

Ionic liquids *in vacuo*; solution-phase X-ray photoelectron spectroscopy

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The *in situ* monitoring of catalysis in Room Temperature Ionic Liquids (RTILs) is fundamental to the understanding of catalytic processes and the role of RTILs in catalytic turnover; we describe how XPS can be used to give information on both pure RTILs and catalytically-active RTIL-based solutions.

X-Ray photoelectron spectroscopy (XPS) is a powerful spectroscopic technique that provides information about both the elemental composition and, more interestingly, the electronic structure of the elements in a huge range of solid samples.¹ Such information would be extremely useful for samples in solution but, until now, the measurement of XPS spectra of liquids has been fraught with difficulty;² the sample simply evaporates under the ultra high vacuum (UHV) conditions required. Here we show that XPS can be easily used to investigate liquid samples based on room temperature ionic liquids (RTILs).

RTILs are sterically-hindered organic salts having melting points below 100 °C. Because they are composed entirely of ions, ionic liquids have *almost zero vapour pressure* and do not evaporate, even under vacuum. We have found that this lack of volatility allows RTILs to be used in a whole range of analytical instruments that require UHV conditions for their operation, thus, opening up a route to fundamentally important information about both pure ionic liquids and, more interestingly, their solutions. We present the first XPS data on a RTIL, 1-ethyl-3-methyl imidazolium ethylsulfate (ECOENG[®] 212), and demonstrate the sensitivity of the technique by monitoring the reduction of Pd²⁺ using *in situ* high resolution XPS.

Under our analysis conditions,³ liquid RTILs emit a surprisingly good photoelectron flux; hence, excellent XPS data can be obtained in a very short collection time (< 5 min). Furthermore, since the RTIL is electrically conducting, none of the problems associated with differential charging are encountered, and charge neutralisation is not required. RTILs appear to be very stable during exposure to the X-ray source; we have observed no evidence of either out-gassing, after initial pump-down, or beam damage to the sample. There is also no visible discolouration of the sample, unlike many other organic based samples, including polymers.⁴

Fig. 1 shows an example of a survey type XPS spectrum of ECOENG[®] 212 (purity > 98%). The data obtained are of high quality and the signal to noise ratio is comparable to that obtained from conducting solid samples under similar conditions. Core level photoemissions are observed for each element within the sample, and the calculated stoichiometry is within experimental error of the

expected values. Observed peak shapes and stoichiometries appear to be constant throughout the experiment, with minimal change or deterioration, even after extended exposure times (up to 10 h).

The most interesting point in Fig. 1 is that trace chemical impurities are detectable, e.g. the Si 2p photoemission at 100 eV (arrowed). The Si appears to originate from the silicone septum on the bottle used to store the ECOENG[®] 212, possibly being introduced into the sample after coring with a syringe needle. After removal of the septum and stringent cleaning of all analytical syringes, the contaminant disappeared. However, this serendipitous observation of Si demonstrates that XPS can be used to detect low concentrations of solutes dissolved in the RTIL.

XPS spectra can also be recorded in high resolution mode. This mode is sufficiently sensitive to distinguish between atoms of the same element in chemically distinct environments. The binding energy of each photoemission is characteristic of the electronic environment in which that particular atom resides.

The high resolution profile of the C1s peak of ECOENG[®] 212 is shown in Fig. 2. This photoemission consists of at least two resolved peaks but, if we consider the structure of the two ions, there are clearly more than two inequivalent C atoms. It is known in such circumstances that it is sufficient merely to distinguish between atoms on the basis of their nearest neighbours. Applying this approach, it can be seen that there are five different types of C atom, as indicated on the structures in Fig. 2. These atom types seem to be a reasonable basis for further analysis of the peak in Fig. 2. However, binding energies for liquid systems have, until now, not been measured. Therefore, we assume that the differences

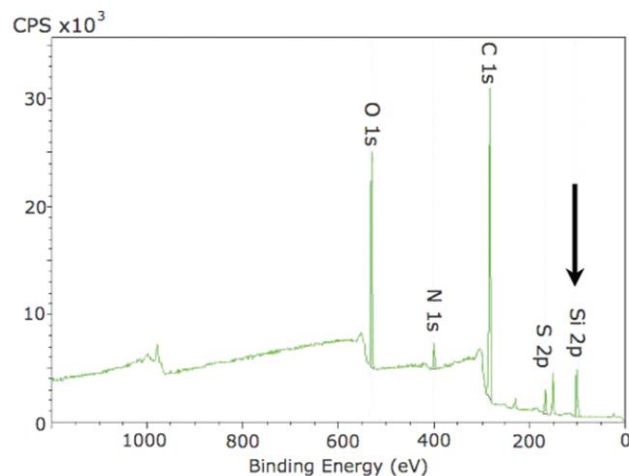


Fig. 1 XPS survey spectrum of RTIL 1-ethyl-3-methyl imidazolium ethylsulfate (ECOENG[®] 212); characteristic photoemissions are observed for each element in the sample. Silicon (arrowed) is also observed, an impurity originating in the septum used to seal the storage vial.

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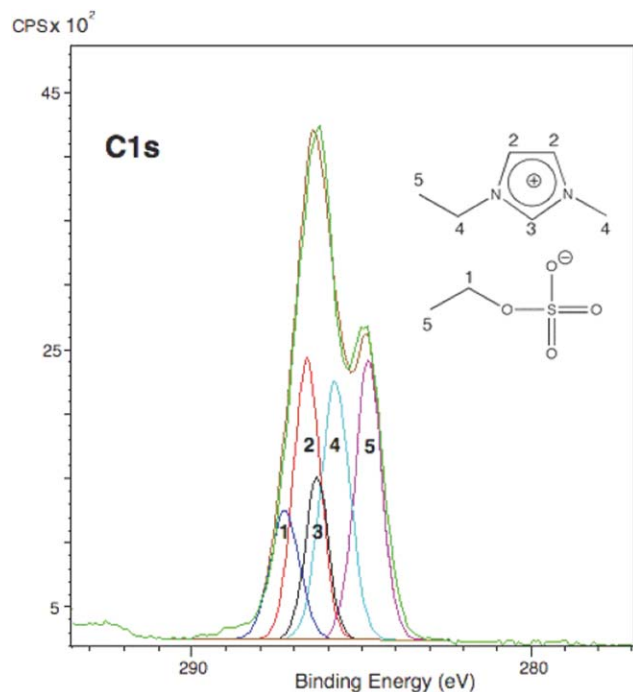


Fig. 2 High resolution XPS spectra of ECOENG[®] 212, detailing the C1s photoemission. The experimental data (green) is compared to a simulated fit where each “non-equivalent” carbon atom has a distinct shift in binding energy. The simple model employed was created using CASAXPS software, peak shape GL(30)—a symmetrical Gaussian (70%) and Lorentzian (30%). The FWHM of each component was constrained to ≈ 1.5 eV. The relative areas of each component peak were fixed by the stoichiometry of the analytical sample. Component 5 was assigned as aliphatic carbon and charge corrected to 285 eV accordingly. Additional components were added to the model using experimentally-determined binding energies measured for isostructural fragments in solid systems.⁵

between solid and liquid samples will be small. With this assumption, we can assign a probable binding energy to each of these types of atom by comparison with experimentally determined binding energies of isostructural fragments measured in solid samples.⁵ The relative intensity of each individual component, and hence its weighting in this simple model, will be fixed by the known stoichiometry of the sample (*e.g.* 1 and 3 will have half the intensity of the other peaks). Our experimental data was then fitted to these five peaks, assuming that the FWHM of each individual component lay between 1.2 and 1.7 eV, depending upon their proximity to electronegative elements. The resulting fit to the observed data is striking. Similar XPS on other RTILs gives differently shaped C1s photoemissions, suggesting that liquid XPS does indeed have the ability to differentiate between atoms in different chemical environments. This renders XPS a potentially very powerful technique for probing catalytic species in solution.

The range of reactions investigated in RTILs is constantly increasing.⁶ Pd-based chemistries, including the ubiquitous Heck reaction, are some of the most widely studied.⁷ Unfortunately, the stability of the Pd catalysts is often unpredictable. In many cases, catalytic activity is reported to remain stable over prolonged periods of time and many successful recycles. By contrast, in some imidazolium-based RTILs, there is evidence for ligand exchange

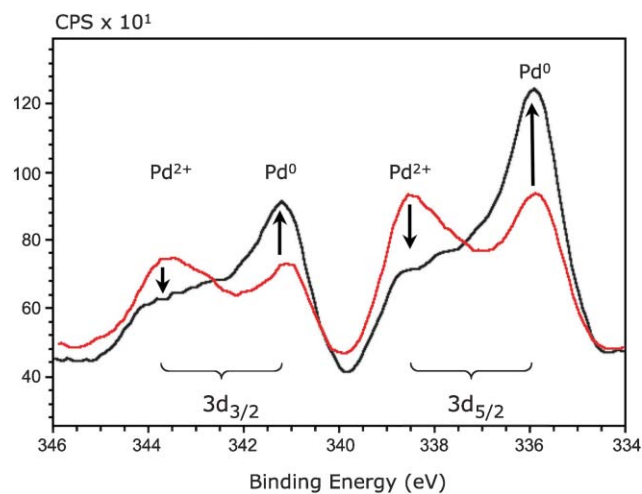


Fig. 3 High resolution XPS spectrum of a solution of Pd(OAc)₂(PPh₃)₂ in ECOENG[®] 212, highlighting the Pd 3d photoemission. The plot illustrates the facile reduction of the Pd²⁺. The red line shows data recorded at the start of the XPS experiment, minutes after the solution was prepared; note Pd⁰ is already observed. The black line presents data recorded 6 h later. 300 data sets were recorded between these points. Also note, the 3d photoemission is observed as a doublet with intensities 2 : 3 due to spin-orbit coupling in the emissive state.

with subsequent formation of *N*-heterocyclic carbene complexes⁸ and eventual reduction to finely dispersed “palladium black”.⁹

We decided to test our XPS approach by investigating the stability of a reported Heck catalyst in ECOENG[®] 212 by monitoring the profile of the Pd 3d photoemission. A freshly prepared solution of Pd(OAc)₂(PPh₃)₂ in ECOENG[®] 212 was split into two aliquots; the first was pumped-down and analysed by XPS at room temperature and the second was kept as a control. Over the course of the analysis (≈ 90 min), the XPS spectrum (see Fig. 3) showed a decay in the amount of Pd²⁺ present and a corresponding increase in the amount of Pd⁰.

The appearance of the samples changed significantly, the transparent straw-coloured solution becoming opaque and very dark in colouration. The simultaneous change of both the analytical and the standard solution indicates that reduction of the Pd species was not due to X-ray exposure alone. This simple observation shows that Pd(OAc)₂(PPh₃)₂ is not stable in ECOENG[®] 212.

In this communication, we have shown that RTILs allow XPS data to be collected for liquids and solutions in quite a new way. Further experiments are under way in our laboratory to explore the wider applications of this approach, including the *in situ* monitoring of electrochemically controlled processes.

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