



Zinc chloride aqueous solution as a solvent for starch



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ABSTRACT

It is important to obtain starch-based homogeneous systems for starch modification. Regarding this, an important key point is to find cheap, low-cost and low-toxicity solvents to allow complete dissolution of starch and its easy regeneration. This study reveals that a ZnCl₂ aqueous solution is a good non-derivatizing solvent for starch at 50 °C, and can completely dissolve starch granules. The possible formation of a “zinc–starch complex” might account for the dissolution; and the degradation of starch, which was caused by the H⁺ in ZnCl₂ aqueous solution, could not contribute to full dissolution. From polarized light microscopic observation combined with the solution turbidity results, it was found that the lowest ZnCl₂ concentration for full dissolution was 29.6 wt.% at 50 °C, with the dissolving time being 4 h. Using Fourier-transform infrared (FTIR), solid state ¹³C nuclear magnetic resonance (NMR), and X-ray diffraction (XRD), it was revealed that ZnCl₂ solution had no chemical reaction with starch glucosides, but only weakened starch hydrogen bonding and converted the crystalline regions to amorphous regions. In addition, as shown by intrinsic viscosity and thermogravimetric analysis (TGA), ZnCl₂ solution caused degradation of starch macromolecules, which was more serious with a higher concentration of ZnCl₂ solution.

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1. Introduction

Starch is one of the most abundant carbohydrates in nature, and has been widely used as a raw material in industry. Furthermore, native starch can be modified into various derivatives to widen its applications. Modified starches such as starch sodium succinate and starch phosphate ester can be used to prepare food additives; and starch can also be converted into value-added chemical products, such as binders and flocculants (Hanselmann & Burchard, 1996; Wu & Hakkarainen, 2014).

However, the modification of starch has been greatly limited by its insolubility in water and most organic solvents. This is especially true if a high degree of substitution (DS) is desired, and in this case modification can only occur in a heterogeneous way. In order to increase the DS, starch esters, for example, were usually prepared in organic solvents, where catalysts may be further added. However, these organic solvents were often volatile, not recyclable, and the catalysts such as pyridine were toxic. These heterogeneous systems have limited the development of starch modification and the application of modified starch (Junistia et al., 2008).

Homogeneous systems have been reported to be beneficial to carbohydrate modification (Heinze & Liebert, 2011; Gao, Luo, & Luo, 2012). As a result, efforts in recent years have been focused on the search for solvents that can completely dissolve starch. Solvents can be classified into derivatizing and non-derivatizing types according to whether or not any chemical reaction is occurring in the dissolution process. Some traditionally- and broadly-used solvents for starch include dimethyl sulfoxide (DMSO) and strong inorganic alkalis (e.g., KOH and NaOH). However, research has shown that alkaline solutions may induce undesirable side reactions such as structural depolymerization and oxidation (Jackson, Choto-Owen, & Waniska, Rooney, 1988; Jordan, Schmidt, Liebert, & Heinze, 2014). DMSO was found to be able to dissolve starch without structural degradation (Everett & Foster, 1959). However, the dissolution process with DMSO is not straight forward. Starch is heated in 90% aqueous DMSO for about 24 h, followed by precipitation and re-dissolution in water (with further heating); and this procedure requires intensive shear and thermal treatment to starch (Chakraborty, Sahoo, Teraoka, & Gross, 2005; Han & Lim, 2004; Zhong, Yokoyama, Wang, & Shoemaker, 2006).

Ionic liquids (IL's) represent a new class of solvents for starch, which have gained much attention recently. IL's have been claimed as “green solvents” for many substances including natural polymers such as starch and cellulose, because of their chemical and thermal

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stability, low vapor pressure, and high ionic activity (Gericke, Schluffter, Liebert, Heinze, & Budtova, 2009; Lu, Yan, & Texter, 2009). However, the research on IL's has just been started and the toxicity of IL's remains uncertain. Jastorff et al. (2003) and Matsumoto, Mochiduki, Fukunishi, and Kondo (2004) have preliminarily studied the toxicity of IL's and proved that the commonly-accepted notion that IL's have low toxicity is incorrect. Most IL's are designed with large organic cations, such as pyridinium, imidazolium and pyrrolidinium while the anions are hexafluorophosphate (PF_6^-), tetrafluoroborate (BF_4^-), dicyanamide ($\text{N}(\text{CN})_2^-$), etc. Their release to aquatic environments could cause severe water and soil contamination due to the potential toxicity and non-biodegradability (Gathergood & Scammells, 2002). Moreover, the high prices of IL's make them difficult to be applied practically in industry. Therefore, the practical application of IL's remains uncertain.

Another class of solvents for natural polymers is inorganic salt hydrates, which are liquids that have a designated water–salt mole ratio close to the coordination number of the strongest hydrated ion. Typical examples are liquid phases of solid salt hydrates, such as $\text{Ca}(\text{SCN})_2/\text{H}_2\text{O}$ (Warwicker, Jeffries, Colbran, & Robinson, 1966), $\text{LiSCN}/\text{H}_2\text{O}$ (Lukanoff, Schleicher, & Philipp, 1983) and $\text{ZnCl}_2/\text{H}_2\text{O}$ (Letters, 1932). They are inexpensive, convenient, and environmentally friendly. They are non-derivatizing solvents not only being regarded as very efficient solvents for most natural polymers such as cellulose (Cao, Xu, Chen, Gong, & Chen, 1994), chitin (Wang, Pedersen, Deng, Qiao, & Hou, 2013), but also have been applied as a medium for the chemical functionalization or derivatization, such as carboxymethylation and esterification, of these natural polymers, within a short reaction time (Leipner, Fischer, Brendler, & Voigt, 2000; Sen, Martin, & Argyropoulos, 2013). For example, Heinze et al. used molten $\text{LiClO}_4/3\text{H}_2\text{O}$ as a solvent for homogeneous carboxymethylation of cellulose with a high DS (i.e., <2) in a one-step synthesis after a short reaction time of 4 h (Fischer, Thümmeler, Pfeiffer, Liebert, & Heinze, 2002). Acetylation could also be carried out at a temperature of 130 °C for a short reaction time (0.5–3.0 h) with DS between 1 and 2.5 (Fischer, Leipner, Thümmeler, Brendler, & Peters, 2003). When cellulose is dissolved in a molten salt hydrate, the formation of a homogeneous phase makes cellulose hydroxyl groups completely available for chemical derivatization. This allows the control of both the degree of substitution and the distribution of functional groups, which can undoubtedly broaden the reaction paths and the diversity of products. However, there has been no report on molten salt hydrates applied as solvents or reaction media for starch.

Thus, the aim of the present work was to investigate the ability of ZnCl_2 aqueous solution, a molten salt hydrate, as a solvent for starch, together with the structure and properties of the regenerated starch from this solvent.

2. Materials and methods

2.1. Materials

Native cassava starch (with moisture content of 14%) was obtained from Dongguan Wenying Starch Trade Co., Ltd., without further treatment. Anhydrous zinc chloride (ZnCl_2) and methanol (analytical grade) were purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China). Other chemicals including hydrazine sulfate and hexamethylenetetramine were of analytical grade and used as received without further purification. All solutions were prepared with distilled water.

2.2. Dissolution and regeneration of starch from zinc chloride solutions

Certain amounts of anhydrous ZnCl_2 were added to a three-neck, round-bottom flask equipped with an electric stirrer to obtain ZnCl_2

aqueous solutions of certain concentrations (65%, 43%, 35% and 29.6%). The ZnCl_2 solution was then mixed with a certain amount of starch (2.0 wt.%, dry weight). Then, the system was stirred at 50 °C for 4 h. In order to prevent degradation by shear force, the revolution speed was set as 60 rpm. Besides, during the dissolution process, the solution was sampled at intervals and observed under a polarized light microscope (Motic BA300POL, Motic Asia, Hongkong) equipped with a digital camera (Moticam Pro 205A, Motic Asia, Hongkong).

Regenerated starch was obtained from the above solutions by adding absolute ethanol with continuous stirring (The absolute ethanol was about 2–5 times the volume of the starch solution). The starch samples were then dried and smashed into powder for further analysis.

ZnCl_2 aqueous solution was acidic (pH=4.09 for 29.6% and pH=0.67 for 65%). For discussing the influence of H^+ on starch, hydrochloric acid (HCl) solution with a pH value of 4.09 was prepared. After that, native cassava starch was treated with the HCl solution under the exactly same processes as with ZnCl_2 aqueous solution. And regenerated starch from HCl solution was collected and compared with those from ZnCl_2 aqueous solution.

2.3. Characterization of starch and regenerated starch

Fourier-transform infrared (FTIR) spectra for native and regenerated starches were obtained in the range of 400–4000 cm^{-1} with a TENSOR27 FTIR model manufactured by Burker, Germany. The samples were mixed with KBr and well ground before being pressed into wafers.

X-ray diffraction (XRD) patterns for native and regenerated starches were obtained on an PW3040/60 X'pert PRO X-ray diffractometer (PANalytical, Netherlands) using the Cu-K α X-ray source operating at 36 kV and 20 mA. The scanning range and rate are 5–90° and 4°/min, respectively.

Solid-state ^{13}C CP/MAS spectra were collected on a Bruker Avance 500 nuclear magnetic resonance (NMR) spectrometer using a 4 mm MAS BB-1H probe head. The spectral width used was 37.6 kHz. The acquisition time was 27 ms, together with 7.7 μs pre-scan delay and 13.3 μs dwell time. All solid experiments were carried out at 125.8 MHz for ^{13}C with 4096 scans accumulating for each spectrum.

To determine the intrinsic viscosity of native and regenerated starches (Islam, Mohd, & Noor, 2001), the samples were dispersed in 0.5 mol/L KOH solutions and stirred in a boiling water bath for 10 min. The solutions were then cooled to room temperature and left overnight. The final concentrations of the solutions were 2.6–6.0 mg/mL. Intrinsic viscosity measurements were obtained using a Ubbelohde dilution capillary viscometer (size 37, Shanghai Liangjing Glass Instrument Factory, China) immersed in a water bath maintained at 25 ± 0.1 °C. The efflux time of solvent and solutions were measured in triplicate and averaged. Results were expressed as relative viscosity (η_r), $\eta_r = \eta/\eta_0$; specific viscosity (η_{sp}), $\eta_{sp} = \eta_r - 1$; and intrinsic viscosity ($[\eta]$). η is the solution viscosity and η_0 is the solvent viscosity. Intrinsic viscosity, $[\eta]$, was then calculated as the zero concentration-limit of the η_{sp}/c value resulting from the plots of η_{sp}/c versus c straight lines (c represents the concentration of solvent).

The thermal decomposition of native and regenerated starches was determined by a thermogravimetric analysis (TGA) apparatus (TGA4000, PerkinElmer, USA) in an open system (Liu, Yu, Liu, Chen, & Li, 2009). Starch samples were heated to 800 °C at 20 °C/min. The weight loss results were also converted to derivative weight percentages to measure and compare the peak temperatures. The temperature calibration was done by the Curie temperatures of nickel and iron.

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