Effect of dissolved CO_2 on the conductivity of the ionic liquid [bmim][PF_6]

Jianmin Zhang,[a] Chunhe Yang,[a] Zhenshan Hou,[a] Buxing Han,*[a] Tao Jiang,[a] Xiaohong Li,[a] Guoying Zhao,[a] Yongfang Li,*[a] Zhimin Liu,[a] Dongbin Zhao[b] and Yuan Kou*[b]

[a] *Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China. E-mail: Hanbx@infoc3.icas.ac.cn; Fax: 86-10-62559373; Tel: 86-10-62562821*
[b] *Department of Chemistry, Peking University, Beijing 100871, China*

Received* (*in Montpellier, France*) *4th July 2002, Accepted 2nd October 2002
First published as an Advance Article on the web 17th December 2002

This work conducts the first study on the effect of compressed CO_2 on the electric conductivity of ionic liquids (ILs), and the CO_2/1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) system is investigated at 40.0 °C and 50.0 °C, and at pressures up to 130 bar. It is found that the conductivity increases with increasing pressure of CO_2 in the pressure range studied, although CO_2 is a non-polar compound.

Introduction

Ionic liquids (ILs) are organic salts which are liquids at room temperature. They are good solvents for a broad range of polar and non-polar organic compounds. Typical ILs have a stable liquid range of over 300 K, very low vapor pressure at room temperature, wide electrochemical windows, and excellent thermal and chemical stability. The solvent properties of ILs can be tailored to meet the requirements of specific applications by variation of the length and branching of the alkane chains of the cationic core and the anionic precursors. These unique properties have suggested their use as environmentally benign solvents that can replace volatile organic compounds as solvents in different processes, such as in chemical reactions and separation and fractionation.[1–5]

Supercritical (SC) CO_2 has emerged as a promising environmentally benign alternative for the toxic organic solvents since it is inexpensive, nontoxic, nonflammable, readily available in large quantities, and has moderate critical temperature and pressure (31.1 °C and 73.8 bar). Moreover, it can be easily recaptured and recycled after use. In recent years, increasing numbers of scientists have begun to study supercritical science and technology related to CO_2.[6–17] Some have been attracted by the possibility to use it as an environmentally benign solvent or reactant, while others have been driven by inherent scientific interest.

Both SC CO_2 and ILs are environmentally benign solvents, and each of them has their own unique properties. Combination of the advantages of the two classes of solvents is a new and interesting topic. Recently, some research has been done on systems containing both ILs and SC CO_2, such as determining the solubility of CO_2 in ILs,[18,19] studying the effect of anionic species of ionic liquids on the molecular state of the dissolved CO_2,[20] carrying out chemical reactions in CO_2–IL systems,[21,22] and extracting solutes or products from ILs using CO_2.[18,21–24]

Reduction of CO_2 is a very important area.[25–27] CO_2 is soluble in some ILs and the solubility increases with increasing pressure.[18,19] Recently, ILs have been used as reaction media for electrocatalytic cycloaddition of CO_2 to epoxides at ambient pressure.[28] Reducing CO_2 electrochemically at higher pressures using ILs as electrolytes may be conducted at greater current densities because the concentration of CO_2 in ILs is larger at higher pressures,[18,19] and practical processes need large current densities.

In this paper, we study the conductivity of the CO_2/[bmim][PF_6] system at different temperatures and pressures. To our knowledge, this is the first work to study the effect of a dissolved gas or supercritical fluid in an IL on the conductivity of ILs, although the conductivities of different ILs[29–36] in the absence of gases and the conductivities of some supercritical fluids with small amount of salts have been determined.[37,38]

Results and discussion

Reliability of the apparatus

In order to verify the reliability of the apparatus, we first determined the conductivities of the KCl aqueous solution and the CO_2-free IL, and compared these with literature values. The conductivity of 0.1 M KCl aqueous solution determined in this work at 25.0 °C is 0.0127 S cm^{-1}, which agrees well with the literature value of 0.0128 S cm^{-1}.[39] The conductivity values of CO_2-free [bmim][PF_6] determined in this work at 25.0 °C, 40.0 °C, 50.0 °C agree with the data reported by Suarez *et al.*,[33] as is shown in Table 1. This confirms the reliability of the apparatus used in this work. The repeatability of our experiments is better than ±3%, and it is estimated that the accuracy of the data is better than ±5%.

Effect of CO_2 pressure on the conductivity

The conductivity data of the CO_2-saturated [bmim][PF_6] determined at 40.0 °C and 50.0 °C and different pressures of CO_2 are illustrated in Fig. 1 and Table 2.

Table 1 Conductivity data ($\times 10^3$) of CO_2-free [bmim][PF_6] (S cm^{-1})

	25.0 °C	40.0 °C	50.0 °C
This work	1.46 ± 0.07	2.97 ± 0.15	4.70 ± 0.25
Ref. 33	1.58 ± 0.16	3.01 ± 0.30	4.58 ± 0.46

DOI: 10.1039/b206526f

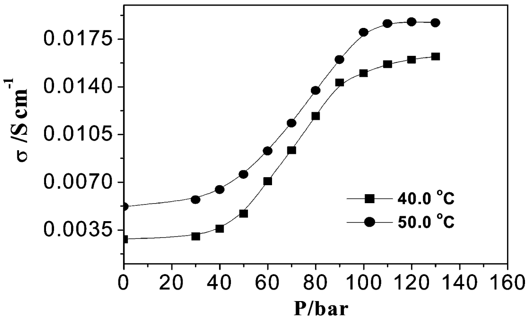

Fig. 1 The conductivity of CO_2-saturated [bmim][PF_6] at different pressures and temperatures.

It is very interesting that the conductivity of the IL increases with increasing pressure in the pressure range studied. The effects of the dissolved CO_2 on the IL are very complex, and are discussed in the following.

The conductivity σ is related to the ion mobility and the number of charge carriers, as can be expressed by the following equation[40]

$$\sigma = \sum n_i \mu_i q_i \tag{1}$$

where n_i is the number of charge carriers of species i, q_i the charge, and μ_i the mobility. Therefore, the conductivity of the IL depends mainly on the viscosity of the IL and the number of charge carriers.

The dissolved CO_2 affects the conductivity of the IL in different ways. First, dissolution of CO_2 in the IL can reduce the viscosity of the IL,[41] which is favorable for increasing the conductivity because the mobility of the species becomes greater. Second, an IR spectroscopy study[20] has recently shown that CO_2 forms weak Lewis acid–base complexes with the anions in [bmim][PF_6]. Formation of the complexes may reduce the degree of association between the ions or increase the number of charge carriers, which is also favorable for increasing the conductivity. Finally, IL is expanded by the dissolved CO_2, and the number of charge carriers per unit volume is reduced, which is not favorable for increasing the conductivity. The significance of all these factors depends on the concentration of CO_2. In this work, we determined the volume expansion coefficient (VE), which is defined by the following equation

$$\mathrm{VE} = (V - V_o)/V_o \tag{2}$$

where V_o and V are the volumes of the CO_2-free IL and CO_2-saturated IL, respectively. The VE of the IL at different temperatures and pressures determined in this work is shown in Fig. 2, which shows that the VE increases with increasing pressure. It is estimated that the accuracy of the volume expansion measurement is better than ±4%. Obviously, VE is closely related to the concentration of CO_2 in the IL. In fact, the shape of the VE *vs.* pressure curves is similar to that of the solubility of CO_2 in the IL *vs.* pressure curves.[19]

Table 2 Conductivity data ($\times 10^3$) of CO_2-saturated [bmim][PF_6] (S cm^{-1}) at different pressures

40.0 °C		50.0 °C	
P/bar	σ	*P*/bar	σ
0	2.97	0.0	4.70
30.0	3.01	30.1	5.71
40.3	3.59	39.8	6.46
50.1	4.69	49.9	7.57
60.0	7.06	60.1	9.29
69.8	9.33	70.4	11.3
80.2	11.9	80.1	13.7
90.7	14.3	89.0	16.0
99.5	15.0	100.0	18.0
110.2	15.6	110.0	18.6
120.1	16.0	120.4	18.8
130.4	16.2	129.9	18.7

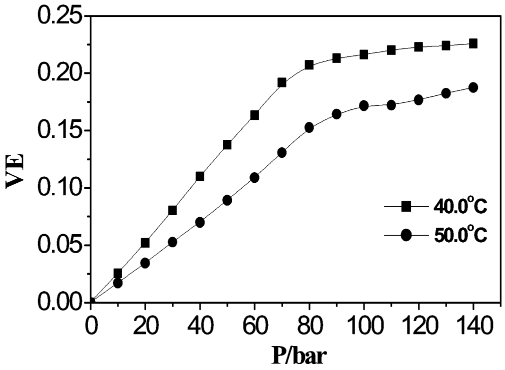

Fig. 2 Dependence of volume expansion coefficient (VE) of [bmim][PF_6] on pressure of CO_2.

The increase of the conductivity with increasing pressure suggests that the first two factors discussed above are dominant. In the high pressure region, the conductivity is not sensitive to pressure mainly because the VE or the concentration of CO_2 in the IL changes slowly with pressure, as can be deduced from Fig. 2.

It is interesting that the effect of pressure on the conductivity is very limited in the low pressure region, although pressure has a pronounced effect on the viscosity[41] and VE. It means that the effect of the first two factors discussed above is nearly compensated by that of the third one. Hussey and coworkers[36] investigated the effects of benzene, acetonitrile, and dichloromethane on the viscosity and conductivity of $AlCl_3$ + 1-methyl-3-ethylimidazolium chloride at 25 °C, and the concentration of the cosolvents was up to 40 wt%. The conductivity *vs.* cosolvent concentration curves of the systems have a similar trend, *i.e.*, the conductivity increases with cosolvent concentration, but slowly in the low cosolvent concentration region.

Effect of temperature

Fig. 2 also illustrates that the conductivity of IL is larger at higher temperature over the entire pressure range. This is easy to understand because the mobility of the charged species should be larger, and more ion pairs are disassociated at the higher temperature.

In conclusion, dissolution of compressed CO_2 in [bmim][PF_6] can increase the conductivity of the IL significantly. From the conductivity aspect, the IL can be used as an electrolyte to reduce compressed CO_2, which is a cleaner process.

Experimental

CO_2 (99.995% purity) was supplied by Beijing Analytical Instrument factory. [bmim][PF_6] was synthesized using the procedures reported by other authors.[42] Residual chloride in the IL prepared was 0.002 mol L^{-1}, which was determined by the method reported by Seddon *et al.*[43] and a chloride-selective electrode produced by Jiangsu Analytical Instrument Factory (China, Model 301) was used. In the experiment, the calibration curve was obtained from aqueous solutions of 1-butyl-3-methylimidazolium chloride.

The IL was dried at 50 °C under vacuum prior to use. Our experiments showed that the weight of IL was constant after a drying time of about 30 h, indicating removal of most of the water. However, we dried the sample for at least 3 days. The amount of water in the IL after drying was 0.1 wt%, which was determined by Karl Fischer analysis. The IL can absorb water from the atmosphere if it is exposed to the air. In order to minimize the absorption of water, IL was charged into the high-pressure stainless steel vessel (Fig. 3b) immediately after drying, and the vessel was sealed as quickly as possible. The IL in the sealed vessel was used to determine the conductivity.

The high-pressure apparatus used in this work is shown schematically in Fig. 3a. It was constructed based on conventional methods. The apparatus consisted mainly of a high-pressure stainless steel vessel, a conductivity cell, a constant temperature water bath, a high-pressure syringe pump, a pressure gauge, a magnetic stirrer, and a gas cylinder. The temperature of the water bath was controlled using a Haake-D8 controller, and the temperature was measured by a mercury thermometer with an accuracy of better than ±0.05 K. The pressure gauge was composed of a pressure transducer (FOXBORO/ICT, Model 93) and an indicator, which was accurate to ±0.25 bar in the pressure range of 0–200 bar. The details of the conductivity cell are shown in Fig. 3b. Both working electrode and counter electrode were made of 0.3 mm thick Pt foil, which were fixed on the two ends of a Teflon tube with an inner diameter of 8 mm, so that the distance between the two electrodes was fixed. There were some holes in the wall of the Teflon tube for mass transfer. A ZAHNER IM6e Electrochemical Workstation (made in Germany) was used to measure the conductivity. The cell constant was calibrated with aqueous 0.01 M KCl at 25.0 °C and the cell constant was 1.60 cm^{-1}.

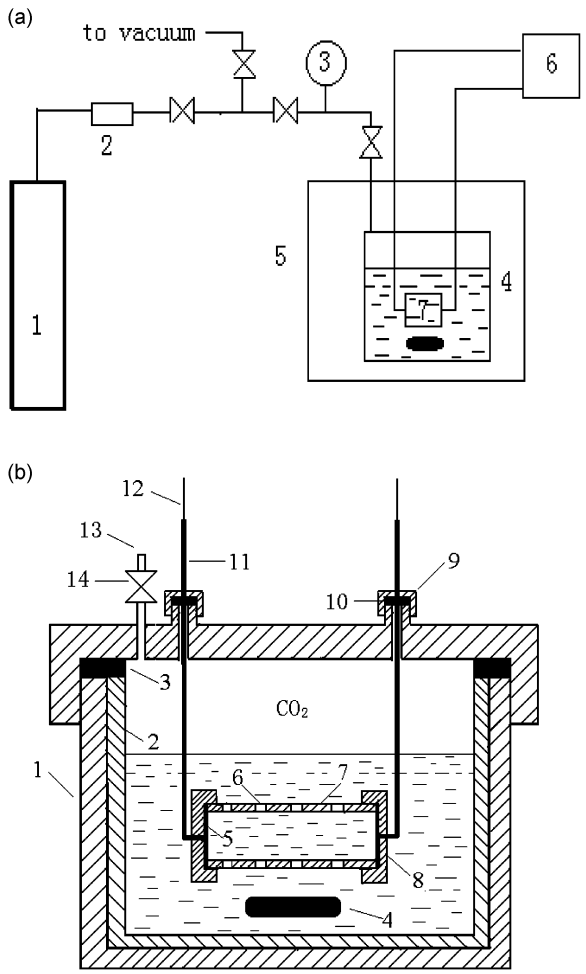

Fig. 3 (a) Schematic diagram of the apparatus. 1, CO_2 cylinder; 2, high pressure pump; 3, pressure gauge; 4, stainless steel vessel; 5, constant temperature water bath; 6, impedence analyzer; 7, conductivity cell (see Fig. 1b). (b) Schematic diagrams of the high pressure vessel and the conductivity cell. 1, Stainless steel vessel; 2, Teflon vessel; 3, Teflon seal; 4; magnetic stirrer; 5, Pt foil; 6, holes in the Teflon tube; 7, Teflon tube; 8, Teflon nut; 9, stainless steel nut; 10, Teflon seal; 11, Teflon insulation; 12, Pt wire; 13, gas inlet or outlet; 14, valve.

In a typical experiment, 30 ml of dried IL was charged into the stainless steel vessel. As discussed above, the vessel was sealed immediately after charging the dried IL in order to minimize the absorption of water from the air. At the same time, the conductivity cell was immersed into the IL, as shown in Fig. 3b. The conductivity cell was full of liquid because there were some holes in the Teflon wall of the conductivity cell. The sealed vessel was placed into the constant temperature water bath. CO_2 was pumped into the system until the desired pressure was reached, and the magnetic stirrer was started to facilitate the dissolution of CO_2 in the IL. The conductivity of the IL at equilibrium was determined; equilibrium was confirmed by the fact that both the pressure and the conductivity were independent of equilibration time.

IL was expanded after dissolution of CO_2. The volume expansion coefficient of the IL was determined by an optical cell which was used previously.[44]

Acknowledgements

This work was financially supported by the National Key Basic Research Project of China (G2000048010), the National Natural Science Foundation of China (20133030), and the UK–China R & D Program.

References

1 P. Wasserscheid and W. Keim, *Angew. Chem., Int. Ed.*, 2000, **39**, 3773.
2 K. R. Seddon, *J. Chem. Technol. Biotechnol.*, 1997, **68**, 351.
3 T. Welton, *Chem. Rev.*, 1999, **99**, 2071.
4 M. J. Earle, P. B. McCormac and K. R. Seddon, *Chem. Commun.*, 1998, 2245.
5 V. P. W. Bohm and W. A. Herrmann, *Chem. Eur. J.*, 2000, **6**, 869.
6 M. A. McHugh and V. J. Ktukonis, *Supercritical Fluid Extraction*, 2nd edition, Butterworth-Heinemann, Boston, 1994.
7 C. A. Eckert, B. L. Knutson and P. G. Debenedetti, *Nature*, 1996, **383**, 313.
8 R. A. Brown, P. Pollet, E. McKoon, C. A. Eckert, C. L. Liotta and P. G. Jessop, *J. Am. Chem. Soc.*, 2001, **123**, 1254.
9 F. Loeker and W. Leitner, *Chem. Eur. J.*, 2000, **6**, 2011.
10 M. G. Hitzler and M. Poliakoff, *Chem. Commun.*, 1997, 1667.
11 K. P. Johnston, K. L. Harrison, M. J. Clarke and S. M. Howdle, *Science*, 1996, **271**, 624.
12 J. F. Brennecke and J. E. Chateauneuf, *Chem. Rev.*, 1999, **99**, 433.
13 A. Baiker, *Chem. Rev.*, 1999, **99**, 453.
14 P. G. Jessop, T. Ikariya and R. Noyori, *Chem. Rev.*, 1999, **99**, 475.
15 J. A. Darr and M. Poliakoff, *Chem. Rev.*, 1999, **99**, 495.
16 J. L. Kendall, D. A. Canelas, J. L. Young and J. M. DeSimone, *Chem. Rev.*, 1999, **99**, 543.
17 P. E. Savage, *Chem. Rev.*, 1999, **99**, 603.
18 L. A. Blanchard, D. Hancu, E. J. Beckman and J. F. Brennecke, *Nature*, 1999, **399**, 28.
19 L. A. Blanchard, Z. Y. Gu and J. F. Brennecke, *J. Phys. Chem. B*, 2001, **105**, 2437.
20 S. G. Kazarian, B. J. Briscoe and T. Welton, *Chem. Commun.*, 2000, 2047.
21 F. C. Liu, M. B. Abrams, R. T. Backer and W. Tumas, *Chem. Commun.*, 2001, 433.
22 R. A. Brown, P. Pollet, E. McKoon, C. A. Eckert, C. L. Liotta and P. G. Jessop, *J. Am. Chem. Soc.*, 2001, **123**, 1254.
23 M. F. Sellin, P. B. Webb and D. J. Cole-Hamilton, *Chem. Commun.*, 2001, 781.

24 L. A. Blanchard and J. F. Brennecke, *Ind. Eng. Chem. Res.*, 2001, **40**, 287.
25 K. Ohta, K. Suda, S. Kaneco and T. Mizuno, *J. Electrochem. Soc.*, 2000, **147**, 233.
26 T. Saeki, K. Hashimoto, N. Kimura, K. Omata and A. Fujishima, *Chem. Lett.*, 1995, 361.
27 P. G. Jessop, T. Ikariya and R. Noyori, *Nature*, 1994, **368**, 231.
28 H. Z. Yang, Y. L. Gu, Y. Q. Deng and F. Shi, *Chem. Commun.*, 2002, 274.
29 P. Bonhote, A. P. Dias, M. Armand, N. Papageorgiou, K. Kalyanasundaram and M. Gratzel, *Inorg. Chem.*, 1996, **35**, 1168.
30 J. Fuller, R. T. Carlin and R. A. Osteryoung, *J. Electrochem. Soc.*, 1997, **144**, 3881.
31 C. Nanjundiah, F. McDevitt and V. R. Koch, *J. Electrochem. Soc.*, 1997, **144**, 3392.
32 R. Hagiwara, T. Hirashige, T. Tsuda and Y. Ito, *J. Fluorine Chem.*, 1999, **99**, 1.
33 P. A. Z. Suarez, S. Einloft, J. E. L. Dullius and R. F. de Souza, *J. Chim. Phys. Phys.-Chim. Biol.*, 1998, **95**, 1626.
34 V. R. Koch, C. Nanjundiah, G. B. Appetecchi and B. Scrosati, *J. Electrochem. Soc.*, 1995, **142**, 116.
35 A. Noda, K. Hayamizu and M. Watanabe, *J. Phys. Chem. B*, 2001, **105**, 4603–4610.
36 R. L. Perry, K. M. Jones, W. D. Scott, Q. Liao and C. L. Hussey, *J. Chem. Eng. Data*, 1995, **40**, 615.
37 A. P. Abbott and C. A. Eardley, *J. Phys. Chem. B*, 2000, **104**, 9351.
38 A. P. Abbott and J. C. Harper, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 3895.
39 *CRC Handbook of Chemistry and Physics*, Ed. D. R. Lide, 82nd edn., CRC Press, Boca Raton, London, New York, Washington DC, 2001–2002, pp. 5–91.
40 H. Every, A. G. Bishop, M. Forsyth and D. R. MacFarlane, *Electrochim. Acta*, 2000, **45**, 1279.
41 S. N. Baker, G. A. Baker, M. A. Kane and F. V. Bright, *J. Phys. Chem. B*, 2001, **105**, 9663.
42 J. G. Huddleston, H. D. Willauer, R. P. Swatloski, A. E. Visser and R. D. Rogers, *Chem. Commun.*, 1998, 1765.
43 K. R. Seddon, A. Stark and M. J. Torres, *Pure Appl. Chem.*, **72**, 2275.
44 D. Li, Z. M. Liu, B. X. Han, G. Y. Yang, Z. H. Wu, Y. Liu and B. Z. Dong, *Macromolecules*, 2000, **33**, 7990.