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Dilute solution properties of carboxymethyl celluloses of various molecular weights and degrees of substitution

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ABSTRACT

The intrinsic viscosities of six carboxymethyl celluloses (CMC) of different degrees of substitution, molecular weights, and molecular weight distributions (MWDs) were measured as a function of pH, ionic strength, and temperature. The molecular weights and MWDs were determined by analytical ultracentrifugation. It was demonstrated that the raw viscosity data could be represented by the Fedors equation allowing for accurate determination of the intrinsic viscosity. Ionic strength, rather than pH or temperature had the strongest effect on the conformation of CMC. An estimate of the Mark–Houwink–Kuhn–Sakurada exponent ($\alpha = 0.83$) and calculations of chain flexibility and expansion factors indicated that CMC has semi-flexible, randomly coiling chains in solution with persistence lengths on the order of 8.8–24.5 nm in distilled water and 11.3–14.8 nm in 0.01 mol/L sodium chloride. It was also found that the lowest molecular weight CMC was most flexible among the tested samples.

1. Introduction

Carboxymethyl cellulose (CMC) is an anionic polysaccharide obtained from cellulose. The non-toxicity, biodegradability and biocompatibility of CMC make it one of the most important cellulose derivatives. CMC readily dissolves in water to form viscous solutions with a range of thickening, stabilizing and film-forming properties. These properties make CMCs attractive polymers for industrial and consumer applications, including textile (Stelzer & Klug, 1980), food (Gilbert, 1994), pharmaceutical (Wade & Weller, 1994), carbon nanotubes (Minami, Kim, Miyashita, Kazaoui, & Nalini, 2006), mineral processing (Pugh, 1989) and the pulp and paper industry (Watanabe, Gondo, & Kitao, 2004). In mineral processing, CMC is commonly used as a depressant of carbonate and talcaceous gangue minerals in the froth flotation of sulfide and Platinum Group Metal ores by adsorbing on the gangue minerals, rendering them hydrophilic and preventing their flotation (Leppinen et al., 2005). Another important application of CMC is in potash flotation as a "blinder" of waste fine water-insoluble minerals such as clays and dolomite. The role of CMC is to adsorb on the waste minerals and prevent the collector from interacting with these unwanted minerals. Structural and physicochemical properties such as conformation, chain flexibility and molecular weight distribution (Fleer, Cohen-Stuart, Scheutjens, Cosgrove, & Vincent, 1993) affect the behavior of CMC, thus knowledge of such properties is required to adequately understand the action of CMC in various industrial applications.

The majority of studies on the use of CMC in mineral processing have focused on the adsorption of CMC on gangue minerals (Beaussart, Mierczynska-Vasilev, & Beattie, 2010; Hoogendam et al., 1998a; Khraisheh, Holland, Creany, Harris, & Parolis, 2005; Mierczynska-Vasilev & Beattie, 2010; Morris, Fornasiero, & Ralston, 2002). The effect of the degree of substitution (DS) and molecular weight (M_W) of CMC on depressant action was also studied (Khraisheh et al., 2005; Mierczynska-Vasilev & Beattie, 2010; Shortridge, Harris, Bradshaw, & Koopal, 2000; Steenberg & Harris, 1984). A few studies on the molecular properties of CMC dealt with the persistence length (Hoogendam et al., 1998b) and conformation in aqueous solution (Brown & Henley, 1964; Kästner, Hoffmann, Dönges, & Hilbig, 1997; Sitaramaiah & Goring, 1962). However, these studies did not systematically investigate the effect of pH and ionic strength on the dilute solution properties of CMC.

In this study, the molecular conformation, chain flexibility, and molecular weight distribution of a series of CMCs of different DS and molecular weights were determined as a function of pH and ionic strength.

2. Materials and methods

2.1. Polymers and other chemicals

Three carboxymethyl cellulose samples with different degrees of substitution (DS = 0.7, 0.9 and 1.2, Acros Organics) designated hereon as DS0.7, DS0.9, DS1.2, respectively, but with similar

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molecular weight (250,000 g/mol), and three samples of similar DS (0.7) but of different molecular weights (80,000, 250,000 and 700,000 g/mol, Polysciences), designated hereon as LM-CMC, MM-CMC, and HM-CMC, respectively, were evaluated. The actual molecular weights used in data analysis were independently determined by sedimentation velocity using the analytical ultracentrifuge and are presented in Section 3.1. The samples were received as dry solids and were used without any further treatment or purification.

Solutions for viscosity measurements were prepared by mixing an appropriate amount of CMC in de-ionized water or in 0.01 mol/L sodium chloride solution at room temperature to give stock concentrations of 1 g/L. The stock solutions were allowed to stand overnight (~10 h) to ensure complete hydration of CMC after which working solutions were prepared by dilution with the appropriate background electrolyte and tested within 2–4 h after dilution. The concentration of residual sodium in the tested solutions was determined by atomic absorption spectrometry, and this sodium assay was used as a correction factor for calculating the actual polymer concentrations.

Reagent grade sodium chloride (NaCl) was used to adjust the ionic strength while small amounts of analytical grade sodium hydroxide and hydrochloric acid were used to adjust the pH.

2.2. Viscosity measurements

The kinematic viscosities of the CMC solutions were measured using two Cannon–Fenske capillary viscometers (Shott-Geräte, GmbH, Germany). The viscometers were calibrated by carrying out carefully controlled viscosity measurements with de-ionized water at 25 °C. When the determined kinematic viscosities deviated from accepted literature values (Weast, 1970), the viscometer constants were re-calculated accordingly. The corrections for the viscometer constants were on the order of 3% but such rather small adjustments were considered important since small differences in kinematic viscosities can have a dramatic impact on the calculated specific viscosities in very dilute solutions, especially since two different capillaries were used, which would then affect the accuracy of the intrinsic viscosities.

After dilution of the stock solution to the desired polymer concentration, 7-mL aliquots were transferred to the capillary viscometer, the viscometer was placed in a water bath at 25 ± 0.1 °C for an equilibration time of 30 min. The actual temperature variation during the viscosity measurements was checked with a highly accurate thermometer and was found to fall within ±0.02 °C. The kinematic viscosity was then determined by allowing the CMC solution to flow down the capillary under gravity. A PVS1 Lauda photo-timing and processing system interfaced with a computer was used to automatically measure three flow times, an average of which was used to calculate the kinematic viscosity. The standard deviation of the flow times was always less than 1 s. In addition, three solutions were usually tested at a given concentration.

For high temperature measurements, with the capillary and sample still in the bath, the temperature of the bath was increased to 50 °C and the sample was equilibrated for 30 min. The CMC solutions were tested in the concentration range from 10 mg/L to 100 mg/L. The upper limit satisfied the general critical concentration (c^*) requirement for dilute solution viscometry ($c^* \approx 1/[\eta]$) for the onset of entanglement formation. The lower limit of the concentration range was arbitrarily chosen to minimize possible polymer adsorption effects on the capillary walls. The relative viscosity of all the tested solutions was less than 2.0.

From the kinematic viscosities, the relative, specific and reduced viscosities of the CMC solutions were calculated at each concentration, pH value (approximately 3, 4.5, 7), and temperature (25 °C, 50 °C). Finally, the intrinsic viscosities were determined with the use of Fedors equation (see Section 3).

In order to test the stability of CMC solutions, the viscosity of a 150 mg/L solution of DS0.7 and the viscosity of a 100 mg/L solution of DS1.2 were measured over a period of 24 h in 1 h intervals. It was found that the viscosity decreased only by 0.15% and 2.5% for the DS0.7 and DS1.2 solutions, respectively. Nonetheless, similar sample preparation procedures and times, dilution steps and testing times were strictly followed.

2.3. Sedimentation velocity analytical ultracentrifugation

Sedimentation velocity (SV) experiments were conducted using a Beckman Coulter ProteomeLab XL-I analytical ultracentrifuge equipped with absorbance and interference optics. Stock solutions of 1 g/L CMC were prepared as described before. Aliquots of the stock solutions were diluted to the final concentration prior to analysis. In order to suppress the non-ideality arising from charge effects, a high ionic strength is recommended for analytical ultracentrifugation analysis of charged macromolecular systems such as CMC (Harding, 2005a). On the other hand, the sample concentration depends on the optical path length of the cell and the optical properties of the sample. A minimum concentration of 200 mg/L is recommended (Harding, 2005b) for sedimentation velocity experiments on the XL-I analytical ultracentrifuge. However, this concentration is well above the critical overlap concentration ($c^* \approx 1/[\eta]$) above which CMC molecules start interacting. To accommodate the above requirements, an ionic strength of 0.1 mol/L NaCl and sample concentration of 100 mg/L were chosen in order to minimize hydrodynamic and thermodynamic non-ideality resulting from molecular co-exclusion and CMC polyelectrolyte behavior. All experiments were run at 25 °C and pH 6.

The diluted CMC solutions (460 μL) and solvent (0.1 mol/L NaCl, 450 μL) were injected into the sample and reference channels of the 12-mm double sector centerpieces (assembled with sapphire windows) and loaded into a 4-hole titanium (AnTi60) rotor. The samples were equilibrated at 25 °C for 1 h prior to the sedimentation velocity run to minimize convection effects in the cells at the start of the sedimentation run. The rotor speed was 40,000 rpm. Rayleigh interference scans were acquired in the continuous mode and the resulting data (fringe displacement vs. radial position) were analyzed by the least-squares (*ls*) regression method incorporated in the program SEDFIT (Schuck & Rossmanith, 2000). The method involves direct linear boundary modeling of the data to obtain an apparent distribution $ls-g^*(s)$ of the sedimentation coefficient s. The $ls-g^*(s)$ model was run with the Tikhonov–Phillips 2nd derivative regularization at a confidence level of $p = 0.95$. The resolution of the $ls-g^*(s)$ distribution (number of points on the s-grid) was 200.

The sedimentation coefficient distributions, $ls-g^*(s)$ were transformed into molecular weight distributions, $f(M)$ using the Extended Fujita method (Harding et al., 2011) for general conformation types of macromolecules. This method is an extension of the Fujita (1962) transformation of a differential distribution $g(s)$ of sedimentation coefficients into a differential distribution $f(M)$ of molecular weights for linear polymers with a random coil conformation, i.e., with $b = 0.5$ in the sedimentation coefficient–molecular weight power law relation, $s = \kappa_s M_W{}^b$, where κ_s is a constant for a given polymer/solvent/temperature system, and b (conformation of the polymer) ranges from 0.4 to 5 for a coil, ~0.15 to 0.2 for a rod and ~0.67 for a sphere (Kulicke & Clasen, 2004). In order to do the transformation, b and at least one pair of $s-M_W$ values need to be known in order to obtain κ_s in the $s-M_W$ relationship above. Values of b and κ_s used in the transformation ($b = 0.29$, $\kappa_s = 0.0101$) were calculated by linear regression of a plot

of log s vs log M_W using published s and M_W data from Brown and Henley (1964) in the molecular weight range from 147,000 g/mol to 1,060,000 g/mol. Then, the corresponding molecular weights of the tested samples were obtained from the sedimentation coefficients s determined by the ultracentrifuge. The Brown and Henley data were obtained under very similar experimental conditions (temperature and ionic strength) as those of the present study, which minimizes uncertainty associated with the interpolation of the sedimentation coefficients from their data.

The Extended Fujita method is built into the sedimentation velocity analysis program SEDFIT (Schuck, 2000; Brown & Schuck, 2006) and was recently applied to polysaccharides and other polymeric systems (Harding et al., 2011; Gillis et al., 2012).

3. Results and discussion

3.1. Molecular weight and molecular weight distribution

The sedimentation coefficient distributions ($ls-g^*(s)$ vs s) for all the samples showed a single major peak located at different sedimentation coefficients depending on the molecular weight of the samples. In accordance with the Svedberg equation (Svedberg & Pedersen, 1940), the high molecular weight (HM-CMC) sample sedimented faster than the other samples based on the sedimentation coefficient value at the peak of the $ls-g^*(s)$ vs s (in units of Svedberg, S) distributions. Under the tested conditions, weight average sedimentation coefficients, S_{av}, obtained by integrating the areas under the $ls-g^*(s)$ distributions increased with molecular weight and ranged from 5.1 S to 21.0 S. The $ls-g^*(s)$ distributions for the higher molecular weight polymers showed several small peaks over a broader span of S values indicative of a small fraction of very high molecular weight material sedimenting at higher S values outside of the main peak. These minor peaks accounted for the higher S_{av} values obtained for the higher molecular weight samples.

The molecular weight distributions for the tested CMCs are plotted in Fig. 1. The weight-average and z-average molecular weights (M_W and M_Z respectively) were extracted from the data by integrating the areas under the molecular weight distributions. A comparison of the manufacturer's values with those obtained using the Extended Fujita approach is provided in Table 1. Also shown in Table 1 are the polydispersity indices (PDI) calculated as the ratio of M_Z to M_W.

It is evident in Fig. 1A that the width of molecular weight distributions increases in the order LM-CMC < MM-CMC < HM-CMC, as is also shown by the increasing polydispersity index in Table 1. The molecular weight distributions and average molecular weights for DS0.7, DS0.9, DS1.2 are indeed quite similar. Generally, the Extended Fujita approach produces fair estimates of the molecular weights provided by the manufacturer, more so for the HM-CMC since the method is primarily intended for large polydisperse macromolecules (Harding et al., 2011).

3.2. Intrinsic viscosities

3.2.1. Remarks on the aggregation state of CMC solutions

The poor solubility of native cellulose arises from strong hydrogen bonding within the cellulose crystalline structure. Partial derivatization, as is often the case for most cellulose derivatives including CMC, leaves unsubstituted OH groups that can interact by *intra*- and *inter*-molecular hydrogen bonding thereby limiting the solubility. According to Schulz, Burchard, and Dönges (1998) and Schulz and Burchard (1993), the specific interaction between OH groups in partially substituted celluloses results in formation of poorly soluble aggregates. The literature on the aggregation of CMC is contradictory. Schulz and Burchard (1993) determined the exponent ν in the scaling law relating the radius of gyration R_g and M_W ($R_g = K_{RG}M_W{}^{\nu}$) to be 0.28 in 0.1 mol/L NaCl and concluded that the CMC solutions contained aggregates. The exponent ν can be correlated with the exponent α in the $[\eta]$–M_W relationship through the equation $\alpha = 3\nu - 1$ (Kulicke & Clasen, 2004). Based on this equation, it can be seen that the value determined by Schulz and Burchard is below the theoretical minimum (0.33) and it is not clear whether such a low value was indeed due to the presence of aggregates in the CMC solutions. However, Hoogendam et al. (1998b) obtained a value of 0.59 in 0.1 mol/L KOH and $NaNO_3$ indicating that CMC contained very little or no aggregates under those conditions. Clasen and Kulicke (2001) determined the value of ν for CMC from $R_g - M_W$ data in 0.1 mol/L NaCl to be 0.53. Those authors also reported a literature value of 0.70 in 0.1 mol/L NaCl. Using the values of exponent α determined in this study for CMC in 0.01 mol/L NaCl (Fig. 7), the exponent ν was found to range from 0.57 to 0.62 depending on pH, indicating good solvent conditions throughout. These values agree well with the values from Clasen and Kulicke (2001) and Hoogendam et al. (1998b). All the intrinsic viscosity data presented in this work were obtained using quite dilute stock and working solutions prepared carefully by gentle mixing in water over a long period of time. These conditions favor the dissolution of the polymer, and though the presence of aggregates in the tested solution cannot be entirely ruled out, the ensuing discussion will be based on the assumption that the presence of aggregates did not significantly affect the experimental data. This is in line with the argument that since aggregates behave as compact spheres, their contribution to the intrinsic viscosity would be negligible (Kratochvil, 1972).

3.2.2. Determination of intrinsic viscosities

The reduced viscosity of a polymer solution can generally be represented by a power series in concentration, c, as follows (Lovell, 1989):

$$\eta_{red} = [\eta] + k_1[\eta]^2 c + k^2[\eta]^3 c^2 + \cdots \quad (1)$$

where $[\eta]$ is the intrinsic viscosity, c is the polymer concentration, k_i are constants, η_{red} is the reduced viscosity. The intrinsic viscosity of dilute nonionic polymers can be determined graphically by truncating Eq. (1) to a linear approximation (the first two terms on the right side of Eq. (1)), and plotting η_{red} vs the polymer concentration, c, which allows evaluation of $[\eta]$ to be made from the intercept. However, the tested CMC solutions showed typical polyelectrolyte behavior and thus could not be described by the linear approximation. Previous results by Arinaitwe and Pawlik (2013) on the intrinsic viscosity of anionic polyacrylamide showed that the Fedors (1979) equation (Eq. (2)) reliably described the raw data by plotting $[2({\eta_{rel}}^{1/2} - 1)]^{-1}$ against $1/c$, and therefore the equation was also applied to anionic CMC.

$$[2(\eta_{rel}^{1/2} - 1)]^{-1} = ([\eta]c)^{-1} - ([\eta]c_m)^{-1}) \quad (2)$$

where c_m is a polymer concentration parameter. The intrinsic viscosity could then be determined from the slope, $1/[\eta]$, of the plot. It should be noted that very good fits to the experimental data were obtained under all experimental conditions (ionic strength, temperature and pH). Most importantly, the equation allowed the intrinsic viscosities to be determined without having to apply the iso-ionic dilution technique (Pals & Hermans, 1948) almost universally used for polyelectrolyte solutions in order to minimize the polyelectrolyte effect especially in low ionic strength solutions.

Fig. 2 shows an example of the concentration dependence of the reduced viscosity for DS1.2 in distilled water at different pH. The error bars shown at the lowest concentration tested (10 mg/L) generally reflect the absolute experimental errors in determining the reduced viscosities. For DS1.2, the highest absolute error in

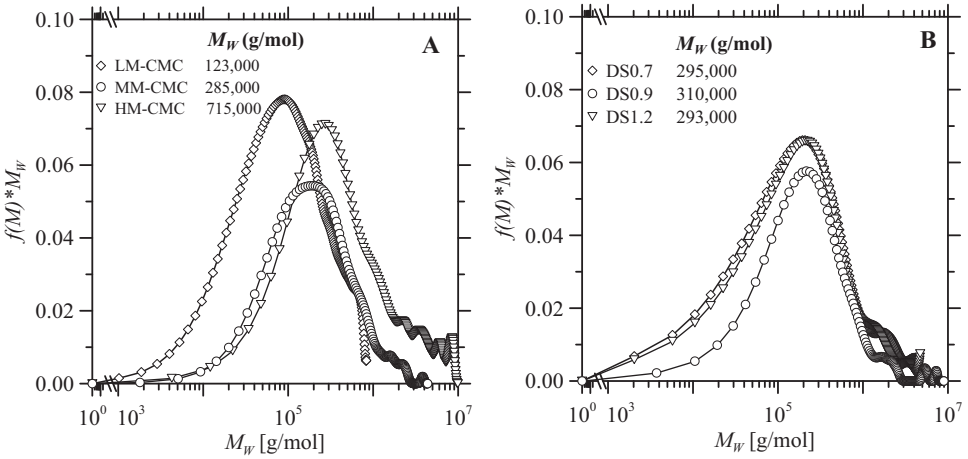

Fig. 1. Molecular weight distributions $f(M)$ vs M_W for LM-CMC, MM-CMC and HM-CMC (DS 0.7) (Graph A); and for DS0.7, DS0.9 and DS1.2 (Graph B).

Table 1
Molecular weights [g/mol] and polydispersities of the tested polymers.

Polymer	M_W (manufacturer's data)	Weight-average M_W (extended Fujita method)	PDI [M_Z/M_W]
LM-CMC	80,000	123,000	2.27
MM-CMC	250,000	285,000	2.74
HM-CMC	700,000	715,000	4.30
DS0.7	250,000	295,000	4.42
DS0.9	250,000	310,000	3.99
DS1.2	250,000	293,000	4.52

obtaining the reduced viscosity was ~6.7 dL/g corresponding to an error in the intrinsic viscosity of ~9.1 dL/g.

The reduced viscosity increases with decreasing polymer concentration as typically seen for polyelectrolytes. Since the degree of dissociation of the weakly acidic carboxylic groups increases at lower polymer concentrations, the increase in η_{red} as concentration decreases is attributed to the gradual expansion of the polymer coil brought about by increasing repulsion between the dissociated carboxylate groups.

Fig. 3 illustrates the Fedors representation of the data from Fig. 2 in which $[2(\eta_{rel}{}^{1/2} - 1)]^{-1}$ is plotted against $1/c$ to produce linear fits whose reciprocal slopes give the intrinsic viscosities. It is interesting to note that the intrinsic viscosities determined by fitting a second-order polynomial equation (the first three terms in Eq. (1)) to the experimental data, as shown by the solid curves in Fig. 2, gave very similar intrinsic viscosities as those determined using the Fedors equation. This provided a good cross-check of the intrinsic viscosity values.

3.2.3. Effect of pH and ionic strength

Fig. 4 shows the intrinsic viscosities for all the CMCs in distilled water and in 0.01 mol/L NaCl at different DS. In distilled water, an increase in the DS from 0.7 to 1.2 brings about a steady increase in the intrinsic viscosity of the CMCs resulting from the increasing content of carboxylic groups that cause stronger repulsion and stretching between the polymer chains. Compared to pH, temperature does not seem to have any significant effect on the intrinsic viscosities. Under all experimental conditions, the

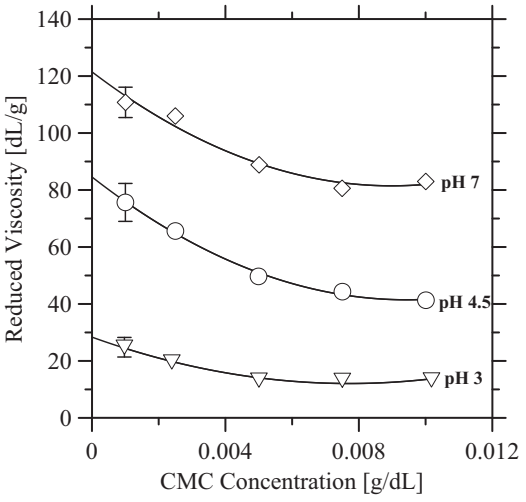

Fig. 2. Reduced viscosity vs. polymer concentration for DS1.2 in distilled water, 25 °C at different pH. The solid lines represent second order polynomial fits to the data.

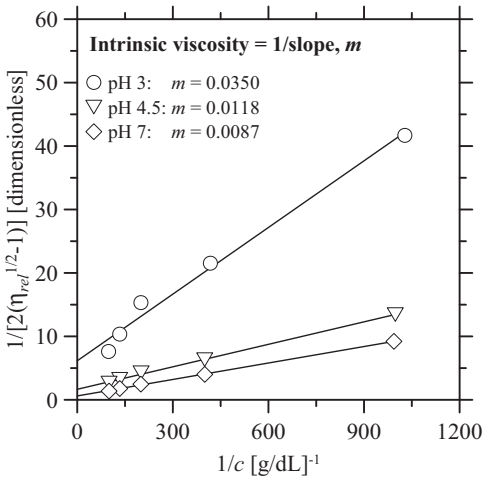

Fig. 3. Fedors representation of the data from Fig. 2 for DS1.2 in distilled water at 25 °C and different pH.

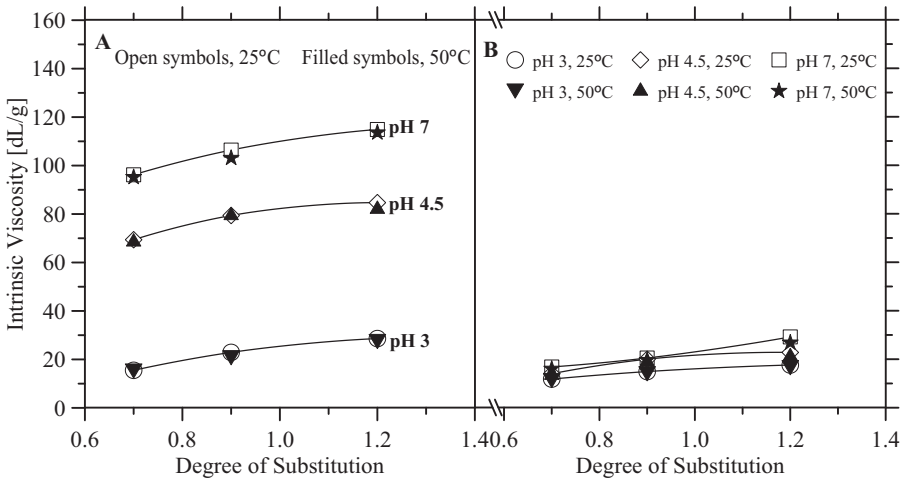

Fig. 4. Effect of pH and temperature on the intrinsic viscosities of the CMCs of different DS. M_W = 293,000–310,000 g/mol. (A) Distilled water and (B) 0.01 mol/L NaCl.

differences between the results at 25 °C and 50 °C are about 3 dL/g which is well within the experimental error.

At all degrees of substitution, the effect of pH in distilled water is apparently quite strong. Increasing the pH from 3 to 4.5 results in a large increase in [η] and a further increase is noted as the pH is increased to 7. This trend is consistent with the degree of dissociation of CMC which increases from pH 3 to ~pH 5 and steadily increases to a maximum around pH 6–7 depending on the ionic strength (Hoogendam et al., 1998b). At pH 7, the degree of dissociation of carboxylic groups is already on the order of 0.999, so pH values higher than 7 should not induce significant additional repulsion between the carboxylic groups of the macromolecule, and the carboxylic groups can be assumed to be completely dissociated.

In Fig. 4B, the effect of ionic strength is shown by plotting intrinsic viscosities in 0.01 mol/L alongside those in distilled water, keeping the same scale to highlight the impact of NaCl. Sodium counterions in solution shield the intramolecular electrostatic repulsive forces, which leads to coiling of the polymer chains, and a large decrease in the intrinsic viscosities.

Fig. 5 shows the effect of ionic strength on the intrinsic viscosities of DS0.7 and DS1.2 at pH 7. The strong impact of sodium ions in suppressing the electrostatic interactions between the polymer coils can clearly be seen. The data in Figs. 4 and 5 allow the effect of pH on the intrinsic viscosity to be de-coupled from the effect of ionic strength. It should be noted that pH 3 in distilled water is equivalent to an ionic strength of 10^{-3} mol/L, and as Fig. 4A shows the intrinsic viscosity of DS1.2 decreases to about 30 dL/g at pH 3 from nearly 120 dL/g at pH 7. If, however, 10^{-3} mol/L sodium chloride is used as the background electrolyte at pH 7, the intrinsic viscosity of DS1.2 also decreases to about 44 dL/g as seen in Fig. 5. The difference between the value at pH 3 in distilled water and the value at pH 7 in 10^{-3} mol/L sodium chloride can then be attributed to pH effects. In other words, 10^{-3} mol/L hydrochloride acid has almost the same effect on the intrinsic viscosity as 10^{-3} mol/L sodium chloride, which strongly suggests that the apparent effect of pH in Fig. 4A is primarily caused by changes in the ionic strength of CMC solutions, and to a smaller extent by association/dissociation of carboxylic groups.

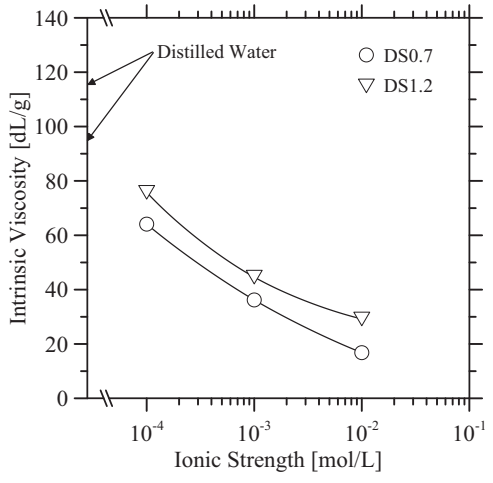

Fig. 5. Intrinsic viscosities of DS0.7 and DS1.2 at pH 7 and 25 °C as a function of ionic strength. Constant M_W of 295,000 g/mol (DS0.7) and 293,000 g/mol (DS1.2).

The same trends can be observed for the DS0.7 sample. Very interestingly, the strong effect of pH observed in distilled water completely disappears in dilute NaCl as seen by comparing Figs. 4A and B. Once the CMC chains are coiled by addition of 0.01 mol/L NaCl, increasing the pH from 3 to 7 does not fully uncoil the chains. Thus, it is the presence of background counterions, not the pH that seems to determine the conformation of CMC over the studied pH range. It should also be noted that the effect of temperature remains very weak under all conditions implying that solvency effects are not significant in the tested CMC solutions.

Along the same lines, Fig. 6A shows that in distilled water, at any pH, an increase in the molecular weight of CMC results in an increase in the intrinsic viscosity. When the molecular weight of a polymer is increased, the effective size of the polymer coil increases which is reflected in the increasing intrinsic viscosity at a given pH value. However, pH seems to have an effect on this expansion. At pH 3, an increase in the molecular weight results in a moderate increase in intrinsic viscosity, but a sharper increase is seen at higher pH values. This effect can be explained by ionic strength effects and association of the polymer at low pH. Adding HCl to adjust the natural pH of the CMC solutions (~pH 6) to pH 3 increases the ionic strength of the solutions which limits stretching of the chain with increasing molecular weight, thus the intrinsic viscosities obtained for LM-CMC, MM-CMC, and HM-CMC at pH 3 do not differ much. Moreover, the anionic CMC macromolecules are associated at low pH, and an increase in the molecular weight does not lead to a corresponding change in intrinsic viscosity as seen in the small difference in the intrinsic viscosity between LM-CMC and HM-CMC.

On the other hand, at pH 7 CMC is fully dissociated and there are few counterions in solution to shield negatively charged carboxylic

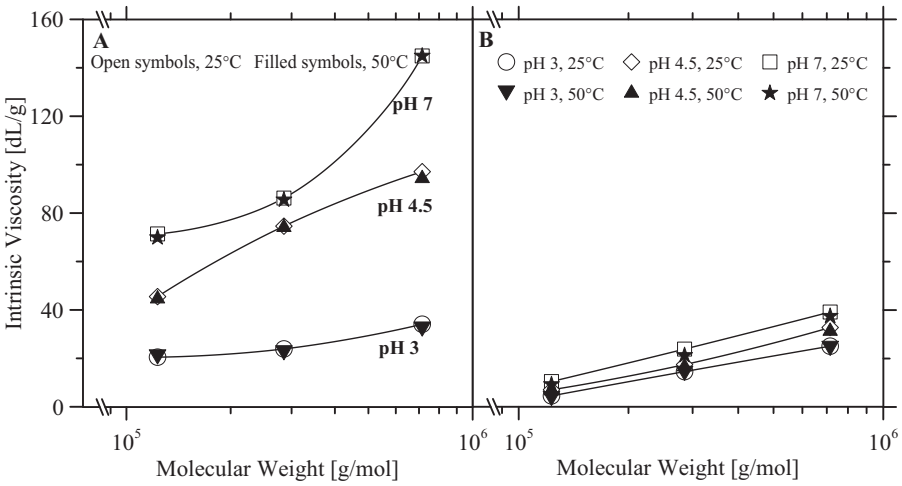

Fig. 6. Effect of pH and temperature on the intrinsic viscosities of the tested CMCs of different M_W (DS = 0.7). (A) distilled water and (B) 0.01 mol/L NaCl.

groups. As a result, expansion of CMC due to increasing molecular weight is much more pronounced. Overall, especially at higher pH values, increasing the molecular weight affects the conformation of the polymers more than increasing the degree of substitution at a given molecular weight.

Fig. 6B shows that 0.01 mol/L NaCl has a similar effect to that seen in Fig. 4-the sharp increase in $[\eta]$ with M_W observed in distilled water disappears with addition of salt. The absolute values of $[\eta]$ decrease due to the screening of the carboxylic groups and therefore coiling of the CMC macromolecules. However, even in 0.01 mol/L NaCl, a significant increase of $[\eta]$ with M_W can still be observed, compared to the smaller increase of $[\eta]$ with DS (Fig. 4B) again indicating the more significant role of M_W over DS in determining the conformation of CMC.

3.2.4. Expansion factor of CMC

The polyelectrolyte expansion can be expressed in terms of the expansion factor α_E, given for cellulose derivatives by (Pals & Hermans, 1952):

$$\alpha_E^2 = \frac{[\eta]}{[\eta]_{I=\infty}} \tag{3}$$

where $[\eta]$ is the intrinsic viscosity in distilled water and $[\eta]_{I=\infty}$ is the intrinsic viscosity at infinite ionic strength. The values of $[\eta]_{I=\infty}$ can be determined graphically from the relation of $[\eta]$ with ionic strength (Pals & Hermans, 1952) given by:

$$[\eta] = A + B\sqrt{I} \tag{4}$$

where I is the ionic strength. It can be seen that as $I \to \infty$, $[\eta] \approx A$, thus A, the intercept with the y-axis of a plot of $[\eta]$ vs $I^{-1/2}$ can be taken as the intrinsic viscosity at infinite ionic strength. Replotting the data from Fig. 5 according to Eq. (4) for DS0.7 and DS1.2 gives $[\eta]_{I=\infty}$ as 15.6 dL/g and 26.1 dL/g respectively (only DS0.7 and DS1.2 were tested at different NaCl concentrations). By comparison, the intrinsic viscosities $[\eta]_{I=0.01}$ for the DS0.7 and DS1.2 in 0.01 mol/L NaCl are 16.8 dL/g and 29.2 dL/g, respectively which indicates that 0.01 mol/L NaCl is sufficient to bring coiling of CMC to intrinsic viscosity values close to those at infinite ionic strength. This comparison also indicates that the expansion factors estimated using $[\eta]_{I=0.01}$ in Eq. (3) instead of $[\eta]_{I=\infty}$ should quite closely describe the expansion of the CMC macromolecules. Thus, the expansion factors presented in Table 2 were obtained as square roots of the ratios of the intrinsic viscosity in distilled water ($[\eta]$) to the intrinsic viscosity in 0.01 mol/L NaCl ($[\eta]_{I=0.01}$):

$$\alpha_E = \sqrt{\frac{[\eta]}{[\eta]_{I=0.01}}} \approx \sqrt{\frac{[\eta]}{[\eta]_{I=\infty}}} \tag{5}$$

Table 2 shows values of α_E evaluated from Eq. (5). A few trends can be noted in the table. Generally, the expansion factors increase with pH at any DS or M_W. However, the apparent effect of pH on chain expansion needs to be viewed with caution since it is affected by the different ionic strengths of the solutions as pH is increased from 3 to 7. As discussed earlier, the ionic strength at pH 3 in distilled water produces nearly the same effect on the intrinsic viscosity as a 10^{-3} mol/L NaCl solution. Since the determination of the expansion factor involves taking a ratio of the intrinsic viscosity in distilled water to the intrinsic viscosity in 0.01 mol/L NaCl, the α_E values at pH 3 would be lower than the values at pH 7 primarily due to the stronger effect of ionic strength on the intrinsic viscosities at pH 3 in distilled water compared to the weaker effect of ionic strength on the intrinsic viscosity at pH 7 in distilled water. However, the effect of DS and M_W on the chain expansion can be seen by comparing the expansion factors at constant pH thus ensuring a constant ionic strength.

The effect of DS on the chain expansion is not so pronounced as that of the molecular weight. The CMC with the lowest molecular weight has the highest ability to expand while the highest molecular weight polymer generally exhibits lower expansion factors. The expansion factor can also be looked at as the ability of the polymer chains to coil or stretch in solution upon transition from low to high ionic strength solutions. Thus, the low expansion factors of HM-CMC are probably due to the increased stiffness within the polymer chain resulting from intrachain hydrogen bonding. The increased rigidity limits the ability of the higher molecular weight polymer (and to some extent the higher DS polymer) to coil or stretch compared to the more flexible lower molecular weight and lower DS polymers.

Table 2
Expansion factors of CMC of different DS and M_W at different pH. The typical error (standard deviation) associated with the expansion factors was on the order of 0.12.

Polymer	α_E			Polymer	α_E		
	pH 3	pH 4.5	pH 7		pH 3	pH 4.5	pH 7
DS0.7	1.15	2.23	2.39	LM-CMC	1.87	2.53	2.86
DS0.9	1.24	1.99	2.28	MM-CMC	1.28	2.06	1.90
DS1.2	1.27	1.93	2.19	HM-CMC	1.17	1.72	1.92

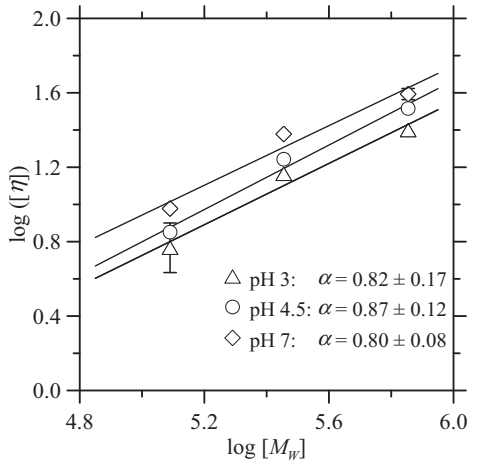

Fig. 7. Logarithmic dependence of the intrinsic viscosity [η] as a function of molecular weight for CMC (M_W range 123,000–715,000 g/mol) in 0.01 mol/L NaCl at 25 °C and different pH, DS = 0.7.

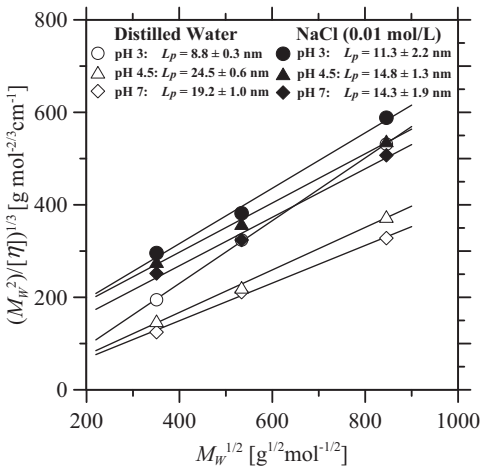

Fig. 8. Bohdanecky plot for CMC in distilled water and in 0.01 mol/L NaCl at different pH conditions.

3.2.5. 3.2.5 [η]–M_W relationship

The conformation of CMC was further analyzed through the Mark–Houwink–Kuhn–Sakurada scaling relationship between intrinsic viscosity and molecular weight (Eq. (6)):

$$[\eta] = K_{[\eta]} M^{\alpha} \tag{6}$$

where $K_{[\eta]}$ and α are constants for a given polymer/solvent/temperature system. The exponent α in the scaling law contains information about the solvent quality and the structural properties of the polymer coil in solution (Kulicke & Clasen, 2004). Fig. 7 shows that a linear relation was obtained between the intrinsic viscosity and molecular weight for CMC samples LM-CMC, MM-CMC, and HM-CMC. The high values of α indicate that 0.01 mol/L NaCl is a good solvent for CMC and that CMC assumes a randomly coiling, semi-flexible conformation under the tested conditions. There is no clear correlation of the exponent α with pH, with an average value of 0.83.

It is difficult to directly compare published α values to the ones determined in the present study due to differences in sample sources (commercial, as in this study vs. well fractionated homogenous samples) and different experimental conditions, such as pH and ionic strength. Also important is the range of the molecular weights used in the studies since α values are only valid for a limited range of molecular weights (Kulicke & Clasen, 2004).

For example, Eremeeva and Bykova (1998) tested CMCs of much lower M_W (8000–92,000 g/mol) than tested in this study and obtained lower α values ranging between 0.73 and 0.83. Brown and Henley (1964) obtained a value of 0.92 at the same ionic strength as that used in the present study. However, their samples had a DS of 1.06 and measurements were performed at 21 °C. Also, the pH of the measurements was not reported. The samples utilized in their study had a much wider range of M_W (~150,000–1,100,000 g/mol), and the PDI (M_z/M_w) of their samples was 1.53–1.77 compared to 2.27–4.30 (LM-CMC–HM-CMC) in the present study. Kulicke et al. (1996) found α to be 0.9 for CMC samples ranging in M_W from ~200,000–2,000,000 g/mol with a DS of 1.0 in 0.01 mol/L NaCl and at 25 °C. It should be pointed out that the differences in the published and present results are not overly significant considering the various conditions under which the studies were performed.

3.2.6. Chain flexibility

The CMC chain flexibility was quantitatively estimated by determining the persistence lengths L_p, from intrinsic viscosity and molecular weight data. Bohdanecky (1983) showed that the dependence of [η] on the molecular weight of stiff-chain polymers can be used for the estimation of the persistence length. The practical limits for persistence length are ~1 nm for a random, flexible coil and ~200 nm for an extra-rigid rod-shaped macromolecule. It should be noted that for charged polymers such as CMC, there are two contributions to the persistence length, L_p: one resulting from the repulsive interactions between charged segments of the chain, the so-called electrostatic persistence length L_{pe}, and the other representing the chain stiffness intrinsic to the polymer backbone L_{p0} and denoted as the intrinsic persistence length (Odjik, 1977; Skolnick & Fixman, 1977). Theoretical considerations of the persistence length of worm-like polyelectrolytes, independently described by Odjik (1977) and Skolnick and Fixman (1977), showed that the two contributions are additive, i.e.,

$$L_p = L_{p0} + L_{pe}. \tag{7}$$

In its simplest form, Bohdanecky's relationship is shown in Eq. (8):

$$\left(\frac{M_W^2}{[\eta]_0}\right)^{1/3} = A_0 M_L \Phi_{0,\infty}^{-1/3} + B_0 \Phi_{0,\infty}^{-1/3} \left(\frac{2L_p}{M_L}\right)^{-1/2} M_W^{1/2} \tag{8}$$

where A_0 and B_0 are tabulated coefficients and can be found in Bohdanecky's article (Bohdanecky, 1983). By plotting $(M_W{}^2/[\eta]_0)^{1/3}$ vs $M_W{}^{1/2}$ linear relationships shown in Fig. 8 were obtained and the L_p values shown in the figure were calculated from the slopes $[B_0 \Phi_{0,\infty}{}^{-1/3}(2L_p/M_L)^{-1/2}]$ of the linear fits to the data. The Flory's constant, $\Phi_{0,\infty}$ was 2.86×10^{23} mol^{-1} (Yamakawa & Fujii, 1974) while the parameter $B_0 = 1.05$ was obtained from Bohdanecky's article. The molar mass per unit length, $M_L = m/l$ where m is the glucose monomer mass (~162 g/mol) and l is the monomer length or the diameter of a monosaccharide (~0.54 nm). For a DS of 0.7, the average monomer mass is approximately 172 g/mol, thus $M_L \approx 319$ g mol^{-1} nm^{-1}.

It should be noted that excluded volume effects are not accounted for in Bohdanecky's method, thus it is worth recalling that the data presented above were obtained using very dilute solutions in which excluded volume effects were negligible. Moreover, the relative stiffness of the CMC chain (as indicated by the persistence length results) should diminish excluded volume effects. It can be seen that the slopes, and therefore the persistence lengths L_p, of the linear fits in distilled water increase with pH while they are approximately constant in 0.01 mol/L NaCl. This trend can be expected in accordance with the data in Fig. 6 which show a strong effect of pH in distilled water and a weak effect of pH in

NaCl. The independence of L_p from pH in 0.01 mol/L NaCl solutions indicates that the electrostatic persistence length L_{pe} is much lower than the intrinsic persistence length L_{p0}. To a good approximation, it can be assumed that the L_p value obtained at pH 3 is equal to L_{p0} since at pH 3, the polymer is in an associated state and the presence of 0.01 mol/L NaCl is sufficient to screen the few dissociated carboxylic groups. With this assumption, L_{pe} values at pH 4.5 and pH 7 calculated using Eq. (7) are 3.0 nm and 3.5 nm respectively. These values are slightly higher than the L_{pe} value (1.37 nm in 0.02 mol/L NaCl) determined by Hoogendam et al. (1998b) but the small difference can be explained by the difference in ionic strength between the two studies. Hoogendam et al.'s value was obtained by setting L_{p0} at 13 nm which gives an L_p value of 14.4 nm, similar to the values obtained in 0.01 mol/L at pH 4.5 and pH 7. Thus, the obtained persistence lengths are in reasonable agreement with those obtained using carefully prepared CMC samples and employing more involved techniques and theories.

In distilled water, L_p increases dramatically from 8.8 nm to 19.2 nm as pH is increased from 3 to 4.5. A further increase in pH to a value of 7 increases the L_p to 24.5 nm. The observed increase in L_p with pH can be explained by the increasing coulomb repulsive forces with increasing pH which leads to a higher L_p at higher pH, though the change in ionic strength of the solutions as pH changes complicates such a direct comparison. However, the L_p values in distilled water are considerably higher than those in 0.01 mol/L NaCl at the same pH and illustrate the importance of ionic strength in affecting L_p. The dependence of L_p on ionic strength indicates that $L_{pe} > L_{p0}$ in distilled water. This can be demonstrated using the assumption made before for the data in 0.01 mol/L NaCl that the L_p value at pH 3 fairly well reflects the chain length in the absence of electrostatic interactions and can be approximated to be close to L_{p0}. Thus, assuming L_{p0} to be 8.8 nm, the calculated L_{pe} values at pH 4.5 and 7 are 10.4 nm and 15.7 nm respectively which are all higher than L_{p0}, and are significantly higher than the L_{pe} values estimated in 0.01 mol/L NaCl.

The results presented above indicate that CMC is a semi-flexible, weakly stiff chain rather than a flexible chain extended by intramolecular excluded volume effects. Admittedly, the number of samples used for the analysis is low, and the method could be sensitive to the molecular weight distribution of the samples. However, the agreement with some of the data obtained using more involved methods, and the presentation of data as a function of pH, which is often lacking in many published works, should further enhance our understanding of the dilute solution behavior of CMC.

4. Conclusions

Analytical ultracentrifugation revealed that the tested CMCs were polydisperse in nature with polydispersity indices ranging from 2.27 to 4.52 and weight average molecular weights ranging from 123,000 g/mol to 715,000 g/mol.

The intrinsic viscosity of CMC solutions was a strong function of the polymer molecular weight while the dependence of the intrinsic viscosity on the degree of substitution was weak. An increase in the molecular weight from 123,000 g/mol to 715,000 g/mol brought about a dramatic increase in the intrinsic viscosity particularly at pH 7 as a result of the extended conformation. On the other hand, an increase in the degree of substitution from 0.7 to 1.2 only had a weak effect on the intrinsic viscosity indicative of the lesser role that the increase in the number of carboxylic groups had on the polymer conformation. The intrinsic viscosity data at constant ionic strength revealed that pH in fact had a very weak effect on the conformation of CMC. The intrinsic viscosity values obtained at pH 3 in distilled water (ionic strength of 10^{-3} mol/L) and at pH 7 in a dilute NaCl solution with a similar ionic strength (10^{-3} mol/L) were almost identical which confirmed that it was the ionic strength, rather than pH that had the strongest influence on the conformation of CMC.

The intrinsic viscosity and molecular weight data analysis using the Mark–Houwink–Kuhn–Sakurada relationship showed that CMC, in a dilute background electrolyte, assumed a randomly coiling, semi-flexible conformation. Further analysis of the data using Bohdanecky's method for determining the persistence length showed that CMC has semi-flexible, weakly stiff chains that are slightly more extended than random coil chains.

The flexibilities of individual CMC samples were quantified from the expansion factors. It was determined that the flexibility depended on molecular weight with the lowest molecular weight sample being the most flexible while the samples of different DS were of comparable flexibilities.

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