The role of entropy in the description of relaxation dynamics of ionic liquids

The molecular dynamics of glass-forming systems is one of the most striking and still unsolved issues in the field of condensed-matter physics. The study of the correlation between the glass formers' dynamics and thermodynamics is an integral approach to this problem. The present thesis addresses the role of entropy, a fundamental thermodynamic quantity reflecting the degree of disorder of the systems, in the description of dynamical properties of ionic liquids in terms of classical Adam-Gibbs theory and the recently established density scaling law.

In the framework of Adam-Gibbs theory, I investigate the relations between the dc-conductivity (σ_{dc}), configurational entropy (S_c) and excess entropy (S_e) of several imidazolium-based ionic liquids. Meanwhile, I also study the connection between shear viscosity (η) and the excess entropy. It turns out that the Adam-Gibbs relation, $\log_{10}(\sigma_{dc}) \propto (TS_c)^{-1}$, does not work when the broad temperature range is considered. On the other hand, the use of excess entropy leads to a satisfactory linear relation between $\log_{10}(\sigma_{dc}$ or $\eta)$ and $(TS_e)^{-1}$ in the entire supercooled range. Additionally, the generalized Adam-Gibbs model, $\log_{10}(\sigma_{dc}) \propto (TS_c^{\alpha})^{-1}$, successfully describes the experimental data of σ_{dc} and S_c with the determined parameter $\alpha < 1$, which indicates that S_c is insufficient to govern the conductivity.

Moreover, based on the recently established 'density-scaling' relation that $x = f(TV^{\gamma_x})$ (where x represents any of the physical variables quantifying the molecular dynamics or thermodynamics, V is the specific volume, T is the temperature, and γ_x is the scaling exponent), the density scaling behavior of dc-conductivity and entropy of 1-ethyl-3-methylimidazolium diethylphosphate ([EMIm][DEP]) has been studied. I found that the scaling exponent of dc-conductivity is constant in a broad range covering volume changes of 13%, while the scaling exponent of entropy being equal to the Grüneisen parameter (γ_G) is a linear function of entropy. Such entropy scaling behavior is proved to be also valid in other ionic liquids within different structures and thus strength of interactions between ions. Notably, the generated slope shows a close relation to the typical interactions (van der Waals and Coulomb forces and H-bond) existing in ionic liquids.

The results presented in this dissertation have been published in the following publications:

1. Shinian Cheng, Małgorzata Musiał, Zaneta Wojnarowska, and Marian Paluch, *The relation between molecular dynamics and configurational entropy in room temperature ionic liquids: Test of Adam-Gibbs model*, J. Chem. Phys. 2020, 152, 091101.

2. Shinian Cheng, Małgorzata Musiał, Zaneta Wojnarowska, K.L. Ngai, Johan Jacquemin, and Marian Paluch, *Universal scaling behavior of entropy and conductivity in ionic liquids*, J. Mol. Liq. 2020, 316, 113824.

3. Shinian Cheng, Zaneta Wojnarowska, Małgorzata Musiał, and Marian Paluch, *Correlation between configurational entropy, excess entropy, and ion dynamics in imidazolium-based ionic liquids: Test of the Adam-Gibbs model*, 2021, J. Chem. Phys. 154, 044502.

4. Shinian Cheng, Małgorzata Musiał, Zaneta Wojnarowska, Adam P. Holt, Charles M. Roland, Eric Drockenmuller, and Marian Paluch, *Structurally related scaling behavior in ionic systems*, J. Phys. Chem. B 2020, 124 (7), 1240.