Mechanism and Conformation Changes for the Whole Regeneration Process of Cellulose in Pyridinium-Based Ionic Liquids

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Research Article

Keywords: Cellulose, ionic liquid, anti-solvent, regeneration, conformation

Posted Date: December 6th, 2021

DOI: https://doi.org/10.21203/rs.3.rs-1087872/v1

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Mechanism and conformation changes for the whole regeneration process of cellulose in pyridinium-based ionic liquids

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Abstract

In this work, mechanism and conformation changes of cellulose regenerated from ionic liquid by anti-solvents (water, ethanol and acetone) were investigated by molecular simulations. Cellulose model consists of seven glucose single chains were constructed. In order to depict the regeneration mechanism, both the dissolution and regeneration processes of cellulose in [Bpy][OAc] IL were simulated. The methyl hydroxyl group of cellulose will change its conformation during dissolution and regeneration. The conformation of initial cellulose crystal is mainly the tg conformation. After dissolved in ILs, the cellulose conformation changes into the gt conformation and the gg conformation. After regenerated by anti-solvent, the proportion of the gg and gt conformation changes, and the gg conformation increased and the gt conformation decreased. Based on energy analysis, it is concluded that the energy for tg is the lowest, and the tg widely exists in cellulose I. After cellulose is dissolved in ILs, the conformation changes into two higher energy conformations, the gt and gg. In the subsequent regeneration process, with the completion of regeneration, the gg conformation increases and the gt conformation decreases.

Keywords
Cellulose \textbullet{} ionic liquid \textbullet{} anti-solvent \textbullet{} regeneration \textbullet{} conformation
Introduction

In recent years, with the rapid development of the social economy and the extensive exploitation and use of traditional fossil energy, the contents of pollutants such as carbon dioxide, carbon monoxide and nitrogen oxides in the atmosphere has been rapidly increased. The shortage of resources and ecological destruction have become a major problem. To protect the environment and follow the basic principles of green chemistry, we focus on renewable biomass resources (Khan et al., 2018; Samikannu et al., 2019; Zhang et al., 2015). Cellulose is one of the most abundant renewable resources, with an annual output of $1.5 \times 10^{12}$ tons (Schmer et al., 2008). Cellulose is the raw material of "green" materials because of its attractive properties such as good chemical stability, non-toxicity, biodegradability and environmental friendliness. Cellulose is composed of covalent $\beta$-1, 4-glycosidic repeated glucose units. It is a linear polycondensation polymer with a degree of polymerization (DP) of 100-20000. However, due to the highly ordered crystal structure and H-bond network in cellulose, cellulose is difficult to dissolve in water and common organic solvents, which dramatically hinders the rational utilization of cellulose (Moon et al., 2011; Yuan et al., 2019).

Ionic liquid (IL) is a kind of material that is wholly composed of cation and anion. ILs become widely available for catalysis, separation, electrochemistry and medicine, because of their excellent thermal and chemical stability, low vapour pressure and strong designability (Cesari et al., 2019; Friess et al., 2021; McNeice et al., 2021; Md Moshikur et al., 2020; Tiago et al., 2020; Xiong et al., 2019; Zhang and Pesic, 2021). The premise of utilization of cellulose is to dissolve cellulose in solvent. However, the dissolution of cellulose is a challenging process because of its stable crystal structure and H-bond network. In 2002, Swatlosky et al. found that 1-butyl-3-methylammonium chloride could effectively dissolve cellulose, and the concentration of cellulose in the solution could up to 10 wt% at $100 \, ^{\circ}C$ (Swatloski et al., 2002). Since then, ILs have been called "green solvents" of cellulose. Moreover, a variety of ILs can effectively dissolve cellulose for the pretreatment of cellulose (Lethesh et al., 2020; Sun et al., 2011; Xu et al., 2015; Zhao et al., 2012). The reason for dissolution of cellulose is to form hydrogen bonds between ILs and cellulose, thus the original crystal structure of cellulose is destroyed (Ishida, 2020).

Then cellulose was regenerated by adding anti-solvent. Because the solubility of cellulose in the anti-solvent was low, resulting in the precipitation of cellulose from the solution. Moreover, the
crystallinity of regenerated cellulose reduces, which is helpful to convert cellulose into biofuel (Huang et al., 2020; Singh et al., 2009). As we all know, after regeneration, the cellulose will change from cellulose I to cellulose II. Many experiments have also confirmed this point. B. Meenatchi et al. reported that ILs could dissolve cellulose well, and the regenerated cellulose was characterized by XRD and SEM, and the decrease in crystallinity and structural changes of cellulose was observed (Meenatchi et al., 2017). Taheri et al. also confirmed that cellulose changes from cellulose I to cellulose II during dissolution and regeneration (Taheri et al., 2019). In addition, Tan et al. found that when the anti-solvent was water, the crystallinity of regenerated cellulose was higher, and the cellulose type was cellulose II. When the anti-solvent is ethanol, the regenerated cellulose has low crystallinity and poor thermal stability, and there is amorphous cellulose (Tan et al., 2019).

Molecular simulation could reveal the mechanism at the micro-level, thus many researchers used the technology to depict the dissolution mechanism of cellulose. Li et al. explored the process of ILs dissolving cellulose through molecular simulation, analyzed the interaction between ions and cellulose, and concluded that cation and anion synergistically dissolve cellulose (Li et al., 2015). Gupta et al. reported the effects of temperature and water concentration on cellulose regeneration and found that the number of cellulose-cellulose hydrogen bonds increases as water concentration increases. In addition, they also found that higher temperature will promote the regeneration of cellulose (Gupta et al., 2013b). However, the reason for the conformational change of cellulose was not reported. Therefore, the regeneration process of cellulose in three kinds of anti-solvent (water, ethanol and acetone) were simulated, focusing on the influence of anti-solvent on cellulose regeneration, the conformational change of cellulose and the reason.

In this work, molecular dynamics simulation was used to explain the conformational changes of cellulose dissolved in ILs and regenerated after adding anti-solvents, which provides a theoretical basis for the conformational changes of cellulose. There are two kinds of cellulose structures, Iα with a triclinic unit cell and Iβ with a monoclinic unit cell. Cellulose Iβ was used in our research, because cellulose Iβ is the most abundant crystalline form of cellulose in plants and is more stable (Wada et al., 2003). The pyridinium-based IL, [Bpy][OAc] is used, and the anti-solvents are water, ethanol and acetone. In particular, different anti-solvent concentrations (15%, 30%, 45%, 60%, 75%, 85%, and 100%) were simulated and analyzed in the regeneration process. The second section briefly introduces
the models and methods used. The simulation results and discussion, as well as cellulose regeneration, are presented in Section 3. Finally, section 4 summarizes the conclusions.

Methodology

Simulation Systems

Fig 1 illustrates the chemical structures of cellulose chains, the cation and anion of [Bpy][OAc], and anti-solvents (water, ethanol and acetone) used in this study. The cellulose model is composed of 7 single glucose chains with a polymerization degree of 8, which is called a 7 * 8 cellulose beam. Because the cell wall of higher plants is mainly composed of Iβ, only cellulose Iβ structure is constructed (Klemm et al., 2005). Cellulose model were built based on experimental crystallographic data (Yoshiharu et al., 2002) by a toolkit named cellulose-builder (Gomes and Skaf, 2012). The simulations include two parts, namely the dissolution and regeneration. The composition of the simulation systems is listed in Table 1 and Table 2. Glycam 06 force field was used for cellulose (Kirschner et al., 2008). For anion [OAc]−, the all-atom force field in the form of AMBER developed by Liu is used (Liu et al., 2004), and for cation [Bpy]+, force field parameters were also taken from the AMBER force field (Wang et al., 2004). Water was represented by using the SPC/E model (Berendsen et al., 1987). The structures of ethanol and acetone were optimized using the Gaussian 09 package at the B3LYP/6-31+G* level (Frisch). Then, the atomic charges were determined by using the restricted electrostatic potential (RESP) method (Lu and Chen, 2012). Due to simulation time and complexity, charge transfer and charge polarization of ILs that occur in the liquid are neglected in the atom charge calculation.

Molecular dynamics simulation details

The dissolution system consists of 7 * 8 cellulose and 1200 pairs of ILs. The regeneration system is composed of dissolved cellulose, ILs and anti-solvent, and the contents are shown in Table 1. The cellulose model and the box boundary are at least 3 nm apart to provide a sufficient dissolution environment. All dynamic simulations are carried out in gromacs5.1.5 (Van Der Spoel et al., 2005). The long-range electrostatic interaction in the system is treated by the particle-mesh Ewald method (Darden et al., 1993). The truncation of electrostatic and van der Waals force is 1.2 nm. Periodic boundary conditions were used in all directions to mimic a bulk system. The simulation details are the same as
that of the dissolved system.

The initial configuration is first minimized by the steepest descent method until the minimum force is less than 100 kJ mol\(^{-1}\) nm\(^{-1}\) to eliminate possible coordinate collisions. Then the systems were equilibrated for 10 ns under NVT ensemble with a temperature of 500 K. Following was a 100 ns equilibration dynamics under NPT ensemble to equilibrate the solvents and the temperature decreased from 500 K to 450 K. In the above equilibrium, a potential of 1000 kJ mol\(^{-1}\) nm\(^{-2}\) is applied to the cellulose bunch model to ensure that the cellulose beam remains in the initial position. After that, the force was cancelled and the cellulose bunch was completely released for simulation of 500 ns in a time step of 2 fs. Atomic coordinates, velocities and energies were collected every 50 ps for further analysis.

In the simulation, the velocity rescaling method is used for temperature control, and the coefficient is 0.2 ps (Bussi et al., 2007); Parrinello-Rahman barostat is used for pressure control, and the coefficient is 2.0 ps (Parrinello and Rahman, 2005). All covalent bonds were constrained using the LINCS algorithm (Hess et al., 1998). The subsequent regeneration process is similar to the dissolution process, except that the temperature is set to 353 K.

**Fig 1.** Molecular structures of (a) cellulose chain, (b) [Bpy]+, (c) [OAc]-, (d) water, (e) ethanol, and (f) acetone. N: blue, C: cyan, O: red, and H: white
Table 1. Composition of the regeneration systems (353K)

| Wt% water | ILs | water   |
|-----------|-----|---------|
| 15%       | 1000| 1911    |
| 30%       | 800 | 3500    |
| 45%       | 600 | 5318    |
| 60%       | 400 | 6500    |
| 75%       | 200 | 6500    |
| 85%       | 150 | 9208    |
| 100%      | 0   | 12000   |

| Wt% ethanol | ILs | ethanol |
|-------------|-----|---------|
| 15%         | 1000| 742     |
| 30%         | 800 | 1454    |
| 45%         | 600 | 2083    |
| 60%         | 400 | 2538    |
| 75%         | 200 | 2538    |
| 85%         | 150 | 3603    |
| 100%        | 0   | 5087    |

| Wt% acetone  | ILs | acetone |
|--------------|-----|---------|
| 15%          | 1000| 593     |
| 30%          | 800 | 1156    |
| 45%          | 600 | 1651    |
| 60%          | 400 | 2026    |
| 75%          | 200 | 2026    |
| 85%          | 150 | 2832    |
| 100%         | 0   | 3214    |

Results and discussion

Dissolution process of cellulose

Fig 2. Structure of cellulose before and after the dissolution
As shown in Fig 2, before dissolution, we can see that cellulose is regularly and closely arranged together. After 500 ns simulated in ILs, the cellulose chains are separated from each other, which means that the cellulose has been completely dissolved in ILs. The single-chain is not straight, but in a disordered state. Hydrogen bond and energy analysis are shown in Supporting Information.

Fig 3. (a) Methyl hydroxyl group in sugar conformation (Liu et al., 2012) and the calculated hydroxyl group orientation in the (b) crystal cellulose Iβ and cellulose Iβ in [Bpy][OAc] solution

One of the critical parameters determining the crystal structure of cellulose is the orientation of the O2-H-O6 hydrogen bond, which determines the position of hydroxymethyl C6-OH (Fig 3). There are three stable staggered rotation conformations: trans-gauche (tg), gauche-trans (gt), and gauche-gauche (gg). Fig 3a shows the three rotator conformations and their corresponding torsion angles ω. Fig 3b shows the torsional angle distribution of cellulose crystal and dissolved cellulose. As shown in Fig 3b, the conformational distribution of torsion angle is tg > gt > gg in cellulose Iβ, consistent with the previous results (Nishiyama et al., 2003; Yoshiharu et al., 2002). However, the conformational
distribution of cellulose dissolved in ILs changed: The tg conformation in cellulose Iβ is disappeared, and then transformed into the gt conformation and the gg conformation, and the gt conformation is the primary one.

**Regeneration process of cellulose in anti-solvent**

**Effect of anti-solvent on cellulose regeneration**

![Figure 4: Structure of cellulose in different mass fractions of water](image)

In this study, three anti-solvents: water, ethanol and acetone were used. Fig 4 and Figs S2, S3 shows the structure diagram of dissolved cellulose in different mass fractions of anti-solvent, and we hope to show the regeneration process of cellulose by continuously increasing the anti-solvent. Comparing the structures of cellulose in different anti-solvents, we can see that the regeneration effect of cellulose in water is better (Fig 4). When the mass fraction of water is 60%, the initially dispersed cellulose single chains have gathered together. From the structure of cellulose in different mass fractions of ethanol (Fig S2), it can be seen that when the mass fraction of ethanol is 85%, the dispersed cellulose chains begin to aggregate. When the anti-solvent is acetone (Fig S3), the cellulose chain presents a dispersed state before 100%. When the mass fraction reaches 100%, the cellulose chains gather together. Therefore, we speculate that the regeneration effects of three anti-solvents on cellulose are as follows: water > ethanol > acetone. This result is consistent with the previous research results.
In the process of cellulose regeneration, a large number of H-bonds will be formed in cellulose, accompanied by the breaking of H-bonds between cellulose and anions. To accurately understand the regeneration process of cellulose in anti-solvent, we counted the H-bonds between cellulose and cellulose and between cellulose and anion in different mass fractions of anti-solvent, as shown in Fig 5. It can be seen that, the number of H-bonds between cellulose and cellulose increases, while the H-bonds between cellulose and anion decrease gradually by increasing the mass fraction of anti-solvent. When the anti-solvent is water, the significant increase in the number of H-bonds between cellulose and cellulose occurs at 60% (Fig 5a), corresponding to the rapid decrease in the number of H-bonds between cellulose and anion (Fig 5b). The cellulose regeneration completed at 75%, and the number of H-bonds is unchanged after that. When the anti-solvent is ethanol, as shown in Fig 5c, the number of H-bonds between cellulose and cellulose is increasing slowly before ethanol being 100 wt%, and the number of H-bonds between cellulose and anion decreased gradually, as shown in Fig 5d. These show that cellulose can be regenerated entirely in the pure ethanol. Besides, when the anti-solvent is acetone, as shown in Fig 5e, the number of H-bonds between cellulose and cellulose is nearly unchanged before acetone being 100 wt%. The number of H-bonds between cellulose and anion in Fig 5f is also unchanged. The reason is that water can interrupt the H-bond between cellulose and anion the most effectively, and promote the formation of H-bond between cellulose and cellulose, followed by ethanol,
Fig 6. The energy between cellulose and cellulose

The regeneration process of cellulose inevitably leads to energy change, so we counted the energy change of cellulose in the regeneration process. As shown in Fig 6, there are two inter-energies: electrostatic interaction (ECoul) and van der Waals interaction (ELJ). The glucose unit in cellulose contains a large number of hydroxyl groups, and a large number of H-bonds will be formed during regeneration (Fig 5). In addition, the changing trend of energy is also consistent with the number of H-bonds, which increases with the continuous aggregation of cellulose chains in the regeneration process. When the anti-solvent is water, the energy increases at 60 wt%. When the mass fraction of anti-solvent above 75 wt%, the energy is unchanged, which means that the cellulose regeneration in 75 wt% water completed. In addition, when the anti-solvent is ethanol, although the energy increases all the time before 100 wt%, indicating that cellulose regeneration completes only in pure ethanol. In addition, when the anti-solvent is acetone, the energy is unchanged until acetone is 100 wt%, indicating that the effect of acetone on the regeneration of cellulose in the system is poor.
Fig 7. Radial distribution function of [OAc]⁻ around cellulose in the systems contain (a) water, (c) ethanol and (e) acetone; Radial distribution function of anti-solvent around cellulose in the systems contain (b) water, (d) ethanol and (f) acetone.

By analyzing the simulation trajectories of the last 100 ns of each system, we calculated the radial distribution function (RDF) of this period to understand the specific effects of anions and anti-solvents on cellulose regeneration. Fig 7 shows the point-to-point RDFs of anions and anti-solvent. H2, H3, and H6 atoms are selected on cellulose, and O atoms are selected for anions and anti-solvent respectively.
First, when the anti-solvent is water, the peak in Figs 7a and b gradually decreases, indicating that the distribution of anions and water around cellulose gradually decreases. The reason is that with the regeneration of cellulose, the interaction between cellulose and cellulose increases, while the interaction between cellulose and anion and water decreases. When the anti-solvent is ethanol, the peaks in Figs 7c and d increase with the increase of the mass fraction of anti-solvent. On the one hand, the peak value in Fig 7c increases because the mass fraction of ILs decreases with the rise of anti-solvent mass fraction, resulting in the decrease of ILs density, so the peak value increases. Therefore, we also counted the number of anions around cellulose. The number of anions decreases with the increase of ethanol. In addition, from Fig 7d, we can see that the interaction between cellulose and ethanol increases gradually, because the impact of ethanol on cellulose regeneration becomes more and more evident with the increase of ethanol mass fraction. When the anti-solvent is acetone, the reason for the rise of the peak value in Fig 7e is the same as that in Fig 7c, so the number of anions around cellulose is also measured. The number of anions is unchanged, indicating that the strong interaction between cellulose and anions. As can be seen from Fig 7f, the peak value does not appear until pure acetone. It implies the weak interaction between acetone and cellulose.

![Fig 8. Spatial distribution functions of cellulose and anti-solvent around anion.](image)

**Red: anti-solvent, white: cellulose. (a) water, (b) ethanol and (c) acetone**

The regeneration of cellulose is accompanied by the breaking and recombination of H-bond, including the breaking of H-bond between cellulose and anion and the recombination of H-bond between celluloses. To explore the reasons why the regeneration effect of water on cellulose is the best, we analyze the spatial distribution around anions. From Fig 10, we can see the spatial distribution functions (SDFs) of anti-solvent and cellulose around the anion \([\text{OAc}^-]\). As shown in Fig 8, water and ethanol molecules mainly distribute around the O1 and O2 sites of \([\text{OAc}^-]\), but acetone is around the
methyl of [OAc]. As the O1 and O2 atoms of [OAc] can form strong H-bonds with hydroxyl groups on cellulose, it means that water and ethanol will hinder the interaction between anions and cellulose, and interrupt the H-bond between cellulose and anions. As shown in Fig 8a, the distribution of water around anions is completely the same with that of cellulose around anions. So water can effectively interrupt the H-bond between cellulose and anions and promote regeneration. In addition, we can see that the distribution of ethanol around anions is inferior to that of water, so the ability of ethanol to break the H-bond between cellulose and anions is less than that of water (Fig 8b). However, from Fig 8c, we can see acetone distribute near the oxygen atom and is completely different from the cellulose, which means that acetone cannot break the H-bond between cellulose and anion. Therefore, we looked at the distribution of anion around cellulose in the 85 wt% acetone system (Fig 9). We saw that anions formed a cluster structure around cellulose. The spatial distribution of acetone around [OAc] determined that acetone could not break the H-bond to regenerate cellulose. In summary, the effect of anti-solvent on cellulose regeneration is: water > ethanol > acetone.

![Cellulose conformation changes](image)

**Fig 9.** The anion distributed around the cellulose chain when the mass fraction of acetone was 85 wt%. Red: O, blue: C, white: H

**Cellulose conformation changes**

![Cellulose conformation changes](image)

**Fig 10.** In the process of cellulose regeneration, the torsion angle ω and its
corresponding conformational changes. (a) water, (b) ethanol and (c) acetone

From the dissolution process, we learned that the conformational distribution of cellulose changed from the tg configuration to the gt and gg configurations, and the tg configuration disappeared. In the regeneration process, we also studied the configuration changes of cellulose again, as shown in Fig 10, and we can obtain the same law. With the increase of anti-solvent mass fraction, it can be seen the decrease of the gt conformations and the growth of the gg conformations. To explore the reasons for the conformational changes of cellulose, we calculated the energy of three conformations through quantum chemical calculation. Taking cellulose dimer as an example (Fig 11), we calculated the energy of different conformations (Based on gt conformational energy), as shown in Table 2. The energy for tg conformation is the lowest, followed by the gg conformation, and the energy for gt conformation is the highest. Therefore, we speculate the reason for the conformational change of cellulose during dissolution and regeneration. The configuration of cellulose I is the tg, which is determined by the crystal structure and is the most stable. After dissolution, the cellulose chain is separated, making cellulose unstable, and the configuration changes to the gt and gg. With the addition of anti-solvent, the cellulose gradually regenerates, cellulose gradually changes from an unstable state to a stable state, because the energy of the gg conformation is the lowest, and it is the most stable. Therefore, in the regeneration process, the gg conformation gradually increases and the gt conformation gradually decreases. Therefore, we speculate that the conformational energy change of cellulose should first increase and then decrease, but the final energy should be higher than the initial energy. Based on the dimer energies, we calculated the conformational energy of initial, dissolved and regenerated cellulose, as shown in Fig 12, which shows a trend of first rising and then falling. The energy of regenerated cellulose is higher than that of initial cellulose. This is consistent with our conjecture.

Fig 11. Cellulose dimer structure
Table 2. Conformational energy (Based on gt energy)

| conformation | tg   | gt   | gg   |
|--------------|------|------|------|
| Δ Energy(kJ/mol) | -12.31 | 0    | -6.88 |

Fig 12. Conformational energy change diagram of cellulose (The regeneration system takes the conformational distribution of 100 wt% ethanol cellulose as an example)

Conclusion

In this work, we used molecular dynamics simulation to study mechanism and conformation changes for the whole dissolution and regeneration process of cellulose in ILs [Bpy][OAc]. Our results show that [Bpy][OAc] destroys the crystal structure of cellulose through the synergistic effect of cation and anion. The impact of anti-solvent on cellulose regeneration was investigated. The stronger ability of anti-solvent to break the H-bond between cellulose and anion, the better regeneration effect on cellulose. We also depicted the conformation change of cellulose from tg conformation to gt and gg...
conformation during dissolution. The conformational change is driven by energy. The conformation of cellulose I is mainly tg, which is determined by the crystal structure and is the most stable. After dissolution, the conformation changes to gt and gg, and the cellulose is unstable. With the addition of anti-solvent, cellulose regenerates, and cellulose gradually changes from unstable state to another stable state. Because the energy of gg conformation is lower than that of gt conformation, the proportion of gg conformation increases and the proportion of gt conformation decreases. We believe that the above results will provide useful information for understanding the whole regeneration process of cellulose, and these findings could also boost further exploration of ILs applications.

Acknowledgment

We cordially acknowledge the financial support from the National Natural Science Foundation of China (22178187, 22108139, 21908222), Natural Science Foundation of Shandong Province (ZR202102180830), and the Taishan Scholars Program of Shandong Province (tsqn201909091). The authors thank the High-Grade Talents Plan of Qingdao University for financial support and all the other friends in this work for their direct and indirect help to me. The authors would also like to thank the journal editors and the reviewers who raised valuable points that help to improve the quality of the presentation of this article.

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