

# Viscosity and scaling of semiflexible polyelectrolyte NaCMC in aqueous salt solutions.

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## Abstract

We investigate the viscosity dependence on concentration and molecular weight of semiflexible polyelectrolyte sodium **carboxymethylcellulose** (NaCMC) in aqueous salt-free and NaCl solutions. Combining new measurements and extensive literature data, we establish relevant power laws and crossovers over a wide range of degree of polymerisation ( $N$ ), polymer ( $c$ ) and salt ( $c_s$ ) concentration. In salt-free solution, the overlap concentration shows the expected  $c^* \propto N^{-2}$  dependence, and the entanglement crossover scales as  $c_e \propto N^{-0.6 \pm 0.3}$ , in strong disagreement with scaling theory for which  $c_e \propto c^*$  is expected, but matching the behaviour found for flexible polyelectrolytes. A second crossover, to a steep concentration dependence for specific viscosity

( $\eta_{sp} \propto c^{3.5 \pm 0.2}$ ), commonly assigned to the concentrated regime, is shown to follow  $c^{**} \propto N^{-0.6 \pm 0.2}$  (with  $c^{**}/c_e \simeq 6$ ) which thus suggests instead a dynamic crossover, possibly related to entanglement. The scaling of  $c^*$  and  $c_e$  in 0.01M and 0.1M NaCl shows neutral polymer in good solvent behaviour, characteristic of highly screened polyelectrolyte solutions. This unified scaling picture enables the estimation of viscosity of ubiquitous NaCMC solutions as a function of  $N$ ,  $c$  and  $c_s$  and establishes the behaviour expected for a range of semiflexible polyelectrolyte solutions.

## Introduction

Water soluble polyelectrolytes play a crucial role as rheology modifiers, stabilisers, and functional ingredients in a wide range of formulated products.<sup>1,2</sup> The scaling of various properties such as viscosity, relaxation times, overlap and entanglement concentrations with molecular weight governs much of their practical use in industry. These have been established and reviewed for flexible polyelectrolytes<sup>3-5</sup> in the presence and absence of salt. However, the behaviour of their semiflexible counterparts, remains less well understood, despite their industrial importance, particularly in salt-free solution.<sup>6-9</sup> From a fundamental perspective, it is also of interest to establish whether the same scaling laws apply for flexible and semiflexible polyelectrolytes.<sup>10,11</sup> In this paper, we review experimental data for the viscosity and crossover concentrations of sodium carboxymethylcellulose (NaCMC) in aqueous solutions at different salt concentrations. Despite the vast literature on this topic, no unified picture of the dependence of viscosity on molecular weight and polymer concentration at different salt concentrations exists. Our own data helps fill gaps where literature data are absent.

## Sodium carboxymethylcellulose (NaCMC)

NaCMC is a polyelectrolyte widely used as a rheology modifier<sup>12</sup> in toothpastes<sup>13</sup> and to control soil re-deposition during domestic washing in detergent liquids and powders.<sup>14,15</sup> Its annual consumption in the U.S. was estimated at  $2.7 \times 10^7$  kg for 1983<sup>15</sup> and its worldwide

market at \$834 million in 2012.<sup>16</sup> Commercial grades of NaCMC have a molecular weight ( $M_w$ ) between  $9 \times 10^4$  and  $7 \times 10^5$  g/mol and a degree of substitution (D.S.) between 0.7 and 1.2.<sup>2</sup> D.S. is defined as the average number of carboxymethyl groups substituted on a glucose unit with a maximum possible value of 3.

The rheology of NaCMC of different  $M_w$  and D.S. in aqueous, salt-free solutions has been studied previously.<sup>6,17-26</sup> A power law dependence of the specific viscosity ( $\eta_{sp} = (\eta - \eta_s)/\eta_s$  where  $\eta$  is the solution viscosity and  $\eta_s$  is the solvent viscosity) in the semidilute non-entangled regime close to the Fuoss law<sup>27</sup> ( $\eta_{sp} \sim c^{1/2}$ ) is usually observed, where  $c$  is the polymer concentration.<sup>6,17-19,23-26</sup> A strong dependence of  $\eta_{sp} \sim c^{3.4-3.8}$  is reported at high concentrations,<sup>6,17,23,26</sup> stronger exponents are sometimes observed<sup>24</sup> as the result of gelation.

Addition of monovalent salts to dilute NaCMC solutions results in typical polyelectrolyte behaviour:<sup>28-39</sup> increasing the salt concentration ( $c_s$ ) leads to decreased electrostatic stiffening and excluded volume,<sup>40-43</sup> resulting in a decrease of solution viscosity. The most extensive investigation of the scaling of NaCMC in salt solution is by Kulickle and co-workers<sup>12,44</sup> who studied NaCMC with D.S.  $\simeq 1$  and  $2 \times 10^5 \leq M_w \leq 2 \times 10^6$  g/mol in 0.01M aqueous NaCl. The intrinsic viscosity  $[\eta]$  was found to scale as  $[\eta] \propto M_w^{0.93}$ , characteristic of a semiflexible polymer in good solvent.<sup>40-43</sup> Plots of  $\eta_{sp}$  as a function of  $c[\eta]$ , in the range  $0.5 \leq c[\eta] \leq 50$  were found to collapse into a single master curve, displaying limiting power laws at high  $M_w$  and  $c$  (c.f. table 12<sup>12</sup>) of  $\eta_{sp} \sim M_w^{3.9}$  and  $c^{4.3}$ , in approximate agreement with scaling theory for polymers in good solvent.<sup>3,45</sup> Results for the longest relaxation times ( $\tau$ ) yielded stronger than expected dependences of  $\tau \sim c^3 M_w^5$ . A similar result for  $\eta_{sp}$  was found<sup>46</sup> for two NaCMC samples of D.S.  $\simeq 0.7-0.8$  and  $M_w = 1.2$  and  $7.7 \times 10^5$  g/mol in 0.1M NaCl. These curves collapsed into the same master plot as other polysaccharides<sup>46,47</sup> that did not show ‘hyperentanglements’,<sup>47,48</sup> where normal entanglements are intensified by attractive forces. Values between 8 and 30 nm for the intrinsic Kuhn length ( $b_0$ ), characteristic of a semiflexible polymer, have been reported for NaCMC.<sup>29,33,49,50</sup> While no consensus exists in the literature, our estimates are closer to the lower values.<sup>51</sup> The effective charge density of NaCMC

has been shown to be approximately independent of D.S. in the range  $0.7 \leq D.S. \leq 1.2$ ,<sup>52</sup> as expected due to counterion condensation on such rigid chains. While this body of work provides great insight into the solution properties of NaCMC, no clear picture for the scaling of various quantities can be obtained due to the limitations of individual datasets, particularly in salt free solution. We resolve this by providing a careful analysis of the available data along with new data presented in this paper. We first briefly review the theoretical framework necessary for the scaling law description of semiflexible polyelectrolytes in order to assist the interpretation of the data.

## Scaling laws for polymer solutions

Polymer solutions are broadly classified into three regimes: dilute, semidilute and concentrated.<sup>45,53</sup> Further, semidilute and concentrated solutions may be entangled or non-entangled. In dilute solution, chains do not overlap and their end-to-end distance  $R_F$  follows:  $R_F \simeq bN_K^\nu$  where  $b$  is the Kuhn length,  $N_K$  is the number of Kuhn segments per chain and  $\nu$  is an exponent which depends on solvent quality: 0.5 for neutral polymers in theta solvent, 0.588 for neutral polymers in good solvent and polyelectrolytes with added salt, and 1 for polyelectrolytes in salt-free solutions. The Kuhn length of polyelectrolytes contains a contribution from the intrinsic Kuhn length and the electrostatic Kuhn length, which depends on the ionic strength of a solution. The overlap concentration  $c^*$  is given by:

$$c^* \simeq \frac{N}{R_F^3} \sim N^{1-3\nu} \quad (1)$$

where  $N$  is the degree of polymerisation ( $N = M_w/M_0$  where  $M_0$  is the molar mass of a monomer). Experimentally,  $c^*$  can be determined as the reciprocal of the intrinsic viscosity  $[\eta]$ .<sup>3,45,54</sup> The specific viscosity of polymers in dilute solution follows the Huggins relation:

$$\eta_{sp} = [\eta]c + k_H([\eta]c)^2 \quad (2)$$

where  $k_H$  is the Huggins constant, found to be  $k_H \simeq 0.3 - 0.5$  for polymers in good and theta solvents. The viscosity at  $c^*$  is therefore  $\eta_{sp}(c^*) \simeq 1.3 - 1.5$ . The range of validity of equation 2 ( $c \lesssim 10/[\eta]$ ) can be increased by adding a third term:<sup>55</sup>  $B(c[\eta])^m$ . Determination of  $k_H$ ,  $B$  and  $m$  along with the dependence with  $[\eta]$  on  $N$  allows the prediction of the viscosity of polymer solutions over a wide range of  $M_w$  and concentration. While equation 2 does not apply to polyelectrolytes in salt-free solution,<sup>27,56-59</sup> the empirical criterion  $\eta_{sp}(c^*) = 1$  yields, however,  $c^*$  values in agreement with those determined by other techniques.<sup>3,60</sup>

At  $c^*$ , chains begin to overlap and the correlation length,  $\xi$ , independent of  $N$ , becomes the relevant lengthscale:  $\xi \simeq R_F \left(\frac{c}{c^*}\right)^\mu$  where  $\mu$  can be shown to be  $\mu = -\nu/(3\nu - 1)$ .<sup>45</sup>

Chains in semidilute solution obey dilute solution statistics for length scales smaller than  $\xi$  and random walk statistics for length scales larger than  $\xi$ . The end-to-end chain size scales as  $R \sim N^{1/2}c^{-(\nu-1/2)/(3\nu-1)}$ . Above  $c^*$ , but below the entanglement concentration ( $c_e$ ), the specific viscosity is predicted to scale according to the Rouse model:<sup>45</sup>

$$\eta_{Rouse} \simeq (c[\eta])^{1/(3\nu-1)} \propto Nc^{1/(3\nu-1)} \quad (3)$$

This equation describes data for neutral polymers well<sup>3,45</sup> but the  $N$  dependence deviates for salt-free polyelectrolyte solutions, where  $\eta_{sp} \propto N^{2-2.5}$  instead of  $\eta_{sp} \propto N^1$  has been reported.<sup>60,61</sup> Further, the concentration dependence predicted by equation 3 for salt-free polyelectrolyte solutions  $\eta_{sp} \sim c^{1/2}$  is not always observed.<sup>6,60</sup> Chains begin to entangle at  $c_e$ , which is predicted to be proportional to  $c^*$ :<sup>3,10,62</sup>

$$c_e = n^{6\nu-2}c^* \quad (4)$$

where  $n$  is the number of chain overlaps required for an entanglement to form. For flexible neutral polymers and polyelectrolytes in salt solution,  $c_e \simeq 10-50c^*$  is generally found.<sup>62,63</sup> For salt-free polyelectrolyte solutions, the observed non-proportionality between  $c_e$  and  $c^*$  for samples of varying  $N$  has been tentatively interpreted as due to  $n$  being chain-length

dependent.<sup>3,60</sup> The viscosity in the semidilute entangled regime is predicted to scale as:<sup>62,63</sup>

$$\eta_{sp} = \eta_{Rouse} \left( \frac{c}{c_e} \right)^{2/(3\nu-1)} \quad (5)$$

The correlation length decreases with concentration and reaches the value of the Kuhn length at  $c_D$ . For  $c \geq c_D$ , the concentrated crossover, the chain's end-to-end distance becomes independent of concentration and the viscosity is expected to vary as  $\eta \sim c^{15/4}$ . This crossover has been experimentally observed for neutral polymers.<sup>3,45,53</sup> For polyelectrolytes in salt-free solution the situation is less clear.<sup>6,64-70</sup> Throughout this paper, we will use the term  $c^{**}$  to refer to the crossover to a viscosity power law of  $\eta_{sp} \propto c^{3-4}$  and  $c_D$  to refer to a crossover to the concentrated regime as identified by small angle scattering or osmotic pressure measurements, as we find here that they generally do not agree.

Having outlined the expected viscosity and crossover concentration scaling laws for polyelectrolytes, we now discuss experimental results for NaCMC in detail. Specifically we examine the  $N$  dependence of  $c^*$ ,  $c_e$ ,  $c^{**}$  and  $\eta_{sp}$  for aqueous NaCMC solutions at different salt concentrations.

## Materials and methods

NaCMC samples with  $M_w = 7 \times 10^4$  g/mol (D.S. =  $0.7 \pm 0.1$ ),  $M_w = 3.2 \times 10^5$  g/mol (D.S. =  $1.2 \pm 0.1$ ) and  $M_w = 1.2 \times 10^6$  g/mol (D.S. =  $0.9 \pm 0.1$ ) were purchased from Sigma-Aldrich (with nominal  $M_w$   $9 \times 10^4$  g/mol,  $2.5 \times 10^5$  g/mol and  $7 \times 10^5$  g/mol, and re-calibrated using triple detection GPC or viscosimetry; see S.I. for further details). NaCl ( $\geq 99.98\%$ ) was obtained from Sigma-Aldrich and deionised (D.I.) water from a miliQ source.

Viscosity measurements were carried out using either a rheometer (Anton Paar Physica MCR 301 or Malvern Kinexus pro, both with a cone and plate geometry) or a viscometer (LV-DVI-Prime Brookfield viscometer with a Couette geometry).

## Results

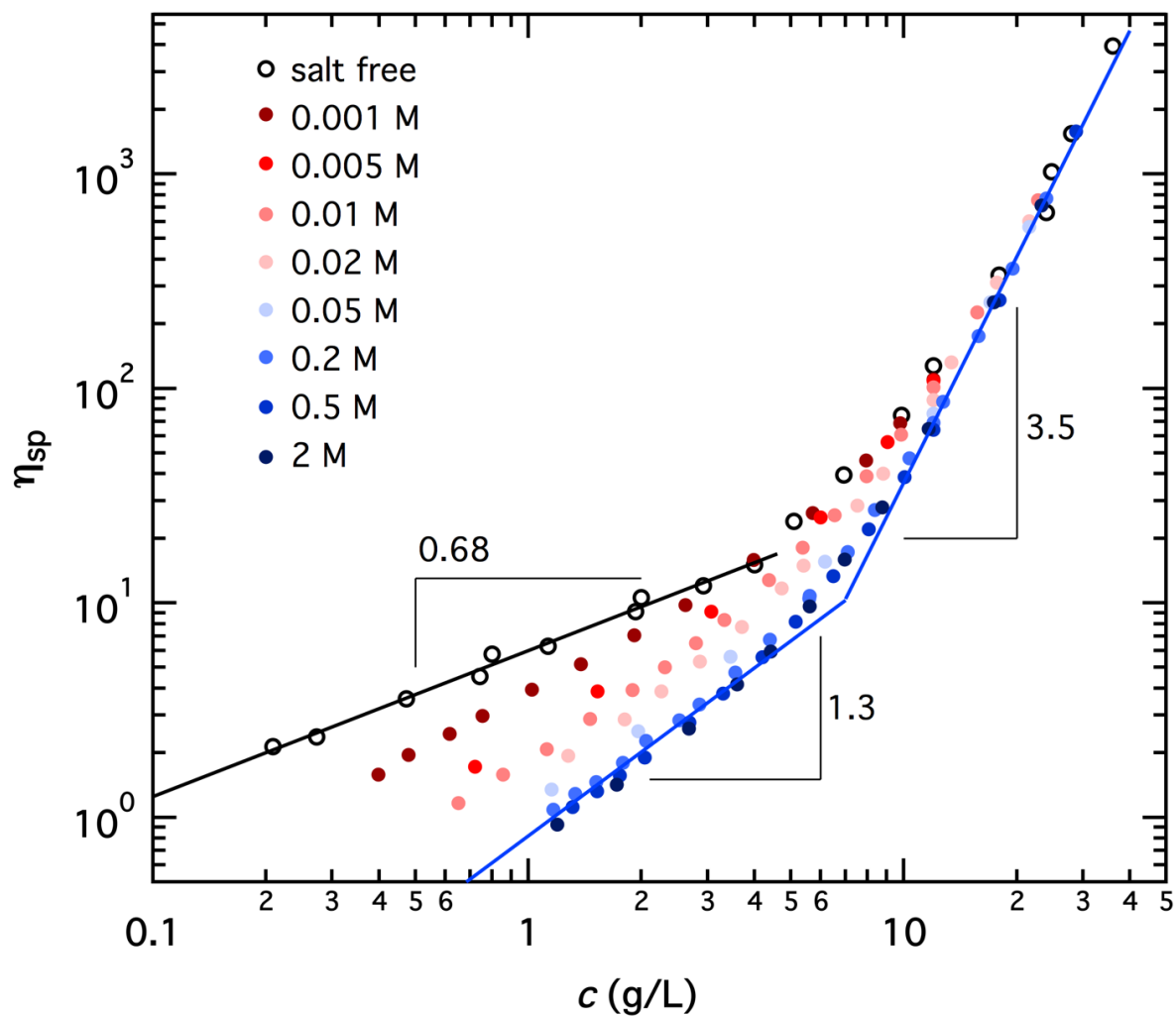


Figure 1: Specific viscosity as a function of polymer concentration and added salt for NaCMC D.S. = 1.2 and  $M_w = 3.2 \times 10^5$  g/mol. Lines indicate limiting slopes. Salt-free data were reported previously.<sup>6</sup>

### Viscosity measurements.

Figure 1 shows the specific viscosity of NaCMC ( $M_w = 3.2 \times 10^5$  g/mol, D.S.  $\simeq 1.2$ ) solutions as a function of polymer and added salt concentration. As expected, solution viscosities decrease with increasing salt, the effect being more pronounced at lower polymer concen-

trations. The effect of added salt appears to saturate at high  $c_s$  values above 0.1M. These results agree with Hayashi et al’s data for sodium hyaluronate,<sup>42</sup> where the intrinsic viscosity was shown to vary only weakly in the same salt concentration range. Following equation 3, the viscosity in the semidilute unentangled regime is also expected to be salt independent. Two regimes can be observed for  $c_S \geq 0.1\text{M}$ , namely  $\eta_{sp} \sim c^{1.3}$  at low  $c$ ,  $\eta_{sp} \sim c^{3.5}$  at high  $c$ . At  $c_s = 0.1\text{M}$ , the inverse Debye-Huckel screening length is  $\simeq 1$  nm. This approximately corresponds to the distance between dissociated charges along the chain<sup>23</sup> and therefore charges along the chain are fully screened from each other for  $c_S \geq 0.1\text{M}$ . Viscosity data and associated crossovers for the  $M_w = 7 \times 10^4$  g/mol and  $M_w = 1.2 \times 10^6$  g/mol samples in salt-free solution are reported in the S.I., exhibiting power laws in agreement with those in Figure 1. We have estimated the salt concentration for the  $M_w = 3.2 \times 10^5$  g/mol sample to be  $\simeq 0.4\text{wt}\%$ , which we designate as ‘salt-free’. Such residual salt content is theoretically expected<sup>10</sup> to cause a decrease in solution viscosity no greater than 3-5%, below the scatter of the data compilation. Further, the salt-free power laws of  $\eta_{sp}$  vs.  $c$  are expected to remain unaffected by residual salt when the ratio of polymer to salt concentration is kept constant, which we have examined experimentally.

## Compilation of literature data.

Values of  $c^*$ ,  $c_e$ ,  $c^{**}$  and  $\eta_{sp}(c)$  for samples of varying  $M_w$  and D.S. in salt-free and salt solutions were obtained from viscosity data from various reports.<sup>6,12,17–19,23,24,26,32,36,37,39,44,46,71–89</sup> Literature data were carefully reviewed and critically reanalysed taking into account well-known artefacts of shear thinning and residual salt. We note that  $M_w$  values reported by manufacturers are not always accurate as systematically examined in section S3 of the S.I. We have therefore only included viscosity data for which  $M_w$  is known to reasonable accuracy. The values presented herein are restricted to a robust subset of measurements, selected as detailed in the S.I. section S.



## Determination of crossover concentrations.

$c^*$  is determined using equation 2 for samples with added salt and from  $\eta_{sp}(c^*) = 1$  for salt free samples. For samples with added salt,  $c_e$  is obtained by fitting data above  $c^*$  with:

$$\eta_{sp} = \eta_{Rouse}(1 + (c/c_e)^q) \quad (6)$$

which interpolates equations 3 and 5 for  $q = 2/(3\nu - 1)$ . For salt free samples  $c_e$  is determined from the crossover of  $\eta_{sp} \sim c^{1/2}$  to  $\eta_{sp} \sim c^{3/2}$ , (Equations 3 and 5 for  $\nu = 1$ ), and  $c^{**}$  is obtained from the crossover of  $\eta_{sp} \sim c^{3/2}$  to  $\eta_{sp} \sim c^{3.4}$ . We find that the best fit power law exponent for salt-free data in the semidilute unentangled regime to be  $\simeq 0.68 \pm 0.06$  (see S.I.), higher than the scaling prediction of  $1/2$ . **Although we do not have a definitive explanation for this discrepancy, chain rigidity and polydispersity may be contributing factors.** The former, related to the relatively large intrinsic persistence length of NaCMC has been discussed in previous work.<sup>6</sup> A large polydispersity can also potentially yield a higher apparent exponent due to the co-existence of chains in the dilute and semidilute regimes, characterised by expected power laws of 1 and  $1/2$ . For this sample however, the dilute chain fraction, over the concentration range studied, appears insufficient to account for the difference observed. We note that both smaller ( $\sim 0.33$ ) and larger ( $\sim 0.9 - 1.1$ ) exponents have also been reported for sodium polystyrene sulfonate (NaPSS),<sup>60</sup> chitosan and sodium hyaluronate<sup>90</sup> We have fit the data with the exponent of  $1/2$  to keep it consistent with literature reports for other polyelectrolytes.<sup>60,91</sup> Both methods produce similar results, with few exceptions detailed in the S.I..

# Discussion and analysis

## Scaling laws in salt-free solutions.

Figure 2a shows  $c^*$ ,  $c_e$  and  $c^{**}$  as functions of degree of polymerisation ( $N$ ) for different NaCMC samples, from the literature and our own measurements. The variation of  $c^*$  with  $N$  ( $c^* \propto N^{-2.5 \pm 0.6}$ ) for salt-free solutions agrees with equation 1 for  $\nu = 1$ :  $c^* \propto N^{-2}$ . The dependence of  $c_e \simeq N^{-0.6 \pm 0.3}$  is however much weaker than the prediction of equation 4, which expects it to be proportional to  $c^*$ . The non-proportionality between  $c^*$  and  $c_e$  can be resolved by considering that  $n$ , the number of chain overlaps required to form an entanglement, depends on  $N$ .<sup>3,60</sup> The collected data imply  $n \propto N^{0.45}$ , as plotted in figure 3.  $\eta_{sp}(c_e)$  should then vary as  $\eta_{sp}(c_e) \simeq n^2 \simeq N^{0.8}$ . This is plotted also as a function of  $N$  in figure 3, where  $\eta_{sp}(c_e) \propto N^{0.8 \pm 0.2}$  is observed. A similar variation for the specific viscosity at  $c^{**}$ :  $\eta_{sp}(c^{**}) \propto N^{1 \pm 0.2}$  is observed.

Surprisingly,  $c^{**}$  shows a weak but clear dependence on  $N$  ( $c^{**} \simeq 6c_e$ ), which is inconsistent with a crossover to the concentrated regime, which corresponds to  $\xi = b_0$ , since both  $\xi$  and  $b_0$  are  $N$  independent (using  $\xi$  values from<sup>6</sup> and  $b_0 = 10$  nm,<sup>49</sup>  $c(\xi = b_0) \simeq 0.03$ M). The scattering profiles for NaCMC in salt-free solution do not exhibit particular changes across  $c^{**}$ .<sup>6</sup> **We recall that  $c^{**}$  was defined by the crossover to the high viscosity power-law regime, and this unexpected  $N$ -dependence suggests therefore a dynamic crossover.** Figure 2b shows the dependence of  $\eta_{sp}$  on  $N$  in the different concentration regimes. In the non-entangled regime, the observed  $\eta_{sp} \propto N^{1.4}$  is in disagreement with the Rouse model prediction  $\eta_{sp} \propto N$ , but consistent with the observed behaviour  $c^* \propto N^{-2}$  and the  $\eta_{sp} \propto c^{0.68}$ , which together lead to  $\eta_{sp} \propto N^{1.4}$ . In the semidilute entangled regime  $\eta_{sp} \propto N^{1.8}$  is observed, in disagreement with equation 5 ( $\eta_{sp} \propto N^3$ ). The disagreement is expected given the difference between the predicted and observed  $N$  dependence of  $c_e$ . As there are not sufficient data to establish the scaling of  $\eta_{sp}$  with  $N$  at a single concentration for  $c \geq c^{**}$ , we fit the viscosity data with  $\eta_{sp} = Kc^{3.4}$  and plot  $K \times 25^{3.4}$  in figure 3. This yields a variation of

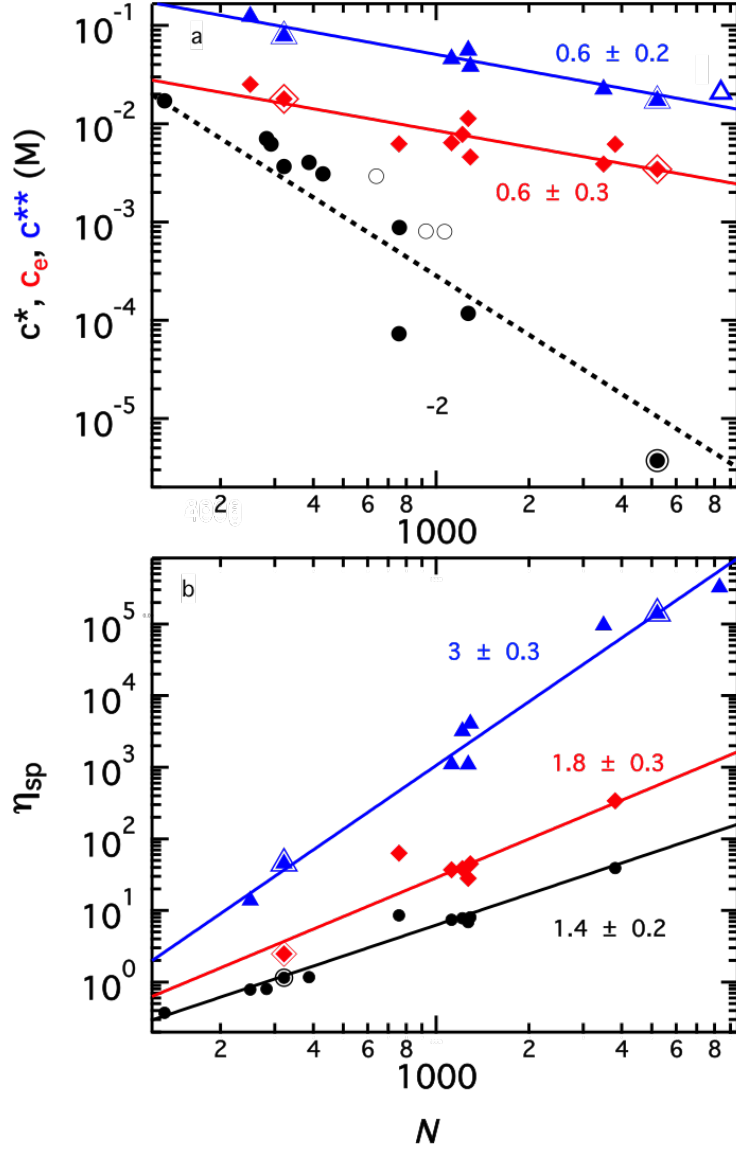


Figure 2: a: Dependence of  $c^*$  (black symbols),  $c_e$  (red symbols) and  $c^{**}$  (blue symbols) on  $N$  for salt-free solutions. Dashed black line is the scaling prediction  $c^* \propto N^{-2}$ , the full red and blue lines are best fit power laws, whose exponent is indicated on the graph. b: specific viscosity  $\eta_{sp}(0.005M)$  as a function of  $N$ , corresponding to data in the  $c^* \leq c \leq c_e$  range (black symbols) and  $\eta_{sp}(0.02M)$  for data in the  $c_e \leq c \leq c^{**}$  range (red symbols). Blue symbols are  $K \times 25^{3,4}$ , which corresponds to the scaling of the specific viscosity for  $c \geq c^{**}$ , as discussed in the text. Lines are best fit power laws, the exponents are indicated on the graph. Data include this work (full symbols surrounded by empty symbols) and references.<sup>6,18,19,26,44,83,92</sup> Open symbols are upper bound estimates.

$\eta_{sp} \propto N^{3 \pm 0.3}$  for  $c \geq c^{**}$ , consistent with the predicted and observed power law dependence of neutral polymer and polyelectrolytes in solution.<sup>55</sup> We thus conclude that  $c^{**}$  measured by this criterion, and not  $c_e$ , corresponds to the entanglement crossover.

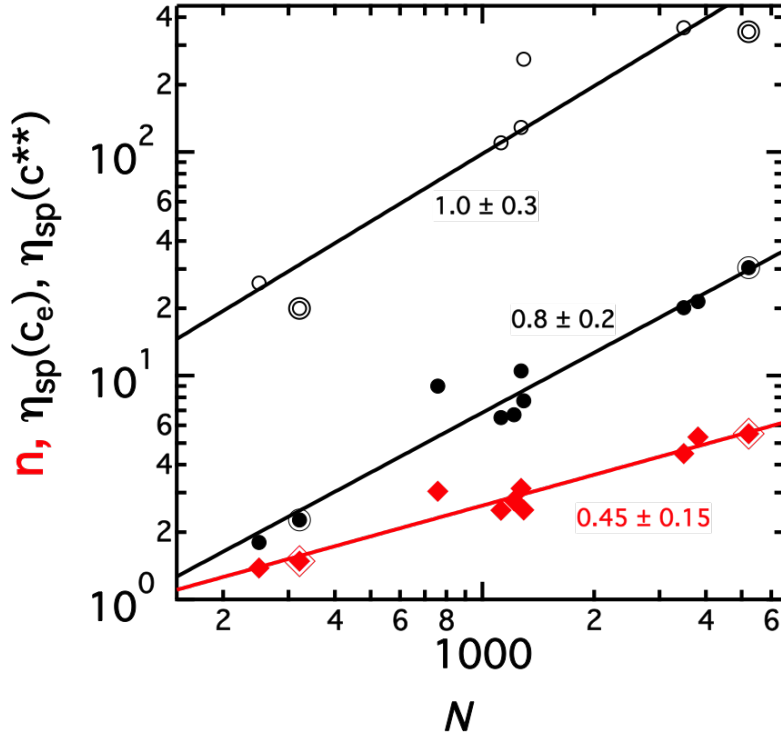


Figure 3: Specific viscosity at  $c_e$ ,  $\eta_{sp}(c_e)$  (full black circles) and at  $c^{**}$   $\eta_{sp}(c^{**})$  (empty black circles) and  $n$  (red points) plotted as a function of  $N$ . Lines are best fit power laws. Data from this work (marked by surrounding hollow symbols) and references.<sup>6,18,26,44,92</sup>

### Scaling laws in salt solutions.

The concentration dependence of the viscosity at high salt concentrations agrees with equation 3 for neutral polymers in good solvent ( $\nu \simeq 0.588$ ). The slope at high  $c$  ( $\gtrsim 12 \pm 2$  g/L) is well described by  $3.5 \pm 0.2$  for all salt concentrations in Fig 1. At these high polymer concentrations,<sup>10,93</sup> chains are highly screened even in salt-free solutions and the fraction of charged monomers may decrease above  $c^{**}$ .<sup>23</sup> It is thus expected that the addition of salt will not contribute strongly to further screening. Power law exponents for flexible<sup>63</sup> and

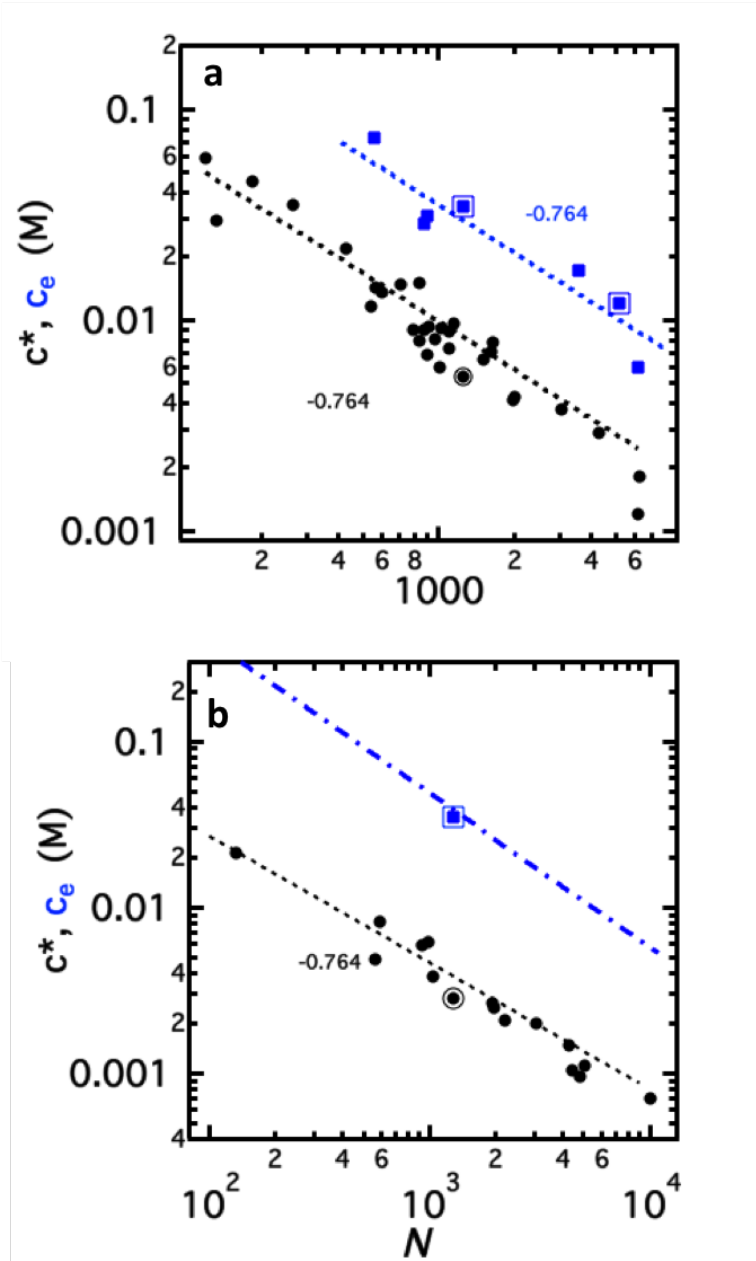


Figure 4: a:  $c^*$  (black symbols) and  $c_e$  (blue symbols) as a function of  $N$  for 0.1 M NaCl solutions and for (b) 0.01M NaCl solutions. Black lines correspond to Zimm's prediction.<sup>45</sup> Dashed-dotted line indicates the trend for  $c_e$  extracted from Kulicke's master curve.<sup>12,44</sup> Data from this work (marked by hollow symbols) and references.<sup>32,44,46,71,74,76,83</sup> Values for  $c_s = 0.1\text{M}$  were interpolated as we did not measure at that  $c_s$ .

semiflexible entangled polymers,<sup>55,94,95</sup> neutral or charged, including polysaccharides<sup>96</sup> have been reported to be within the 3.2-4 range.

Using eqs. 1 and 4 for polymers in good solvent<sup>45</sup> ( $\nu = 0.588$ ), expects  $c_e \propto c^* \propto N^{-0.764}$ , which compare well with the best fit power law exponents of  $-0.9 \pm 0.2$  for both  $c^*$  and  $c_e$  in 0.1M solution. This prediction along with the experimental results is plotted in figure 4a. Data from this work and references<sup>46,74,76,82</sup> can be described by a single master curve according to the expanded version of equation 2, as shown in Figure S6. The different parameters are collected in table 1 and yield a scaling of  $\eta_{sp} \propto N^{3.5}c^4$  at high  $c$  and  $N$ , consistent with equation 5 .

Figure 4b shows  $c^*$  and  $c_e$  for NaCMC in 0.01M NaCl aqueous solutions. The best fit power law exponent to the overlap concentration data is  $c^* \propto N^{-0.8 \pm 0.2}$ , again in reasonable agreement with Zimm’s exponent<sup>45</sup> of -0.764. The  $c_e$  value for our sample agrees with the trends extracted from Kulicke and co-workers master curve<sup>12,44</sup> (dashed-dotted line) for samples in the  $10^5 \leq M_w \leq 10^6$  g/mol range. Kulicke’s data show  $\eta_{sp} \propto N^{3.9}c^{4.3}$  for entangled samples, in reasonable agreement with equation 5 ( $\eta_{sp} \propto N^3c^{3.75}$ ), and with the power law observed for concentrated salt-free solutions ( $\eta_{sp} \sim c^{3.5}$  in Figure 1).

The number of chain overlaps required to form an entanglement is calculated according to equation 4 as:  $n = 3 \pm 1$  in 0.1M NaCl and  $n = 5 \pm 1$  in 0.01M NaCl. These are similar to  $4 \leq n \leq 16$  calculated by Heo and Larson<sup>63</sup> for flexible polymers in good solvent using a different method.

## Salt-free vs. salt solutions

Based on the collected data, we compile the Mark-Houwink-Sakurada (MHS) relations for NaCMC in salt-free and 0.01 and 0.1M salt solutions, shown in Table 1. These allow the determination of  $N$  of NaCMC from dilute viscosity data over a wide range of  $N$ . Further, parameters  $k_H$ ,  $B_m$  and  $m$  which, along with the MHS relations describe  $\eta_{sp}$  over a wide range of  $c$ , are also collected. Since equation 2 does not hold for salt-free polyelectrolyte solutions, we use an alternative plot, first proposed by Krause et al,<sup>61</sup> to obtain a unified description of solution viscosities for all three salt concentrations studied. We write the

specific viscosity as:

$$\eta_{sp} = \eta_{sp}(c^*)(c/c^*)^\gamma(1 + Q(c/c_e)^p) \quad (7)$$

where  $\gamma$  describes the concentration dependence of  $\eta_{sp}$  in semidilute non-entangled solutions,  $Q$  is a crossover parameter and  $p$  is set by the concentration dependence of  $\eta_{sp}$  at high concentrations. The values of these parameters are collected in Table 1. Trivially, for 0.1M  $Q = 1$  since equation 6 is used to determine  $c_e$ . According to equation 7, plots of  $\eta_{sp}c^*/c$  against  $c/c_e$  should collapse data for different  $M_w$  into a single curve. This is indeed observed for data in salt-free and salt solutions (see S.I. section 2). The different crossover concentrations can be estimated as:  $c^* = 1/[\eta]$  with  $[\eta] = KN^a$ ,  $c_e = EN^\alpha$  and  $c^{**} = CN^\beta$ .

## Comparison with flexible polyelectrolytes

Krause et al<sup>61</sup> report  $Q \simeq p \simeq 1$  for NaPAMS in salt-free solution. Analysis of maleate copolymers gives  $Q \simeq 0.2$  and  $p \simeq 1.8$ . It therefore appears that these parameters are system-dependent, but a correlation with molecular architecture is not clear at this point. Figure 5 compiles data for  $c^*$  and  $c_e$  for NaCMC along with flexible ( $b_0 \simeq 2$  nm) polyelectrolytes NaPSS (following the compilation in reference<sup>60</sup> for  $N \geq 100$ ), poly(isobutylene-alt-sodium maleate) (NaIBMA),<sup>91</sup> poly(acrylamide-co-sodium 2-acrylamido-2-methyl-1-propanesulfonate) (NaPAMS)<sup>61</sup> in aqueous solution (a point is omitted for clarity), Poly(N-methyl-2-vinyl pyridinium chloride) (QP2VP-Cl) in ethylene glycol<sup>69</sup> and Poly(N-methyl-2-vinyl pyridinium iodide) (QP2VP-I) in N-methylformamide (NMF)<sup>97</sup> as a function of the reduced contour length  $Nb/B$  where  $b$  is the monomer size calculated from bond lengths and  $B$  (the stretching parameter which takes into account short range folding of chains<sup>10</sup>) is obtained from small angle neutron or X-ray scattering (SANS/SAXS).<sup>6,91,98,99</sup> The scaling of  $c^* \propto N^{-2}$  and  $c_e \propto N^{-0.6 \pm 0.3}$  is common to NaCMC, NaPSS and NaIBMA.<sup>3,60,91</sup> Our result for the  $N$ -dependence of  $\eta_{sp}$  in the non-entangled regime lies between that observed for NaPSS and

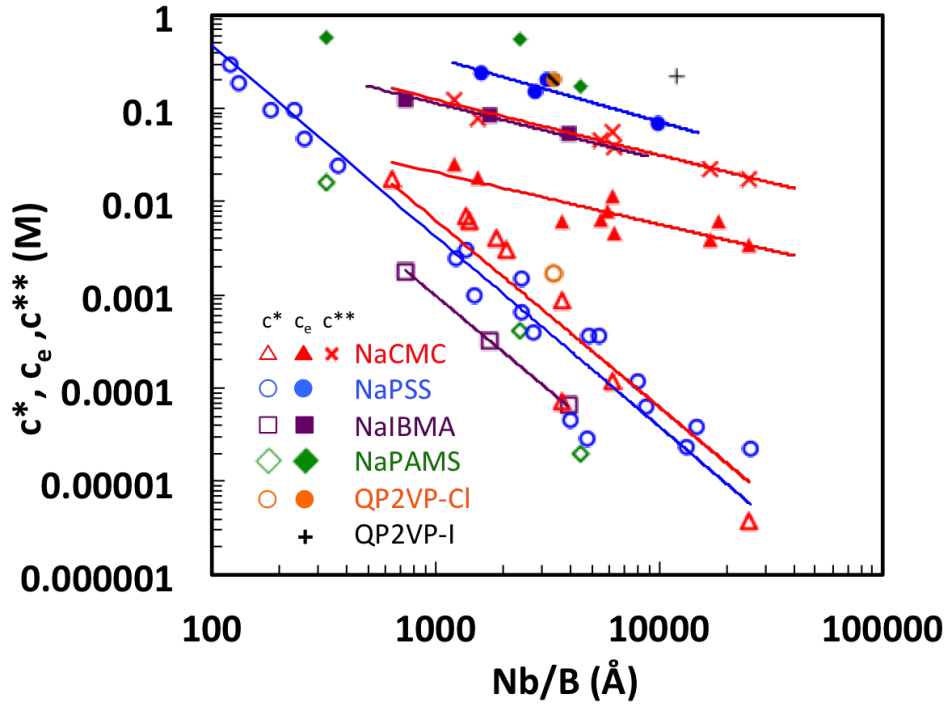


Figure 5: Crossover concentrations for salt free solutions of different polyelectrolyte systems:  $c^*$  (hollow) and  $c_e$  (full symbols) for: NaPSS (blue circles), NaIBMA (purple squares), NaCMC (red triangles) NaPAMS (green diamonds), QP2VP in ethylene glycol (orange circle), QP2VP in NMF<sup>97</sup> (black +),  $c^{**}$  for NaCMC (red crosses).

NaPAMS ( $\eta_{sp} \sim N^{2-2.4}$ ) and that for NaIBMA ( $\eta_{sp} \sim N^1$ ). The dependence of  $\eta_{sp}(c_e) \propto N^{0.8}$  is similar to that reported earlier for NaPSS.<sup>60</sup> If we force the same power law dependence of  $n$  on  $N$  for NaCMC as for flexible systems, following equation 4 (with  $\nu = 1$ ), the compiled data for NaCMC indicate  $n \simeq 0.138(Nb/B)^{0.35}$ . Data for NaPSS,<sup>60</sup> NaIBMA<sup>91</sup> and NaPAMS,<sup>61</sup> imposing the same power law dependence on  $Nb/B$ , show similar relations:  $n = 0.3(Nb/B)^{0.35}$ ,  $n = 0.32(Nb/B)^{0.35}$  and  $n = 0.45(Nb/B)^{0.35}$  respectively. Within the limits of the datasets considered, this suggests that fewer chain overlaps are required to form an entanglement for semiflexible chains.



Table 1: Parameters for MHS and entanglement, concentrated crossover relations for different salt concentrations:  $[\eta] = KN^a$  in L/mol,  $c_e = EN^\alpha$  and  $c^{**} = CN^\beta$ .  $[\eta]$  is obtained from the Huggins equation for salt solutions and from  $\eta_{sp}(c = 1/[\eta]) = 1$  for salt-free solutions. Parameters  $k_H$ ,  $B$  and  $m$  are obtained from fits to  $\eta_{sp} = c[\eta] + k_H(c[\eta])^2 + B(c[\eta])^m$ ,  $Q$  and  $p$  to equation 7.

	K	a	$k_H$	$B$	$m$	E	$\alpha$	C	$\beta$	$\eta_{sp}(c^*)$	$\gamma$	$Q$	$p$
D.I water	0.00015	2.5	-	-	-	0.4	-0.56	3.0	-0.60	1	0.68	0.08	2.7
0.01M	0.81	0.82	0.28	$4.8 \times 10^{-4}$	4.34	29	-0.93	-	-	-	-	-	-
0.1M	0.29	0.87	0.45	0.018	4	9.5	-0.8	-	-	1.45	1.3	1.4	2.7

## Conclusions

Based on analysis of viscosity literature data and new experimental results, the scaling of  $c^*$ ,  $c_e$ ,  $c^{**}$  and  $\eta_{sp}$  with  $N$  for NaCMC in salt-free and in aqueous salt solutions is established. In salt solutions (0.1 and 0.01M NaCl), scaling laws characteristic of neutral polymers in good solvent are observed, in agreement with data for other systems. MHS relations are established for three different salt concentrations. We find the scaling laws in salt-free solution for this semiflexible polyelectrolyte are similar to those for other flexible systems, namely  $c^* \sim N^{-2}$  and  $c_e \sim N^{-0.6}$ . Unexpectedly, the  $\eta_{sp} \sim c^{3.4}$  relation observed at high concentrations cannot be assigned to a crossover to the concentrated regime, instead appearing to be a dynamic crossover related to entanglement. Finally, our results enable calculation of rheological properties for NaCMC of varying  $N$ ,  $c$  and  $c_s$  using parameters in Table 1.

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## References

- (1) Glass, J.; Zukoski, C.; Schultz, D. *Polymers as rheology modifiers: An overview*; ACS Symp. Ser., 1991.
- (2) Ashland Bulletin VC-531C Aqualon<sup>TM</sup> Cellulose Gum *Behavior in Water*.
- (3) Colby, R. H. Structure and linear viscoelasticity of flexible polymer solutions: comparison of polyelectrolyte and neutral polymer solutions. *Rheol. Acta* **2010**, *49*, 425–442.
- (4) Dobrynin, A. V.; Rubinstein, M. Theory of polyelectrolytes in solutions and at surfaces. *Progress in Polymer Science* **2005**, *30*, 1049–1118.
- (5) Dobrynin, A. V. Theory and simulations of charged polymers: From solution properties to polymeric nanomaterials. *Current Opinion in Colloid & Interface Science* **2008**, *13*, 376–388.
- (6) Lopez, C. G.; Rogers, S. E.; Colby, R. H.; Graham, P.; Cabral, J. T. Structure of sodium carboxymethyl cellulose aqueous solutions: A SANS and rheology study. *Journal of Polymer Science Part B: Polymer Physics* **2015**, *53*, 492–501.
- (7) Yu, F.; Zhang, F.; Luan, T.; Zhang, Z.; Zhang, H. Rheological studies of hyaluronan solutions based on the scaling law and constitutive models. *Polymer* **2014**, *55*, 295–301.
- (8) Fouissac, E.; Milas, M.; Rinaudo, M. Shear-rate, concentration, molecular weight, and temperature viscosity dependences of hyaluronate, a wormlike polyelectrolyte. *Macromolecules* **1993**, *26*, 6945–6951.
- (9) Wyatt, N. B.; Liberatore, M. W. Rheology and viscosity scaling of the polyelectrolyte xanthan gum. *J. Appl. Polym. Sci.* **2009**, *114*, 4076–4084.
- (10) Dobrynin, A. V.; Colby, R. H.; Rubinstein, M. Scaling Theory of Polyelectrolyte Solutions. *Macromolecules* **1995**, *28*, 1859–1871.

- (11) Odijk, T. Possible scaling relations for semidilute polyelectrolyte solutions. *Macromolecules* **1979**, *12*, 688–693.
- (12) Clasen, C.; Kulicke, W.-M. Determination of viscoelastic and rheo-optical material functions of water-soluble cellulose derivatives. *Prog. Polym. Sci.* **2001**, *26*, 1839 – 1919.
- (13) Garlick, T.; Miner, P. Low stringing toothpaste. 1993; US Patent 5,192,529.
- (14) Francis, L. D. Soil anti-redeposition agents, their use and detergent compositions containing same. 1971; US Patent 3,597,416.
- (15) Whistler, R.; BeMills, J. *Industrial Gums: Polysaccharides and Their Derivatives 3rd Ed*, Academic Press; Elsevier, 1993.
- (16) Carboxymethyl Cellulose Market - Global Industry Analysis, Size, Share, Growth, Trends and Forecast, 2013 - 2019.
- (17) Kastner, U.; Hoffmann, H.; Donges, R.; Hilbig, J. Structure and solution properties of sodium carboxymethyl cellulose. *Colloids Surf., A* **1997**, *123*, 307 – 328.
- (18) Guillot, S.; Delsanti, M.; Desert, S.; Langevin, D. Surfactant-Induced Collapse of Polymer Chains and Monodisperse Growth of Aggregates near the Precipitation Boundary in Carboxymethylcellulose-DTAB Aqueous Solutions. *Langmuir* **2003**, *19*, 230–237.
- (19) Tam, K.; Tiu, C. Improved correlation for shear-dependent viscosity of polyelectrolyte solutions. *J. of Non-Newtonian Fluid Mech* **1993**, *46*, 275–288.
- (20) Dolz, M.; Bugaj, J.; Pellicer, J.; Hernandez, M.; Gorecki, M. Thixotropy of highly viscous sodium (carboxymethyl)cellulose hydrogels. *J. Pharm. Sci.* **1997**, *86*, 1283–1287.
- (21) deButts, E. H.; Hudy, J. A.; Elliott, J. H. Rheology of Sodium Carboxymethylcellulose Solutions. *Ind. Eng. Chem.* **1957**, *49*, 94–98.

- (22) Elliot, J.; Ganz, A. Some rheological properties of sodium carboxymethylcellulose solutions and gels. *Rheol. Acta* **1974**, *13*, 670–674.
- (23) Truzzolillo, D.; Bordi, F.; Cametti, C.; Sennato, S. Counterion condensation of differently flexible polyelectrolytes in aqueous solutions in the dilute and semidilute regime. *Phys. Rev. E* **2009**, *79*, 011804.
- (24) Lim, S.; Kim, S.; Ahn, K. H.; Lee, S. J. The effect of binders on the rheological properties and the microstructure formation of lithium-ion battery anode slurries. *Journal of Power Sources* **2015**, *299*, 221–230.
- (25) Wu, Q.; Du, M.; Shangguan, Y.; Zhou, J.; Zheng, Q. Investigation on the interaction between C16TAB and NaCMC in semidilute aqueous solution based on rheological measurement. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2009**, *332*, 13–18.
- (26) Wu, Q.; Shangguan, Y.; Du, M.; Zhou, J.; Song, Y.; Zheng, Q. Steady and dynamic rheological behaviors of sodium carboxymethyl cellulose entangled semi-dilute solution with opposite charged surfactant dodecyl-trimethylammonium bromide. *J Colloid Interf. Sci.* **2009**, *339*, 236–242.
- (27) Fuoss, R. M.; Strauss, U. P. Polyelectrolytes. II. Poly-4-vinylpyridonium chloride and poly-4-vinyl-N-n-butylpyridonium bromide. *J. Polym. Sci. A Polym. Chem.* **1948**, *3*, 246–263.
- (28) Brown, W.; Henley, D. Studies on cellulose derivatives. Part IV. The configuration of the polyelectrolyte sodium carboxymethyl cellulose in aqueous sodium chloride solutions. *Makromolekulare Chemie* **1964**, *79*, 68–88.
- (29) Davis, R. M. Analysis of dilute solutions of (carboxymethyl)cellulose with the electrostatic wormlike chain theory. *Macromolecules* **1991**, *24*, 1149–1155.

- (30) Nandi, P.; Bhattarai, A.; Das, B. Intrinsic viscosities of sodium carboxymethylcellulose in acetonitrile–water mixed solvent media using isoionic dilution method. *J. Pol. Sci. Part B: Pol Phys* **2007**, *45*, 1765–1770.
- (31) Sitaramaiah, G.; Goring, D. Hydrodynamic studies on sodium carboxymethyl cellulose in aqueous solutions. *J Pol Sci* **1962**, *58*, 1107–1131.
- (32) Schneider, N. S.; Doty, P. Macro-ions. IV. The ionic strength dependence of the molecular properties of sodium carboxymethylcellulose. *J. Phys. Chem.* **1954**, *58*, 762–769.
- (33) Hoogendam, C. W.; de Keizer, A.; Cohen Stuart, M. A.; Bijsterbosch, B. H.; Smit, J. A. M.; van Dijk, J. A. P. P.; van der Horst, P. M.; Batelaan, J. G. Persistence Length of Carboxymethyl Cellulose As Evaluated from Size Exclusion Chromatography and Potentiometric Titrations. *Macromolecules* **1998**, *31*, 6297–6309.
- (34) Trap, H. J. L.; Hermans, J. J. Light-scattering by polymethacrylic acid and carboxymethylcellulose in various solvents. *The Journal of Physical Chemistry* **1954**, *58*, 757–761.
- (35) Trivedi, H.; Patel, R. Studies on carboxymethyl cellulose. Quantitative analysis of the huggins constant  $k'$ . *Die Angewandte makromolekulare Chemie* **1986**, *141*, 11–18.
- (36) Trivedi, H.; Patel, C.; Patel, R. Studies on carboxymethyl cellulose. Viscosity dependence on polymer concentration and electrolyte content. *Die Angewandte Makromolekulare Chemie* **1981**, *95*, 155–170.
- (37) Fujita, H.; Homma, T. Non-Newtonian viscosities in dilute aqueous solutions of sodium carboxymethylcellulose. *Journal of Polymer Science* **1955**, *15*, 277–295.
- (38) Pals, D. T. F.; Hermans, J. J. Sodium salts of pectin and of carboxy methyl cellulose in aqueous sodium chloride. I. Viscosities. *Recueil des Travaux Chimiques des Pays-Bas* **1952**, *71*, 433–457.

- (39) Arinaitwe, E.; Pawlik, M. Dilute solution properties of carboxymethyl celluloses of various molecular weights and degrees of substitution. *Carbohydrate polymers* **2014**, *99*, 423–431.
- (40) Yashiro, J.; Hagino, R.; Sato, S.; Norisuye, T. Chain stiffness and excluded-volume effects in polyelectrolyte solutions: Characterization of sodium poly (2-acrylamido-2-methylpropanesulfonate) in aqueous sodium chloride. *Polymer journal* **2006**, *38*, 57–63.
- (41) Iwamoto, Y.; Hirose, E.; Norisuye, T. Electrostatic contributions to chain stiffness and excluded-volume effects in sodium poly (styrenesulfonate) solutions. *Polymer journal* **2000**, *32*, 428–434.
- (42) Hayashi, K.; Tsutsumi, K.; Norisuye, T.; Teramoto, A. Electrostatic contributions to chain stiffness and excluded-volume effects in sodium hyaluronate solutions. *Polymer journal* **1996**, *28*, 922–928.
- (43) Tsutsumi, K.; Norisuye, T. Excluded-volume effects in sodium hyaluronate solutions revisited. *Polymer journal* **1998**, *30*, 345–349.
- (44) Kulicke, W.-M.; Kull, A. H.; Kull, W.; Thielking, H.; Engelhardt, J.; Pannek, J.-B. Characterization of aqueous carboxymethylcellulose solutions in terms of their molecular structure and its influence on rheological behaviour. *Polymer* **1996**, *37*, 2723–2731.
- (45) Rubinstein, M.; Colby, R. H. *Polymer Physics*; Oxford, 2003.
- (46) Castelain, C.; Doublier, J.; Lefebvre, J. A study of the viscosity of cellulose derivatives in aqueous solutions. *Carbohydrate polymers* **1987**, *7*, 1–16.
- (47) Morris, E. R.; Cutler, A.; Ross-Murphy, S.; Rees, D.; Price, J. Concentration and shear rate dependence of viscosity in random coil polysaccharide solutions. *Carbohydrate polymers* **1981**, *1*, 5–21.

- (48) Doyle, J. P.; Lyons, G.; Morris, E. R. New proposals on "hyperentanglement" of galactomannans: Solution viscosity of fenugreek gum under neutral and alkaline conditions. *Food Hydrocolloids* **2009**, *23*, 1501–1510.
- (49) Kamide, K.; Saito, M.; Suzuki, H. Persistence length of cellulose and cellulose derivatives in solution. *Makromol Chem Rapid Commun.* **1983**, *4*, 33–39.
- (50) Dogsa, I.; Tomsic, M.; Orehek, J.; Benigar, E.; Jamnik, A.; Stopar, D. Amorphous Supramolecular Structure of Carboxymethyl Cellulose in Aqueous Solution at Different pH Values as determined by Rheology, Small Angle X-ray and Light Scattering. *Carbohydrate Polymers* **2014**, *111*, 492–504.
- (51) Lopez, C. G. Thesis, Imperial College London - London, 2015.
- (52) Ray, D.; De, R.; Das, B. Thermodynamic, transport and frictional properties in semidilute aqueous sodium carboxymethylcellulose solution. *J. Chem. Thermodyn.* **2016**, *101*, 227–235.
- (53) Graessley, W. W. Polymer chain dimensions and the dependence of viscoelastic properties on concentration, molecular weight and solvent power. *Polymer* **1980**, *21*, 258–262.
- (54) Ying, Q.; Chu, B. Overlap concentration of macromolecules in solution. *Macromolecules* **1987**, *20*, 362–366.
- (55) Kulicke, W.-M.; Kniewske, R. The shear viscosity dependence on concentration, molecular weight, and shear rate of polystyrene solutions. *Rheologica acta* **1984**, *23*, 75–83.
- (56) Wolf, B. A. Polyelectrolytes revisited: reliable determination of intrinsic viscosities. *Macromol. Rapid Commun.* **2007**, *28*, 164–170.
- (57) Eckelt, J.; Knopf, A.; Wolf, B. A. Polyelectrolytes: Intrinsic viscosities in the absence and in the presence of salt. *Macromolecules* **2008**, *41*, 912–918.

- (58) Eich, A.; Wolf, B. A. Intrinsic Viscosities of Polyelectrolytes: Determination and Modeling of the Effects of Extra Salt. *ChemPhysChem* **2011**, *12*, 2786–2790.
- (59) Nishida, K.; Kaji, K.; Kanaya, T.; Fanjat, N. Determination of intrinsic viscosity of polyelectrolyte solutions. *Polymer* **2002**, *43*, 1295–1300.
- (60) Boris, D. C.; Colby, R. H. Rheology of Sulfonated Polystyrene Solutions. *Macromolecules* **1998**, *31*, 5746–5755.
- (61) Krause, W. E.; Tan, J. S.; Colby, R. H. Semidilute solution rheology of polyelectrolytes with no added salt. *J. Polym. Sci., Part B: Polym. Phys.* **1999**, *37*, 3429–3437.
- (62) Raspaud, E.; Lairez, D.; Adam, M. On the number of blobs per entanglement in semidilute and good solvent solution: melt influence. *Macromolecules* **1995**, *28*, 927–933.
- (63) Heo, Y.; Larson, R. G. The scaling of zero-shear viscosities of semidilute polymer solutions with concentration. *Journal of Rheology* **2005**, *49*, 1117–1128.
- (64) Lorchat, P.; Konko, I.; Combet, J.; Jestin, J.; Johner, A.; Laschewski, A.; Obukhov, S.; Rawiso, M. New regime in polyelectrolyte solutions. *EPL (Europhysics Letters)* **2014**, *106*, 28003.
- (65) Nishida, K.; Kaji, K.; Kanaya, T. High concentration crossovers of polyelectrolyte solutions. *J. Chem. Phys.* **2001**, *114*, 8671–8677.
- (66) Lorchat, P. Structure des solutions aqueuses de polyelectrolytes fortement charges. Ph.D. Thesis, Institut Charles Sadron - Strasbourg , 2012.
- (67) Takahashi, Y.; Matsumoto, N.; Iio, S.; Kondo, H.; Noda, I.; Imai, M.; Matsushita, Y. Concentration Dependence of Radius of Gyration of Sodium Poly(styrenesulfonate) over a Wide Range of Concentration Studied by Small-Angle Neutron Scattering. *Langmuir* **1999**, *15*, 4120–4122.



- (68) Takahashi, Y.; Iio, S.; Matsumoto, N.; Noda, I. Viscoelastic properties of polyelectrolyte solutions in non-entangled concentrated regions. *Polymer International* **1996**, *40*, 269–273.
- (69) Dou, S.; Colby, R. H. Charge density effects in salt-free polyelectrolyte solution rheology. *J. Polym. Sci., Part B: Polym. Phys.* **2006**, *44*, 2001–2013.
- (70) Waigh, T. A.; Ober, R.; Williams, C. E.; Galin, J.-C. Semidilute and concentrated solutions of a solvophobic polyelectrolyte in nonaqueous solvents. *Macromolecules* **2001**, *34*, 1973–1980.
- (71) Brown, W.; Henley, D.; Ohman, J. Sodium carboxymethyl cellulose, an experimental study of influence of molecular weight and ionic strength on polyelectrolyte configuration. *Arkiv for Kemi* *22*.
- (72) Brown, W.; Henley, D. Studies on cellulose derivatives. Part IV. The configuration of the polyelectrolyte sodium carboxymethyl cellulose in aqueous sodium chloride solutions. *Die Makromolekulare Chemie* **1964**, *79*, 68–88.
- (73) Rinaudo, M.; Danhelka, J.; Milas, M. A new approach to characterising carboxymethylcelluloses by size exclusion chromatography. *Carbohydrate polymers* **1993**, *21*, 1–5.
- (74) Meyer, F. Korrelation rheo-mechanischer und rheo-optischer Materialfunktionen. Ph.D. thesis, Universität Hamburg, 2008.
- (75) Pfefferkorn, P. M. J. Analytik von wasserlöslichen Polysacchariden und Polysaccharidderivaten mittels Groβenausschlusschromatographie kombiniert mit Vielwinkellaserlichtstreuung und Konzentrationsdetektion. Ph.D. thesis, Universität Hamburg, 2004.
- (76) Barba, C.; Montané, D.; Farriol, X.; Desbrières, J.; Rinaudo, M. Synthesis and characterization of carboxymethylcelluloses from non-wood pulps II. Rheological behavior of CMC in aqueous solution. *Cellulose* **2002**, *9*, 327–335.

- (77) Barba, C.; Montané, D.; Rinaudo, M.; Farriol, X. Synthesis and characterization of carboxymethylcelluloses (CMC) from non-wood fibers I. Accessibility of cellulose fibers and CMC synthesis. *Cellulose* **2002**, *9*, 319–326.
- (78) Barba, C. Síntesis de carboximetilcellulosa (CMC) a partir de pastas de plantas anuales. Ph.D. thesis, Universitat Rovira i Virgili, 2002.
- (79) Moan, M.; Wolff, C. Etude viscosimétrique de solutions de polyélectrolytes par dilution isoionique. Effet de la densité de charge sur la conformation du polyion. *Die Makromolekulare Chemie* **1974**, *175*, 2881–2894.
- (80) Matsumoto, T.; Mashiko, K. Influence of Added Salt on Dynamic Viscoelasticity of CMC aqueous systems. *Polym. Eng. Sci.* **1988**, *28*, 393–402.
- (81) Picton, L.; Merle, L.; Muller, G. Solution behavior of hydrophobically associating cellulosic derivatives. *International Journal of Polymer Analysis and Characterization* **1996**, *2*, 103–113.
- (82) Charpentier, D.; Mocanu, G.; Carpov, A.; Chapelle, S.; Merle, L.; Müller, G. New hydrophobically modified carboxymethylcellulose derivatives. *Carbohydrate polymers* **1997**, *33*, 177–186.
- (83) Lohmander, U.; Strömberg, R. Non-Newtonian flow of dilute sodium carboxymethyl cellulose solutions at different ionic strengths and of dilute solutions of cellulose nitrate and polystyrene in moderately viscous solvents studied by capillary viscometry: Experimental results. *Die Makromolekulare Chemie* **1964**, *72*, 143–158.
- (84) Vink, H. Viscosity of polyelectrolyte solutions. *Die Makromolekulare Chemie* **1970**, *131*, 133–145.
- (85) Nakagaki, M.; Kawamura, M. Physicochemical studies on the suspension syrup. VI. The

- viscometric behavior of sodium carboxymethylcellulose in aqueous sucrose solutions. *Yakugaku Zasshi* **1968**, *88*, 852–856.
- (86) Chatterjee, A.; Das, B. Radii of gyration of sodium carboxymethylcellulose in aqueous and mixed solvent media from viscosity measurement. *Carbohydrate polymers* **2013**, *98*, 1297–1303.
- (87) Inagaki, H.; Sakurai, H.; Sasaki, T. Distinct Maximum Appearing in the Viscosity Curve of Dilute Polyelectrolyte Solutions. *Bulletin of the Institute for Chemical Research, Kyoto University* **1956**, *34*, 74–86.
- (88) Truzzolillo, D.; Cametti, C.; Sennato, S. Dielectric properties of differently flexible polyions: a scaling approach. *Phys. Chem. Chem. Phys.* **2009**, *11*, 1780–1786.
- (89) Ye, T.; Du, M.; Song, Y.; Zheng, Q. Effect of Alkyl Trimethylammonium Bromide on Rheology of Entangled Semi-dilute Solution of Sodium Carboxymethylcellulose. *Acta Polymerica Sinica* **2015**, 827–834.
- (90) Del Giudice, F.; Calcagno, V.; Taliento, V. E.; Greco, F.; Netti, P. A.; Maffettone, P. L. Relaxation time of polyelectrolyte solutions: When  $\mu$ -rheometry steps in charge. *Journal of Rheology (1978-present)* **2017**, *61*, 13–21.
- (91) Di Cola, E.; Plucktaveesak, N.; Waigh, T. A.; Colby, R. H.; Tan, J. S.; Pyckhout-Hintzen, W.; Heenan, R. K. Structure and Dynamics in Aqueous Solutions of Amphiphilic Sodium Maleate-Containing Alternating Copolymers. *Macromolecules* **2004**, *37*, 8457–8465.
- (92) Tam, K.; Tiu, C. Steady and dynamic shear properties of aqueous polymer solutions. *Journal of Rheology* **1989**, *33*, 257–280.
- (93) Muthukumar, M. Double screening in polyelectrolyte solutions: limiting laws and crossover formulas. *The Journal of chemical physics* **1996**, *105*, 5183–5199.

- (94) Ohshima, A.; Yamagata, A.; Sato, T.; Teramoto, A. Entanglement effects in semiflexible polymer solutions. 3. Zero-shear viscosity and mutual diffusion coefficient of poly (n-hexyl isocyanate) solutions. *Macromolecules* **1999**, *32*, 8645–8654.
- (95) Ohshima, A.; Kudo, H.; Sato, T.; Teramoto, A. Entanglement Effects in Semiflexible Polymer Solutions. 1. Zero-Shear Viscosity of Poly (n-hexyl isocyanate) Solutions. *Macromolecules* **1995**, *28*, 6095–6099.
- (96) Risica, D.; Barbetta, A.; Vischetti, L.; Cametti, C.; Dentini, M. Rheological properties of guar and its methyl, hydroxypropyl and hydroxypropyl-methyl derivatives in semidilute and concentrated aqueous solutions. *Polymer* **2010**, *51*, 1972–1982.
- (97) Dou, S.; Colby, R. H. Solution Rheology of a Strongly Charged Polyelectrolyte in Good Solvent. *Macromolecules* **2008**, *41*, 6505–6510.
- (98) Ermi, B. D.; Amis, E. J. Influence of backbone solvation on small angle neutron scattering from polyelectrolyte solutions. *Macromolecules* **1997**, *30*, 6937–6942.
- (99) Nierlich, M.; Williams, C.; Boue, F.; Cotton, J.; Daoud, M.; Famoux, B.; Jannink, G.; Picot, C.; Moan, M.; Wolff, C.; Rinaudo, M.; de Gennes, P. Small angle neutron scattering by semi-dilute solutions of polyelectrolyte. *Journal de Physique* **1979**, *40*, 701–704.

# Graphical TOC Entry

