Structural evidence of charge renormalization in semi-dilute solutions of highly charged polyelectrolytes

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Abstract. We show experimentally that Manning counterion condensation also leads to a renormalization of the charge density at high concentrations of highly charged, flexible, hydrophilic polyelectrolytes. Investigations by small angle neutron and X-ray scattering of semi-dilute solutions of poly(acrylamide-co-sodium-2-acrylamido-2-methylpropane sulfonate) at different charge densities above the condensation threshold, show that the scattering function is invariant with the charge density.

PACS. 61.25.Hq Macromolecular and polymer solutions; polymer melts; swelling – 61.10.Eq X-ray scattering (including small-angle scattering) – 61.12.Ex Neutron scattering techniques (including small-angle scattering)

1 Introduction

Polyelectrolytes contain a variable proportion of ionizable monomers. In polar solvents such as water, the charges are dissociated; the charges of one sign are localized on the chain whereas the counterions, of opposite sign, are mobile in the solution. The linear charge density is an important parameter which regulates the behaviour of a polyelectrolyte chain. When the distance between charges along the chain, b, is such that the coulombic interaction is smaller than \( k_B T \), entropic effects have to be taken into account. In the opposite limit, for highly charged polyelectrolytes, \( b \) is small and the solution behaviour is dominated by electrostatic interactions. This strong coupling regime starts at \( b = l_B = e^2/\varepsilon kT \), where \( l_B \) is the Bjerrum length; in water at \( T = 25°C \), \( l_B = 7.13\,\text{Å} \). Thus for vinylic polymers it corresponds to a linear charge density \( f \) of about 0.36. Above that charge density the electrostatic potential at the chain becomes very large and some counterions are confined in a small volume around the chain in order to reduce the electrostatic interactions between monomers. Thus the chain has an effective charge density \( f_{\text{eff}} \) smaller than the nominal charge density \( f \). The concept of counterion condensation \([1,2]\) has been first formalized by Manning who found that the effective charge is renormalized to a constant value such that \( b = l_B \) above a condensation threshold \([3]\). A large body of experimental data have confirmed the validity of the model at sufficiently high dilution.

At higher concentrations the situation is less clear. Various calculations \([4–6]\) have attempted to take into account the effects of finite concentration on charge renormalization, also including possible effects on the chain conformation and have predicted strong deviations from Manning’s model for the single chain. Attractive interactions have also been found between chains surrounded by their sheath of counterions. Measurement of the effective charge is difficult in that concentration range, mostly due to the complex structure of concentrated polyelectrolyte solutions which prevents the determination of the amount of free counterions by the usual techniques, e.g. osmometry, electrical conductivity or electrophoretic mobility.

The semi-dilute, salt-free solutions of intrinsically flexible, highly charged polyelectrolytes are well described by de Gennes’ isotropic model in which the entangled chains form an isotropic transient network \([7,8]\). The mesh size of the network, also called correlation length \( \xi \), is the most important feature of the model. On length scales smaller than \( \xi \) the portions of the chain are extended, similarly to their conformation in dilute solution. But on length scales larger than \( \xi \) the chain obeys random walk statistics. \( \xi \) is independent of the chain length \( N \) and is of the same order as (but not necessarily equal to \([9]\)) the Debye-Hückel screening length \( \kappa^{-1} = (\varepsilon kT/4\pi e^2 c)^{1/2} \) where \( c \) is the number of free counterions that are able to move in order to screen
the electrostatic interactions in the solution. Hence measuring $\xi$ provides a way of monitoring the amount of free (and therefore of condensed) counterions in the solution. Scattering techniques are most adequate to this end since they probe directly the monomer pair correlations at different length scales [10]. It is particularly easy to probe $\xi$ in polyelectrolyte solutions since one signature of the model is the existence of a broad maximum in the light, X-ray and neutron small angle scattering intensity profiles whose position scales as $\xi^{-1}$ [11–13].

Previous experiments have shown that below the condensation limit and at constant polymer concentration in the semi-dilute regime, the position of the peak was a function of the charge fraction $f$; it scaled first as $f^{1/3}$ then leveled off slowly [14]. Above the condensation limit it remained constant [15]. In this paper we want to extend our previous measurements and give more evidence to the interpretation that a charge renormalization does indeed take place for highly charged chains in semi-dilute solutions, akin to Manning’s condensation for single chains. This conclusion is reached not only by monitoring the position of the broad peak but also by showing the invariance of all those structural properties which depend only on electrostatic interaction, when the charge density is varied above the onset of Manning condensation for a single chain.

Comparison of X-ray and neutron scattering (SAXS and SANS) measurements allows one to obtain complementary information on the chains and the counterions since the origin of the contrast is different; both the chain and its counterions contribute to the X-ray intensity whereas the counterions are not seen by neutrons. The polymer is a random copolymer of acrylamide and sodium-2-acrylamido-2-methyl propane sulfonate, with a hydrophilic backbone so that the hydrophobic interactions which could alter the solution properties remain negligible [16]. It should be added that at the same nominal charge fractions as those investigated here, i.e. between 0.3 and 1, direct osmotic pressure measurements at very low concentrations have demonstrated that the effective charge is renormalized according to Manning’s model for single chains [17]. In what follows, the effect of the charge fraction on the SAXS and SANS structural features will be analyzed at constant polymer concentration in the semi-dilute regime. Then for each charge fraction the effect of polymer concentration and added salt concentration will be investigated independently.

2 Experimental section

Poly(acrylamide-co-sodium-2-acrylamido-2-methylpropa-
ne sulfonate), abbreviated as AMAMPS, was synthesized by radical copolymerisation of acrylamide with acry-
lamido methyl propane sulfonic acid according to a standard procedure [18] which was optimized to obtain highly charged polyelectrolytes. The charge density was varied between 0.3 and 1, above the onset of Manning condensation for a single chain. The polymers had a $M_w = 670 000$ and a polydispersity $M_w/M_n = 2.6$.

Semi-dilute solutions were prepared by dissolving the desired amount of dry polyelectrolyte in deionised H$_2$O (for SAXS) or D$_2$O (for SANS) with a conductivity of about 0.05 $\mu$S and let to rest for two days before investigation. All concentrations are expressed in monomole/l., using an average molecular weight for the monomers at each chain composition. For the SAXS measurements, the samples were enclosed in 1.2 mm thick cells with 50 $\mu$m kapton windows. For the SANS measurements, the samples were put in 5 mm thick cells with quartz windows. All measurements were performed at room temperature.

The structure of the solutions has been analysed by Small Angle X-ray Scattering (SAXS) and Small Angle Neutrons Scattering (SANS). SAXS measurements were performed on beam line D22 at LURE (Orsay, France) using the DCI synchrotron radiation source. The intense beam was monochromated with two Ge (111) parallel crystals to a wavelength $\lambda = 1.37$ Å ($\Delta \lambda/\lambda = \text{a few} 10^{-3}$) and collimated to 0.5 × 0.5 mm$^2$ at the sample. The scattered X-ray-photons were detected by a gas filled, one dimensional position sensitive detector with a resolution of 217 $\mu$m. The scattering vector $q \left( q = (4\pi/\lambda)\sin(\theta/2) \right)$, where $\theta$ is the observation angle) was varied from 0.005 to 0.35 Å$^{-1}$ by using two sample-to-detector distances $D$ of 930 mm and 1630 mm. The recorded intensity was corrected for incident beam intensity, sample thickness and transmission and a background scattering was subtracted. The scattering profiles are plotted as intensity $I(q)$ versus $q$, in relative units. Absolute measurements would require multiplying by a constant instrumental factor and by the chain/solvent contrast.

SANS measurements were performed on the PACE spectrometer, at the Orphée reactor, Laboratoire Léon Brillouin (Saclay, France). The wavelength was set by a velocity selector. To cover a $q$-range between 0.003 and 0.08 Å$^{-1}$, two set-ups were used, characterized by $D = 5$ m, $\lambda = 8$ Å ($\Delta \lambda/\lambda = 0.1$) and $D = 2$ m, $\lambda = 9.5$ Å. The scattered intensity was recorded by a multidetector with 30 concentric, 1 cm wide rings. The response of each ring was normalized to the (flat) incoherent scattering of water. The recorded intensity was corrected for sample thickness and transmission, incoherent and background scattering. Using direct beam measurements the intensities are obtained in absolute units of cross-section [19]; they are then divided by the contrast factor $K^2$ [20], to yield the structure factor $S(q)$. The SANS data are plotted as $S(q)$ versus $q$. For all profiles the peak position was determined as the centerpoint of the full width at half-maximum.

3 Results

In order to investigate the effect of the chain charge content on the overall structure of the solution, the polymer concentration and the concentration of added salt have been varied systematically for each charge fraction in a range between 0.3 and 1. The main features of the scattering profiles of semi-dilute solutions of flexible polyelectrolytes have been described at length previously ([21] and