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ORIGINAL CONTRIBUTION

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# Conductometric and microcalorimetric analysis of the alkaline-earth/alkali-metal ion exchange onto polyacrylic acid

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**Abstract** The specificity of the exchange between divalent ($Di^{2+}$ = $Ca^{2+}$ or $Ba^{2+}$) and monovalent ($M^{+}$ = $Li^{+}$, $Na^{+}$ or $K^{+}$) ions onto a polyacrylic chain is examined using conductometric and microcalorimetric techniques. Assuming the formation of a bidentate complex between the $Di^{2+}$ and the carboxylate groups, the conductometric data give the exchange ratio ($Di^{2+}/M^{+}$) and the speciation of the acrylic groups. No significant difference is observed between the three alkali-metal ions for a given $Di^{2+}$ ion. Comparisons between $Ca^{2+}$ and $Ba^{2+}$ show a stronger hydrophobicity of the former as it precipitates at a complexation ratio $r = 0.33$ versus $r = 0.45$ for the $Ba^{2+}$ salt. Microcalorimetric data show that all $Di^{2+}/M^{+}$ exchange energies are positive and depend significantly on the type of cations. The largest displacement energy (the more positive) is found for the binding of $Ca^{2+}$ with sodium polyacrylate (8.13 kJ · $mol^{-1}$) and the smallest for $Ba^{2+}$ with lithium polyacrylate (1.88 kJ · $mol^{-1}$). The interpretation of the data leads to the conclusion that specificity of the $Di^{2+}$ binding originates in the dehydration phenomenon and specificity between the three alkali-metal ions is due to the decrease in the electrostatic bond strength with an increase in the ionic radii. The $Di^{2+}/M^{+}$ exchange is entropically driven.

**Key words** Conductometry · Poly(acrylic acid) · Barium(II) ion · Calcium(II) ion · Complexation

## Introduction

Interactions between polyelectrolytes and counterions are relevant phenomena in a number of applications. For example polyelectrolytes are used as additives in cement pastes to control the rheological properties and the setting behaviour [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 flocculation, mineral flotation and sewage purification, etc. In all cases the polyelectrolyte performance may be profoundly altered by interacting ionic species. This is particularly true in solutions containing high salt concentrations and when counterions (e.g. $Ca^{2+}$, $Al^{3+}$, $La^{3+}$, $SO_4^{2-}$, $PO_4^{3-}$, etc.) induce precipitation of the polymer, gelification of the system or increase the adhesion between mineral surfaces [3]. In addition, ion binding plays an important role in the physicochemical properties of biomolecules [4].

Due to the wide theoretical and practical interest, 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), the effect of salts on the ionisation properties has been extensively analysed, resulting in affinity series for cations on the basis of their influence on the ionisation constant [5]. The binding of multivalent cations with polyelectrolytes has also been measured directly, but results are not always consistent. The formation of both bidentate [6, 7] and monodentate [8] $Ca^{2+}$/acrylate ligand complexes has 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. $Ba^{2+}$ counterions have not been examined as much as $Ca^{2+}$, $Mg^{2+}$ and transition-metal cations in the presence of carboxylic polymers. For $Ba^{2+}$, Koda et al. [9] report a simple electrostatic interaction with PAA, whereas $Cu^{2+}$, $Zn^{2+}$ and $Mn^{2+}$ bind chemically with the acrylate groups.

Divalent ($Di^{2+}$) counterion binding is also affected by the concentration and the type of coexisting monovalent ($M^+$) counterions. As an example, $Ca^{2+}$ binds with dextran sulphate 10–30% more in the presence of $Na^+$ than in the presence of $K^+$ [10]. In the case of PAA and partly hydrolysed poly(acryl amide), polymers precipitate above a critical $Ca^{2+}$ concentration that depends on the polymer concentration, size and ionisation ratio; but the precipitate may redissolve by addition of an excess of $Na^+$ with respect to $Ca^{2+}$ [7]. The specificity in $Di^{2+}$ counterion binding may derive from differences in the intrinsic binding strength, but also from differences in hydration changes accompanying the binding of competing $M^+$ because the latter phenomenon causes significant entropic variations [11, 12]. Indeed, dilatometric studies show a large difference between the volume changes of the trimethyl ammonium salt of PAA due to the binding of protons (12–25 ml/mol), $Mg^{2+}$, $Ba^{2+}$ (26 ml/mol) and $Li^+$ (4.35 ml/mol) and $K^+$ (2.75 ml/mol) [13]. Similarly volume changes have been used to differentiate the so-called site-binding of $Mg^{2+}$ and $Ca^{2+}$ with PAA and the atmospheric binding with poly(styrene sulphonate), since in the first case the $Di^{2+}$ are more dehydrated than in the second case [14–16]. At the present time, in view of the literature, neither the physical state of the $M^{n+}$/polyelectrolyte bonds, nor the binding mechanism are clearly established.

The present paper is the second of a series reporting experiments aimed at understanding the specific effects of small ions in the adsorption of polyelectrolytes. When a weak polyelectrolyte such as PAA adsorbs on a charged surface, both the ionisation of the polymer and the surface charge increase or decrease, depending on the respective charge signs and on the adsorption level. Another important phenomenon in the adsorption process is the competitive (or induced) binding of electrolyte ions. In some cases, depending on the relative strength of the bonds, the polymer displaces ions from the surface or it drags the counterions into the adsorption layer [2, 17–19]. As a result, quantitatively and qualitatively, the addition of small ions may profoundly alter the adsorption isotherms as much as it influences the phase separation and the solution viscosity. In order to understand the dependence of adsorption on the presence of electrolytes one should therefore examine more precisely the ionic interactions with both the substrate and the polymer. Previously we addressed the binding of $Ba^{2+}$ in solutions of PAA salts of $M^+$ ($Li^+$, $Na^+$, $K^+$) using conductivity and potentiometric measurements [20]. Results were consistent with the formation of a bidentate complex. No significant difference was found in the $Ba^{2+}$/polymer binding between the three solutions of the different electrolytes. The displacement ratio onto the chain between $Ba^{2+}$ and electrostatically condensed $Na^+$ was measured and the $Ba^{2+}$ binding constant was evaluated ($\log K = 6.5$). We now investigate more precisely the specificity of the $M^+/Di^{2+}$ binding strengths for the same PAA salts. Comparison will be made between the complexations of $Ba^{2+}$ and $Ca^{2+}$ and between the displacement energies of the three different $M^+$ by $Ba^{2+}$. In addition to the conductometric determination of the binding and displacement ratios, microcalorimetric measurements will provide a sensitive and original insight into the binding mechanism.

## Experimental

### Materials

Sodium polyacrylate (PANa), molecular weight 5100, was supplied by Fluka as a sodium salt and was purified by two successive precipitations in pure methanol. Amberlite IRN-77 cationic resin was used to obtain the acidic form of the polymer from the purified PANa. The $M^+$ PA solutions (PAM where $M^+ = Li^+$, $Na^+$ or $K^+$) were obtained by adding the corresponding alkali-metal hydroxide to PAA solutions until complete neutralisation at pH 9. The total monomer concentration $c_{pol}$, was determined by acid/base titrations of the polyacid solution and was equal to $9.5 \times 10^{-3}$ mol · dm$^{-3}$ for all the experiments in the present study.

All other chemicals were of analytical grade and were purchased from Prolabo. Water was twice deionised with a Milli-Q Millipore system.

### Methods

#### *Microcalorimetry*

Calorimetric experiments were carried out in a Tian–Calvet-type calorimeter described elsewhere [21]. The heat flow, registered by thermocouples, was processed by a Keithley 181 nanovoltmeter and the signal was stored on a computer, where the numerical integration of the peak was carried out. The computer was also used to control the salt injections.

All experiments were carried out at 25 °C. The system containing the samples was allowed to equilibrate for 4 days before the experiment was started. The calorimetric cell was filled with 30 ml of the PAM solution (pH = 9 and $c_{pol} = 9.5 \times 10^{-3}$ mol · dm$^{-3}$) and additions of 1-ml aliquots of the salt solutions were made ($BaCl_2$ or $CaCl_2$ at a molarity of $2 \times 10^{-2}$ mol · dm$^{-3}$). The salt solution was contained in a glass reservoir above the PAM solution in the calorimetric cell and was injected into this cell using a peristaltic pump; it was also adjusted to pH 9.

The first injection did not give reproducible data, probably due to a significant change in the suspension viscosity. The change in ionic strength in the system is too low (from $4.75 \times 10^{-3}$ mol · dm$^{-3}$ in the initial solution of PAM to

$5.40 \times 10^{-3}$ mol · dm$^{-3}$ after the first injection) to explain this lack of reproducibility. For this reason, we systematically ignored the first measurement in the computation of the experimental data. In each case the heat effects are the sums of the heat due to the $M^+/Di^{2+}$ counterion exchange on the polyion and the heat of dilution of the mother salt solution. The dilution of the polymer solution is negligible in view of the volumes of salt solution added. In order to determine the heat of dilution of the salt solution and the heat effect due to the changes in the ionic strength, the same experiments were carried out with deionised water at pH 9 instead of the polymer solution. In the present case, heats of dilution were found to be negligible in comparison with other calorimetric effects.

### $Di^{2+}$ complexation measurements

The complexation of $Di^{2+}$ ($Ba^{2+}$ or $Ca^{2+}$) on fully neutralised PAMs (pH 9) was monitored by the conductometric method described elsewhere [20]. This technique allows the determination of the complexation isotherm of the $Di^{2+}$ and the speciation of the acrylic groups [COOM, $COO^-$ and $(COO)_2Di$] of the polyion as a function of the complexation ratio. All conductometric analyses were performed with a Knick 702 conductometer at 25 °C under a nitrogen atmosphere. The experimental parameters were the same as in the calorimetric experiments, which allowed the easy comparison of the enthalpy change with the complexation ratio.

Turbidity measurements were made (Metrohm 662 photometer at 600 nm) in order to detect the solubility limit of PABa.

## Results

### $M^+/Di^{2+}$ exchange on PA

Analysis of the $M^+/Di^{2+}$ exchange on the polyelectrolyte chain consists of the measurement of the conductivity, $K_T$, of PAM solutions as a function of aliquots of $BaCl_2$ or $CaCl_2$ solutions added [20]. Comparison is made between the experimental values and the calculated ones using the two-state approximation, where ions are considered as being either condensed with the polymer or free in the bulk solution. In the first case, they do not contribute to the solution conductivity; in the second case, they behave as free ions in a regular electrolytic solution [22].

The word "complexation" is used for the binding of PA with $Di^{2+}$ and "condensation" is conventionally used for the binding of PA with $M^+$. In both cases, it is an electrostatic interaction, but the binding of $Di^{2+}$ leads to the formation of bidentate $(COO)_2Di$ complexes until complete neutralisation of the polymer, whereas there is no real binding of $M^+$, but rather a distribution of $M^+$ near the polymer chain.

When the chloride salt of $Di^{2+}$ is added to a PAM solution, the conductivity per mole of monomer groups, $\Lambda_T$, is

$$\Lambda_T = f_M\lambda_M + rf_{Di}\lambda_{Di} + 2r\lambda_{Cl} + f_p\lambda_p \quad . \tag{1}$$

$r$ is the concentration ratio between added $Di^{2+}$ and monomer units. $f_i$ is the unbound fraction of species $i$ ($i = M^+, Di^{2+}$ or $p$). Note that all chloride ions are free in the solution. $\lambda_i$ is the equivalent molar conductivity at 25 °C of species $i$ respectively. Using the Eisenberg procedure [23], $\Lambda_T$ is measured with different $M^+$ ($Li^+$, $Na^+$ and $K^+$) and plotted as a function of the equivalent molar conductivity, $\lambda_M$, of $M^+$ for different values of $r$. The plot of $\Lambda_T$ versus $\lambda_M$ is linear under the assumption that $f_M$ does not depend on the nature of $M^+$, i.e. there are no specific interactions between $M^+$ and the polyion [9]. Practically, as shown in Figs. 1 and 2, Eq. (1) applies fairly well, producing a slope $f_M$ at different values of $r$ and the corresponding intercept $B(r)$ which reads

$$B(r) = (rf_{Di}\lambda_{Di} + 2r\lambda_{Cl} + f_p\lambda_p) \quad . \tag{2}$$

Assuming the formation of a bidentate ligand complex $(COO)_2Di$ [6, 24], the fraction of unbound acrylate groups $f_p$ is

$$f_p = f_M - 2r(1 - f_{Di}) \quad . \tag{3}$$

Namely, the number of unbound carboxylate groups equals the number of free $M^+$ minus twice the number of complexed $Di^{2+}$. $f_{Di}$ can further be calculated from the intercept $B(r)$ by combining Eqs. (2) and (3)

$$f_{Di} = \frac{B(r) + 2r(\lambda_p - \lambda_{Cl}) - \lambda_p f_M}{r(\lambda_{Di} + 2\lambda_p)} \quad . \tag{4}$$

The complete procedure, based on the formation of a bidentate complex [25] and the Manning concept of condensed $M^+$ [26], gives the distribution of all species on the polyelectrolyte [COOM, $COO^-$ and $(COO)_2Di$] and in the solution ($M^+$ and $Di^{2+}$). The results are given in Figs. 3 and 4 with respect to the total concentration of $Ca^{2+}$ and $Ba^{2+}$ salt added, respectively. It is important to note that, using conductivity measurements, the binding of $Di^{2+}$ does not show any dependence on the type of $M^+$, confirming the results obtained by Manning [26] and Eisenberg [23]; therefore,

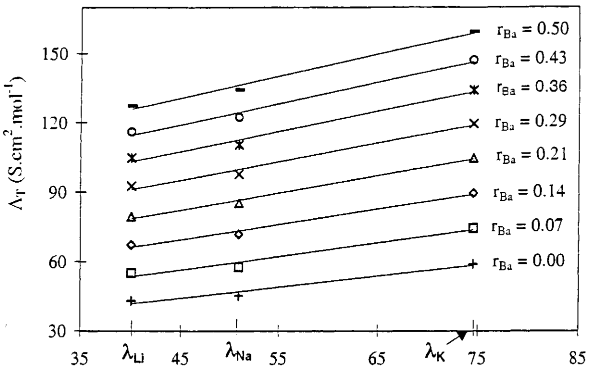

**Fig. 1** Total molar conductivity of alkali-metal polyacrylate (*PAM*) solutions against the equivalent molar conductivity of the corresponding $M^+$ ($Li^+$, $Na^+$, $K^+$) for different concentrations of $BaCl_2$. $r_{Ba}$ represents the ratio $[Ba^{2+}]_{added}$ over $c_{pol}$

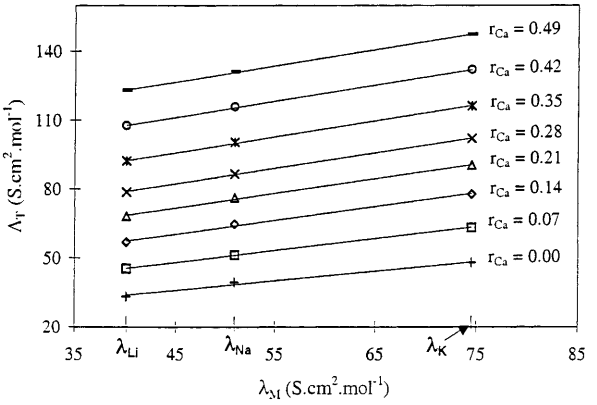

**Fig. 2** Same as Fig. 1 but with $CaCl_2$ instead of $BaCl_2$. $r_{Ca}$ is the ratio $[Ca^{2+}]_{added}/c_{pol}$

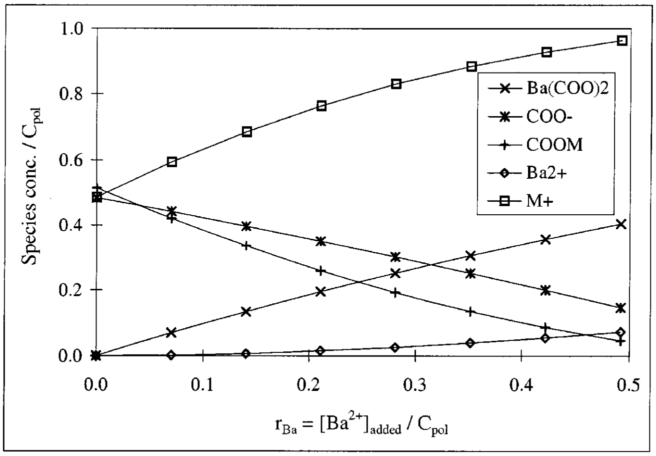

**Fig. 3** Distribution of the $COO^-$, COOM, $M^+$, $Ba^{2+}$ and $(COO)_2Ba$ species (expressed as the ratio of species concentration on $c_{pol}$) during the $Ba^{2+}$/PAM complexation reaction against $r_{Ba}$

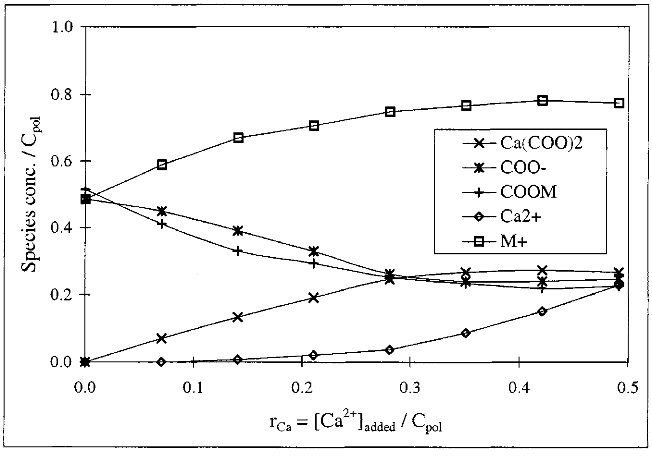

**Fig. 4** Same as Fig. 3 but with $CaCl_2$ instead of $BaCl_2$

our data do not distinguish the different $M^+$ species. As we shall see later, the results are different when considering calorimetric measurements. In fully neutralised, uncomplexed PAM solutions, $M^+$ divide almost equally between condensed and freelike species [20, 27, 28]. Complexation with $Di^{2+}$ implies a monotonous release of condensed $M^+$, accompanied by a decrease in the ionised carboxylate groups. At full complexation with $Ba^{2+}$ ($r_{Ba}$ = 0.45), almost all $M^+$ are free in the solution, but a small percentage remain condensed. The $COO^-$ concentration is almost zero. In the case of $Ca^{2+}$, the polymer precipitates sooner (at $r_{Ca}$ = 0.33) which implies a fraction of condensed $M^+$ and of ionised acrylate groups on the complexed polyion greater than in the case of $Ba^{2+}$ complexation. Up to half of the maximum complexation ratio, all $Ba^{2+}$ and $Ca^{2+}$ bind with the PA molecule (Fig. 5). This is consistent with the strong complexation affinity reported by Ikegami and Imai [24] and by Shimizu and Minakata [29]. There is a difference at higher complexation ratios where the $Ca^{2+}$ salt precipitates at $r$ = 0.33 and the $Ba^{2+}$ salt at $r$ = 0.45. Ogawara et al. [30] also reported precipitation of PAA (60000 g mol$^{-1}$) salts with $Di^{2+}$ at a complexation ratio of about 0.40. In both cases, as mentioned previously for $Ca^{2+}$ [17, 20], precipitation and complete complexation occur at $r$ values below 0.50. Indeed, a fraction of $M^+$ counterions has been found in precipitated PACa salts [17]. This is attributed to the fact that some acrylic groups are not available for bonding with $Di^{2+}$ because of the chain's lack of flexibility and also for steric reasons [17, 28]. The precipitation of $Di^{2+}$/PA molecules, illustrated in Fig. 6, is a well-known phenomenon, caused by the hydrophobic properties of the fully neutralised polyelectrolyte [6]. Considering the difference in the complexation ratio at the onset of

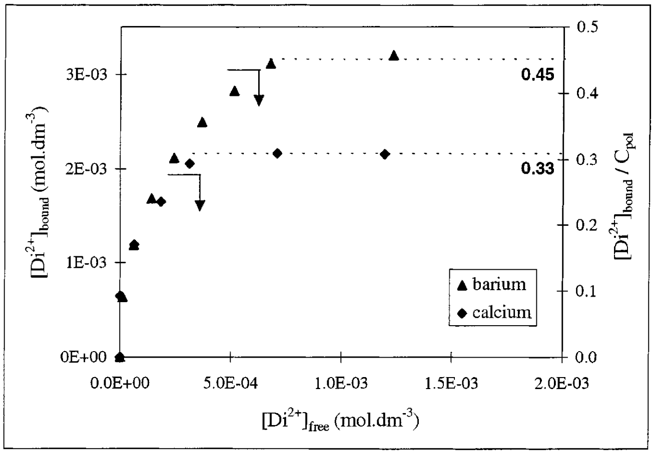

**Fig. 5** Isotherm of the $Ba^{2+}$ and $Ca^{2+}$ complexation on PAM at pH 9 and $c_{pol}$ = 9.5 × 10$^{-3}$ mol dm$^{-3}$

precipitation, we conclude that the $Ca^{2+}$ salt is more hydrophobic than the $Ba^{2+}$ salt.

Table 1 shows that the displacement ratio, i.e. the ratio between released $M^+$ counterions and complexed $Di^{2+}$, varies almost linearly between 1.36 and 1.12 for $Ba^{2+}$ and between 1.21 and 0.81 for $Ca^{2+}$. Values less than 2 show that the release of $M^+$ does not result from a stoichiometric exchange with $Di^{2+}$ ions on the acrylic groups. $Di^{2+}$ ions react simultaneously with $M^+$ condensed PA groups (COOM) and ionised acrylate groups ($COO^-$). Presumably, the release of $M^+$ depends on the decrease in the mean electrostatic potential of the chain, due to the binding of $Di^{2+}$ [25].

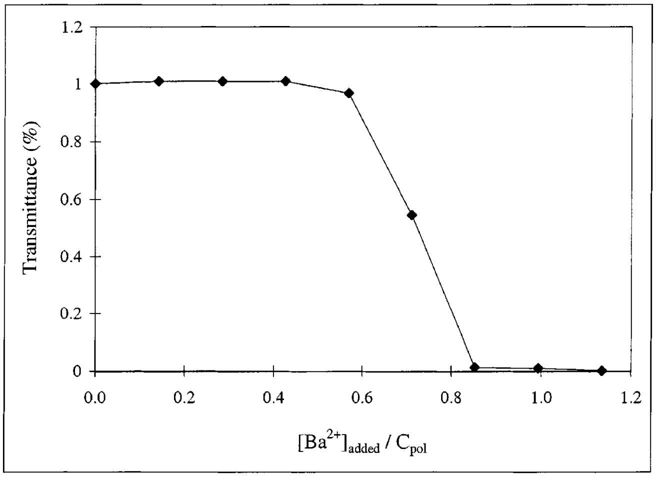

**Fig. 6** Transmittance of a PAM solution where $BaCl_2$ is added. The $x$-axis represents the concentration of $BaCl_2$ added. The drop in transmittance indicates the precipitation of the fully complexed polyelectrolyte

## Microcalorimetric measurements of the $Di^{2+}$/PA complexation

The integral enthalpy change due to the successive addition of $BaCl_2$ and $CaCl_2$ solutions to PANa solutions is shown in Fig. 7, whilst Fig. 8 shows the integral enthalpy change for the addition of $BaCl_2$ to three different PAM solutions (M = $Li^+$, $Na^+$ or $K^+$). The $x$-axis gives the concentration of bound $Di^{2+}$ as obtained previously by conductivity measurements. Straight lines are observed with a slope corresponding to the molar enthalpy changes, $\Delta H_{tot}$ (kilojoules per mole of complexed $Di^{2+}$). The $\Delta H_{tot}$ values are summarised in Table 2 for the four experiments presented here.

In all cases the complexation reaction is an endothermic phenomenon ($\Delta H_{tot} > 0$). A similar result was obtained by Böhmer et al. [19] for the PANa/$CaCl_2$ system. The principal features in Table 2 are that the

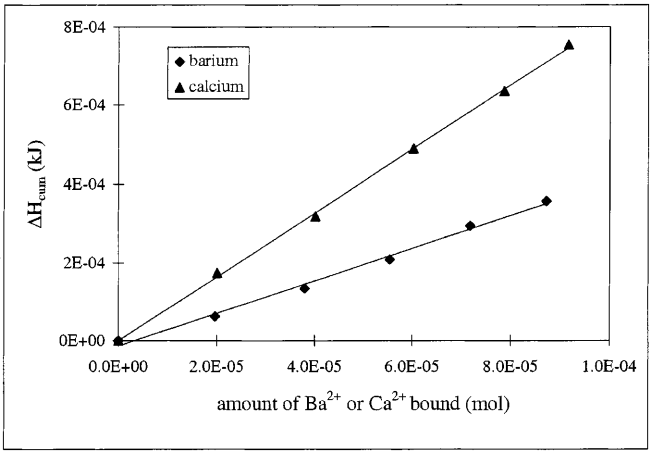

**Fig. 7** Integral enthalpy changes occuring while complexing PANa with either $Ba^{2+}$ or $Ca^{2+}$. The $x$-axis represents the bound quantity of $Ba^{2+}$ or $Ca^{2+}$

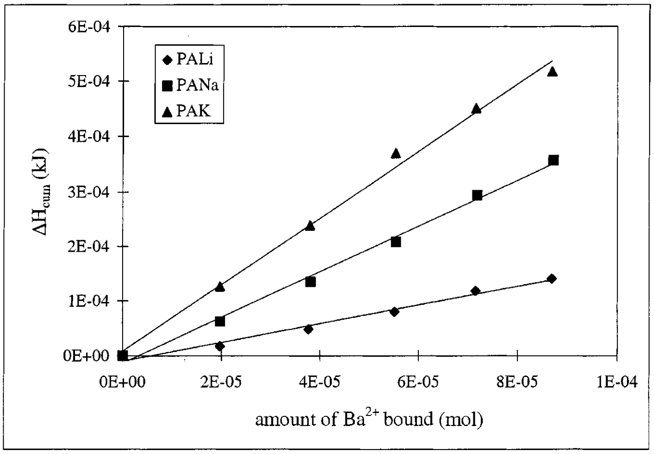

**Fig. 8** Integral enthalpy changes occuring while complexing PAMs with $Ba^{2+}$. The $x$-axis represents the bound quantity of $Ba^{2+}$

**Table 1** Monovalent cation ($M^+$) divalent cation ($Di^{2+}$) displacement stoichiometry, $A$, versus complexation ratio, $r$, of alkali-metal polyarrylates (*PAM*) by $Ba^{2+}$ or $Ca^{2+}$ at pH 9

| $r$ | 0.07 | 0.14 | 0.21 | 0.28 | 0.35 | 0.42 | 0.50 |
|---|---|---|---|---|---|---|---|
| $A_{Ca} = [M^+]_{rel}/[Ca^{2+}]_b$ | 1.23 | 1.13 | 0.91 | 0.81 | – | – | – |
| $A_{Ba} = [M^+]_{rel}/[Ba^{2+}]_b$ | 1.36 | 1.28 | 1.27 | 1.25 | 1.22 | 1.17 | 1.12 |

**Table 2** $Ba^{2+}$ and $Ca^{2+}$ displacement enthalpies with PAM (PALi or PANa or PAK). The overall entholpy change, $\Delta H_{tot}$, is expressed in kilojoules per mole of $Di^{2+}$ complexed (data from Fig. 7)

| | $Ba^{2+}$/PALi | $Ba^{2+}$/PANa | $Ba^{2+}$/PAK | $Ca^{2+}$/PANa |
|---|---|---|---|---|
| $\Delta H_{tot}$ (kJ/mol) | 1.88 | 4.44 | 5.93 | 8.13 |

molar complexation enthalpy for the $Ca^{2+}$/PANa system is twice that for $Ba^{2+}$/PANa (4 $kJ \cdot mol^{-1}$ for $Ba^{2+}$ and 8 $kJ \cdot mol^{-1}$ for $Ca^{2+}$) and that the complexation enthalpy depends on the $M^+$ species. The $\Delta H_{tot}$ values increase with the nonhydrated ionic radius of the counterion (1.88 $kJ \cdot mol^{-1}$, 4.44 $kJ \cdot mol^{-1}$ and 5.93 $kJ \cdot mol^{-1}$ for exchange between $Ba^{2+}$ and $Li^+$, $Na^+$ and $K^+$, respectively). Interestingly the latter result is contrary to the conductivity data, where no difference was observed between the three $M^+$ ions. The binding property trend in the $M^+$ series has been examined many times in the past. In the case of PAA, Ikegami and Imai [24] found an increase in the critical salt concentration as the ionic radius of $M^+$ decreases, which means that the hydrophobicity of the chain decreases with the solvated radius of the counterion. In the same way, it is generally accepted that the electrostatic attraction between PAA and $M^+$ is stronger when the hydrated radius of the ion decreases [31]. Similar trends were also observed in the case of DNA and RNA nucleobases [4, 14, 32], which has led to the so-called Hofmeister series [33]. Finally, it is relevant to indicate that the sudden precipitation of the polymer at the end of the complexation reaction does not lead to any heat effects.

## Discussion

In order to discuss the change of $\Delta H_{tot}$ with the nature of the ions involved in the complexation phenomenon, we have attempted to subdivide the reaction into several elementary contributions. Let us write the overall reaction as follows:

$$\begin{aligned} &A(\mathrm{COOM},\ a\mathrm{H_2O}) + (2\text{-}A)(\mathrm{COO^-}, p\mathrm{H_2O} \\ &\quad + \mathrm{M^+}, m\mathrm{H_2O}) + \mathrm{Di^{2+}}, d\mathrm{H_2O} \\ &\quad \rightarrow (\mathrm{COO})_2\mathrm{Di}, q\mathrm{H_2O} \\ &\qquad + 2\ \mathrm{M^+}, m\mathrm{H_2O} + h\mathrm{H_2O} \end{aligned} \tag{5}$$

Assuming that 2 mol acrylate groups bind with 1 mol $Di^{2+}$, we consider that before the bond is established, $A$ mol formed a condensed species with $M^+$ (COOM) and (2-$A$) mol is free polycarboxylate species ($COO^-$) associated with the same amount of free $M^+$ in the so-called electrostatic atmosphere. Values of $A$ against $r$ were calculated using the conductometric data and are listed in Table 1 for both $Ca^{2+}$ and $Ba^{2+}$/COOM exchange. In addition to the ionic species balance, Eq. (5) accounts for the solvation stoichiometry. It is readily seen that all species are allowed a different hydration number ($a$, $p$, $m$, $d$ and $q$) and that $h$ free moles of water result from the solvation balance:

$$A\ a + (2\text{-}A)(p + m) + d = q + 2m + h\ . \tag{6}$$

We see that $a$ is the sum of the hydration numbers of the bound carboxylate groups ($a_1$) and the bound $M^+$ ($a_2$). Similarly, $q$ is the sum of the hydration numbers of the bound carboxylate groups ($q_1$) and the bound $Di^{2+}$ ($q_2$). Introducing these variables in Eq. (6), we get

$$A[(a_1 - p) + (a_2 - m)] + 2(p - q_1) + (d - q_2) = h\ . \tag{7}$$

Equation (7) shows that the gain in free water molecules $h$, is equal to the number of water molecules released by dehydration of $Di^{2+}$ ($d - q_2$) and 2 $COO^-$ [$2(p - q_1)$] minus the rehydration number of $A$ mol of COOM groups ($A$ [$(a_1 - p) + (a_2 - m)$]).

In accordance with Eq. (5), we may now write the following enthalpy balance:

$$\begin{aligned} \Delta H_{tot} = &-A\Delta H_{cond} \\ &+ A\left[(p - a_1)\Delta H^{COO}_{hyd} + (m - a_2)\Delta H^{M}_{hyd}\right] \\ &+ 2(q_1 - p)\Delta H^{COO}_{hyd} + (q_2 - d)\Delta H^{Di}_{hyd} + \Delta H_{comp}\ . \end{aligned} \tag{8}$$

The different enthalpy terms are defined as follows. $A$ mol PAM groups dissociate (enthalpy increase: $-A\Delta H_{cond}$) and rehydrate as ionic species (enthalpy release: $(p - a_1)\Delta H^{COO}_{hyd}$ and $(m - a_2)\Delta H^{M}_{hyd}$). Two moles of acrylate groups and 1 mol $Di^{2+}$ undergo a partial dehydration (enthalpy increase: $(q_1 - p)\Delta H^{COO}_{hyd}$ and $(q_2 - d)\Delta H^{Di}_{hyd}$) and form 1 mol of the complex $(COO)_2$-Di (enthalpy release: $\Delta H_{comp}$). Note that the displacement of noncondensed $M^+$ counterions from the diffuse shell to the bulk solution is not taken into account. On this basis, we may discuss further the influence on $\Delta H_{tot}$ of the different natures of the ionic species; namely, the different $M^+$ and $Di^{2+}$.

### Effect of the nature of $Di^{2+}$

The endothermic feature of the $Ba^{2+}$ (or $Ca^{2+}$)/PAM complexation implies an entropy gain in the system, which is produced by the partial desolvation of the complexing species i.e. the $Di^{2+}$ as well as the carboxylate groups [14, 19, 34]. The loss of water accompanying the complexation of multivalent cations with polyelectrolytes has been well established by Satoh et al. [11]. Moreover, the precipitation of the polymer at the end of the complexation reaction without any heat effect proves that individual binding of $Di^{2+}$ with the carboxylate groups produces a progressively dehydrated chain, until precipitation takes place with no subsequent heat effect: in other words, $q = q_1 + q_2$ should be low. It is interesting to see that the linearity of the calorimetric data in Figs. 7 and 8, i.e. the constancy of the molar displacement enthalpy for a given PAM/$Di^{2+}$ system, corroborates the dilatometric measurements by Satoh et al. [12]. In other words, both results show no significant dependence of the complexation mechanism on the complexation ratio.

Concerning the difference in the displacement enthalpy between $Ca^{2+}$ and $Ba^{2+}$ with PANa, we may consider the different terms in Eqs. (7) and (8). According to Satoh et al. [11], the factor of $A$ in Eq. (7) amounts to about 2 mol in comparison with 12–13 mol for the sum of the second and third terms. We may then neglect the corresponding enthalpic contribution in Eq. (8) which now reads

$$\Delta H_{\mathrm{tot}} = -A\Delta H_{\mathrm{cond}} + 2(q_1 - p)\Delta H_{\mathrm{hyd}}^{\mathrm{COO}} + (q_2 - d)\Delta H_{\mathrm{hyd}}^{\mathrm{Di}} + \Delta H_{\mathrm{comp}} \ . \tag{9}$$

For a given PAM, $\Delta H_{\mathrm{cond}}$ is constant. In addition, the apparent constancy of $\Delta H_{\mathrm{tot}}$ with regards to $r$ (see values of $A$ versus $r$ in Table 1) shows that the first term on the right-hand side of Eq. (9) does not vary significantly. Finally, since it is also reasonable to suppose that the free carboxylate group's dehydration term is the same for $Ca^{2+}$ and $Ba^{2+}$ complexations [35], the difference between $\Delta H_{\mathrm{tot}}$ for the two $Di^{2+}$ originates in the two last contributions, i.e.

$$\Delta H_{\mathrm{tot}} = (q_2 - d)\Delta H_{\mathrm{hyd}}^{\mathrm{Di}} + \Delta H_{\mathrm{comp}} \ . \tag{10}$$

The relevant solvation data and the ionic radii for both cations are summarised in Table 3. The hydration numbers were measured by Satoh et al. [11] using compressibility measurements and the thermodynamic data (free energies, enthalpies and entropies) refer to the transfer of ions from gas to water at 25 °C [36]. The binding energy, $\Delta H_{\mathrm{comp}}$, is likely to increase (be more exothermic) as the ionic radius decreases; therefore, $\Delta H_{\mathrm{comp}}$ should be more exothermic for $Ca^{2+}$ than for $Ba^{2+}$ if they both form an inner-sphere complex. Similarly, the desolvation energy $(q_2 - d)\Delta H_{\mathrm{hyd}}^{\mathrm{Di}}$, should be higher (more endothermic) for $Ca^{2+}$ than for $Ba^{2+}$. On this basis, the experimental data ($\Delta H_{\mathrm{tot}}$ more positive for $Ca^{2+}$ than for $Ba^{2+}$) indicate that the desolvation term dominates the $Di^{2+}$/$M^+$ displacement energy balance. Although it does not prove anything, note that the ratio of the total enthalpy change for $Ca^{2+}$ and $Ba^{2+}$ (1.83) happens to equal that of the squared unsolvated radius of $Ba^{2+}$ and $Ca^{2+}$ (1.86). This is expected theoretically for the purely electrostatic ion/water dipole interaction energy [37].

## Effect of the nature of $M^+$ counterions

A very similar approach may be used to explain the trend of the enthalpy change for the displacement of the different $M^+$ by $Ba^{2+}$. Application of Eq. (8) shows that the difference between $\Delta H_{\mathrm{tot}}$ for two $M^+$ and a given $Di^{2+}$ reads

$$\Delta H_{\mathrm{tot}} = -A\Delta H_{\mathrm{cond}} + A\left[(m - a_2)\Delta H_{\mathrm{hyd}}^{M}\right] \ . \tag{11}$$

All terms related to $Di^{2+}$ have been deleted and $\Delta H_{\mathrm{hyd}}^{\mathrm{COO}}$ has been considered to be independent of $M^+$. Since $A$ does not depend on the type of $M^+$, as shown by conductivity measurements, two terms are left: $\Delta H_{\mathrm{cond}}$ and $(m - a_2)\Delta H_{\mathrm{hyd}}^{\mathrm{M}}$.

A size effect seems to be the more obvious explanation for the influence of $M^+$ on the $Di^{2+}$/PAM complexation energy [31]. Actually, the hydrated $Li^+$ is bigger than $Na^+$ one, which is in turn bigger than the $K^+$ one (Table 4). The condensation of $M^+$ on PA being an electrostatic phenomenon, the $M^+$/polyion binding energy increases ($\Delta H_{\mathrm{cond}}$ is more negative) in the order $Li^+ < Na^+ < K^+$, which makes $\Delta H_{\mathrm{tot}}$ vary with positive values in the same order. A very good correlation is actually obtained between $\Delta H_{\mathrm{tot}}$ and $R_{\mathrm{H}}$ (see Fig. 9).

According to the Manning condensation theory, $(m - a_2)$ should be very close to zero since no change in $M^+$ hydration is expected upon binding. Satoh and coworkers [11, 12] showed, however, that $M^+$ lose a small part of their hydration sphere upon binding with PAA (typically, about 1 mol water per mole of condensed $M^+$). In that case, the release of condensed $M^+$ would contribute $A(m - a_2)\Delta H_{\mathrm{hyd}}^{\mathrm{M}}$ to the overall displacement enthalpy. This term would be increasingly negative in the order $K^+ < Na^+ < Li^+$, which makes $\Delta H_{\mathrm{tot}}$ more positive in the reverse order.

**Table 3** Hydration numbers ($d$ and $q_2$), free enthalpies ($\Delta G_{\mathrm{H}}$), enthalpies ($\Delta H_{\mathrm{H}}$) and entropies ($\Delta S_{\mathrm{H}}$) of solvation at 25 °C, and ionic radii ($R_{\mathrm{ion}}$) of $Ca^{2+}$ and $Ba^{2+}$ [36]. Hydration number values from compressibility experiments [12]

| | d | $q_2$ | $\Delta G_{\mathrm{H}}$ (kJ/mol) | $\Delta H_{\mathrm{H}}$ (kJ/mol) | $\Delta S_{\mathrm{H}}$ (J/mol K) | $R_{\mathrm{ion}}$ (Å) |
|---|---|---|---|---|---|---|
| Calcium | 9 | 2.9 | −1592 | −1667 | −254 | 0.99 |
| Barium | 11 | 3.5 | −1317 | −1377 | −202 | 1.35 |

**Table 4** Hydration numbers ($m$ and $a_2$), free enthalpies, enthalpies and entropies of solvation hydrated, ($R_H$) and ionic radii of $Li^+$, $Na^+$ and $K^+$ ions [36]. Hydration number values are from compressibility experiments [12] and calculations from this study, and hydrated radii are from Ref. [36]

| | $m$ | $a_2$ | $\Delta G_H$ (kJ/mol) | $\Delta H_H$ (kJ/mol) | $\Delta S_H$ (J/mol K) | $R_{ion}$ (Å) | $R_H$ (Å) |
|---|---|---|---|---|---|---|---|
| Lithium | 5.0 | 3.6 | −516 | −558 | −141 | 0.60 | ~6 |
| Sodium | 4.4 | 3.2 | −411 | −443 | −109 | 0.95 | ~4 |
| Potassium | 3.8 | 2.8 | −338 | −360 | −74 | 1.33 | ~3 |

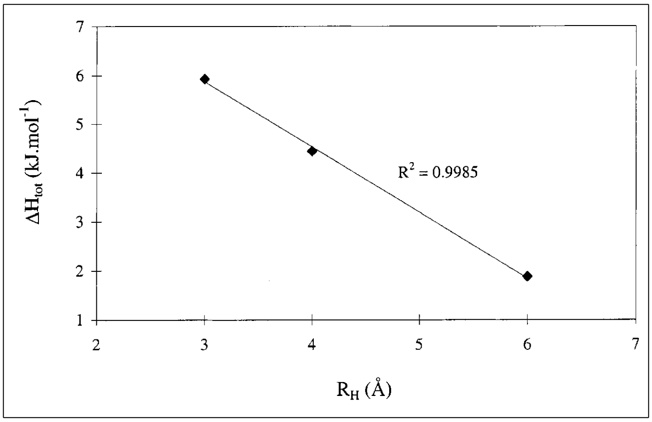

**Fig. 9** Enthalpy change measured during the $Ba^{2+}$/PAM complexation versus the $M^+$ hydrated radius

Both the binding energy and the solvation energy may thus explain qualitatively the variation of the overall enthalpy change for the binding of $Ba^{2+}$ with different PAM. The lack of accurate knowledge about the change of hydration between condensed and free $M^+$ does not allow further and more quantitative discussion. In our opinion, however, it is more likely that the binding energy, $\Delta H_{cond}$, rather than the rehydration energy rules the overall displacement en- thalpy order in accordance with Manning theory [26] and the analyses of Satoh et al. [11].

## Conclusion

The combination of conductometric and calorimetric techniques proves to be very useful to analyse the specificity of ion/polyelectrolyte binding. In the present example, $Ba^{2+}$ and $Ca^{2+}$ have been exchanged with ($Li^+$, $Na^+$ and $K^+$) onto polyacrylic chains. Conductivity measurements, using Eisenberg plots, give the distribution of all species on the polyelectrolyte [COOM, $COO^-$, $(COO)_2Di$] and in solution ($M^+$ and $Di^{2+}$) for different $Di^{2+}$/acrylate groups ratios. Comparison between $Ba^{2+}$ and $Ca^{2+}$ exchange with PANa does not show any obvious difference in terms of complex stability, but it does show a difference when considering the displacement ratios and the complex solubility. The $M^+/Di^{2+}$ exchange ratio varies between 1.36 and 1.12 in the case of $Ba^{2+}$ and between 1.21 and 0.81 for $Ca^{2+}$. PACa is more hydrophobic: it precipitates at a complexation ratio of 0.33 in comparison with 0.45 for PABa. In constrast to conductometric measurements, microcalorimetric data show a strong difference between the displacement energies of $Ba^{2+}$ and $Ca^{2+}$. They are both positive but about twice as much for $Ca^{2+}$ ($8.13\ kJ \cdot mol^{-1}$) than for $Ba^{2+}$ ($4.44\ kJ \cdot mol^{-1}$). Another interesting feature is that the displacement en-thalpy for $Ba^{2+}$ is more positive in the series $Li^+ < Na^+ < K^+$, although no difference was observed in the binding equilibria. Qualitatively, the microcalorimetric data can be explained by considering the contribution of the dehydration energies for $Ba^{2+}$ and $Ca^{2+}$ upon binding. In the case of $M^+$, the difference arises from the increase in the binding strength when the hydrated radius of the ion decreases. The calorimetric data are fully consistent with previous dilatometric studies of $M^+$ and $Di^{2+}$ binding with polyacrylic chains. It would be interesting to study the complexation of $Di^{2+}$ onto a polyelectrolyte which does not develop any condensation with $M^+$ counterions in order to rid the microcalorimetric measurements of this condensation effect.

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## References

1. Pierre A, Mercier R, Foissy A, Lamarche JM (1989) Adsorp Sci Technol 6:179–246
2. Dupont L, Couchot P, Foissy A, Mottet B (1997) J Chim Phys 94:1257–1273
3. Berg JM, Claesson PM, Neumann RD (1993) J Colloid Interface Sci 161:182–189

4. Cerda BA, Wesdemiotis C (1996) J Am Chem Soc 118:11884–11892
5. Gunnarson G, Gustavsson H (1982) J Chem Soc Faraday Trans I 78:2901–2910
6. François J, Truong N, Medjahdi G, Mestdagh M (1997) Polymer 38:6115–6127
7. Axelos M, Mestdagh M, François J (1994) Macromolecules 27:6594–6602
8. Miyajima T, Mori M, Ishiguro S (1997) J Colloid Interface Sci 187:259–266
9. Koda S, Nomura H, Nagasawa M (1983) Biophys Chem 18:361–367
10. Joshi YM, Kwak JCT (1981) Biophys Chem 13:65–75
11. Satoh M, Hayashi M, Komiyama J, Lijima T (1990) Polymer 31:501–505
12. Satoh M, Kawashima T, Komiyama J (1991) Polymer 32:892–896
13. Begala AJ, Strauss UP (1972) J Phys Chem 76:254–260
14. Strauss UP, Leung YP (1965) J Am Chem Soc 87:1476–1480
15. Mattai J, Kwak JCT (1986) Macromolecules 19:1663
16. Mattai J, Kwack JCT (1982) J Phys Chem 86:1026
17. Geffroy C (1997) Mécanismes d'interaction entre les minéraux solubles et les polyélectrolytes anioniques. Université de Franche-comté, Besançon
18. El Attar SY, Carquille C, Lamarche JM, Foissy A (1990) Prog Colloid Polym Sci 82:43–51
19. Böhmer MR, El Attar Sofi Y, Foissy A (1994) J Colloid Interface Sci 164:126–135
20. Pochard I, Couchot P, Foissy A (1998) Colloid Polym Sci 276:1088–1097
21. Partyka S, Lindheimer M, Zaini S, Keh E, Brun B (1986) Langmuir 2:101–105
22. Gonzales-Mozuelos P, Olivera De La Cruz M (1995) J Chem Phys 103:3145–3157
23. Eisenberg H (1958) J Polym Sci 30:47–66
24. Ikegami A, Imai N (1962) J Polym Sci 56:133–152
25. Morishima Y, Sato T, Kamachi M (1996) Macromolecules 29:3960–3964
26. Manning GS (1978) Q Rev Biophys II:179–246
27. De Jong HG, Lyklema J, Van Leeuwen HP (1987) Biophys Chem 27:173–182
28. Ludwig H, Loebel KH (1996) Ber Bunsenges Phys Chem 100:863–868
29. Shimizu T, Minakata A (1981) Biophys Chem 14:333–339
30. Ogawara K, Kawazoe S, Tamura T, Kawauchi S, Satoh M, Komiyama J (1998) Polymer 39:437–440
31. Kim HG, Lee JH, Lee HB, Jhon MS (1993) J Colloid Interface Sci 157:82–87
32. Strauss UP, Helfgott C, Pink H (1967) J Phys Chem 71:2550–2556
33. Edsall J, Wyman J (1958) Biophysical chemistry, vol 1. Academic Press, New York
34. Wu CF, Lee JF (1996) J Colloid Interface Sci 183:236–242
35. Kankia BI, Funck T, Uedaira H, Buckin UA (1997) J Solution Chem 26:877–888
36. Handbook of Chemistry and Physics, 54th edn. Weast RC (ed) CRC Press, Cleveland
37. Israelachvili J (1985) Intermolecular and surface forces. Academic Press, London