K for temperature, and 0.001 for mole fraction.

Special Issue: John M. Prausnitz Festschrift

Received: October 20, 2010
Accepted: January 10, 2011
Published: February 23, 2011

Table 1. Experimentally Measured Solubility Data (Bubble-Point Curves) for Hydrogen (1) in [hmim][Tf_2N] (2)

x_1	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa
0.0328	300.67	6.119	308.21	5.899	315.67	5.699
	323.15	5.509	323.22	5.509	330.65	5.338
	330.70	5.339	338.20	5.098	338.20	5.169
	338.21	5.119	345.69	5.009	345.74	4.999
	353.23	4.839	353.25	4.868	360.77	4.748
	368.23	4.579	368.26	4.598		
0.0427	300.88	8.053	308.36	7.783	315.90	7.493
	323.31	7.289	323.37	7.168	323.43	7.163
	330.85	6.928	330.87	7.044	338.40	6.713
	338.41	6.803	345.85	6.463	345.87	6.503
	345.88	6.583	353.38	6.303	353.40	6.373
	360.89	6.103	360.90	6.173	368.36	5.923
	368.41	5.993				
0.0521	300.75	9.873	308.35	9.483	315.94	9.143
	323.34	8.853	323.37	8.969	330.90	8.664
	338.30	8.403	338.37	8.293	345.90	8.163
	353.35	7.913	353.38	7.803	360.88	7.663
	368.39	7.443				
0.0612	300.74	11.853	308.22	11.373	315.73	10.993
	323.19	10.473	323.21	10.782	323.21	10.592
	330.67	10.422	330.71	10.133	338.19	10.072
	338.22	9.793	345.73	9.513	345.73	9.724
	353.17	9.233	353.22	9.414	360.73	8.943
	360.75	9.144	368.25	8.703	368.27	8.904

Table 2. Interpolated Isothermal Solubilities for Hydrogen (1) in [hmim][Tf_2N] (2)

	P/MPa			
T/K	x_1 = 0.0328	x_1 = 0.0427	x_1 = 0.0521	x_1 = 0.0612
293.15	6.354	8.392	10.228	12.303
313.15	5.764	7.583	9.301	11.133
333.15	5.265	6.904	8.542	10.152
353.15	4.853	6.334	7.892	9.330

3. RESULTS

Table 1 presents hydrogen solubilities in the form of bubble-point pressures required to dissolve hydrogen at four different concentrations. The above-mentioned data were also converted by interpolation, the results of which are presented in Table 2 in the form of isothermal solubility data. The data in Tables 1 and 2 are presented visually in Figures 2 and 3, respectively.

Figure 2 indicates that the hydrogen solubility increases with increasing temperature. This is in contrast to the usual trend of decreasing solubility with increasing temperature found for most other gases, but it seems to be a normal behavior in the case of hydrogen gas in some ionic liquids. The same trend has been observed for dissolution of hydrogen in 1-butyl-3-methylimidazolium hexafluorophosphate[16] and 1-butyl-3-methylimidazolium methyl sulfate[17] as well as in 1-butyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide.[18] As can be seen in Figure 2, the data for this system were not fully reproducible as time progressed for each sample. We suspect that reaction(s) may occur over time within the equilibrium cell containing hydrogen, [hmim][Tf_2N], and mercury.

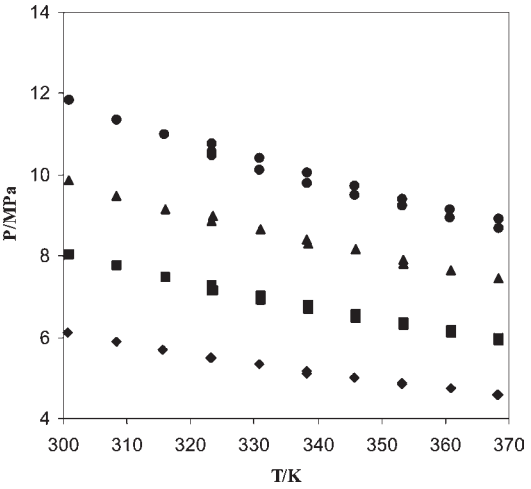

Figure 2. Experimentally measured bubble-point data for the binary system H_2 + [hmim][Tf_2N] at four different compositions with the following H_2 mole fraactions: ◆, 0.0328; ■, 0.0427; ▲, 0.0521; ●, 0.0612.

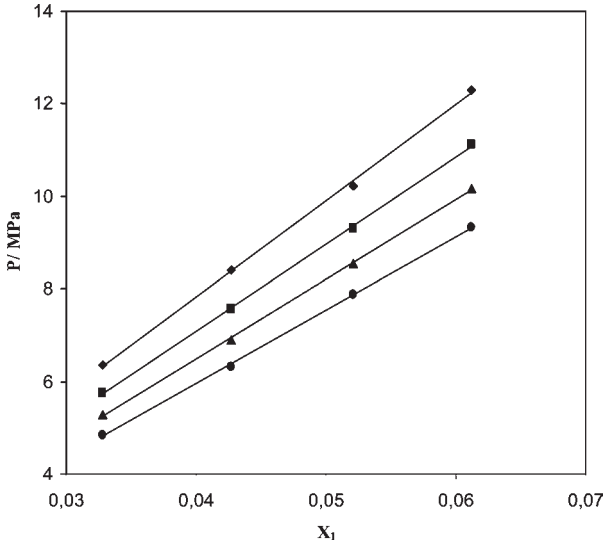

Figure 3. Molar solubilities of H_2 in [hmim][Tf_2N] at the following temperatures: ◆, 293.15 K; ■, 313.15 K; ▲, 333.15 K; ●, 353.15 K.

Table 3. Values of Henry's Constant (H) for Hydrogen Solubility in [hmim][Tf_2N] at Various Temperatures

T/K	H/MPa
293.15	198.1376
313.15	179.5456
333.15	164.0452
353.15	150.9919

Figure 3 indicates that the solubility of hydrogen in [hmim][Tf_2N] is limited to very small amounts. For example, pressures higher than 12 MPa are required to obtain a H_2 mole fraction of 0.06 in [hmim][Tf_2N] at 293 K. Figure 3 also indicates that at a fixed temperature, the hydrogen solubility increases more or less linearly with pressure. Values of Henry's constant were also determined at several different temperatures for this binary system;

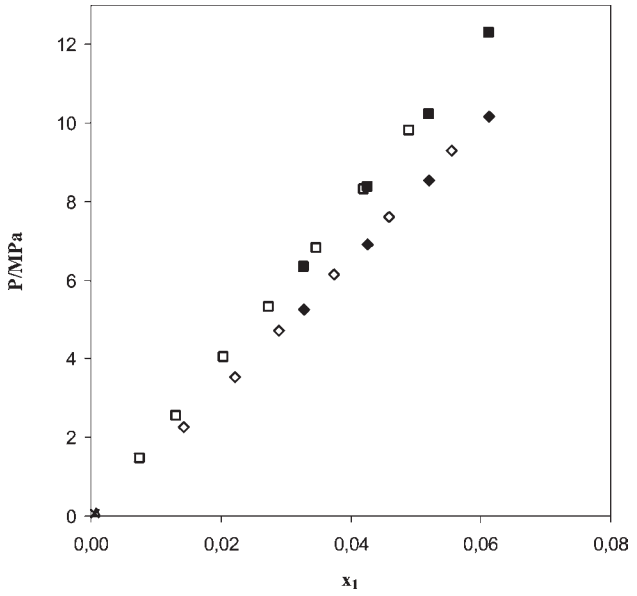

Figure 4. Comparison of hydrogen solubilities in [hmim][Tf_2N] with literature data: □, Kumelan et al.[3] at 293.2 K; ■, this work at 293.15 K; △, Costa Gomes[6] at 293.56 K; ◇, Kumelan et al.[3] at 333.2 K; ◆, this work at 333.15 K; ×, Costa Gomes[6] at 333.17 K.

these values, which are applicable to hydrogen mole fractions up to 0.06, are presented in Table 3.

Figure 4 compares the data from this work with the data for the same binary system measured by two other laboratories of the IUPAC task force, one at only low pressure[6] and the other up to high pressures.[3] Both of these laboratories used the same ionic liquid sample (provided by the University of Notre Dame) as was used in this work. The match between the three sets of data is very good.

AUTHOR INFORMATION

Corresponding Author

*Tel: +98-711-2303071. E-mail: raeissi@shirazu.ac.ir.

ACKNOWLEDGMENT

Thanks are due to Dr. M. J. Muldoon of the University of Notre Dame and Dr. A. Widegren of NIST for synthesizing and analyzing the ionic liquid sample. S.R. also thanks Shiraz University and Delft University of Technology for facilitating this joint research.

REFERENCES

(1) 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.

(2) Kumelan, J.; Kamps, A. P. S.; Tuma, D.; Maurer, G. Solubility of the Single Gases Methane and Xenon in the Ionic Liquid [hmim][Tf_2N]. *Ind. Eng. Chem. Res.* **2007**, *46*, 8236–8240.

(3) Kumelan, J.; Kamps, A. P. S.; Tuma, D.; Maurer, G. Solubility of H_2 in the Ionic Liquid [hmim][Tf_2N]. *J. Chem. Eng. Data* **2006**, *51*, 1364–1367.

(4) 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.

(5) 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.

(6) 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 K and 343 K. *J. Chem. Eng. Data* **2007**, *52*, 472–475.

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

(8) Widegren, J. A.; Magee, J. W. Density, Viscosity, Speed of Sound, and Electrolytic Conductivity for the Ionic Liquid 1-Hexyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide and Its Mixtures with Water. *J. Chem. Eng. Data* **2007**, *52*, 2331–2338.

(9) See: http://www.iactweb.org/ (accessed Jan 10, 2011).

(10) Koch, V. R.; Nanjundiah, C.; Battista Appetecchi, G.; Scrosati, B. The Interfacial Stability of Li with 2 New Solvent-free Ionic Liquids: 1,2-Dimethyl-3-propylimidazolium Imide and Methide. *J. Electrochem. Soc.* **1995**, *142*, L116–L118.

(11) Bonhôte, P.; Dias, A.; Papageorgiou, N.; Kalyanasundaram, K.; Grätzel, M. Hydrophobic, Highly Conductive Ambient-Temperature Molten Salts. *Inorg. Chem.* **1996**, *35*, 1168–1178.

(12) Pringle, J. M.; Golding, J.; Baranyai, K.; Forsyth, C. M.; Deacon, G. B.; Scott, J. L.; MacFarlane, D. R. The Effect of Anion Fluorination in Ionic Liquids: Physical Properties of a Range of Bis(methanesulfonyl)-amide Salts. *New J. Chem.* **2003**, *27*, 1504–1510.

(13) Raeissi, S.; Peters, C. J. A potential ionic liquid for CO_2-separating gas membranes: Selection and gas solubility studies. *Green Chem.* **2009**, *11*, 185–192.

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

(15) Raeissi, S.; Peters, C. J. Carbon Dioxide Solubility in the Homologous 1-Alkyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide Family. *J. Chem. Eng. Data* **2009**, *54*, 382–386.

(16) Kumelan, J.; Kamps, A. P. S.; Tuma, D.; Maurer, G. Solubility of H_2 in the Ionic Liquid [bmim][PF_6]. *J. Chem. Eng. Data* **2006**, *51*, 11–14.

(17) Kumelan, J.; Kamps, A. P. S.; Tuma, D.; Maurer, G. Solubility of Single Gases H_2 and CO_2 in the Ionic Liquid [bmim][CH_3SO_4]. *Fluid Phase Equilib.* **2007**, *260*, 3–8.

(18) Raeissi, S.; Peters, C. J. Unpublished data.