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Direct probe electrospray (and nanospray) ionization mass spectrometry of neat ionic liquids†

Paul J. Dyson,*[a] Isam Khalaila,[a] Sarah Luettgen,[b] J. Scott McIndoe*[b] and Dongbin Zhao[a]

[a] Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne, EPFL-BCH, CH-1015, Lausanne, Switzerland. E-mail: paul.dyson@epfl.ch.; Fax: +41 (0)21 693 98 85; Tel: +41 (0)21 693 98 54
[b] Department of Chemistry, University of Victoria, P.O. Box 3065, Victoria, Canada BC V8W 3V6. E-mail: mcindoe@uvic.ca.; Fax: +1 (250) 721 7147; Tel: +1 (250) 721 7181

Electrospray ionization mass spectrometry of neat ionic liquids does not require continuous sample injection and the presence of a molecular solvent facilitates analysis of the ionic liquid itself and dissolved analytes.

Ionic liquids (ILs) continue to attract considerable interest as solvents for multiphasic catalysis[1] as well as for other applications.[2] Since ILs are composed entirely of ions, they are inherently involatile and consequently their analysis and that of analytes dissolved in them requires special protocols. Consequently, we reported a dilution method for analysing ILs and catalysts (although potentially any analyte) dissolved in an IL by electrospray ionisation mass spectrometry (ESI-MS).[3] We pointed out that a potential limitation of the technique might be interference of the analyte (catalyst) by the molecular solvent and a subsequent report by Jackson and Duckworth showed that remarkably, ILs could be analysed without dilution using ESI-MS.[4] They were also able to show that an organic salt additive could be detected, potentially overcoming the limitations of the dilution method.

However, direct injection of neat ionic liquid even at low flow rates consumes many orders of magnitude more sample than is required if the IL is diluted. While quantities remain small in an absolute sense, contamination of the instrument remains a real problem, but one that can be avoided by using a simplified version of Shiea's direct probe (DP) method.[5] A short length (~20 mm) of fine stainless steel wire was bent and clipped directly to the commercial inlet (Fig. 1).[6] The wire was orientated so its tip lay on the same axis as the capillary and the IL was applied to the wire using a glass fibre. Switching on the desolvation gas resulted in immediate and copious ion production, even when the gas was at ambient temperature. The ion current soon abated, however, and could only be recovered upon raising the temperature of the gas to above ca. 150 °C. High temperatures resulted in extensive decomposition (exact temperatures in each case were dependent on the particular ionic liquid). It was proposed that the actual temperature

of the IL is only likely be ca. 80 °C with a desolvation gas at 250 °C,[4] but given that decomposition of the IL was observed at a desolvation gas temperatures of about 300 °C, the temperature match between gas and sample is probably much closer. The reproducibility of these results led us to investigate this behaviour in more detail, hence the ion current was recorded as a function of temperature. In each case, a profile was obtained in which three regimes (sometimes only two) of ion production could be identified (Fig. 2). With the source at 30 °C (ambient), switching on the desolvation gas resulted in a sudden surge of ion production (regime A), which diminished to baseline after about a minute. Regime A is likely to be due to efficient desolvation of residual (neutral, non-IL) solvent from the IL. Brief invigoration of this process occurs when heating the desolvation gas, suggesting further evaporation of the remaining, residual solvent. [BuPy][BF$_4$], like most ionic liquids, is hygroscopic and contains 1.09% water (as determined by Karl–Fischer analysis) unless rigorously dried and stored in a glove box. Above 100 °C and peaking at about 200 °C more ions erratically appear (regime B), and these are attributed to ion evaporation[7] directly from the IL.[8] At temperatures above 300 °C (regime C) a substantial, moderately steady ion current is recorded, during which period the IL decomposes.

Fig. 3 shows the mass spectra obtained for regimes A, B and C (summations; spectra varied little within each region). The regime A spectrum closely resembles that obtained from a diluted solution of the IL (in a typical electrospray solvent such as water, methanol, acetonitrile or dichloromethane). The presence of aggregates of the form $[(BuPy)_n(BF_4)_{n-1}]^+$ is as expected,[3,4] and the negative ion spectrum displays corresponding ions of the type $[(BuPy)_n(BF_4)_{n+1}]^-$. Isotopomer envelopes for each of the peaks matched calculated patterns, and two comparisons are shown as insets. One so highlighted indicates the presence of Cl$^-$ in addition to the expected BF$_4^-$; residual Cl$^-$ is a problem in the purification of ILs[9] and we are investigating ESI-MS as a method for quantifying this impurity. The second mass spectrum, regime B, resembles the first, though aggregation is more extensive, and this was found to be a feature of ion production in this higher
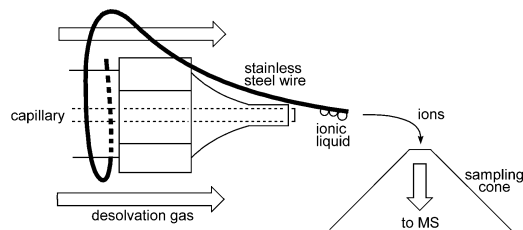

Fig. 1 Suspension of ionic liquid in the path of desolvation gas to enable direct probe analysis (diagram not to scale).
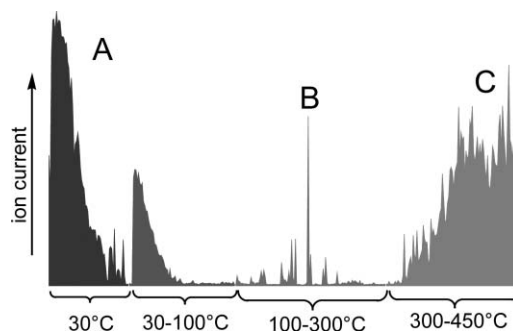
DOI: 10.1039/b407217k

Fig. 2 Plot of ion current vs. time (temperature) for the direct probe analysis of neat [BuPy][BF$_4$]. Total acquisition time of 7 min.
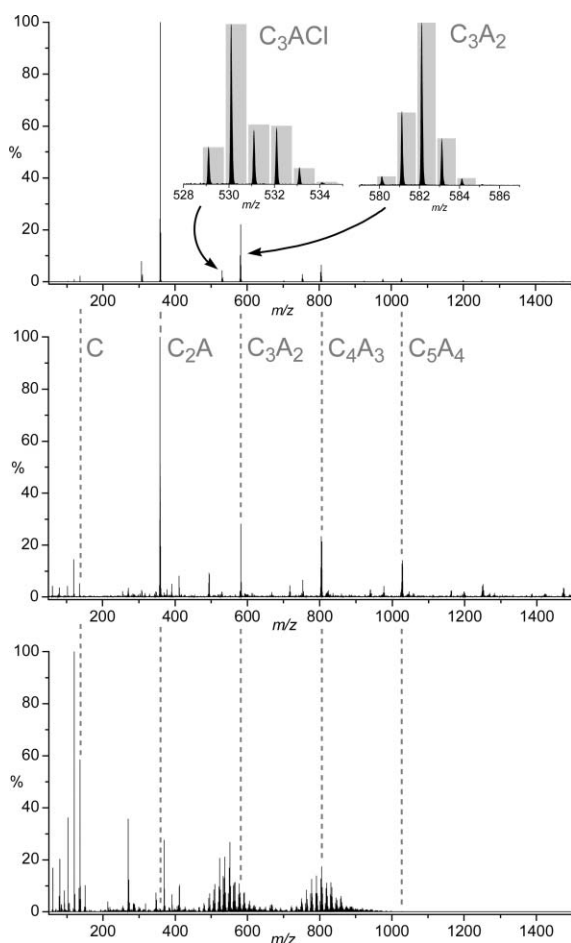
Fig. 3 Positive ion electrospray ionization mass spectra of neat [BuPy][BF₄] collected in regimes A (top), B (middle) and C (bottom).

Fig. 4 The positive-ion nanospray mass spectra of [Ru(η^6-p-cymene)-(η^2-triphos)Cl]⁺ in (top) neat [bmim][PF₆], 1 mM; (middle) [bmim][PF₆]-methanol 1:1, 0.5 mM; (bottom) neat MeOH, 0.5 mM Acquisition time 5 min per spectrum (zoomscans). Absolute intensity (ion count) is indicated to the right of each spectrum.

increasingly important for the analysis of ionic liquids[12] and to study catalyst species in ionic liquids.[13] From the work described herein, the presence of a molecular solvent (and the use of low temperatures) considerably facilitates analysis.

temperature regime for most of the ILs studied. The total ion current observed in regime B was found to wildly fluctuate for different ILs; essentially no ions were produced in regime B for the alkyne functionalised ionic liquid [C₇H₉N₂][Tf₂N],[10] for example (see supporting information). Careful setting of the temperature and desolvation gas flow rate can allow ion production over a period of minutes in this regime. Further increasing the desolvation gas temperature to over 300 °C results in decomposition of the IL, and the products of this process may be observed in the third mass spectrum.

The observations of Jackson and Duckworth are consistent with ion production in regimes A or B. However, as the IL is being continuously injected into the source, we suspect that significant assistance from residual solvent evaporation is occuring, *i.e.* regime A, and that the putative advantages of conducting ESI-MS of IL without dilution are, in fact, minimal. The consequences of a high desolvation gas temperature might also be detrimental to the sample being analysed, and the detection of analytes in ILs under these conditions appears to be possible only in regime A, where ion evaporation is facilitated by residual water. In fact, using a commercial nanospray source[9,11] to analyse catalysts in ILs (1 μL of sample may be sprayed over a period of 1 h, minimising contamination problems) we found that dilution in MeOH significantly facilitated analysis. The spectra of [Ru(η^6-p-cymene)-(η^2-triphos)Cl][PF₆] in [bmim][PF₆], [bmim][PF₆]/MeOH (1:1) and MeOH recorded under identical conditions are compared in Fig. 4, illustrating the benefit of dilution. The presence of a molecular solvent results in a much higher ion current leading to a vast improvement in signal-to-noise ratio and hence detection limit.

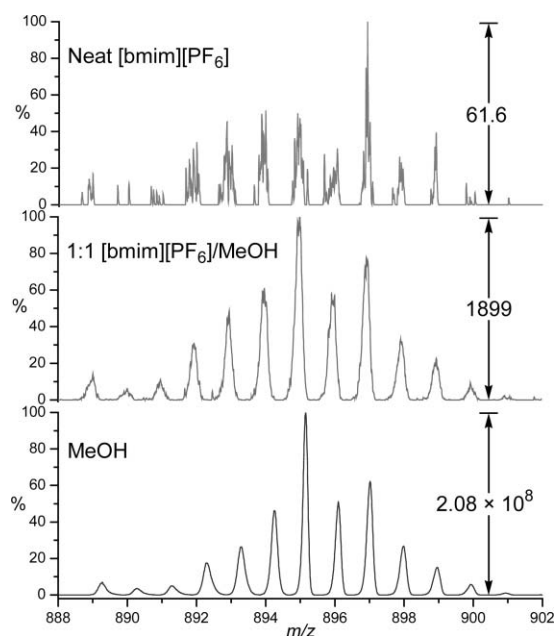In conclusion, mass spectrometric methods are becoming

Notes and references

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