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Scattering studies of the size and structure of cellulose dissolved in aqueous hydroxide base solvents

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ABSTRACT

Combining NaOH with other hydroxide bases with superior dissolution properties can be a means of improving dissolution of cellulose. However, this raises questions about how the size and structure of cellulose vary when dissolved in different hydroxide bases. Here, cellulose in aqueous solutions of NaOH, Tetramethylammonium hydroxide (TMAH), Benzyltrimethylammonium hydroxide (Triton B) and previously studied equimolar solutions of NaOH/TMAH and NaOH/Triton B were investigated using small angle X-ray scattering, static and dynamic light scattering. The results show that cellulose in NaOH(aq) is largely aggregated and that the more hydrophobic TMAH and Triton are capable of molecularly dissolving cellulose into worm-like conformations, stiffer than in NaOH. The dissolution properties of mixtures are highly dependent on the compatibility of the individual bases; in line with previous observations of the properties of the solutions which now could be correlated to the structure of the cellulose on a nano- and microscale.

1. Introduction

Dissolution of cellulose is required for many applications and analytical methods. A few examples of when dissolution is crucial is spinning of textile fibres from cellulose pulp, homogeneous derivatization of cellulose and analysis of the molecular weight using gel permeation chromatography. One of the few classes of direct and water-based solvents for cellulose is the hydroxide bases in aqueous solution. One base that has received much attention both from industry and from academia is NaOH. The dissolution conditions under which NaOH(aq) dissolves cellulose are however rather limited, namely to temperatures around 0 °C and NaOH(aq) concentrations close to 2 M. There is also a limitation as to what type of cellulose that can be dissolved (Budtova & Navard, 2016). Most often a degree of polymerization below 400–500 is required and even then the dissolution capacity is not high, around 2 to 3 wt% depending on the cellulose and on the method of determining the dissolution capacity (Swensson et al., 2020a, 2020b; Wang et al., 2018). The solutions also have stability issues as they will gel or precipitate upon increasing cellulose concentration, storage time or temperature, as exemplified by the rheological study by Roy et al. (2003). Even though there are several studies on cellulose dissolution in cold NaOH(aq) performed on cellulose with similar properties and dissolved through similar procedures, there are conflicting reports on whether the solutions contain truly molecularly dissolved cellulose or not. In the rheological study of Roy et al. the authors conclude that microcrystalline cellulose (MCC) which is dissolved in 9 wt% NaOH(aq) and brought down to a minimum of −6 °C is not a true solution but rather a suspension of small aggregates. In another study of MCC dissolved in 2 M NaOH(aq) at a minimum of −20 °C, NMR and SAXS data showed a molecularly dissolved solution while SLS data showed large aggregates (Hagman et al., 2017). It can be noted that, in general, cellulose in solution appear to often exist in a colloidally stable but aggregated state (Schulz et al., 2000).

Besides NaOH, there are a number of quaternary ammonium- or phosphonium hydroxide bases that can dissolve cellulose when in aqueous solution. The temperature reported for dissolution varies depending on the base, ranging from room temperature to lower temperatures around 0 °C, similar to what is required for NaOH (Abe et al., 2012; Kostag et al., 2018). Tetrabutylammonium hydroxide (TBAH) and Benzyltrimethylammonium hydroxide (also known as Triton B) are two examples of quaternary ammonium hydroxides that are reported to dissolve more cellulose than NaOH (Wang et al., 2018; Zhong et al.,

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2013). This has been proposed to be due to their relatively hydrophobic nature, which is advantageous for dissolution due to the slight amphiphilic character of the cellulose chain (Lindman et al., 2010; Wang et al., 2018). Even though the quaternary ammonium hydroxide bases seem to be superior in dissolving cellulose there is still an interest in using NaOH since it is readily available, cheap and non-toxic (but still corrosive). Therefore research has aimed at improving the properties of the NaOH (aq) solutions by mixing in additives as for example urea (Cai & Zhang, 2005) or ZnO (Davidson, 1937; Liu et al., 2011; Väisänen et al., 2021).

In our previous work, we have combined NaOH with TMAH or Triton in solution to dissolve cellulose and investigated their impact on solution properties as well as a possible preference of cellulose for one base over the other. Combining hydroxide bases is a rather overlooked concept compared to the use of additives, as in our search we could only find a patent from 1924 (Lilienfeld, 1924) which mentions that "The presence of (the) caustic soda enhances the solvent action of the bases", but with no systematic investigations of the resulting properties. We however, have shown that combining NaOH with TMAH increased the stability of the solutions over time but combining NaOH with Triton had no such effect, despite the fact that Triton alone is superior over NaOH or TMAH in dissolving cellulose (Swensson et al., 2020a, 2020b). Because of this, the question arose how these stability and solubility effects correlate with the structure of the cellulose in solution: Is cellulose molecularly dissolved and, in general, to which extent does the amphilicity and size of the base affect the structure and organization of dissolved cellulose? Therefore, three methods for measuring the size and structure of cellulose when dissolved in NaOH(aq), TMAH(aq), Triton(aq) and in two combined solvents of 50/50 NaOH and TMAH and 50/50 NaOH and Triton were chosen for this study: X-ray scattering, dynamic light scattering and static light scattering.

It should be noted that all of the solvents used for this study require that the solution is brought to temperatures below 0 °C in order for dissolution to occur (at 4 mol% base). Because of this the scattering measurements were performed at the lowest available temperature on the respective instruments and on freshly prepared samples without storage time. This was in order to view the size and structure of the cellulose as close to the state upon dissolution as possible.

2. Materials and methods

2.1. Materials

Microcrystalline cellulose (MCC), Avicel PH-101 purchased from FMC BioPolymer, a purified partially depolymerized cellulose made by acid hydrolysis of specialty wood pulp was used throughout the study. It has been characterized to have a Mn of 11.7 $\times$ 10^3 g/mol (Degree of Polymerization (DP_n)72), Mw 29 $\times$ 10^3 g/mol (DP_w 179) and Mz 58 $\times$ 10^3 g/mol (DP_z 358) as obtained from GPC-MALS in DMAc/LiCl (personal communication with Majid Ghasemi at Södra skogsägarnas ekonomiska förening). Granulated sodium hydroxide (NaOH) known commercially as Emplura, benzyltrimethylammonium hydroxide (Triton or Triton B) 40 wt% (aq), tetramethylammonium hydroxide (TMAH) 25 wt% (aq) were purchased from Merck (previously Sigma-Aldrich) and used as received.

2.2. Dissolution of cellulose

A 4 mol% base(aq) solution was prepared and then placed in an ice bath to cool, cellulose was added and the solution left to stir for 10 min. The solution was then stored in a freezer at −20 °C for 20 min before being stirred in an ice bath for ca. 5 min to remove any ice crystals that might have formed, and to ensure a more homogeneous sample. The method used is the same as described in (Swensson et al., 2020a) and for the stirring a standard magnetic stirrer was used.

2.3. Small angle X-ray scattering (SAXS)

Small angle X-ray measurements were performed using a Mat:Nordic from SAXSLAB with a Rigaku 003+ high brilliance microfocus Cu-radiation source and a Pilatus 300K detector. Samples of dissolved cellulose were always prepared in direct conjunction to the SAXS measurement and measured within 8 h while under temperature control. The measured q-range was 0.007–0.25 $Å^{-1}$, the two-dimensional scattering pattern was radially averaged using either the SAXSGui software or in PyFAI and the sample data was subtracted by the solvent data. The concentrations of cellulose ranged between 1 and 2.5 $\times$ 10^{-2} g/ml, see Table S1 in the supporting information for the exact concentrations. The modelling of the data was performed using SasView. Temperature control was achieved using a JULABO recirculating bath with cooling liquid.

2.4. Dynamic light scattering (DLS)

DLS measurements were performed using 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. Upon preparation of samples for DLS the solvents were filtered with 0.22 μm filters before addition of cellulose to minimize any dust in the samples. After preparation of the cellulose solutions, they were measured as soon as possible and both unfiltered and filtered using a 1.2 μm acrylic copolymer filter or a 0.22 μm PES filter. The concentration measured was kept at a fixed molar ratio of 268 mol base per anhydroglucose unit (AGU) and 24 mol base per H_2O, corresponding to ca 0.125 wt% of MCC in ca 2 M solvent or ca 1.4 * 10^{-3} g/ml depending on the weight and volume of the base. The built-in software was used for analysis, both a cumulant fit and a distribution fit ("general purpose mode", a non-negative least squares method) was applied. The viscosity of each solvent was measured at 20 °C through flow sweeps and the measured viscosity was used for the data analysis (see Table S2 in the supporting information).

2.5. Static light scattering (SLS)

SLS measurements were performed using a CGS-8F from ALV GmbH with a 50 mW laser operating at a wavelength of 532 nm. The measurements were made at a scattering angle of 17° to 152° with a maximum step size of 4°. The cellulose solutions were measured directly after preparation at concentrations in the range of 5 $\times$ 10^{-4} to 1.6 $\times$ 10^{-2} g/ml (see Table S1 in the supporting information) and measured either unfiltered or filtered using a 1.2 μm acrylic copolymer filter or a 0.22 μm wwPTFE filter. Each concentration was prepared individually and not diluted from a stock solution.

2.6. Refractive index measurements

The refractive index of the solvents was measured and used for the DLS and SLS measurements (see Table S2 in the supporting information). The instrument was an Abbemat 550 from Anton Paar using a wavelength of 589 nm at 20 °C.

3. Results and discussion

3.1. Dynamic light scattering

Dynamic light scattering was used to measure the hydrodynamic size of the cellulose in solution when dissolved at a dilute concentration. Clarification of samples for light scattering by filtering or centrifugation is standard procedure to remove dust particles that might interfere with the measurement. It is however important to consider that by doing so one might alter the composition of the sample in addition to removing dust. Therefore, we chose to measure the samples both unfiltered and filtered with a 1.2 or 0.22 μm filter when studying the dissolution state

of the cellulose chains, probing for possible aggregation as well as molecularly dissolved cellulose chains. The normalized raw correlation curves are presented in Fig. 1 and in order to calculate the effective hydrodynamic radius both a cumulant fit (see Table 1) and a multimodal distribution was applied (see Fig. 2 and in the supporting information: Figs. S1 and S2 for the drawn distributions and Table S3 for the corresponding values). The fitted cumulant and multimodal model curves can also be found in the supporting information (Figs. S4 to S13).

If first the single base solutions are examined, the results show that cellulose in NaOH(aq) can be fractionated through filtering as seen both on the effect on the correlation curves (Fig. 1a) and on the subsequent sizes obtained through a cumulant analysis (Table 1). The obtained

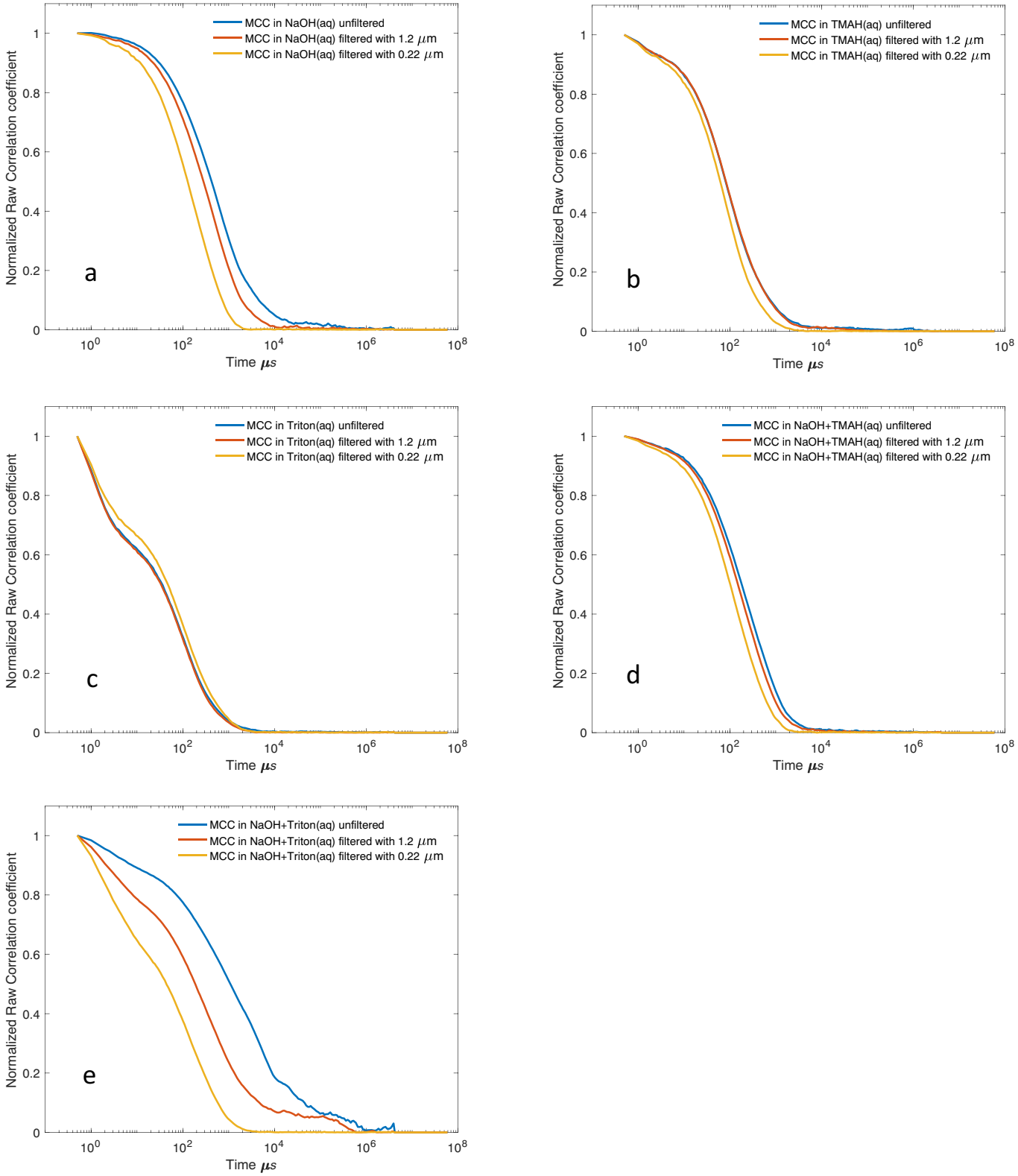

Fig. 1. a to e: Normalized raw correlation data from DLS measurements.

Table 1
Results from a cumulant analysis of the DLS data of cellulose in 4 mol% base(aq).

Solvent	Unfiltered		Filtered with 1.2 μm		Filtered with 0.22 μm	
	$R_{h,z}$ [nm]	PDI	$R_{h,z}$ [nm]	PDI	$R_{h,z}$ [nm]	PDI
NaOH	81	0.81	48	0.99	28	0.62
TMAH	16	0.64	15	0.72	12	0.65
Triton	9	0.96	10	0.93	11	0.95
50/50 NaOH/ TMAH	32	0.91	27	0.95	21	0.61
50/50 NaOH/ Triton	120	0.91	36	0.61	8	1.0

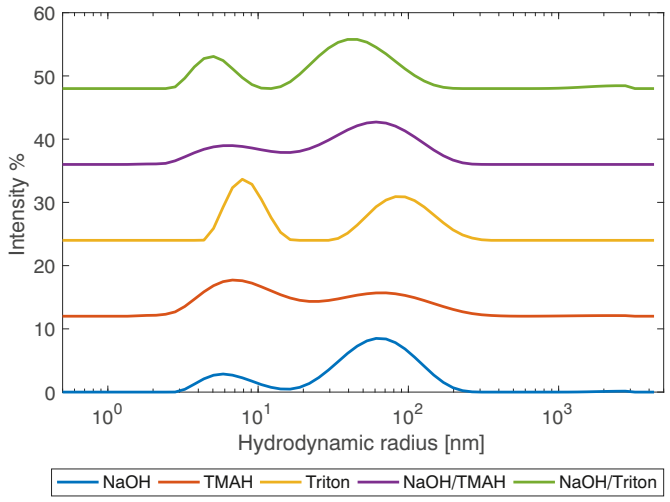

Fig. 2. Size distributions of cellulose solutions filtered with a 0.22 μm filter, obtained through a multimodal fit. The curves are baseline shifted for improved readability.

values for the Poly Dispersity Index (PDI) for the three NaOH samples are high, indicating that they are not monomodal. When applying a distribution fit instead of a cumulant fit for the NaOH solutions, results reveal that there are aggregates with a radius of ca 0.4 μm present that are removed upon filtration with the 0.22 μm filter, leaving two populations with a radius of 7 nm and 70 nm, respectively (see Fig. 2 and Table S3 in the supporting information). Compared to NaOH(aq), the cellulose dissolved in the more powerful bases TMAH(aq) and Triton(aq) is unaffected by filtration and well-dissolved as indicated by the small radii obtained from the cumulant analysis (Table 1), which are in line with those expected for molecularly dissolved MCC. Yet, in the correlation curves (Fig. 1b and c) there is a feature indicating that there are two populations of cellulose, most distinctly seen in the correlation curves of cellulose in Triton(aq) (Fig. 1c): there is an initial steep decrease, followed by a plateau before the curve decreases again. The multimodal distributions for the TMAH and Triton solutions show that there is a high intensity scattering from the small-sized population of ca 10 nm (Fig. 2 and Table S3 in the supporting information), which is what is reflected in the cumulant analysis, but also a fraction with a size of ca 80–100 nm. As smaller particles scatter less light, the high intensity from the 10 nm population reflects that the majority of the cellulose in these samples is molecularly dissolved despite the presence of aggregates. In Triton(aq), the two populations are clearly separated (see Fig. 2), as could be expected from the appearance of the correlation curve (Fig. 1c).

When NaOH is combined with TMAH(aq), the cumulant analysis shows that the cellulose is more well-dissolved than in NaOH(aq) but larger in size than in TMAH(aq). Even though there is no sign of multiple populations in the correlation curves for NaOH/TMAH(aq) (Fig. 1d), the PDI obtained from the cumulant analysis is high and the distribution fit indicates two populations with a radius of around 10 nm and 70–100 nm, respectively (see Fig. 2 and Table S3 in the supporting information).

For cellulose dissolved in the combination of NaOH and Triton(aq), the solutions are heavily affected by filtration as can be viewed by the difference in the correlation data (see Fig. 1e) and in the cumulant analysis (see Table 1). This indicates that a comparatively large portion of the sample is aggregated and that this combination did not improve the solution structure as compared to pure NaOH(aq). In fact, another interesting feature related to this was observed already in the preparations for the DLS measurements. When the solvents viscosities were measured prior to DLS the solution of NaOH with Triton(aq) showed slightly shear-thinning behavior as opposed to the expected Newtonian behavior, which was observed for the other solvents (see Fig. S3 in supporting information). A subsequent DLS measurement of the 50/50 NaOH/Triton(aq) solvent showed a slight correlation for a particle size of 1 nm, indicating aggregation of the solvent itself. From our previous study of the dissolution capacity and properties of cellulose dissolved in NaOH(aq) combined with Triton(aq) it was clear that this combination did not improve the solvent quality but instead it was a slightly poorer solvent than expected from the mere average of the two individual solvent bases (Swensson et al., 2020b). This indicates that even though NaOH and Triton are both soluble in water to a large extent, they might not be completely miscible, as the Triton base might be aggregating in the presence of NaOH. In fact, if one considers that Triton B is a weak surfactant it is likely to show self-aggregation behavior, particularly at high ionic strength (Attwood & Florence, 2012), which is in line with this observation. This could explain the observed solution properties and be an indication that it is not preferable to mix NaOH with a more hydrophobic base. The fact that the radius of the sample of unfiltered cellulose in 50/50 NaOH/Triton(aq) is closer to that in NaOH(aq) but upon filtering with a 0.22 μm filter it is closer to that in Triton(aq) (Table 1) could be interpreted as a sign that there are two populations of cellulose: one interacting with NaOH and one with Triton, but to conclude this would require further investigation.

In summary, from the distribution fit it appears that in all the solutions there is a population of well-dissolved cellulose with a radius of ca 10 nm and a portion of intermediate-sized cellulose with a radius of ca 50–100 nm which we interpret as aggregated cellulose (Fig. 2). While in this study the DLS measurements were made on one dilute concentration another extensive DLS study by Lu et al. on cellulose dissolved in NaOH/urea(aq) showed that upon increasing concentrations of cellulose, increasing temperature or storage time, cellulose continued to aggregate further (Lu et al., 2011). A similar behavior might be expected for the solvents used in this study, even though the temperature stability might differ between the solvents, as our previous study has indicated that the more hydrophobic bases might give more stable solutions at higher temperatures compared to NaOH (Swensson et al., 2020b).

3.2. Static light scattering

To investigate the aggregation state of the solutions, static light scattering was performed to measure the z-average radius of gyration and the apparent weight average molecular weight. A Zimm-plot analysis (see Figs. S14–S25 in the supporting information) of unfiltered and filtered solutions of dissolved cellulose yielded the results as seen in Table 2. Since more concentrated samples were used for SLS than DLS it also became apparent that the Triton solutions were easier to filter, an observation that also agrees with the superior dissolution properties of Triton. On the other hand, and in line with the DLS findings, the NaOH solutions were difficult to filter. The second lowest concentration used for SLS (1.4×10^{-3} g/ml) was the same as that used for DLS and unfortunately above that concentration the samples of cellulose in NaOH (aq) could not be filtered with the 0.22 μm filter and lower concentrations gave a weak signal. Because of this only a partial Zimm-analysis on the lowest measured concentration (0.7×10^{-3} g/ml) was performed for

Table 2
Results from a Zimm-plot analysis on the data from the static light scattering measurements made on 4 mol% base(aq) solutions.

Solvent	Unfiltered			Filtered 0.2 μm		
	$R_{g,z}$ [nm]	$M_{w,ave}$ [g/mol]	$A_2 \times 10^{-6}$ [mol × ml × g^{-2}]	$R_{g,z}$ [nm]	$M_{w,ave}$ [g/mol]	$A_2 \times 10^{-6}$ [mol × ml × g^{-2}]
NaOH	294	7.5 × 10^6	21	47[a]	3.3 × 10^5[a]	N/A
TMAH	173	2.4 × 10^6	490	24	4.5 × 10^4	160
Triton	103	2.0 × 10^5	160	35	6.3 × 10^4	1400
50/50 NaOH/TMAH	152	1.6 × 10^6	14	85	3.3 × 10^5	530
50/50 NaOH/Triton	162	3.3 × 10^6	160	75	1.9 × 10^5	−16

[a] Partial Zimm-analysis.

this sample.

The results show large radii and high molecular weights for the unfiltered samples, indicating that there are aggregates in all of the solutions but the largest in NaOH(aq). The solutions (except for cellulose in TMAH(aq) and Triton(aq)) were also measured after filtration with a 1.2 μm filter and gave similar results to the unfiltered samples (see Table S5 in the supporting information). If we compare the results on the molecular weights after filtration with a 0.2 μm filter, to that of 2.9 × 10^4 g/mol obtained from GPC-MALS in DMAc/LiCl, it appears that TMAH(aq) and Triton(aq) can dissolve part of the cellulose on a molecular level. If the obtained values of $R_{g,z}$ from the filtered samples are compared to theoretical ones (see Table S4 in the supporting information), they indicate that the cellulose chains exist as stiff worm-like chains rather than Gaussian chains. The combined solvents show slightly better dissolution than NaOH(aq) but appear to contain aggregates even after filtration with a 0.22 μm filter.

The second virial coefficient A_2 provides a measure of the interactions between the solvent and the cellulose. A value close to zero would correspond to a theta solvent (Schärtl, 2007). The obtained results vary between the unfiltered and filtered samples, but two results stand out: the high value obtained for the filtered cellulose in Triton(aq), indicating strong interactions between the cellulose and the solvent, and the negative value obtained for the filtered cellulose in NaOH/Triton (aq), indicating repulsive interactions between the cellulose and the solvent.

The ratio between R_h and R_g has been used to give more information on the structure of cellulose (Schulz et al., 2000). Our results show that the radius of gyration is always larger than the radius of hydration (see Table 3), indicating that there is a core to the coils/aggregates where the solvent cannot diffuse freely. The same trend was reported by Saalwächter et al. for the same type of cellulose (Avicel MCC) in Cuoxam (Saalwächter et al., 2000). In the work by Chen et al. it was found that for cellulose dissolved in NaOH/urea(aq) the R_g/R_h ratio was 1.4 (Chen et al., 2007) which agrees with the value below 2 that we obtained for NaOH(aq), indicating a slightly more compact structure compared to those in TMAH(aq) or Triton(aq) (showing somewhat higher R_g/R_h ratios). The large values for the ratios obtained for the combined solvents are difficult to interpret but might suggest that the structure of the aggregates is very loose.

Table 3
Results of the radius of gyration, the hydrodynamic radius and the ratio between them for samples filtered with 0.22 μm filters.

Solvent (aq)	R_g	R_h	R_g/R_h
NaOH	47	28	1.7
TMAH	24	12	2.0
Triton	35	11	3.2
50/50 NaOH/TMAH	85	21	4.1
50/50 NaOH/Triton	75	8	9.4

3.3. Small angle X-ray scattering (SAXS)

SAXS measurements were made to provide information on the structure of the cellulose to complement the size information obtained from DLS and SLS. The solutions did not scatter much and therefore in most cases the concentration had to be increased to between 1 and 2.5 g/ml (above that which was used for DLS and SLS) in order to get good statistics within a reasonable measurement time. Because of this, the solutions were most likely in the semi-dilute state. The cellulose in the solutions were thus influenced by interactions between cellulose chains and – based on the knowledge obtained from DLS and SLS – consisted of both dissolved and undissolved cellulose fractions of different aggregate sizes. Adding the fact that cellulose is inherently polydisperse will further increase the difficulties of modelling these systems and therefore one should take caution when interpreting the results. Because of this, as a first step, the power law behavior within the q-range of 0.01–0.1 $Å^{-1}$ (corresponding to a distance of 6.3–63 nm) was fitted to provide information about the structure of the cellulose without assuming a model (see Fig. 3). The results was an exponent of −1 and −1.1 for cellulose in Triton(aq) and TMAH(aq), respectively, which according to scattering theory suggests that at this length scale we are probing a stiff rod-like structure (Glatter, 2018). This suggests that in these two solvents the cellulose is closer to a stiffer worm-like chain than a fully flexible random coil, which could indicate a strong association of the quaternary ammonium cations to cellulose. For cellulose in NaOH(aq), the result of $q^{-1.65}$ is typically associated with swollen chains in a good solvent (Glatter, 2018), but since all other measurements indicate that it is indeed a rather poor solvent we interpret this as an indication that the cellulose is more flexible in NaOH(aq) than in Triton(aq) or TMAH(aq). For the combined equimolar solvents, the exponents of −1.35 for NaOH/TMAH and −1.4 for NaOH/Triton are close to the average between NaOH and TMAH (−1.38) or NaOH and Triton (−1.33). These values are more difficult to interpret but reflect that the solutions structure is somehow in between a well-dissolved solution as in TMAH(aq) or Triton (aq) and the aggregated state of NaOH(aq). It can both indicate that the two bases are distributed randomly along the chains (resulting in a semi-flexible chain) or that there is a mix of flexible and stiff chains. Based on the knowledge obtained through the DLS measurements, showing a

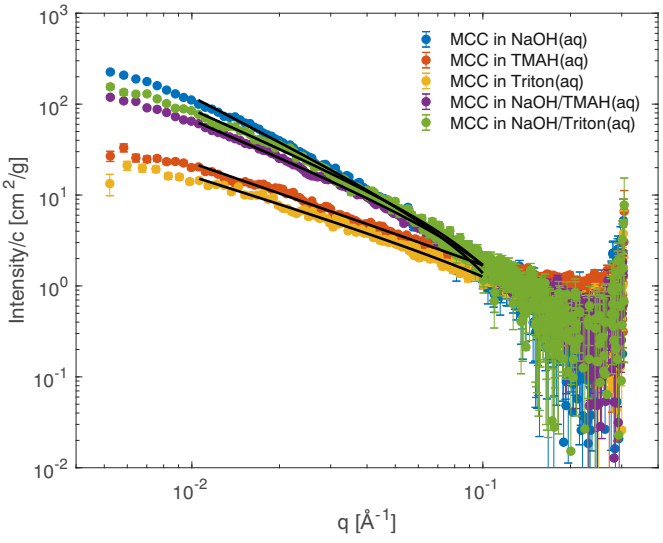

Fig. 3. SAXS data normalized by concentration with the black lines showing the power law fitted to the q region in the range from 0.01 to 0.1 $Å^{-1}$.

Triton-like behavior of cellulose in NaOH/Triton(aq) solutions after removal of large aggregates, it is possible that the first case applies to cellulose dissolved in 50/50 NaOH/TMAH(aq) while in 50/50 NaOH/Triton(aq) there might also be a possibility of two populations of cellulose existing due to poor miscibility of the two bases and aggregation of Triton.

The data was subsequently fitted using a model for a semiflexible polymer with excluded volume where the fitting parameters are the contour length, Kuhn length (2 times the persistence length Lp for a worm-like chain) and the radius of the cellulose chain (see Figs. 4, 5 and Tables 4 and S6) (Pedersen & Schurtenberger, 1996). This model does not take into account any aggregation of the cellulose and therefore might be less suited for the low q-range.

The result obtained for cellulose in NaOH(aq) reflect a very long and flexible chain, but the contour length of 356 nm (see Table 4) is longer than the maximum zeta average contour length of 184 nm as calculated from GPC-MALS data (see supporting info). We interpret this as that the scattering signal is affected by agglomerates in NaOH(aq) and that this is not the true contour length for the single cellulose chains.

The results for cellulose dissolved in TMAH(aq) or Triton(aq) reflect a stiffer chain than in NaOH(aq) as seen by the ratio of length over persistence length (junction points, see Table 4). The contour lengths obtained for cellulose in TMAH respectively in Triton are shorter than expected since they correspond to a DP of 119 and 83 which are close to the number average DP of 72 as measured by GPC-MALS (assuming that the length of an anhydroglucose unit is 0.515 nm) (Schulz et al., 2000). SAXS data should be closer to reflecting the weight average or zeta average since the intensity is proportional to the volume of the particle to the power of 6 and therefore the longer chains should scatter more. One explanation for a shorter chain could be degradation of the cellulose chain but the samples were measured at close to 0 °C and so we do not expect any degradation to occur. Another explanation for the short contour length might be that the obtained radius of the chain is larger than expected for a single cellulose chain (within the order of 2 Å, not including the counterion), and so the true contour length might be longer if the chain is taking a longer path inside the flexible cylinder that the model is representing.

For the two combined solvents the results of applying the model for the semi-flexible chain are very similar to each other. They both return a contour length corresponding to a DP of ca 235 (which is slightly above the weight average), persistence lengths of ca 4.5 nm and radii in line with that obtained for the other solutions (see Table 4).

It is difficult to compare this data with other published results as often the same model can give several fits to the same data and it is up to the researcher to judge what is a reasonable result. With this in mind, Gubitosi et al. dissolved the same type of microcrystalline cellulose as used in this study in 40 wt% Tetrabutylammonium hydroxide(aq) at 30 °C. They used a model of a semiflexible chain with excluded volume interactions combined with a core-shell cross section together with a random phase approximation. They found that a cellulose core with a radius of 5 Å surrounded by a 5 Å shell of TBA+ ions, contour length of 181 nm, persistence length of 2 nm (ca 4 AGU) and interaction parameter of 5 described their sample (Gubitosi et al., 2016). Their results suggest a more flexible cellulose chain compared to the results for MCC in TMAH(aq) found in this study. Despite the similarities of the bases, they do differ in dissolution properties as they dissolve cellulose at different temperatures and concentrations, and the temperature at which the measurements were performed differ. If turning to two published studies on MCC in cold NaOH(aq), Hagman et al. found that a model of a semiflexible polymer with excluded volume with a contour length of 82 nm, radius of 2.5 Å and a Kuhn length of 2.3 nm (4 AGU) combined with a structure factor with a mesh size of 103 nm reflected their data (Hagman et al., 2017). In another article investigating the same type of cellulose dissolved at low temperatures in 2.0 M NaOH(aq) and measured at room temperature a different result was found: a semiflexible polymer with excluded volume with a radius of 4.1 Å, persistence length of 10 nm and a contour length of 60 nm (Martin-Bertelsen et al., 2020). The latter study points to a very stiff cellulose chain in solution. Besides the fact that dissolution of cellulose in these systems have been shown to be sensitive to temperature and time - which might result in different structures depending on how one treats the samples - this also highlights the need for continued studies on cellulose in solution and model development.

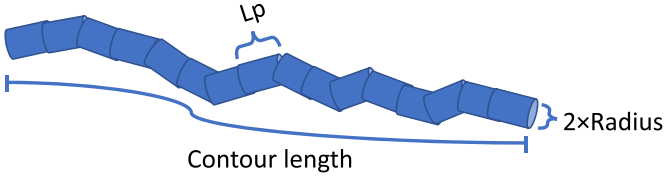

Fig. 4. An illustration of a worm-like semi flexible cellulose chain and the fitted parameters.

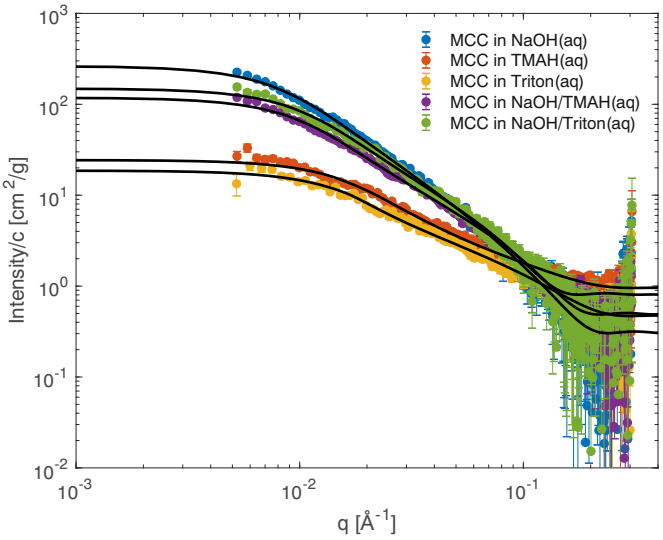

Fig. 5. SAXS data together with black lines showing the fitted curves of the model for a semi-flexible worm-like chain.

Table 4
Results from the fitting of the model to the SAXS data.

	NaOH	TMAH	Triton	50/50 NaOH/TMAH	50/50 NaOH/Triton
Contour length L [nm]	356 ± 88	61 ± 2	43 ± 2	118 ± 2	121 ± 4
Kuhn length [nm]	3.2 ± 1.1	7.7 ± 0.5	19 ± 1.0	9.5 ± 0.3	8.6 ± 0.5
Persistence length Lp [nm]	1.6	3.6	9.4	4.8	4.3
L/Lp	220	17	4.6	25	28
Chain radius [Å]	16 ± 1.0	12 ± 0.1	13 ± 0.4	18 ± 0.2	22 ± 0.4

3.4. The effect of different bases on the structure of cellulose

In general, our SAXS findings show that the cellulose is stiffer and more well-dissolved in Triton(aq) and in TMAH(aq) than in NaOH(aq) or the combined solvents as viewed by the persistence lengths and the number of junction points. The influence that the base and more specifically the cation (since the anion is the same for all bases) has on the structure of cellulose in solution can be viewed through several aspects. Firstly, they differ in their amphiphilic properties as all are well-soluble

in water but increasingly hydrophobic in the order of NaOH < TMAH < Triton. As mentioned in the introduction to this paper, it has been shown that the ability of the base to match the slightly amphiphilic character of cellulose can be advantageous for dissolution and a stronger interaction between the charged cation and the cellulose could lead to a stiffer chain - similar to the effect that charge has on polyelectrolytes, which would explain the stiffer chain observed in Triton and TMAH solutions. Secondly, there might be a difference in the strength of the bases in the order of Triton > TMAH > NaOH, as indicated by the Beta parameter measured with solvatochromic dyes in our previous work (Swensson et al., 2020b). This would directly affect the deprotonation of cellulose hydroxyls and the resulting charging contribution to the stabilization of the dissolved chains (with the strongest effect in Triton and weakest in NaOH solutions). Thirdly, they differ in size and a larger cation associated to the chain might prevent chain-chain interactions more effectively than a small one although the impact of the steric hindrance of the cation on dissolution is uncertain. In a study by Brownsett et al. they investigated if the size of the cation is related to the extension of the lattice in the crystalline zones through X-ray diffraction. They could see that when cellulose is subjected to different quaternary ammonium hydroxide bases to form so-called alkali-cellulose, it is accompanied by an extension of the lattice but only to a certain extent. Between the larger bases they could not see a significant difference (Brownsett & Clibbens, 1941). If comparing NaOH with TMAH, the TMA^+-ion has been reported to be about twice as large as Na^+ in the hydrated form (García-Tarrés & Guàrdia, 1998; Mähler & Persson, 2012). The comparably smaller size of the Na^+ ion might allow it to effectively diffuse into and swell the cellulose, but its lack of additional more hydrophobic interactions makes it a rather poor solvent.

4. Conclusions

Through this study we can see that the solution properties of cellulose, when dissolved in aqueous solutions of hydroxide bases, can be related to the size and structure of cellulose on a micro- and nanoscale. The poor solution properties of cellulose in NaOH(aq) is reflected by the fact that even at low concentrations there are large aggregates present, indicating that a portion of the cellulose is never dissolved but merely swollen cellulose particles. DLS and SAXS measurements indicate that TMAH and Triton have the capability to dissolve cellulose on a molecular level and that the chains exist as worm-like chains rather than flexible coils. Through this study it also appears that, when mixing/combining hydroxide bases in aqueous solution to dissolve cellulose, it is not enough that both bases are well-soluble in water at the same temperature. One also needs to consider their miscibility as indicated by the fact that Triton B seems to aggregate in the presence of NaOH, resulting in poor solution properties. When cellulose is dissolved in a combination of NaOH and TMAH(aq) the results from DLS, SLS and SAXS in general point to a cellulose with a size and structure representing almost an average of the two cases, but not truly molecularly dissolved. This however shows that combining NaOH with TMAH can improve the dissolution as compared to only NaOH(aq).

CRediT authorship contribution statement

Beatrice Swensson: Conceptualization, Formal analysis, Investigation, Writing – original draft, Visualization. **Sebastian Lages:** Methodology, Investigation, Writing – review & editing. **Barbara Berke:** Investigation, Writing – review & editing. **Anette Larsson:** Conceptualization, Writing – review & editing, Supervision, Funding acquisition. **Merima Hasani:** Conceptualization, Writing – review & editing, Supervision, Project administration, Funding acquisition.

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Appendix A. Supplementary data

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