

Construction of High-Pressure Apparatuses with High-Impact Engineering Plastics for Supercritical Fluid Solutions

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We have newly developed two kinds of high-pressure cells for electric conductivity and X-ray diffraction measurements with a high-impact engineering plastic of poly(etherether ketone). It was confirmed that the two high-pressure cells can withstand temperatures and pressures, at least, up to ~35 MPa and ~403 K. With the developed apparatuses, the pressure effects of carbon dioxide on 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid were studied in view of transport phenomena and liquid structures. The electric conductivity of the ionic liquid exhibited a remarkable increase due to the dissolution of carbon dioxide in the pressure range between 0.1 and 10 MPa. In harmony with these results, it was found that a few new peaks appeared and increased as a function of carbon dioxide pressure in the intermolecular distribution functions, which were obtained from X-ray diffraction measurements.

1. Introduction

The solvent-free technology to reduce the use of harmful volatile organic compounds is one of the most crucial research subjects for the achievement of environmentally benign green chemical processes. There have been several approaches proposed so far, for example, to use no-solvent systems, aqueous solutions, supercritical fluids, and ionic liquids. The latter two media of supercritical fluids and ionic liquids have recently gained much attention, and also are expected to have a promising wide application such as extraction, separation, chemical reaction, and material processing media [1, 2]. Supercritical fluids, consisting of water and carbon dioxide, have the merits of economical benefit, easy solvent removal, and readily tunable solvent properties by temperature and pressure. On the other hand, ionic liquids with lower melting points are non-volatile, non-flammable, and the solvent properties can be modified by a choice of cation and anion combinations. Thus, such a new class of solvents has several advantages over conventional liquid organic solvents. Recently, we have found that the biphasic media composed of ionic liquid and supercritical carbon dioxide have potential abilities for chemical reactions [3]. However, a lack of fundamental properties

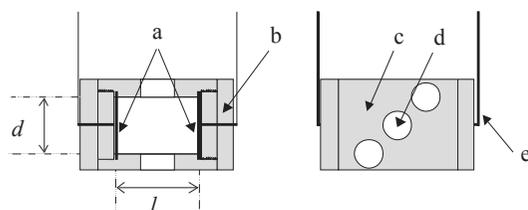
frequently prevents much progress of its utility. In order to remove such barriers, we have developed a variety of high-temperature and high-pressure spectroscopic techniques for in-situ observation of supercritical fluid solutions and have made efforts to understand the solvent properties [4-6]. In particular, we favorably used some kinds of engineering plastics such as polyimide and poly(etherether ketone) because they have relatively high tensile strength, good machinability, and excellent stability for a wide range of chemicals; moreover, they are relatively cheap, non-magnetic, and transparent for radio waves. We have constructed high-resolution NMR [5, 6] and MRI [7] cells from polymer materials, which are usable, at least, up to ~35 MPa and ~403 K.

In this study, two kinds of high-pressure cells for electric conductivity and X-ray diffraction measurements are newly developed. We present the details of high-pressure instrumentation and discuss the solution behaviors of ionic liquid in contact with supercritical carbon dioxide.

2. Experimental Methods

2.1. Electric Conductivity Cell Although several kinds of high-pressure cells for electric conductivity measurements have been proposed so

far [8], we develop a new type of cell for the measurement of certain solution in a multi-phasic system. A schematic drawing of electrode is given in Fig. 1. The electrode consists of a cylindrical tube (c) and two caps (b) at both ends, where a pair of Pt disks (a) is fixed. The sample solution can come and go to the inside of the electrode through several open holes (d) in the cylindrical tube. The distance (l) between a pair of Pt disks was fixed at 15 mm. Several cylindrical tubes with different inner diameters ($d = 5, 7, 10$ mm) were used tentatively. These parts were made of a strong and easy-machinable poly(etherether ketone), which was also a good insulator. Because this kind of electrode is very simple and compact, we can locate it in arbitrary position in the high-pressure cell.



(I) side cut-away view (II) out side view

Fig. 1. A schematic drawing of electrode for high-pressure conductivity measurements: (a) Pt plate, (b) cap, (c) tube, (d) open hole, and (e) electric lead

2.2. X-ray Diffraction Cell A schematic drawing of high-pressure cell for X-ray diffraction measurements is given in Fig. 2. The structure is very simple. A head cap (a) made of SUS 316 has a gas inlet/outlet hole (b). A cell body (d) is again made of poly(etherether ketone) with the dimensions of 15 mm inner diameter, 29 mm outer diameter, and 35 mm length. The seal between the head cap and cell body can be kept with an O-ring

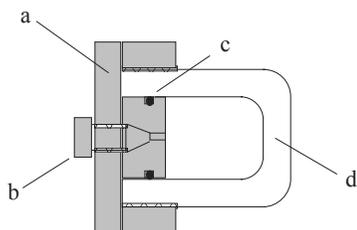


Fig. 2. A schematic drawing of high-pressure cell for X-ray diffraction measurements: (a) head cap, (b) gas inlet/outlet, (c) O-ring, and (d) cell body.

(c). Since poly(etherether ketone) consists of relatively light elements, the wall thickness of the cell body will not bring about serious background noise in X-ray diffraction measurements.

2.3. Sample Preparation and High-Pressure Experiments The samples of 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF₆) ionic liquid were synthesized in our laboratory according to the previous procedure [9]. The synthesized [BMIM]PF₆ was purified with activated charcoal and filtered through neutral alumina column. The obtained colorless liquid was dried under vacuum at 343 K for 30 h to remove any excess water. The purified ionic liquid was transferred into each high-pressure cell in a dry glove box.

Before high-pressure experiments, it was confirmed that each high-pressure cell withstands temperatures and pressures, at least, up to ~35 MPa and ~403 K under hydrostatic condition.

Pure-grade carbon dioxide (Showa-Tansan, 99.99% in purity) was pressurized with a cooled liquid chromatography pump (JASCO, SCF-Get). After the system was allowed to equilibrate, the pressure was measured with a digital indicator (Druck, DPI 145).

2.4. Instruments Electric conductivities (κ) were recorded with an electric conductivity measurement system 369 presented by Fuso Electro Chemical System Co. The cell constants of the electrodes were determined with a known value of κ of 0.1 mol dm⁻³ KCl aqueous solution at 25.00 °C [10]. The temperature dependence of the cell constant was negligibly small. The frequency was fixed at 1 kHz. During the experiments, the sample temperature was controlled at 39.97±0.01 °C.

X-ray diffraction measurements were carried out using a Rigaku diffractometer with Mo K_α radiation ($\lambda = 0.7107 \times 10^{-10}$ m). The diffraction data were collected over a wide 2θ range between 3 and 150° at intervals of 0.2°. The experiments were performed at room temperatures.

3. Results and Discussion

3.1. Pressure Effect of Carbon Dioxide on Electric Conductivity of [BMIM]PF₆ The electric conductivity ($\kappa = 0.146 \pm 0.005$ S m⁻¹) of [BMIM]PF₆ determined with the developed cell at 25.00 °C and at atmospheric pressure is in a quite good agreement with the reported value of

$0.158 \pm 0.016 \text{ S m}^{-1}$ [11] within the experimental errors.

Carbon dioxide was introduced into the ionic liquid in the high-pressure cell at certain pressure at $39.97 \text{ }^\circ\text{C}$, and the time-dependence of the conductivity was observed with the solution being stirred. After the stirring was stopped, it was confirmed that the variations in the sample pressure and the conductivity remained virtually constant within $\pm 0.003 \text{ MPa}$ and $\pm 0.5 \%$, respectively. Then, the electric conductivity of [BMIM]PF₆ solution was recorded with the reading of the pressure indicator. It took a few hours to equilibrate at low pressures.

The pressure dependence of electric conductivity of [BMIM]PF₆ solution saturated with carbon dioxide was given in Fig. 3. It was found that the conductivity increases remarkably and almost linearly with a raise of pressure up to $\sim 10 \text{ MPa}$ and is less sensitive to pressure above $\sim 10 \text{ MPa}$. This is mainly attributable to the fact that at low pressures carbon dioxide smoothly dissolves into the ionic liquid in proportion to pressure, whereas at higher pressures dissolution of carbon dioxide is expected not to be large very much [12]. Similarly, Liu et al. [13] recently reported that viscosity of [BMIM]PF₆ rapidly decreases due to dissolution of carbon dioxide.

The developed high-pressure cell is very simple and enables us to precisely measure the electric conductivity of arbitrary solution in a multi-phasic system. Moreover, it has become apparent that transport phenomena in very viscous ionic liquids can be improved effectively by the addition of carbon dioxide.

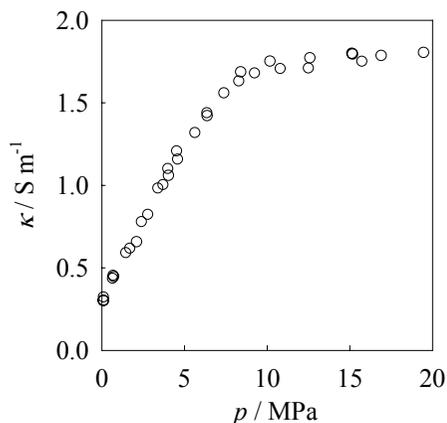


Fig. 3. Pressure effect of carbon dioxide on electric conductivity of [BMIM]PF₆ at $39.97 \text{ }^\circ\text{C}$.

3.2. Pressure Effect of Carbon Dioxide on X-ray Diffraction of [BMIM]PF₆ X-ray diffraction measurements were carried out for three samples of neat [BMIM]PF₆ and [BMIM]PF₆ solutions saturated with carbon dioxide at 4 and 13 MPa. The molar ratios (x) of [BMIM]PF₆ in the three samples are obtained to be 1, 0.5, and 0.3, respectively, from the solubility data [12]. The density of the neat sample was reported [14], and the densities of the saturated solutions were estimated from the compositions and volume expansions of the ionic liquid [12-14]. We also measured the empty high-pressure cell, which had broad peaks only at $2\theta < 15^\circ$. The background correction was made for the collected diffraction data preliminary to further analyses. The X-ray diffraction profiles arising from the intramolecular contributions were calculated from the structural

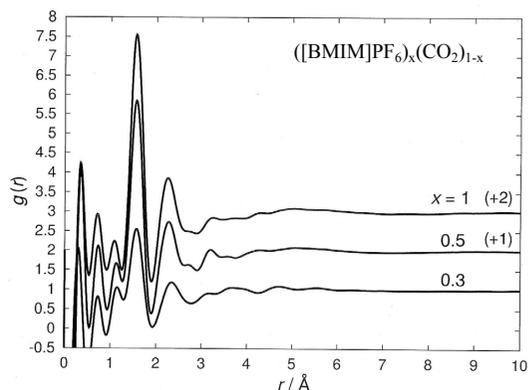


Fig. 4. Total distribution functions of [BMIM]PF₆-carbon dioxide solutions with different compositions at room temperature of $25 \pm 3 \text{ }^\circ\text{C}$.

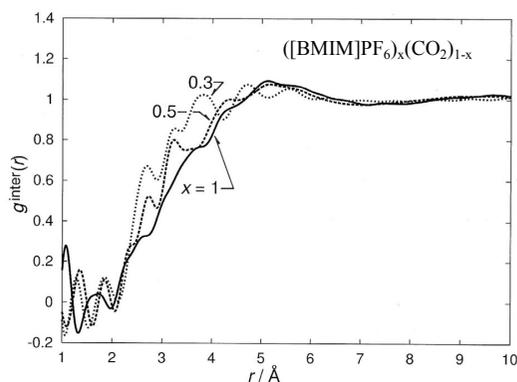


Fig. 5. Intermolecular distribution functions of [BMIM]PF₆-carbon dioxide solutions with different compositions at room temperature of $25 \pm 3 \text{ }^\circ\text{C}$.

data of the cation [15] and the anion [16] species. The intermolecular interference term was obtained by subtracting the intramolecular interference contribution from the total interference term, and then the distribution functions were determined by the Fourier transforms of the interference terms.

The total distribution functions ($g(r)$) of the three sample solutions are shown in Fig. 4. Since the dissolution of carbon dioxide brings about a decrease in density of the solution, the peaks become weaker with decreasing the molar ratio of x . The intermolecular distribution functions ($g^{\text{inter}}(r)$) are also given in Fig. 5. It is clearly found that two peaks appear at around 2.8 and 3.2×10^{-10} m in $g^{\text{inter}}(r)$ of the sample solution with $x = 0.5$. These two peaks appreciably increase in $x = 0.3$; moreover, there is another peak at $\sim 3.8 \times 10^{-10}$ m. Although these new peaks cannot be assigned at present, the X-ray results show that carbon dioxide can dissolve and interact with the ionic liquid. This is in harmony with the results of electric conductivity measurements.

4. Conclusions

We have newly developed two kinds of high-pressure cells for electric conductivity and X-ray diffraction measurements with a high-impact engineering plastic of poly(etherether ketone). It was demonstrated that some kinds of engineering plastics are very suitable for the material of high-pressure experiments. With the developed apparatus, moreover, the pressure effect of carbon dioxide on ionic liquid was investigated. Understanding of both transport phenomena and liquid structures can provide reliable pictures for complicated matters in solutions.

Acknowledgements

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References and Notes

- [1] P. G. Jessop, W. Leitner eds, in *Chemical Synthesis Using Supercritical Fluids*, (Wiley-VCH, New York, 1999).
- [2] P. Wasserscheid, T. Welton eds, in *Ionic Liquids in Synthesis*, (Wiley-VCH, New York, 2002).
- [3] H. Kawanami, A. Sasaki, K. Matsui, and Y. Ikushima, *Chem. Commun.*, **2003**, 896.
- [4] M. Kanakubo, T. Aizawa, T. Kawakami, O. Sato, Y. Ikushima, K. Hatakeda, and N. Saito, *J. Phys. Chem. B*, **104**, 2749 (2000).
- [5] T. Umecky, M. Kanakubo, and Y. Ikushima, *J. Phys. Chem. B*, **106**, 11114 (2002).
- [6] T. Umecky, M. Kanakubo, and Y. Ikushima, *J. Phys. Chem. B*, **107**, 12003 (2003).
- [7] M. Kanakubo, T. Umecky, Y. Masuda, T. Aizawa, and Y. Ikushima, in *the proceeding of 28th International Conference on Solution Chemistry*, p. 104 (2003).
- [8] See for example, M. Ueno, *Denki Kagaku* (presently *Electrochemistry*), **65**, 934 (1997).
- [9] S. Carda-Bronch, A. Berthod, D. W. Armstrong, *Anal. Bioanal. Chem.*, **375**, 191 (2003).
- [10] J. -C. Justice, in *Conductance of Electrolyte Solutions, Comprehensive Treatise of Electrochemistry*, (Plenum, New York, 1983), Vol. 5, Chapter 3.
- [11] P. A. Z. Suarez, S. Einloft, J. E. L. Dullius, and R. F. de Souza, *J. Chim. Phys. Phys.-Chim. Biol.*, **95**, 1626 (1998).
- [12] L. A. Blanchard, D. Hancu, E. J. Beckman, and J. F. Brennecke, *J. Phys. Chem. B*, **106**, 7315 (2002).
- [13] Z. Liu, W. Wu, B. Han, Z. Dong, G. Zhao, J. Wang, T. Jiang, and G. Yang, *Chem. Eur. J.*, **9**, 3897 (2003).
- [14] Z. Gu and J. F. Brennecke, *J. Chem. Eng. Data*, **47**, 339 (2002).
- [15] J. Andrade, E. S. Böes, and H. Stassen, *J. Phys. Chem. B*, **106**, 13344 (2002).
- [16] B. Milliken, L. Borer, J. Russell, M. Bilich, M. M. Olmstead, *Inorg. Chim. Acta*, **348**, 212 (2003).