### Ultraviolet Spectra and Structure of Zinc–Cellulose Complexes in Zinc Chloride Solution

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**ABSTRACT:** The spectral characteristics of aqueous zinc chloride solutions (67% w/w) containing cellulose, cellobiose, maltose,  $\beta$ -methyl glucoside, and glucose were compared. The results suggest that zinc ion forms loose complexes with the C2 or C3 hydroxyl groups of glucose or methyl glucopyranoside. The absorption of light in the 200–220 nm range indicates the formation of these types of complexes. In solutions containing cellobiose or cellulose, zinc ion forms complexes with the hemiacetal oxygen atom of the anhydroglucose at the nonreducing end and a hydroxyl group of an anhydroglucose unit at the reducing end. This type of complex absorbs at 290 nm. Light absorption of cellobiose solutions at 235 nm was also correlated with similar complexes involving the anomeric oxygen at the reducing end of cellobiose. The absorption at 290 nm was proportional to the zinc chloride concentration. The presence of calcium ion also enhances the absorption; however, ion alone cannot form a complex with cellulose. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1441–1446, 1999

Key words: cellobiose; cellulose; zinc-sugar complexes; zinc chloride; optical density

### **INTRODUCTION**

Cellulose fibers can be produced by spinning zinccellulose solutions in a coagulation bath. The fiber characteristics depend on the configuration of the cellulose molecules during the spinning process. Whatever type of zinc-cellulose complex exists in the dissolved cellulose solution affects the shape and flexibility of the cellulose molecules in the coagulated fiber. By varying processing conditions, such as zinc chloride concentration and reaction temperature,<sup>1</sup> zinc ion forms complexes of variable structure and stoichiometry with the hydroxyl groups of cellulose. These differences are reflected by various changes in the physical and chemical properties, such as viscosity and light absorbency.

According to the literature, the presence of other cations in zinc chloride solutions can affect the molecular structure of zinc chloride. It is a known fact

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that calcium and zinc ions can form complexes with cellulose.<sup>2–5</sup> It is a logical expectation that the molecular structures of zinc–cellulose complexes could be influenced by the presence of such ions. To predict and control the quality of the product, the effect of these ions on the characteristics of the cellulose fiber should be understood. The ultraviolet (UV) spectra of various complexes may provide relevant information. Because calcium chloride is the most common contaminant in the production and recycling of zinc chloride, the spectra of cellulose solutions containing calcium chloride were investigated, and the effect of calcium chloride on the formation of zinc–cellobiose and zinc–cellulose complexes were investigated.

#### MATERIALS AND METHODS

#### Preparation of Zinc Chloride Solutions Containing Glucose, Methyl-β-D-glucopyranoside, Cellobiose, Maltose, and Cellulose

Granular zinc chloride (Mallinckrodt Chemical, Inc., Paris, KT) was dried in an oven at 110°C

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overnight and dissolved in distilled water at concentrations (w/w) of 12%, 60%, 64%, 66%, 67%, 68%, 69%, 70%, and 72% zinc chloride. To prepare cellulose solutions, 0.81 g of microcrystalline cellulose (Avicel PH101, FMC, Philadelphia, PA), equivalent to 0.05 mol of anhydrous glucose units (molecular weight = 162) was mixed with 1.6 mLof water to form a paste. The zinc chloride solutions and cellulose paste were equilibrated at 65°C. Twelve milliliters of zinc chloride solution at each concentration was then added to the paste. The mixtures containing 6.2% (w/v) of cellulose were incubated at 65°C for 30 min with constant stirring. For the preparation of glucose, methyl-β-D-glucopyranoside, and cellobiose solutions, 0.05 mol of each compound was dissolved in each one of the zinc chloride solutions as described.

#### Preparation of Solutions of Zinc–Cellulose Complexes Containing Cations

To study the effect of cations on the viscosity of cellulose solutions, the chloride salt of each cation, at a molar ratio of Zn/cation of 30/1 was added to 67% (w/w) zinc chloride solution. The cations selected were ammonium, potassium, calcium, magnesium, aluminum ion, and ferrous ion. Cellulose solutions were prepared as described herein. To study the effect of calcium ion, zinc chloride solutions containing different molar ratios of calcium ion to zinc ion (0, 0.007, 0.015, 0.03, and 0.045) were used for the dissolution of cellulose.

#### UV Spectroscopy of the Cellulose, Cellobiose, Maltose, Methyl-β-D-glucopyranoside, and Glucose Solutions

Zinc chloride solutions containing glucose, methyl- $\beta$ -D-glucopyranoside, cellobiose, maltose, and cellulose were scanned from 200 to 340 nm with a UV-Vis spectrophotometer (Lambda 3B, Perkin-Elmer Corp., Norwalk, CT) with distilled water as a reference. Solutions containing the same molar concentrations of cellobiose, methyl-β-D-glucopyranoside, glucose, and zinc chloride solutions with and without cations were also scanned. The spectra of the zinc-cellobiose, zinc-maltose, zincmethyl- $\beta$ -D-glucopyranoside, and glucose complexes were obtained by subtracting the optical densities of the controls. Because cellulose is not soluble in water, an aqueous cellobiose solution equivalent to the same molar concentration of anhydroglucose units in cellulose was used as a



Wavelength (nm)

**Figure 1** UV spectra of cellobiose in 12% ZnCl<sub>2</sub> solutions and 50% CaCl<sub>2</sub> solutions, and the spectra of methyl- $\beta$ -glucopyranoside and glucose in a 67% ZnCl<sub>2</sub> solution.

control for the UV spectrum of the zinc–cellulose complex.

#### **RESULTS AND DISCUSSION**

#### UV Spectrum of Glucose and Methyl-β-Dglucopyranoside in Zinc Chloride Solution

The spectrum of glucose in zinc chloride solution showed only a small negative peak at  $\sim 205$  nm (Fig. 1). This spectrum serves as the baseline for comparisons with the spectra of other sugars.

When the reducing end of glucose is substituted by a methyl group, such as in  $\alpha$ - and  $\beta$ -methyl-glucopyranoside, the negative peak at 205 nm remains, and a new peak at 220 nm appeared (Fig. 1). These data indicate that the 1,4 linkage is involved in the formation of complexes between zinc ion and anhydroglucose. Because the methyl group cannot complex with zinc, interactions between sugars and metal ions must involve the oxygen at C2 or C3; these absorbed light at 220 nm. Richards and Williams<sup>6</sup> reported that methyl- $\beta$ -D-glucopyranoside showed only a slight absorption peak at 257 nm; however, UV spectroscopy of both  $\alpha$ - and  $\beta$ -methyl-glucopyranosides conducted in the present study gave different results.

# UV Spectrum of Cellobiose and Cellulose in Zinc Chloride Solution

Cellobiose consists of two D-glucose units joined by a  $\beta$ -1,4 linkage. As shown in Figure 2, the



Figure 2 UV spectra of cellobiose in a 67% (w/w)  $ZnCl_2$  solution with and without  $CaCl_2$ .

spectrum of cellobiose in 67% zinc chloride solution showed three peaks at ~ 210, 235, and 290 nm. The two new peaks at 235 nm and 290 nm must therefore be attributable to the  $\beta$ -1,4 linkage between two glucose units.

Comparing the structures of cellobiose and methyl-glucopyranoside, cellobiose has two adjacent glucose units that provide a pair of oxygen atoms across the  $\beta$ -1,4 linkage. However, in methyl- $\beta$ -D-glucopyranoside, the methyl group does not provide an oxygen atom to pair with this oxygen in the C1 and C4 linkage. This indicates that an oxygen pair across the  $\beta$ -1,4 linkage is essential for the formation of a zinc complex that absorbs at 290 nm and 235 nm, respectively. Richards and Williams<sup>6</sup> also suggested that an oxygen pair was required for the formation of a zinc complex.

In comparison with cellulose, cellobiose has a high concentration of reducing groups. The anhydroglucose unit at the reducing end is less bulky than the other anhydroglucose units in the interior of the cellulose chain. After complex formation with zinc ion, the hydrogen bond between C3 and C5 is ruptured. The glucose unit at the reducing end can adopt a conformation that offers less hindrance to rotation about the 1,4 linkage. An examination of the stick model of the molecule suggests that this may be the boat conformation. Therefore, the 1-4 bond in cellobiose is more free to rotate than the 1.4 linkages in the interior of the cellulose polymer. The UV spectrum of cellobiose shows a peak at 235 nm, but the cellulose solution does not show this peak. Therefore, the peak at 235 nm may be assigned to the zinchydroxyl complex involving the reducing end. However, as described, complex formation requires a 1,4 linkage and a pair of oxygen atoms from different glucose units. It is possible that the conformation of cellobiose is such that a nonreducing glucose unit is able to provide a hydroxyl group for the formation of zinc complexes that absorb at 235 nm. This peak is specific to cellobiose only. In other glucose dimers, such as maltose, it is not possible for two oxygen atoms to participate in the formation of zinc complexes because no significant absorption band was observed at 235 nm (Fig. 3). This assumption requires more proof.

In dilute (12%) zinc chloride solution, cellobiose showed a major peak (Fig. 1) at 220 nm and a



Figure 3 UV spectra of maltose in a 67% (w/w)  $\text{ZnCl}_2$  solution with and without  $\text{CaCl}_2$ .



**Figure 4** Optical density of zinc-cellulose complexes at 290 nm at various concentrations of ZnCl<sub>2</sub>.

minor peak at 310 nm, but none at 235 nm. Under these conditions, zinc ion possibly forms a complex (absorbing at 220 nm) only with hydroxyl groups at C2 and C3, whereas the complexes that absorb at 235 nm only occur in concentrated zinc chloride solutions. At this level, the Hammett acidity of the zinc chloride solution is lower than -2, and the hydroxyl groups of the anhydroglucose units are protonated. Under this condition, the conformation of the zinc-cellobiose complex provides an oxygen atom that, in combination with the oxygen at the reducing ends, can form a zinc ion complex.

Referring to standard interpretations of UV spectra, the spectral peaks at 210 and 220 nm are usually associated with C—O bonds. The peak at  $\sim 290$  nm is associated with the carbonyl group.<sup>7,8</sup> Increasing the concentration of zinc chloride intensified the absorption at 290 nm. At zinc chloride concentrations >69% (w/w), the absorbency at 290 nm of the cellulose solution increased drastically (Fig. 4). There are two possible explanations for this phenomenon. One explanation is that when the concentration is >69% (10*M*), zinc chloride starts to become polymerize. Because the heat of dilution of concentrated zinc

chloride solution is strongly exothermic, it indicates that a high bond energy level may exist in these polymers. If this is the case, the bond energy of the zinc polymers may provide extra energy to form complexes. The other possible explanation is that the acidity of the zinc chloride increases rapidly as the zinc chloride concentration is increased. At 70% or above, the pH of the solution is lowered to less than -2 (see refs. 9 and 10) and the pKa of the acid-base reaction is -2 (see ref. 11).

$$ROH_2^+ \rightarrow ROH + H^+$$
 (pK = -2)

At such a low pH, the hydroxyl groups of cellulose become protonated. Once a hydroxyl group is protonated, further reactions with zinc chloride result in cellulose–OH<sub>2</sub><sup>+</sup>Cl–Zn–Cl (aq) structures that drive the reaction further. When the concentration of zinc chloride increases to the point that protons become unavailable, zinc ions would replace hydrogen ions and attach directly to oxygen atoms. Cellulose dissolved in 64-67% zinc chloride has a low and similar optical density, because the zinc-cellulose complex over this range of zinc chloride concentrations has similar chemical bonds. A minimal absorbency at 67% may indicate a low degree of zinc-cellulose complex formation at this concentration, or may simply reflect the fact that this particular zinc-cellulose complex has a low extinction coefficient. Above 68%, the water molecules that bind zinc ions diminish; therefore, the extinction coefficient increases.

Because the polymeric structure of zinc chloride plays an important role in complex formation, the addition of other cations may interfere with the polymeric structures in zinc chloride solution. The addition of potassium, magnesium, ammonium, aluminum, and calcium ions increased the optical density at 290 nm. The most effective ion was calcium ion (Fig. 5). The effect of ferrous ion was not clear because ferrous ion in water absorbs at 290 nm.

## Effect of Calcium Chloride on the Optical Density of the Complexes

The UV spectrum of cellobiose in 50% calcium chloride is similar to the spectrum of cellobiose in 12% zinc chloride (Fig. 1). There is only a single peak at 210 nm. Because the addition of calcium chloride to the zinc chloride solution enhanced the absorbency of cellulose and maltose solutions at 290 nm (Figs. 3 and 6), it was surprising to note the absence of the 290 nm peak in 50% calcium chloride (Fig. 1). It is possible that there is either no complex formation between cellobiose and calcium chloride, or if there is some complex formation, the complexes do not absorb at 290 nm.

Trace amounts of calcium chloride (Ca/Zn ratio: 0.015) increased the absorbency of zinc-cellulose complexes at 210 and 290 nm in zinc chloride solution (Fig. 6), but had little effect on the absorbency of cellobiose (Fig. 2). Because spectroscopy of cellobiose in 50% calcium chloride solution showed no absorption peak at 290 nm, calcium ions alone cannot form complexes with the oxygen atom between C1 and C4. It is likely that the complex absorbing light at 290 nm only occurs at low pH (i.e., in concentrated zinc chloride solution). Once the zinc-cellulose complex is formed, calcium chloride can replace zinc chloride in the complex because calcium chloride provides free  $Cl^{-}$  ions that can neutralize  $OH_{2}^{+}$ . After chloride ions enter this region, the cellulose molecules are spread apart, and the formation of additional



**Figure 5** Optical density of cellulose at 290 nm in a 67% ZnCl<sub>2</sub> solution with cation/zinc molar ratios of 0.03.



Figure 6 UV spectra of cellulose in a 67% ZnCl<sub>2</sub> solution with and without CaCl<sub>2</sub>.

zinc–OH complexes becomes possible. This spreading effect does not apply to cellobiose, which is a small molecule. Detail of these interactions require further studies, for example by nuclear magnetic resonance (NMR) spectroscopy.

#### CONCLUSIONS

At low concentrations (12%) of zinc chloride, complexes between glucose residues and metal ions form only at C3. This complex does not absorb at 290 nm. At high concentrations of zinc chloride (64-72%), a possible complex involving C1, C3, and C5 gives rise to a species with an absorption peak at ~ 290 nm. Such complexes could involve intermolecular or intramolecular bonding; but, the latter is more likely to occur. NMR spectroscopy and comparative analysis of zinc complexes with starch, maltose, and isomaltose might further clarify the structures of the complexes. The literature suggests that zinc chloride forms poly-

meric tetrahedral structures, at concentrations > 67% w/w. We assume that polymeric zinc chloride would persist after the formation of complexes with cellulose. In viscosity studies, calcium ions were found to lower the apparent viscosity of 72% w/w solution of zinc chloride. Calcium ions are thought to break up zinc chloride polymers, as suggested in the literature. However, at zinc chloride concentrations of 64%, there are no polymers. The addition of calcium ion did not significantly change the apparent viscosity of zinc-cellulose solutions. At zinc chloride concentrations > 67%, tetrahedral zinc chloride starts to appear. The zinc-cellulose complex could therefore be one involving polymeric tetrahedral zinc chloride. Obviously, these complexes would have a higher extinction coefficient. At a zinc chloride concentration of 10*M*, the metal ions are predominantly in polymeric tetrahedral form. Further increases in zinc chloride concentration failed to increase the UV absorption.

The addition of calcium chloride to zinc chloride solutions enhanced the UV absorption of zinc-cellulose complexes. This indicates that there are more than two species that absorb at 290 nm. One type is a complex of cellulose with polymeric zinc chloride; the other type is a complex of cellulose with free chloride ions. Because neither of these species has been isolated, their extinction coefficients cannot be ascertained. The absorbency at 290 nm can only be used as an indicator of zinc-cellulose complex formation. The enhancement of UV absorption at 290 nm by calcium chloride can be interpreted in terms of repulsive forces between chloride ions that spread the zinc-cellulose molecules apart. This spreading could expose more reactive sites, leading to more zinc-cellulose complexes, which would make the cellulose molecules rod-like and rigid. This structure would affect the physicochemical properties of fibers regenerated from zinc-cellulose complexes. The optical density at 290 nm may be used as a parameter to monitor the state of zinc-cellulose complex formation, and it may therefore be useful in monitoring fiber formation. Further confirmation of the proposed complex structures will require further study by NMR spectroscopy and by the measurement of physical properties, such as viscosity and light scattering.

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