Aqueous Calcium Thiocyanate Solution as a Cellulose Solvent. Structure and Interactions with Cellulose

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ABSTRACT: Dissolution of cellulose into aqueous (aq) calcium thiocyanate solution was investigated with emphasis on solvent structure and interactions with cellulose. The aq calcium thiocyanate ($Ca(SCN)_2$) solution with concentration (C_{CaT}) more than 48.5 wt% could dissolve any celluloses. Solvation measurement revealed that in $C_{CaT} \geq 48.5$ wt%, the solvent system is formulated by $Ca(NCS)_2 \cdot xH_2O$ ($x \leq 4$) + yH_2O ($y \leq 6$), which exhibits mainly non-dissociated thiocyanate with high specific viscosity, as proved by electric conductivity, specific viscosity and IR or ^{13}C NMR measurements on solvent as a function of concentration of calcium thiocyanate. In this regard, the most stable 4 hydrate calcium thiocyanate is concluded from energy calculation as *trans–trans* configuration of $Ca(-N=C=S) \cdot 4H_2O$. DSC and IR analyses suggested that dissolution of cellulose takes place by first attack of $Ca(NCS)_2 \cdot xH_2O$ ($x \leq 4$) towards ring oxygen in cellulose. $Ca(NCS)_2 \cdot xH_2O$ ($x \leq 4$) becomes 4-hydrates-like structure (sixcoordinate complex of Ca) and cellulose forms a 5-membered ring by coordinating two oxygen atoms (O(5) and O(6)) in the glucopyranose unit, and then cellulose dissolves on heating. In this process, some ligand exchange might occur if the hydration number is more than 2. This coordination of cellulose is quite characteristic, compared with other solvents, such as cuprammonium hydroxide, which coordinate with O(2) and O(3) hydroxyl groups.
KEY WORDS Cellulose / Aqueous Calcium Thiocyanate Solution / Solvation / Interaction of Solvent with Cellulose / Infrared / Differential Scanning Calorimetry / Nuclear Magnetic Resonance /

Concentrated aqueous (aq) calcium thiocyanate ($Ca(SCN)_2$) solution dissolves cellulose at elevated temperature[1–4] and authors have reported that cellulose-I (Cell-I) crystal in natural cellulose is denaturated to form new cellulose–$Ca(SCN)_2$ addition compound which has some ordered structure detected by X-ray diffraction when in contact with 55 wt% aq $Ca(SCN)_2$ solution.[5] Such molecular adducts of cellulose have been reported also for aq lithium thiocyanate[6] and aq zinc chloride solutions.[7] However, the structures of all these cellulose adducts have not been clear yet. In other studies on cellulose dissolution into aq sodium hydroxide solution, Kamide *et al.*[8–11] pointed out the importance of solvent and cellulose structures: For the complete cellulose dissolution the intramolecular hydrogen bonds in cellulose solid should be broken to some extent and aq sodium hydroxide soln. should form a specific hydration structure in a very narrow concentration range at low temperature. The latter view point seems necessary in consideration of the cellulose dissolution into aq $Ca(SCN)_2$ solution although taking account of cellulose structure is not needed because $Ca(SCN)_2$ solution is able to completely dissolve even highly crystalline cellulose.

In this paper we attempt to clarify the solvent structure required for cellulose dissolution and elucidate a tentative cellulose–$Ca(SCN)_2$ adduct structure based on infrared, DSC, and NMR data.

EXPERIMENTAL

Materials

A conifer pulp (viscosity-average degree of polymerization $DP_v = 968$, prepared by sulfite pulping method) was supplied from Alaska Pulp Co., Ltd. (U.S.A.). As reference materials the followings were used to investigate interactions with aq calcium thiocyanate ($Ca(SCN)_2$) solution; cellulose triacetate (CTA) (LT-35, $DP_v = 300$, degree of substitution $DS = 2.92$, Daicel Co., Ltd., Japan), methyl cellulose (MC) (prepared from cellulose/NaOH soln. with dimethyl sulfate at our laboratory, $DS = 1.88$), starch (guaranteed grade, Kishida Chemicals Co., Ltd., Japan), xylan (JANSSEN CHIMICA, Belgium), poly(vinyl alcohol) (PVA) (guaranteed grade, $DP_v = 2000$, Wako Pure Chemical Industries Ltd., Japan), polyethylene glycol (PEG) (#4000, Nakalai Chemicals Ltd., Japan), atactic polyacrylonitrile (PAN) (synthesized by radical polymerization in our laboratory). Guaranteed grade calcium thiocyanate with $4H_2O$ ($Ca(SCN)_2 \cdot 4H_2O$) was supplied from Wako Pure Chemical Industries Ltd.

Preparation of $Ca(SCN)_2$ Solution

About 60 wt% aq $Ca(SCN)_2$ solution was prepared as follows: $Ca(SCN)_2 \cdot 4H_2O$ was dissolved in distilled water and the solution was subjected to centrifugation to discard the undissolved part, and filtered through G4 grade glass-filter. The correct concentration of $Ca(SCN)_2$, C_{CaT} (wt%), was determined as follows: 3.00 g of the above solution were diluted by ion-exchange water 10 times and 50 ml of 0.1 N aq silver nitrate solution and 5 ml of 6 N aq nitric acid solution were added to 5.00 g of the diluted solution, and the final solution was back titrated with 0.1 N aq potassium thiocyanate standard solution using aq ferric ammonium sulfate solution as indicator.

The $Ca(SCN)_2$ solution was diluted by distilled water to give solutions with desired concentrations ($C_{CaT} = 5$—60 wt%).

Adiabatic Compressibility Measurement

Sonic velocities of pure water and aq $Ca(SCN)_2$

solutions (v_0 and v_s) were measured at 60°C as a function of C_{CaT} using NUSONICS model 6080 CONCENTRA-TION ANALYZER (Mapco Inc., U.S.A.) and the densities of water and Ca(SCN)$_2$ solutions (ρ_0 and ρ_s) at 60°C were determined by picnometric method. The number of solvated water molecules on 1 mol of Ca(SCN)$_2$ molecule h was calculated as[12,13]

$$h = (1 - \beta_s/\beta_0)(n_0/n_s) \qquad (1)$$

$$\beta_k = 1/(\rho_k v_k{}^2) \qquad (k = 0 \text{ or s}) \qquad (2)$$

Here, β_k is adiabatic compressibility of water ($k = 0$) or Ca(SCN)$_2$ solution ($k = s$) and n_0 and n_s are the molar concentrations of water and calcium thiocyanate in a given Ca(SCN)$_2$ solution.

Electric Conductivity, Viscosity, and ^{13}C NMR Measurements of Ca(SCN)$_2$ Solutions

Electric conductivity (Λ) and specific viscosity (η_{sp}) of aq Ca(SCN)$_2$ solution were measured at 60°C as a function of C_{CaT} on an electric conductometer model CM24 (Toa Denpa Co., Ltd., Japan) and by an Ub-belohde type viscometer, respectively. ^{13}C NMR spectra of Ca(SCN)$_2$ solution at 60°C were recorded on an FT-NMR spectrometer (GSX-400; JOEL, Japan) using TSP as the internal standard.

Infrared Spectroscopy

IR measurements on Ca(SCN)$_2$ solution sandwiched between polyethylene films were made on an IR instrument model JIR-3505 (JEOL, Japan) by transmission method against polyethylene films as reference at a resolving power of 2 cm^{-1} and 20 accumulation times.

In order to clarify the interactions of Ca(SCN)$_2$ solutions with cellulose, a regenerated cellulose film recovered from its dimethylacetamide–lithium chloride (9:1, w/w) solution was utilized. IR measurements were made for the films absorbing small amounts of Ca(SCN)$_2$ solution with different C_{CaT}.

Ab Initio Quantum Chemical Calculation

The most stable structure of calcium thiocyanate tetrahydrate was obtained by the ab initio quantum chemical method. The following three structures as an initial state were prepared using Insight II: trans-[Ca(–N=C=S)$_2$·4H$_2$O], cis-[Ca(–N=C=S)$_2$·4H$_2$O] and isomeric trans type [Ca(–S–C≡N)$_2$·4H$_2$O]. Quantum chemical calculation was carried out on SGI Workstation using split valence (SV) as a basis function and Turbomole soft ware (Turbomole program pakage commercially available from BYOSYM, San Diego, U.S.A.).

Differential Scanning Calorimetry

About 20 mg of Ca(SCN)$_2$ solution with given C_{CaT} were dropped on cellulose sample (ca. 5 mg) placed in a stainless seal cell and immediately the cell was sealed at room temperature and stood for given times t_d ($t_d = 0$ means the instance when cell was sealed). The cell was loaded in a DSC apparatus (DSC-200, Seiko Electronic Co., Ltd., Japan), followed by cooling to 5°C for 5 min. Measurements were carried out at heating rate of $3°\text{C min}^{-1}$ in the temperature range from 5°C to 155°C
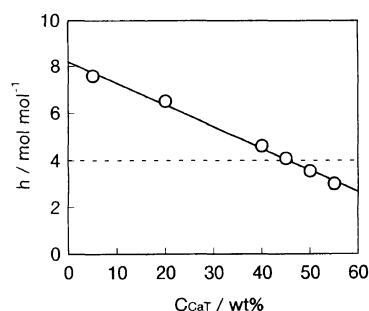

Figure 1. Calcium thiocyanate concentration C_{CaT} dependence of the number of solvated water molecules h in aqueous calcium thiocyanate solution at 60°C.
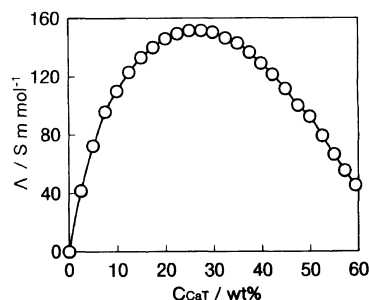

Figure 2. Calcium thiocyanate concentration C_{CaT} dependence of conductivity Λ of aqueous calcium thiocyanate solution at 60°C.

under nitrogen purging.

RESULTS AND DISCUSSION

Structure of aq Calcium Thiocyanate Solution Capable of Dissolving Cellulose

The aq calcium thiocyanate solutions with concentrations C_{CaT} more than 48.5 wt% were proved to dissolve pulp, cotton linter, regenerated cellulose and even bacterial cellulose at elevated temperature. This means that cellulose crystal form and crystallinity are not factors controlling dissolution in the Ca(SCN)$_2$ solution and rather the structure of the Ca(SCN)$_2$ solution depending on its concentration is a key factor for cellulose dissolution.

Figure 1 shows the hydration number h on 1 mol of Ca(SCN)$_2$ as a function of C_{CaT}. Clearly, h decreases with increase in C_{CaT}, being less than 4 for Ca(SCN)$_2$ solution capable of dissolving cellulose. The Ca(SCN)$_2$ solution contains ca. 6 mol/1 mol of solute of free water (not solvated by solute). Thus, the composition of the Ca(SCN)$_2$ solution is Ca(SCN)$_2$: solvated H$_2$O : non-solvated H$_2$O = 1 : 4 : 6 (mol/mol/mol).

Figure 2 shows the electric conductivity Λ as a function of C_{CaT}. Up to $C_{CaT} = 25$ wt%, Λ of aq calcium thiocyanate soln. increases with C_{CaT} and decreases monotonically above this point. This might mean that in a dilute region, calcium thiocyanate molecules dissociate into Ca^{2+} and SCN$^-$ ions, whose content increases with C_{CaT}, but the dissociation of the molecules is suppressed above $C_{CaT} = 25$ wt%.

Figure 3 shows the relationship between $\eta_{sp}/(C_{mCaT})^{1/2}$ and $(C_{mCaT})^{1/2}$. Here, C_{mCaT} is molar concentration of Ca(SCN)$_2$. According to Jones–Dole's equation[14] for dilute electrolyte solution, where perfectly dissociated ions and solvent interact together only through electro-
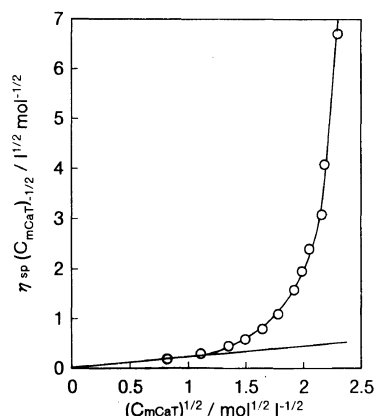
Figure 3. Plot of $\eta_{sp}/(C_{mCaT})^{1/2}$ as a function of $(C_{mCaT})^{1/2}$ for aqueous calcium thiocyanate solution at 60°C.
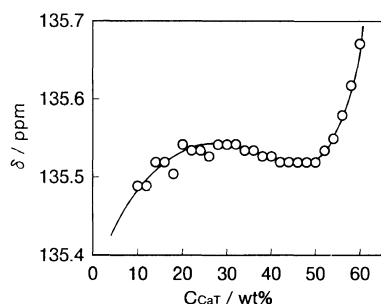

Figure 4. Calcium thiocyanate concentration C_{CaT} dependence of carbon chemical shift δ of ^{13}C NMR peak for aqueous calcium thiocyanate solution.

static Coulomb force, $\eta_{sp}/(C_{mCaT})^{1/2}$ can be expressed as a function of $(C_{mCaT})^{1/2}$ as follows:

$$\eta_{sp}/(C_{mCaT})^{1/2} = A + B(C_{mCaT})^{1/2} \qquad (3)$$

Here A and B are ion–ion and ion–solvent interaction coefficients, respectively and independent of C_{mCaT}. In the region of $(C_{mCaT})^{1/2}$ lower than 1, $\eta_{sp}/(C_{mCaT})^{1/2}$ is almost proportional to $(C_{mCaT})^{1/2}$ and A is zero, indicating that ion–ion interaction is negligible and calcium thiocyanate molecules perfectly dissociated in solution. However, above $(C_{mCaT})^{1/2} = 1$, the data points show deviation from the Jones–Dole's relation, probably corresponding to increase of interaction between ion and ion or ion and solvent molecules.[15,16] Especially, $\eta_{sp}/(C_{mCaT})^{1/2}$ drastically increases in the range of $(C_{mCaT})^{1/2} \geq ca.$ 2, which corresponds to $C_{CaT} = ca.$ 48 wt%.

^{13}C NMR chemical shift δ is plotted against C_{CaT} in Figure 4. δ shifts to a lower field with increase in C_{CaT} in the range of $C_{CaT} \leq 20$ wt%, passing through some plateau region (rather slightly higher field shift region) $(20 < C_{CaT} < 50$ wt%) and then again steeply shifts to a lower field in the range of $C_{CaT} \geq 50$ wt%.

Figures 5a and b show the IR spectrum of a Ca(SCN)$_2$ solution with $C_{CaT} = 55$ wt% and the C_{CaT} dependence of the wave numbers of HOH bending and CN stretching vibration (v_{HOH} and v_{CN}, respectively) for Ca(SCN)$_2$ solutions. v_{HOH} and v_{CN} are observed around at 1625 and 2070 cm^{-1}, respectively. From IR analysis on various salts of isothiocyanate and thiocyanate complex, Savatini and Bertini[17] indicated that v_{CN} of NCS group (N-bonded type) appears around 2060—2100 cm^{-1}, while that of
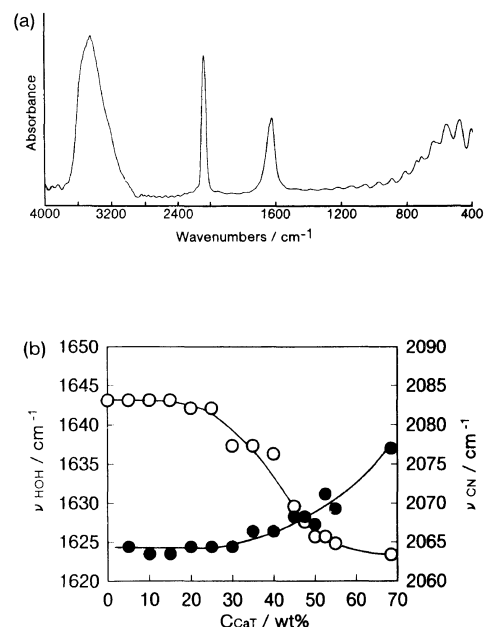

Figure 5. IR spectrum of aqueous calcium thiocyanate solution (a) and concentration C_{CaT} dependence of wave number of HOH bending (v_{HOH}, O) and CN stretching (v_{CN}, ●) vibration (b).

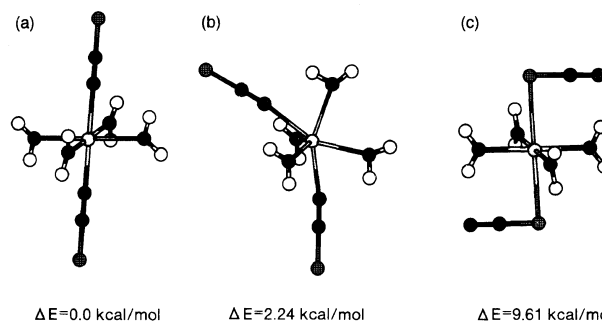ΔE=0.0 kcal/mol   ΔE=2.24 kcal/mol   ΔE=9.61 kcal/mol

Figure 6. Most stable structures for Ca(SCN)$_2 \cdot$4H$_2$O with *trans*, *cis*, and isomeric *trans* conformation obtained by computer simulation. ΔE, potential energy.

SCN group (S-bonded type) was observed above 2100 cm^{-1}. Therefore the v_{CN} of 2070 cm^{-1} in this study implies that the NCS group coordinates with calcium atom at nitrogen atom site, *i.e.*, Ca(NCS)$_2$. In figure 5b v_{HOH} seems almost constant in the $C_{CaT} < 25$ wt%, and shifts to a shorter wave number up to *ca.* $C_{CaT} = 50$ wt%, approaching an asymptotic value. v_{CN} also seems roughly constant in the $C_{CaT} < 25$ wt% and abruptly shifts to a longer wave number.

Figure 6 depicts the most stable structures for three calcium thiocyanate tetrahydrates; *trans*-[Ca(–N=C= S)$_2 \cdot$4H$_2$O], *cis*-[Ca(–N=C=S)$_2 \cdot$4H$_2$O] and isomeric *trans* type [Ca(–S–C≡N)$_2 \cdot$4H$_2$O]. Potential energy ΔE was calculated for each most stable structure and the result is shown below each illustration, taking ΔE = 0 for Ca(–N=C=S)$_2 \cdot$4H$_2$O with *trans–trans* configuration. The calculation elucidated that *trans–trans* configuration is the most stable for Ca(NCS)$_2 \cdot$4H$_2$O.

From the above, the dissolved state of calcium thiocyanate molecules in water is speculated as follows: In a sufficiently dilute region of $C_{CaT} < 15$ wt% the molecules are perfectly dissociated. Above 15 wt% and below 25 wt%, the molecules might be in equilibrium

represented by $Ca^{2+} + NCS^- \leftrightarrow [CaNCS]^+$, because of the deviation from Jones–Dole's relation of $\eta_{sp}/(C_{mCaT})^{1/2}$ and decrease in increasing rate of Λ. Increase in the concentration of calcium thiocyanate in this region brings about increase in partially dissociating ion $[CaNCS]^+$, which makes the NCS group an electron donor to Ca^{2+} ions, leading to lower carbon chemical shift. In the region of $25\% < C_{CaT} < 50\%$, NCS^-, $[CaNCS]^+$ and undissociated $Ca(NCS)_2$ are considered to be in equilibrium as $[CaNCS]^+ + NCS^- \leftrightarrow Ca(NCS)_2$, as suggested by the decrease in Λ. NCS^- in $Ca(NCS)_2$ might be strongly bound to Ca^{2+} by ion–ion interaction from the result that the wave number due to CN stretching vibration shifts to a higher wave number. Above $C_{CaT} = 50\,wt\%$, the hydrated $Ca(NCS)_2$ with *trans–trans* conformation might mainly exist in the solution, while the hydration number monotonically decreases with C_{CaT} in this region. The reason why δ steeply shifts towards lower field with increase in C_{CaT} in $C_{CaT} \geq 50\,wt\%$ could be explained in the following way: The decrease in the numbers of the solvated water and free water surrounding $Ca(NCS)_2$ might allow the formation of cross-link like structure between $Ca(NCS)_2$ molecules themselves and might lower exchange chance between Ca^{2+} and thiocyanic ions due to increase in the existence probability of non-dissociated $Ca(NCS)_2$ in the system, all which might lead to abrupt increase in η_{sp} and more energetically stable NCS group (longer wave number shift of v_{CN}). A cross-link like structure has been known for aq inorganic salts, as exemplified by $[Pd(SCN)_4]^{2-}$ complex.[18]

Interaction between Cellulose and aq $Ca(NCS)_2$ Solution

Figure 7a shows DSC curves for the cellulose/aq $Ca(NCS)_2$ solution with several C_{CaT} measured at standing time $t_d = 0$. It is obvious that an exothermic peak appears in $C_{CaT} \geq 50\,wt\%$ and its peak temperature shifts towards higher temperature with increase in C_{CaT}. The former indicates the existence of interactions between cellulose and aq $Ca(NCS)_2$ and the latter is likely related to lowering of diffusional penetration of aq $Ca(NCS)_2$ solution into cellulose owing to the increase in viscosity of the solvent induced by increase in C_{CaT}. Exothermic heat ΔH linearly increases with C_{CaT}, as shown in Figure 7b. Extrapolation to $\Delta H = 0$ gives $C_{CaT} = 48.5\,wt\%$, which precisely coincides with the lower concentration limitation of $Ca(NCS)_2$ for cellulose dissolution. Authors[5] have found that cellulose and aq $Ca(NCS)_2$ with $C_{CaT} = 55\,wt\%$ interact with each other at room temperature forming some stable structure for 60 min and as a result hydrogen bonds in cellulose solid are disrupted. Such stable adducts might be formulated from the above discussion as follows:
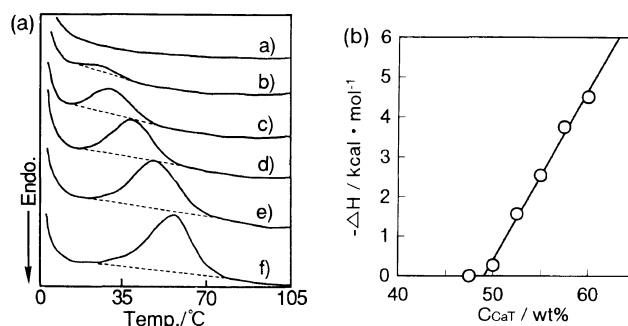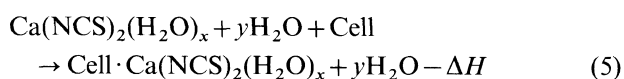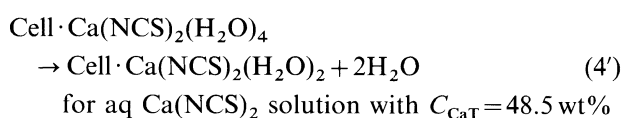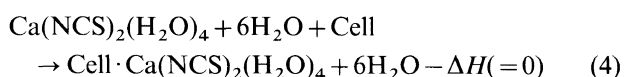
$$Ca(NCS)_2(H_2O)_4 + 6H_2O + Cell$$
$$\rightarrow Cell \cdot Ca(NCS)_2(H_2O)_4 + 6H_2O - \Delta H(=0) \qquad (4)$$
$$Cell \cdot Ca(NCS)_2(H_2O)_4$$
$$\rightarrow Cell \cdot Ca(NCS)_2(H_2O)_2 + 2H_2O \qquad (4')$$
for aq $Ca(NCS)_2$ solution with $C_{CaT} = 48.5\,wt\%$
$$Ca(NCS)_2(H_2O)_x + yH_2O + Cell$$
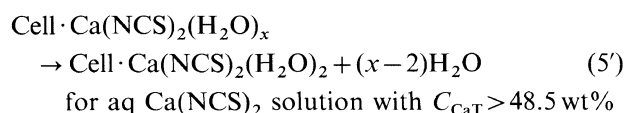$$\rightarrow Cell \cdot Ca(NCS)_2(H_2O)_x + yH_2O - \Delta H \qquad (5)$$

Figure 7. DSC thermogram of conifer pulp in aqueous calcium thiocyanate solution with various C_{CaT} (a) and exothermic ΔH plotted against C_{CaT} (b).

$$Cell \cdot Ca(NCS)_2(H_2O)_x$$
$$\rightarrow Cell \cdot Ca(NCS)_2(H_2O)_2 + (x-2)H_2O \qquad (5')$$
for aq $Ca(NCS)_2$ solution with $C_{CaT} > 48.5\,wt\%$

Here, x and y are less than 4 and 6, respectively, and the molar ratio of cellulose is far smaller than that of thiocyanate. The sign of endothermic heat is taken as positive. ΔH might include contribution from energies necessary to form adducts with cellulose and break hydrogen bonds within cellulose solid.[5] The above formula could explain the fact that ΔH is 0 for aq $Ca(NCS)_2$ solution with $C_{CaT} = 48.5\,wt\%$ (stable 4 hydrate type) and becomes larger when aq $Ca(NCS)_2$ solution with higher C_{CaT} (hydration number is less than 4) interacts with cellulose so as to satisfy 4 hydrates-like thiocyanate. In other words, cellulose might act as a supplier of R–O–R moiety like water (H–O–H moiety) directly interacting with aq $Ca(NCS)_2$ with evolution of heat. Equations 4' and 5' assume that cellulose (one glucopyranose unit) has two interaction sites against the $Ca(NCS)_2$ structure again so as to form 4 hydrates-like thiocyanate. Thus, when x approaches 4 (C_{CaT} becomes smaller), the probability of a direct adduct formation on cellulose is reduced with smaller exothermic heat, and then the resultant adduct is subject only to a ligand-exchange reaction for stable cellulose/$Ca(NCS)_2$ complex formation. Here, 6-valence coordination for Ca is of course assumed.

The fact that cellulose has two reaction sites in a cellobiose units is reconfirmed in Figure 8, where DSC curves for other polymers contacted with aq $Ca(NCS)_2$ solution with $C_{CaT} = 55\,wt\%$ are shown. Polymers having ether oxygen such as cellulose, CTA, MC, starch, xylan, and PEG generate heat when in contact with the $Ca(NCS)_2$ solution. This means that heat evolution by the thiocyanate requires ether oxygen, especially O–C–C–O repeat units in polymers to form more stable cyclic complex. In contrast, PVA having alcoholic OH shows endothermic behavior and PAN having no ether linkage and alcohol OH is athermal. Thus, ether oxygen–$Ca(NCS)_2$–ether oxygen or ether oxygen–$Ca(NCS)_2$–alcohol oxygen type complexes for cellulose are possible and more stable.

Figure 9a shows the IR spectrum of cellulose film in contact with aq $Ca(NCS)_2$ with $C_{CaT} = 55\,wt\%$ for 60 min at room temperature. v_{CN} derived from solvent clearly splits into two peaks by interaction with cellulose. A stick diagram for v_{CN} and v_{HOH} when cellulose is con-
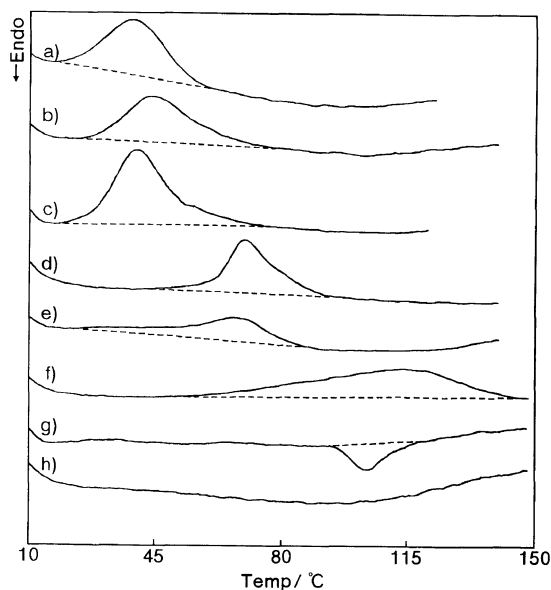
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Figure 8. DSC thermograms of various polymers in aqueous calcium thiocyanate solution with 55 wt% salt concentration. a) conifer pulp; b) CTA; c) MC; d) starch; e) xylan; f) PEG; g) PVA; h) atactic PAN.
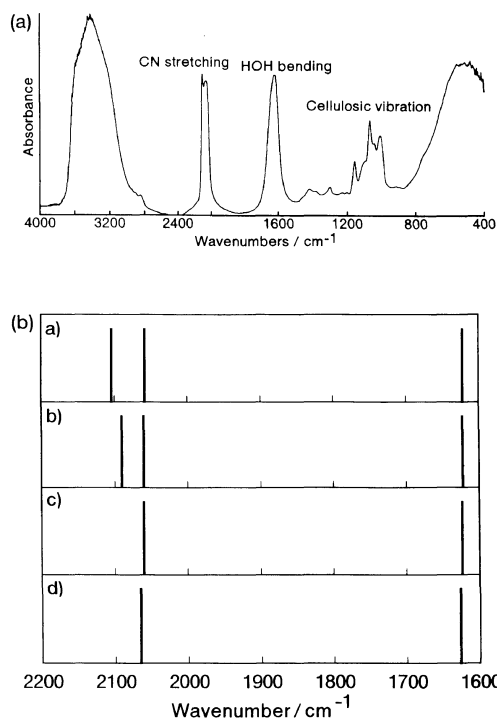

Figure 9. IR spectrum of cellulose film in contact with 55 wt% aq calcium thiocyanate soln. for 60 min (a) and stick diagram for wave number of CN stretching around 2100 cm^{-1} and HOH bending at 1626 cm^{-1} from aq Ca(NCS)$_2$ contacted with cellulose. a) $C_{CaT} = 55$ wt%; b) 25 wt%; c) 21.5 wt%; d) 5 wt%.
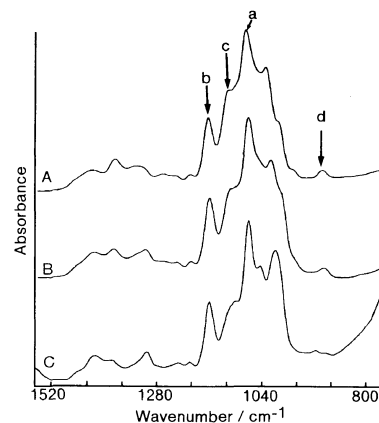

Figure 10. IR spectra of cellulose (A), cellulose absorbing 5 wt% (B), and 55 wt% aq calcium thiocyanate solution (C).

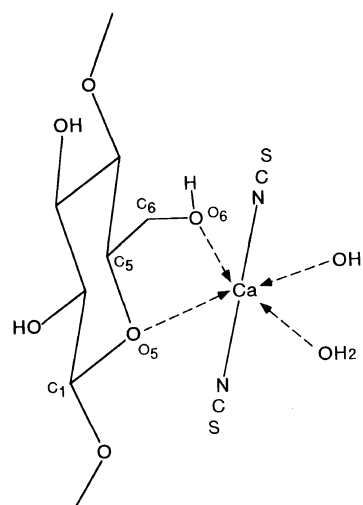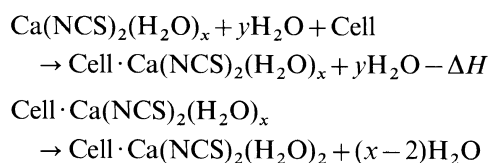**Figure 11.** Schematic representation of interaction between cellulose and calcium thiocyanate–water complex.

tacted with aq Ca(NCS)$_2$ with different C_{CaT} is shown in Figure 9b, revealing that the splitting of v_{CN} occurs in $C_{CaT} \geq 25$ wt%. Strictly speaking, a new absorption appears at longer wave number besides the original absorption when in contact with cellulose. In the C_{CaT} range of ca. 25—ca. 48 wt%, where half-dissociated and non-dissociated Ca(NCS)$_2$ coexist and are solvated by 7.5—4 mol of waters with relatively abundant free water, cellulose can only act as a hydroxyl group supplier since the Ca(NCS)$_2$ is not in the state which requires ether

oxygen as interaction site. In $C_{CaT} > 50$ wt%, Ca(NCS)$_2$ requires ether oxygen as an interaction site, as proved in DSC analysis, leading to the appearance of a new v_{CN} at far longer wave number region. The longer wave number absorption is generated as a result of interaction with cellulose.

To clear the interaction between cellulose and aq Ca(NCS)$_2$ solution with $C_{CaT} > 50$ wt%, which dissolves cellulose, IR analysis was carried out on cellulose absorbed by Ca(NCS)$_2$ solution and the results for the wave number range of 800—1520 cm^{-1} are shown in Figure 10. The figure shows IR spectra of the original cellulose film (A), cellulose film absorbing aq Ca(NCS)$_2$ with $C_{CaT} = 5$ wt% (B) and cellulose film absorbing aq Ca(NCS)$_2$ with $C_{CaT} = 55$ wt% (C). Absorption bands are responsible for CO stretching (a), antisymmetrical bridge C–O–C stretching (b), antisymmetrical in-phase ring stretching (c) and antisymmetrical out-of-phase ring stretching (d).[19−21] IR for A and B are much the same but that for C is quite different, giving denaturated patterns in the range 1020—960 cm^{-1} and depressed c and d absorption. This means that aq Ca(NCS)$_2$ solution capable of dissolving cellulose might form a stable complex-like structure with cellulose. Quantitative analysis using a (CO stretching) absorption as standard reveals that b (bridge C–O–C) absorbance does not

change by contact by $Ca(NCS)_2$ solution. These results with those by DSC lead us to the conclusion that preferable interaction site of cellulose is ring oxygen (O(5)) and a stable complex-like structure is cyclic because of the depression of ring vibration. An attack of the $Ca(NCS)_2$ solution on O(5) oxygen is equivalent to breakdown of intramolecular hydrogen bonds of cellulose, as proposed by Kamide and Okajima[23] as a fundamental for cellulose dissolution in a solvent. The above cyclic structure requires for cellulose to have at least one more interaction site with $Ca(NCS)_2$ besides the ring oxygen. The most possible structure is illustrated in Figure 11 where the 5-membered ring is formed by interacting oxygen atoms at O(5) and O(6) with assumption of 6-valence coordination of Ca and –NCS coordination to Ca. This structure is basically the same as in eq 4' and 5'. In this structure the cationic Ca is neutralized by electrons from oxygen atoms contained in cellulose and the –NCS coordinated to Ca might exist as $-N=C-S^-$, giving an appearance of v_{CN} at longer wave number, and also can depress the vibration of ring oxygen. Such a situation has been reported for $[CoNCS(NH_3)_5]Cl_2$.[24] This coordination of cellulose is quite characteristic, compared with other solvent, such as cuprammonium hydroxide,[25] which coordinates with O(2) and O(3) hydroxyl groups.

CONCLUSION

Regarding dissolved calcium thiocyanate in aqueous solution and interaction of cellulose with the aq calcium thiocyanate, it was proved that only $Ca(NCS)_2 \cdot xH_2O$ $(x \leq 4) + yH_2O$ $(y \leq 6)$ which exhibits mainly non-dissociated type of the thiocyanate with high specific viscosity, can dissolve any celluloses. DSC and IR analyses lead to the conclusion that swelling of cellulose might take place by first attacking of ring oxygen in cellulose towards $Ca(NCS)_2 \cdot xH_2O$ $(x \leq 4)$ so as to fulfill the 4-hydrates-like form (6-valence coordination of Ca) and finally forms 5-membered cyclic structure by coordinating two oxygen atoms (O(5) and O(6)) in glucopyranose unit to centered Ca atoms probably in $Ca(NCS)_2 \cdot xH_2O$ $(x \leq 4)$ as shown below:

$$Ca(NCS)_2(H_2O)_x + yH_2O + Cell$$
$$\rightarrow Cell \cdot Ca(NCS)_2(H_2O)_x + yH_2O - \Delta H$$

$$Cell \cdot Ca(NCS)_2(H_2O)_x$$
$$\rightarrow Cell \cdot Ca(NCS)_2(H_2O)_2 + (x-2)H_2O$$

where, ΔH is exothermic heat evolving when cellulose contacts with aq $Ca(NCS)_2$ soln. with concentration higher than 48.5 wt%, and then cellulose could dissolve on heating.

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