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ORIGINAL CONTRIBUTION

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Potentiometric and conductometric analysis of the binding of Barium ions with alkali polyacrylate

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Abstract The interaction between Poly(acrylic acid) and barium ions is analyzed using potentiometric (barium specific electrode) and conductometric titrations. At full ionization of the polyelectrolyte, in the presence of M^+ counterions ($M^+ = Li^+$, Na^+ and K^+), the binding ratio $[Ba^{2+}]_{bound}/C_p$ on the chain is determined, showing no significant difference between the three alkali ions. When the added Ba^{2+} concentration does not exceed $0.2 \times C_p$, all barium ions bind with the polymer, i.e. none can be detected in the solution with the barium selective electrode. Assuming that monovalent counterions divide the electrostatically condensed and "atmospheric" ions and using Eisenberg plots of the conductivity excess, the experimental data allows to calculate the distribution of the different acrylic species on the fully deprotonated chain (free carboxylate groups, bound groups with M^+ and with Ba^{2+} ions). Assuming the formation of a bidentate $Ba(COO)_2$ species and taking into account that part of the remaining groups bind with M^+ ions, the calculated complexation constant ($\log K_c = 6.5$) is satisfactorily independent of the complexation ratio. The displacement ratio of M^+ ions by attaching Ba^{2+} ions is also calculated, showing interestingly a continuous decrease between 1.4 and 0.9 as r increases. The latter result is attributed to the change of the averaged electrostatic potential of the chain, in relation with the binding of barium ions.

Key words Conductometry – polyacrylic acid – barium II ion – complexation – counterions condensation

Introduction

Interactions between counterions and polyelectrolytes are a relevant phenomenon in a number of applications. As an example polyelectrolytes are used as additives in cement pastes to control the rheological properties and the setting behavior [1], in concentrated suspensions of particles to ensure the dispersion stability and the fluidity of the system [2], in many industrial processes such as selective floculation, mineral flotation and used water clarification [3], etc. In all cases, there is much evidence that the polyelectrolyte performance can be profoundly altered by interacting ionic species. This is particularly true for solutions containing high salt concentrations and when multivalent counterions (e.g. Ca^{2+}, $A1^{3+}$, La^{3+} SO_4^{2-}, PO_4^{3-}, etc.) induce precipitation of the polymer, gelification of the system or increase in the adhesion between mineral surfaces [4].

Our interest aims at the comprehension of the effect of dissolved ions in the adsorption of polyelectrolytes on inorganic materials. In the case of anionic polymers (e.g. poly(acrylic) and poly(sulfonic) acids) it is well established that multivalent cations increase considerably the adsorption on particles [5–7]. The cations effect in however limited in the concentration range where the polymer remains soluble and where the cations act as a bridge between the negative sites of the surface and the negative functional groups on the macromolecule. The last point suggests that the bridging process depends on the relative affinity of the cations for the polyelectrolyte and the surface. It also depends on the coordination number of the metal/ligand complex. If M^{2+} ions form strongly bound bidentate species, no positive charge remains to bind the polymer with the surface sites. In the latter case, the retention of the polyelectrolyte by the particles relates more to precipitation than to adsorption phenomena.

Due to the wide field of theoretical and practical interests, extensive investigations have been made of the interaction between small ions and polyelectrolytes. Considering only weakly acidic polymers such as poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMA), the effect of salts on the ionization properties has been largely analyzed, producing affinity series for cations on the basis of their influence on the ionization constants [8]. Much less is established concerning the binding of metallic ions with the functional groups. Studies divide between two principal approaches. One was introduced by Manning [9] which postulates that counterions of different valency are considered either electrostatically bound (condensed) to the polymer or free in the bulk. The other one considers that counterions bind specifically with the carboxylic groups, forming definite complex species. In the latter case, the coordination number and the intrinsic complexation constants vary between different studies, which may be derived from differences in the experimental design or in theoretical assumptions. Both the formation of bidentate [10, 11] and monodentate [12] calcium/acrylate ligand complexes have been proposed. According to the latter study, Cu^{2+} and Pb^{2+} ions form bidentate or monodentate species with the carboxylate functional groups, depending on the binding ratio. Barium counterions have not been examined as much as calcium, magnesium and transition cations in the presence of carboxylic polymers. For Ba^{2+}, Koda [13] reports a simple electrostatic interaction with PAA, different from Cu^{2+}, Zn^{2+} and Mn^{2+} which bind chemically with the acrylate groups.

The present study deals with the complexation properties of polyacrylate salts (PAM) with barium ions. A combination of conductometric and potentiometric (using a barium specific electrode) titrations have been used to study the Ba^{2+}/M^{+} exchange ratio ($M^{+} = Li^{+}, Na^{+}, K^{+}$) and to determine the unbound carboxylate groups at full ionization of the polymer chain. Conductometric titrations of the polyacid are also made with the three MOH alkali to examine the interaction of M^{+} ions with the chain in terms of condensation phenomena as defined in the Manning theory [14]. In order to proceed with the calculation, several approximations are discussed. Finally, assuming the formation of a bidentate ligand complex, the complexation constant is calculated. The latter appears satisfactorily independent on the complexation ratio.

Definitions

Generalities on polyelectrolytes

For a given degree of neutralization, α, the charge density parameter ξ of a polyelectrolyte is defined as follows [14, 9]:

$$\xi = \frac{\alpha l_B}{b} , \tag{1}$$

where l_B is the Bjerrum length, α is the degree of neutralization of the polymer, b is the average charge spacing along the polymer chain (2.5×10^{-10} m for fully ionized polyacrylic acid [15]).

$$l_B = \frac{q^2}{DkT} = 7.1\ \text{Å} \quad \text{in water at 298 K} , \tag{2}$$

where q is the elementary charge, D is the bulk solvent dielectric constant, k is the Boltzmann's constant and T is the temperature in Kelvin.

The degree of neutralisation, α, is the ratio between the number of neutralized acrylate groups and the total number of monomer groups on the polyion

$$\alpha = \frac{[\text{–COO}^-]}{[\text{–COOH}]_{\text{tot}}} , \tag{3}$$

where $[\text{–COOH}]_{\text{tot}} = C_p$: concentration of monomer groups.

According to the Manning theory [14], counterions are free in the solution, i.e. they fully contribute to the bulk conductivity, up to the critical value $\xi = 1/|Z|$, where Z is the counterions valency.

Definition of the conductivity excess [16, 17]

The excess of conductivity K_E due to the complexation of barium ions on PAM is equal to the total conductivity K_T of the PAM/$BaCl_2$ solution minus the initial conductivity of alkali polyacrylate K_{pol} (without any addition of barium chloride) and the conductivity of $BaCl_2$ in pure water K_B

$$K_E = -(K_T - K_B - K_{pol}) . \tag{4}$$

The negative sign is conventional in order to obtain positive values of K_E. The expressions of K_T, K_B and K_{pol} are given below:

$$K_T = f_{Ba}C_{Ba}\lambda_{Ba} + 2C_{Ba}\lambda_{Cl} + f_p C_p \lambda_p + f_M C_p \lambda_M , \tag{5}$$

$$K_B = C_{Ba}(\lambda_{Ba} + 2\lambda_{Cl}) , \tag{6}$$

$$K_{pol} = f^0_M C_p(\lambda_p + \lambda_M) . \tag{7}$$

By combining Eqs. (4)–(7) K_E may be expressed as follows:

$$K_E = C_p(\lambda_M + \lambda_p)(f^0_M - f_M) + C_{Ba}(1 - f_{Ba})(\lambda_{Ba} + 2\lambda_p) \tag{8}$$

Where C_i, λ_i and f_i are, respectively, the concentration, the equivalent molar conductivity at 25 °C and the free fraction of the i species. f^0_M is the fraction of free alkali ions in a pure solution of PAM and f_p is the fraction of ionized carboxylic groups bound neither with Ba^{2+} nor with M^+. Comparison between the experimental and calculated conductivities is made using the two state-approximation where ions are considered to be either bound to the polymer or free in the bulk solution. In the first case, they are imperceptible in conductometric measurements, in the second case, they undergo no influence of the polyion and behave as regular electrolyte [18]. The first term on the right-hand side of Eq. (8) is related to the gain in conductivity due to the release of alkali ions from the polymer, whereas the second term is due to the loss of conductivity because of the binding of barium ions by the polyion.

Materials and methods

Polyacrylic acid (PAA) of 5100 g mol^{-1} molecular weight was supplied as a sodium salt powder containing less than 15% w/w of water. Purification of the salt was made by dissolution/precipitation using successively water and addition of methanol. A gel permeation chromatographic analysis of this polymer exhibits a Gaussian distribution of the molecular weight centered at 5100 g mol^{-1} and a degree of polydispersity equal to 2.10. The pH of a 1% w/w solution of the precipitated powder is between 6.0 and 8.0. Preparation of the polyacrylic acid solution was made by ions exchange, using the above sodium salt (PANa) and a cationic resin (Amberlite IRN-77). The resin was added into the PANa solution until the pH reaches a constant value of about 3.

All electrolytes (sodium, lithium, potassium hydroxides and barium chloride) were analytical grade reagents and were used without further purification. Water was purified by a Millipore Milli-Q purification system. Its conductivity was about 1 μS cm^{-1}.

All conductometric analyses were performed using Knick 702 conductometer with a Schott LF1100T cell including a PT1000 thermal probe. The cell constant (0.96 cm^{-1}) was periodically checked and calibrated with a 10^{-2} mol dm^{-3} sodium chloride solution. Potentiometric titrations of free barium ions were performed with an Elit 081 Ionic Selective Electrode (ISE) combined with a calomel electrode. Calibration was made before each experiment with 10^{-4} to 10^{-2} mol dm^{-3} barium chloride solutions at pH 9 and ionic strength 0.3 mol dm^{-3} NaCl. pH, free barium concentration and conductivity measurements were accomplished under a nitrogen stream and at 25 °C.

Solutions of alkali polyacrylate of varying charge density were prepared from the stock PAA solution by adding the corresponding alkali hydroxide (MOH) solution. The total concentration of acrylic groups was determined by full titration of the initial PAA solution using sodium hydroxide and a Crison micropH pHmeter.

Complexation of barium ions by alkali polyacrylate

The conductivity or the ISE electrode potential (depending on the nature of the analyses) were measured in 150 ml of alkali polyacrylate solution ($C_p = 7 \times 10^{-3}$ M) after every addition of 500 μl of 0.15 mol dm^{-3} barium chloride solution. The conductivity, K_B, of 150 ml of water containing the same aliquots of $BaCl_2$ was added, was also measured in order to calculate the conductivity excess. The initial pH of the PAM and $BaCl_2$ solutions were set at 9 with alkali hydroxide so that the polymer was fully neutralized (at pH 9, the degree of neutralisation of PAM equals 1 and no alkali hydroxide is in excess). Finally, the conductivity of sodium polyacrylates of different molecular weight (from 2100 to 170 000 g mol^{-1}) was measured at pH 9 in order to determine the size influence of the macroion on its equivalent molar conductivity.

Neutralization of polyacrylic acid

pH and conductivity were measured during the titration of 150 ml of a polyacrylic acid solution ($C_p = 7.67 \times 10^{-3}$ mol dm^{-3}) using 1N alkali hydroxide solutions (lithium, sodium or potassium hydroxide).

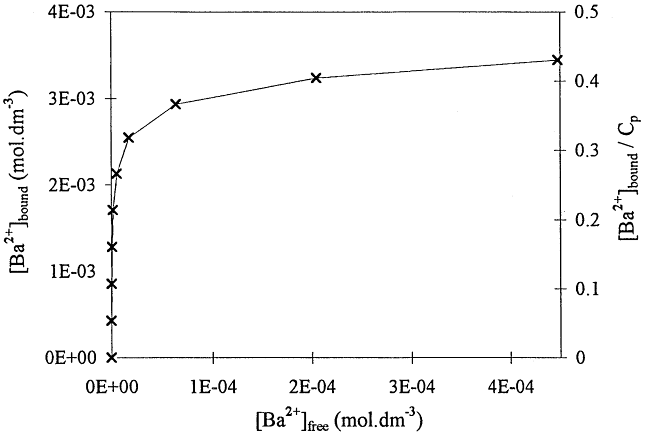
Results

Complexation of barium ions by sodium polyacrylate

Figure 1 represents the concentration of barium ions bound to the polymer versus the free Ba^{2+} concentration. The bound fraction of Ba^{2+} ions is calculated from the difference between the added and the free barium ions concentrations. The latter is obtained by ISE measurements. The experiment was made as described previously, using a PANa solution at pH 9. As found elsewhere [19], there is no detectable free barium ions at low concentration. The ratio of bound barium ions to acrylic monomers levels off at a value of 0.42.

Using the same titration procedure, conductivity data versus $r = [Ba^{2+}]_{\mathrm{added}}/C_p$ present two straight lines with an intercept point close to $r = 0.50$ (Fig. 2). The initial conductivity of the sodium polyacrylate solution is equal to 0.316 mS cm^{-1}. The change of slope is attributed to the end of the barium ions complexation with PANa [10] and to the formation of a white precipitate in the solution. To interpret the conductivity results in terms of bound fractions of monovalent and divalent cations onto the polyion, it is more convenient to consider the excess of conductivity K_E as defined by Eq. (8). The latter gets rid of the initial conductivity of the solution and the contribution of unexchangeable ions (chloride ions). It accounts explicitly for the variation of conductivity due to the Ba^{2+}/PAM interactions [9, 16]. Figure 2 presents also the plot of a $BaCl_2$ solution conductivity (Eq. (6)) and the conductivity excess obtained as described by Eq. (4). K_{pol} is given by the intercept of K_T at zero barium concentration. K_E is zero at $r = 0$ because $f_M^0 = f_M$ and $C_{Ba} = 0$ (see Eq. (8)). At the intersection point of the two sections of K_T, K_E levels off because no more interaction takes place between PANa and Ba^{2+}. Actually, as said above, the polyelectrolyte precipitates.

Fig. 1 Complexation curve of barium ions onto PANa at pH = 9 and $C_p = 7 \times 10^{-3}$ mol dm^{-3} measured by ionic selective electrode



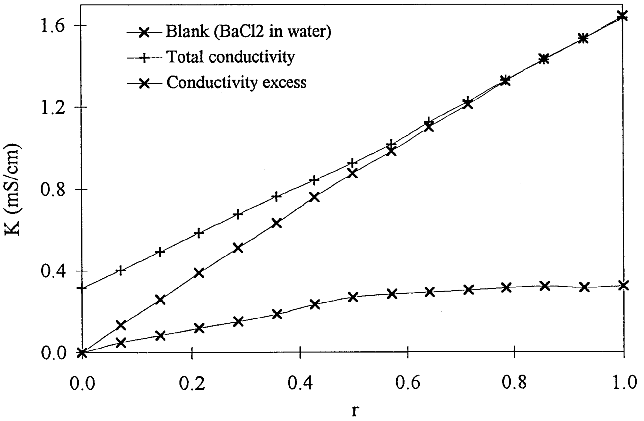


Fig. 2 Conductivity of PANa ($C_p = 7 \times 10^{-3}$ mol dm^{-3}) and water solutions when adding $BaCl_2$. r is the ratio between the concentration of Ba^{2+} added and C_p

Conductivity of alkali polyacrylate in the presence of divalent cations

Conductometric titrations with barium chloride solutions were also performed using PALi and PAK solutions. Results were totally similar in shape to that using PANa but with different conductivity values at a given value of r when using the three different alkali hydroxides. The whole data are presented in Fig. 3 using Eisenberg plots [20]. It gives the molar conductivity of the solutions (S cm^2 per mole of monomer groups) for different values of r (from zero to 0.50) as a function of the equivalent molar conductivity of the alkali ions used. All experiments were performed with the same PAM concentration which is 7×10^{-3} M. Figure 3 shows a linear dependence of the total molar conductivity of alkali polyacrylate solutions as a function of the alkali counterion's equivalent molar conductivity [20]. This has been shown to apply when no specific binding of the counterions takes place with the polyelectrolyte [13]. The plots in Fig. 3 also show that this rule applies at any concentration of barium ions, but with different slopes (from 0.49 to 0.96) and intercepts (22.22–87.63 S cm^2 mol^{-1}) which we shall discuss in the next section.

Neutralisation of PAA

Figure 4 shows the conductometric titrations of polyacrylic acid solutions with alkali hydroxides. The molar

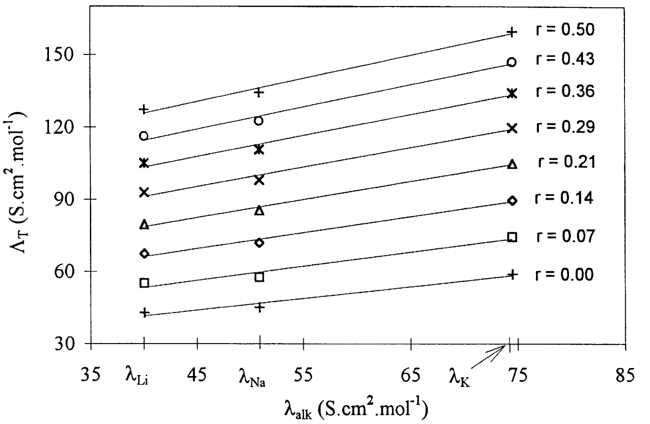


Fig. 3 Total conductivity of PAM solutions against the equivalent molar conductivity of the corresponding alkali counterions (Li^+, Na^+ or K^+). Curves are carried out with increasing concentration of barium chloride ($r = 0$ to 0.50)

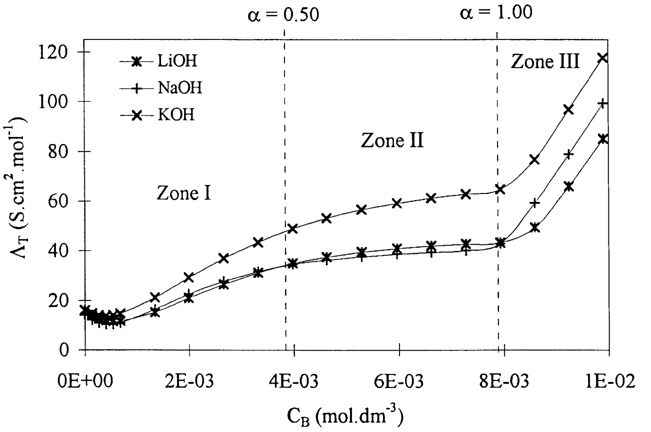


Fig. 4 Evolution of the total conductivity of a PAA solution during its neutralization by LiOH, NaOH and KOH ($C_p = 7.67 \times 10^{-3}$ M)

conductivity first decreases from the initial value 15 S cm^2 mol^{-1} (for $C_p = 7.67 \times 10^{-3}$ mol dm^{-3}) due to the neutralization of free protons produced by the self-ionization of the polyacid [21, 22]. The conductivity then increases smoothly, exhibiting three distinct and roughly linear sections (zone I, II and III). The first one develops between $\alpha = 0.10$ to about 0.50, the second one, above $\alpha = 0.50$, has a lower slope and the third one, strictly linear, corresponds to a titrant excess [23].

The change in slope is formally set at the titrant concentration C_B^*, corresponding to the intersection of the extrapolated linear parts of the conductivity curves in domains I and II. The values of C_B^* differ slightly between the three alkali hydroxide. They are given in Table 1 together with the corresponding values of the ionisation ratio α^*.

Discussion

Stoichiometry of the barium/PANa complexation (ISE analyses)

The vertical slope at the beginning of the curve of Fig. 1 indicates that barium ions present a strong affinity for acrylate groups [24]. Furthermore, the ratio between the concentrations of bound barium ions and carboxylate groups at the plateau gives the apparent stoichiometry of the complexation reaction. Thus, the Ba^{2+}/PANa complexation seems to be bidenate as the ratio between the bound Ba^{2+} concentration and C_p is close to 0.50 (0.42) at the plateau. This result was also obtained with the system Ca^{2+}/PAA [10, 24]. The lack of sensitivity of ISE analyses does not allow the measurement of equilibrium concentrations of free barium ions at low complexation ratio. However, in the barium concentration range where enough accuracy is obtained (between 2×10^{-5} and 10^{-4} M of free barium concentration), the Ba^{2+}/PANa complexation constant K_c can be evaluated, assuming bidentate species and the following definition:

$$K_c = \frac{[(\text{–COO})_2\text{Ba}]}{[\text{–COO}^-]^2[\text{Ba}^{2+}]} . \tag{9}$$

This approach implies that the sodium/carboxylate interactions are not taken into account and all ionized carboxylate groups are considered free for binding. Experimental data lead to Log K_c between 8.0 ± 0.1 and 8.5 ± 0.1 in the range of free Ba^{2+} concentrations at equilibrium $[Ba^{2+}]_{free} = 1.74 \times 10^{-5}$–$6.38 \times 10^{-5}$ mol dm^{-3}. This value compares well with the other data in the literature using the same procedure. As an example, Log K_c equals 5 and 8 for the binding with PAA of Ca^{2+} and Cu^{2+}, respectively [12]. *It is clear however that a more precise approach should consider that part of the ionised groups actually bind with monovalent ions, the remaining part being free or bound with* Ba^{2+} *ions. When additional* Ba^{2+} *ions bind with the polyion, they displace some of the pre-condensed monovalent counterions. Analysis of such an ion exchange has been also described in the literature* [17, 25].

Conductometric analyses

The conductometric measurements (Fig. 2) confirm the formation of bidentate species as r is close to 0.50 at the onset of the conductivity excess plateau, like with ISE analyses. It may be noticed that, at the onset of full complexation, r is slightly lower than 0.50 ($r = 0.45$). Ludwig [26] and Geffroy [27] found a similar result for the calcium/polyacrylate binding ($r = 0.36$). We explain this value slightly below the 1/2 stoichiometry by the fact that some acrylic groups are not available for bonding with divalent cations due to the lack of chain's flexibility and also on account of steric matters. Although some acrylate groups do not bind with barium ions, the polyelectrolyte precipitates, indicating that alkali ions probably balance the remaining electrical charge. Precipitation of divalent cations/polyacrylate molecules is a well-known phenomenon, caused by the hydrophobic property of the fully neutralized polyelectrolyte [10]. In order to determine the effective complexation constant, it is necessary to evaluate the fractions of bound barium ions and free carboxylate groups i.e., $1 - f_{Ba}$ and f_p, respectively. This is done using Eq. (8) and a few assumptions allowing the calculation of f_M^0, f_M and λ_p. Therefore, the following sections will be devoted to the determination of these parameters and hence of the Ba^{2+}/PAM complexation constant. For that purpose, as explained later, we will also assume the formation of a bidentate ligand complex $Ba(COO)_2$.

Determination of f_M^0

f_M^0 is the fraction of free counterions M^+ in a solution of fully neutralized polyelectrolyte at zero divalent ions concentration. A method to estimate f_M^0 is to use the Manning's theory of ions condensation onto polyelectrolytes [14]. On this ground, condensation of monovalent counterions occurs at a threshold value $\xi = 1$, which corresponds to $\alpha = 0.36$ in the case of polyacrylate [28]. A discontinuity is therefore predicted in the polyacid conductometric titration curve at $\xi = 1$. Considering the conductivity data in Fig. 4, we may assume that the change of slope between zone I and II indicates the beginning of the condensation phenomenon. At this point, the free M^+ ions concentration reaches a maximum and constant value up to full neutralization of the polyacid. Table 1 shows that experimental threshold values range very closely for the three monovalent ions Li^+, Na^+ and K^+ between 0.46 and 0.51, which is significantly higher than predicted by Manning theory, but close to Ludwig [26] *and De Jong* [16] data. The discrepancy between theory and experiments may be attributed to an underestimation of the b value (see previous section). *It is also important to realise that Manning's theory holds for a line charge, which may not fit perfectly with a real macromolecule containing discrete charged groups at small separation.* In the following part of the paper, we shall use the common value $f_M^0 = 0.47 \pm 0.02$ for the three alkali ions.

Table 1 Fractions of free alkali counterions in a polyacrylate solution and the threshold value of charge density at which condensation occurs

	Lithium	Sodium	Potassium
C_p [mol dm^{-3}]	7.67×10^{-3}	7.67×10^{-3}	7.67×10^{-3}
C_B^* [mol dm^{-3}]	3.85×10^{-3}	3.52×10^{-3}	3.92×10^{-3}
$f_M^0 = \alpha^*$	0.50	0.46	0.51
ξ (at $\alpha = \alpha^*$)	1.25	1.14	1.27

Determination of f_M

The fraction f_M of free M^+ ions in the bulk can be determined as a function of the barium concentration at full neutralization of the polyelectrolyte (pH = 9) using Eq. (5). By dividing K_T by C_p, we obtain the total molar conductivity, Λ_T:

$$\Lambda_T = f_M \lambda_M + r f_{Ba} \lambda_{Ba} + 2r\lambda_{Cl} + f_p \lambda_p \; . \qquad (10)$$

Equation (10) shows that the slope of Λ_T versus λ_M gives f_M under the assumption that f_M does not depend on the nature of M^+, i.e. there are no specific interactions of the alkali ions with the polyion. Practically, as shown by Fig. 3, Eq. (10) applies fairly well, producing f_M at different values of r and the corresponding intercepts $B(r)$. From Eq. (10), when $\lambda_M = 0$:

$$B(r) = (r f_{Ba} \lambda_{Ba} + 2r\lambda_{Cl} + f_p \lambda_p) \qquad (11)$$

f_M values are plotted in Fig. 5 as a function of r. At $r = 0$, $f_M^0 = 0.49$, which is very coherent with the value found previously ($f_M^0 = 0.47$). At full complexation, f_M is slightly less than 1 ($f_M = 0.96$ for $r = 0.50$) which indicates a residual binding of alkali ions with the polyelectrolyte. Note that this result is qualitatively consistent with the binding ratio lower than 0.50 for barium ions. Actually, the precipitated polymer should be composed of $-(COO)_2Ba$ groups and few $-COOM$ groups. This result is confirmed by Geffroy [27] who found 6% of residual Na^+ ions on the precipitated calcium polyacrylate by Atomic Absorption Spectroscopy analyses.

Determination of λ_p

Several methods are available to calculate the molar conductivity λ_p of polyacrylic acid from the previous measurements. The simplest one is to use the conductivity data at pH 9 and Eq. (7) [29] that we may write for sodium counterions

$$\lambda_p = \frac{K_{pol} - C_p f_{Na}^0 \lambda_{Na}}{C_p f_{Na}^0} \; . \qquad (12)$$

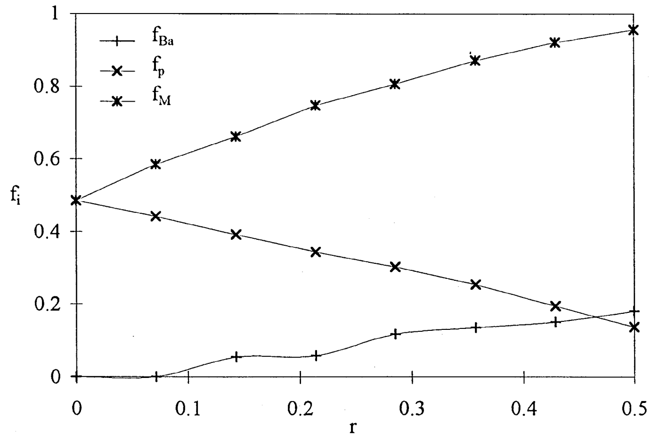


Fig. 5 Variation of the free fractions of acrylate groups, f_p, alkali, f_M, and barium, f_{Ba}, ions in an alkali polyacrylate solution where barium chloride is added

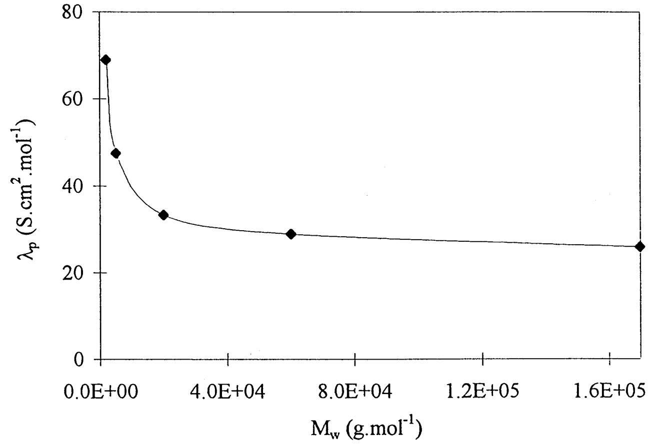


Fig. 6 Variation of the equivalent molar polyacrylate conductivity against the mean molecular weight of the polymer

Using $f^0_{Na} = 0.47$, $\lambda_{Na} = 50.9\ \mathrm{S\,cm^2\,mol^{-1}}$ [30], $K_{pol} = 0.316\ \mathrm{mS\,cm^{-1}}$ and $C_p = 7 \times 10^{-3}\ \mathrm{mol\,dm^{-3}}$, we get $\lambda_p = 45.15\ \mathrm{S\,cm^2\,mol^{-1}}$.

λ_p may also be derived from the intercept, $B(r)$, of the first line of Fig. 3 (for $r = 0$, $B(r) = 22.22$). In that case, it is clear that $B(r) = f_p \lambda_p$ (see Eq. (11)). Furthermore, as there are only monovalent cations on the solution, the fraction of ionized carboxylate groups f_p is equal to the fraction of free alkali ions ($f_p = f^0_M = 0.47$). Thus, we obtain $\lambda_p = 45.7\ \mathrm{S\,cm^2\,mol^{-1}}$ which is fairly consistent with the value found above.

It has been established that the molar conductivity of large polyelectrolytes does not vary with the molecular weight [20, 29]. The conductivity increases however for small molecules and oligomers as shown in Fig. 6 for five sodium polyacrylate salts with molecular weight varying between 2100 and 170 000 g mol^{-1}. The data of Fig. 6 have been obtained by single measurements of the PANa salts conductivity at pH 9 and using the same values as above for C_p, f^0_M and λ_{Na}. We see that λ_p increases considerably from 30 S cm^2 mol^{-1} for $M_w \geq 50\,000$ g mol^{-1} to about 70 S cm^2 mol^{-1} for $M_w = 2100$ g mol^{-1}. This λ_p value for high degrees of polymerization of polyacrylate was also found by Ikegami [24]. For small polyelectrolytes, Benegas found between 46 and 49 S cm^2 mol^{-1} for 26 000 g mol^{-1} polymethacrylate [31]. Some other works are in accordance with these values [20, 29].

The range of polymer concentrations employed in all these experiments is sufficiently narrow $(7.0 \pm 0.5) \times 10^{-3}$ mol dm^{-3}, to assume that the variations of λ_p with c_p is negligible. Nevertheless, it is essential to keep in mind that the molar conductivity would be sensitive to large variations of the polymer concentration [16, 17, 23].

Determination of K_c

In order to calculate the Ba^{2+}/PAM complexation constant K_c, the last step consists in determining f_p and f_{Ba} as a function of the barium concentration ratio r. For that purpose, we shall assume the formation of a bidentate ligand complex Ba(COO)$_2$, which gives for f_p the following identity:

$$f_p = f_M - 2r(1 - f_{Ba}) \qquad (13)$$

Namely, the number of unbound carboxylate groups equal the number of free alkali ions minus twice the number of complexed barium ions. f_{Ba} can be calculated from the intercept $B(r)$ of the Eisenberg plots and the combination of Eqs. (11) and (13):

$$f_{Ba} = \frac{B_{(r)} + 2r(\lambda_p - \lambda_{Cl}) - \lambda_p f_M}{r(\lambda_{Ba} + 2\lambda_p)} . \qquad (14)$$

The plot of f_p in Fig. 5 shows a monotonous, almost linear decrease between $f_p = 0.47$ ($r = 0$) to $f_p = 0.14$ ($r = 0.50$). As expected from ISE measurements (Fig. 1), f_{Ba} is zero i.e., Ba^{2+} ions are totally bound up to r values between 0.20 and 0.25. Then, f_{Ba} increases continuously up to 0.18 at $r = 0.50$.

Finally, the complexation constant K_c can be calculated from its basic expression (Eq. (9)), since all the terms are now known:

$$K_c = \frac{C_{Ba}(1 - f_{Ba})}{(C_p f_p)^2 C_{Ba} f_{Ba}} . \qquad (15)$$

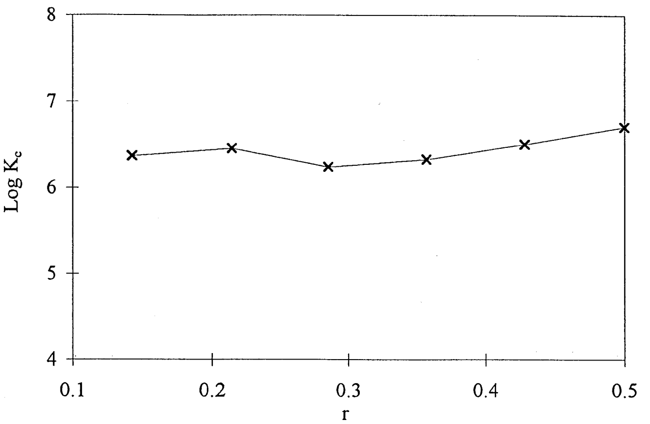


Fig. 7 Variation of the logarithm of the Ba^{2+}/PAM complexation constant, K_c, with *r*

Figure 7 shows the variation of the logarithm of K_C with *r*. The first two values of Log K_c (for $r = 0.00$ and 0.07) cannot be calculated because f_{Ba} equal zero. The complexation constant shows a fairly stable value in the range 6.50 ± 0.25 which attests a strong affinity of Ba^{2+} ions for acrylate groups in the polymer. This result also demonstrates that the binding of barium ions does not depend on the electrostatic potential of the polymer chain. In the latter case, considering that the reaction free energy sums up the chemical and electrical terms, we would have the following identity for the experimental complexation constant:

$$K_c = e^{-(\Delta G_{exp}/RT)} = e^{-(\Delta G_{chim} + \Delta G_{el})/RT} , \qquad (16)$$

where ΔG_{chim} is a purely chemical term and ΔG_{el} is an electrical term which may be identified to $- 2F\Psi_{chain}$, where "2" is the electrical charge number of barium ions and Ψ_{chain} is the mean electrical potential of the chain. Ψ_{chain} certainly varies with the complexation ratio, we therefore conclude that ΔG_{el} is negligible in comparison with ΔG_{chim}. In addition, our calculation is consistent with the formation of a bidentate ligand complex when using the site binding mode approach [26, 32, 33]. In the present work, the calculated Log K_c values differ by about two units between conductometric and ISE measurements. The conductometric result seem however more reliable as it takes into account the binding of monovalent counterions in the evaluation of free carboxylate groups. Miyajima et al. [12, 34] studied the complexation of various cations onto polyacrylic acid. They calculated the constants for the calcium and cadmium/polyacrylate interactions and found Log K_c, respectively, equal to 5.0 and 7.5 with $\alpha = 1$ and $I = 10^{-2}$ M. The value found for the Ba^{2+}/PAM complexation constant in our study is thus in very good agreement with these other works as cadmium is known to be a better complexing ion than barium which is in turn more complexing than calcium. *It is also interesting to compare the present value of* Log K_c *with those obtained using simple monomeric species. As an example, values were given for the association constant of* Ba^{2+} *with glycinate* (Log $K_1 = 0.77$), *oxalate* (Log $K_1 = 2.33$) *and citrate ions* (Log $K_1 = 3.00$) [35] *with* $K_1 = (BaP^{(n-2)-})/(Ba^{2+})(P^{n-})$, where (P^{n-}) and $(BaP^{(n-2)-})$ *are the concentration of the free and bound ligand molecules and n is the ligand's valency. Using the same definition for the complexation constant in the* Ba^{2+}/PAM *system, considering moreover that a binding site P contains two carboxylate groups* $P = (CH_2CHCOO^-)_2$ *and* $n = 2$, K_1 *for* PAA *reads*:

$$K_c = \frac{C_{Ba}(1 - f_{Ba})}{[(C_p f_p)/2](C_{Ba} f_{Ba})} . \qquad (17)$$

Calculations give $\log K_1 = 4.0 \pm 0.1$, *which fits very well with the series above since the binding strength is known to increase with the number of binding sites* [35].

Calculation of the total conductivity of the $BaCl_2$/PAM system

To control the coherence of all the parameters derived from the conductivity equations, the total conductivity of the solution (Eq. (5)) has been calculated at full neutralization as a function of *r*. It is seen from Fig. 8 that the calculated result compares very well with the experimental data taken from Fig. 2. In our view, the quality of the fit and the constancy of the complexation constant legitimate the main assumptions used in the work i.e., the formation of $Ba(COO)_2$ species, the presence of non active alkali ions in conductivity measurements and the constancy of λ_p in the whole titration range.

Distribution of carboxylate species and M/Ba displacement ratio

Knowledge of the different f_i values allows the calculation of the concentrations of the three species formed in the course of barium titration of a fully neutralized polyacrylic molecule, namely free carboxylate groups (COO^-), complexed groups ($Ba(COO)_2$) and alkali bound groups (COOM). Figure 9 presents the three roughly linear plots of the respective concentrations as a function of *r*.

From the previous curves, it is also possible to calculate the M^+/Ba^{2+} displacement ratio i.e., the amount of displaced alkali ions in comparison to that of bound barium ions. It is seen from Table 2 that the displacement ratio decreases almost linearly from 1.36 to 0.92 when *r* varies from 0 to 0.5. Values less than 2 show indeed that

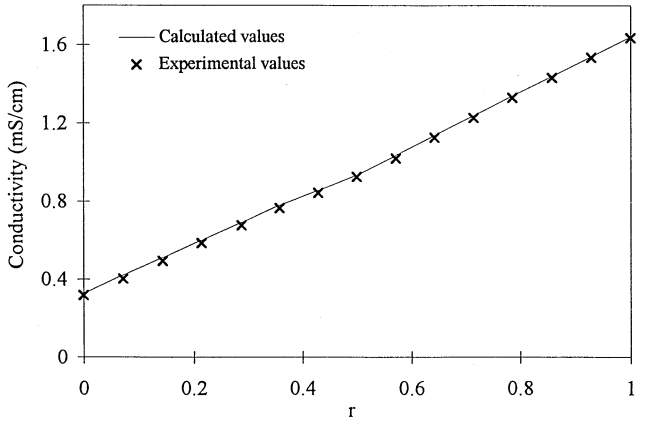


Fig. 8 Comparison of the experimental values (see Fig. 2) and the calculated ones from Eq. (5) of the total conductivity of a PANa/BaCl$_2$ solution

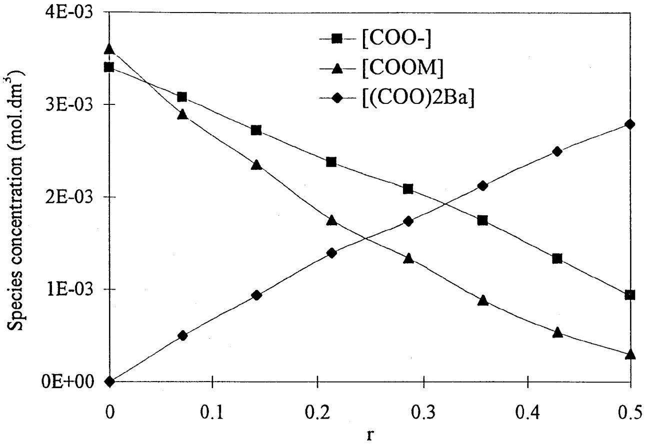


Fig. 9 Distribution of COO$^-$, COOM and (COO)$_2$Ba species concentration along the complexation of PAM by Ba^{2+}

Table 2 M$^+$/Ba^{2+} displacement ratio along the complexation of PAM by Ba^{2+} at pH = 9

r	0.07	0.14	0.21	0.29	0.36	0.43	0.50
$f_M/[\mathrm{Ba}]_{\mathrm{bound}}$	1.36	1.21	1.20	1.10	1.06	1.00	0.92

the release of alkali ions does not result from a simple exchange of ions on the binding sites, but is more likely to occur from a decrease of the mean potential of the polyelectrolyte.

Conclusion

Conductometry can be a useful technique to study the ions/polyelectrolyte interactions and especially the release of monovalent counterions by the binding of divalent ions onto polyion. In this way, it has been shown that barium ions form bidentate complexes with alkali polyacrylate. The conductometric measurements and calculations lead to the fractions of released alkali counterions, bound barium ions and ionized carboxylate groups and allow one to calculate the complexation constant, K_c, of the Ba^{2+}/PAM interactions. Log K_c is found to be equal to 6.50 ± 0.25 which is in good agreement with other studies on ions/polyion binding. Furthermore, the fraction of non-condensed alkali counterions in a polyacrylate solution found by this method is equal to 0.47 ± 0.02 which is slightly higher than the predictions of the Manning's theory. Finally, the conductometric feature of polyelectrolytes is pointed out by the calculation of the polyacrylate equivalent molar conductivity, λ_p. This parameter is found to be dependent on the polyion's degree of polymerization. For the polyacrylate studied (DP = 54), λ_p has been found equal to 45 S cm^2 mol^{-1} which is in accordance with literature's values.

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