

Investigation of solubility in protic ionic liquids and its implications for biotransformation reactions

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Protic ionic liquids (PILs) are often touted as a more environmentally and economically viable alternative to “traditional” aprotic ionic liquids.^{1,2} However, the presence of a labile proton in these PILs leads to their solvent interactions being very complex. As such, whilst there are currently applications of PILs which take advantage of their acidity and basicity,^{3,4} the lesser understanding of the solvent properties of PILs limits their broader adoption in research and industry. As such, it is imperative that the factors which govern the solvent properties of PILs are well understood.

The work described here highlights recent efforts to systematically investigate the physicochemical properties of PILs which affect mechanisms of solvation, and how these properties apply to chemical reactions. High-throughput NMR spectroscopic methods were performed to assess the solubility of model non-polar solutes in a series of PILs. The measured solubilities were then correlated with the solvent properties of these PILs, from solvatochromic parameters to fundamental physicochemical properties.

These correlations were also used to rationalise how PILs affected enzymatic reactions. Two enzymatic hydrolysis reactions were examined in the presence of a series of PILs, with particular focus on the role of the structural properties of the PILs. Corresponding enzyme-containing mixtures were studied using small-angle X-ray scattering to assess the effect of the PILs on the structure of these enzymes in order to further rationalise differences in how PILs affected the enzymatic hydrolysis reactions.

References

- (1) Greaves, T. L.; Drummond, C. J. Protic Ionic Liquids: Properties and Applications. *Chem. Rev.* **2008**, *108* (1), 206-237. DOI: 10.1021/cr068040u.
- (2) Peric, B.; Sierra, J.; Martí, E.; Cruañas, R.; Garau, M. A.; Arning, J.; Bottin-Weber, U.; Stolte, S. (Eco)toxicity and biodegradability of selected protic and aprotic ionic liquids. *J. Hazard. Mater.* **2013**, *261*, 99-105. DOI: 10.1016/j.jhazmat.2013.06.070.
- (3) George, A.; Brandt, A.; Tran, K.; Zahari, S. M. S. N. S.; Klein-Marcuschamer, D.; Sun, N.; Sathitsuksanoh, N.; Shi, J.; Stavila, V.; Parthasarathi, R.; et al. Design of low-cost ionic liquids for lignocellulosic biomass pretreatment. *Green Chem.* **2015**, *17* (3), 1728-1734. DOI: 10.1039/C4GC01208A.
- (4) Elwan, H. A.; Mamlouk, M.; Scott, K. A review of proton exchange membranes based on protic ionic liquid/polymer blends for polymer electrolyte membrane fuel cells. *J. Power Sources* **2021**, *484*, 229197. DOI: 10.1016/j.jpowsour.2020.229197.



Kenny completed his PhD in Chemistry at the University of New South Wales with Associate Professor Jason Harper, where he investigated the physicochemical properties of geminal ionic liquids and their use as solvents for organic reactions. Kenny is currently working with Professor Tamar Greaves at RMIT University, where he is studying the solvent properties of protic ionic liquids and their applications in biotransformations and self-assembly.