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Short Communication

Effect of Solvent Quality on the Behaviour of Highly Charged Polyelectrolytes

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Résumé. — Une étude par diffusion de RX aux petits angles et émission de fluorescence de solutions aqueuses de polystyrène sulfonate de sodium (squelette hydrophobe) et de 2-acrylamido-2-méthyl-propane sulfonate de sodium (squelette hydrophile) a montré l'importance de la qualité du solvant sur la structure de ces solutions. La fraction de monomères chargés, entre 0,35 et 1, est supérieure au seuil de condensation de Manning-Oosawa pour les contre-ions. Le polyélectrolyte hydrophile suit qualitativement les modèles théoriques proposés, contrairement au polyélectrolyte hydrophobe dont le comportement ne peut être confronté aux prédictions théoriques.

Abstract. — We show experimentally that the solutions properties of highly charged polyelectrolytes depend on the solvent quality for the backbone. Sulfonated Polystyrene, with hydrophobic backbone, and Poly(acrylamide-co-sodium-2-acrylamido-2-methylpropane sulfonate), with hydrophilic backbone, have been investigated by SAXS and fluorescence emission in a charge fraction range between 0.35 and 1, above the onset of Manning-Oosawa counterion condensation. The hydrophilic polyelectrolyte follows the prediction of the current models whereas the behaviour of polystyrene sulfonate cannot be reconciled with any existing model.

1. Introduction

Polyelectrolytes are polymer chains containing ionizable groups. Once dissolved in a suitable polar solvent such as water, the ions pairs dissociate. The electrostatic charges of one sign are localized on the chain, whereas the oppositely charged counterions are scattered in whole the solution. For highly charged chains, this dissociation will lead to prohibitively high coulombic...
repulsion between the chain charges. Such system evolves to a more stable state characterised by weaker repulsive interactions monitored by the counterion condensation. This approach is based on the Manning-Oosawa [1, 2] theory which relies on a reduced charge parameter \( l_b/b \) where \( b \) is the average linear charge spacing between charges along the polyion chain and \( l_b \), the Bjerrum length is the distance where the thermal energy exactly compensates the coulombic interaction i.e. \( l_b = e^2/\varepsilon k T \) where \( e \) is the electron charge, \( \varepsilon \) the dielectric constant of the solvent, \( k \) the Boltzmann constant and \( T \) the absolute temperature.

When \( l_b/b < 1 \), all counterions are free in the solution. When \( l_b/b > 1 \), it is assumed that sufficient counterions will "condense" on to the polyion to renormalize the reduced charge parameter to unity; thus a fraction \( 1 - 1/(l_b/b) \) of the charged monomers, in the case of monovalent counterions, is completely neutralised by the condensation of the counterions on the chain.

In water, at room temperature \( l_b = 7.12 \, \text{Å} \). For most synthetic polyelectrolytes, based on a polyvinylic backbone, the monomer size is of the order of 2.5 Å and thus the condition \( l_b/b > 1 \) for counterion condensation will hold for all charge contents larger than about 0.35. In this regime, the fraction of condensed counterions will increase with \( f \) to reach a constant effective charge density on the order of 0.35. Consequently for these polyelectrolytes, the electrostatic interactions are equivalent and thus all characteristic features that are governed by the electrostatics of the chain should not vary. Among them, the structure of the solution, as evidenced by its small angle scattering properties.

In the semi-dilute regime, the chains are entangled and form an isotropic transient network. In the scaling picture [3–5] the solution is described by a dense assembly of blobs of size \( \xi \), the correlation length, which is of the same order as the Debye electrostatic screening length \( K_p^{-1} (K_p^2 = 4\pi \varepsilon c e^2/\varepsilon k T = 4\pi \varepsilon c l_b \) where \( c \) is the concentration of free counterions). At length scales smaller than \( \xi \), electrostatic forces are dominant and the polyelectrolyte has a rodlike conformation similar to that in dilute solution. For scales larger than \( \xi \), the interactions are screened out and each chain is a random walk.

This isotropic model is characterised in reciprocal space, by a broad peak in the scattering profile whose position depends on \( \xi^{-1} \) and thus scales with polymer concentration \( c_p \) as \( c_p^{1/2} \). This dependence has been verified for a large domain of concentration by means of light, neutrons and X-ray scattering [6–8] particularly for fully charged polystyrene sulfonate (\( f = 1 \)).

If the fraction of charged monomers is lowered \( (f < 1) \), at constant polymer concentration, but still above the onset of polymer condensation \( (f \geq 0.35) \), it is predicted that the position of the scattering peak should remain unchanged since the number of free counterions remains constant. Scattering experiments should therefore provide a sensitive test of the model.

The aim of this paper is to show that this prediction is not verified in the case of poly(styrene-co-styrene sulfonate) (PSS) where the peak position is found to vary almost linearly with \( f \) in the range \( 0.3 < f < 1 \). This behaviour will be contrasted to that of poly(acrylamide-co-sodium-2-acrylamido-2-methylpropane sulfonate) (AMAMPS), where the peak position is constant in the same conditions. The results will be discussed in terms of solvent quality since PSS has a very hydrophobic backbone as opposed to the hydrophilic AMAMPS backbone.

### 2. Experimental Section

The chemical structure of the polymers used in this study are shown in Figure 1. A random copolymer of styrene and Na styrene sulfonate (PSS) was prepared by post sulfonation of polystyrene (\( M_w = 250000 \) and a polydispersity = 2) based on the Makowski procedure [9, 10]. The charge density was varied between 1 (fully charged) and 0.3 (the limit of solubility in
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N°9

PSSNa

\[(\text{CH-CH}_2)_{x}-(\text{CH-CH}_2)_{y} \quad f = x/x+y\]

SO$_3$Na

SAMPS

\[(\text{CH-CH}_2)_{x}-(\text{CH-CH}_2)_{y} \quad f = x/x+y\]

\[\text{C}=\text{O} \quad \text{NH-C(CH}_3)_2\text{-CH}_2\text{-SO}_3\text{Na}\]

AMAMPS

\[(\text{CH-CH}_2)_{x}-(\text{CH-CH}_2)_{y} \quad f = x/x+y\]

\[\text{C}=\text{O} \quad \text{NH}_2 \quad \text{NH-C(CH}_3)_2\text{-CH}_2\text{-SO}_3\text{Na}\]

Fig. 1. — Chemical structure of the polyelectrolytes used in this study

water), a range never explored before this study. Poly(acrylamide-co-sodium-2-acrylamido-2-methylpropane sulfonate) was synthesized by copolymerisation of acrylamide with methyl propane sulfonic acid according to a standard procedure [11] which was slightly modified to obtain highly charged polyelectrolytes.

The structure of the solution has been measured by the Small Angle X ray Scattering (SAXS). SAXS measurements were performed on beam line D22, at L.U.R.E using the DCI synchrotron radiation source. The intense beam was monochromated with two Ge (111) parallel crystals to a wavelength $\lambda = 1.37$ Å and collimated to $0.5 \times 0.5$ mm$^2$. The scattered X ray-photons were detected with a one dimensional position sensitive detector with a resolution of 217 μm. The explored q range was included between 0.005 and 0.22 Å$^{-1}$ ($q = 4\pi \sin \theta/\lambda$, where $q$ is one half the scattering angle). “Salt-free” semi dilute solutions at a concentration of 0.32 monomol l$^{-1}$ were prepared by dissolving the dry polyelectrolyte in deionized water at 50 °C for 30 minutes, then let to rest for two days at room temperature before the investigation. Great care was taken to keep the residual salt concentration at a minimum value ($\approx 10^{-5}$ mol l$^{-1}$). For the SAXS measurements, the samples were enclosed in a 1.2 mm thick cell with 50 μm kapton windows. The resulting scattered intensity was corrected for the incident beam intensity, the sample thickness and transmission and the background scattering.

Fluorescence measurements of pyrene in dilute solutions of $2.72 \times 10^{-2}$ monomol l$^{-1}$ of PSS or AMAMPS in water were performed. The pyrene was first dissolved in ethanol at a concentration of $6 \times 10^{-4}$ mol l$^{-1}$ and was then added to the polyelectrolyte solutions up to a final concentration of $6 \times 10^{-7}$ mol l$^{-1}$. The fluorescence experiments were conducted at 25 °C with an AMINCO 500-SPF spectrometer. The excitation wavelength was 334 nm and the
band pass were set at 5 nm for excitation and 0.5 nm for emission. The emission intensities of the first and third emission peaks at 373 nm and 384 nm respectively, were used to calculate the $I_1/I_3$ ratio which characterizes the local polarity averaged over all pyrene solubilisation sites.

3. Results and Discussion

The effect of charge density on the structural properties has been investigated by SAXS for the two polyelectrolytes differing by the nature of the backbone, namely PSS (hydrophobic) and AMAMPS (hydrophilic). The fraction of charged monomers $f$ has been varied between 0.3 and 1 and the solutions are in the semi-dilute range. The behaviour of PSS is found to be strikingly different from that of AMAMPS. Firstly, for PSS the position of the characteristic polyelectrolyte peak varies continuously with $f$, as already reported [10] and it is found that $q^*$ scales as $f^{0.9\pm0.1}$, as opposed to AMAMPS where $q^*$ is constant with $f$. Figure 2a shows the corresponding evolutions at a fixed polymer concentration of 0.32 monomol $l^{-1}$ and in the absence of added salt. Secondly, the intensity at $q^*$, $I(q^*)$, decreases as $f$ increases for PSS whereas it increases for AMAMPS (Fig. 2b). Let us recall that the contrast for X-rays is mainly due to the counterions and should be very sensitive to the number of condensed ions which can be considered as decorating the chain. Therefore the intensity is expected to increase with $f$ as indeed observed for AMAMPS but not for PSS. A third important feature of the scattering profiles is the intensity extrapolated to $q = 0$ which is related to the osmotic pressure $\pi$ by $S(q \rightarrow 0) = Tc_p(\partial c_p/\partial \pi)$. For AMAMPS, $S(q \rightarrow 0)$ is almost constant as $f$ varies indicating constant $\pi$, i.e. a constant number of free counterions. This is consistent with the constant position of the peak $q^*$, which in the isotropic model depends only on $K_p^{-1}$, i.e. the number of free counterions. For PSS, however, the situation is quite different: the scattered intensity at $q \rightarrow 0$ decreases as $f$ increases, indicating that the osmotic pressure due to the free counterions increases with $f$; this variation is qualitatively consistent with the variation of $K_p^{-1}$, as measured by the peak displacement. However the strong excess scattering in the low angle range (see Fig. 3) can also be a signature of large scale inhomogeneities in the solution giving rise to a superposed signal which hides the effect of the osmotic compressibility at low angles. It is important to note that the scattered intensity does not evolve with time and

Fig. 2. — Variation of the SAXS peak position $q^*$ (a) and its intensity $I(q^*)$ (b) with charge content $f$ for PSS (●) and AMAMPS (○) at a constant polymer concentration of 0.32 monomol $l^{-1}$.
is reproducible once the polymer has been completely dissolved; it is therefore an equilibrium feature of the PSS solutions. The same effect of charge content has been observed at all concentrations between 0.16 and 1.3 monomol l$^{-1}$. Furthermore it has been verified that for both polyelectrolytes $q^* \sim c_p^{1/2}$ at constant $f$, a rather general prediction for polyelectrolytes in semi-dilute solutions.

These results clearly show that the solvent quality for the uncharged backbone has a definite influence on the solution properties. Indeed, whereas the scattering features of the hydrophilic polyelectrolyte AMAMPS agree well with the predictions of counterions condensation in the framework of the isotropic model, those of PSS can not be reconciled with the existing models. In order to ascertain that this effect is not fortuitous, we have compared the aforementioned results to those obtained in a parallel investigation with a polyelectrolyte having intermediate backbone properties [12]; it deals with SAMPS, a copolymer of the charged hydrophilic monomer AMPS (one of the building blocks of AMAMPS) and the uncharged hydrophobic one, styrene. As shown on Figure 3, for a charge density of 0.55 and a polymer concentration of 0.32 monomol l$^{-1}$ for the three polyelectrolytes, the scattering features, i.e. $q^*$, $I(q^*)$ and $I(q \to 0)$ are intermediate between those of PSS and AMAMPS, although, as far as electrostatic interactions are concerned, the three polyelectrolytes are equivalent. The only difference between them remains the quality of the solvent; as it changes from good to bad, the peak is displaced to smaller $q$ and its intensity increases. In conclusion, it appears from all these scattering experiments where the electrostatic interactions are kept constant that the hydrophobic interactions also have to be taken into account for highly charged polyelectrolyte.

The existence of hydrophobic regions in aqueous PSS solutions has been evidenced by measuring the local polarity of the pyrene probe in dilute PSS solutions. This technique is based on the utilization of the extrinsic fluorescence probe, pyrene which is able to detect the presence of hydrophobic microdomains, owing to the sensitivity of its fluorescence characteristics to the
polarity of its immediate envirement [13,14]. If the pyrene molecule is found in an hydrophilic environment, the fluorescence emission of the probe is characterised by a high value of the ratio $I_1/I_3$; on the contrary if hydrophobic regions exist in the solution in which pyrene prefers to reside, the fluorescence emission is characterised by a small value of the ratio $I_1/I_3$. Typical values are 1.9 in water and 1.1 in hydrophobic micelles. Note that $I_1/I_3$ gives a measure of the polarity averaged over all solubilization sites for pyrene and thus does not provide site specific information. Figure 4 shows the evolution of $I_1/I_3$ of the pyrene emission spectra as a function of the charge density for the two polyelectrolytes. For AMAMPS, $I_1/I_3$ is constant and close to the value in pure water, consistent with the fact that the medium is highly polar. For PSS, however, $I_1/I_3$ increases linearly with $f$, from a low value of 1.32 at $f = 0.38$, typical of a low polarity microenvironment to a high value of 1.7 at $f = 1$, indicative of a higher local polarity. However it never reaches the value for AMAMPS, which shows that even for the fully charged chain, pyrene can find a slightly hydrophobic environment. This evolution with charge is very progressive; there is no evidence of a transition to a micellar microphase such as commonly observed with hydrophobically modified polyelectrolytes [15] and which would give rise to a discontinuity in the plot. Figure 4 also shows the measured value for pyrene dissolved in micelles of the surfactant $C_{12}H_{25}(C_6H_4)SO_3Na$. It is interesting to note that it coincides with the extrapolation of the experimental curve to $f = 0$.

The existence of localized hydrophobic regions in such highly charged polyelectrolytes can be better understood if one recalls that, at low fraction of charged monomers, PSS is only soluble in apolar organic solvents and behaves as a typical ionomer [16]: the ion pairs do not dissociate in the low dielectric constant medium and ionic aggregation occurs due to attractive dipolar interactions. In this case, we tentatively propose that close to sequences of uncharged hydrophobic monomers, the dielectric constant is low and the charged monomers are not dissociated thus increasing the size of the hydrophobic domains. This effect will evidently be stronger for the least charged polymers. Similar effects have been proposed to explain the collapse of weakly charged polyelectrolyte gels [17].
4. Conclusion

This experimental study has shown the anomalous behaviour of highly charged sulfonated polystyrene in salt free aqueous solutions. For fractions of charged monomers higher than 0.3 and up to 1, the effective charge on the chain is renormalized by the process of counterion condensation and all electrostatic interactions are equivalent. This is indeed observed for a polyelectrolyte with an hydrophilic backbone where the characteristic length measured by SAXS in semidilute solutions does not vary with charge. On the contrary, for PSS, that length varies with f although here too, the electrostatic interactions should be the same; this shows that another parameter has to be taken into account, the hydrophobicity of the backbone. Furthermore, fluorescence emission measurements of pyrene in dilute solutions of PSS show the existence of hydrophobic regions; this effect increases as the charge decreases. These preliminary results do not allow us to propose a detailed model. More experiments, such as osmotic pressure measurements, are necessary to determine the fraction of uncondensed counterions as a function of the charge density.

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References