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Ionic Transport Properties and Structures of Room Temperature Ionic Liquids

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Introduction

Room temperature ionic liquids (RTILs) possess unique physicochemical properties, such as negligible vapor pressure, non-flammability, high thermal, chemical and electrochemical stability, and high ionic conductivity. It is not therefore surprising that ionic liquids, while attracting significant attention of the academicians of multidisciplinary areas, have been studied to find practical applications, such as batteries, capacitors, fuel cells, solar cells, and actuators. However, the fundamental understanding of a relationship between microscopic dynamics of the ions and the ionic structures is essential for molecular (ionic) design of RTILs to achieve desirable physical and chemical properties.

In this study, ion transport behaviors of common RTILs were investigated by changing the cationic and anionic structures. The determination of self-diffusion coefficients by PGSE-NMR method is an effective strategy to explore the ion transport properties and the ion association/dissociation in the ionic liquids, which may be considered as the most important propertiy for the unique phenomena. We will present experimental results on the relationship between the ionic structures and ionicity determined by the combination of the PGSE-NMR diffusion and UV-visible spectral polarity measurements.

Experimental

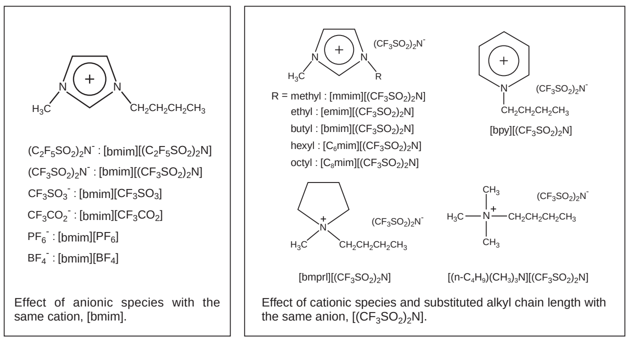
The RTILs with different structures, by changing cationic and anionic structures, were synthesized as shown in Figure 1. The physicochemical properties, such as thermal properties, density, viscosity, ionic conductivity, and self-diffusion coefficients of cation and anion, have been studied by correlating with the change in the anionic structure for a fixed cationic species, and *vice versa*, to provide a deep insight into the relationship with the ionic structure. The donor ability of anion and the acceptor ability of cation were estimated by UV-visible spectral polarity measurements.

Results and Discussion

The self-diffusion coefficients, individually determined by PGSE-NMR for the cation and anion, exhibit higher values for the cation, compared to the anion over a wide temperature range. The summation of the cationic and anionic diffusion coefficients for the RTILs well contrasts to the viscosity data. The analysis of the diffusivity and the fluidity by the use of the Stokes-Einstein equation and a comparison of the self-diffusion coefficients of each ionic species indicate that the ionic diffusion in the ionic liquids appear to have significant influence from the factors like the ionic size, shape and the state of aggregation.

The influence of ionic association is further revealed from the ratio of the molar conductivity obtained from impedance measurement (Λ_{imp}) and that calculated from the ionic diffusivity using Nernst-Einstein equation (Λ_{NMR}), which The ratio, $\Lambda_{imp}/\Lambda_{NMR}$, provides quantitative information on the ions contributing to ionic conduction as the diffusion component. The ratio for the [bmim] based RTILs follows the order [PF_6] > [BF_4] > [$(C_2F_5SO_2)_2N$] > [$(CF_3SO_2)_2N$] > [CF_3SO_3] > [CF_3CO_2] (see Figure 2). In the case where the anionic structure is fixed as [$(CF_3SO_2)_2N$] and the cationic skeletal structures were changed by keeping the same butyl-substituent, the ratio follows the order [bmprl] > [$(n\text{-}C_4H_9)(CH_3)_3N$] > [bpy] > [bmim]. With increasing the alkyl chain length of [Rmim][$(CF_3SO_2)_2N$], the ratio further decreases. The difference in the $\Lambda_{imp}/\Lambda_{NMR}$ represents the difference in ionic character; in other words, "ionicity" of the ionic liquids. By using the difference of ionicity, some of physical properties of the [Rmim][$(CF_3SO_2)_2N$] can be explained.

The order of the ionicity for [bmim] based RTILs is in good agreement with the anionic donicity determined by solvatochromism, and also correlates with ^{1}H-NMR chemical shift. Correspondingly, the ionicity of the butyl substituted cation based RTILs with [$(CF_3SO_2)_2N$] is dominated by the acceptor ability of cation.



Effect of anionic species with the same cation, [bmim].

Effect of cationic species and substituted alkyl chain length with the same anion, [$(CF_3SO_2)_2N$].

Figure 1 Molecular Structures of RTILs.

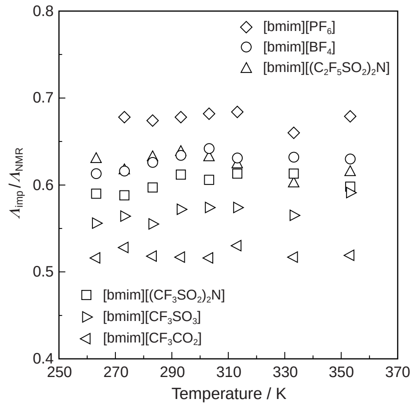


Figure 2 Molar Conductivity Ratios ($\Lambda_{imp}/\Lambda_{NMR}$) for [bmim] based RTILs plotted against temperature.

References

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