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## NATURAL POLYMERS

# Probing the Cellulose-Ionic Liquids Interaction by X-ray Photoelectron Spectroscopy[1]

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**Abstract**—X-ray photoelectron spectroscopy is used as a probe to demonstrate the interaction between cellulose and 1-butyl-3-methylimidazolium chloride. The fitting models of C 1*s* spectra for the ionic liquid, cellulose and cellulose containing solutions are developed. The measured binding energy of $C^2$ 1*s* component is used to indicate the ionic liquid-cellulose interaction. In the case of the cellulose containing solution, due to the weaker charge-transfer effect between hydrophilic groups of cellulose and the imidazolium cation, the $C^2$ atom is in a more electropositive environment and thus exhibits higher binding energy.

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## INTRODUCTION

To date, ionic liquids have found applications in a large range of sources such as homogeneous catalysis [1, 2], organic/inorganic synthesis [3, 4], phase separation [5, 6], $CO_2$ capture [7] and electrochemistry [8, 9]. The widespread applications of ionic liquids are ascribed to their fascinating properties, i.e. high thermal stability, high conductivity, wide liquid range and excellent solvation properties.

Ever since 2002, ionic liquids have been successfully employed in the processing of cellulose [10]. Many investigations have been conducted aiming to improve the solubility of cellulose in ionic liquids and decrease the temperature of dissolution. For this target, design and synthesis of functionalised ionic liquids have been successfully carried out. Furthermore, the mechanism of the dissolution of cellulose in ionic liquids has also been revealed [11]. The impact of both the cation and the anion upon dissolution of cellulose in ionic liquids has been suggested. Among all techniques, NMR is the most commonly employed one. Unfortunately, most of the time, NMR data are obtained when samples have to be diluted in deuterated solvents.

X-ray photoelectron spectroscopy (XPS) has been used as an effective technique to investigate pure ionic liquids [12, 13], ionic liquid mixtures [14] and ionic liquid-based solutions [15–17]. Due to the negligible volatility of ionic liquids, the cellulose containing ionic liquid solutions can be analyzed directly by XPS, which offers an opportunity to provide information on the ionic liquid-cellulose interaction.

In this study, XPS is used to probe the interaction between cellulose and 1-butyl-3-methylimidazolium chloride ($[C_4C_1Im]Cl$). The fitting models of C 1*s* spectra for $[C_4C_1Im]Cl$, cellulose and cellulose containing solutions are developed. The measured binding energy of $C^2$ 1*s* component is used to indicate the ionic liquid-cellulose interaction. In the case of the cellulose containing solution, due to the weaker charge-transfer effect between hydrophilic groups of cellulose and the imidazolium cation, when compared to that of $Cl^-$, the $C^2$ atom is in a more electropositive environment and thus exhibits higher binding energy.

## EXPERIMENTAL

### *Materials*

All chemicals were obtained from Chinese Market and were used as received except for 1-methylimidazole, which was distilled over calcium hydride prior to use.

Synthesis of $[C_4C_1Im]Cl$: 1-methylimidazole was placed in a two necked round-bottomed flask fitted with a water condenser topped with a blue silica tube. 1-Chlorobutane (1.2 molar equivalents) was added drop wise into the flask with stirring at 70°C. The reaction was allowed to proceed for 48–72 h. The

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[1] The article is published in the original.

product was then recrystallized in the mixture of acetonitrile and ethyl acetate. The desired product, $[C_4C_1Im]Cl$, was firstly dried using a rotary evaporator and then under high vacuum at 60°C for 12 h to yield a white solid [18].

### *Dissolution of Cellulose into the Ionic Liquid*

2 g of dried microcrystallized cellulose (MCC) was added into a 500 mL flask containing 48 g of the dried ionic liquid. The flask was sealed and the mixture was heated at 60°C and stirred under nitrogen atmosphere. After the solution became optically clear under a polarization microscope, additional MCC was added until the cellulose solution became saturated, judged by the fact that cellulose could not be dissolved further within 2 h. It was found that the solubility of the MCC used in this study was up to 12 wt %.

### *XPS Data Collection*

All XP spectra were recorded using a PHI Quantera II spectrometer employing a focused, monochromated $AlK_\alpha$ source ($h\nu = 1486.6$ eV), hybrid (magnetic/electrostatic) optics, hemispherical analyzer 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 analyzed area was 100 × 100 μm, and 16 different spots of each sample were analyzed.

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 [19].

### *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%) [20, 21]. All XP spectra in this study were charge corrected by setting the measured binding energy of the aliphatic C 1*s* component ($C_{aliphatic}$ 1*s*) to 285.0 eV [22].

## RESULTS AND DISCUSSION

### *Fitting Procedure for C 1s Region of $[C_4C_1Im][X]$*

The high resolution C 1*s* XP spectra of imidazolium-based ionic liquids have been fitted based upon several established models by other research groups all over the world [22–25]. Here we describe our fitting model by demonstrating the representative example in this paper, $[C_4C_1Im]Cl$, as shown in Fig. 1. The high resolution C 1*s* XP spectrum of non-functionalised imidazolium-based ionic liquids is composed of two unresolved peaks. However, by carefully analyzing the electronic environment of the carbon atoms, there should be three electronic equivalent carbon components, showing binding energies at 285.0, 286.3 and 287.2 eV respectively. Therefore a three-component model was used to fit the C 1*s* XP spectrum for $[C_4C_1Im]Cl$. The peak at 285.0 eV is fitted as $C_{aliphatic}$ 1*s*; the peak at 286.3 eV is fitted as $C_{hetero}$ 1*s*; the peak at 287.3 eV is fitted as $C^2$.

### *Fitting Procedure for C 1s and O 1s Regions of Cellulose*

The high resolution C 1*s* XP spectrum of cellulose is composed of three unresolved peaks. Taking into account the structure of the anhydroglucose unit of cellulose, there should be two carbon components, which can be defined as $C_{O-C-C}$ and $C_{C-O}$. Apart from these two components, the aliphatic carbon atoms are also present in cellulose. The signals of this component originate from the hydrocarbon compound contaminations in cellulose, as has been reported in the literature [26]. The aliphatic carbon component is not influenced by the charging generated during XP spectra acquisition and is therefore used as the internal reference for the charge correction. Consequently, a three-component model was used to fit the C 1*s* XP spectrum for cellulose. The peak at 285.0 eV is fitted as $C_{aliphatic}$ 1*s*; the peak at 286.7 eV is fitted as $C_{C-O}$ 1*s*; the peak at 288.2 eV is fitted as $C_{O-C-O}$. The O 1*s* spectrum is also fitted into two components according to ref. [26]. The component at 532.9 eV is fitted as $O_{OH}$ 1*s*; the component showing binding energy at 533.4 eV is fitted as $O_{C-O}$ 1*s*. A detailed demonstration of the fittings of C 1*s* and O 1*s* spectra for MCC is shown in Fig. 2.

### *Fitting Procedure for C 1s Region of Cellulose Containing Solutions*

The high resolution C 1*s* XP spectra for all cellulose containing solutions can be then fitted with a five-component model taking fitting models for cellulose and $[C_4C_1Im]Cl$ into account. The five components are defined as $C_{O-C-O}$ 1*s*, $C_{C-O}$ 1*s*, $C^2$ 1*s*, $C_{hetero}$ 1*s* and $C_{aliphatic}$ 1*s*, respectively. Figure 3 shows a representative example in this study, a 12 wt % cellulose solution in $[C_4C_1Im]Cl$.

### *The Ionic Liquid-Cellulose Interaction*

In order to give a spectroscopic probe of the ionic liquid-cellulose interaction, C 1*s* XP spectra of pure $[C_4C_1Im]Cl$, cellulose and a 12 wt % cellulose solution

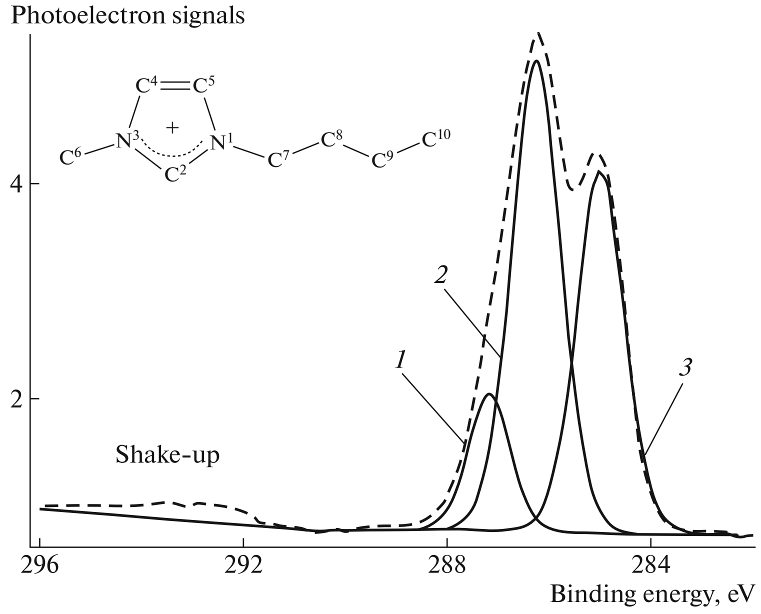

**Fig. 1.** C 1*s* XP spectrum with fittings for $[C_4C_1Im]Cl$. The spectrum was fitted using three components: (*1*) $C^2$, (*2*) $C_{hetero}$ ($C^4$–$C^7$), and (*3*) $C_{aliphatic}$ ($C^8$–$C^{10}$).

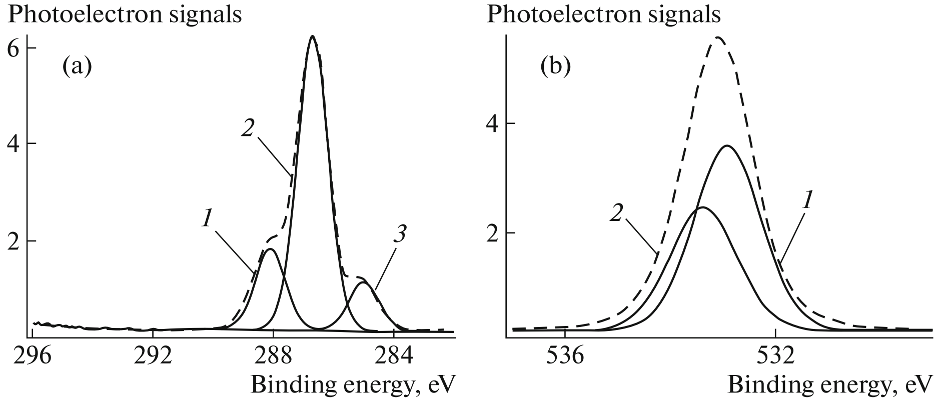

**Fig. 2.** XP spectra with fittings for MCC: (a) C 1*s* and (b) O 1*s*. The C 1*s* spectrum was fitted using three components: (*1*) $C_{O-C-O}$, (*2*) $C_{C-O}$ and (*3*) $C_{aliphatic}$; the O 1*s* spectrum was fitted into two components: (*1*) $O_{OH}$ and (*2*) $O_{C-O}$.

in $[C_4C_1Im]Cl$ are demonstrated in Fig. 4. At first glance, the shift in binding energy for $C^2$ 1s between $[C_4C_1Im]Cl$ and the 12 wt % cellulose solution is greater than the experimental error, as shown in Figs. 4a, 4b. The $C^2$ 1*s* binding energy for the cellulose solution shifts more than 0.2 eV to higher, when compared to that of $[C_4C_1Im]Cl$.

Due to the higher basicity of $Cl^-$, the charge transferred from $Cl^-$ to the imidazolium cation must be significant, as has been reported in the literature. Moreover, it has also been illustrated that the ionic liquid mixture contains intimate mixtures of cations and different anions, not pockets of the cation and one type of anion, with other pockets of the cation and the other anion. Consequently, in the cellulose solution, the imidazolium cation is surrounded by $Cl^-$ and the hydrophilic groups of cellulose, i.e. $OH^-$. The charge-transfer effect between these hydrophilic groups and the imidazolium cation can be carried out by the formation of hydrogen bonding, which is apparently weaker than that of $Cl^-$. Therefore, in the cellulose solution, less charge is transferred to the cation head-group, which consequently leads to the $C^2$ atom in a more electropositive environment and thus with higher binding energy. Table 1 lists binding energies of all carbon components for $[C_4C_1Im]Cl$, cellulose and cellulose solutions with different weight fraction. It

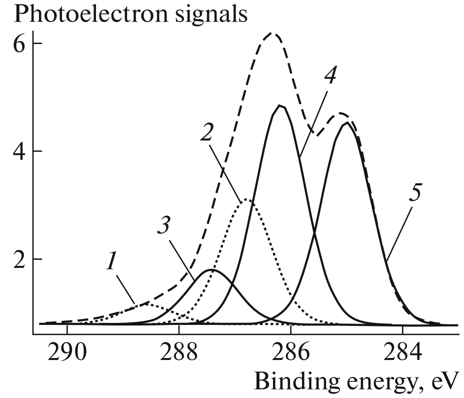

**Fig. 3.** C 1*s* XP spectrum with fittings for cellulose containing ionic liquid solution (12 wt %). The spectrum was fitted using five components: (*1*) $C_{O-C-O}$, (*2*) $C_{C-O}$, (*3*) $C^2$, (*4*) $C_{hetero}$, and (*5*) $C_{aliphatic}$.

indicates that the more amount of cellulose dissolved in [$C_4C_1$Im]Cl, the higher binding energy for $C^2$ 1*s* component, as shown in Fig. 5.

It is not trivial that the measured binding energy of $C_{O-C-O}$ 1*s* component for all cellulose solutions is more than 0.5 eV higher than that of cellulose. It is well known that upon dissolution of cellulose in ionic liquids, the intra/inter-molecular hydrogen bonding of cellulose can be completely destroyed but simultaneously replaced by the ionic liquid-cellulose interaction. The $C_{O-C-O}$ atom is bonded to two oxygen atoms. Therefore the change in electronic environment due the decomposition of hydrogen bonding should be more remarkable.

## CONCLUSIONS

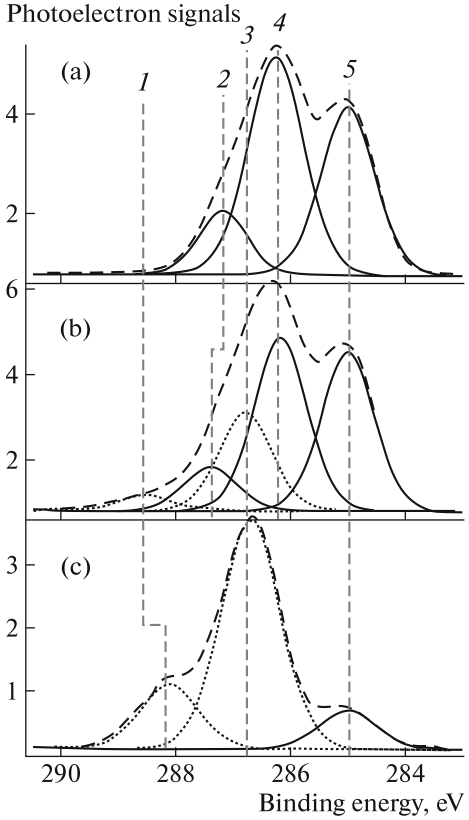

**Fig. 4.** C 1*s* XP spectra with fittings for (a) [$C_4C_1$Im]Cl, (b) cellulose solution (12 wt %) and (c) cellulose. (*1*) $C_{O-C-O}$, (*2*) $C^2$, (*3*) $C^2$ $C_{C-O}$, (*4*) $C_{hetero}$, and (*5*) $C_{aliphatic}$.

XPS is successfully used to probe the interaction between cellulose and [$C_4C_1$Im]Cl. The fitting models of C 1*s* spectra for [$C_4C_1$Im]Cl, cellulose and cellulose containing solutions are developed. The measured binding energy of $C^2$ 1*s* component is used to indicate the ionic liquid-cellulose interaction. In the case of cellulose containing solutions, due to the weaker charge-transfer effect between hydrophilic groups of cellulose and imidazolium cation, the $C^2$ atom is in a more electropositive environment and thus exhibits higher binding energy.

**Table 1.** C 1*s* binding energies of all components for [$C_4C_1$Im]Cl, cellulose and cellulose solutions with different weight fraction

| Sample | Binding energy, eV | | | | |
|---|---|---|---|---|---|
| | $C^2$ 1*s* | $C_{hetero}$ 1*s* | $C_{aliphatic}$ 1*s* | $C_{C-O}$ | $C_{O-C-O}$ |
| [$C_4C_1$Im]Cl | 287.2 | 286.3 | 285.0 | | |
| Cellulose | | | 285.0 | 286.7 | 288.1 |
| 2% solution | 287.3 | 286.2 | 285.0 | 286.8 | 288.7 |
| 5% solution | 287.3 | 286.2 | 285.0 | 286.8 | 288.6 |
| 8% solution | 287.4 | 286.2 | 285.0 | 286.8 | 288.6 |
| 10% solution | 287.4 | 286.2 | 285.0 | 286.8 | 288.6 |
| 12% solution | 287.4 | 286.2 | 285.0 | 286.8 | 288.6 |

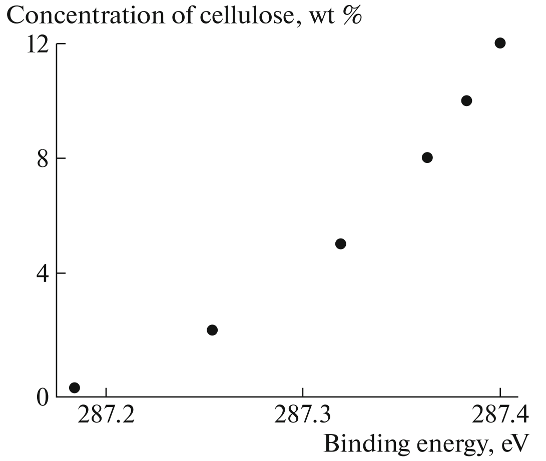

**Fig. 5.** Binding energy of $C^2$ 1*s* as a function of the concentration of cellulose in $[C_4C_1Im]Cl$.

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