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Mechanistic study on the cellulose dissolution in ionic liquids by density functional theory☆

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ABSTRACT

Ionic liquids (ILs) have attracted many attentions in the dissolution of cellulose due to their unique physicochemical properties as green solvents. However, the mechanism of dissolution is still under debate. In this work, computational investigation for the mechanisms of dissolution of cellulose in [Bmim]Cl, [Emim]Cl and [Emim]OAc ILs was performed, and it was focused on the process of breakage of cellulose chain and ring opening using cellobiose as a model molecule. The detailed mechanism and reaction energy barriers were computed for various possible pathways by density functional theoretical method. The key finding was that ILs catalyze the dissolution process by synergistic effect of anion and cation, which led to the cleavage of cellulose chain and formation of derivatives of cellulose. The investigation on ring opening process of cellobiose suggested that carbene formed in ILs played an important role in the side reaction of cellulose, and it facilitated the formation of a covalent bond between cellulose and imidazolium core. These computation results may provide new perspective to understand and apply ILs for pretreatment of cellulose.

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1. Introduction

Cellulose is an abundant renewable compound on earth and has very attractive properties, such as biocompatibility, biodegradability, and thermal and chemical stability [1]. It consists of linear β-(1 → 4)-linked glucose chains which contain numerous intermolecular and intramolecular hydrogen bonds. The highly ordered structure of cellulose makes it a challenge to find appropriate solvents for dissolution and follow-up use [2].

Ionic liquids (ILs) have attracted much attention in cellulose investigation since they show great potential to dissolve cellulose compared to transitional cellulose solvents [3–8]. ILs are regarded as a new class of stable, green organic solvents which offer a variety of remarkable physical properties, such as high thermal stability, low melting points, negligible vapor pressure, nonflammability, reusability, and designability [9–13]. ILs consisting of imidazolium, pyridinium cations and OAc^-, $HCOO^-$, $(MeO)_2PO_2^-$, Cl^- anions have the high ability to dissolve cellulose, and were widely investigated [14]. However, the mechanism of dissolution of cellulose in ILs remains elusive and needs more detailed analysis.

Experimental and molecular simulation studies have shown that both anions and cations were involved in the dissolution process. Numerous reports have proposed that anions formed hydrogen bonds with cellulose, which may be the major reason for dissolving cellulose in ILs [15–17]. On the other hand, cation was suggested to play an indirect role in dissolution process instead of forming strong direct hydrogen bonds with cellulose [18]. A proposed dissolution mechanism of cellulose in ILs was supposed that the anion and cation of ILs formed hydrogen bonds with the hydrogen and oxygen atoms of the cellulose respectively [19], which primarily occurred between C6 and C3 hydroxyl groups of neighbored cellulose chains [20]. The interaction between ILs and cellulose which resulted in the separation of hydroxyl groups of different chains, may be one possibility leading to the dissolution of cellulose in ILs [19,21]. However, little derivative reactions in the process of dissolution of cellulose in ILs were taken into account.

Heinze et al. [22] also studied the mechanism of cellulose dissolution in ILs. They investigated the interaction between cellooligomers and ILs by NMR spectroscope and found that the C1 signal of glucose unit was not present if the cellooligomers were dissolved in [Emim]OAc. In accordance with these results, authors gave an explanation that the C1 carbon of the reducing end of cellooligomer may be covalently bonded with C2 carbon of the imidazolium core, forming a carbon–carbon bond. The proposed structure for the covalent product is shown in Fig. 1.

Antje Potthast et al. [23] observed that carbonyl groups were present after cellulose dissolution in imidazolium-based ILs. Further, imidazolium-based ILs deprotonated at C2 under basic condition were

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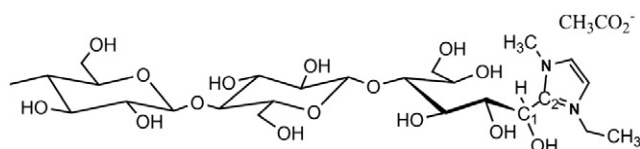   E-mail addresses: xqyao@ipe.ac.cn (X. Yao), sjzhang@ipe.ac.cn (S. Zhang).

Fig. 1. Proposed structure for a covalent binding of [Emim]OAc to cellooligomer (DP 6–10).

suggested to be able to react with electrophiles, for instance, benzaldehyde [24]. Ebner *et al.* [25] combined above, and gave a series of ¹³C-isotopic labeling and fluorescence labeling experiments. The experimental evidence verified the hypothesis that the C2 carbon of 1-alkyl-3-methylimidazolium cation may form covalent bond with reducing end of cellulose [25]. Surprisingly, this was not the case when cellooligomer was dissolved in [Emim]Cl, [22] which was subsequently supported by experiments of Matthew *et al.* [26] A series of experiments were then conducted to investigate cellulose dissolution in 1-ethyl-3-methyllimidazolium chloride, [Emim]Cl [27–29]. It was reported that [Emim]Cl penetrated into wood and liquefied wood components by depolymerizing them [27]. Subsequent studies investigated the reaction behavior of cellulose in [Emim]Cl at 373, 393, and 413 K. They showed that the solubilized cellulose in [Emim]Cl was depolymerized into various low molecular weight compounds including cellobiose, cellobioam, glucose, and levoglucosan, but the carbon–carbon covalent bond mentioned above still cannot be detected [28]. These results not only suggested that the dissolution of cellulose in ILs may lead to complex reactions but also highlighted the role ILs may play in the dissolution process.

Some studies used quantum mechanical calculations to understand the interaction between cellulose and ILs. The solution of cellulose in [Emim]OAc was studied by density functional theory (DFT) calculation to evaluate the ionic influence on the dissolution mechanism [30]. Their results showed that the interaction between ILs and cellulose was stronger than the intermolecular interaction of cellulose. Further, the acetate anion formed strong hydrogen bond with cellulose. R. S. Payal and coworkers investigated the dissolution mechanism of cellulose in explicit solvent ([Emim]OAc) by DFT analysis, chosen cellobiose as model [31]. The calculation data suggested that both cation and anion were responsible for dissolution process of cellulose, and the results demonstrated the interaction between ion (anion or cation) and cellulose. Du *et al.* [32] explored the reaction of ring opening by *ab initio* calculations with an implicit solvent model, and showed that breakage of the C–O bond on the glucose ring was the critical step [32]. Wei *et al.* [33] also investigated the reactivity of cellulose with ILs using glucose as a model by DFT calculation. It was found that TEA facilitated the ring opening of glucose. The theoretical analyzed above mainly focused on the investigation of the interaction between cellulose and ILs, few effects were made to study cleavage of cellulose chain and ring opening of side reaction during the dissolution of cellulose in ILs. Thus, our work was aimed to explore the detailed paths about the cleavage of cellulose chain and the formation of covalent bond between reducing end of cellulose and cation in ILs. The roles that cations and anions played in the process of dissolution were also investigated.

In this work, reaction path calculations were performed to study the key steps in cellulose depolymerization to form levoglucosan and glucose through cleavage of glycosidic bond and side reaction in ILs by DFT method. The cellobiose (shown in Fig. 2) was used as a model molecule for cellulose. [Bmim]Cl, [Emim]Cl and [Emim]OAc would be used to investigate how cations and anions influence the reaction of cleavage of cellobiose and ring opening. These ILs have been widely studied in the promising field of cellulose processing. Potential energy surface (PES) scan and the intrinsic reaction coordinate (IRC) theory were carried out to search and construct the minimum-energy path. The key finding was that the anions and cations of ILs would promote the cleavage of cellulose chain. Further, ILs with acetate anion would be reactive to reducing end of the cellulose, whereas not with chloride

anion. The similarities and differences between the role of cations and anions played in the reaction process were discussed. Such fundamental information may provide new perspective to understand and apply ILs for pretreatment of cellulose.

2. Computational Methods

All QM calculations were carried out by using Gaussian 09 program packages [34]. Ground- and transition-state geometries of the investigated species were optimized by density functional theory (DFT) using B3LYP/6-311 + G (d, p) (Becke's three-parameter nonlocal-exchange functional with the nonlocal correlation of Lee–Yang–Parr method) [35]. The B3LYP/6-311 + G (d, p) and similar level methods were found to be reliable for the calculation of geometry and energy of ionic liquids [36–39]. The potential energy surface (PES) scan was performed to search for corresponding minima or saddle points. The number of imaginary frequency indicates whether a minimum or a transition state was located: all positive frequencies for a minimum and one imaginary frequency for a transition state. The connectivity between a given TS and the reaction/product minima, was verified in each case by performing intrinsic reaction coordinate (IRC) [40,41] calculations at the same level of theory.

3. Results and Discussion

[Bmim]Cl, [Emim]Cl and [Emim]OAc were used to investigate the influence of different kinds of cations and anions on the reaction of cleavage of cellobiose and ring opening. The structures of intermediates and transition states involved in these processes were determined, and the relative energies of these species were calculated. PES scan and IRC theory were carried out to search and construct the minimum-energy path.

3.1. The cleavage of cellobiose

To compare with the reaction catalyzed by ILs quantitatively, the reaction which formed levoglucosan and glucose by cleavage of the glycosidic bond in absence of ILs was investigated firstly. The schematic for cleavage of cellobiose in ILs is shown in Fig. 3 [29].

In our computational exploration, the reaction in the absence of ILs proceeds through the cleavage of a O–H bond of hydroxyl and a C–O bond connecting two rings of cellobiose, and finally leads to the formation of a 5-C ring of levoglucosan and glucose. Geometries of reactant compound (cellobiose), transition state and products (glucose and levoglucosan) for this reaction are optimized at the B3LYP/6-311 + G (d, p) level and plotted in Fig. 4. The energy diagram of the possible pathway is also shown in Fig. 4.

The reaction progresses with the formation of a transition state (cello-ts), which further decomposed into glucose and levoglucosan, in which C–O bond connecting two rings of cellobiose and an O–H bond of hydroxyl will cleavage, and a 5-C ring of levoglucosan will form. In transition state (cello-ts), the distances of C1–O20, C1–O44 and O44–H45 are 0.243, 0.267 and 0.140 nm, respectively. The energy barrier of this step is about 207.9 $kJ \cdot mol^{-1}$. The calculations show that the formation of glucose and levoglucosan from cellobiose is endothermic with reaction energy of 32.2 $kJ \cdot mol^{-1}$. The total energy of glucose and levoglucosan was 15.0 $kJ \cdot mol^{-1}$ higher than the energy of the product in which glucose and levoglucosan are hydrogen bonded. Previous literature proposed a similar mechanism of cellulose thermal decomposition using DFT method and implicit THF solvent [42]. The result reveals that the energy barriers for the reaction of cleavage of glycosidic bond to form glucose and levoglucosan are affected by solvents.

Therefore, our investigation will focus on the influence of different anions and cations on the reaction of cleavage of cellobiose. There are several possible interaction sites for ions that probably lead to cleavage of the C–O bond connecting two rings of cellobiose in each process. The candidates for active sites are selected through optimizations of