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Influence of the counter-ion on the effective charge of polyacrylic acid in dilute condition

Jean-Philippe Boisvert*, Alexandre Malgat, Isabelle Pochard, Claude Daneault

Centre de recherche en pâtes et papier, Pavillon Suzor-Côté, Université du Québec à Trois-Rivières, 3351, boul. des Forges, Trois-Rivières, Que., Canada G9A 5H7

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Abstract

Osmotic pressure measurements were satisfactorily used to compute the effective charge of poly(acrylic) acid (PAA) at different pHs and with different monovalent and divalent counterions. This experimental method is sensitive to the osmotically active species (polymer and counterions). After correction for the polymer contribution to the total osmotic pressure (solvency and excluded volume), the remaining pressure can be attributed to the polyelectrolyte counterions and processed with Donnan and equation of state in order to compute the effective charge number per polymeric chain (Z^{eff}). The behavior of Z^{eff} against the chain concentration and pH was investigated after neutralization of PAA with LiOH, NaOH, and TMAOH. The results clearly indicate that the nature of the monovalent counterion has no effect on Z^{eff} leading to the conclusion that the interaction between monovalent counterions and the acrylate functionality is purely electrostatic in agreement with conductimetric and potentiometric results reported in the literature. The behavior of Z^{eff} against the degree of ionization of the polymer and its concentration is also in good agreement with the theoretical expectations of the theory of ionic condensation. Osmotic measurements were also used in order to understand the influence of divalent cations (Mg^{2+}, Ca^{2+}, Ba^{2+}) on Z^{eff} of the sodium salt of PAA at pH 9 and at different divalent/acrylate molar ratio. All the divalent cations depress Z^{eff} each of one at different degrees, confirming a specific divalent/polymer interaction. The energy of hydration of cations can explain most of the observed results with divalents. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(acrylic) acid; Ionic condensation; Effective charge

1. Introduction

The poly(acrylic) acid (PAA) is widely used as additive in coatings, paints, ceramics, and cosmetics industries in order to improve the rheological properties of mineral slurries by increasing the repulsion between particles [1–5]. The performance of PAA in stabilizing mineral particles is in part related to its 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}). It then appears that this effective charge is a very important parameter that should be monitored and correlated to the stabilizing efficiency of the polyelectrolyte when used as a dispersant, for example.

The effect of ionic condensation has been observed for solutions of linear polyelectrolytes by Katchalsky 35 years ago [11]. The theory that rationalized this phenomenon was developed few years latter by Oosawa [12] and Manning [13]. The theory of ionic condensation is developed elsewhere [14–18] and predicts an effective charge number (Z^{eff}) which increases with the bare charge number (Z^{str}) up to the point where the thermal energy of the ions balances the reversible work necessary to remove ions from the charged species. From that point on, the effective charge of the polymer remains constant. Thus, a maximum effective charge can be expected and all additional charges added to the polyelectrolyte above this maximum value will condense (ionic condensation) leading to a constant Z^{eff}. Recent models and experimental work can predict such ionic condensation [17,19]. 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 usage to replace the bare charge

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* Corresponding author. Tel.: +1-819-376-5075; fax: +1-819-376-5148.

E-mail address: jean-philippe_boisvert@uqtr.uquebec.ca (J.-P. Boisvert).

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by a so-called 'renormalized' charge (effective charge) [15,16,20].

In this work it is investigated the influence of the pH, the nature of the monovalent counter-ion and the presence of complexing divalent cations upon the effective charge of PAA of molecular weight (MW) 35 kg mol^{-1}. Equation of state and osmotic measurements were used in order to compute Z^{eff} for this polyelectrolyte. This straightforward approach can be used to compute an experimental Z^{eff} with very few approximations and a priori assumptions (on the form of the interaction potential, charge distribution, etc). Moreover, this experimental method allows very low osmotic pressures to be measured and thus allowing dilute conditions to be used. The polymer solvency parameter χ (Flory–Huggins parameter) accounting for the solute–solvent interactions 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.

2. Theoretical background

Osmometry has been widely used to characterize colloidal suspensions. It is possible with this very simple experimental method to access to the effective charge via equation of state. In this method, a Donnan equilibrium is established by the distribution of a diffusible electrolyte in two compartments separated by a semi-permeable membrane when a non-diffusible polyion (charged particle) is localized in one of the compartments. This compartment will be referred below to as the *inside* compartment while the other will be referred to as the *outside* compartment (reservoir). The charge of the polymer creates an uneven distribution of the small ions across the membrane which is at the origin of the net osmotic pressure Π experienced by this system.

The predictions of the colloidal behavior of concentrated suspensions has been the subject of many theoretical studies [15,18,21–24]. As demonstrated elsewhere [21,22] it is clearly shown that small ions in a 1:1 electrolyte with a concentration up to 0.1 M in presence of polyelectrolyte with a chain concentration up to 0.001 M and an effective charge number up to 30–40 behave as ideal solution. Under these conditions, one can neglect the activity coefficients of the small ions and the net osmotic pressure is then

$$\frac{\Pi}{kT} \cong \gamma_{\text{p}}\varphi_{\text{p}} + \varphi_{+}^{\text{i}} + \varphi_{-}^{\text{i}} - \varphi_{+}^{\text{o}} - \varphi_{-}^{\text{o}} \quad (1)$$

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 non-ideality 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 B_n [25,26]:

$$\frac{\Pi}{kT} \cong \varphi_{\text{p}}(1 + B_2\varphi_{\text{p}} + B_3\varphi_{\text{p}}^2 + \cdots) + \varphi_{+}^{\text{i}} + \varphi_{-}^{\text{i}} - \varphi_{+}^{\text{o}} - \varphi_{-}^{\text{o}}$$

Thus,

$$\gamma_{\text{p}} \cong (1 + B_2\varphi_{\text{p}} + B_3\varphi_{\text{p}}^2 + \cdots) \quad (2)$$

By considering low concentrations ($\varphi_{\text{p}} \to 0$), we are allowed to neglect all high-order terms. Then, Eq. (2) reduces to

$$\gamma_{\text{p}} \cong 1 + B_2\varphi_{\text{p}} \quad (3)$$

where B_2 is the second virial coefficient accounting for the excluded volume and solvency effects. It is shown elsewhere [27] that the development of Eq. (1) for low φ_{p} leads to

$$\frac{\Pi}{kT} \cong \varphi_{\text{p}}\left(1 + \frac{(1/2 - \chi)\bar{V}_{\text{p}}^2}{1000\bar{V}_1 N_{\text{A}}}\varphi_{\text{p}} + \nu\varphi_{\text{p}}\right) + 2\varphi_{+}^{\text{o}}\left[\left\{\left(\frac{\varphi_{\text{p}}Z^{\text{eff}}}{2\varphi_{+}^{\text{o}}}\right)^2 + 1\right\}^{1/2} - 1\right] \quad (4)$$

where χ is the Flory–Huggins interaction parameter, N_{A} is the Avogadro number, $\bar{V}_{\text{p}}$ and $\bar{V}_1$ 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 $\nu = 4(4/3\pi(a^{\text{eff}})^3)$ is the excluded volume for a spherical polymer molecule with effective radius a^{eff}. The effective radius is defined as $a^{\text{eff}} = a + \kappa^{-1}$ where $\kappa = (8\pi L_{\text{B}} I)^{1/2}$ is the inverse of the Debye length, where L_{B} is the Bjerrum length. It should be noted that in the equation $\nu = 4(4/3\pi(a^{\text{eff}})^3)$, the excluded volume implicitly considers the volume of non-interpenetrating double layers. Although the concept of excluded volume is usually much more appropriate for 'hard' surfaces (proteins, latex, mineral colloids, etc) than 'diffuse' surfaces (random coiled polymers), one can consider as a first approximation that the electrostatic charge present with the polyelectrolyte induce some stiffness on the polymer conformation.

As shown elsewhere [28], the exact value of χ and ν for PAA depends upon the ionic strength I. Here, the ionic strength (mol dm^{-3}) is defined as $I = (1000N_{\text{A}})^{-1}[\varphi_{\text{s}}^{\text{i}} + 1/2\varphi_{\text{p}}Z^{\text{eff}}]$ where $\varphi_{\text{s}}^{\text{i}}$ is the salt concentration (number per cubic meter) inside the polymer compartment. The solvency parameter for the PAA is known to be a linear function of $I^{-1/2}$. The empiric relation between χ and $I^{-1/2}$ is [28]

$$\chi = -(0.02167I^{-1/2}) + 0.5232 \quad (5)$$

The effective radius of gyration for the PAA of MW 15,000 is [28]

$$R_{\text{G}} = -3.539 + 0.5273I^{-1/2} - 0.01279I^{-1} \quad (6)$$

Assuming a spherical geometry, one can compute the effective polymer radius $a^{\mathrm{eff}} = R_G(5/3)^{1/2}$ from Eq. (6) and access to the excluded volume ν. Since all the terms but Z^{eff} in Eq. (4) are known, one can take Z^{eff} as an adjustable parameter and find by iteration the value of Z^{eff} necessary to match the experimental osmotic pressure as a function of φ_p.

Interestingly, when $\varphi_+^o > \varphi_p$ the last term in Eq. (4) simplifies [29] and Eq. (4) reduces to

$$\frac{\Pi}{kT} \cong \varphi_p\left(1 + \frac{(1/2 - \chi)\bar{V}_p^2}{1000\bar{V}_1 N_A}\varphi_p + \nu\varphi_p + \frac{(Z^{\mathrm{eff}})^2\varphi_p}{4\varphi_+^o}\right) \tag{7}$$

From Eq. (7), it may be seen that the last term of Eq. (4) can be associated with a second virial coefficient in connection with the charge of the polymer. Thus, Eq. (4) can be transcripted in the following form

$$\Pi \cong \Pi^{\mathrm{ID}} + \Pi^{\chi} + \Pi^{\mathrm{exc}} + \Pi^{\mathrm{Donnan}}$$

where Π^{ID} is the limiting osmotic pressure (ideal gas 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.

Moreover, it should be mentioned that the osmotic pressure for polyions can also be computed using the so-called 'virial' route that takes into account the repulsive interaction between two charged spheres with charges homogeneously distributed on the particle surface. This approach uses the virial Eq. (8) as a starting point [25]

$$\frac{\Pi}{kT} = \rho_p - \frac{2\pi}{3kT}\rho_p^2 \int g(r)\frac{\partial \upsilon(r)}{\partial r} r^3 \,\mathrm{d}r \tag{8}$$

where $\upsilon(r)$ is the total interaction energy, r is the mean center-to-center distance between monodisperse spherical particles, $g(r)$ is the radial distribution function. Unfortunately, $g(r)$ and $\upsilon(r)$ are unknown functions for many-body interactions and in order to use Eq. (8), many approximations have to be done. A very usual approximation is to only consider pair interactions. According to the DLVO theory for spherical and monodisperse particles, the screened coulombic pair wise potential for the electrostatic contribution is [25]

$$\upsilon^{\mathrm{DLVO}}(r)/kT = \frac{(Z^{\mathrm{eff}})^2 L_B}{r}\frac{\exp[-\kappa(r - 2a)]}{(1 + \kappa a)^2} \tag{9}$$

By replacing Eq. (9) into Eq. (8) and in the limit of the linear Debye–Hückel theory [25], Eq. (8) reduces to

$$\frac{\Pi}{kT} = \rho_p + \rho_p^2\left[\frac{16\pi a^3}{3} + \frac{(Z^{\mathrm{eff}})^2}{4\rho_+^o}\right] \tag{10}$$

which is very close to Eq. (7). Actually, the only difference between Eqs. (10) and (7) is the absence of the solvency effect. Some refinements of the interaction potential can include attractive interactions [21].

3. Material and method

3.1. Chemical reagents

All electrolytes (LiOH, NaOH, Tetramethyl ammonium hydroxide (TMAOH), $MgCl_2$, $CaCl_2$, $BaCl_2$) are 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 stressor for the osmotic pressure experiments.

3.2. Osmotic stress

This method has been used by other workers on other systems [30–33] and was adapted to the present study. In this method, the osmotic pressure of PEG solutions having different weight concentrations is first measured by osmometry as described elsewhere [30,32]. 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 PAA solutions of known concentrations ($c_p > 3 \times 10^{-3}$ 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 PAA solutions. Therefore, the dependence of the PAA concentration on the osmotic pressure is known and yields the equation of state of the polyelectrolyte solution, as described in the theoretical background.

The dialysis tubes of regenerated cellulose were provided by Roth. The nominal cut off of the membrane is 12–14 kg mol^{-1}, i.e. neither the PAA 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 three 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.

4. Experimental details

The influence of three main parameters on the effective charge were investigated: the pH, the nature of the monovalent counter-ion and the nature 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 MW of the purified PAA was measured by osmotic pressure measurements

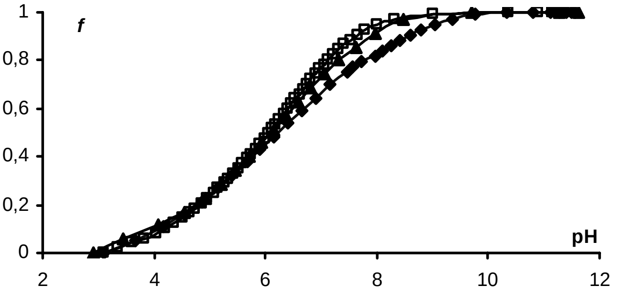

Fig. 1. Degree of neutralization of PAA upon alcalimetric titration with (□) LiOH, (▲) NaOH, and (◆) TMAOH. The degree of neutralization is defined as the number of neutralized acrylic acid functional groups over the total number of functional groups. The monomer concentration c_p is 4.5×10^{-2} monomol dm^{-3}.

as reported elsewhere [27] and found to be 35 kg mol^{-1}. The precipitated and purified PAA 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.

4.1. pH adjustment

Solutions of sodium, lithium and tetramethylammonium (TMA) poly(acrylate) at different pHs were prepared from the PAA solution by addition of LiOH, NaOH, TMAOH, respectively. The pHs investigated were pH 4, 6.5, 7.5, 8, and 9. These are the equilibrium pHs of the polyacrylate solutions in the dialysis bag. The total concentration of acrylate functional groups was determined by full titration of the initial PAA solution with an Orion 720A pHmeter. The degree of neutralization *f* of PANa, PALi and PATMA against pH is presented in Fig. 1. This degree of neutralization represents the number of neutralized carboxylic groups over the total number of functional groups.

4.2. Divalent addition

$MgCl_2$, $CaCl_2$, $BaCl_2$ were added to the PANa solution (pH 9) up to molar ratios $r\ X^{2+}/c_p = 0.12$, 0.22 and 0,33, where X^{2+} is the molar concentration of Mg^{2+}, Ca^{2+} or Ba^{2+}. No divalent cations were detectable in the PEG reservoir at equilibrium confirming the strong affinity of divalents for the PAA at pH 9 when $X^{2+}/c_p < 0.33$.

Turbidity measurements on the PANa + XCl_2 solutions at pH 9 were performed against $r\ X^{2+}/c_p$ in order to find the critical r_c above which precipitation of Mg, Ca or Ba polyacrylate becomes apparent. The measurements were performed by a Hach instrument calibrated with standards of known turbidities. The initial c_p was 2×10^{-3} monomol dm^{-3} and the added volume of the XCl_2 solution was less than 10% of the initial volume.

In all cases, the pH of both the PAA and the PEG solutions as well as the remaining volume in each bag were measured at equilibrium. The latter is used to calculate the equilibrium concentration of the PAA and the PEG. The concentration of cations and anions in the reservoir were determined by atomic adsorption spectroscopy for Na^+, Mg^{2+}, Ca^{2+}, Ba^{2+} and by ionic chromatography for Cl^-. The concentration of LiOH and TMAOH were determined by conductivity using calibration curves.

5. Results and discussion

5.1. Experimental considerations regarding the dilute and semi-dilute conditions

The theory of ionic condensation is particularly suitable for polyelectrolyte concentrations belonging to the dilute regime [15]. It is then important to make sure that the range of the PAA concentrations studied in the present work belongs to this regime. Theoretical studies [34,35] 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 relationship differs depending on whether the solution is in the dilute or semi-dilute regime. In the dilute regime, the slope should be within 1.05 and 1.13 and should increase to 2.25 for the semi-dilute regime [34,35].

In order to find to which regime our systems belong, osmotic pressure measurements were performed on PAA solutions at pH 9 with monovalent (Li^+, Na^+, TMA^+) and divalent (Mg^{2+},Ca^{2+}, Ba^{2+}) counter-ions. The experimental slopes on a log–log scale Π vs C_p for $C_p < 5 \times 10^{-4}$ mol dm^{-3} were always within or close to the expected values (1.05–1.13) for a dilute solution. It is then fully justified to use the theory of the ionic condensation to interpret the results. (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})).

5.2. Influence of monovalent counter-ions on the effective charge

Using Eq. (4), the effective charge (Z^{eff}) of the polymer can be computed as a function of the chain concentration (C_p) at different pHs. In these experiments, the PAA was acidified to pH 3 by using a cationic resin and then ionised with LiOH, NaOH or TMAOH to the selected pHs. The results are reported in Figs. 2–4, respectively. Three main observations can be made from these figures: Firstly, Z^{eff} does not depend on the pH within pH 7 and 9 but does so below pH 7; Secondly, Z^{eff} is not very sensitive to C_p (or the volume fraction ϕ) unless C_p is very low. Both observations agree pretty well with predictions of the charge renormalization theory. Actually, osmotic measurements were performed at very low C_p only for PANa at pH 9. These data are reported in Figs. 2–4, for comparison. Thirdly, the results are very similar no matter the counter-ion (Li^+, Na^+, or TMA^+).

1. The saturation of Z^{eff} against Z^{str}, predicted by the theory of ionic condensation [15,17,18], is observed in

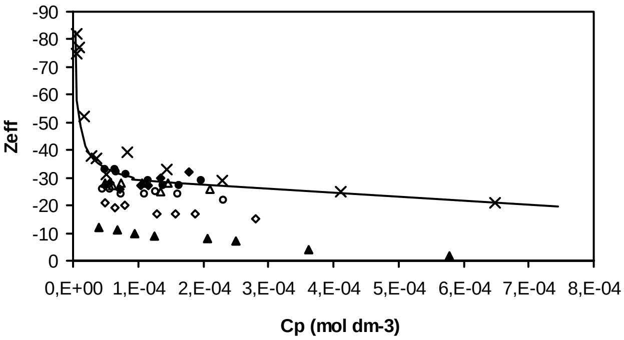

Fig. 2. Effective charge Z^{eff} of PALi calculated from Eq. (4) against chain concentration for different pHs. (▲) pH 4.2, (◇) pH 5, (○) pH 6.2, (◆) pH 7, (△) pH 7.5, (●) pH 10.2, (×) PANa at pH 9.

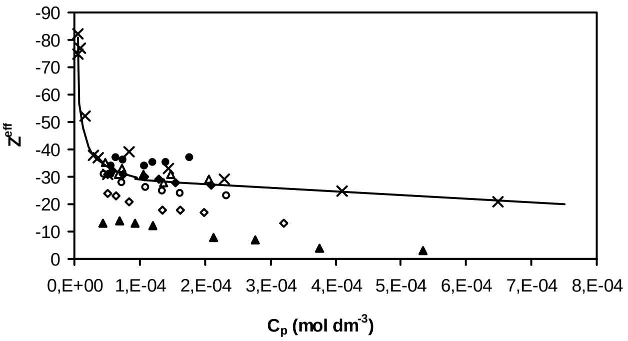

Fig. 4. Effective charge Z^{eff} of PATMA calculated from Eq. (4) against chain concentration for different pHs. (▲) pH 4.2, (◇) pH 5, (○) pH 6, (◆) pH 6.8, (△) pH 7, (●) pH 10, (×) PANa at pH 9.

Figs. 2–4; the maximum Z^{eff} value is already reached at pH 6.5–7 and remains constant over pH 7. At pHs over 7, the maximum Z^{eff} value is roughly 40 to 20 per chain for chain concentrations higher than 1×10^{-4} mol dm^{-3}, no matter the counter-ion. The ratio Z^{eff}/Z^{str} saturates to about 0.10 at pHs over 7 and increases to 0.20 at lower pHs. This ratio is very similar to results reported elsewhere [9,36–38] but lower than the one reported in other studies [39,40]. The relation between Z^{str} and Z^{eff} is reported in Fig. 5. This figure clearly illustrates the saturation of Z^{eff} against Z^{str} as predicted.

2. The theory of ionic condensation also predicts that Z^{eff} increases very sharply as C_p (or ϕ) decreases to zero [17] and reaches its bare value Z^{str} in the infinite dilution limit [15]. In this limit, the polyelectrolyte solution is ideal and concept of ionic condensation becomes obsolete [12,41]. The leveling off of Z^{eff} when C_p increases is also in agreement with the theory of ionic condensation. As shown in Fig. 5, the results for PANa at pH 9 agree very well (at least qualitatively) with the theoretical expectations of the ionic condensation theory for the wide range of chain concentration. Such a behavior is predicted [15,17,18] and observed for colloids [42,43]. It seems then to be a behavior common to any charged specie no matter if it is polymer, micelle, latex, mineral, etc.
3. The results reported in Fig. 5 also show that Z^{eff} does not depend on the nature of the monovalent counter-ion. According to osmotic pressure measurements, the interaction between a monovalent counter-ion and the acrylate functionality is thus purely electrostatic. This finding is in agreement with conductimetric and potentiometric measurements on similar polymers [39,40,44] and legitimates the starting hypothesis of theories on ionic condensation that consider counter-ions as point charges without any distinct particularity. According to this, the electrostatic properties of PAA should remain the same no matter the counter-ion. Consequently, any possible difference in the dispersing efficiency of PALi, PANa or PATMA could not be explained with electrostatic arguments.

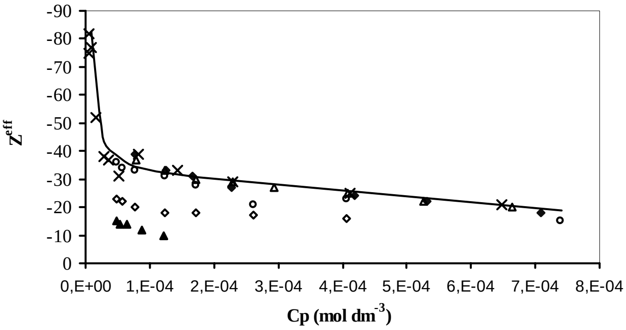

Fig. 3. Effective charge Z^{eff} of PANa calculated from Eq. (4) against chain concentration for different pHs. (▲) pH 4.5, (◇) pH 5.3, (○) pH 6.8, (◆) pH 7.5, (△) pH 8, (×) pH 9.

5.2. Influence of divalent cations on the effective charge

It is now well known that multivalent cations induce an entropically driven complexation of acrylate functional groups [45–47] leading to the precipitation of weak polyelectrolytes above a critical r_c X^{2+}/c_p which depends on the nature of the divalent [48,49]. Thus, before proceeding to osmotic measurements on PANa/XCl$_2$ solutions at various r X^{2+}/c_p, turbidity measurements were made at different r in order to detect the apparent critical r_c above which the

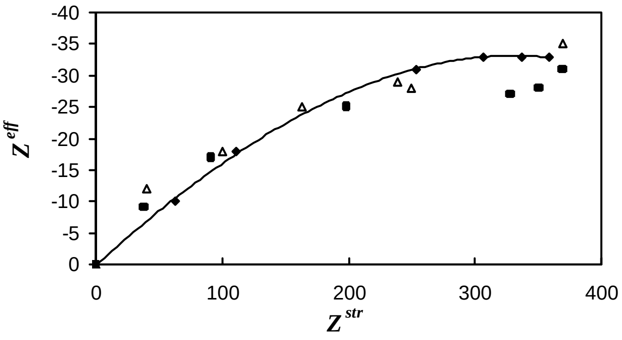

Fig. 5. Effective charge of PAA calculated from Eq. (4) against the structural charge following neutralization with (■) LiOH, (◆) NaOH, and (△) TMAOH. The concentration c_p is 4×10^{-2} monomol dm^{-3}.

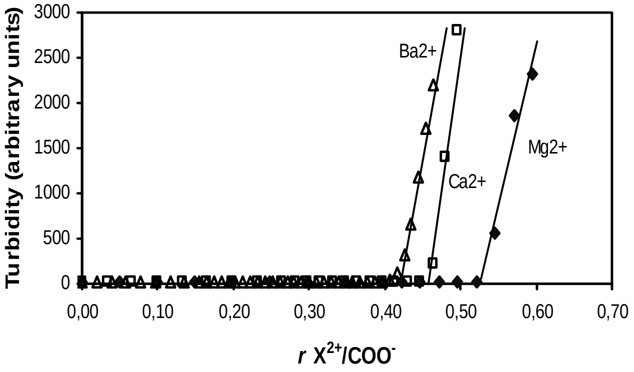

Fig. 6. Influence of the molar ratio X^{2+}/c_p on the turbidity of PANa solutions, where X^{2+} is (◆) Mg^{2+}, (□) Ca^{2+}, and (Δ) Ba^{2+}. Initial $c_p = 2.5 \times 10^{-2}$ monomol dm^{-3}.

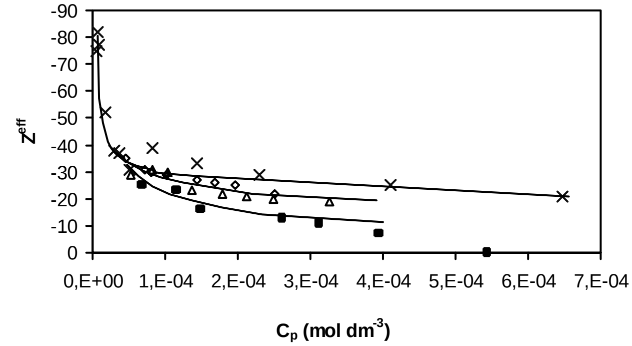

Fig. 7. Influence of the complexing Mg^{2+} ion on the effective charge Z^{eff} of PANa at pH 9. (×) no Mg^{2+} salt, (◇) $r\,Mg^{2+}/c_p = 0.12$, (Δ) $r = 0.22$, and (■) $r = 0.33$.

polymer precipitates. As reported in Fig. 6, r_c depends on the nature of the divalent cation indicating a specific interaction with the polymer. This feature can be correlated to the hydration energy. The magnitude of hydration energy is $Mg^{2+} > Ca^{2+} > Ba^{2+}$ [50,51]. According to this, among the three cations, Ba^{2+} should be the easiest to desolvate and consequently easier to complex with the acrylate functionality leading to the formation of the precipitate detected by turbidimetric measurements. The same trend should apply to the other cations explaining the order $r_c\,Mg^{2+}/c_p = 0.55 > r_c\,Ca^{2+}/c_p = 0.44 > r_c\,Ba^{2+}/c_p = 0.42$ observed in Fig. 6. The present results are in agreement with other studies showing that Ba^{2+} has a higher affinity than Ca^{2+} for PAA as well as for similar polyelectrolytes [10,52].

Other workers report precipitation at $r_c\,Ca^{2+}/c_p = 0.37$ with PAA MW 60 kg mol^{-1} [6]. Of course, the higher the MW, the lower r_c should be [53] explaining then the various r_c reported in the literature. Moreover, as reported in the literature and in the present study precipitation occurs with Ca^{2+} and Ba^{2+} before all functional groups are complexed i.e. at $r < 0.5$ indicating that a complete neutralization is not a necessary condition for the precipitation to begins.

Interestingly, Mg^{2+} seems to be so much hydrated that precipitation begins only when the functional groups are 'oversaturated' with respect to Mg^{2+}, i.e. $r_c > 0.5$. Indeed, a high hydration energy should lower the tendency for this ion to form Mg-polyacrylate precipitate. Hence, an higher ionic 'pressure' (concentration) is required to induce desolvation and force precipitation. However, it is clearly shown elsewhere [10] that although divalent ions (like Mg^{2+}) may not be dehydrated by the carboxylate functional groups at low $r\,X^{2+}/c_p$ they remain in the vicinity of the functional group as hydrated counter-ions and then they are not free in solution, at least for $r\,X^{2+}/c_p$ lower than 0.3. In addition to that, the results presented in Fig. 6 show that the PANa remains fully soluble for $r\,X^{2+}/c_p$ lower than 0.4. According to these experimental evidences, we proceeded with the osmotic pressure measurements on PANa solutions at $r\,X^{2+}/c_p = 0.12$, 0.22, and 0.33. These experiments will show the influence of $r\,X^{2+}/c_p$ on the effective charge of PANa at pH 9. The results are reported in Figs. 7–9 for Mg^{2+}, Ca^{2+}, and Ba^{2+}, respectively.

As shown in Figs. 7–9, the presence of divalent cations influences the effective charge of PANa. As a general trend, the higher r the lower the Z^{eff}. The exact magnitude of this influence seems to depend on the nature of the divalent cation but there is no simple relation between their order in the periodic table and their efficiency in reducing Z^{eff}. Barium is the most perturbing cation, probably because of its lower hydration energy. The presence of precipitate at high C_p with $r\,Ba^{2+}/c_p = 0.33$ in Fig. 9 reported for the data points with open squares confirms that the interaction between the functional groups and the Ba^{2+} is strong enough (or one could that say the hydration energy of Ba^{2+} is weak enough) to lead to the formation of insoluble (non-hydrated) barium polyacrylate. Obviously, for Ba^{2+} the critical ratio r_c at which the precipitate appears depends on the concentration of the polymer; at $c_p = 0.025$; $r_c = 0.42$, at $c_p = 0.2$; $r_c = 0.33$. This observation indicates a complex behavior that should be investigated in future work.

Moreover, as can be seen in Fig. 9, there is no simple relation between Z^{eff} and the presence of a precipitate; on one hand the apparition of a precipitate with Ba^{2+} seems to

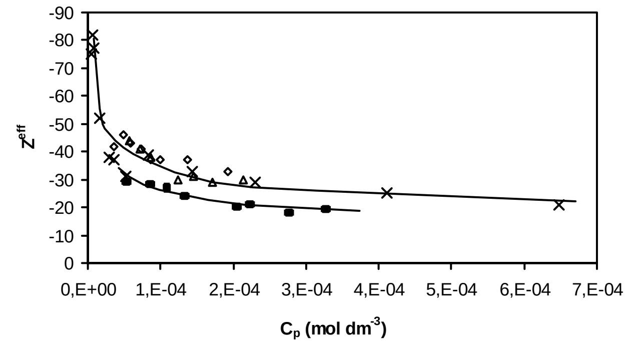

Fig. 8. Influence of the complexing Ca^{2+} ion on the effective charge Z^{eff} of PANa at pH 9. (×) no Ca^{2+} salt, (◇) $r\,Ca^{2+}/c_p = 0.12$, (Δ) $r = 0.22$, and (■) $r = 0.33$.

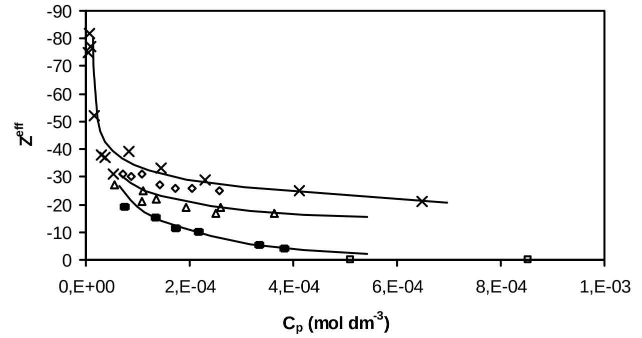

Fig. 9. Influence of the complexing Ba^{2+} ion on the effective charge Z^{eff} of PANa at pH 9. (×) No Ba^{2+} salt, (◇) r Ba^{2+}/$c_p = 0.12$, (Δ) $r = 0.22$, and (■) $r = 0,33$. Open squares refer to polymer solutions in which a precipitate was observed at equilibrium. The precipitate was not observed at initial concentration.

be related to the falloff of Z^{eff} to zero but on another hand a zero effective charge does not lead to any detectable precipitation with Mg^{2+} (see Fig. 7). Interestingly, with Mg^{2+} at $r = 0.33$ and $Z^{\text{eff}} = 0$ the experimental osmotic pressure can be perfectly modelled with the terms in the first bracket of Eq. (4), i.e. with no adjustable parameter. If this result is not fortuitous, it would mean that Mg^{2+} does not perturb the conformation of the polymer (at least at this r) and consequently that Mg^{2+} is condensed but not complexed with the functional groups leading to a neutral and highly hydrated magnesium polyacrylate specie. Such an explanation is compatible with the high hydration energy of Mg^{2+}. By using the same arguments, the interaction of the Ba^{2+} and the functional groups seems very deleterious to the polymer since there is no way the experimental osmotic pressure can be modeled with Eq. (4) taking $Z^{\text{eff}} = 0$; at this condition, the experimental osmotic pressure is always much lower than that computed with the use of Eq. (4) This would mean that the solvency parameter χ and/or the excluded volume ν depend on r with Ba^{2+}. Such a dependence is much less pronounced with Mg^{2+}. The situation with Ca^{2+} is intermediate.

6. Conclusion

Osmotic pressure measurements in combination with equation of state have allowed the computation of the effective charge of the weak PAA, against pH in dilute condition and in presence of various monovalent and divalent counterions. In presence of monovalents the results agree pretty well with the expectations of the theory of ionic condensation on linear polyelectrolyte. The results clearly indicate that no matter with which base (LiOH, NaOH, TMAOH) the PAA is neutralized its effective charge increases the same way. Above a neutralization degree of about 0.6 corresponding to a pH of 7, the effective charge levels off to a limiting value. These two observations lead to the conclusion that the interaction between the monovalent counterion and the polyelectrolyte is non-specific, i.e. is the same no matter the counterion. The practical implication of this finding is that any difference in the stabilizing efficiency between PALi and PATMA observed following adsorption on mineral particles, for example, could not be explained by using the usual arguments of electrostatic repulsion since the effective charge responsible for the electrostatic repulsion is the same. Another practical implication would be that any difference in the stabilizing efficiency of the polymer between pH 7 and 10 could not be attributed to the increase of the electrostatic repulsion, again because the effective charge is the same.

Concerning the interaction of the polymer with divalent counterions, the results show a specific interaction with the acrylate functionality. The strength of this interaction seems to be related to the energy of hydration of the cations; the lower the energy, the stronger the interaction and the easier the complexation with the polymer leading to insoluble divalent polyacrylate species. The Mg^{2+} counterion has a much higher tendency than Ba^{2+} or Ca^{2+} to condense with the acrylate. Below a critical molar ratio Mg^{2+}/c_p the Mg-polyacrylate species remain fully soluble and behave like a neutral but hydrated polymer. Above this critical ratio, the Mg-polyacrylate species begin to precipitate.

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