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Citation for the original published paper (version of record):

Naserifar, S., Swensson, B., Bernin, D. et al (2021). Aqueous N,N-dimethylmorpholinium hydroxide as a novel solvent for cellulose. European Polymer Journal, 161.
http://dx.doi.org/10.1016/j.eurpolymj.2021.110822

European Polymer Journal 161 (2021) 110822

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Aqueous *N,N*-dimethylmorpholinium hydroxide as a novel solvent for cellulose

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ARTICLE INFO

Keywords:
Quaternary ammonium hydroxide
Cellulose dissolution
Microscopy
DLS
SEC
NMR

ABSTRACT

N,N-dimethylmorpholinium hydroxide was synthesized and its ability to dissolve microcrystalline cellulose and pulp was assessed for the first time. Microscopy and UV–Vis measurements showed that dissolution occurred over a range of 1–2 M concentration of the solvent and a maximum solubility of 7 wt% microcrystalline cellulose could be achieved. The stability of cellulose solutions was evaluated by size exclusion chromatography, which did not detect degradation to any noticeable extent. This observation was further confirmed by ^{13}C NMR measurements. Finally, DLS studies confirmed that most of the cellulose was molecularly dissolved, with intrinsic viscosity values indicating cellulose chains expansion in this solvent.

1. Introduction

Growth in the world's population and rapid changes in the climate highlight the urgency in shifting from fossil-based-materials towards the utilization of renewable resources, which would lead to a more sustainable society. Biobased materials derived from sustainable renewable resources such as forest biomass (cellulose, lignin and hemicellulose), agricultural residues, etc. are gaining increased importance as alternatives to oil-derived materials and chemicals in attaining this goal [1]. Among renewable polymers, cellulose, which is the most abundant biopolymer on Earth, has thus far received considerable attention and both native fibres and man-made cellulose are widely processed for various applications. In such a context, the development of sustainable technologies that enable the reshaping of cellulose into textile fibres, films and membranes is of great importance [2,3], especially with respect to the fast increasing demand for textile materials.

Yet, to be able to shape cellulose, processing through dissolution is a requisite, while a major existing challenge is cellulose insolubility in water and common organic solvents [4]. The poor solubility of cellulose originates from its semi-crystalline fibrils being arranged in a complex hierarchical morphology, resulting from extended inter and intra-molecular H-bondings as well as hydrophobic interactions. Cellulose thus has an amphiphilic structure, and the biggest challenge is to introduce a dissolution medium that has the potential to overcome this amphiphilicity. Over the past decades, a number of dissolving systems for cellulose have been reported, namely aqueous solutions of amines coupled with transition metals (e.g. Cuam, Cadoxen, Cuen [5]), aqueous solutions of bases or acids (e.g. NaOH(aq) [6,7], quaternary ammonium hydroxides(aq) [8], phosphoric acid(aq) [9]), organic solvents with salts (such as DMAC/LiCl [10] and DMSO/TBAF [11]) and ionic liquids (ILs) [12]. The challenge that remains is to minimize the limitations associated with existing solvents, which include instability of the dissolved state, low dissolution capacity, specific temperature requirements, chemical instability of the solvent, narrow concentration range required for dissolution and undesired reactions that cause a decrease in the degree of polymerization (DP) of cellulose [13]. Further research is therefore focused on understanding critical cellulose-solvent interactions along with identifying new compounds/compound systems capable of providing dissolution power towards overcoming these limitations.

In this respect, water-based solvents are of considerable interest due to their applicability in large scales. Alongside NaOH(aq), which has been studied extensively and used in the cellulose industry particularly in viscose process [14], aqueous solutions of quaternary ammonium hydroxides (QAHs(aq)) were reported to dissolve cellulose as early as in 1924, in a patent by Lilienfeld [15]. Since then, cellulose dissolution in water solutions of QAHs such as tetra-n-butylammonium hydroxide [16], tetra-n-butylphosphonium hydroxide (TBPH) [17], tetramethylammonium hydroxide (TMAH) [18], tetraethyl ammonium hydroxide [19], triethylmethyl ammonium hydroxide and benzyltrimethyl

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https://doi.org/10.1016/j.eurpolymj.2021.110822
Received 4 September 2021; Received in revised form 5 October 2021; Accepted 8 October 2021
Available online 12 October 2021

ammonium hydroxide (Triton B) [20] have been studied both theoretically and experimentally.

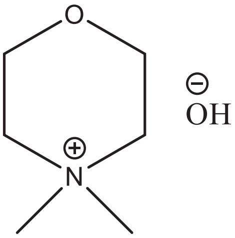
Investigations on the dissolution mechanism of cellulose in aqueous hydroxide base solutions such as NaOH showed that dissolution probably relies on the disruption of H-bonding by competitive intermolecular interaction of solvent hydroxide with cellulose hydroxyl groups, which also includes partial deprotonation. Moreover, it is likely that the cation contributes to preventing the re-association of dissolved cellulose by distribution between individual chains [21]. Higher hydrophobicity of the cation has been reported to enhance both dissolution and higher stability of the solution [20]. In that regard, the role of the hydrophobic assembly effect and the amphiphilic structure of cellulose on its dissolution in aqueous systems [22] should also be considered.

Recently in our group, dissolution of cellulose in QAHs using TMAH and Triton B, as well as their combination with NaOH (aq) have been investigated,[23,24] the favourable interactions of the quaternary ammonium cations being accentuated. In continuation to that work as well as being inspired by the well-known and industrially-used solvent NMMO, and bearing in mind the relatively low toxicity and good stability [25] reported for ionic liquids based on morpholinium cations, we envisioned that combining *N*-methylmorpholinium with a hydroxide counterion to create an *N,N*-dimethylmorpholinium hydroxide (NDMM-OH) would yield a potential cellulose solvent (scheme 1). In this paper, we report on the synthesis of this QAH and the properties of its water solutions as a cellulose solvent. The dissolution studies were performed using microscopy and UV–Vis measurements, along with intrinsic viscosity and dynamic light scattering (DLS) measurements that were used to evaluate the size and structure of cellulose in the solution. Finally, size exclusion chromatography (SEC) and NMR were conducted to probe the occurrence of degrading side reactions in the cellulose solutions.

2. Experimental

2.1. Materials

Microcrystalline cellulose (MCC), Avicel PH-101 made by acid hydrolysis of specialty wood pulp with a degree of polymerization (DP) of 180 measured by GPC-MALLS (personal communication with Majid Ghasemi at Södra skogsägarnas ekonomiska förening, Sweden) was purchased from FMC BioPolymer. A prehydrolysis kraft dissolving grade hardwood pulp from Eucalypt and a sulfite dissolving grade pulp from softwood with viscosities 283 cm^3/g and 442 cm^3/g (measured by pulp dissolution in bis (ethylenediamine) copper (II) hydroxide solution (CED) using capillary viscosimetry according to the SCAN-C 15:99 method) were provided by Bracell and Domsjö respectively. *N*-methyl morpholine, Iodomethane, acetonitrile, diethyl ether, HCl, NaOH and, Potassium hydrogen Phthalate were purchased from Merck (previously Sigma-Aldrich) and silver(I) oxide was purchased from Alfa Aesar and used as received. Distilled water was used to dilute the solutions.



Scheme 1. The structure of *N,N*-dimethylmorpholinium hydroxide (NDMM-OH).

2.2. Solvent synthesis

2.2.1. Synthesis of N,N-dimethylmorpholinium iodide

A general way to synthesize quaternary ammonium hydroxides is methylation of the amine followed by an ion exchange using silver(I) oxide in water [26]. Here 0.18 mol *N*-methylmorpholine (19.79 ml) was added to 120 ml acetonitrile. The solution was placed in an ice bath because the methylation of *N*-methylmorpholine is exothermic, and 0.18 mol iodomethane (11.20 ml) was added dropwise to it. A few minutes after iodomethane addition, white precipitates were formed. Once all the iodomethane had been added, the reaction mixture was stirred for an additional 1 h to make sure the precipitation was in fact complete. The product was then purified and isolated by adding diethyl ether to the solution and the mixture was stirred for an additional 1 h. This step was performed twice to ensure complete removal of the impurities/side products formed during the course of the reaction. Finally, the obtained precipitates with 84.4% yield were dried at ambient temperature.

2.2.2. NDMM-OH synthesis

0.06 mol of *N,N*-dimethylmorpholinium iodide (14.58 g) was added to 20 ml distilled water in a 45 ml centrifuge vial and 0.04 mol of silver (I) oxide (9.26 g) was added to the solution. The vial was sealed tightly to avoid further contact with air and the mixture was stirred at room temperature for approx. 5 h. Yellow precipitates of silver iodide were formed as soon as stirring began and by the end of the reaction, the excess grey silver(I) oxide remained unreacted. Lastly, the obtained solution was centrifuged, and the supernatant containing NDMM-OH (76% yield) was isolated and kept refrigerated.

2.3. Dissolution of MCC and pulp

A range of NDMM-OH concentrations from 0.8 M to 2.3 M was prepared by diluting the concentrated solvent with distilled water. The desired amount of MCC was added to each solution to a final concentration of 3 wt% and stirred at room temperature for 5 min to yield a well-dispersed suspension. The suspension was then placed in a freezer at -25 °C for 20 min, after which it was thawed under constant stirring to remove any ice formed and thereby yield a transparent solution. The same procedure was followed to evaluate pulp dissolution in NDMM-OH (aq). For investigation of solubility at higher temperatures 4 samples were prepared by adding MCC corresponding to 3% to a 1.3 M NDMM-OH(aq) solution. The dissolution was evaluated under constant stirring at different temperatures: at 5 °C, room temperature and 38 °C.

3. Characterization methods

3.1. ^1H and ^{13}C NMR characterization

Nuclear magnetic resonance spectra were recorded on a Varian (400-MHz) spectrometer equipped with One NMR Probe in D_2O at 25 °C to confirm the synthesis of NDMM-OH.

^{13}C NMR experiments to probe the stability were carried out on an 800 MHz (^1H) magnet with a TXO probe and Bruker Avance HDIII console using a z-restored spin echo sequence to avoid a rolling baseline.

3.2. Determination of NDMM-OH concentration

Titration was performed using an SI analytics autotitrator. 1 ml of the NDMM-OH(aq) was diluted with 30 ml of distilled water and titrated against HCl 0.5 M. The concentration was calculated using the titrant volume at the equivalence point. The titrations were run in duplicates.

3.3. Determination of the maximum solubility of MCC in solutions

4–10 wt% cellulose solutions in 1.3 M NDMM-OH were prepared as described above (Dissolution of MCC cellulose and pulp). Shortly after the dissolution, microscopic observations were made by placing a small droplet of the solution on a slide glass that was pressed using a glass window in a microscope (ZEISS SteREO Discovery.V12) using cross-polarized light equipped with a camera at ambient temperature. Dissolution was confirmed when no particles could be detected, whereas the solubility limit was reached as soon as a crystal could be observed. Additionally, UV–Vis method was used to measure the transmittance of light as a means of assessing the turbidity of the samples.

3.4. *UV–Vis measurements*

A double-beam spectrometer Specord 205 with a spectral bandwidth of 1.4 nm was used to record UV–Vis measurements. WinASPECT software was used to control the device, collect the spectra and analyze them. For each measurement, 1.5 ml of the blank and sample solutions, were transferred into plastic cuvettes respectively. A measurement was run initially on water as the background and NDMM-OH as the sample solution in order to determine the wavenumber at which the transmittance was 100%. Thereafter, 851 nm was selected for further analysis and comparisons.

3.5. *Size exclusion chromatography (SEC)*

A chromatography system from Polymer Laboratories, comprised of a PL-GPC 220 with an RI detector, was employed for SEC. It included a set of Guard column Mixed-A 20 μm (7.5 * 50 mm) and 2 Mixed-A 20 μm (300 * 7.5 mm), also from Polymer Laboratories, connected in series. The mobile phase contained 0.5 w/v% LiCl /DMAc with flow rate of 1 ml/min operating at 70 °C. Pullulan polysaccharides obtained from Polymer Lab with molecular masses of 708000, 344000, 200,000, 107,000, 47,100, 21,100, 9600 and 6100 Da, were used as calibration standards.

Prior to analysis, 25 mg of the sample was solvent-exchanged 3 times with 5 ml of methanol for 30 min, followed by a further 3 time solvent exchange step using DMAc for 30 min. The excess of DMAc was then removed and 5 ml of 8% (w/v) LiCl/DMAc was added and left overnight at ambient temperature with mild magnetic stirring. This sample was thereafter diluted with 20 ml of DMAc.

3.6. *Intrinsic viscosity*

Cellulose solutions were prepared, as mentioned above in the dissolution section, in the concentration range 0.15–0.55 wt% and, in addition, a solution without cellulose was prepared. All the solutions were kept in a water bath at 25 °C for 30 min after dissolution. Viscosity measurements were performed using a capillary viscometer equipped with circulating water bath to maintain a temperature of 25 °C, and the time (t) taken for the solutions to pass down the timing marks in the capillary was recorded. Each measurement was run in triplicate and the average measured time was used in the relative viscosity (η_{rel}) calculations. The specific viscosity (η_{sp}) was then calculated using Eq. (1), and η_{sp}divided by concentration (C) was plotted vs C g/dL. The intrinsic viscosity was obtained from linear regression, with a coefficient of determination of at least 0.97.

$$\eta_{rel} = t_{solution}/t_{solvent}$$

$$\eta_{sp} = \eta_{rel} - 1 \tag{1}$$

3.7. *Refractive index measurements*

The refractive index of the solvent was measured using a refractometer (Abbemat 550, Anton Paar) with a wavelength of 589 nm at 20 °C.

3.8. *Dynamic light scattering (DLS)*

A Zetasizer Nano ZS from Malvern Panalytical, with a 4 mW 632.8 nm red laser at a scattering angle of 175° at 20 °C, was used to perform DLS. The samples were measured both unfiltered and filtered using a 0.22 μm wwPTFE filter. The built-in software was used for the analysis, with the “general purpose mode” (a non-negative least squares method) being selected for analysis when applying a distribution fit. The viscosity of the solvent was measured at 20 °C through flow sweeps and the measured viscosity (1.7 mPa) together with the refractive index (1.36) were used for the data analysis.

4. Results and discussion

4.1. *Synthesis of NDMM-OH*

NDMM-OH was synthesized via a two-step procedure: (1) methylation of *N*-methylmorpholine to yield *N,N*-dimethylmorpholinium iodide (^{1}H NMR and ^{13}C NMR can be found in the supporting information) and (2) an ion exchange step to replace iodide with hydroxide ion (Fig. 1a). The resulting aqueous solution of NDMM-OH was characterized and used with required concentration adjustments. The formation of NDMM-OH was confirmed with ^{1}H NMR and ^{13}C NMR (Fig. 1b and c) as well as the pH of the solution (2.3 M), which was measured to be 14.7.

With regard to stability and recyclability of this solvent pertaining to potential applicability in cellulose dissolution processing, it should be mentioned that QAHs are mainly prone to Hoffman degradation at higher temperatures. Studies on stability of QA cations in alkaline conditions have been carried out before showing the impact of QA cation structures and water content on its stability [27–29]. At high water content, hydroxide is sufficiently solvated to prevent a nucleophilic attack on the QA cation while at low water content, the cation degradation is accelerated at room temperature. However, under the conditions generally used for cellulose dissolution (i.e. low temperature and high water content) the impact of this degradation pathway is probably of minor importance. In this study after weeks of storing NDMM-OH(aq) in the fridge at 5 °C no significant changes in concentration of the solvent could be detected by titration.

Recyclability of the solvent base itself after precipitation of the solute (e.g. cellulose) relies on the fact that the cation itself does not undergo any chemical changes and can be recovered as a salt by appropriate precipitation, while its hydroxide counterion can be restored by for instance an ion exchange approach. In addition, during the solvent synthesis when doing the ion exchange step,silver(I) oxide is transformed to silver iodide from which both iodine and grey silver powder can be recovered [30].

4.2. *Analysis of cellulose dissolution in NDMM-OH(aq)*

4.2.1. *Determination of the dissolution window for MCC*

A series of NDMM-OH(aq) solutions was prepared, with concentrations in the range 0.8–2.3 M (71.4–89.8 % water content), to assess the dissolution of 3 wt% MCC (Fig. 2a). UV–Vis spectroscopy (Fig. 2b) was used to measure the amount of light transmitted through the solution and thus as a tool to measure turbidity [31], which is indicative of undissolved particles. In the range of 1–2 M of NDMM-OH, transparent solutions were achieved shortly after thawing (see Dissolution of MCC and pulp), UV–Vis measurements recorded a transmittance of 92–96% and no undissolved cellulose could be detected by the microscope. It is important to note that the presence of dust particles, microbubbles, traces of silver oxide or even a scratch on the measuring cell could have caused the transmittance to fall short of 100%. Nevertheless, at a lower concentration (0.8 M) and concentrations over 2 M, the solutions were opaque, the transmittance values were lower than 80% and undissolved cellulose could be detected easily both by the naked eye and a microscope (Fig. 3).

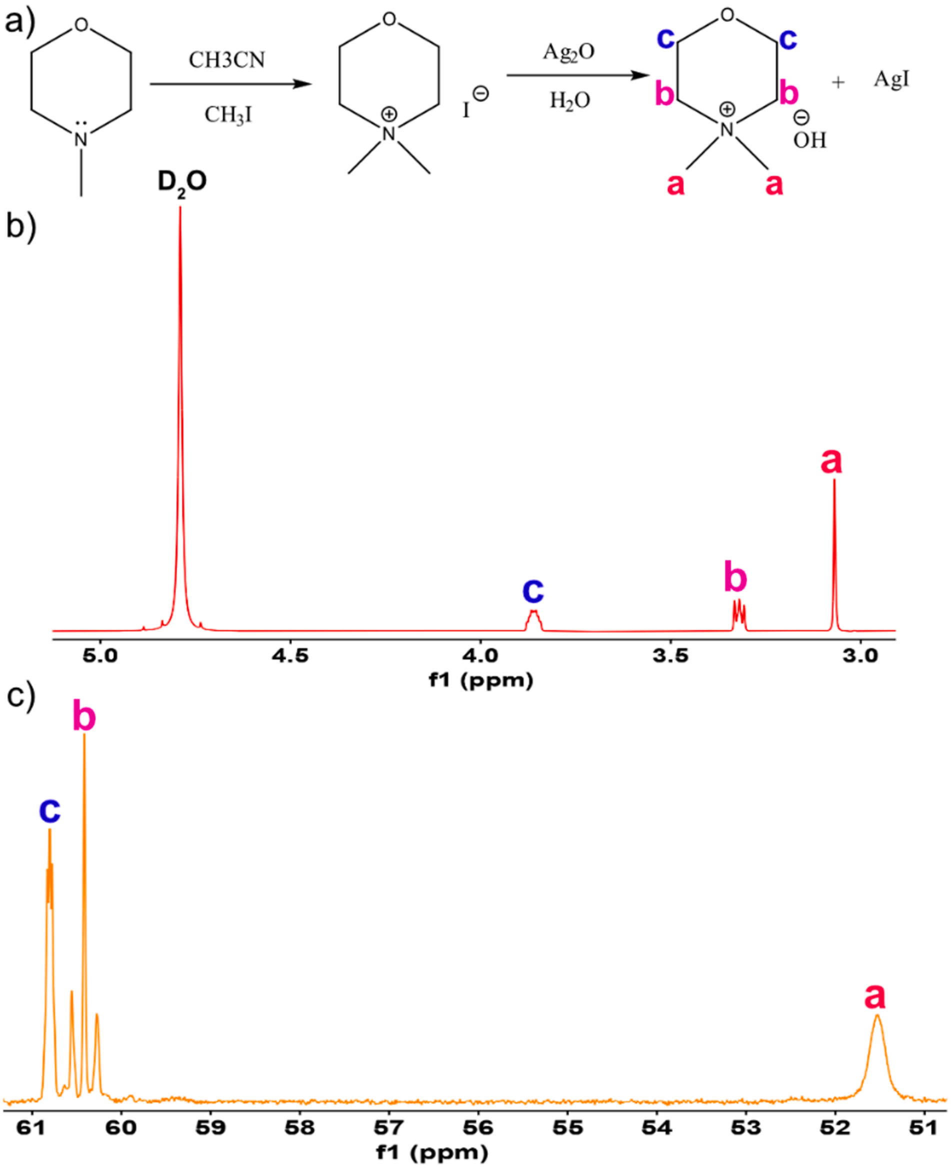


Fig. 1. a) Scheme of NDMM-OH synthesis and its corresponding. b) ^{1}H NMR. c) ^{13}C NMR spectra.

The narrow concentration window required for cellulose dissolution has been commonly reported for these aqueous systems specifically for NaOH in the range 1.5–2.5 M [32,33]. The underlying reasons for this might be that a certain basicity is required for deprotonation (lower base concentration limit) along with the requirement for solvation and the specific size of the hydrated ions formed at certain concentrations (upper base concentration limit) [34–36]. It appears that solvated ions of a particular hydrodynamic diameter are required in order to penetrate both the amorphous and crystalline regions of cellulose. Likewise, the narrow concentration limit observed in this study is probably determined on the one hand by the basicity of the solvent setting the lower limit to 1 M (pH of 14.7 could be measured in 2.3 M NDMM-OH(aq), compared to 13.5 measured in 2.3 M NaOH(aq)) and, on the other hand, by the specific hydration levels of the solvent ions necessary for the dissolution, setting the higher limit to 2 M. Hence For the purpose of comparison, it may be noted here that 2.4 M TEAOH(aq) was reported to dissolve 3 wt% [19], and 2.7 M TMAH dissolved 4 wt% MCC [37].

At higher temperatures (5 °C, room temperature and 38 °C) no dissolution could be detected after 2 h of stirring: as shown in Fig. 4, the samples remained as suspensions. Yet, dissolution temperature dependence will be thoroughly investigated in the coming studies.

4.2.2. *Is NDMM-OH able to dissolve pulp?*

Dissolution of cellulose pulp fibres in aqueous hydroxide solvents usually goes through the so-called ballooning, a precursor dissolution step comprising heterogeneous swelling and partial dissolution of the differently oriented cellulose microfibrils layers in the fibre walls. Primary investigations on 0.5 wt% hardwood pulp (visc. 283 cm^{3}/g, pulp A) in 1.3 M NDMM-OH resulted in a transparent solution with 92.4% transmittance and clear microscopy images with only traces of the remained ballooning structures. When the pulp concentration was increased to 1 wt%, 77% transmittance was obtained and a few more balloons could be observed. However, an increase of the NDMM-OH(aq) concentration to 1.6 M or an additional freeze–thaw step increased the transmittance to 84.6 % and 86.5% respectively (Fig. 5).

In addition a softwood pulp with a higher viscosity of 442 cm^{3}/g (pulp B) was investigated at 0.5 wt% and 1 wt% pulp concentrations in 1.3 M NDMM-OH(aq) in which 83.8% and 76.6% transmittance were achieved respectively. Here, clear microscopy images with few fibre ballooning could be detected too (Fig. 5).

4.2.3. *Maximum MCC dissolution*

Further analysis of the dissolution capacity with varied MCC

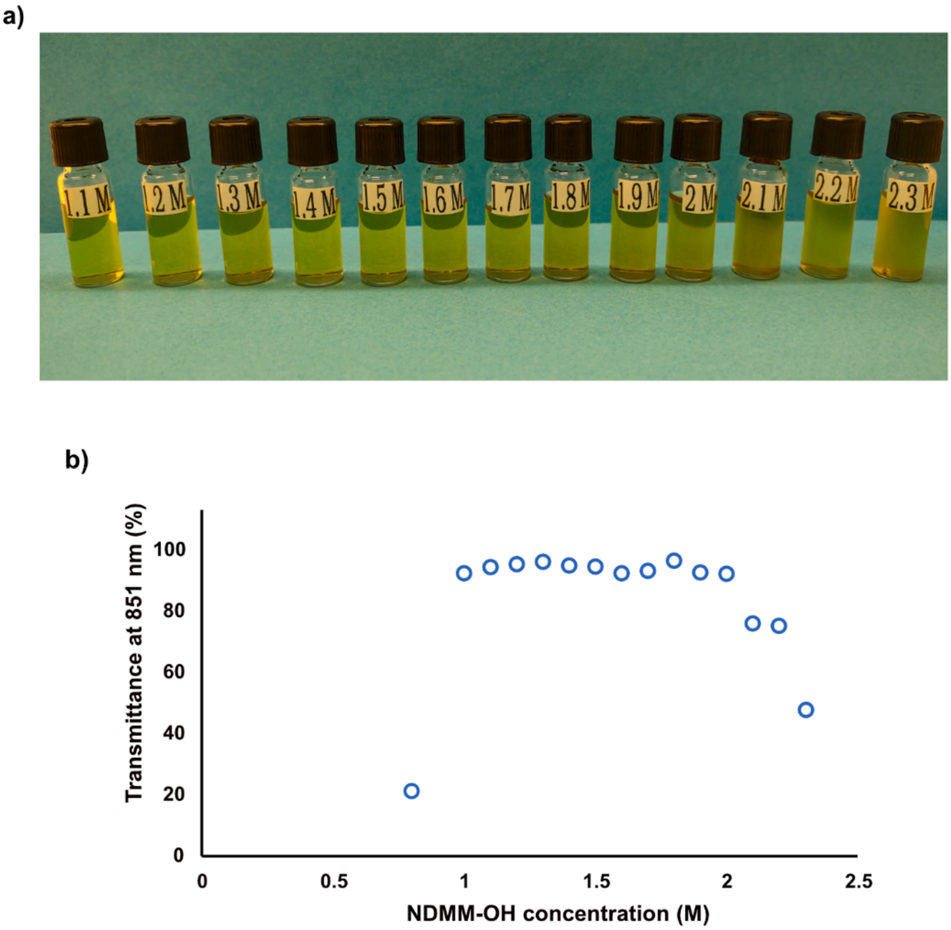


Fig. 2. a) MCC 3 wt% in NDMM-OH(aq) 1.1–2.3 M from left to right. b) Transmittance of the corresponding solutions at 851 nm.

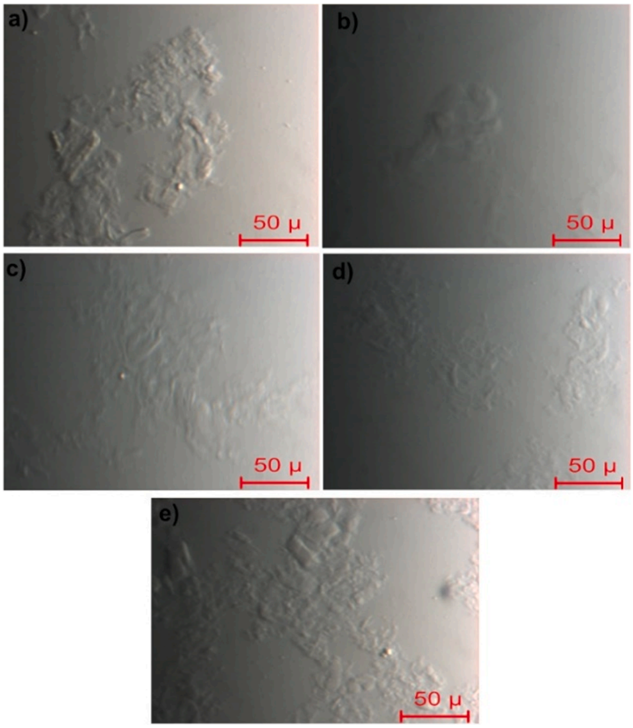


Fig. 3. Microscopy images of MCC 3 wt% in NDMM-OH(aq). a) 0.8 M, b) 2 M, c) 2.1 M, d) 2.2 M, e) 2.3 M.

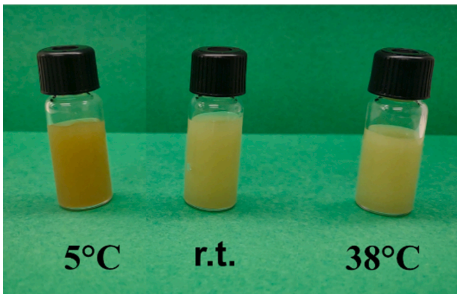


Fig. 4. MCC 3 wt% in 1.3 NDMM-OH at higher temperatures.

concentrations was carried out in 1.3 M NDMM-OH to determine the maximum solubility, as summarized in Fig. 6. The results showed that the addition of MCC up to 7 wt% yielded not only high transmittance but also clear microscopy images, with no traces of undissolved cellulose. Yet, at concentrations above 7 wt%, the solutions gelled immediately after thawing and microscopy images showed undissolved cellulose clearly. These values can be compared to the maximum dissolution capacity of NaOH(aq) reported to be 5 wt%, where cellulose was initially dissolved in NaOH(aq) 2.3 M and then diluted to 1.3 M [38] and 2 M NaOH, with a maximum dissolution of 2 wt% MCC [39].

The observed dissolution window and the maximum solubility of cellulose, places NDMM-OH(aq) among the QAHs capable of dissolving relatively high concentrations of cellulose at relatively low base concentrations, thereby justifying further investigations being undertaken on dissolution at higher temperature ranges and hydration/

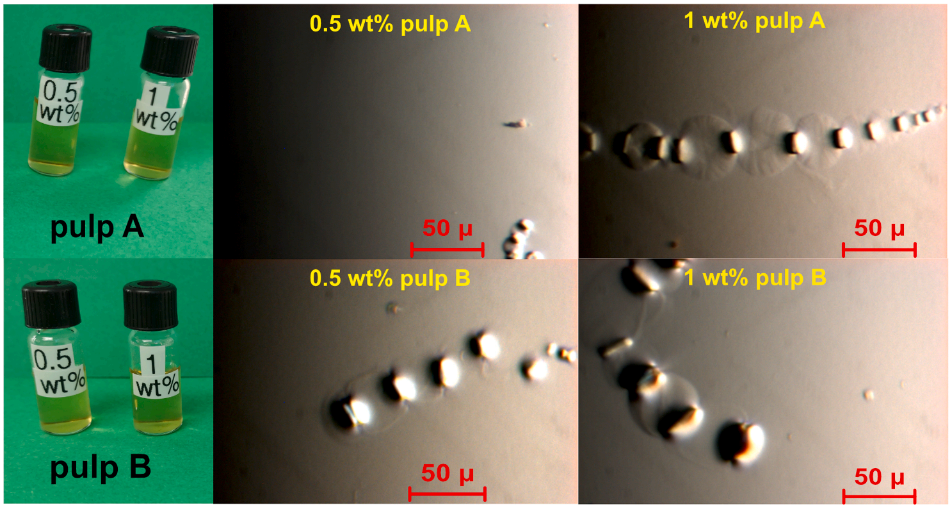


Fig. 5. Dissolution of pulp in 1.3 M NDMM-OH.

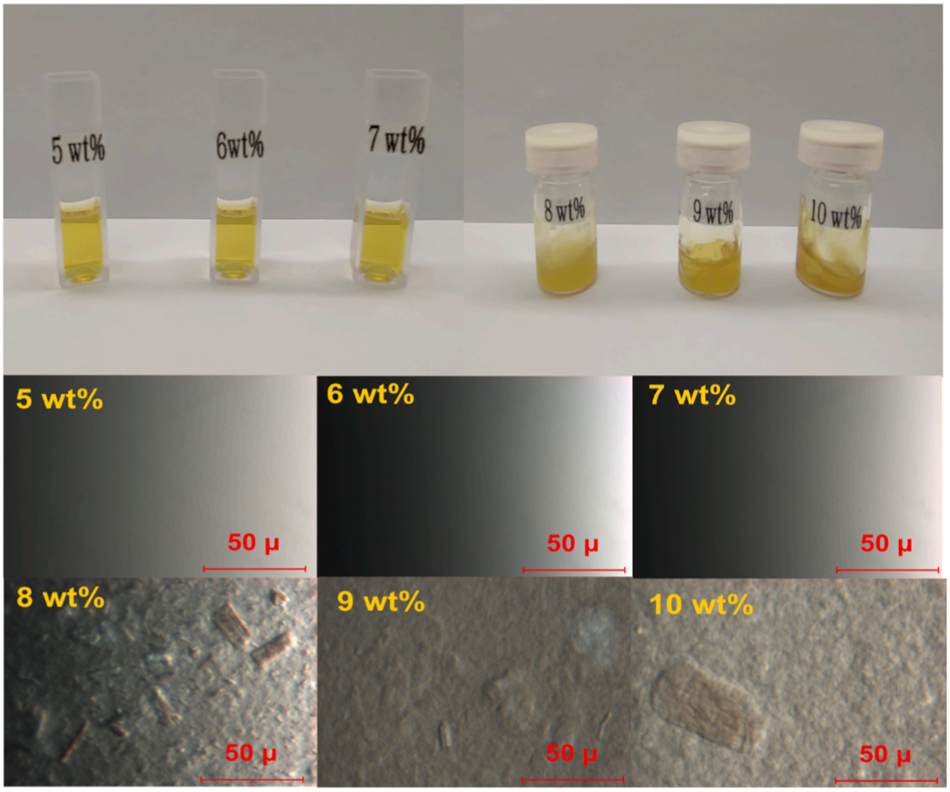


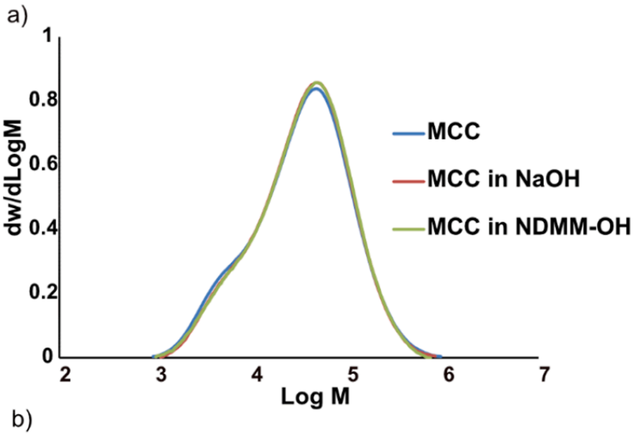
Fig. 6. Varying amounts of MCC in NDMM-OH(aq) 1.3 M and their corresponding microscopy images.

concentration regimes as well as on cellulose pulp substrates.

4.3. *Chemical stability of cellulose dissolved in NDMMOH(aq)*

Fig. 2 shows that, upon the dissolution of MCC in NDMM-OH(aq), the solution turned yellow and subsequently darkened as the concentration of MCC increased. Since a yellow colour in alkaline solutions is usually a sign of degradation, this called for an investigation of changes in the cellulose DP, as well as a search for side products in the solution detectable by NMR. SEC (in DMAc/LiCl) measurements were therefore run on MCC precipitated from a 3 wt% solution in 1.3 M NDMM-OH(aq), as well as in 2.1 M NaOH(aq) (8 wt%) as a comparison, to evaluate the molecular weight distribution (MWD) after 15 h refrigerated storage (Fig. 7). It is evident that the chromatograms (Fig. 7a) of the sample precipitated from NDMM-OH(aq) is almost identical to the reference MCC and the MCC precipitated from NaOH(aq) with regard to shape, and the polydispersity values do not differ significantly from each other (Fig. 7, Table b). Moreover, the values in Table b clearly show a minor decrease towards lower Mw values in NaOH(aq) and NDMM-OH(aq) compared to MCC, indicating a slight shortening in the chain. It is likely that this is related to the reducing end chemistry and beta elimination commonly observed in alkaline systems with good cellulose accessibility.

Nevertheless the ^{13}C NMR measurements run on freshly dissolved MCC in NDMM-OH(aq) (Fig. 8, pink spectrum) and an aged sample that had been refrigerated for 16 h after dissolution (Fig. 8, blue spectrum)



b)

Sample name	Mw (kg/mol)	Mp (kg/mol)	Mn (kg/mol)	Mv (kg/mol)	PD
MCC	60.6	48.1	16.0	139.0	3.8
MCC in NaOH	60.3	49.2	17.3	131.6	3.5
MCC in NDMM-OH	59.7	47.0	17.0	125.0	3.5

Fig. 7. a) Molecular weight distribution (determined by SEC in DMAc/LiCl) for MCC reference (blue) and MCC samples dissolved and precipitated after 15 h storage from NDMM-OH (green) and NaOH (orange) b) Detailed analysis values.

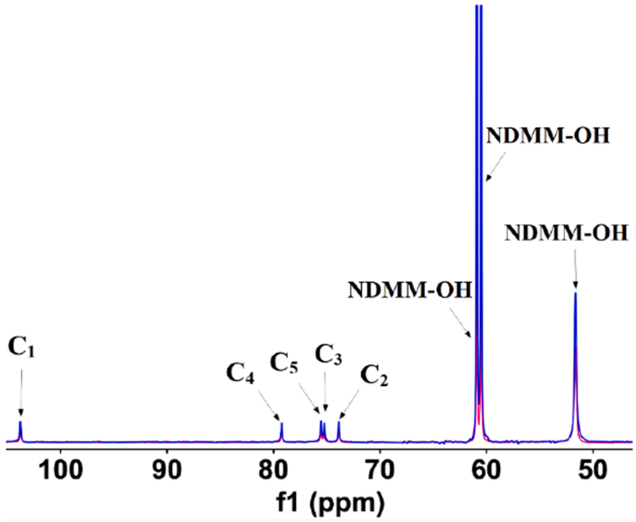


Fig. 8. ^{13}C NMR measurements of freshly dissolved MCC 3 wt% in NDMM-OH (aq) (pink) and an aged solution kept refrigerated for 16 h post dissolution (blue).

did not detect any signs of degradation products. Both spectra show 8 distinct peaks at 103.78, 79.22, 75.53, 75.21 and 73.86 ppm assigned to C_1, C_4, C_5, C_3 and C_2 positions in cellulose, respectively. Moreover, the three other peaks at 60.90, 60.51 and 51.64 ppm correspond to NDMM-OH. It is noteworthy here that C_6 in cellulose appears at around ca. 60 ppm, which overlaps with these NDMM-OH peaks, yet the spectra of both samples look exactly the same: neither shifts in the peaks nor extra peaks could be detected. This observation further confirms that MCC solutions in NDMM-OH are stable over the time range investigated.

4.4. Properties of cellulose solutions in NDMM-OH(aq)

4.4.1. Intrinsic viscosity

To assess the quality of the solvent, intrinsic viscosity of cellulose solutions in 1.3 M NDMM-OH(aq) was measured as indicative of spatial extension of a supramolecule in a solution. Since a good solvent leads to the extension of polymer chains, the higher intrinsic viscosity (n(sp)/C), usually indicates a better solvent. As shown in Fig. 9, the extrapolated value extracted from plotting η_{sp}/C vs C yields the intrinsic viscosity corresponding to 1.11 dL/g. Previously, Swensson et al. [23] have investigated dissolution of MCC in 2.3 M TMAH(aq), NaOH(aq) as well as their mixture and the values they reported for intrinsic viscosity were 0.88 dL/g for NaOH(aq), 0.92 dL/g for TMAH(aq) and 1.14 dL/g for NaOH(aq)/TMAH(aq). A quick comparison of the values clearly reveals that the intrinsic viscosity in these systems is quite similar, with those in NDMM-OH(aq), TMAH(aq) and NaOH(aq)/TMAH(aq) being slightly higher than in NaOH, which can indicate that most likely the stabilizing interactions in these solutions are of the same nature.

4.4.2. Is cellulose molecularly dissolved (DLS)?

DLS was used to investigate whether cellulose could be molecularly dissolved in this novel solvent by measuring the hydrodynamic radius of the cellulose at a dilute concentration (Fig. 10a and b). A sample of 0.5 wt% cellulose in 1.3 M NDMM-OH(aq) was measured, both unfiltered and filtered, with a 0.22 μm filter so that aggregates and well-dissolved cellulose chains could be observed. The results of a cumulant analysis of the unfiltered sample were a z-average radius of 122 nm and a PDI of 0.65, while those of the filtered sample were 17 nm and 0.37, respectively. The unfiltered sample thus contained some larger particles, presumably aggregated cellulose, although it is also possible that dust had caused contamination. A distribution fit was applied in order to separate the different populations of cellulose, the results of which are reported in the graphs and tables in Fig. 10. They show that, despite there being larger particles present in the unfiltered sample, the majority of the sample consists of smaller objects approx. 10 nm in size (based on the volume and number distributions), which correlates well with the expected size of molecularly dissolved MCC chains [40].

Upon filtration of the sample, the distribution fit resolves the signal into two populations of cellulose: the fraction identified previously in the unfiltered sample as molecularly dissolved chains and an even smaller, fraction. It may be that the latter fraction originates from the shorter chains of the cellulose because it is inherently polydisperse, which is also indicated by the high values obtained for the polydispersity index.

5. Conclusions

In this study, NDMM-OH(aq) was synthesized and its potential use as a new solvent for the dissolution of microcrystalline cellulose and pulp via freeze-thawing method was evaluated. The results show that solutions of NDMM-OH in a narrow concentration window of 1–2 M are able to dissolve microcrystalline cellulose shortly after being thawed. In

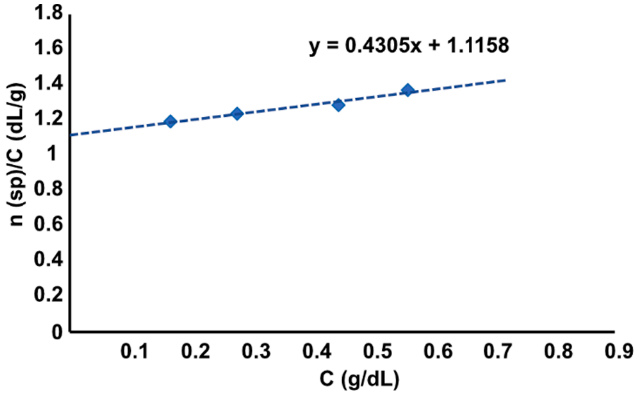
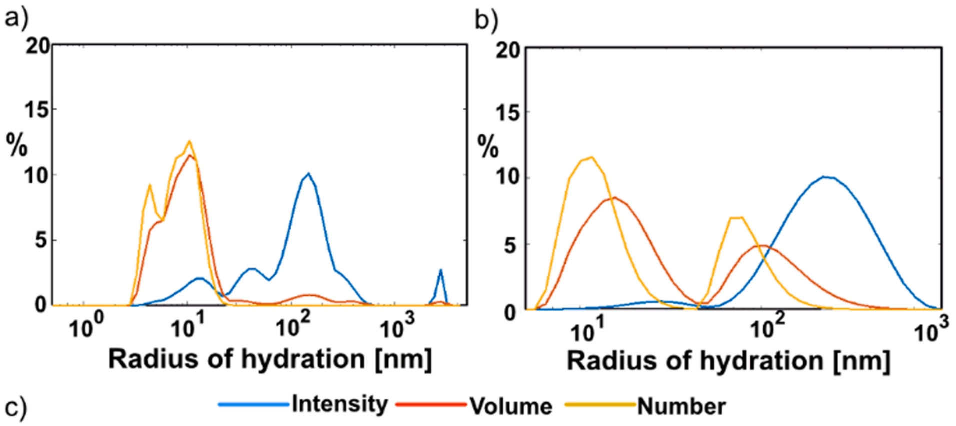


Fig. 9. Intrinsic viscosity extrapolated from η_{sp}/C plotted vs. C g/dL in 1.3 M NDMM-OH(aq).



c)

Unfiltered solution	Peak 1*R (%) [nm]	Peak 2 R (%) [nm]	Peak 3 R (%) [nm]
Intensity	164±79 (68.7%)	42±11 (15.1%)	13±4 (12.9%)
Volume	10±6 (92.8%)	159±60 (5.4%)	400±78 (1.1%)
Number	10±3 (69.5%)	4.6±0.8 (30.5%)	-

* Radius

d)

Filtered, 0.22 µm	Peak 1 R (%) [nm]	Peak 2 R (%) [nm]
Intensity	26±14 (96%)	3±1 (4%)
Volume	13±7 (36%)	2±1 (64%)
Number	9±3 (33.4%)	1±0.5 (66.6%)

Fig. 10. a) Unfiltered sample of 0.5 wt% MCC in 1.3 M NDMM-OH(aq) and b) Filtered sample of 0.5 wt% MCC in 1.3 M NDMM-OH(aq). Tables: distribution analysis of c) unfiltered sample of 0.5 wt% MCC in 1.3 M NDMM-OH(aq) and d) filtered sample of 0.5 wt% MCC in 1.3 M NDMMOH(aq).

addition, dissolving up to 7 wt% of MCC in 1.3 M NDMM-OH(aq) was achieved successfully. Investigations on two different pulps yielded clear microscopy images with traces of fiber ballooning. Intrinsic viscosity measurements (1.11 dL/g) indicate a similar nature of stabilizing solvent-cellulose interactions as in other aqueous hydroxide solvents, which will be subject to further investigation. Degradation of the cellulose to any noticeable extent could not be detected, even after refrigerating the solution for 15–16 h after dissolution. Hence, the easy synthesis of NDMM-OH(aq), coupled with the relatively low solvent concentration required for cellulose dissolution and its rapid and good dissolution capacity make it a promising solvent with the potential of being employed in future cellulose applications. Also, in light of the work we have done on combining different bases to tune the solution properties, access to a new QAH base with good affinity to cellulose and high dissolution capacity is very valuable. Further investigations on this solvent will focus on solubility and dissolution mechanisms, as well as applicability on other temperature ranges and pulp substrates.

CRediT authorship contribution statement

Shirin Naserifar: Conceptualization, Formal analysis, Investigation, Writing – original draft, Visualization. **Beatrice Swensson:** Investigation, Writing – review & editing. **Diana Bernin:** Investigation, Writing – review & editing, Supervision. **Merima Hasani:** Conceptualization, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The Knut and Allice Wallenberg Foundation is gratefully acknowledged for financial support within Wallenberg Wood Science Center and the Swedish NMR Centre is acknowledged for providing spectrometer time. We also thank Professor Johan Bergenholtz at The University of Gothenburg for the kind use of the equipment for the DLS measurements.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.eurpolymj.2021.110822.

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