Effects of Formamides on Intermolecular Vibrations of 1-Methyl-3-octylimidazolium Tetrafluoroborate

([1]*Department of Chemistry, Chiba University,* [2]*Graduate School of Science and Engineering, Saga University,* [3]*Faculty of Science and Engineering, Saga University*) ○Masatoshi Ando,[1] Yue Peng,[1] Atsuya Tashiro,[2] Masahiro Kawano,[2] Toshiyuki Takamuku,[3] Hideaki Shirota[1]

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In this study, we have investigated the low-frequency spectra of 1-methyl-3-octylimidazolium tetrafluoroborate ([MOIm][BF_4]) mixtures with formamide (FA), *N*-methylformamide (NMF), and *N*,*N*-dimethylformamide (DMF) using femtosecond Raman induced Kerr effect spectroscopy (fs-RIKES).[1,2] Because these formamides have different hydrogen-bonding (HB) abilities, we can examine the effects of the hydrogen bonds between formamides and [MOIm][BF_4] on the intermolecular vibrations in detail.

Figure 1 shows the low-frequency spectra of [MOIm][BF_4] mixtures with FA, NMF, and DMF. As increasing the molecular liquid (ML) mole fraction X_{ML}, the spectral intensity for the [MOIm][BF_4] mixtures gradually increased. In neat liquids, FA has a peak at 100 cm^{-1} and a shoulder at 200 cm^{-1} and NMF also has a shoulder at 130 cm^{-1}. Quantum chemical calculations for clusters of FA and NMF have reported that FA and NMF have the vibrational bands of linear HB network at 100 cm^{-1} and FA also has those of two-dimensional HB network at 200 cm^{-1}.[3] Thus, the peak and shoulder of FA at 100 and 200 cm^{-1} and the shoulder of NMF at 130 cm^{-1} observed in this study can be attributed to the HB vibrations. The spectral shapes of the mixtures gradually changed from neat [MOIm][BF_4] to each formamide liquid with increasing X_{ML}.

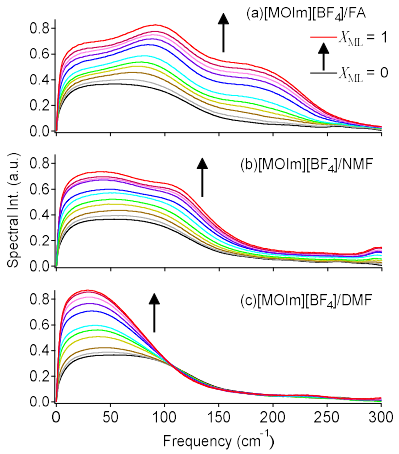

Figure 1. Low-frequency spectra of [MOIm][BF_4] mixtures with (a) FA, (b) NMF, and (c) DMF.

To characterize the X_{ML} dependence of the low-frequency spectra, the plots of the first moment M_1, which is the center frequency of the spectrum, vs. X_{ML} for the mixtures are shown in Figure 2. As increasing X_{ML}, the M_1 of the low-frequency spectra for the [MOIm][BF_4]/FA increased and that for the [MOIm][BF_4]/DMF decreased. FA has the vibrational bands of the two-dimensional HB network even at low X_{ML}, so the M_1 has shifted to the higher frequency side. DMF may invade to the polar region in [MOIm][BF_4] and make the interionic interaction weaken. On the other hand, the [MOIm][BF_4]/NMF showed almost no concentration dependence of the M_1 in $X_{ML} \leq 0.7$ but the M_1 increased in $X_{ML} \geq 0.8$. This X_{ML} dependence is similar to those of [MOIm][BF_4] mixtures with methanol, acetonitrile, and dimethyl sulfoxide.[4] It implies that NMF does not much influence on the ionic network of [MOIm][BF_4] in $X_{ML} \leq 0.7$ but break it in $X_{ML} \geq 0.8$.

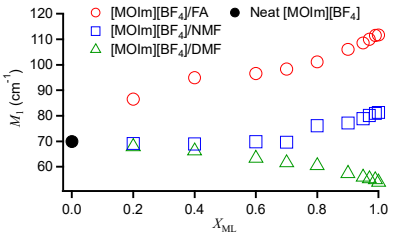

Figure 2. Plots of M_1 vs. X_{ML} for [MOIm][BF_4] mixtures with FA, NMF, and DMF.

References

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