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LIMITING LAWS AND COUNTERION CONDENSATION IN POLYELECTROLYTE SOLUTIONS. IV. THE APPROACH TO THE LIMIT AND THE EXTRAORDINARY STABILITY OF THE CHARGE FRACTION

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The limiting laws for polyelectrolyte solutions developed in previous papers of this series have been amply confirmed by measurement. A surprising result of the accumulated data is that the limiting polyelectrolyte charge fraction (fraction of fixed charges uncompensated by condensed counterions in the limit of zero concentration), persists up to concentrations of 0.1 M or even higher. Here the theory is extended in a simple manner to finite concentrations, and the stability of the charge fraction is found to be firmly based on consequences of the long-range polyelectrolyte field. The associated counterions are assumed to translate freely in a region centered on the contour axis of the polyion. The numerical value of the free volume is determined self-consistently from the axial charge density of the polyelectrolyte and is used as the general framework within which specific binding effects are treated.

1. Introduction

Modern polyelectrolyte theory [1–6] rests on the concept of counterion condensation, which affirms the thermodynamic instability of reduced linear charge densities ξ greater than a critical value

$$\xi_{\text{crit}} = |z|^{-1}, \tag{1}$$

where z is the valence of the counterions. The reduced density ξ is defined as

$$\xi = b_B/b, \tag{2}$$

where b_B is the Bjerrum length $q^2/\epsilon kT$, with q the protonic charge and ϵ the dielectric constant, and b is the average polyelectrolyte charge spacing projected onto the contour axis. The instability is resolved by association of counterions with the polyelectrolyte chain to exactly that extent which reduces the net value of ξ to the critical value $|z|^{-1}$. Therefore, for the class of polyelectrolytes (in practice, nearly all) structurally characterized by charge densities in the range $\xi > |z|^{-1}$, the effective charge density including associated counterions is an invariant. (The situation is more complicated if the counterions are a mixture of species with different valences [3,7,8].

Oosawa [3] has aptly compared the associated counterions to a condensed phase in which the fixed charges on the polymer chain provide the cohesive forces. If an increase in the amount of associated counterions (condensed phase) is effected by an increase in the number of fixed charges on each chain (that is, by an increase of the polyelectrolyte structural charge density), then the number of free counterions (vapor pressure) remains constant. There is therefore, to a limited extent, a nice analogy to a condensed phase in equilibrium with its vapor. Unlike an ordinary liquid–vapor or solid–vapor equilibrium, however, the complex formed by the polymer chain and its associated counterions interacts at long range with the free counterions, since the charge density of the complex is not zero, but rather equal to ξ_{crit}.

Insofar as the theory has previously been developed, the instability of reduced linear charge densities greater than $|z|^{-1}$ is of restricted nature. If the density is carried by a continuous line charge in the presence of point counterions, the instability exists at all concentrations. If, however, the polyelectrolyte chain and counterions are realistically endowed with finite dimensions (short-range repulsive cores), then the instability exists only in the limit of zero concentration [2,4–6]. The experimental status of the polyelectrolyte charge fraction, by contrast, suggests a much deeper aspect to the instability. The charge fraction is defined as the fraction of the structural polyelectrolyte charge uncompensated by associated counterions. Being equal in general to the ratio of the net value of ξ to its structural value, the theoretically predicted result for the charge fraction is therefore $|z|^{-1}\xi^{-1}$. It is an experimental fact not only that the charge fraction is equal to $|z|^{-1}\xi^{-1}$ at low ionic strength, but also that the same value persists at very *high* concentration, possibly as large as 1 M in some cases. A review of the pertinent data is given in appendix A, and it is noted there that specific effects (short-range stabilizing forces) cannot be the dominant cause of this phenomenon, since the same charge fraction is found for all polyelectrolytes studied, including those for which specific effects are known to be small.

It is proposed here to extend the theory by analyzing a self-consistent model that allows calculation of the charge fraction as a function of ionic strength. Only long-range electrostatic forces are included and are found sufficient to explain the extraordinary stability of the charge fraction against wide variations of ionic strength.

2. Theory

Consider a linear array of fixed monovalent charges $\pm q$ with spacing b together with an associated fraction r of counterions, so that the array is effectively composed of charges of magnitude $(1-r)q$ with spacing b. The charge fraction is $1-r$. In the presence of excess simple salt the Debye–Hückel approximation for the free energy of formation of this array, in units of n_pRT, where n_p is the number of moles of fixed charges (designated by n_e in previous articles), is [9]

$$\bar{g}_{el} = -(1-r)^2\xi\ln(1-e^{-\kappa_s b}), \tag{3}$$

where κ_s is the Debye screening parameter in the simple salt solution with no polyelectrolyte. Bailey [5] has concluded that for charge fractions in the neighborhood of those anticipated, namely $|z|^{-1}\xi^{-1}$, the Debye–Hückel approximation (sum of Mayer cycle diagrams) is highly accurate. The scheme is now to enumerate all other contributions to the free energy of the solution, evaluate them as functions of r, and then find the value of r that minimizes the free energy.

Let G_u be the contribution to the free energy arising from the mixing of unassociated counterions. Then

$$G_u \doteq RT[\nu n_s + (1-r)|z|^{-1}n_p] \times \ln\{10^{-3}\gamma[\nu c_s + (1-r)|z|^{-1}c_p]\}, \tag{4}$$

where n_s is the number of moles of salt, ν the number of moles of counterion in each mole of salt, n_p the number of moles of fixed charges and c_s and c_p the corresponding molarities. The argument of the logarithm is the activity of unassociated counterions in mole cm^{-3}; the quantity $(1-r)|z|^{-1}c_p$ is the molarity of unassociated counterions originating from the polyelectrolyte salt, while νc_s is the molarity of those originating from the simple salt, and γ is the activity coefficient of unassociated counterions. If this expression is divided by n_pRT to obtain $\bar{g}_u$ and then expanded with neglect of terms higher-order in c_p/c_s, the result is

$$\bar{g}_u = [\nu c_s/c_p + (1-r)|z|^{-1}]\ln(10^{-3}\gamma_s\nu c_s) + (1-r)|z|^{-1} - \tfrac{1}{2}(1-r)^2\xi\nu'(\nu+\nu')^{-1}, \tag{5}$$

where ν' is the number of moles of coion per mole of simple salt and γ_s is the activity coefficient of the counterion in the salt solution if polyelectrolyte is absent. The details leading to eq. (5) are given in appendix B; proper treatment of the activity coefficient is required.

Let the contribution to the free energy from mixing of the coions, all of which are unassociated, be designated by G'_u. Then

$$G'_u = RT\nu' n_s\ln(10^{-3}\gamma'\nu' c_s), \tag{6}$$

where the symbols have the same meaning as in the preceding paragraph but for the prime referring to the coion. Division by n_pRT and expansion in powers of c_p/c_s gives for the leading term (see appendix B),

$$\bar{g}'_u = (\nu' c_s/c_p)\ln(10^{-3}\gamma'_s\nu' c_s) - \tfrac{1}{2}(1-r)^2\xi\nu(\nu+\nu')^{-1}, \tag{7}$$

where γ'_s is the activity coefficient of the coion in the absence of polyelectrolyte.

If G_{H_2O} is the contribution from the solvent,

$$G_{H_2O} = -RT\phi[(\nu+\nu')n_s + (1-r)|z|^{-1}n_p], \tag{8}$$

where ϕ is the osmotic coefficient. Again, division by n_pRT to get $\bar{g}_{H_2O}$, followed by expansion in powers of c_p/c_s with retention of the lead term, gives (see appendix B),

$$\bar{g}_{H_2O} = -\phi_s(\nu+\nu')c_s/c_p - (1-r)|z|^{-1}\phi_s + \tfrac{1}{2}(1-r)^2\xi, \tag{9}$$

where ϕ is the osmotic coefficient of the simple salt solution in the absence of polyelectrolyte.

The final free energy contribution is from the mixing of associated counterions. To calculate it, let us specify that all associated counterions can translate freely within a free volume symmetrically positioned with respect to the linear polyelectrolyte charge array. With the assumption that all electrostatic interactions among associated counterions and between polyion and associated counterions are adequately built into eq. (3), the mixing free energy of associated counterions is given by

$$G_a = RT|z|^{-1}rn_p \ln(|z|^{-1}rn_p/n_pV_p), \tag{10}$$

since $|z|^{-1}rn_p$ is the total number of moles of associated counterions, and n_pV_p, where V_p is the free volume per mole of polyelectrolyte charge available for translation of associated counterions, is the total volume to which they are confined. Division by n_pRT yields:

$$\bar{g}_a = |z|^{-1}r\ln(|z|^{-1}rV_p^{-1}); \tag{11}$$

the quantity V_p has units of cm^3 to be consistent with the factor 10^{-3} in eqs. (5) and (6).

If the derivative with respect to r of the sum of the free energy components in eqs. (3), (5), (7), (9), and (11) is set equal to zero, the value of r for the equilibrium state is found to satisfy the following transcendental relation,

$$r = 10^{-3}\gamma_s e^{-\phi_s\nu|z|}V_pc_s(1-e^{-\kappa_s b})^{-2|z|\xi(1-r)}. \tag{12}$$

It is interesting that the last terms on the rhs of eqs. (5), (7), and (9), which represent the linear effect of polyelectrolyte on the small ion activity coefficients and osmotic coefficient (see appendix B), cancel when added and hence do not enter into the equilibrium relation (12).

The first step in analyzing the structure of eq. (12) is to note that a unique solution $r > 0$ exists if $c_s > 0$. For the lhs, considered as a function of r in the first quadrant, is a straight line of slope one passing through the origin, while the rhs is positive at $r = 0$ and decreases monotonically as r increases, tending to zero as r becomes infinite. Hence, as functions of r in the first quadrant, there is one and only one positive value of r at which the lhs and rhs intersect. Since the rhs is always positive, there is no solution in the range $r < 0$.

Now consider the rhs of eq. (12) in the limit $c_s \to 0$. Recalling that $\kappa_s^2 = O(c_s)$, we analyze two cases: $\xi < |z|^{-1}$ and $\xi \geqslant |z|^{-1}$. For the case $\xi < |z|^{-1}$, the rhs of eq. (12) tends to zero as $c_s \to 0$ for any value of $r > 0$; hence, in the limit $c_s \to 0$, the unique solution of eq. (12) is $r = 0$. For the case $\xi \geqslant |z|^{-1}$, the rhs of eq. (12) tends to zero as $c_s \to 0$ if $r > 1 - |z|^{-1}\xi^{-1}$, but tends to $+\infty$ if $r < 1 - |z|^{-1}\xi^{-1}$. Therefore, if $\xi \geqslant |z|^{-1}$, the only possible solution of eq. (12) in the limit $c_s \to 0$ is $r_0 = 1 - |z|^{-1}\xi^{-1}$. This value of r will actually be a solution if V_p is chosen self-consistently, that is, as the value which makes the rhs of eq. (12) equal to r_0 when $r = r_0$. Because the full definition of κ_s^2 is, if L equals Avogadro's number and z' is the valence of the coion,

$$\kappa_s^2 = (4\pi)\times 10^{-3}\,L(\nu+\nu')|zz'|\xi bc_s, \tag{13}$$

the self-consistant value of V_p as $c_s \to 0$ is

$$V_p^0 = 4\pi eL|z'|\nu^{-1}(\nu+\nu')(\xi-|z|^{-1})b^3. \tag{14}$$

In this formula, e is the base of natural logarithms, and b has units of cm.

Let us collect the results of the preceding paragraph. In the limit $c_s \to 0$ there is a critical value of ξ equal to $|z|^{-1}$, where z is the valence of the counterion. Below this critical value, the charge fraction of the polyelectrolyte is unity; there are no associated counterions. Above the critical value the charge fraction is $|z|^{-1}\xi^{-1}$; the fraction $r_0 = 1 - |z|^{-1}\xi^{-1}$ of the polyelectrolyte charge is compensated by associated counterions. The associated counterions move freely within a region of volume V_p^0 (cm^3/mole polyion charge) given by eq. (14).

The qualitative behavior of eq. (12) for low values of c_s is easily described. By low values, we mean in the

Table 1
Charge-fraction parameters for 1 : 1 salt at zero ionic strength

ξ	b (Å)	r_0	V_p^0 (cm^3/mole P)	a_0 (Å)
10.0	0.7	0.90	127	9.8
8.0	0.9	0.88	210	11.1
6.0	1.2	0.83	355	12.5
4.0	1.8	0.75	720	14.5
2.0	3.6	0.50	1919	16.8
1.2	6.0	0.17	1777	12.5
1.0	7.1	0.00	0	0.0

Table 2
Charge-fraction parameters for 2 : 1 salt at zero ionic strength

ξ	b (Å)	r_0	V_p^0 (cm^3/mole P)	a_0 (Å)
10.0	0.7	0.950	201	12.3
8.0	0.9	0.938	337	14.1
6.0	1.2	0.917	586	16.1
4.0	1.8	0.875	1259	19.2
2.0	3.6	0.750	4317	25.2
1.0	7.1	0.500	11040	28.7
0.7	10.1	0.286	12712	25.8
0.5	14.2	0.000	0	0.0

range such that $\kappa_s b \ll 1$, wherein $\exp(-\kappa_s b)$ may be linearized. Then, except for relatively small effects due to the factor $\gamma_s \exp(-\phi_s)$ that account for nonideality of the simple salt solution, the pair of values (r_0, V_0) remains a solution of eq. (12). Since typical values of b are of the order of 3 Å, the constraint $\kappa_s b \ll 1$ is very mild, stating merely that $c_s \ll 1$ M. Thus, we expect the value and physical structure of the charge fraction to be stable over a concentration range up to 0.1 M and possibly higher.

3. Numerical results

Calculations were done for a polyanion in the presence of both a 1 : 1 salt like NaCl and a 2 : 1 salt like $CaCl_2$. In tables 1 and 2, values of $r_0 = 1 - |z|^{-1} \xi^{-1}$ and V_p^0 given by eq. (14) are listed as functions of ξ for 1 : 1 and 2 : 1 salts, respectively. Along with V_p^0 are listed values of a_0, obtained by assuming a cylindrical free volume of radius a_0 centered axially on the linear array of polyelectrolyte charges,

$$V_p^0 = \pi a_0^2 bL, \tag{15}$$

with a_0 and b in cm and L equal to Avogadro's number. The trend is for V_p^0 and a_0 to increase gradually as the reduced charge density ξ decreases, then to decrease precipitously to zero as ξ approaches its critical value (1.0 for the 1 : 1 salt, 0.5 for the 2 : 1 salt). Local concentrations of associated (condensed) counterions in mole ℓ^{-1} are given by $1000\ V_p^{-1} r_0 |z|^{-1}$. At $\xi = 4$ (the approximate value for DNA), the concentration of condensed univalent counterions is 1.04 M; the concentration of condensed divalent counterions is 0.35 M. Remember that these local concentrations are under conditions for which the bulk concentration is zero!

In tabulating results at finite values of c_s, we are faced with a choice of using $V_p = V_p^0$ in eq. (12) and solving for r, or using $r = r_0$ in the same equation and solving for V_p. There is no physical motivation for the former procedure, but the latter is attractive because of the copious data (appendix A) that indicate experimental charge fractions near $|z|^{-1}\xi^{-1} = 1 - r_0$ over a wide concentration range. Therefore in tables 3 and 4, for 1 : 1 and 2 : 1 salts, respectively, the listed values of a [which bears the same relation to V_p as does a_0 to V_p^0 in eq. (15)] are those that satisfy eq. (12) when r is set equal to r_0. Under these conditions, of course, eq. (12) is trivially solved for V_p,

$$V_p = 10^3 \gamma_s^{-1} e^{\phi_s} (\nu c_s)^{-1} |z|^{-1} r_0 (1 - e^{-\kappa_s b})^2, \tag{16}$$

its transcendental character being manifested only if r is the dependent variable. Values of the counterion activity coefficients are taken as those of Na^+ in NaCl solutions for the 1 : 1 case and Ca^{2+} in $CaCl_2$ solutions

Table 3
Radius of the free volume as a function of salt concentration for NaCl

c_s (M)	κ_s^{-1} (Å)	a (Å; $\xi = 4.0$)	a (Å; $\xi = 2.0$)	a (Å; $\xi = 1.2$)
0	∞	14.5 (0)	16.8 (0)	12.5 (0)
10^{-2}	30.4	14.6 (0.3)	16.3 (1)	11.8 (3)
10^{-1}	9.6	14.4 (3)	15.2 (10)	10.2 (22)
1	3.0	12.6 (20)	–	–

Table 4
Radius of the free volume as a function of salt concentration for $CaCl_2$

c_s (M)	κ_s^{-1} (Å)	a (Å; $\xi = 4.0$)	a (Å; $\xi = 2.0$)	a (Å; $\xi = 0.7$)
0	∞	19.2 (0)	25.2 (0)	25.8 (0)
10^{-2}	17.6	25.1 (1)	31.2 (3)	27.2 (19)
10^{-1}	5.5	31.7 (8)	35.7 (23)	–

in the 2 : 1 case; the sodium and calcium ion activity coefficients are estimated from mean activity data in Robinson and Stokes [10], with the assumption that the chloride ion activity coefficient equals the mean activity coefficient in KCl solutions of identical ionic strength. Osmotic coefficients for the 1 : 1 and 2 : 1 salts are taken as those for NaCl and $CaCl_2$ solutions, respectively [10].

To assess the meaning of tables 3 and 4, account must be taken of an essentially artifactual feature of eq. (12), which becomes strikingly apparent in the asymptotic limit as c_s tends to infinity,

$$r \simeq 10^{-3} \gamma_s e^{-\phi_s} \nu |z| V_p c_s . \tag{17}$$

In this limit polyelectrolyte effects are swamped; the value of r, the degree of association of counterions due to long-range polyionic forces, should approach zero. Instead, eq. (17) asserts (ignoring for the moment the nonideality correction $\gamma_s e^{-\phi_s}$) that the counterion normality $10^3 r V_p^{-1}$ within the free volume is the same as in the rest of the solution, a correct but misleading result, since in this limit counterions are found in the free volume (along with an equivalent number of coions) only because their concentration is uniform throughout the solution and not because they are associated with the polyelectrolyte charge. The appearance of the factor $\gamma_s e^{-\phi_s}$ in eq. (17) compounds this modeling inconsistency.

Rather than undertake the task of removing the inconsistency at the probable cost of increased complexity, it may be more useful at present simply to evaluate it and throw out those results for which the inconsistency is deemed too large. Thus, I have proceeded by computing V_p from eq. (16), wherein r has been set equal to r_0; then, with this value of V_p, the "residual" r (call it r_∞) has been obtained from eq. (17), divided by r_0, and expressed as a percentage $100 r_\infty / r_0$. This "% inconsistency" appears in parentheses next to each entry for a in tables 3 and 4. I have arbitrarily decided that inconsistencies less than 25% are tolerable; vacancies in the tables signify intolerable inconsistency.

The extraordinary stability of the structure of the charge fraction as a function of ionic strength emerges clearly from tables 3 and 4. For a given ξ the value of a varies only slightly up to salt concentrations exceeding 0.1 M. The only exception is in table 4 for $\xi = 0.7$, close to the critical value $\frac{1}{2}$; for this entry a is stable up to about 10^{-2} M, beyond which the model fails. The highest concentrations in table 3 and 4 represent minimum values for which the charge fraction retains its zero-concentration limiting value and structure; at still higher concentrations, it is the model that breaks down, not necessarily the physical reality of the stable charge fraction.

The qualitative difference between the small concentration dependence of a and "screening behavior" is apparent from comparison with the Debye screening length κ_s^{-1}, also listed in the tables. Whereas $\kappa_s^{-1} = \infty$ at $c_s = 0$, a is a finite length at all concentrations; while κ_s^{-1} decreases by an order of magnitude when c_s increases by two orders of magnitude, a scarcely changes at all.

4. Specific effects

The association of counterions with polyelectrolytes is accompanied by partial dehydration of both polyion and counterion. For a given counterion, the extent of dehydration varies with polyion species; for a given polyion, the dehydration depends on counterion species [11]. In most cases the free energy of stabilization due to this short-range effect is expected to be fairly small compared to the nonspecific long-range polyelectrolyte effect on stabilization of the charge fraction. Nevertheless, short-range effects due to dehydration of ions and ionic or polar groups, may be the key to some of the most crucial problems in biology, ranging from the origin of specificity of ionic transport in nerves and synapses [12] to the regulation of genetic expression by means of specific recognition by a protein of short base-pair sequences on DNA [13].

An estimate of the free energy of short-range stabilization of associated counterions is made possible

Table 5
Results for the short-range stabilization free energy ψ

Polyion	d (Å)	a (Å)	ψ/RT
PP	3.0	15.6	3.3
PA	5.0	15.6	2.3
PSS	9.2	15.6	1.1

by coupling the theory presented here to recent NMR data. Suppose, as is likely, that the free volume V_p is actually a composite parameter that incorporates not only the translational degrees of freedom of the counterion, but also the short-range forces. Explicitly, eq. (10) for the mixing free energy of associated counterions is modified by replacing V_p with V_p^{int}, the intrinsic free volume, and adding a term equal to $|z|^{-1} r n_p \psi$ where ψ is the contribution to the counterion chemical potential of short-range interactions. The expression thus modified leads to eq. (12), but now with

$$V_p = V_p^{int} \exp(-\psi/RT). \qquad (18)$$

In terms of a, the radius of the cylindrical free volume,

$$a = a_{int} \exp(-\psi/2RT). \qquad (19)$$

Leyte and his colleagues have measured relaxation rates of ^{23}Na in the presence of polyphosphate (PP), polyacrylate (PA), and polystyrenesulfonate (PSS) [14]. They interpret the rate in terms of the radially averaged electric field experienced by the Na nucleus and, by applying a simple expression for the field which incorporates the value r_0 for the fractional number of sodium ions near the polyelectrolyte chain, are able to extract values for a parameter d, which equals the reciprocal of the root-mean-square reciprocal distance of a Na nucleus from the polyion axis. With full awareness of the roughness of the approximation involved, I have identified d with a_{int} in eq. (19) and used for a the value of a_0 corresponding to $\xi = 2.8$ (the common structural value for PP, PA, and PSS), obtained in the same way as the values listed in table 1. The results for ψ calculated in this manner from eq. (19) are given in table 5. The magnitude is characteristic of weak forces, and the order of strength PP > PA > PSS is exactly that expected on the basis of dilatometric measurements of the extents of dehydration [11].

Appendix A

The first direct measurement of a polyelectrolyte charge fraction was performed by Ikegami [4,15] who used as a probe of counterion–polyion close interaction the perturbation of index of refraction caused by mutual penetration of the hydration layers about the ionic species. He established that the charge fraction of polyacrylate in a sodium ion environment is close to ξ^{-1}, which equals 0.35 for fully neutralized polyacrylate. Concentrations used by Ikegami were between 0.01 M and 0.1 M. Strauss (unpublished data) has confirmed the validity of Ikegami's analysis by direct measurement (dilatometry) of the volume increase responsible for the index of refraction changes. Strauss finds a charge fraction for sodium polyacrylate close to ξ^{-1} at an ionic strength 0.2 M. Ultrasonic absorption may also be used to detect mutual penetration of hydration layers with consequent volume increases. By this technique Zana et al. [16] found that the charge fraction of carboxymethylcellulose is close to ξ^{-1} in a sodium environment at least up to 0.3 M.

Rinaudo [17] has observed that the dependence of titration curves on univalent counterion species occurs only when neutralization of a polyacid exceeds that degree which corresponds to $\xi \approx 1$. Her experiments with carboxymethylcellulose and vinylic polyacids were at concentrations between 10^{-3} M and 10^{-2} M.

NMR studies by Leyte's group [14] show charge fractions ξ^{-1} for the sodium salts of polyphosphate, polyacrylate, and polystyrenesulfonate at concentrations over 0.1 M. Spegt and Weill [18] have combined NMR and EPR measurements to analyze the structure of the charge fraction of manganese polyphosphate at about 10^{-3} M. They find that the overall charge fraction is about equal to the predicted value $\frac{1}{2}\xi^{-1}$ and that the associated manganese ions are composed of two distinct populations, roughly half being completely dehydrated, while the other half is only slightly perturbed. Their valuable analysis provides an opportunity for further theoretical progress in the direction of a more sophisticated view of the charge fraction than that presented in this paper, wherein the associated counterions are treated as a single population.

Although the measurement of thermodynamic and transport properties cannot provide direct information on the charge fraction, close agreement between measured and predicted values is consistent with physical accuracy of the model on which the predictions are based. The remarkable coincidence found by Kwak et al. [19] of experimental and theoretical values of mean activity coefficients of NaCl, KCl, $CaCl_2$, and $MgCl_2$ in polystyrenesulfonate solutions containing only one counterion species therefore supports the assertion that the charge fraction is ξ^{-1} for Na^+ and K^+ and $\frac{1}{2}\xi^{-1}$ for Mg^{2+} and Ca^{2+}. (The significant deviation under conditions of excess polyelectrolyte over simple salt for NaCl and KCl probably reflects theoretical problems with the unassociated small ions.) Successful comparison of experimental heats of mixing [20] and tracer diffusion coefficients [21,22] with theoretical prediction may also be cited as strong support for the charge fraction ξ^{-1} for univalent counterions. In all these cases, concentrations ranged up to 0.1 M.

It is difficult to attribute the persistence at higher concentrations of a charge fraction dependent only on polyelectrolyte linear charge density and counterion valence to specific short-range stabilizing forces (although the latter are important and manifest themselves in other ways). Polystyrenesulfonate, in particular, is known to generate only very weak short-range forces [11]. Another polyion, similar to polystyrenesulfonate in its low *surface* charge density (as opposed to high axial density), hence in the weakness of its specific ionic effects, is DNA. Evidence bearing on the charge fraction of this important biopolyelectrolyte is presented in another paper [13].

Appendix B

Kwak et al. [19] have generalized to arbitrary valences the theoretical expressions of ref. [1] for the activity coefficients of univalent counterions and coions and the osmotic coefficient of a polyelectrolyte solution with added 1 : 1 salt. With the notation of the text, the formulas needed here are

$$\ln(\gamma/\gamma_s) = -\tfrac{1}{2}\xi(\nu'/\nu)(\nu + \nu\ )^{-1}c_p/c_s + O[(c_p/c_s)^2], \qquad (20)$$

$$\ln(\gamma'/\gamma'_s) = -\tfrac{1}{2}\xi(\nu/\nu')(\nu + \nu')^{-1}c_p/c_s + O[(c_p/c_s)^2], \qquad (21)$$

$$\phi = \phi_s - \tfrac{1}{2}\xi(\nu + \nu')^{-1}c_p/c_s + O[(c_p/c_s)^2], \qquad (22)$$

where the subscript s denotes a quantity characteristic of the pure simple salt solution ($c_p = 0$). These relations were derived for $\xi < \xi_{crit}$, so that they apply in the absence of associated counterions. In the present context the polyelectrolyte unit is the polyion with its associated counterions, and the coion activity coefficient, osmotic coefficient, and activity coefficient of *unassociated* counterions for any value of ξ are required. These quantities are obtained with the replacement of ξ and c_p in eqs. (20)–(22) by $(1 - r)\xi$ and $(1 - r)c_p$, respectively. Use of the resulting formulas accounts for the appearance of γ_s, γ'_s, and ϕ_s in eqs. (5), (7), and (9) and for the last terms on the right-hand sides of these equations.

Note added in proof:

Private correspondence has indicated that the procedure of section 3 can give rise to some confusion. The primary point of that section is simply that (r_0, V_p^0) is an approximate solution of eq. (12) even at high concentrations. The main point of the entire paper, however, is contained in the last paragraph of section 2: subject to the mild restrictions that the ionic strength not exceed values of order 0.1 M and that activity coefficient effects be neglected for the simple salt solution, (r_0, V_p^0) is an *exact* solution of eq. (12) for any ionic strength.

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