

Glass Transitions and Low-frequency Dynamics of Room-temperature Ionic Liquids

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The glass transition and boson peak are two major research subjects in current physics of complex systems. We have studied these subjects using molecular systems for a long time and recently started the experiments on a new type of glass-former, “ionic liquids”.

Ionic compounds usually have melting temperatures T_m higher than room temperature because of their strong and long-range interionic interactions. Recently, it was found that a series of organic ionic compounds have T_m lower than room temperature and they are called “room temperature ionic liquids” or simply “ionic liquids”. These compounds have various useful properties as a solvent, e.g., low vapor-pressure, amphiphilicity, etc. We have measured heat capacities and neutron scattering spectra of some salts of 1-butyl-3-methylimidazolium ion $[bmim]^+$, which is a typical cation of ionic liquids [1].

Fig.1 shows the heat capacities of $[bmim]Cl$ and $[bmim]FeCl_4$. The former compound is important as a prototype ionic liquid and the latter is recently remarked as a magnetic ionic liquid [2]. A glass transition with a large C_p jump was found at 225 K in $[bmim]Cl$ and 182 K in $[bmim]FeCl_4$. The temperature dependence of configurational entropy demonstrated that both ionic liquids are of fragile liquids as molecular liquids. This result was quite unexpected since the ionic interaction generally causes ordering of liquid structure.

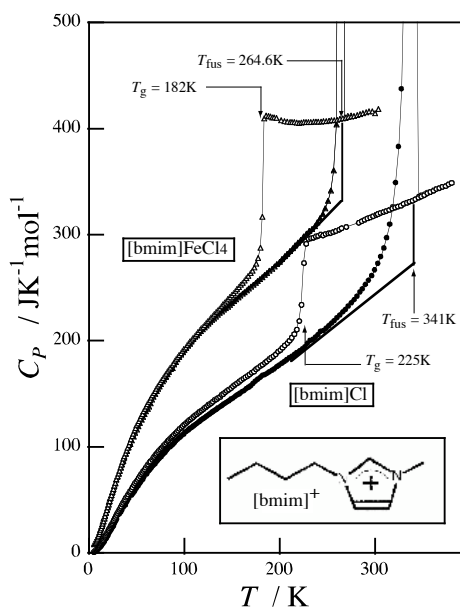


Fig. 1 Heat capacities of $[bmim]Cl$ and $[bmim]FeCl_4$ measured by an adiabatic calorimeter. Open symbols denote the data of glassy and liquid states and closed symbols those of crystalline one. T_g and T_{fus} represent glass transition and fusion temperatures, respectively.

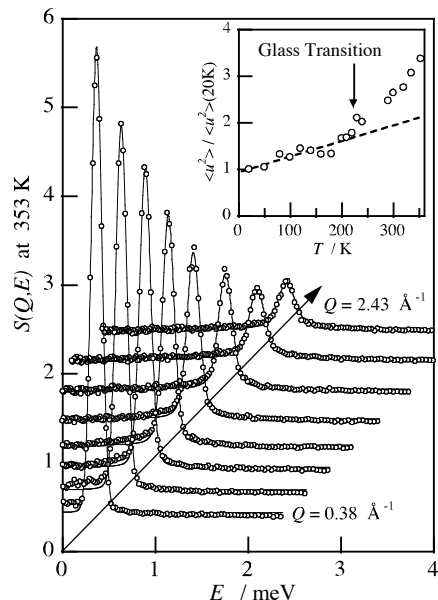


Fig. 2 Quasielastic neutron scattering spectra of $[bmim]Cl$ measured at 353 K for several momentum transfer values on AGNES spectrometer of ISSP. The data are fitted to Lorentzian functions to obtain self-diffusion coefficients. The inset gives the temperature dependence of the mean square displacements divided by the value at 20 K.

In both ionic liquids, quasielastic neutron scattering was observed as shown in Fig.2. The inset reveals an anomalous increase of $\langle u^2 \rangle$ showing an onset of some fast relaxation process around T_g . This is similar to the fast β relaxation observed in molecular and polymer glasses. The activation energy calculated from the temperature dependence of self-diffusion coefficients is 11 kJ/mol, which is considerably smaller than that of the intramolecular rotation of butyl-group in organic molecules, 13-15 kJ/mol.

Both calorimetric and neutron scattering data clearly revealed that the $[bmim]^+$ ions are highly disordered and flexible, and entropically stabilizing ionic liquid phase. In the workshop, we will show the results also on the boson peaks of ionic glasses and give a systematic comparison between ionic and molecular glasses for both glass transitions and boson peaks.

References

- [1] O. Yamamuro, Y. Inamura, S. Hayashi, and H. Hamaguchi, Chem. Phys. Lett., to appear.
- [2] S. Hayashi and H. Hamaguchi, Chem. Lett. 33 (2004) 1590.