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Limiting-laws of polyelectrolyte solutions. Ionic distribution in mixed-valency counterions systems.
I: The model

Sergio Paoletti *, Julio Benegas [1], Attilio Cesàro, Giorgio Manzini
Dipartimento di Biochimica, Biofisica e Chimica delle Macromolecole, Università di Trieste, via A. Valerio 22, I-34127 Trieste (Italy)

Federico Fogolari
SISSA - Scuola Internazionale Superiore di Studi Avanzati, Strada Costiera 11, I-34136 Trieste (Italy)

Vittorio Crescenzi
Dipartimento di Chimica, Università "La Sapienza", Piazzale A. Moro 5, I-00100 Rome (Italy)

Abstract

An extension of the counterion-condensation (CC) theory of linear polyelectrolytes has been developed for the case of a system containing a mixture of counterions of different valency, *i* and *j*. The main assumption in the derivation of the model is that the relative amount of the condensed counterions of the type *i* and *j* is strongly correlated and it is determined by the overall physical bounds of the system. The results predicted by the model are consistent, in the limiting cases of single species component, with those of the original CC theory. The most striking results are obtained for the cases of low charge density and excess of counterion species: in particular, an apparent positive "binding" cooperativity of divalent ions is revealed for small, increasing additions of M^{2+} ions to a solution containing a swamping amount of monovalent salt and a polyelectrolyte of low charge density. Apparent "competitive binding" of mono- and divalent ions derives as a bare consequence of the electrostatic interactions. Theoretical calculations of experimentally accessible quantities, namely single-(counter) ion activity coefficients, confirm the surprising predictions at low charge density, which qualitatively agree with the measured quantities.

Keywords: Counterion condensation theory; Linear polyelectrolytes; Mixed valency counterion systems; Ion activity coefficients

1. Introduction

Within the framework of the counterion-condensation (CC) theory of linear polyelectrolytes, the problem of the description of the system in the case of mixtures of counterions of different valency was already tackled. Both approximate [1] and more exact [2–5] expressions have been reported, and comparison with experimental results was performed [6–9]. Still, it does not appear useless to reconsider the problem and look for new formalisms, especially if aiming at avoiding limited experimental conditions (e.g. excess of one of the counterion species, high ionic strength, etc.).

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* To whom correspondence should be addressed.

[1] And International Center for Theoretical Physics, ICTP, Trieste, Italy. On leave from: Escuela de Fisica, Universidad Nacional de San Luis, 5700 San Luis, Argentina.

The scope of this paper is to derive the model and to discuss its main features and implications; we defer a detailed comparison with experimental data to a forthcoming paper.

The procedure which will be followed hereafter is to write suitable expressions for the different terms contributing to the (excess) free energy of a 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 valency.

2. Theory

2.1 The model

The real polyelectrolyte chain is idealized by a linear uniform array of charges (uniform charge density), 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 (in Å): the ensuing dimensionless charge density parameter ξ is defined as $\xi = l_B/b$ where l_B is the Bjerrum length (in Å).

For simplicity, two types of counterions, i and j with valency z_i and z_j, respectively, will be considered, taking $z_i = 1$ with no loss of generality. Coions stemming from added simple electrolytes may be present: for simplicity, they will be assumed to be the same for both types of added simple salts.

The treatment of the so-called "chemical model", as firstly developed by G.S. Manning [10], will be followed, much in the same way as recently reported, e.g., for the derivation of the $\Delta pK_a(\alpha)$ of linear weak polyacids [11]. Briefly, it amounts to factorize the total reduced molar (rm) excess free energy of polyelectrolytic nature, g^{ion}, into two main contributions: (1) a purely electrostatic term, g^{el}, and (2) a rm-free energy of mixing of mobile species, g^{mix}.

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

The reference state is provided by a solution (at the same temperature, pressure and in the same solvent) containing the same type and concentration of charges of all kinds including those fixed on the polyelectrolyte, where the latter, however, are assumed to be simple mobile ions instead ("iso-ionic strength condition"). The expression for g^{el} is the "classical" one given by the CC theory:

$$g^{\mathrm{el}} = -\xi q_{\mathrm{eff}}^2 \ln(1 - \exp(-Kb)) \tag{2}$$

where q_{eff} is the net, "effective" charge on each ionized site on the polylectrolyte and K is the reciprocal of the Debye length. In the case of no condensation,

$$q_{\mathrm{eff}} = q_{\mathrm{struct}} \tag{3}$$

q_{struct} is the value of the fixed charge on the polyion: in what follows q_{struct} is assumed unity. In the presence of condensation in systems containing counterions of only one valency, q_{eff} is given by:

$$q_{\mathrm{eff}} = q_{\mathrm{struct}}(1 - rz_i) \tag{4}$$

where r is the (molar) fraction of condensed counterions of valency z_i, which will effectively shield the fraction rz_i of fixed charge and whose numerical value stems from the condition of stability of the system at infinite dilution (limiting law condition [12]:

$$r = z_i^{-1}(1 - 1/z_i\xi) \tag{5}$$

3. The new approach

The new derivation starts by assuming that in the presence of counterions of mixed valency the total fraction of condensed counterions, r, is given by:

$$r = r_i + r_j = r(x_i + x_j) \tag{6}$$

where:

$$x_i = \frac{[\mathrm{Me_i}]_{\mathrm{cond}}}{[\mathrm{M_i}]_{\mathrm{cond}} + [\mathrm{M_j}]_{\mathrm{cond}}} \tag{7}$$

and

$$x_j = 1 - x_i \tag{8}$$

Equation (4) will take the form:

$$q_{\mathrm{eff}} = q_{\mathrm{struct}}(1 - r_i z_i - r_j z_j) \tag{9}$$

For the commonly encountered case $z_i = |q_{\text{struct}}| = 1$ and $z_j = 2$, and making use of eqs. (6) and (8) one has:

$$\begin{aligned} q_{\text{eff}} &= 1 - r(x_1 + 2(1 - x_1)) \\ &= 1 - r(2 - x_1) \end{aligned} \tag{10}$$

In general, the final form of g^{el} will then be:

$$\begin{aligned} g^{\text{el}} = & -\xi\big(1 - r\big(z_j - x_i(z_j - z_i)\big)\big)^2 \\ & \times \ln(1 - \exp(-Kb)) \end{aligned} \tag{11}$$

For g^{mix} the contributions of the different mobile species to the change of the entropy of mixing will be considered:

$$\begin{aligned} g^{\text{mix}} = & \, g_i^{\text{cond}} + g_j^{\text{cond}} + g_i^{\text{free}} + g_j^{\text{free}} \\ & + g_{\text{coions}} + g_{\text{solv}} \end{aligned} \tag{12}$$

The following relations will hold:

$$g_i^{\text{cond}} = rx_i \ln\big(rx_i/(1 + R_i)V_pC_p\big) \tag{13}$$

$$g_j^{\text{cond}} = r(1 - x_i) \ln\big(r(1 - x_i)/R_jV_pC_p\big) \tag{14}$$

$$\begin{aligned} g_i^{\text{free}} = & (1 + R_i - rx_i) \ln\big((1 + R_i - rx_i) \\ & /\big((1 + R_i)(1 - V_pC_p)\big)\big) \end{aligned} \tag{15}$$

$$\begin{aligned} g_j^{\text{free}} = & \big(R_j - r(1 - x_i)\big) \ln\big(\big(R_j - r(1 - x_i)\big) \\ & /\big(R_j(1 - V_pC_p)\big)\big) \end{aligned} \tag{16}$$

$$g_{\text{coions}} = \big(R_i + z_jR_j\big) \ln\big(1/(1 - V_pC_p)\big) \tag{17}$$

$$g_{\text{solv}} = r_i + r_j = r \tag{18}$$

where R_i and R_j stand for the molar ratios between the concentrations of the ith (e.g. uni-univalent) and the jth (e.g. bi-univalent salt), respectively, and that of the polymer, C_p; V_p is the molar volume of the condensed phase, expressed in liters per mole of fixed charge.

The system is therefore characterized by the usual variables (temperature, pressure, dielectric constant of the solvent, concentration of macroscopic solutes), the two independent variables r and x_i, and V_p, which is a physical parameter of the system whose equilibrium value is not numerically known as yet. For the determination of r and x_i it was found convenient to resort to the free energy minimization procedure following the original treatment of Manning [10]; according to such established procedure, the r- and the x_i-derivatives of V_p and of the dielectric constant will be neglected, and the minimization conditions will read:

$$\delta g^{\text{ion}}/\delta r = 0 \tag{19}$$

and

$$\delta g^{\text{ion}}/\delta x_i = 0 \tag{20}$$

The following expression derives from eqs. (11)–(18) by performing the operation of eq. (19):

$$\begin{aligned} & 2\xi\big(1 - r\big(z_j - x_i(z_j - z_i)\big)\big)\big(z_j - x_i(z_j - z_i)\big) \\ & \quad \ln(1 - \exp(-Kb)) \\ & \qquad + \Big[\xi\big(1 - r\big(z_j - x_i(z_j - z_i)\big)\big)^2 \\ & \quad \times \big(x_i\big(z_i^2 - z_j^2\big) + z_j^2\big)Kb\Big] \\ & \qquad /[2DEN(\exp(Kb) - 1)] \\ & \quad + x_i \ln\big(\big[x_ir(1 - V_pC_p)\big]/\big[(R_i + 1 - rx_i)V_pC_p\big]\big) \\ & \quad + (1 - x_i) \ln\big(\big[(1 - x_i) \\ & \quad \times r(1 - V_pC_p)\big]/\big[\big(R_j - r(1 - x_i)V_pC_p\big)\big]\big) \\ & \qquad + 1 = 0 \end{aligned} \tag{21}$$

where

$$\begin{aligned} DEN = & 1 + R_i\big(z_i^2 + z_i\big) + R_j\big(z_j^2 + z_j\big) \\ & - r\big(x_i\big(z_i^2 - z_j^2\big) + z_j^2\big) \end{aligned}$$

upon linearization of the exponential for the condition $Kb \ll 1$, eq. (21) can be rearranged into the form:

$$\begin{aligned} & 2\xi\big(1 - r\big(\big(z_j - x_i(z_j - z_i)\big)\big)\big) \\ & \quad \times \big(z_j - (z_j - z_i)x_i\big) \ln(Kb) \\ & \quad + \Big[\xi\big(1 - r\big(z_j - x_i(z_j - z_i)\big)\big)^2 \\ & \quad \times \big(x_iz_i + z_j^2(1 - x_i)\big)\Big]/[2DEN] \\ & \quad + x_i \ln\big(\big[x_ir(1 - V_pC_p)\big] \\ & \quad /\big[(R_i + 1 - x_i)V_pC_p)\big]\big) \\ & \quad + (1 - x_i) \ln\big(\big[(1 - x_i)r(1 - V_pC_p)\big] \\ & \quad /\big[(R_i + 1 - x_i)V_pC_p\big]\big) + 1 = 0 \end{aligned} \tag{22}$$

Exploring the condition of infinite dilution, much in the same way as in the original "limiting law" treatment [12], it is immediately revealed that the system will be physically unstable for all r and x_i values not obeying the following condition, necessary to avoid divergence of the ratio of C_p-containing terms for C_p approaching zero:

$$\xi(1 - rx_i(z_j - (z_j - z_i))(z_i x_i + z_j(1 - x_i))) = 1 \tag{23}$$

Equation (23) implies that, at equilibrium, for the limiting conditions:

$$r = \frac{1}{(z_i x_i + z_j(1 - x_i))}\left[1 - \frac{1}{\xi(z_i x_i + z_j(1 - x_i))}\right] \tag{24}$$

It can be easily verified that eq. (24) reduces to eq. (5) for the two extreme cases of purely monovalent ($x_i = 1$) and purely divalent counterions ($x_j = 1$). Similarly, eq. (20) leads to:

$$\begin{aligned}&-2\xi(1 - r(z_j - x_i(z_j - z_i)))\\ &\quad\times (z_j - z_i)\ln(1 - \exp(-Kb))\\ &\quad+ [\xi(1 - r(z_j - x_i(z_j - z_i)))^2\\ &\quad\times Kb(z_i^2 - z_j^2)]/[2\cdot(\exp(Kb) - 1)DEN]\\ &\quad+ \ln([x_i(R_j - r(1 - x_i))]\\ &\quad/[(1 - x_i)(R_i + 1 - rx_i)]) = 0\end{aligned} \tag{25}$$

The system at equilibrium is then uniquely determined, regarding the two variables r and x_i, by the simultaneous solution of the transcendental eq. (25) and the linear eq. (24). Once the values of r and x_i (which, in general, are *not* functionally dependent on V_p) have been calculated, the equilibrium value of the parameter V_p can be determined from the numerical solution of eq. (22). Before proceeding further on commenting the results, it seems convenient to present some remarks on the procedure followed hitherto:

(i) the *total* fraction of condensed counterions *and* the molar fraction of *one* of the two species have been treated as the independent "condensation" variables;

(ii) in general, the (molar) volume of the condensed phase, V_p, is *not* functionally dependent on the independent variables of the system. Only the *equilibrium value* of V_p turns out to be dependent on the concentrations of mobile ions;

(iii) *negligible but non-zero* values of x_i are found for ϵ values lower than the critical value $\xi_{crit} = 1/z_i$ (e.g. $x_1 \neq 0$ for $\xi \leq 1$). Formally, this stems from the requirement of non-divergence of the entropy of mixing of *all* counterions in relation to a condensation volume common to *all* such species;

(iv) although conveniently obtained at infinite dilution, the solutions given by eqs. (25) and (26) are assumed to be valid at *finite* values of C_p by the same token as originally reported for the "single species" case [10]. Strictly confining to the $C_p \to 0$ case, only the trivial condition of convergence: $x_i = 0$ would hold, being $i < j$.

4. Results and discussion

For practical reasons, the more frequently encountered case of a mixture of mono- and divalent counterions (i.e. $i \equiv 1$ and $j \equiv 2$; $z_i = 1$ and $z_j = 2$) will be considered in the following calculations.

The dependence of r, r_1 and r_2 on x_1 is reported in Fig. 1 for $\xi = 1.5$. The plot, which is the graphical representation of eq. (24), is independent of the composition variables C_p, R_i, R_j, etc. Clearly non-linear relations hold among those

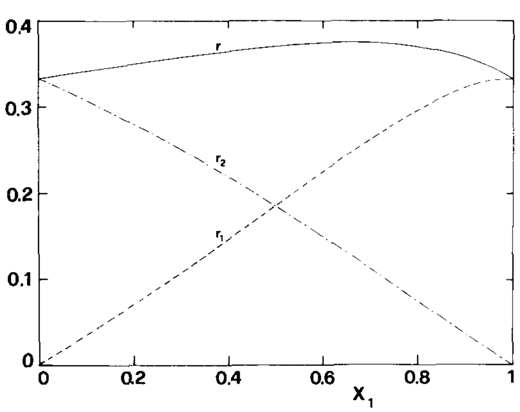

Fig. 1. Dependence of r (————), r_1 (— — —) and r_2 (· – · – ·) on x_1 for $\xi = 1.5$, according to eq. (24).

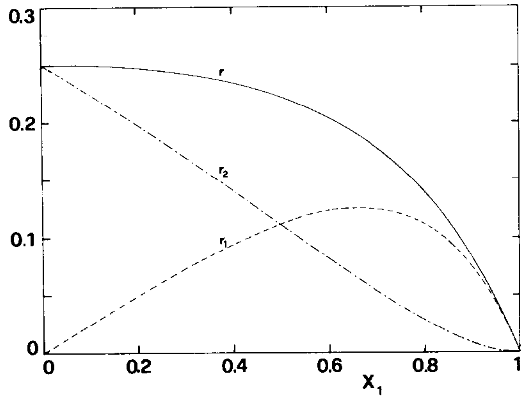

Fig. 2. Dependence of r (———), r_1 (— — —) and r_2 (–·–) on x_1 for $\xi = 1$, according to eq. (24).

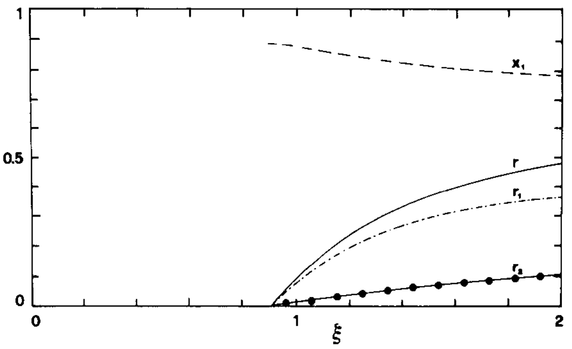

Fig. 3. Dependence of x_1 (— — —), r (———), r_1 (–·–) and r_2 (●———●) on ξ for $C_p = 0.0001$ M, $R_1 = 100$ and $R_2 = 1$.

quantities, which render non-obvious any prediction. Such a behavior is even more clearly shown by the curves of Fig. 2 which display r, r_1, r_2 as a function of x_1, for $\xi = 1$. The last case reveals a striking behaviour: the fraction of condensed monovalent counterions, r_1, attains the value of zero as predicted by the "simple" CC theory only for the limiting condition of the "one-type-of-counterion" case, i.e. $x_1 = 1$ (and $R_2 = 0$, "pure monovalent"), and for $x_1 = 0$ ("pure divalent"). For all finite values of R_2 the value of r_1 is non-zero, indicating that the condensation of divalent ions, which is required anyway by the CC theory for $\xi > 0.5$, also "induces" the condensation of monovalent ions. This surprising result, which has already been addressed in the preceding point (iii) of Section 3, is illustrated also by the plots given in Figs. 3 and 4, showing the dependence on ξ of r, r_1, r_2 and x_1 for the experimentally interesting cases of excess monovalent salt, and equal concentrations of mono- and divalent salts, respectively. The plots for the extreme case of excess divalent counterions (not shown) reduce to those predicted by the original CC theory, under the same assumptions, inasmuch as all condensed counterions are divalent.

Generally, the functional dependence of r, r_1, and r_2 on ξ will in turn depend on the complicated interplay of C_p, R_1, and R_2 values given by eqs. (24) and (25). However, the most interesting feature of the model is that there is the presence of a unique value of ξ, ξ_{crit}, marking the onset of the condensation of *all* the counterions. The numerical value of ξ_{crit} does, in turn, depend on the chemical composition of the system (i.e. C_p, R_1, R_2), varying continuously from $\xi = 1$ for the "pure monovalent" case to $\xi = 0.5$ for the "pure divalent" system.

The plot of Fig. 5 helps to visualize the interesting effect of the "induced condensation" of monovalent ions by the presence of divalent ions (i.e. $R_2 > 0$). As can be seen r_2 always increases with R_2: the increase is monotonous, reaching the limiting value $r_2 = r = \frac{1}{2}(1 - (2\xi)^{-1})$ for $r_2 \to \infty$. The behavior of r_1 is by far more exciting. For all non-zero values of R_2, r_1 assumes non-zero values, reducing to $r_1 \to 0$ only for $R_2 \to \infty$. A sharp increase with a maximum is shown by $r_1(R_2)$ for small values of R_2, followed by a monotonous decrease, which may be more readily understood on an intuitive basis. For the given conditions and for the sample case $R_2 = 0.5$ (i.e. R_2 much higher

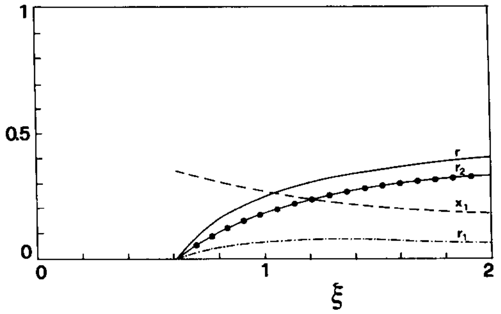

Fig. 4. Dependence of x_1 (— — —), r (———), r_1 (–·–) and r_2 (●———●) on ξ for $C_p = 0.0001$ M and $R_1 = R_2 = 10$.

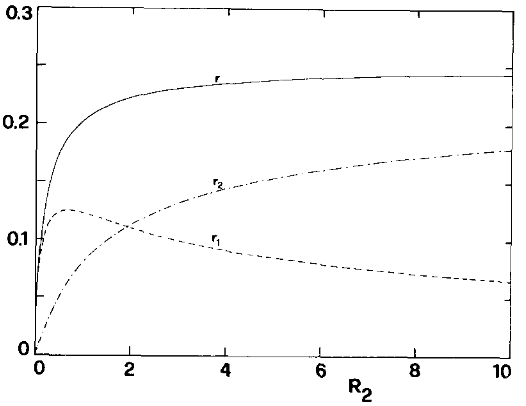

Fig. 5. Dependence of r (———), r_1 (— — —) and r_2 (–·–) on R_2 for $\xi = 1$, $C_p = 0.001$ M and $R_1 = 10$.

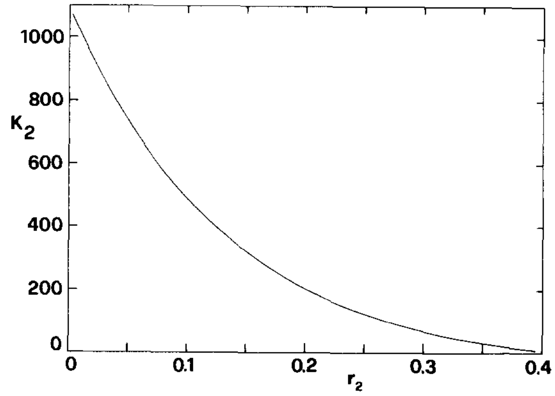

Fig. 6. Scatchard plot ($K_2 = r_2/(R_2 - r_2)C_p$ vs. r_2) for $\xi = 4.2$, $C_p = 0.001$ M and $R_1 = 50$.

than the r_2 value predicted by Manning's limiting law, $r_2 = 0.25$), the model predicts that the r_2 fraction is as low as 0.05, whereas r_1 is 0.124. Therefore, monovalent counterions not only do condense for $\xi = 1$, but, for this particular case, they account for more than 70% of the total number of condensed ions! (Similar behaviour is found for ϵ values ranging from 0.5 to 1).

Concepts like "competition" between i-valent and j-valent ions, which are widely spread in the scientific literature, may conveniently be addressed by considering the relative extent of "binding" (i.e. condensation) of the species for given boundary conditions. The value of the fraction of condensed divalent ions, r_2, has been the master variable in the Scatchard-plot which has been calculated and reported in Figs. 6 to 9 for mono-/divalent mixtures and for different experimental conditions. In the plots, the ordinate is $K_2 (K_2 = r_2/((R_2 - r_2)C_p))$ and the abscissa is r_2. For $\xi = 4.2$, i.e. for the charge density of the B-helix of DNA, Figure 6 shows that for low r_2 values the affinity of the chain for a divalent ion is rather high, but it rapidly decreases upon increasing the amount of bound ions. Such a behaviour could be interpreted as a "negative cooperativity" or "anti-cooperativity" but it is nevertheless the simple outcome of the interplay of electrostatic interactions between ions of different valency. Similarly (and still for $\xi = 4.2$), in Fig. 7 the higher level of binding of divalent ions in the presence of a lower concentration of the monovalent ones shows that interionic competition has to appear in polyelectrolyte systems simply as a result of the role of the entropy of mixing without the need to invoke any "specific" interaction. The results of Fig. 8, obtained for $\xi = 2$, confirm the above mentioned trend, but with a smaller effect due to the reduced electrostatic interaction. Even lower binding levels are reported in Fig. 9 for $\xi = 1$; in this case, however, a new effect comes into play, that is: a marked *positive* cooperativity is shown at low binding levels, which was totally undetectable in the curves calculated for higher values of the linear charge density. This result is clearly much more striking than the former ones: no *a priori* argument might have suggested that, for small values of ξ and low binding levels, the polymer affinity for the more charged ions would be rather

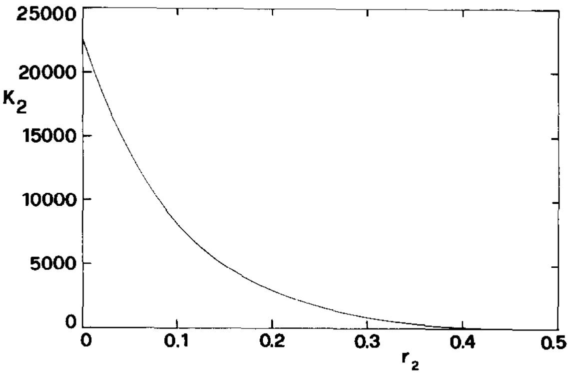

Fig. 7. Scatchard plot ($K_2 = r_2/(R_2 - r_2)C_p$ vs. r_2) for $\xi = 4.2$, $C_p = 0.001$ M and $R_1 = 10$.

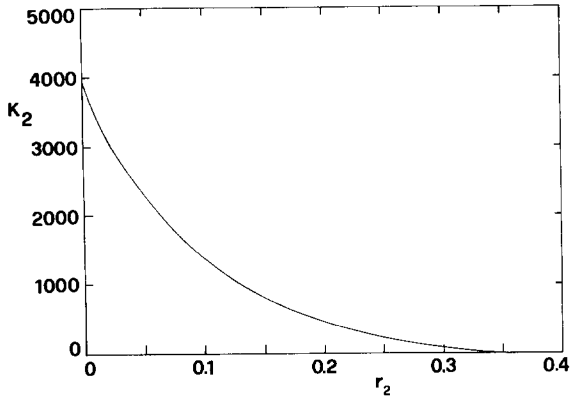

Fig. 8. Scatchard plot ($K_2 = r_2/(R_2 - r_2)C_p$) vs. r_2) for $\xi = 2$, $C_p = 0.001$ M and $R_1 = 10$.

low and that further binding would increase such an "intrinsic" affinity in a rather marked (positive) cooperative way.

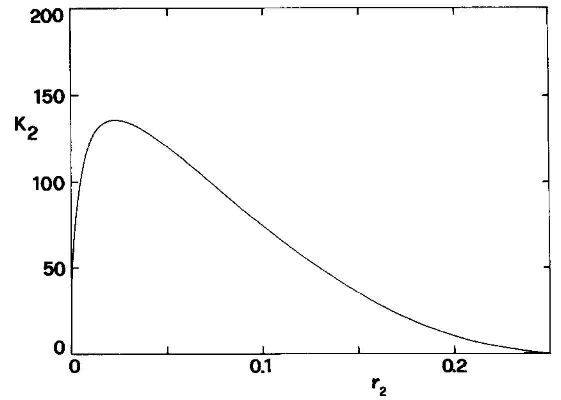

Fig. 9. Scatchard plot ($K_2 = r_2/(R_2 - r_2)$ C_p vs. r_2) for $\xi = 1$, $C_p = 0.001$ M and $R_1 = 10$.

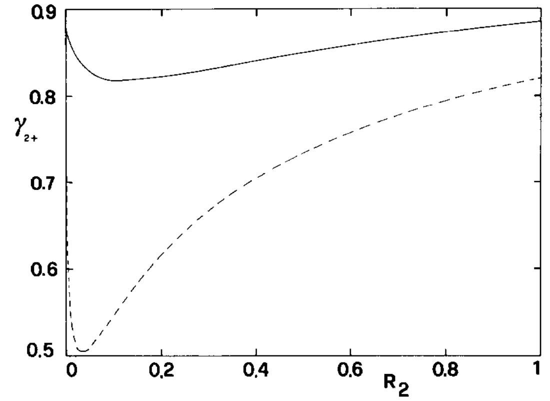

Fig. 10. Dependence of the activity coefficient of divalent counterions (eq. 25]) on R_2 for $\xi = 1$. $C_p = 0.001$ M, $R_1 = 10$ (upper curve) and $C_p = 0.0001$ M, $R_1 = 10$ (lower curve).

The apparent oddity of the previous result obviously makes it even more compelling to resort to the calculation of experimental quantities to test the theoretical predictions. An extensive comparison between the prediction of the present approach and the experimental data is beyond the scope of this paper; still, to derive some indication from the experimental literature was necessary to assess the general trend of the theoretical predictions. It was already known to the authors for some years that careful determinations of the single-ion activity coefficient of Cu(II) ions ($\gamma_{Cu^{2+}}$) in the presence of different polycarboxylates in various conditions all have shown the presence of a behavior of $\gamma_{Cu^{2+}}$ strongly reminiscent of the positive cooperativity of Fig. 8 [13]. This has prompted us to derive the proper expression for γ_j from the free energy expressions of eqs. (11) and (12):

$$\ln \gamma_j = -\left[\xi\left(1 - r\left(z_j - x_1\left(z_j - z_i\right)\right)\right)^2 \times Kbz_j^2\right] / \left[2(\exp(Kb) - 1)DEN\right] + \ln\left(\left[R_j - r(1 - x_i)\right] / \left[R_j(1 - V_pC_p)\right]\right) \qquad (26)$$

The calculated curves of γ_2 for given system conditions are reported in Fig. 10. Surprisingly, the "positive cooperativity" behavior of the Scatchard-plot of Fig. 8 has found an exact counterpart in the behavior of $\gamma_2(R_2)$. Changes in the experimental conditions (e.g. polymer concentration, ionic strength, etc.) qualitatively affect the calculated curves in the same way as the experimental ones [13].

5. Conclusion

The present, novel approach to the problem of the distribution of counterions in mixed-valency systems seems to yield predictions in agreement both with experimental findings and with reasonable expectations about polyelectrolytic behavior. However, a totally new outcome of the theory is reported for conditions which are often met in practical cases, i.e. excess monovalent salt and low values of the linear charge density. It has to be recalled that several biologically relevant polyelectrolytes (in particular, ionic polysaccharides) show ξ values ranging from about 0.5 to about 2, which is the interval where the intriguing "cooperative" and "competitive" behavior appears in its most pronounced form. If they were proved to be realistic, the present findings could certainly have profound bearings on some currently established ideas on small ion – polyelectrolyte interactions. For this reason, extensive comparison with experimental data, especially if of very different nature, is mandatory for a sound assessment of the model and prior to further developments. Work with this scope is in progress.

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Notation

b	average distance between the projections of the loci of charge onto the polyelectrolyte axis, Å
C_p	equivalent polymer concentration (mol fixed charge/L), M
C_i	molar concentration of counterion of valency i, M
C_j	molar concentration of (multivalent) counterion of valency j, M
γ_i	single-ion activity coefficient of ion species i
γ_j	single-ion activity coefficient of ion species j
ξ	dimensionless linear charge density parameter $\xi = l_B/b$
g	dimensionless reduced molar (ꜰm) free energy: $g = G/n_p RT$
K^{-1}	Debye length: $K^2 = 8\pi l_B \mu$, Å
l_B	Bjerrum length: $l_B = e^2/Dk_B T$; e is the value of the elementary charge, iD is that of the dielectric costant of the solvent, k_B is Boltzmann's constant; for water at 298 K, $l_B = 7.135$ Å
$[M_{i,j}]_{\text{cond}}$	molar concentration of condensed counterions of species i or j, M
μ	ionic strength: $\mu = \frac{1}{2}\Sigma_1 C_1 z_1^2$, M
r	(molar) fraction of total number of condensed counterions per fixed charge
R	gas constant, J/mol K
R_i	molar ratio of the total concentration of species i to the polymer concentration
R_j	molar ratio of the total concentration of species j to the polymer concentration
T	absolute temperature, K
V_p	molar volume of the condensed phase (L/mol fixed charge), M^{-1}
x_i	molar fraction of condensed counterions of species i
z_i	valency of counterions of species i; in the paper: $z_i \equiv 1$
z_j	valency of (multivalent) counterion of species j
z_1	valency of ionic species 1

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