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Chemical and Electrostatic Association of Various Metal Ions by Poly(acrylic acid) and Poly(methacrylic acid) As Studied by Potentiometry

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Potentiometric titrations have been performed for poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMA) in solution in the presence of different metals (Ca, Mg, Zn, and Cu) by titrating with KOH without additional salt. For the Me/PAA system, experimentally obtained apparent dissociation constants (pK_a) appear to decrease in the initial part of the titration curve, which was found to be most pronounced in case of Cu. This was also found for the Cu/PMA system. For all systems studied, an increase in pK_a was observed at higher degrees of dissociation. Analytical expressions for the change in apparent pK_a upon ionization have been derived on the basis of counterion condensation theory taking into account both electrostatic and chemical binding of counterions of different valences. Taking also into account the effects of the flexibility of the polymer, the agreement between calculated and experimentally obtained data is certainly satisfying for the larger part of the titration curve. The agreement is completely lost by considering only electrostatic interactions between metal ions and the polyanions. An increase in chemical binding as indicated by a more negative value of the intrinsic reduced free energy of binding (g_b) is observed in the order $Mg \approx Ca < Zn < Cu$ for both polyelectrolytes. The present approach allows us to quantify the contributions of the individual physicochemical processes related to the overall distribution of counterions around charged macromolecules.

Introduction

Knowledge of association phenomena of metal ions with charged macromolecules is of importance for the understanding of their physicochemical behavior in environmental and biological systems. From an experimental point of view, information is usually obtained with respect to the *overall* distribution of counterions around the charged macromolecules without having the ability to distinguish between different fractions which might be attributed to various underlying interaction processes, like electrostatic and chemical binding. Recently, we have presented an extension of the counterion condensation theory, which takes into account a number of association phenomena of counterions around linear charged polyelectrolytes.¹ The contribution of the territorial and site-specific association processes to the overall distribution has been discussed and illustrated from the theory for a wide range of different chemical conditions, including polyelectrolyte charge density, concentrations of polymer and monovalent and divalent counterions, etc.

The proton dissociation of weak polyacids in solutions with its own counterions and with added 1:1 simple salt is one of the physicochemical processes largely studied theoretically and used experimentally.^{2–7} However, potentiometric analysis for the case of polyelectrolyte solutions containing a mixture of counterions of different valence has received little attention.^{8–13} Ishikawa⁹ and Zhang and Nilsson¹¹ have used the solution of the Poisson–Boltzmann equation to interpret their results, assuming only electrostatic interactions between the polyelectrolyte and the low molecular ions in the solution. On the other hand, and on the basis of potentiometric experiments, chemical binding of Cu to polymethacrylate polyion was proposed as part

of the association process.⁸ Benegas et al.¹³ have analyzed potentiometric titration data of various Cd/poly(acrylic acid) systems, by assuming chemical binding of the cadmium ions to the polymer as well as electrostatically bound potassium counterions. Chemical binding was introduced in a simplified manner by assuming complete charge compensation of the macromolecule due to the association of cadmium ions by the polyanion.

The counterion condensation (CC) theory of linear polyelectrolytes^{14,15} is well-known for giving rather simple analytical equations for the different thermodynamic functions that describe the electrostatic interactions of linear polyelectrolytes in solution. Recent theoretical developments¹ allow us to introduce both electrostatic and chemical binding of counterions of different valences in analyzing metal/polyelectrolyte solutions. On the basis of these new insights, analytical expressions for the change in apparent pK upon ionization are derived in this paper.

The aim of the present paper is to study the association of divalent metals ions to the polymer upon charging of the polyelectrolyte from both experimentally and theoretically. Potentiometric titrations have been carried out for poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMA) (both widely used synthetic polymers) in solution in the presence of different earth alkaline metals (Ca and Mg) and heavy metals (Zn and Cu) by titrating with potassium hydroxide. In analyzing the data theoretically, the effects of the flexibility of the polymer are taken into account.^{16,17}

Theory

Counterion Condensation. Starting point in our theoretical approach (as usual in the CC-theory) is to assume that the

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polyelectrolyte in solution can be modelled by a uniform linear array of charges. Under this assumption the structural polyelectrolyte charge density, ξ_{str} , is defined as

$$\xi_{\text{str}} = l_b/b = e^2/\epsilon kTb \quad (1)$$

where l_b is the Bjerrum length, b represents the average spacing between charges on the linear polyion, e is the elementary charge, ϵ is the dielectric constant of the bulk solution, k is the Boltzmann constant, and T is the absolute temperature.

As shown by Paoletti et al.,¹⁸ counterions of species i and j (of valences z_i and z_j) will be condensed onto a condensation volume V_p , which surrounds the polyelectrolyte, by a total fraction r per polymeric-charged group, under the condition that the polyelectrolyte charge density ξ be greater than a critical value ξ_{crit} . In this model the fraction of condensed counterions, r , is always made up of contributions of both counterions. Therefore

$$r = r_i + r_j = r(x_i + x_j) \quad (\text{with } x_i + x_j = 1) \quad (2)$$

where x_i and x_j stand for the fractions of condensed counterions per polymer charge of valences z_i and z_j , respectively. Therefore, on average, each polymeric charge is compensated by counterion condensation by an amount $z_i x_i + z_j x_j$.

To obtain the equilibrium values of the parameters r and x_i , the total free energy, given by the sum of the ionic free energy (including electrostatic and entropic mixing contributions) and the binding energy¹

$$G^{\text{tot}} = G^{\text{ion}} + G^{\text{bin}} = G^{\text{el}} + G^{\text{mix}} + G^{\text{bin}} \quad (3)$$

is minimized with respect to r and x_i . The free energy of binding is given by¹

$$G^{\text{bin}} = \sigma G_0^{\text{bin}} \quad (4)$$

where G_0^{bin} is the intrinsic free energy for chemically binding a counterion to the polyelectrolyte site. The bonded fraction of counterions results in a reduction of each polymeric charge by a fraction σ . This reduced polymeric charge then interacts electrostatically with all remaining counterions in the solution to determine the fraction of condensed counterions. In the limit of infinite dilution, the total fraction of condensed counterions is given by¹

$$r = \frac{1}{(z_j - x_i(z_j - z_i))} \left[1 - \frac{1}{\alpha \xi_{\text{str}}(z_j - x_i(z_j - z_i))(1 - z_j\sigma)} \right] \quad (5)$$

where σ denotes the fraction of counterions chemically bound per polymeric charge and α is the degree of dissociation (cf. eq 15).

The Apparent Dissociation Constant pK_a . The apparent dissociation constant, pK_a , for the proton ionization of a weak polyelectrolyte, is given by⁵

$$pK_a(\alpha) = pK_0 + \frac{1}{n_p 2.303RT} \frac{\partial G^{\text{ion}}}{\partial \alpha} \quad (6)$$

where n_p is the number of polymeric charge units and R is the gas constant. The change in pK_a is a function of all thermodynamic variables of the aqueous solution

$$\Delta pK_a(\alpha) = \frac{1}{n_p 2.303RT} \frac{\partial G^{\text{ion}}}{\partial \alpha} = F(\alpha, \xi_{\text{str}}, c_p, c_1, c_2, T, \epsilon, \sigma_0) \quad (7)$$

where σ_0 is the maximum amount of bound counterions per polymeric unit and c_p , c_1 , and c_2 stand for the analytical concentration of polymer ionizable groups, monovalent, and divalent counterions, respectively. For the general case of a mixture of two counterions of valences z_i and z_j , eq 7 takes the following forms for the regions below and above the onset of condensation, for $\xi \leq \xi_{\text{crit}}$,

$$2.303\Delta pK =$$

$$-\alpha(1 - z_j\sigma)^2 \xi_{\text{str}} \left[2 \ln(1 - e^{-\kappa b_\sigma}) + \frac{\alpha \kappa b_\sigma}{(e^{\kappa b_\sigma} - 1)} \text{SU} \right] \quad (8)$$

where $b_\sigma = b_{\text{str}}/(\alpha(1 - z_j\sigma))$ and κ is defined as the inverse of the Debye length, usually presented in the form

$$\kappa^2 = l_b c_p \text{DEN} \quad (9)$$

SU stands for:

$$\text{SU} = \frac{1 - z_j^2\sigma}{2\text{DEN}} - \frac{1}{\alpha} \quad (10)$$

and

$$\text{DEN} = \alpha + R_i(z_i + z_i^2) + R_j(z_j + z_j^2) - \alpha z_j^2\sigma \quad (11)$$

In eq 11, $R_i = c_i/c_p$ and $R_j = c_j/c_p$.

For $\xi > \xi_{\text{crit}}$, we obtain:

$$2.303\Delta pK = -\alpha(1 - z_j\sigma)^2 \xi_{\text{str}} \times$$

$$\begin{aligned} & (1 - r(z_j - x_i(z_j - z_i)))^2 \left[2 \ln(1 - e^{-\kappa b_\sigma}) + \frac{\alpha \kappa b_\sigma}{(e^{\kappa b_\sigma} - 1)} \text{SU} \right] + \\ & x_i r (1 - z_j\sigma) \ln \left[\frac{x_i r \alpha (1 - z_j\sigma)}{(\alpha + R_i) V_p c_p} \right] + \\ & (1 - x_i r (1 - z_j\sigma)) \ln \left[\frac{\alpha + R_i - x_i r \alpha (1 - z_j\sigma)}{(\alpha + R_i)(1 - V_p c_p)} \right] + \\ & (1 - x_i) r (1 - z_j\sigma) \ln \left[\frac{(1 - x_i) r \alpha (1 - z_j\sigma)}{R_j V_p c_p} \right] - \\ & (1 - x_i) r (1 - z_j\sigma) \ln \left[\frac{R_j - (1 - x_i) r \alpha (1 - z_j\sigma)}{R_j (1 - V_p c_p)} \right] \end{aligned} \quad (12)$$

where SU has now become:

$$\text{SU} = \frac{1 - z_j^2\sigma - r(1 - z_j\sigma)^2(x_i(z_i^2 - z_j^2))}{2\text{DEN}} - \frac{1}{\alpha} \quad (13)$$

and

$$\text{DEN} = \alpha + R_i(z_i + z_i^2) + R_j(z_j + z_j^2) - \alpha(z_j^2\sigma + r(x_i(z_i^2 - z_j^2) + z_j^2)) \quad (14)$$

We note that in the case in which no chemical binding occurs (i.e., $G^{\text{bin}} = 0$), the previous equations can be applied just by taking $\sigma = 0$. In this case, the calculated change in pK_a can be

TABLE 1: pH and (α) Values of the Initial Metal/Polymer Solution (without any KOH) ($R_2 = c_2/c_p = 0.1$ and 0.2 for the PAA and PMA system, respectively; $c_p = 2.5 \times 10^{-3} \text{ mol L}^{-1}$; no additional salt)

metal	none	Ca	Cu	Mg	Zn
PAA	4.26 (0.022)	4.12 (0.030)	3.70 (0.080)	4.11 (0.031)	4.05 (0.036)
PMA	4.02 (0.038)	4.08 (0.033)	3.81 (0.062)	4.15 (0.028)	4.09 (0.033)

derived from the theoretical model described in ref 18 and is presented here for the first time.

Experimental Section

Materials. The poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMA) solutions were obtained from Acros (lot/product number A010694201/18501-2500) and BDH Chemicals (lot/product number 6013180C/29805), respectively, and used without further treatment. According to the manufacturers, PAA and PMA concentrations were 25 and 20% weight units, respectively. Stock solutions of approximately 0.1 mol L^{-1} (in monomers) were prepared by dilution with water. Concentrations of carboxylic groups were determined by potentiometric titration with potassium hydroxide. Until usage, stock solutions were kept in the refrigerator at approximately 7°C . All other reagents were obtained by Merck: copper(II) nitrate and zinc(II) nitrate were of analytical-reagent grade, whereas calcium nitrate and magnesium nitrate were of Suprapur quality. Titrisol potassium hydroxide solutions at a concentration of 0.100 mol L^{-1} were used as titrating solutions. Titrisol buffer solutions were used for calibrating the potentiometer.

Methods. The potentiometric measurements were performed using a digital pH meter from Radiometer (model PHM 95) in combination with a combined glass/calomel electrode (GK2401C). The electrode system was daily calibrated using two buffers (pH 4 and 7) and controlled with a standard buffer solution of pH equal to 6.88.

The potentiometric titrations were carried out with potassium hydroxide charging the poly(acrylic acid) and poly(methacrylic acid) at a fixed concentration of $2.5 \times 10^{-3} \text{ mol L}^{-1}$ in the presence of various metal nitrates. The pH readings (± 0.01 pH unit) were carried out after a sufficient stabilization period. The titration vessel was thermostated at 25°C . Experiments are performed under a nitrogen atmosphere. The degree of polymer dissociation (α) was calculated from the monitored pH value and the degree of neutralization, as given by the added amount of the KOH solution

$$\alpha = ([\text{KOH}]_a + [\text{H}^+] - [\text{OH}^-])/c_p \quad (15)$$

where $[\text{KOH}]_a$ is the concentration of the added KOH solution and c_p is the overall poly(meth)acrylic acid concentration (in terms of functional groups, thus including both carboxylic and carboxylate groups).

Results and Discussion

In Table 1, the initial pH is presented for both the poly(acrylic acid) and poly(methacrylic acid) system at a polymer concentration of $2.5 \times 10^{-3} \text{ mol L}^{-1}$ in the presence of various metal nitrates at concentrations of 0.25×10^{-3} and $0.5 \times 10^{-3} \text{ mol L}^{-1}$, respectively, without additional salt. Thus, these data represent the first point in the potentiometric titrations, which are shown for the different metal/PAA systems in Figure 1. Using eq 15, the initial degree of dissociation α has been calculated and is included in Table 1. The initial pH appears to be dependent on the metal/polymer system and increases in the

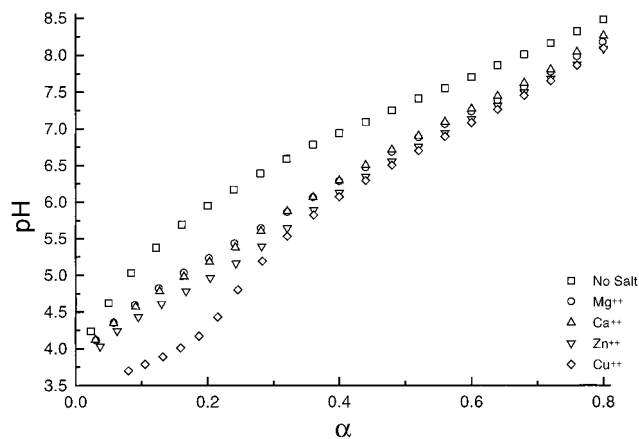


Figure 1. Potentiometric titration curves of various metal/PAA systems: $c_p = 2.5 \times 10^{-3} \text{ mol L}^{-1}$; $c_2 = 0.25 \times 10^{-3} \text{ mol L}^{-1}$; no additional salt ($c_1 = 0$).

order $\text{Cu} < \text{Zn} < \text{Mg} \leq \text{Ca}$ for the poly(acrylic acid) system. For the poly(acrylic acid) in water, an initial pH of 4.26 is found, which is the result of self-dissociation of the polymer. A smaller initial pH means that the corresponding metal is able to replace more protons from the polyelectrolyte chain compared to other metal/polymer systems, which show an elevated pH. Differences in pH may be attributed to differences in association of the metal with the polymer. From a theoretical point of view, the association of the metal with poly(acrylic acid) should be of chemical binding nature, since the polymeric charge densities are all well below the critical value for condensation. Note that an initially lower value for pH results in an initially larger degree of proton dissociation. For all metal/poly(acrylic acid) systems, a smaller pH is observed over the whole potentiometric titration curve, compared to the reference curve. In addition, this deviation is the largest for the case of Cu up to a degree of dissociation of approximately 0.3. From here the potentiometric behavior is approximately the same for the various metal/poly(acrylic acid) systems. For the poly(methacrylic acid) system, initial binding of metals is less pronounced, since most obtained pH values are approximately equal to the pH resulting from self-dissociation of the PMA solution. In case of Cu the initial pH is certainly lowered compared to that of the other systems, indicating (chemical) binding of the metal with to the macro-molecule.

In Figure 2, the apparent dissociation constant (pK_a) of the Ca/PAA system and the Zn/PAA system are plotted as a function of the degree of dissociation (α). The pK_a values have been calculated from the measured pH with

$$\text{pK}_a = \text{pH} + \log [(1 - \alpha)/\alpha] \quad (16)$$

For the Mg/PAA system and the Cu/PAA system, pK_a values are plotted versus α in Figure 3. In all cases, the concentrations were $[\text{PAA}] = 2.5 \times 10^{-3} \text{ mol L}^{-1}$ and $[\text{Me}] = 0.25 \times 10^{-3} \text{ mol L}^{-1}$ with no additional salt. The experimental data for the (salt-free) reference curve show the normal pattern of protolytic behaviour of linear polyelectrolytes under salt-free conditions. The protolytic behavior of all metal/poly(acrylic acid) systems is certainly different compared to the reference curve. The experimentally obtained pK_a values appear to decrease in the initial part of titration curve and increases before α becomes approximately 0.2. This observation seems to be dependent on the metal under investigation and is most pronounced for the case of copper. It is obvious that the binding of the various metals influence the protolytic behavior of the polyacrylate anion

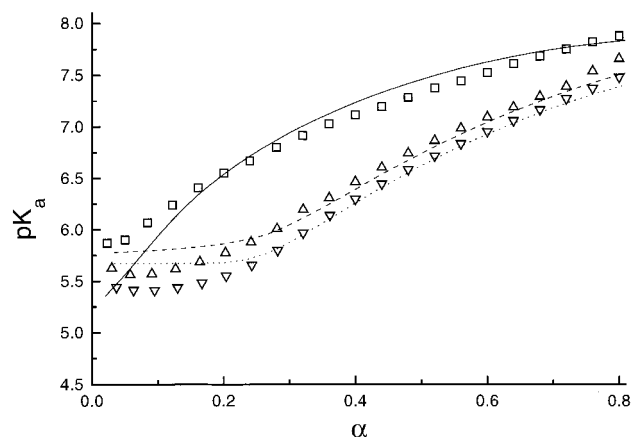


Figure 2. Experimental and theoretical pK_a data for the Ca/PAA and Zn/PAA as a function of the degree of dissociation (α) of the poly(acrylic acid). Included are data for the metal-free case ($c_2 = 0$): $c_p = 2.5 \times 10^{-3} \text{ mol L}^{-1}$; $c_2 = 0.25 \times 10^{-3} \text{ mol L}^{-1}$; $\xi_{\text{str}} = 2.85$. Symbols are as in Figure 1. Lines: (—) salt-free case, semiflexible polymer; (---) $g_b = -9.5RT$; (···) $-12RT$.

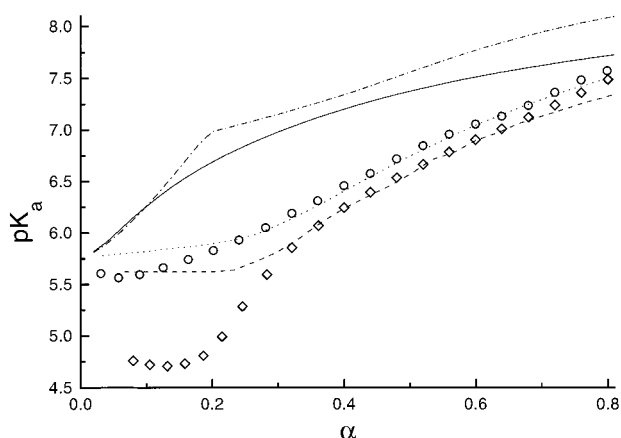


Figure 3. Experimental and theoretical pK_a data for the Mg/PAA and Cu/PAA as a function of the degree of dissociation (α) of the poly(acrylic acid). Included are theoretical curves based on the absence of chemical binding: $c_p = 2.5 \times 10^{-3} \text{ mol L}^{-1}$; $c_2 = 0.25 \times 10^{-3} \text{ mol L}^{-1}$. Symbols are as in Figure 1. Lines: (—) salt-free case, semiflexible polymer; (---) salt-free case, rigid polymer; (---) $g_b = -15RT$; (·-·) $-9RT$.

in different ways, in a process which is not well understood by us yet. This modification of the titration curves has also been shown by Morishima et al.,¹² although not in such a striking form as here, because they refer only to a point at the end of the titration curve ($\alpha \sim 1$), where the effect is least noticeable.

Using eqs 8 and 12 and a value of 2.85 for the structural charge density parameter of the polyelectrolyte, theoretical pK_a values have been calculated taking into account the flexibility of the polymer,^{16,17} and are presented as lines in Figures 2 and 3. The calculated semiflexible curves are obtained using a rigidity parameter (k) equal to $0.24 \text{ kcal mol}^{-1} \text{ \AA}^{-2}$, as in previous calculations for the poly(acrylic acid) system.¹³ For the reference situation, pK_a values were calculated considering only the ionic and mixing contributions to the Gibbs free energy, whereas the theoretical curves for the various metal/polyelectrolyte systems have been calculated using different values for the intrinsic reduced free energy of binding g_b and pK_0 (see Table 2). In all cases, the shape of the theoretical curve consists of a more or less initially flat part at low α , followed by a gradual increase, which starting point depends highly on the chosen value for g_b . In fact, increasing the value of g_b shifts this point to larger values of α , which can be clearly seen by

TABLE 2: pK_0 and g_b Values for Various Me/PAA and Me/PMA Systems as Obtained by Theoretical Analysis of Potentiometrically Obtained Acid–Base Dissociation Data ($R_2 = c_2/c_p = 0.1$ and 0.2 for the PAA and PMA system, respectively; $c_p = 2.5 \times 10^{-3} \text{ mol L}^{-1}$; no additional salt)

	metal	none	Ca	Cu	Mg	Zn
PAA	pK_0	5.25	5.78	5.62	5.78	5.67
	g_b (RT)	0	−9.5	−15	−9	−12
PMA	pK_0	5.65	6.35	6.25	6.35	6.35
	g_b (RT)	0	−9	−15	−9	−12

comparing for example the theoretical curves of Mg/PAA system and the Cu/PAA system. For all systems, the final part of the theoretical curve is convex with the convexity decreasing with increasing α .

For illustration, in Figure 3 theoretical pK_a curves are included for a metal/polyelectrolyte system with $c_2 = 0.25 \times 10^{-3} \text{ mol L}^{-1}$ and $c_p = 2.5 \times 10^{-3} \text{ mol L}^{-1}$, without additional salt, assuming *no* chemical binding, thus $g_b = 0$, for a rigid and semiflexible polymer. Note, that the shape of both curves is certainly different from the curve calculated assuming binding. For the rigid case, the initial part of the curve has a steep rise, followed by a rather flat region that begins at the critical charge density of the polyelectrolyte. This curve shows the same features as the calculated pK_a curve with only monovalent counterions, which has been widely used in analyzing potentiometric titration data.^{5,6} Taking into account the thermodynamic averaging by considering the flexibility of the polymeric chain, the discontinuity in the slope is lost, but the overall shape is still not in accordance with our experimental data.

Assuming chemical binding, the agreement between theoretically calculated and experimentally obtained data is certainly satisfying for α values larger than 0.3 for the Cu/PAA system. For the other metal/PAA systems, the agreement between model and experiment is already obtained at smaller values of α , e.g., in case of Mg/PAA for which the agreement is fairly good for $0.2 < \alpha < 0.8$. The observed decrease in g_b (see Table 2; $\text{Mg} > \text{Ca} > \text{Zn} > \text{Cu}$) is consistent with our observation of the behavior of the initial pH values for the various potentiometric titration curves (see Table 1). A decrease in g_b corresponds with an increase in chemical binding. For both earth alkaline metals, the chemical binding to PAA is quite comparable, whereas for Zn and Cu the binding strength is larger and much larger, respectively.

For various metal/PMA systems, theoretical and experimental values for pK_a are plotted versus α , in Figures 4 and 5. The concentrations in this case are $c_p = 2.5 \times 10^{-3} \text{ mol L}^{-1}$ and $c_2 = 0.5 \times 10^{-3} \text{ mol L}^{-1}$ with no additional salt added. We note that the acid–base potentiometric behavior for PMA is somewhat more complicated than in the case of PAA, due to a conformational transition in the region of low values for α (see for example, ref 20), which is clearly seen for the reference salt-free case curve. To avoid the extreme complexity of the system due to the conformational transition, here we focus on the final part of the curves. Theoretical curves have been calculated using g_b and pK_0 values as presented in Table 2. Again a good agreement is obtained between experimentally obtained and theoretically calculated data. In the initial part of the experimental curves there is a small increase in pK_a for Ca, Mg and Zn, whereas for Cu a clear initial decrease is observed. The intermediate region is rather flat, a characteristic obtained only by assuming chemical binding. In this case, the flat region extends up to approximately $\alpha = 0.45$, because the total analytical metal concentration has been increased by a factor of 2 compared to the polyacrylate system. For these metal/PMA

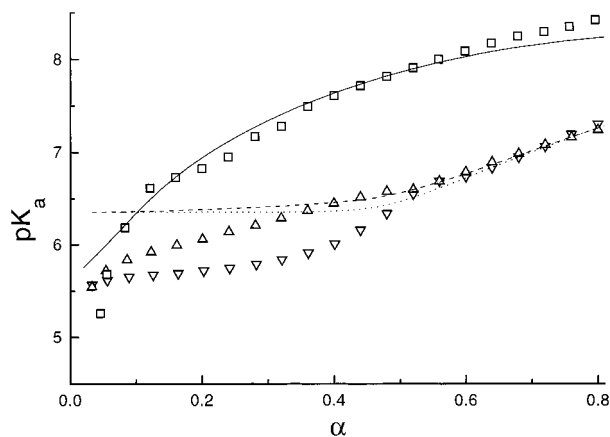


Figure 4. Experimental and theoretical pK_a data for the Ca/PMA and Zn/PMA as a function of the degree of dissociation (α) of the poly(methacrylic acid). Included are data for the metal-free case ($c_2 = 0$); $c_p = 2.5 \times 10^{-3} \text{ mol L}^{-1}$; $c_2 = 0.5 \times 10^{-3} \text{ mol L}^{-1}$. Symbols are as in Figure 1. Lines: (—) salt-free case, semiflexible polymer; (---) $g_b = -9RT$; (···) $-12RT$.

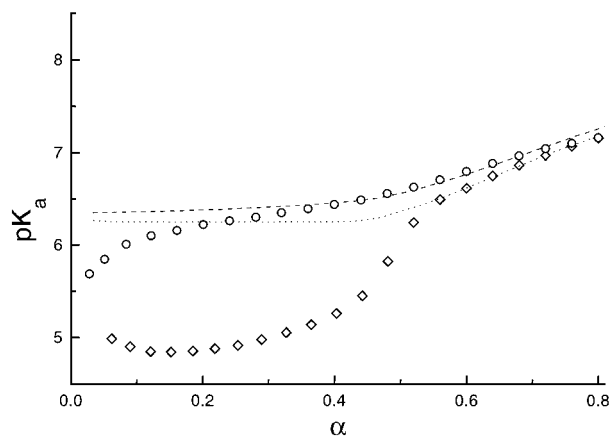


Figure 5. Experimental and theoretical pK_a data for the Mg/PAA and Cu/PAA as a function of the degree of dissociation (α) of the poly(methacrylic acid): $c_p = 2.5 \times 10^{-3} \text{ mol L}^{-1}$; $c_2 = 0.5 \times 10^{-3} \text{ mol L}^{-1}$. Symbols are as in Figure 1. Lines: (---) $g_b = -9RT$; (···) $-15RT$.

systems, the intrinsic reduced free energy of binding g_b appears to be equal or almost equal to the ones found for the PAA system. This observation is in line with expectation, since both polyelectrolytes consist of an array of monomeric units of almost comparable chemical complexing groups, i.e., carboxylate.

For illustration, in Figure 6, the concentration of chemically bound (c_2^b) and electrostatically associated (c_2^c) divalent counterions are plotted versus the degree of dissociation for two values of g_b , a polymer concentration of $2.5 \times 10^{-3} \text{ mol L}^{-1}$ and a total divalent metal concentration of $0.25 \times 10^{-3} \text{ mol L}^{-1}$. It appears that for these values of g_b , the association of divalent metals is mainly due to chemical binding certainly for smaller degrees of dissociation, whereas the concentration of metals associated by the polyanion due to electrostatic interaction is very small and only observed at higher degrees of polymer dissociation.

It can be concluded that association phenomena of divalent counterions with linear polyelectrolytes as studied by potenti-

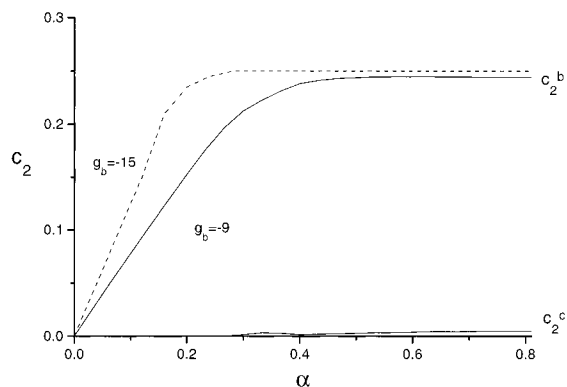


Figure 6. Theoretically calculated concentrations of chemically bound and electrostatically associated divalent counterions to the polyelectrolyte as a function of the degree of dissociation (α) for various values of g_b : $c_p = 2.5 \times 10^{-3} \text{ mol L}^{-1}$ and $c_2 = 0.25 \times 10^{-3} \text{ mol L}^{-1}$.

metric titrations can be fairly well described by the counterion condensation approach presented here which takes into account both chemical binding and electrostatic interactions. Hence, in this way we are able to distinguish the individual contributions of both physicochemical processes to the overall distribution of counterions in polyelectrolytic solutions containing linear charged polyelectrolytes.

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