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Intrinsic binding effects in mixed counterionic polyelectrolyte systems: extension of condensation theory and comparison with voltammetric data

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Abstract

Voltammetric speciation data for the potassium/zinc/polymethacrylate system, recently obtained for various charge densities of the polyelectrolyte (Díaz-Cruz et al., Anal. Chim. Acta, 264 (1992) 163) and for different concentrations of monovalent counterions (van den Hoop and van Leeuwen, Anal. Chim. Acta, 273 (1993) 275), are compared with theoretical predictions computed according to a new thermodynamic model developed by Paoletti et al. (Biophys. Chem., 41 (1991) 73) and recently extended by Benegas and Paoletti (in preparation). The model allows: (i) the simultaneous condensation of both monovalent and divalent counterions and (ii) can account for a certain specific affinity of the polyelectrolyte for one type of the counterion over the other. For various charge densities of the polyelectrolyte, experimentally obtained speciation data for the K/Zn/PMA system agree well with theoretical predictions by considering an extra reduced molar affinity energy of $-4RT$ for the Zn^{2+} polyelectrolyte binding. The agreement between experimental and theoretical values for the distribution of Zn^{2+} ions over the free and bound state becomes less perfect for relatively high concentrations of monovalent counterions.

Keywords: Voltammetry; Polyelectrolyte theory; Mixed-valency counterions system; Intrinsic affinity

1. Introduction

Electrochemical methods such as polarography and voltammetry are widely used for the determination of the distribution of metal ions over different chemical and/or physical–chemical forms in natural water systems. This is largely due to their metal-specificity, their high sensitivity and the allowance of direct speciation. However, the applicability of voltammetry to speciation in rather involved systems such as polyelectrolyte solutions is relatively new [1,2]. In general, voltammetry is a technique that measures the diffusion properties of the electroactive component. One of the complications in the analysis of metal/polyelectrolyte systems in terms of frac-

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tions of free and bound counterions is related to the differences between the diffusion coefficients of the free and bound metal ions. One can overcome this problem by taking into account the overall mean diffusion coefficient ($\bar{D}$) of the complex system [3]. For the case of labile metal/complex systems, analysis of complexation curves, i.e. curves of the voltammetric response versus the concentration of the complexing agent at constant total metal concentration, leads to stability values of the metal/complex involved [2,4]. Once the stability has been obtained, the distribution of metal ions over the free and bound state can be calculated for any ligand concentration. This procedure has been shown to work satisfactorily well for model polyelectrolyte systems such as Zn^{2+}/polyacrylate [5] and Zn^{2+}/polymethacrylate [6,7], and natural polyelectrolyte systems, like Zn^{2+}/humate and Cd^{2+}/humate [7].

The theoretical consideration of an aqueous polyelectrolyte system, consisting of a very dilute solution of a linear polyelectrolyte of known charge density in the presence of variable amounts of counterions of different valencies, has been done within different frameworks, including the solution of the Poisson–Boltzmann equation [8] and Monte Carlo simulations [9]. In this paper we follow the approach of the counterion condensation theory, mainly developed by Manning [10,11], but with the formalism proposed recently by Paoletti et al. [12]. Working along this line, all ionic free energy terms are considered, both of electrostatic and entropic nature. In the present data analysis we found it necessary to include an affinity-free energy term to take into account the preference of the polyelectrolyte for one type of counterion over the other one present in the solution. It will be shown that with the inclusion of this affinity, interaction the theory gives good quantitative agreement with the experimental results, providing a consistent overall description of the phenomena under consideration. In Section 2 a short theoretical outlook of both stripping voltammetry and counterion condensation theory is given. In Section 4 the theory is applied to the analysis of stripping voltammetric speciation data of the Zn^{2+}/polymethacrylate system for different charge densities of the polyelectrolyte and different concentrations of monovalent counterions, which were recently published by Díaz-Cruz et al. [6] and van den Hoop and van Leeuwen [7].

2. Theory

2.1. Counterion condensation in systems with ionic mixtures

For the calculation of fractions of free monovalent and divalent cations, we follow the theoretical approach of Paoletti et al. [12]. Briefly it amounts to splitting the polyelectrolytic ionic contribution, g^{ion}, to the total reduced molar Gibbs free energy of the system into two main contributions:

- a purely electrostatic term, g^{el}, and
- a free energy of mixing of the non-polyionic species, g^{mix}.

$$g^{\text{ion}} = g^{\text{el}} + g^{\text{mix}} \tag{1}$$

The reduced molar Gibbs free energy is defined as:

$$g = \frac{G}{n_{\text{p}} RT} \tag{2}$$

where n_{p} is the number of moles of polyionic charged groups (assumed univalent), i.e. the molar concentration c_{p} times the volume of the solution. Expressions for g^{el} and g^{mix} have been presented previously [12] and are recalled in the Appendix. The reference state is a solution at the same temperature, pressure and in the same solvent, containing the same type and concentration of all ions, but with the fixed ions being mobile. The main assumption of the model is that in the presence of counterions of different valencies all ions may condense, with the total molar fraction of condensed counterions, r, given by:

$$r = r_1 + r_2 \tag{3}$$

where r_1 and r_2 are the fractions of monovalent and divalent counterions condensed per polymeric charge, respectively. We let $r_1 = rx_1$ and $r_2 = rx_2$, where x_i is the mol fraction of counterions i in the condensation volume, so

$$r = r(x_1 + x_2) \tag{4}$$

The fractions of free monovalent and divalent counterions, f_1 and f_2, respectively, can be calculated according to:

$$f_i = \frac{c_i^{\text{tot}} - r_i c_\text{p}}{c_i^{\text{tot}}} \tag{5}$$

where c_i^{tot} denotes the analytical molar concentration of counterions of type i, and c_p is the equivalent volume concentration of deprotonated groups on the polyion. In the case of solutions with monovalent and divalent counterions, the effective charge of each polymeric charged group is reduced due to the condensation of counterions, so:

$$q_{\text{eff}} = q_{\text{str}}(1 - r_1 z_1 - r_2 z_2) = q_{\text{str}}[1 - r(2 - x)] \tag{6}$$

where q_{str} and z_i represent the structural linear charge density and the valency of the counterion i, respectively. For the case where some affinity of the polyion for the divalent counterion exists, we take this interaction into account by considering a reduced free energy term [13]:

$$g^{\text{aff}} = g^\circ \times r_2 \tag{7}$$

so, the total free energy of the system is:

$$g^{\text{t}} = g^{\text{ion}} + g^{\text{aff}} \tag{8}$$

For each type of counterion (in the present case monovalent and divalent), the polyelectrolyte may have some additional binding energy, g^{aff}. However, for monovalent counterions g^{aff} can be taken as 0, based on the results of conductometric experiments that show little or no affinity of monovalent counterions for polymethacrylic acid [14]. Thus, a negative value of g° in Eq. (7) means a relative preference of the polyelectrolyte for the divalent counterion with respect to the monovalent one.

The system is fully defined by the state variables (temperature, pressure, concentrations of polymer and solutes), and characterized by the two independent variables r and x, and by the molar condensation volume, V_p, expressed in litres per mole of fixed charge (see Appendix). The values of r, x and V_p, are determined by the condition that the molar Gibbs free energy be minimized with respect to both x and r [11,12], and therefore we impose:

$$(\partial g^{\text{t}}/\partial r)_x = 0 \tag{9}$$

and

$$(\partial g^{\text{t}}/\partial x)_r = 0 \tag{10}$$

If we further require that Eq. (9) remains finite in the limit of infinite dilution, we obtain the so-called limiting condition for the fraction of condensed counterions [12]:

$$r = \frac{1}{(2-x)}\left(1 - \frac{1}{\xi(2-x)}\right) \tag{11}$$

where ξ is the structural charge density parameter as defined in the Appendix. Simultaneous use of Eqs. (9) and (11) results in an analytical expression for V_p. The value of x is obtained independently from Eq. (10). It can be easily verified that Eq. (11) reduces to the well-known limiting conditions for the two extreme cases of solutions with only monovalent ($x = 1$) and only divalent counterions ($x = 0$) [10,12].

2.2. Voltammetric methodology

The distribution of metal ions over the free and bound states in systems containing macromolecules on the basis of a voltammetric method has been described in detail before by van den Hoop and van Leeuwen [7]. However, for the purpose of the present paper, i.e. a comparison of voltammetric speciation data with theoretical predictions, it is useful to recall the main aspects and assumptions of the voltammetric analysis of metal/polyelectrolyte systems in terms of a stability K. Starting-point in the voltammetric treatment of metal/polyelectrolyte solutions is to consider that the voltammetric response is not only a function of the transport of the electroactive free metal ion (in the present case Zn^{2+}) from the bulk solution to the electrode surface, but that it also depends on the simultaneous diffusion of the electroinactive metal complex. Hence, the association/dissociation reactions of Zn^{2+} with the charged group on the polyelectrolyte (denoted as P) play an important role:

$$\text{Zn}^0 \leftrightarrows \text{Zn}^{2+} + \text{P} \underset{k_\text{a}}{\overset{k_\text{d}}{\leftrightarrows}} \text{ZnP} \tag{12}$$

where k_a and k_d are the rate constants for association and dissociation, respectively. Charges of the polyionic species are omitted for simplicity. The complexation equilibrium in the bulk is expressed by the stability K:

$$K = \frac{c_{\mathrm{ZnP}}}{c_{\mathrm{Zn}} c_{\mathrm{P}}} \tag{13}$$

where the c_{ZnP}, c_{Zn} and c_{P} denote bulk concentrations of the bound metal, the free metal and the ligand, respectively. When a large excess of ligand is present $(c_{\mathrm{P}} \gg c_{\mathrm{Zn}}^{\mathrm{tot}}[= c_{\mathrm{Zn}} + c_{\mathrm{ZnP}}])$ Eq. (13) may be written as follows:

$$K = \frac{r_{\mathrm{Zn}}}{f_{\mathrm{Zn}} c_{\mathrm{Zn}}^{\mathrm{tot}}} \tag{14}$$

The analysis of the voltammetric current runs through [7]:

$$\Phi = \left(\frac{\bar{D}}{D_{\mathrm{Zn}}} \right)^{p} = \left(\frac{1 + \epsilon K c_{\mathrm{p}}}{1 + K c_{\mathrm{p}}} \right)^{p} \tag{15}$$

where Φ is defined as the ratio between the peak current for the complex system and the reference peak current under conditions of no complexation. The power p is a hydrodynamically determined parameter with a value between 1/2 and 2/3 for stripping voltammetries and 1/2 for direct voltammetries and $\bar{D}$ is the mean diffusion coefficient of the Zn/P complex system, given by

$$\bar{D} = D_{\mathrm{Zn}} \frac{c_{\mathrm{Zn}}}{c_{\mathrm{ZnP}} + c_{\mathrm{Zn}}} + D_{\mathrm{ZnP}} \frac{c_{\mathrm{ZnP}}}{c_{\mathrm{ZnP}} + c_{\mathrm{Zn}}} \tag{16}$$

which actually incorporates the speciation over the fractions of free and bound metal. Eqs. (15) and (16) express that by voltammetry one can measure free metal concentrations that are very small compared to those of the bound metal. However, the application of the presented relationship between the voltammetric current and the stability of the complex involved is only allowed if certain conditions are obeyed. The metal/polyelectrolyte system must be voltammetrically labile, i.e., the kinetics of the association/dissociation reactions (12) must be sufficiently fast to maintain equilibrium for any relevant value of space and time [3]. Lability criteria for the dynamic case and for stripping voltammetries have been derived in the literature [3,15,16]. Furthermore, there must be a large excess of complexing agent (in the present case carboxylate groups of the polyacid PMA) over the metal. The reason for this condition is to be sure that the equilibrium ratio $c_{\mathrm{ZnP}}/c_{\mathrm{Zn}}$ is constant over the whole voltammetric diffusion layer. This is necessary to ensure a constant mean diffusion coefficient [see Eq. (16)] from the bulk of the solution to the surface of the electrode.

3. Experimental

The experimental data were taken from the literature [6,7]. For the sake of clarity, we will briefly summarize the main aspects of the experimental approach. The procedure is based on adding ligand (in the present case polymethacrylic acid obtained from BDH) to the solution of the metal [here zinc(II)] and measuring the reoxidation current. The concentration levels were such that the values measured of Φ all refer to excess ligand while the region $K c_{\mathrm{p}} \approx 1$ is sufficiently covered. Under these conditions, the voltammetric response can be analysed according to Eq. (15) with the total metal concentration constant over the whole complexation curve. In order to ensure proper protolytic control, the pH of the metal ion solution was set at the pH of the polymethacrylic acid solution in the presence of $\mathrm{KNO_3}$. In each point of the titration, the pH was measured. Thus, it could be verified that the degree of dissociation (α) is constant during the titration. This justifies the computation of the complex stability K using Eq. (15) as explained before [6]. For fully deprotonated PMA, the structural charge density parameter (ξ, defined in the Appendix as l_{b}/l) is 2.85. For a particular degree of dissociation (α), ξ becomes $\alpha * l_{\mathrm{b}}/l$.

4. Results and discussion

In this section we present theoretical results aimed at the interpretation of experimental stripping voltammetric speciation data obtained for the association of Zn^{2+} ions with polymethacrylic acid (PMA) for various charge densities of the polyelectrolyte [6] and different concentrations of supporting electrolyte [7]. According to the polyelectrolyte model adopted here [12], the fractions of monovalent and divalent counterions condensed on the polyelectrolyte depend on the charge density of the polyelectrolyte ξ and also on the physico-chemical conditions of the solu-

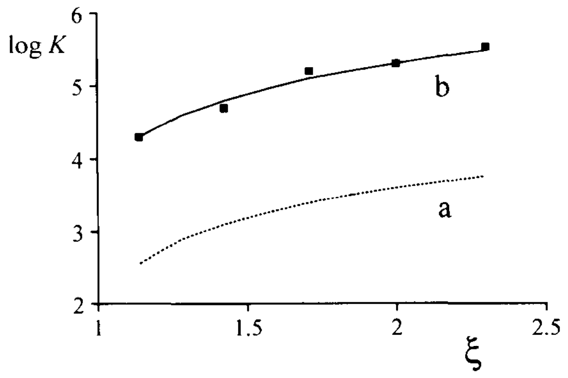

Fig. 1. Experimental (symbols) and theoretical values (solid curve, $g^\circ = -4$; dashed curve $g^\circ = 0$) of the stability K as a function of the charge density ξ. Experimental data are taken from the literature [6] and were obtained for the Zn/PMA system with $c_{Zn} = 10^{-6}$ mol l^{-1} and c_{KNO_3} 0.01 mol l^{-1}.

tion. Therefore we investigate the charge density dependency of K as well as the effect of changing the ionic strength of the solution at constant charge density of the polyelectrolyte.

4.1. Charge density dependency of K

In Fig. 1 the stability K of the Zn/PMA system is presented as a function of the charge density ξ for $c_{Zn} = 10^{-6}$ mol l^{-1} and $c_{KNO_3} = 0.01$ mol l^{-1}. Since PMA undergoes a conformational transition at low values of the degree of ionization, i.e. at low charge densities [17], we will consider in the following discussion only experimental and theoretical results obtained for charge densities larger than 1.15.

The Zn/PMA was found to be voltammetrically labile, and hence, the Φ, c_p curves could be analyzed according to Eq. (15) using $p = 2/3$. The exact value of the power of $(\bar{D}/D_{Zn})$ in Eq. (15) affects log K by only 0.1 units [5], i.e. within the order of the experimental error. The theoretical results are presented as solid curves on the same figure for two values of the intrinsic affinity reduced free energy: $g^\circ = 0$ and $g^\circ = -4$, which represents an extra affinity free energy $-4RT$. The theoretical curves for the stability are calculated using Eq. (14). The values of the fractions of condensed and free Zn^{2+} counterions are computed directly from the calculated r and x values obtained from Eqs. (9) and (10).

It can be seen from Fig. 1 that a qualitative agreement between experimental and theoretical values is obtained assuming no affinity interactions, i.e taking $g^\circ = 0$ (curve a). By assuming a relative affinity of the polyelectrolyte for the divalent counterion with respect to the monovalent one, the calculated curve is shifted upwards. The quality of the agreement becomes excellent for an intrinsic affinity $g^\circ = -4$ (curve b). We note that the interaction of potassium ions with PMA has been found to be of a non-specific nature [14] and hence, in the present case, the relative affinity can be considered as an absolute measure of the intrinsic affinity of PMA for the Zn^{2+} counterion.

An equation analogous to Eq. (8) can be written for the stability K, which reads:

$$\log K^{t} = \log K^{\text{ion}} + \log K^{\text{aff}} \tag{17}$$

where $\log K^{\text{aff}} = \log[\exp - (g^\circ)]$, which in the present case ($g^\circ = -4$) corresponds to about 1.7 units of log K. It is interesting to note that this value of the parameter g° is in reasonable agreement with the value of $\log K^{\text{aff}} = 1.1$, experimentally obtained by Cleven et al. [18] on the basis of a tentative extrapolation procedure.

Finally, it can be seen that although log K increases with the charge density of the polyelectrolyte, the slope $\mathrm{d}\log K/\mathrm{d}\xi$ is decreasing. This behaviour is related to the dependence of the polyelectrolytic free energy with the charge density. This feature already showed up in the change in pK_a in

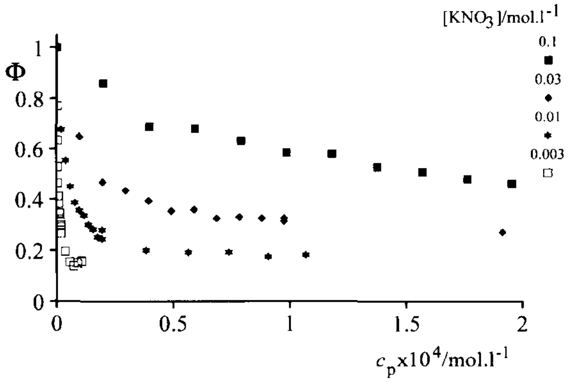

Fig. 2. Stripping voltammetric complexation curves for the KNO_3/Zn^{II}/PMA system for different KNO_3 concentrations. $c_{Zn} = 10^{-7}$ mol l^{-1}; $\xi = 2.3$ [7].

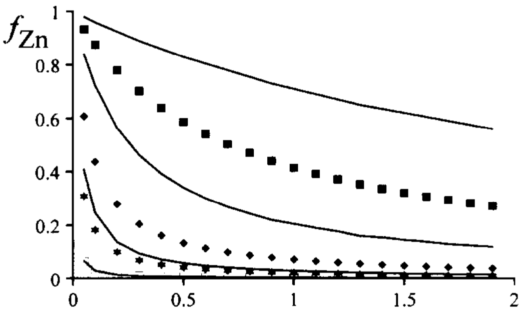

Fig. 3. Fractions free Zn^{2+} ions as a function of the polymethacrylate concentration deduced from stripping voltammetric experiments (symbols) and calculated with theoretical model (curves) for different concentrations of KNO_3. $c_{Zn} = 10^{-7}$ mol l^{-1}; $\xi = 2.3$; $g° = -4$. Symbols as in Fig. 2.

the potentiometric titration of weak polyelectrolytes [19].

4.2. Ionic strength dependency of *K*

A typical set of voltammetric complexation curves is presented in Fig. 2, where the normalized peak current Φ is plotted versus the polymethacrylate concentration c_p for various concentrations of KNO_3 for $\xi = 2.3$ and a total Zn^{2+} concentration of 10^{-7} mol l^{-1} [7]. The polymethacrylate species have diffusion coefficients much lower than D_{Zn}. Hence, Φ decreases as the result of the association of Zn^{2+} with the polyanion and reaches a certain plateau value $(D_{ZnP}/D_{Zn})^p$ with further increase of ligand concentration. Under these experimental conditions the Zn/PMA system was found to be definitely labile on the stripping voltammetric time-scale [7]. Hence, stability values were satisfactorily calculated with Eq. (15) using $p = 2/3$. With the stability K thus derived and making use of Eq. (14), experimental values of the fraction of free Zn^{2+} ions, f_{Zn}, can be calculated. In Fig. 3, the resulting f_{Zn} values are presented as a function of the polymer concentration for different concentrations of KNO_3. Included in Fig. 3 are the theoretical f_2 values calculated with $g° = -4$. There is a good quantitative agreement between the theoretical and experimental values for the curves corresponding to low salt concentrations. For $[KNO_3] = 0.1$ and 0.03 mol l^{-1} the agreement between theoretical and experimental data is less satisfactory. This might be due, among other things, to the fact that the salt concentration is very high. Under these conditions, the activity of the free zinc ions in the bulk of the solution is seriously reduced. Furthermore, since the reciprocal Debye length (κ) increases with increasing salt concentration, κ_i is not much smaller than one, and hence, ligand–ligand interactions may be expected. As an illustration we have finally plotted in Fig. 4 the stability log K versus the log $[KNO_3]$ for the same values of the parameters as in Fig. 3. Again the agreement is better at low 1–1 electrolyte concentrations. The observed difference between theory and experiment at the high salt level deserves further analysis from the theoretical point of view considering factors like bulk activity effects and ligand–ligand interaction (reduced screening), which are not regarded in the present model.

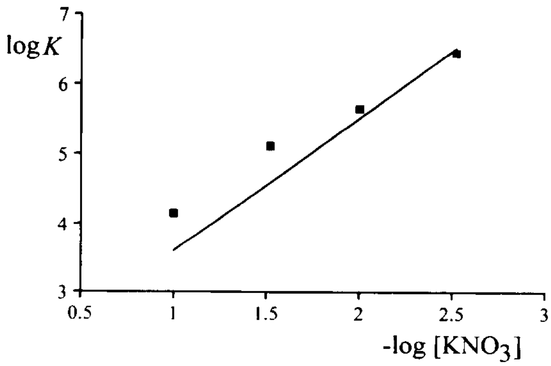

Fig. 4. Experimental (symbols) and theoretical values (solid curve) for the stability K as a function of the concentration of KNO_3 for the system KNO_3/Zn/PMA. $c_{Zn} = 10^{-7}$ mol l^{-1}; $\xi = 2.3$; $g° = -4$.

5. Conclusions

The model correctly describes the main features of the polyelectrolyte–counterion interactions, including the competition of counterions of different valencies for the condensation volume. It has also been shown that in addition to purely electrostatic interactions, an extra affinity of the polyelectrolyte for one of the counterionic species over the other is necessary to obtain a good quantitative agreement between theory and experimental data of the $KNO_3/Zn/PMA$ system. For the different physicochemical conditions of the polyelectrolyte system studied, such as various charge densities, metal-to-ligand ratios and different salt concentrations, certain finite fractions of both monovalent and divalent counterions are always in condensed and free forms. This feature is particularly interesting for polymers with $\xi_{str} < 1$, i.e, for the case where the charge density is too low for classical [10] condensation of monovalent counterions. For the Zn/PMA system, this is the region where conformational changes occur and hence, the association of Zn^{2+} with the polymethacrylate anion becomes very complex. For future comparison in this regime appropriate experimental data are necessary, as well as the extension of the theory to include transition between conformations which might have different affinities for a given counterion.

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Appendix 1

In the presence of salt and under conditions where polyion–polyion interactions is negligible, the electrostatic free energy g^{el} of a polyelectrolytic system is given by the counterion condensation theory [20]:

$$g^{el} = -\xi(q_{eff})^2 \ln(1 - e^{-\kappa l}) \quad (A1)$$

where q_{eff} is the net charge (i.e. site charge minus counter charge) on each ionized site on the polyelectrolyte, κ is the reciprocal Debye length and ξ is the structural charge density parameter defined as $\xi = l_B/l$ with l_B being the Bjerrum length and l represents the spacing between charged sites on the linear polyion. In the case of no condensation, q_{eff} equals the polyionic charge.

For g^{mix} the following contributions of the different non-polyionic species to the change of the entropy of mixing are considered:

$$g^{mix} = (g_1)^{cond} + (g_2)^{cond} + (g_1)^{free} + (g_2)^{free} + g_{coions} + g_{sol} \quad (A2)$$

which according to [12] are written as:

$$(g_1)^{cond} = rx_1 \ln\frac{rx_1}{(1+R_1)V_p c_p} \quad (A3)$$

$$(g_2)^{cond} = rx_2 \ln\frac{rx_2}{R_2 V_p c_p} \quad (A4)$$

$$(g_1)^{free} = (1 + R_1 - rx_1)\ln\frac{1 + R_1 - rx_1}{(1+R_1)(1 - V_p c_p)} \quad (A5)$$

$$(g_2)^{free} = (R_2 - rx_2)\ln\frac{R_2 - rx_2}{R_2(1 - V_p c_p)} \quad (A6)$$

$$g_{coions} = (R_1 + 2R_2)\ln\frac{1}{(1 - V_p c_p)} \quad (A7)$$

$$g_{sol} = r \quad (A8)$$

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 ratio between the amounts of monovalent counterions and charged groups on the polymer. V_p is the molar condensation volume expressed in litres per mole of fixed charge. Finally, Eq. *A*8 takes into account the lowering of the concentration of ions of the solution.

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