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Theoretical study on interactions between lignocellulose components and ionic liquids

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Abstract. Interactions between lignocellulose and ionic liquids have been studied by designed lignocellulose components models, and their complexes with 1-butyl-3-methylimidazolium chloride. All the structures were optimized by DFT methods and hydrogen bonds within lignocelluloses components, and their complexes with 1-butyl-3-methylimidazolium chloride were investigated by AIM calculations. Our calculated results demonstrate that when dissolved in ionic liquids, the stable intermolecular hydrogen bonds and weak π -stacking interactions between ionic liquids and lignocelluloses components reduce the energy of complex systems, which are advantageous for lignocelluloses components dissolution in ionic liquids. Moreover, there are deformation accrued for both lignocelluloses components and ionic liquids, which may be a prerequisite for lignocelluloses components dissolution in ionic liquids.

1 Introduction

The world's increasing demands for energy and the need for the reduction of the air pollution have led to the quest of new alternative energy sources that would also be environmental friendly. Biomass energy has been recognized as an ideal energy especially for chemical applications, but it has not been available for extensive commercial use yet. One of the major reasons for this has been the difficulty to break down lignocelluloses nanostructures to obtain fuels and chemical intermediates. Lignocelluloses pretreatment methods often require extremes of temperature, pressure, and reagent reactivity, which are incompatible with "green" biomass energy production [1].

Ionic liquids (ILs), defined as organic salts which are liquid below 100 °C, are a kind of promising solvents in lignocelluloses dissolution and separation [2]. Since Rogers [3] firstly reported the cellulose dissolution in 1-butyl-3-methylimidazolium chloride ionic liquids in 2002, nowadays there is an intensive research in lignocelluloses dissolution and has been proposed that the solution of lignocelluloses dissolution will become from the design, synthesis of new targeted ionic liquids, or the development of already existing ionic liquids with special properties. For example, Fort and his co-workers have investigated the dissolution of mason pine, poplar, eucalyptus, and oak in [C₄mim]Cl/dimethyl sulfoxide, and found that [C₄mim]Cl/dimethyl sulfoxide could be able to partially dissolve up the lignocelluloses with heating 24 h at 100 °C [4]. Li and his co-workers have designed a new ionic liquid/acid mixed system to dissolve up lignocellulosic materials, and their experimental results revealed that in the [Bmim]Cl/HCl(7wt%) mixed system, reducing sugar yield of straw and pine for an hour at 100°C is 74% and 81%, respectively [5].



Following the previous literature [6-10], some general guidelines can be proposed for the lignocelluloses dissolution and separation in ionic liquids. The main factors that enhance solution of lignocelluloses components in ionic liquids are chemical structures of ionic liquids and lignocellulosic materials, particle size of the lignocellulosic materials, interactions between ionic liquids and lignocelluloses components, and the moisture content of lignocellulosic materials. So, the detailed discussion of above mentioned factors is advantageous to understand the mechanisms of lignocelluloses components dissolution and separation in ionic liquids.

In this paper, the molecular behaviors of cellulose, hemicelluloses, and lignin models in the 1-butyl-3-methylimidazolium chloride [Bmim][Cl] [11, 12], one of the effective ionic liquids, were carried out to investigate the interactions between lignocelluloses components and ionic liquids. The lignocelluloses components (cellulose, hemicelluloses and lignin) and their complexes with ion pair of [Bmim][Cl] ionic liquids were fully optimized and frequency calculated. AIM calculations were also performed to investigate the hydrogen bonding patterns of the lignocelluloses components during their dissolution in ionic liquids. These results would provide mechanistic insights and suggestions for future experiments on lignocelluloses dissolution and separation.

2 Computational Methods

Taking into account that lignocelluloses are tough composite of rigid cellulose crystals embedded in hemicelluloses sugars and lignin poly-phenols, we have designed the dimer models for cellulose, hemicelluloses, and lignin which have been intercepted from lignocelluloses and could reflect the chemical properties of lignocelluloses components. The cutoff functional groups are saturated by hydrogen. The construction of the initial crystal structures for ionic liquid and lignocelluloses components were followed by an optimization procedure, using Gaussian 09 suite of electron structure programs [13]. Density functional theory with B3LYP/6-31++G (d, p) has been carried out to obtain the optimized geometries for all the species [14]. Self-consistent field calculations and geometry optimizations use tight convergence criteria. Frequency calculations at B3LYP/6-31++G (d, p) level of theory have confirmed that all optimized geometries are local minima on the potential energy surface. Single point energy corrections have been performed at B3LYP//6-311++G(2d, 2p)//B3LYP /6-311+G(d, p) level of theory, including the basis set superposition error (BSSE) correction.

Atoms-in-molecules method (AIM) [15], proposed by Bader, were carried out to analyze, evaluate, and classify the nature of the interactions between ionic liquids and lignocelluloses components. All AIM calculations were carried out based on the optimized geometries at B3LYP /6-31++G (d, p) level of theory.

3 Results and Discussion

3.1 Geometries

The insolubility of lignocelluloses components in water and organic solvents, mainly attributed to the large number of intramolecular hydrogen bonds, has become a bottleneck for lignocelluloses' further wide applications on fuels and chemical intermediates. The dissolution and separation of the lignocelluloses components in ionic liquids requires first breaking down their intramolecular hydrogen bonds. So it is necessary to investigate hydrogen bonds within lignocelluloses components and their complexes with ionic liquids. This was done in two steps. First we investigated the hydrogen bonds within ionic liquids and lignocelluloses components.

The most stable geometries and topological parameters for both [Bmim][Cl] ionic liquid and lignocelluloses components are presented in Figure 1 and Table 1.

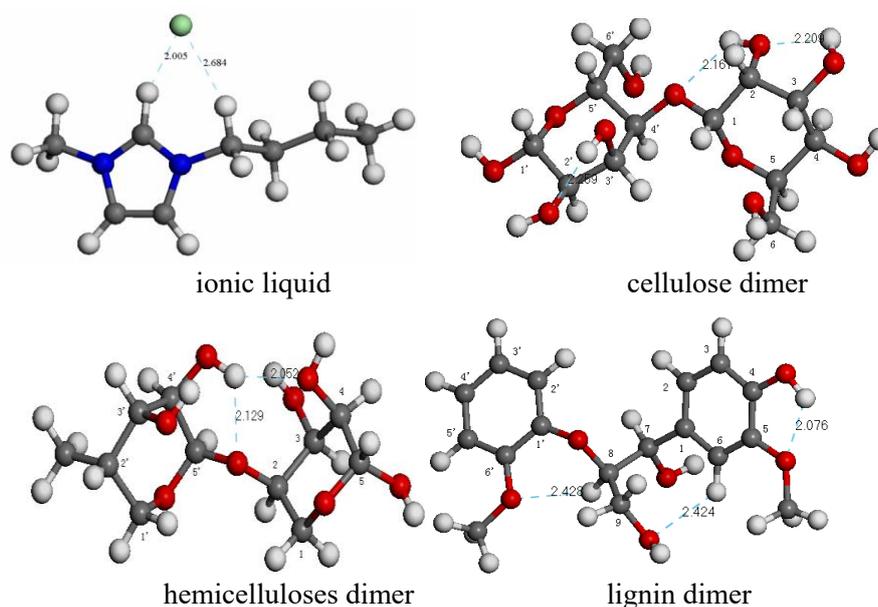


Figure 1. The most stable geometries of the ionic liquid and the lignocelluloses components dimer models. Carbon, oxygen, nitrogen, chlorine, and hydrogen atoms are shown as grey, red, blue, green, and white colors, respectively. Length (Å) of partial hydrogen bonds has been given.

As it can be seen, the 1-butyl-3-methylimidazolium cation interacts with chloride anion through two C-H...Cl intermolecular hydrogen bonds, which can also be confirmed by the bond critical points of H-bonds in supporting information. The hydrogen bond distances, bond angles and charge density given in Figure 1 and Table 1, show that hydrogen bond strength involved the proton on the imidazole ring of cation is larger than that of the other H-bond in the [Bmim][Cl] ionic liquids.

For the convenience of discussion, carbon atoms in the cellulose dimer, hemicelluloses dimer and lignin dimer have been numbered as shown in Figure 1. Two types O-H...O intramolecular hydrogen bonds have been found in the cellulose dimer. The hydroxyl at No.2 position forms a hydrogen bond with oxygen atom of the near glucose unit (Type A H-bond), which plays an important role for the maintenance of the cellulose molecule skeleton. The hydroxyl at No.2' position interacts with another hydroxyl at No.3' position of the same glucose unit through a hydrogen bond (Type B H-bond). Electron density of all hydrogen bond critical points within cellulose dimer is greater than zero ($\rho_{\text{bcp}} > 0$), while energy density is less than zero ($H_{\text{bcp}} < 0$), indicating greater strength of hydrogen bonds, and the nature of the partial covalent bond. It should be noted that the strength of type A H-bond is much greater than that of type B H-bond.

Similarly, two types O-H...O intramolecular hydrogen bonds have been found in the hemicelluloses dimer. The hydroxyl at No.4' position forms an intramolecular hydrogen bond with oxygen atom of the near glucose unit (Type C H-bond), which maintains the hemi-cellulose molecule skeleton. And the hydroxyl at No.3 position forms an intramolecular hydrogen bond with another hydroxyl at No.4 position of the near unit (Type D H-bond).

In lignin dimer, the two phenol rings of the lignin are connected with hydroxyl methyl as it is in bulk lignin polyphenols [16, 17], which confirms that the selected model is structurally suitable for mimicking the real lignin polyphenols. As shown in Figure 1, the methoxy at No.5 position forms an O-H...O hydrogen bond with the hydroxyl at No. 4 position of the same benzene unit (Type E H-bond), while the methoxy at No.6' position forms a C-H...O hydrogen bond with the hydrogen at 8 position of the near benzene unit (Type F H-bond). Moreover, as it can be seen from supporting information, the existence of ring critical points in the lignin dimer reveals weak π -stacking interactions in the lignin due to the intramolecular hydrogen bonds, which are disadvantageous for lignin dissolution in ionic liquids.

Table 1. Properties of partial hydrogen bonds within the ionic liquids and the lignocelluloses components ^a

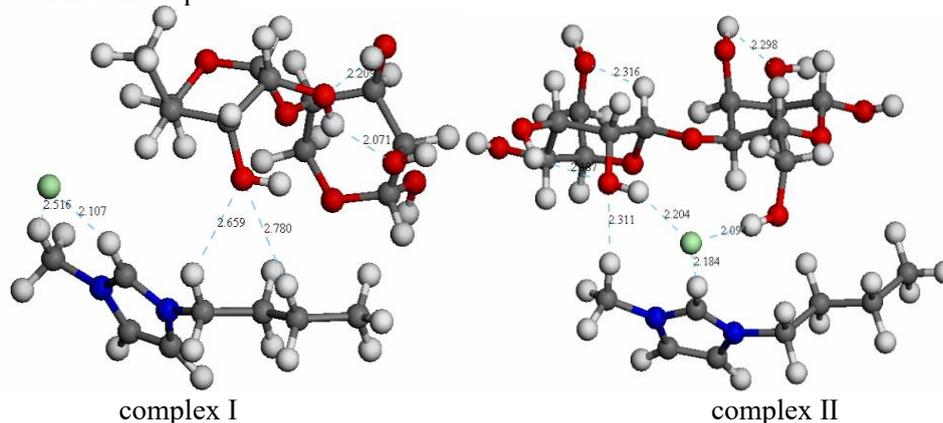
species	H-bonds	Length(Å)/ bond angle(°)	ρ_{bcp}
Ionic liquid	C-H(imidazole)---Cl	2.005/159.1	0.04212
	C-H---Cl	2.684/138.1	0.01120
Cellulose	O-H---O(skeleton)	2.161/113.2	0.01842
	O-H---O(hydroxy)	2.209/112.3	0.01273
hemicellulose	O-H---O(skeleton)	2.129/112.4	0.02126
	O-H---O(hydroxy)	2.052/149.4	0.01909
lignin	C-H---O	2.404/109.5	0.01261
	O-H---O	2.102/114.3	0.01994

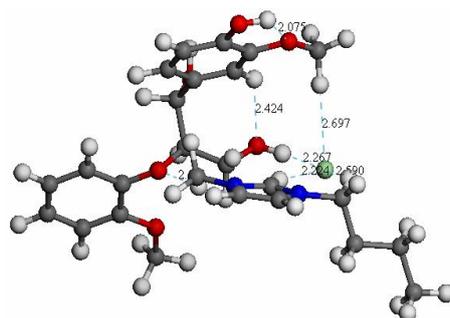
^a All topological quantities are in atomic units.

3.2 Interactions between lignocellulose components and ionic liquids

And afterward we focused on investigations of the dissolution mechanisms of cellulose, hemicelluloses, and lignin in [Bmim][Cl] ionic liquids. For convenience, the complexes which ionic liquid interacts with cellulose, hemicelluloses, and lignin are represented by complex I, II, and III, respectively.

Our calculated results for both the most stable geometry and topological parameters of complex I, II, and III, are demonstrated in Figure 2 and Table 2. As it can be seen, in the complex I cellulose dimer forms a C-H---O intermolecular hydrogen bond with the cation, and simultaneously forming two O-H---Cl intermolecular hydrogen bonds with anion, with length (bond angle) being 2.311 Å (117.337 °), 2.204 Å (156.450 °), and 2.094 Å (175.3°), respectively. Moreover, the existence of (3, +1) ring critical point in supporting information indicates that the complex characters with weak π -stacking interactions due to the intermolecular hydrogen bonds between cellulose dimer and ionic liquids. The stable intermolecular hydrogen bonds and weak π -stacking interactions between ionic liquid and cellulose dimer reduces the energy of the complex system, which are advantageous for the cellulose dissolution in ionic liquids.





complex III

Figure 2. The most stable geometries of the ionic liquid interacting with lignocelluloses components. Carbon, oxygen, nitrogen, chlorine, and hydrogen atoms are shown as grey, red, blue, green, and white colors, respectively. Length (\AA) of partial hydrogen bonds has been given.

Compared with the free cellulose dimer, one of the most significant changes is the disappearance of type A H-bond of the cellulose dimer in the complex I due to the ionic liquids involved in, which has played an important role for the maintenance of the free cellulose molecule skeleton. Furthermore, charge density of type B intramolecular hydrogen bond of the cellulose in the complex I shows that the strength of type B H-bond has decreased when the cellulose dimer interacts with ionic liquids.

Qualitatively, deformation energy could be used to estimate the deformation degree of ionic liquid and lignocelluloses components in the complexes. It can be evaluated from the format: $\Delta E_{\text{def}} = E_{\text{monomer}} - E_{\text{(optimized monomer)}}$. In the complex I, the deformation energy of cellulose dimer is 24.25 kJ/mol, while that of ionic liquid being 13.32 kJ/mol (see Figure 3). We predicted that the deformation of cellulose dimer and ionic liquid in the complex I may be a prerequisite for cellulose dissolution in ionic liquids.

In the complex II, the hemicelluloses dimer forms two C-H...O hydrogen bonds with the cation of ionic liquid, with bond distance (bond angle) being 2.659 \AA (134.7°), and 2.780 \AA (129.8°), respectively. Topological parameters in Table 2 also show that the strength of intermolecular hydrogen bonds in the complex II with respect to those in the complex I is decreased. Correspondingly, the deformation energy of hemicelluloses dimer in the complex II is 1.96 kJ/mol, while the deformation energy of ionic liquid in the complex II being 5.19 kJ/mol.

Similarly with the complex I, one of the most significant changes is the disappearance of type C H-bond of the hemicelluloses dimer in the complex II due to the ionic liquids involved in, which has played an important role for the maintenance of the free cellulose molecule skeleton. Furthermore, the strength of type D H-bond has decreased in the complex II when the hemi-cellulose dimer interacts with ionic liquids.

Table 2. Properties of partial hydrogen bonds within the complex I, II, and III ^a

species	H-bonds		Length(Å)/ bond angle(°)	ρ_{bcp}
complex I	C-H _(cation) ---O		2.311/171.3	0.01253
	O-H---Cl _(anion)		2.204/156.4	0.02467
	O-H---Cl _(anion)		2.094/175.3	0.03254
	Type B H-bond	C-H---O	2.316/121.7	0.01342
		O-H---O	2.298/107.9	0.00992
		C-H---Cl	2.184/174.1	0.02798
complex II	C-H _(cation) ---O		2.659/134.7	0.00634
	C-H _(cation) ---O		2.780/129.8	0.00514
	Type D H-bond	O-H---O	2.209/163.6	0.01485
		O-H---O	2.071/145.3	0.01938
		C-H _(imidazole) ---Cl	2.107/153.7	0.03358
		C-H---Cl	2.516/150.1	0.01471
complex III	C-H _(cation) ---O		2.671/136.8	0.00608
	O-H---Cl _(anion)		2.267/157.0	0.02189
	C-H---Cl _(anion)		2.697/171.9	0.01000
	Type E H-bond	O-H---O	2.075/115.2	0.02110
	Type F H-bond	C-H---O	2.424/127.5	0.01165
		C-H _(imidazole) ---Cl	2.224/151.0	0.02589
		C-H---Cl	2.590/139.8	0.01299

^a All topological quantities are in atomic units.

In the complex III, lignin dimer forms a C-H---O intermolecular hydrogen bond with the cation, and simultaneously forming a O-H---Cl intermolecular hydrogen bond and a C-H---Cl intermolecular hydrogen bond with anion, with bond length (bond angle) being 2.671 Å (136.8 °), 2.267 Å (157.0 °), and 2.697 Å (171.9°), respectively. Moreover, there are two (3, +1) ring critical points between the ionic liquid and lignin (see supporting information), which are advantageous for the lignin dissolution in ionic liquids. The deformation energy of lignin dimer in the complex III is 6.12 kJ/mol, while the deformation energy of ionic liquid in the complex III being 5.34 kJ/mol. Compared with the free lignin oligomer, the intramolecular hydrogen bonds of lignin dimer in the complex III have not almost changed when dissolved up in the ionic liquids.

On the other hand, the weak cation-anion interactions and deformation of ionic liquids have been investigated, and our calculated results indicate that the weak cation-anion interactions of ionic liquids are decreased when dissolving up the lignocelluloses components. From Figure 3, we can find that the deformation energy of cellulose dimer is biggest among the lignocelluloses components, following by that of lignin dimer, and that of hemicelluloses dimer being smallest. The same order is applicable for ionic liquid in the complex I, II, and III. The deformation energy of ionic liquid in complex I, II, and III has confirmed our prediction that the deformation of lignocelluloses components and ionic liquid may be a prerequisite for lignocelluloses components dissolution in ionic liquids.

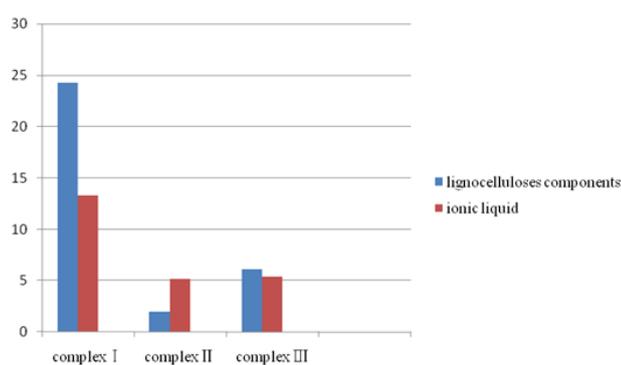


Figure 3. The deformational energy (kJ/mol) of lignocelluloses components and ionic liquid in the complexes.

4 Conclusion

In this paper, we proposed the dimer models for lignocelluloses components and their complexes with [Bmim][Cl] ionic liquid, their structural characteristics and the interactions between lignocelluloses components and ionic liquid were investigated by multiscale theoretical techniques. Our calculated results demonstrate that the insolubility of lignocelluloses components in water and organic solvents is mainly attributed to the large number of intramolecular hydrogen bonds. When dissolved in [Bmim][Cl] ionic liquid, the stable intermolecular hydrogen bonds and weak π -stacking interactions between ionic liquid and lignocelluloses components dimer reduces the energy of the complex system, which are advantageous for lignocelluloses components dissolution in ionic liquids. Compared with the free cellulose dimer, one of the most significant changes is the disappearance of type A H-bond of the cellulose dimer in the complex I due to the ionic liquids involved in, similarly with type C H-bond of the hemicelluloses dimer in the complex II. In the complex III, the intramolecular hydrogen bonds of lignin dimer have not almost changed when dissolved up in ionic liquids. Moreover, there are deformation accrued for both lignocelluloses components and ionic liquids, which may be a prerequisite for lignocelluloses components dissolution in ionic liquids.

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