

Predicting Reaction Outcomes in Ionic Liquids and their Mixtures: A Unified Framework Based on Dynamics and Nucleofugality

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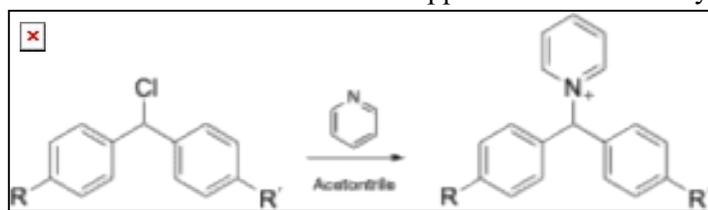
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Ionic liquids (ILs) have attracted considerable attention as alternatives to molecular solvents,¹ though unusual solvent effects have limited their application.² Significant research has been conducted to explain and understand these solvent effects in ILs, particularly noting that solvent effects are dependent on both the proportion of ionic liquid in the reaction mixture and nature of the constituent ions. Importantly, an understanding of how the solvent might interact with species along the reaction coordinate, the solvent effects can be explained and even predicted. However, in all cases, any efforts at prediction are qualitative.³

Nucleofugality, N_f , is a solvent parameter that describes a leaving group's ability to depart from a reagent.⁴ Recently studies have determined this parameter in mixtures containing an ionic liquid for chloride,⁵ bromide,⁶ and dimethyl sulfide.⁷ This information allows for quantitative prediction of reaction outcome.⁷

This presentation will discuss the measurements of the nucleofugality of chloride in ionic liquid mixtures. Along with comparing reaction outcomes between different ionic liquids and hence discussion of the key microscopic interaction, the importance of different co-solvents will be introduced, extending N_f measurements from IL–ethanol to IL–acetonitrile mixtures (Scheme 1). Further, correlations between the measured nucleofugality and the diffusion of the species in solution will be investigated measured across different timescales. Together, this work lays the foundation for a unified, quantitative model of IL solvent effects that applies across solvent systems.



Scheme 1. Reaction being studied in varying amounts of ionic liquid and ionic liquid species.

References:

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Maxwell is currently a Ph.D student in the Harper group at UNSW Sydney, researching ionic liquid solvent effects. He is investigating nucleofugality in ionic liquid–acetonitrile mixtures. His work aims to unify this fundamental reactivity parameter with solvent effects using a combination of analytical techniques.