Chemistry Letters Vol.32, No.6 (2003)

Raman Spectra, Crystal Polymorphism, and Structure of a Prototype Ionic-liquid [bmim]Cl

Satoshi Hayashi, Ryosuke Ozawa, and Hiro-o Hamaguchi*

Department of Chemistry, School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033

(Received March 5, 2003; CL-030192)

A prototype ionic-liquid [bmim]Cl shows crystal polymorphism, having two crystal forms, Crystal (1) and Crystal (2), characterized by distinct X-ray powder patterns and Raman spectra. Two sets of characteristic Raman bands of Crystals (1) and (2), which are mutually exclusive with each other, do coexist in the spectrum of liquid [bmim]Cl. It seems that two distinct structures of the $[\text{bmim}]^+$ ion, one corresponding to that in Crystal (1) and the other to that in Crystal (2), exist simultaneously in the ionic liquid state.

Although ionic liquids (ILs) or room-temperature ionic liquids (RILs) attract much attention of chemists,[1] there still remain some fundamental questions to be answered regarding the nature of the liquid state. In spite of early infrared and NMR spectroscopic studies, which elucidated some aspects of hydrogen-bonding interactions between the cation and anion, there is no established view on the microscopic structure of the ionic liquid state.[2–6] In the present letter, we report our preliminary studies on the structure of a prototype ionic-liquid, 1-butyl-3-methyl-imidazolium chloride, [bmim]Cl. Having a melting point of 65 °C,[7] this compound is suitable for X-ray crystallographic analyses at room temperature and also for Raman spectroscopic investigations of the solid state, the liquid state ($t > 65\,^\circ\text{C}$) and supercooled liquid states ($t < 65\,^\circ\text{C}$).

By chance, we found that [bmim]Cl shows crystal polymorphism. By cooling liquid [bmim]Cl down to −18 °C and keeping it for 48 h, two different types of crystals, Crystal (1) and Crystal (2), were obtained. Crystal (2) dominantly formed with this procedure but Crystal (1) also formed occasionally. Upon leaving Crystal (2) for more than 24 h at dry-ice temperature, Crystal (2) was converted to Crystal (1). Therefore, it is most likely that Crystal (2) is a metastable form and Crystal (1) is the stable form at dry-ice temperature. Figure 1 shows the powder X-ray patterns of Crystals (1) and (2) sealed in glass capillaries, which were obtained with the synchrotron radiation (wavelength 0.1 nm) at the SPring-8 BL02B2 of the Japan Synchrotron Radiation Research Institute. Both of the two forms show a number of sharp peaks at different scattering angles. It is clear from these patterns that Crystals (1) and (2) have two distinct crystal structures. It is also noted that the continuous background in the X-ray powder pattern is higher in Crystal (2) than in Crystal (1), indicating that Crystal (2) contains more disordered structure than Crystal (1).

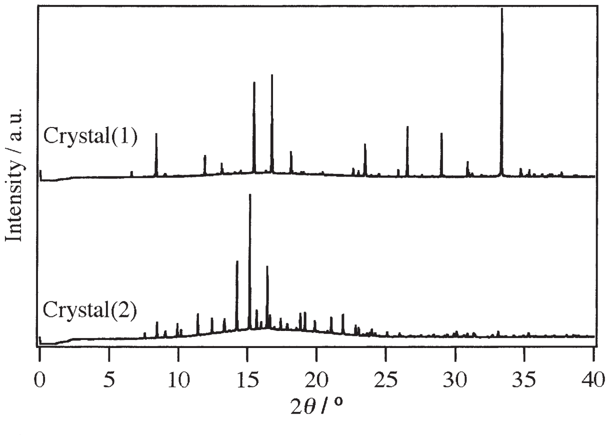

Figure 1. The X-ray powder patterns of Crystal (1) (upper) and Crystal (2) (lower).

In order to study in more detail the structural difference between Crystals (1) and (2), we measured the Raman spectra of [bmim]Cl samples sealed in glass capillaries using a laboratory made near-infrared multichannel Raman system. The 1064 nm line of a cw Q-switched Nd: YAG laser was used for excitation. The results are shown in Figure 2, together with the Raman spectrum of [bmim]Cl in a supercooled liquid state. The Raman spectrum of Crystal (1) is markedly different form that of Crystal (2), in harmony with the two distinct X-ray powder patterns. The difference is most notable in the 500 up to 800 cm^{-1} wavenumber region. The bands at 625, 730, and 790 cm^{-1} are observed only for Crystal (1) and not for Crystal (2), while those at 500, 600, 700 cm^{-1} are observed only for Crystal (2) and not for Crystal (1). It is most probable that several skeletal modes of the imidazolium ring give rise to Raman bands in this wavenumber region. In fact, a preliminary *ab initio* calculation (Gaussian 98, B3LYP/6-31G+** level) located a ring deformation mode at 600 cm^{-1}. We, therefore, suspect that the $[\text{bmim}]^+$

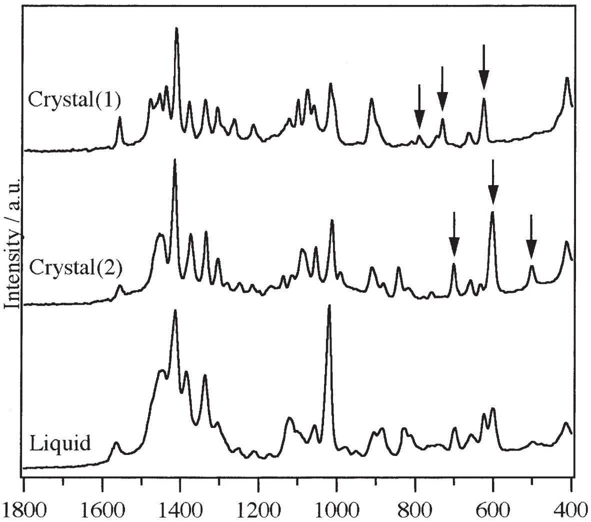

Figure 2. Raman spectra of Crystal (1) (top), Crystal (2) (middle) and liquid, [bmim]Cl in a supercooled liquid state (bottom). Arrows indicate characteristic Raman bands of Crystal (1) and (2).

ion has two distinct ring structures in the crystalline state, one corresponding to the structure in Crystal (1) and the other to that in Crystal (2). It is then extremely interesting that both sets of the characteristic Raman bands, the 625, 730, and 790 $\mathrm{cm^{-1}}$ bands of Crystal (1), and the 500, 600, 700 $\mathrm{cm^{-1}}$ band of Crystal (2), exist simultaneously in the Raman spectrum of a supercooled liquid state (Figure 2). If we add the two crystalline spectra using a scale factor that makes the relative intensity $I(600\,\mathrm{cm^{-1}})/I(625\,\mathrm{cm^{-1}})$ equal to that in the liquid spectrum, we obtain the spectrum shown in Figure 3. The synthesized Raman spectrum thus obtained resembles very much, not only the spectrum of [bmim]Cl in a supercooled liquid state but also that of a prototype room-temperature ionic liquid [bmim]$\mathrm{BF_4}$. This finding leads us to a conjecture that two distinct structures of the [bmim]$^+$ ion coexist in the ionic liquid states of [bmim]Cl and [bmim]$\mathrm{BF_4}$.

If the Raman band at 600 $\mathrm{cm^{-1}}$ and that at 625 $\mathrm{cm^{-1}}$ originate from the two distinct structures of the [bmim]$^+$ ion, they are likely to show different response against external perturbations. As a first step, we examined their temperature dependence, as shown in Figure 4. In this experiment, the temperature of the sample was changed from 110 °C, where [bmim]Cl was in the liquid state, to 50 °C, where [bmim]Cl was in a supercooled liquid state. The Raman spectrum was measured after keeping the sample for 30 min at each temperature. The Raman spectrum changed meaningfully, though not markedly, when the temperature was decreased. The 600 $\mathrm{cm^{-1}}$ band behaves in parallel with the other two characteristic Raman bands (500 and 700 $\mathrm{cm^{-1}}$) of Crystal (2). The intensities of those three bands increase with decreasing temperature. On the other hand, the 625 $\mathrm{cm^{-1}}$ band of Crystal (1) barely changed. These findings support the interpretation that the Raman bands at 600 and 625 $\mathrm{cm^{-1}}$ originate from the two distinct structures of the [bmim]$^+$ ion. During the course of this experiment, we noticed that the time needed for the [bmim]Cl liquid to be thermally equilibrated was very long when the experiment was initiated by melting a crystalline sample and then temperature was raised. It took more than three hours before a melted sample was thermally equilibrated at 110 °C. It seems that some local structures (probably crystal-like) exist in the liquid [bmim]Cl, giving rise to such a long equilibration time even at a temperature well above the melting point.

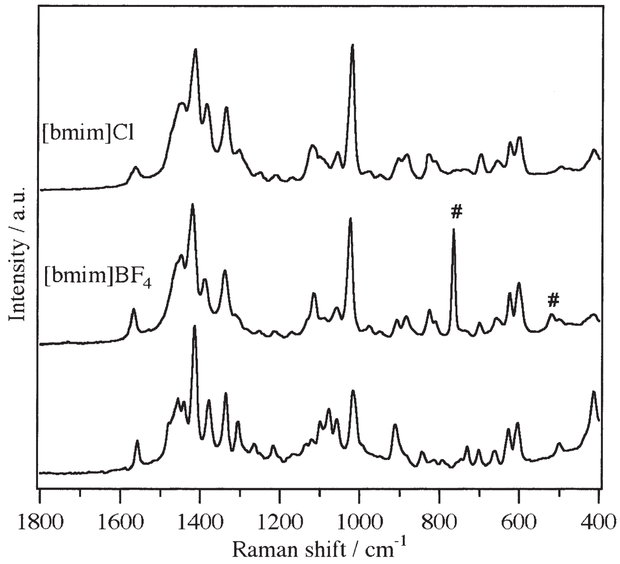

Figure 3. Raman spectra of [bmim]Cl in a supercooled state (top), [bmim]$\mathrm{BF_4}$ (middle) and the synthesized Raman spectrum (bottom, see text). # denotes the $\mathrm{BF_4}^-$ bands.

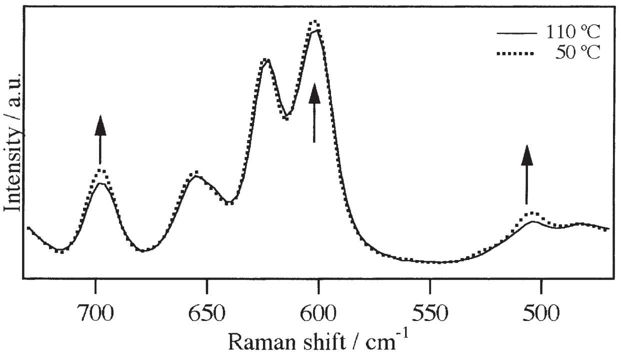

Figure 4. Temperature dependence of the Raman spectrum of liquid [bmim]Cl, when the sample temperature was changed from 110 °C to 50 °C. Arrows indicate the characteristic Raman bands of Crystal (2).

Further X-ray crystallographic and Raman spectroscopic investigations are under way.

The authors are grateful to Professor Akiko Kobayashi of Research Centre of Spectrochemistry, School of Science, the University of Tokyo, for the measurements of the X-ray powder patterns at the SPring-8. This study was supported by a Grant-in-aid for the 21st Century COE Program "Frontiers in Fundamental Chemistry" from the Ministy of Education, Culture, Sports, Science and Technology.

References

1 P. Wasserscheid and W. Keim, *Angew. Chem., Int. Ed.*, **39**, 3772 (2000).
2 A. Elaiwi, P. B. Hitchcock, K. R. Seddon, N. Srinivasan, Y.-M. Tan, T. Welton, and J. A. Zora, *J. Chem. Soc., Dalton. Trans.*, **1995**, 3467.
3 A. G. Avent, P. A. Chaloner, M. P. Day, K. R. Seddon, and T. Welton, *J. Chem. Soc., Dalton. Trans.*, **1994**, 3405.
4 S. Tait and R. A. Osteryoung, *Inorg. Chem.*, **23**, 4352 (1984).
5 K. M. Dieter, C. J. Dymek, Jr., N. E. Heimer, J. W. Rovang, and J. S. Wilkes, *J. Am. Chem. Soc.*, **110**, 2722 (1988).
6 J.-F. Huang, P.-Y. Chen, I.-W. Sun, and S. P. Wang, *Inorg. Chim. Acta*, **320**, 7 (2001).
7 J. S. Wilkes, J. A. Levisky, R. A. Wilson, and C. L. Hussey, *Inorg. Chem.*, **21**, 1263 (1982).

Published on the web (Advance View) May 6, 2003; DOI 10.1246/cl.2003.498