Intermolecular Dynamics of Lithium Salt-Amide Deep Eutectic Solvents

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Deep eutectic solvents (DESs) are mixtures of two or more solids that exhibit a melting point far lower than their individual components, making them a liquid at room temperature. Here, we have investigated the intermolecular dynamics, including intermolecular vibration and orientational dynamics, of five DESs based on lithium bis(trifluoromethylsulfonyl)amide (Li[NTf$_2$]) and organic amides, using dynamic Kerr effect spectroscopy: femtosecond Raman-induced Kerr effect spectroscopy (fs-RIKES)[1] and subpicosecond optical Kerr effect spectroscopy (ps-OKES).[2] The former one was used for the intermolecular vibrations and the latter one was used for the collective orientational dynamics. The five organic amides were acetamide (AcAm), propanamide (PrAm), *N*-methylacetamide (NMAc), butyramide (BuAm), and urea. The DESs were prepared by mixing Li[NTf$_2$] and organic amides at a 1:3 molar ratio. In addition, liquid properties such as density, surface tension, and viscosity were measured and compared with the spectroscopic results.

The low-frequency spectra obtained from the fs-RIKES measurements of different DES systems exhibited differences in the line shape and peak frequency. For example, Li[NTf$_2$]/NMAc showed a trapezoidal spectrum, while other DESs exhibited a bimodal one. In the bimodal spectrum, the shoulder peak at ~20 cm^{-1} was mainly due to the cross-term and anion, and the high-frequency band at ~60 or 70 cm^{-1} was attributed to the intermolecular amide hydrogen bonding (N–H···O=C). The peak frequency of the higher frequency bands of Li[NTf$_2$]/urea and Li[NTf$_2$]/AcAm were 71.0 and 69.2 cm^{-1}, respectively, whereas Li[NTf$_2$]/PrAm and Li[NTf$_2$]/BuAm showed peaks at ~60 cm^{-1}. The first moments of the low-frequency spectral band of Li[NTf$_2$]/urea and Li[NTf$_2$]/AcAm were also higher than those of the other three DESs. These findings suggest that the microscopic intermolecular interactions in the urea- and acetamide-based DESs are comparatively stronger than the other three DES systems. The surface tension values of the present DESs were also correlated with this tendency. Furthermore, the analysis of intramolecular vibrational bands of [NTf$_2$]$^-$ anion showed that the population of transoid [NTf$_2$]$^-$ was slightly higher in Li[NTf$_2$]/urea. This indicates that the lithium cation solvation via hydrogen bonds is larger in Li[NTf$_2$]/urea than in the other four DESs. Regarding the collective orientational dynamics, the ps-OKES results revealed that the slow relaxation dynamics depend on organic amides. However, the slow relaxation time did not exhibit a linear correlation with viscosity and thus did not follow the Stokes-Einstein-Debye hydrodynamic model.

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