A thermal behavior of low-substituted hydroxyethyl cellulose and cellulose solutions in NaOH-water

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ABSTRACT: Hydroxyethyl cellulose (HEC) with low molar substitution has better solubility in 8%NaOH-water solution than pure cellulose. The thermal behavior of ternary HEC/NaOH/water mixtures was investigated by DSC, and the results are compared with those of cellulose/NaOH/water solutions, aiming at providing better understanding about cellulose dissolution mechanism in NaOH-water. At low polymer concentrations and below 0°C, HEC and cellulose solutions exhibit a similar thermal behavior with ice, eutectic and/or melting and recrystallization peaks, showing that the overall interactions between NaOH, water and cellulose or HEC are identical. However, when the concentration increases above 2%, the eutectic peak of HEC solutions disappeared, leaving only the ice peak, which is different from previous results for cellulose where the disappearance of the eutectic peak was related to the maximum solubility of cellulose (around 8 wt%). This implies that the dissolution behavior of HEC in NaOH solution is changed due to possible changes of chain flexibility and/or increased attractions to water caused by the hydrophilic hydroxyethyl groups. The melting and recrystallization peaks visible only at low concentrations of HEC or cellulose in solution also support the conclusion that dissolution of cellulose and HEC at low concentrations bears features which are not yet understood.

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Cellulose dissolution has been an active field of research and technology since cellulose was identified and isolated (Liebert 2010; Navard et al. 2012). The reason for such research efforts at early times (broadly speaking before mid-twentieth century) was that cellulose was one of the cheapest polymers available in large quantities. At the present time, the driving forces for cellulose research are different. The research is pushed by such considerations as its renewable, natural, CO_2 neutral, biodegradable and biocompatible characters. Since cellulose is not melting,

it is possible to process it only through three ways: i) using cellulose fibres as is (for example, from cotton seeds or wood), ii) dissolving cellulose in a solvent to produce fibres, sponges and films (as presently used in the Lyocell process (Wendler et al. 2012)) or iii) derivatizing cellulose to further process it from solution or from a melt. In addition, the search for new sources of energy alternative to fossil ones requires de-structuring lignocellulosics into smaller molecular "bricks", a process where the recalcitrance of cellulose has very clear connections with its difficulty to be dissolved.

Cellulose is not soluble in common solvents, which is causing many difficulties for its processing. A good review of the various solvent options can be found in Liebert (2010). Among the potential solvents, the NaOH family has a special "status", mainly because of its easy-to-use character. Sodium hydroxide is a well-known chemical widely used in many industrial sectors due to its cheapness, easy handling, reasonable safety, low polluting hazards and good recyclability. It thus very early attracted interest as a solvent in the process called mercerisation, able to improve the quality of cellulose fibres or for making viscose fibers. The first scientist to report cellulose dissolution in aqueous (6-10)%NaOH was Davidson (1934; 1936). However, the dissolution power of this solvent turned out to be rather weak and additives like ZnO (Davidson 1937) or urea (Laszkiewicz, Wcislo 1990) were used to help dissolution. These results were never used in practice due to the low dissolution yield, the need to perform dissolution at temperatures below zero and the impossibility to dissolve high molar masses. In the 1980's, Japanese researchers from Asahi Corporation looked again at the possibility to dissolve cellulose in NaOH-water and they found that it was possible to overcome some of these difficulties by using steam exploded pulps (Kamide et al. 1987; Matsui et al. 1995; Yamashiki et al. 1988). Many physical and chemical studies of cellulose-alkali aqueous solutions were performed at that time but they did not bring this new process to the industrial level.

In the last decade, several groups took again this topic and revisited cellulose dissolution in NaOH-water without or with additives, such as ZnO, urea, thiourea and their combinations. It was found that these additives are helping dissolution, enabling to use cellulose of larger molar mass and retarding the formation of gel at room temperatures, allowing thus to produce fibres, membranes, aerogels and films at laboratory scale (Cai, Zhang 2006; Cai et al. 2004; Egal et al. 2007; Gavillon, Budtova 2007; Roy et al. 2003; Zhou et al. 2004). However, the NaOH process is still too complicated to be efficiently used for manufacturing industrial products. The low cellulose concentration (below 10%), the use of sub-ambient temperatures for dissolution, the need to

recycle mixtures of solvents are among the difficulties which have not yet been overcome at the industrial level.

The dissolution of cellulose in NaOH-water occurs at NaOH concentrations between 6 and 10% and temperatures around and below -6°C. Freezing of cellulose-NaOH-water also helps dissolution. The thermal behavior of NaOH-water is well known, with a classical eutectic behavior in the region of low NaOH concentrations, of interest here (Egal et al. 2007). The eutectic composition is a crystalline mixture of sodium pentahydrate and four water molecules (NaOH·5H$_2$O; 4 H$_2$O) with a melting peak around -33°C and melting enthalpy of 187 J/g measured at the eutectic composition (20% of NaOH in water). At temperatures below -33°C and NaOH concentrations below 20%, there is a mixture of eutectic crystals and ice. Upon increasing temperature, the eutectic mixture is melting, giving a mixture of liquid hydrates and ice; further heating leads to ice melting. The DSC trace is thus composed of two peaks: the narrow eutectic melting peak and a wide melting peak of ice which extends over a large temperature range (Egal et al. 2007; Roy 2002; Roy et al. 2001). The addition of cellulose is not changing the behavior of the melting of ice meaning that the liquidus is not influenced by the presence of cellulose. The eutectic melting peak also remains at the same temperature, but the area of the peak is reduced (Egal et al. 2007; Roy 2002; Roy et al. 2001). The enthalpy of this eutectic peak is decreasing with the increase of cellulose concentration until its complete disappearance. It was supposed that when all "available" NaOH are "captured" by cellulose, dissolution stops and no more cellulose can go in solution. The addition of a polymer is not leading to the presence of the polymer in the NaOH-water eutectic mixture which always stays with the same composition as in the pure solvent. But the addition of a polymer is influencing the amount of eutectic crystals in the system. Based on this reasoning, cellulose dissolution limit was deduced as being four NaOH per one anhydroglucose unit (AGU) or roughly equal weight concentrations of NaOH and cellulose (Egal et al. 2007).

However, there were two intriguing facts. The first is reported in (Roy 2002). It was noticed that at low cellulose concentrations and temperatures below the melting of the eutectic peak, there was the appearance of a melting and immediate re-crystallisation of a crystalline phase. It was supposed that some instable species were created at low cellulose concentrations, but that they were not directly linked to cellulose, since they disappeared with the increase of cellulose concentration in solution (above 1-2wt%). No more study was done to understand the origin of these peaks. The second intriguing fact was the number of NaOH which is supposed to be linked to each AGU. Above 3% of cellulose, the proportion between NaOH and AGU was 4:1 (see *Fig 5* in Egal et al. 2007) while at lower cellulose concentrations, the number of NaOH linked to each AGU increases enormously with the decrease of cellulose concentration (see *Fig 5* in Egal et al. 2007). At the lowest cellulose concentrations reported in Egal et al. (2007), up to 20 NaOH molecules seemed to be linked to each AGU. We recall that this calculation was made by considering that NaOH

molecules are linked to cellulose and not anymore to eutectic crystal. It was supposed in previous papers (Yamashiki et al 1988; Zhou et al, 2004), and in this paper that Na$^+$ ions are solvating cellulose, not considering the possibility that cellulose could be solvated by OH$^-$. From all points of views, in particular steric ones, to accommodate 20 Na$^+$ hydrated shells around each AGU is difficult to conceive. No clear explanation of this fact was given in the paper of Egal et al. (2007).

The mechanisms behind the dissolution of cellulose in NaOH-water are still not fully clear. One point of view is that NaOH is able to break the dense network of hydrogen bonds (Zhang et al. 2010) and form a sort of shell of hydrated Na$^+$ ions around the cellulose chain, bringing them into solution (Egal et al. 2007). A similar mechanism with the formation of inclusion complexes has also been advocated when urea or thiourea is added (Jiang et al. 2014), considering that there are no interactions either between urea and NaOH, or between urea and cellulose (Egal et al. 2008). Other points of views consider that dissolution requests to weaken cellulose-cellulose hydrophobic interactions that prevent dissolution, which would be the role of urea (Lindman et al. 2010; Medronho, Lindman 2014). One of the reasons of cellulose poor solubility is said to be its chain rigidity and thus very small gain in conformational entropy during dissolution. The same lack of conformational mobility is the reason for the impossibility to dissolve oligomers of cellulose and cellulose itself in water, apparently because of the non-destruction of O3-O5 hydrogen bonds (Bergenstrahle et al. 2010). It is the same bonds that were already identified by Kamide et al. (1984) who reported that regenerated cellulose from a cupramonium solution and ball milled amorphous cellulose dissolves in aqueous alkali and that the solution is stable over a long period of time if the hydrogen bond intramolecular (O3- O5) is weakened.

One possible way to use NaOH-based solvents and increase cellulose dissolution limit and stability is to derivatize cellulose at low substitution. This is what has been tested recently by synthesising hydroxyethyl cellulose (HEC) with low molar substitution (*MS*) between 0.2 to 1 (Wang et al. 2013). It was possible to make HEC fibres wet spun from 9%cellulose in NaOH-water based solvents. This way seems to be an alternative to the viscose process.

Since it is possible to dissolve high concentrations of HEC, it is of interest to study the thermal behavior of the HEC-NaOH-water solutions and compare it to cellulose solutions. In particular, since the limit of solubility of HEC seems to be higher than the one of cellulose, to compare the influence of HEC and cellulose on the behavior of the NaOH eutectic peak might bring some clues regarding the understanding of cellulose dissolution mechanism in NaOH-water.

Materials and Methods
Materials
Cotton linters were purchased from Xiangtai Corporation (Hubei Province, China) with degree of polymerization

(*DP*) of 1000 as provided by the manufacturer. Microcrystalline cellulose Avicel PH-101 ("cellulose" in the following) with a DP of 170 was from Sigma-Aldrich and was used to prepare cellulose-8wt% NaOH solutions. Commercial HEC used in this study was purchased from Sigma-Aldrich. According to the manufacturer, the weight-average molecular weight (M_w) of the commercial HEC is around 250 000, and the *MS* is 2.0. Sodium hydroxide in pellets was supplied by Merck with purity higher than 97%. Ethylene oxide (EO) was purchased from Sinopharm Chemical Reagent Co., Ltd. Glacial acetic acid of analytical grade was supplied by Enterprise group chemical reagent Co., LTD and used without further purification. Distillate water was used for making solutions. All concentrations are in wt%.

Preparation of hydroxyethyl cellulose (HEC)

The synthesis of HEC was conducted in heterogeneous conditions as described in a previous publication (Wang et al. 2013). Cellulose was first dried in the vacuum and immersed in 21% NaOH aqueous solution under vigorous stirring for 1 h at ambient temperature. The excess of NaOH solution was removed, and then alkaline cellulose was mixed with different amounts of ethylene oxide (EO) and placed under vacuum in a 2 l stainless steel autoclave equipped with a mechanical stirrer. The mixture was stirred at 40°C for 100 min. The obtained polymer was neutralized with acetic acid, repeatedly rinsed with distilled water and dried under vacuum. Three samples were prepared with mass ratio of EO to cellulose in the reaction medium of 0.13 (MS = 0.24), 0.15 (MS = 0.28) and 0.20 (MS = 0.38). The samples will be noted in the paper as HEC-0.13, HEC-0.15 and HEC-0.20, respectively.

Preparation of cellulose and HEC solutions in 8%NaOH-water

Dried cellulose was swollen in distilled water at 5°C for 1 h and then was mixed with an aqueous solution of NaOH (18-20% of NaOH) cooled to -6°C. The resulting mixture of cellulose and 8% NaOH solution was stirred at 800-1000 rpm for 2 h at -6°C to obtain the cellulose solutions of various concentrations.

Dry HEC samples were immersed into the 8%NaOH aqueous solution pre-cooled to -6°C. Transparent solutions with various HEC concentrations were obtained after mixing at about -6°C and stirring at about 1400 rpm for 2 h. Then, the resultant HEC solutions were subjected to centrifugation at 6000 rpm for 20 min in order to remove the air bubbles.

Both the cellulose and HEC solutions were kept in closed vessels at 5°C to avoid gelation and oxygen-induced degradation.

DSC

Differential scanning calorimetry (DSC) experiments were performed on a PerkinElmer DSC-4000, 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 +20°C to -60°C, maintained at -60°C for 1 h and then heated up to +10°C. Cooling and heating

rates were 1 °C/min. This rate was chosen to compare results with previously published data (Egal et al. 2007) and because of the high heat capacity of gold-plated stainless steel caps.

Results

Fig 1 is showing the typical behavior of 8%NaOH-water and its solutions with cellulose and HEC. We see three types of peaks: Peak I at the highest temperature (melting of ice), Peak II around -33°C (melting of the eutectic mixture) and Peak III (a melting-recrystallisation process with two peaks). *Fig 2* is giving the DSC traces for solutions of various polymer concentrations prepared with the four HEC samples and *Table 1* shows the characteristics of the peaks.

It is possible to draw the following conclusions from this series of results. Peak I is the melting of ice upon increasing temperature, when moving from solidus to liquidus. The precision of enthalpy measurement is not very good due to the difficulty of estimating the beginning of the melting process, but the general conclusion is that there is no variation of its enthalpy of melting as a function of concentration or type of HEC as it is also the case for cellulose. The same has been reported for cellulose-8%NaOH-water (Egal et al. 2007).
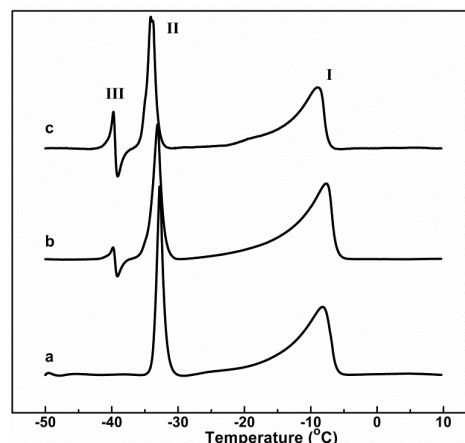

Fig 1 - Typical DSC traces of solutions of a) 8%NaOH-water; b) 0.5% cellulose-8%NaOH-water and c) 0.5% HEC-0.13-8%NaOH-water solutions.
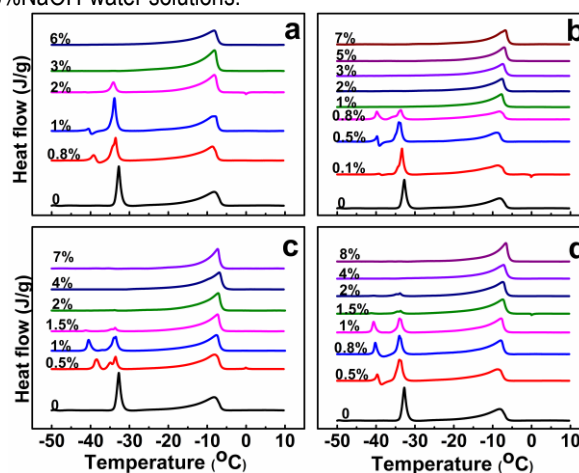

Fig 2 - DSC melting thermograms of solutions in 8 wt% NaOH solution at different polymer concentrations (baseline has been subtracted) for a) commercial HEC; b) HEC-0.13; c) HEC-0.15 and d) HEC-0.20.

Table 1 - Examples of enthalpy and temperature of the peaks observed for cellulose and the four HEC-8%NaOH-water solutions. The melting temperature of a compound is taken at the maximum of the peak. T_{ice}, T_{eut}, T_{melt} and T_{crys} stand for the temperature corresponding to the peak summit of ice (peak I), eutectic mixture melting (peak II), and melting and recrystallisation at low temperature (peak III), respectively. ΔH_{ice}, ΔH_{eut}, ΔH_{melt} and ΔH_{crys} are the corresponding enthalpies.

$C_{polymer}$, (%)	Peak I (ice)		Peak II (eutectic mixture)		Peak III (melting and recrystalllization)	
	T_{ice}, (°C)	ΔH_{ice}, (J/g)	T_{eut}, (°C)	ΔH_{eut}, (J/g)	T_{melt} /T_{crys}, (°C)	ΔH_{melt}/ΔH_{crys}, (J/g)
Cellulose						
0	-8.23	151.49	-32.74	74.25		
0.5	-7.68	161.67	-33.07	71.48	-39.15/-39.51	-4.38/4.30
1	-8.58	113.67	-33.71	58.94	-39.58/-40.56	-5.72/9.87
2	-8.45	134.67	-33.45	46.74	-39.14/-41.38	-13.31/18.37
6	-6.79	109.24	-33.45	2.71		
HEC-0.13						
0.1	-8.66	136.96	-33.34	72.08	-38.45/-39.26	-1.22/1.03
0.5	-7.95	160.86	-33.37	67.72	-38.84/-39.62	-11.12/8.97
1	-7.77	188.88				
2	-7.6	173.86				
4	-7.45	160.19				
5	-7.08	176.59				
7	-6.78	171.93				
HEC-0.15						
0.5	-8.11	163.30	-33.58	35.45	-38.45	21.10
1	-7.63	160.47	-33.52	41.34	-40.50	21.41
1.5	-7.34	156.83	-33.71	8.94	-41.22	1.09
2	-7.18	171.32	-33.85	1.27		
4	-6.89	171.19				
7	-7.33	160.93				
HEC-0.20						
0.5	-8.78	155.68	-33.99	70.26	-38.55/-39.70	-9.76/9.90
0.8	-7.94	153.43	-34.01	47.29	-38.08/-40.21	-9.78/18.3
1	-7.81	132.50	-33.95	40.40	-40.63	22.08
1.5	-7.44	167.01	-33.7	9.95	-41.23	0.78
2	-7.41	149.31	-33.85	9.48	-40.56	0.82
4	-7.23	155.88				
8	-6.6	171.20				
Commercial HEC						
0.8	-8.37	148.95	-33.62	52.15	-37.54/-39.34	-3.11/10.23
1	-8.67	135.48	-33.88	57.74	-39.64/-40.52	-8.21/2.88
2	-8.05	131.81	-34.09	6.67		
3	-8.12	126.86	-33.99	0.21		
6	-8.22	155.22				

The temperature of the end of the peak T_{end} reflects the position of the liquidus on the ternary phase diagram. It seems that there is no decrease of T_{end} with HEC concentration, but the absolute value seems to slightly depend on *MS*. However, this absolute value is similar, if not identical, regarding the rather large error made in its estimation, to the one of 8%NaOH-water solution without dissolved polymer. The overall behavior of Peak I is very similar between HEC and cellulose, expressing the fact that there is no major change in the shape of the phase diagram between solidus and liquidus. It means that ice crystals present at low temperature are formed in the same manner with or without polymer dissolved.

Peak II is the melting of the eutectic mixture. As for cellulose-8%NaOH-water solutions (Egal et al. 2007), the position of the peak in the presence of HEC is the same as in pure 8%NaOH-water. This shows that eutectic mixture is not perturbed by the presence of HEC. As for cellulose, the enthalpy ΔH is decreasing when polymer concentration is increasing. *Fig 3* is giving the value of

the melting enthalpy of the eutectic peak II as a function of polymer concentration for the four HEC solutions and cellulose solutions (from two sources, one from Egal et al. 2007, and the other one from the present work).

The most striking result is that the melting enthalpy of the eutectic mixture of HEC solutions reaches zero at about 2% HEC. It means that all NaOH are used by HEC at only 2% concentration since they are not anymore able to participate to the formation of the eutectic mixture.

However, this is not preventing HEC to be dissolved at much higher concentrations. This means that the approach taken for cellulose dissolved in 8%NaOH-water where the disappearance of the eutectic peak was associated to the maximum solubility of cellulose is not applicable to HEC dissolved in the same solvent. As shown on *Fig 3*, there is no visible difference in the decrease of ΔH with concentration for the four HEC polymers, but more strangely, the values of ΔH for cellulose are very similar to the ones of HEC in the concentration region below 2-3%. A straight line is shown
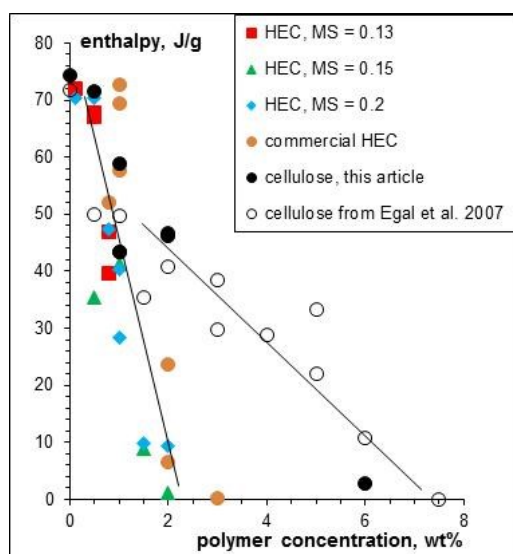
Fig 3 - Enthalpy of the eutectic peak as a function of polymer concentration for cellulose and the four HEC samples in 8%NaOH-water.

on *Fig 3* in this low concentration region demonstrating that ΔH is decreasing in the same manner for cellulose and HEC.

Peak III is present in all cellulose and HEC solutions at low polymer concentration. Its intensity is not very regular and repeating the same DSC experiment on the same solution did not always give the same values of enthalpies. In most cases, the enthalpies of the melting and crystallization parts of peak III were identical (with some few exceptions). It is the melting and recrystallization of unknown species which appear only when cellulose or HEC concentration is low.

Discussion

DSC traces of all HEC and cellulose solutions in 8%NaOH-water are very similar, meaning that the same overall interactions phenomena occur between the solvent and these two types of polymers. Except for Peak III, DSC thermograms of HEC and cellulose solutions are similar to the one of the solvent, with eutectic and ice melting peaks located at the same temperatures. This means that the structure of NaOH-water is not perturbed by these polymers. At low polymer concentration, below 2% of either cellulose or HEC, the behavior of HEC and cellulose solutions is identical as far as Peaks I, II and III are concerned. The overall interactions between NaOH, water and cellulose or HEC should thus be identical, leading to the same ternary phase diagram structure.

However, the fact that the dependence of the melting enthalpy of the eutectic mixture is similar at low concentrations but strongly differ at higher concentration is questioning the possibility to detect the maximum polymer concentration by using the method reported in Egal et al. (2007). It is probably valid when the dissolution mechanism is such that a certain minimum amount of solvent species is needed to dissolve the polymer. When the amount of these species is exhausted due to the increase of polymer concentration, dissolution stops. This is what is happening with cellulose, but not with HEC as far as NaOH is concerned. A small amount

of substitution is drastically affecting the dissolution behavior in NaOH-water. Even when there are no more available Na^+ ions as seen by the disappearance of the eutectic crystals, it is still possible to dissolve HEC at higher concentration. There is thus a change of the dissolution mechanism, already seen at the lowest substitution degree, where it is not Na^+ ions that play the most important role in the dissolution, but water (highly substituted HEC are water soluble). Solubility is strongly increasing, due to changes in both solvent – solute interactions and solute-solute interactions. This means that an additional parameter is at stake in the case of HEC, and not present in cellulose.

Several reasons can explain these differences. A first one is that there could be an increase of conformational entropy in the case of HEC compared to pure cellulose, with even a very low amount of substitution being able to induce enough flexibility so that the number of accessible conformations in solution largely exceeds the ones in solid state, thus helping dissolution. This remains to be checked and it does not seem to follow the usual trend which is that some cellulose derivatives are more rigid than pure cellulose (Navard et al. 2012). Another possibility is that hydrophilic hydroxyethyl groups attract water increasing the dissolution power in addition to NaOH which dissolves non-derivatised cellulose. Hydroxyethyl groups help "separating" cellulose chains one from another and also prevent the formation of cellulose-cellulose hydrogen bonds due to steric reason. Many questions remain, among which is why there are so many NaOH molecules unable to form the eutectic mixture when cooling, at low polymer concentrations, and where Egal et al. (2007) postulated that these molecules were around the cellulose chains on the basis of the behavior at high cellulose concentrations. The results obtained with HEC solutions seem to suggest that this is incorrect, at least for low polymer concentration. The role of Peak III, only present in this low temperature range and at low polymer concentrations, was not fully considered previously but must well be involved in the dissolution process. Peak III is never seen without cellulose or HEC; it is suggesting that the phase diagram might be more complicated than the simple eutectic one considered up to now.

Conclusions

These new results are bringing several conclusions. The first is that the dissolution mechanisms of cellulose and HEC at low polymer concentrations are similar, with probably a complex structure of hydrates that are linked to the polymer chain and are preventing NaOH to participate to the eutectic mixture. At higher concentration, we can postulate that either some additional chain flexibility is present in HEC or that there is a splitting of interactions (water bonding to hydroxyethyl moieties and Na hydrates to AGU) leading to an increased dissolution power without having to "rely" only on NaOH content.

The second conclusion is that all experiments (NMR for example) must be conducted in the low and high concentration regions in order to avoid having half the picture of dissolution mechanisms.

A third conclusion is that kinetics does not seem to play a role, since the mechanisms are seen whatever the molar mass is. The final conclusion is that the difference seen between low and high concentration ranges has nothing to do with the interaction of chains since the overlap concentration of polymer with low and very high degrees of polymerisation is very different, which is here the case of low DP microcrystalline cellulose and high DP HEC. This argument is somehow of the same nature as the one related to kinetics.

Acknowledgments

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