Studies on Structure of Cuprammonium Cellulose I.
A Circular Dichroism Study on the Dissolved State of
Cellulose in Cuprammonium Solution

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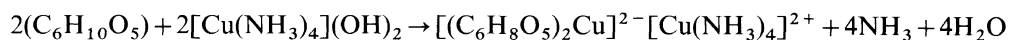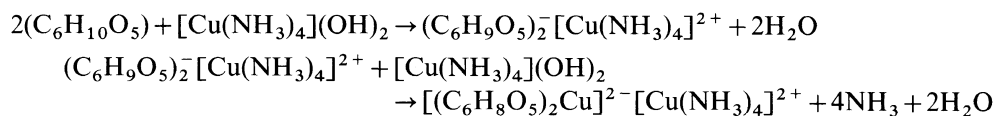Takatsuki, Osaka 569, Japan*

ABSTRACT: An attempt was made to clarify the dissolved state of cellulose in aq cuprammonium hydroxide solution using ultraviolet (UV) and circular dichroism (CD) spectrophotometry on cellulose and its oligomers in the solution. Negative Cotton effect and positive Cotton effect for the cellulose–cuprammonium solution are observed at 300—350 nm and *ca.* 600 nm. The former Cotton effect seems to originate from charge transfer (CT) excitation and the latter from d–d excitation of cupric ion due to coordination of cuprammonium complex to hydroxyl group of cellulose. The experimental fact that intensity of CD for almost C_2–C_3 substituted methyl cellulose in cuprammonium hydroxide is nearly zero leads us to an conclusion that cuprammonium complex coordinates preferentially to hydroxyl groups at C_2 and C_3, giving δ chelate form. As a dissolved state of cellulose in aq cuprammonium hydroxide, an equilibrium state between cellulose–cuprammonium complex, cellulose and cuprammonium hydroxide was predicted where copper–cellulose molar ratio of *ca.* 0.6—0.8 is stable for the cellulose–cuprammonium complex.
KEY WORDS   Cuprammonium Cellulose / Circular Dichroism / Cotton Effect / Charge Transfer Excitation / Chelate Conformation / Methyl Cellulose / Equilibrium State /

Discovery of a cuprammonium solution as a cellulose solvent by Schweitzer[1] as early as in 1857 brought about the embryo stage of regenerated cellulose fiber industries.[2] The technology using this solvent remains still now active for fiber and hollow fiber productions[3,4] though within very limited countries in the world.

Many cellulose chemists undoubtedly had believed for long years that cellulose dissolves forming certain cellulose–cuprammonium complex in cuprammonium solution and made significant efforts in 1920 to 1950 to speculate the structure of cellulose–cuprammonium complex,[5-8] but most of them were based on an elementary analysis of the products recovered from cellulose–cuprammonium solution. For example, Traube[5] proposed the reaction mechanism between cellulose and cuprammonium hydroxide as follows:
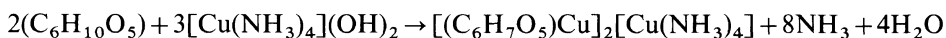
$$2(C_6H_{10}O_5) + [Cu(NH_3)_4](OH)_2 \rightarrow (C_6H_9O_5)_2^- [Cu(NH_3)_4]^{2+} + 2H_2O$$

$$(C_6H_9O_5)_2^- [Cu(NH_3)_4]^{2+} + [Cu(NH_3)_4](OH)_2$$
$$\rightarrow [(C_6H_8O_5)_2Cu]^{2-} [Cu(NH_3)_4]^{2+} + 4NH_3 + 2H_2O$$

$$2(C_6H_{10}O_5) + 2[Cu(NH_3)_4](OH)_2 \rightarrow [(C_6H_8O_5)_2Cu]^{2-} [Cu(NH_3)_4]^{2+} + 4NH_3 + 4H_2O$$

Lieser[6] proposed another chemical structure of cuprammonium cellulose solid as follows:

$$(C_6H_{10}O_5)(C_6H_7O_2) \begin{bmatrix} OH \\ OH \\ OH-[Cu(NH_3)_4](OH)_2/2 \end{bmatrix} > Cu(OH)_2 \end{bmatrix} .$$
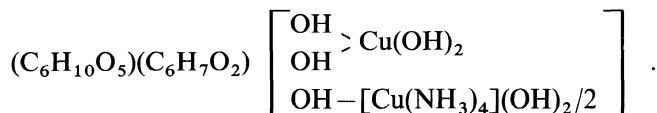
On the one hand, Neale reported that one mole of copper bonds to one mole of glucose residue for his cuprammonium cellulose.[7] Thus, these analyses unavoidably proved that structure of cuprammonium cellulose might be greatly influenced by removal or separation method. Furthermore, chemical structure of solid cuprammonium cellulose might not always be the same as that in solution.

In order to avoid these effects of treatment,

Hess and his coworkers[8] studied the optical rotation and electrophoresis of cellulose–cuprammonium solution system and found that optical rotation is determined by the concentration of cuprammonium cellulose in solution and complex formed between copper and decomposed cellulose was precipitated on cathode by electrophoresis, proposing the following reaction scheme:

$$2(C_6H_{10}O_5) + [Cu(NH_3)_4]^{2+}(OH)_2^- \rightarrow (C_6H_9O_5)_2 - [Cu(NH_3)_4]^{2+} + 2H_2O$$
$$(C_6H_9O_5)_2 - [Cu(NH_3)_4]^{2+} + 2[Cu(NH_3)_4]^{2+}(OH)_2^-$$
$$\rightarrow [C_6H_7O_5)_2Cu]_2^- [Cu(NH_3)_4]^{2+} + 8NH_3 + 4H_2O$$

$$2(C_6H_{10}O_5) + 3[Cu(NH_3)_4](OH)_2 \rightarrow [(C_6H_7O_5)Cu]_2[Cu(NH_3)_4] + 8NH_3 + 4H_2O$$

Later in 1944, Reeves[9] also carried out the optical rotation study finding that cuprammonium cellulose solution exhibited a levorotation at 436 nm and he stressed that the levorotation was caused by the existence of cuprammonium cellulose complex. He also synthesized β-methyl glucose derivatives of which the hydroxyl groups at C_2, C_3, C_4, or C_6 positions were selectively masked and found that the solution has almost the same value in molecular rotatory power as the solution of cellulose only when both hydroxy group at C_2 and C_3 positions of the glucose was not substituted, leading to a conclusion that the optical rotatory power of the solution was originated by a complex in which copper coordinates to C_2, C_3 hydroxyl groups of glucose residue. He proposed that the structure of cellulose–cuprammonium complex is a 1 : 1 mol salt of cuprammonium complex cation and diol anion at C_2 and C_3 positions on pyranose ring of cellulose. This structure is believed as a cellulose–cuprammonium complex structure in the cuprammonium solution. His studies are elegant and more reliable because of free of separation procedure of the complex. However, these results are not quantitative in strict sense and much more will be needed for explaining the origin of optical rotation in relation to more detailed nature of the complex. Other voluminous studies on cuprammonium cellulose solid or its solution had been made, but even the molar ratio of copper and glucopyranose unit was not settled down.

In 1960s, the development of optical rotatory dispersion (ORD) and circular dichroism (CD) measurements encouraged to study the conformation or configuration of complexes in solvents. Bukhari et al.[10,11] studied the CD spectra of cyclic 1,2 diols and 1,2 amino alcohols in aqueous cuprammonium hydroxide solution having variety of configuration, revealing that 1) two CD peaks near 600 and 300 nm are detected for the case where two

hydroxyl groups are placed in gauche conformation, 2) no peak is detectable when two hydroxyl groups are in trans conformation, 3) Cotton effect is reversed when the gauche angle goes from positive to negative. They pointed out that copper ion forms chelate coordination with two hydroxyl groups and conformation of the chelate might determine the nature of Cotton effect. These results might be applicable to cellulose–cuprammonium solution system. Bukhari et al. have succeeded to clarify that the origin of asymmetry is chelate conformation but reserved to clear the origin of absorption band for generating Cotton effect.

In this study, an attempt was made to elucidate the coordination cite on cellulose of copper, coordination molar ratio of copper to cellulose, and conformation of the complex for cellulose–cuprammonium solution system from their ultra-violet (UV)-visible light absorption spectra and CD spectra.

EXPERIMENTAL

Materials

Cellulose. Alaska pulp with viscosity-average molecular weight $M_v = 1.72 \times 10^5$ and α-cellulose content $= 90.1$ wt% was treated by steam-explosion method under the conditions described in the previous study.[12] M_v of the treated cellulose sample was estimated as 5.36×10^4 through the equation $[\eta] = 3.85 \times 10^{-2} M_w^{0.76}$ (cm^3 g^{-1}) established for cellulose–cadoxen system,[13] where $[\eta]$ and M_w are the limiting viscosity number in cadoxen (cadmium oxide–ethylendiamine–NaOH–H$_2$O = 5 : 29 : 1.4 : 166, w/w/w/w) and the weight-average molecular weight, respectively. And its degree of break-down of intramolecular hydrogen bond ($\chi_{am}(C_3 + C_6)$) determined by CP/MASS ^{13}C NMR method[14] was 48%.

Cellulose Oligomer. Cellobiose, cellotriose, cellotetraose, and cellopentaose/supplied from Aldrich Co., Ltd. (U.S.A.) were used as received.

Methyl Cellulose (MC). Non-regioselective-ly-substituted MC (RMC with total degree of substitution $\langle\!\langle F \rangle\!\rangle = 1.98$) was supplied from Kishida Chemicals Co., Ltd. (Tokyo). Regio-selectively-substituted MC at C_2 and C_3 position with $\langle\!\langle F \rangle\!\rangle = 1.68$ (SMC) was synthesized by the procedure proposed by Kondo et al.[15] using the cellulose described above. Probability of substitution at C_2, C_3, and C_6 ($\langle\!\langle fk \rangle\!\rangle$, $k = 2, 3, 6$) was determined from methyl carbon peak intensities of MC dissolved in dimethyl sulfoxide (DMSO) in ^{13}C NMR spectrum.[16] The ^{13}C NMR measurements using a FT-NMR spectrometer (GSX 400, JEOL) were made under the following conditions: Frequency on carbon atom, 100.2 MHz; data point, 32768; accumulation, 20000; flip angle, 45°; pulse mode, gated proton-decouple without NOE; pulse interval, 5s; solvent, DMSO-d_6; internal standard, tetramethyl silane.

Preparation of Solutions. A 25 wt% of aq ammonia (NH$_3$) solution (supplied from Kishida Chemicals Co., Ltd.) was diluted by deionized water giving aq ammonia solution with desired concentrations. Into the solution, an excess amount of cupric hydroxide was added saturatedly at room temperature and the solution obtained was stood for 10 h at 5°C. Then we filtered off the excess cupric hydroxide in the solution and obtained the cuprammonium solution with the composition of Cu/NH$_3$ = 0.089/7.94 and 0.055/7.94 (mol/mol) for the case using 12.5 wt% aq ammonium solution. The compositions of the above aq cuprammonium solution is expressed in weight basis as Cu/NH$_3$/H$_2$O = 0.8/12.5/86.7 and 0.5/12.5/86.4 for the sake of simplicity. Note that in practical cellulose dissolving process an addition of small amount of NaOH in the aq cuprammonium hydroxide solution is said to facilitate the dissolution of cellulose, but in the present study this effect is neglected.

Polymer–aq Cuprammonium Hydroxide Solution Systems. Cellulose and MC were added into 10 g of the aq cuprammonium hydroxide solution with the afore-mentioned compositions at 5°C stood for 24 h with intermittent

agitation, so as to give the desired concentrations. When we prepare the cellulose solution with different copper concentrations, the cellulose solution with $Cu/NH_3/H_2O = 0.5/12.5/86.4$ was diluted by 12.5% aq NH_3 solution. 0.025 g of cellulose oligomer was dissolved into 10 g of the aq cuprammonium solution with $Cu/NH_3/H_2O = 0.5/12.5/86.4$ following to the same procedure as the case of cellulose and MC. Copper concentration in the aq cellotetraose and cellopentaose soln was changed by putting the $Cu(OH)_2$ powder into 2 g of each oligomer solution with oligomer concentration of 1 wt%. The resultant solutions were subjected to UV and CD measurements. As a reference solution, the cellulose–aq sodium hydroxide solution system reported in the previous study[14] was used.

CD Measurement. CD spectra of the solutions were recorded on a spectrophotometer model J-720 (JASCO, Japan) at 25°C in a quart cell with light pass length = 1 mm or 0.1 mm under the following conditions: Band width, 1.0 nm; sensitivity, 1000 mdeg; response, 0.5 s; scan speed, 500 nm min^{-1}; wavelength range, 800—200 nm.

UV Measurement. UV spectra of the solutions were recorded on a UV spectrophotometer (UV-3400 spectrophotometer, Hitachi Co., Ltd., Japan) in a quart cell with light pass length = 1 mm at 25°C in wavelength (λ_{UV}) range of 800—200 nm.

Cu Contents in the Cellulose–aq Cuprammonium Systems during Coagulation. Cellulose–cuprammonium solution (Cell/Cu/NH$_3$/H$_2$O = 0.68/0.62/4.16/47.86 mol l^{-1}) was cast on a glass plate so as to give thickness of the solution of 0.27 mm and the plate was immersed into the deionized water at temperatures of 9 and 40°C. Copper contents of the films obtained after desired time lapse were estimated by Iodo-titration method.

RESULTS AND DISCUSSION

Figure 1 shows UV spectra of aq 15 wt%

NH_3 solution (a), aq cuprammonium hydroxide solution $(Cu/NH_3/H_2O = 0.8/12.5/86.7)$ (b), 0.8 wt% cellulose solution dissolved in the above solution (c), 0.8 wt% cellulose solution dissolved in 8.7 wt% aq NaOH solution (d). The aq cuprammonium hydroxide solution apparently shows UV absorption near $\lambda_{UV} = 260, 300, 330$, and 630 nm where no absorption was detected for the aq ammonium solution. A dissolution of cellulose into the aq cuprammonium solution brings about remarkable increase in the absorbance near $\lambda_{UV} = 330$ nm, while the absorbance at other wavelength is almost invariant.

Generally, the following excited states are important for organometallic complex[17]: 1) L–F or d–d excitation: Change in electron displacement between d-orbitals of metal ion. 2) IL excitation: Change in electron displacement within ligand molecules. 3) Charge transfer (CT) excitation: Donation or acceptance of electron between metal and ligand. Besides the above, other effects such as an electron transfer from metal complex to solvent and an excitation of electron on metal-metal bondage might occur but may be minor ones.

It is a well-known fact that copper forms copper-ammnine complex in ammonia solution and the band at 630 nm has been identified as the d–d transition of cupric ion.[18] Since the peaks observed at less than 400 nm for the
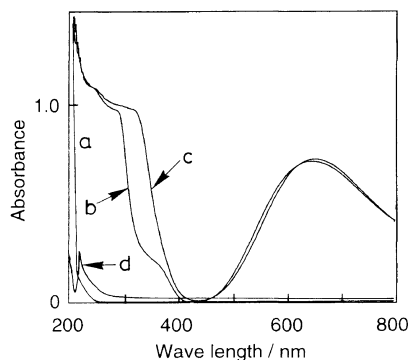

Figure 1. Absorption spectra of aq 15 wt% NH$_3$ solution (a), aq cuprammonium solution (b), cellulose–aq cuprammonium solution (c), and cellulose–aq sodium hydroxide solution (d).

cuprammonium solution were not detected for aq NH_3 solution and the appearance of absorption in near UV region due to d–d transition of cupric ion has never been reported, then these three peaks (330, 300, 260 nm) may be responsible for CT absorption derived from a formation of complex between Cu and NH_3, OH, H_2O. It is well-known as an empirical fact for aq cobalt complex $Co(NH_3)_6^{3+}$ that the CT absorptions between cobalt ion and NH_3, OH, H_2O are observed in UV region and the peak wave length shifts to longer wavelength side by the ligand species in the order of NH_3, H_2O, OH^{-}[19]. If we dare to apply the above fact to the present aq cuprammonium solution, the absorption at 260, 300, and 330 nm might be attributed to the complexes mainly formed between Cu–NH_3, Cu–H_2O, Cu–OH, respectively. This indirectly predicts that peak wavelength for absorption depends strongly on the stability or strength of the complex caused by circumstances.

Regarding absorption spectrum of the cellulose–cuprammonium solution (c), the absorption peak near $\lambda_{UV} = 630$ nm due to d–d transition of cupric ion seems to slightly shift to higher wave length but almost constant in its intensity by dissolution of cellulose, indicating that transition energy level of d–d transition of cupric ion is not so influenced by dissolution of cellulose. In contrast to this, the band around at 330 nm observed for aq cuprammonium solution strongly increases in its intensity by addition of cellulose. The increase of the intensity (ΔI) for the band (ca. 330 nm) is accelerated by increase of cellulose amount in the systems, as demonstrated in Figure 2, where the subtracted spectra obtained by subtracting the spectra of aq cuprammonium hydroxide solution from those of cellulose solution are shown. Inspection of Figure 1(d) reveals that the cellulose in aq NaOH solution does not show any absorption around at $\lambda_{UV} = 330$ nm. In the figure the small absorbance at $\lambda = 230$ nm is considered due to contamination of lignin and hemicellulose. These facts indicate
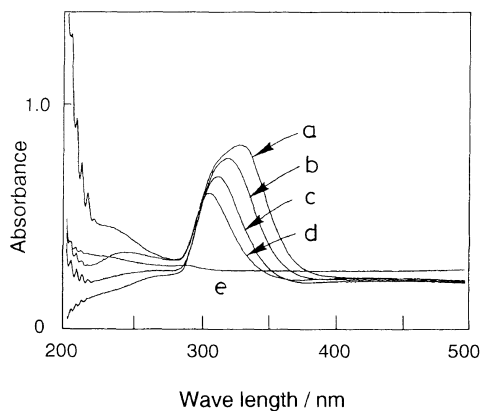

Figure 2. Subtracted spectra of cellulose–aq cuprammonium solution with cellulose concentration of 1.6 wt% (a), 0.8 wt% (b), 0.4 wt% (c), 0.2 wt% (d), and 0 wt% (e).
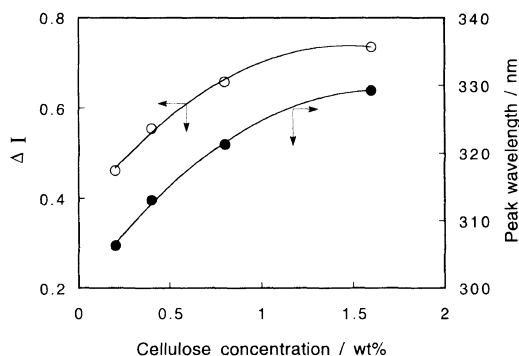

Figure 3. Plots of the peak intensity and peak wavelength of absorption spectra in Figure 2 against cellulose concentration.

that this band is attributable to CT excitation between cupric ion and oxygen atom of hydroxyl group of cellulose. The above conclusion might be supported by the report[20] that CT excitation of complex of cupric ion and amino acids takes place in UV range.

Cellulose concentration (C_p) dependence of the peak wavelength and the intensity (ΔI) of CT absorption is indicated in Figure 3. With an increase in cellulose amount in the system, the peak wavelength shifts to higher wavelength and the intensity monotonically increases. In Figure 4, the effect of the concentration of copper and cellulose on the UV spectra is shown for the cellulose–cupram-
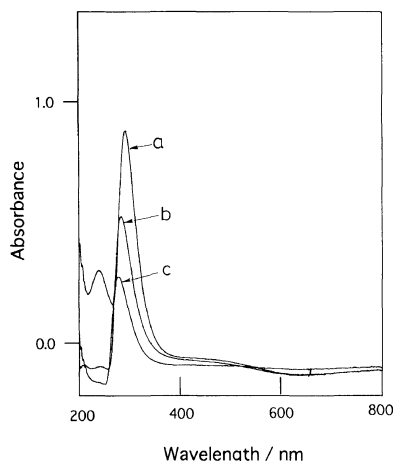
Figure 4. Absorption spectra of cellulose–aq cuprammonium–cellulose solution $Cu/NH_3/H_2O(wt\%) = 0.5/12.5/0.32$ (a), $Cu/NH_3/H_2O(wt\%) = 0.25/12.5/0.16$ (b), and $Cu/NH_3/H_2O(wt\%) = 0.16/12.5/0.10$ (a).

Figure 5. Subtracted spectra of cellulose–aq cuprammonium and cellulose oligomer–aq cuprammonium solution. Cu concentration $= 0.5$ wt%; NH_3 concentration $= 12.5$ wt%; cellulose oligomer and cellulose concentration $= 0.25$ wt%. a) glucose; b) cellobiose; c) cellotriose; d) cellotetraose; e) cellulose.

monium solution in which the weight ratio of copper and cellulose is maintained constant. Each subtracted spectrum of the cellulose solution in the figure is obtained by subtracting the spectrum of aq cuprammonium solution from that of the cellulose solution with the same Cu, NH_3, H_2O composition. When the concentration of copper, accordingly cellulose, decreases, the peak wavelength of CT transition shifts to lower wavelength and the differential absorbance at $\lambda_{UV} = 330$ nm remarkably decreases. This indicates that copper amount in the solution is another factor to determine the peak wavelength and its intensity, as far as the CT transition is concerned.

Intensity for the CT excitation might be a function of cellulose–cuprammonium complex concentration in the system if cellulose, cuprammonium complex, and cellulose–cuprammonium complex in the system are in equilibrium. It is important to reveal the molar ratio of copper/glucopyranose unit (hereafter, simply referred to Cu/Cell ratio) for the cellulose–cuprammonium complex in the system. Unfortunately, cellulose could not be completely dissolved in aq cuprammonium hydroxide unless Cu/Cell ratio surpass 0.5 and
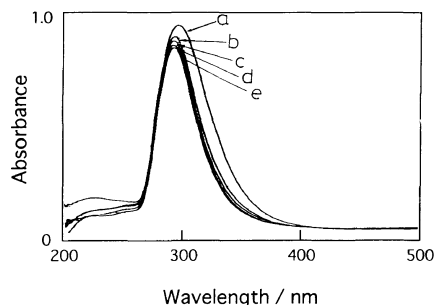
then cellulose oligomers were used for this purpose. Figure 5 shows subtracted UV spectra of glucose, cellobiose, cellotriose, cellotetraose, and cellulose dissolved with the solute concentration of 0.25 wt% in aq cuprammonium hydroxide. The spectrum of every solution exhibits the absorbance peak around $\lambda_{UV} = 290$ nm due to CT transition. The peak position is almost independent of the solute, but the peak height tends to decrease with increasing number of glucose units for the solute molecules. As discussed later (see Figures 12 and 13), cupric ions possibly coordinate with hydroxyl groups of the oligomer and cellulose molecules in the solution , forming chelate and the number of chelates per glucose unit should decrease with an increase in the length of the solute molecule. This is considered to cause the lowering of the peak height. Since the peak position is independent of the samples, the effect of Cu/Cell ratio on the absorption intensity of CT transition was investigated using cellotetraose and cellopentaose as models of cellulose.

Figure 6 shows the plot of intensity difference (ΔI) of the CT absorption against Cu/Cell ratio initially charged for the systems of cellotetraose (a) and cellopentaose (b). ΔI for both systems rapidly increases with an increase in Cu/Cell ratio in the Cu/Cell range less than 0.6 and tends to level off at Cu/Cell ratio more
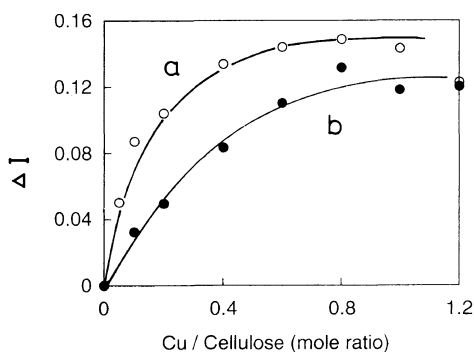
Figure 6. The Intensity($\triangle$) and peak wavelength of CT absorption bands of cellulose oligomer–cuprammonium systems plotted against the initial Cu/Cell ratio. a) cellotetraose; b) cellopentaose.
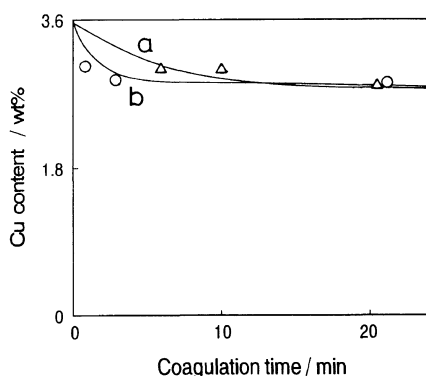

Figure 7. Coagulations time dependence of the liberation of copper from cellulose–aq cuprammonium solution by water at 9°C (a) and 40°C (b). Concentration of initial solution: $Cu = 3.6\,wt\%$; $NH_3 = 7.0\,wt\%$; cellulose $= 10$ wt%.

Figure 8. CD spectra of aq cuprammonium solution with $Cu/NH_3/Cell = 0.8/12.5/1.0\,wt\%$ (a) and cellulose–aq sodium hydroxide solution (b).

than 0.6. If this result is applicable to cellulose in aq cuprammonium hydroxide, in the Cu/Cell range more than 0.6—0.8 the liberated cuprammonium complex coexists with cellulose–cuprammonium complex in the system. This does not contradict the past observation that cellulose does not dissolve in aq cuprammonium hydroxide at the cellulose concentration up to 10 wt% when Cu/Cell ratio initially charged for the system is less than unity.[21]

Figure 7 demonstrates that liberation of copper from cellulose–aq cuprammonium hydroxide solution with Cu/Cell ratio of unity by water at 9°C (a) and 40°C (b). The liberation
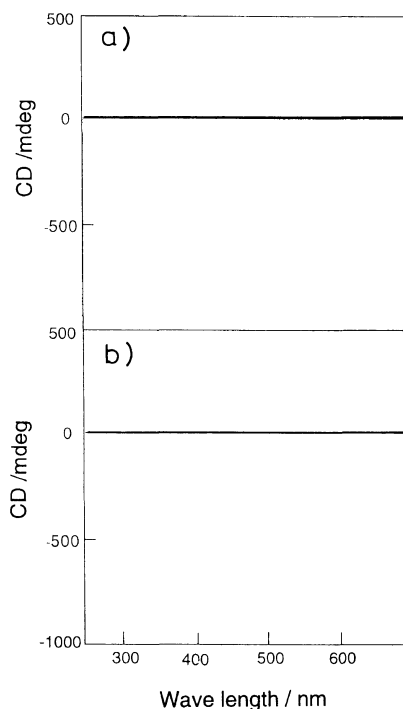
of copper at both temperatures saturates to 20—25%, which coincides with the Cu/Cell ratio giving level-off ΔI. These phenomenogical facts should be considered in relation to conformation of cellulose–cuprammonium complex and ligand position.

Figure 8 shows CD spectra of aq cuprammonium hydroxide (a) and cellulose–aq NaOH (b) and Figure 9 shows CD spectra of cellulose–aq cuprammonium hydroxide systems. Obviously, no CD peak is observed for the former system. For the latter system, a negative CD peak around 300 nm and a broad positive CD peak around 600 nm are observed. The CD peak around 300 nm increases in its intensity and shifts towards higher wave length as cellulose content increases, which just corresponds to the peak shift and change in its intensity of UV absorption near $\lambda_{UV} = 300$ nm, indicated in Figure 3. Of course, the latter peak

intensity increases with an increase of cellulose concentration. As a rule, Cotton effect can be detected 1) when the absorption exists in the observed wave length range and 2) when asymmetric molecules exist in the system. Aq cuprammonium hydroxide system satisfies condition 1) (see Figure 1) but not satisfy condition 2). For cellulose–aq NaOH, condition 1) is not satisfied so that no CD peak is detectable. The cellulose–aq cuprammonium hydroxide system accords with the both conditions because there are observed d–d excitation (ca. 600 nm) and CT excitation (ca. 300 nm) absorptions and the formation of cellulose–cuprammonium complex which probably has asymmetric nature. Origin of the
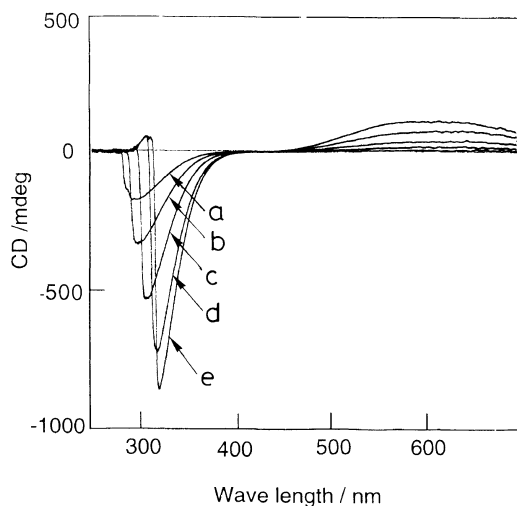
asymmetric cite of organometallic complex is mainly related to the following three effects: 1) Configuration of chelate ligand, 2) conformation of chelate ligand, 3) optical activity ligand itself. As described before, Bukhari et al. reported that symbols of CD peak for chelate compound of cyclic 1,2 diols containing copper are reversed depending on whether the chelate comformation takes a form of δ or λ structure (see Figure 10 and corresponding CD patterns are shown in Figure 1 in ref 11). Judging from CD spectrum pattern of cellulose–aq cuprammonium solution, cellulose–cuprammonium complex might take a form of δ structure. A monomer unit of cellulose, that is β-D-glucose takes 6-membered chair conformation and all hydroxyl groups at C_2, C_3, and C_6 are arranged equatorially. In this case, the angle between hydroxyl groups at C_2 and C_3 is $60°$ and is only possible to give δ structure with copper, as shown in Figure 11.

Figure 12 shows CD spectra of cellulose oligomers in cuprammonium hydroxide. Obviously, positive CD peak around 300 nm is observed for glucose and cellobiose although peak intensity is higher for the former than that for the latter. In contrast to this, negative CD peak appears for cellotriose, cellopentaose, and cellulose and its intensity increases with an increase in number of glucose units. For glucose, chelating of copper is possible at C_1–C_2, C_2–C_3, and C_3–C_4 positions and except for C_2–C_3 position λ structure is stable, as shown in Figure 13. Therefore, λ structure is numerically superior δ structure, generating relatively large positive CD peak. Since for cellobiose one reducing end C_1 and one non-

Figure 9. CD spectra of cellulose–aq cuprammonium solution with Cu and NH_3 concentrations of 0.8 and 12.5 wt%, respectively. a) 0.1 wt%; b) 0.2 wt%; c) 0.4 wt%; d) 0.8 wt%; e) 1.6 wt%.
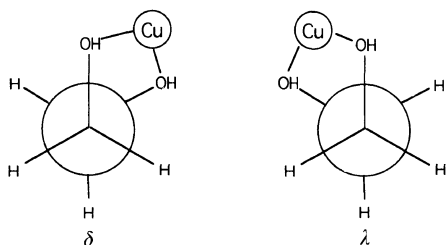

Figure 10. Newman's projections of δ and λ structures of copper chelate.
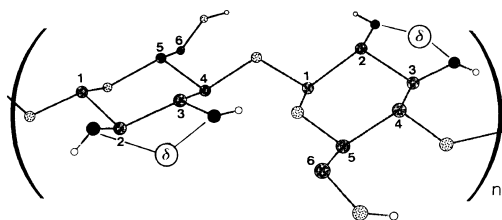

Figure 11. Schematic representation of conformation of the cellulose–cuprammonium complex.
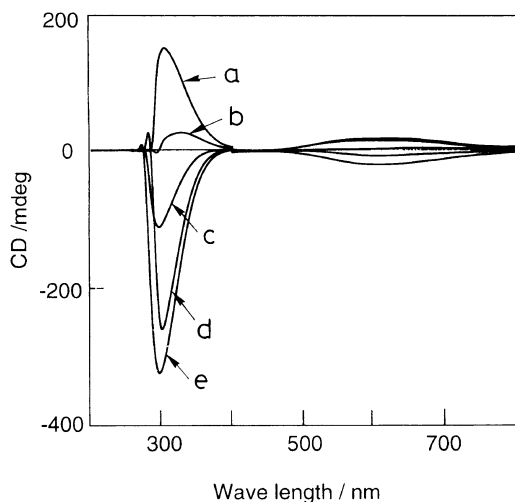
Figure 12. CD spectra of cellulose oligomer–aq cuprammonium solution. a) glucose, b) cellobiose, c) cellotriose, d) cellopentaose, and e) cellulose. Cu concentration = 0.8 wt%; NH_3 concentration = 12.5 wt%; oligomer concentration = 1.0 wt%.
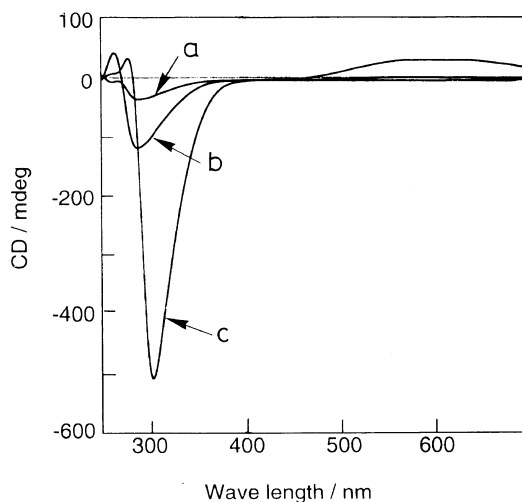
Figure 14. CD spectra of cellulose–aq cuprammonium solution and MC–aq cuprammonium solution a) SMC, b) RMC, and c) cellulose. Cu concentration = 0.8 wt%; NH_3 concentration = 12.5 wt%; polymer concentration = 1.0 wt%.
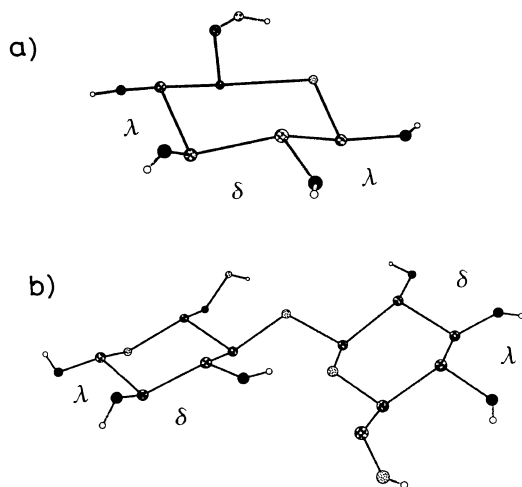

Figure 13. Considerable chelate conformation of copper and cellulose oligomer. a) glucose; b) cellobiose.

reducing end C_4 are linked by β-glycosidic linkage, the probability of δ and λ structures are equal, leading to a depressed positive CD peak. Likewise, for cellulose oligomers with more than 3 glucose units, the probability of δ structure increases with an increase in molecular chain length, giving larger negative CD

peaks. This consideration gives plausible explanation for the above experimental facts although discussion is needed on the energetical stability of δ and λ structures in the solution. As mentioned before, Reeves *et al.* reported on the methyl glucose (MG)–cuprammonium solution system that the MG substituted by methyl group at C_2 and C_3 positions indicates lower levorotation, comparing to the case of MG which is free from methyl group at the both positions, and MG with no methyl groups at C_4, C_2, and C_3 shows far lower levorotation. These very interesting results support our speculation, because equal occurring probability of δ and λ structures which may be realized for MG with unsbstituted hydroxyl groups at C_2, C_3, and C_4 positions, leads to very low circular dichroism.

Figure 14 demonstrates that C_2–C_3 positions are suitable site for coordination of cuprammonium complex. Here, CD spectra of RMC, SMC, and cellulose in aq cuprammonium hydroxide are shown. Intensity of CD peak attributed to charge transfer is in the order of Cellulose $\gg$ RMC $>$ SMC. This means that

methylation of hydroxyl group leads to the lowering in CT intensity. Since $\langle\!\langle F \rangle\!\rangle$ is larger for RMC than SMC and if all hydroxyl groups participate in the complex formation, the itensity of CT excitation should be larger for SMC than RMC.

CONCLUSION

An attempt was made to clarify the dissolved state of cellulose in aq cuprammonium hydroxide solution using UV and CD spectrophotometry on cellulose and its oligomers in the solution. Negative Cotton effect and positive Cotton effect for the cellulose–cuprammonium solution are observed at 300— 350 nm and *ca.* 600 nm. The former Cotton effect seems to originate from CT excitation and the latter from d–d excitation of cupric ion due to coordination of cuprammonium complex to hydroxyl group of cellulose. The former CD strength becomes larger depending on cellulose concentration and at the same time its position shifted toward longer wave number.

Consideration on conformation of glucopyranose unit and the experimental fact that intensity of CD for almost C_2–C_3 substituted methyl cellulose in cuprammonium hydroxide is nearly zero leads us to an conclusion that cuprammonium complex coordinates preferentially to hydroxyl groups at C_2 and C_3, giving δ chelate form. As a dissolved state of cellulose in aq cuprammonium hydroxide, an equilibrium state between cellulose–cuprammonium complex, cellulose and cuprammonium hydroxide was predicted where copper/cellulose molar ratio of *ca.* 0.6—0.8 is stable for the cellulose–cuprammonium complex.

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