Ionic strength control of sulfated cellulose nanocrystal suspension viscosity

STEPHANIE BECK AND JEAN BOUCHARD

ABSTRACT: The effect of added electrolyte on the viscosity behavior of 3–9 wt% cellulose nanocrystals (CNC) suspensions was investigated for three different grades of CNCs extracted from wood pulp with sulfuric acid at increasing hydrolysis temperature. The viscosity of aqueous CNC suspensions decreases significantly when small amounts of electrolyte are added because of a reduction in electroviscous effects caused by compression of the electrical double layer surrounding the particles. As the ionic strength increases further, the suspension viscosity reaches a minimum and then increases again with the formation of an attractive gel.

Application: A simple, easy-to-implement online technique can be used to control CNC suspension flow properties, thereby facilitating processing and increasing the range of applications for CNC suspensions.

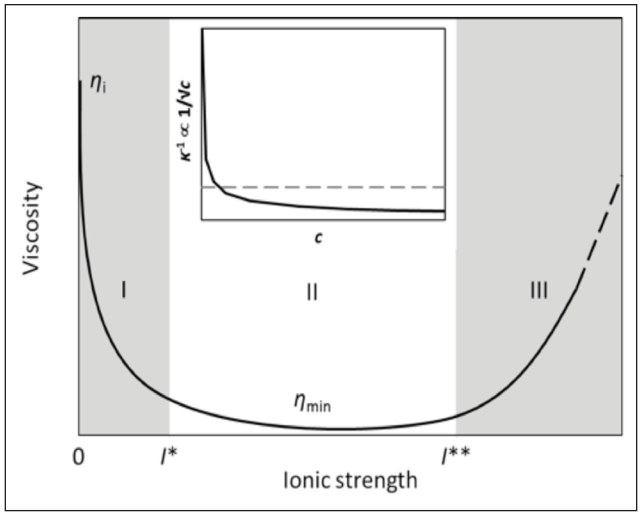
During their manufacture by sulfuric acid hydrolysis, cellulose nanocrystals (CNCs) are typically handled as low (<10 wt%) concentration suspensions for ease of purification. Following purification, increasing the CNC concentration as much as possible reduces the energy input needed for drying. Higher-concentration aqueous CNC formulations might also be required for some applications, as well as reducing the cost of drying or transportation. However, CNC suspension viscosity increases dramatically with concentration; the abrupt increase typically occurs at concentrations between 5 wt% and 10 wt% for wood-derived CNCs [1-4]. This might cause problems such as hollow fiber membrane fouling during purification and concentration.

Several studies [1-7] of CNC suspensions under shear have indicated that, above a critical concentration [8], they are shear-thinning (non-Newtonian) fluids whose viscosity decreases significantly with increasing applied shear rate. Shear-thinning properties are often desirable in a material, as they can provide suspension stability or drip resistance when at rest but also ease of spreading, pouring, or pumping when a shear stress is applied. The zero-shear viscosity is the viscosity of a material at a shear rate of zero (i.e., the viscosity at rest), which is typically the condition to use when studying stability. The material is undergoing no significant deformation forces apart from that of gravity.

Cellulose nanocrystals have an electrostatic charge from the anionic sulfate half-ester groups ($-OSO_3^-$) covalently bound to the surface cellulose chains. The net negative surface charge allows the CNCs to remain stable in aqueous suspension with an increased concentration of cationic counterions close to the particle surface; an electrical double layer (EDL) surrounds each particle, extending into the bulk medium (water) [9]. In industry, however, formulations are rarely made with pure water. Because formulations to which CNCs are added often contain significant concentrations of various salts and other species, we examined the effects of ionic strength on CNC suspension rheology.

The distortion of the EDL when the particle is in a shear flow leads to increased dissipation of energy and an increase in the suspension viscosity, known as the primary electroviscous effect [10]. Electrical double layers repel each other, increasing the effective particle diameter [11,12]; a secondary electroviscous effect can be observed when the EDLs of neighboring particles overlap. Double layer interactions contribute significantly to the low-shear viscosity of dispersions of charged colloidal spheres [13-15]. Charged colloidal rods such as CNCs have larger interaction volumes relative to their size; therefore, electroviscous effects are observed at much lower particle concentrations and ionic strengths than for colloidal spheres [10]. In the presence of salts, the thickness of the EDL is proportional to the inverse square root of the concentration of ions in solution [16], affecting the viscosity (via electroviscous effects).

At low shear rates, colloidal factors such as ionic strength and surface forces contribute to the rheological behavior of a suspension of charged colloidal particles [17]. For suspensions of negatively charged sulfated CNCs, the viscosity is thus controlled by the ionic strength of the aqueous phase [8,11,18,19] and the CNC surface charge density [3,20] in addition to the CNC concentration [2,3,8,11,18-22]. Added salt has little or no effect on the viscosity at higher shear rates (e.g. during pump-



1. Theoretical schematic diagram of viscosity of a suspension of charged rod- or spindle-shaped colloidal particles as a function of the ionic strength. Inset is a schematic diagram of the electrical double layer thickness $\varkappa^{-1}$ as a function of the ion concentration c.

ing or mixing), as hydrodynamic effects control the rheology under those conditions [17].

The viscosity behavior of charged rod suspensions in the presence of added electrolyte is represented in **Fig. 1**. In region I ($0 \le I < I^*$) when no background electrolyte is present, the EDL swells, leading to large repulsion interactions between adjacent particles. At low shear, the EDL interactions dominate, competing with shear flow and making it difficult for particles to pass over each other [11]; thus, the suspension has high initial viscosity, ηi. At high particle concentrations, double layer overlap might strongly reduce particle diffusion and lead to the formation of a stiff repulsive gel.

In region II ($I^* \le I < I^{**}$) when small concentrations of electrolyte are added to the aqueous phase, the surface charges are shielded, compressing the EDL [11]. This reduces the primary and secondary electroviscous effects; thinner double layers are less distorted by shear flow and overlap to a lesser extent. The low-shear viscosity therefore drops significantly as the motion of the rods becomes less restricted, facilitating shear flow [21]. If enough salt is added, a balance between repulsive and attractive interactions between the particles is attained and the viscosity levels off and reaches a minimum value, ηmin. For the viscosity versus ionic strength curves obtained in these experiments, we have defined the ionic strength boundaries I* and I** of this pseudoplateau region of low viscosity so that the values of viscosity at the boundaries are no more than 20% higher than the value of the measured minimum viscosity.

In region III ($I \ge I^{**}$) as even more salt is added, the EDL compression reaches a limit with increasing ionic strength. Suspension viscosity increases again as electrostatic repulsion is swamped and van der Waals attractions between particles dominate the suspension behavior [21]. Flocculation or gelation can occur if the structure of agglomerated particles is strong enough, causing the viscosity to increase rapidly [10]. When an attractive gel forms, particles agglomerate to produce space-filling networks that might be either homogeneous or heterogeneous [21].

Recent works have examined the effect on the CNC rheological behavior profile of parameters such as the hydrolysis agent, CNC surface charge [3,20], CNC concentration [2,3], CNC aspect ratio [23], temperature [2], liquid crystalline microstructure of the suspension at high CNC concentration [19,21], and added polymers [24]. However, many studies have focused on redispersed dried CNCs at concentrations much lower than those of interest for industrial processing. Boluk et al. have investigated the effect of sodium chloride (NaCl) electrolyte concentration on the viscosity under shear of dilute (isotropic) CNC suspensions up to 1.0 wt% [8]; González-Labrada and Gray also examined the viscosity of a dilute (0.06–2 wt%) CNC suspension containing 0–5 mM NaCl with a rolling ball viscometer [18]. Shafiei-Sabet et al. performed a detailed study on the addition of 0–15 mM NaCl to 1–15 wt% CNC suspensions, finding that the concentration-dependent liquid crystalline microstructure of the suspension, itself altered by ionic strength [12,25,26,27], influenced the effects of salt on the suspension rheology [19].

This report investigates the effect of electrolyte concentration on the viscosity of several as-produced, never-dried CNC suspensions at concentrations of industrial use. Viscosity and rheological behavior of colloidal dispersions are key parameters in many industries, as they have great impact on processing and on defining the final products and applications. Our aim was to examine the range of viscosities generated by adding electrolyte to control suspension flow properties with a simple and easy-to-implement online technique, thereby facilitating processing and increasing the range of applications for CNC suspensions.

EXPERIMENTAL METHODS

CNC extraction

Aqueous CNC suspensions containing a small concentration of background electrolyte were prepared from bleached softwood kraft pulp in a pilot-scale CNC reactor according to a procedure modified from the literature [28]. CNCs were extracted by hydrolysis with 64 wt% sulfuric acid for 25 min at different hydrolysis temperatures (**Table I**). The low-, medium-, and high-temperature (CNC-45, CNC-50, and CNC-65) CNC grades exhibit increasing surface charge from sulfate half-ester groups [1]. The z-average hydrodynamic diameter measured by dynamic light scattering (82 ± 4 nm) and the particle size distributions of the different batches were similar. At lower hydrolysis temperatures, oligosaccharides derived from hydrolyzed cellulose form a layer on the surface of the CNCs [29].

CNC suspensions were dialyzed extensively against running deionized water (Spectra/Por 4 [Spectrum Laboratories; Rancho Dominguez, CA, USA], 12–14 kDa MWCO, minimum 3 days) until the pH and conductivity of the dialysis water was

CNC Grade	CNC-45	CNC-50	CNC-65
Hydrolysis temperature, °C	45	50	65
Sulfate half-ester content, mmol S/kg CNC*	240 ± 10	260 ± 10	280 ± 10
Oligosaccharide layer	+++	++	0
z-average particle size, nm**	83 ± 3	78 ± 5	86 ± 3

* Measured by elemental analysis (inductively coupled plasma-atomic emission spectroscopy) after extensive dialysis against deionized water.
** Intensity mean z-average hydrodynamic diameters of equivalent spheres, averaged over 12–19 CNC batches for each grade.

I. Extraction temperature and properties of the cellulose nanocrystals (CNC) suspensions studied.

constant and identical to that of fresh deionized water, to give samples containing zero background electrolyte.

CNC suspensions as produced in the pilot plant are in the acid form (H-CNC). To obtain the neutral sodium form (Na-CNC), dilute aqueous sodium hydroxide (NaOH) (0.2 N) was added to acidic CNC suspensions until a stable pH value of 7.0 was reached.

To obtain different CNC concentrations, suspensions were diluted with high-resistivity ultrapure water (18.2 MΩ·cm, Milli-Q purification system, Merck Millipore; Billerica, MA, USA) or concentrated by evaporating water from the suspension at ambient conditions with mechanical stirring.

An aliquot (10 g) of CNC suspension was transferred to a 20-mL glass vial and the appropriate amount of sodium sulfate (Na_2SO_4) solution (0.2 or 1.0 M) was added and the suspension mixed by vortex for 15 s. The total volume change was less than 2%.

Viscosity of CNC samples

Viscosity measurement can be performed with simple capillary viscometers, making it ideal for industrial quality control monitoring. Cannon-Fenske viscometers (Cannon Instrument Co.; State College, PA, USA) with an efflux time of 150–700 s were selected. Portions (6–7 mL) of well-mixed CNC suspensions containing a range of sodium sulfate concentrations were transferred to viscometers. The capillary tube was lubricated by drawing some suspension into the tube before measurement. Measurements were made in a water bath at 25 ± 0.1°C after 5 min equilibration. Measurements were done in triplicate; the variation in the measurements was typically less than 1%.

The suspension viscosity, η, at 25°C was calculated according to $\eta = Ct\varrho$, where C is the viscometer constant (K factor), t is the efflux time, and ϱ is the suspension density. The suspension density was determined by weighing 5-mL aliquots of well-mixed suspension (in triplicate). By this gravimetric method, the water density was 1.01 g/mL.

Characterization of CNC grades

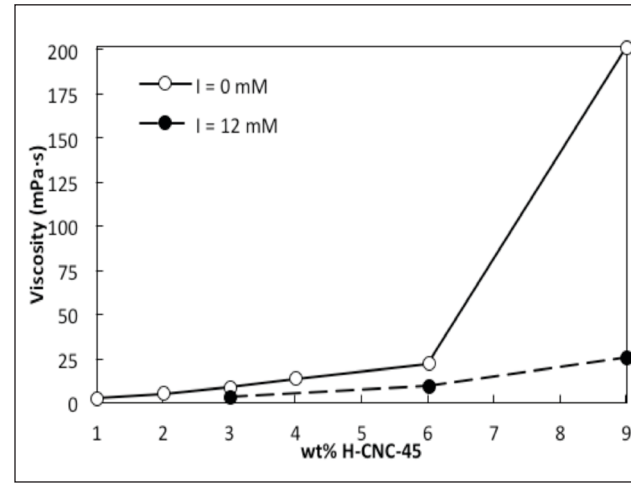
Sulfur, and hence sulfate half-ester, contents of the CNC grades were determined by freeze drying purified CNC samples and analyzing for total S content by inductively coupled plasma–optical emission spectroscopy (ICP-OES). CNC particle size (equivalent hydrodynamic diameter) was determined by dynamic light scattering (DLS) on a Malvern Zetasizer Nano ZS as described in the literature [30].

RESULTS AND DISCUSSION

Viscosity of CNC suspensions

We have generally observed that the viscosity of suspensions of pure, never-dried, sulfuric acid-extracted, wood-derived CNCs increases greatly at concentrations around 6 wt%, above which gel networks form. However, at concentrations of added Na_2SO_4 such that the suspension viscosity lies in the minimum viscosity plateau region where electroviscous effects are smallest [21], the viscosity increase as CNC concentration increases is much less pronounced. **Figure 2** shows that the viscosity of 9 wt% H-CNC-45 drops from 202 to 25 mPa·s with the addition of 4 mM Na_2SO_4 (ionic strength I = 12 mM).

Adding small amounts of electrolyte significantly reduces the viscosity of suspensions of charged rodlike particles, as shown recently for the addition of NaCl to dilute CNC suspen-



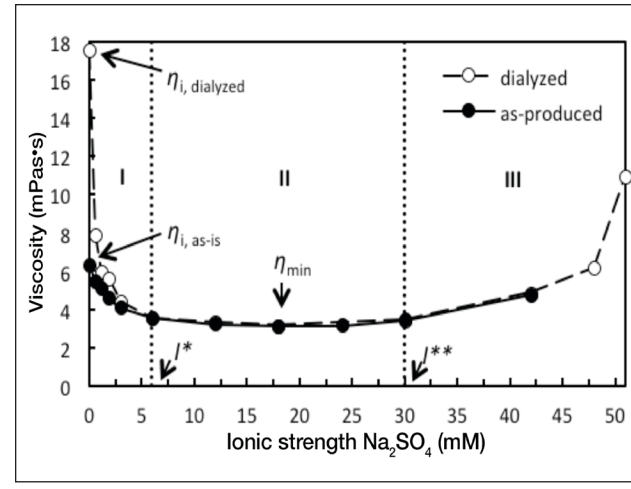
2. Viscosity of H-CNC-45 suspensions as a function of CNC concentration at constant ionic strengths (I) from sodium sulfate of 0 and 12 mM. Lines are intended as a visual guide. Error bars are smaller than the data points.

sions [8,19]. At ionic strengths above 6 mM, the Debye length (EDL) does not shrink significantly with further salt addition; eventually attractive forces dominate and particle agglomeration and gel formation occur [17,21]. This has been confirmed by DLS measurements on CNC suspensions, for which the hydrodynamic radius decreases with added salt at ionic strengths up to 5 mM, where agglomeration occurs and measured particle sizes increase significantly [19]. Boluk et al. also observed agglomeration in 1 wt% CNC suspensions at 10 mM added salt concentrations and higher [8]. CNC particle size (hydrodynamic radius) was not measured as a function of salt concentration because the suspension concentrations are high compared to those required for DLS measurements. Furthermore, the CNC concentration also affects the overall ionic strength of the suspension because of the anionic sulfate half-ester groups at the nanocrystal surfaces [12].

Figure 3 depicts the effect of increasing sodium sulfate concentration on the viscosity of 3 wt% H-CNC-45. The curves have the general shape of the theoretical diagram given in Fig. 1. In region I the viscosity drops sharply; at a critical ionic strength I*, a plateau region containing a minimum viscosity, η_{min}, begins (region II). Finally, at I** the viscosity begins significantly increasing again with increasing ionic strength (region III). All CNC grades, concentrations, and counterions that were investigated show similar viscosity behavior profiles with added sodium sulfate. Boluk et al. and Shafiei-Sabet et al. observed similar decreases in the viscosity of CNC suspensions at concentrations up to 3 wt% containing up to 10 mM added NaCl [8,19].

During purification and concentration of CNCs by dialysis (i.e., sulfuric acid removal), the suspension viscosity increases significantly. The dialyzed samples have much higher initial viscosities than the as-produced samples because of the much lower ionic strength of the background electrolyte. The viscosity drops as Na_2SO_4 is added and compresses the EDL, minimizing electroviscous effects. A plateau in which the viscosity varies by less than 20% of the minimum measured viscosity value (region II) is seen between approximately 6 and approximately 30 mM ionic strength. The viscosity then begins to increase more significantly; a sharper increase occurs above approximately 50 mM ionic strength as an attractive, shear-thinning CNC gel begins to form (data not shown).

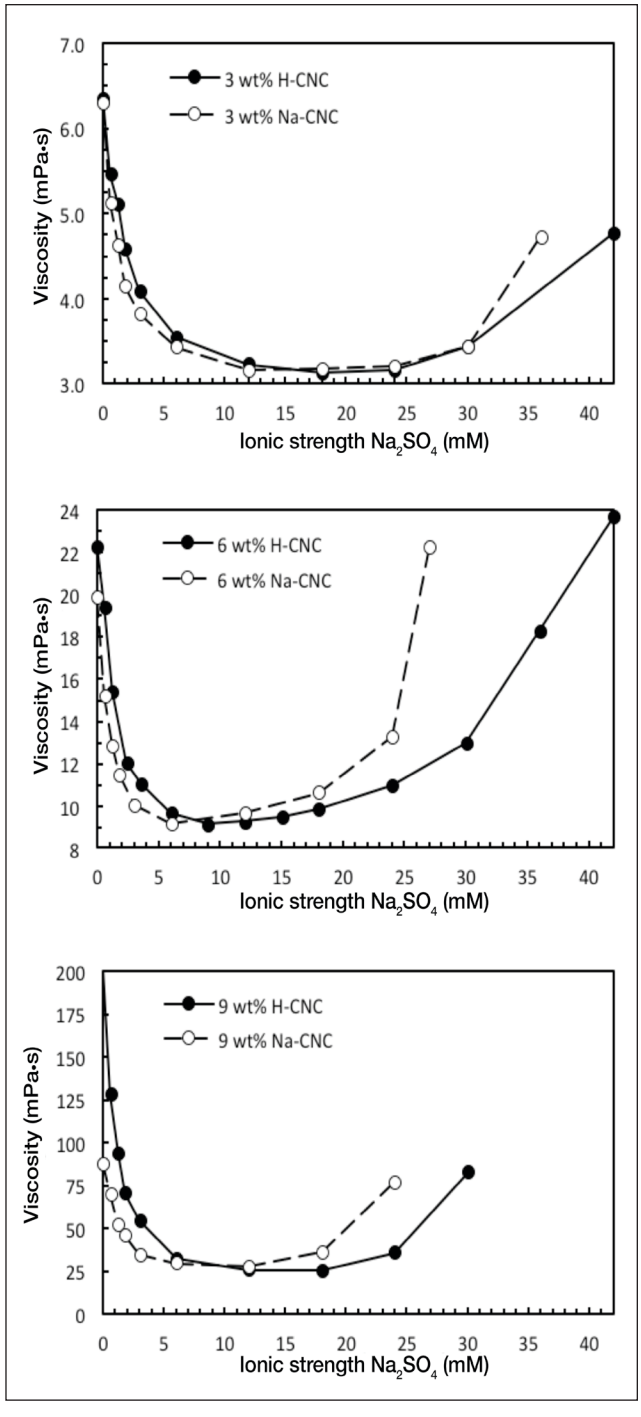
The initial viscosity of the dialyzed H-CNC-45 sample is nearly three times higher than the initial viscosity of the as-produced sample, indicating that residual ionic material is left at the end of the pilot-scale production process and that most or all background ions are removed by the dialysis step. However, adding approximately 2 mM molar concentration of sodium sulfate to all CNC grades fully offsets the viscosity increase imparted by dialysis, yielding the same viscosity as as-produced CNCs containing the same amount of sodium sulfate (Fig. 3). It therefore appears that the CNC suspensions produced at pilot scale have an ionic strength of approximately 6 mM from residual ions. Added sulfuric acid has the same effect as sodium sulfate on the viscosity behavior of dialyzed CNC suspensions (results not shown). As-produced CNC suspensions are used in the rest of the current study; although they have a less pronounced curve in region I, they are simpler to prepare, are more industrially relevant, and have identical values of I*.



3. Viscosity of as-produced and dialyzed 3 wt% H-CNC-45 suspensions as a function of ionic strength adjusted using sodium sulfate. Vertical lines indicate the approximate boundaries of the three viscosity behavior regions. Error bars are smaller than the data points.

The ionic strength, I, of an electrolyte solution is given by $I = \frac{1}{2}\sum_{i=1}^{n}(c_i z_i^2)$ where c_i is the molar concentration of ion i and z_i is the valency of ion i. Multivalent ions (e.g., sulfate anions) contribute more strongly to the ionic strength; the ionic strength of a sodium sulfate solution is three times its molar concentration. For a 3 wt% H-CNC-45 suspension, the ηmin plateau region begins at I* = ~5–6 mM (Fig. 3), in good agreement with Shafiei-Sabet and coworkers' results using monovalent NaCl [19]. In addition, adding NaCl to a CNC suspension led to an observed increase in viscosity at an ionic strength of about 26 mM NaCl, which corresponds roughly to the value of I** for Na_2SO_4 seen in Fig. 3. Electrolytes with divalent anions, such as Na_2SO_4 or sulfuric acid, are thus recommended for use in controlling the CNC suspension viscosity because smaller molar quantities are needed to achieve the same ionic strength. Divalent or trivalent cations are not recommended for viscosity reduction because ionic crosslinking between sulfate half-ester groups on adjacent CNCs will tend to increase the suspension viscosity and promote gelation [30,31].

The relative timing of sample preparation and viscosity measurement is vital to obtaining meaningful data. The minimum viscosity of CNC suspensions containing electrolyte increases somewhat with resting time (i.e., standing without shear after addition of electrolyte). This effect is more pronounced at higher ionic strengths and is presumably caused by the slow structure building leading to an attractive gel



4. Viscosity of (top) 3 wt%, (middle) 6 wt%, and (bottom) 9 wt% H- and Na-CNC-45 suspensions as a function of ionic strength adjusted using sodium sulfate. Error bars are smaller than the data points.

network, agglomerates, or both. The kinetics of this process in CNC suspensions near I* (and thus within 20% of the minimum viscosity value) are such that the viscosity can increase by 25%–65% in only 3 h. To avoid variability in results, all viscosity measurements in this report were made at similar (< 30 min) resting times following mixing.

Redispersed and never-dried CNC suspensions are shear thinning [7,8,10,11,18,32], owing to the alignment of the acicular spindle-shaped particles in a shear flow, so applied shear such as pumping will reduce their viscosity further in combination with added electrolyte. Although CNC suspensions are generally processed under shear, this increase in viscosity over time is a concern if concentrated suspensions containing added salt will be stored before use.

Effect of CNC counterion

Acidic H-CNCs cannot be redispersed when fully dried [33,34]; therefore, they are typically neutralized with NaOH to give the commercial sodium Na-CNC form, which is fully redispersible and neutral in pH when in aqueous suspension. Sodium counterions appear to induce a shift of the viscosity curves toward lower ionic strength values (**Fig. 4**). We observed H-CNC suspensions to have somewhat higher viscosities than Na-CNC suspensions of a given CNC concentration, at ionic strengths from 0–5 mM; thus, less salt is needed to drop the viscosity to a given value for low added ionic strengths. However, the shift also occurs at high added ionic strengths and the steep increase in viscosity and gelation also occur at lower salt concentration in Na-CNC suspensions; at ionic strengths above I**, Na-CNC suspension viscosities are larger and increase more steeply with ionic strength. Na-CNC suspensions are slightly more sensitive to ionic strength of added electrolyte, but the plateau regions still overlap significantly for both H-CNCs and Na-CNCs. Replacing proton counterions with sodium counterions may interfere with hydrogen-bonding between cellulose nanocrystals, resulting in lower viscosity. The higher viscosity and steeper increase at ionic strengths above I** observed in Na-CNC suspensions may be related to the nature of the counterion and caused by differences in ionic activity.

Effect of CNC concentration

Above a certain particle concentration, the rotational diffusion of spindle-shaped particles in suspension will be prevented by overlapping EDLs and other electroviscous effects, causing the viscosity to increase sharply and diverge from Newtonian behavior. The low-shear viscosity of a dispersion of charged rods such as CNCs is expected to diverge at lower particle concentrations than for spheres or uncharged rods [10]. Increasing the CNC concentration inherently increases the ionic strength of the medium and also results in the spontaneous formation of liquid crystal microstructures (**Table II**) depending on the concentration [12,19,21]. These variations may cause changes in the attractive interactions with increasing CNC concentration [21].

The liquid crystal microstructure of the CNC suspensions also controls their rheology in the presence of electrolytes [19,21]. Dilute (isotropic) suspensions have been found to show a decrease in viscosity with increasing ionic strength up to 10 mM because of weakening electroviscous effects

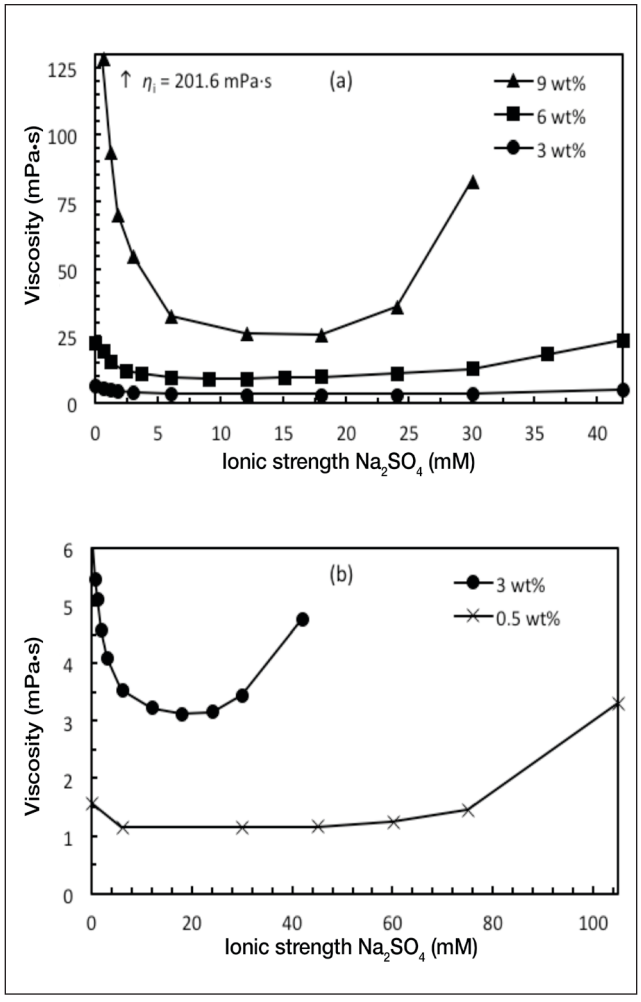
CNC Grade	CNC-45		CNC-50		CNC-65	
Counterion	H^+	Na^+	H^+	Na^+	H^+	Na^+
*c**, wt% CNC*	3.1	3.4	1.9	2.1	1.1	1.5
*c***, wt% CNC**	6.5	6.8	5.3	5.0	4.1	4.0
State at Rest						
3 wt%	Isotropic	Isotropic	Biphasic	Biphasic	Biphasic	Biphasic
6 wt%	Biphasic	Biphasic	Anisotropic	Anisotropic	Gel***	Gel***
9 wt%	Anisotropic	Anisotropic	Gel***	Gel***	Gel***	Gel***

* Concentrations for initial anisotropic liquid crystal phase formation from isotropic suspension (*c**) and for disappearance of the isotropic phase to give a fully anisotropic-at-rest suspension (*c***).

** The value of *c*** was calculated by extrapolating the linear regression line of a plot of anisotropic phase volume fraction as a function of CNC concentration to a volume fraction of 1.

*** The sample is designated as a gel when it is not possible to measure its viscosity with the capillary viscometer.

II. Lyotropic phase separation properties in the absence of electrolyte of the CNC suspensions studied.



5. Viscosity of (a) 3–9 wt% and (b) 0.5 wt% H-CNC-45 suspensions as a function of ionic strength adjusted using sodium sulfate. Error bars are smaller than the data points.

[19]. This effect was observed in 3 wt% CNC-45 suspensions (**Fig. 5**).

More concentrated CNC suspensions (c > c* in Table II), which phase separately at equilibrium to give an anisotropic liquid crystal (chiral nematic) phase and an isotropic phase, demonstrated an increase in viscosity with 0–15 mM added NaCl [19] because of an increase in chiral interactions caused by compression of the EDL [12]; this results in a smaller pitch and a decrease in chiral nematic domain size [12,19,35]. The increase in number of smaller chiral nematic domains contributes to increasing the suspension viscosity [19,21]. The biphasic suspension viscosity continued to increase with NaCl concentration above 15 mM, as the interparticle repulsion decreased and agglomeration and gelation occurred. In contrast, the 6 wt% CNC-45 samples invariably demonstrated a decrease in viscosity at low ionic strengths up to approximately 12 mM, followed by an increase at I > I*, as for the isotropic samples (Fig. 5); the weakening of the electroviscous effects dominates any change in suspension microstructure.

The observed differences in biphasic suspension viscosity at low shear in the presence of added electrolyte may be due to the dispersion technique used to prepare the samples: the suspensions studied in this work consist of never-dried, as-produced CNC suspensions, whereas those studied in [19] were prepared from freeze-dried CNCs redispersed to a high concentration (15 wt%), then diluted to the appropriate concentration and sonicated to an input of 1000 J/g CNC after dilution. This procedure may result in incomplete dispersion [36] and hence the presence of agglomerates of various dimensions, which might alter the effect of electrolyte on the suspension microstructure. In addition, variations in CNC concentration and added electrolyte might cause changes in attractive interactions between the nanocrystals because of their combined effect on the ionic strength of the medium [22].

CNC Sample	CNC, wt%	η_i, mPa·s†	η_{min}, mPa·s	I*, mM	I**, mM	Plateau Width, mM
H-CNC-45	3	6.4	3.1	~5–6	~33	27–28
	6	22.2	9.1	~3.5	~24	~20.5
	9	202	25.5	~3	~21	~18
Na-CNC-45	3	6.3	3.2	~3	~32	~29
	6	19.8	9.6	~2	~19	~17
	9	87.9	27.2	~4	~16	~12
H-CNC-50	3	12.1	4.6	~3	~24	~21
	6	138	18.4	~5	~18	~13
Na-CNC-50	3	9.2	4.3	~2.5	~20.5	~18
	6	93.0	18.5	~4.5	~12.5	~8
H-CNC-65	3	57.7	8.2	~2.5	~15	~12.5
Na-CNC-65	3	39.2	8.8	~2.5	~12	~9.5

† As-produced suspensions containing trace residual electrolyte.

III. Summary of the viscosity behavior of CNC suspensions.

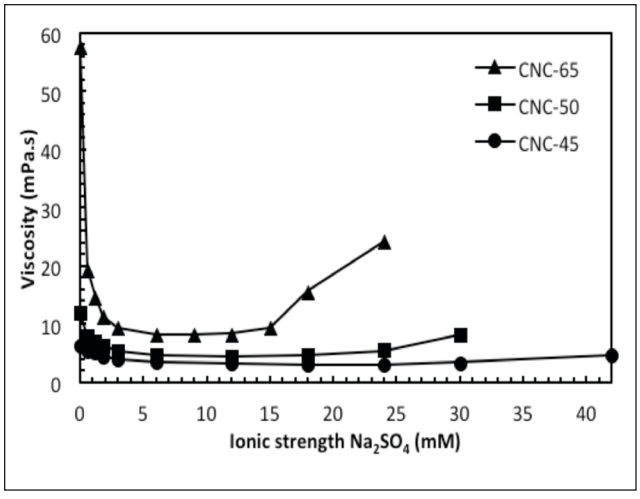
Higher concentration CNC suspensions, including anisotropic and gel samples with no liquid crystal texture (both with c > c**) have been found to demonstrate a decrease in viscosity at low ionic strengths of added salt, followed by a viscosity increase as the ionic strength increases further [19]. This behavior was confirmed for the anisotropic H-CNC and Na-CNC samples (9 wt% CNC-45 and 6 wt% CNC-50) studied. It was not possible to measure the viscosity of 9 wt% CNC-50 and 6 9 wt% and 9 wt% CNC-65 samples with the viscometer, as they yielded gel forms that were too viscous to flow through the capillary (Table II).

Figure 5 shows the response of H-CNC-45 suspension viscosity to the addition of sodium sulfate at a range of CNC concentrations. As the concentration increases, the colloidal particles are more densely packed; therefore, there is stronger friction because of increased electrical double layer overlap (secondary electroviscous effect), which will strongly reduce particle diffusion and lead to the formation of a gel. This is confirmed by the increasing initial viscosities, η_i, of 6.4, 22.2, and 202 mPa·s at CNC concentrations of 3 wt%, 6 wt%, and 9 wt%, respectively. The values of ηmin (near I = 10–15 mM) also increase with CNC concentration, but to a lesser extent (from 3 to 25 mPa·s). This corresponds to a decrease in viscosity upon electrolyte addition of 88% at 9 wt% CNCs and a 57% decrease at 3 wt% CNCs. Although this effect is detectable in CNC suspensions as dilute as 0.5 wt%, it is clear that added electrolyte causes a much more significant decrease in the viscosity as the CNC concentration increases.

As the overall viscosity increases with CNC concentration, a concurrent narrowing of the span of ionic strength of added salt defines the viscosity plateau region containing ηmin. For both H- and Na-CNCs, I* (at which the viscosity is 20% higher than the measured minimum value) varies slightly (**Table III**) with increasing CNC concentration, whereas I** decreases significantly with increasing CNC concentration. The viscosity plateau begins at I* around 3–6 mM for all CNC concentrations in Fig. 5; I** decreases from around 33 mM to around 21 mM between 3 wt% and 9 wt% CNCs. At increasing CNC concentrations, cellulose nanocrystals approach each other more closely, such that the attractive forces that induce gelation or agglomeration begin to dominate at lower ionic strengths of added electrolyte (i.e., it does not take as much electrolyte to compress the EDL sufficiently for attractive forces to overcome the electrostatic repulsion). This effect is easily seen in the laboratory, where CNC suspensions are often diluted to facilitate salt addition and avoid the formation of agglomerates, clumps, or gel.

Effect of CNC extraction conditions

Suspensions of CNCs extracted at higher hydrolysis temperatures have higher viscosities at a given CNC concentration, making them more difficult to handle and pump. The viscosities of 3 wt% H-CNC-45, H-CNC-50, and H-CNC-65 suspensions as a function of added sodium sulfate are shown in **Fig. 6**. Table III summarizes the viscosity behaviors of the CNC suspensions studied. Results are compared for 3 wt% CNCs; comparisons were not possible at higher CNC concentrations because the viscosities of 9 wt% CNC-50 suspensions and 6 wt% and 9 wt% CNC-65 suspensions were too high to be measured by this technique even in the presence of sodium



6. Viscosity of 3 wt% suspensions of different grades of H-CNCs as a function of ionic strength adjusted using sodium sulfate. Error bars are smaller than the data points.

sulfate.

CNC-65 suspensions have significantly higher overall viscosity than CNC-45 (8-fold increase) or CNC-50 (3.75-fold increase) at a given concentration. However, with added sodium sulfate, the viscosity of 3 wt% CNC-65 approaches that of CNC-45 or CNC-50, its minimum viscosity being only 1.8 times higher than for CNC-50.

For all CNC concentrations and grades, the minimum viscosity plateau is reached at a molar concentration of about 0.8–2 mM added Na_2SO_4 (an ionic strength I* of about 2.5–6 mM [Table III]). As the CNC extraction temperature increases, the sodium sulfate ionic strength window over which the minimum viscosity plateau (region II in Fig. 3) occurs becomes narrower, decreasing from a range of about 28 mM to a narrow window of about 10–12 mM ionic strength from added sodium sulfate for 3 wt% CNC-45 to CNC-65 suspensions. CNCs extracted at 65°C thus form an attractive gel at lower concentrations of added electrolyte. While I* remains approximately constant with hydrolysis temperature (or increases slightly), I** decreases significantly with extraction temperature for both H- and Na-CNCs. The plateau width appears to decrease more or less linearly with increasing hydrolysis temperature.

The hydrolysis conditions used in CNC extraction, including sulfuric acid concentration and temperature, affect the kinetics and extent of the cellulose hydrolysis and hence the properties and behavior of cellulose nanocrystals and suspensions thereof. The main differences in the CNC grade properties (Table I) are the total sulfur (sulfate half-ester) content [1] and the thickness of the oligosaccharide layer at the CNC surface [29].

The viscosity of suspensions of spindle-shaped or other anisometric particles also depends partially on their axial ratio, with longer and thinner rods resulting in higher viscosities [10]. However, it is not possible to quantitatively compare the particle dimensions of the CNC grades because their particle size distributions are polydisperse and there is no significant difference in their z-average mean particle diameter (or the particle size distribution curves) measured by light scattering.

Increasing the hydrolysis temperature increases the sulfur content of extracted CNCs [28]. The sulfur contents measured by ICP-OES after extensive dialysis of CNC-45, CNC-50, and CNC-65 are listed in Table I and range from 240 to 280 mmol S/kg CNC. The total sulfur content of purified CNCs is equivalent to the sulfate half-ester content [37]. The sulfate half-ester content determines the surface charge density of the cellulose nanocrystals, which controls the extent of electroviscous effects and thus the suspension viscosity and flow behavior [3,20].

Experiments in the literature have shown that increasing surface charge tends to reduce the viscosity of CNC suspensions. Araki et al. found that increasing degree of sulfation led to decreasing suspension viscosities compared with HCl-extracted CNCs, which have minimal surface charge [7,20]. Working with suspensions of redispersed freeze-dried sodium-form CNCs having different degrees of sulfation, Shafiei-Sabet et al. also observed a smaller viscosity in the sample having higher surface charge [3].

Our present experiments do not follow the above trend; both the initial and minimum viscosity values increase with hydrolysis temperature (Fig. 6), despite the concurrent increase in CNC surface charge (Table I). Several factors might contribute to this discrepancy. The conditions under which the viscosities were determined are not identical. Here, suspension viscosities are measured in a capillary viscometer, whereas the data in the literature were obtained using a rotational rheometer with parallel plate geometry. Perhaps most significantly, variations in the hydrolysis temperature might affect CNC properties other than surface charge and dimensions. Whereas the increase in the hydrolysis temperature from 45°C to 65°C has a relatively small influence on parameters such as CNC dimensions and degree of sulfation (≤ 17% increase), the viscosity of aqueous CNC suspensions is strongly affected (up to 800% increase), as well as their propensity to form a gel at lower ionic strengths from added salt (Table III).

The phenomena described above might be caused by variations in quantities of cellulose-derived oligosaccharides precipitated onto CNCs during the water quenching of the hydrolysis reaction in the production process. An oligosaccharide surface layer (OSL) has been found to be present at the CNC surface in varying amounts depending on the hydrolysis temperature. This OSL is substantial at low hydrolysis temperature (45°C) and becomes negligible at high temperature (65°C).

It is possible that the OSL is responsible for the lower viscosity of the CNC suspensions produced at lower hydrolysis temperatures by altering the interaction between CNCs and free water. Nanometric particles in suspension have water molecules strongly bound to their surface in a bound water layer (BWL). Li and Akinc [38] have demonstrated that the

viscosity of a nanometric alumina suspension can be significantly reduced by adding 1–20 wt% fructose based on dry weight of alumina. They conclude that fructose displaces the BWL from the particle surface or otherwise alters the nature of the particle/bulk water interaction, resulting in a reduction of the suspension viscosity. Oligosaccharides may displace water molecules on the CNC surface in a similar fashion, weaken the hydrogen bonding between water molecules, or both, leading to higher mobility of water molecules near the particle surface. Steric repulsions between the OSLs might also reduce the viscosity in CNC suspensions at higher ionic strengths.

All of the parameters and variables discussed here previously are interrelated to some extent. In particular, the CNC surface charge is not independent of the OSL in our CNC samples produced at different hydrolysis temperatures. The CNC surface charge might be varied independently by changing the acid-to-pulp ratio [3] at constant hydrolysis temperature, or suspensions might be desulfated to varying degrees by, for example, heating acidic H-CNC suspensions for increasing lengths of time [35,39], which should not alter the OSL. As described earlier, Shafiei-Sabet et al. found that increasing the surface charge without affecting the OSL resulted in a decrease in suspension viscosity over a range of shear rates [3]. The effects of the varying surface charge and OSLs might be competing, as the oligosaccharides most likely become sulfated during acid hydrolysis of the cellulose. In addition, rotational diffusion coefficient of cellulose nanocrystals depends on their dimensions and geometry, as well as the surface charge density, which in turn affects the bound water layer thickness and electrical double layer interactions (electroviscous effects). Further in-depth research is needed to determine the fundamental differences among the CNC grades to explain the observed variations in other properties (e.g., viscosity). Studying the rheological behavior of CNC suspensions prepared at different hydrolysis temperatures under applied shear in the presence of added electrolyte might also yield additional insights.

CONCLUSIONS

When the acid hydrolysis temperature is increased from 45°C to 65°C, the CNC suspension viscosity increases with increasing temperature in the absence of electrolyte as follows: CNC-45 < CNC-50 << CNC-65. These experiments indicate the effect of added electrolyte on the viscosity behavior of CNC suspensions. Adding small amounts of salt such as sodium sulfate equivalent to about 6–12 mM ionic strength of electrolyte minimizes the suspension viscosity. Typically, a plateau region of minimal viscosity (varying by less than 20% of the measured minimum viscosity value) exists in a window between ionic strengths I^* and I^{**} of around 2.5–6 mM and 30–10 mM, respectively. Above I^{**}, the viscosity increases steeply and gelation may occur. CNC suspensions display increased sensitivity to added electrolyte as a function of hydrolysis temperature, as evidenced by lower I^* and I^{**} values. From these results, it appears that the viscosity of CNC suspensions can be fine-tuned by controlling the ionic strength. **TJ**

ACKNOWLEDGEMENTS

The authors thank Jie Wang and Myriam Méthot for meticulously performing the viscosity measurements; George Sacciadis, Guy Njamen, Allan Matudio, Damien Mauran, Carole Fraschini, and Annie Dorris for experimental contributions and insightful discussions; and Giuseppa Zambito for performing the ICP-OES measurements.

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ABOUT THE AUTHORS

In general, the rheology behavior of colloidal suspensions is an industrially relevant topic. It affects so many aspects of production, processing, and transportation, even before considering how it defines and limits possible applications. A simple, easily implemented method of regulating the viscosity of CNC suspensions using minimal additives was a highly desirable objective.

Our research complements an in-depth study examining the effects of hydrolysis temperature on CNC surface properties, and thus on suspension behavior, by providing data that support the theory proposed. In addition, our findings are consistent with those of Shafiei-Sabet et al., who examined the effect of ionic strength on the rheology of CNC suspensions using a rheometer, as well as the effect of varying the CNC surface charge by means other than varying pulp hydrolysis temperature.

Sulfated CNCs exhibit complex behavior in aqueous suspension. The sodium sulfate did not always simply lower or raise the suspension viscosity to a given value; it also resulted in the development of microstructure (gelation) over time, which changed the value of the measured viscosity depending on when the measurement was performed. To eliminate this effect, all viscosity measurements were made the same amount of time after mixing the salt and suspension.

Beck

Bouchard

CNC suspensions reach minimum viscosity at almost identical amounts of added electrolyte regardless of hydrolysis temperature, which is surprising considering how widely the viscosities of the as-produced suspensions vary in the absence of added electrolyte.

Beck is a scientist and Bouchard is principal scientist and research leader, cellulosic biomaterials, at FPInnovations, Pointe-Claire, QC, Canada. Email Beck at stephanie.beck@fpinnovations.ca.