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End Effects in Polyelectrolytes by the Mayer Cluster Integral Approach

Charles P. Woodbury, Jr.*

Department of Medicinal Chemistry, College of Pharmacy, University of Illinois at the Medical Center, Chicago, Illinois 60680

G. V. Ramanathan

Department of Mathematics, University of Illinois at Chicago Circle, Chicago, Illinois 60680.

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ABSTRACT: We apply the Mayer cluster expansion theory to the interaction of point ions with a polyion, modeling the polyion as a line charge of length $2L$ with suitable polyion–mobile ion distances of closest approach. By summing over all simple ring clusters we obtain limiting law expressions for contributions to the excess free energy and various colligative properties of the solution due to mobile ion–polyion interactions. These expressions include explicit end-effect corrections to the expressions derived by Manning for the case of an infinitely long polyion. We show that for a polyion of *fixed* dimensions, even though its length may be very large, cluster terms of higher order than the simple ring terms do not diverge in the limit of infinite dilution but instead disappear more rapidly than the ring terms. This indicates the absence of counterion condensation in this limit and validates the simple ring term expressions as limiting law expressions.

I. Introduction

In 1969 Manning[1,2] presented a theory of polyelectrolyte solutions based on the Mayer[3] cluster theory of ionic solutions. The Manning theory models the polyion as a uniformly charged line of infinite length interacting with a solution of mobile ions (taken as point charges), with assumption of a suitable distance of closest approach of mobile ions to the polyion. Interactions between polyions are neglected, and "uncondensed" (see below) mobile ions are treated in the Debye–Hückel approximation; that is, only simple "ring term" contributions to the free energy for "uncondensed" mobile ions are considered.

A fundamental quantity in the Manning theory is a (dimensionless) polyion charge-density parameter, ξ, defined by

$$\xi = \frac{e\sigma}{DkT} = \frac{e^2}{bDkT}$$

where e is the magnitude of the electronic charge, D the pure bulk solvent dielectric constant, k Boltzmann's constant, T the absolute temperature, and σ the polyion's charge density, equal to e/b with b the equivalent axial charge spacing distance on the polyion. For a polyion in a solution of univalent ions, if ξ is initially greater than 1, the condensation hypothesis requires that (in the limit of infinite dilution) sufficiently many counterions "condense" on the polyion to reduce ξ effectively to 1; if ξ is less than 1 initially, no counterion condensation occurs.

The theoretical justification given by Manning[1,2] for hypothesizing condensation involves the divergence of certain free energy terms in the limit of infinite dilution. Specifically, Manning showed that the leading ("ring") term in the Mayer cluster expansion corresponded to that obtained in the Debye–Hückel approximation; this term diverged logarithmically with increasing dilution of the system. Manning then analyzed the next higher order terms in the cluster expansion and showed that for $\xi \geq 1$, certain of these terms diverged even more rapidly than the ring term. Manning interpreted this result as implying counterion condensation.

In more recent work, Manning[4-7] and Iwasa[8,9] have treated polyion–counterion interactions by minimizing the free energy of the polyelectrolyte solution with respect to transfer of counterions from a bulk ("free") phase to a polyion-bound ("condensed") phase; the results obtained agree with the original condensation hypothesis. In a

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reexamination of the Poisson–Boltzmann (PB) equation for linear polyions, Fixman[10] has shown that a two-phase (or condensation) model can be obtained as an approximation to the PB model. Anderson and Record[11] have analyzed the low-salt limiting behavior of the Donnan coefficient from the cylindrical PB model and have found that a high local concentration of counterions remains close to the polyion at low ionic strength for polyion charge densities above the critical value; this is consistent with the condensation hypothesis.

The above treatments all take the polyion to be infinitely long and so neglect the effects of ends. However, end effects have received some recent attention through the work of Skolnick and Grimmelmann[12] on the potential of a finite line segment of charge in an ionic solution. Although these workers allow for screening effects in the interaction of mobile ions with the oligoion, they do not specifically address the problems of counterion condensation and the definition of an effective oligoion charge density.

Record and Lohman[13] have presented a semiempirical treatment of end effects that includes both screening and condensation effects. In their model of the oligoion, counterion condensation at the ends of the molecule is reduced over that in the interior; ξ_{end} is thus taken as greater than ξ_{interior}. With certain simplifying assumptions on the proportionality of counterion condensation at the ends vs. the interior of the oligoion, and on the length of the end regions, Record and Lohman use the observed length dependence of the melting temperature of a series of d(A-T) oligomers[14] to calibrate empirically the effect of ends. The calibrated model is then successfully applied to several other oligo- and polynucleotide systems.

Since real polyelectrolytes are composed of discrete charges that perhaps form a linear or helical lattice or are embedded in a medium of different dielectric constant than that of the bulk solvent, several variations on the continuous line-charge model have been examined. Bailey[15] has shown that at extreme dilution the continuous line-charge model and a straight line of regularly spaced charges yield equivalent results for the Debye–Hückel approximation to the excess electrostatic free energy. Moreover (for $\xi \leq 1$) Bailey claims that the contribution of higher order cluster terms to the free energy is small compared to the simple ring term, thus supporting Manning's neglect of these terms. It should be mentioned, however, that this neglect of higher order terms has been contested by Iwasa and co-workers.[16,17]

Soumpasis[18] has considered more elaborate lattice models for the polyion with a discrete charge array and has concluded (with Bailey[19]) that at infinite dilution the effects of charge discreteness are negligible, as are the effects of ionic size. Skolnick and Fixman[20] and Skolnick[21] have examined the electrostatic free energy for helical arrays or stripes of charges on the surface of a dielectric cylinder, following Hill's[22] earlier work on infinitely long, uniformly charged cylinders as polyion models. Again, for sufficiently low salt concentrations, predictions agree with those of the simple line-charge model.

The present paper is an extension of Manning's treatment of infinitely long polyelectrolytes,[1,2] in which we seek explicit end-effect corrections (in the Debye–Hückel approximation) to Manning's expression for the excess free energy and certain of its derivatives. Following Manning, we shall use the Mayer cluster integral approach, first examining the simple ring term to obtain the Debye–Hückel approximation to the free energy and to various colligative properties. We then turn to the behavior at infinite dilution of the higher order cluster terms that reflect the short-range interactions of mobile ions with the polyion. Manning has cited the divergence of such terms, in the limit of infinite dilution and when the charge density exceeds a certain critical value, as evidence for "condensation" of counterions onto the polyion. We shall show that, regardless of the value of ξ, these terms vanish at infinite dilution more rapidly than the ring term contribution in the case of a polyion of *fixed* length, which implies the absence of counterion condensation and justifies our use of the simple ring terms for deriving limiting law expressions. In a subsequent paper we shall return to the relation between counterion condensation and polyion charge density and length, and we shall offer there criteria for the onset of counterion condensation.

II. Theory

A. Preliminaries. We define the three-dimensional Fourier transform $\tilde{f}(\mathbf{k})$ of a function $f(\mathbf{r})$ as

$$\tilde{f}(\mathbf{k}) = \int f(\mathbf{r}) e^{-i\mathbf{k}\cdot\mathbf{r}} \, d\mathbf{r} \tag{1}$$

The inverse transform is

$$f(\mathbf{r}) = (1/2\pi)^3 \int \tilde{f}(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}} \, d\mathbf{k} \tag{2}$$

In what follows we shall have occasion to use the three-dimensional "box" function

$$B(\mathbf{r},L) = \delta(x)\delta(y)b(z,L) \tag{3}$$

where $\delta(x)$ and $\delta(y)$ are Dirac δ functions, and the function $b(z,L)$ is defined by

$$\begin{aligned} b(z,L) &= 0 \qquad |z| > L \\ &= 1 \qquad |z| \leq L \end{aligned} \tag{4}$$

The Fourier transform of $B(r,L)$ is given by

$$\tilde{B}(\mathbf{k},L) = \frac{2 \sin (k_z L)}{k_z} \tag{5}$$

We shall also need the Fourier transforms of the Coulomb potential function r^{-1} and the "screened" potential function $r^{-1}e^{-\kappa r}$

$$\widetilde{(1/r)} = 4\pi/k^2 \tag{6a}$$

and

$$\widetilde{\left(\frac{e^{-\kappa r}}{r}\right)} = \frac{4\pi}{k^2 + \kappa^2} \tag{6b}$$

B. Uniformly Charged Line Model. We take as our model for a finite polyion a line charge along the z axis from $-L$ to $+L$, carrying a total charge Q with a uniform charge density σ of $Q/2L$. We suppose the polyion to be immersed in a solution of mobile ions, the ith species of which has a charge $z_i e$ and a number density n_i. The Debye parameter κ is given as usual by

$$\kappa^2 = \frac{4\pi e^2}{DkT} \sum n_i z_i^2 \tag{7}$$

According to the cluster theory of ionic solutions,[3,23] the major contribution to the excess Helmholtz free energy A^{ex} comes from the sum over simple closed chains (rings) of ions and corresponds to the Debye–Hückel limiting law result. Let us denote by C_n the term corresponding to a chain of n mobile ions joining a polyion and a test charge q. C_n is given by

$$C_n = \frac{\sigma q}{D}(-\kappa^2)^n \int g_{q1} g_{12} g_{23} \cdots g_{n-1,n} h_{n,p} \, d\mathbf{r}_1 \ldots d\mathbf{r}_n \tag{8}$$

Here $\mathbf{r}_i$ is the position of the ith mobile ion; g_{ij} is proportional to the spherically symmetric Coulomb potential for each of the mobile ions

$$\begin{aligned} g_{ij} &= g(r_{ij}) \\ &= (4\pi r_{ij})^{-1} \end{aligned} \tag{9}$$

and $h_{n,p} = h(r_{np})$ is proportional to $\psi_L(\mathbf{r})$, the Coulomb potential due to the polyion at the position of the nth mobile ion.

The potential $\psi_L(\mathbf{r})$ can be written as the integrated potential at $\mathbf{r}$ due to each infinitesimal line segment of charge in the polyion

$$\psi_L(\mathbf{r}) = \frac{\sigma}{D}\int_{-L}^{L} \frac{\mathrm{d}z_1}{(\rho^2 + (z - z_1)^2)^{1/2}} \tag{10}$$

where (ρ, ϕ, z) are the cylindrical coordinates of the vector $\mathbf{r}$. In terms of the B function defined earlier, $\psi_L(\mathbf{r})$ can be written as a convolution of the Coulomb potential function r^{-1} with the B function

$$\psi_L(\mathbf{r}) = \frac{\sigma}{D}(r^{-1}) * B(\mathbf{r},L) \tag{11}$$

The Fourier transform of C_n may now be obtained through the Fourier convolution theorem

$$\tilde{C}_n = \frac{\sigma q}{D}\left(\frac{-\kappa^2}{k^2}\right)^n \frac{\tilde{B}(\mathbf{k},L)}{k^2} \tag{12}$$

where we have taken $\tilde{h} = k^{-2}\tilde{B}(\mathbf{k},L)$. We sum over all chains, for $n = 0$ to ∞

$$\begin{aligned} \tilde{C} &= \sum_{n=0}^{\infty} \tilde{C}_n \\ &= \frac{\sigma q}{D}\tilde{B}(\mathbf{k},L)\left(\frac{1}{k^2 + \kappa^2}\right) \end{aligned} \tag{13}$$

Transforming back we have

$$C = \frac{\sigma q}{D}B(\mathbf{r},L) * \left(\frac{e^{-\kappa r}}{r}\right) \tag{14}$$

having used eq 6b for the screened Coulomb potential transformation.

To calculate the excess Helmholtz free energy in the Debye–Hückel approximation, we need to sum over *closed* chains, or rings, of ions. We replace the test charge q with the line charge on which the ring begins and ends, writing the counterpart of eq 8 as

$$R_n = \frac{\sigma^2}{2D}(-\kappa^2)^n \int h_{q1}g_{12}\ldots g_{n-1,n}h_{n,q'}\,\mathrm{d}\mathbf{r}_1\ldots\mathrm{d}\mathbf{r}_n \tag{15}$$

the factor of two arising from the combinatorics of requiring the chain to begin and end on the same ion. Using the definition of the box function, we have

$$R_n = \frac{\sigma^2}{2D}(-\kappa^2)^n \int B(\mathbf{r}_q,L) \int B(\mathbf{r}_{q'},L) \int g_{q1}g_{12}\ldots g_{n,q'}\,\mathrm{d}\mathbf{r}_1\ldots\mathrm{d}\mathbf{r}_n\,\mathrm{d}\mathbf{r}_{q'}\,\mathrm{d}\mathbf{r}_q \tag{16}$$

where $\mathbf{r}_q$ and $\mathbf{r}_{q'}$ are (different) positions on the same polyion.

Summing over rings from $n = 1$ to ∞, and using eq 13 and 14, we have

$$R = \frac{\sigma^2}{2D}\int B(\mathbf{r}_q,L)\left[B(\mathbf{r},L) * \left(\frac{e^{-\kappa r}}{r} - \frac{1}{r}\right)\right]\mathrm{d}\mathbf{r}_q \tag{17}$$

The single convolution $B(\mathbf{r},L) * (e^{-\kappa r}/r)$ may be written as

$$\begin{aligned} B(\mathbf{r},L) * \frac{e^{-\kappa r}}{r} &= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\delta(x_1)\delta(y_1)b(z_1,L) \times \\ &\quad \frac{\exp\{-\kappa[(x - x_1)^2 + (y - y_1)^2 + (z - z_1)^2]^{1/2}\}}{[(x - x_1)^2 + (y - y_1)^2 + (z - z_1)^2]^{1/2}}\,\mathrm{d}x_1\,\mathrm{d}y_1\,\mathrm{d}z_1 \\ &= \int_{z-L}^{z+L} \frac{\exp[-\kappa(\rho^2 + \zeta^2)^{1/2}]}{(\rho^2 + \zeta^2)^{1/2}}\,\mathrm{d}\zeta \end{aligned} \tag{18}$$

with $\zeta = (z - z_1)$ and $\rho^2 = x^2 + y^2$. Similarly

$$B(\mathbf{r},L) * \frac{1}{r} = \int_{z-L}^{z+L} \frac{\mathrm{d}\zeta}{(\rho^2 + \zeta^2)^{1/2}} \tag{19}$$

Then eq 17 can be written as

$$R = \frac{\sigma^2}{2D}\int_{-L}^{L}\mathrm{d}z \int_{z-L}^{z+L} \frac{[e^{-\kappa|\zeta|} - 1]}{|\zeta|}\,\mathrm{d}\zeta \tag{20}$$

where application of the second box function has removed the dependence on ρ. Integration by parts yields

$$R = \frac{\sigma Q}{D}\int_0^{2L} \frac{(e^{-\kappa z} - 1)}{z}\,\mathrm{d}z + \frac{\sigma Q}{D} - \frac{\sigma^2}{\kappa D}(1 - e^{-2\kappa L}) \tag{21}$$

having used the definition $Q = 2\sigma L$. Then with the relation

$$\int_0^x \frac{e^{-u} - 1}{u}\,\mathrm{d}u = -\gamma - \ln x - \mathrm{Ei}\,(x)$$

where γ is Euler's constant ($\gamma = 0.5772\ldots$) and $\mathrm{Ei}\,(x)$ the exponential integral

$$\mathrm{Ei}\,(x) = \int_x^{\infty} (e^{-u}/u)\,\mathrm{d}u$$

we find the excess free energy A_1^{ex} by multiplying R by N_{p}, where N_{p} is the total number of polyions in the volume V of the system

$$A_1^{\mathrm{ex}} = \frac{\sigma Q N_{\mathrm{p}}}{D}\left[-\mathrm{Ei}\,(2\kappa L) - \ln\,(2\kappa L) - \gamma + 1 + \frac{1}{2\kappa L}(e^{-2\kappa L} - 1)\right] \tag{22}$$

Defining n_{p} as $|Q|N_{\mathrm{p}}/eV$, we have

$$A_1^{\mathrm{ex}}/VkT = -\xi n_{\mathrm{p}}\left[\mathrm{Ei}\,(2\kappa L) + \ln\,(2\kappa L) + \gamma - 1 - \frac{1}{2\kappa L}(e^{-2\kappa L} - 1)\right] \tag{23}$$

Notice that as κL becomes very large we have

$$A_1^{\mathrm{ex}}/VkT = -\xi n_{\mathrm{p}} \ln\,(2\kappa L) \tag{24}$$

so that in the Debye–Hückel approximation the excess free energy diverges logarithmically, as predicted by Manning[1,2] for an infinite line charge. However, for *fixed* polyion length in a sufficiently dilute system (i.e., $\kappa L \ll 1$) the excess free energy due to the polyion varies as

$$A_1^{\mathrm{ex}}/VkT \simeq -\xi n_{\mathrm{p}}\kappa L \tag{25}$$

as may be shown by expanding $e^{-2\kappa L}$ and $\mathrm{Ei}\,(2\kappa L)$ for $\kappa L \ll 1$.

We can easily obtain end-effect corrections to the colligative properties of polyion solutions by taking the appropriate derivative of the excess free energy. For example, the activity coefficient γ_i of the ith mobile ion species is given by

$$\ln \gamma_i = \left(\frac{\partial[A^{\mathrm{ex}}/VkT]}{\partial n_i}\right)_{T,V,n_{i\neq j}}$$

Retaining only the contribution to $\ln \gamma_i$ from the presence of the polyion species while ignoring higher order cluster terms and the contribution from bulk salt (see Wells[24] for an empirical correction for bulk salt effects and Iwasa and Kwak[25] for a discussion of its theoretical basis), we can use eq 23 to obtain

$$\ln \gamma_i = \frac{-\lambda \xi n_p}{2\kappa^2}\left[1 + \frac{(e^{-2\kappa L} - 1)}{2\kappa L}\right] \tag{26}$$

The mean activity coefficient is also easily shown to be

$$\begin{aligned}\ln \gamma_\pm &= \tfrac{1}{2}[\ln \gamma_1 + \ln \gamma_2] \\ &= \frac{-\lambda \xi n_p}{2\kappa^2}\left[1 + \frac{(e^{-2\kappa L} - 1)}{2\kappa L}\right]\end{aligned} \tag{27}$$

The contribution Π^{ex} of the polyion to the excess osmotic pressure is (to the same level of approximation)

$$\Pi^{ex} = -(\partial A_1{}^{ex}/\partial V)_{T,\text{composition}}$$

and using eq 23, with the relation

$$(\partial \kappa/\partial V)_{\text{composition}} = -\kappa/2V$$

we find

$$\frac{\Pi^{ex}}{kT} = -\tfrac{1}{2}N_p\left[1 + \frac{(e^{-2\kappa L} - 1)}{2\kappa L}\right] \tag{28}$$

The osmotic coefficient ϕ is defined by

$$kT(\phi - 1)(n_1 + n_2) = \Pi^{ex}$$

It is then easy to show that

$$\phi = 1 - \tfrac{1}{2}\xi\frac{n_p}{n_1 + n_2}\left[1 + \frac{(e^{-2\kappa L} - 1)}{2\kappa L}\right] \tag{29}$$

If we define $X = n_p/n_s$ and use the relations $n_1 = n_s + n_p$, $n_2 = n_s$, we have

$$\phi = 1 - \tfrac{1}{2}\xi\frac{X}{X + 2}\left[1 + \frac{(e^{-2\kappa L} - 1)}{2\kappa L}\right] \tag{30}$$

which may be compared to eq 28 of Manning.[1]

C. Higher Order Terms. In this section we examine the cluster terms of next higher order to the ring terms. These describe the close interaction of a pair of ions, one of which is the polyion; the terms we consider here correspond to those in eq 29 of Manning[2] or eq 7 of Bailey[15] (see also Chapter 17 of Friedman[23]). The divergence of this class of terms at infinite dilution for an infinitely long polyion of sufficiently high charge density was cited by Manning as indicating the onset of counterion condensation. We shall show that for a polyion of *fixed, finite* dimensions, divergences at infinite dilution do not appear for this class of terms, and further, that this class is negligible in its contribution to the excess free energy compared to the ring term, at extreme dilution.

For a finite polyion with a cylindrical hard core of radius a, length $2L'$ (where a is the radial distance of closest approach, and $L' = L + a'$, with a' an axial distance of closest approach to the end of the polyion), we define

$$\begin{aligned} u^*{}_{ip} &= 0 && \text{for } \rho > a \text{ or } |z| > L' \\ &= \infty && \text{for } \rho < a \text{ and } |z| < L' \end{aligned}$$

Then we write the next higher order free energy contribution as (see Friedman,[23] especially Chapter 17)

$$\begin{aligned}\frac{A_2{}^{ex}}{VkT} = {}& \sum_i n_i \sum_{\nu=0}^{2} 2\pi \int_{-\infty}^{\infty} \mathrm{d}z \int_0^{\infty} \mathrm{d}\rho \\ & \rho\frac{N_p}{\nu! V}(\pm\xi z_i)^\nu \left(\frac{\exp[-\kappa r_{ip}]}{r_{ip}} * B(\mathbf{r}_p,L)\right)^\nu - \\ & \sum_i n_i \sum_{\nu=0}^{\infty} 2\pi \int_{-\infty}^{\infty} \mathrm{d}z \int_0^{\infty} \mathrm{d}\rho\ \rho(1 + k_{ip}) \times \\ & \frac{N_p}{\nu! V}(\pm\xi z_i)^\nu \left(\frac{\exp[-\kappa r_{ip}]}{r_{ip}} * B(\mathbf{r}_p,L)\right)^\nu\end{aligned} \tag{31}$$

We have used here

$$k_{ip} = \exp[-u^*{}_{ip}/kT] - 1$$

Defining for convenience

$$I_\nu \equiv \left[\frac{\exp[-\kappa r_{ip}]}{r_{ip}} * B(\mathbf{r}_p,L)\right]^\nu$$

taking account of the effects of $(k_{ip} + 1)$ on the limits of integration of z and ρ, and finally changing to dimensionless variables of integration $t = \kappa z$, $u = \kappa\rho$, and $\upsilon = \kappa\zeta$, we have

$$\frac{-A_2{}^{ex}}{VkT} = \frac{2\pi N_p}{V\kappa^3}\sum n_i[H + K + P - M] \tag{32}$$

$$H = \sum_{\nu=3}^{\infty}(\nu!)^{-1}(\pm\xi z_i)^\nu \int_{\kappa L'}^{\infty}\mathrm{d}t \int_0^{\infty}\mathrm{d}u\ (uI_\nu)$$

$$K = \sum_{\nu=3}^{\infty}(\nu!)^{-1}(\pm\xi z_i)^\nu \int_{-\infty}^{-\kappa L'}\mathrm{d}t \int_0^{\infty}\mathrm{d}u\ (uI_\nu)$$

$$P = \sum_{\nu=3}^{\infty}(\nu!)^{-1}(\pm\xi z_i)^\nu \int_{-\kappa L'}^{\kappa L'}\mathrm{d}t \int_{\kappa a}^{\infty}\mathrm{d}u\ (uI_\nu)$$

$$M = \sum_{\nu=0}^{2}(\nu!)^{-1}(\pm\xi z_i)^\nu \int_{-\kappa L'}^{\kappa L'}\mathrm{d}t \int_0^{\kappa a}\mathrm{d}u\ (uI_\nu)$$

In eq 31 and 32 the upper sign is to be taken for a polyanion, the lower sign for a polycation.

Consider the integral terms in M first, the νth term M_ν of which is of the general form

$$M_\nu = \int_{-\kappa L'}^{\kappa L'}\mathrm{d}t \int_0^{\kappa a}\mathrm{d}u\ (uI_\nu) \tag{33}$$

Changing to the reduced variables $x = t/\kappa L$, $y = u/\kappa a$, and $z = \upsilon/\kappa L$, we write

$$I_\nu = \left[\int_{x-1}^{x+1}\frac{\exp[-\kappa L(z^2 + (ay/L)^2)^{1/2}]}{(z^2 + (ay/L)^2)^{1/2}}\,\mathrm{d}z\right]^\nu \tag{34}$$

Now

$$I_\nu \le \left[\int_{x-1}^{x+1}\frac{\mathrm{d}z}{(z^2 + (ay/L)^2)^{1/2}}\right]^\nu \tag{35}$$

Since $z^2 + (ay/L)^2 \ge 2a|yz|/L$, we have

$$I_\nu \le (L/2a)^{\nu/2}\left[\int_{x-1}^{x+1}\frac{\mathrm{d}z}{|yz|^{1/2}}\right]^\nu \tag{36}$$

so that

$$M_\nu \le \kappa L(\kappa a)^2(2L/a)^{\nu/2}\int_{-L'/L}^{L'/L}(|x + 1|^{1/2} - |x - 1|^{1/2})^\nu\,\mathrm{d}x \int_0^1 y^{1-\nu/2}\,\mathrm{d}y \tag{37}$$

Since the integral on the right-hand side exists and is independent of κ, we see that all M_ν go to zero at least as fast as $\kappa L(\kappa a)^2$; hence M also goes to zero at least as fast as $\kappa L(\kappa a)^2$.

Consider next the integral terms in L, the νth of which is of the form

$$P_\nu = \kappa L(\kappa a)^2 \int_{-L'/L}^{L'/L} \mathrm{d}x \int_1^\infty y I_\nu \, \mathrm{d}y \tag{38}$$

Now

$$I_\nu \leq \left[\frac{2L}{ay}\right]^\nu \text{ for } \nu \geq 3$$

and so

$$P_\nu \leq \kappa L(\kappa a)^2 \int_{-L'/L}^{L'/L} \mathrm{d}x \int_1^\infty y \left[\frac{2L}{ay}\right]^\nu \mathrm{d}y \tag{39}$$

Since $y \geq 1$ and $\nu \geq 3$, we have $y^{-2} \geq y^{1-\nu}$, so that

$$P_\nu \leq \kappa L(\kappa a)^2 \left(\frac{2L'}{L}\right)\left(\frac{2L}{a}\right)^\nu \int_1^\infty \frac{\mathrm{d}y}{y^2} = (2\kappa L')(\kappa a)^2 \left(\frac{2L}{a}\right)^\nu \tag{40}$$

Thus P_ν in general will go to zero at least as fast as $\kappa L'(\kappa a)^2$.

To obtain P, each P_ν is multipled by $(\nu!)^{-1}(\pm\xi z_i)$ and the terms are summed from $\nu = 3$ to ∞. Since this sum converges, we have

$$P \leq 2\kappa L'(\kappa a)^2 \times (\text{constant independent of } \kappa) \tag{41}$$

and so P goes to zero at least as fast as $\kappa L'(\kappa a)^2$.

Turning to the integral terms in H, we have

$$H_\nu = \kappa L(\kappa a)^2 \int_{L'/L}^\infty \mathrm{d}x \int_0^\infty y I_\nu \, \mathrm{d}y \tag{42}$$

Observing that $x > 1$, we have

$$I_\nu \leq \frac{2^\nu \exp\{-\nu\kappa L[(x-1)^2 + (ay/L)^2]^{1/2}\}}{[(x-1)^2 + (ay/L)^2]^{\nu/2}} \tag{43}$$

Defining $S^2 = (x-1)^2 + (ay/L)^2$, we then have

$$H_\nu \leq \kappa L(\kappa a)^2 \int_{L'/L}^\infty \left\{\frac{L^2}{a^2} \int_{x-1}^\infty \frac{e^{-\nu\kappa LS}}{S^{\nu-1}} \, \mathrm{d}S\right\} \mathrm{d}x \tag{44}$$

Integrating by parts yields

$$H_\nu \leq (\kappa L)^3 \int_{L'/L-1}^\infty \frac{e^{-\nu\kappa LS}}{S^{\nu-2}} \, \mathrm{d}S \tag{45}$$

For $\nu \geq 4$ it is straightforward to show that $H_\nu \leq (\kappa L)^3 \cdot (L/a')^\nu$, and for $\nu = 3$

$$H_3 \leq (\kappa L)^3 \int_{L'/L-1}^\infty \frac{e^{-3\kappa LS}}{S} \, \mathrm{d}S = -(\kappa L)^3 \ln(\kappa a') + \mathcal{O}(\kappa^3 L^3) \tag{46}$$

Since the sum

$$\sum_{\nu=4}^\infty (\nu!)^{-1}(\pm\xi z_i L/a')^\nu \tag{47}$$

converges, H goes to zero at least as fast as $(\kappa L)^3 \ln(\kappa a')$.

Finally, we claim that by arguments similar to those applied to the term H, we can show that the term K will also go to zero at least as fast as $(\kappa L)^3 \ln(\kappa a')$.

Returning now to A_2^{ex}/VkT, noting that $\sum n_i$ is proportional to κ^2 and using our inequalities for H, K, P, and M, we find that at extreme dilution ($\kappa a' \ll 1$), A_2^{ex}/VkT goes to zero with κ at least as rapidly as $(\kappa L)^2 \ln(\kappa a')$. Since the simple ring term contribution to the free energy is proportional to κL at low salt (cf. eq 25), A_2^{ex} for finite polyions is indeed negligible by comparison to A_1^{ex} in the limit of infinite dilution.

III. Conclusion

We have studied the statistical mechanics of a polyelectrolyte solution for rigid polyions of fixed, finite length. We have specifically included end effects in deriving expressions for the excess electrostatic free energy and various colligative properties of the solution. For a finite line charge with appropriate distances of closest approach, we have shown that the higher order cluster terms are insignificant in the limit of infinite dilution. As a consequence, there is no counterion condensation in this limit, regardless of the polyion's charge density, so long as the polyion dimensions are fixed and finite. This stands in contrast to Manning's theory, according to which counterion condensation at infinite dilution is a result of a sufficiently high charge density on an infinitely long polyion.

It should be stressed that in the analysis presented here we have required that L, a, and a' be *fixed*. However, if L/a is allowed to go to infinity, the upper bounds to the higher order cluster terms in the last section can become infinitely large. In that case, the free energy contribution can become infinite, indicating condensation of counterions. In fact, even if $L/a \rightarrow \infty$ but $\kappa L \rightarrow 0$, it is possible to demonstrate condensation, and we shall discuss in a future paper the precise limiting conditions for counterion condensation.

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