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Electrospray mass spectrometry of undiluted ionic liquids†

Glen P. Jackson and Douglas C. Duckworth*
Chemical Sciences Division, Oak Ridge National Laboratory, P. O. Box 2008, Oak Ridge, TN, 37831-6375, USA. E-mail: duckworthdc@ornl.gov; Fax: 01 (865) 574-6906; Tel: 01 (865) 576-6296

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Ionic liquids have been analyzed in undiluted form using electrospray mass spectrometry (ES-MS); results indicate that signal-to-noise ratios for minor constituents are comparable to those observed in conventional, diluted ES-MS and that this approach could be readily applied for mass spectrometric analysis of ionic liquids and ionic impurities/additives dissolved therein, especially those that are solvent reactive.

Room temperature ionic liquids (RTILs) have received major attention recently as replacements for conventional solvents in synthesis,[1] catalysis,[2–3] electrochemistry[4] and separations.[5–6] With their widespread application comes an inherent requirement to determine the nature and purity of synthesized ionic liquids, and to characterize and quantify the variety of compounds dissolved within them. This poses an interesting analytical problem, because the properties of RTILs do not always readily lend themselves to conventional analytical techniques.

Early attempts to obtain electron ionization (EI) mass spectra and chemical ionization (CI) mass spectra were unsuccessful,[5] presumably because RTILs have very little vapor pressure and cannot be readily transferred to the gas phase. Because of their inherently low vapour pressure, fast atom bombardment (FAB) MS has been the most extensively used MS technique for characterizing RTILs. The RTILs may be dissolved in a matrix such as glycerol, or analyzed without dissolution.[5,7] FAB-MS spectra of RTILs are typically characterized by a dominant peak for the unbound cation followed by clusters of the form $[(AB)_nA]^+$, where A is the cation and B is the anion. One may also perform mass analyses of RTILs by dissolving them in a suitable solvent and performing electrospray mass spectrometry.[8]

Very recently, Dyson, McIndoe and Zhao demonstrated the ability to analyze charged catalysts dissolved within ionic liquids using electrospray mass spectrometry (ES-MS).[9] ES-MS of diluted RTILs allowed the observation of charged catalysts at concentrations four orders of magnitude more dilute than the ionic liquid. Although ES-MS holds considerable promise for the analysis of RTILs and dissolved species, there are significant challenges to overcome. For example, Dyson and coworkers show that although mass-analysis of dissolved catalyst-containing RTILs gives better signal-to-noise for the catalyst at higher final concentrations than at lower final concentrations, clustering of the RTIL components is more prevalent at the higher concentrations.[9] In a few cases this clustering could interfere with the catalyst signal. Therefore, one must find an optimal dilution factor to balance deleterious interferences and useful signal-to-noise. In addition, some catalysts are likely to react with methanol or aqueous solvents. In these cases, replacement solvents may be required. In instances where ionic liquid aggregates overlap the spectral region of interest, alternative ionic liquid matrixes could be used. However, identifying another RTIL with the desired characteristics could prove challenging.

In an effort to alleviate problems associated with dissolution and solvent effects, we have performed the first studies to evaluate the possibility of generating mass-spectrometric information from undiluted ionic liquids. Two reports can be found in the literature on the electrospray of undiluted ionic liquids,[10] although these reports are not analytical in nature. In addition, these reports utilize an electrospray plume under vacuum and not at atmospheric pressure.

Applying a heated curtain gas in opposition to the electrospray plume enables consistent ion signals to be recorded from an undiluted sample of 1-butyl-3-methyl imidazolium pentafluorophosphate (BMIM-PF_6). However, the effect of the heated curtain gas (250 °C) is not immediate. The benefit arises from the reduced viscosity of the heated ionic liquid in the electrospray needle caused by convective heating by the curtain gas. Very little, and in some cases no ion signal is observed in the absence of the heated curtain gas. The exact temperature of the ionic liquid was not determined under heated conditions, but was probably not greater than 80 °C. Future work will need to clarify the heating effect and any potential problems regarding the heating of thermally sensitive analytes that might decompose at these operating temperatures. ES-MS of undiluted ionic liquids was usually performed at an infusion rate of 2 μL min^{-1}, but stable ion signal could often be achieved with no active infusion. Unlike ES plumes generated from conventional solvents such as methanol, the electrospray plume was not observable with the naked eye or under significant magnification.

Fig. 1(a) shows a mass spectrum obtained from an undiluted and unpurified sample of BMIM-PF_6 containing 4×10^{-4} M tetrabutylammonium iodide (TBAI).‡ Clearly evident is the $BMIM^+$ cation signal at *m*/*z* 139, and the trimolecular cluster $[(BMIM)_2PF_6]^+$ at *m*/*z* 424. The peak at *m*/*z* 84 is due to the

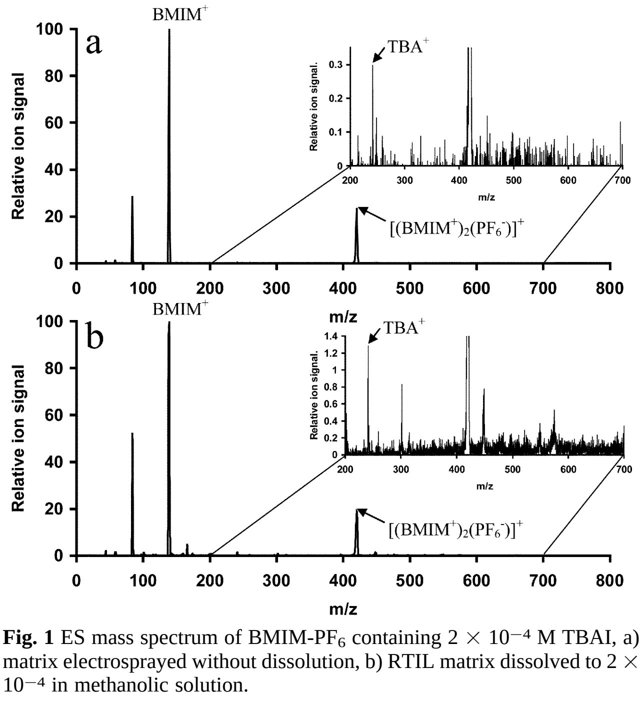

Fig. 1 ES mass spectrum of BMIM-PF_6 containing 2×10^{-4} M TBAI, a) matrix electrosprayed without dissolution, b) RTIL matrix dissolved to 2×10^{-4} in methanolic solution.

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fragmentation of the BMIM$^+$ cation, the extent of which could be readily altered by the acceleration potential between the capillary exit and the skimmer cone. MS/MS of isolated BMIM$^+$ also gave this peak as one of the major fragmentation products.

The TBA$^+$ peak is readily observable at *m*/*z* 242 and the spectrum is relatively free from other major peaks. Fig. 1(b) shows the same sample dissolved to 2×10^{-4} M BMIM-PF$_6$ in the methanolic solution (final concentration of TBA$^+$ $\approx 1 \times 10^{-7}$ M). In general, the two spectra show the same major ions in similar relative abundance. Although the plots have been normalized to the largest peak in each case, absolute ion abundances were reasonably similar for the two methods when using a 50 ms injection period. Closer inspection of the baseline of the two spectra, shown in the insets, reveals interesting differences. The spectrum for the undissolved RTIL displays considerably less chemical noise and shows the TBA$^+$ peak at ~0.3% of the base peak height, whereas the baseline for the dissolved RTIL shows significant ion signal at nearly every mass and a TBA$^+$ peak at 1.3% of the base peak height. In this example, dissolution of the RTIL matrix provides better absolute signal response for the dissolved "impurity" ions, but at the expense of higher background noise. The minor peaks in the *m*/*z* 200–700 window have not been identified; presumably, they are due to methanol or water clusters of impurity ions. Calculation of the signal-to-noise ratio for the two methods (dilution *versus* no dilution) gave very similar results. Approximate detection limits for TBAI dissolved in BMIM-PF$_6$ (based on three times the standard deviation of a blank) are on the order of $0.5–1.0 \times 10^{-4}$ M, or 10–20 ppm in the ionic liquid.

Although ES-MS of dissolved RTILs will suffice for most analyses, Dyson *et al.* noted[9] that some RTILs and their dissolved catalysts are water or solvent reactive. In these cases ES-MS of undiluted RTILs could be a more direct approach to obtaining mass spectrometric information of the RTILs and their contents, without any significant loss in analytical performance.

Analyses of various other cation/anion combinations of RTILs were also performed. These spectra typically gave ion signals comparable in stability to conventional ES-MS, but using lower operating voltages (details given below‡). Higher operating voltages were attempted without success. The signal for BMIM$^+$ from a sample of BMIM-PF$_6$ showed no measurable drift over a ten minute acquisition period and gave RSD = 13%, providing similar performance to conventional electrospray signals. However, ion signal was found to deteriorate after several hours of analysis such that the source and heated capillary needed to be cleaned to restore performance. It was also necessary to clean the skimmer cone and hexapole ion guide at the end of each week, which is an unfortunate result of this approach. The degree of internal contamination could almost certainly be reduced using a more optimal source geometry than the one employed here (*i.e.* orthogonal ES instead of normal ES).

Lower-viscosity RTILs, such as BMIM-Tf$_2$N (Tf$_2$N = bis[(trifluoromethyl)sulfonyl]amide), are electrosprayed more readily than higher-viscosity RTILs and do not require as much heating in order to form a stable spray. Samples containing mixtures of cations and anions display all possible combinations of trimolecular cluster spectra in positive ion mode. However, the relative gas-phase abundances of the cations and trimolecular clusters are not always representative of the condensed-phase molar proportions. These observations seem to correlate qualitatively with the strength of the cation–anion binding energy; for example, strongly-binding anions form a larger proportion of the trimolecular clusters than do weakly-binding anions. If this relationship proves to be quantitative, this phenomenon could help predict condensed-phase characteristics of cation–anion combinations that have yet to be isolated.

This communication demonstrates the ability to obtain simple mass spectra from undiluted RTILs using a conventional ES-MS interface with a heated drying gas. The advantage of this approach is that ionic liquids do not have to be dissolved in a solvent in order to electrosprayed. This aspect could be most beneficial for reactive RTILs such as chloroaluminate salts and for reactive contents such as precious-metal-containing catalysts. Undiluted ES-MS of RTILs is also able to identify dissolved ions, which could be beneficial for analyzing catalysts, reagents and impurities, depending on the application.

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Notes and references

‡ Data was collected on a Teledyne Discovery II quadrupole ion trap (formerly Mountainview, CA) with an Analytica ES ion source and hexapole ion guide (Brandford, CT). Instrumentation details will be provided in a full-length article to follow. Ionic liquids were purchased from Solvent Innovation GmbH (Köln, Germany) and used without purification. Settings for ESI of 2×10^{-4} M BMIM-PF$_6$ in 80/20/0.2% vol MeOH/H$_2$O/CH$_3$COOH were as follows: sample flow rate 2 μL min^{-1}, N$_2$ drying gas set at 15 psi, 250 °C, ESI needle = 0 V, cylinder = −3800 V, plate = −4500 V, capillary entrance = −5500 V, capillary exit = 100 V, skimmer cone = 24 V, hexapole dc bias = 4.5 V, Gate electrodes = −180 V, ionization time = 50 ms with low mass cut off = 41 amu. For neat/undissolved BMIM-PF$_6$ all settings were the same, except cylinder = −2600 V and plate = −2500 V.

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