

The Liquid-Liquid Phase Transition in Ionic Liquids at Ambient and Elevated Pressure

Abstract: -

As one of the most intriguing physical phenomena, liquid-liquid phase transition (LLT) between two liquid states of single-component material is strategically significant in the field of condensed matter physics. It has attracted considerable attention recently due to its potential applications in various areas. The present thesis investigates the LLT phenomenon in a series of phosphonium ionic liquids (ILs) using calorimetry, dielectric spectroscopy, and other techniques (rheology, Raman measurements, small-angle X-Ray scattering). The effects of different IL structures on LLT are analyzed, focusing on both cation and anion variations. By tailoring the alkyl chain of trihexyl-tetradecyl-phosphonium ($[P_{666,14}]^+$) cation, it demonstrates that the C_{14} alkyl chain is the critical length driving the generation of nonpolar local domains and thus observing two distinct supercooled states in the single-component system (LLT). In contrast, although there is no calorimetric evidence of LLT in the case of ILs with $[P_{666,m}]^+$ ($m=2,6,8,12$), their ion dynamics show similar changes to LLT in Stickel analysis near the liquid-glass transition, and the nanoscale ordering still occurs.

On the other hand, anions change in $[P_{666,14}]^+$ -based ILs subtly affects the LLT behavior. Specifically, the ion dynamics reveal anomalous behavior during LLT for all examined ILs, i.e., the conductivity relaxation times τ_σ are significantly longer, and their distribution gets broader; however, this signature of LLT occurs at slightly different τ_σ being anion specific. However, when $[P_{666,14}]^+$ was combined with bulky anions (i.e., $V_{vdW} > 0.2 \text{ nm}^3$), the LLT was prevented and could not be directly detected by calorimetry scanning and dielectric spectroscopy. Furthermore, ion dynamics follows the typical behavior of ion glass-formers in a supercooled liquid state, i.e., the temperature dependence of the conductivity relaxation time ($\log \tau_\sigma(1000/T)$) obeys the Vogel–Fulcher–Tammann (VFT) law, and the shape of the conductivity relaxation process satisfies the time-temperature superposition (TTS) rule.

Furthermore, the decoupling between ion diffusion and structural dynamics has been detected for the first time in neat aprotic ionic liquids due to the occurrence of LLT. The self-assembly of liquid 2 is suggested as the physical origin behind this phenomenon and can be tuned by pressure. Pressure-induced nanostructure of liquid 2 depends on anion size leading to different pressure effects on ion transport. In addition, the time scale of relaxation dynamics of examined aprotic ILs under high pressure is sample-dependent; however, it exhibits an isochronal behavior at LLT, i.e., $\tau_\sigma(T_{LL}, P_{LL})$ remains constant for a given system. The pressure sensitivity and entropy fluctuations offer the possibility to estimate specific volume changes during LLT and suggest that the order parameter controlling LLT may not be density. It is worth mentioning that some other interesting physical phenomena were also found to exist in the studied ILs, such as polyamorphism, indicating two or more amorphous states, and the inflection point in pressure dependence of relaxation dynamics. These results provide insight into the nature of LLT phenomenon and diverse opportunities for designing highly effective electrolytes that utilize ionic liquids with self-assembly properties.

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

Beibei Yu

1. **Beibei Yao**, Marian Paluch, Mateusz Dulski, Courtney Quinn, Shannon McLaughlin, Anne McGrogan, Malgorzata Swadzba-Kwasny, and Zaneta Wojnarowska, *Tailoring Phosphonium Ionic Liquids for a Liquid–Liquid Phase Transition*, **J. Phys. Chem. Lett.**, 14, 2958-2964 (2023)
2. Zaneta Wojnarowska, Shinian Cheng, **Beibei Yao**, Malgorzata Swadzba-Kwasny, Shannon McLaughlin, Anne McGrogan, Yoan Delavoux, and Marian Paluch, *Pressure-induced liquid-liquid transition in a family of ionic materials*, **Nat. Commun.**, 13, 1342 (2022)
3. **Beibei Yao**, Marian Paluch, and Zaneta Wojnarowska, *Effect of bulky anions on the liquid-liquid phase transition in phosphonium ionic liquids: Ambient and high-pressure dielectric studies*, **Sci. Rep.**, 13, 3040 (2023)
4. **Beibei Yao**, Marian Paluch, Jaroslaw Paturej, Shannon McLaughlin, Anne McGrogan, Malgorzata Swadzba-Kwasny, Jie Shen, Beatrice Ruta, Martin Rosenthal, Jiliang Liu, Danuta Kruk and Zaneta Wojnarowska, *Self-assembled nanostructures in aprotic ionic liquids facilitate charge transport at elevated pressure*, **ACS Appl. Mater. Interfaces**, under review.

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