

Ionic Liquids in Lewis Acid Catalysis

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Ionic liquids are molten salts with very low melting points; below 100 °C by a popular definition, and often below room temperature. Conventional ionic liquids consist exclusively of ions, typically organic cations and/or inorganic anions, which imparts them some unique properties. In contrast to most organic solvents and water, most ionic liquids do not evaporate, do not burn and intrinsically conduct electricity. Most importantly, since there are plenty of cation/anion combinations, as well as tertiary and quaternary mixtures of ions available, physico-chemical properties of ionic liquids are incredibly tuneable.

The study of catalytic applications of ionic liquids pre-dates the name itself.^[1] Decades of research have been devoted to the study of Friedel-Crafts chemistry and similar Lewis acid catalysed reactions, all catalysed by halometallate ionic liquids, which continue to attract considerable industrial interest. The best example is the recently-announced ISOALKY process, which constitutes the first major innovation in the field of alkylate gasoline, introduced at an industrial scale, since eight decades.^[2,3]

Despite the breadth of investigated reactions, halometallate acidic ionic liquids have had very limited structural diversity, with most examples combining a 'spectator' organic cation with anions of a general formula $[M_xX_y]$, where $M = e.g.$ AlIII, ZnII, GaIII or FeIII, and $X = Cl$ or Br .^[4] This talk will be an overview of our research into more innovative liquid Lewis acids: from inexpensive, Lewis acidic liquid coordination complexes, tailored to particular industrial processes,^[5] through superacidic ionic liquids based on borenium cations and other main group cations,^[6] to investigations into frustrated Lewis pairs in ionic liquids.^[7] The presentation will cover aspects of multi-technique speciation studies, spectroscopic measurements of Lewis acidity, and applications in catalysis.

^[1] G. W. Parshall, *J. Am. Chem. Soc.*, 1972, **94**, 8716.

^[2] https://www.uop.com/?press_release=honeywell-uop-introduces-ionic-liquids

^[3] <https://results2021.ref.ac.uk/impact/1359711d-d304-4fc0-b86a-9c6d7011babf?page=1>

^[4] J. Estager, J. D. Holbrey, M. Swadźba-Kwaśny, *Chem. Soc. Rev.*, 2014, **43**, 847.

^[5] J. M. Hogg, F. Coleman, A. Ferrer-Ugalde, M. P. Atkins, M. Swadźba-Kwaśny, *Green Chem.* 2015, **17**, 1831.

^[6] J. M. Hogg, A. Ferrer-Ugalde, F. Coleman, M. Swadźba-Kwaśny, *ACS Sus. Chem. Eng.*, 2019, **7**, 15044.

^[7] L. C. Brown, J. M. Hogg, M. Gilmore, L. Moura, S. Imberti, S. Gärtner, H. Q. N. Gunaratne, R. O'Donnell, N. Artioli, J. D. Holbrey, M. Swadźba-Kwaśny, *Chem. Commun.*, 2018, **54**, 8689.



Małgorzata Swadźba-Kwaśny (Gosia) is the Director of the QUILL Research Centre and the Director of Research at the School of Chemistry and Chemical Engineering at Queen's University Belfast. She obtained her MSc (2005) from the Silesian University of Technology, Poland (Chrobok group), and her PhD (2009) from the QUILL Research Centre at Queen's University Belfast (Seddon group). Her doctoral and post-doctoral projects included collaborations with several industrial partners, including Petronas, BP and Evonik. In 2015, Gosia has secured Queen's University Fellowship and established her own research group. She was promoted to Senior Lecturer (Assistant Professor) in 2019 and to Full Professor in 2021.

Gosia works on ionic liquids and other advanced liquid materials. Her group designs and synthesises new acidic and metal-containing ionic liquids, harnessing discoveries in the field of main group chemistry, with particular focus on Group 13. They study the structure and reactivity of liquids at a molecular level, using both in-house spectroscopic and scattering techniques and synchrotron-based techniques (XAS and neutron scattering). In parallel, Gosia is involved in applied projects in collaboration with industrial partners (Petronas, The Lycra Company, Chevron), where they use ionic liquids and other functional liquids as sustainable alternatives to existing catalysts and solvents. Examples include the use of acidic ionic liquids as catalysts in the valorisation of plastic waste streams, as precursors in the synthesis of semiconductor materials, or as additives in technological fluids formulations.

