Studies on Structure of Cuprammonium Cellulose II. Structural Change of Cellulose–Cuprammonium Complex as a Function of Hydroxyl Ion Concentration

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ABSTRACT: As an extension of our previous study on cellulose–cuprammonium system,[1] an attempt was made to clarify the structure of cellulose–cuprammonium complex in the solid–liquid coexisting system by applying the fact that dissolution of cellulose into cuprammonium solution depends strongly on OH^- concentration in the system. Electro-conductivity measurements on aqueous (aq) cuprammonium complex revealed that the complex existed as dissociated type at C_{OH} (OH concentration for aq solution) $< 0.3 \, mol \, l^{-1}$ and as undissociated type at $C_{OH} > 0.5$. Absorption reaction of aq cuprammonium complex on solid cellulose was also dependent on C_{OH}, revealing that the reaction order of OH^- ion for the solid–liquid absorption reaction is unity and 0 for the system with C_{OH} less than $0.3 \, mol \, l^{-1}$ and for the system with $C_{OH} > 0.5 \, mol \, l^{-1}$, respectively. Meanwhile, the reaction order of copper to cellulose was found unity regardless the C_{OH} value. The latter fact might deny the random reaction of 3 OH groups in glucopyranose unit with copper ion and suggests indirectly the regio-selective complex formation of cuprammine and OH groups at C_2 and C_3 as previously proved. It was found that even if the molar ratio of copper ion in aq cuprammine complex to solid cellulose is more than unity, copper absorbed on solid cellulose is at most $0.65 \, mol \, mol^{-1}$. This value is quite near to that evaluated for the cellulose dissolved in cuprammonium solution. Using the above results a tentative new cellulose dissolving process is proposed, in which the less amount of copper and NH_3 are employed, compared with those used for conventional process.
    KEY WORDS   Cuprammonium Cellulose / Hydroxyl Ion / Electro-conductivity / Glucopyranose / Cupric Ion / Absorption Reaction /

In the previous study[1] we carried out analysis on cellulose and regio-selective cellulose derivative dissolved in cuprammonium solution by ultraviolet (UV) and circular dichroism (CD) spectrometries, revealing that 1) copper selectively coordinates to hydroxyl groups at C_2 and C_3 positions of glucopyranose units in cellulose giving a cellulose–cuprammonium complex with charge transfer (CT) excitation around 300 nm, 2) the CT excitation relates to negative Cotton effect for cellulose with degree of polymerization (*DP*) more than 3, 3) the origin of the Cotton effect might be related to δ chelate conformation of cellulose–cupram-

monium complex, and 4) intensity of CT absorption levels off when molar ratio of copper to glucopyranose unit of cellulose (Cu/Cell) in the solution exceeds 0.6—0.7, predicting the existence of some chemical equiriblium state (and saturated states) between cellulose, cuprammonium complex and cellulose–cuprammonium complex in the solution. The above results mostly support the idea proposed by Reeves[2] that cellulose–cuprammonium complex is a salt of cuprammonium complex cation and diol anion at C_2 and C_3 positions on glucopyranose ring but differs from his prediction that Cu/Cell ratio is unity

for the above cellulose–cuprammonium complex. Concerning the reaction equiriblium study between cellulose, cuprammonium complex, and cellulose–cuprammonium complex in the above solution was first reported by Hess and his coworkers[3] by measuring optical rotation of the cellulose–cuprammonium solution assuming that the optical rotation of the system is result of the formation of the cellulose–cuprammonium complex. They found that the following relationship held as a result of the equilibrium of the complex-forming reaction between one mol of cellulose and one mol of cuprammonium complex.

$$\frac{[\text{Cellulose–Cuprammonium complex}]}{[\text{Cellulose}] \times [\text{Cuprammonium complex}]} = K$$

(K, constant; [ ], concentration)

However, they neglected the effect of sodium hydroxide (NaOH) on the above equilibrium despite of their findings that an addition of small amount of NaOH into a cellulose–cuprammonium solution system resulted in an increase of optical rotation of the system. Further, it has been known that NaOH concentration in cuprammonium solutions influenced their dissolving power giving maximum dissolving ability at $100 \, \text{mmol} \, \text{l}^{-1}$ and losing dissolving power at more than $200 \, \text{mmol} \, \text{l}^{-1}$ for purified ramie under the initially charged cellulose concentration of 0.8%.[4] Sobue[5] also described that solubility of cellulose was very low in a cuprammonium solution containing $770 \, \text{mmol} \, \text{l}^{-1}$ of NaOH. Considering these facts we can choose the experimental conditions under which cellulose does not dissolve in cuprammonium solution but apparently absorbs Cu. In this solid–liquid coexisting system, separation of Cu-absorbing cellulose from the solution becomes much easier without severe morphological change, hence compositional change, compared with those recovered from the cellulose dissolved in cuprammonium solution.[6–9] As mentioned before, our previous study[1] showed that com-

plex-forming copper is at most 0.6—0.7 mol per glucoside residue and the excess amount of cuprammonium complex coexists with cellulose–cuprammonium complex. And if the complex-forming equilibrium between cellulose and cuprammonium complex also exists in this solid–liquid coexisting system similarly as the equilibrium in the solution the Cu-absorbing cellulose might also take some specified complex structure. Therefore, it is very interesting to compare the structure of cellulose–cuprammonium complex in the solution with that for solid state Cu-absorbing cellulose for the much more detail understandings of dissolved state of cellulose in cuprammonium solution. For the purpose, an attempt was made to analyze a kind of absorption equilibrium as a function of NaOH or OH$^-$ ion concentration in the cuprammonium solution for elucidation of cellulose–cuprammonium complex structure.

EXPERIMENTAL

Materials

A regenerated cellulose sample (the viscosity-average degree of polymerization $DP_v = 364$) recovered from its cuprammonium solution was used. A commercially available cuprammonium solution (viscosity-measurement grade) was supplied from Kishida Chemicals Co., Ltd., Japan, and its initial copper (Cu) and ammonia (NH$_3$) concentrations (C_{Cu} and C_{NH_3}, respectively, expressed by mol l^{-1}) were adjusted by diluting with deionized water in order to lower its solubility power. And its initial hydroxyl ion (OH$^-$) concentration (C_{OH} expressed by mol l^{-1}) was adjusted to give 0.07—2.5 mol l^{-1} by adding $4N$ of aqueous (aq) sodium hydroxide. The resulting solutions (Cu/NH$_3$/sucrose/OH$^-$ = 0.052/2.4/0.011/ 0.07—2.5, mol l^{-1}) were employed for the treatment of the cellulose sample. C_{Cu} in the solution was examined by chemical analysis, and C_{OH} was determined by pH measurement. C_{NH_3} and sucrose content in the solution were

calculated by considering dilution factor from those described by supplier.

Sample Treatment and Analytical Procedure

For better understanding of the analytical procedure, one concrete example is described below and the procedure is schematically shown in Figure 1. About 1.7 g of the regenerated cellulose with equilibrium water retention was immersed in 142.8 g of cuprammonium solutions ($Cu/NH_3/sucrose/OH^- = 0.052/2.4/0.011/0.07 \, mol \, l^{-1}$) stocked in an Erlenmeyer flask with silicon rubber stopper at 25°C for 1 h in a dark place and the undissolved crude blue cellulose solid (hereafter denoted as CBC) was separated from the resulting solution (hereafter denoted as liq. A) by passing through a glass filter (ISO G-4 grade) under vacuum. The CBC was washed with *ca.* 20 ml of methanol, dried at 50°C for 2 h. The resulting washing liquids separated in this stage were mixed with liq. A. The dried blue cellulose sample (hereafter denoted as DBC) was subjected to chemical analyses to determine Cu content absorbed by the cellulose solid. The liq. A was acidified with 1 N hydrochloric acid (HCl) to precipitate the cellulose dissolved in the solution. The precipitates (crude recovered cellulose) in the neutralized media are centrifuged at 10000 rpm for 40 min by using a centrifugal apparatus (Type CR 20B2, Hitachi

Co., Ltd., Japan), filtered out by a glass filter (ISO G-4 grade), washed by water, followed by drying at 90°C for 2 h and then weighed (w_s g). The acidified solution was stocked for chemical analysis. DBC samples were subsequently subjected to regeneration process where DBC was regenerated with 1 N HCl at 25°C for 2 h, washed by water, dried in air and finally dried at 90°C for 2 h, and weighed (w_{ns}). The resultant washing liquids were subjected to Cu analysis to estimate Cu content absorbed by the cellulose. The procedure described above were applied for the systems where the amount of cellulose varies from 0.2 g to 3.00 g in each 142.8 g of cuprammonium solutions with different C_{OH} ($=0.07$—$2.5 \, mol \, l^{-1}$) but keeping the concentrations of other components constant.

Analyses

The viscosity-average degree of polymerization DP_v of the regenerated cellulose used was determined to be 364 from the limiting viscosity number $[\eta]$ in cadoxen at 25°C using following equation[10]:

$$[\eta] = 3.85 \times 10^{-4} M_w^{0.76} \tag{1}$$

$$DP_v = M_w/162 \tag{2}$$

Electro-Conductivity (EC) Measurements
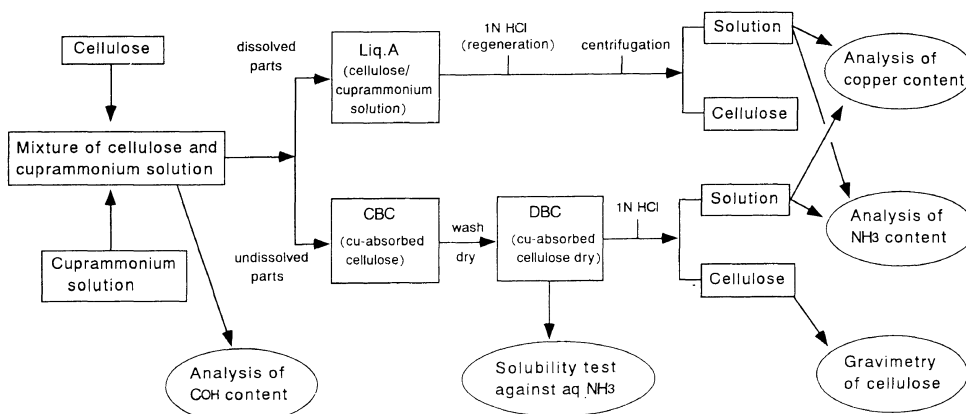
EC of cuprammonium solution was mea-

Figure 1. Shematic procedure of sample treatment and analysis.

sured by a conduct-o-meter (model CM-2A, Toa Denpa Co., Ltd., Japan) with platinum-black conductivity cell (Type CG201PL, cell constant $=0.995 \times 1$) at $25.0°C$ by adding $4N$ of aq NaOH solution slowly and dropwisely (0.2 ml min^{-1}) with aid of a burette to the original cuprammonium solution (Cu/NH$_3$/sucrose $=0.071/3.4/0.016$, mol l^{-1}) in order to avoid rapid temperature rise caused by the addition of alkali with stirring, as a function of NaOH concentration. Care was also taken to avoid vaporization of ammonia from the system. The similar measurement was carried out for the the same cuprammonium solution with 0.55 mol l^{-1} cellulose and 3.4 mol l^{-1} aq NH$_3$ solution (of which NH$_3$ concentration is the same as that for starting cuprammonium solution), by adding $4N$ NaOH as reference.

Hydroxyl Ion Concentration of the Cuprammonium Solution

pH of cuprammonium solutions with different C_{OH} was measured by a glass electrode type pH meter (Model HM-18, Toa Denpa Co., Ltd., Japan) at $20°C$. Before measurement the pH meter was attenuated at $20°C$ to precisely indicate pH $= 13.1$ by using $0.10N$ aq NaOH standard solution. The measured pH value was translated to OH$^-$ ion concentration using the following equation:

$$C_{OH} = 10^{(PH-14)} \qquad (3)$$

Solubility of Cellulose in Cuprammonium Solutions (S_c)

S_c was defined as following equation.

$$S_c = 100 \times w_s/(w_s + w_{ns}) \quad (\%) \qquad (4)$$

Here, w_s and w_{ns} are weights for dissolved and undissolved parts of cellulose.

Initial cellulose concentration C_{Cell} charged to cuprammonium solution is defined as;

$$C_{Cell} = 1000 \times (w_s + w_{ns})/162/142.8/\rho$$
$$(\text{mol l}^{-1}) \qquad (5)$$

Here, ρ is density of cuprammonium solution at $25°C$.

Copper Content

Copper contents (w_{Cu}) were determined gravimetrically by converting cupric ion into cupric sulfide (CuS) in the following manner; 2.0 g of sodium sulfide 9 hydrates (Na$_2$S·9H$_2$O) was added in the cuprammonium solution and stood at room temperature for 8 h to produce black precipitate of CuS completely. The CuS was separated on a glass filter, whose weight (W_g) was measured in advance after drying at $105°C$ for 3 h, and the total weight of the CuS with the glass filter (W_{gc}) was measured after drying at $105°C$ for 3 h.

$$w_{Cu} = (W_{gc} - W_g) \times 63.55/95.61 \qquad (6)$$

C_{Cu} (expressed in mol l^{-1}) of starting cuprammonium solution with precise volume (at $25°C$) was also determined in the same manner after acidifying the cuprammonium solution with $1N$ HCl. Molar absorption of Cu on the undissolved cellulose at equilibrium (M_{Cu}/M_{Cell}) is defined as;

$$M_{Cu}/M_{Cell} = (w_{Cu}/63.55)/(w_{ns}/162) \qquad (7)$$
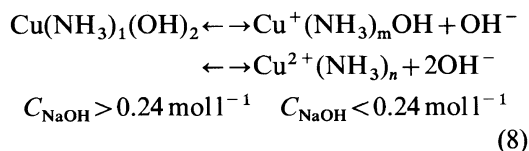
Production of Cellulose–Cuprammonium Solution

The DBC sample obtained by using the cuprammonium solution of $C_{OH} = 0.60$ mol l^{-1} was washed by water at $5°C$, methanol and dried at $50°C$ for 2 h to remove an excess NaOH absorbed on the sample. 7.5 g of this washed DBC sample was mixed with 42.5 g of 2.5% aq ammonia solution in a flask and immediately strong agitation was done by the mechanical stirrer for 2 min. The DBC sample was completely soluble in this condition and cellulose–cuprammonium solution was obtained. The cellulose concentration of this solution calculated by the analytical data of the DBC sample was 9.1, and this value is almost equal to the conventional cellulose–cuprammonium solution using in the cellulose industry. The ratio of copper and cellulose (M_{Cu}/M_{cell}, mol/mol) in the solution calculated in a same manner was 0.52, and this value is almost a half to the conventional cellulose–cuprammonium solu-

tion. The ammonia concentration of this solution was 2.1%, and this value is almost one third to the conventional cellulose–cuprammonium solution.

RESULTS AND DISCUSSION

Figure 2 shows electro-conductivity EC of cuprammonium solutions and cuprammonium solution dissolving cellulose as a function of C_{OH} added in the system. On the horizontal axis the corresponding NaOH concentration (C_{NaOH}) is also shown. Here, a reference line obtained for aq $3.4 \, mol \, l^{-1}$ NH_3 solution is also shown. EC of aq NH_3 seems to have two linear regions against C_{OH} or C_{NaOH}. In the first linear region $(C_{NaOH} < 0.02 \, mol \, l^{-1})$ there might exist dissociation form of NH_3 (that is, NH_4^+) and in the second linear C_{OH} region $(C_{NaOH} \geqq 0.02 \, mol \, l^{-1})$ the dissociation of NH_3 might be restricted because dissociation constant of $NH_3 (= 10^{-9.24})$ is very low even in water.[11] EC of cuprammonium solution deviates significantly to higher side from the two linear lines obtained for aq NH_3 in low C_{NaOH} region and seems to fall on the second linear line for aq NH_3 in C_{NaOH} region more than $ca.$ $0.24 \, mol \, l^{-1}$. This strongly suggests that cuprammonium complex exists in its undissociated state in the region of $C_{NaOH} > ca.$ $0.24 \, mol \, l^{-1}$. Therefore, the following example

of dissociation equilibria of cuprammonium complex might be anticipated depending on C_{NaOH} in the system:

$$Cu(NH_3)_1(OH)_2 \leftarrow \rightarrow Cu^+(NH_3)_m OH + OH^-$$
$$\leftarrow \rightarrow Cu^{2+}(NH_3)_n + 2OH^-$$
$$C_{NaOH} > 0.24 \, mol \, l^{-1} \quad C_{NaOH} < 0.24 \, mol \, l^{-1}$$
$$(8)$$

These dissociation equilibria of cuprammonium complex might also exist in the cellulose–cuprammonium coexisting system. But the EC line on the figure was detected as a little lower than the cuprammonium system in the cellulose-soluble composition because of the higher viscosity of the solution.

Since the concentration of OH or NaOH in cuprammonium solution has long been pointed out to influence the solubility of cellulose,[8,9] the solubility S_c of the regenerated cellulose sample in cuprammonium solutions with different C_{OH} were measured under the conditions of constant C_{Cell}, C_{Cu}, and C_{NH_3} (0.068, 0.052, and $2.4 \, mol \, l^{-1}$, respectively). The results are shown in Figure 3. Figure 3 clarifies that S_c is 0 in C_{OH} region less than $0.08 \, mol \, l^{-1}$ (that is, $C_{NaOH} = ca.$ $0.004 \, mol \, l^{-1}$) and increases rather steeply with an increase in C_{OH} approaching a maximum value ($ca.$ 50%) at $C_{OH} = ca.$ $0.35 \, mol \, l^{-1}$ (that is, $C_{NaOH} = ca.$ $0.16 \, mol \, l^{-1}$), then rapidly decreases to $S_c = 0$ in the C_{OH} region more than $0.6 \, mol \, l^{-1}$ (corresponding to $C_{NaOH} = ca.$ $0.5 \, mol \, l^{-1}$). The C_{OH} value giving maximum S_c roughly corresponds to the C_{OH} value where cuprammonium complex in the solution goes into the
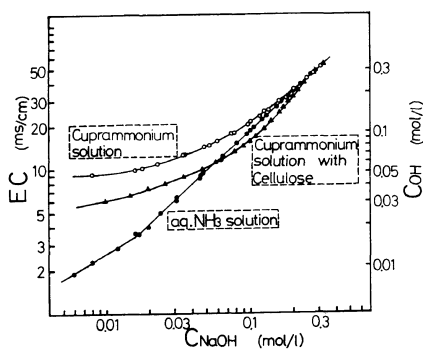
Figure 2. Electro-conductivity (EC) of cuprammonium solution as a function of NaOH concentration (C_{NaOH}): ●, aq NH_3 system; ○, cuprammonium solution system; ▲, cuprammonium solution system with cellulose.
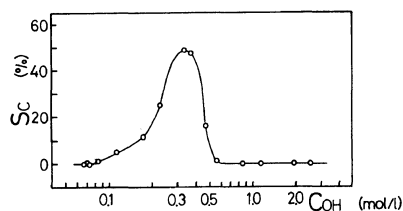
Figure 3. Solubility of the regenerated cellulose sample (S_c) in cuprammonium solution with different hydroxyl ion concentration (C_{OH}).

undissociated state. The experimental fact that dissolving power of cuprammonium solution rapidly decreases in the region $C_{NaOH} > 0.5$ $mol\,l^{-1}$ quite well corresponds to the results given by Sobue[5] and the C_{NaOH} value which gives the maximum value of S_c ($C_{NaOH} = 0.16$ $mol\,l^{-1}$) also well corresponds to the results given by Hess.[4] The results also show that if we choose two C_{OH} regions ($C_{OH} < 0.08\,mol\,l^{-1}$ and $C_{OH} \geqq 0.6\,mol\,l^{-1}$) where no dissolution of cellulose takes place, the solid cellulose simply absorbs copper dissolved in the solution and this phenomenon might be approximately attributed to a kind of absorption equilibrium between Cu, solid cellulose and solid Cu-absorbing cellulose.

Figure 4 shows the plot of molar absorption of Cu absorbed on cellulose M_{Cu}/M_{Cell} vs. initial cellulose concentration C_{Cell} ($mol\,l^{-1}$) charged in a cuprammonium solution with constant C_{OH} (a, $C_{OH} = 0.83\,mol\,l^{-1}$; b, $C_{OH} = 0.18\,mol\,l^{-1}$; c, $C_{OH} = 0.07\,mol\,l^{-1}$). Absolute value of M_{Cu}/M_{Cell} for the system with $C_{OH} = 0.83\,mol\,l^{-1}$ is far larger than that for the system with $C_{OH} = 0.07\,mol\,l^{-1}$. For the system with $C_{OH} = 0.83\,mol\,l^{-1}$ there are two regions: region A, $C_{Cell} \leqq 0.04\,mol\,l^{-1}$ where M_{Cu}/M_{Cell} is constant ($= 0.65$); region B, $C_{Cell} > 0.04\,mol\,l^{-1}$ where M_{Cu}/M_{Cell} decreases monotonically with increase in C_{Cell}. Similar line
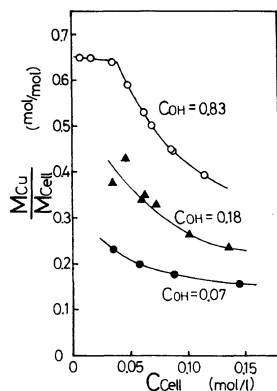

Figure 4. Plot of molar absorption of Cu absorbed by cellulose (M_{Cu}/M_{Cell}) vs. initial cellulose concentration (C_{Cu}) in cuprammonium solution: ○; $C_{OH} = 0.83\,mol\,l^{-1}$, ▲; $C_{OH} = 0.18\,mol\,l^{-1}$; ●, $C_{OH} = 0.07\,mol\,l^{-1}$.

as observed in the region B was obtained at $C_{Cell} > 0.035\,mol\,l^{-1}$ for the system with $C_{OH} = 0.18\,mol\,l^{-1}$ and $C_{OH} = 0.07\,mol\,l^{-1}$. The appearance of region A suggests that cellulose has its upper limit of absorption cite for cuprammonium complex. Constant ($= 0.65$) value of M_{Cu}/M_{Cell} in the system where cuprammonium complex exists far larger than cellulose well coincides with our previous result shown for cellulose dissolved in cuprammonium solution,[1] predicting that structure of the present Cu-absorbing cellulose might have one to one correspondence to the structure of cellulose–cuprammonium complex in its solution.

In a separate experiment we confirmed that the cotton linter and soft wood pulp with different DP_v and morphology dispersed in the same system with $C_{OH} = 0.83\,mol\,l^{-1}$ proved to show almost same upper limit value of $M_{Cu}/M_{Cell}(= 0.65)$ obtained here, suggesting that this absorption reaction has some simple stoichiometrical chemical reaction nature irrespective of the super-molecular structure of cellulose. The region B ($C_{Cu}/C_{Cell} \leqq 1.4$) is useful when we analyze an absorption equilibrium between cellulose and cuprammonium complex at constant C_{OH}. Note that cuprammonium complex is dissociated in the system with $C_{OH} = 0.18\,mol\,l^{-1}$ and $C_{OH} = 0.07\,mol$ l^{-1}, and not dissociated in the system with $C_{OH} = 0.83\,mol\,l^{-1}$.

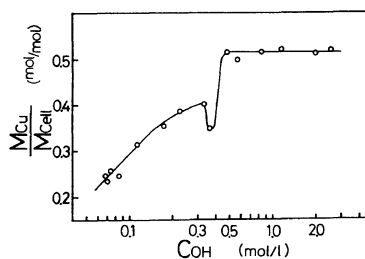Figure 5 shows the molar absorption of Cu on undissolved cellulose (M_{Cu}/M_{Cell}) treated by

Figure 5. Relation between the molar absorption of Cu on undissolved cellulose (M_{Cu}/M_{Cell}) and hydroxyl ion content (C_{OH}) of the solution.

above cuprammonium solutions under the constant $C_{Cu}/C_{Cell}(=ca.\ 0.75)$ as a function of C_{OH}. M_{Cu}/M_{Cell} seems to increase almost linearly in C_{OH} region less than $0.6\ \text{mol}\,l^{-1}$ with one exception at $C_{OH}=0.38\ \text{mol}\,l^{-1}$, attaining an asymptotic value $(M_{Cu}/M_{Cell}=0.52)$ in the region of $C_{OH}\geqq0.6\ \text{mol}\,l^{-1}$.

According to Hess and his coworker[4] who studied an equilibrium for the cellulose–cuprammonium solution system, the present case can be described by Cu-absorbing equilibrium on cellulose solid in the solid–liquid coexisting system with cellulose and cuprammonium solutions as followed:

$$\frac{[Cell\cdot Cu]}{[Cell]\times[Cu]}=K \qquad (9)$$

Here, symbols are defined as follows:

[Cu·Cell], concentration of Cu-absorbing cellulose (that is, $1000\times(w_{Cu(a)}/63.55)/(142.8/\rho)$); [Cu], concentration of Cu remained in cuprammonium solution (that is, $1000\times(w_{Cu(na)}/63.55)/(142.8/\rho)$); [Cell], concentration of cellulose not absorbing Cu
(that is, $C_{cell}-[Cu\cdot Cell]$)

[Cu·Cell]/[Cu] [Cell] is shown as a function of C_{Cu}/C_{Cell} in Figure 6 using the data points obtained in Figure 4 (region B in the system with $C_{OH}=0.83\ \text{mol}\,l^{-1}$). [Cu·Cell]/[Cu]×[Cell] has almost constant value irrespective of C_{Cu}/C_{Cell} in every three C_{OH} concentration ($C_{OH}=0.83$, 0.18, and $0.07\ \text{mol}$ l^{-1}). Here, we assumed as a zero-th order
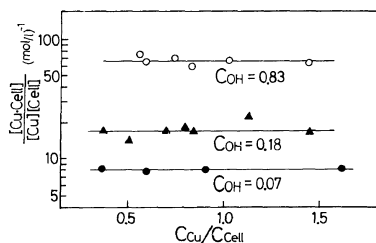
approximation in the case of systems with $C_{OH}=0.18\ \text{mol}\,l^{-1}$ where a part of cellulose dissolves, that the dissolved cellulose absorbs cuprammonium complex in the same molar ratio as determined for undissolved cellulose. The basic equilibrium of cellulose–cuprammonium complex formation reaction between one mol of cellulose and one mol of cuprammonium complex can be expected also in the solid–liquid coexisting system as followed:

$$[Cu]+[Cell]\longleftrightarrow[Cu\cdot Cell] \qquad (10)$$
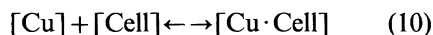
Using the above results and the data points obtained under constant C_{Cu}/C_{Cell} (=0.75) in Figure 5 the similar analysis was carried out to clarify the influence of OH^- on the absorption equilibrium. Following equilibrium and relationship might be expected for the present case:

$$[Cu]+[Cell]+Y[OH^-]\longleftrightarrow[Cu\cdot Cell] \qquad (11)$$
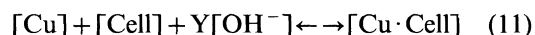
$$\frac{[Cell\cdot Cu]}{[Cell]\times[Cu]\times[OH^-]^Y}=K \qquad (12)$$

$$\log\frac{[Cell\cdot Cu]}{[Cell]\times[Cu]}=\log K''+Y\log[OH^-] \qquad (13)$$

Here, symbols are defined as follows:

$[OH^-]$, concentration of OH^- ion (We use the initial C_{OH} in the cuprammonium solution because the change of C_{OH} by the complex formation reaction is small.); Y, reaction order of OH^-

The results are shown in Figure 7. Here, we assumed as a zero-th order approximation that, in the C_{OH} region where a part of cellulose dissolves, the dissolved cellulose absorb cuprammonium complex in the same molar ratio as determined for undissolved cellulose. Thus, the accuracy for this analysis is expected to be low in the C_{OH} region around $0.35\ \text{mol}\,l^{-1}$ where cellulose shows higher solubility in cuprammonium solution. Figure 7 shows that reaction order of OH^- (Y) is almost 1.0 in the region of $C_{OH}<0.3\ \text{mol}\,l^{-1}$ but Y is $ca.$ 0 in the
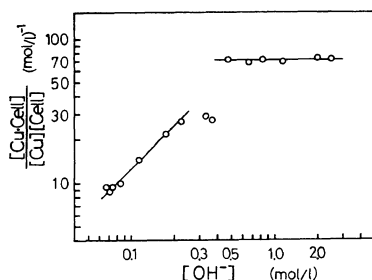
Figure 6. A plot of $\log[Cu\cdot Cell]/[Cu]\times[Cell]$ $vs.$ C_{Cu}/C_{Cell} in the cuprammonium–cellulose system: $\bigcirc$, $C_{OH}=0.83\ \text{mol}\,l^{-1}$; $\blacktriangle$, $C_{OH}=0.18\ \text{mol}\,l^{-1}$; $\bullet$, $C_{OH}=0.07$ $\text{mol}\,l^{-1}$.
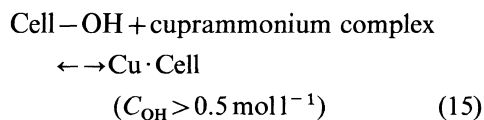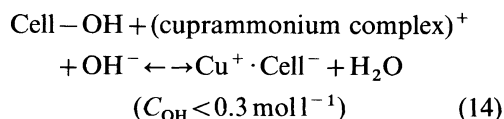
Figure 7. A plot of $\log[\text{Cu} \cdot \text{Cell}]/[\text{Cu}] \times [\text{Cell}]$ *vs.* $\log[\text{OH}^-]$ in the cuprammonium–cellulose system which shows the reaction order of the hydroxyl ion.

region of $C_{OH} > 0.5\,\text{mol}\,1^{-1}$. This suggests that when cuprammonium complex is dissociated into OH^- ion and cation, the OH^- ion contributes to the Cu-absorption reaction equilibrium, but when cuprammonium complex is expected not to be dissociated, the OH^- ion has no contribution to the Cu-absorption reaction despite large amount of OH^- ion existing in the system. The whole absorption schemes are shown in the following equations:

$$\text{Cell} - \text{OH} + (\text{cuprammonium complex})^+$$
$$+ \text{OH}^- \leftarrow \rightarrow \text{Cu}^+ \cdot \text{Cell}^- + \text{H}_2\text{O}$$
$$(C_{OH} < 0.3\,\text{mol}\,1^{-1}) \qquad (14)$$

$$\text{Cell} - \text{OH} + \text{cuprammonium complex}$$
$$\leftarrow \rightarrow \text{Cu} \cdot \text{Cell}$$
$$(C_{OH} > 0.5\,\text{mol}\,1^{-1}) \qquad (15)$$

The study of Reeves[2] was carried out under the condition of $C_{OH} < 0.3\,\text{mol}\,1^{-1}$ in the initial cuprammonium solution and he proposed the diol anion structure of the cellulose–cuprammonium complex, which coincides with scheme (14) in this study. Scheme (14) also explains the findings by Hess[4] that an addition of NaOH resulted in an increases in optical rotary power of the cellulose–cuprammonium solution system, because the addition of OH^- ion into the system promotes the cellulose–cuprammonium complex forming reaction and the Cu-absorbing reaction equilibrium in the region of $C_{OH} > 0.5\,\text{mol}\,1^{-1}$ are firstly reported in this study.

Considering our previous study,[1] the formation of cellulose–cuprammonium complex, if any, in the present system may be tentatively illustrated as follows;
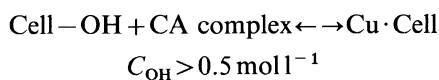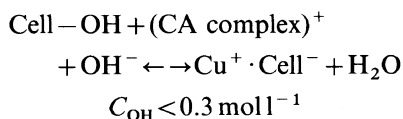

$$C_{OH} < 0.3\,\text{mol}\,1^{-1}$$

$$C_{OH} > 0.5\,\text{mol}\,1^{-1}$$
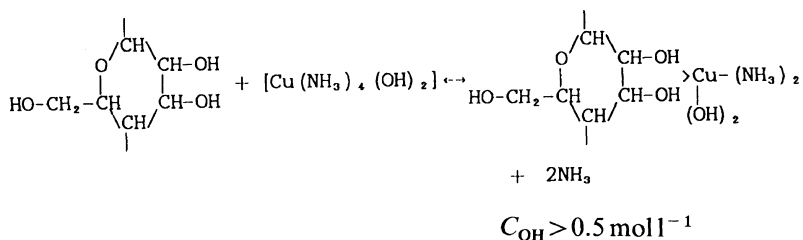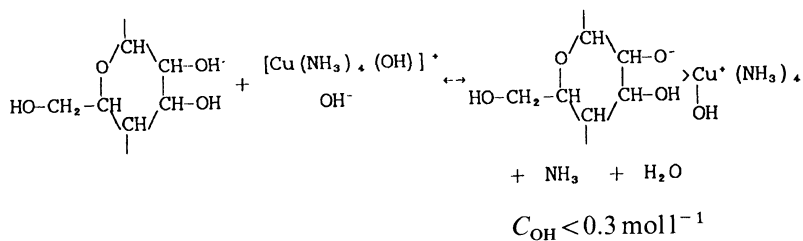
In this connection, sodium cation (Na^+) might not contribute in the above process because similar analysis using Na^+ concentration $([Na^+])$ instead of $[OH^-]$ term in Figure 7 did not give any linear line.

The absorption equilibrium proposed here together with our previous study[1] also suggests that as the dissolved state of cellulose in cuprammonium solution all glucopyranose units constituting cellulose do not always coordinate cuprammonium complex. This means that when about a half of glucopyranose units are substituted as a diol anion salt of the cuprammonium complex, this cellulose derivative is soluble in the aq cuprammonium solution or water, and about a half of cuprammonium complex exists away from cellulose molecular in the cellulose–cuprammonium solution. If we can make the cellulose derivative described above or at least copper-coordinated cellulose derivative in a separate process, they might be soluble in aq ammonia or water. This principle might lead us to a new way producing the cellulose–cuprammonium solution which has low concentration of copper and ammonia. In fact, we succeeded in preparing the above solution as described in Experimental section: First, a DBC sample with C_{Cu}/C_{cell} value$(=ca.$ 0.52) was prepared by treating cellulose with cuprammonium solution which has no cellulose dissolving power $(C_{OH} \geq 0.5 \, mol \, l^{-1})$. The DBC contains copper and NaOH (or OH^-) but lose ammonia by drying process. The DBC sample was proved to give clear solution by mixing with aq 2 wt% ammonia solution at polymer concentration level of $ca.$ 5 wt%. By this method we can produce the cellulose–cuprammonium solution which contains 1/2 copper and 1/3 ammonia in thier amounts, compared with those employed in conventional cellulose–cuprammonium solution.

CONCLUSION

An attempt was made to clarify chemical reaction nature of cellulose when dissolved in a cuprammonium solution in more detail. For this purpose an absorption experiment of cuprammonium complex in the solid–liquid coexisting system was carried out by either varying initial molar ratio of solid cellulose to cupric ion or varying hydroxyl ion strength in aq cuprammonium complex. Analysis in view of absorption equilibrium revealed that the following absorption equilibria held depending on OH ion strength $(C_{OH}; \, mol \, l^{-1})$ in the system:

$$Cell-OH+(CA \, complex)^+$$
$$+OH^- \leftarrow \rightarrow Cu^+ \cdot Cell^- + H_2O$$
$$C_{OH} < 0.3 \, mol \, l^{-1}$$
$$Cell-OH+CA \, complex \leftarrow \rightarrow Cu \cdot Cell$$
$$C_{OH} > 0.5 \, mol \, l^{-1}$$

The above schemes were found to reasonably explain the results obtained past. It was also confirmed that saturated absorbing copper is at most 0.65 mol per glucopyranose unit, which well coincides with the value evaluated for the cellulose–cuprammonium system in our previous study. Using this above results as tentative new cellulose dissolving process is proposed, in which the less amount of copper and NH_3 are employed, compared with those used for conventional process.

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