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Limiting-laws of polyelectrolyte solutions. Ionic distribution in mixed-valency counterions systems. II. A comparison of conductometric data and theoretical predictions

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Abstract

The competitive binding of monovalent and divalent counterions (M^+ and M^{2+}, respectively) has been studied by a conductometric procedure as described by De Jong et al. (Biophysical Chemistry 27 (1987) 173) for aqueous solutions of alkali metal polymethacrylates in the presence of $Ca(NO_3)_2$ or $Mg(NO_3)_2$. The experimentally obtained fractions of conductometrically free counterions are compared with theoretical values computed according to a new thermodynamic model recently developed by Paoletti et al. (Biophysical Chemistry, 41 (1991) 73). For the systems studied, the fractions of free monovalent and divalent counterions can be fairly well described by the theory. In fact, the results support the assumption that under the present conditions the conductometrically obtained distribution parameters f_1 and f_2 approximate the equilibrium fractions of free monovalent and divalent counterions. For a degree of neutralization of 0.8 and a molar concentration ratio of divalent counterions and charged groups on the polyion up to 0.25, the mean M^+/M^{2+} exchange ratio ν has been found to be 1.39 ± 0.03 and 1.33 ± 0.03 for the alkali metal/Ca/PMA and alkali metal/Mg/PMA systems, respectively. These values agree well with the theoretical value, which for this particular case is 1.38.

Keywords: Conductometry; Polyelectrolyte theory; Mixed-valency counterions system

1. Introduction

The competitive binding of monovalent and divalent counterions in polyelectrolytic systems has been the subject of many theoretical and experimental studies [1–8]. Manning [3] has de-

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scribed condensation phenomena in solutions of linear polyelectrolytes; systems with counterions of different valencies are considered in what is called the two-variable theory. Since then, many workers, including Manning himself [4], have reported various expressions to describe quantitatively condensation phenomena. Recently, Paoletti et al. [2] have developed an extension of the counterion condensation theory of linear polyelectrolytes for the case of a system containing a mixture of counterions of different valency. The main element of their model is that the relative amounts of the condensed counterions of different types, for example monovalent and divalent ones, are accurately accounted for in the pertaining entropy-of-mixing terms.

Recently, De Jong et al. [1] described a procedure for the analysis of the conductivity of solutions of anionic polyelectrolytes in which both monovalent and divalent counterions are present. They used a combination of the Eisenberg procedure together with the conductivity excess function for analyzing the conductivity of Zn/alkali metal polyacrylate systems and found that conductometry indeed allows the computation of bound fractions of both the monovalent and divalent counterions.

The aim of the present work is to extend the study by De Jong et al. [1] and to compare the competitive behavior of monovalent and divalent counterions in polyelectrolyte solutions as obtained by conductometry with values computed with the model proposed by Paoletti et al. [2]. Alkali metal polymethacrylate solutions with a degree of neutralization of 0.8 have been titrated with $Ca(NO_3)_2$ or $Mg(NO_3)_2$, respectively, in the absence of any additional simple salt. From the conductometric titration data obtained, fractions of free monovalent and divalent counterions have been calculated. The changes of these fractions in the course of the titration give information about the M^+/M^{2+} exchange ratio. The fractions free monovalent and divalent counterions as well as the exchange ratio have been compared with the theoretical values as computed with the model proposed by Paoletti et al. [2].

2. Theory

2.1 Conductivity of mixed-valency counterion-polyelectrolyte solutions

For the interpretation of conductometric titration of an aqueous polyelectrolyte solution (with a monovalent counterion) with a solution of a divalent metal salt in systems without any additional salt, we follow the procedure previously described by De Jong et al. [1]. In short, the procedure includes the following basic equations and assumptions.

According to the two-state approximation [9], the specific conductivity of a polyelectrolyte solution, which consists of negatively charged polyions together with monovalent and divalent counterions and monovalent co-ions, may in general be written as:

$$K = f_1\lambda_1 c_1 + f_2\lambda_2 c_2 + f_p\lambda_p c_p + \lambda_A c_A \qquad (1)$$

where c_1, c_2 and c_A denote the analytical molar concentrations of monovalent and divalent counterions and co-ions, respectively; c_p is the molar volume concentration of deprotonated groups on the polyion (which equals the degree of dissociation α times the analytical concentration of total amount of groups c_c); λ_i denotes the molar conductivity of ion type i; and f_i is the fractional distribution parameter of i [9].

In the two-state approximation, we simplify the real situation by disregarding the gradual change from fully free polyionic groups and counterions on one hand to a perfect associate, i.e., a state of complete annihilation of charges, on the other. However, the two-state approximation has been shown to be operationally helpful and very effective in many practical situations. Considering the experimental evidence from independent sources [10], it seems not unreasonable to assume that the evaluated distribution parameters f_1 and f_2 come close to the equilibrium fractions of free monovalent and divalent counterions.

In the case of purely electrostatic (i.e. non-specific) interactions, f_1 and λ_p values can be determined from Eisenberg plots [11], i.e., plots of the molar conductivity Λ [equal to $K/(c_p + c_A)$] versus λ_1^0, the molar conductivity of different monovalent counterions in pure solvent. For different metal/polyelectrolyte systems, these plots have been found to be linear [1,11,12].

Values of f_2 can be calculated from the conductivity excess function ΔK, defined by the difference between the specific conductivity of a mixed metal/polyelectrolyte system and the sum of the conductivities of the metal salt solution and the polyelectrolyte solution before mixing. For the case of adding $Me(NO_3)_2$ to an alkali metal polycarboxylate solution we have:

$$\Delta K = (f_{1,0} - f_1)(\lambda_1^0 + \lambda_p)c_1 + (1 - f_2)(\lambda_2^0 + 2\lambda_p)c_2 \qquad (2)$$

where $f_{1,0}$ is the fraction of conductometrically free monovalent counterions in the polyelectrolyte solution without added 2:1 salt. The first term in eq. (2) is due to the liberation of monovalent ions and the second one represents the effects of binding divalent ions.

2.2 Theoretical model of ionic distribution in mixed-valency counterions systems

For the calculation of the fractions of free monovalent and divalent cations, we use the model recently proposed by Paoletti et al. [2], which basically follows the so-called "chemical model" of counterion-condensation (CC) of linear polyelectrolytes as firstly developed by Manning [13]. As usual, in this approach, the linear polyelectrolyte chain is idealized by a linear uniform array of charges, supposed to be of infinite length to neglect end effects. The average distance between the projections of the charges onto the polymer axis is b. The charge density parameter ξ is defined as $\xi = l_B/b$ with l_B being the Bjerrum length. The total reduced molar (rm) excess free energy of polyelectrolytic nature, g^{ion}, is factorized into two main contributions:
(i) a purely electrostatic term, g^{el}, and (ii) a rm-free energy of mixing of the non-polyionic species, g^{mix}.

$$g^{ion} = g^{el} + g^{mix} \qquad (3)$$

An expression for g^{el} is given by the CC theory:

$$g^{el} = -\xi(q_{eff})^2 \ln(1 - e^{-\kappa b}) \qquad (4)$$

where q_{eff} is the net, "effective" normalized charge on each ionized site on the polyelectrolyte and κ is the reciprocal Debye length. The total fraction of condensed monovalent and divalent counterions, r, is given by:

$$r = r_1 + r_2 = 2 - f_1 - f_2 \qquad (5)$$

with $r_1 = rx_1$ and $r_2 = rx_2$.
x_i is the mol fraction in the condensation volume according:

$$x_1 = \frac{r_1}{r_1 + r_2} = \frac{1 - f_1}{2 - f_1 - f_2} \qquad (6)$$

and

$$x_2 = 1 - x_1 \qquad (7)$$

In this case the effective charge is given by:

$$q_{eff} = 1 - r(x_1 + 2(1 - x_1)) = 1 - r(2 - x_1) \qquad (8)$$

For g^{mix} the following (entropic) contributions of the different non-polyionic species to the change of the free energy of mixing are considered:

$$g^{mix} = (g_1)^{cond} + (g_2)^{cond} + (g_1)^{free} + (g_2)^{free} + g_{coions} + g_{solv} \qquad (9)$$

which are given by:

$$(g_1)^{cond} = rx_1 \ln(rx_1/(1 + R_1)V_p c_p) \qquad (10)$$

$$(g_2)^{cond} = rx_2 \ln(rx_2/R_2 V_p c_p) \qquad (11)$$

$$(g_1)^{free} = (1 + R_1 - rx_1) \ln((1 + R_1 - rx_1)/(1 + R_1)(1 - V_p c_p)) \qquad (12)$$

$$(g_2)^{free} = (R_2 - rx_2) \times \ln((R_2 - rx_2)/R_2(1 - V_p c_p)) \qquad (13)$$

$$g_{coions} = (R_1 + 2R_2) \ln(1/(1 - V_p c_p)) \qquad (14)$$

$$g_{solv} = r \qquad (15)$$

where R_1 and R_2 stand for the analytical concentrations of the (added) 1:1 and 2:1 salt, divided by c_p. Thus, $(1 + R_1)$ is the amount ratio between monovalent counterions and charged groups on the polymer. The molar condensation volume, V_p, is expressed in liters per mole of fixed charge.

The system is characterized by the usual variables (temperature, pressure, macroscopic concentration of solutes), and in addition by the two independent variables r and x, and by V_p. For the determination of r, x and V_p it was found convenient to resort to the free energy minimization procedure similar to the original treatment of Manning [13]. The minimization conditions have been defined as:

$$\partial g^{\text{ion}}/\partial r = 0 \tag{16}$$

and

$$\partial g^{\text{ion}}/\partial x = 0 \tag{17}$$

Equation (16) implies that the following condition is necessary to retain stability for all r and x in the limit $c_p \to 0$:

$$r = \frac{1}{(2-x)}\left(1 - \frac{1}{\xi(2-x)}\right) \tag{18}$$

It can be easily verified that eq. (18) reduces to the well-known limiting conditions for the two extreme cases of purely monovalent ($x = 1$) and purely divalent counterion ($x = 0$) [4]. Regarding the two variables r and x, the system at equilibrium is fully determined by the simultaneous solution of eqs. (17) and (18).

3. Experimental

Poly(methacrylic acid) (PMA, with an average relative molecular mass of 26000) was obtained from BDH and used without pretreatment. All chemicals used were of analytical-reagent grade. All samples were prepared using demineralized tap water, produced by a Millipore Super-Q reverse osmosis system. After removing CO_2, the conductivity of this water never exceeded 0.6 μS cm^{-1}. The equipment has been described elsewhere [1].

Solutions of alkali metal polymethacrylates were prepared by neutralizing the polyacid with the appropriate hydroxide solution to a degree of neutralization of 0.8. For such high values, the difference between the degree of neutralization and that of dissociation is negligible. Aliquots of 50 μl of 0.05 M $Ca(NO_3)_2$ or $Mg(NO_3)_2$ solution were added to 50 ml of the sample solution. Prior to measurements, the samples were stirred and kept in a constant-temperature vessel for 60 min to achieve thermal equilibrium, while purging with CO_2-free, water-saturated nitrogen. All experiments were done in duplicate at 25.00 ± 0.02°C.

4. Results and discussion

Figures 1(a) and 1(b) show the conductivity excess for the three alkali metal polymethacrylate solutions as a function of the concentration of Ca^{2+} and Mg^{2+}, respectively, with [PMA] = 2.5 mM and a degree of neutralization of 0.8. Under these conditions, the contributions of H^+ and OH^- can be ignored because their concentrations are sufficiently negligible with respect to the other charged species.

From Eisenberg plots, which were found to be linear for both the Ca/PMA and Mg/PMA systems at all metal concentrations, the corresponding f_1 and λ_p values have been calculated. The observed linearity illustrates the non-specific nature of the interaction between alkali metal ions and the polymethacrylate anion, also in their competition with both Ca^{2+} and Mg^{2+} for binding by the polyion. This is in agreement with various earlier observations. For example, Rinaudo and Milas [15] have found that the binding of Ca^{2+} to carboxymethylcellulose appeared to be purely electrostatic. As discussed before by De Jong et al. [1], accurate values of $f_{1,0}$ and λ_p are obtained by extrapolation of f_1 to zero R_2 (Figs. 2a and 2b). For the Ca/PMA and Mg/PMA systems, $f_{1,0}$ values were found to be 0.498 ± 0.007 and 0.494 ± 0.004, respectively. λ_p values of 46.0 ± 1.4 and 48.9 ± 0.8 S cm^2 mol^{-1} were obtained for the two independent samples. From the obtained values of f_1 and $f_{1,0}$, together with the value of λ_p for the blank polyelectrolyte

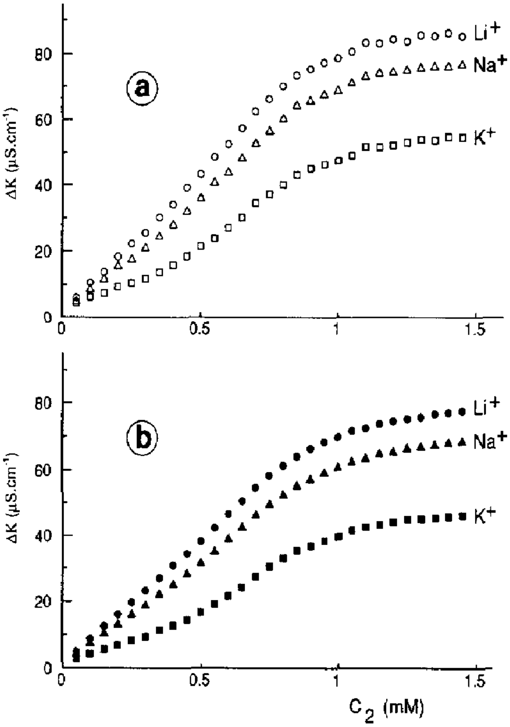

Fig. 1. Conductivity excess curves of three alkali metal polymethacrylate solutions for various concentrations of Ca^{2+} (a) and Mg^{2+} (b); [PMA] = 2.5 m*M*; $\alpha = 0.8$.

solution [1], the fractions of free divalent counterions can be calculated from the conductivity excess. This can easily be done with eq. (2), with an apparently constant λ_p [1] over the considered titration range. Note that the calculated f_2 values are average values for the three alkali metal polymethacrylate solutions.

In Figs. 2(a) and 2(b), the resulting f_1 and f_2 values are plotted as a function of the ratio R_2 for the Ca/PMA and the Mg/PMA systems, respectively. For the PMA polyion, the results obtained with Ca system agree with those of Mg within the limits of experimental error. Satoh et al. [5] have studied the activity coefficients as a function of the divalent cation concentration for sodium poly(styrenesulfonate)/$MgCl_2$ or $CaCl_2$ and sodium poly(L-glutamate)/$MgCl_2$ or $CaCl_2$ for the salt free case. They have also observed the similarity of behavior of the two earth alkali metal cations.

The theoretical f_1 and f_2 values are presented as solid curves in Figs. 2(a) and 2(b). They have been calculated for $c_p = 2$ m*M* and $\xi = 2.29$ [12]. For both systems the theoretical data agree fairly well with the experimental ones. The theoretical $f_{1,0}$ value is fixed by the limiting-law condition in eq. (18). According to eq. (18), only the charge density parameter ξ can account for the observed difference. The difference could be attributed to some uncertainties with respect to (i) the real charge distribution along the polyelectrolyte chain, (ii) the analytical error in α_n and (iii) the value of ξ as taken from the literature [12]. Use of a somewhat smaller value of ξ in the computation, certainly leads to an increased quality of the fit. Figures 2(a) and 2(b) show that a better agreement is obtained between experimental and theoretical f_1 values for $\xi = 2.0$ (see dashed curves). For this ξ value, however, the model overestimates the fractions of free divalent counterions for higher values of R_2. It has to be mentioned that both the interpretation of the experiments and the model rely on the simplifica-

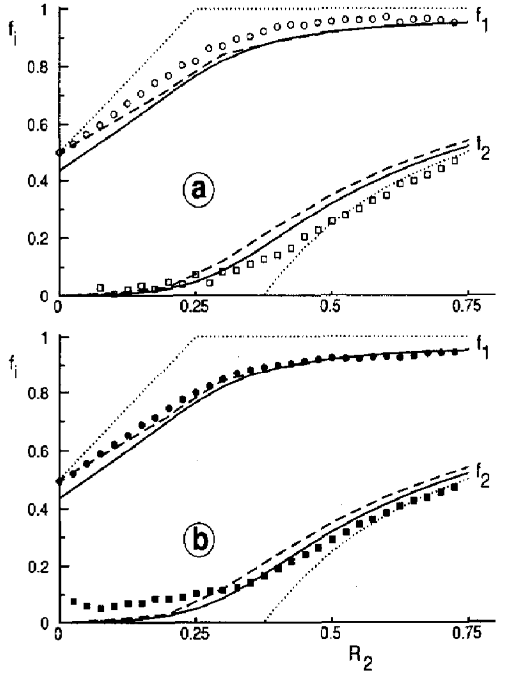

Fig. 2. Experimental (symbols) and theoretical values (solid curves, $\xi = 2.29$; dashed curves, $\xi = 2.0$; dotted curves, complete charge compensation model) of f_1 and f_2 as a function of the ratio R_2 for the Ca/PMA (a) and Mg/PMA (b) systems; [PMA] = 2.5 m*M*; $\alpha = 0.8$. Further explanation in the text.

tion of the two phase model. Some unexpected aspects of the competition between divalent and monovalent counterions could arise from this oversimplification.

In Figs. 2(a) and 2(b), the dotted curves represent the behavior of the fractions of free monovalent and divalent counterions in the case of complete charge compensation, as would be predicted for the salt-free case by Manning's counterion condensation theory [3], for $\xi = 2.0$. The salt concentration of the initially salt-free M^+/PMA solution increases along the titration and affects, therefore, the theoretical pattern of complete charge compensation as plotted in Figs. 2(a) and 2(b). Our analysis, however, refers to the initial section of the titration curves and the resulting f values hold for the limit $c_{\text{salt}} \to 0$. For this limit Manning has shown that the binding of divalent ions approaches the salt-free case of complete charge compensation [3].

The increase of f_1 with increasing R_2 is due to the exchange of condensed monovalent ions for divalent ions. In the initial part up to $R_2 \approx 0.25$, the liberation of monovalent cations is proportional to the increase of added M^{2+}, whereas the added divalent ions are practically quantitatively bound (cf. the prediction according to the case of complete charge compensation, i.e. dotted curves in Figs. 2a and 2b). This is readily shown by considering the charge fractions of bound monovalent and divalent counterions per deprotonated monomer

$$\Theta_i = z_i(1-f_i)c_i/c_p \tag{19}$$

In Figs. 3(a) and 3(b), Θ_1, Θ_2 and $\Theta_{\text{sum}}(=\Theta_1 + \Theta_2)$ are plotted as a function of R_2 for the Ca/PMA and the Mg/PMA systems, respectively. Taking into account a typical experimental error of 0.04, both figures show that under these conditions practically all added divalent cations are quantitatively bound in the range $0 \le R_2 \le 0.25$. For the Zn/PAA system, similar results have been obtained under comparable conditions [1].

Assuming a constant λ_p, the M^+/M^{2+} exchange ratio ν is easily computed using

$$\nu_{1,2} = -\frac{\Delta[(f_{1,0}-f_1)c_1]}{\Delta[(1-f_2)c_2]} = \frac{\Delta f_1 c_1}{\Delta[(1-f_2)c_2]} \tag{20}$$

Up to $R_2 = 0.25$, Figs. 2(a) and 2(b) show that the release of monovalent counterions is linear upon addition of divalent counterions for both systems (with statistics for the Mg/PMA system: $n = 10$, $R^2 = 0.998$, slope $= 1.25 \pm 0.02$). Using eq. (20), a mean exchange ratio ν has been calculated for the range $0 < R_2 \le 0.25$, taking for $(1-f_2)$ an average value of 0.94 ± 0.01 for the Mg/PMA system. Using the same procedure for the Ca/PMA system, the mean exchange ratios $\nu_{1\text{Ca}}$ and $\nu_{1\text{Mg}}$ were found to be 1.39 ± 0.03 and 1.33 ± 0.03, respectively, for the range $0 \le R_2 \le 0.25$. Using $\xi = 2.29$, the mean exchange ratio $\nu_{1,2}$ calculated from the theory is 1.38, which is in remarkable agreement with the experimental data. For the PAANa/Mg^{2+} and Ca^{2+} with $\alpha = 1$, Satoh et al. [8] have estimated exchange ratios in the range 1.5–1.8 from activity coefficient data in the same R_2 range. These results seem to confirm that at lower charge densities a divalent counterion replaces less monovalent counterions

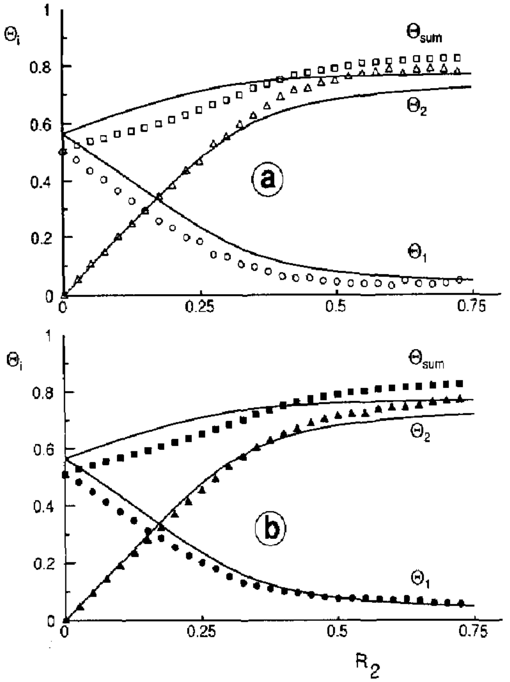

Fig. 3. Experimental (symbols) and theoretical values (solid lines, $\xi = 2.29$) of Θ_1, Θ_2 and Θ_{sum} as a function of the ratio R_2 for the Ca/PMA (a) and Mg/PMA (b) systems; [PMA] = 2.5 mM; $\alpha = 0.8$.

than for higher charge densities. A similar result has been found for DNA [16].

Furthermore, these experimental results show that in different regimes of charge density values and counterion concentrations, both monovalent and divalent counterions are always condensed (provided that $\xi > \xi_{\mathrm{crit}}$, see ref. [2] for further discussion). This feature is not considered in the model of ref. [4]. The point can be further considered by calculating the net effective charge density

$$\xi_{\mathrm{net}} = \xi_{\mathrm{str}}(1 - \Theta_1 - \Theta_2) \tag{21}$$

Due to the release of monovalent counterions and the binding of divalent counterions in a ratio less than 2:1, the net effective charge density will decrease upon addition of divalent ions. According to the limiting law conditions, this will continue until the asymptotic value of one half is reached [13]. This work reveals that some condensation of monovalent counterions still occurs in the range of R_2 up to 0.25, i.e. under conditions where ξ_{net} is below unity.

5. Conclusions

It can be concluded that conductometry is a useful tool in counterion distribution studies of polyelectrolytic systems. For the Ca/alkali metal PMA and Mg/alkali metal PMA systems, the experimentally obtained fractions of free monovalent and divalent counterions are in good agreement with the theoretical values computed according to a new thermodynamic theory recently developed by Paoletti et al. [2]. For $\alpha = 0.8$ and $0 \leq R_2 \leq 0.25$, the mean exchange ratio ν has been found to be 1.33 ± 0.03 and 1.39 ± 0.03 for the Mg/PMA and Ca/PMA systems, respectively, and this compares well with the theoretical value of 1.38. The results seem to support the assumption that under the present conditions the conductometrically obtained distribution parameters f_1 and f_2 approximate the equilibrium fractions of free monovalent and divalent counterions. Apparently, non-equilibrium effects are small.

It may be noted that the small disagreement between experimental data and theoretical calculations ($f_{1,0}$) might be attributed to other phenomena, like polyelectrolyte flexibility and specific affinity for certain counterions, which have not been included in the present model. Further work along these lines is in progress.

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