

# Chemical Engineering Doctoral Defense

## Self-Assembly at Ionic Liquid-Based Interfaces: Fundamentals and Applications

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### abstract

On a liquid surface, small particles can interact and spontaneously form structures through a process called self-assembly. This process is important in the fabrication of micron-sized devices and emulsion formulation. At oil/water interfaces, these structures can range from ordered lattices to close-packed aggregates. In this study, we replace oil and/or water with an ionic liquid (IL) at the interface, and find that new self-assembly phenomena emerge. ILs are ionic compounds that are liquid at room temperature (essentially molten salts) and have remarkable properties such as negligible volatility and high chemical stability, and can be synthesized for nearly any application. The nature of IL-fluid interfaces has not yet been studied in depth. Consequently, the corresponding self-assembly phenomena have not yet been explored.

We demonstrate how the unique molecular nature of ILs allows for new self-assembly phenomena to take place at their interfaces. These phenomena include droplet bridging (the self-assembly of both solid particles and liquid droplets), spontaneous particle transport through the liquid-liquid interface, and various gelation behaviors. In droplet bridging, self-assembled layers of particles effectively “glue” droplets to one another, allowing the droplets to self-assemble into large networks. With particle transport, it is experimentally demonstrated that the ILs overcome the strong adhesive nature of the liquid-liquid interface and extract solid particles from the bulk phase without the aid of external forces. These phenomena are quantified and corresponding mechanisms are proposed.

These experimental investigations are supported by molecular dynamics (MD) simulations, which allow for a molecular view of the self-assembly process. In particular, we show that particle self-assembly depends primarily on the surface chemistry of the particles and the non-IL fluid at the interface. Free energy calculations show that the attractive forces between nanoparticles and the liquid-liquid interface are unusually long-ranged, due to capillary waves. Furthermore, IL cations can exhibit molecular ordering at the IL-oil interface, resulting in a slight residual charge at this interface. We also explore the transient IL-IL interface, revealing molecular interactions responsible for the unusually slow mixing dynamics between two ILs. This dissertation, therefore, contributes to both experimental and theoretical understanding of particle self-assembly at IL-based interfaces.



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