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# Influence of counterion type on the scattering of a semiflexible polyelectrolyte

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Understanding the influence of counterion and backbone solvation on the conformational and thermodynamic properties of polyelectrolytes in solution is one of the main open challenges in polyelectrolyte science. To address this problem, we study the scattering from semidilute solutions of a semiflexible polyelectrolyte, carboxymethyl cellulose (CMC) with alkaline and tetra-alkyl-ammonium (TAA) counterions in aqueous media using small-angle neutron scattering (SANS), and small-angle x-ray scattering (SAXS), which allow us to probe concentration fluctuations of the polymer backbone and counterions. In SAXS, the calculated contrast arises primarily from the polymer backbone for both alkaline and TAA salts of CMC. In SANS, however, the contrast is dominated by the counterions for the TAA salts and the polymer backbone for the alkaline salts. Solutions are found to display a correlation peak in their scattering function, which at low concentrations is independent of counterion type. At high concentrations, the peak positions obtained from SANS and SAXS for the CMC salts with the TAA counterions differ. This divergence suggests a decoupling in the lengthscale over which the counterions and the polymer fluctuate. Upturns in the scattering intensity in the low- $q$  region signal the presence of long-ranged compositional inhomogeneities in the solutions. The strength of these decreases with increasing counterion-solvent interaction strength, as measured by the viscosity  $B$  coefficient, and are strongest for the corresponding sodium salt of CMC.

## I. INTRODUCTION

Polyelectrolytes are polymers with charged groups covalently bonded to their backbone. The presence of these charges lends them an array of properties leading to a significantly different behaviour compared to their neutral counterparts.<sup>1-3</sup> These properties can be further modified by altering the interaction between the charges by, for instance, the addition of low molecular weight salts, or by varying the counterion type.<sup>3-10</sup> The importance of biological polyelectrolytes such as DNA, RNA, hyaluronic acid or proteoglycans makes understanding the physics of charged polymers crucial for understanding fundamental biological phenomena and molecular interactions.<sup>11-13</sup>

The role of counterion solvation, which was usually not considered in early polyelectrolyte solution theories<sup>14-19</sup>, has received attention in recent years<sup>5,20-23</sup> and is thought to be responsible for some of the hitherto unexplained phenomena in polyelectrolyte solutions, such as the low- $q$  upturn observed in the structure factor of solutions of low ionic strength. Several recent simulation studies discuss the effect of counterion solvation on the properties of polyelectrolyte solutions. For example, it is known that the relative quality of the solvent for the polymer backbone and counterions can influence the distribution of counterions around the chain.<sup>24</sup> Using a coarse-grained model of polyelectrolyte solutions with explicit solvents, Chremos and Douglas concluded that with increasing affinity of the counterions to the solvent, the solution becomes increasingly heterogeneous due to chain clustering.<sup>25,26</sup> This

phenomenon gave rise to a stronger upturn at low- $q$ , a phenomenon ubiquitously observed in synthetic polyelectrolytes, as well as proteins, and many other biomolecule solutions.<sup>20</sup> This finding was further backed by another molecular dynamics simulation study that investigated the effect of altering the relative solvation of the counterions and the backbone. The latter study indicated a stronger upturn at low- $q$  for a preferential solvation of the counterion.<sup>22</sup> Another Molecular dynamics (MD) simulation study found that the stronger solvation of the charged species (counterion and backbone alike) leads to the disappearance of the correlation peak and a strong low- $q$  upturn<sup>21</sup>, a behaviour observed in aggregan<sup>27</sup> and other highly charged bottlebrush polyelectrolyte molecules in which the sidegroups are highly hydrophilic. This was interpreted as arising from the appearance of short and long-ranged attractive forces induced by the better-solvated counterions, which leads to the formation of heterogeneous multichain structures. The work of Wang et al.<sup>28</sup> provides additional evidence for the importance of solvent-specific effects<sup>29</sup> on the electrostatic interactions between charged objects in solution, that is not captured by continuum electrostatics. According to their model, polar solvents can order around charged objects in a way that strongly depends on the sign of the charge on the object, suggesting another level of subtlety in the interactions between charged particles and polymers in solution.

The existence and behaviour of the multichain domains in polyelectrolyte solutions have been studied in the literature, primarily using dynamic light scattering (DLS).<sup>3,5,30-37</sup> These domains have been recognised as the source of the slow mode

on the DLS correlation curves, and the low- $q$  upturn in small-angle neutron scattering (SANS)/small-angle X-ray scattering (SAXS)<sup>35,38,39</sup> and have been found to exist for a range of systems. Their response to different stimuli, such as ionic strength<sup>31</sup> and mechanical filtration<sup>33,36</sup>, and their stability over time<sup>34</sup> have been reported. These domains have been found to be stable for long periods of time under no-added salt conditions for systems such as sodium polystyrene sulfonate, and ionised solutions of polyacrylic acid and polymethacrylic acid.<sup>34</sup> Filtering has been shown to transiently alter their properties and non-equilibrium effects have sometimes been observed.<sup>33,36</sup>

In the present work, we study the scattering of carboxymethyl cellulose aqueous solutions as a function of counterion type. Carboxymethyl cellulose (CMC) usually employed as its sodium salt NaCMC is a weak, semiflexible polyelectrolyte which is widely employed as a rheology modifier in food, drinks, pharmaceutical products and in drilling muds.<sup>40–43</sup> With a market size of over USD (United States Dollars) 1 billion<sup>44</sup>, it is the most widely employed cellulose ether as well as the most important ionic derivative of cellulose.<sup>45</sup>

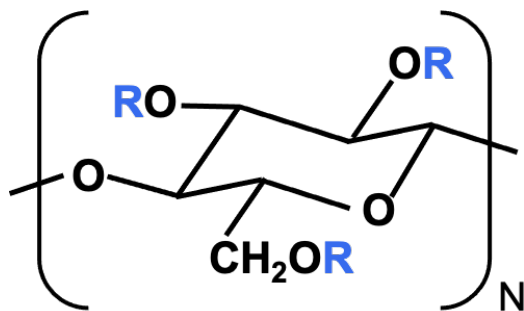


FIG. 1. Carboxymethyl cellulose monomer where  $R = H$  or  $CH_2COO^-X^+$  and  $X^+$  is the counterion. The degree of substitution is the number of  $R = CH_2COO^-X^+$  per monomer, out of a maximum of three.

The monomer structure of CMC is shown in Figure 1.  $R = H$  in all three positions corresponds to cellulose. The degree of substitution (DS) is the average number of  $R = CH_2COO^-X^+$  groups per monomer, out of a maximum of 3. The structural and rheological properties of NaCMC have been extensively studied in earlier publications.<sup>46–56</sup> Grades with  $DS \gtrsim 1$  are labelled as "highly substituted" and usually display "hydrophilic" behaviour in aqueous solution<sup>49,51</sup>, meaning that inter-chain associations are relatively weak and no crystalline aggregates of unsubstituted cellulose are present.<sup>47,48,57–60</sup> In aqueous solution, NaCMC displays a locally rigid conformation<sup>47,48,61</sup>, independent of degree of substitution. Its rheological properties in excess salt show similar features to those of other semiflexible polysaccharides (neutral or charged).<sup>40,62,63</sup> Despite extensive investigations into the properties of CMC, literature on the influence of counterion on the solution behaviour of CMC are limited to a few studies on their electrical conductivity.<sup>64,65</sup>

## II. BACKGROUND THEORY

The relatively expanded nature of polyelectrolytes in salt-free solutions, compared to their uncharged counterparts, means that the overlap concentration<sup>2,49</sup> is very low, and semidilute or concentrated solutions are usually of interest. The scaling theory of Dobrynin et al.<sup>14</sup> models semidilute polyelectrolyte solutions is based on the assumption of well dispersed chains with a characteristic mesh size known as the correlation length  $\xi$ , which, in the absence of added salts, is predicted to scale with concentration as,

$$\xi = \left(\frac{B_s}{bc}\right)^{1/2} \quad (1)$$

where  $b$  is the monomer length and  $B_s$  is a stretching parameter which quantifies the degree of folding of the polyelectrolyte chain inside a correlation blob. A value of  $B_s = 1$  corresponds to fully stretched chains and  $B_s > 1$  indicates local folding. While this is an idealized model that does not address the long-range attraction effects that arise from ion solvation, this model nonetheless captures many observed trends in polyelectrolyte solutions, and we refer to the predictions of this model in our discussion below.

For example, the predicted variation of  $\xi \propto c^{-1/2}$  from this model is consistent with reports on many experimental studies on flexible<sup>2,66–69</sup>, semiflexible<sup>47,48,61,70</sup> and rigid polyelectrolyte systems<sup>71</sup>. In this scaling model, the correlation length ( $\xi$ ) characterizes the lengthscale at which polyelectrolyte chains become flexible, in agreement with experimental observations for polystyrene sulfonate.<sup>72</sup>

Although a scaling exponent having a magnitude near 1/2 is common, this exponent is not universal. A scaling exponent value having a value near 1/3 has been observed in mucin bottlebrush polyelectrolytes<sup>73</sup> and proteoglycan molecules from cartilage<sup>74</sup> where strongly hydrating side-groups exist, as in the case of aggrecan. This exponent also matches the observation of Kaji et al. for polyelectrolytes in dilute solutions.<sup>75,76</sup> Chremos and Douglas<sup>26</sup> found by simulation with an explicit solvent that the magnitude of this scaling exponent can be reduced from 1/2 when the counterions or polymer are strongly hydrating and a smaller magnitude exponent has been observed in polyionene solutions with certain counterions.<sup>77</sup> Simulation and measurement also indicated an exponent having a value near 1/3 in star polymer polyelectrolytes<sup>78,79</sup> and an exponent value near 1/3 has been observed in dendrimer polyelectrolytes<sup>80,81</sup>, globular proteins<sup>82,83</sup> and other relatively compact-shaped charged polymers and charged particles such as charged micelles.<sup>84,85</sup> Changes in the value polyelectrolyte scaling exponent might then provide a clue about new physics in these solutions becoming important. We will see this situation arise below in our discussion of tetraalkylammonium counterions of carboxymethyl cellulose.

## A. Partial structure factors and scattering contrast

### SANS

Following the notation of van der Maarel et al.,<sup>86</sup>, the neutron scattering of a polyelectrolyte solution, in the absence of added salts can be written as:

$$I(q) = \rho_m \bar{b}_m^2 S_{mm}(q) + 2\sqrt{\rho_m \rho_c} (\bar{b}_m \bar{b}_c) S_{mc}(q) + \rho_c \bar{b}_c^2 S_{cc}(q) \quad (2)$$

where  $S(q)_{m,m}$ ,  $S(q)_{m,c}$  and  $S(q)_{c,c}$  are the partial structure factors, for monomer-monomer, monomer-counterion and counterion-counterion correlations respectively and  $\rho_m$  and  $\rho_c$  are the concentrations in number per unit volume for the monomer and the counterion respectively. If  $x$  is the degree of substitution,  $\rho_c = x \times \rho_m$ , and therefore:

$$\frac{I(q)}{\rho_m} = \bar{b}_m^2 S_{mm}(q) + 2\sqrt{x} (\bar{b}_m \bar{b}_c) S_{mc}(q) + x \bar{b}_c^2 S_{cc}(q) \quad (3)$$

The contrast factors for SANS are given by:

$$\bar{b}_i = b_i - b_s \frac{v_i}{v_s} \quad (4)$$

where  $b_i$  and  $v_i$  are the scattering length and volume of the unit. The subscript  $s$  refers to the solvent and  $i = c$  or  $i = m$ .

If the concentration fluctuations of counterions and the polymer backbone occur on the same lengthscale, which is expected, for example, if a large fraction of the counterions are condensed onto the backbone, we can simplify Eq. 2 using the approximation  $S_{m,m}(q) \simeq S_{m,c}(q) \simeq S_{c,c}(q)$ . The structure factor can then be calculated from the scattering intensity as:

$$S(q) \simeq (\bar{b}_{eff})^{-1} \frac{I(q)}{\rho_m} \quad (5)$$

where we define the effective contrast factor as:

$$\bar{b}_{eff} = \bar{b}_m^2 + 2\sqrt{x} (\bar{b}_m \bar{b}_c) + x \bar{b}_c^2 \quad (6)$$

### B. Scattering functions for semidilute polyelectrolyte solutions

The total structure factor  $S(q)$  can be written as the sum of an interparticle contribution, known as the form factor ( $P(q)$ ) and an intermolecular term  $H(q)$ :

$$S_{m,m}(q) = NP(q) + \rho H(q) \quad (7)$$

For sufficiently high wave-vectors,  $H(q) \simeq 0$ <sup>86,87</sup>, and we approximate  $S_{m,m} \simeq NP(q)$ . Chains are expected to be in a rigid configuration inside the correlation blob, so that for  $q \gg 2\pi/\xi$ ,  $P(q)$  may be approximated by the form factor of a rod<sup>86</sup>:

$$I(q) \simeq \rho_m \bar{b}_{eff} \left[ \frac{\pi}{b'q} \right] e^{-q^2 R_C^2/2} + I_{Bck} \quad (8)$$

where  $R_C$  is the cross-sectional radius of the chain,  $b'$  is the  $z$ -projected monomer length,  $c$  the concentration in number

of monomers per unit volume.<sup>88</sup> The term in square brackets corresponds to the form factor of an infinitely thin-rod and the exponential takes into account the finite lateral dimensions of the chain. The constant  $I_{Bck}$ , which is left as a free parameter accounts for the  $q$ -independent scattering. This includes contributions from incoherent scattering (spin incoherence), arising primarily from <sup>1</sup>H isotopes as well as coherent  $q$ -independent contributions (known as compositional incoherent or Laue scattering).

Polyelectrolytes, normally, display a peak in their scattering function at wave-vector  $q^*$ , which can be related to the correlation length as:<sup>14,16</sup>

$$\xi = \frac{2\pi}{q^*} \quad (9)$$

Experimentally, a large upturn in the scattering intensity is observed at low scattering wave-vectors, the origin of which remains controversial because the very low osmotic compressibility of salt-free polyelectrolyte solutions is expected to strongly suppress concentration fluctuations over long length-scales. The origin of the upturn has been assigned to multichain clusters of polyelectrolyte chains, undissolved aggregates, or long-ranged concentration fluctuations, as discussed in the introduction.<sup>20,35</sup> Simulations that have not included a description of solvation have not observed this phenomenon.

For wave-vectors  $R_{g,C} \lesssim q \ll 2\pi/q^*$ , where  $R_{g,C}$  is the radius of gyration of the clusters, the scattering intensity can be described by a power-law:

$$I(q) = Dq^{-m} \quad (10)$$

where  $m$  is the apparent fractal dimension of the clusters, which can take values between 1 (rod-like clusters) and 3 (compact clusters). Exponents larger than 3 are characteristic of surface fractals and compact objects with sharp interfaces.<sup>89,90</sup> Experimentally,  $m$  has been observed to vary between -4.3 to -2.1.<sup>35,47,48,91,92</sup>

For sufficiently small wave-vectors  $q \lesssim 1/R_{g,C}$ , the Guinier law describes the scattering intensity:

$$I(q) = I(0) e^{-q^2 R_{g,C}^2/3}$$

where  $I(0)$  is proportional to the contrast between the polyelectrolyte and solvent and the concentration of clusters and their molar mass. Most static scattering experiments, with few exceptions<sup>31,89</sup> do not cover a sufficiently broad  $q$ -range to make determination of the cluster size possible. Dynamic light scattering experiments yield apparent hydrodynamic sizes of the clusters in the range of a few hundred nanometers.<sup>89,93,94</sup>

## III. MATERIALS AND METHODS

**Materials:** NaCMC was purchased from Sigma-Aldrich, with a nominal mass average molar mass ( $M_w$ ) of 250 kg/mol and degree of substitution (DS) = 1.2. Characterisation of the sample in an earlier study<sup>93</sup> yielded  $M_w \simeq 2.1 \times 10^5$  g/mol

and DS = 1.3. The Spectra/Por dialysis membranes<sup>95</sup> with a Molecular Mass Cut-Off of 6 to 8 kDa were used and were purchased from VWR. A viscosity standard solution N2 purchased from VWR. The bases used for the preparation of CMC salts were acquired from Sigma Aldrich and their characteristics are reported in Table ST2 in the Supporting Information.

**Preparation of CMC salts:** As a precursor to the CMC salt preparation, the NaCMC was converted to its acid form (HCMC) by displacement using 0.1 mol/L HCl at pH  $\approx$  2 and then dialysing the resulting solution against DI water to remove the excess ions. The end point of the dialysis was determined by examining the conductivity of the dialysis bath at the point when the conductivity stayed below  $2 \mu\text{S cm}^{-1}$  beyond, at least, 4 h of the last exchange. The resulting solution was frozen using liquid nitrogen and dried under vacuum at a pressure of 0.4 mbar for 72 h to 96 h.

For the preparation of the CMC salts with alkali metal and quaternary ammonium counterions, the resulting dry HCMC was neutralized with excess of the respective bases. The neutralized solutions were again subjected to the same dialysis and freeze-drying process to obtain the pure salts.

**Sample preparation:** The CMC salts were stored in the vacuum freeze dryer for  $\approx$  24 h before any samples were prepared. The samples were prepared in polypropylene microcentrifuge tubes, previously washed with deionized (DI) water and dried at 60 °C. All the sample components were added by weight using a weighing balance with a least count of 0.1 mg and, therefore, a typical error of  $\pm$  0.05 mg.

**Densitometry:** The density measurements were performed using the Anton Paar DMA 5000 densitometer with a least count of  $10^{-6} \text{ g cm}^{-3}$ . The accuracy of the instrument was calibrated using DI water.

**Thermogravimetric Analysis:** The PerkinElmer STA 6000 was used for the thermogravimetric measurements to estimate the residual water content in all the CMCs. The sample temperature was increased to 120 °C at 10 °C/min, and was allowed to reach equilibrium. The temperature was then increased to 550 °C to estimate the point of CMC degradation.

**Conductivity and pH:** The conductivity measurements were made using the Mettler Toledo S47 SevenMulti conductivity meter. All the pH measurements were made using the Metrohm 744 pH meter at room temperature.

**Small-Angle Neutron Scattering:** The SANS measurements were carried out at NG30m at NIST Center for Neutron Research (NCNR), Maryland, USA, D11 at Institut Laue-Langevin (ILL), Grenoble, France and SANS-1 at Paul Scherrer Institute (PSI), Switzerland. The sample-to-detector distances (SDD) used at NCNR were 1.5 m and 7 m which covered a  $q$ -range of (0.003 to 0.42)  $\text{\AA}^{-1}$  ( $\lambda = 6 \text{ \AA}$ ). The measurements at D11 were performed at five different SDDs (1.7 m, 5.5 m, 8 m, 12 m and 28 m) covering a  $q$ -range of (0.002 to 0.55)  $\text{\AA}^{-1}$  ( $\lambda = 6 \text{ \AA}$ ). The measurements at SANS-1 were conducted at two different SDDs (3 m and 11 m) covering a  $q$ -range of (0.005 to 0.36)  $\text{\AA}^{-1}$  ( $\lambda = 6 \text{ \AA}$ ). The samples were measured in banjo cells with path lengths of 1 mm, 2 mm or 5 mm depending on polymer concentration. The reduced scattering intensities are tabulated in the supporting information.

**Small-Angle X-Ray Scattering:** The SAXS measurements were carried out at SPring-8, Hyogo, Japan and at the Institute of Physical Chemistry, Rheinisch-Westfälische Technische Hochschule (RWTH) Aachen using an in-house instrument. The sample-to-detector distances of 2 m and 4 m were used at SPring-8, providing a  $q$ -range of (0.0023 to 0.2)  $\text{\AA}^{-1}$  using a beam energy of 10 keV. A Peltier heating system was used to maintain the sample temperature at 25 °C. The in-house instrument consists of a 3-pinhole S-Max3000 system with a MicroMax002+ X-ray microfocus generator from Rigaku and a 2D multiwire detector with an active diameter of 200 mm. The sample-to-detector distance of 2.6 m was used, which covered a  $q$ -range of (0.005 to 0.4)  $\text{\AA}^{-1}$  ( $\lambda = 1.54 \text{ \AA}$ , Cu radiation). The samples were measured in sealed 1.5 mm borosilicate capillaries from WJM Glas Müller GmbH. The reduced scattering intensities are tabulated in the supporting information for all measurements.

All the measurements were performed at 25 °C, except the conductivity and pH measurements, which were carried out at room temperature ( $\approx$  22 °C). All the data for this study are provided in tabulated form in the supporting information.

## IV. RESULTS AND DISCUSSION

### A. Density measurements

The partial molar volume ( $\bar{v}$ ) of various CMC salts were determined from density measurements of solutions using:<sup>98</sup>

$$\bar{v} = \frac{1}{d_s} - \frac{1}{C} \left( \frac{d}{d_s} - 1 \right) \quad (11)$$

where  $d$  and  $d_s$  are the densities of the solution and the solvent ( $\text{H}_2\text{O}$  in all cases), and  $C$  is the concentration in units of mass of solute per volume of solution. The partial molar volume (PMV) of the CMC monomer without the counterion is estimated as follows: Firstly, the PMV of LiCMC was calculated from its solution density. This was used to determine the molar volume of the CMC monomer by subtracting the molar volume of  $\text{Li}^+$  ion obtained from literature<sup>96</sup>. Assuming that the contribution of the CMC monomer to the partial molar volume of the salt is independent of the counterion, we calculate  $\bar{v}$  for the various counterions studied, see table I. Values for the PMV of counterions available in literature have also been provided in the table. These are found to be in reasonable agreement with our data except for  $\text{K}^+$  and  $\text{Cs}^+$ .

Table I lists the contrast factors for the CMC monomer and the various counterions studied in  $\text{D}_2\text{O}$ . Both SANS and SAXS contrast factors for alkali salts in  $\text{D}_2\text{O}$  and  $\text{H}_2\text{O}$  respectively are dominated by the polymer backbone so that  $I(q) \propto S_{m,m}(q)$ . On the other hand, for the TAA salts in  $\text{D}_2\text{O}$ , the SANS contrast is dominated by the counterions, such that  $I(q) \propto S_{c,c}(q)$ . The SAXS contrast for the TAA salts in  $\text{H}_2\text{O}$ , however, arises primarily from the polymer backbone (Eq. 2). The contrast conditions are summarised in table II, see the supporting information for more details.

Scattering Unit	$b_i$ SANS [fm]	$b_i$ SAXS [fm]	$\bar{b}_i^{-2}$ SANS [fm <sup>2</sup> ]	$\bar{b}_i^{-2}$ SAXS [fm <sup>2</sup> ]	PMV (lit.) [cm <sup>3</sup> /mol]
CMC <sup>-</sup> Monomer	54.39	360.39	7680	22800	133.90
Li <sup>+</sup>	-1.90	5.64	7.7	18.8	0.83 <sup>a</sup>
Na <sup>+</sup>	3.63	28.2	1.0	591	2.47 (2.68 <sup>a</sup> )
K <sup>+</sup>	3.67	50.7	110	892.9	13.3 (6.63 <sup>a</sup> )
Cs <sup>+</sup>	5.42	155	960	10300	34.3 (12.39 <sup>a</sup> )
TMA <sup>+</sup>	-8.91	121	11030	418	90.6 (84.85 <sup>b</sup> )
TEA <sup>+</sup>	-12.24	211	3620	2610	168 (143.53 <sup>b</sup> )
TBA <sup>+</sup>	-18.90	392	141600	18200	337 (271.18 <sup>b</sup> )

TABLE I. SANS contrast factor ( $\bar{b}_i$ ) with respect to D<sub>2</sub>O (SANS) and H<sub>2</sub>O (SAXS) and partial molar volume for the CMC monomer (DS = 1.3) and the various counterions studied. The values in brackets for the PMV are taken from literature. <sup>a</sup>: Reference 96, <sup>b</sup>: Reference 97

Salts	SANS	SAXS
Alkaline	$I(q) \sim S_{mm}(q)$	$I(q) \sim S_{mm}(q)$
TAA	$I(q) \sim S_{cc}(q)$	$I(q) \sim S_{mm}(q)$

TABLE II. Contrast conditions for alkaline (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup> and Cs<sup>+</sup>) and tetra-alkyl-ammonium (alkyl = methyl, ethyl, butyl) salts.

## B. Influence of counterion on scattering properties of CMC

### 1. High- $q$ scattering: local conformation.

SANS profiles for the alkaline salts of CMC in D<sub>2</sub>O were fitted to Eq. 8. This requires three free parameters: The background term  $I_{Bck}$  (which contains contributions from spin and compositional incoherent scattering), the chain cross-sectional radius  $R_C$  and the pre-factor  $A$ , which is a function of polymer concentration and contrast. Following earlier work<sup>39</sup>, we set  $R_C = 3.5$  Å for all fits. The background term and the concentration are left as fitting parameters. The fitted concentration ( $c_{fit}$ ) is found to be  $\simeq 0.7 \times c_g$ , where  $c_g$  is the concentration calculated from the weights of the polymer and solvent used to prepare the solution. A part of the discrepancy between these two quantities may be taken to indicate a small amount of residual water in the polymer which is not removed by the freeze-drying process. This is confirmed by TGA experiments, which show a mass loss of  $\approx 5$  % for the tetrabutylammonium carboxymethyl cellulose (TBACMC) powder when heated to 120 °C under nitrogen, see figure S1. Further sources of error, which arise due to uncertainties in the calculation of the scattering contrast, are discussed in the supporting information. TGA experiments reveal a consistent mass loss of 5 % to 10 % upon heating to 120 °C for all the CMC salts studied, and in the following, we assume that to be the water content for all the freeze-dried polymers.

### 2. Mid- $q$ : The polyelectrolyte peak.

Figure 2 shows the SANS intensities for CMC with alkali counterions at  $c = 0.05$  mol/L and  $c = 0.15$  mol/L in D<sub>2</sub>O solution. The procedure for subtracting the background term follows our earlier discussion and is detailed in the supporting information curves display a correlation peak at  $q = q^*$ . The value of  $q^*$  is determined by fitting a polynomial to the

curves (see the supporting information), and found to be independent of counterion type, as indicated by the vertical lines. The peak intensity is seen to depend on the counterion type. These differences are primarily the result of the different scattering length densities of the ions. If the scattering intensity is normalised by the effective contrast (eq. 6), the resulting apparent structure factors  $S(q)$  largely overlap, as shown in the supporting information.

The SANS profiles of CMC with tetra-alkyl-ammonium counterions, where the alkyl chain = C1, C2 and C4 in D<sub>2</sub>O solutions are plotted in Figure 3a. At  $c = 0.05$  mol/L, there is no discernible influence of counterion type on the position of the maxima  $q^*$ . At  $c = 0.1$  mol/L, the correlation peak broadens and moves a lower  $q$  for the larger counterions (see SI). For sufficiently high concentrations ( $c \simeq 0.15$  mol/L), the peak in TBACMC solutions develops into a scattering plateau (i.e. no discernible maxima) where a polynomial fit is no longer possible. Here, we fit two linear functions to either side of the scattering plateau, following the approach of Salmon et al.,<sup>70</sup> and take their point of the intersection to be the 'position' of the scattering plateau. If this method is applied for samples with a distinct peak, the difference in  $q^*$  is always smaller than  $\approx 20$  %. A more detailed discussion of this can be found in the Supporting Information. The viscosity  $B$ -coefficients of tetraalkylammonium halide characterizing the relative strength of the hydration of these ions<sup>99,100</sup> are tabulated over a range of temperatures by Kay et al.<sup>101</sup> These ions are strongly kosmotropic, i.e., have large  $B$ -coefficient values), except for the case of tetramethylammonium ion, where the  $B$ -coefficient near 0.

The concentration dependence of the correlation length for the alkaline salts of CMC agrees well with the scaling prediction (Eq. 1), as expected based on previous SANS and SAXS studies on aqueous solutions of NaCMC.<sup>47,48,61</sup> Applying Eq. 1 and 9, the stretch parameter is estimated to be in the range of  $B_s \simeq 1.3 \pm 0.1$  for all samples, see table III. These values are similar to the stretch parameter of  $B_s \simeq 1.1 \pm 0.1$  reported by Lopez et al. for solutions of NaCMC with DS  $\simeq 1.06$ .<sup>47</sup>

The independence of the peak position on counterion type for the alkaline series contrasts with results for aqueous solutions of ionenes, where the scaling of the peak position with concentration of halide salts of the same polymer depends on the counterion.<sup>77,102,103</sup> Note that Kaji et al. report a weak dependence of the peak position on counterion type for the alkaline salts of poly(vinyl hydrogen sulfate).<sup>104</sup> These results

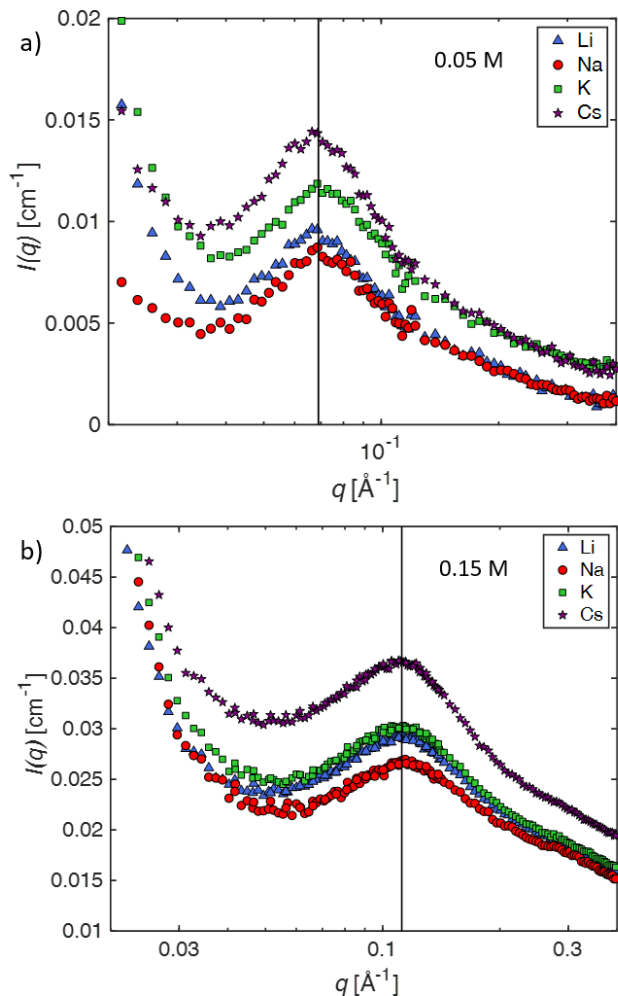


FIG. 2. Background subtracted scattering intensity as a function of scattering wavevector  $q$  for alkaline salts of CMC in salt-free  $D_2O$ , see legend for the colour scheme. a:  $c = 0.05$  mol/L and b:  $0.15$  mol/L. Lines indicate the peak positions (a:  $q^* = 0.069 \text{ \AA}^{-1}$ , b:  $q^* = 0.112 \text{ \AA}^{-1}$ ).

are apparently in line with the simulations observations of Chremos and coworkers discussed previously indicating that stronger ion and polymer solvation, acting together, can alter the concentration scaling of  $q^*$ .

The tetra-alkyl-ammonium salts of CMC display similar behaviour to the alkaline salts at low concentrations: the correlation length is independent of ion type, matching the values observed for alkaline CMCs (see Figure 4b), the maxima in  $S_{mm}(q)$  and  $S_{cc}(q)$  coincide and the common scaling  $q^* \sim c^{1/2}$  is observed. These observations are in agreement with the literature reports for polystyrene sulfonate (PSS). Prabhu et al. report the correlation lengths for TMAPSS in  $D_2O$  ( $3.7 < c < 46$  g/L), measured by SANS<sup>105</sup>, which are nearly identical values to those reported for NaPSS in  $H_2O$  obtained using SANS and SAXS.<sup>75,106–109</sup>

At high concentrations, the behaviour of TAA salts differs in several ways from those of alkaline salts. First, the peak

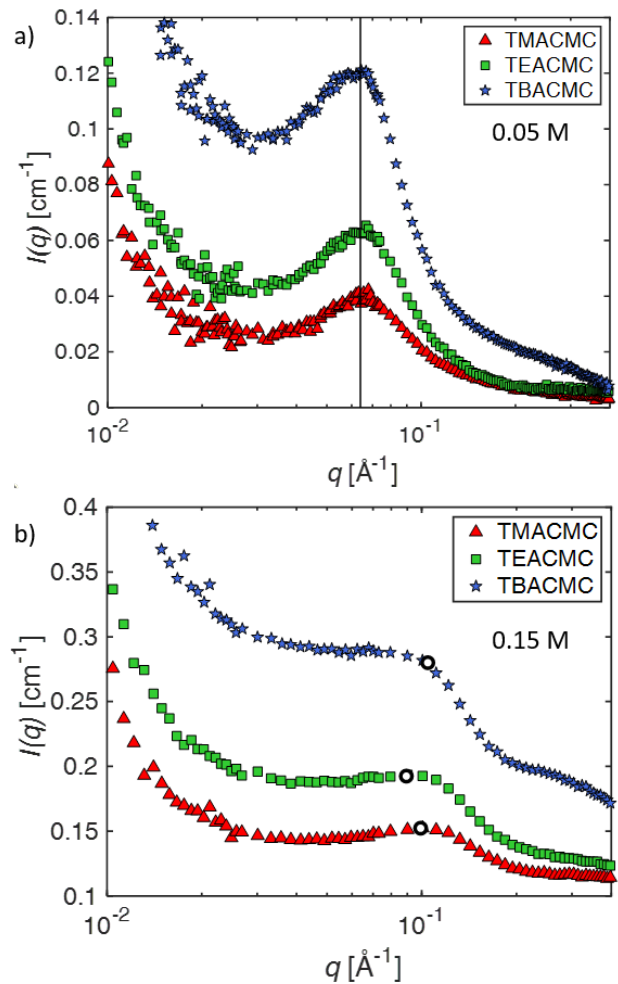


FIG. 3. Scattering intensity  $I$  as a function of scattering wavevector  $q$  for tetra-alkylammonium salts of CMC, see legend for colour scheme. a:  $c = 0.05$  mol/L and b:  $0.15$  mol/L. The line indicates the position of the peaks at that concentration ( $q^* = 0.064 \text{ \AA}^{-1}$ ). The hollow points represent the peak positions in TMACMC and TEACMC and the scattering plateau position in TBACMC.

position in the SANS signal, which measures  $S_{cc}(q)$ , shifts to lower  $q$  values and its shape becomes broader, eventually morphing into a scattering plateau. The magnitude of these changes depends on the length of the alkyl chain, with larger ions showing more pronounced effects, see for example 4b. The maxima in the SAXS signal, which corresponds approximately to  $S_{mm}(q)$  is almost the same as for the alkaline counterions. These results indicate that 1) polymer mesh size (inferred from  $q^*$ ) is not strongly influenced by the nature of the counterions and 2) the concentration fluctuations of the polymer backbone and the counterions become decoupled at high concentrations if the counterions are hydrophobic.

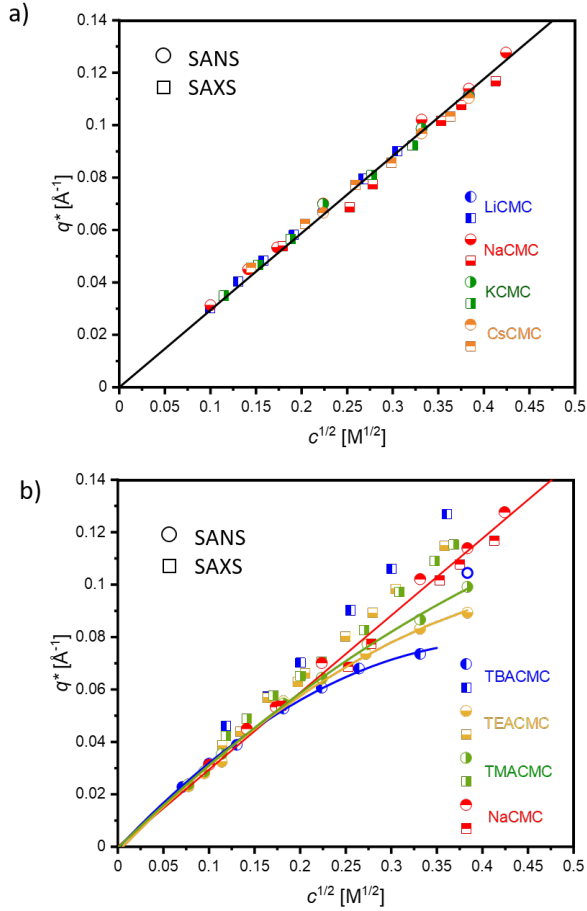


FIG. 4. Peak positions ( $q^*$ ) as determined from SANS (circles) and SAXS (squares) curves for CMCs with a) alkaline and b) tetra-alkylammonium counterions in water as a function of concentration, see legend for the colour scheme. Hollow symbols are for the fit scattering plateaus.

CMC salt	$B_{s,SANS}$	$c$ -range [M]	$B_{s,SAXS}$	$c$ -range [M]
LiCMC	1.4	0.05 to 0.147		
NaCMC	1.2	0.01 to 0.18	1.4	0.033 - 0.15
KCMC	1.36	0.05 to 0.147		
CsCMC	1.43	0.05 to 0.147	1.3	0.02 - 0.07
TMACMC	1.22	0.006 to 0.033	1.0	0.014 - 0.04
TEACMC	1.32	0.006 to 0.05	1.03	0.013 - 0.039
TBACMC	1.18	0.003 to 0.017	0.89	0.014 - 0.13

TABLE III.  $B_s$ -parameter estimated from SANS and SAXS measurements using Eq. 1 over the concentration ranges indicated.

### 3. The low- $q$ upturn: large scale inhomogeneities.

Figure 5a plots the scattering intensity of carboxymethyl cellulose with four different counterions at a concentration of  $c = 0.11$  mol/L. The low- $q$  upturn can be fitted to a power-law in the low- $q$  region (Eq.10), although it is unclear if the data follow a single power-law over a wide  $q$ -range. The

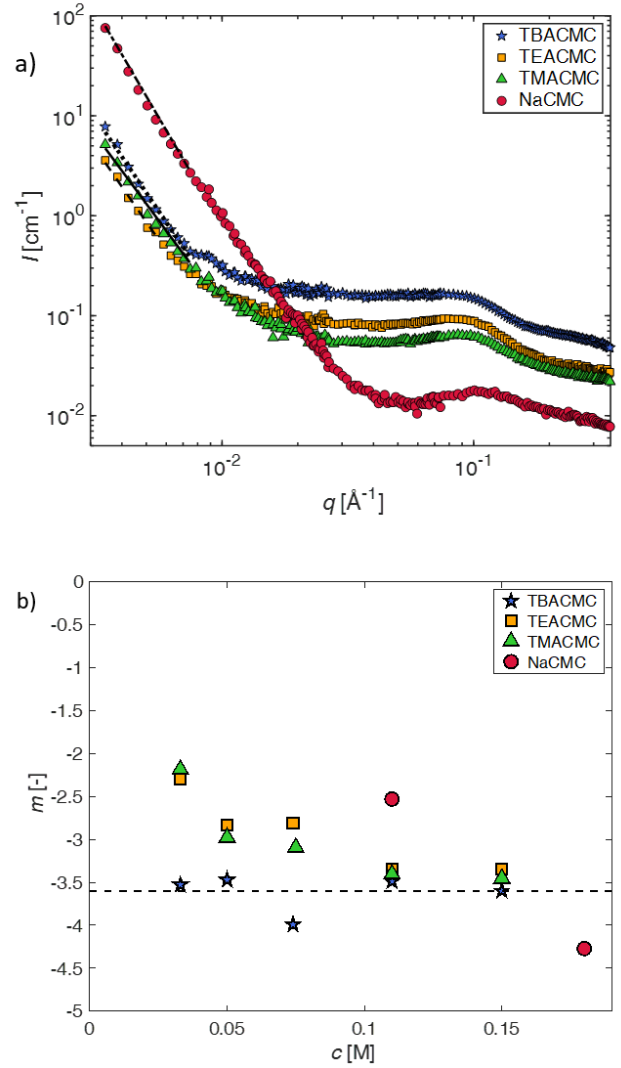


FIG. 5. a: Scattering intensity of CMC with different counterions for a fixed concentration of  $c = 0.11$  mol/L. Lines are power-law fits (Eq. 10) to the low- $q$  upturn region. b: best-fit exponent  $-m$  as a function of polymer concentration for various salts of CMC.

best-fit exponent is plotted as a function of concentration in figure 5b. The exponent for the TMA and TEA salts shows a decrease with concentration, and for  $c \geq 0.11$  mol/L it converges with the value  $m \approx 3.6$  observed for TBACMC over the entire concentration range, indicated by the dashed line. The same value was reported by Lopez et al. for NaCMC in  $D_2O$  in an earlier study.<sup>39</sup> The large value of the exponents suggests that the entities responsible for the upturn are surface fractals or have diffuse interfaces.

The pre-factor,  $D$ , to the low- $q$  power-law in Eq. 10 is plotted as a function of ion type in Figure 6a for  $c = 0.11$  mol/L and  $c = 0.15$  mol/L. For this plot, we use fits with the exponent  $m$  fixed to a value of 3.6, so that the units of the pre-factor are independent of concentration. We have divided  $D$  by  $\bar{b}_{eff}$  to reduce the influence of neutron contrast. Further, we compare the scattering intensity at the lowest measured wave vec-



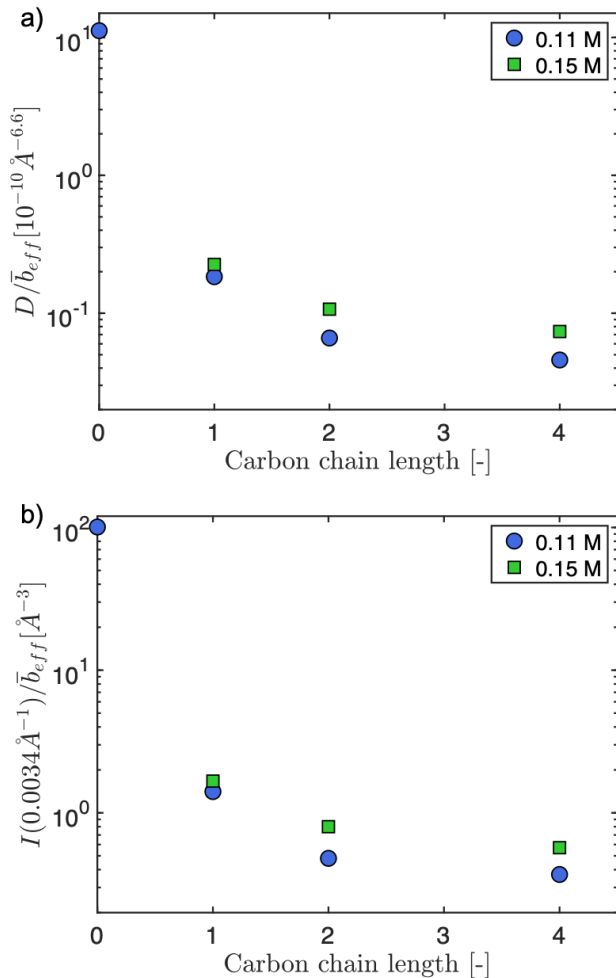


FIG. 6. a: Pre-factor to clustering power-law ( $D$ ), normalised by effective scattering contrast ( $\bar{b}_{eff}$ ) as a function of counterion type. The parameter  $D/\bar{b}_{eff}$  serves as a measure of clustering strength. b: scattering intensity at  $q = 0.0034 \text{ \AA}^{-1}$  normalised by effective contrast. Data for carbon chain length = 0 is for NaCMC.

tor ( $q = 0.0034 \text{ \AA}^{-1}$ ) at  $c = 0.11 \text{ mol/L}$  for the various salts studied. Lacking a more rigorous framework to evaluate the low- $q$  region, both  $D/\bar{b}_{eff}$  and  $I(0.0034 \text{ \AA}^{-1})/\bar{b}_{eff}$  serve as measures for the 'clustering strength'. The trends observed in figure 6 therefore support an earlier finding by molecular dynamics simulations<sup>26</sup> that preferential counterion solvation can lead to enhanced clustering in polyelectrolyte solutions. The general increase of the clustering strength parallels the growth of the viscosity  $B$ -coefficient values<sup>101</sup> of the tetra-alkylammonium counterions.

## V. CONCLUSIONS

We have studied the scattering properties of semiflexible polyelectrolyte carboxymethyl cellulose with different counterions in aqueous solutions. The correlation peak of the var-

ious alkaline salts studied follows the same  $q^* \propto c^{1/2}$  scaling law and the peak positions measured by SANS and SAXS agree, indicating that concentration fluctuations of the polymer backbone and counterions occur on approximately the same lengthscales.

Solutions with hydrophobic counterions display similar features to the alkaline salts at low concentrations. However, beyond a characteristic concentration, a different scaling behaviour emerges. First, in this regime, the  $c$ -dependence of  $q^*$ , obtained from SANS, becomes increasingly weaker with an increasing degree of counterion hydrophobicity. However, the  $q^* \propto c^{1/2}$  scaling persists in the results obtained from SAXS, even for the most hydrophobic counterion studied. We interpret this as a "decoupling" of the concentration fluctuations of the polymer backbone and counterions, but we, currently, lack any convincing explanation for the physical mechanism underpinning this behaviour. A further examination of the nature of counterion-solvent interactions using other techniques, such as rheology, could provide better insights into this behaviour. Another key observation at higher concentrations is the broadening of the SANS correlation peaks with increasing counterion hydrophobicity. This is accompanied by a shift in the correlation peak position as well.

As with other polyelectrolyte systems, the solutions studied here displayed an upturn at low  $q$ , which signals the presence of large-scale inhomogeneities in the solution. A comparison of solutions of sodium and tetra-alkyl-ammonium salts of CMC revealed that the clustering intensity, when adjusted for contrast, *decreases* as the viscosity  $B$ -coefficient becomes larger or the ions become more kosmotropic.<sup>99-101</sup> Interpreting this trend in  $B$  coefficient values is non-trivial however since the tetra-alkylammonium ions with larger  $B$ -coefficients are also larger in size and presumably more "hydrophobic". The nature of hydration in these complex ions requires further investigation.

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## VII. DATA AVAILABILITY STATEMENT

All the scattering datasets from this study are included in xls format as supporting information.

## VIII. AUTHOR CONTRIBUTIONS

CRedit: **Anish Gulati**: formal analysis, investigation, data curation, methodology, writing-original draft, writing-review & editing. **Jack F. Douglas**: formal analysis, investigation, writing-original draft, writing-review & editing. **Olga Mat-sarskaia**: data curation, investigation, methodology, writing-review & editing. **Carlos G. Lopez**: conceptualization, formal analysis, funding acquisition, investigation, data curation, methodology, supervision, writing-original draft, writing-review & editing.

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