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Anomalous counterion condensation in salt-free hydrophobic polyelectrolyte solutions: Osmotic pressure measurements

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Abstract. – The effective charge fraction f_{eff} of a highly charged hydrophobic polyelectrolyte (poly(styrene)-co-styrene sulphonate, sodium salt) has been measured as a function of the bare chemical charge fraction f between 0.38 and 1 by osmotic-pressure measurements complemented by cryoscopy. It was found that f_{eff} is highly reduced, compared to the prediction of counterion condensation theory and the measurements we made on a model hydrophilic polyelectrolyte. Furtheremore, f_{eff} varies linearly with the chemical charge fraction and extrapolates to zero effective charge at a chemical charge fraction of 0.18, a value close to the limit of solubility of the polyelectrolyte in water. We relate this anomalous behaviour to the variations of the local dielectric constant, measured previously with the same polyelectrolyte, a parameter which is not considered in the structural models for hydrophobic polyelectrolytes.

Polyelectrolytes are polymers with a fraction of ionizable monomers. Most biopolymers are polyelectrolytes and many water-soluble, synthetic polymers of technological relevance carry ionizable groups. In a polar solvent such as water, the ion pairs dissociate. The electrostatic charges of one sign are localized on the chain whereas the numerous oppositely charged counterions are distributed in the solution, thus gaining entropy. Overall the behaviour of polyelectrolytes is dominated by electrostatic forces [1, 2].

In solution, the highly mobile counterions play a leading role in screening electrostatic interactions and their distribution may not be uniform. For instance, for a highly charged polyelectrolyte chain (*e.g.*, when all of the N monomers are ionizable), it is generally assumed that the charge density is renormalized by condensation of the counterions along the chain [3,4] in such a way that the average distance between effective charges, b, is of the same order as the Bjerrum length, l_B, which measures the characteristic distance in the solvent where the electrostatic energy is compensated by the thermal energy k_BT ($l_B = e^2/\varepsilon k_BT$ with e the electronic charge and ε the solvent dielectric constant). In water, at 25 °C, $l_B = 0.71\,\text{nm}$;

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thus for vinylic polymers with a monomer size of 0.25 nm, the effective charge should remain constant above a charge fraction f along the chain of about 0.3. This implies that the number of *free* counterions that will contribute to the osmotic pressure of the solution and to the screening of the electrostatic interactions in the system, is also constant. These calculations are valid only for rod-like polyelectrolyte chain and even those using Poisson-Boltzmann theory give a continuous but non uniform distribution of counterions in the solution [5]. Despite considerable interest in the properties of highly charged polyelectrolytes, surprisingly few systematic experiments have been reported in this charge range [6]. They are however so much more necessary that theoretical descriptions of counterion condensation rely on severe approximations because of the presence of strong long-range Coulomb interactions which limits the applicability of the Debye-Hückel theory. Manning's approach [4] even though qualitatively verified for flexible chains, strictly applies to an infinite, rod-like, single chain of zero thickness with a uniform charge density and the onset of counterion condensation is set *a priori* at $b = l_B$. The more quantitative aspects of this theory have been challenged by more elaborate calculations [7–9] and by molecular-dynamics simulations [10, 11]. However, the very existence of counterion condensation is not questioned.

Polyelectrolytes can be dissolved in poor solvent such as partially sulfonated polystyrene (PSS) in water and we deal here with a class of polyelectrolytes called hydrophobic polyelectrolytes. The PSS behaviour will be compared to that of AMAMPS, a polyelectrolyte in good solvent in water. Indeed, previous findings of a small-angle scattering study of the same polymers [12–16] showed that their semi-dilute solution structure is very different and depends drastically on the solvation characteristics of the backbone. These experimental results emphasize the importance of solvent quality for the backbone (a parameter not considered until that time for modelling highly charged systems) and corroborate the predictions of the pearl-necklace model [17–19] in which the single-chain conformation is made of compact, charged beads, "the pearls", joined by charged narrow strings. As the solvent quality and electrostatic charge vary, the chain is unstable and undergoes a cascade of abrupt transitions between necklace configurations with different number of beads.

This letter deals with an experimental determination of the amount of free counterions, hence of the effective charge fraction using osmotic-pressure measurements, complemented by cryoscopy, on two series of polyelectrolytes, hydrophobic and hydrophilic, with (chemical) linear charge fractions f above the condensation threshold (f ranging from 0.3 to 1) as a function of concentration. The results show that the effective charge is indeed renormalized to a constant value for the polyelectrolyte chain in a good solvent (hydrophilic backbone) in striking agreement with Manning's theory. In contrast, the polyelectrolyte in poor solvent (hydrophobic backbone) has an anomalously high counterion condensation that cannot be reconciled with conventional theories.

The samples are flexible random copolymers of charged and uncharged monomers; the resulting polyelectrolytes contain either *hydrophobic* units of styrene and sodium-styrene sulfonate (noted PSS) or *hydrophilic* units of acrylamide and sodium-2-acrylamide-2-methyl propane sulfonate (noted AMAMPS). The latter was synthesized by copolymerisation of acrylamide with methyl propane sulfonic acid according to a standard procedure [20] which was slightly modified to obtain highly charged polyelectrolytes. The resulting polymers had a molecular weight of 650000 ($N = 4850$) and a polydispersity of 2.6. As for the PSS samples, they were prepared by post sulfonation of polystyrene based on the Makowski procedure [13, 21]. For the first series, the parent polystyrene had an average molecular weight of 250000 ($N = 2400$) and a polydispersity of 2.0 while for the second series, three molecular weights of 42600 ($N = 410$), 96700 ($N = 930$) and 137000 ($N = 1320$) and a polydispersity of 1.1, were used [22]. A fully charged PSS ($f = 1$) was also prepared, by polymerisation of

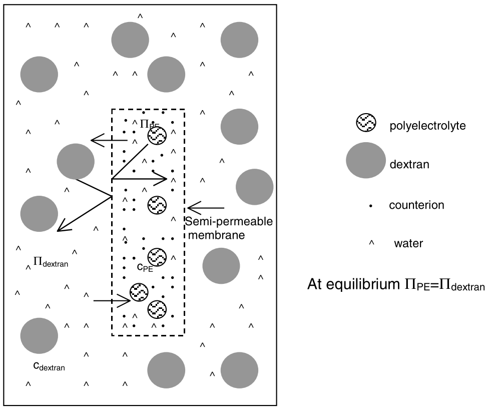

Fig. 1

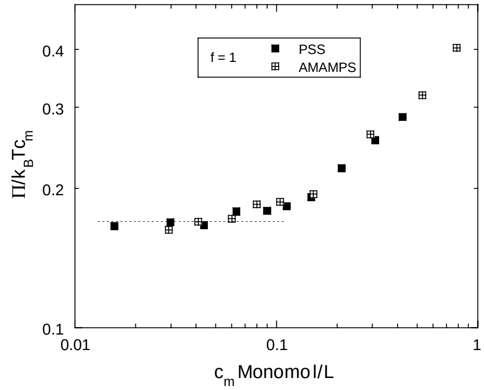

Fig. 2

Fig. 1 – Osmotic stress device.

Fig. 2 – Reduced osmotic pressure $\Pi/c_m T k_B$ as a function of monomer concentration c_m for the fully charged PSS and AMAMPS; ($f_{AMAMPS} = 1$; $f_{PSS} = 1$). The investigated concentrations cover two regimes with a transition to the second regime at c_m around 0.1 monomol/L. (Note that the asymptotic regime is not reached yet).

the styrene sulfonate monomer in order to be sure that all the monomers were charged. The charge fractions of PSS were necessarily restricted to a range between $f = 0.3$, a practical limit of solubility in water and $f = 1$, where the properties of PSS have been thoroughly investigated and shown to be those of a classic hydrophilic polyelectrolyte. The same charge fractions were chosen for AMAMPS which served as a hydrophilic reference system. Note that both polyelectrolytes bear $SO_3{}^-$ anions as side groups, with Na^+ counterions so that they only differ by their solvation characteristics.

The osmotic pressure has been measured by the osmotic stress method [23–25] by which a small volume (ca. 2 mL) of the polyelectrolyte solution of interest, contained in a container only permeable to water (Spectra/Por dialysis membrane of molecular weight cut-off 3500 Daltons) comes to osmotic equilibrium with a larger volume (ca. 40 mL) of a solution of an uncharged water soluble polymer (here, dextran of molecular weight 500000 and purchased from Pharmacia Biotech) (fig. 1) of known osmotic pressure at various concentrations. Once equilibrium is reached by transfer of water through the membrane, the concentration of both polyelectrolyte and dextran (close to nominal concentration) in each compartment is determined by measuring the amount of total carbon in each solution [26]. To obtain the osmotic pressure of dextran (equal to that of polyelectrolyte), we have used an empirical formula derived by Prouty and Vink [27,28] from measurements with a membrane osmometer in a broad concentration range ($\Pi_{\text{dex}}(w) = 10^{(1.75+1.03w^{0.383})}$, Π: pressure in Pa and w: % in weight of dextran). All experiments were performed at room temperature and particular care was taken that no charged impurities were introduced during the manipulations. The residual salt concentration is estimated to be $3 \cdot 10^{-5}$ M, as close as possible to "salt free" conditions. We estimate the experimental uncertainties in the measurements of Π to be about 10%.

The osmotic pressure of a polyelectrolyte solution in the absence of a simple electrolyte, is the sum of two contributions, that of the polymer chains, Π_p, and that of the counterions, Π_i. At low polymer concentrations, the osmotic pressure is dominated by the counterions and the chain plays a negligible role; indeed if all fN ionizable monomers of each chain of degree of polymerization N are dissociated, the ratio Π_p/Π_i is of the order of $(fN)^{-1} \sim 10^{-3}$ in our case. Thus Π is directly related to the number of counterions in the solution. Addition of

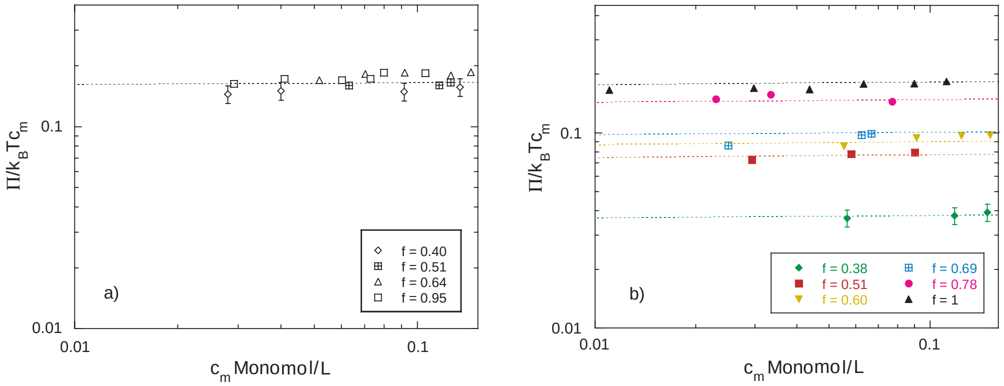

Fig. 3 – Reduced osmotic pressure Π/c_mTk_B as a function of monomer concentration c_m in the counterion-dominated dilute range, for different bare (chemical) charge fractions f of the hydrophilic polyelectrolyte AMAMPS (a) and of the hydrophobic one PSS (b). The horizontal lines corresponding to each bare charge fraction are guides for the eye.

salt changes the distribution of counterions to satisfy the condition of local electroneutrality and results in a decrease of Π. We did not consider this case in our experiments. When all counterions are free in the solution (ideal case) the osmotic pressure is k_BTc_mf, where c_m is the monomer concentration. When counterion condensation takes place, the bound counterions do not contribute to the osmotic pressure and the c_mf_{eff} free counterions behave as a gas of charges, polarized by the rodlike polyelectrolyte chains of effective charge $f_{eff} = a/l_B$ (a is the monomer size). For a Debye-Hückel gas of counterions and for a rodlike chain Manning has shown [2,4] that

$$\Pi = 1/2k_BTc_mf_{eff}\,.$$

As the polymer concentration increases, Π no longer scales as c_m as already mentioned in previous works [17,29,30]. This region is of no interest to us here since it does not provide direct information on the counterion condensation.

The first regime (counterions only) and the crossover to the second one are clearly seen in fig. 2 which shows the evolution of the reduced osmotic pressure $\Pi/(k_BTc_m)$ as a function of c_m in an extended range between 0.015 and 0.8 monomol/L for fully charged ($f = 1$) PSS and AMAMPS. The features are identical for both polymers and the plots are superposable: there is an experimentally accessible region where Π scales approximately as c_m; and the value of $\Pi/(k_BTc_m)$, extrapolated to $c_m = 0$, of 0.18, agrees with Manning's estimate of 0.178 ($a/(2l_B)$) and previous experimental values for PSS [31] and other vinylic polyelectrolytes; the deviation from linearity appears at c_m around 0.1 monomol/L (see also [30]).

Although the backbone characteristics do not affect the condensation process for the fully charged chains, the dichotomy between hydrophilic and hydrophobic polymers appears for all charge fractions smaller than 1. For AMAMPS (fig. 3a), Π/k_BTc_m is constant at 0.17 for $f = 0.95$ and 0.64; it decreases slightly at $f = 0.51$ to 0.155 to reach 0.15 at $f = 0.4$. The behaviour of this hydrophilic polyelectrolyte agrees surprisingly well with the predictions of Manning's theory, given the severe approximations involved. The slight decrease of 12% (just outside experimental errors) for the lowest f's can be ascribed to a continuous onset of counterion condensation at finite concentration [7], rather than a sharp threshold at some fixed f. These results imply that treating the (single) flexible chain as a uniformely charged wire does indeed give a good physical insight into counterion condensation. For PSS, however, the behaviour is strikingly different (fig. 3b). As f decreases the reduced osmotic pressure decreases steadily from 0.184 at f close to 1 (a value equal to that for AMAMPS, within experimental error) to reach the low value of 0.04 at $f = 0.38$, just above the solubility limit.

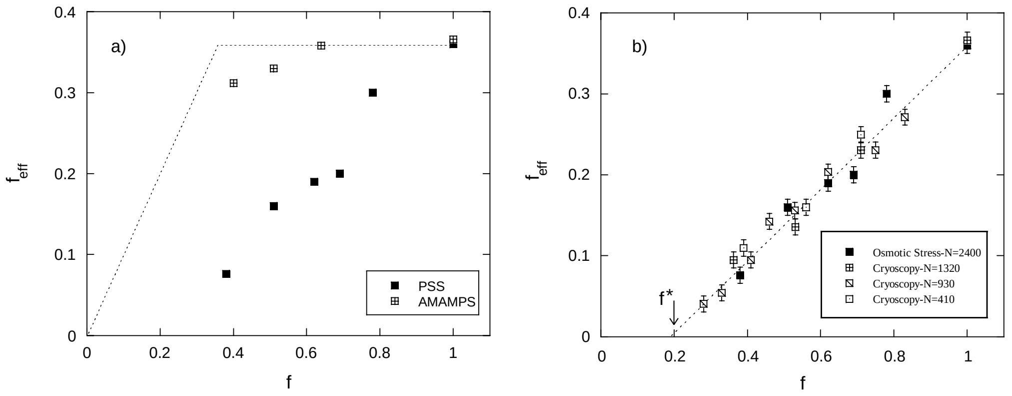

Fig. 4 – Evolution of the effective charge f_{eff} as a function of the bare charge fraction f_{eff}, for PSS and AMAMPS, obtained by extrapolation to zero concentration of the reduced osmotic pressure (osmotic stress method). The dotted line corresponds to Manning Oosawa counterion condensation (a) and the evolution of f_{eff} as a function of f, for PSS obtained by the cryoscopy technique at a concentration of 0.1 mol/L for three different chain lengths N and compared to that obtained by the osmotic stress method (b).

It is interesting to note that the same kind of behaviour was observed by static light scattering measurements of $S(q = 0)$ on these PSS as a function of c_m and f, which is related to the osmotic compressibility of the system in the thermodynamic limit [32]. Figure 4a shows the variation of the effective charge fraction as a function of the bare charge fraction for PSS and AMAMPS deduced from the extrapolation at zero concentration of the osmotic measurements. Figure 4b includes the data for PSS just described together with the results of complementary experiments using the related colligative technique of cryoscopy [33, 34]. The latter data are taken at one value of c_m below 0.1 monomol/L for a series of PSS as a function of f and N. The plot reveals that the effective charge f_{eff} varies linearly with f in the whole range, independently of N and the same evolution of f_{eff} with f is obtained either by osmotic or by cryoscopy techniques, which confirm obviously the validity of these experimental data. At $f = 1$, and only there, f_{eff} has the value predicted by Manning-Oosawa condensation theory; it extrapolates to zero effective charge (neutral chain) at a value f^* of the order of 0.18 close

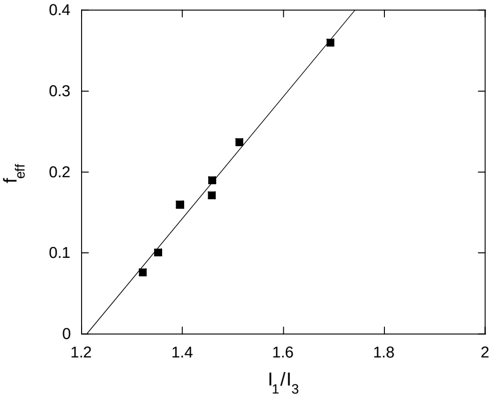

Fig. 5 – Evolution of the effective charge f_{eff} as a function of the fluorescence emission ratio I_1/I_3 for pyrene in dilute PSS solution at a monomer concentration of $2.72 \cdot 10^{-2}$ monomol/L and pyrene concentration of $6 \cdot 10^{-7}$ mol/L.

to the limit of solubility of PSS in water (~ 0.25). This is consistent with the fact that water is not a solvent of polystyrene and it is only the presence of charges that impart solubility to the chain. In between these two points, f_{eff} is proportional to f and more particularly f_{eff} can be expressed as $f_{eff} = 0.36^*(f - f^*)/(1 - f^*)$.

It has been shown previously [13] that the backbone hydrophobicity of PSS promotes the formation in solution of hydrophobic domains with a locally low dielectric constant and that the effect increases as the bare charge fraction f decreases. Indeed the fluorescence emission of an extrinsic pyrene probe, which is sensitive to the local polarity averaged over all solubilisation sites, shows a continuous variation of its characteristic intensities as a function of f. These hydrophobic domains have locally a much lower dielectric constant than that of water. If we assume that the PSS chain in dilute salt-free solutions has a necklace-like shape [16] with compact beads joined by narrow strings, this implies that the hydrophobic domains correspond to the beads where the local dielectric constant ε can be very low. It is important to note that neither theory nor simulations consider a local variation of the dielectric constant ε. However, this can have important consequences: if ε is sufficiently low (low charge content and few water molecules), the ion pairs in the core of the beads cannot be dissociated and only those near the interface with bulk water can be dissociated. The charges would be localized in a charged shell of undetermined thickness [35]. Indeed as shown in fig. 5, f_{eff} is found to be strongly correlated with the fluorescence emission ratio I_1/I_3 for pyrene in dilute PSS solution, *i.e.* with the local dielectric constant. This phenomenon can give a qualitative explanation to the reduction of osmotically active counterions in case of the hydrophobic polyelectrolyte, beside that only for geometrical arguments the condensation on beads is higher than that on strings [19]. Furthermore, it has been demonstrated experimentally that the pearl size D_p increases when f decreases [36], in agreement with the scaling prediction of the pearl-necklace model. When the pearl size becomes larger, the increase in the volume of hydrophobic zones is accompanied by a decrease in I_1/I_3 as well as an increase in the number of counter-ions trapped within the hydrophobic pearls. A quantitative calculation has not been possible, mainly because of the coupling between the chemical charge and solvent quality.

Finally, we conclude that the solvent quality governs the effective charge value of the highly charged hydrophobic polyelectrolytes chain; the effective charge varies with the chemical charge and the Manning-Oosawa condensation law is violated. The chain can be assumed to have a necklace-like shape. This behaviour is markedly different from that of the hydrophilic polyelectrolyte where the Manning-Oosawa condensation law is verified and the chain has an extended-like conformation. As an extension of this work, it will be interesting to investigate the evolution of the effective charge as a function of the chemical charge content for another hydrophobic polyelectrolyte in the same solvent (water), in order to check if this evolution is intrinsic to PSS or valid also for other hydrophobic polyelectrolytes.

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