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Abstract. We present a study of the clustering counterion of iodine counterions around a cationic rodlike polyelectrolyte in aqueous solution. The novel synthetic polyelectrolyte used here has a poly(p-phenylene) backbone and can be considered as rodlike in good approximation. The correlation of the counterions with the macroion in aqueous solution is determined by small-angle x-ray scattering which is mainly sensitive to the I^- counterions. The measured intensities agree with the prediction of the Poisson–Boltzmann cell model if radius of the macroion is treated as an adjustable parameter. The small value of radius of the macroion found here shows that the cell model underestimates the correlation of the counterions to the macroion.

1. Introduction

The clustering of counterions around highly charged macromolecules in solutions was predicted a long time ago [1, 2]. Due to the strong electric field of the macroions, a fraction of the counterions will be 'condensed' on the macroion [3, 4]. Depending on ionic strength, the charges along the chains will more or less be screened and the interaction between the charges and the dissolved macroions can be tuned by adding salt. In case of flexible polyelectrolytes the increased repulsive interaction between the charged groups in salt-free solutions will be followed by a stretching of the coiled macromolecules [5–7]. The coupling between electrostatic interaction and chain conformation in case of flexible polyelectrolytes is still not fully understood [6–8]. Rodlike polyelectrolytes, however, retain their shape regardless of the strength of electrostatic interaction and present theoretically much simpler systems. Hence, rodlike polyelectrolytes present ideal model systems to study the correlation of counterions with the macroion in solution, in particular when comparing the experimental result to the predictions of the classical cell model of rodlike polyelectrolytes [1, 2, 9–12]. In addition to this, the possible counterion-mediated attractive interactions between rodlike macroions in solutions can be investigated by use of these systems [13, 14].

While rodlike polyelectrolytes have been the subject of intense theoretical research for these reasons, the number of experimental studies is still scarce. This is due to the fact that most of the model polyelectrolytes studied so far, e.g. poly(styrenesulphonate), are based on flexible backbones [10]. Helical polymers, e.g. DNA [9, 10], or colloidal structures like certain viruses, e.g the TMV virus [15], or wormlike micellar structures [16] that assume a nearly rodlike shape

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in solution may provide model systems for cylindrical polyelectrolytes. The extended shape of these structures, however, is restricted to certain concentrations, temperatures or solution conditions which may hamper seriously a comprehensive study of rodlike polyelectrolytes.

Recently, we presented a novel class of rodlike polyelectrolyte based on the poly(*p*-phenylene) backbone (PPP) [17]. The fully aromatic backbone exhibits a excellent chemical stability and has a persistence length which is ∼20 nm [18]. The degree of polymerization is located between 20 and 40 so that the contour length equals approximately one persistence length at most. Therefore these polyelectrolytes present nearly ideal model systems for the study of rodlike macroions in solution.

Here we give a first account of our recent investigations of the cationic PPP-polyelectrolyte **1** (figure 1) by small-angle x-ray scattering (SAXS). The goal of this investigation is to elucidate the spatial distribution of the counterions around the macroions and to compare the results to the prediction of the Poisson–Boltzmann (PB) cell model [1, 12]. Small-angle scattering methods such as SAXS and small-angle neutron scattering (SANS) have been repeatedly used to study the counterion cloud around dissolved polyelectrolytes (see [19–22] and further citations given there). In many cases the contributions of the macroion to the measured SAXS intensity $I(q)$ ($q = (4\pi/\lambda \sin(\theta/2))$; λ: wavelength of the used radiation; θ: scattering angle) exceeds by far the one of the counterions. For these systems SANS is indispensable since the contrast can be adjusted by appropriate mixtures of H_2O and D_2O [23]. The hydrocarbon backbone of polyelectrolyte **1**, however, exhibits a low excess electron density in water. Hence, its SAXS intensity is small and the contribution of the counterions may become the leading term. By changing the counterions from Cl^- to I^- the contrast can be changed quite drastically: while the electron density of Cl^- ions is nearly matched by water, I^- ions exhibit a strong contrast in aqueous solution. Hence, if I^- counterions are used, their correlation with the macroion should be easily visible. In the case of Cl^- counterions, on the other hand, the measured scattering intensity mainly originates from the macroions.
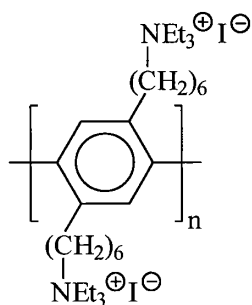

Figure 1. Chemical structure of polyelectrolyte **1**.

2. Experiment

The polyelectrolyte **1** has been synthesized as described recently through a precursor route [17]. The uncharged precursor can be characterized by NMR spectroscopy and osmometry. The degree of substitution of the polyelectrolyte was higher than 99% as determined by NMR spectroscopy. Purification was achieved by prolonged reverse osmosis against pure water (Millipore Milli-Qplus). From synthesis iodine counterions result that may be exchanged with Cl^- ions through ultrafiltration using 0.2 M KCl solution. Afterwards the KCl solution is
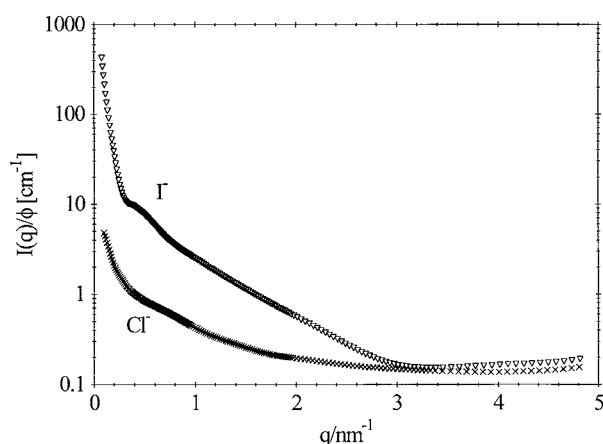
Figure 2. SAXS scattering intensity of polyelectrolyte **1** in salt-free solution as a function of the magnitude of the scattering vector q. Upper curve: iodine counterions; lower curve: chlorine counterions. Both measurements have been taken at a polymer concentration of 19.9 g l^{-1}. The data have been normalized to the volume fraction ϕ of the polyelectrolyte.

replaced by pure water again and the reverse osmosis is continued until all co-ions are removed.

SAXS measurements were performed on dilute solutions of **1** in pure water using a Kratky Kompakt camera supplied by Paar (Graz, Austria). Details of the measurements and the data corrections are described elsewhere [24]. In all cases to be discussed here absolute intensities have been obtained. The partial specific volume v_2 of polyelectrolyte **1** having Cl$^-$ or I$^-$ counterions was determined by measuring the density of dilute aqueous solutions of **1** by use of a DMA60 apparatus (Paar, Graz, Austria). The value of $v_2 = 0.80$ cm^3 g^{-1} obtained from these measurements served for the calculation of the volume fraction ϕ of the dissolved polymer through $\phi = (N/V)v_2$.

3. Theory

The absolute scattering intensities $I(q)$ following from SAXS measurements may be rendered as [25]

$$I(q) = \frac{N}{V} I_0(q) S(q) \tag{1}$$

where N/V is the number of dissolved polyelectrolyte molecules per volume. $S(q)$ is the structure factor which takes into account the effect of intermolecular interferences. Its influence is restricted to the region of small scattering angles. The scattering intensity $I_0(q)$ of a single rodlike polyelectrolyte molecule can be formulated as [19, 23]

$$I_0(q) = \int_0^1 [F(q, \alpha)]^2 \, d\alpha \tag{2}$$

where α is the cosine of the angle between the scattering vector q and the long axis of the molecule. The scattering amplitude of the rod with orientation α follows as

$$F(q, \alpha) = L \frac{\sin(qaL/2)}{qaL/2} \int_0^\infty \Delta\rho(r_c) J_0[qr_c(1 - \alpha^2)^{1/2}] 2\pi r_c \, dr_c. \tag{3}$$

The measured scattering intensity $I_0(q)$ is thus related to the Hankel transform of the radial excess electron density $\Delta\rho(r_c)$ that may be calculated from the radial density of the macroions

and the distribution of the counterions around the macroion. Since the macroion has a small radius termed a its radial electron density may be rendered in good approximation by a constant excess electron density $\Delta\rho_{rod}$. This quantity in turn may derived from the partial specific volume of the macroion in solution.

The counterion distribution function $n(r_c)$ may be calculated from the solution of the Poisson–Boltzmann equation within the frame of the cell model [1, 12]. Here the polyelectrolyte is characterized by the charge parameter ξ which is defined through the ratio of the Bjerrum length λ_B to the contour distance per unit charge b:

$$\xi = \frac{\lambda_B}{b} \tag{4}$$

with λ_B being defined through

$$\lambda_B = \frac{e^2}{4\pi\varepsilon_0\varepsilon k_B T} \tag{5}$$

where e is unit charge, ε the dielectric constant of the medium and ε_0, k_B and T have their usual meanings. In order to obtain $n(r_c)$ the solution of uniform cylindrical polyelectrolytes of length L is treated as a system of N parallel rods. The cell radius R_0 follows from the number concentration N/V of the rods as $(N/V)\pi R_0^2 L = 1$. The distribution function $n(r_c)$ is given by [12]

$$\frac{n(r_c)}{n(R_0)} = \left\{ \frac{2|\beta|}{\kappa r_c \cos[\beta \ln(r_c/R_M)]} \right\}^2.$$

From the known parameters ξ, a, R_0 the first integration constant can be obtained through

$$\arctan\left(\frac{\xi-1}{\beta}\right) + \arctan\left(\frac{1}{\beta}\right) - \beta \ln\left(\frac{R_0}{a}\right) = 0.$$

The second integration constant R_M may be regarded as the radial distance within which the counterions are condensed [12]. It follows as

$$R_M = a \exp\left[\frac{1}{\beta}\arctan\left(\frac{\xi-1}{\beta}\right)\right]. \tag{6}$$

The screening constant κ and the number $n(R_0)$ of counterions at the cell boundary are related through $\kappa = 8\pi\lambda_B n(R_0) = 4(1+\beta^2)/R_0^2$.

With $n(r_c)$ being known, the excess electron density within the cell, i.e. for $a \leqslant r_c \leqslant R_0$, the integration equation (3) can be performed. The number of excess electrons per counterion $\Delta\rho_{ci}$ can be calculated in good approximation by use of their crystallographic radii. For I^- we obtain $\Delta\rho_{ci} = 39$ e$^-$/ion whereas for Cl^- a value of 11 excess electrons per ion results. Hence, $\Delta\rho(r_c)$ follows as

$$\Delta\rho(r_c)\begin{cases} = \Delta\rho_{rod} & 0 \leqslant r_c \leqslant a \\ = n(r_c)\Delta\rho_{ci} & a < r_c \leqslant R_0 \\ = 0 & r_c > R_0. \end{cases} \tag{7}$$

Insertion of (7) into (3) and subsequent numerical integration of (3) and (2) then leads to the scattering intensity $I_0(q)$. The total scattering intensity of a system of non-interacting rods follows from equation (1) with $S(q) = 1$.

4. Results and discussion

Figure 2 displays the absolute SAXS scattering intensities of polyelectrolyte **1** in aqueous solution. The upper curve refers to **1** with I^- counterions whereas the lower curve shows the SAXS intensity resulting for **1** having Cl^- counterions. In both cases salt-free solutions with a polymer concentration of $19.9 \, g \, l^{-1}$ have been measured at $25 \, °C$. The scattering intensities obtained for both systems as a function of q may be roughly subdivided into three regions. In an intermediate q-range both curves decrease roughly as q^{-1} whereas in the region of smallest values ($q < 0.4 \, nm^{-1}$) there is a strong rise of the measured scattering intensity $I(q)$. At highest q-values ($q > 2.8 \, nm^{-1}$) both curves merge and increase again with rising q. It must be noted that in both cases the good contrast allows us to take measurements up to high scattering angles with sufficient accuracy. This allows a meaningful discussion of both curves in the q-range displayed in figure 2.
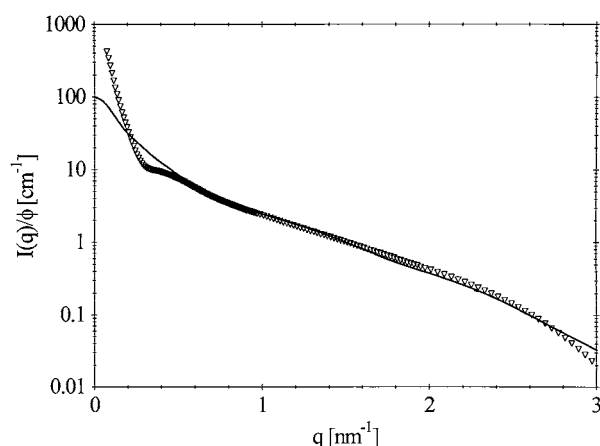
Figure 3. Comparison of measured and calculated scattering intensities. The triangles give the SAXS intensity of a solution of polyelectrolyte **1** in water whereas the solid line displays the optimal fit by equations (2) and (3).

It is immediately obvious that changing the counterions from Cl^- to I^- leads to a strong increase of the measured scattering intensity. As mentioned above the Cl^- ions have a much smaller contrast than the I^- ions. Hence, $I(q)$ measured for solutions of **1** with Cl^- counterions is governed by the scattering intensity of the macroions. The much higher scattering intensity measured for solutions of **1** with I^- counterions as compared to $I(q)$ measured for Cl^- counterions must therefore be traced back to the counterions themselves. Evidently, a solution of free iodine ions in water would not lead to a strong increase of $I(q)$ because in this case the intensities of single ions add up. If n is the number of counterions per volume, the scattering intensity extrapolated to vanishing scattering angle scales with n. If the counterions are strongly correlated to macroion, however, their amplitudes add up (cf equation (3)) and the forward scattering of a single macroion $I_0(q–0)$ scales with n^2. The marked difference of both scattering curves therefore points immediately to a strong correlation of most of the counterions with the macroions, i.e. to the effect of a strong clustering of the counterions around the macroion [3, 4].

At high q-values both curves merge within given limits of error. Also, $I(q)$ is increasing, which cannot be explained by equation (2). We assign this additional scattering contribution to the hydrocarbon side chains which constitute no rigid part of the macroion but their

conformation will exhibit spatial fluctuations. A further reason for this term may be given by fluctuations of the cloud of counterions parallel to the macroion. These fluctuations are not included in the mean-field description of the cell model (equation (4)) and may cause a weak attraction between the macroions and have been the subject of recent theoretical considerations [13, 14]. Both terms have no cross term with the scattering amplitude of the macroion because these fluctuations are statistically independent. Their contribution can therefore be subtracted using techniques developed recently for the analysis of polymer latexes [26]. Details of this procedure will be given elsewhere [24].

From its structure charge parameter $\xi = 3.3$, all other parameters necessary for the fit are fixed experimentally. The only adjustable parameter a is given by the minimum distance to which counterions may approach the macroion. This distance is identical to the sum of the radii of counterion and the macroion. In the cell model the counterions are treated as point-like objects. Therefore this minimum distance is given by the radius a of the macroion. In the fit procedure a is treated as an adjustable parameter.

Figure 3 gives the comparison of measured and calculated scattering intensities for **1** having I^- counterions. For the fit according to equations (2) and (3) data have only been taken for q-values greater 0.49 nm^{-1}. Good agreement of theory and experiment can be achieved for these data. Trial calculations have shown that for $q > 0.49$ nm^{-1} the influence of mutual interactions of the polyelectrolytes may be safely dismissed. The deviations of theory and experiment for $q < 0.49$ nm^{-1} point to a strong correlation of the macroions in solutions and indicates a weak attractive interaction between the rods. The interactions of the macroions **1** will be treated elsewhere [24].

The resulting fit of the data is displayed in figure 3. From this fit the radius a of the macroion follows as 0.7 nm. This figure is considerably smaller than the value which would follow from the density of **1** in solution (minimum distance of contact of macroion and I^- counterions: ~ 1 nm). No meaningful description of the present data would be possible if the value of $a = 1$ nm were assumed. This finding shows that the correlation of the counterion to the macroion is significantly stronger than predicted by the cell model: a smaller value of a within the frame of the PB-cell model indicates a much higher concentration of the counterions at the surface of the macroion than anticipated from structural data of polyelectrolyte **1**. This is in accord with recent measurements of the osmotic coefficient of **1** in aqueous solution conducted in our laboratory [27] which show that the density of osmotically active ions is significantly smaller than calculated from the cell model.

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