

Rotational dynamics in $[C_n\text{mim}][\text{PF}_6]$ ionic liquids

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We performed classical molecular dynamics simulation on 1-alkyl-3-methylimidazolium hexafluorophosphate ionic liquids (ILs). The bonded parameters of potential are based on OPLS-AA force field, and nonbonded parameters utilize Lennard-Jones formula with the Lorentz-Berthelot combining rules for different atomic pairs. All the force field parameters are taken from Zhong *et al.*, [1] where the hydrogens on the alkyl chain are incorporated within the carbon but the ones on the imidazolium ring are sustained. All the computer simulations are conducted by open source code package LAMMPS [2]. The simulated systems include 1000 ionic pairs, which are contained in a cubic box.

Important relaxation modes in these ILs include the translational dynamics of the center of mass, rotational dynamics of the imidazolium ring, and orientational dynamics of the alkyl chain. In our simulation study, we found the orientational dynamics of the alkyl chain is the slowest relaxation mode in the ILs with long alkyl chain, and accounts for the slow structural relaxation in the liquid. In order to highlight the role played by the rotational dynamics of the alkyl chain, we change the alkyl-chain length, i.e., in $[C_n\text{mim}][\text{PF}_6]$ ($n = 2, 4, 6, 8, 10, 12$) ILs.

Upon cooling down the $[C_n\text{mim}][\text{PF}_6]$ ILs, structural relaxation time drastically increases with temperature decreasing. At the same temperature, the structural relaxation time also increases with alkyl-chain length. Transport coefficients, including self diffusion coefficient and shear viscosity, are calculated at dif-

ferent temperatures with the variation of alkyl chain. Stokes-Einstein relation, which connects diffusivity and viscosity in liquids, found to be broken down at low temperatures. The critical temperature points for the onset of the breakdown is found to decrease with the increment of alkyl chain length.

In order to reveal the coupling and decoupling behavior between the translational and rotational dynamics in these ILs. We measured the characteristic time for the translational dynamics via self-intermediate scattering function, and the time scale for rotational dynamics via self-correlation function of rotational vectors in terms of second Legendre polynomial.

At high temperatures, the translational and rotational dynamics couple with each other. But they decouple with each other at low temperatures. The critical temperatures for the decoupling behavior is found to decrease with the alkyl-chain length. This decoupling behavior can possibly be connected with the breakdown of Stokes-Einstein relation. Further analysis is required to reveal the underlying mechanism.

References

- [1] X. J. Zhong, Z. P. Liu, and D. P. Cao: *J. Phys. Chem. B* **115** (2011) 10027.
- [2] S. Plimpton: *J. Comput. Phys.* **117** (1995) 1.