



## Research on the structure of amino acid ILs and its solubility for chitosan with chemical software



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### ABSTRACT

In the present study, some different amino acid ionic liquids (ILs) were designed in order to find new solvent which is of excellent solubility and poor degradation for chitosan. The designed ILs contain different amino acid cations and organic acid anions: amino acids cations included [Gly], [Pro], [Thr] and [Ser]; organic acids anions included [HCOOH], [CH<sub>3</sub>COOH], [CH<sub>3</sub>CH<sub>2</sub>COOH], [CH<sub>2</sub>aCHCOOH] and [CH<sub>2</sub>aC(CH<sub>3</sub>)COOH]. At the same time we used chemical software to construct the original structure of three excellent-dissolving ILs which were selected from the amino acid ILs we prepared, and the calculation results of chemical software showed [Thr][CH<sub>3</sub>CH<sub>2</sub>COO] that of  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  are  $-0.17699$  and  $-0.02997$  which was the easiest to form hydrogen bond with chitosan and caused the dissolution of chitosan. The present work could guide us to design more new solvent to dissolve chitosan, which can enlarge the usage range of chitosan.

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## 1. Introduction

Chitosan is the deacetylated derivative of chitin which is widely used in tissue engineering [1–4], heavy metal disposal [5–7], drug delivery, filtration, and biosensors and so on [8–14]. However, chitosan is insoluble in many conventional organic solvents, which restricts their applications. Resembling the structure of cellulose, chitosan has the structure of N-acetamino-2-desoxy-β-D-glycopyranose, but bearing one amino group in place of the hydroxyl group in the C-2 position [15]. Its origin and the high number of amino groups along the polymer chain provide the chitosan macromolecule with exceptional properties, namely, its bioactivity and biocompatibility in combination with a high synthetic potential [16]. The key point of preparing excellent chitosan products is the choice of solvent. The traditional solvents of chitosan are some acids which are highly volatile and hard recycling, and do harm to environment and equipments. Consequently, it is highly desirable to seek effective and sustainable solvents for chitosan dissolution.

Recently, ionic liquids (ILs) have outstanding solvation potential, have been claimed to be green solvents which are capable of dissolving complex macromolecules such as chitosan and polymeric

materials with high efficiency [17–20], in addition to their potential as environmentally affable solvents with a myriad of synthetic and industrial applications [21–23]. However, only a few studies have been performed to explore the effects of cationic structure on the biopolymer dissolution [24–26], many research preferred to imidazoles ILs while the study of amino acids ILs are rare. Furthermore, nobody used ChemDraw or Chem3D to construct the original structure of ILs. It is worth noting that previous research on the solubility of chitosan in ILs also paid little attention to the degradation of chitosan.

Our group has tried to use [Gly]Cl to dissolve chitosan and improved the shortcomings of traditional solvents [27], but [Gly]Cl had a great impact on chitosan's structure, and caused a higher degradation rate of chitosan, which had a great impact on the follow-up chitosan products such as chitosan fibre, textile and hydrogel etc. In order to find some kinds of ILs that can dissolve chitosan efficiently, easily recycling, and have a lower degradation rate of chitosan, a lot of work has been done. In the present study, some different amino acid ILs were designed in order to find new solvent which is of excellent solubility and poor degradation for chitosan. The designed ILs contain different amino acid cations and organic acid anions: amino acids cations included [Gly], [Pro], [Thr] and [Ser]; organic acids anions included [HCOOH], [CH<sub>3</sub>COOH], [CH<sub>3</sub>CH<sub>2</sub>COOH], [CH<sub>2</sub>aCHCOOH] and [CH<sub>2</sub>aC(CH<sub>3</sub>)COOH]. At the

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same time we used chemical software to construct the original structure of ILs to guide us to design more new solvent to dissolve chitosan, which can enlarge the usage range of chitosan.

## 2. Experimental

### 2.1. Materials

Chitosan was obtained from Shengyang chemical limited company (Qingdao, China), with a degree of deacetylation (DD) value of 86.9%, and its average-molecular weight ( $M_w$ ) was  $1.49 \times 10^6$  by measuring viscosity. It was used directly with no pretreatment. Glycine, proline, serine, threonine, methanoic acid, acetic acid, propionic acid, acrylic acid, methacrylic acid, and acetone were all AR, purchased from Aldrich and Alfa Aesar, and used without purification.

### 2.2. Preparation and characteristic of ILs

Preparation of ILs were done according to known procedures [28] with minor modifications. Briefly, a mixture of amino and organic acid of which the mole ratio is 1:1.2 was heated at 50 °C for 5–6 h in 20 g deionized water. During the process a transparent aqueous solution formed. The solution was dried in vacuum at 60 °C for 24 h. After cooling to room temperature, a white solid formed. The solid was washed with ethyl acetate (3 × 30 ml) and dried in vacuum at 50 °C for 12 h. Amino acids included Gly, Pro, Thr and Ser; organic acids included HCOOH, CH<sub>3</sub>COOH, CH<sub>3</sub>CH<sub>2</sub>COOH, CH<sub>2</sub>=CHCOOH and CH<sub>2</sub>aC(CH<sub>3</sub>)COOH.

### 2.3. Dissolution and recycling

#### 2.3.1. Dissolution of chitosan

Prepare IL aqueous solution (4 wt%) by dissolving 2 g IL in 48 ml deionized water, and 1 g chitosan was dissolved in it under continuous magnetic stirring for 5 h, then obtained clarify chitosan gel solution.

#### 2.3.2. Recycling of chitosan and ILs

Acetone was added into the chitosan-ILs solution at room temperature, and then the dissolved chitosan would precipitate from ILs. The precipitated chitosan was dried for 24 h at 50 °C. The average-molecular weight ( $M_w$ ) of chitosan was evaluated by measuring viscosity based on Ubbelohde' method and the structure of recycled chitosan was characterized by XRD (D/max2500 PW3040/60) X-ray diffractometer with Cu K $\alpha$  radiation ( $k = 0.15405981$  nm). The ILs-acetone solution was distilled to remove acetone. The recycled ILs was characterized by FT-IR (Nicolet-510 P FTIR, America) using KBr discs in the range of 4000–500 cm<sup>-1</sup>, and NMR (Bruker AV500, D<sub>2</sub>O; TMS).

## 3. Results and discussion

### 3.1. Degradation of chitosan

The mechanism of chitosan dissolution in amino acids ILs is thought that both anions and cations are involved in the dissolution process. The oxygen and hydrogen atoms of the chitosan form electron donor-electron acceptor complexes with the charged species of the IL. It has been suggested that this occurs primarily between the C-2 amino groups and C-5 hydroxyl groups. This interaction resulted in the separation of the amino groups and hydroxyl groups of the different chitosan chains leading to dissolution of the chitosan in the ILs [29] (see Fig. 1).

ILs linked to chitosan molecular chain in the form of hydrogen

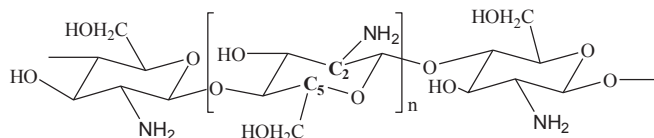


Fig. 1. Chemical structure of chitosan.

bond, and amino acid cations and acid anions were introduced. When the number of hydrogen bond was not so many, the charge were dispersed, which made slightly degradation of chitosan; when the number of hydrogen bond increased, the same charge excluded each other, which caused serious degradation of chitosan during the molecular movement. Therefore, degradation happened every moment during dissolution process of chitosan.

Table 1 showed the effects of different kinds of ILs on degradation rate of chitosan under the same condition such as the same dissolving time, the same concentration of ILs and chitosan.

Amino acid existed as cation in aqueous liquid and easily formed hydrogen bond [31] (Fig. 2). As we can see in Fig. 2, glycine formed a five-membered ring and the hydroxyl on the carboxyl easily formed hydrogen bond with chitosan from every direction which made chitosan molecular chain link a lot compact positive charge. Cations excluded each other easily which caused macromolecule chain of chitosan broken down and resulted a molecular failure. The other three ILs all formed double-ring structure and were not so easy to form hydrogen bond like glycine cations, as a result, the degradation rates of them were lower than glycine series ILs.

During dissolving process, degradation happened every moment [32]. Except the structure of amino acid cation, the degradation rate of chitosan had something to do with the concentration of acid and the steric hindrance. [Pro][CH<sub>3</sub>COO] and [Ser][CH<sub>3</sub>COO] were of stronger the acidity than that of [Thr][CH<sub>3</sub>CH<sub>2</sub>COO]. The stronger the acid was, the more the chitosan degraded [33]. Therefore, the degradation rates of chitosan in [Pro][CH<sub>3</sub>COO] and [Ser][CH<sub>3</sub>COO] were close, and higher than that in [Thr][CH<sub>3</sub>CH<sub>2</sub>COO]. Besides, steric hindrance showed the same law: the acetate's volume of [Thr][CH<sub>3</sub>CH<sub>2</sub>COO], [Pro][CH<sub>3</sub>COO] and [Ser][CH<sub>3</sub>COO] in Fig. 2 was similar, so the probabilities of attacking chitosan molecular chain were the same. The acid ion of [Pro][CH<sub>3</sub>COO] and [Ser][CH<sub>3</sub>COO] were acetate, the volume of which was smaller than that of [Thr][CH<sub>3</sub>CH<sub>2</sub>COO], which made [Pro][CH<sub>3</sub>COO] and [Ser][CH<sub>3</sub>COO] were easier to attacking chitosan molecular chain, as a result, the chitosan molecular chain linked more charged groups, which caused degradation in the constant movement of molecular. The discussion above equated with the experiment result in Table 1.

Entries 23 and 24 showed that [Thr][ClCH<sub>2</sub>COO] and [Ser][ClCH<sub>2</sub>COO] had a large degradation rate of chitosan. The carbo-chain linked Cl was negative which caused large molecular weight failure when Cl formed hydrogen bond with H on chitosan molecular chain based on the theory that the same type of charge is mutually exclusive. The exclusive degree caused the expansion of chitosan molecular chain which was much more serious than the expansion of the ordinary macromolecule's dissolving in solvent. As a result, the serious failure of chitosan molecular weight happened [34].

### 3.2. Measurements of $E_{HOMO}$ and $E_{LUMO}$ parameters of the ILs

ILs have been used for dissolving biological macromolecules that linked together by intermolecular hydrogen bonds such as carbohydrates, cellulose, silk fibroin [35–40]. In order to research the structure stability of ILs and the ability of forming hydrogen

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