# Types of adsorbed water in relation to the ionic groups and their counter-ions for some cellulose derivatives

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The sorption of moisture by different cellulose derivatives was examined as a function of relative humidity, to evaluate the influence of counter-ions and different charged groups on the moisture adsorption mechanism. Studies were made on cellulosic materials containing sulfate ($-O-SO_3H$) and carboxylic ($-COOH$) groups in different ionic forms ($H^+$, $Li^+$, $Na^+$, $K^+$ and $Ca^{2+}$). Uncharged cellulose and amylose were also examined for comparison. It was shown that the choice of counter-ions had a large influence on the moisture uptake by the studied polymers. Moisture adsorption by cellulose containing sulfate acid groups was favoured by the counter-ion $H^+$, rather than, in order of decreasing efficiency, by $Li^+$, $Na^+$, $Ca^{2+}$ and $K^+$. Two types of differently adsorbed water were found: non-freezing bound water and freezing bound water. Most of the differences in total moisture content were due to differences in the freezing water content. The counter-ion favouring water adsorption in the case of the cellulose containing carboxylic acid groups was $Li^+$, followed, in decreasing order of efficiency, by $Na^+$, $K^+$, $Ca^{2+}$ and $H^+$. In this case, the differences in total water content were found in both the non-freezing and freezing water. It was furthermore shown that the presence of charged groups was necessary for the adsorption of freezing water when the relative humidity was less than 100%. The large influence of the counter-ions on water adsorption may be associated with the ionic radius (size of the counter-ion), which influences the degree of hydration. Differences in water adsorption for the protonated form may be explained by the observation that carboxylic acids are weak acids with limited dissociation, whereas the stronger sulfate acid groups facilitate a more complete dissociation.

**(Keywords: cellulose derivatives; moisture adsorption; ionic effects)**

## INTRODUCTION

It is well known that moisture sorption has a significant influence on the physical properties of lignocellulosic materials, affecting both swelling and softening. Moisture sorption is affected by the number of ionic groups in the material as well as by the nature of these ionic groups and the type of counter-ion present. The important binding sites for water molecules on wood polymers are: hydroxyl groups, carboxylic acid groups (mainly present in the xylan of the pulp) and sulfonic acid groups (predominantly present in lignin after sulfonation reactions). Several studies have been performed to obtain an understanding of the adsorption mechanism and the characteristics of water molecules adsorbed to a polymer system. An understanding has been achieved using a variety of techniques, such as infra-red absorption (i.r.)[1], nuclear magnetic resonance (n.m.r.)[2-7] and differential scanning calorimetry (d.s.c.)[5,7-11]. Adsorption has been explained either as the development of hydrous molecular layers[2,8,12], or as hydrous multi-clustering[2,3,12-19].

Studies on the effects imposed on the water adsorption of pulp by the presence of different charged groups are rather limited[7,20]. Most of the previous studies on the cellulose adsorption mechanism, involving different charged groups and their counter-ions, have been devoted to wet conditions where the range of moisture content has varied from anhydrous to far beyond the fibre saturation point[4,21-23]. In this work, the nomenclature adopted by Yoshida *et al.*[24] has been employed. Water showing a first-order phase transition (melting or crystallization) was called freezing water, and water showing no transition down to 130 K was called non-freezing water.

In order to elucidate the role of the ionic groups and their counter-ions on the amounts and types of differently adsorbed water, this study has investigated the sorption of moisture by several cellulosic derivatives. Uncharged cellulose and amylose were also examined as reference substances.

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## EXPERIMENTAL

### *Materials*

*Viscose.* Viscose (MoDoCell AB, Alfredshem, Sweden) was used to manufacture cellulose gels. Crude viscose was purified by ion exchange on Amberlite IRA-400 saturated with hydroxide ions. The viscose solution was then carefully placed under vacuum (to remove any air) before being transferred to glass tubes. Physically crosslinked gels were produced by keeping the viscose solution at 40°C for 14 h, followed by 5 h at 60°C, under nitrogen[25]. Washing procedures are described elsewhere[25].

Gels at different relative humidity (r.h.) were prepared by keeping them at r.h. = 76% for 10 days to remove all traces of excess water after washing and then exposing them to a specific r.h. The crystallinity of the gels was determined by X-ray diffraction to be approximately 40%.

*Amylose.* Amylose (Avebe, Veendam, Holland) with a crystallinity of approximately 15% determined by X-ray diffraction was used in this work.

*Cotton.* The cotton used here has a crystallinity of approximately 70% determined by X-ray diffraction.

*Carboxymethylated cellulose (CMC).* Two different types of carboxymethylated cellulose were used: a lightly carboxymethylated pulp (Buckeye, USA) with a degree of substitution (*DS*) of 0.7, and an amorphous carboxymethylcellulose powder of three different *DS*, 0.7, 1.1 and 1.6. These samples were called CMC(0.7), CMC(1.1) and CMC(1.6). The pure CM pulp was prepared in five different ionic forms ($H^+$, $Li^+$, $Na^+$, $K^+$ and $Ca^{2+}$) whilst the three water-soluble CMCs were prepared in two different ionic forms ($H^+$ and $Na^+$) before being conditioned at different r.h., as described below.

*Cellulose sulfate (CS).* CS (Kelco, USA) with a *DS* of 2.1 was used. The CS was ion exchanged to four different ionic forms ($H^+$, $Li^+$, $Na^+$ and $Ca^{2+}$).

*Dextran sulfate (SD).* SD (Pharmacia, Sweden) with a *DS* of 1.9 was prepared in four ionic forms: $H^+$, $Na^+$, $K^+$ and $Ca^{2+}$ as described below.

*Table 1* summarizes the different materials used and how they were prepared.

### *Procedures*

*Ion exchange.* Ion exchange was performed by keeping samples in solutions of 0.1 M HCl, 0.1 M XOH (where X corresponds to Li, Na or K), or 0.1 M $Ca(OH)_2$ for 24 h under moderate stirring. Afterwards the samples were thoroughly washed with distilled water to pH 6. For easily soluble samples such as cellulose sulfate (CS) and carboxymethylated cellulose (CMC), mixtures of ethanol/XOH solution, 70/30 and 80/20 (v/v) respectively, were used to avoid solubilization.

*Relative humidity (r.h.).* The different moisture levels used were obtained by exposing the gels to the vapour of different saturated salt solutions in closed desiccators at appropriate temperatures: $CuSO_4{\cdot}5H_2O$ for 98%; $K_2HPO_4$ for 92%; $NaC_2H_3O_2{\cdot}3H_2O$ for 76%; $Ca(NO_3)_2{\cdot}4H_2O$ for 56%; $K_2CO_3{\cdot}2H_2O$ for 44%; $CrO_3$ for 35%; NaBr for 22%; and $P_2O_5$ for 0% r.h. Samples were conditioned in desiccators for periods of 3 weeks to ensure equilibrium as measured by a thermogravimetric analyser (Perkin Elmer TGA7). The different relative humidities were measured with a humidity and temperature indicator (Vaisala HMI 31). The accuracy of the relative humidities was ± 1.5%. The temperature was kept at 20°C. Two different sets of relative humidities (r.h.) were used throughout these experiments: set (I) = 98, 92, 76, 44, 22, 0%, and set (II) = 98, 92, 76, 56, 35, 0%. The risk of capillary condensation was minimized by keeping the temperature as constant as possible throughout the experiments.

*Charge density.* The charge densities were determined by conductimetric titration. Titrations were performed at 25°C under nitrogen, using a Tacussel CD78 conductimeter with a Tacussel XE120 electrode. Samples were transformed to their protonated forms by ion exchange in 0.1 M HCl and titrated with 0.1 M NaOH.

*Degree of crystallinity.* The crystallinity was determined by X-ray diffraction, using a Philips PW-1720 X-ray generator, 30 kV.

**Table 1** Materials and testing conditions used

| Material | *C* (meq/g) | Molecular mass of monomeric unit under different ionic forms (g mol$^{-1}$) $H^+$ | $Li^+$ | $Na^+$ | $K^+$ | $Ca^{2+}$ | Relative humidity Set (I) | Set (II) |
|---|---|---|---|---|---|---|---|---|
| Viscose | | | | | | | X | |
| Amylose | | | | | | | X | |
| Cotton | | | | | | | X | |
| CM pulp | 3.3 | 199.6 | 203.5 | 213.9 | 224.3 | 212.0 | | X |
| CMC | 6.3 | 254.8 | | 290.0 | | | | X |
| CMC | 5.0 | 225.8 | | 250.0 | | | | X |
| CMC | 3.4 | 202.6 | | 218.0 | | | | X |
| CS | 5.6 | 331.2 | 343.9 | 377.8 | 411.6 | 371.4 | | X |
| SD | 5.3 | 311.5 | 322.7 | 352.6 | 382.5 | 347.0 | | X |

*Differential scanning calorimetry.* A Perkin Elmer differential scanning calorimeter (DSC7) equipped with a cooling device was used to determine the amount of freezing water. D.s.c. curves were obtained in the temperature range from −60 to +25°C for the carboxymethylated pulp in fibre form, and from −90 to +25°C for the rest of the samples. Indium ($T_m = 156.60$°C) and n-dodecane ($T_m = -9.65$°C) were used for calibration. Ds.c. curves were obtained upon heating at a scanning rate of 1 or 2°C min$^{-1}$. The cooling speed was 200°C min$^{-1}$, and 5 min were allowed for equilibration at the starting temperature ($T_{start}$). Sample enthalpies were calculated using pure water as reference. Sample weights varied between 5 and 15 mg. The samples were weighed in aluminium capsules, which were then sealed. During sealing, the samples were exposed to ambient atmosphere (ca. 50% r.h.) for approximately 1 min.

*Thermogravimetric analysis.* A Perkin Elmer thermogravimetric analyser (TGA7) was used to determine the total water content of the samples. The weights of hydrated sample varied between 3 and 15 mg. The scanning rate and temperature interval were respectively 5–20°C min$^{-1}$ and 20–130°C. Tests were continued until the second derivative of the weight-loss curve reached zero. During loading, samples were exposed to the ambient atmosphere for an average period of 1 min.

Total water ($W_c$) was determined by t.g.a.:

$$W_c = \frac{m_{(H_2O\,evap)}}{m_s} \quad \text{(g/g)} \qquad (1)$$

freezing water ($W_f$) by d.s.c.:

$$W_f = \frac{\Delta H_s}{\Delta H_{H_2O} m_s} \quad \text{(g/g)} \qquad (2)$$

and non-freezing water ($W_{nf}$) in accordance with Hatakeyama *et al.*[5]:

$$W_{nf} = W_c - W_f \quad \text{(g/g)} \qquad (3)$$

in which $m_{(H_2O\,evap)}$ is the mass of evaporated water in grams, $m_s$ the dried weight of the sample, $\Delta H_{H_2O}$ the enthalpy of melting of the bulk water per gram and $\Delta H_s$ the enthalpy for the observed phase transition.

## RESULTS

### *Types of adsorbed water*

The freezing water adsorbed by the cellulosic samples was investigated by d.s.c. measurements. *Figure 1* shows the melting peaks for the adsorbed water for CMC(1.6)-Na$^+$ as the relative humidity progressively increased from 76% to 98%. The average degree of substitution of carboxylic acid groups per glucose unit was 1.6. The peak obtained for bulk water is shown as a reference.

At 76% r.h., no melting peak was observed although the total water content ($W_c$) was as high as 0.47 g water/g dry gel. At 92% r.h., two peaks were observed, peak I ($T_m - 20$°C) and peak II ($T_m - 9$°C). Neither the position nor the magnitude of peak I changed as the relative humidity increased from 92 to 98%. At 98% r.h., peak I and peak II were almost coincidental although peak I was still clearly detectable. The coexistence of several peaks superimposed upon each other has also been reported by Hatakeyama *et al.*[23]. The change in shape and position of peak II when the r.h. increased from 92% to 98% was mainly found on the right-hand side of peak II$_{92\%\ \mathrm{r.h.}}$.

In *Figure 2*, the evolution of the d.s.c. peaks can be followed for CMC(1.6)-H$^+$ as the relative humidity

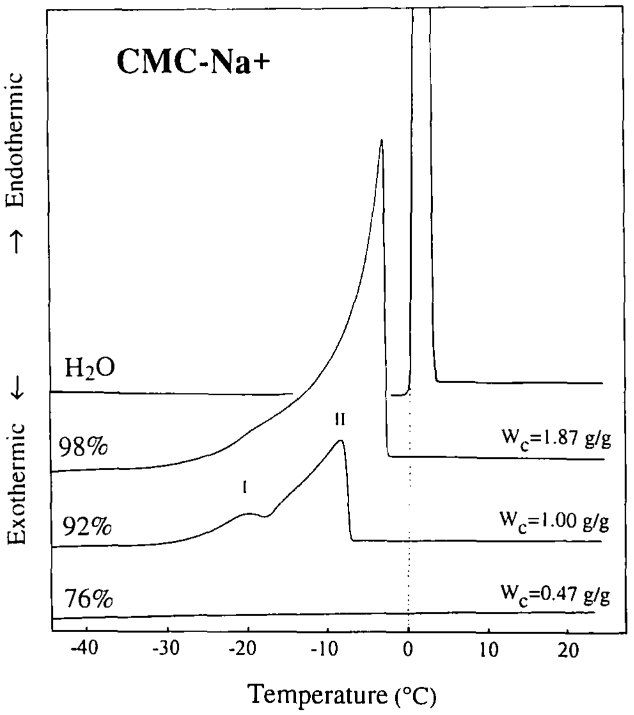

**Figure 1** Temperature scans showing melting peaks for the weak acid system CMC-Na$^+$ at relative humidities between 76 and 98%. The progression of the total water content in g/g is indicated to the right in this figure. A reference curve for bulk water has been added as a comparison

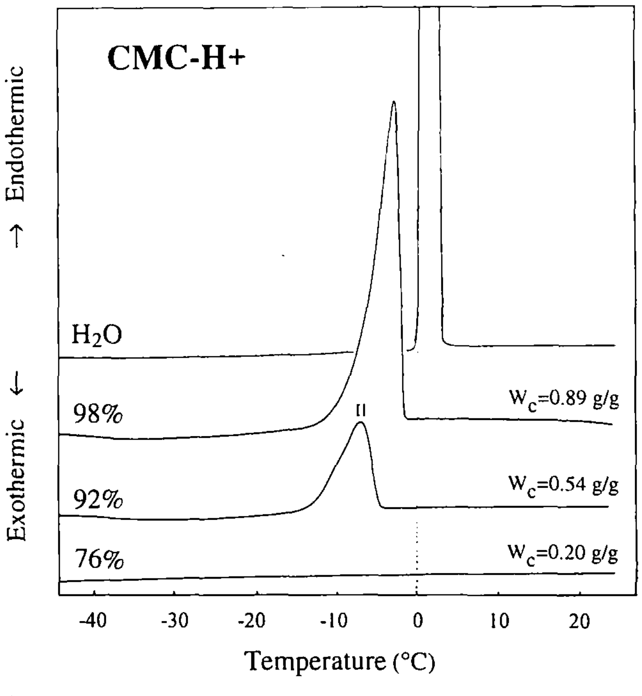

**Figure 2** Temperature scans showing melting peaks for the weak acid system CMC-H$^+$ at relative humidities between 76 and 98%. The progression of the total water content in g/g is indicated to the right in this figure. A reference curve for bulk water has been added as a comparison

increased from 76% to 98%. Unlike CMC(1.6)-$Na^+$, peak I was not detected. Peak II was observed, with $T_m \approx -8°C$ at r.h. = 92%. As the moisture content increased from 92% to 98% r.h., the maximum of peak II moved closer towards the melting peak of bulk water.

*Figure 3* illustrates the progression of the observed melting peaks of adsorbed water for cellulose sulfate, CS-$Na^+$, as the relative humidity increased from 76% to 98%. At a r.h. of 76%, no peak was observed (total water content 0.31 g/g). At 92% r.h., a single peak (peak I) was detected with $T_m \approx -10°C$. As the relative humidity increased to 98%, peak II appeared with $T_m \approx -5°C$. Peak I was clearly detectable at r.h. = 98%.

The results for CS-$H^+$ from 56% to 98% r.h., *Figure 4*, differ somewhat from the results for the CMC samples previously presented. In the case of CS, the charged groups are strong sulfate (-O-$SO_3H$) acid groups, whereas, in the case of CMC, they are weak carboxylic acids. At a r.h. of 56%, no melting peak was recorded. At 76% r.h., a recrystallization and a melting peak, peak III, were observed. Peak III extended all the way to about 12°C. The integral of peak III from −40 to 20°C (incorporating both the recrystallization and melting) was equal to zero. As the relative humidity increased to 92%, peaks I and II appeared at −15 and −8°C respectively. Peak III was still detectable at 92% r.h. When the relative humidity was increased to 98%, the maximum of peak II approached the reference peak of bulk water.

For uncharged cellulose samples such as viscose, no freezing water was observed even at 98% r.h., although the adsorbed total water content was as high as 0.47 g/g.

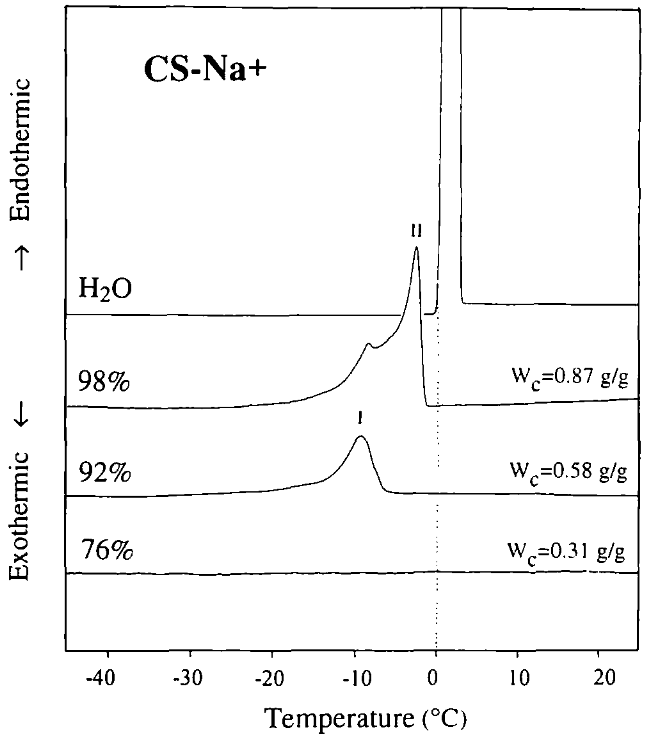

**Figure 3** Temperature scans showing melting peaks for the strong acid system CS-$Na^+$ at relative humidities between 76 and 98%. The progression of the total water content in g/g is indicated to the right in this figure. A reference curve for bulk water has been added as a comparison

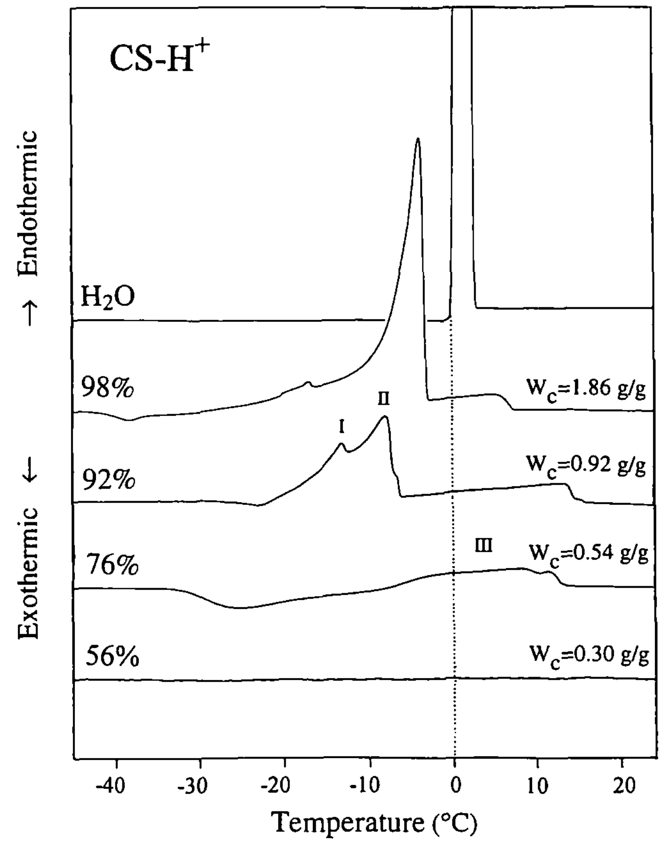

**Figure 4** Temperature scans showing melting peaks for the strong acid system CS-$H^+$ at relative humidities between 76 and 98%. The progression of the total water content in g/g is indicated to the right in this figure. A reference curve for bulk water has been added as a comparison

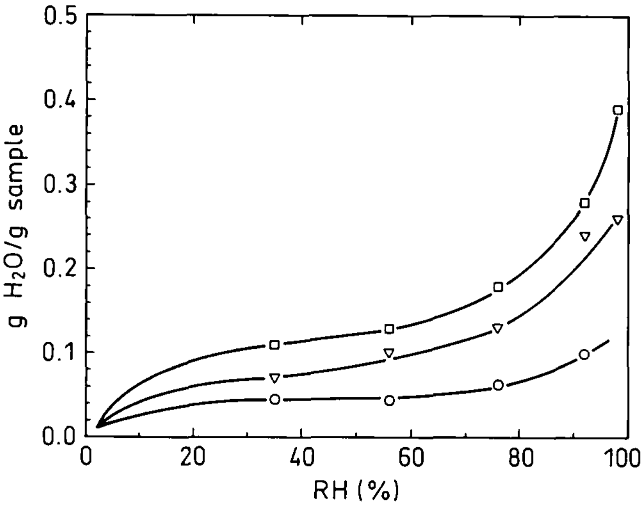

**Figure 5** The total water adsorption for three uncharged carbohydrates, cotton (○), viscose (▽) and amylose (□), with degrees of crystallinity of 70, 40 and 15% respectively as a function of relative humidity. Only non-freezing water is adsorbed by these carbohydrates

### *Amount of total water, freezing water and non-freezing water*

The quantities of the different types of water adsorbed in different samples were examined by combining the t.g.a. and d.s.c. techniques. In *Figure 5*, the total moisture adsorption for three uncharged carbohydrates (viscose, cotton and amylose) with different degrees of crystallinity is plotted against r.h. Amylose, which had the lowest degree of crystallinity (15%), adsorbed most moisture, whereas cotton, with the highest degree of crystallinity (70%), adsorbed the least. In the range of relative humidities tested, no freezing water was detected by d.s.c. for these uncharged carbohydrates, implying that all the water was present as non-freezing water.

The total moisture sorption isotherms for carboxymethylated fibres under different ionic forms are shown in *Figure 6a*. The nature of the counter-ions had little influence on the total water uptake at a r.h. less than 80%. For the carboxymethylated fibres, freezing water appeared at 92% r.h. for $Li^+$, $Na^+$ and $K^+$, and thereafter increased with increasing r.h., *Figure 6b*. Only small amounts of freezing water were detected in the case of the $H^+$ and $Ca^{2+}$ forms at 98% r.h. The occurrence of freezing water coincided with a pronounced increase in the amount of non-freezing water in the system as shown in *Figure 6c*. The non-freezing water adsorption reached a plateau as the moisture level approached 98% r.h.

The total moisture sorption isotherms for CS in different ionic forms are presented as a function of relative humidity in *Figure 7a*. The total water adsorbed was only slightly affected by the nature of the counter-ions when the relative humidity was less than 90% except for the protonated form, which, at all r.h. levels studied, adsorbed more water than the other ionic forms. The protonated form of CS was the only sample that adsorbed freezing water at 76% r.h., as is shown in *Figure 7b*. The protonated form adsorbed considerably more freezing water than the lithium form, which in turn adsorbed more than the sodium and calcium forms. In the case of the non-freezing water, as is shown in *Figure 7c*, the adsorption was not at all affected by the type of counter-ion. For CS, the sequence favouring total water adsorption was $H^+$, followed , in order of decreasing efficiency, by Li+, $Na^+$ and $Ca^{2+}$.

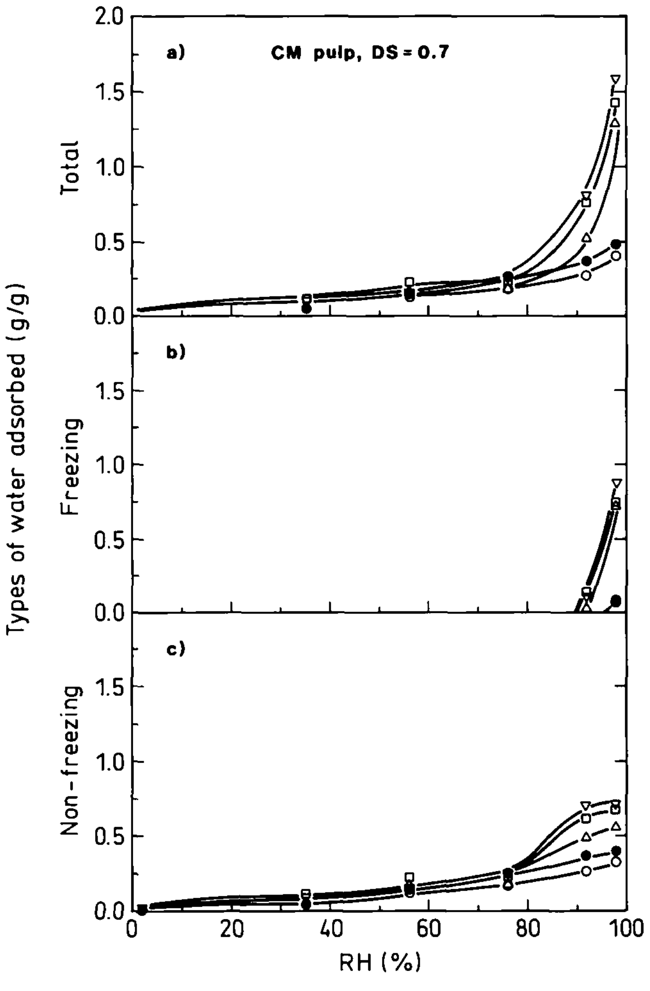

**Figure 6** Total, freezing bound and non-freezing water sorption isotherms at 20°C for carboxymethylated fibres, in different ionic forms: (▽) $Li^+$, (□) $Na^+$, (△) $K^+$, (●) $Ca^{2+}$ and (○) $H^+$

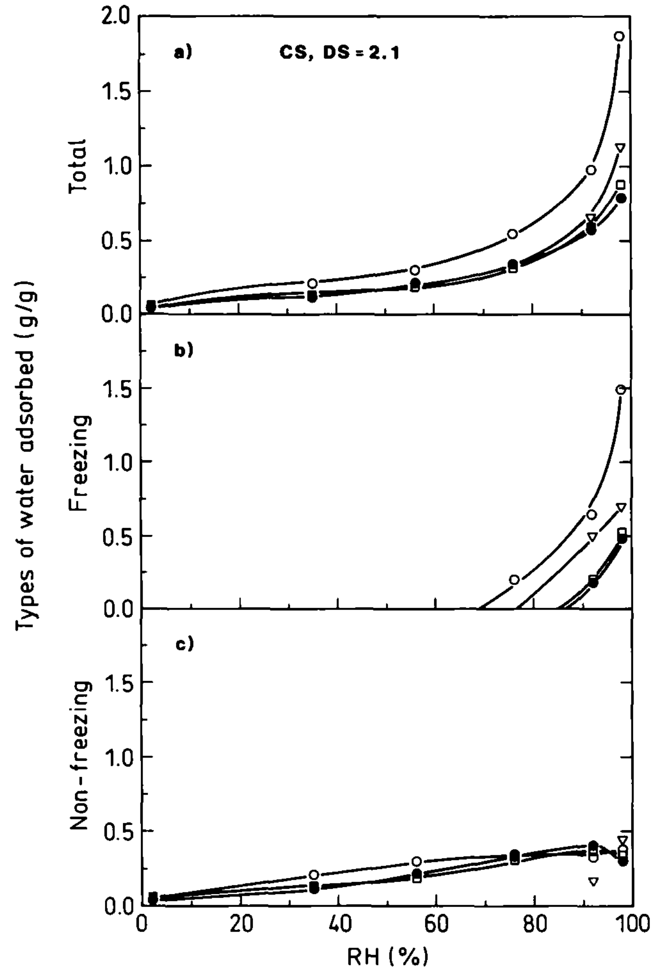

**Figure 7** Total, freezing bound and non-freezing water sorption isotherms at 20°C for cellulose sulfonate, CS, in different ionic forms: (▽) $Li^+$, (□) $Na^+$, (△) $K^+$, (●) $Ca^{2+}$ and (○) $H^+$

## DISCUSSION

### *Moisture adsorption*

The sorption mechanism may be regarded in several ways. In the present discussion, the view is adopted that to achieve water adsorption specific interactions between water molecules and the polymer system must be possible. The interactions may arise between water molecules and ionic groups with counter-ions or hydroxyl groups active as sorption sites for the water molecules. For the ionic groups and their counter-ions, the electrostatic fields due to these groups are important[1]. Steric conditions[16,17], the ability to form bonds between the molecules involved and the nature of the ionic groups (weak acid groups or strong acid groups) are important parameters affecting the interactions. The nature of the counter-ion is probably also important as the electrostatic field decreases for the earth metals (group IA in the periodic table), the sequence being $Li^+$, followed, in decreasing order of electrostatic field intensity, by $Na^+$, $K^+$, $Rb^+$ and $Cs^+$. The ionic radii increase according to the same sequence[1]. The stronger the field, the stronger the effect on the surrounding water molecules. The results indicate that the way in which charged groups and their counter-ions combine has a large influence on the type of water adsorbed.

*Types of differently adsorbed water*

As the first water molecules enter the cellulose derivative system, they presumably attach to the thermodynamically most attractive sites. These water molecules then experience attractive forces strong enough to prevent any phase transition, although the molecules are still mobile, as shown by n.m.r.[26]. All the cellulose derivative systems tested in the current study show the presence of this tightly interacting, non-freezing water.

Peak I (*Figures 1* and *3*), observed for carboxymethylated cellulose and cellulose sulfate, demonstrated a disordered ice structure possessing thermodynamic parameters quite different from those of normal ice. The area of peak I was almost constant as the r.h. increased, suggesting that the number of water molecules forming this unorganized ice structure was almost constant as the relative humidity increased and further water molecules were adsorbed. With increasing distance to the adsorption sites, the attractive forces become weaker. In the d.s.c. curves this is observed as an evolution of peak II with increasing relative humidity. The higher the r.h., the more bulk-like becomes the water adsorbed for peak II. The absence of peak I for CMC(1.6)-$H^+$ can probably be explained as being due to the low dissociation of weak acid systems[27]. Conversely, in the case of CS-$H^+$, a strong acid ($-O-SO_3H$) in its protonated form demonstrates a high degree of dissociation. In this case, water that recrystallized at very low temperatures at 76% r.h. was observed. This recrystallization peak was found to be independent of the cooling rate (between 200 and $5°C\,min^{-1}$) preceding the scan. The adsorbed water molecules that recrystallize form some kind of ice structure that melts at abnormally high temperatures (peak III in *Figure 4*). As this peak was detected only in the presence of strong acid (sulfonic acid) under its protonated form, some relation to its protonated form can be suspected.

*Amounts of total, freezing and non-freezing water*

In interpreting the quantities of the differently adsorbed types of water, it should be borne in mind that the enthalpy for melting ice depends on the energy of interaction between molecules. The enthalpy for melting bulk water may therefore not be a perfect reference against which to interpret peaks of polymers interacting with water molecules.

It was observed that the weak acid system, the carboxymethylated cellulose, adsorbed more water than the strong acid system, the cellulose sulfate, the greatest exception being CS-$H^+$. The total water adsorption in gram $H_2O$/gram dry material (g/g) for the sequence of different counter-ions followed, for both CMC and CS, the behaviour previously noted for polymer acid systems in electrolyte solutions[27]. A significant difference between CMC and CS was found when the influence of counter-ions on non-freezing water adsorption was examined. For the carboxymethylated cellulose, the non-freezing water adsorption for the different counter-ions was well separated, whereas there were virtually no differences in non-freezing water adsorption between the different ionic forms of cellulose sulfate. The explanation for this may be found in the nature of the ionic groups.

*Number of water molecules per ionic site*

The adsorption of water by strongly hydrophilic polymers (i.e. those having hydroxyl groups) may be regarded as being a sorption of water on the hydroxylic sites[8,28]. Under this assumption, disregarding clusters or multiple layer absorption, saturation should occur when each hydroxyl group has bound one water molecule. To investigate this hypothesis, an attempt was made to calculate the number of water molecules adsorbed to the hydroxyl groups of a sugar unit in a cellulose chain at different r.h. values. This value could subsequently be used to interpret the effects that ionic groups and counter-ions have on water sorption. It would thus also be possible to determine the number of non-freezing and freezing water molecules per ionic group and counter-ion in accordance with equation (5) discussed below. In the following calculations, only the three OH groups present on the glucose unit have been considered as potential binding sites for hydrogen bonding to water for the uncharged cellulose. No contribution from the oxygen in the glucose ring, between C5 and C1, nor from the oxygen between sugar units has thus been considered. Any possible contribution to the interaction between cellulose and water due to these oxygens[17] would thus be considered as being a contribution from the three OH groups. It is further assumed that the interaction between water and the OH groups on the cellulose is the same with and without ionic groups with counter-ions. Furthermore, these calculations are assumed to be independent of the nature of the ionic group and the charge density.

Using the adsorption data in *Figure 5* for glucans with different degrees of crystallinity, it was possible, using their respective degrees of crystallinity, to calculate the

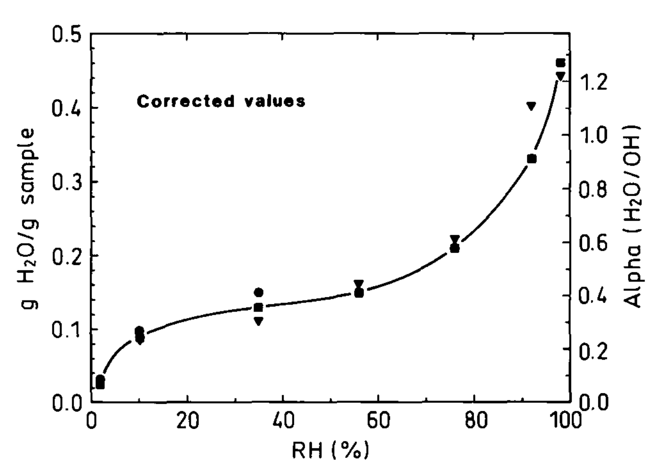

**Figure 8** The total water adsorption for three uncharged carbohydrates: cotton, viscose and amylose. The total water sorption has for each sample been recalculated to an estimated 100% amorphous material based on the degree of crystallinity of each material

adsorption for 100% amorphous materials as plotted in *Figure 8*. Amylose, which differs only in the type of glycosidic linkage and otherwise consists of the same glucose units, is considered relevant in the comparison made here. A fair correlation between the different samples was found, in accordance with the results of Valentine[29], in the linear relationship between the water sorption ratio and the degree of crystallinity. Slight divergences from this model have been explained as being due to differences in the size of the crystallites for different types of cellulose tested[1]. As previously stated, all water was adsorbed as non-freezing water throughout the whole r.h. range (i.e. no freezing water was found in the case of the uncharged carbohydrates). Thus, the curve for the calculated 100% amorphous material permits the estimation of an empirical value $\alpha$ (the number of water molecules per OH) at different r.h.:

$$\alpha = \frac{W_c M_{\text{cellulose}}}{M_{\text{water}}(1-\theta/100)n_{\text{OH}}} \tag{4}$$

where $W_c$ is the non-freezing water content (according to equation (3) since $W_f = 0$), $\theta$ is the degree of crystallinity, $M_{\text{cellulose}} = 162\ \text{g mol}^{-1}$, $M_{\text{water}} = 18\ \text{g mol}^{-1}$ and $n_{\text{OH}} = 3$ is the number of hydroxyl binding sites. At an r.h. of 98%, $\alpha$ is calculated to be 1.27, which is comparable with the value of 1.25 based on viscose and cotton calculated by Nakamura *et al.*[8], presumably for conditions of 100% r.h. The condition where one $H_2O$ is adsorbed per OH was calculated to be at about 92% r.h. The number of water molecules calculated per hydroxyl group as a function of r.h. is given in *Table 2*.

**Table 2** Number of water molecules per hydroxyl group of cellulose ($\alpha$) as a function of the relative humidity. The values are determined from *Figure 8*

| R.h. (%) | $\alpha(n(H_2O)/OH)$ |
|---|---|
| 98 | 1.27 |
| 92 | 1.00 |
| 76 | 0.66 |
| 56 | 0.48 |
| 35 | 0.36 |
| 0 | – |

With this number of bound water molecules per sugar unit, it is possible to calculate the number of bound water molecules adsorbed per ionic site (in this study carboxylic acid groups ($-COO^-$) and sulfate acid groups ($-O-SO_3^-$)) from the amount of non-freezing water adsorbed:

$$n_{(H_2O\ \text{bound/site})} = \frac{X-(n_{\text{OH}}-DS)\alpha}{DS} \tag{5}$$

with

$$X = \frac{W_b M_c}{M_{\text{water}}} \tag{6}$$

where $W_b$ is the number of water molecules adsorbed per monomeric unit and $M_c$ is the molecular weight of the

**Table 3** The water adsorption for carboxymethylated pulp, CMC, CS and SD expressed in number of non-freezing (nf) water molecules per sugar unit and per charged group

| Materials studied | Counter-ions | Ads. (g/g) | DS | M (g mol$^{-1}$) | Non-freezing water | |
|---|---|---|---|---|---|---|
| | | | | | $n(H_2O)$/sugar | $n(H_2O)$/site[a] |
| CM-pulp | $H^+$ | 0.39 | 0.65 | 199.6 | ≈3.5 | ≈1 |
| | $Li^+$ | 0.60 | 0.65 | 203.5 | ≈7.5 | ≈7 |
| | $Na^+$ | 0.55 | 0.65 | 213.9 | ≈6 | ≈5.5 |
| | $K^+$ | 0.47 | 0.65 | 224.3 | ≈5.5 | ≈5 |
| | $Ca^{2+}$ | 0.38 | 0.65 | 212.0 | ≈4.5 | ≈3 |
| CMC | $Na^+$ | 0.50 | 1.6 | 290.0 | ≈8.6 | ≈4 |
| | $Na^+$ | 0.50 | 1.1 | 250.0 | ≈6.9 | ≈4 |
| | $Na^+$ | 0.40 | 0.7 | 218.0 | ≈4.3 | ≈4 |
| CMC | $H^+$ | 0.30 | 1.6 | 254.8 | ≈4.9 | ≈2 |
| | $H^+$ | 0.30 | 1.1 | 225.8 | ≈4.2 | ≈2 |
| | $H^+$ | 0.35 | 0.7 | 202.6 | ≈3.6 | ≈2 |
| Yoshida *et al.*[24] | $Na^+$ | – | 0.33 | – | – | 10.9 |
| | $K^+$ | – | 0.6 | – | – | 7.2 |
| CS | $H^+$ | 0.32 | 2.1 | 331.2 | ≈6 | ≈2.5 |
| | $Na^+$ | 0.35 | 2.1 | 377.8 | ≈7 | ≈3 |
| | $Ca^{2+}$ | 0.35 | 2.1 | 371.4 | ≈6.8 | ≈3 |
| SD | $H^+$ | 0.35 | 1.9 | 311.5 | ≈6.3 | ≈3 |
| | $Na^+$ | 0.30 | 1.9 | 352.6 | ≈6 | ≈2.5 |
| | $K^+$ | 0.18 | 1.9 | 382.5 | ≈3.8 | ≈1.5 |
| | $Ca^{2+}$ | 0.28 | 1.9 | 347.0 | ≈5.4 | ≈2.5 |
| Froix *et al.*[2] | $Na^+$ | – | – | – | – | 3.3 |
| Zundel[1] | cations in general | – | – | – | – | ≈5 |

[a] Site = carboxylic or sulfonic acid and counter-ion

monomeric unit in the derivatized cellulose. The results of these calculations are given in *Table 3*. It is interesting to note that the degree of substitution does not influence the amount of non-freezing water molecules adsorbed per ionic site in the range studied ($DS = 0.7$–$1.6$). The differences in amount of adsorbed non-freezing water molecules for different counter-ions are greater for the weak carboxylic acid (carboxymethylated cellulose, –COOH) than for the strong sulfonic acid (cellulose sulfate, $-O-SO_3H$).

## CONCLUSIONS

From these studies, it can be deduced that all cellulosic systems tested probably have a layer of interacting non-freezing water in close proximity to the binding sites. Differently adsorbed freezing water may then surround this non-freezing water. The presence of charged groups is a necessary condition for the adsorption of freezing water at moisture levels below 100% r.h.

The type of ionic site and counter-ion influence the extent and properties of the water that is adsorbed. The sequences found favouring the water adsorption at a relative humidity less than 100% r.h. are in agreement with the sequences found for polymers with weak and strong acids in solutions.

The choice of counter-ion is more important for the number of non-freezing water molecules adsorbed in a weak acid system than in a strong acid system.

The number of water molecules adsorbed per hydroxyl group reaches one $H_2O$/OH group at 92% r.h.; this result involves a specific binding, and thus does not favour cluster or pure multilayer adsorption models, as sometimes suggested in the literature.

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