Dynamics of the mixture of deep eutectic solvent and water

K. Yoshida[A], T. Nagai[A], S. Shiegto[A], T. Takekiyo[B], Y. Ohmasa[C], H. Akiba[C], O. Yamamuro[C]

[A] *Fukuoka Univ.*, [B] *National Defense Academy*, [C] *ISSP-NSL, Univ. of Tokyo*

Deep eutectic solvents (DES) are mixtures of hydrogen-bonding acceptor compounds and hydrogen-bonding receptor compounds (both solids) in specific ratios and are liquid at room temperature. In addition to having advantages similar to ionic liquids, they are highly environmentally compatible. The disadvantage of DES for applications is high viscosity. In practical use, it is often mixed with water to decrease the viscosity.

In this study, we investigated the dynamics of the mixture of reline (mixture of choline chloride and urea), a representative DES, and water at various ratios. The molecular ratio of choline chloride and urea is 1:2. The DES was mixed with H_2O at 1, 11, 21, and 60 wt% of water (DESh01, h11, h21, and h60). Instead of urea and H_2O, urea-d_4 and D_2O were used for preparation of deuterated samples. The contents of water are 21 and 60 wt% (DESd21 and d60) for deuterated samples.

The chemical formulas are shown as follows:

choline chloride $[(CH_3)_3NCH_2CH_2OH]Cl$

urea $(NH_2)_2CO$

urea-d_4 $(ND_2)_2CO$

The sample solutions were sealed in double aluminum cylindrical cell. The thickness of the sample is 0.2, and 0.5 and 1 mm for protonated and deuterated samples, respectively.

Quasi-elastic neutron scattering (QENS) spectra were obtained using an AGNES spectrometer installed in the research reactorJRR-3 owned by the Japan Atomic Energy Agency (JAEA). The energy resolution is 120 μeV, and the Q range is 0.38-2.63 Å^{-1}. The spectrum of DESh01 at 3 K was used as a resolution function. The measuring temperature was from 288 K to 328 K.

Dynamic structure factors obtained from QENS measurement were fitted with three Lorentzian functions. Fig. 1 shows the Q-dependence of HWHM of the narrowest component for DESd60 at various temperatures. The jump diffusion model was applied to obtain the diffusion constant and the residence time. The HWHM of the widest component is about 5 meV and that of the middle component is about 0.5 mV. These do not show Q dependence. These could be assigned to the methyl group rotation of choline and water rotational motion. For DESh01, the spectrum was fitted with two Lorentzian functions. The HWHM of the narrower component for DESh01 is considerably small.

The diffusion constant decreased with decreasing water content. This is consistent with the fact that the viscosity increases with decreasing water content. Compared with the result of deuterated sample, the temperature dependence of the diffusion constant for protonated samples is larger than that for deuterated samples at the same water content. This is because water molecules bind to other water molecules and urea via hydrogen bonds.

MD simulation study is in progress to reveal the details of the dynamics of DES-water mixtures.

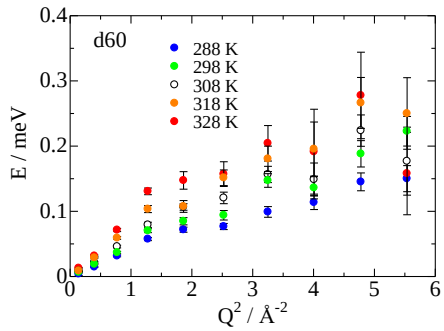

Fig. 1 Q-dependence of HWHM of the narrowest component for DESd60 sample.