Supporting Information: Influence of counterion type on the scattering of a semiflexible polyelectrolyte

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I. PARTIAL MOLAR VOLUME CALCULATION

The partial molar volume for Lithium carboxymethyl cellulose (LiCMC) was calculated from the density of the 5 g/L aqueous LiCMC solution as follows:

$$\bar{v} = \frac{1}{\rho_s} - \frac{1}{C}\left(\frac{\rho}{\rho_s} - 1\right) \tag{1}$$

where $\bar{v}$ is the partial molar volume (PMV), C is the concentration in g/mL, ρ_s is the solvent density and ρ is the solution density.

$$\bar{v} = \frac{1}{0.99705} - \frac{1}{0.005339}\left(\frac{0.999465}{0.99705} - 1\right)$$

$$v_m = \bar{v} * M_0 \tag{2}$$

where v_m is the molar volume and M_0 is the mass average molecular mass.

$$v_m(CMC) = v_m(LiCMC) - v_m(Li^+)$$

$$v_m(CMC) = 134.74 - 0.83 = 133.91$$

$$v_m(X^+) = v_m(XCMC) - v_m(CMC) \tag{3}$$

where X represents the respective counterion. The LiCMC solution density was found to be 0.999465 g/mL and, hence, its PMV ($\bar{v}$) was calculated to be 0.5493 g/cm^3. The molar volume (v_m) was calculated as the product of $\bar{v}$ and its molar mass (245.29 g/mol). v_m for Li$^+$ was taken from the literature to be 0.83 cm^3/mol. On subtracting this from v_m(LiCMC) (134.74 cm^3/mol), v_m(CMC) was calculated to be 133.91 cm^3/mol. This was used to calculate the v_m for each counterion by subtracting it from the v_m for the respective salt for CMC.

II. LOW-Q UPTURN EXPONENTS

Table ST1 lists the low-q upturn exponents for the various CMC salts in D$_2$O at different concentrations determined as shown in figure 5 in the main text.

III. BASES USED FOR CMC PREPARATION

PE	c [mol/L]	Exponent (m)
TBACMC	0.15	-3.6
TBACMC	0.11	-3.5
TBACMC	0.074	-4.0
TBACMC	0.05	-3.5
TBACMC	0.033	-3.5
TEACMC	0.15	-3.4
TEACMC	0.11	-3.4
TEACMC	0.074	-2.8
TEACMC	0.05	-2.8
TEACMC	0.033	-2.3
TMACMC	0.15	-3.5
TMACMC	0.11	-3.4
TMACMC	0.075	-3.1
TMACMC	0.05	-3.0
TMACMC	0.033	-2.2
NaCMC	0.11	-2.5
NaCMC	0.18	-4.3

TABLE ST1. Low-q upturn exponents for the different CMC salts in D_2O.

Base	Grade/Purity	Notes
LiOH	99.95%	Trace Metals basis
KOH	8.0 M	by HCl titration
CsOH	99.9%	Trace Metals basis
TMAOH	25 wt.% in H_2O	Quality Level 200
TEAOH	35 wt.% in H_2O	Quality Level 100
TBAOH	20 wt.% in H_2O	Quality Level 100

TABLE ST2. Bases used for the preparation of CMC salts
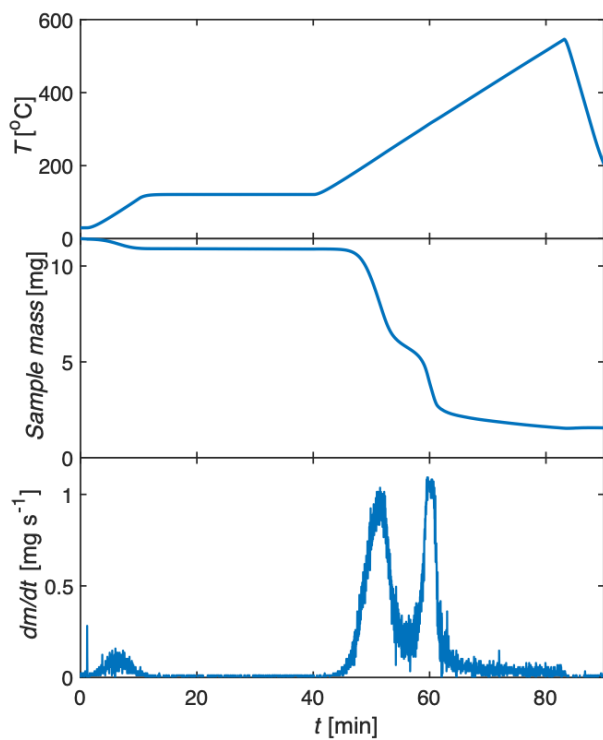

FIG. S1. Thermogravimetric analysis for tetrabutylammonium carboxymethyl cellulose (TBACMC) under N_2
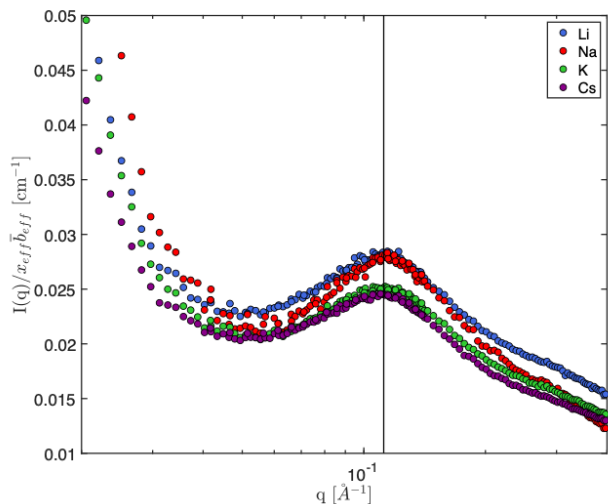
FIG. S2. Background subtracted SANS scattering intensity (normalized by the respective effective contrasts) as a function of scattering wavevector q for alkaline salts of CMC in salt-free D_2O, see legend for colour scheme at $c = 0.15$ mol/L. The line indicates the peak positions ($q^* = 0.112$ Å^{-1}).
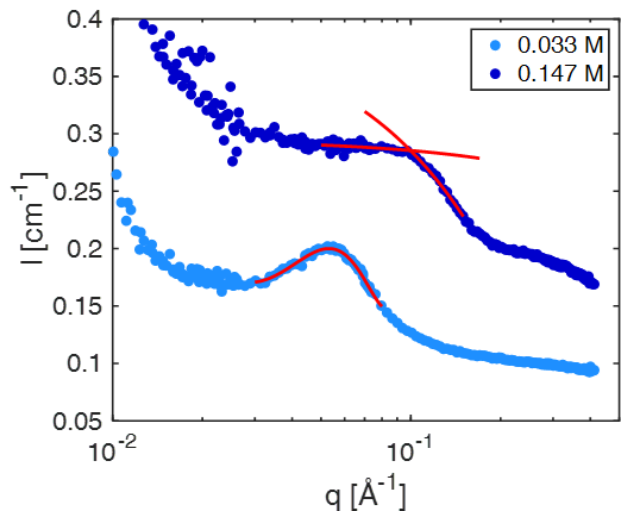

FIG. S3. Representative plot to illustrate the fitting methods used to determine the peak/shoulder position from scattering intensity vs wavevector q curves. This plot shows the scattering curves for TBACMC in D_2O. At $c = 0.033$ M, a polynomial fit has been used to fit a distinct peak to determine the correlation peak position (q^*). At $c = 0.147$, q^* has been determined from the crossover point of the two linear curves fit to either side of the shoulder.
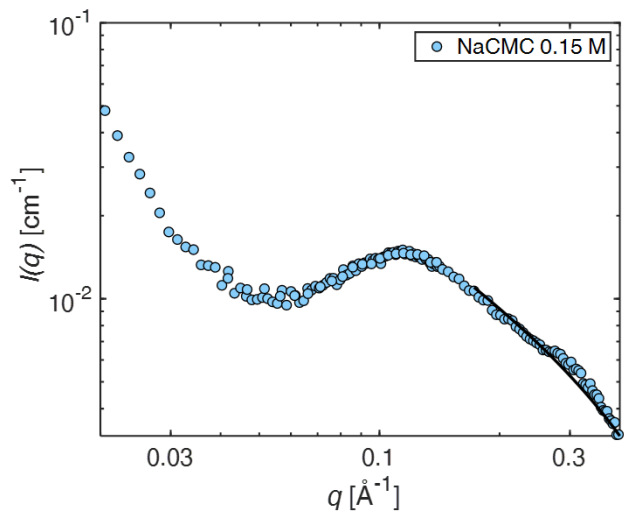
FIG. S4. Representative plot to illustrate the fit to equation 8 of the main text to the high-q region ($q \geq 1.5q^*$) of the non-background subtracted scattering intensity vs wavevector q curves. This fit (solid black line) is used to determine the factor I_{Bck}, which is then subtracted from the total scattering intensities at each wavevector to compute the background subtracted scattering curves. This plot shows the scattering curves for NaCMC in D_2O at $c = 0.15$ M