Carbohydrate Polymers 127 (2015) 316–324

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Experimental and theoretical study of carbohydrate–ionic liquid interactions

El-Sayed R.E. Hassan, Fabrice Mutelet*, Mohammed Bouroukba

Université De Lorraine, Ecole Nationale Supérieure des Industries Chimiques, Laboratoire Réactions et Génie des Procédés (UMR CNRS 7274), 1 rue Grandville, 54000 Nancy, France

ARTICLE INFO

Article history:
Received 17 October 2014
Received in revised form 27 February 2015
Accepted 9 March 2015
Available online 30 March 2015

Keywords:
Cellulose
Glucose
Ionic liquids
Ab initio calculations

ABSTRACT

With increasing interest in the use of lignocellulosic biomass for the production of renewable transportation fuels, new approaches for biomass pretreatment have been of considerable interest. The conversion of biomass cellulose to water-soluble sugars is currently one of the most intensive demands worldwide. The use of ionic liquids has been described as a new potentially viable development in this area. Indeed, previous work indicates that carbohydrates are soluble in some imidazolium based ionic liquids. For a better understanding of the behavior of such systems, theoretical quantum chemical calculation have become complementarities of experimental measurements. The goal of this work is to investigate the fundamental natures of the interaction between glucose or cellulose and imidazolium based ionic liquids using ab initio calculations and comparing these results with experimental data. Furthermore, a characterization study was made to investigate the changes in the cellulose structure during the process of solubility and regeneration with ionic liquids.

1. Introduction

Since ILs are interesting for so many different fields, these solvents are currently being intensively studied by using a great variety of experimental and theoretical methods (Khelassi-Sefaoui, Mutelet, Mokbel, Jose, & Negadi, 2014; Mutelet, Hassan El-Sayed, Stephens, Acree, & Baker, 2013; Weingaertner, 2008). Among these methods, ab initio calculations play an important role in understanding the special nature of ILs and their interactions with dissolved components or interfaces (Hunt & Gould, 2006; Ji et al., 2012; Kiefer et al., 2008). Recently, ionic liquids have become of great interest in the field of bioengineering, chemical and physical processes (Park & Kazlauskas, 2003; Sheldon, Lau, Sorgedrager, van Rantwijk, & Seddon, 2002; van Rantwijkl, Lau, & Sheldon, 2003). Ionic liquids efficiently dissolve carbohydrates (Lee, Dang, Ha, Chang, & Koo, 2008), cellulose (Swatloski, Spear, Holbrey, & Rogers, 2002), and lignocellulosic biomass (e.g., miscanthus) (Fort et al., 2007; Kilpeläinen et al., 2007). Hydrogen bonding in ILs has been extensively studied because it plays an important role in cation–anion and solvent–solute interactions, as revealed by both experimental and theoretical investigations (Kolle & Dronskowski, 2004; Remsing, Wildin, Rapp, & Moyna, 2007; Wulf, Fumino, & Ludwig, 2010). For example, the hydrogen bond characteristics of ILs was said to be vitally important to design ILs as potential solvents for cellulose (Ohno & Fukaya, 2009; Zhang et al., 2012).

Xu, Pan, Wang, Zhang, and Liu (2012) showed that both chloride anions and imidazolium cations of the IL interact with the cellulose via hydrogen bonds. However, the anions occupy the first coordination shell of the oligomer, and the strength and number of hydrogen bonds and the interaction energy between anions and the oligomer are much larger than those between cations and the oligomer. It is observed that the intra molecular hydrogen bond in the oligomer is broken under the combined effect of anions and cations. The present results emphasize that the chloride anions play a critically important role and the imidazolium cations present a remarkable contribution in the cellulose dissolution. This point of view is different from previous one that only underlines the importance of the chloride anions in the cellulose dissolution. The present results improve our understanding for the cellulose dissolution in imidazolium chloride ILs. Ding et al. (2012) use DFT calculations to investigate the mechanism and regeneration of cellulose in acetate based IL. The study indicates that acetate anion forms strong H-bond with hydroxyl groups of (1,4)-dimethoxy-β-D-glucose. These H-bonds are weakened or destroyed by the addition of water. These results agrees well with the ab initio dynamic molecular results obtained on a monomer of b-cellulose (Payal & Blasubramanian, 2014). However, the role of the cation in the solvation of cellobiose cannot be completely ignored. Strong electrostatic

* Corresponding author. Tel.: +33 03 83 17 51 31; fax: +33 03 83 32 29 75.
E-mail address: fabrice.mutelet@univ-lorraine.fr (F. Mutelet).

http://dx.doi.org/10.1016/j.carbpol.2015.03.042
0144-8617/

interactions between the cation and the anion necessitate that the cation be proximal to the anion. Thus, a few cations are indeed present in the first coordination shell of cellobiose.

The first part of this work aims to study, using ab initio quantum chemical methods, the optimized structures and H-bonding between cations and anions in different imidazolium based ionic liquids. In addition, the interaction of carbohydrates, glucose and cellulose building unit, with ionic liquids was investigated and compared with experimental results. The second part of the study is devoted to the evaluation of the process of dissolution and regeneration of cellulose from ionic liquids using the antisolvent method. A characterization study using various analytical techniques, such as X-ray diffraction, infrared spectra, scanning electron microscope, was performed to evaluate the efficiency of the produced cellulose to be used for biofuel production.

2. Methodology

The ab initio calculations were carried out using GAUSSIAN 98 (Frisch et al., 2003). The minimum energy geometry of the cations and anions studied in this work were determined by performing calculations with density functional theory (DFT). The hybrid Becke 3−Lee−Yang−Parr, B3LYP, exchange-correlation function with the 6-311+G(d) basis set is employed for the geometry optimizations in this work (Becke, 1993; Stephens, Devlin, Chabalowski, & Frisch, 1994). It is known that the B3LYP/6-311+G(d) level is an excellent compromise between the computational cost and accuracy of the computational results. Moreover, the basis set was found to be suitable for the study of systems containing ILs and carbohydrates systems (Ding et al., 2012; Zhang, Yang, & Blasiak, 2011). The geometry optimizations of the cation–anion pairs were carried out in a sequential process at the RHF/6-31G, B3LYP/6-31G(d), and B3LYP/6-311+G(d) levels of theory. The geometry of the cation–anion pairs was firstly optimized at the RHF/6-31G level. The resulting RHF/631G optimized structures were used as the initial structures for subsequent B3LYP/631G(d) geometry optimizations, and these optimized structures were in turn used as initial structures for the B3LYP/6-311+G(d) optimizations. Partial atomic charges were derived from the ion pair geometries using the CHELPG (Breneman & Wiberg, 1990) method.

3. Experimental techniques

3.1. Materials

Microcrystalline cellulose (MCC) and avicel cellulose (AvC) were purchased from Sigma–Aldrich. The ionic liquids used in this work, 1-butyl-3-methylimidazolium chloride (BMIMCl), 1-ethanol-3-methylimidazolium chloride (EtOHMIMCl) and 1,3-dimethyl-imidazolium methyl phosphonate (DMIMMPh), with purity 98%, were from Solvionic, and 1-ethyl-3-methylimidazolium thiocyanate (EMIMSCN) with purity 95% was from Sigma–Aldrich. These ionic liquids were dried under vacuum for 3 h at 363 K before use.

3.2. Solubility and regeneration of cellulose

The solubility experiments of MCC and AvC cellulose in ionic liquids have been performed in jacketed glass cells at atmospheric pressure and at temperature ranges starting from 300 to 400 K using a dynamic method described in our previous work (Hassan El-Sayed, Mutelet, Pontvianne, & Moise, 2013; Hassan El-Sayed, Mutelet, & Moise, 2013).

For the extraction of cellulose, water was added as an antisolvent to the resulting clear liquors, and a cellulose-rich extract was reconstituted from the liquor. This extract was washed with water until the IL completely removed and then dried overnight in an oven at 373 K prior to use.

The characterization of original and regenerated cellulose was performed using FTIR, XRD, ^{13}C NMR and SEM analyses. X-ray diffraction (XRD) of the untreated miscanthus, cellulose-rich extracts and residues were determined with Cu Kα1 radiation at 30 kV and 15 mA. Patterns were recorded in the range of $2\theta = 5–80^{\circ}$ with a scan speed of $1^{\circ}\,min^{-1}$, using a Rigaku MiniFlex II X-ray diffractometer. For solid-state nuclear magnetic resonance (NMR) analysis, untreated and treated miscanthus samples ground to pass a 40-mesh screen were packed in 4-mm-diameter zirconium oxide rotors fitted with Kel-F caps. Cross-polarization/magic angle spinning (CP/MAS) ^{13}C NMR experiments were performed on a Bruker Avance-400 spectrometer operating at a ^{13}C frequency of 100.59 MHz. Glycine was used for the Hartman–Hahn matching procedure and as an external standard for the calibration of the chemical shift scale relative to tetramethylsilane. All spectra were acquired at ambient temperature using a Bruker 4-mm MAS probe. The IR spectra of the untreated miscanthus, cellulose-rich extracts and residues were determined using an ALPHA Fourier Transform IR spectrometer with an OPUS/Mentor software. A small amount of samples, enough to cover the surface of platinum diamond ATR crystal probe was used. Twenty-four scans were acquired for each spectrum. Then, SEM images were obtained using a JSM6700F scanning electron microscope. Samples were fixed to a metal-base specimen holder using double-sided adhesive tape, coated with Au/Pd and observed at 20 kV accelerating voltage.

4. Results and discussion

4.1. Ionic liquids structure optimization and hydrogen bond formation

The optimized structures for cations and anions of ionic liquids studied in this work, glucose and cellulose building unit were obtained using the procedure described in section 2 (see Figs. S1–S3, supporting information). The partial atomic charges for the optimized geometries, derived using the CHELPG method, are given in Table S1, supporting information.

4.1.1. Optimized structures of ionic liquids

The interaction energy ΔE can be calculated using the following equation (Ji et al., 2012; Zhou, Mao, & Zhang, 2008)

$$\Delta E(\text{KJ mol}^{-1}) = 2625.5^{*}[E[\text{cation}]^{+}[\text{anion}]^{-} - (E[\text{cation}]^{+} + E[\text{anion}]^{-})] \quad (1)$$

where $E[\text{cation}]^{+}\,[\text{anion}]^{-}$ is defined as the total energy of the system and $E[\text{cation}]^{+} + E[\text{anion}]^{-}$ is defined as the sum of the energy of the pure compositions.

The interaction energies are corrected by the basis set superposition error (BSSE) and zero-point energy (ZPE). Thus, the corrected interaction energy ΔE_{Corr} could be calculated as follows (Ji et al., 2012; Zhou et al., 2008):

$$\Delta E_{Corr} = \Delta E + \Delta E_{BSSE} + \Delta E_{ZPE} \quad (2)$$

where ΔE_{BSSE} is the correction of BSSE and ΔE_{ZPE} is the correction of ZPE.

To obtain the stable configurations of DMIMMPh, the anion MPh^{-} is located at several different positions around the cation. The initial configurations are fully optimized. Three representative configurations, A_1, A_2 and A_3 are selected, where the MPh^{-} anion is placed at carbon number 2, 4 and 5 of the imidazolium ring in $DMIM^{+}$ cation, respectively. The interaction energy of A_1 is larger