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Structure of Aqueous Solutions of Microcrystalline Cellulose/Sodium Hydroxide below 0 °C and the Limit of Cellulose Dissolution

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The aim of the paper is to investigate the structure of solutions of microcrystalline cellulose in NaOH/water mixtures and to determine the limit of cellulose solubility. The binary NaOH/water and the ternary cellulose/NaOH/water phase diagrams in the area of cellulose dissolution (7−10% NaOH below 0 °C) are studied by DSC. The NaOH/water binary phase diagram has a simple eutectic behavior. Because of the existence of this eutectic structure, it is possible to measure the influence of the addition of pure low molar mass microcrystalline cellulose. This shows that a minimum of four NaOH molecules should be linked to one anhydroglucose unit to allow for the dissolution of microcrystalline cellulose. The proportions between bound Avicel, NaOH, and water molecules as a function of cellulose concentrations are calculated. A tentative explanation about the origin of the dissolving power of NaOH/water is given.

1. Introduction

Aqueous solutions of sodium hydroxide of 7−10 w/w % are promising cellulose solvents because of the ease of solution preparation and low pollution. One of the drawbacks of this solvent is that dissolution is not complete for high molecular weight celluloses. It is not a good solvent, which is why it has never become a commercial process.

Several publications report different dissolution procedures, but all of them show that cellulose can be dissolved in a narrow range of NaOH concentrations, from 7 to 10%, and temperatures (for example, at −5 to −6 °C[1,2]) and also through a freeze−thaw process[3] at +4 °C.[4] There is a lack of understanding of the cellulose/aqueous sodium hydroxide solution structure and properties despite that they are a key issue for the adequate processing of these solutions and the shaping of cellulose objects.

The goal of this article is to clarify the structure of cellulose/sodium hydroxide solutions in a NaOH concentration range of 7−9% at cellulose dissolution temperatures (i.e., below zero). To do so, we used microcrystalline cellulose that is free of other polysaccharides and is of a low molecular weight, knowing that using cotton of high DP or wood pulp does not allow a full dissolution.[5,6] Above 0 °C, the structure and properties of cellulose/NaOH solutions change drastically: they gel with a time and temperature increase due to a noticeable decrease of solvent thermodynamic quality,[7] NaOH/water being unable to dissolve cellulose in these conditions. This case will not be considered here.

X-ray scattering[1] and NMR[4] showed that sodium hydroxide hydrates composed of NaOH and several water molecules are bound to cellulose. A model of cellulose/NaOH/water solutions at low temperatures was proposed.[8] In the present article, this model will be revised according to new results. In particular, the presence of amorphous or unbound water in cellulose/NaOH/water solutions suggested in ref 8 turned out not to be true, due to an incorrect estimation of the melting enthalpies of the water component. Because of the way the eutectic phase diagram is, the melting of ice begins at the eutectic point, with very small amounts of ice melting at each temperature. This was not properly measured in ref 8. The limit of cellulose dissolution in an aqueous sodium hydroxide solution will be introduced, and its reasons will be discussed.

This work focused on the study of the dissolution of pure, low molar mass cellulose (microcrystalline cellulose) in NaOH/water. The article is composed of two parts. First, the phase diagram of pure sodium hydroxide aqueous solution at NaOH concentrations from 0 to 20% will be given. The main thermodynamic parameters will be measured. Several papers report the formation of stable sodium hydrates in which the number of water molecules depends on the NaOH concentration and on the solution temperature;[9−11] liquidus and solidus curves are well-identified.[9,11] All this will be briefly presented to be used for the further study of the structure of cellulose/NaOH/water solutions.

In the second part of the article, the solutions of microcrystalline cellulose in aqueous sodium hydroxide solutions will be studied using the same technique and methodology as described in the first part. The proportions between bound cellulose/NaOH and cellulose/water molecules will be determined. The cellulose dissolution limit in NaOH/water will then be calculated.

2. Experimental Procedures

2.1. Materials and Solution Preparation. The cellulose used was AvicelPH-101 microcrystalline cellulose, called cellulose for the remainder of the article, which was from the FMC Corporation. It is a purified partially de-polymerized α-cellulose, with a mean degree of polymerization of 170, as given by the manufacturer. Before use, cellulose was dried in an oven at 60 °C to remove the remaining water.

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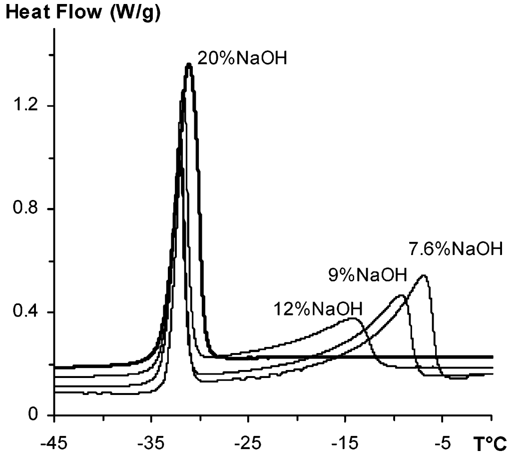

Figure 1. DSC melting thermograms for NaOH/water solutions. Peaks are shifted vertically for better clarity.

Table 1. Melting Temperatures of Each Peak at Different Sodium Hydroxide Concentrations

NaOH (%)	T_m (onset) of the eutectic peak (°*C*)	T_m (end) of ice peak (°*C*)
7.6	−32.9	−5.1
8	−33.2	−5.9
9	−33.6	−7.7
12	−33.5	−11.7
20	−33.3	no peak

Sodium hydroxide was purchased from Prolabo, in pellets, with a purity superior to 98%. NaOH was dissolved in distilled water; its concentration C_{NaOH} varied from 0 to 20% for the studies of the NaOH/water phase diagram. When cellulose was dissolved in the NaOH/water solutions, the quantity of NaOH was either 7.6 or 8 g in 100 g of solution.

NaOH was dissolved in water at concentrations around 12% and was cooled down to −6 °C. At the same time but in another vessel, water was added to cellulose pulp for cellulose swelling, and the cellulose/water system was left at +5 °C for about 2 h. A cold NaOH/water solution was added to this swollen-in-water cellulose in such a proportion that in 100 g of final solution, there were from 0.5 to 7.6 g of cellulose and 7.6 or 8 g of NaOH. The weight proportions between the components in 100 g of solution are noted as *X*cellulose/*Y*NaOH/water, which means *X* g of cellulose, *Y* g of NaOH, and $(100 - X - Y)$ grams of water. Cellulose/NaOH/water mixtures were placed into a thermobath at −6 °C and stirred at ∼1000 rpm for 2 h. Then, the solutions were removed from the bath and stored at +5 °C.

2.2. Methods. Differential scanning calorimetry (DSC) experiments were carried out on a PerkinElmer DSC-7, composed of two thermally insulated ovens. Stainless steel gold-plated screwed caps (PerkinElmer B0182902) were used instead of typical aluminum or stainless steel ones because of corrosion induced by NaOH. Samples were cooled down from room temperature to −60 °C, maintained at −60 °C for 5 min for NaOH/water or 15 h for cellulose/NaOH/water solutions, and then heated up to +10 °C. Cooling and heating rates were 1 °C/min. This rate was chosen because of the high heat capacity of gold-plated stainless steel caps. The experimental errors of temperatures and enthalpies were below 10%.

3. Results and Discussion

3.1. Binary Phase Diagram. Structure of Sodium Hydroxide Aqueous Solutions at $T < 0$ °C and $C_{NaOH} = 0-20\%$. An example of DSC melting thermograms of the NaOH + H_2O solutions is shown in Figure 1. Two peaks clearly can be seen; they are similar to the ones observed in ref 8. The melting temperature T_m of each peak is shown in Table 1. Figure 1 is the characteristic DSC trace of a eutectic phase diagram, as shown in the phase diagram of the NaOH/water solution (Figure 2),[9,10] where at low sodium hydroxide concentrations (<30% NaOH in water), the eutectic mixture and ice should melt at low and high temperatures, respectively.

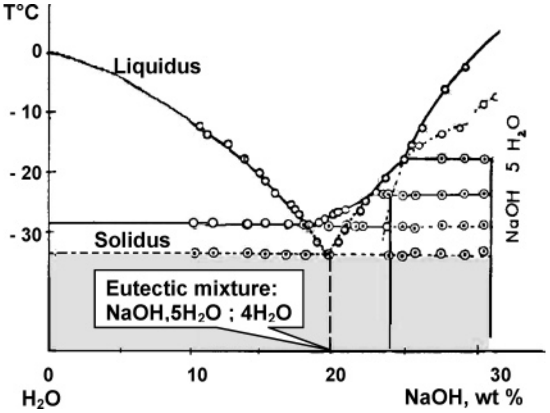

Figure 2. Part of the NaOH/water phase diagram[10,11] for NaOH concentrations lower than 30%. The dashed line corresponds to the $NaOH{\cdot}5H_2O$ metastable hydrate.

The melting peak at low temperature, around −33 °C, is independent of the NaOH concentration and is the trace of the melting of the eutectic mixture. The peak at higher temperature is the trace of the melting of ice.

3.1.1. Eutectic Peak at Low Temperature. Figure 1 and Table 1 allow the following observations: (1) at 20% NaOH/water, there is no pure ice melting at higher temperatures (no peak in Figure 1, curve is shown in bold). Only the eutectic mixture is present in the solution. Thus, the proportion between NaOH and water molecules in the eutectic mixture is 20% NaOH/80% H_2O in weight percent and 1 NaOH/9 H_2O in mol. (2) The rate of cooling/heating temperature is low, 1 °C/min, which means that a metastable hydrate, sodium pentahydrate $NaOH{\cdot}5H_2O$, should be formed[10] (a stable hydrate is formed with a high cooling temperature and corresponds to $NaOH{\cdot}7H_2O$ composition[9]). (3) The melting temperature found corresponds to the one of metastable sodium pentahydrate, reported in ref 10.

Thus, the substance melting around −33 to −34 °C is a crystalline eutectic mixture composed of one metastable sodium pentahydrate and four water molecules ($NaOH{\cdot}5H_2O$; $4H_2O$). Its melting enthalpy is $\Delta H_{eut,pure} = 187$ J/g, measured at $C_{NaOH} = 20\%$.

3.1.2. Peak at Higher Temperature. This peak corresponds to the melting of ice (see liquidus curve in Figure 2). Higher is the sodium hydroxide concentration, and lower is the melting temperature because of the decrease of ice fractions in solution. Such behavior is typical for binary phase diagrams.

3.1.3. Proportions between Eutectic Mixture and Ice in NaOH/Water Solutions at $C_{NaOH} < 20\%$. Applying the level rule on the NaOH/water phase diagram, it is possible to calculate the fractions of the eutectic mixture $f_{eut,calcd}$ and of ice $f_{ice,calcd}$ at any NaOH concentration. It is also straightforward to determine the corresponding fractions from the experimental data, $f_{eut,exp}$ and $f_{ice,exp}$ (i.e. from experimentally measured melting enthalpies ΔH_{eut} and ΔH_{ice} at a given NaOH concentration), and knowing the melting enthalpies of pure compounds (ice and eutectic), $\Delta H_{eut,pure}$ and $\Delta H_{ice,pure}$, respectively. Next, we give an example of such calculations; they will serve as a basis for the determination of cellulose/NaOH/water proportions in cellulose/NaOH/water solutions. As will be shown in the

Table 2. Fractions of Eutectic Mixture in NaOH/Water Solution below 0 °C at a Given Sodium Hydroxide Concentration C_{NaOH}, Determined from DSC Thermograms, $f_{\mathrm{eut,exp}}$, and Calculated from Phase Diagram Level Rule, $f_{\mathrm{eut,calcd}}$

C_{NaOH} (%)	ΔH_{eut}[a] (J/g)	$f_{\mathrm{eut,exp}}$	$f_{\mathrm{eut,calcd}}$
4	*39*	*0.2*	*0.20*
7	*72*	*0.36*	*0.35*
7.6	72	0.39	0.38
8	74	0.40	0.40
9	83	0.44	0.45
9	*80*	*0.43*	*0.45*
12	*111*	*0.59*	*0.60*
15	*157*	*0.79*	*0.75*
18	188	0.94	0.90
20	187 = $\Delta H_{\mathrm{eut,pure}}$	1	1.0
20	*200* = $\Delta H_{\mathrm{eut,pure}}$	*1*	*1.0*

[a] ΔH_{eut} is a measured melting enthalpy of the eutectic mixture. Values shown in italics correspond to reanalyzed experimental results taken from ref 8. Each fraction was calculated taking into account the corresponding $\Delta H_{\mathrm{eut,pure}}$ value.

Table 3. Fractions of Ice in NaOH/Water Solution below 0 °C at Given Sodium Hydroxide Concentration C_{NaOH}, Determined from DSC Thermograms, $f_{\mathrm{ice,exp}}$, and Calculated from Phase Diagram Level Rule $f_{\mathrm{ice,calcd}}$

C_{NaOH} (%)	ΔH_{ice}[a] (J/g)	$f_{\mathrm{ice,exp}}$	$f_{\mathrm{ice,calcd}}$
0	358 = $\Delta H_{\mathrm{ice,pure}}$	1	1
7.6	197	0.55	0.62
9	173	0.48	0.55
12	133	0.37	0.40

[a] ΔH_{ice} is measured ice melting enthalpy.

following paragraphs, measured and predicted fractions coincide within the experimental errors. This methodology will be applied to cellulose/NaOH/water solutions.

The fraction of eutectic mixture f_{eut} in the system depends on the NaOH concentration in the solution. As far as the eutectic mixture corresponds to $C_{\mathrm{NaOH}} = 20\%$ (only eutectic is present in the solution, see Figures 1 and 2), f_{eut} at other than $C_{\mathrm{NaOH}} = 20\%$ is obviously calculated as follows (level rule of phase diagram):

$$f_{\mathrm{eut,calcd}} = \frac{C_{\mathrm{NaOH}}}{20} \qquad (1)$$

In the same way, the fraction of melting ice is determined as

$$f_{\mathrm{ice,calcd}} = \frac{20 - C_{\mathrm{NaOH}}}{20} \qquad (2)$$

As far as experimental data are concerned, $f_{\mathrm{eut,exp}}$ and $f_{\mathrm{ice,exp}}$ are determined as follows:

$$f_{\mathrm{eut,exp}} = \frac{\Delta H_{\mathrm{eut}}}{\Delta H_{\mathrm{eut,pure}}} \qquad (3)$$

where $\Delta H_{\mathrm{eut,pure}} = 187$ J/g was obtained at $C_{\mathrm{NaOH}} = 20\%$ and

$$f_{\mathrm{ice,exp}} = \frac{\Delta H_{\mathrm{ice}}}{\Delta H_{\mathrm{ice,pure}}} \qquad (4)$$

$\Delta H_{\mathrm{ice,pure}} = 358$ J/g was obtained by a separate measurement of the melting of pure ice.

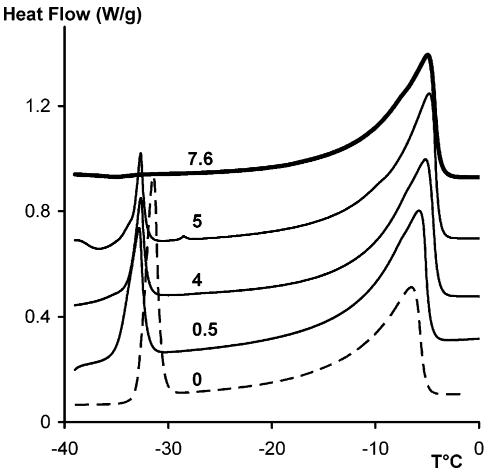

Figure 3. DSC melting thermograms of *X*Avicel/7.6NaOH/water solutions with $X = 0$, 0.5, 4, 5, and 7.6 g in 100 g of solution. Dashed line corresponds to $X = 0$ (solution without cellulose). Curves are shifted vertically for clarity.

Table 4. Melting Temperatures of Peaks at Lower and Higher Temperatures for Different Cellulose Concentrations in Avicel/7.6NaOH/Water Solutions

X (g of Avicel in 100 g solution)	T_{m} (onset) of eutectic peak (°*C*)	T_{m} (end) of ice peak (°*C*)
0	−32.9	−5.1
0.5	−34.9	−4.8
1	−33.7	−4.1
2	−33.5	−4.3
3	−33.2	−3.9
4	−33.4	−3.7
5	−33.5	−3.9
7.5	no peak	−3.8

The comparison of the fractions calculated and determined from DSC thermograms is shown in Tables 2 and 3 for the eutectic compound and ice fractions, respectively.

Tables 2 and 3 show that fractions calculated and determined from experimental data coincide, within experimental error. This match is satisfactory for the enthalpy of the eutectic compound, which has a well-defined melting peak. The match is less satisfactory for the melting of ice, which occurs over a large range of temperatures with a peak having a tail at low temperatures difficult to extract from the baseline. This effect was the reason for the wrong estimate of the melting enthalpy in ref 8. The hypothesis that the phase diagram is of a eutectic type is valid, and all the fractions of the components are known at all concentrations. This can be applied now to the ternary phase diagram of cellulose/NaOH/water solutions.

3.2. Ternary Phase Diagram. Structure of Cellulose/NaOH/Water Solutions at $T < 0$ °C. In this part, detailed DSC experiments were performed on Avicel/sodium hydroxide/water solutions in the region of cellulose dissolution, as determined by a phase diagram.[1] The goal is to determine the type of phase diagram and the amount of NaOH and water linked to cellulose using the methodology described in the first part. A concentration of NaOH of 7.6 or 8% was chosen in the following examples as being in the middle of the dissolution range. An example of DSC melting thermograms for solutions of different cellulose concentrations is given in Figure 3. Melting temperatures of each peak for the curves shown and for some other cellulose concentrations are presented in Table 4. The meaning of the peak at lower and higher temperatures is discussed next.

3.2.1. Eutectic Peak at Low Temperature. Whatever the concentration of cellulose and sodium hydroxide is, the melting temperature of the peak at lower temperatures is constant (Table 4). It coincides with the melting temperature of the eutectic mixture in a pure aqueous sodium hydroxide solution of 7.6% but with a systematic shift of about 1 °C toward lower temperatures. This means two things. First, the same eutectic mixture ($NaOH\cdot5H_2O$; $4H_2O$) is present in cellulose/sodium hydroxide aqueous solutions in this region of temperatures and NaOH concentrations, owing to the fact that the temperature shift is very small. The presence of cellulose does not change its composition. Second, because there is a change in the molecular environment due to the presence of cellulose, there is a slight shift in the melting temperature. We will see in the next paragraph that this change due to the presence of cellulose is also visible in the melting peak of pure water.

The result obtained means that here we are not in the presence of a ternary phase diagram where each of the components makes eutectic mixtures two by two (there is no solubility of cellulose in pure water or in pure NaOH). Nevertheless, the presence of cellulose drastically changes the amount of the water/NaOH eutectic mixture. The influence of cellulose concentration on the eutectic peak can be seen from the variation of enthalpy values: the enthalpy decreases down to zero with the increase of cellulose concentration (see Figure 3: curve in bold corresponding to $X = 7.6$ does not show any eutectic peak at −34 °C). Such behavior means that cellulose interacts with sodium hydroxide. The higher the cellulose concentration is, the smaller the amount of the eutectic compound that can crystallize and then melt at −34 °C is. Since NaOH is present only in the eutectic compound, the decrease of its melting enthalpy allows the calculation of the number of NaOH molecules linked to cellulose, and thus, it is not able to participate in the $NaOH\cdot5H_2O$ crystal fraction of the eutectic mixture. The calculations of the proportions between anhydroglucose unit, sodium hydroxide, and water molecules will be performed after the analysis of the peak at higher temperatures.

3.2.2. Pure Water Peak at Higher Temperatures. Figure 3 and Table 4 show that the temperature of the peak at higher temperatures is slightly changing when the cellulose concentration is increased. Again, this change is small, as in the case of the eutectic peak. This increase of the melting temperature of ice with increasing cellulose concentration reflects the fact that the molecular environment of the crystallizing ice is changed when cellulose traps NaOH.

3.2.3. Proportions between Bound Cellulose, NaOH, and Water Molecules in (0.5−9)Cellulose/(7−9)NaOH/Water Solutions. The dependence of reduced eutectic melting enthalpy on cellulose/NaOH weight ratio $M_{cell}/M_{NaOH} = X/Y$ in solutions *X*cellulose/*Y*NaOH/water with X varying from 0.5 to 7.6 g and $Y = 7.6$ and 8.0 g in 100 g of solution is presented in Figure 4. The reduced eutectic enthalpy is $\Delta H_{eut}/\Delta H_{eut,0}$ where ΔH_{eut} is the eutectic melting enthalpy value for either *X*cellulose/7.6NaOH/water or *X*cellulose/8NaOH/water and $\Delta H_{eut,0}$ is the enthalpy of the eutectic peak at $M_{cell} = 0$ at the corresponding NaOH content (either 72 or 74 J/g, respectively; see Table 2). The following very important conclusion concerning the limit of cellulose dissolution can be made from this graph.

The fact that ΔH_{eut} reaches zero at a certain cellulose concentration means that all sodium hydroxide molecules have been trapped by the cellulose chains. This corresponds to the dissolution limit since there are no more NaOH molecules able to solvate any additional cellulose chain that could be brought in the mixture. At this dissolution limit, we can calculate the proportion between cellulose anhydroglucose unit (AGU) and NaOH molecules. In our case, the eutectic peak disappears when the weight ratio $M_{cell}/M_{NaOH} = 1$. In mol, this proportion is four NaOH per AGU ($m_{AGU} = 162$ g/mol and $m_{NaOH} = 40$ g/mol). The data from ref 8 for Avicel dissolved in 9% NaOH aqueous solution give a similar result (triangles in Figure 4).

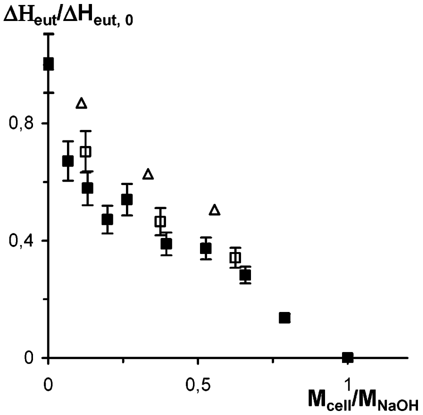

Figure 4. Reduced enthalpy as a function of cellulose/NaOH weight ratio in solution. Dark squares: cellulose/7.6NaOH/water; open squares: cellulose/8NaOH/water; and triangles: cellulose/9NaOH/water from ref 8.

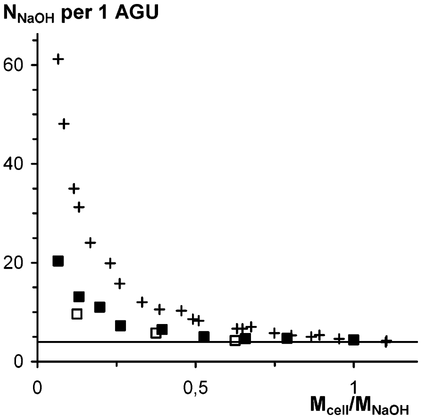

Figure 5. Number of NaOH molecules linked to one anhydroglucose unit, calculated from melting enthalpy data, as a function of cellulose/NaOH weight ratio in solution. Dark squares: cellulose/7.6NaOH/water; open squares: cellulose/8NaOH/water; and crosses: data from ref 12 for NaOH concentrations of 4.5, 6.2, and 7.9%.

Figure 4 allows the calculation of the proportion between linked AGU and NaOH at any weight ratio of the components. The fraction of eutectic linked to cellulose is as follows:

$$f_{eut,linked} = \frac{\Delta H_{eut,0} - \Delta H_{eut}}{\Delta H_{eut,0}} \quad (5)$$

Thus, the amount of eutectic (or NaOH) linked to cellulose, in mol, is given by

$$N_{NaOH} \text{ per 1 AGU} = f_{eut,linked} \frac{M_{NaOH}}{m_{NaOH}} \frac{m_{AGU}}{M_{cell}} \quad (6)$$

The amount of NaOH molecules linked to one anhydroglucose unit as a function of the weight ratio M_{cell}/M_{NaOH} for the systems Avicel/7.6NaOH/water and Avicel/8NaOH/water is shown in Figure 5 (squares). At $M_{cell}/M_{NaOH} > 0.4-0.5$, the proportion between AGU and NaOH molecules is constant and equal to the limit of cellulose dissolution, which is four NaOH per AGU. At low cellulose concentrations, $M_{\mathrm{cell}}/M_{\mathrm{NaOH}} < 0.25$, up to 20 NaOH molecules seem to be linked to one anhydroglucose unit. The change of the slope in Figure 5, as well as in Figure 4, may be caused by the transition of the cellulose solution from a dilute to semidilute state. In ref 7, the overlap concentration for Avicel in a 9%NaOH/water solution was reported to be $C_{\mathrm{cell}} \approx 1\%$. Figures 4 and 5 show that the slope change corresponds to $C_{\mathrm{cell}} \approx 1.5-2\%$. It may be possible that due to the steric hindrance caused by the transition from the dilute to semidilute state, the number of NaOH molecules linked to cellulose strongly decreases.

The same proportion between NaOH and anhydroglucose unit corresponding to the limit of cellulose dissolution, four NaOH per AGU, can be calculated if taking the results of the study of Kuo and Hong, who investigated Avicel solubility in NaOH aqueous solutions of different concentrations.[12] Using turbidimetry, the authors measured the amount of undissolved cellulose as a function of cellulose and NaOH concentration. We recalculated their data (Figure 2 in ref 12) as the weight of NaOH per 1 g of dissolved cellulose, converted the obtained figures into mol ratios, and plotted their data together with our data as a function of $M_{\mathrm{cell}}/M_{\mathrm{NaOH}}$. The result is presented in Figure 5 (crosses): at higher cellulose concentrations, the results of ref 12 coincide with ours and show that at least four NaOH molecules are needed to dissolve one AGU. At low cellulose concentrations, $M_{\mathrm{cell}}/M_{\mathrm{NaOH}} < 0.25$, the amount of NaOH linked to one anhydroglucose unit calculated from ref 12 is twice as high as that obtained by us using the DSC technique. These results do not seem to be an artifact since the proportion (20−50) NaOH per one AGU at cellulose concentrations around 1−2% was obtained independently by two different methods. The question is why it is so. Above the melting temperature of all crystalline structures, in the liquid phase of the NaOH/water mixture, there should be two species fully mixed: the one that will make the eutectic compound (i.e., water on one hand) and a $NaOH{\cdot}5H_2O$ hydrate on the other. According to Figure 5, in dilute solutions, when cellulose traps one NaOH hydrate, this prevents a large amount of the NaOH neighbors from crystallizing. It is an indication that these hydrates are strongly interacting in the liquid state, forming a sort of network. To change the state of one of these hydrates seems to drastically affect the state of the others around, preventing them from participating in the crystallization of the eutectic compound. When the cellulose concentration increases, the clouds of these affected NaOH hydrates touch each other, and this decreases the effective number of affected NaOH per AGU, down to the minimum case where there are only NaOH hydrates that directly interact with the cellulose chain.

The final step was to calculate the proportion between linked water, NaOH, and cellulose molecules. In cellulose/NaOH/water solutions, H_2O is present in three forms or compounds: (1) as a free water frozen to ice below the liquidus curve; (2) in the eutectic mixture that is not linked to cellulose below the crystallization point of the eutectic mixture; and (3) in the mixture linked to cellulose through NaOH.

As far as the amount of free water not changing with adding cellulose, this means that the number of water molecules linked to NaOH that are bound to cellulose has the same composition as the eutectic mixture. The number of water molecules linked to one anhydroglucose unit is then straightforward to calculate: it is a product of $N_{\mathrm{NaOH}} \times 9$; N_{NaOH} calculated according to eq 6, and nine being the number of water molecules in the eutectic mixture.

4. Conclusion

DSC experiments and careful analysis of experimental data allowed the understanding of the thermodynamic behavior and structure of microcrystalline cellulose/sodium hydroxide aqueous solutions at temperatures below 0 °C, in the region of cellulose dissolution. It was possible to determine the limit of cellulose dissolution in NaOH/water as being at least four NaOH molecules per one anhydroglucose unit or the weight ratio of cellulose/NaOH being one. If the concentration of cellulose is higher, it will not be dissolved. Because cellulose can be dissolved only in a narrow range of sodium hydroxide concentrations, from 7 to 10%, this means that the maximal amount of cellulose that can be dissolved in NaOH/water solutions is 10%.

This result is compatible with what was found experimentally when preparing cellulose/NaOH/water solutions for processing. There is a strong limitation if one wishes to use such a solvent in commercial applications since the amount of polymer is rather low. It has two side effects. One is the cost of processing. The second is the fact that the properties of the final products may not be good due to the small amount of polymer material in the solution. It should be remembered that the dissolution limit in NaOH/water was determined for a low DP cellulose sample. For entropic reasons, increasing the molecular weight probably further decreased the ability to dissolve cellulose. As shown in refs 4 and 5, many insoluble parts are present in the solutions with high DP pulps or cotton.

The structure of the liquid solvent seems to be rather complex, with $NaOH{\cdot}5H_2O$ hydrates interacting strongly at low temperatures. It seems that the presence of such hydrates is important to dissolve cellulose. We can make the following tentative explanation about the dissolution power of NaOH/water solutions. The NaOH concentration plays a key role. If too much water is present (below 6−7% of NaOH), there is not enough NaOH to dissolve cellulose, and it is not a solvent. It may also be that the size of the hydrate is too large to penetrate the cellulose fibers. When the amount of water is low (NaOH concentrations higher than 18−20%), NaOH prefers to stay close to the cellulose chains forming a Na/cellulose crystal: it is the mercerization process with the formation of Na/cellulose. When the amount of water is in between these two cases (i.e., NaOH is 7−10%), NaOH hydrates penetrate into the cellulose fibers and bind to each chain but without forming Na/cellulose crystal. This pushes the detachment of individual chains out of the cellulose fiber and makes a solution. It seems that at these concentrations, there is a sort of unstable equilibrium between NaOH hydrates bonded to each other and to cellulose, which makes all the entities in solution.

The action of temperature could be as follows. The lower the temperature, the stronger the network of NaOH hydrates, probably due to the increase of the strength of the hydrogen bonding. At low temperatures, when cellulose is dissolved, this network will prevent the cellulose chains from interacting with each other and forming interchain hydrogen bonds. When the temperature is raised, the hydrogen bonds are weaker, and the network of hydrates is gradually destroyed.

The dissolution of cellulose thus needs NaOH hydrates as active compounds to penetrate into the cellulose fiber, in a certain equilibrium between bonding cellulose and water. The fact that at low temperatures there is probably a strong network of NaOH hydrates may explain why dissolution only occurs at low temperatures and why upon heating a slow physical bonding of cellulose chain occurs, seen as a gelation process. We assume that a combination of hydrates able to penetrate into the cellulose structure and able to prefer forming some type of network with themselves rather that bind to the cellulose only (as in the mercerization case) is found only in this small concentration and temperature region.

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References and Notes

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