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Note

Chitosan-LiOH-urea aqueous solution—a novel water-based system for chitosan processing

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ABSTRACT

A solution of partially N-deacetylated chitosan in aqueous lithium hydroxide (LiOH)/urea was prepared successfully through a freeze-thawing process and the dissolution behavior was studied. The results indicated that chitosan can directly dissolve in LiOH/urea aqueous solution. LiOH mainly contributed to the breakage of intramolecular and intermolecular hydrogen bonds in chitosan. Urea, LiOH, and chitosan formed inclusion compound (IC) with urea as the IC host, and the LiOH-chitosan complex as the guest. Aqueous 4.8 wt % LiOH/8.0 wt % urea was verified to be the optimal solvent for chitosan. The results of rheology and viscosity characterizations revealed that chitosan/4.8 wt % LiOH/8.0 wt % urea aqueous solution was pseudoplastic fluid, and was more stable than the solution of chitosan in acetic acid at ambient temperature.

For a long time, the widespread use of chitosan has been seriously restricted due to its poor processibility resulting from its poor solubility.[1] Chitosan can only dissolve in some specific organic acids and a few inorganic solvents.[2,3] However, chitosan is unstable in acid. Its hydrolysis is accompanied with the cleavage of glycosidic-bonds,[4] which results in the decrease and higher dispersivity of molecular weight, and therefore the poor properties of chitosan products. Owing to the above-mentioned reasons, various studies were carried out to improve the solubility of chitosan and the stability of its solution. With respect to the solubility, the work mainly focused on the following three aspects. (1) Modification of the degree of deacetylation (DD).[5–7] (2) Degradation.[8,9] (3) Chemical modification.[10–15]

Recently, novel cellulose fibers have been successfully prepared from aqueous cellulose/alkali urea solution,[16] and the dissolution behavior has also been studied.[17] Moreover, many works concerning alkali chitin have been carried out.[18–24] In addition, this alkali chitin solution has been applied to prepare chitin product, such as hydrogels[25] and other products.[26] Chitosan is chemically similar to chitin and cellulose. Therefore, it is possible for chitosan to dissolve or swell in alkali aqueous solution. However, few works have been carried out in this field. Herein, we present a new method to prepare the solution of partially N-deacetylated chitosan with relatively high molecular weight by using 4.8 wt % lithium hydroxide (LiOH)/8.0 wt % urea aqueous solution as the solvent. A primary understanding of the dissolution behavior of N-deacetylated chitosan was studied by ^{13}C nuclear magnetic resonance (NMR), X-ray diffraction (XRD), and Transmission Electron Microscope (TEM). The rheological behavior and stability of the solution were also studied. It is our intention that the results may contribute to a new solvent system for chitosan, a meaningful pathway to develop the production of chitosan materials and a broader application of chitosan in wide pH range. And recently, we have successfully prepared chitosan membrane and scaffolds from this kind of solution.

Figure 1 shows the image of the solutions of 2.0 wt % CS80 in aqueous 4.8 wt % LiOH/8.0 wt % urea, with or without freeze-thawing treatment. Compared with the treatment without freeze-thawing, which only results in swelling in the given solvent system, it is evident that the freezing treatment has crucial role in the dissolution of CS80. Such dissolution behavior for crystalline chitosan in alkali solvent has seldom been reported. On the contrary, alkali is traditionally used as a coagulant for chitosan.

^{13}C NMR spectra of solutions of CS80 in 4.8 wt % LiOH/8.0 wt % urea/D_2O and 4.8 wt % LiOH/D_2O and 4.8 wt % LiOH/8.0 wt % urea in pure D_2O are shown in Figure 2. The peaks at 105.3, 81.7, 78.7, 77.0, 63.6, 60.1, and 19.9 ppm. for CS80 in LiOH/urea/D_2O are assigned to the C-1, C-4, C-5, and C-3, C-6, C-2 as well as acetyl of chitosan, respectively. These chemical shifts are similar to those for chitosan in trifluoroacetic,[27] which is good solvent for chitosan. No new peaks are observed in ^{13}C NMR spectra of the chitosan solutions. The results show that CS80 can directly dissolve in 4.8 wt % LiOH/8.0 wt % urea aqueous solution without any derivatization. Comparing the spectra of CS80 in LiOH/urea with those

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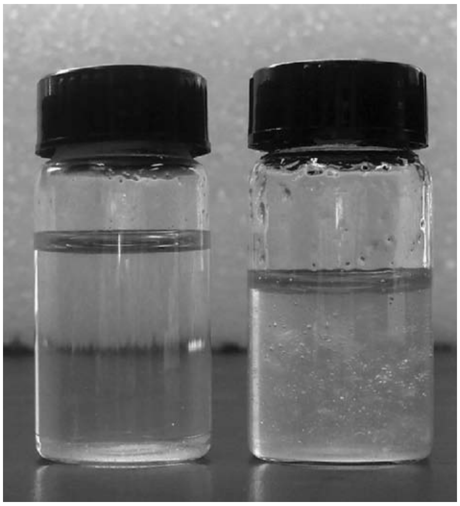

Figure 1. Solutions of 2.0 wt % CS80 in 4.8 wt % LiOH/8.0 wt % urea/H_2O with and without freezing–thawing process.

in LiOH, the chemical shifts are similar, suggesting that the existence of LiOH mainly contributed to the breaking of the intramolecular and intermolecular hydrogen bonds in CS80, and making it soluble in LiOH/urea/H_2O mixture. Figure 3 shows XRD spectra of the powdered samples. All the samples are prepared by the freeze-dried method. The major peaks at $2\theta = 33.5°$, 36.8°, 31.8°, and 29.9° are assigned to the crystal structure of LiOH·H_2O and $2\theta = 22.6°$, 36.4°, and 30.1° are observed for pure urea illustrated in Figure 3a and b,[28] respectively. With respect to the freeze-dried sample of CS80 in LiOH aqueous solution, the spectra of it exhibit high similarity to those of lithium hydroxide monohydrate (LiOH·H_2O) powder, except for several new peaks, which are not characteristics of LiOH and chitosan, suggesting the formation of a new complex. The diffraction pattern of the freeze-dried sample of CS80 in LiOH/urea solution is very similar to a combination of that of urea and LiOH·H_2O. But comparing the diffraction pattern of freeze-dried sample of CS80 in LiOH aqueous solution with that of LiOH, it can be found that the diffraction intensity of LiOH in the former is much weaker, and it is notable that the absence of diffraction peaks which are attributed to chitosan. The peaks of urea remain in the CS80/LiOH/urea system while those of LiOH and chitosan weaken, and disappear, respectively. Since the ^{13}C NMR spectra and XRD spectra of frozen-dried sample of CS80 in LiOH aqueous solution discussed before show clear evidence for the presence of CS80, we can conclude that CS80 and LiOH are shielded by urea.[17,28] Urea has been proven to be an inclusion compound host, with guests, either small molecules or polymers, such as PEO, polypropylene and cellulose, engaged in its channels.[17,28] Based on these results it is presumed that as a guest CS80–LiOH complex is included in the ICs hosted by urea hydrates, creating a stable solution through low-temperature process.

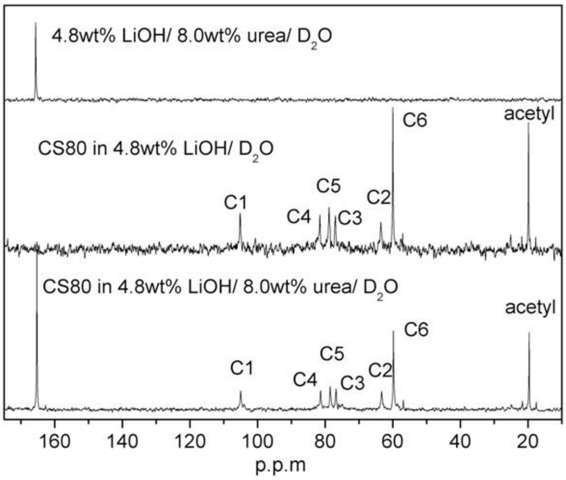

Figure 2. ^{13}C NMR spectra of 4.8 wt % LiOH/8.0 wt % urea/D_2O and of CS80 in 4.8 wt % LiOH/D_2O and in 4.8 wt % LiOH/8.0 wt % urea/D_2O at ambient temperature.

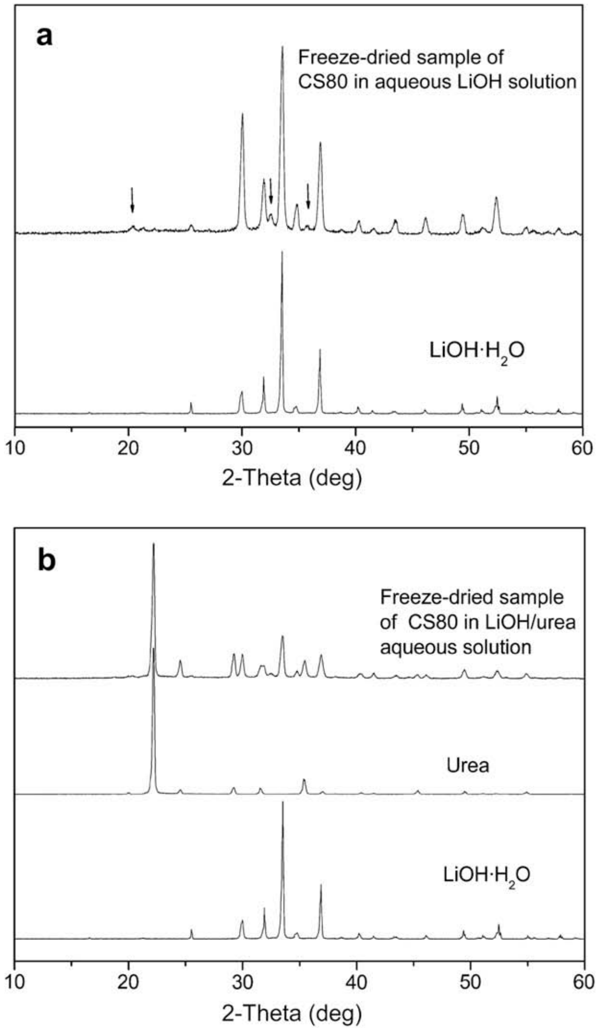

Figure 3. (a) XRD spectra of LiOH·H_2O (powder) and a frozen-dried sample of CS80 in LiOH aqueous solution; (b) XRD spectra of LiOH·H_2O (powder), urea (powder), and a frozen-dried sample of CS80 in LiOH/urea aqueous solution.

UV–vis spectrophotometry is used to optimize the formation condition of the inclusion composites. As shown in Figure 4a, the transmittance of the solution of CS80 in aqueous LiOH is low when the concentration of LiOH is low, and CS80 can only swell at this concentration. As the concentration of LiOH rises, the transmittance of the corresponding solution increases, and reaches the maximum at the concentration of 4.8 wt %. Therefore, a concentration of 4.8 wt % for LiOH is chosen. Fixing the concentration of LiOH at 4.8 wt %, the effect of the introduction of urea on the transmittance of the solution is shown in Figure 4b. When the concentration of urea is low, the addition of urea hinders the dissolution of CS80. The transparency of the solution reaches the maximum when the concentration of urea is 8.0 wt %. Thus, aqueous 4.8 wt % LiOH/8.0 wt % urea is chosen as the optimal solvent for CS80.

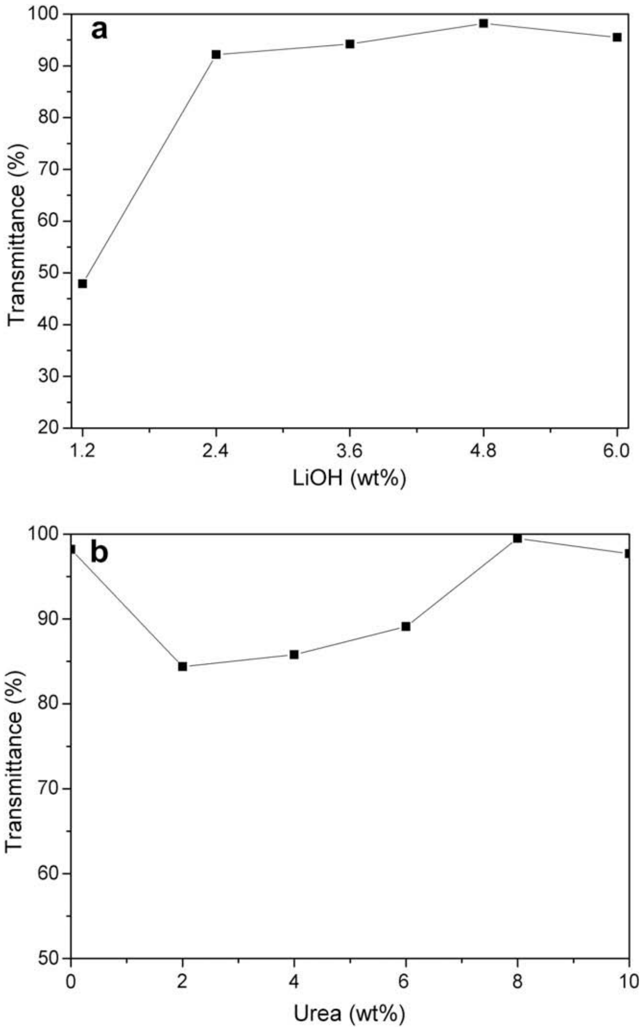

Figure 4. Effect of the composition of the solvent on the solubility of CS80.

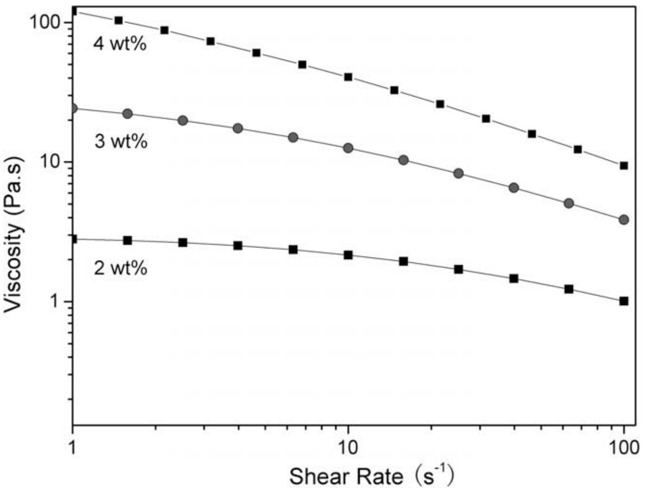

Figure 5. Dependence of the steady shear viscosity on the shear rate for the CS80 solutions with different concentrations at 20 °C.

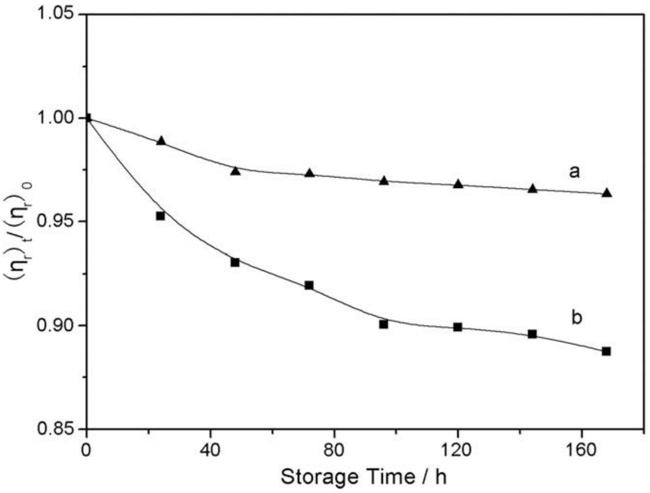

Figure 6. Viscosity change with the storage time of CS80 solution in (a) 4.8% LiOH/8.0% urea/H_2O, and (b) 0.2 M CH_3COOH.

The steady shear viscosity dependence on the shear rate of CS80 aqueous solution with different concentrations in 4.8 wt % LiOH/8.0 wt % urea at 20 °C is shown in Figure 5. The rheological behavior of CS80 in LiOH/urea aqueous solution was influenced by the concentration of CS80. When the concentration rises, the shear viscosity values increase, and all the solutions present pseudoplastic behavior, in the range of the shear rate used, with the shear-thinning behavior becoming more obvious with the increase of the concentration.

The poor stability of chitosan solution is a critical issue that restricts the production of chitosan materials. Therefore, research has been devoted to improve the stability of it for decades. Figure 6 shows the change of viscosity of CS80 solution in 4.8 wt % LiOH/8.0 wt % urea/H_2O and 0.2 M acetic acid (CH_3COOH) with the increase of storage time. Obviously, the solution of CS80 in LiOH/urea is more stable than that in CH_3COOH. Although the viscosity of both solutions decreases with prolonged time, the decrease of viscosity of CS80 in 4.8 wt % LiOH/8.0 wt % urea/H_2O is slower than that of CS80 in 0.2 M CH_3COOH, with a platform stage appearing after storage for 72 h, a phenomenon that does not show up in the solution of CS80 in 0.2 M CH_3COOH. It was found that the glycosidic (1→4)—linkages in cellulose are alkali stable when the temperature is below 170 °C.[29] The chemical structure of the chitosan is very similar to that of cellulose, so chitosan is also alkali stable at ambient temperature presumably.

1. Experiment

1.1. Materials

Partially N-deacetylated α-chitosan (coded as CS80) was prepared in our laboratory by heterogenous N-deacetylation from commercial chitin. The viscosity-average molecular weights (M_η) and degree of deacetylation (DD) of resulted chitosan were 2.7×10^5 Da and 80.2%, respectively.

HCl, $LiOH{\cdot}H_2O$, NaOH, KOH, and urea were obtained from Sinopharm Chemical Reagent Co. Ltd. (China). All reagents were of analytical grade, and were used without further purification.

1.2. Dissolution of chitosan

$LiOH{\cdot}H_2O$, urea, and deionized water with a mass ratio of 4.8:8:87.2 were mixed to form a transparent solution at first, and then a certain amount of dried CS80 powder (2.0 wt %) was added in and mixed with. After the treatment of freeze-thawing between −40 and 20 °C, a transparent solution was obtained.

1.3. Measurement

^{13}C NMR spectra of LiOH/urea/D_2O and CS80 solution in LiOH/urea/D_2O and LiOH/D_2O were carried out on a NMK-300 MHz NMR spectrometer (Varian, Inc., USA) at ambient temperature. The chemical shifts were referenced to internal sodium 3-(trimethylsilyl)-1-propanesulfate (DSS). X-ray diffraction (XRD) patterns were obtained by a Bruker AXS D8 Advance X-ray diffractometer, 40 kV and 34 mA with Cu Kα radiation at k 1.5406 Å. TEM images of chitosan in aqueous LiOH/urea solution were obtained by a Philips-CM200 transmission electron microscope with an accelerating voltage of 160 kV. The condition of the formation of the inclusion composites was optimized from the transmittance of their solutions. A UV–vis spectrophotometer using a quartz cell with an optical path length of 1 cm at 600 nm was used to record the transmittance of the solution.[30] The concentration of the sample was 5 mg/mL. Rheological measurements of CS80 solutions were carried out on a Rheometric Scientific ARES controlled strain rheometer (TA Instruments, New Castle, USA). The steady shear viscosities of CS80 solutions were determined rheometrically at 20 °C, angular frequency 1 rad s^{-1}, and rate 1–100 s^{-1}. The stability of chitosan solution was evaluated by the change of viscosity versus storage time. The prepared solution was maintained at ambient condition, and the viscosity was measured every 24 h.

^{13}C NMR (D_2O): δ 19.87–20.12 (acetyl of chitosan), 59.84–60.34 (C-6 of chitosan), 63.57 (C-2 of chitosan), 76.98–77.72 (C-3 of chitosan), 78.96 (C-5 of chitosan), 81.44–81.94 (C-4 of chitosan), 105.03–105.53 (C-1 of chitosan) 165.35–165.89 (C=O of urea).

Acknowledgements

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