



Superadsorption of LiOH solution on chitosan as a new type of solvent for chitosan by freezing/blasting

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ABSTRACT

The adsorption behavior and mechanism of chitosan in aqueous LiOH solution was studied systemically. The results showed that the adsorption of chitosan was mainly due to the breakage of its hydrogen bonds, which were destroyed by the reaction of LiOH with the acetyl and the hydroxyl groups of chitosan. Low temperature also played a crucial role in the adsorption of chitosan. The adsorption of chitosan decreased with increased DD. The adsorption ratio of LiOH to chitosan ($n_{\text{LiOH}}/n_{\text{CS}}$) increased linearly while the adsorption ratio of water to chitosan ($n_{\text{H}_2\text{O}}/n_{\text{CS}}$) decreased with the increased DD. All chitosans reached their maximal swelling degree when the concentration of LiOH was 4.8 wt%. Chitosan was stable in LiOH aqueous solution. The LiOH solution may be a potential favorable solvent for chitosan.

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1. Introduction

It has been a long term effort to seek appropriate solvents for chitosan ever since its discovery (Austin, Brine, Castle, & Zikakis, 1981). Dilute acids have been chosen as the solvents for chitosan for decades (Muzzarelli et al., 2012; Wang, Turhan, & Gunasekaran, 2004). However, chitosan is unstable in acid. Its hydrolysis is accompanied with the cleavage of glycosidic-bonds, which results in decreased molecular weights and higher dispersivity (Aiba, 1991; Muzzarelli, 2012).

Recently, novel chitin products with good mechanical properties have been successfully prepared from aqueous chitin/alkali solution (Goycoolea et al., 2007; Hu et al., 2007; Rinaudo, 2008). And plenty of works concerning the system of chitin and alkali solution have been carried out (Feng, Liu, & Hu, 2004; Liu, Liu, Pan, & Wu, 2008; Noishiki et al., 2003). Moreover, it is proved that the β -(1→4) glycosidic-bonds of chitin and cellulose are stable in alkali at a temperature lower than 170 °C (Knill & Kennedy, 2003), which contributes to the good mechanical properties of the products.

Chitosan is chemically similar to chitin, so it is possible for it to dissolve or swell in alkali aqueous solution with high stability, and to be processed into products with good mechanical properties

(Muzzarelli, Tosi, Francescangeli, & Muzzarelli, 2003). However, few works have been carried out in this field (Fan & Hu, 2009; Fan, Hu, & Shen, 2009).

In our current work, chitosans with high molecular weight ($M_n \geq 1.5 \times 10^6$) and different DD were prepared by a modified two-step deacetylation process. And they were used to study the adsorption behavior of chitosan in LiOH aqueous solutions.

This work focused on acquiring basic understanding of the adsorption behavior of chitosan in LiOH aqueous solution and providing guidance for the further development of this new-type solvent for chitosan.

2. Materials and methods

2.1. Materials

α -Chitin and α -Chitosan (shrimp shell, powders) supplied by Zhejiang Golden-shell Biochemical Co. Ltd. (China) were used without further treatment.

LiOH·H₂O, NaOH, HCl, CH₃COOH, and CH₃COONa were obtained from Sinopharm Chemical Reagent Co. Ltd. (China). All the reagents were of analytical grade, and used without further purification.

2.2. Preparation of partially N-deacetylated chitosan

N-deacetylated chitosan was prepared heterogeneously under the preparing conditions by a modified two-step deacetylation

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process shown as below. 10 g dried α -chitin powder was stirred with 300 mL NaOH in a flask for a certain time. Then the mixture was cooled by the addition of 1000 ml deionized water. After standing at room temperature for 12 h, the solid was washed to neutral with deionized water, and then dried at 60 °C in the oven for 24 h. The prepared N-deacetylated chitosans were coded as CS65, CS70, CS75 and CS80, for the DD of them were 64.2%, 71.9%, 76.7% and 81.4% respectively. And the preparation conditions are as follows:

CS65–90 °C, 50% NaOH and stirred for 1 h;
 CS70–80 °C, 55% NaOH and stirred for 2 h;
 CS75–85 °C, 50% NaOH and stirred for 2 h;
 CS80–90 °C, 55% NaOH and stirred for 4 h.

2.3. The adsorption experiment of chitosan

2.3.1. The adsorption experiment at room temperature

0.500 g chitosan powders were soaked in 100 g LiOH aqueous solution with different concentration ranging from 1.2 wt% to 6.0 wt%. After standing at room temperature for 4 h and adsorbing fully, the sample was filtered with a 60 mesh nylon net and its surface water was removed by a ashless quantitative filter paper with a pore size of 30 μ m. The mass of resulted sample was measured precisely and recorded as m_1 .

2.3.2. The adsorption experiment with the treatment of freezing–blasting

0.500 g chitosan powders were soaked in 100 g LiOH aqueous solution with different concentration ranging from 1.2 wt% to 6.0 wt%. After standing for 4 h and frozen for 5 h at –60 °C, the sample was taken out from the freeze-dryer and thawed at the low temperature (0–5 °C). The obtained sample was filtered with a 60 mesh nylon net and the mass was recorded as m_2 after precise measurement.

The adsorption of sample was calculated from Eq. (1):

$$A = \frac{m - 0.500}{0.500} \times 100\% \quad (1)$$

where m is the mass of the swollen samples.

For each sample, three parallel experiments were carried out and the average values were taken.

2.4. Measurement

The amount of LiOH and water adsorbed in samples could be determined by conductometric titrations, using a conductivity meter DDS-307 equipped with a Pt electrode. After the adsorption experiment, 5 ml resultant LiOH solution was took and put into a beaker, diluted with 50 ml deionized water, and then titrated with 1.0 M HCl. A curve of the conductivity against the volume of HCl with two inflectional points was obtained. The volume difference of these two points corresponded to the remaining LiOH in the solution after the adsorption. Then the concentration of LiOH after adsorption could be calculated. The amount of LiOH and water adsorbed in samples were calculated according to Eqs. (2) and (3).

$$\text{Adsorbance}_{\text{LiOH}} = C_{\text{LiOH}} \times 100 - \frac{1.0 \times V_{\text{HCl}} \times 24 \times V_{\text{LiOH}}}{5.0} \quad (2)$$

$$\text{Adsorbance}_{\text{H}_2\text{O}} = m_2 - \text{adsorbance}_{\text{LiOH}} \quad (3)$$

For each sample, three parallel experiments were carried out and the average values were taken.

The DD was determined by conductometric titrations according to Raymond, Morin, and Marchessault (1993).

The M_η of prepared samples was calculated from the classical Mark–Houwink relationship,

$$[\eta] = kM^\alpha \quad (4)$$

where $[\eta]$ is the intrinsic viscosity, $\alpha = -1.02 \times 10^{-2} \times \text{DD} + 1.82$, $k = 1.64 \times 10^{-30} \times \text{DD}^{14} \text{ cm}^3 \text{ g}^{-1}$ (Fan et al., 2009). The intrinsic viscosity was measured with an Ubbelonde viscometer at 30 °C using 0.2 M CH_3COOH –0.1 M CH_3COONa as solvent. The solutions were filtered through a P30 glass filter before determining $[\eta]$.

The stability of chitosan in LiOH aqueous solution was evaluated by DD and M_η of the swollen chitosan after adsorption for 1, 3, 5, and 7 days.

In order to characterize the composition of the prepared chitosan, solubility of the prepared chitosan in acid was evaluated by the transmittance of their solution in 0.2 M acetic acid by a UV–vis spectrophotometer (UV-2550, Shimadzu) with a quartz cell and an optical path length of 1000–600 nm. The sample concentration was 5 mg ml^{-1} (Kubota, Tatsumoto, Sano, & Toya, 2000).

X-ray diffraction patterns of powdered samples were obtained by a Bruker AXS D8 Advance X-ray diffractometer, 40 kV and 34 mA with Cu $K\alpha$ radiation at k 1.5406 Å. The relative intensity was recorded in the scattering range (2θ) of 5–60° with steps of 0.1° s^{-1} . The crystalline index (CrI) was determined by the Hermans–Weidinger equation (Zhang, Haga, Sekiguchi, & Hirano, 2000).

FT-IR spectra were measured on a Vector 22 spectrometer (Bruker) in KBr pellets at ambient temperature. All spectra were recorded with an accumulation of 32 scans and a resolution of 4 cm^{-1} in the range from 4000 cm^{-1} to 500 cm^{-1} .

3. Results and discussion

By dispersing CS65 in the LiOH aqueous solution and freezing–blasting afterward in a covered bottle, CS65 can adsorb large amount of aqueous LiOH and swell highly in the LiOH aqueous solution, with the particles turning into transparent hydrogel.

3.1. Effect of the structure of chitosan

3.1.1. Structural change during the two-step deacetylation

The adsorption behavior of chitosan is closely related to its structure. The structure parameters of prepared chitosan with different DD are shown in Table 1. All the four chitosan can dissolve in 0.2 M acetic acid completely, indicating that the original chitin deacetylates quite homogeneously by our two-step deacetylation process, and the composition of the obtained product is totally chitosan. Generally, with the increase of DD, the molecular weight of chitosan decreases gradually, the crystallinity decreases at first and then increases, and the d -spacing increases at first and then decreases except for CS75. This fact indicates the structure of the prepared chitosan is loose at first and then becomes relatively denser with the increase of DD. However, due to their different preparing conditions, CS75 has exceptional looser structure.

3.1.2. Influence of structure on the adsorption

As expected, the adsorption behavior of chitosan prepared by the two-step method shows dependency on the DD. Moreover, by data fitting, the relationship among swelling degree, DD and the concentration of LiOH can be expressed as follows:

$$A = 7346.834 + 60851.79 \times C_{\text{LiOH}} - 7782.139 \times \text{DD} \quad (5)$$

$(R = 0.874, F = 33.99)$

The adsorption capacities of CS65, CS70, CS75, and CS80 in water ($C_{\text{LiOH}} = 0 \text{ wt}\%$) are 676%, 675%, 675% and 626%, respectively, which

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