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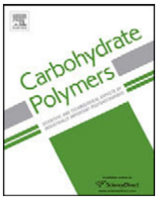

Molecular simulation of the complex of konjac glucomannan–borate in water

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ABSTRACT

The formation of konjac glucomannan–borate complex in water solution has been investigated by experimental and molecular simulation methods. The energy, radical distribution function of borate anion ($B(OH)_4{}^-$), and mean square displacement of the complex were studied during the molecular simulation, and the results indicate that one type of helical complex can be formed based on the hydrogen bonds between borate anion and helical chain of KGM. The hydrogen bond is formed by the interaction of borate anion and –OH groups on C (6) of mannose and glucose. Temperature has little effect on the helical conformation of the complex. It was proposed that the complex can form gel through the aggregation arrangement of helical chain.

1. Introduction

Konjac glucomannan (KGM) is an essential polysaccharide that is the main component of the konjac flour produced from the tubers of *Amorphophallus konjac* C. Koch. It consists of â-1-4-linked glucose and mannose units, and the ratio of glucose: mannose is between 1:1.5 and 1:1.6 (Pang, Lin, & Zhang, 2003). KGM could form gel with the metal salts which could be hydrolyzed into multi-hydroxy hydrate (Li, Wang, & Sun, 2003). Borate is a good buffer agent, which could be fully hydrolyzed into borate anion ($B(OH)_4{}^-$) in water solution. Because of the tetrahedron conformation, borate anion could coordinate with KGM molecular chain easily to form network structure, and finally form gel (Li et al., 2003a; Li, Pang, & Liao, 2004).

In our previous work, the structure of KGM–borate complex has been studied by ^{11}B NMR, ^{1}H NMR, IR, and Raman characterizations (Li et al., 2004). The characteristic vibration of B–O bound in 1380 cm^{-1} in infrared spectrum, and B–H vibration in 2640 cm^{-1} in Roman spectrum indicate that the coordination complex is formed. The main reaction site was the hydroxyl at C (6) of mannose and glucose, and the hydroxyl at C (2), C (3) of mannose. One type of intramolecular complex can be formed when the ratio of KGM:borate anion was 1:1. Because of the diversity of helical conformation of KGM in solution, and the limit of traditional experimental methods, the conformation and formation mechanism of KGM–borate complex have not been fully understood (Li & Xie, 2003; Yui, Ogawa, & Sarko, 1992; Ogawa, Yui, & Mizuno, 1991).

So far, molecular docking and molecular dynamic simulation method have been widely used in the study of macromolecule conformation and the interaction with their complexes (Pang, Sun, & Guan, 2005; Pang, Sun, & Sun, 2006; Pang, Xu, & Bai, 2009). In the previous studies, we investigated the formation mechanism, formation sites, and microscopic conformation of KGM molecular helices by molecular dynamics and experiment (Jian, Yao, & Wang, 2010). In this work, we investigated the conformation, potential energy, and radical distribution function of the KGM–borate complex using molecular dynamic simulation in order to disclose the coordination and gelatin mechanism. This work will provide a new method and theoretical guide for the coordination mechanism between natural biological macro-molecules and inorganic molecules.

2. Method

2.1. Establishment of KGM model

Based on the primary structure of KGM (Fig. 1), the primary model of left-handed helical KGM was established by Build Biopolymer Module in Sybyl 8.1 software, using the dihedral angle of glycoside bond $\varphi = -123$, $\psi = -90$ as parameters. The primary model was optimized by molecular mechanics, followed by the molecular dynamics simulation on O2 workstation. The parameters in molecular dynamics were set as follows: isothermal system with $T = 300$ K, relaxation method utilized to adjust the tempera-

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G-M-M-M-M-G-M-G
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G= glucose residue, M= mannose residue, Ac= acetyl

Fig. 1. Structural composition diagram of KGM.

ture, integration step of calculation to 0.001 ps. The system was run for 1000 ps.

2.2. *Establishment and optimization of borate anion model*

The primary model of borate anion was established in Sybyl 8.1 software, and was optimized by molecular mechanics and molecular dynamics simulation. Parameters in molecular dynamics simulation on Borate anion were set as follows: isothermal system with T = 300 K and coupling of 0.1 ps with cutoff = 8, dielectric constant = 1.0, integration step of calculation to 0.001 ps. The system was also run for 1000 ps.

2.3. *Molecular docking*

Molecular docking was carried out by Surflex-dock module in Sybyl 8.1 software, using the KGM model as receptor and borate anion model as ligand, respectively. The intramolecular KGM–borate complex was achieved after docking. Parameters for docking were set as follows: surflex-dock mode with automatic protomol generation, and threshold value = 0.50 with bloat = 0.

2.4. *Molecular dynamics simulation on the complex*

Molecular dynamics simulation was carried out on the complex model in periodic boundary conditions in water solution with Tripos force field. The parameters for molecular dynamics simulation were set as follows: algorithm for solvating: silverware, temperature: 300 K, initial velocity: Boltzmann, step: 0.001 ps, length: 50,000 ps, dielectric constant: 1.0, the length of box was 30.99187, respectively, in three dimensions.

2.5. *Preparation of KGM–borate complex solution*

One gram of purified KGM was added into 1000 ml water and dissolved completely. The solution was filtrated. Then 10 ml 1% (w/v) borate solution was added into the filtrate in a stirring condition. After stirring for 1 h and then placed for 24 h, the complex solution was obtained.

2.6. *Optical rotation analysis on complex solution*

Optical activity of KGM–borate complex solution was measured with 1 dm polarization tube using sodium light at 293 K. Distilled water was used as blank. Optical activity was calculated by the following equation:

$$\text{specific optical rotation} = [\alpha]_\lambda^t = \frac{\alpha}{L \times c}$$

where L is the length of polarization tube(dm) and c is the concentration of sample.

3. Results and discussion

3.1. *Energetic curve of complex during MD simulation*

As suggested in Fig. 2, the potential energy of the complex increased sharply in the first 10 ns because of heightening temperature. An energy oscillation can be observed during 10–23 ns, which may be the result of the conformation adjustment of the complex, and the non-bounding interaction between KGM and borate anion, when borate anion began to enter the helical cavity of KGM. Finally, the energy declined, and became stable (about 620 kcal/mol) due to the formation of complex with optimized conformation between 30 ns and 50 ns.

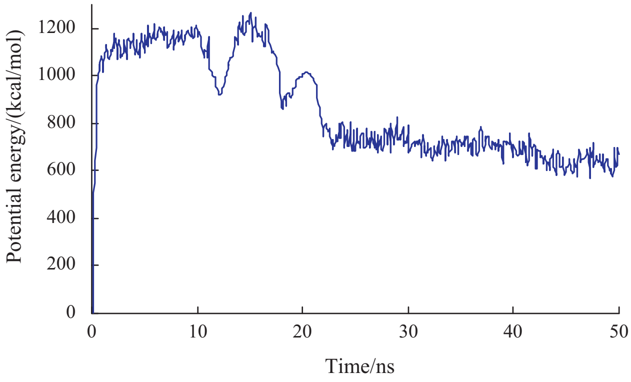

Fig. 2. Energy curve of the KGM–borate complex.

3.2. *Radius of gyration of the complex*

Radius of gyration is a physical quantity which shows the molecular coil dimension during the MD simulation. The definition is shown as follows:

$$R_{gyr}(t)=\left[\frac{1}{N_{at}}\sum_{i=1}^{N_{at}}(r_i(t)-r_{CM}(t))^2\right]^{1/2}$$

Here $r_i(t)$ means the coordinate of atom (i) at time t and $r_{CM}(t)$ means coordinate of the molecule at time t; N_{at} means the total number of atoms in the system.

As shown in Fig. 3, the radius of gyration of the complex increased in the first 10 ns, and then descended in a periodic changing mode. It kept constant between 6.4 and 6.6A after 40 ns. Its changing trend was similar to that of the potential energy. Both indicated the interacting process of KGM and borate anion. In this process, the molecular chain of KGM expanded appreciably to facilitate the entering of borate when borate approached KGM's helical cavity. The molecular chain shrinked slightly when the system reached the dominant conformation.

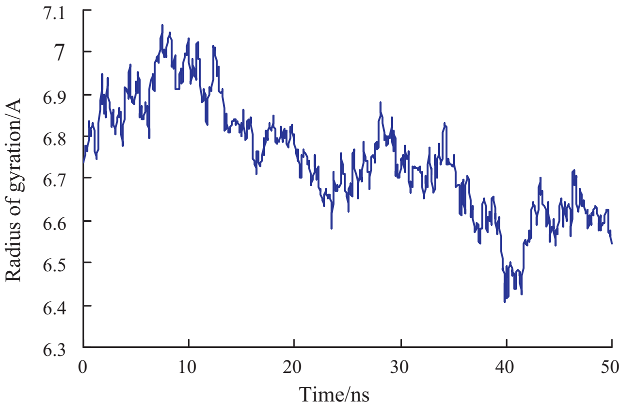

Fig. 3. The change of radius of gyration with time.