

## Structures of [BMIM]I and [BMIM]BF<sub>4</sub> studied by ATR and Raman spectroscopy

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Structures of ionic liquids with different anions were studied by Attenuated Total Reflection (ATR) infrared absorption and Raman spectroscopy using the mixtures of 1-butyl-3-methylimidazolium iodide ([BMIM]I) and [BMIM]BF<sub>4</sub> ionic liquids with water. As in Fig.1 the ATR spectrum of [BMIM]I in CH<sub>x</sub>(x=1,2,3) vibration region between 2800 cm<sup>-1</sup> and 3200 cm<sup>-1</sup> is very different from that of [BMIM]BF<sub>4</sub>. The spectrum of [BMIM]I in this region has much more absorption, and looks like lying on top of some broad feature centered around ~3050 cm<sup>-1</sup>. All the spectral features in this region should have come from the butyl chain and the imidazolium ring of the cation. This difference is very unusual as both [BMIM]I and [BMIM]BF<sub>4</sub> consist of same cation, and the number densities of cations per unit volume are also very similar. We propose the relative position of anion with respect to the cationic imidazolium core is responsible for this difference in the vibrational spectra: for [BMIM]BF<sub>4</sub>, the BF<sub>4</sub><sup>-</sup> anion is on top of imidazolium ring, while for [BMIM]I the I<sup>-</sup> anion is in the plane of imidazolium ring along the C(2)-H bond direction, as proposed for the similar ionic liquid [1,2]. The strong electric field from the anion at the side (along the C(2)-H bond direction) is creating the asymmetric distribution of  $\pi$ -electrons in the imidazolium ring, which works to increase the dipole strength of the CH-bond dramatically. The Raman spectra in this region showed similar behavior to the ATR spectra. We then used Raman spectroscopy to probe the gauche- and trans conformations of the butyl chain around 620 cm<sup>-1</sup> [3]. For pure samples, gauche- and trans peaks were similar in strength for [BMIM]BF<sub>4</sub>, while for [BMIM]I the trans peak was much bigger. This difference could also have originated from the relative position difference of the anion with respect to the butyl chain. Both the ATR and the Raman spectra of [BMIM]BF<sub>4</sub> and [BMIM]I looked after the other as we added more water to the solution and became indistinguishable for very dilute mixtures.

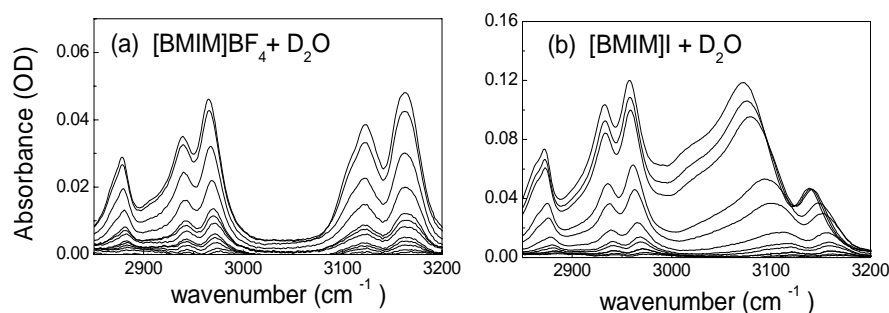


Fig.1. ATR absorption spectra of (a) [BMIM]BF<sub>4</sub> + D<sub>2</sub>O mixture, (b) [BMIM]I + D<sub>2</sub>O mixture. D<sub>2</sub>O concentration increases from top to bottom in each figure.

### References

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