A differential scanning calorimetry study of the phase transition of the water–sodium cellulose sulphate system

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(Received 23 June 1986; revised 26 September 1986; accepted 28 November 1986)

Phase transition temperatures of water–sodium cellulose sulphate systems with various water contents ranging from 0 to 2.0 (grams of water per gram of polymer) were evaluated by differential scanning calorimetry. When the system was quenched from the isotropic liquid state to ~170 K, four kinds of phase transition were observed: a glass transition, cold crystallization, melting and a transition from the mesophase to the isotropic liquid state. When the system cooled gradually from the isotropic liquid state, or cooled from the mesophase, melting and a transition from the mesophase to the isotropic liquid were observed. The enthalpy of the transition indicated that each (OSO_3Na) group was surrounded by about three water molecules, which were strongly associated with the ionic groups, and behaved as non-freezing water, the transition of which could not be detected separately. A mesophase observed with water content ranging from 0.5 to 1.7, from 280 to 330 K, showed a time of reorganization of 50 to 300 s, which strongly suggests long-range order of the system.

(Keywords: cellulose sulphate; sodium salt; water; differential scanning calorimetry; glass transition; cold crystallization; melting; mesophase; non-freezing water)

INTRODUCTION

The molecular motion of water associated strongly with the hydrophilic group of a polymer is different from that of pure water. It is known that a water molecule attached directly to a hydroxyl group of a polymer through hydrogen bonding shows no phase transition, such as melting or crystallization[1]. A water molecule showing no phase transition is categorized as non-freezing water. The amount of non-freezing water associated with hydrophilic polymers that are insoluble in water is generally about one molecule to each hydroxyl group in the monomer unit, as reported previously[1–6], although the amount varies slightly, being affected by the molecular conformation. In the case of water-soluble polyelectrolytes, the amount of non-freezing water increases through ionic hydration. Owing to this, molecular motion of water in polyelectrolytes becomes difficult to treat as an independent component. The water–polyelectrolyte system in the highly concentrated region from 0 to 2.0 (grams of water per gram of polymer) is considered to be a model system whose phase transition is expected to change significantly depending on the water content of the system[7].

Sodium cellulose sulphate (NaCS) is a typical polyelectrolyte. Recently, Kamide and coworkers[8–10] studied NaCS as an anticoagulant from a physiological viewpoint. In the present study, water–NaCS systems with a water concentration from 0 to about 2.0 g/g were chosen and phase transition temperatures were investigated using differential scanning calorimetry (d.s.c.). At the same time, the bound water content was determined from the enthalpy of the transition.

EXPERIMENTAL

Sample

The NaCS used was obtained from Scientific Polymer Products, Inc. The degree of substitution (*DS*) was determined according to the procedure reported by Whistler and Spencer[11]. The obtained *DS* was 2.26.

Measurements

A Perkin–Elmer differential scanning calorimeter, DSC-II, equipped with cooling apparatus, was used. D.s.c. curves were obtained in the temperature range from 150 to 330 K; sample weights were 3–5 mg; and the scanning rate was varied from 1 to 20 K min^{-1}. Temperature and enthalpy of crystallization of the sample

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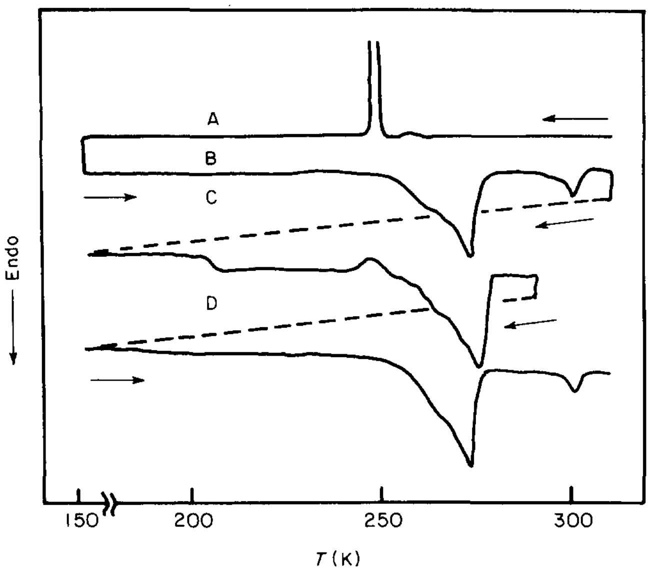

Figure 1 D.s.c. curves of water–Na cellulose sulphate: curve A, cooling curve; B, heating curve; C, heating curve of the sample quenched from 330 K; D, heating curve of the sample quenched from a temperature between the melting peak and the subpeak. Heating rate = 10 K min^{-1}

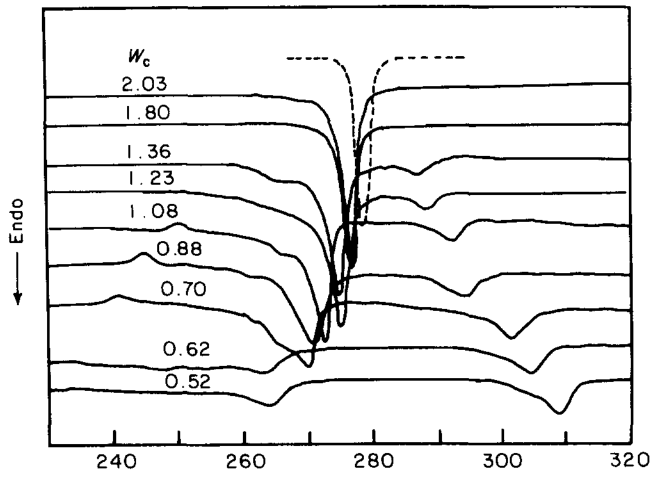

Figure 2 D.s.c. heating curves of water–Na cellulose sulphate with various water contents, W_C (g/g). The broken curve is for pure water. Heating rate = 10 K min^{-1}

were calibrated using pure water as the standard. The sample was weighed using a Sartorius microbalance with a precision of ±0.001 mg. After the d.s.c. measurement, the sample was weighed again to confirm that no weight loss had taken place.

The water content of the system was defined as:

$$\text{water content } (W_c) = \text{water/dry NaCS} \qquad (g/g) \quad (1)$$

The bound water content was calculated by a method reported previously[1-6].

The isothermal crystallization was carried out by Kamide's method[12].

A Leitz Orthoplan polarized light microscope was used for observing phase transitions.

RESULTS AND DISCUSSION

Figure 1 shows the schematic d.s.c. curves of the water–NaCS system ($W_c = 0.88$). When the sample was cooled from 330 K at the rate of 10 K min^{-1}, two exotherms were found at 255 and 248 K (curve A). When the sample was cooled from 330 K faster than a rate of 20 K min^{-1}, the peak observed at the higher-temperature side disappeared. Two peaks were resolved more clearly with decreasing cooling rate. In the heating curve B, two endothermic peaks are observed at 273 and 298 K. In curve C for the sample quenched from 330 to 150 K, a step in the baseline around 205 K, a broad exotherm whose peak is at ~245 K and an endothermic peak are observed. However, when the sample was quenched from a temperature between the two endothermic peaks observed in curve B, for example from 290 K, as shown in curve D in *Figure 1*, only two endotherms were observed, similar to the curve B. Even when the cooling rate was fast, the heating curve showed a similar pattern to curve D.

Figures 2 and *3* show the d.s.c. heating and cooling curves of quenched water–NaCS systems with various amounts of water. By comparing the curve of pure water (broken curves) with those of *Figures 1* and *2*, the endotherm at around 270 K was attributed to the melting of water in the system. The peak temperature of melting

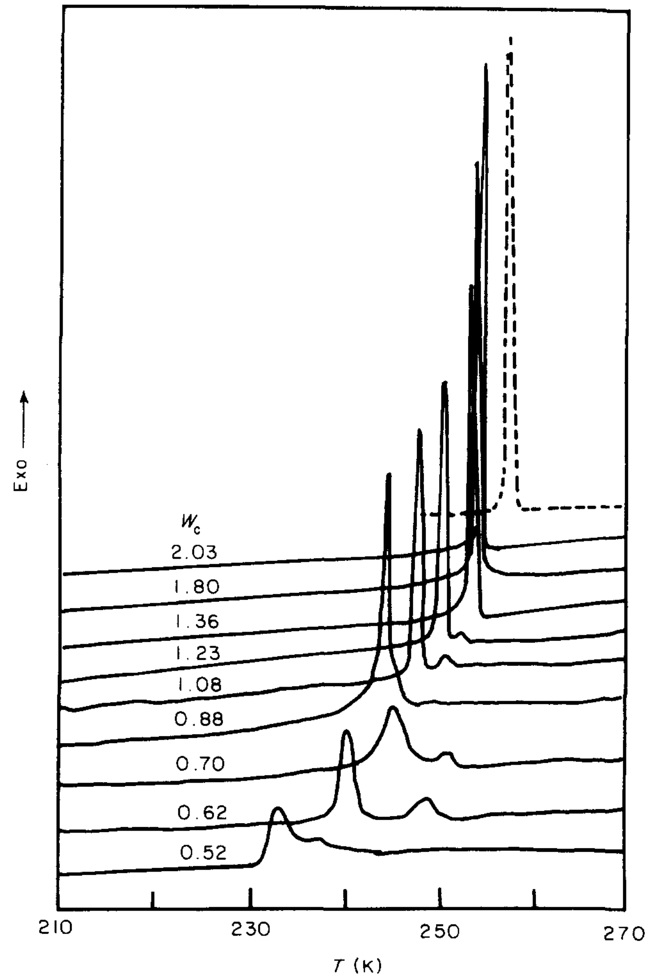

Figure 3 D.s.c. cooling curves of water–Na cellulose sulphate with various water contents, W_C (g/g). The broken curve is for pure water. Cooling rate = 10 K min^{-1}

shifts to the low-temperature side and the peak width becomes broader and more asymmetric with decreasing water content. These facts suggest that the structure of freezing water in the system is affected by the NaCS. The melting temperature and peak shape varied not only with water content but with the thermal history of each sample. The melting peak shifted slightly to the higher-temperature side when the sample cooled slowly.

The main exotherm around 252 K in *Figure 1*, and those in *Figure 3*, can be attributed to the crystallization of water in the system. The crystallization temperature changed as a function of water content as shown in *Figure 3*.

The d.s.c. heating curve C in *Figure 1* indicates that a glassy sample is formed by quenching from a temperature higher than the subpeak, which is named T^*. The temperature of the step in the baseline increased with increasing heating rate. At the same time, enthalpy relaxation was observed by slow cooling or annealing at a temperature lower than the endothermic deviation of the baseline. The above facts indicated that the step in the baseline was regarded as the glass transition temperature (T_g). When the system contained a water content > 1.4, T_g could not be detected. The result indicates that the glassy state of the water–NaCS system can be obtained by quenching from a temperature higher than T^* in systems whose water contents are up to 1.4 (g/g). This will be discussed further in a later section.

The water–NaCS system takes a random arrangement when it is quenched from a temperature higher than T^*. The above fact indicates that the molecular chain assumes an ordered state at a temperature between T_m and T^*. In order to obtain more detailed characteristics of the intermediate state between T_m and T^*, the enthalpy of transition of the melting of the subpeak was calculated as a function of water content. The enthalpy of transition (ΔH) decreases linearly with increasing water content, and it becomes undetectable at a water content of 1.80. The maximum value (~ 20 J/g (total weight of water and NaCS)) is obtained at a water content of 0.40, which is the critical water content. The critical water content corresponds to the water content from which the first-order phase transition of water becomes detectable by d.s.c. This is clearly seen in the d.s.c. curves in *Figures 2* and *3*.

The texture of the sample was observed using a polarized light microscope equipped with a temperature controller from -70 to 50°C. Nitrogen gas cooled by liquid nitrogen passed through the sample cell and similar thermal hysteresis was applied to the sample. Although the W_c of the sample could not be kept entirely constant owing to the structure of the sample cell, the texture showing the nematic type molecular arrangement was observed at a temperature between T_m and T^*. From the results obtained by microscopy and d.s.c., it is considered that the intermediate phase appears in a very narrow water content region, and the excess amount of water disturbs the formation of the mesophase.

It was also found that the rate of formation of this intermediate phase was slow, compared with the crystallization rate of water in the system. The temperature difference between T_m and T^* increased with decrease of the cooling rate. Two endothermic peaks merged when the cooling rate exceeded 20 K min^{-1}.

Figure 4 shows the isotherms of the water–NaCS system ($W_c = 0.88$) at various temperatures. Each system was kept at a temperature higher than T^* (310 K) for a minute, and then cooled rapidly to the crystallization temperature. The exothermic heat was recorded as a function of time. As shown in the figure, smooth and monotonic isotherms are observed at 250 and 252 K, and the crystallization is completed in 1 to 2 min. However, a shoulder is observed in the isotherm at 253 K, indicating that two different crystallization mechanisms are concerned in the transition from the liquid state to the mesophase. After the crystallization was completed, each sample was heated at a rate of 10 K min^{-1}. The endothermic peak showed a smooth curve with a broad tail on the low-temperature side. The peak was observed at 300 K, regardless of the crystallization temperature. In this experiment, the molecular significance of the two-step crystallization has not been elucidated. We carried out the isothermal crystallization of water in the system at various crystallization temperatures. The crystallization was completed in several seconds. This means that the time interval during which the temperature of the d.s.c. sample holder reached an isothermal state could not be neglected. This shows that the formation of the mesophase takes far longer than the crystallization of free water in the system. This suggests that both water and NaCS were connected with the transition from the liquid state to the mesophase.

Figure 5 shows the phase diagram of the quenched water–NaCS system, indicating that the quenched system consists of glassy, crystalline, meso and isotropic liquid states, respectively. The phase diagram of the water–NaCS system, obtained by slow cooling, lacks T_g and T_{cc}. The temperatures T_m and T^* were the same for both quenched and slowly cooled samples.

Figure 6 shows the relationship between W_c and weight of water calculated from the enthalpy of melting (W_f). In the system, the first-order transition was not detected when W_c was smaller than 0.38. By the subtraction of W_f from W_c, the amount of non-freezing water (W_{nf}) was calculated:

$$W_{nf} = W_c - W_f \tag{2}$$

W_{nf} is also shown in *Figure 6*. The slight increase of W_{nf}

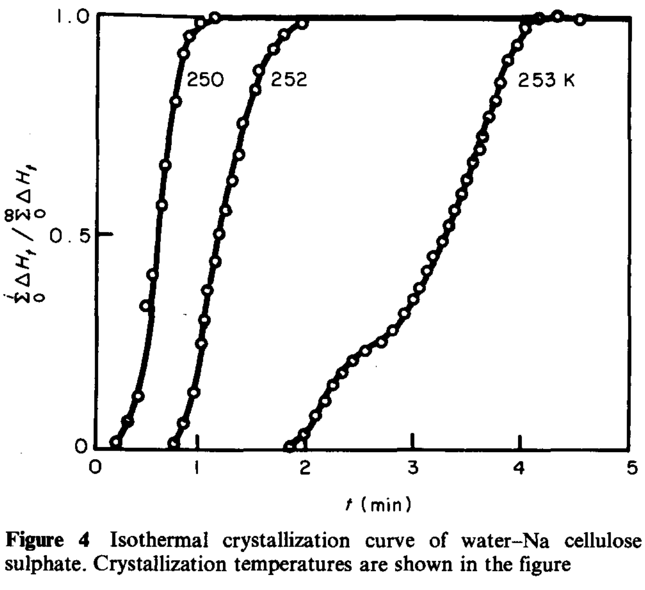

Figure 4 Isothermal crystallization curve of water–Na cellulose sulphate. Crystallization temperatures are shown in the figure

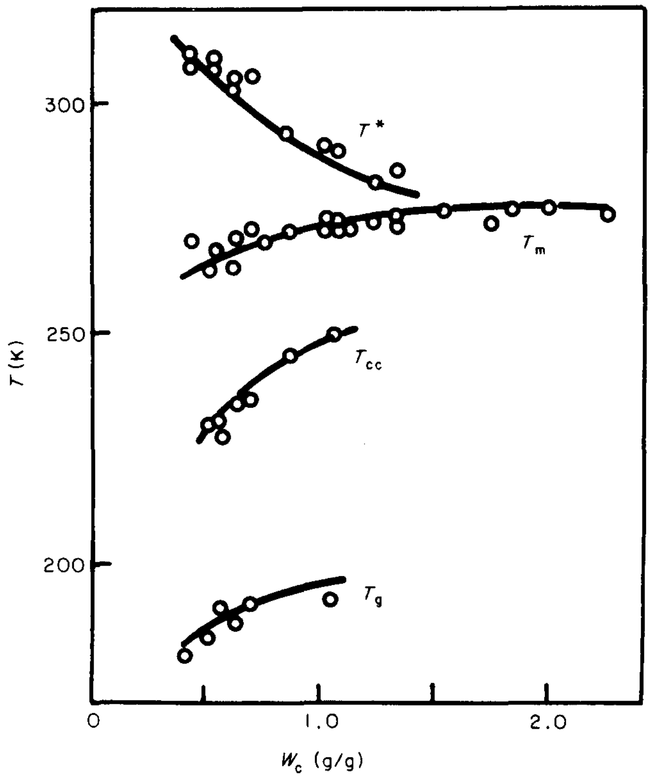

Figure 5 Phase diagram of quenched water–Na cellulose sulphate system

with increasing W_c suggests that the higher-order structure of NaCS changes as a function of W_c. It is reasonable to consider that the extended W_{nf} line (dotted line in *Figure 6*) intersects with the ordinate at 0.38, since freezing water appears at 0.38. As the degree of substitution of the SO_3 group was 2.26, as described in the 'Experimental' section, the amount of water molecules attached to NaCS as non-freezing water was calculated to be three molecules. In this calculation the W_{nf} bonded to the hydroxyl group, which was not substituted to the sulphate group, was assumed to be one molecule. By previous results obtained by n.m.r. relaxation[13,14], an activation energy for the reorientational process of water molecules in the hydration shell of sodium ions was 2.9 kcal mol^{-1}, which was calculated from the correlation time. This also indicates the strong interaction between water molecules and sodium ions in the first hydration shell.

The glassy state of the water–NaCS system was observed from the $W_c \simeq 0.4$. This value was almost the same as the maximum value of W_{nf} ($=0.38$). The glassy state could not be detected when the number of free water molecules in the system was more than about eight (corresponding to $W_c \simeq 1.4$). It is reasonable to assume that the free water in the system crystallizes during cooling from 330 to 150 K when the system contains many free water molecules. It is known that the temperature of supercooling of free water depends on the size of the molecular assembly[15]. Therefore, it is thought that the thermal hysteresis applied to the sample may be sufficiently long to complete the crystallization of free water when $W_c > 1.4$. The random arrangement of molecular chains in the liquid state of the water–NaCS system is frozen at low temperatures and forms the glassy state only when the W_c of the system is of sufficient magnitude. An adequate amount for molecular movement is $W_c \simeq 0.4$, but this is not sufficient for the crystallization of free water. It is also noteworthy that the mesophase is observed in a similar W_c range where T_g was observed. The glassy state and the mesophase of the water–NaCS system seem to be related to the homogeneity of the system, which contains a moderate amount of water that enables simultaneous molecular movement.

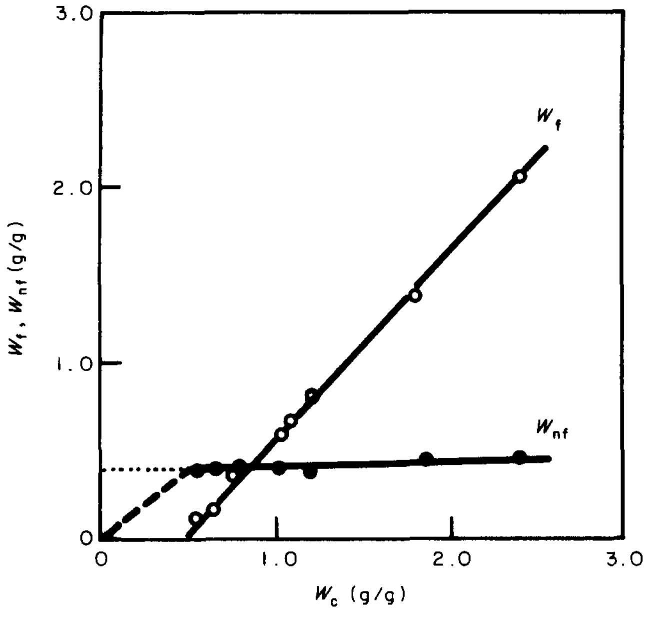

Figure 6 Relationship between water content (W_c) and freezing water content (W_f) or non-freezing water content (W_{nf})

Therefore, it is appropriate to consider that our data obtained by d.s.c. suggest the presence of water molecules that contact directly sodium ions. Especially, when three water molecules attach to the sodium ion and one water molecule to the hydroxyl group of NaCS, the water molecules become 'non-freezing water'. Phase transition behaviour of the system clearly relates to the homogeneous nature of water and polyelectrolytes.

ACKNOWLEDGEMENT

We are grateful to Dr Kunio Nakamura, Industrial Research Institute of Kanagawa Prefecture, for helpful discussions.

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