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Test of Oosawa–Manning condensation in a semiflexible polyelectrolyte across solvents of varying Bjerrum length

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Abstract

The effective charge of polyelectrolytes is a crucial parameter that determines their conformational and thermodynamic properties in solution. The Oosawa–Manning condensation model predicts that when the distance between charges becomes smaller than the Bjerrum length (l_B), additional charges condense onto the backbone, rendering the effective charge independent of the chemical charge density. This implies that above the condensation threshold the effective charge is inversely proportional to l_B. This prediction has remained largely untested due to the limited solubility of common polyelectrolytes in apolar media. Here we use a semiflexible polyelectrolyte, carboxymethyl cellulose with organic counterions, which extends its solubility across a wide range of solvents, enabling a test over a broad range of l_B. The effective charge is found to be inversely proportional to l_B in the low dielectric region and independent of l_B when $l_B \lesssim 0.7$ nm, in agreement with the theory.

1 Introduction

The distribution of counterions around charged polymers in solution governs their thermodynamic and transport properties.[1, 2, 3] Oosawa[4, 5] and Manning[6] predicted that when the linear charge density on the backbone exceeds one charge per Bjerrum length (l_B) counterions condense onto the backbone, renormalising the effective charge to this limiting value. The fraction of monomers with a free counterion is:

$$f = \frac{1}{uZ_C}, \tag{1}$$

where $u = l_B/b_c$ is the coupling parameter, b_c is the distance between charged groups on the backbone and Z_C is the counterion valence.

Although Eq. 1 is derived for isolated chains, it applies in semidilute solutions above the overlap concentration, as shown experimentally by Wandrey et al[7] and explained theoretically by Tang and Rubinstein.[8] Equation 1 yields three predictions for $u > 1$:

(i) for a given solvent (i.e., fixed dielectric constant) the effective charge is independent of the chemical charge density,

(ii) the fraction of monomers with a dissociated counterions is inversely proportional to the counterion valence,

(iii) for the same polymer in different solvents, the effective charge density scales inversely with l_B.

The first two of these predictions have been tested experimentally[9, 2, 10, 11] but the dependence of the effective charge on l_B remains largely unexplored because of the limited solubility of common polyelectrolytes in non-aqueous media. Here we test this prediction using carboxymethyl cellulose (CMC), a highly charged, semiflexible polyelectrolyte ($\simeq 0.97$ carboxymethyl units per glucose unit, Kuhn length $\simeq 10$ nm)[12]. We study the sodium and tetrabutylammonium (TBA) salts, the latter due to its broad solubility in organic media.[13]

2 Determination of effective charge fraction

The fraction of free counterions is obtained from electrical conductivity using the model of Colby et al:[14, 15]

$$\Lambda = f\left[\lambda_0 + f\frac{k_BT}{6\pi\eta_s\xi}\ln\left(\frac{\xi}{D}\right)\right], \tag{2}$$

where λ_0 is the limiting molar conductivity of the counterion, η_s the solvent viscosity, ξ the correlation length, and D the chain diameter. We take $D = 7$ Å from previous work.[16] The values of λ_0 were obtained from ref. [17] for pure solvents and interpolated for solvent mixtures assuming $\lambda_0 \propto 1/\eta_s$.

Equation 2 can be used to calculate the fraction of free counterions from the electrical conductivity of a solution if the correlation length is known. Example results for the scattering profiles of TBACMC in dimethylformamide (DMF) are shown in figure 1a. The correlation length is obtained from the SAXS patterns as $\xi = 2\pi/q^*$, where q^* is the scattering wave-vector at the maxima of the correlation peak. For some mixed solvents, the value of ξ in mixed solvents was obtained by interpolating the value between pure solvents. A power-law relation between ξ and c is obtained (fig 1b) and Eq. 2 is applied to conductivity data to calculate f as a function of concentration. The value of f is found to be independent of concentration, as shown in fig. 1c. The average value of f over all measured concentrations is taken to correspond to the f value in that particular solvent. The same procedure as in figure 1 was applied to 35 solvents or solvent mixtures to cover a very broad range of dielectric permittivity ($\epsilon_r \simeq 180 - 20$). Results over a narrower dielectric constant range for NaCMC were reported in an earlier publication.[18]

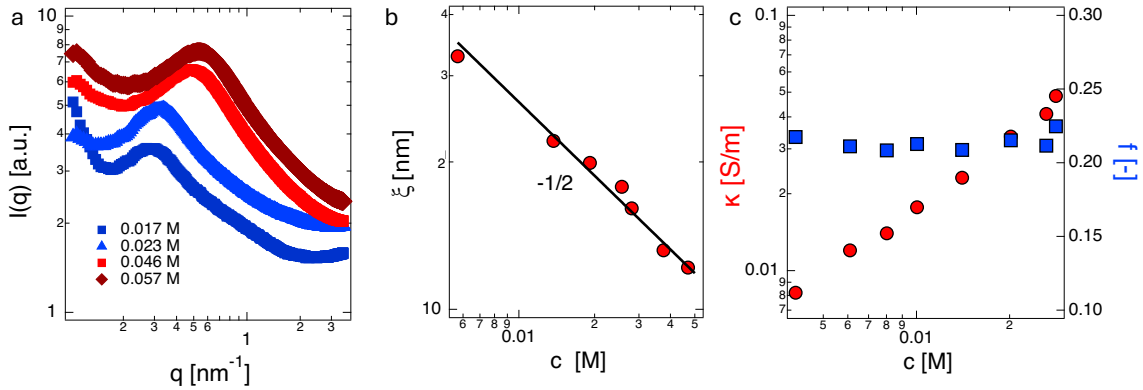

Figure 1. a: SAXS patterns for TBACMC in DMF solutions without added salts. b: Correlation length as a function of concentration. Line is a best-fit with the exponent forced to the theoretical value of -1/2. c: electrical conductivity of TBACMC solutions in DMF as a function of concentration (red symbols) and calculated fraction of monomers with a free counterions (blue symbols).

3 Test of Oosawa-Manning theory

Figure 2 plots f as a function of l_B for NaCMC and TBACMC. The data for both salts of CMC fall onto a single curve, indicating minimal role of counterion-solvent interaction effects. When the Bjerrum length decreases below $\simeq 0.5$ nm, f plateaus. This value is close to the average distance between charges ($b/DS \simeq 0.53$ nm). At larger Bjerrum lengths, f decreases as $1/l_B$. Both features are in agreement with the Oosawa and Manning theories, but the experimental data consistently lie below Eq. 1, shown by the dashed line. Manning[19] predicts that f obtained from conductivity is $\simeq \times 0.87$ lower than the fraction of free counterions because the motion of free counterions is slowed down by the electric field of the polyion, this is shown by the full line in fig. 2, and agrees with the data within $\simeq 15\%$. The remaining discrepancy is most likely due to the limited accuracy of Eq. 2. Specific ion effects are unlikely, as no systematic deviation is observed between NaCMC and TBACMC, and experimental scatter is too small to account for the offset. This interpretation is consistent with our earlier finding that the conductivity/SAXS method tends to underestimate f relative to osmotic pressure and potentiometric measurements.

These results provide direct experimental validation of the predicted dependence on Bjerrum length. This contrasts with earlier studies on flexible polyelectrolytes,[20, 2] where $f \propto l_B^{-1}$ was not observed. In those cases, f was inferred from chain size or intrinsic viscosity, requiring assumptions that link chain conformation to effective charge. Additionally, for flexible chains the distance between charges may depend on the polyion's effective charge, complicating the application of

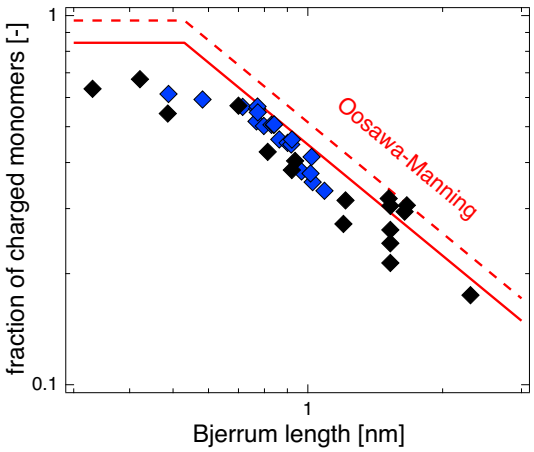

Figure 2. Fraction of monomers with a free counterion, f, as a function of solvent Bjerrum length for sodium (blue diamonds) and tetrabutylammonium (black squares) salts of CMC. Dashed line is the theory of Oosawa, where we identify f from Eq. 2 with the fraction of free counterions in Oosawa's two-phase model. The full line is Manning's theory, which expects f from electrical conductivity to be $\simeq 0.87\times$ the fraction of free counterions.

Eq. 1. In CMC, the large persistence length suppresses this coupling, enabling a direct test of the theory.

4 Conclusions

SAXS and conductivity measurements on the semiflexible polyelectrolyte carboxymethyl cellulose across a broad range of solvent dielectric constants provide direct experimental support for the central prediction of the Oosawa–Manning theory. It remains an open question whether the inverse proportionality between charge fraction and solvent Bjerrum length predicted by the OM theory also applies to flexible polyelectrolytes, where the effective distance between charges may depend on the charge fraction.

Materials and Methods

Chemicals: Sodium carboxymethylcellulose (NaCMC) and the solvents methanol (99.8%, suitable for EPA 1613), ethanol (99.5%, EMSURE), 2-propanol (99.5%), acetone (99.5%, EMSURE), ethyl methyl ketone (99%), ethylene glycol (99.9%, EMSURE), dimethyl sulfoxide (99.9%, EMSURE), *N*,*N*-dimethylformamide (99.8%) and *N*-methylacetamide (99%) were procured from Sigma-Aldrich. The NaCMC used was the same as in ref. [18], with a molar mass of 360 kg mol^{-1}.

The NaCMC was dialysed against excess hydrochloric acid until the initial mixture pH was below 2 to obtain HCMC. The HCMC was subsequently neutralised with TBAOH until the initial pH was around 13 and dialysed against DI water. Both dialyses were deemed complete when the conductivity of the external water was approximately 2×10^{-4} S m^{-1}, measured using a SevenMulti Dual pH/conductivity meter (Mettler Toledo).

Conductivity: A SevenMulti Dual pH/conductivity meter equipped with a Cond Sensor InLab 710 probe (Mettler Toledo) was used. The probe was immersed in 10 mL polypropylene vials containing 3–4 mL of sample. The vial was placed in a temperature-controlled water bath, with the probe sensor positioned below the bath water level. Measurements were recorded once both the bath sensor and the conductivity meter indicated a temperature of 25 °C.

SAXS: Scattering data for TBACMC in various solvents were collected at beamline BL40B2 at SPring-8. Detector distances of 1 m and 2 m were used, corresponding to q-ranges of 0.009–0.78 Å^{-1}, 0.0047–0.37 Å^{-1} and 0.0023–0.2 Å^{-1}, respectively. The beam energy was approximately 12 keV.

Sample temperature was controlled using a Peltier unit and set to 25 °C for all samples, except for TBACMC in pure *N*-methylacetamide, where it was set to 35 °C.

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