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Donnan equilibrium and the effective charge of sodium polyacrylate

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Abstract Osmometry using an external stressor is a very useful method to measure the equilibrium osmotic pressure for dilute solutions of polyelectrolyte. By taking into account the contribution of the ideal gas law, the excluded volume, the solvency effect, and the Donnan equilibrium effect on the measured pressure it is possible to estimate the effective charge of sodium polyacrylate 35 kgmol^{-1} as a function of the polymer concentration, the pH, the ionic strength, and the presence of Ca^{2+} ion. The numerical resolution of state equations has shown that the effective charge increases with the ionic strength or with the decreasing polymer concentration, in agreement with recent theoretical models. On the other hand, the effective charge is pH-independent. This statement remains valid as long as the degree of neutralization of the polyacrylate is over 0.5. Above this degree of neutralization, any further neutralization promoted by NaOH addition leads to the condensation of the Na^+ counterion, in agreement with the general concept of ionic condensation. The effective charge represents only 10–20% of the total number of monomer units for pH within 6 and 9 and ionic strength below 0.1 M. The polymer can tolerate the presence of Ca^{2+} at least up to a molar ratio Ca^{2+}/–COOH = 0.222 without any influence on the effective charge.

Key words Polyacrylate · Ionic condensation · Effective charge · Polyelectrolyte · Osmotic pressure

Introduction

Water-soluble polyelectrolytes, such as the sodium salt of poly(acrylic) acid (PANa), are widely used as additives in coatings, paints, ceramics, and cosmetics to improve the rheological properties of mineral slurries [1–5]. The performance of weak polyelectrolytes in stabilizing mineral slurries is in part related to their adsorption capability, which, in turn, depends upon the surface charge of the mineral, the ionic strength of the bulk, the presence of complexing species such as divalent cations, the degree of neutralization of the polymer, etc [4, 6–8]. The latter parameters are known to influence the effective charge of the polymer (Z_{eff}) [9, 10] as well as the double-layer thickness (also called the Debye length, κ^{-1}), which both control the electrostatic interactions between a polyelectrolyte molecule and a charged surface, for example.

The concept of effective charge for polyelectrolytes was introduced many decades ago by Manning [11] and is still of interest. The effective charge number for charged species can be predicted on the basis of the theory of ionic condensation developed elsewhere [12–16]. Recent models and experimental work have shown that a large fraction of the counterions near the functional groups of the polyelectrolyte are actually "condensed" [15, 17]. The excess of the remaining uncondensed charges is referred to as the "effective" particle charge number, Z_{eff}, contrasting with the "bare" charge, Z_{str}. It is now common to replace the bare charge by a so-called "renormalized" charge (effective charge) [13, 14, 18]. The theory of ionic condensation predicts an effective charge number which increases with the bare charge number up to the point where the thermal energy of the ions balances the reversible work necessary to remove the ions from the charged species. From that point on, the effective charge remains constant. Thus, a maximum effective charge can be expected and all additional charges added to the polyelectrolyte above this maximum value will condense, leading to a constant effective charge number.

The goal of the present work is to highlight the influence of the polyelectrolyte concentration, the pH, the ionic strength, and the presence of complexing cation upon the effective charge of PANa, of molecular weight (MW) 35 kgmol^{-1}. We use the theory of the Donnan equilibrium across a semipermeable membrane to compute Z_{eff} for this polyelectrolyte. This approach is much more straightforward than any other to find an experimental Z_{eff} because very few approximations and a priori assumptions (of the form of the interaction potential, charge distribution, etc) have to be done. Moreover, this experimental method allows very low osmotic pressures to be measured, thus allowing dilute conditions to be used. The polymer solvency parameter χ (Flory–Huggins parameter) and the effective excluded-volume effect of the polymer were taken into account in the computation of Z_{eff}. Hence, the effective charge computed this way would reflect only Coulombic interactions between the polyelectrolyte molecules and small ions.

Theoretical background

A Donnan equilibrium is established by the distribution of a diffusible electrolyte between two compartments separated by a semipermeable membrane when a nondiffusible polyelectrolyte is localized in one of the compartments. The charge of the polymer creates an uneven distribution of the small ions across the membrane which is part of the net osmotic pressure, Π, experienced by this system. This osmotic pressure is the sum of many contributions; the limiting pressure described by the van't Hoff law (Π_{vH}), the excluded-volume pressure (Π_{exc}), the solvency pressure (Π_{χ}), and the activity coefficient pressure (Π_{γ}), taking account of the nonideal behavior of all charged species. Rigorously, a state equation for the hard-sphere contribution to the osmotic pressure should be used instead of the van't Hoff law; however, the volume fractions reported in this work are so small that the state equation for hard spheres reduces to the van't Hoff law.

Much recent theoretical work has been done in order to predict the nonideal behavior coming from the charge of the species in concentrated systems [13, 16, 19–22]. Some of these works [19, 20] clearly show that the ideal behavior can be met in "realistic" experimental conditions, i.e., 1:1 electrolyte with a concentration up to 0.1 M, a polyelectrolyte concentration up to 0.001 M, and an effective charge up to 30–40 per polyelectrolyte molecule. Under these conditions, one can neglect the activity coefficients of small ions and the net osmotic pressure is then

$$\frac{\Pi}{kT} \cong \gamma_{\mathrm{p}}\varphi_{\mathrm{p}} + \varphi_{+}^{\mathrm{i}} + \varphi_{-}^{\mathrm{i}} - \varphi_{+}^{\mathrm{o}} - \varphi_{-}^{\mathrm{o}} \ , \tag{1}$$

where φ is the number concentration (number per cubic meter), the superscripts i and o refer to the inside and outside of the polymer compartment, respectively, and the subscripts p, +, and − refer to polymer, cation, and anion, respectively. The activity coefficient γ_{p} takes into account the nonideality of the polymer with regard to the excluded-volume and solvency effects. This activity coefficient can be written as a function of the virial coefficients [23]:

$$\frac{\Pi}{kT} \cong \varphi_{\mathrm{p}}\left(1 + B_2\varphi_{\mathrm{p}} + B_3\varphi_{\mathrm{p}}^2 + \ldots\right) + \varphi_{+}^{\mathrm{i}} + \varphi_{-}^{\mathrm{i}} - \varphi_{+}^{\mathrm{o}} - \varphi_{-}^{\mathrm{o}} \ .$$

Thus,

$$\gamma_{\mathrm{p}} \cong \left(1 + B_2\varphi_{\mathrm{p}} + B_3\varphi_{\mathrm{p}}^2 + \ldots\right) \ . \tag{2}$$

By considering only pair interactions ($\varphi_{\mathrm{p}}\rightarrow 0$) in a one-component model, we are allowed to neglect all high-order terms. Then, Eq. (2) reduces to

$$\gamma_{\mathrm{p}} \cong 1 + B_2\varphi_{\mathrm{p}} \ , \tag{3}$$

where B_2 is the second virial coefficient accounting for the excluded-volume and solvency effects. This coefficient can be written as a combination of both contributions:

$$B_2 = B_2^{\chi} + B_2^{\mathrm{exc}} \ , \tag{4}$$

where B_2^{χ} is the second virial coefficient accounting for the solvency effect and B_2^{exc} is for the excluded-volume effect. These coefficients are described by the following statistical thermodynamic relations [23, 24]:

$$B_2^{\chi} = \frac{(1/2 - \chi)\overline{V_{\mathrm{p}}^2}}{1000\overline{V_1}N_{\mathrm{A}}} \ , \tag{5}$$

and

$$B_2^{\mathrm{exc}} = v/2 \ , \tag{6}$$

where χ is the Flory–Huggins interaction parameter, N_{A} is the Avogadro number, $\overline{V_{\mathrm{p}}}$ and $\overline{V_1}$ are the partial molar volumes of the polymer (15.38 dm^3 mol^{-1}) and solvent (0.018 dm^3 mol^{-1}), respectively, and where v is the excluded volume for one polymer molecule.

The solvency parameter for the PANa is known to be a linear function of $I^{-1/2}$ as reported elsewhere [25], where I is the ionic strength. The ionic strength is defined as $I = (1000N_A)^{-1}(\varphi_s^i + 1/2\varphi_p Z_{eff})$, where φ_s^i is the salt concentration (number per cubic meter) inside the polymer compartment. The empiric relation between χ and I is [25]:

$$\chi = -(0.02167I^{-1/2}) + 0.5232 \ . \tag{7}$$

The effective radius of gyration for the PANa of MW 15,000 is [25]

$$R_G = 3.539 + 0.5273I^{-1/2} - 0.01279I^{-1} \ . \tag{8}$$

Assuming a spherical geometry, one can compute the effective polymer radius $a_{eff} = R_G(5/3)^{1/2}$ from Eq. (8). The polymer radius is defined as $a = a_{eff} - \kappa^{-1}$, where $\kappa = (8\pi L_B I)^{1/2}$, where L_B is the Bjerrum length. Finally, the excluded volume is $v = 4(4/3\pi a^3)$. On inserting Eqs. (3), (4), (5), and (6) into Eq. (1), one finds

$$\frac{\Pi}{kT} \cong \varphi_p\left(1 + \frac{(1/2-\chi)\overline{V_p^2}}{1000\overline{V}_1 N_A}\varphi_p + \frac{v}{2}\varphi_p\right) + \varphi_+^i + \varphi_-^i - \varphi_+^o - \varphi_-^o \ . \tag{9}$$

The expression of the Donnan equilibrium for ideal systems is

$$\varphi_+^i\varphi_-^i = \varphi_+^o\varphi_-^o \ . \tag{10}$$

Electroneutrality on either side of the membrane demands that

$$\varphi_+^o = \varphi_-^o \tag{11}$$

and

$$\varphi_-^i + Z_{eff}\varphi_p = \varphi_+^i \ . \tag{12}$$

On inserting Eqs. (10), (11), and (12) into Eq. (9), we find

$$\frac{\Pi}{kT} \cong \varphi_p\left(1 + \frac{(1/2-\chi)\overline{V_p^2}}{1000\overline{V}_1 N_A}\varphi_p + \frac{v}{2}\varphi_p\right) + 2\varphi_+^o\left\{\left[\left(\frac{\varphi_p Z_{eff}}{2\varphi_+^o}\right)^2 + 1\right]^{1/2} - 1\right\} \ . \tag{13}$$

With $\varphi_+^0 > \ \varphi_p$ the last term of Eq. (13) simplifies [26] and Eq. (13) reduces to

$$\frac{\Pi}{kT} \cong \varphi_p\left(1 + \frac{(1/2-\chi)\overline{V_p^2}}{1000\overline{V}_1 N_A}\varphi_p + \frac{v}{2}\varphi_p + \frac{(Z_{eff})^2\varphi_p}{4\varphi_+^o}\right) \ . \tag{14}$$

From Eq. (14), it may be seen that the last term of Eq. (13) can be associated with a second virial coefficient in connection with the polymer charge. Thus, Eq. (13) can be transcripted in the following form:

$$\Pi \cong \Pi_{vH} + \Pi_\chi + \Pi_{exc} + \Pi_{Donnan} \ ,$$

where Π_{vH} is the limiting osmotic pressure (van't Hoff law), Π_χ is the pressure coming from the solvency effect, Π_{exc} is the excluded-volume contribution to the net osmotic pressure, and Π_{Donnan} is the contribution of the polymer charge via the Donnan equilibrium. (Again, a state equation for the hard-sphere contribution to the osmotic pressure should be used instead of the van't Hoff law; however, the volume fractions reported in this work are so small that the state equation for hard spheres reduces to the van't Hoff law.) By taking Z_{eff} as an adjustable parameter in Eq. (13), one can find by numerical iteration the value of Z_{eff} necessary to match the experimental osmotic pressure as a function of φ_p.

It should be mentioned that, neglecting solvency effects and in the limit of the previously mentioned experimental conditions, the remaining terms in Eq. (14) can also be found using the so-called "virial" route that takes into account the repulsive interaction between two charged spheres with charges distributed on the particle surface. The system can be modeled as a one-component system with spherical particles having identical size (monodisperse) and interacting through the screened Coulombic potential in the form [23]:

$$\frac{w(r)}{kT} = \frac{(Z_{eff})^2 L_B}{r}\frac{\exp[-\kappa(r-2a)]}{(1+\kappa a)^2} \ , \tag{15}$$

where r is the center-to-center distance between the spheres. Equation (15) can be used to model the experimental osmotic pressure for a given system by taking Z_{eff} as an adjustable parameter. Some refinements of the interaction potential can include attractive interactions [19, 27].

Materials and methods

Chemical reagents

All the electrolytes (sodium hydroxide, sodium chloride, and calcium chloride) were analytical grade reagents and were used without further purification. Distilled, deionized water was used throughout. Poly(ethylene glycol) (PEG) of MW 35 kg mol^{-1} purchased from Fluka was used as a stressor for the osmotic pressure experiments.

Osmotic stress

This method has been used by other workers on other systems [28–31] and was adapted to the present one. In this method, the osmotic pressure of PEG solutions having different weight concentrations is first measured by osmometry as described elsewhere [28, 30]. An empirical relation between the osmotic pressure, Π, and the weight concentration of PEG is found. Then, the osmotic pressure for each PEG concentration is known with precision. Different dialysis tubes were filled with the PANa solution of known concentration ($c_p > 3 \times 10^{-3}$ monomol dm^{-3}) and were immersed in different reservoirs of PEG solutions. The PEG then plays the role of an osmotic stressor. At equilibrium, the osmotic pressure is the same on both side of the dialysis membrane. If one knows the PEG concentration, one can find the osmotic pressure of the PANa solution; therefore, the dependence of the PANa concentration on the osmotic pressure is known and yields the state equation of the polyelectrolyte solution, as described in the Theoretical background.

The dialysis tubes of regenerated cellulose were provided by Roth. The nominal cutoff of the membrane is 12–14 kgmol^{-1}, i.e., neither the PANa nor the PEG can pass through the membrane. The only diffusible species are the electrolyte ions and the solvent molecules. Membrane conditioning was done as prescribed by the manufacturer. The tubes were hermetically closed and rested for 3 weeks for equilibrium as described earlier. Next, the solutions were carefully recovered and accurately weighted. In all cases, the mass transfer of the solvent towards the finite PEG reservoir was taken into account in determining the equilibrium osmotic pressure.

Experimental details

The influences of three main parameters on the effective charge were investigated: the pH, the ionic strength, and the presence of divalent cations. The polyelectrolyte was purified by dissolution/precipitation using successive water and methanol additions. At the end of this process, the recovered precipitate was dried to evaporate the water/methanol solvent. The molecular weight of the purified PANa was measured by osmotic pressure measurements (see later). The precipitated and purified PANa was redissolved in water and its pH was adjusted to pH 3 using a cationic resin (Amberlite IRN-77). At this pH, the polyelectrolyte is in its acidic form; poly(acrylic) acid.

pH adjustment

Solutions of sodium polyacrylate at different pH were prepared from the poly(acrylic) acid solution by sodium hydroxide addition. The pHs investigated were pH 4, 5, 6.5, 7.5, 8, and 9. These are the equilibrium pHs of the PANa solution in the dialysis bag. The total concentration of acrylate functional groups was determined by full titration of the initial poly(acrylic) acid solution with an Orion 720A pH meter. The degree of neutralization, *f*, of PANa as a function of pH is presented in Fig. 1. This degree of neutralization represents the number of neutralized carboxylic groups over the total number of functional groups.

Ionic strength adjustment

The pH of the PANa solutions for this set of experiments was adjusted to 9. The ionic strength in the PANa compartment and the PEG reservoir was adjusted with NaCl. At equilibrium, the ionic strength in the PANa compartment was about 1.5×10^{-3} [$I = (1000N_A)^{-1}(1/2\varphi_p Z_{eff})$ for zero salt added], 6×10^{-3}, 1.1×10^{-2}, 5.5×10^{-2}, and 1.1×10^{-1} mol dm^{-3}.

Calcium addition

$CaCl_2$ was added to the PANa solution (pH 8) up to the molar ratio $Ca^{2+}_{total}/c_p = 0.116$ and 0.222. As shown elsewhere [10], all the Ca^{2+} ions are bound to the polyion when the ratio $Ca^{2+}_{total}/c_p < 0.30$ and, thus, no Ca^{2+} is free in the bulk for $Ca^{2+}_{total}/c_p = 0.116$ and 0.222.

In all cases, the pHs of both the PANa and the PEG solutions as well as the remaining volume in each bag were measured. The latter is used to calculate the equilibrium concentration of the PANa and the PEG. The concentrations of sodium, calcium and chloride ions in the reservoir were determined by atomic adsorption spectroscopy for cations and by ionic chromatography for anions.

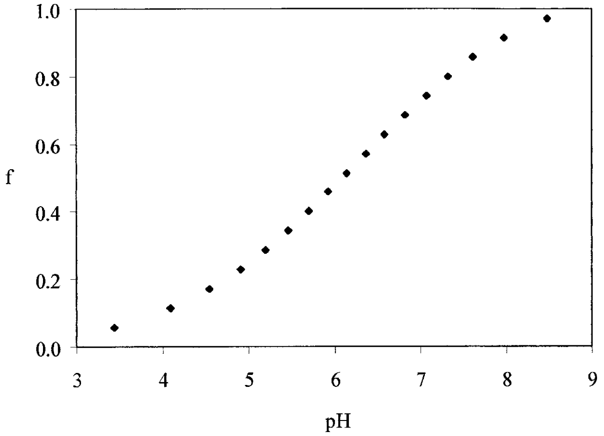

Fig. 1 Degree of neutralization of poly(acrylic) acid upon NaOH titration. The degree of neutralization is defined as the number of neutralized acrylic acid functional groups over the total number of functional groups. The monomer concentration, c_p, is 0.09 monomol dm^{-3}

Results and discussion

Experimental considerations regarding the dilute and semidilute conditions

As reported elsewhere, the theory of charge renormalization is only suitable for polyelectrolyte concentrations belonging to the dilute regime [13]. It is then important to make sure that the range of the PANa concentrations studied in the present work belongs to this regime. Theoretical studies [32, 33] have shown that a linear relationship on a log–log scale exists between the osmotic pressure (Π) of the polyelectrolyte solution and its concentration (C_p). This linear relation differs depending on whether the solution is in the dilute or semidilute regime. In the dilute regime, the slope should be within 1.125 and 1.05 and should increase to 2.25 for the semidilute regime [32, 33].

In order to find to which regime our systems belong, osmotic pressure measurements were performed on salt-free PANa solutions at a pH between 6.5 and 9. The results are reported in Fig. 2. In this figure the linear relation is obvious and the experimental slope (1.09) is within the expected values (1.05–1.13) for a dilute solution. It is then fully justified to use the theory of the charge renormalization to interpret the results within the chain concentrations (C_p) reported in Fig. 2.[1] It should be mentioned that the ionic strength

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[1] Note the symbol for chain concentration is C_p (mol dm^{-3}) and should not be confused with the monomer concentration c_p (monomol dm^{-3})

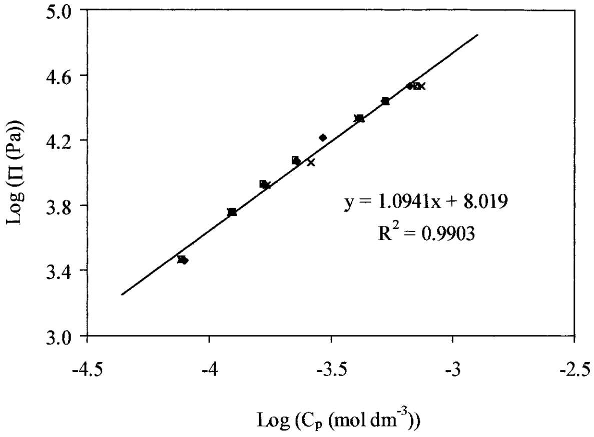

Fig. 2 Influence of the pH (or degree of neutralization) on the osmotic pressure of the sodium salt of poly(acrylic) acid (*PANa*) 35 kg mol^{-1} measured by the osmotic stress method. pH 6.5 (×), pH 7.5 (△), pH 8 (◆), pH 9 (□)

in the salt-free condition simplifies to $I=(1000N_A)^{-1}(1/2\varphi_p Z_{eff})$ (see the Theoretical background for details).

Influence of the pH on the effective charge

Moreover, an interesting behavior is observed in Fig. 2; no matter what the pH is, the osmotic pressure is the same. Using Eq. (13), one can compute the effective charge of the polymer as a function of the chain concentration. As expected from Fig. 2, Z_{eff} is pH-independent; this is reported in Fig. 3. Two main observations can be made from this figure: Z_{eff} does not depend on the pH within the range 6.5–9 but does so below pH 6; Z_{eff} increases as C_p (or the volume fraction, ϕ) decreases to zero. On the other hand, Z_{eff} levels off as C_p increases. Both observations agree very well with the predictions of the charge renormalization theory.

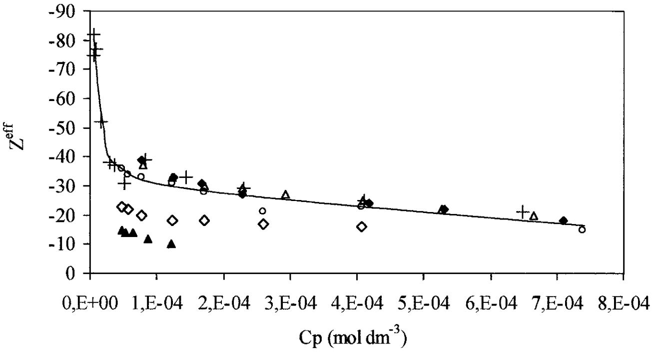

Fig. 3 Influence of the pH (or degree of neutralization) on the effective charge, Z_{eff}, of PANa calculated from the Donnan equation and the state equation. pH 4 (▲), pH 5 (◇), pH 6.5 (○), pH 7.5 (◆), pH 8 (△) and 9 (+)

1. Regarding the first observation, the theory of ionic condensation predicts an effective charge number, Z_{eff}, which increases with the bare charge number, Z_{str}, up to the point where Z_{eff} remains constant. Thus, a maximum Z_{eff} can be expected and all charges added to the polyelectrolyte above this maximum value will condense, leading to a constant Z_{eff} (see the Introduction and Refs. [13, 15, 17]). As shown in Fig. 3, the maximum Z_{eff} is already reached at pH 6.5 and corresponds to about 20–10% of the total number of monomer units (375 units for PANa MW 35 kg mol^{-1}). The exact percentage depends on the concentration. In other words, 20–10% of the monomer's counterion (H^+ or Na^+) is uncondensed between pH 6 and 9. This percentage is similar to results reported elsewhere [9, 34–36], while it is lower than that reported in other studies [37, 38]. At pH 4, Z_{eff} is very low and is expected to be very close to Z_{str} since the degree of neutralization, f, is close to zero (Fig. 1). As soon as f has reached 0.5 (pH 6, Fig. 1), Z_{eff} remains the same no matter what Z_{str} is. Thus, any differences in the adsorption capability of the polymer on a charged surface following pH readjustments (between pH 6.5 and 9) should not be attributed to changes in the electrostatic properties of the polymer. When such differences are observed, changes in the electric properties of the surface or in the chemical affinity of the polymer for the surface could explain these differences.
2. At very low ϕ (or C_p), the charge renormalization theory predicts that Z_{eff} increases very sharply as C_p decreases [15] and reaches its bare value, Z_{str}, in the infinite-dilution limit [13]. In this limit, the polyelectrolyte solution is ideal and there is no condensation [39, 40]. The results shown in Fig. 3 also agree very well with the theoretical expectations for the infinite-dilution limit. The consequence of this would be that the electrostatic affinity of the polymer for a positively charged surface at the onset of an adsorption isotherm might be higher than that at the end of it where the equilibrium concentration is higher.

Influence of the ionic strength on the effective charge

The influence of the ionic strength on $\Pi/1000m_pRT$ is reported in Fig. 4 (m_p is the polymer concentration in units of grams per cubic decimeter). In the zero-salt limit, $\varphi^1_- \ll Z_{eff}\varphi_p$ and $I \cong (1000N_A)^{-1}(1/2\varphi_p Z_{eff})$; Eq. (12) can thus be approximated by $\varphi^1_+ \cong Z_{eff}\varphi_p$. Under this condition, the osmotic coefficient reaches a plateau very quickly and, neglecting the contribution of the excluded-volume and the solvency effects, Eq. (13) reduces (after appropriate unit transformations) to $\Pi/(1000m_pRT) \cong (1 + Z_{eff})/\mathrm{MW}$ [27, 41]; i.e., Π/m_pRT becomes independent of m_p. Such behavior is observed

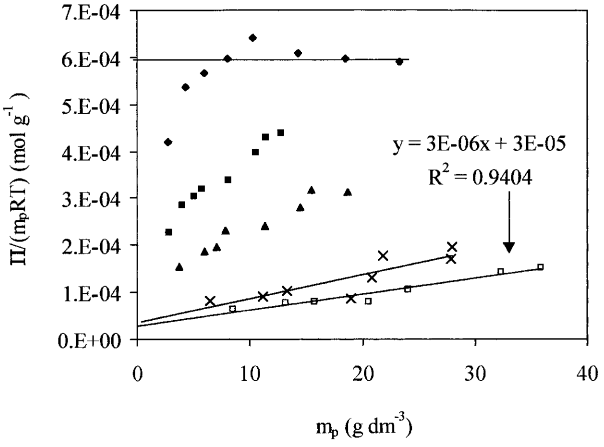

Fig. 4 Reduced osmotic pressure of PANa solutions versus C_p for different ionic strengths (NaCl). The equation corresponds to the regression line through the points for $I = 1.2 \times 10^{-1}$ M. 0 M (◆), 5×10^{-3} M (■), 1.1×10^{-2} M (▲), 6×10^{-2} M (×), 1.2×10^{-1} M (□)

in Fig. 4. From this figure one can compute $Z_{\mathrm{eff}} = -22$. On the other hand, at high ionic strength, Eq. (13) reduces to the linear equation $\Pi/(1000 m_p RT) \cong 1/\mathrm{MW} + (Z_{\mathrm{eff}}^2\ m_p N_A)/(4\varphi_+{}^{\circ}\mathrm{MW}^2)$, still neglecting excluded-volume and solvency effects [27, 41]. The linear behavior is observed for $I = 6 \times 10^{-2}$ and 1.2×10^{-1} M. With the linear regression parameters, one computes MW = 35 kg mol^{-1} and $Z_{\mathrm{eff}} = -40$. The perfect agreement of the MW computed with both ionic strengths increases our confidence in the results. Taking into account the excluded-volume and solvency effects, the exact resolution of Eq. (13) leads to $Z_{\mathrm{eff}} = -21$ and -35 in the low and high ionic strength limits, respectively (Fig. 5).

The increase in Z_{eff} with I as reported earlier is clearly demonstrated in Fig. 5. This has been theoretically predicted elsewhere [42]. In our opinion, this can be explained by the increase of the screening effect as I goes up. As a consequence, the range of the electrostatic repulsive interaction between two neighboring charges becomes smaller and more counterions can thus "decondense". According to our results, this "decondensation" becomes apparent for a Debye length $\kappa^{-1} < 3$ nm.

Of course, the decondensation would lead to an increase in Z_{eff} but, on the other hand, the κ^{-1} decreases when I increases; one effect compensates for the other and Z_{eff} becomes proportional to κ for $\kappa a \gg 1$ [13]. This relation between Z_{eff} and κ for $\kappa a \gg 1$ is observed in Fig. 6. The result in this figure is very similar to the one predicted from the hypernetted chain model (see Fig. 11 of Ref. [13]). The physical and practical meaning of this would be that any charge increase of the polymer promoted by salt addition with a view to increase the electrostatic interaction between a charged polymer and a charged surface, for example, is compensated by the screening of the polymer, unless κa is near 1. In other words, the addition of salt makes the charge become higher but in doing so it also makes the electrostatic interaction become short ranged (unless κa is near 1).

Moreover, the increase in Z_{eff} when $C_p \to 0$ in Fig. 3 is still observed in the presence of salt (Fig. 5). The ideal state of the polyelectrolyte solution observed at low concentrations does not seem to be very sensitive to the ionic strength, at least for ionic strengths below 0.1 M.

Influence of Ca^{2+} on the effective charge

As reported in Fig. 7, the calcium ion does not have any effect on Z_{eff} under the present experimental conditions (molar ratios $Ca^{2+}_{\mathrm{total}}/c_p = 0.116$ and 0.222). Since all Ca^{2+} ions complex with the $-COO^-$ functional groups of the polymer at these ratios, no free Ca^{2+} ions were

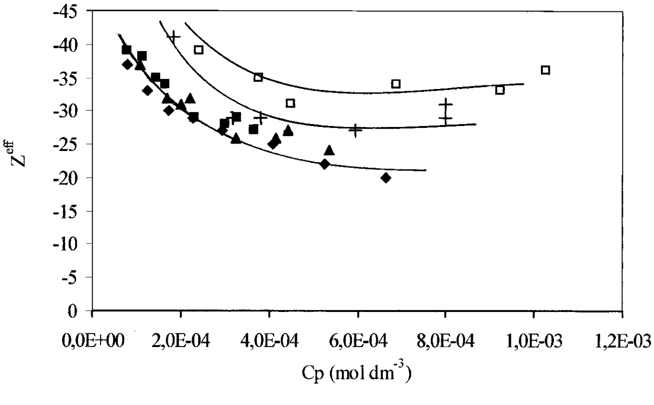

Fig. 5 Influence of the ionic strength (NaCl) on the Z_{eff} of PANa at pH 8. 0 M (◆), 5×10^{-3} M (■), 1.1×10^{-2} (▲) and 6×10^{-2} M (+), 1.2×10^{-1} M (□)

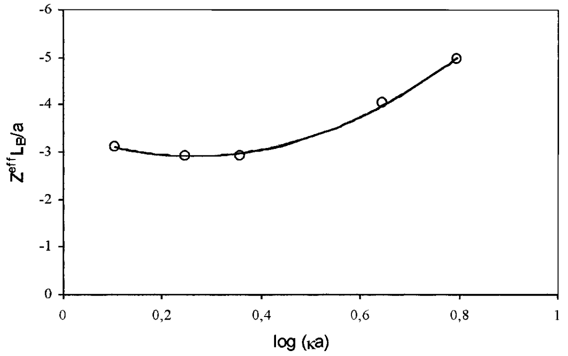

Fig. 6 Z_{eff} as a function of κa (on a semilog scale) at constant PANa concentration, $C_p = 2.5 \times 10^{-4}$ mol dm^{-3} and pH 8. κ is the inverse of the Debye length (nm), a is the polymer radius (nm) calculated with Eq. (8) and L_B is the Bjerrum length (0.70 nm at 298 K)

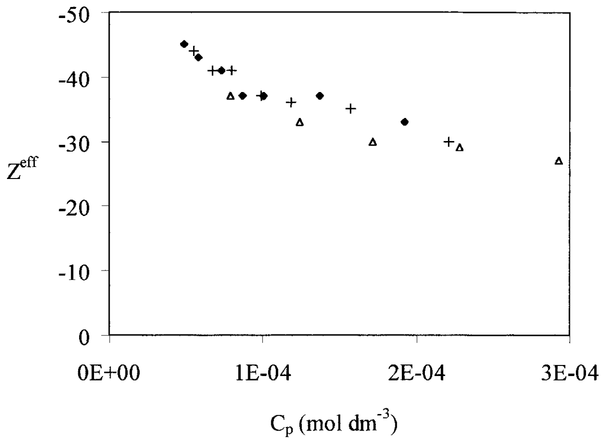

Fig. 7 Influence of the complexing Ca^{2+} ion on the Z_{eff} of PANa at pH 8. No salt (Δ), $r = 0.116$ (◆) and $r = 0.222$ (+)

present in the bulk, as expected [6, 43]. According to the results in Fig. 7, the polymer can "tolerate" a high degree of complexation without losing its effective charge. Indeed, a molar ratio of 0.222 corresponds to almost half of the functional groups monopolized by Ca^{2+} ions. This finding is in agreement with the low percentage of uncondensed functional groups (about 10%) under normal conditions; since about 80–90% of the functional groups are not ionized, many of them can be complexed without having any influence on Z_{eff}. Other workers have reported the precipitation of this polymer when the Ca^{2+}/c_p molar ratio reaches 0.37 [6, 43]. For the moment, we do not know what would happen with Z_{eff} near this critical ratio.

The complexation with Ca^{2+} is expected to have a dramatic influence on the structural conformation of the polymer as well as on its solvency parameter since the interaction Ca^{2+}/polymer is known to change the solubility of the polymer. The computation of Z_{eff} with Eq. (13) did not take these effects into account. However, the contribution of the excluded-volume and solvency effects on the total osmotic pressure is weak and any deviation from the expected behavior because of the complexation should not induce a large error on the computed Z_{eff}.

Conclusion

The effective charge number of a polyelectrolyte can be calculated satisfactorily from osmotic pressure measurements. The results have shown that no more than 35–80 acrylate functional groups on PANa 35 kg mol^{-1} are not condensed i.e., their sodium counterion is "free" as long as the degree of neutralization is above 0.5 (pH > 6). Under this condition, the highest effective charge can be reached with chain concentrations below 1×10^{-4} mol dm^{-3}. At higher concentrations only 35–40 counterions are uncondensed. This charge number represents about 10% of the total number of monomer units (375 units for PANa MW 35 kg mol^{-1}). In other words, 10% of the monomer's counterion (H^+ or Na^+) are uncondensed between pH 6 and 9 and this percentage is roughly concentration-independent for chain concentrations above 1×10^{-4} mol dm^{-3}. The increase in the ionic strength leads to a slight increase in the effective charge for $I > 6 \times 10^{-2}$ mol dm^{-3} (i.e., for $\kappa^{-1} < 3$ nm) and can be explained by a screening effect reducing the repulsive interaction between two neighboring charges. All of the reported experimental behaviors agree very well with recent models based on the theory of ionic condensation. The practical meanings of these findings are the following:

1. Between pH 6 and 9 and at constant concentration, the electrostatic properties of polyacrylate cannot account for any observed differences regarding the interaction between the polyelectrolyte and another charged species (colloid, micelle, surface, etc.) because its effective charge is the same.
2. Since the charge increases when the polymer concentration decreases, the electrostatic contribution of the interaction between PANa and another charged species should not be the same when the concentration changes. This effect is very important for chain concentrations below 1×10^{-4} mol dm^{-3} and any ΔG of adsorption computed from adsorption isotherms for such systems is highly questionable.
3. Regarding the salt addition, the effective charge is proportional to $I^{1/2}$ for $I > 6 \times 10^{-2}$ mol dm^{-3} (i.e., for $\kappa^{-1} < 3$ nm); however, any charge increase of the polymer promoted by salt addition with a view to increase the electrostatic interaction between a charged polymer and a charged surface, for example, is compensated by the higher extent of screening of the polymer.
4. The closure of industrial water circuits, a high hardness index of water, or the use of partly soluble calcium salts ($CaCO_3$ or $CaSO_4$) in industrial processes can lead to a high level of Ca^{2+} pollution. As far as the electrostatic behavior is concerned, the efficiency of PANa under these conditions should not be affected as long as the ratio Ca^{2+}/c_p is at least 0.222 or lower because the polymer can stand the presence of Ca^{2+} below this ratio without losing its effective charge.

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