Dissolution of cellulose using a combination of hydroxide bases in aqueous solution

Beatrice Swensson · **Anette Larsson** · **Merima Hasani**

Abstract In order to further understand the role of the cation when dissolving cellulose in aqueous solutions of hydroxide bases, different bases were combined in solution. Up to 5 wt.% of microcrystalline cellulose was dissolved using a combination of NaOH and the organic base tetramethylammonium hydroxide (TMAH) in water at low temperatures. Thermoscans of solutions containing both NaOH(aq) and TMAH(aq) indicated that cellulose interaction with TMAH seems to be favoured over NaOH. Dynamic rheology measurements of the solutions revealed that combining the two bases delayed gelation significantly when compared to cellulose dissolved in NaOH(aq) or TMAH(aq) alone. Intrinsic viscosity of cellulose in the combined NaOH- and TMAH(aq) solutions was slightly higher than that of the single-base solutions, indicating a slight increase in solvent quality. This shows that combining bases may lead to synergies that improve solvent stability without requiring the use of other additives.

B. Swensson · A. Larsson · M. Hasani (✉)
Department of Chemistry and Chemical Engineering,
Chalmers University of Technology, 412 96 Gothenburg,
Sweden
e-mail: beatrice.swensson@chalmers.se

A. Larsson
e-mail: anette.larsson@chalmers.se

M. Hasani
e-mail: merima.hasani@chalmers.se

A. Larsson · M. Hasani
Wallenberg Wood Science Center, The Royal Institute of
Technology, Chalmers University of Technology,
10044 Stockholm, Sweden

Graphic abstract
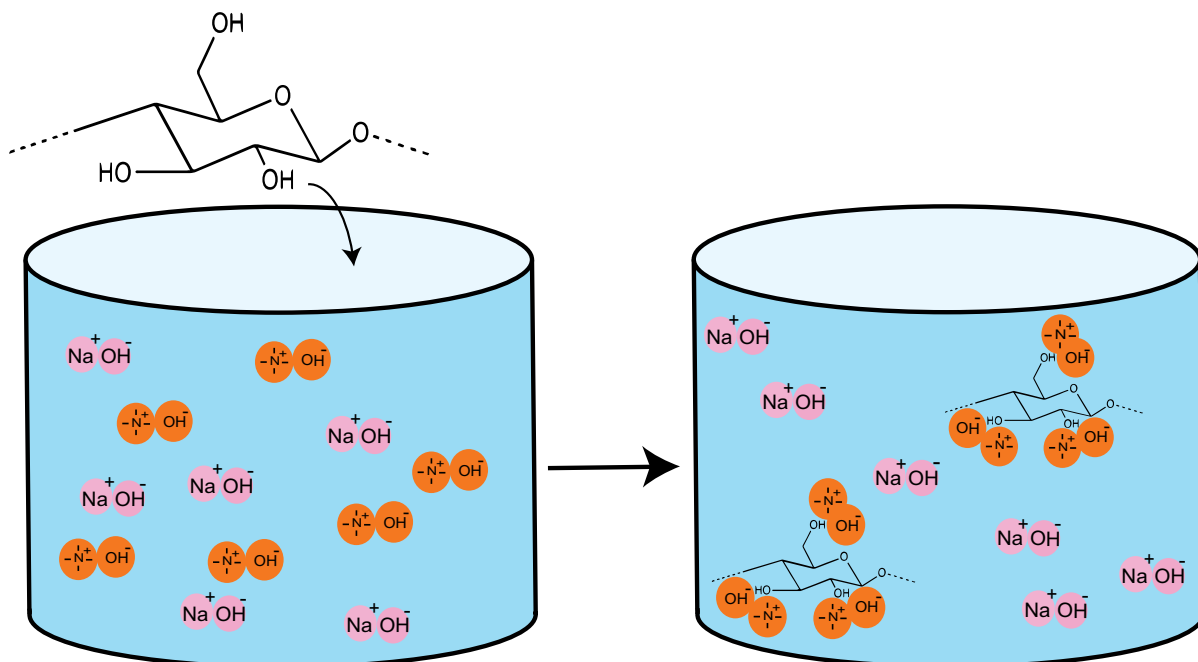
Introduction

Cellulose is an excellent raw material for the development of renewable, biodegradable materials that can replace or complement, for example, single-use plastic articles and fossil-based textiles. Many of these applications require processing in order to shape the cellulose into films, membranes, textile fibers, etc. This requires dissolution-based processing, however, since cellulose degrades before it melts. In order to dissolve cellulose, cellulose-solvent interactions are required to overcome the attractive stabilising forces between the cellulose chains: cellulose chains are, namely, stabilised through strong intra- and intermolecular hydrogen bonding as well as hydrophobic interactions and are, as such, organized in semicrystalline fibrils that are further assembled in complex layered hierarchical morphology. Despite this, numerous solvents have been developed and most of them are complex systems, such as ionic liquids (Wang et al. 2012), specific salt-solvent combinations

[e.g. DMAc/LiCl (McCormick et al. 1985), DMSO/TBAF (Liebert and Heinze 2001)], aqueous solutions of bases or acids [e.g. NaOH(aq) (Sobue et al. 1939; Davidson 1934), quaternary ammonium hydroxides(aq) (Powers and Bock 1935), phosphoric acid(aq) (Boerstoel et al. 2001)], hydrated metal amine salts [e.g. Schweizer's reagent (Schweizer 1857)] as well as those relying on the derivatization of cellulose [e.g. industrially important CS_2/NaOH(aq)]. Aqueous solution of NaOH is of particular interest since it is inexpensive, non-toxic, readily available and already in use in the pulp and paper industry. Dissolution of cellulose in NaOH(aq), however, only occurs below +1 °C and in solutions with a NaOH concentration between 7 and 10 wt.% (Budtova and Navard 2016). The use of this solvent system has also been held back, partly due to its inability to dissolve cellulose with a DP over ca 200 and partly due to problems with the instability of the solutions as they gel with increasing time, temperature and/or concentration of cellulose (Roy et al. 2003). Considerable efforts have therefore been made to improve dissolution in the cold NaOH(aq) system and different additives have been identified, including urea (Zhou and Zhang 2000), thiourea (Zhang et al. 2002), ZnO (Yang et al. 2011) and polyethylene glycol (Yan and Gao 2008). Whilst a

general stabilisation mechanism for these additives has not been established, emphasis in current research is now being placed on the importance of hydrophobic interactions in solvent systems, since the amphiphilic nature of cellulose has been investigated widely. It has been shown, for example, that increasing concentrations and molecular weights of cellulose can be dissolved by increasing the hydrophobicity of the cation in quaternary ammonium hydroxide bases (Wang et al. 2018).

The aim of this work was to increase understanding of the dissolution of cellulose in aqueous solvents and, more specifically, the role of the cation, by combining different hydroxide bases and investigating whether or not cellulose displays an affinity for different cations. The resulting solutions were investigated using differential scanning calorimetry to identify the hydrate structures of the bases in solution, and how these are affected by each other and by cellulose. Moreover, NMR spectra of selected solvents were analysed to shed additional light on molecular interactions. In order to investigate if these solutions displayed properties different to those of single-base solutions, intrinsic viscosity analysis was used to compare the solvent quality, while dynamic rheology measurements were performed to investigate effects on solution stability.

Experimental

Materials

Microcrystalline cellulose (MCC), Avicel PH-101 purchased from FMC BioPolymer, a purified partially depolymerized cellulose made by acid hydrolysis of specialty wood pulp, with a degree of polymerization of 180 as measured by GPC-MALLS (personal communication with Majid Ghasemi at Södra skogsägarnas ekonomiska förening), was used. Granulated sodium hydroxide (NaOH) known commercially as Emplura, tetrabutylammonium hydroxide (TBAH) 40 wt% in H_2O, methyl-α-D-glucopyranoside (99%) and deuterium oxide (D_2O, 99.9%) were purchased from Merck (previously Sigma-Aldrich) and used as received. Potassium hydroxide (KOH) pellets (analysis grade) were purchased from Merck. Tetramethylammonium hydroxide (TMAH) aqueous solutions made from either TMAH

pentahydrate or 25 wt% TMAH solution in water, were also purchased from Merck and diluted with deionized water.

Dissolution of cellulose

The solvent was prepared by dissolving the desired amount of base in deionized water. MCC was added to the solvent under stirring in an ice bath and left to stir for 5 min or until dispersed. The solution was then stored in a freezer at $- 20\ ^{\circ}C$ for 20 min before being stirred in an ice bath for up to 5 min to remove any ice crystals that might have formed, and to ensure a more homogeneous sample.

Determination of the maximum solubility of MCC in solutions

Solutions of cellulose were prepared as described above (see "Dissolution of cellulose") with increasing concentrations of cellulose, starting from 3 wt% MCC. Immediately after dissolution, a droplet of solution was placed on a glass plate and pressed between it and a glass window before being observed in a microscope (ZEISS SteREO Discovery.V12) using cross-polarized light at room temperature. When several undissolved crystals were observed, the dissolution limit was deemed reached. It is relevant to mention that this does not determine whether the cellulose is molecularly dissolved or not but it is a quick method to estimate a rough dissolution limit.

Intrinsic viscosity

Cellulose solutions were prepared as described above (see "Dissolution of cellulose") with cellulose concentrations in the range of 0.1 to 1.1 g/dL. Solutions, with or without cellulose, to be used for determining intrinsic viscosity were placed in a 25 °C water bath directly after dissolution for 30 min; the viscosity was then measured using a capillary viscometer with circulating water (for the purpose of temperature control) at 25 °C. Three measurements were made for each sample and the average was used to calculate the relative viscosity, which was determined with a maximum error of 2%. The intrinsic viscosity was obtained from linear regression with a coefficient of determination of at least 0.97.

Dynamic rheology

Oscillatory dynamic rheology measurements were performed to monitor stability of solutions over time. A TA Discovery Hybrid Rheometer (HR-3), with a sandblasted 40 mm plate-plate geometry with a gap of 1 mm, was employed and the temperature was controlled by a Peltier plate with circulating cooling liquid. Strain (γ) sweeps were conducted to determine the linear viscoelastic region and can be found in the supplementary information in Figures S2–S7. From these an angular frequency of 1 rad/s and a strain of 10% were chosen for samples with 3 wt% MCC to increase measurement sensitivity and an angular frequency of 1 rad/s and a strain of 1% for samples with 5 wt% MCC. Samples were measured directly after dissolution with a water-filled solvent trap and brought to the desired temperature in the rheometer without pre-shearing. The point of gelation was taken when G'=G''. Even though this is a rough estimation, it is here used for comparative purposes under the same conditions.

Differential scanning calorimetry (DSC)

Aqueous solutions of bases with and without cellulose were prepared as described above (see "Dissolution of cellulose") and thermoscans of the solutions were performed using a DSC 250 from TA Instruments Discovery series equipped with stainless steel pans. Aqueous solutions of bases were cooled at a cooling rate of 10 °C/min down to − 70 °C and kept at − 70 °C for 5 min; all of the samples were then heated up to 80 °C at a heating rate of 1 °C/min, with the exception of 2.3 M NaOH(aq), which was heated up to 10 °C. The procedure for solutions with dissolved cellulose was the same as for NaOH(aq).

Nuclear magnetic resonance (NMR)

NMR analysis was performed on samples containing methyl-α-D-glucopyranoside (0.4 M) dissolved in D_2O with 2.3 M NaOH, 2.3 M TMAH and 2.3 M 50/50 mol% NaOH/TMAH, respectively. The NMR measurements were run on an 800 MHz magnet equipped with a Bruker Avance HDIII console and a TXO cryoprobe. Spectra were recorded with a low-angle radio frequency pulse to minimize relaxation-weighting using a single pulse experiment with [1]H

decoupling during acquisition and a relaxation delay set to 5 s; 8 scans were collected. A capillary containing D_2O with 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt (DSS) was placed inside the tube as an internal reference.

Results and discussion

Solubility of cellulose in aqueous solutions of combined hydroxide bases
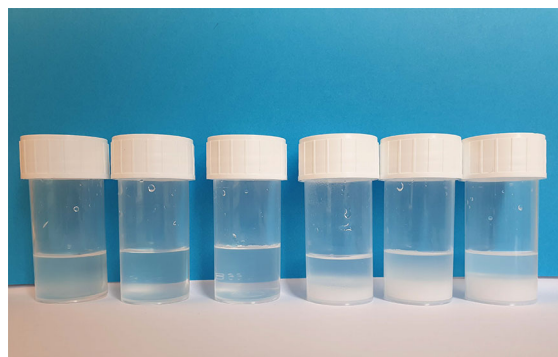
Several combinations of bases were studied to investigate whether it was possible to combine hydroxide bases in water to dissolve cellulose, and to determine the demands this would place on the cation, including combinations where only one or both of the bases have been reported to dissolve cellulose. One of the combinations tested was NaOH with KOH. Unlike NaOH, KOH is unable to dissolve cellulose in aqueous solution, but it is a stronger base. It has been proposed that the inability of KOH to dissolve cellulose arises from its loose hydration shell: where the water in the hydration shell can easily exchange with bulk water (Xiong et al. 2013). Bearing this in mind, discovering if the presence of NaOH would aid KOH to interact with cellulose is therefore of interest. The results show that solutions of KOH with NaOH or TMAH in 2.3 M 50/50 mol% aqueous solution were unable to dissolve 3 wt% of cellulose. This indicated that reaching a high concentration of [OH⁻], i.e. high pH, was insufficient: both cations need to be able to stabilise cellulose. We therefore moved on to combining NaOH and tetra-butylammonium hydroxide (TBAH) in 2.3 M 50/50 mol% aqueous solution: this was also unsuccessful in dissolving cellulose, even though cellulose can be dissolved in solutions of the respective bases (Sobue et al. 1939; Lilienfeld 1924). The sample also differed from the others in that, after the addition of cellulose, it turned from being a liquid to having a more solid consistency, as Fig. 1 shows. This indicated a lack of (or significantly reduced amount of) unbound water in the sample. Dissolution of cellulose in TBAH has been reported to occur around room temperature and not at the temperatures required for NaOH to dissolve cellulose (Alves et al. 2016), because TBAH crystallises below ca 30 °C (depending on its hydration). This led to the assumption that, in order to dissolve cellulose, the two bases should have a

Fig. 1 From left to right: 3 wt% MCC in 2.3 M 50/50 mol.% KOH/TMAH(aq), 2.3 M 50/50 mol% KOH/NaOH(aq), 2.3 M 50/50 mol% NaOH/TBAH(aq) and 2.3 M 50/50 mol% NaOH/TMAH(aq)

Fig. 2 From left to right: 3 wt% MCC in 2.3 M NaOH(aq), 2.3 M 50/50 mol% NaOH/TMAH(aq), 2.3 M TMAH(aq), 1.15 M NaOH(aq), 1.15 M 50/50 mol% NaOH/TMAH(aq) and 1.15 M TMAH(aq)

temperature interval in common where they can dissolve cellulose. Based on these conclusions, tetramethylammonium hydroxide (TMAH) and NaOH, both of which are known to dissolve cellulose at low temperatures, were chosen and 3 wt.% MCC was dissolved successfully in 2.3 M 50/50 mol% NaOH/TMAH(aq), as can be seen in Fig. 1.

In 2.3 M 50/50 NaOH/TMAH(aq) solution, the respective concentrations of NaOH and TMAH corresponded to 1.15 M; the solubility of 3 wt% MCC in 1.15 M of each base was tested in order to confirm that neither NaOH nor TMAH alone were responsible for dissolution. The solubility of 3 wt% of MCC in 1.15 M of the combined bases was also tested to see if the total amount of base needed for dissolution could be lower than 2.3 M. The results showed that cellulose could not be dissolved in any of the solvents at 1.15 M, as can be seen in Fig. 2; here it can be observed that MCC dissolved in 2.3 M NaOH(aq), 2.3 M TMAH(aq) and in 2.3 M 50/50 mol% NaOH/TMAH(aq) but not in the corresponding solutions containing only 1.15 M of one single base, as observed by the sedimentation of cellulose. This confirms that, in the 2.3 M 50/50 mol% NaOH/TMAH(aq) solution, the two bases do not disturb the dissolution capacity of each other but rather that they must be able to coexist, or even cooperate, to dissolve cellulose. The results also showed that, in order to dissolve cellulose, a certain minimum concentration of base is required; for this particular combination of bases, it corresponds to base concentrations between 1.15 and 2.3 M.

The observation that a certain minimum concentration of base is required to dissolve cellulose has also been made for the cold NaOH(aq) system (Sobue et al. 1939), and seems to be applicable to solvents consisting of these types of hydroxide bases in water. When phase diagrams of NaOH(aq) (Egal et al. 2007) or TMAH(aq) (Mootz and Seidel 1990) are viewed it is clear that, for concentrations of base below the minimum required to dissolve cellulose, still the same eutectic hydrate structure is present but diluted in this case by bulk (unbound) water. This indicates that it is not just the hydrated base that is crucial for dissolution: these hydrates need to exceed a certain critical concentration to provide dissolution. Another driving force for cellulose to go into solution could be deprotonation of hydroxyl groups: as this only occurs when a high pH is reached, it therefore requires a high concentration of base.

Maximum solubility of MCC in solution

Solubility tests were continued to determine the dissolution limit of cellulose by using a microscope to identify undissolved fibres. Although this method does not determine whether the cellulose is molecularly dissolved or merely very swollen, it does give a quick and rough estimation of the dissolution capacity of the solvent. It was found that up to and including 5 wt% of MCC could be dissolved in 2.3 M 50/50 mol% NaOH/TMAH(aq), 6 wt% in 2.3 M TMAH(aq) and 3 wt% in 2.3 M NaOH(aq). Although the dissolution capacity of 2.3 M 50/50 mol% NaOH/TMAH(aq) doesn't reach that of 2.3 M TMAH(aq), it nevertheless

indicates that interactions between cellulose and TMAH/NaOH are affected by combining the two bases, which could be related to a change in the hydrate structure of the dissolved bases.

Whilst combining hydroxide bases for dissolution of cellulose in water has been researched only scarcely, it isn't entirely novel. It is interesting to note that, in a patent from 1924 (which also appears to be one of the first times aqueous solutions of quaternary ammonium hydroxides are reported as being used as solvents for cellulose), it is stated that "the presence of caustic soda enhances the solvent action of the bases". This shows that observations of some type of improved dissolution upon addition of NaOH to solutions of, for example, TMAH(aq) (Lilienfeld 1924) had also been made.

Investigating the structure of hydrates in solution using differential scanning calorimetry (DSC)

Thermoscans were performed using DSC to identify melting temperatures and enthalpies of different hydrates in order to investigate the structure of the hydrated bases in the water solutions when NaOH and TMAH are combined, and to study their interactions with cellulose.

Aqueous solutions of NaOH and TMAH

NaOH forms different hydrates when dissolved in water and for NaOH concentrations around 2.3 M, both an eutectic hydrate salt with a reported composition of NaOH • 9 H_2O (melting temperature of − 34 °C) and free water are present (Roy et al. 2001). Navard et al. characterized the dissolution of MCC in NaOH(aq) and found that the enthalpy of the eutectic hydrate salt decreases with increasing dissolution of cellulose, suggesting that the hydrates interact with the dissolved cellulose chains which prevents them from crystallizing (Egal et al. 2007).

Thermoscans of 2.3 M TMAH(aq) solution confirmed that it contained an eutectic hydrate salt with a melting point of − 26.3 °C and unbound water, as given in Table 1. This is in agreement with a previously reported investigation of TMAH hydrates: from the published phase diagram, the structure of the eutectic hydrate salt can be calculated as being TMAH • 16 H_2O and the melting temperature read as − 28 °C (Mootz and Seidel 1990). From our results we also

observed that the melting enthalpy of ice was lower for TMAH(aq) than for NaOH(aq), supporting the theory that the TMAH hydrate contains more bound water than the NaOH hydrate. Traces of other hydrates were also found in the 2.3 M TMAH(aq) solution, but these are not believed to be involved in the dissolution of cellulose since they have a melting point well above the interval for cellulose dissolution: these are reported in Table S1 found in the supporting material.

Aqueous solutions of NaOH and TMAH combined

Varying ratios of the bases with increasing level of TMAH were measured, as can be seen in Table 1, in order to investigate how the hydrates of NaOH and TMAH would be affected by each other when combined. In a solution of 75/25 mol% NaOH/TMAH(aq), hydrates of NaOH and TMAH are formed with the same structures as in the reference solutions of 100 mol% NaOH(aq) and 100 mol% TMAH(aq), based on the fact that there was no significant shift in their melting temperatures. The enthalpy of the NaOH hydrate, however, decreased significantly, indicating only a modest formation of NaOH hydrates. When the concentration of TMAH was increased further to 50/50 mol% NaOH/TMAH(aq), two hydrate salts were again observed: the melting temperature of the NaOH hydrate had however shifted to − 27.8 °C, which is closer to the melting point reported for NaOH • 7H_2O than for NaOH·9H_2O (Pickering 1893). Upon increasing the concentration of TMAH even further to 25/75 mol% NaOH/TMAH(aq), only one peak (besides that of ice) was observed, with a melting temperature and enthalpy consistent with a TMAH salt. This could have several explanations: the peak of NaOH hydrate is hidden under the peak of TMAH hydrate; no NaOH hydrate salt could be formed at this high TMAH concentration; together, NaOH, TMAH and water formed an eutectic salt.

These measurements indicate that the presence of TMAH can disturb both the level and structure of the NaOH salt formed in the solution whereas TMAH probably retains its structure, with its melting temperature affected only slightly by a change in its surrounding molecular environment. Another observation that was made is that the enthalpy of the TMAH hydrate in the 2.3 M TMAH(aq) solution is roughly the same as in the 2.3 M 50/50- and 25/75 NaOH/TMAH(aq) solutions, i.e. around 70 J/g. This shows

Table 1 Melting temperature (T_m) (°C) and enthalpy (ΔH) (J/g sample) of hydrates in 2.3 M(aq) base with the specified ratio of NaOH and TMAH, measured using DSC

Ratio of base	T_m (°C) NaOH	ΔH (J/g) NaOH	T_m (°C) TMAH	ΔH (J/g) TMAH	T_m (°C) Ice	ΔH(J/g) Ice
100/0 NaOH/TMAH	− 33.7	95.0			− 9.7	170.6
75/25 NaOH/TMAH	− 34.4	16.1	− 25.3	41.5	− 13.2	30.6
50/50 NaOH/TMAH	− 27.8	15.3	− 25.1	72.2	− 14.7	42.1
25/75 NaOH/TMAH			− 27.3	69.4	− 16.0	41.9
0/100 NaOH/TMAH			− 26.3	68.0	− 17.3	27.8

that there is the same amount of hydrate in all three solutions, despite the lower concentration of TMAH in the two solutions that also contain NaOH. It indicates that the addition of NaOH favours the formation of TMAH • 16 hydrate; the additional hydrates probably arise from other hydrates of TMAH, which act as a depot and reform into TMAH • 16 hydrate upon the presence of NaOH.

Cellulose dissolved in aqueous solutions of base

Measurements were made for 3 wt% MCC in 2.3 M 50/50 mol% NaOH/TMAH(aq) as well as in 2.3 M NaOH(aq) and 2.3 M TMAH(aq). It was observed that when cellulose was dissolved in the NaOH(aq) solution, the melting temperature of the NaOH hydrate decreased slightly and the enthalpy decreased significantly, as can be seen in Table 2. This indicates that whilst the structure of the NaOH • 9 H_2O salt remains the same, only a small amount is formed, which is the same behaviour that was observed when TMAH and NaOH were combined. The drastic decrease in NaOH hydrate cannot only be explained by the addition of cellulose: there is about 11 NaOH per anhydroglucose unit (AGU) at 3 wt% MCC in 2.3 M NaOH(aq) solution (and it is more likely to be 1 – 3 NaOH

molecules interacting with one AGU), which should be sufficient to form the NaOH • 9 H_2O salt even with cellulose present. One plausible explanation, previously proposed by Egal et al. (2007), is that interaction of NaOH hydrates with cellulose affects the surrounding network of the hydrates preventing them from crystalizing in the eutectic salt. What is observed however, is that upon addition of cellulose the enthalpy of ice decreases significantly. This is probably due to the water hydrating the cellulose, but it also means that there is less unbound water in the solution and could also explain why the formation of the NaOH eutectic hydrate salt is partly disturbed by the addition of cellulose.

Upon dissolution of cellulose in 2.3 M TMAH(aq) or 2.3 M 50/50 NaOH/TMAH(aq), the same hydrate structures were formed as in cellulose-free solutions but only the enthalpy of the TMAH hydrate decreased, possibly indicating a preferred cellulose interaction with the TMAH hydrate.

A series with increasing concentrations of MCC in 2.3 M 50/50 mol% NaOH/TMAH was therefore measured in order to further investigate whether cellulose favours one base over another. Only minor shifts in the melting temperatures of the hydrates were observed when the concentration of MCC was
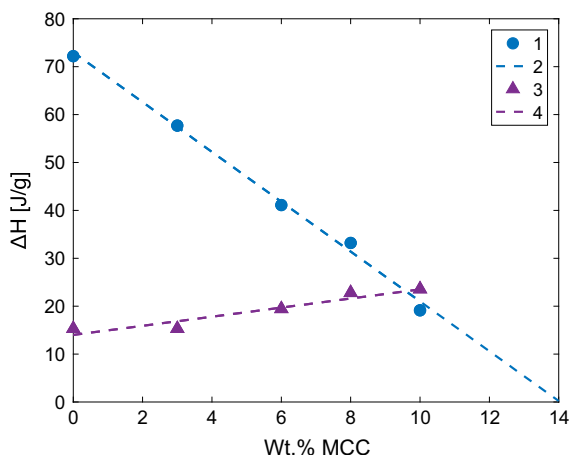
Table 2 Melting temperature (T_m) (°C) and enthalpy (ΔH) (J/g sample) of hydrates in solutions of 3 wt% MCC dissolved in 2.3 M base with the specified ratio of NaOH and TMAH, measured using DSC

Ratio of base	T_m (°C) NaOH	ΔH (J/g) NaOH	T_m (°C) TMAH	ΔH (J/g) TMAH	T_m (°C) Ice	ΔH(J/g) Ice
100/0 NaOH/TMAH	− 34.5	13.7			− 9.0	68.7
0/100 NaOH/TMAH			− 26.4	63.2	− 15.6	34.3
50/50 NaOH/TMAH	− 28.16	15.3	− 25.4	57.7	− 12.7	50.6

increased, indicating that no essential changes in their structures took place. The enthalpy of the hydrate salt of TMAH decreased linearly with increased concentration of MCC, whereas the enthalpy of the hydrate salt of NaOH slightly increased, as can be seen in Fig. 3. The implication here is that TMAH interacts with the cellulose instead of forming a hydrate salt in the solution; the slight increase in the enthalpy of the NaOH hydrate salt could be due to less TMAH hydrate salt being formed and interfering with the NaOH structure.

It is interesting to note that although both bases are required for dissolution, the DSC results indicate that only TMAH seems to be interacting with the cellulose. Another significant feature is that, at the observed dissolution limit of 5 wt% MCC, the levels of the eutectic salts do not reach zero (5 wt% MCC corresponds to ca 3 TMAH/AGU). If the linear trend of decreasing TMAH-hydrate would continue, it would reach zero at 14 wt% MCC (as seen in Fig. 3), corresponding to ca 1 TMAH/AGU.

These results depict a scenario where cellulose is dissolved in a solution containing both NaOH and TMAH hydrates but only interacts with TMAH, whilst NaOH hydrates are affected by the presence of both the cellulose and TMAH through a change in the water structure but are not associated to either one. This raises the question of whether the properties of the solution would be similar to cellulose dissolved in either TMAH(aq) or NaOH(aq), or a mixture thereof.

Intrinsic viscosity

It has been reported that TMAH and other similar cations increase the amount of cellulose that can be dissolved through hydrophobic interactions (Wang et al. 2018), which allows the simple conclusion to be drawn that these solvents have a better solvent quality than NaOH(aq). This was investigated here by measuring the intrinsic viscosity of the combined 2.3 M 50/50 mol% NaOH/TMAH(aq) solvent, 2.3 M NaOH(aq) and 2.3 M TMAH(aq). Intrinsic viscosity is a measure of how extended the polymer is in the solvent, and thereby the quality of the solvent since a better solvent should cause the polymer to extend more. The combination of NaOH/TMAH(aq) showed a slightly higher intrinsic viscosity of 1.14 dL/g than that of TMAH(aq) at 0.92 dL/g which, in turn, is slightly higher than that of NaOH(aq) at 0.88 dL/g, as seen in Fig. 4.

Taking into consideration that there is an error margin of 2% when determining the relative viscosities and a linear regression is made using these values, the differences between the intrinsic viscosities measured for TMAH(aq) and NaOH(aq) are not significant. This implies that the inherent hydrophobicity of a cation such as TMAH, does not improve the solvent's quality significantly compared to NaOH, at least when measured by intrinsic viscosity. It is reasonable to
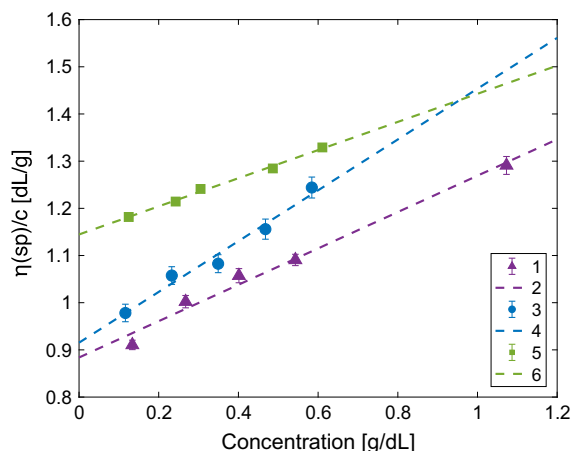
Fig. 3 Enthalpy of TMAH-hydrate (1) with linear trendline (2) and NaOH-hydrate (3) with linear trendline (4) as a function of cellulose concentration in solutions of 2.3 M 50/50 mol% NaOH/TMAH(aq)

Fig. 4 Specific viscosity divided by concentration (ηsp/c) as a function of cellulose concentration, used to extrapolate values of intrinsic viscosity at 25 °C for MCC dissolved in 2.3 M NaOH(aq) (1) with linear trendline (2), 2.3 M TMAH(aq) (3) with linear trendline (4) and 2.3 M 50/50 mol% NaOH/TMAH(aq) (5) with linear trendline (6)

assume that dissolution in NaOH(aq) and TMAH(aq) occurs through similar mechanisms and that the effects on the conformation and subsequent entanglement of the cellulose will be similar. This is possibly why the intrinsic viscosity of NaOH(aq) and TMAH(aq) are comparable. Combining the two bases did improve the quality slightly; the results from DSC indicate that a change in the hydrate structure could be the cause, but this requires further investigation.

NMR

NMR analysis was performed in order to shed light on molecular interactions in the solutions. Replacing NaOH(aq) with TMAH(aq) led to a downfield displacement of all the ^{1}H chemical shifts observed. For the signal originating from water, a displacement in the chemical shifts corresponding to 0.15 ppm downfield could be observed upon replacement of 50% NaOH and, finally, displacement corresponding to additional 0.1 ppm when dissolved in TMAH only, as can be seen in Fig. 5. It is in agreement with the effect observed previously of dissolving relatively hydrophobic cations in water solutions and is commonly interpreted as being evidence of the formation of stronger H-bonding. It is, in fact, rather an effect of

the perturbation of the water structure in close proximity to TMAH, causing the water structure to have lower mobility. [1]H chemical shifts of the model glucose compound are also displaced downfield: this is indicative of the displacement of electron density away from the glucose C–H protons and is possibly due to the proximity of the TMAH cation.

Furthermore, changes in ^{13}C chemical shifts (see Figure S1 in the supporting information), albeit modest, additionally witness of perturbation of electron density experienced by the glucose ring upon addition of TMAH in the NaOH(aq) system. Carbon atoms in positions 2, 4 and 6 show deshielding effects when the amount of TMAH is increased (displacement of the chemical shift downfield corresponding to 0.2 ppm when going from NaOH(aq) to TMAH(aq)), while those in positions 1, 3 and 5 seem to experience a very poor shielding effect (a modest chemical shift displacement upfield).

Interestingly enough, this does not comply with the deprotonation signature commonly observed: an upfield displacement of ^{1}H chemical shifts together with a downfield displacement of the ^{13}C signals originating from the C atoms carrying deprotonable OH-groups. Consequently, the presence of TMAH is probably not associated with enhanced deprotonation
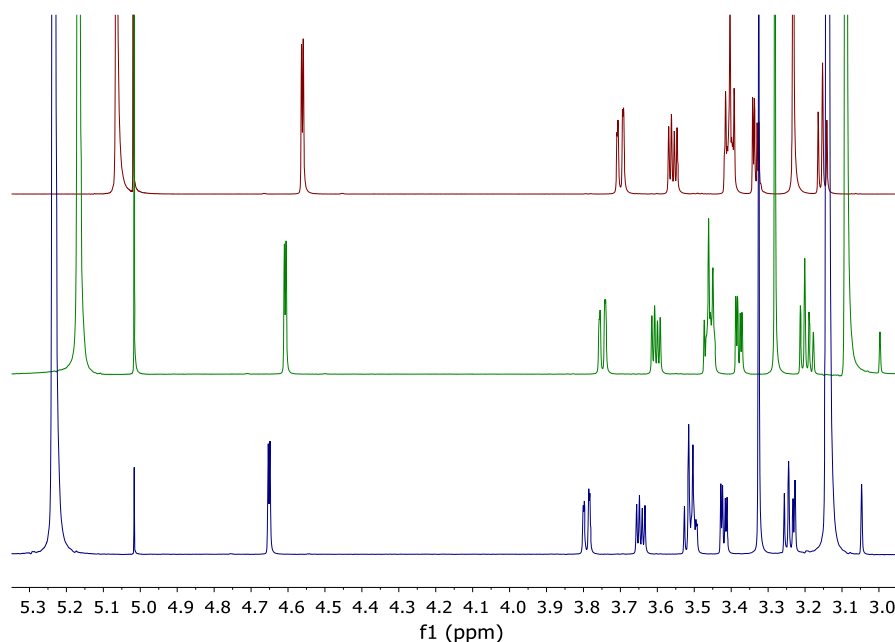
Fig. 5 ^{1}H NMR spectra of methyl-α-D-glucopyranoside dissolved in 2.3 M NaOH (red spectra), 2.3 M 50/50 mol% NaOH/TMAH (green spectra) and 2.3 M TMAH (blue spectra), all in D2O

of the carbohydrate, it is more likely involved in other interactions responsible for deshielding of the glucose C–H moieties.

Stability of cellulose/base solutions

The instability of cellulose solutions over time might present a problem when processing cellulose dissolved in cold NaOH(aq) and similar solvents, so dynamic oscillatory viscosity measurements were performed to record the stability of solutions over time by monitoring gelation.

The evolution of G' and G'' for 5 wt% MCC solutions at 15, 25 and 35 °C can be seen in Fig. 6 and the results for 3 wt% MCC solutions can be found in the supplementary material in Figures S8 and S9. Overall trends observed comply with previous findings and show that solutions gel faster with increasing cellulose concentration and temperature. Observations from the measurements on the 3 wt% MCC solutions show a tendency of the NaOH solutions to be more stable than TMAH solutions at lower temperatures, while the opposite could be observed at higher temperatures. At a concentration of 5 wt% MCC, the solutions in 2.3 M NaOH were gelled already from the start of the measurement at all temperatures. This is also an indication that not all of the cellulose at 5 wt% was dissolved. The solutions in 2.3 M TMAH gelled within minutes at 15 °C and at 25 and 35 °C were already gelled from the start. Interestingly, in the case of the combined solvent, the results show that combining bases delays gelation significantly, which could be observed at all investigated temperatures and concentrations. An increase in turbidity was often observed after the samples had gelled, which makes it important to note that the observed gelation is most likely accompanied by aggregation or micro-phase separation of the cellulose from the solvent.

The reason for the delayed gelation needs more investigation but the implication from time-resolved rheology is that the two bases have somewhat different stabilisation mechanisms: the more hydrophobic TMAH provides better stabilisation of the dissolved cellulose when the temperature is increased whereas NaOH provides better stabilisation at lower temperatures. One possible explanation here is that attractive hydrophobic interactions between cellulose molecules are less pronounced at lower temperatures since cellulose adapts a conformation that minimises the
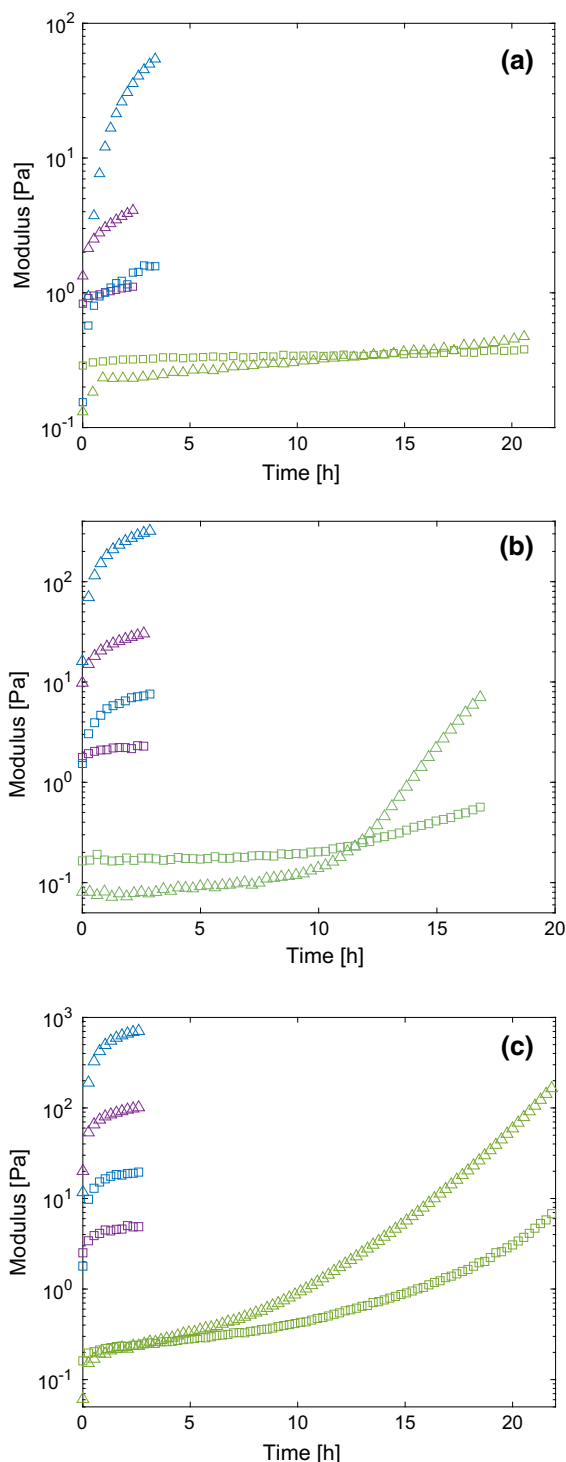
Fig. 6 Storage modulus G'(triangles) and loss modulus G'' (squares) of 5 wt% MCC in 2.3 M NaOH(aq) (purple), 2.3 M TMAH(aq) (blue) and 2.3 M 50/50 mol% NaOH/TMAH(aq) (green) as a function of time at **a** 15 ° C, **b** 25 °C, **c** 35 °C

exposed hydrophobic surfaces and thus minimises hydrophobic cellulose-cellulose interactions (Lindman and Karlström 2009), thereby making stabilisation through hydrophobic interactions less important. At higher temperatures, on the other hand, the inherent hydrophobic properties of TMAH inhibit hydrophobic attractive forces between the cellulose chains and stabilises the solution.

Moreover, the combined solvent does not display the properties of either pure solvents or an average of the two. Based on the DSC results discussed earlier, it could be concluded that the presence of NaOH might have favoured the formation of TMAH • 16 H_2O hydrate so that there was the same amount of hydrate in a 2.3 M 50/50 mol% NaOH/TMAH(aq) solution as in a 2.3 M TMAH(aq) solution. This could be an indication as to why the combined solvent displays increased stability: the cellulose gains a more hydrophobic cation to interact with at the same time as NaOH is present in solution.

Conclusions

Up to 5 wt% of MCC can be dissolved using a combination of NaOH and the organic base TMAH in water. These are levels at which each of the bases cannot dissolve cellulose alone, indicating that the two bases can cooperate to do so. The solution of the combined bases exhibits a slightly higher intrinsic viscosity than NaOH(aq) or TMAH(aq) alone, showing that combining the two bases improves the quality of the solvent slightly. DSC measurements revealed that the amount of eutectic salt of TMAH decreases linearly with increasing concentration of cellulose, thereby indicating that cellulose interacts preferably with TMAH rather than NaOH. The combined NaOH and TMAH solvent delayed gelation over time significantly: this is an interesting result, the cause of which needs to be elucidated further.

Compliance with ethical standards

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