

Ethanol Cluster Formation in Imidazolium-based Ionic Liquids

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Room-temperature ionic liquids may be miscible with not only polar solvents, but also non-polar solvents, despite electrolytes. The microscopic interactions among the ionic liquid-cation, -anion, and molecular liquid contribute to the miscibility. We are interested in how the non-polar alkyl chain of molecular liquids affects the mixing state of imidazolium-based ionic liquids with molecular liquids. Imidazolium-based ionic liquids, 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide, $C_n\text{mImTFSA}$ (n gives the alkyl chain length), has the alkyl chain with various lengths. In contrast, aliphatic alcohols, such as methanol and ethanol, also involve the different alkyl chain lengths. The interaction between the ionic liquid-alkyl chain and the alcohol-alkyl chain should influence the mixing state of ionic liquid with alcohol.

In the present investigation, we have observed the mixing state of methanol and ethanol with $C_n\text{mImTFSA}$ with $n = 2, 4, 6, 8, 10,$ and 12 using small-angle neutron scattering (SANS) technique on the mesoscopic scale. Based on the SANS results, the effects of the alkyl chain of alcohol molecules on the mixing with the ionic liquids have been discussed.

The ionic liquids $C_n\text{mImTFSA}$ synthesized were mixed with deuterated methanol $\text{MeOH-}d_4$ and ethanol $\text{EtOH-}d_6$ at various alcohol mole fraction x_A . SANS experiments were performed on the binary solutions at 298.2 K using the SANS-U spectrometer. The sample solutions were kept in a quartz cell with 2 mm-thickness. The camera lengths were set at 1 and 4 m. The accumulation times for the scattered neutrons at the camera lengths were 10 and 60 min, respectively. The transmittance of the solutions was determined at the camera length of 8 m for 2 min. The observed scattering intensities were corrected for the absorbance, background, and incoherent scatterings.

Fig. 1 shows the representative SANS profiles

of $C_4\text{mImTFSA-EtOH-}d_6$ solutions as a function of x_A . The SANS intensities for all the solutions are observed, but not strong. Thus, the ionic liquids weakly forms clusters in the alcohol solutions. The profiles were fitted by the Ornstein-Zernike equation to estimate the correlation length ξ . The x_A dependence of the ξ values is depicted in Fig. 2. Interestingly, the value for the $\text{MeOH-}d_4$ system increases with elongating the alkyl chain, while that for the $\text{EtOH-}d_6$ system decreases with the alkyl chain. The cluster formation of $C_n\text{mImTFSA}$ is surely affected by the alcohol alkyl chain. The present results reveal that the alkyl chain of the ionic liquid cation more easily interacts with ethanol than methanol even by just one longer ethyl group.

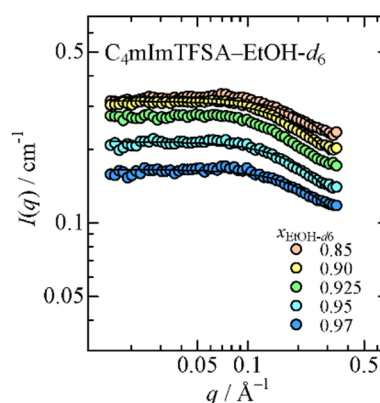


Fig. 1. SANS profiles of $C_4\text{mImTFSA-EtOH-}d_6$.

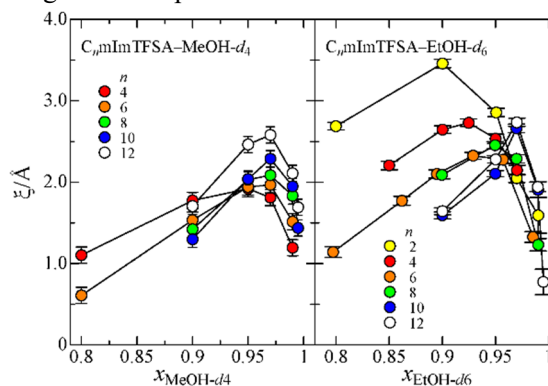


Fig. 2 Correlation lengths ξ for $C_n\text{mImTFSA-MeOH-}d_4$ and $-EtOH-}d_6$.