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Studies on Bound Water of Cellulose by Differential Scanning Calorimetry

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ABSTRACT

The crystallization and melting of adsorbed water on cellulose samples such as cotton, kapok, linen, jute, various rayons, and wood cellulose have been studied using a differential scanning calorimeter (DSC). Two exothermic peaks of crystallization of adsorbed water on the cellulose samples are observed. One is a sharp peak (Peak I) observed at about 255 K in a DSC curve; the other is a broad peak (Peak II) observed at about 230–250 K. Judging from the amounts of water calculated from the results obtained by the DSC study, there seems to be some nonfreezing water which does not crystallize. Therefore, we have categorized water adsorbed on cellulose samples as one of three different kinds: free water (Peak I), freezing bound water (Peak II), and nonfreezing bound water.

The bound water content is dependent on the degree of crystallinity of cellulose samples. The amounts of bound water estimated are from 1.0 to 2.2 moles per one glucose unit of cellulose. However, the amount of water bound to each glucose unit was 3.4 moles, if we took into consideration that water diffuses only into the amorphous region of each cellulose sample.

Introduction

Many different workers have shown that water sorbed by natural polymers has properties that are markedly different from free water. It has been considered that the molecular motion of the water is restricted by polymers. However, different names such as "bound," "ordered," "ice-like," or "nonfreezing" have been given to the water. Magne *et al.* [15, 16] and other authors [1, 6, 9, 19, 20] reported that melting and crystallization temperatures of the bound water in polymers such as cellulose and keratin are lower than those of free water or ordered water. Amounts of bound water have been already reported by several authors. However, the definition and the amounts of bound water in cellulose have been reported differently by authors [2, 7, 9, 18, 21].

In this paper, therefore, we define in the following experiments that "free water" is the unbounded water in polymers whose transition temperature, enthalpy, and peaks in DSC curves are equal to those of pure water. "Bound water" is the water restricted by hydroxyl groups of cellulose molecules, the transition temperature of which is lower than that of pure water. We also define "nonfreezing water" as a kind of bound water whose transition is not detected in the first-order transition.

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There have been many techniques reported for detecting the water adsorbed on polymers [4]. However, differential scanning calorimetry (DSC) is a useful technique to evaluate quantitatively free and bound water contents [10]. We have measured the phase transition of water adsorbed on different kinds of cellulose by DSC. The amount of adsorbed water depends on the amount of amorphous material, which is evaluated from x-ray analysis.

Experimental

MATERIALS

Cellulose samples used in this experiment are natural celluloses such as cotton lint, cotton yarn, linen yarn, jute, kapok, wood cellulose, and regenerated celluloses such as viscose rayon, cupra rayon, polynosic rayon, etc. These cellulose samples were purified by extracting contaminants with toluene, carbon tetrachloride, and *n*-hexane successively using a Soxhlet extractor. The cellulose samples were cut to a fine powder to eliminate the effect of fiber orientation.

MEASUREMENTS

X-Ray Diffractometry

A Rigaku Denki Co. x-ray diffractometer Rotaflex RU-100-PL was used to evaluate the degree of crystallinity of the cellulose samples. The x-ray diffraction patterns were recorded employing a scintillation counter and a rate-meter using CoKα radiation with a crystal monochrometer operated at 42.5kV and 30mA. The degree of crystallinity was calculated according to the integral intensity method by integrating the area between diffraction angle 2θ from 8° to 42° compensating for Compton scattering by air. The scattering angle range decided by Hermans [12, 13] was adopted in this experiment. The degree of crystallinity was calculated from the following equation:

$$\text{Degree of crystallinity} = \frac{\text{integral intensity of crystalline region}}{\text{integral intensities of amorphous and crystalline regions}} \times 100(\%) \quad (1)$$

Differential Scanning Calorimetry (DSC)

A Perkin Elmer differential scanning calorimeter DSC-1B equipped with cooling cells was used to measure the phase transition of water adsorbed on the cellulose samples. DSC curves were obtained by cooling at the scanning rate of 8 K/min from room temperature to 200 K and then heating to room temperature at the same rate. The temperature of crystallization and melting of adsorbed water were calibrated using melting and crystallization peaks of pure water. The enthalpy of water adsorbed on samples was calculated according to the enthalpy of possible polymorphism of ice. The cellulose samples were dried in a vacuum desiccator for about 1 week, and then each 5-mg sample was weighed in an aluminum pan for a volatile sample. The aluminum pan had been previously heated at 373 K in an autoclave with water to eliminate any reaction between the aluminum surface and water. A certain amount of water was added to each sample by a micro-syringe and then the pan was sealed. The water content was calculated as follows:

$$\text{Water content} = (\text{weight of water}/\text{weight of sample}) \times 100(\%) \quad (2)$$

Each sample pan was heated at 70°C for 1 h and was allowed to stand for a few days in order to have samples with the same thermal history.

A Seiko Co., Ltd. differential scanning calorimeter SSC/560 was also used to measure the samples at lower than 300 K. Using the apparatus, it was possible to obtain the cooling curves of samples from room temperature to 130 K. Heating rate was 5 K/min, and each sample weight was *ca.* 5mg.

Results and Discussion

Figure 1 shows the schematic DSC curves of cooling and heating of water adsorbed on cellulose samples. When a sample containing water was cooled from room temperature to 200 K, the first-order transition of water was not recognized at first unless the water contents exceeded a certain amount. This phenomenon was also confirmed by cooling to 130 K using a Seiko DSC SSC/560. The amount of the first-order transition of water varied according to the chemical structure and/or the higher order structure of each sample. Before exceeding this water content, a broad crystallization peak (Peak II) appeared at about 230–250 K. This peak shifted to higher range of temperature with increasing amounts of adsorbed water. The enthalpy calculated from the area of Peak II increased with increasing water content until it attained a certain value; this water content depends on the number of

hydrophilic groups. A new sharp peak (Peak I) appears when the amount of water in each sample exceeds that needed to show a constant Peak II in a DSC curve. The shape and temperature of Peak I accords well with that for the crystallization of pure water, as shown in the dotted curves in Figure 1, although Peak I is broadened slightly in the low-temperature side. In general, with further increase of water the enthalpy of Peak I increases, whereas that of Peak II remains constant.

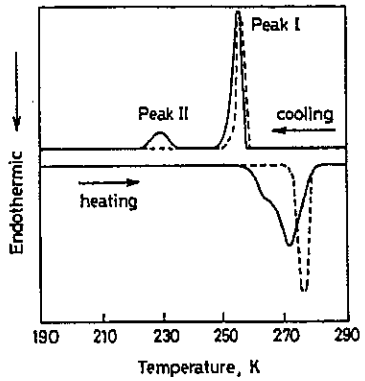

FIG. 1. Schematic DSC curves of water adsorbed on various cellulose samples. Heating and cooling rate is 8 K/min. —— = adsorbed water, ----- = pure water.

The schematic heating curves of adsorbed water starts from a lower temperature than that of pure water, as shown in the dotted line. The shape varies according to the water content and/or properties of a sample such as cotton or jute. In some cases a shoulder was found in the low-temperature side of a melting peak. In general, asymmetry was observed as a characteristic pattern of the melting of adsorbed water. If water is added to hydrophobic polymers such as polystyrene, DSC heating and cooling curves of water show a pattern similar to that of pure water.

In the case of the crystallization of water adsorbed on cellulose samples, the sum of the weight of water calculated from enthalpies of Peak I and Peak II is less than the total weight of added water. The amount of water corresponding to the difference between the added water and the amount of water calculated from DSC must be present somewhere. It is very obvious that water cannot move to the outside of a volatile sample pan in our experimental conditions, because no first-order transitions were observed except for crystallization or melting in each of cooling and heating curves. Accordingly, the only possibility is that the water combined very tightly to cellulose molecules. Therefore, the following equations can be obtained:

$$W_t = W_{p1} + W_{p2} + W_{nf} \quad ; \tag{3}$$

$$W_t = W_m + W_{nf} \quad , \tag{4}$$

where W_t = total weight of water added to a sample, W_{p1} = weight of water calculated from the enthalpy of crystallization Peak I, W_{p2} = weight of water calculated from the enthalpy of crystallization Peak II, W_{nf} = weight of nonfreezing water, and W_m = weight of water calculated from the enthalpy of melting.

From Equations 3 and 4, W_m can be shown as follows:

$$W_m = W_{p1} + W_{p2} \quad . \tag{5}$$

The weight of bound water can be shown as follows:

$$W_b = W_{p2} + W_{nf} \quad , \tag{6}$$

where W_b = weight of bound water. The percent bound water content is calculated by the following equation:

$$C_b = W_b / W_s \times 100(\%) \quad , \tag{7}$$

where C_b = percent bound water and W_s = weight of sample. It will be noted that the amounts of bound water (W_b) shown by Equation 6 can be obtained directly from a DSC cooling curve (Equation 3), while W_{p2} of crystallization Peak II is difficult to evaluate from a DSC heating curve, because of the difficulty in separating the melting peaks as represented by W_m from W_{p1} and W_{p2} of Equation 5. Therefore, the bound water content (C_b) can only be calculated by using DSC cooling curves.

Figure 2 shows DSC heating and cooling curves of various amounts of water adsorbed on viscose rayon. Any kind of first-order transition of adsorbed water is not recognized until the water content exceeds 19.6% by weight. The broad crystallization peak (Peak II) appears at about 230–250 K in the water content region from 19.6–23.0%. A new sharp crystallization peak (Peak I) appears at about 255 K when the water content exceeds 23.0%. The DSC heating curve of water adsorbed on a sample also shows a broad peak in the region of 23.0% of water. The overlapping of broad and sharp peaks is clearly observed if the water content exceeds 23.0%.

Figure 3 shows crystallization of water adsorbed on various kinds of cellulose samples. In the case of cotton and linen celluloses, the starting point of crystallization Peak II is observed at about 232 K as a very small peak. However, in the case of polynosic rayon, kapok, jute, and wood celluloses, Peak II is observed at a higher temperature than those of cotton and linen

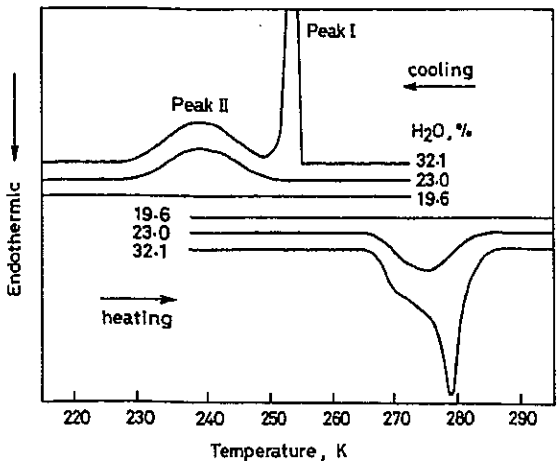

FIG. 2. DSC cooling and heating curves of various amounts of water adsorbed on viscose rayon. Cooling and heating rates are 8 K/min.

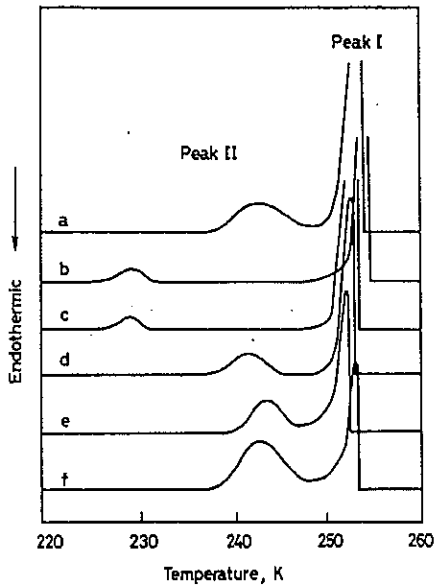

FIG. 3. DSC cooling curves of water adsorbed on various kinds of cellulose samples. Heating rate is 8 K/min. a = polynosic rayon, b = cotton, c = linen, d = jute, e = kapok, f = wood cellulose.

celluloses. Moreover, in these cases Peak II is observed as a larger peak than those of cotton and linen celluloses. The above facts suggest that the water which appeared as Peak II is affected by the higher-order structure of cellulose samples.

Figure 4 shows melting curves of water adsorbed on various cellulose samples. It is clearly seen that the

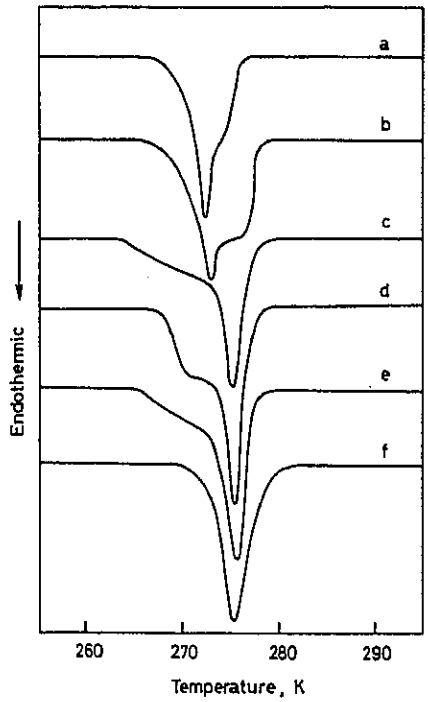

FIG. 4. DSC melting curves of water adsorbed on various kinds of cellulose samples. Cooling rate is 8 K/min. a = cotton, b = polynosic rayon, c = jute, d = wood cellulose, e = linen, f = Kapok.

broad and sharp melting peaks overlap together in the melting peak. The starting temperature of the broad peak is found at about 265 K, and the pattern of each broad peak is quite similar to that of viscose rayon, containing only bound water (melting curve of 23.0% of water in Fig. 2). Moreover, the sharp melting peaks of jute, linen, kapok, and wood cellulose are found at 276 K, which accords well with that of pure water at the heating rate of 8 K/min.

Figure 5 shows x-ray diffraction patterns of cellulose samples. In the case of cotton and linen celluloses, the diffraction peaks of (101), ($10\bar{1}$), and (002) are observed at 2θ of 17°, 19°, and 26°, respectively. However, in the case of other native celluloses such as kapok, jute, and wood cellulose, diffraction peaks of (101) and (002) are observed at 2θ of 18° and 26°, respectively. The (101) diffraction peaks of jute and kapok include the ($10\bar{1}$) diffraction peak; the (002) diffraction peak includes the (021) diffraction peak. In the case of regenerated celluloses of cupra rayon and viscose rayon, x-ray patterns apparently separate into three diffraction peaks of (101) at about 15°, ($10\bar{1}$) at about 23°, and (002) at about 26°. The (101) diffraction peaks of cupra rayon and viscose rayon include the (021) diffraction peaks.

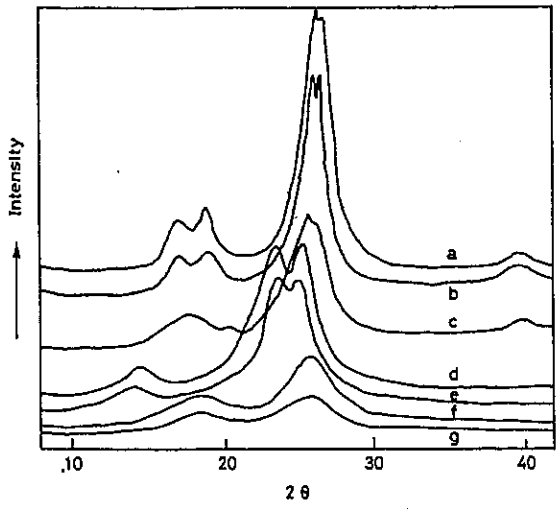

FIG. 5. X-ray diffraction patterns of various kinds of cellulose samples. a = linen, b = cotton, c = wood cellulose, d = cupra rayon, e = viscose rayon, f = jute, g = Kapok.

The degree of crystallinity was calculated by the integral intensity method, as shown by Equation 1. The degree of crystallinity of kapok, jute, viscose rayon, cupra rayon, wood cellulose, polynosic rayon, cotton lint, cotton yarn, and linen yarn were calculated as 33, 36, 42, 43, 44, 46, 52, 54, and 69%, respectively.

The above facts reveal that water molecules in the amorphous region of cellulose samples have a strong relation with the bound water content. It is well known that the moisture regain depends on the molecular structure of the amorphous part of a polymer [6, 15]. Moreover, it is known that the interaction between water molecules and the adsorption site of a polymer is appreciable [17, 18]. It is also well known that the diffusion coefficient generally depends on the higher structure of a polymer [3, 14]. In a previous report [11], the diffusion coefficient was shown to have a strong relation with the amorphous fraction of cellulose, since the water molecule can diffuse only through the amorphous part of cellulose samples. Accordingly, the establishment of the relationship between water molecules and the adsorption sites of cellulose samples is very necessary.

It is appropriate to consider that there are three kinds of adsorbed water: *i.e.*, nonfreezing water, freezing bound water, and free water, due to the interaction of cellulose molecules and water. Nonfreezing water having none of the first-order transition does not seem to have any kind of crystalline structure. Freezing bound water (Peak II) and free water having crystallization and melting must have certain kinds of crystalline structure which may be the same as the structure of natural ice, regardless of the crystalline morphism. There are nine polymorphic forms of ice: *i.e.*, ice I, Ic, II, III, IV, V, VI, VII, and VIII [5]. The structures from ice IV to ice VIII are found only at very high pressures. Therefore, in our experimental conditions the possible structures of ice for freezing bound water can be considered as ice I, Ic, II, and III. The maximum value of melting enthalpy of ice (ice I) is estimated as 334J/g, and the minimum value of melting enthalpy of ice (ice III) is estimated as 311J/g, from the phase diagram of water [5]. Table I shows the bound water contents calculated using enthalpy values of both ices I and III.

Figure 6 shows the relationship between the degree of crystallinity of cellulose samples and contents of bound water and nonfreezing water shown in Table I. The cited values [8] of the moisture regain in the relative humidity (RH) of 65% at 25°C are also presented in this figure. Both bound water and nonfreezing water contents decrease with increasing degree of crystallinity of cellulose samples; furthermore, the bound water content approaches the nonfreezing water content with increasing degree of

TABLE I. Characteristics of cellulose samples.

	Degree of crystallinity, %	Regain, %	Non-freezing water, %	Peak II, %	Bound water, %	M_b, mole	M_{bo}, mole
Linen yarn	69	7	10.5	0.8	11.3	1.0	3.3
Cotton yarn	54	8	14.0	2.0–2.1	16.0–16.1	1.5	3.2
Cotton lint	52	8	17.8	2.1–2.2	19.9–20.0	1.8	3.8
Wood cellulose	44	11	18.6	3.8–4.1	22.4–22.7	2.0	3.6
Jute	36	12	18.4	5.5–5.9	23.9–24.3	2.2	3.4
Kapok	33	10	14.9	7.9–8.5	22.8–23.4	2.1	3.1
Polynosic rayon	46	12	19.8	1.4–1.5	21.1–21.2	1.9	3.5
Cupra rayon	43	11	18.0	3.7–4.0	21.7–22.0	2.0	3.5
Viscose rayon	42	11	19.6	3.2–3.4	22.8–23.0	2.1	3.7

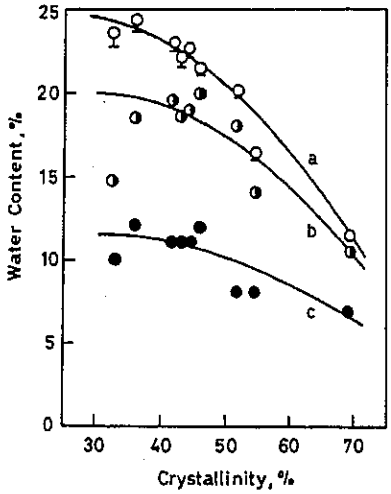

FIG. 6. The relationship between degree of crystallinity of cellulose samples and contents of bound water, nonfreezing water, and cited regain at RH 65%, 25°C [8]. a = content of bound water, b = content of nonfreezing water, c = cited regain at RH 65%, 25°C.

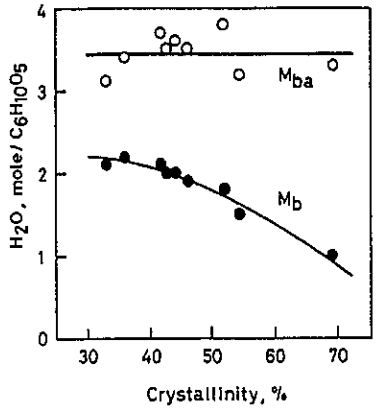

FIG. 7. The relationship between degree of crystallinity of cellulose samples and the moles of bound water adsorbed on the glucose unit ($C_6H_{10}O_5$) of cellulose molecules and those in the amorphous region of samples. M_b = moles of bound water adsorbed per glucose unit of cellulose samples; M_{ba} = moles of bound water adsorbed per glucose unit in the amorphous region of cellulose samples.

crystallinity of samples. This means that the amount of crystallizable bound water (Peak II) decreases with increasing degree of crystallinity of cellulose samples. The moisture regain also decreases with increasing degree of crystallinity of samples. These facts indicate that only the amorphous region in cellulose molecules can be regarded as the adsorption site of water molecules.

The moles of water adsorbed on a glucose unit ($C_6H_{10}O_5$) of cellulose can be calculated by the following equation:

$$M_b = \frac{162 \times W_b}{18 \times W_s} = \frac{9 \times W_b}{W_s} = 0.09C_b \quad , \qquad (8)$$

where M_b = the moles of water adsorbed on a glucose unit, and the numbers 162 and 18 are molecular weights of a glucose unit of cellulose and water, respectively. The moles of bound water adsorbed on a glucose unit in the amorphous region of cellulose samples are calculated by the following equation:

$$M_{ba} = \frac{M_b \times 100}{100 - \text{degree of crystallinity}} \quad , \qquad (9)$$

where M_{ba} = the moles of bound water adsorbed on a glucose unit in the amorphous region of cellulose samples.

The curve M_b in Figure 7 shows the relation between the degree of crystallinity and the moles of bound water adsorbed on a glucose unit of cellulose molecules. It is clearly seen from Figure 7 that M_b decreases with increasing degree of crystallinity of samples in a similar manner as in the case of bound water content. However, it is necessary to correct the values of M_b, since the water molecules can only be adsorbed in the amorphous region of cellulose samples. The curve M_{ba} in Figure 7 shows the moles of bound water adsorbed on a glucose unit in the amorphous region as calculated from the results obtained by x-ray diffractometry of cellulose samples. M_{ba}, the corrected value of M_b that shows the moles of water adsorbed on a glucose units in the amorphous region of cellulose molecules, is nearly constant at about 3.4 moles per glucose unit. This fact suggests that water molecules of bound water attach three hydroxyl groups in the amorphous region of cellulose molecules.

From the results, it is clear that three different kinds of water exist in the adsorbed water on cellulose samples: *i.e.*, free water (Peak I), freezing bound water (Peak II), and nonfreezing bound water. The bound water molecules are in the amorphous region of cellulose and attach to the three hydroxyl groups of each glucose unit.

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