Alkyl chain length dependence of conformational distribution in ionic liquids.

([1]*Graduate School of Science and Engineering, Doshisha University*, [2]*Faculty of Science and Engineering, Doshisha University*) ○Hiroki Sumida,[1] Yoshifumi Kimura,[1,2] Takatsugu Endo[2]
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Ionic liquids (ILs) are defined as salts with melting point below 100 °C. Since the melting point is the crucial physical property for ILs, numerous investigations have been made to answer why ionic liquids have such a low melting point as salts. Thermodynamically, melting point (T_m) is expressed by $T_m = \Delta_{fus}H/\Delta_{fus}S$ where $\Delta_{fus}H$ is the fusion enthalpy and $\Delta_{fus}S$ is the fusion entropy. Contrary to the conventional discussion[1)], we have found that $\Delta_{fus}S$ plays a more important role than $\Delta_{fus}H$ in lowering melting point of ILs[2)], i.e., large $\Delta_{fus}S$ of ILs drastically lowers their T_m. Since most ILs have flexible alkyl chains, the conformational entropy (S_{conf}) in the liquid state may contribute to the large $\Delta_{fus}S$ of ILs. In this research, conformations of the alkyl chain, e.g., trans, gauche, gauche', were analyzed by molecular dynamics (MD) simulations and NMR spectroscopy to estimate S_{conf} of ILs in the liquid state. 1-Alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([$C_n$mim][NTf_2]) were used for both simulations and experiments.

First, S_{conf} of the ILs with different alkyl chain lengths in the liquid states were estimated from *NPT* MD trajectories (Fig. 1. (a)). The black line in the figure represents maximum S_{conf} where the population of all conformations of the alkyl chain exists equally. Estimated S_{conf} in the ILs (red circles) was always lower than the maximum S_{conf} and the gap was widened when the alkyl chain was lengthened. It was found that the small S_{conf} originated from the large population of the trans conformation (e.g., Fig. 1. (b)). A similar result was also obtained from J-coupling constants of NMR experiments. NMR measurement suggested that strong interactions among the alkyl chains were feasible in the trans conformation.

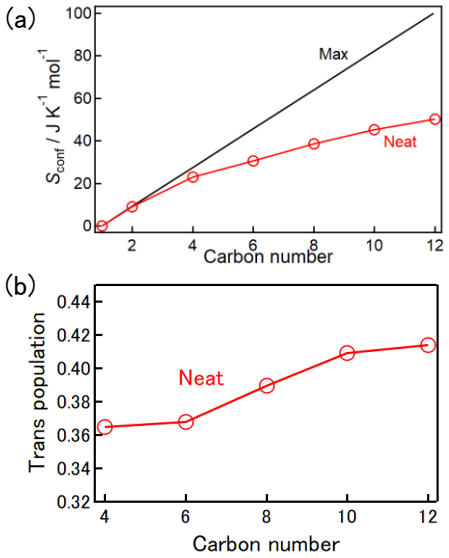

Fig. 1. (a) S_{conf} versus the carbon number of the alkyl chain in the IL cation. (b) Population of the trans conformation of N-C-C-C versus the carbon number of the alkyl chain in the IL cation.

1) E. A. Turner, *et al., J. Phys. Chem. A* **2003**, 107, 13, 2277. 2) T. Endo, *et al., 11th Symposium on Ionic Liquids in Japan* **2021**, 2O12.