Spectroscopic analysis of 1-butyl-2,3-dimethylimidazolium ionic liquids: cation-anion interactions

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Abstract

In this study, four 1-butyl-2,3-dimethylimidazolium ionic liquids are analysed by X-ray photoelectron spectroscopy, together with three 1-butyl-3-methylimidazolium ionic liquids. A reliable fitting model for the carbon 1s region of 1-butyl-2,3-dimethylimidazolium ionic liquids is modified according to established models. The effect of the anion on the electronic environment of the cation is explored based upon the comparison between measured binding energies of nitrogen 1s and hydrogen bond acceptor ability. The effect of the cation on the cation-anion interactions is also demonstrated by carefully comparing the hydrogen bond donating ability of different cations, with a definite anion.

Introduction

Ionic liquids, possessing many fascinating properties, in particularly negligible vapour pressures, have been widely investigated by X-ray photoelectron spectroscopy (XPS) since 2005[1, 2]. XPS has been used to investigate the elemental composition, surface enrichment and the subtle change of the electronic environment of a certain component present in an ionic liquid[3-6], as well as the cation-anion interaction of ionic liquids[7-9]. Apart from that, XPS analysis can also focus on the demonstration of the catalyst-ionic liquids interaction[10, 11] and the catalyst-ligand interaction in ionic liquids[12]. Binding energy can even be correlated to NMR data[13] and Kamlet-Taft parameters[7] to allow further understanding of the physico-chemical properties of ionic liquids.

As conducting samples, ionic liquids which are liquids at room temperature can dissipate the charge built up at the sample surface as a result of prolonged photoemission effect[3, 14] and therefore give well-resolved peaks in core level XP spectra[3]. Consequently, the effect of charging is negligible and charge neutralisation is not normally necessary. However, measurable shifts in binding energy can still be observed for ionic liquids photoelectron peaks recorded over prolonged periods of time[7]. To overcome this potential problem and obtain comparable information between different spectra, standard charge correction methods should always be applied[7]. Among all charge correction methods, the internal referencing of the aliphatic carbon has been widely used to get comparable binding energies. This method relies on the referencing of the aliphatic carbon to a certain binding energy, which consequently needs the development of the fitting model of C 1s spectra of ionic liquids.

Over the past decade, investigation of ionic liquids by XPS has been focused on many families of cations, such as imidazolium[7, 13, 15], pyrrolidinium[8, 16], pyridinium[9] and ammonium[17]. Apart from 1-alkyl-3-methylimidazolium ionic liquids, 1-alkyl-2,3-dimethylimidazolium ionic liquids have also been analysed by XPS, especially as a part of lubricants[18, 19] and functionalised metal nanoparticles[20]. However, a systematic investigation of this family of ionic liquids has not been conducted yet.

In this study, four 1-butyl-2,3-dimethylimidazolium ($[C_4C_1C_1Im]^+$) ionic liquids are analysed by XPS, together with three 1-butyl-3-methylimidazolium ($[C_4C_1Im]^+$) ionic liquids. A reliable fitting model for the C 1s region is modified according to established models. The charge correction method is discussed. The electronic effect of the anion on the electronic environment of the cation is explored based upon the comparison between measured binding energies of N 1s and hydrogen bond acceptor ability (β). Meanwhile, the effect of the cation on the cation-anion interactions is also demonstrated by carefully comparing the hydrogen bond donating ability (α) of different cations, with a definite anion.

Experimental

Materials: All chemicals were purchased from Jiayijia Glassware and Chemicals Company of Shenyang (China) or Sigma-Aldrich and were used as received except for 1-methylimidazole, which was distilled over calcium hydride prior to use. The procedures of synthesis of ionic liquids, NMR data and survey 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 Kα 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, θ, 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.

The 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 ≈ 10^{-7} mbar. The samples were then transferred to the main analytical vacuum chamber. The pressure in the main chamber remained below 1×10^{-8} mbar during all XPS measurements, suggesting that all volatile impurities, such as water, are removed, leading to high purity samples[21].

XPS Data Analysis: 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%)[22, 23].

To aid visual interpretation of the XP spectra, all spectra were normalised to the fitted area of N_{cation} 1s peak of $[C_4C_1C_1Im][Tf_2N]$. This peak was used for normalisation simply because nitrogen atoms are present in both used cations studied in this work in 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. It allows simple visual comparison of the same element for different ionic liquids as any differences in intensity will be due to the variation in the stoichiometric composition of that particular element of interest.

Results and Discussion

Electronic environment of carbon regions and charge correction

Here we describe the fitting model of C 1s for $[C_4C_1C_1Im]^+$-based ionic liquids by demonstrating the representative example in this paper, $[C_4C_1C_1Im][Tf_2N]$, as shown in Figure 1. The high resolution C 1s XP spectrum of $[C_4C_1C_1Im][Tf_2N]$ is composed of two peaks, a singlet peak showing binding energy at 292.9 eV, which has been assigned to $-CF_3$, and an unresolved multiplet peak between 290.0 eV and 283.0 eV. By carefully considering the electronic environment of the carbon atom within $[C_4C_1C_1Im]^+$ cation, the unresolved multiplet peak can be fitted using a three-component model. The peak showing binding energy at 287.8 eV is fitted as C^2 1s, because this component is more positively charged as it is bonded directly to two nitrogen atoms. The peak at 286.6 eV is fitted as C_{hetero} 1s, which includes four carbon atoms directly bonded to the nitrogen atom, *i.e.* C^4-C^7. The peak at 285.2 eV is fitted as $C_{aliphatic}$ 1s, including C^8-C^{10}. Meanwhile, according to the ^{13}C NMR data, C^{11} exhibits surprisingly the lowest chemical shift (δ_C = 9.78). By carefully comparing the point charges of atoms within the cation, it is found that C^{11} is with higher electron density than any other carbon atoms bonded directly to the cation headgroup including C^2-C^7[24]. Consequently, C^{11} has similar electronic environment to those of C^8-C^{10} and should be fitted into $C_{aliphatic}$ 1s component as well. A satisfactory fitting can be obtained by constraining the area ratio of these three components to 1:4:4. The obtained FWHM ratio for C^2: C_{hetero}: $C_{aliphatic}$ is 1.09: 1.17: 1.27, which is reasonable as the aliphatic carbon signal is actually an overlap of several carbon signals and therefore has been shown to produce a characteristic broader signal than other carbon components[25, 26].

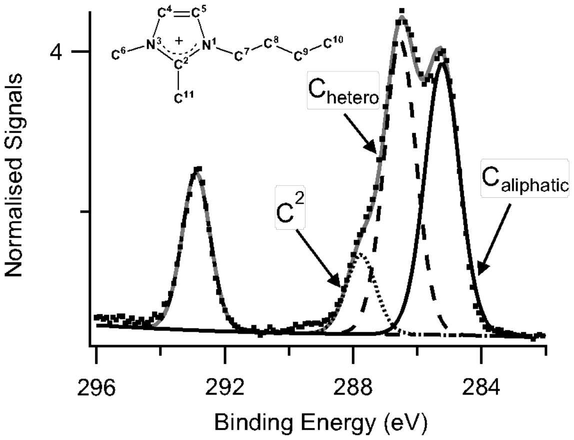

Figure 1 C 1s XP spectrum with fittings for $[C_4C_1C_1Im][Tf_2N]$. The spectrun was fitted using three components: C^2, C_{hetero} (C^4-C^7) and $C_{aliphatic}$ (C^8 onwards). The inset structure shows the numbering system used in the deconstruction.

The same procedures for the fitting of C 1s spectra of $[C_4C_1C_1Im]Br$ and $[C_4C_1C_1Im][TfO]$

were also carried out. $[OAc]^-$ comprises new carbon contributions. Consequently, their additional contributions have been included in the fitting model by amending the appropriate weighting to the existing component, *i.e.* carbon signal from the carboxylate group is fitted into C^2; the electronic environment of the methyl group of the anion is similar to that of C^{11}, therefore it is fitted into $C_{aliphatic}$ (see Figure S2).

Previous investigations about the charge correction methods for a series of families of ionic liquids have concluded that for the anion with lower basicity, due to the electronic impact of the positive charge on the cation headgroup, the binding energy of $C_{aliphatic}$ 1s shifts to a higher value with the decreasing of the alkyl chain length. Consequently, this internal reference is only reliable when the alkyl chain is long enough, *i.e.* octyl; for other alkyl chains, charge corrections can be carried out by referencing the N 1s peak to the value measured for octyl-based analogous. For a definite anion with higher basicity, *i.e.* Cl^-, Br^- and $[OAc]^-$, $C_{aliphatic}$ 1s is always reliable as an internal reference[7, 13, 15]. Unfortunately, full data set of XP spectra for 1-alkyl-2,3-dimethylimidazolium ionic liquids is insufficient. Consequently, in this study, for $[C_4C_1C_1Im]Br$ and $[C_4C_1C_1Im][OAc]$, $C_{aliphatic}$ 1s is used as the internal reference (set to 285.0 eV). For $[C_4C_1C_1Im][Tf_2N]$ and $[C_4C_1C_1Im][TfO]$, charge corrections are carried out by referencing the corresponding F 1s peak to values reported in the literature (688.8 eV for $[Tf_2N]^-$ and 688.4 eV for $[TfO]^-$ respectively[7]), as the F 1s peak in $-CF_3$ group is thought consistent during XPS measurement[7, 27].

In order to get comparable data, C 1s spectra for $[C_4C_1Im]^+$-based ionic liquids used in this study are also fitted using the similar model for $[C_4C_1C_1Im]^+$ by amending corresponding area ratio of three components (see Figure S3 in Supplementary Information).

Electronic environment of nitrogen regions

The effect of the anion on the charge transferred to the cation has been investigated for three $[C_4C_1C_1Im][X]$ ionic liquids, where X = $[Tf_2N]^-$, $[TfO]^-$ and Br^-. The binding energies for N 1s (also C^2 1s and C_{hetero} 1s) follow the trend: $[Tf_2N]^- > [TfO]^- > Br^-$, as shown in Figure 2. The higher binding energy corresponds to a more electropositive cation. Therefore, more charge is transferred from anion to the cation for the more basic anion. These results suggest that the anion can significantly influence the electronic environment of the cation, for $[C_4C_1C_1Im]^+$-based ionic liquids.

The binding energy N 1s can be correlated to the anion basicity (β)[28]. For low basicity anions such as $[Tf_2N]^-$ (with $[C_4C_1C_1Im]^+$ cation, $\beta=0.44$[29]), the N_{cation} 1s binding energy is relatively high (401.9 eV), meaning that the cation is relatively electropositive. Clearly, low basicity anions transfer less charge to the cation. The basicity of $[TfO]^-$ (with $[C_4C_1C_1Im]^+$ cation, $\beta=0.59$[29]) is higher than that of $[Tf_2N]^-$, which means that more negative charge is transferred from $[TfO]^-$ to $[C_4C_1C_1Im]^+$ cation, leading to a slightly lower N 1s binding energy (401.7 eV). Br^- is considered as one of the most basic anions, which can transfer the most negative charge to the counter cation. The measured N 1s binding energy for [$C_4C_1C_1$Im]Br is 401.5 eV, which is the lowest among three [$C_4C_1C_1$Im]$^+$-based ionic liquids. Unfortunately, the β value for Br^- (with [$C_4C_1C_1$Im]$^+$ cation) is unavailable to give a visual correlation. However, it is quite apparently that the N_{cation} 1s binding energy follows the same trend as the basicity of the anion (β). This observation is in good agreement with previous XPS investigations of the cation-anion interactions of ionic liquids[13, 30]. The same conclusion can also be made to [OAc]$^-$, as the measured binding energy of N 1s for [OAc]$^-$ is the same with that of Br^- (see Table 1). It must be noted that, due to the different technique for the calculation of the basicity of anions (β) and acidity of caitons (α), it is better to cite these values from the same literature to avoid introducing errors.

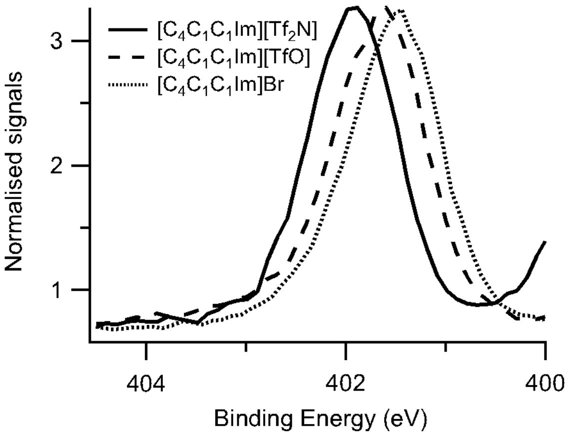

Figure 2 N 1s spectra for [$C_4C_1C_1$Im][Tf_2N], [$C_4C_1C_1$Im][TfO] and [$C_4C_1C_1$Im]Br.

[$C_4C_1C_1$Im]X versus [C_4C_1Im]X

Table 1 lists binding energies of all elements for all ionic liquids studied herein. At the first glance, it is apparently that for a definite anion, binding energy of N_{cation} 1s for the [$C_4C_1C_1$Im]$^+$-based ionic liquid is lower than that of the [C_4C_1Im]$^+$-based analogues; whilst the value for C^2 1s is higher. For example, the measured N 1s binding energy for [$C_4C_1C_1$Im]Br is 401.5 eV, which is ~0.2 eV lower than that of [C_4C_1Im]Br (401.7 eV). On other hand, binding energies of C^2 1s for [$C_4C_1C_1$Im]Br and [C_4C_1Im]Br are 287.4 eV and 287.2 eV, respectively. It is well known that the positive charge within imidazolium cation is delocalised[31]. Due to the inductive effect of the additional methyl group on C^2 position, the distribution of partial charges spreading over atoms within the cation headgroup would be changed. As a result, C^2 atom bears more positive point charges, with two nitrogen atoms being left more negatively charged (on an average)[24]. Consequently, in the case of [$C_4C_1C_1$Im]$^+$, C^2 atom shows higher binding energy, whilst two nitrogen atoms exhibit lower binding energies, when compared to those of [C_4C_1Im]$^+$.

The acidity of the cation (α) and the sterically effect of long alkyl chains have also found to influence the charge-transfer from anion to cation[17]. Due to the inductive effect of the methyl group on C^2 position, the α value of $[C_4C_1C_1Im]^+$ (0.44 with $[Tf_2N]^-$ anion) is found lower than that of $[C_4C_1Im]^+$ (0.55 with $[Tf_2N]^-$ anion)[29]. Consequently, the acidity of the H atom which is bonded to the carbon atom in vicinity to the positively charged nitrogen atom for $[C_4C_1C_1Im]^+$ is weaker, when compared to that of $[C_4C_1Im]^+$. It should cause the decrease of the charge-transfer from anion to cation, and thus lead to a more negatively charged anion.

Table 1 Binding energy of all elements for all ionic liquids in this study. [a]Data available according to Ref [7].

	Binding energy / eV									
Ionic liquids	F 1s	O 1s	N_{cation} 1s	N_{anion} 1s	$C_{aliphatic}$ 1s	C_{hetero} 1s	C^2 1s	C_{CF3} 1s	S $2p_{3/2}$	Br $3d_{5/2}$
$[C_4C_1Im][Tf_2N]$	688.8	532.7	402.1	399.5	285.2	286.7	287.7	293.0	169.0	
$[C_4C_1C_1Im][Tf_2N]$	688.8	532.7	401.9	399.5	285.2	286.6	287.8	292.9	169.0	
$[C_4C_1Im][TfO]$[a]	688.5	532.0	402.0		285.2	---	287.6	292.5	168.4	
$[C_4C_1C_1Im][TfO]$	688.4	532.0	401.7		285.1	286.4	287.6	292.5	168.3	
$[C_4C_1Im][OAc]$		530.3	401.7		285.0	286.3	287.3			
$[C_4C_1C_1Im][OAc]$		530.4	401.5		285.0	286.3	287.4			
$[C_4C_1Im]Br$			401.7		285.0	286.3	287.2			67.5
$[C_4C_1C_1Im]Br$			401.5		285.0	286.2	287.4			67.3

For the low basic anion, *i.e.* $[Tf_2N]^-$, as the charge-transfer effect is negligible, the measured binding energies of all anion-based elements for $[C_4C_1C_1Im][Tf_2N]$ are the same with those of $[C_4C_1Im][Tf_2N]$, within the experimental error, as shown in Table 1.

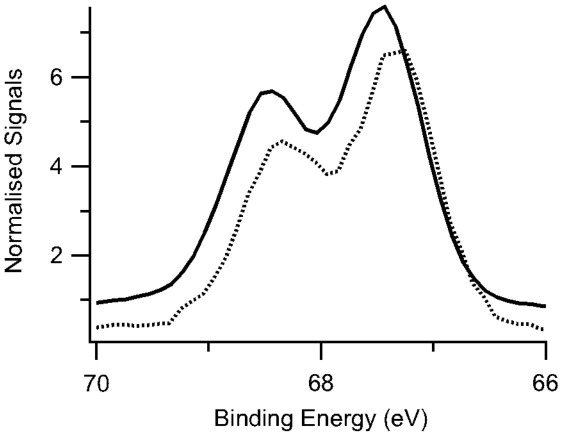

Figure 3 Br 3d spectra for $[C_4C_1Im]Br$ (black) and $[C_4C_1C_1Im]Br$ (dot).

For the high basic anion, *i.e.* Br^-, since the charge transferred from anion to caion is significant, the weaker acidity of the cation can effectively shield the charge-transfer effect. As shown in Figure 3, the Br 3d binding energy for $[C_4C_1C_1Im]Br$ is ~0.2 eV lower than that of $[C_4C_1Im]Br$, meaning that in the case of $[C_4C_1C_1Im]Br$, Br^- is left with much higher electron density. It must be noted that the experimental error associated with XPS is of the order ± 0.1 eV. Consequently, any reported binding energy shift should be larger than 0.2 eV; otherwise, one has to report a series of samples to give a trend to demonstrate the change in binding energy. As has been stated above, the shift in Br 3d binding energy in this study is ~0.2 eV, meaning that the shift is not perfectly noticeable. The acidity of the cation can be influenced through inductive effect and sterically shielding effect. In the case of $[C_4C_1C_1Im]^+$, since the methyl group bonded to C^2 position is with lower sterical effect, the impact of the decrease in acidity of the cation upon charge-transfer is not as much to be reflected on binding energy. However, it inspires an idea on the investigation of the effect of the acidity of caiton on the cation-anion interactions.

Conclusions

Four $[C_4C_1C_1Im]^+$-based ionic liquids are successfully analysed by XPS, together with three $[C_4C_1Im]^+$-based ionic liquids. A reliable fitting model for the C 1s region is modified according to established models. The charge correction method is discussed. The electronic effect of the anion on the electronic environment of the cation is explored based upon the comparison between measured binding energies of N 1s and β values. The effect of the cation on the cation-anion interactions is also demonstrated by carefully comparing α values of different cations, with a definite anion.

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