

Synthesis and Properties of Ionic Liquids for Application in Supported Ionic Liquid Phase (SILP) Catalysis

3rd September 2024, Harwell Campus

Programme

10:30	Tea/Coffee	
11:00	Duncan Bruce (York)	Introduction and Welcome
11:05	Marco Haumann (Erlangen) Advanced SILP Concepts for Continuous Homogeneous Catalysis	Plenary
11:50	Matt Costen (Heriot Watt)	Background and Introduction
11:55	Paul Lane (Heriot Watt) New methods for Characterising Ionic Liquids for Applications in SILP Catalysis	Invited Speaker
12:25	Lunch & Posters	
13:30	John Slattery (York)	Background and Introduction
13:35	Naomi Elstone (York) The Properties and Structure of Ionic Liquid Mixtures as Applied to SILP Catalysis	Invited Speaker
14:05	Max Skoda (RAL) Applications of <i>in situ</i> Neutron Reflectivity at the air-liquid interface	Invited Speaker
14:35	Marco Haumann (Erlangen)	Background and Introduction
14:40	Sharmin Antara (Erlangen) Gas-phase Hydrogenation with Dissolved Pt and Rh Complexes in Ionic Liquids – Adjusting the Location of Reaction by Ligand Design	Invited Speaker
15:10	Refreshment Break	
15:30	Walter Leitner (Aachen) Multifunctional Catalysts based on Metal Nanoparticles at SILP-Type Supports: <i>From Flexible to Adaptive</i>	Plenary
16:15	Chris Hardacre (Catalysis Hub/Manchester)	Summary and Overview
16:35	Ken McKenrick (Heriot Watt)	Concluding Remarks
16:40	CLOSE	

Poster abstracts

Miscible or Immiscible? Alkyl- and semiperfluoroalkyl-imidazoles and the Role of Charge

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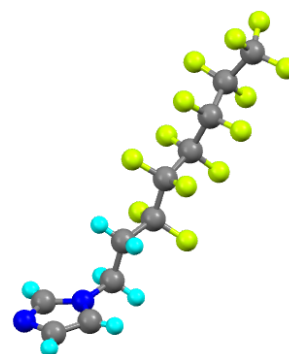
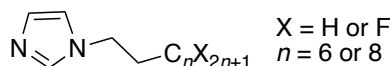
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The preparation of mixtures of ionic liquids is attractive as it allows for continuous variation in physicochemical properties as a function of composition, rather than trying to dial in the required response by preparing a new and bespoke material each time. Our motivation for studying such mixtures stems from their potential application in supported ionic liquid phases (SILPs) for catalysis, where it is of interest to be able to understand and therefore control aspects of local organisation in the bulk as well as the nature of the surface. Both such environments will have a material effect of the activity of the catalytic process.

While previous studies have looked at IL mixtures of imidazolium bistriflimides functionalised with long and short alkyl chains,^{1,2} more recent work has studied analogous mixtures where one component bears a semiperfluoroalkyl chain. Interestingly, for all the chain lengths we studied the different components were co-miscible at all compositions.³⁻⁶

Given the known immiscibility between hydrocarbons and fluorocarbons, it was then of interest to determine the contribution of the electrostatic charge of the imidazolium cation to the observed mutual solubility. As such, we have undertaken the preparation of neutral equivalents of the ILs (Figure) and have made mixtures between hydrogenous and fluororous materials of the same overall chain length. At ambient temperature, the two components are miscible where $n = 6$, but not when $n = 8$, in contrast to the findings for their ionic analogues where both series are miscible.^{5,6} The surface tension of the neutral mixtures has been evaluated and their bulk organisation probed by small-angle X-ray and neutron scattering. The results of these studies will be discussed.



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Fine tuning the ionic liquid-vacuum outer atomic surface

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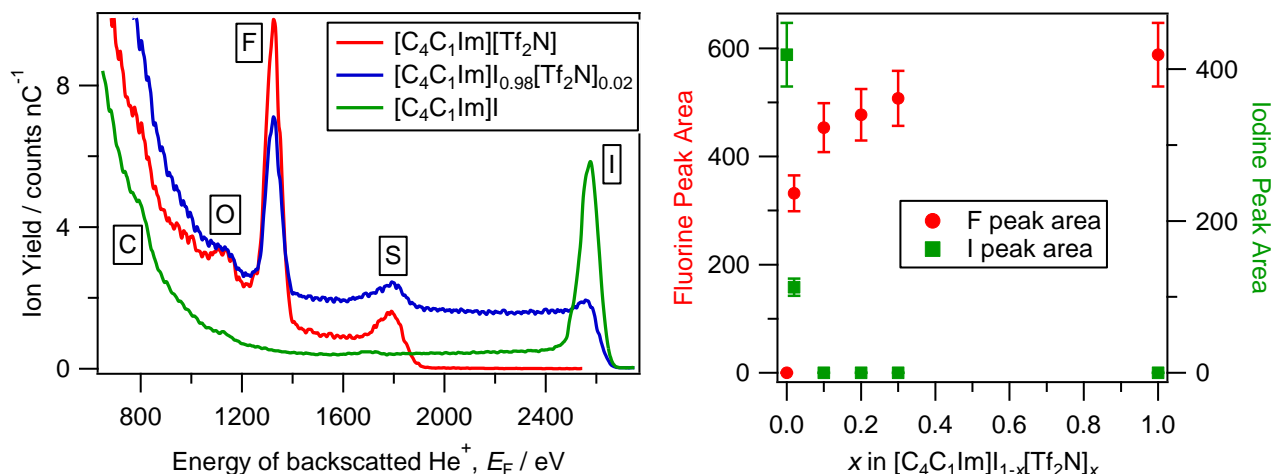
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The ionic liquid-gas surface underpins applications such as gas storage, gas separation, nanoparticle synthesis and supported ionic liquid phase catalysis.[1] For all of these applications, one needs to know which elements of the ionic liquid-based system are located at the outer surface. Ionic liquids have sufficiently low vapour pressures at room temperature that they can be studied under ultrahigh vacuum conditions (system pressure $<10^{-9}$ mbar). Low energy ion scattering (LEIS) is the most surface sensitive, element specific technique available. We have used LEIS to identify the elements present at the outer atomic ionic liquid-gas surface for 40+ ionic liquids, systematically varying both the cation and the anion charged headgroups, their alkyl chain lengths (where feasible), and their anion composition using anion mixtures. We have found that the nitrogen atoms on the imidazolium ring are “visible” at the outer surface for only one of the 40+ ionic liquids investigated, $[C_2C_1Im][OAc]$. [2] For ionic liquids with long alkyl chains, these chains dominate the outer surface, but are not sufficiently densely packed to completely hide the anions, *e.g.* Cl is observed for $[C_8C_1Im]Cl$. [2] For both cations and anions a variety of orientations are observed, with some anion orientations having a higher probability than others. [2] Most surprisingly, for a mixture of containing a small quantity of the $[NTf_2]^-$ anion, $[C_4C_1Im]I_{0.98}[Tf_2N]_{0.02}$, we find a huge positive surface excess of the $[NTf_2]^-$ anion (Figure 1). [3]



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Understanding and Predicting the Reactivity of Trifluoroborate Anion Organic Reagents Using XPS and Resonant XPS

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Boron is a main group, non-metallic, earth-abundant element with growing potential in the field of organic synthesis.¹ Boron's wide ranging reactivity as a reagent, low cost and toxicity is useful to bulk manufacturing. The ability of organoboron compounds to mediate C-C bond formation through the Suzuki reaction (Nobel Prize for Chemistry, 2010) means it is of great importance to pharmaceutical and agrochemical industries.² Traditionally, three coordinate boron reagents are used.¹ However, four coordinate trifluoroborate anion reagents, [RBF₃]⁻, have in recent years become very popular, due mainly to their ability to be thermochemically stable but reactive after photoactivation. Electrochemical oxidation potential has been used as a parameter to judge the reactivity of [RBF₃]⁻ reagents, with a variation with different R groups of ~0.75 V.¹ [RBF₃]⁻-based ionic liquids (ILs) have become popular recently due to their relative ease of synthesis,³ with K[RBF₃] salts widely available as a starting material for IL synthesis. However, no measurements of electronic structure of [RBF₃]⁻ have been made; therefore, there is limited understanding of the link between geometric structure and electronic structure.

We have recorded synchrotron non-resonant and resonant X-ray photoelectron spectroscopy (XPS) for both [C₄C₁Im][BuBF₃] and [C₄C₁Im][BF₄] on beamline B07 at Diamond Light Source, along with performing density functional theory calculations. We measured a range of electronic structure descriptors for [BuBF₃]⁻ and [BF₄]⁻: (a) boron + carbon + fluorine atomic charges, (b) ionisation energy, (c) highest occupied valence state identity (*i.e.* which part of the anion is most readily ionised). We found that the C-BF₃ carbon in [BuBF₃]⁻ is negatively charged, a hugely rare occurrence for carbon, only previously observed by XPS for metal carbides and silicon carbide. This finding matches well to ¹H NMR spectroscopy. Furthermore, we found that the ionisation energy of [BuBF₃]⁻ is ~ 2 eV smaller than the ionisation energy for [BF₄]⁻, due to the presence of the Bu chain. These electronic structure descriptors will be used to understand and interpret photo-oxidation potentials.

References

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Crosslinked Poly(ionic liquids) – Potential Sorbents for the Removal of Antimony, Chromium and Iodine

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Charged/ionic polymers from ionic liquids has recently attracted in many emerging fields due to their ease of synthesis, tuneable solution and binding properties, and stability of ionic liquids^{1,2}. Crosslinked poly(ionic liquids) (C-PILs) represent an advanced class of functional materials, engineered through the crosslinking of ionic liquids to achieve exceptional stability while retaining the ionic liquid properties³. This study was focused on the design and development of C-PILs with cationic and selective binding sites for targeted applications, specifically for the effective removal of antimony, chromium and iodine, and deciphering the binding mechanisms. A robust crosslinked poly(ionic liquid), crosslinked poly(1-butyl-3-vinyl imidazolium bromide) (C-P(BVIm-Br)), was synthesised, using an ionic liquid functional monomer, 1-butyl-3-vinyl imidazolium bromide, and a crosslinker, N,N'-methylenebis(acrylamide) in the presence of thermal free radical initiator through bulk polymerisation in an aqueous medium. The synthesized C-P(BVIm-Br) selectively bind oxyanions of low-level of antimony ions in complex aqueous matrices through anion exchange, demonstrating the ability to differentiate between various oxidation states of antimony. Additionally, C-P(BVIm-Br) effectively immobilizes all forms of iodine from different streams with very high capacity - including molecular and ionic species - through halogen bonding and ion exchange, respectively. This performance of C-P(BVIm-Br) surpasses that of traditional monomers in both form factor and capacity. Further investigations with a non-ionic counterpart poly(ionic liquid), crosslinked poly(vinylimidazole) (C-P(VIm)), revealed that C-P(BVIm-Br) exhibits better selectivity for antimony removal and is capable of removing all forms of iodine, unlike C-P(VIm), which remove only molecular iodine. Furthermore, given the charged nature of the binding sites and the importance of mitigating chromium pollution, the potential suitability of C-P(BVIm-Br) was demonstrated through the efficient removal chromium from contaminated water sources and tannery effluent. Additionally, a series of C-PILs, including poly(1-butyl-3-vinyl imidazolium) cation with different counter ions (chloride, bromide, iodide, tetrafluoroborate, hexafluorophosphate, bis(trifluoromethanesulfonyl imide) and poly(1-alkyl-3-vinyl imidazolium) bromide with different alkyl chain length (ethyl, butyl, hexyl and octyl) were synthesised. These materials were subjected to various characterisation techniques including spectroscopic (FT-IR), microscopic (SEM-EDX) and gravimetric (TGA) analyses and their sorption properties were evaluated. The results revealed significant effects of counter ion and alkyl chain length variations on structural (thermal and swelling properties) and sorption properties (towards antimony, chromium and iodine). The superior properties of these C-PILs make them highly promising for practical applications, including nuclear waste management, and advancements in waste treatment technologies and environmental protection strategies.

References

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