2Pb1-6

Proceedings of Symposium on Ultrasonic Electronics, Vol. 32 (2011) pp. 187-188
8-10 November, 2011

Acoustic study of glass transition of ionic liquids for application to cryoprotective agents

凍結防御剤への応用を目指した音波によるイオン液体のガラス転移の研究

Takahiro Ishii[1†], Takuto Kurokawa[1], Miwa Nakano[1], Harutaka Takayama[1], and Seiji Kojima[1] ([1]Graduate School of Pure and Applied Sciences, University of Tsukuba)

石井　貴大[1†]，黒川　拓都[1]，中野　美和[1]、高山　晴貴[1]，小島誠治[1] (筑波大学 数理物質科学研究科)

1. Introduction

Ionic liquids (ILs) are general term for group of substance in a liquid state around room temperature even though it is only the salts consisting of cations and anions. Recently, their unique natures have been extensively studied, for example, low vaper pressure, low melting point, strong glass-forming tendency[1], ILs solvent as protein[2] etc[3,4]. In this paper, acoustic properies of typical ILs, 1-alkyl-3-methylimidazolium, were studied in order to examine the application of ILs to cryoprotective agents in cryobiology.

2. Experimental

1-Butyl-3-methylimidazolium chloride ([bmim]Cl) and 1-Ethyl-3-methylimidazolium chloride ([emim]Cl) were purchased from Tokyo Chemical Industory and Sigma Aldrich, respectively. The schematic illustration of [bmim]Cl molecule is shown in **Fig. 1**. They were used without further chemical purification. The refractive index is measured using a Metricon Prism Coupler Model 2010. The Acoustic properties were measured by micro-Brillouin scattering spectroscopy as described in ref. 5. The temperature of a sample was controlled by a heating/cooling stage (Linkam) with the temperature stability of ± 0.1 °C.

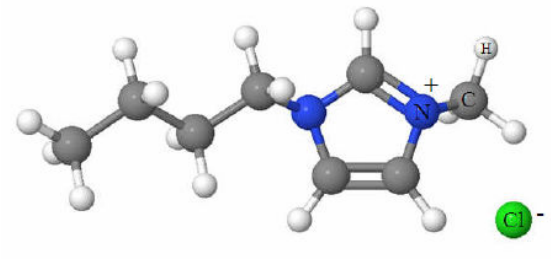

Fig. 1 Schematic illustration of a molecule of 1-Buthyl-3-methylimidazolium

e-mail address: s-tishii@ims.tsukuba.ac.jp

3. Results and Discussion

3.1 Refractive index

The refractive index was measured accurately to determine sound velocity from Brillouin frequency shift. **Table 1** shows the refractive index, concentration and temperature of [bmim]Cl solutions. As the IL concentration increases, the the refractive index of [bmim]Cl solutions increases. While on heating, the refractive index decreases.

Table 1 Values of refractive index of [bmim]Cl aqueous solutions.

[bmim]Cl concentration	298 K	308 K	318 K
30 wt%	1.3895	1.3880	1.3869
40 wt%	1.4103	1.4084	1.4068
50 wt%	1.4300	1.4286	1.4268
60 wt%	1.4494	1.4485	1.4468
70 wt%	1.4785	1.4761	1.4748

3.2 Brillouin scattering

The temperature dependence of Brillouin scattering spectra was measured. Only longitudinal acoustic (LA) mode is observed as shown in **Fig. 2**. On heating form glassy state at 83 K, Brillouin shift shows marked decrease, while the FWHM shows a maximum above a few tens degree above the glass transition temperature T_g.

The temperature dependence of the sound velocity and absorption [bmim]Cl 70 wt% and [emim]Cl 70 wt% is shown in **Fig. 3**. On heating, sound velocity decreases, whereas attenuation factor shows a peak above T_g [6] and then decrease for further heating. Such behaviors indicate a typical structural relaxation as a precursor dynamic process of a liquid-glass transition of structural glass.

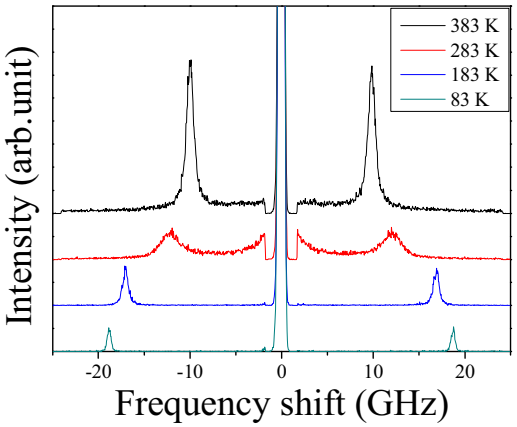

Fig. 2 Temperature dependence of Brillouin scattering spectra of [emim]Cl 70 wt% aqueous solution.

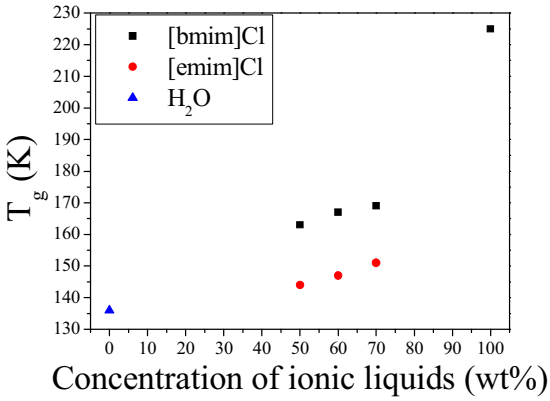

Fig. 4 Concentration dependence of glass transition temperature T_g of [bmim]Cl and [emim]Cl aqueous solution. T_g of H_2O [7] is also plotted.

The relation between the IL concentration of ionic liquids and the glass transition temperature T_g is shown in **Fig. 4**. The range of glass transition temperatures is similar to that of typical cryoprotective agents. For pure water, T_g in literature[7] is about 140 K, and T_g increases as the IL concentration increases. While, at concentrations below 50 wt% the crystallization tendency is enhanced and it is difficult to undergoes into a glassy state within the available cooling rate of the present cooling apparatus.

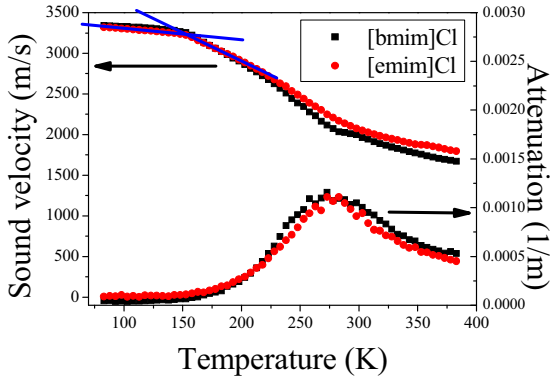

Fig. 3 Temperature dependences of sound velocity and attenuation of [bmim]Cl 70 wt% and [emim]Cl 70 wt% aqueous solution.

4. Conclusion

The aqueous solutions of ILs are studied by micro-Brillouin scattering spectroscopy to clarify their glass-forming tendency at low temperatures. Temperature and concentration dependences of refractive index are also determined accurately. The [bmim]Cl and [emim]Cl aqueous solutions show typical structural relaxation above T_g, and undergo a liquid-glass transition at low temperatures. Our results verify that the glass transition behavior of ILs of 1-alkyl-3-methylimidazolium is very similar to typical cryoprotective agents such as glycerol[8].

References

1. O. Yamamuro, Y. Minamimoto, Y. Imamura, S. Hayashi, H. Hamaguchi, Chem. Phys. Lett. **423** (2006) 371.
2. J. A. Laszlo, D. L. Compton, J. Mol. Catalysis B: Enzymatic **18** (2002) 109.
3. H. Ohno, K. Fukumoto, Acc. Chem. Res. **40** (2007) 1122.
4. Z. Wang, L. Dang, Y. Han, P. Jiang and H. Wei, J. Agric. Food Chem. **58** (2010) 5444.
5. S. Kojima, Jpn. J. Appl. Phys. **49** (2010) 07HA01.
6. J. Kieffer, Phys. Rev. B. **50** (1994) 17.
7. V. Velikov, S. Borick, and C. A. Angell, Science, **294** (2001) 2335.
8. S. Jabrane, J. M. lettofe, J. J. Counioux, P. Cloudy, Thermochimica Acta. **290** (1996) 31.