Probing the electronic environment of binary and ternary ionic liquid mixtures by X-ray photoelectron spectroscopy

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Abstract
X-ray photoelectron spectroscopy is used to probe the electronic environment of cations and anions for three binary and one ternary chlorostannate ionic liquid mixtures. The impact of the weighting of Cl\(^-\) on the electronic environment of cation-based nitrogen atoms is revealed in detail. With the increasing of the concentration of Cl\(^-\), the measured binding energy of N 1s is decreased. The electronic environment of anion-based component is also compared based upon measured Sn 3d\(5/2\) and Cl 2p\(3/2\) binding energies. It is found that with the increasing of the weighting of Cl\(^-\), both of the Sn 3d\(5/2\) and Cl 2p\(3/2\) binding energies decrease.

Introduction
Ionic liquids, which are also known as low temperature molten salts, have found applications in both academic and industrial sources, attributing to their fascinating properties [1], especially negligible volatility and non-flammability. By varying the functionality of either the cation or the anion, it is potential to tune physico-chemical properties of ionic liquids [2-5]. Halometallate ionic liquids have been extensively investigated for electrochemical and catalytic applications [6, 7]. Many metal halides, e.g. AlCl\(_3\) and FeCl\(_3\), can be dissolved in halide-based ionic liquids, e.g. Cl\(_-\), to form different metal-complex anions which are dependent upon the metal halide/ionic liquid ratio. Apart from AlCl\(_3\) and FeCl\(_3\), a large range of different chlorostannate anions with varying molar fractions of SnCl\(_2\) can be prepared. These chlorostannate-based ionic liquids have been reported to interact with Pt catalyst in hydroformylation reactions to form a more catalytic active species [8].

Over the past decade, X-ray photoelectron spectroscopy (XPS) has shown ability to reveal information, such as the elemental composition, surface enrichment, the subtle change of the electronic environment of a certain component present in an ionic liquid [9, 10], the cation-anion interaction [11-13] and catalyst-ionic liquids interaction[14, 15]. XPS analysis has also been used to provide detailed information on metal-based speciation formed in ionic liquids, through interaction between metal complexes and either the cation [14] or the anion [16] of ionic liquids. In some cases, metal complexes are innocent in ionic liquids. However, higher probability has been realised that metal complexes can interact with ionic liquids, and lead to either reduction of the metal complex [9, 15] or formation of metal-carbene complexes [14]. By properly dissolving metal complexes in ionic liquids, it is possible to tune the electronic environment of both the cation and the anion of ionic liquids.

In this study, three binary and one ternary chlorostannate ionic liquid mixtures are analysed by XPS, together [C\(_6\)C\(_1\)Im]Cl. The electronic environment of cation-based component is compared based upon measured N 1s binding energy. The impact of the weighting of anions on the electronic environment of anion-based component is also demonstrated in detail based on binding energies of Sn 3d and Cl 2p. It is found that with
the increasing of the weighting of Cl, the measured binding energies of Sn 3d$_{5/2}$ and Cl 2p$_{3/2}$ both decrease.

**Experimental**

**Materials:** All chemicals were purchased from Jiayijia Glassware and Chemicals Company of Shenyang (China) with high purity and were used as received except for 1-methylimidazole, which was distilled over calcium hydride prior to use. The procedure for the synthesis of ionic liquids, NMR data and XP spectra of ionic liquids can be found in more detail in Supplementary Information.

**XPS Data Collection:** All XP spectra were recorded using a PHI Quantera II spectrometer employing a focused, monochromated Al K$_\alpha$ source ($h\nu = 1486.6$ eV), hybrid (magnetic/electrostatic) optics, hemispherical analyser and a multi-channel plate and delay line detector (DLD) with a X-ray incident angle of 30° and a collection angle, $\theta$, of 0° (both relative to the surface normal). The analysed area was 100 µm×100 µm, and 16 different spots of each sample were analysed.

Ionic liquid samples were presented as thin films (approx. thickness 0.5-1 mm) on a stainless sample bar. Pumping of ionic liquids was carried out with care as the high viscosities associated with these samples meant that significant bubbling due to removal of volatile impurities was observed. The preparation chamber pressure achieved was $\approx 10^{-7}$ mbar. The samples were then transferred to the main analytical vacuum chamber. The pressure in the main chamber remained below $1 \times 10^{-8}$ mbar during all XPS measurements, suggesting that all volatile impurities, such as water, are removed, leading to high purity samples.

**XPS Data Analysis:** Fitting of XP spectra was carried out in CasaXPS. For data interpretation, a spline linear background subtraction was used. Peaks were fitted using GL(30) lineshapes; a combination of a Gaussian (70%) and Lorentzian (30%) [17]. Fitting of C 1s spectra for all ionic liquids were conducted according to Ref. [18]. All XP spectra in this study were charge corrected by setting the measured binding energy of C$_{aliphatic}$ 1s equal to 285.0 eV [11, 12, 19-21].

To aid visual interpretation of the XP spectra, all spectra were normalised to the fitted area of N$^{cation}$ 1s peak of [C$_6$C$_1$Im]Cl. This peak was used for normalisation simply because the nitrogen atoms are present in all cations studied in this work with the same amount. The normalisation is applied to all XP spectra for a particular ionic liquid, and therefore does not affect the relative ratios of different elements within the ionic liquid.

**Results and Discussion**

**Electronic environment of the cation**

The effect of the anion on the electronic environment of the cation is investigated for the ternary ionic liquid mixture and three binary ionic liquid mixtures. The N 1s spectra for all ionic liquid mixtures are shown in Figure 1.

As shown in Figure 1, the N 1s binding energy for all samples follows the trend:
The measured binding energy of $N_{\text{cation}}$ 1s for $[\text{C}_8\text{C}_1\text{Im}]\,[\text{SnCl}_3]$ is found at 402.0 eV [22], which is 0.1 eV lower than that $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$ [21]. When $\text{Cl}^-$ is involved to form the mixture, $N$ 1s binding energy of $[\text{C}_8\text{C}_1\text{Im}][\text{SnCl}_3]_{0.5}\text{Cl}_{0.5}$ shift 0.2 eV to the lower value than that of the primary ionic liquid, i.e. $[\text{C}_8\text{C}_1\text{Im}][\text{SnCl}_3]$ [22]. $\text{Cl}^-$ as one of the most basic anions, transfers more negative charge to $[\text{C}_8\text{C}_1\text{Im}]^+$ cation which leads to the nitrogen atom with higher electron density and thus exhibits lower binding energy. With the increasing of the weighting of $\text{Cl}^-$ in the mixture, the $N$ 1s binding energy is found decreased.

In the case of the ternary ionic liquid mixture, $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]_{0.5}[\text{SnCl}_3]_{0.25}\text{Cl}_{0.25}$, since the weighting of $\text{Cl}^-$ is lower, the amount of negative charge transferred from $\text{Cl}^-$ to $[\text{C}_8\text{C}_1\text{Im}]^+$ is relatively low, which leads to the nitrogen atom more positively charged, when compared to that of $[\text{C}_8\text{C}_1\text{Im}][\text{SnCl}_3]_{0.5}\text{Cl}_{0.5}$. The $N$ 1s binding energy for the ternary ionic liquid mixture is 402.1 eV, as shown in Table 1, higher than that of $[\text{C}_8\text{C}_1\text{Im}][\text{SnCl}_3]_{0.5}\text{Cl}_{0.5}$, but is found the same with that of $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$ [21].

**Figure 1** N 1s spectra for $[\text{C}_8\text{C}_1\text{Im}]^+$ ionic liquids: (a) $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]_{0.5}[\text{SnCl}_3]_{0.25}\text{Cl}_{0.25}$, (b) $[\text{C}_8\text{C}_1\text{Im}][\text{SnCl}_3]_{0.5}\text{Cl}_{0.5}$, (c) $[\text{C}_8\text{C}_1\text{Im}][\text{SnCl}_3]_{0.2}\text{Cl}_{0.8}$, (d) $[\text{C}_8\text{C}_1\text{Im}][\text{SnCl}_3]_{0.1}\text{Cl}_{0.9}$ and (e) $[\text{C}_8\text{C}_1\text{Im}]\text{Cl}$. 
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Note:
¹Cl component for [SnCl₃].
²Cl component for Cl.
Electronic environment of the anion

The Cl 2p and Sn 3d_{5/2} high resolution spectra of all chlorostannate ionic liquid mixtures are shown in Figure 2. A typical Cl 2p spectrum is composed of a doublet peak with a spin-orbital coupling energy difference of 1.6 eV [22] and area ratio of 2p_{3/2} : 2p_{1/2} is 2:1. As shown in Figure 2a, it is obvious that Cl centres are in two different electronic environments. A satisfactory fitting could be achieved by setting the area ratio of the two different environments to 3:1 and both chlorine environments with spin-orbital coupling energy gap of 1.6 eV [22]. The component showing higher binding energy corresponds to the Cl atom present in [SnCl_3]. The component showing lower binding energy represents Cl-. The Goodness of Fit (R^2) is also included in the caption of Figure 2 to identify the quality of fittings.

Figure 2 (a) Cl 2p and (b) Sn 3d_{5/2} spectra for [C_8C_1Im]+ ionic liquids: [Tf_2N]_{0.5}[SnCl_3]_{0.25}Cl_{0.25} \ (R^2=0.9989), \ [SnCl_3]_{0.5}Cl_{0.5} \ (R^2=0.9976), \ [SnCl_3]_{0.2}Cl_{0.8} \ (R^2=0.9969) \ and \ [SnCl_3]_{0.1}Cl_{0.9} \ (R^2=0.9948).

The measured binding energy of Cl 2p_{3/2} (corresponding to Cl) for the equimolar binary mixture, [C_8C_1Im][SnCl_3]_{0.5}Cl_{0.5}, is 197.3 eV, which is 0.3 eV higher than that of [C_8C_1Im]Cl.
According to the measured binding energy of $N_{cation}$ 1s, the basicity of $[SnCl_3]^-$ should sit between $[Tf_2N]^-$ and $Cl^-$. Therefore, $[SnCl_3]^-$ is less basic than $Cl^-$. When $[SnCl_3]^-$ is involved in preparing binary ionic liquids, due to the lower basicity of $[SnCl_3]^-$, the charge transferred from $[SnCl_3]^-$ to the cation is low [24]. Therefore the $[C_6C_1Im]^+$ would be more capable to accept point charges from $Cl^-$, which leads to the $Cl^-$ centre bearing lower electron density and thus showing higher binding energy. The same observation is also found for $[SnCl_3]^-$.

It is found that binding energies of $Sn$ 3d$5/2$ and $Cl$ 2p$3/2$ (corresponding to $[SnCl_3]^-$) for $[C_6C_1Im][SnCl_3]_{0.5}Cl_{0.5}$ are 486.9 eV and 198.6 eV respectively, both of which are 0.2 eV lower than those of $[C_6C_1Im][SnCl_3]$ [22].

When $[Tf_2N]^-$ is involved in preparing the ternary ionic liquid mixture, due to the lowest basicity of $[Tf_2N]^-$, the amount of charge transferred from the anion to the cation is even lower. Therefore the $[C_6C_1Im]^+$ would be more capable to accept point charges from $[SnCl_3]^-$ and $Cl^-$, which leads to both of the $Sn$ centre and the $Cl^-$ centre being less negatively charged and thus show higher binding energy. As shown in Figure 2 and Table 1, the binding energies for $Sn$ 3d$5/2$ and $Cl$ 2p$3/2$ (corresponding to $Cl^-$) are 687.0 eV and 197.4 eV respectively, both of which are the highest.

The opposite is also true when the larger amount of the more basic anion, $Cl^-$, is involved. It is found that with the increasing of the weighting of $Cl^-$, the measured binding energies of both of $Sn$ 3d$5/2$ and $Cl$ 2p$3/2$ (corresponding to $[SnCl_3]^-$) decrease. However, $Cl$ 2p$3/2$ binding energies (corresponding to $Cl^-$) for both of samples are 0.1 eV higher than that of $[C_6C_1Im]Cl^-$.

**Conclusions**

Three binary and one ternary chlorostannate ionic liquid mixtures, together with $[C_6C_1Im]Cl^-$, are successfully analysed by XPS. The electronic environment of the cation-based component is compared based upon measured $N$ 1s binding energy. It is found that with the increasing of the weighting of $Cl^-$, the amount of negative charge transferred from $Cl^-$ to $[C_6C_1Im]^+$ is relatively high, which leads to the nitrogen atom less positively charged. It is reflected on the measured $N$ 1s binding energy.

The impact of using binary and ternary anions on the electronic environment of the anion-based component is also demonstrated in detail based on binding energies of $Sn$ 3d and $Cl$ 2p. Due to the presence of less basic anions, $[C_6C_1Im]^+$ would be more capable to accept point charges from $Cl^-$, which leads to $Cl^-$ being less negatively charged and thus show higher binding energy. Meanwhile, with the increasing of the weighting of $Cl^-$, $[C_6C_1Im]^+$ would be less capable to accept point charges from $[SnCl_3]^-$.

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