In situ Raman Study of Dissolved Carbon-Dioxide Induced Changes of Imidazolium-Based Ionic Liquids

Takashi Makino
Department of Applied Chemistry, Kobe City College of Technology
8-3 Gakuen-higashi, Nishi-ku, Kobe 651-2194, Japan
E-mail: makino@kobe-kosen.ac.jp

Abstract. In situ Raman spectroscopic analysis has been performed for room temperature ionic liquid (RTIL) + CO₂ systems under two-phase equilibrium conditions at room temperature. The Raman spectra indicate the followings: the vibration state and configuration of 1-ethyl-3-methylimidazolium tetrafluoroborate change by CO₂ dissolution; the liquid structure of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide barely changes by addition of CO₂ pressure up to 30 MPa. In addition, the information of the RTIL structure suggests that the large change of the vibration state and configuration of the RTIL does not necessarily relate to the high CO₂ solubility in the RTIL.

1. Introduction
Room temperature ionic liquids (RTILs) are organic salts of liquid state under ambient temperatures. The RTIL generally contains a large asymmetric cation and an organic or inorganic anion. It is believed that the asymmetry of the cation results in low melting points of RTILs, whereas a number of physical and chemical properties of RTILs are considered to be determined by the nature of the anion [1]. RTILs have unique properties, i.e., negligible vapor pressure, nonflammable, thermal and chemical stabilities. Furthermore, RTILs are good solvents for organic and inorganic compounds.

The solubility of CO₂ is remarkably high in all the RTILs investigated although there are some differences. CO₂ solubilities in RTILs reach as high as 70 mol % or more under high pressures [2]. An IR study found evidence of the Lewis base-acid interaction between the dissolved CO₂ molecule and anion of the RTIL [3]. The same paper reported that specific interaction between the CO₂ molecule and imidazolium cation are not observed. CO₂ solubility depends largely on the nature of the anion, and it is suggested that the interaction of CO₂ with the anion is index of CO₂ solubility [4]. However, another IR research insisted that the interaction has no promotional effect on the solubility of CO₂ [5].

The partial molar volume of CO₂ in the RTIL phase is much smaller than that in bulk supercritical CO₂ phase [6], thus, very small volume expansion of the RTIL phase is observed by CO₂ addition [4]. Cadena et al. proposed in the same report that cations and anions construct a framework and the dissolved CO₂ molecule occupies the void space in the RTIL framework. Huang et al. reported that the initial void space is not sufficient for the CO₂ molecule [6]; the sufficient space is generated by small angular rearrangements of the anion without expansion of the RTIL phase.

1 Corresponding Author. e-mail: makino@kobe-kosen.ac.jp
The present study has investigated dissolved CO₂ induced changes of vibrations and configurations of RTILs and the relation between the changes and CO₂ solubility. Because the RTIL has attracted much attention as medium for the gas separation [7] and extraction [8] processes, insights obtained from the present work are useful for the process development. In order to study the vibration and configuration of the RTIL, in situ Raman spectroscopic analysis has been performed for two RTIL + CO₂ systems under two-phase equilibrium conditions at room temperature. 1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)amide ([emim][Tf₂N]), the other is 1-ethyl-3-methyl-imidazolium tetrafluoroborate ([emim][BF₄]). [emim][Tf₂N] is one of the RTILs of which CO₂ solubility is especially high [9]. The CO₂ solubility of [emim][BF₄] is smaller than that of [emim][Tf₂N] [10]. Thus, the [emim][Tf₂N] + CO₂ system has been paid particular attention.

2. Experimental

2.1. Materials
[emim][Tf₂N] and [emim][BF₄] (purity: > 99.9 %; water content: < 10 ppm; halide content: < 10 ppm) were purchased from Toyo Gosei Co., Ltd. CO₂ (purity: 99.99 %) was obtained from Takachiho Trading Co., Ltd. All the materials were used without further purification.

2.2. Apparatus and Procedure
Experimental apparatus consisted of the following parts: a high-pressure optical cell with sapphire windows, high-pressure pump to supply liquid CO₂, and a pressure gauge. The maximum working pressure of the optical cell was 35 MPa. Equilibrium pressure was recorded by a pressure gauge (Valcom VPRT) calibrated by RUSKA quartz Bourdon tube gauge. Temperature was measured by a thermistor probe (Takara D-641) calibrated by a Pt resistance thermometer (25°C) defined by ITS-90. The uncertainties of equilibrium pressure and temperature were 0.07 MPa and 0.02 K, respectively.

The freshly bottled RTIL was introduced into the high-pressure optical cell under dried N₂. After the cell was evacuated to remove N₂, liquid CO₂ was supplied successively for pressurization. Next, the contents were agitated by vibrating an enclosed ruby ball from outside of the cell to establish two-phase equilibrium under room temperature condition (around 298 K). RTIL phase was analyzed by in situ Raman spectroscopic analysis using a laser Raman microprobe spectrometer with a multichannel CCD detector (Jobin-Yvon T64000). Ar ion laser beam (wave length: 514.5 nm, generation power: 100 mW) condensed to 2 µm in spot diameter, was irradiated from the object lens through the sapphire window. The backscatter was taken in with the same lens. The spectral resolution was 0.7 cm⁻¹. Raman peaks were calibrated with the Ne emission lines in the air. The CCD detector was maintained at 140 K by liquid N₂ to reduce heat noise. Raman spectra were fitted by Voigt curve equation.

3. Results and Discussion
Figures 1 and 2 show typical Raman spectra obtained from RTIL phase. The symbols of $\tilde{\nu}$ and $p$ stand for Raman shift and equilibrium pressure, respectively. The Raman spectra of the pure [emim][BF₄] and [emim][Tf₂N] agree with the reported spectra [11,12]. Raman peaks of filled and open diamonds were assigned to Raman peaks derived from the anion and cation, respectively [11,13,14]. Reversed triangles in Figs. 1 and 2 indicate Fermi resonance peaks derived from the dissolved CO₂ molecule.

3.1. [emim][BF₄] + CO₂ system
The Raman spectrum of the [emim][BF₄] + CO₂ system (Fig. 1 b) and c)) is different in shape and wavenumber from that of the pure [emim][BF₄] system (Fig. 1 a)). This difference indicates that the CO₂ molecule interacts with the [emim][BF₄] and the interaction causes the change of the vibration state and configuration of the [emim][BF₄]. The Raman peak detected at 764 cm⁻¹ was attributed to the FBF symmetric stretching vibration. Thus, there is the interaction between the [BF₄] anion and the CO₂ molecule in the [emim][BF₄] + CO₂ system. In addition, it is suggested in the earlier report [5] that the strength of the anion-CO₂ interaction depends on the basicity of the anion.
Raman peaks at 597, 701, 1337, and 1425 cm\(^{-1}\) were related to the vibration of the imidazolium ring [11]. These peaks show the shift of 1-3 cm\(^{-1}\) by the dissolution of CO\(_2\). The MD simulation has reported that CO\(_2\) is found around the imidazolium ring and alkyl tail of the imidazolium ring [6]. It is suggested that the resultant complex of the interaction (the [BF\(_4\)-CO\(_2\)] anion) interacts with the imidazolium ring and causes the vibrational change. While, the Raman peak at 1455 cm\(^{-1}\) was derived from the methyl group, therefore, it is speculated that the significant vibration change is not observed. In addition, the CO\(_2\) dissolution induces the change of spectral shape in the wavenumber range of 1400-1500 cm\(^{-1}\). The most recent study has reported as follows: the spectral shape change, that is, the configuration equilibrium change of the imidazolium cation is caused by the presence of CO\(_2\) [15]. The [emim] cation has the planar and nonplanar configurations [14]. Therefore, the configuration equilibrium change of the [emim] cation might be caused by the CO\(_2\) dissolution in the [emim][BF\(_4\)] + CO\(_2\) system.

3.2. [emim][Tf\(_2\)N] + CO\(_2\) system

In contrast to the [emim][BF\(_4\)] + CO\(_2\) system, the dissolution of CO\(_2\) has little effect on the

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig1}
\caption{Raman spectra obtained from RTIL phase in the [emim][BF\(_4\)] + CO\(_2\) system. a) pure RTIL, b) \(p=2.58\) MPa, c) \(p=6.51\) MPa. Filled diamond: Raman peak of the anion, open diamond: Raman peak of the cation, reverse triangle: Fermi resonance peak of CO\(_2\).}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig2}
\caption{Raman spectra obtained from RTIL phase in the [emim][Tf\(_2\)N] + CO\(_2\) system. a) pure RTIL, b) \(p=6.50\) MPa, c) \(p=29.45\) MPa. Filled diamond: Raman peak of the anion, open diamond: Raman peak of the cation, reverse triangle: Fermi resonance peak of CO\(_2\).}
\end{figure}
vibration state and configuration of [emim][Tf₂N] as shown in Fig. 2. Raman peaks at 571, 743, 1244, and 1336 cm⁻¹ were related to vibrations of the CF₃, SO₂, or SNS groups [13]. Even under the pressure of 29.45 MPa (the equilibrium CO₂ mole fraction in the [emim][Tf₂N] phase is more than 0.7 [16]), no significant change of the wavenumber and spectral shape was observed (Fig. 2 c)). This result reveals the following: the interaction between the CO₂ molecule and the [Tf₂N] anion is so weak that the structure of the anion is unchanged by addition of CO₂ pressure. The wavenumber and spectral shape of the [emim] cation are unchanged similar to the [Tf₂N] anion except for the Raman spectrum in the wavenumber range of 1400-1500 cm⁻¹ (the spectral shape change of the wavenumber range might be due to the configuration equilibrium change similar to the [emim][BF₄] system). It is concluded that the liquid structure of [emim][Tf₂N] barely changes under CO₂ pressure conditions up to 30 MPa.

[emim][Tf₂N] is a better solvent for CO₂ than [emim][BF₄] as mentioned above. If the strength of the interaction between the CO₂ molecule and anion species gave rise to high CO₂ dissolution, the spectral change of the [emim][Tf₂N] system would be more pronounced than that of the [emim][BF₄] system. Therefore, it is suggested that the strong interaction between the CO₂ and RTIL does not necessarily relate to the high CO₂ solubility. Other factors, like void space, might be more important for the CO₂ dissolution. A similar suggestion has been reported in an ATR-IR study [5].

3.3. Raman peaks of the CO₂ molecule dissolved in RTIL

Fermi resonance peaks of the dissolved CO₂ molecule were detected at the following positions: 1278 cm⁻¹ and 1384 cm⁻¹ for the [emim][BF₄] + CO₂ system (Fig. 1-B); 1279 cm⁻¹, 1384 cm⁻¹, and 1404 cm⁻¹ for the [emim][Tf₂N] + CO₂ system (Fig. 2-B). It is suggested that the small difference of wavenumber is caused by the difference of polarities between RTILs. The wavenumbers are lower than those of the Raman bands of the gaseous CO₂ molecule (1287 and 1389 cm⁻¹) and seem to increase gradually with an increase of equilibrium CO₂ pressure.

Figure 3 represents a peak area ratio of Fermi resonance peaks of the dissolved CO₂ molecule (peak area of 2ν₂ vibration to that of ν₁ vibration) as a function of equilibrium CO₂ pressure. The symbol of A stands for the Raman peak area. A Raman study has reported that the peak area ratio increases with a rise of number density of CO₂ [17]. Therefore, Fig. 3 indicates that a number of the CO₂ molecule per unit volume in the [emim][Tf₂N] phase is larger than that in the [emim][BF₄] phase under isobaric conditions. It is reported that the volume of the void space per unit RTIL volume of [emim][Tf₂N] is almost the same as that of [emim][BF₄] [18]. Therefore, the present result shows a possibility that the rearrangement of the [Tf₂N] anion provides more sufficient space for the dissolution of CO₂ than that.
of the [BF₄]⁻ anion. However, further experiments should be performed to elucidate the effect of the void space on the solubility of CO₂ in the RTIL.

4. Conclusion

The RTIL + CO₂ systems have been investigated under two-phase equilibrium conditions by in situ Raman spectroscopy. The vibrational and conformational properties of [emim][BF₄] are affected by the dissolution of CO₂, whereas the liquid structure of [emim][Tf₂N] barely changes by addition of CO₂ pressure up to 30 MPa. This result suggests that the strong interaction of CO₂ with RTIL does not necessarily cause the high CO₂ solubility in the RTIL.

The vibration state of the dissolved CO₂ molecule in [emim][BF₄] is similar to that in [emim][Tf₂N]. The difference between the [emim][BF₄] and [emim][Tf₂N] systems is observed in the peak area ratio of the Fermi resonance peak, which indicates that the number density of CO₂ in the [emim][Tf₂N] phase is larger than that in the [emim][BF₄] phase.

Acknowledgements

The author is grateful to the Division of Chemical Engineering, Graduate School of Engineering Science, Osaka University for the scientific support by "Gas-Hydrate Analyzing System (GHAS)."

Reference

[1] Dzyuba S V and Bartsch R A 2002 Chem. Phys. Chem. 3 161
[2] Noda A and Watanabe M 2000 Electrochem Acta 45 1265
[3] Kazarian S G, Briscoe B J, and Welton T 2000 Chem. Comm. 2047
[4] Cadena C, Anthony J L, Shah J K, Morrow T I, Brennecke J F, Maginn E J 2004 J. Am. Chem. Soc. 126 5300
[5] Seki T, Grunwaldt J-D, Baiker A 2009 J. Phys. Chem. B 113 114
[6] Huang X, Margulis C J, Li Y, Berne B J 2005 J. Am. Chem. Soc. 127 17842
[7] Baltus R E, Counce R M, Culbertson B H, Luo H M, Depaoli D W, Dai S, and Duckworth D C 2005 Sep. Sci. Technol. 40 525.
[8] Scuroto A M, Aki S N V K, and Brennecke J F 2002 J. Am. Chem. Soc. 124 10276
[9] Scovazzo P, Camper D, Kieft J, Poshusta J, Koval C, and Noble R 2004 Ind. Eng. Chem. Res. 43 6855
[10] Finotello A, Bara J E, Narayan S, Camper D, Noble R D 2008 J. Phys. Chem. B 112 2335
[11] Heimer N E, Del Sesto R E, Meng Z, Wilkes J S, Robert Carper W 2006 J. Mol. Liq. 124 84
[12] Lassegues J, Grondi J, Holomb R, and Johansson P 2007 J. Raman Spectrosc. 38 551
[13] Castriota M, Caruso T, Agostino R G, Cazzanelli E, Henderson W A, Passerini S 2005 J. Phys. Chem. A 109 92
[14] Umebayashi Y, Fujimori T, Sukizaki T, Asada M, Fujii K, Kanzaki R, and Ishiguro S 2005 J. Phys. Chem. A 109 8976
[15] Andanson J-M, Jutz F, and Baiker A 2009 J. Phys. Chem. B 113 10249.
[16] Shin E-Y, Lee B-C, and Lim J S 2008 J. Supercritical Fluids 45 282
[17] Garrabos Y, Tufeu R, Le Neindre B 1980 J. Chem. Phys. 72 4637
[18] Larriba C, Yoshida Y, de la Mora J F 2008 J. Phys. Chem. B 112 12401