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Thermochimica Acta 266 (1995) 343–354

thermochimica
acta

The liquid crystalline state of water–sodium cellulose sulphate systems studied by DSC and WAXS ☆

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Abstract

The liquid crystal formation of sodium cellulose sulphate (NaCS)–water systems was investigated by differential scanning calorimetry (DSC), polarizing light microscopy (POL) and wide-angle X-ray diffractometry (WAXS). The liquid crystalline state was observed at a water content (W_c) ranging from 0.4 to 1.5 (g water)/(g NaCS) (g/g), and at a temperature ranging from 260 to 310 K depending on W_c. DSC and WAXS data indicated that each sodium ion is sandwiched by two cellulose molecules coexisting with 4–20 water molecules in the liquid crystalline state. When W_c exceeds the critical value, free water molecules enhance the molecular movement of NaCS and molecular chains are arranged in a random form.

Keywords: DSC; Liquid crystal; Sodium cellulose sulphate; Water; WAXS

1. Introduction

It is known that molecular chains of polyelectrolytes form an aligned structure in a dilute aqueous solution as a result of their electrical repulsion forces [1]. X-ray diffractograms indicate that the molecular assemblies are organized in an aqueous solution of synthetic polyelectrolytes in a solution [2]. We reported that water–polysaccharide electrolytes form the liquid crystalline state in water contents ranging from approx. 0.4 to 2.0 (g water)/(g dry saccharide) (g/g), when the repeating units of polysaccharide are connected by β-1,4 linkage [3, 4], regardless of the species of counter ion, i.e. mono- or divalent ions [5, 6]. The liquid crystal formation of

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☆ Dedicated to Hiroshi Suga on the Occasion of his 65th Birthday.

SSDI 0040-6031(95)02445-X

polysaccharide electrolytes relates closely to the number of water molecules attached to the hydroxyl groups and ions. It was found that the liquid crystalline state is observed when each repeating unit holds 2–10 water molecules [4, 5]. If an excess amount of water molecules are present in each repeating unit, the system takes a more random structure and does not form the liquid crystalline state. These findings suggest that characteristic numbers of water molecules are necessary to break intermolecular interaction and provoke the alignment of polysaccharide molecules. At the same time, molecular ordering is disturbed, when an excess amount of water exists in the system and the molecular motion of polysaccharides is enhanced by the free motion of water molecules [8].

In this study, differential scanning calorimetry and X-ray diffractometry of water–sodium cellulose sulphate (NaCS) systems were carried out as functions of temperature and water content in order to fully understand the molecular order in a highly concentrated aqueous polyelectrolyte system.

2. Experimental

2.1. Sample

NaCS is a polyelectrolyte derived from cellulose. Fig. 1 shows the chemical structure of NaCS. Na ion is preferentially substituted at the 6-position carbon in the glucopyranose ring [1]. Sodium salt of cellulose sulphate (NaCS) was obtained from Scientific Polymer Products Co. Ltd. The degree of substitution (DS) was 2.26.

The water content (W_c) of the sample is defined as (g water)/(g dry sample) (g/g) [9, 10].

2.2. Measurements

DSC

A Perkin–Elmer DSC IIc and a Seiko DSC 200 were used. Sample weight was approx. 3 mg and the scanning rate was varied from 1 to 20 K min^{-1}. The temperature

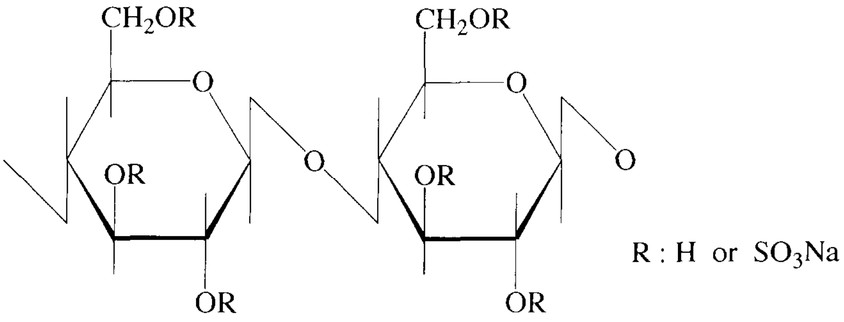

Fig. 1. Chemical structure of sodium cellulose sulphate (NaCS).

was varied from 150 to 330 K using low-temperature equipment. The temperature was calibrated with cyclohexanone and water.

WAX

A Mac Science MXP18 with monochromatic Cu Kα was operated at 40 kV and 300 mA. The temperature was varied from 263 to 298 K using a temperature controller. The temperature was maintained during the measurements at an accuracy of ± 0.5 K.

POL

A Leitz polarizing microscope Orthoplan Pol was used for the morphological observation of the liquid crystals. The temperature was controlled using a Linkam THMS 600 unit (150–400 K, ± 1 K).

3. Results and discussion

NaCS is an amorphous polysaccharide in the dry state. The main chain motion of NaCS is not observed in the dry state due to strong intermolecular interaction [11]. From the differential scanning calorimetry (DSC) results, NaCS showed no phase transition from 150 to 470 K. Thermal decomposition gradually started from 470 K.

NaCS is readily solved in water in the same manner as other polyelectrolytes. When NaCS sorbs a small amount of water, the molecular motion of NaCS is enhanced by the plasticizing effect of water, and glass transition is observed at around a water content of 0.2 g/g.

Fig. 2 shows the representative DSC heating curves of water–NaCS in the temperature range 150–330 K at a heating rate of 10 K min^{-1}. The sample with $W_c = 0.21$ (g/g) (curve I in Fig. 2) showed only glass transition and no first-order phase transition. The glass transition temperature (T_g) markedly decreased with increasing W_c as shown in curves II–IV. Cold-crystallization (T_{cc}) (curves II–IV), melting of ice (T_m) (curves II–IV), and transition from the liquid crystalline state to the liquid state (T^*) (curves II–V) are observed.

The phase diagram of the water–NaCS system was established using the transition temperature obtained by DSC. Fig. 3 shows the phase diagram of water–NaCS. It was found that the liquid crystalline phase is formed with a W_c ranging from 0.4 to approx. 1.5 (g/g) and the temperature range of the liquid crystalline state decreased with increasing W_c. The melting temperature of ice (T_m) in a W_c ranging from 0.4 to 1.5 (g/g) is lower than 273 K, indicating that the structure of ice in the system is not ordinal.

The specific heat capacity jump observed at T_g (ΔC_p) was estimated from DSC heating curves. It was found that ΔC_p values are larger than those reported for other amorphous polymers [12–15]. T_g decreased in the W_c range from approx 0.2 to 0.5 and increased with increasing W_c as shown in Fig. 3. In contrast, ΔC_p values increased with increasing W_c until W_c reached 0.5 (g/g). The minimum T_g value corresponded to the maximum ΔC_p.

Although DSC cooling curves are not shown, it was observed that the crystallization of water did not commence until 258 K at a cooling rate of 10 K min^{-1} due to super

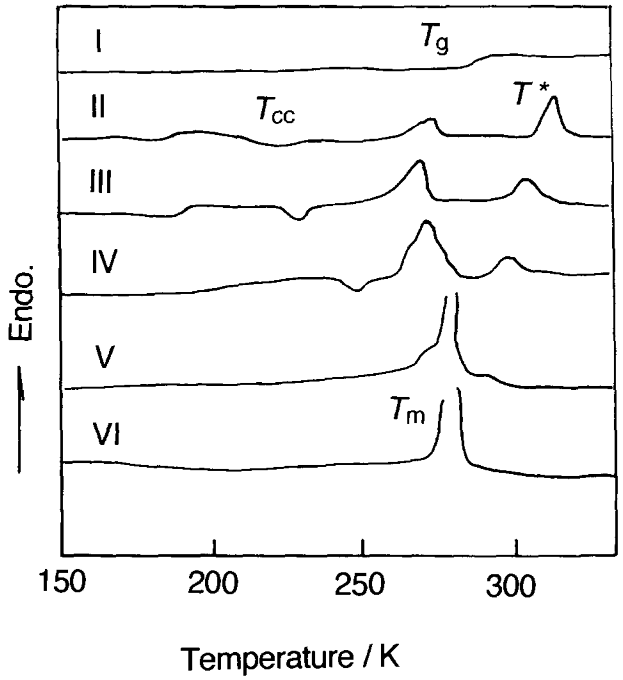

Fig. 2. Representative DSC curves of the water–NaCS systems. Heating rate, 10 K min^{-1}; water content (g/g): I, 0.2; II, 0.50; III, 0.60; IV, 0.80; V, 1.23; VI, 1.80. T_g, glass transition; T_{cc}, cold crystallization; T_m, melting; T^*, liquid crystal to liquid transition.

cooling. The transition from the liquid state to the liquid crystalline state was also observed.

Using polarizing light microscopic observations, the liquid crystalline structure was clearly seen for the sample with $W_c \approx 1.0$ (g/g) at 300 K. After the evaporation of water in the above sample, the structure remained exactly as in the wet state. The liquid crystalline state was reversible if the W_c of a sample was kept at a constant value.

When the endotherm of the liquid crystal transition measured at 10 K min^{-1} (Fig. 2, curve II indicated as T^*) was enlarged, it was found that the endotherm was not a smooth peak but had a shoulder on the high temperature side of the main peak. A schematic illustration of the transition peak from the liquid crystalline state to the liquid state is presented in Fig. 4.

The sample with $W_c = 0.6$ was chosen and measured at various heating rates after quenching from 320 to 150 K. With slow heating, the size of the high temperature side peak (T^*_H) became larger than that of the low temperature side peak (T^*_L). Fig. 4 shows the peak temperatures of T^*_H and T^*_L, and the peak height ratio of the two peaks (H/h) as a function of heating rate. At a heating rate of 20 K min^{-1}, only T^*_L was observed. The height of the T^*_L peak decreased linearly with increasing heating rate. The temperatures of both T^*_H and T^*_L increased with increasing heating rate, suggesting the viscoelastic

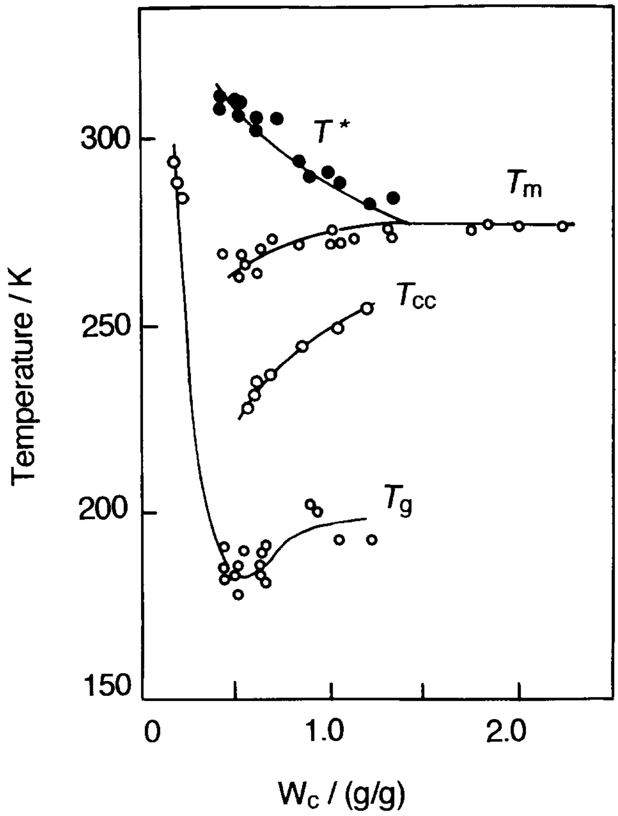

Fig. 3. Relationship between the temperatures of transition and W_c of water–NaCS systems: T_g, glass transition; T_{cc}, cold crystallization; T_m, melting; T^*, liquid crystal to liquid transition.

nature of this phenomenon. These facts suggest that the structure of the liquid crystal is influenced by the thermal history of the sample, i.e. a more stable molecular arrangement is formed during slow heating.

The liquid crystalline formation can be observed not only by dynamic measurements, but also by isothermal measurements. An exothermic peak due to liquid crystallization can be observed as a function of time.

Fig. 5 shows the isothermal liquid crystallization curves of water–NaCS systems with $W_c = 0.6$. The samples were maintained at 320 K for 5 min, quenched to 245, 246, 247 and 248 K, respectively. Then they were maintained at the above temperatures for 10 min in order to complete the liquid crystallization. Dotted lines in the figure show the time interval where the temperature was not controlled isothermally. Two peaks can clearly be seen in the isothermal liquid crystallization curve at 248 K.

The time needed to reach the exothermic peak (t_{max}) increased with increasing temperature of isothermal liquid crystallization (T_c^*) as shown in Fig. 6.

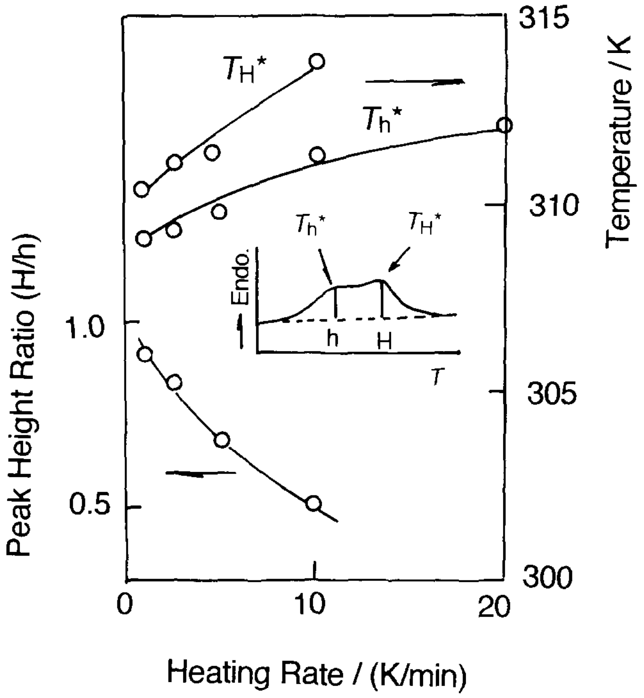

Fig. 4. Relationships between peak temperatures (T_H^*, T_h^*), peak height ratio (H/h) and heating rate of water–NaCS system with $W_c = 0.6$ (g/g).

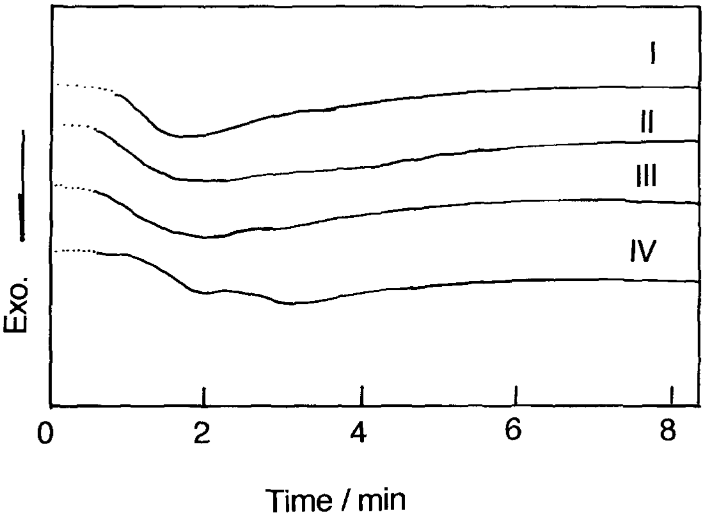

Fig. 5. Isothermal liquid crystallization curves of water–NaCS with $W_c = 0.6$ at various temperatures. Liquid crystallization temperatures: I, 245 K; II, 246 K; III, 247 K; IV, 248 K.

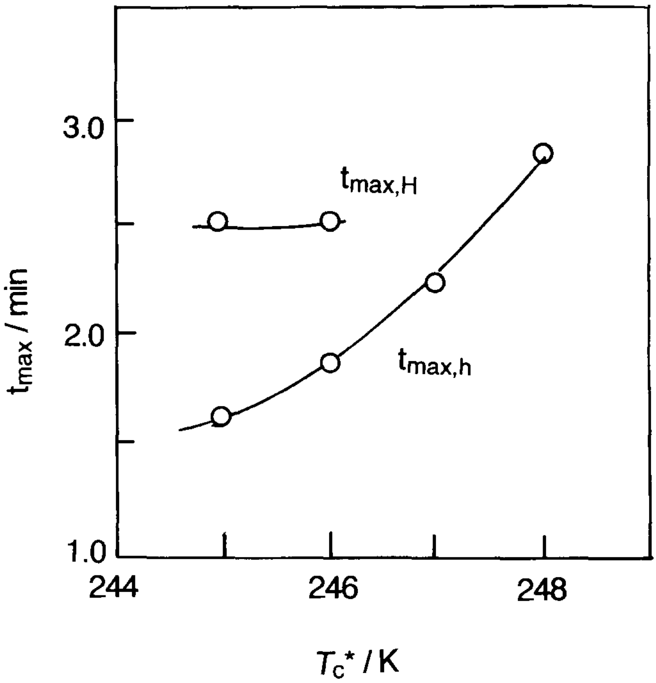

Fig. 6. Relationships between times of endothermic peaks ($t_{\text{max,h}}$, $t_{\text{max,H}}$) and liquid crystallization temperature (T_c^*).

Immediately after completing the isothermal liquid crystallization at various values of T_c^*, the sample was heated from the T_c^* to 320 K at 10 K min^{-1}. An endothermic peak with a shoulder on the low temperature side was observed. At a high temperature of liquid crystallization, the high peak (T_H^*) was formed, indicating that holding the sample isothermally at a high temperature yields almost the same results as obtained with the slow heating rate. The time interval of the liquid crystallization was influenced by W_c, T_c^* and also by other dynamic factors, such as thermal histories.

The liquid crystallization was stopped before completion and the sample was heated immediately at the heating rate of 10 K min^{-1}. For example, the isothermal liquid crystallization of the sample with $W_c = 0.5$, which takes place at 259 K, was stopped at various time intervals ranging from 15 to 80 s. In DSC, heating curves for the sample crystallized for a short time showed a broad exothermic peak from 260 to 280 K before the endothermic peak T^* was observed. When the sample was annealed in the temperature range of the liquid crystalline state, the exothermic deviation disappeared, and the enthalpy of the transition from the liquid crystalline state to the liquid state (ΔH^*) increased. These results also suggest that the liquid crystallinity increased after annealing.

When the sample was annealed at a temperature in the liquid state prior to the liquid crystallization, the liquid crystallization was completed in a short time, and in consequence $t_{\max}$ decreased. The same results were obtained by decreasing the annealing temperature. By annealing in the liquid state, an increase of the enthalpy of transition (ΔH^*) was observed.

Fig. 7 shows the relationship between the enthalpy of the transition from the liquid crystalline state to the liquid state and W_c. By annealing, ΔH^* increased over the whole range of W_c.

In order to obtain direct evidence of the liquid crystal formation of the water–NaCS system, X-ray diffractometry was carried out as a function of temperature. Fig. 8 shows X-ray diffractograms of water–NaCS with $W_c = 0.89$ at various temperatures. A peak appearing at $2\theta = 7°$ is attributed to ice in the system. After the melting of the ice in the system, a small peak at 2θ = approx. 6° remains. This peak disappears at 287 K. Although X-ray measurements were carried out isothermally, the results agreed well with those obtained by DSC.

By cooling the same sample, the liquid-to-liquid crystal transition was observed reversibly as shown in Fig. 9. Similar experiments were carried out for other systems with various W_c values.

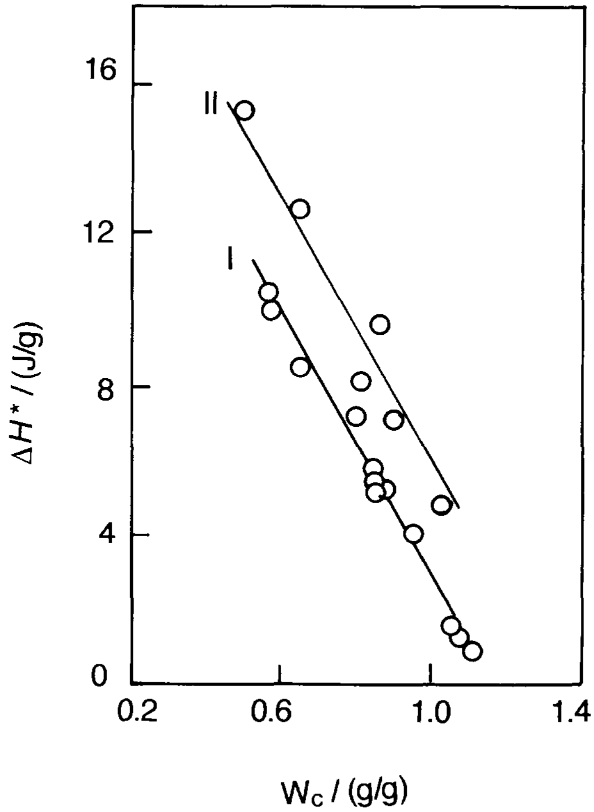

Fig. 7. Relationships between enthalpy of liquid crystal transition (ΔH^*) and W_c: I, quenched sample; II, annealed sample.

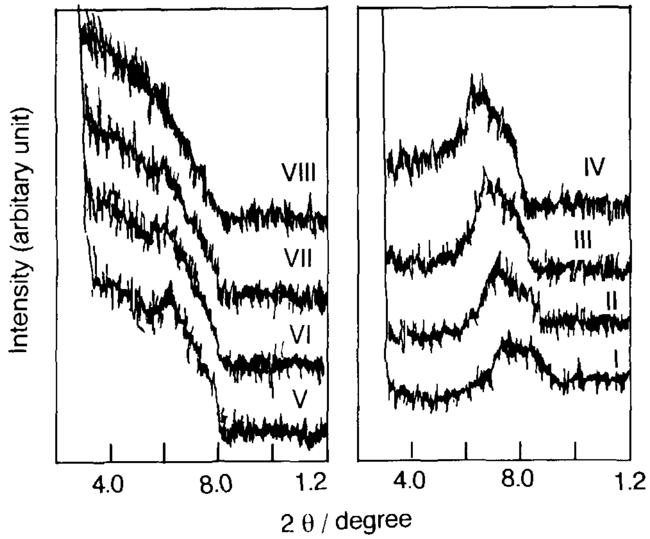

Fig. 8. X-ray diffractograms of water–NaCS systems of $W_c = 0.89$ (g/g) at various temperatures in the heating stage: I, 263 K; II, 267; III, 270; IV, 273; V, 276; VI, 279; VII, 282; VIII, 287.

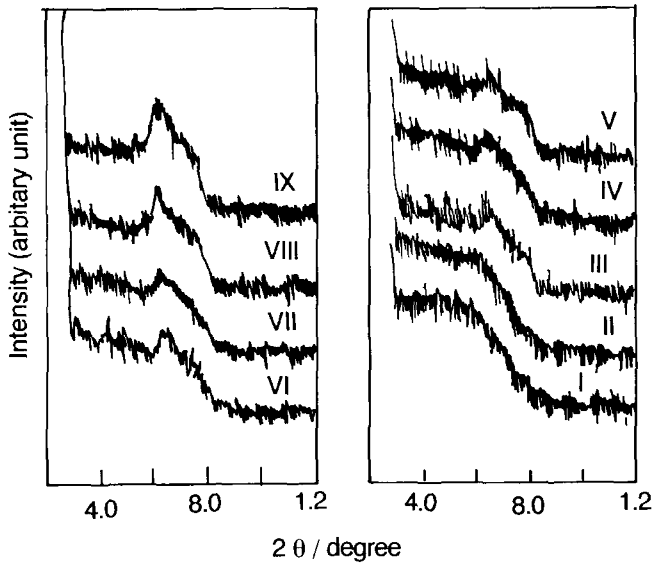

Fig. 9. X-ray diffractograms of water–NaCS systems of $W_c = 0.89$ at various temperatures in the cooling stage: I, 406 K; II, 294; III, 290; IV, 289; V, 286; VI, 283; VII, 280; VIII, 275; IX, 272.

Fig. 10 shows the relationships between the intermolecular distance calculated from X-ray diffractograms (d) and the temperature of water–NaCS systems with $W_c = 0.7$, 0.89, 1.25 and 1.40 g/g, respectively. The d values increased during the melting of ice in the system and reached a constant value. In this figure, the temperature range shows

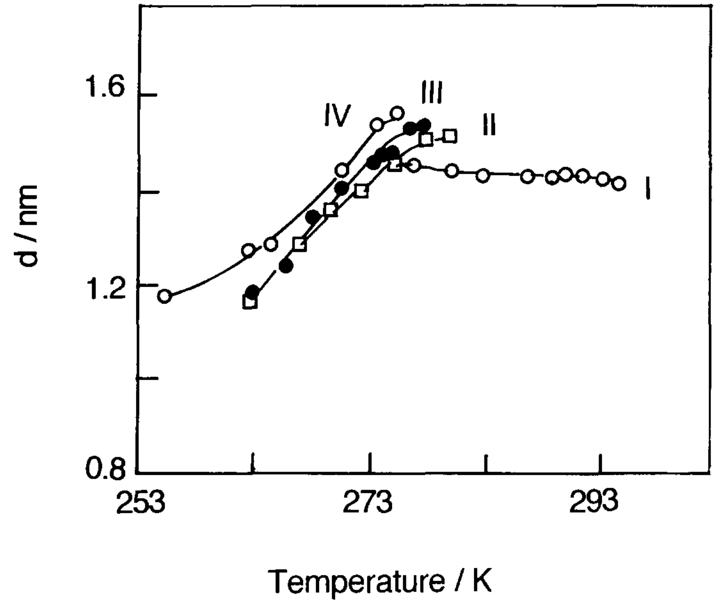

Fig. 10. Relationships between *d* and temperature of water–NaCS systems at different W_c (g/g): I, 0.7; II, 0.89; III, 1.25; IV, 1.40.

a levelling off of *d* values which corresponds to the liquid crystalline state. When W_c is 0.7, the liquid crystalline range is wide. The levelling off in temperature range decreases with increasing W_c. This agrees well with the results obtained by DSC (Fig. 3). At the same time, *d* values in the liquid crystalline region increased with increasing W_c.

Fig. 11 shows the relationship between the mean *d* values of the liquid crystalline state and W_c. It is clear that *d* expands with increasing W_c.

The main chain motion of cellulose sulphate is enhanced when approximately two water molecules are attached to one repeating unit. The main chain of cellulose units starts to align in one direction with increasing number of water molecules. The molecular arrangement is established when 4–5 water molecules are restrained by one hydroxyl group and two Na^+ ions per repeating unit.

The liquid crystalline state was observed at temperatures ranging from 265 to 310 K at a W_c of 0.4 g/g. As stated in the experimental section, the DS of this sample is approx. 2.2, and this implies that one hydroxyl group of the glucopyranose ring restricts one water molecule as non-freezing water and the other water molecules are mainly attracted by Na^+ ions. In this situation, the T_g of the system shows the lowest value, since almost all the water molecules sandwiched between the cellulose sulphate molecules form amorphous ice [15] and contribute to the molecular enhancement of saccharides. The intermolecular distance, 1.4–1.5 nm, observed by X-ray diffractometry (Figs. 8–11), corresponds to the structure where Na^+ ions are sandwiched between two cellulosic chains. This molecular structure is observed as a nematic-type liquid crystal by the observation of POL. With increasing W_c, the intermolecular

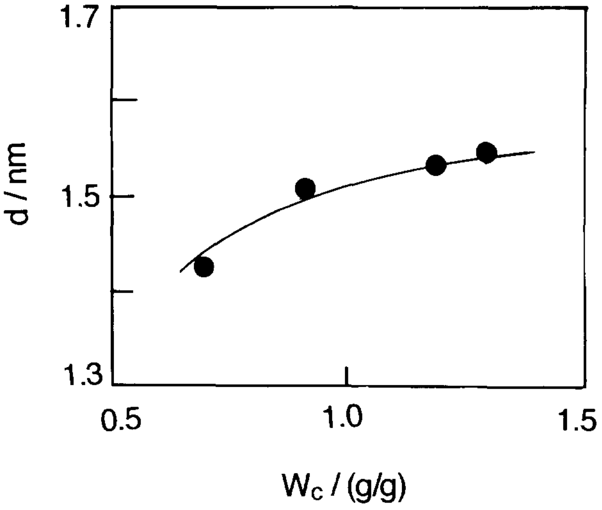

Fig. 11. Relationship between *d* and W_c of water–NaCS systems in the liquid crystalline state.

distance (*d*) increases (Fig. 11) and the liquid crystalline phase is not formed at W_c values higher than the critical value of 1.5 g/g (Fig. 3). This suggests that due to the molecular motion of free water molecules [7], cellulose molecules do not readily maintain a regular molecular arrangement and the liquid crystalline state disappears. When W_c exceeds this critical amount ($W_c = 1.5$ g/g), ordinal ice is formed in the system. T_m increased with increasing W_c and levels off at 273 K at around $W_c = 1.5$ g/g (Fig. 3).

The fact that isothermal liquid crystallization takes place in two stages indicates that there are two structures in the liquid crystalline state; one is regularly organized and the other has a slightly distorted arrangement (Figs. 4 and 5). The change in enthalpy of liquid crystal transition by annealing supports this suggestion.

The above results indicate that water–NaCS systems form unique molecular assemblies in the presence of 4–15 water molecules in one repeating unit of glucopyranose ring.

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