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Counterion Condensation. Effects of Site Binding, Fluctuations in Nearest-Neighbor Interactions, and Bending

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ABSTRACT: A direct binding approach to counterion condensation is proposed that incorporates both site binding and fluctuations in nearest-neighbor interactions as well as mean-field interactions between more distant neighbors. The predicted counterion binding ratio is identical to Manning's limiting law at zero salt concentration and departs only slightly from Manning's mean-field result up to 4 mM salt. The present theory is generalized to incorporate the effects of bending, especially the increase in configurational entropy due to the decrease in electrostatic bending rigidity caused by counterion binding. With this modification, the present theory predicts a much more rapid onset of counterion condensation as ξ increases beyond 1.0 than is exhibited by the straight-chain theories. Comparison with experiment suggests that this predicted enhancement of counterion binding due to bending may be responsible for much or all of the discrepancy between the observations of Klein and Ware and the results of straight-chain theories. The present results also suggest a mechanism whereby the rapid onset of counterion condensation as ξ increases past 1.0 might trigger a structural transition from a more compact or folded state to a more extended conformation.

Introduction

Manning developed a theory of counterion condensation for straight linear polyions that yields predictions in remarkably good agreement with a number of experimental observations.[1,2] By means of electrophoretic light scattering, Klein and Ware determined the effective charge on a particular polyion (6,6-ionene) as a function of the dielectric constant (ϵ) of the solvent through the region where counterion condensation is predicted to begin.[3] Their results constitute one of the most incisive tests of Manning's theory and indeed of the whole concept of counterion condensation. The effective charge (in units of electronic charges per monomer unit) can be expressed as $1 - r$, where r is the fraction of counterions that are condensed. In Figure 1, the experimental values of $1 - r$ are plotted vs $\xi = q^2/(\epsilon bkT)$, where b is the distance between intrinsic charges on the polyion. It is clear that counterion condensation begins precisely at $\xi = 1.0$, as predicted by Manning's theory. However, as ξ increases beyond 1.0, the condensation in this case sets in much more rapidly, or strongly, than is predicted by Manning's theory. Understanding the possible origins of this discrepancy in the region $\xi > 1.0$ is the principal aim of the present work. Discrepancies in the region $\xi < 1.0$, which may be linked to structural transitions near $\xi = 1.0$,[20] will also be considered in the final section of this work.

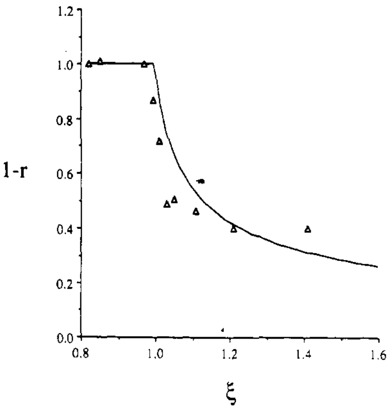

Figure 1. Fraction of the polyion charge ($1 - r$) that is not compensated by counterion condensation vs the reduced charge density parameter (ξ). The triangles were calculated from the measured electrophoretic mobilities of 6,6-ionene by Klein and Ware[3] using Poisson–Boltzmann theory for a cylinder with radius $a = 5.5$ Å and a uniform charge density equivalent to that of 6,6-ionene, which has single positive charges separated by $b = 8.73$ Å. The temperature is $T = 293$ K and the prevailing salt concentration is $c_s = 4.0$ mM KBr. The solid line is calculated using eq 32 for $\xi < 1.0$ and eq 48 together with eqs 53, 49, 34, and 36 for $\xi \geq 1.0$. Parameters employed in the calculation are $T = 293$ K, $c_s = 4$ mM, charge $q = e_0$ (protonic charge), assumed intrinsic persistence length $P_0 = 10$ Å, and values of ξ reported by Klein and Ware.[3]

In Manning's theory, it is assumed that the bound counterions are not localized to specific sites but instead occupy a common (adjustable) free volume extending over the entire length of the polyion. While this might adequately describe the binding of alkali metal cations,[4] it evidently does not accurately portray the binding of divalent alkaline earth and transition metal ions.[5-7] The question arises whether binding into a free volume is actually essential to the predicted binding isotherm or whether the same, or nearly the same, binding isotherm would result from a theory in which the bound counterions are localized to sites (or specific volumes) associated with the individual polyion charges. Using a modified Scatchard approach to the binding isotherm, Schmitz has shown that explicit consideration of site binding with a particular fixed geometry of the bound ions still leads to condensation-like behavior.[8] In that treatment, it is assumed that the ligands bind in stacks, which does not properly account for fluctuations in the occupations of nearest-neighbor sites and, hence, in the interactions between those sites. In fact, runs or stacks of *unfilled* (or unbound) sites with no bound counterions are energetically very unfavorable. Hence, it would be desirable to treat the nearest-neighbor interactions more exactly. The question arises whether either site binding per se or the effects of fluctuations in nearest-neighbor interactions could account for the rapid onset of counterion condensation reported by Klein and Ware. In this work, we develop a theory of counterion binding that admits site binding and accounts exactly for nearest-neighbor interactions within the framework of a two-state model (i.e., each binding site is either filled or empty), but still incorporates the mean-field interactions

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between more distant neighbors. The theoretical procedure to accomplish this is based on a grand partition function method similar to that employed previously to treat ligand binding to supercoiled DNAs.[9] Dewey recently used a related method to investigate the binding of counterions into a "delocalized" state on polyions of finite length.[10] The present straight-chain theory yields Manning's limiting law in the limit of zero salt concentration and exhibits only a small departure from Manning's mean-field theory at higher salt concentration. Hence, it cannot account for the results of Klein and Ware.[3] The present theory does *not* avoid the problem of the adjustable free volume, but merely replaces that with an adjustable site-binding constant. It is noted, however, that the singularity due to the mean-field interactions is so strong that Manning's limiting law is obtained *at zero salt concentration* regardless of the particular choice of that binding constant.

None of the extant theories of counterion condensation treats the effect of counterion binding and its attendant reduction of the electrostatic bending rigidity on the bending partition function. The resulting increase in the bending partition function acts indirectly to enhance counterion binding. The present theory is generalized to incorporate both direct and indirect effects of bending. This theory now predicts a very rapid onset of counterion binding as ξ increases beyond 1.0 and shows good agreement with the observations of Klein and Ware. It is suggested that this enhancement of counterion binding by bending very likely accounts for much or all of the difference between the results of Klein and Ware and the straight-chain theories. It is also suggested in the final section that the rapid enhancement of the bending partition function as ξ increases past 1.0 could potentially trigger a structural transition from a more compact and stiffer state to a more extended and flexible conformation.

Theory

The Model. We consider a very large volume V containing N_0 solvent molecules, N_s "molecules" of completely ionized 1:1 univalent salt (s), an extremely small number of very long linear polyions (P) with a single univalent charge per subunit, and their complement of counterions (C), which are identical to one of the salt ions. In this treatment, the solvent is largely neglected except for its contribution of a uniform dielectric constant. Each subunit of the naked polyion is assumed to provide a single site to which a counterion could bind. The reaction for association of n_C counterions with *naked* polyion P to form a particular complex $D_J(n_C)$ in which the n_C bound counterions are distributed among the different sites in a particular configuration J is

$$\mathrm{P} + n_C\mathrm{C} \rightleftarrows \mathrm{D}_J(n_C) \tag{1}$$

General Binding Theory. All solute species, including ions of the salt, are assumed to be sufficiently dilute that they obey Henry's law:

$$\mu_j = \mu_j{}^\circ + kT \ln X_j = \mu_j{}^\circ + kT \ln\left(\frac{m_j}{m_0}\right) \tag{2}$$

wherein X_j and m_j are the mole fraction and molarity, respectively, of the jth solute species, $m_0 = N_0/(6.02 \times 10^{23})$ is the molarity of the solvent, k is Boltzmann's constant, and T is the absolute temperature. If the salt concentration is sufficiently high that nonideality becomes significant, an activity coefficient $\gamma_C{}^s$ can be included as a multiplicative factor along with m_C. In that case, m_C is simply replaced by $\gamma_C{}^s m_C$ in the sequel. The condition for equilibrium of reaction 1 is

$$\mu_P + n_C\mu_C = \mu_{D_J(n_C)} \tag{3}$$

Inserting eq 2 into eq 3 and rearranging yield

$$\frac{m_{D_J(n_C)}}{m_P} = \left(\frac{m_C}{m_0}\right)^{n_C} \exp[-(\mu_{D_J(n_C)}{}^\circ - \mu_P{}^\circ - n_C\mu_C{}^\circ)/kT] \tag{4}$$

The quantity in parentheses in the exponential function is just the standard-state free-energy change for reaction 1. It is assumed that this standard-state free-energy change can be partitioned into a contribution from long-range electrostatic interactions *between subunits* and a contribution from configurations and interactions *within the binding site of a single subunit.* That is

$$\mu_{D_J(n_C)}{}^\circ - \mu_P{}^\circ - n_C\mu_C{}^\circ = A^{el}(n_C,J) - A^{el}(0) + n_C\Delta A^\circ \tag{5}$$

wherein $A^{el}(n_C,J)$ is the long-range electrostatic free energy of the complex $D_J(n_C)$ with n_C bound counterions in configuration J, $A^{el}(0)$ is the long-range electrostatic free energy of the naked polyion P with no bound counterions, and ΔA° is the free-energy change upon transferring a counterion in its standard state to a single binding site in its standard state. Upon defining the intrinsic equilibrium constant $\beta \equiv \exp[-\Delta A^\circ/kT]$ and combining eqs 4 and 5, one obtains

$$\frac{m_{D_J(n_C)}}{m_P} = \left(\frac{m_C\beta}{m_0}\right)^{n_C} \exp[-(A^{el}(n_C,J) - A^{el}(0))/kT] \tag{6}$$

The concentration of all possible complexes with all possible configurations is $m_D = \sum_{n_C}\sum_J m_{D_J(n_C)}$; hence

$$\frac{m_D}{m_P} = \sum_{n_C=1}^{N}\left(\frac{m_C\beta}{m_0}\right)^{n_C}\sum_J \exp[-(A^{el}(n_C,J) - A^{el}(0))/kT] = \chi(m_C,T,N) \tag{7}$$

wherein the last equality defines the *grand partition function* $\chi(m_C,T,N)$ and N is the number of subunits, or lattice sites, in the polyion. The relation $m_D = m_P\chi$ from eq 7 is combined with the conservation condition $m_P{}^\circ = m_P + m_D$ to yield

$$m_D = \left(\frac{\chi}{1+\chi}\right)m_P{}^\circ \tag{8}$$

where $m_P{}^\circ$ is the total analytical concentration of polyions. Under conditions when no counterions are bound (i.e., $n_C = 0$), then $\chi = 0$ and $m_D = 0$, so there are no complexes present. Under conditions when many counterions on the average are bound (i.e., $\bar{n}_C \gg 1.0$), then $\chi \gg 1.0$, $m_D \cong m_P{}^\circ$, and essentially all polyions exist as complexes with one or more bound ions. It is not necessary to consider here the intermediate case in which $\chi \sim 1.0$ and m_P is intermediate between 0 and $m_P{}^\circ$. The average number of bound counterions *per complex* is

$$\bar{n}_C = \frac{\sum_{n_C=1}^{N}\sum_J n_C m_{D_J(n_C)}}{\sum_{n_C=1}^{N}\sum_J m_{D_J(n_C)}} = m_C\frac{\partial \ln \chi}{\partial m_C} \tag{9}$$

The average number of bound counterions *per polyion,* whether naked or complexed, is

$$\bar{n} = \bar{n}_C \frac{m_D}{m_P^\circ} = 0, \quad \text{when no counterions are bound (i.e., } \bar{n}_C = 0\text{)}$$
$$= \bar{n}_C, \quad \text{when many counterions are bound per complex} \quad (10)$$

When many counterions are bound, one may approximate $\ln \chi$ by the natural logarithm of its maximum term in the sum over n_C.[11,12] This was previously shown to be a good approximation.[13] The extremum condition for that maximum term (from eq 7) is

$$\frac{\partial}{\partial n_C}\left\{ n_C \ln\left(\frac{m_C \beta}{m_0}\right) + \ln\left[\sum_J \exp[-(A^{el}(n_C,J) - A^{el}(0))/kT]\right]\right\} = 0 \quad (11)$$

We now assume that $A^{el}(n_C,J)$ consists of two contributions, namely, a *local* term $(A^{el}_{loc}(n_C,J))$ arising from electrostatic interactions *between nearest-neighbor subunits* and a *global* term $(A^{el}_{glo}(n_C))$ that represents the *mean-field* electrostatic interactions *between all nonadjacent subunits* (i.e., separated by one or more intervening subunits). This global term is calculated under the assumption that all nonadjacent sites exhibit the *average* occupation, or binding ratio, $r = n_C/N$, so it is *independent of the particular configuration J*. Incorporating this assumption, namely

$$A^{el}(n_C,J) - A^{el}(0) = A^{el}_{glo}(n_C) - A^{el}_{glo}(0) + A^{el}_{loc}(n_C,J) - A^{el}_{loc}(0) \quad (12)$$

into eq 11 yields

$$\ln(m_C\beta/m_0) - \frac{\partial}{\partial n_C}[A^{el}_{glo}(n_C) - A^{el}_{glo}(0)]/kT + \frac{\partial \ln W(n_C)}{\partial n_C} = 0 \quad (13)$$

wherein the quantity

$$W(n_C) \equiv \sum_J \exp[-(A^{el}_{loc}(n_C,J) - A^{el}_{loc}(0))/kT] \quad (14)$$

is called the *degeneracy factor*. The value of n_C that satisfies eq 13 is denoted by $\bar{n}_C$ and the corresponding binding ratio by $\bar{r} = \bar{n}_C/N$. Upon taking the antilog of eq 13, multiplying both sides by $\bar{r}$, and rearranging, we obtain a *formal* result for the binding isotherm

$$\frac{\bar{r}}{m_C} = \frac{\beta}{m_0}\exp\left[-\frac{\partial}{\partial n_C}A^{el}_{glo}(\bar{n}_C)/kT\right]F(\bar{r}) \quad (15)$$

wherein $F(\bar{r}) \equiv \bar{r}\exp[\partial \ln W(\bar{n}_C)/\partial n_C]$ is called the *occupation factor*. The derivatives in the exponents are to be evaluated at $\bar{n}_C$. The important point is that the degeneracy factor, which contains the effects of nearest-neighbor interactions, is the same function of n_C *whether or not* the global mean-field interactions are taken into account. Hence, the occupation factor $F(\bar{r})$ is the same function of $\bar{r}$ (or $\bar{n}_C$) even when $A^{el}_{glo}(\bar{n}_C) - A^{el}_{glo}(0)$ is arbitrarily set to zero. In that case, the binding isotherm corresponding to eq 15 is easily derived by an alternate route, as shown below, and the occupation factor $F(\bar{r})$ is explicitly identified. However, first it is necessary to determine the form of the electrostatic interactions and show that they can be partitioned as assumed in eq 12.

Figure 2. Schematic illustration of a very long linear polyion with a single univalent charge per subunit. The quantity q is the subunit charge, f is the average fraction of the charge that is not compensated by counterion condensation, and j denotes a particular subunit on the polyion.

Electrostatic Free Energy of the Straight Chain. Following Manning, the polyion is represented by a (straight) line of discrete charges with separation b. This polyion is immersed in a salt solution with Debye screening parameter $\lambda = (8\pi q^2/\epsilon kT)^{1/2}c_s^{1/2}$, wherein $c_s = N_s/V$ is the salt concentration, q is the ionic charge, and ϵ is the solvent dielectric constant. To compute the average electrostatic potential at the jth polyion charge, we employ the exact charges $f_{j-1}q$ and $f_{j+1}q$ at positions $j - 1$ and $j + 1$, respectively, but use the average charge $fq = (1 - r)q$ at all more distant positions, as indicated in Figure 2. The value of r will ultimately be determined by solving the final equation for the binding isotherm. In the Debye–Hückel approximation, the average electrostatic potential at the jth ion in the middle of the chain (due to all other ions) is

$$\langle\psi_j\rangle = 2\sum_{l=2}^{N/2}\frac{fq}{\epsilon b l}\exp[-\lambda b l] + (f_{j-1} + f_{j+1})\frac{q}{\epsilon b}\exp[-\lambda b] = -\frac{2fq}{\epsilon b}\ln(1 - e^{-\lambda b}) - \frac{2fq}{\epsilon b}\exp[-\lambda b] + (f_{j-1} + f_{j+1})\frac{q}{\epsilon b}\exp[-\lambda b] \quad (16)$$

The polyion chain is assumed to be infinitely long (i.e., $N \rightarrow \infty$) for the summation in eq 16, and the second equality follows from the first by exact evaluation of that infinite sum.[1,13,14] The charge factors (f_j) are defined by the rule $f_j = 0$, if a counterion is bound at the jth site, and $f_j = 1$, if that site is unoccupied. The first two terms in the second equality of eq 16 represent the global mean-field (or mean-occupation) contribution of distant sites to $\langle\psi_j\rangle$, whereas the last term represents the exact contribution of the nearest-neighbor sites for the particular configuration involved. The *electrostatic free energy of the jth site* is given by

$$A_j = \int_0^q \mathrm{d}q_j\langle\psi_j\rangle = \int_0^q f_j\,\mathrm{d}q\langle\psi_j\rangle = -f_j f\frac{q^2}{\epsilon b}\ln(1 - e^{-\lambda b}) - f_j f\frac{q^2}{\epsilon b}\exp[-\lambda b] + (f_j f_{j-1} + f_j f_{j+1})\frac{q^2}{2\epsilon b}\exp[-\lambda b] \quad (17)$$

The *total* electrostatic free energy of the chain is just the sum of the electrostatic free energies of the N individual sites. Ignoring end effects and using $\sum_j f_j = Nf$, one can write

$$A^{el}(n_C,J) = -\frac{Nf^2q^2}{\epsilon b}\ln(1 - e^{-\lambda b}) - \frac{Nf^2q^2}{\epsilon b}\exp[-\lambda b] + \frac{q^2}{\epsilon b}\exp[-\lambda b]\sum_{j=1}^{n} f_j f_{j+1} \quad (18)$$

The last term in eq 18 follows from the last term in eq 17 by noting that any particular term (except those containing $f_0 = 0$ and $f_{N+1} = 0$) occurs twice. The first two terms in eq 18 depend only on n_C (through $f = (1 - n_C/N)$), while the last term clearly depends on both n_C and the particular configuration J of the bound charges. Hence, $A^{el}(n_C,J)$ in eq 18 has the form assumed in eq 12, and one can make the identifications

$$A^{\mathrm{el}}_{\mathrm{glo}}(n_{\mathrm{C}}) = -\frac{Nf^2q^2}{\epsilon b}\ln(1 - e^{-\lambda b}) - \frac{Nf^2q^2}{\epsilon b}\exp[-\lambda b] \tag{19a}$$

$$A^{\mathrm{el}}_{\mathrm{glo}}(n_{\mathrm{C}}) - A^{\mathrm{el}}_{\mathrm{glo}}(0) = -\frac{N(f^2-1)q^2}{\epsilon b}\ln(1 - e^{-\lambda b}) - \frac{N(f^2-1)q^2}{\epsilon b}\exp[-\lambda b] \tag{19b}$$

$$A^{\mathrm{el}}_{\mathrm{loc}}(n_{\mathrm{C}},J) = \frac{q^2}{\epsilon b}\exp[-\lambda b]\sum_{j=1}^{N} f_j f_{j+1} \tag{20a}$$

$$A^{\mathrm{el}}_{\mathrm{loc}}(n_{\mathrm{C}},J) - A^{\mathrm{el}}_{\mathrm{loc}}(0) = \frac{q^2}{\epsilon b}\exp[-\lambda b]\sum_{j=1}^{N}(f_j f_{j+1} - 1) \tag{20b}$$

If it is desired to treat the nearest-neighbor interactions, as well as nonadjacent neighbor interactions, using just the mean-field (or mean-occupation) approach, then one must set $A^{\mathrm{el}}_{\mathrm{loc}}(n_{\mathrm{C}},J) - A^{\mathrm{el}}_{\mathrm{loc}}(0) = 0$ in eq 20b and simultaneously omit the second term in $A^{\mathrm{el}}_{\mathrm{glo}}(n_{\mathrm{C}}) - A^{\mathrm{el}}_{\mathrm{glo}}(0)$ in eq 19b.

Determination of $F(r)$ from Exact Nearest-Neighbor Statistics in the $N \to \infty$ Limit. We now set $A^{\mathrm{el}}_{\mathrm{glo}}(n_{\mathrm{C}}) - A^{\mathrm{el}}_{\mathrm{glo}}(0) = 0$, which is equivalent to neglecting interactions between *nonadjacent* subunits and treating only the nearest-neighbor interactions. Upon substituting this assumption and eq 20b into eq 12, which is in turn substituted into eq 7, the latter can be written as

$$\chi(m_{\mathrm{C}},T,N) = B\sum_{n_{\mathrm{C}}=1}^{N}\sum_{f_1}\sum_{f_2}\cdots\sum_{f_N}\left(\frac{m_{\mathrm{C}}\beta}{m_0}\right)^{\sum_{j=1}^{N}(1-f_j)} \times \sum_{j=1}^{N}(1 - f_j) = n_{\mathrm{C}}$$
$$\exp[-(q^2/\epsilon bkT)\exp[-\lambda b]\sum_{j=1}^{N} f_j f_{j+1}] \tag{21}$$

where $B = \exp[A^{\mathrm{el}}_{\mathrm{loc}}(0)/kT] = \exp[(Nq^2/\epsilon bkT)e^{-\lambda b}]$. The sum over each f_j runs from 0 to 1 and is subject to the indicated constraint. In the usual way, one can simultaneously omit the constraint and delete the sum over n_{C}, provided one also subtracts 1.0, corresponding to the case when all $f_j = 1$ (i.e., zero bound counterion at every site). We define new indices for successive subunits, $k = 1 + f_j$ and $l = 1 + f_{j+1}$, which run from 1 (bound counterion) to 2 (no bound counterion), and also the indexed free energies

$$F(1) = -kT\ln(m_{\mathrm{C}}\beta/m_0) \tag{22a}$$

$$F(2) = 0 \tag{22b}$$

$$F(1|1) = F(1|2) = F(2|1) = 0 \tag{22c}$$

$$F(2|2) = \frac{+q^2}{\epsilon bkT}\exp[-\lambda b] \tag{22d}$$

and note that χ can be written as

$$\chi(m_{\mathrm{C}},T,N) = B\{[\sum_{k=1}^{2}\sum_{l=1}^{2}\sum_{m=1}^{2}\cdots\sum_{z=1}^{2} e^{-F(k)/kT}e^{-[F(k|l)+F(l)]/kT} \times$$
$$e^{-[F(l|m)+F(m)]/kT}\cdots e^{-[F(y|z)+F(z)]/kT}] - 1.0\} \tag{23}$$

Equation 23 has the form of a continued matrix product in which the so-called transfer matrix has elements $M_{kl} = \exp[-(F(k|l) + F(l))/kT]$. Hence

$$\chi(m_{\mathrm{C}},T,N) = B\left\{\left(\frac{m_{\mathrm{C}}\beta}{m_0},1\right)\mathbf{M}^{N-1}\begin{pmatrix}1\\1\end{pmatrix} - 1.0\right\} \tag{24}$$

where

$$\mathbf{M} = \begin{pmatrix} X & 1\\ X & H\end{pmatrix} \tag{25}$$

and $X = m_{\mathrm{C}}\beta/m_0$ and $H = \exp[-q^2\exp[-\lambda b]/\epsilon bkT]$. The 1.0 term in eq 24 is negligible for $n_{\mathrm{C}} \geq 1$ and will henceforth be ignored. If $\mathbf{P}$ is the matrix that diagonalizes $\mathbf{M}$ by similarity transformation (i.e., $(\mathbf{P}^{-1}\mathbf{MP})_{lm} = \delta_{lm}\Lambda_m$), then one has

$$\chi(m_{\mathrm{C}},T,N) = B\left(\frac{m_{\mathrm{C}}\beta}{m_0},1\right)\mathbf{P}\begin{pmatrix}\Lambda_1^{N-1} & 0\\ 0 & \Lambda_2^{N-1}\end{pmatrix}\mathbf{P}^{-1}\begin{pmatrix}1\\1\end{pmatrix} \tag{26}$$

Since $\mathbf{M}$ is positive definite, its largest eigenvalue Λ_1 is nondegenerate. Hence, $\Lambda_1 > \Lambda_2$, and in the large-N limit Λ_2^{N-1} is negligible compared to Λ_1^{N-1}. One has finally in the large-N limit that

$$\chi(m_{\mathrm{C}},N) = \nu\Lambda^N \tag{27}$$

wherein $\Lambda = \Lambda_1$ is the largest eigenvalue of $\mathbf{M}$ and ν is a sum of terms, none of which contains m_{C} to a higher power than 1.0.

The next objective is to calculate the binding ratio $\bar{r}$ using eqs 9 and 27

$$\bar{r} = \frac{\bar{n}_{\mathrm{C}}}{N} = \frac{1}{N}X\frac{\partial\ln\nu\Lambda^N}{\partial X} \cong X\frac{\partial\ln\Lambda}{\partial X} \tag{28}$$

The characteristic equation for the transfer matrix $\mathbf{M}$ yields a relation between Λ and X, which can be combined with eq 28 to express Λ and $\partial\Lambda/\partial X$ in terms of $\bar{r}$ (instead of X), as shown in Appendix A. The final expressions for $\Lambda(\bar{r})$ and $\bar{r}/m_{\mathrm{C}}$ are given in eqs A5 and A6, respectively. Comparison of eq A6 with eq 15 for the case $A^{\mathrm{el}}_{\mathrm{glo}}(n_{\mathrm{C}}) - A^{\mathrm{el}}_{\mathrm{glo}}(0) = 0$ yields the occupation factor

$$F(\bar{r}) = \frac{2}{\Lambda H}\left[\Lambda\frac{(1-\bar{r})}{2} - \left(\bar{r} - \frac{1}{2}\right)(1 - H)\right] \tag{29}$$

This formula reduces to the well-known limit $F(\bar{r}) = 1 - \bar{r}$ when $H = 1$, which corresponds to no interactions between counterion binding sites. Equation A5 should be employed to determine Λ as a function of $\bar{r}$. With $F(\bar{r})$ from eq 29 and Λ from eq A5, eq 15 can now be evaluated for any choice of $A^{\mathrm{el}}_{\mathrm{glo}}(\bar{n}_{\mathrm{C}}) - A^{\mathrm{el}}_{\mathrm{glo}}(0)$.

Counterion Condensation for the Straight Chain. Upon inserting eq 19a into eq 15, taking the indicated derivative, setting $\bar{r} = r$ for simplicity, and rearranging somewhat, we obtain

$$\frac{r}{m_{\mathrm{C}}} = \frac{\beta}{m_0}(1 - e^{-\lambda b})^{-2(1-r)\xi}(\exp[e^{-\lambda b}])^{-2(1-r)\xi}F(r) \tag{30}$$

where $\xi \equiv q^2/\epsilon kbT$ is Manning's reduced linear charge density parameter. In fact, m_{C} is the total concentration of free counterions, *including those in the salt*, and practically $m_{\mathrm{C}} \cong c_{\mathrm{s}}$, where c_{s} is the salt concentration, because the polyions are so extremely dilute. In the case of low salt concentration, one has $\lambda b \ll 1.0$, $\exp[e^{-\lambda b}] \cong e$, and $H \cong \exp[-q^2/\epsilon bkT]$.

Equation 30 is very similar to the corresponding equation of Manning for the particular case of 1:1 univalent salt.[1,2] The quantity β/m_0 in eq 30 is equivalent to the free volume for counterion binding in Manning's theory. In addition, Manning's theory contains a counterion activity coefficient, which could also have been simply incorporated along with

m_C in the present theory, as noted above. The factor $\exp[-\phi_s]$, where ϕ_s is the osmotic coefficient of the salt, appears in Manning's result, but not in the present theory. The reason for this difference is not clear. In any case, Manning's theory is typically evaluated in the limit $\phi_s = 1.0$. Finally, the factor $(\exp[e^{-\lambda b}])^{-2(1-r)\xi}F(r)$ in eq 30 represents the effects of site binding with explicit consideration of fluctuations in nearest-neighbor interactions, which are due to fluctuations in nearest-neighbor occupations. This factor does not appear in Manning's theory, which treats nonlocal, or regional, binding of counterions into a free volume with only mean-field (or mean-occupation) interactions.

It is instructive to consider what modifications of the present approach yield Manning's theory. As noted by Dewey,[10] Manning's theory is equivalent to assuming that the entire polyion is a single large binding site onto which all of the counterions bind in the single most probable uniform configuration. In that case, the electrostatic free energy of the chain is just the mean-field contribution of the *first term* on the right-hand side of eq 18. This is substituted directly into eq 11 and the sum over configurations is, of course, omitted with the result that the last term (containing the degeneracy factor $W(n_C)$) on the left-hand side of eq 13 and the occupation factor $(F(\bar{r}))$ on the right-hand side of eq 15 are now absent. Finally, the factor $(\exp[e^{-\lambda b}])^{-2(1-r)\xi}F(r)$ in eq 30 is replaced by 1.0. In this modification of eq 30, the effects of both local site binding and fluctuations in nearest-neighbor interactions, or occupations, have been removed, and the result is essentially equivalent to Manning's theory.

With appropriate modifications, eq 30 can be applied to other special cases. For example, one can retain the effects of site binding (as opposed to regional binding into a common free volume) but remove the effects of fluctuations in nearest-neighbor interactions by setting both $(\exp[e^{-\lambda b}])^{-2(1-r)\xi} = 1.0$ and $F(r) = 1 - r$, which results from setting $H = 1.0$. One can also remove all effects of interactions between nonadjacent neighbors by replacing the factor $(1 - e^{-\lambda b})^{-2(1-r)\xi}(\exp[e^{-\lambda b}])^{-2(1-r)\xi}$ by 1.0 in eq 30.

It remains to determine $\beta = \exp[-\Delta A°/kT]$. $\Delta A°$ is that part of the standard free energy change upon ion binding that is attributable to configurations and interactions *within* the binding site. There is a surface surrounding the polyion outside of which the electrostatic potential is of the linear Debye–Hückel type. In the case of purely electrostatic binding, the bound counterions are considered to be confined to the domain inside this surface by the nonlinear part of the electrostatic potential. Here we determine β following the self-consistency argument of Manning.[1] We set $m_C = c_s$, $\lambda = Kc_s^{1/2}$, and take the limit $c_s \rightarrow 0$. In this limit we note that $1 - \exp[-\lambda b] \cong \lambda b = Kb\, c_s^{1/2}$, where $K \equiv (8\pi q^2/\epsilon kT)^{1/2}$. Equation 30 is rearranged to give

$$r = \frac{\beta}{m_0}(c_s)^{1-(1-r)\xi}(Kb)^{-2(1-r)\xi}e^{-2(1-r)\xi}F(r) \qquad (31)$$

The solution of eq 31 is different depending on whether or not $\xi \geq 1.0$.

(1) If $\xi < 1.0$, then the exponent of c_s, namely, $1 - (1 - r)\xi$, is *always positive* for r in its allowed range $0 \leq r \leq 1$. In this case, the factor containing c_s always vanishes in the limit $c_s \rightarrow 0$. Of course, $F(r)$ is finite when r lies in its allowed range $0 \leq r \leq 1.0$. Hence, the entire right-hand side of eq 31 vanishes in the limit $c_s \rightarrow 0$ for any allowed value of r. The left-hand side vanishes only for $r = 0$, which is the unique solution in this case. Hence

$$r = 0 \quad \text{when } \xi < 1.0 \qquad (32)$$

(2) If $\xi > 1.0$, then the exponent of c_s can be either positive or negative. Now, in the limit $c_s \rightarrow 0$, there is no self-consistent solution for r *except that which causes the exponent of* c_s *to vanish*, namely, $1 - (1 - r)\xi = 0$, or $r = 1 - \xi^{-1}$.[1,2] This is easily seen by noting that the factor containing c_s vanishes (in the limit $c_s \rightarrow 0$) when its exponent is positive, which occurs for $r > 1 - \xi^{-1}$. Hence, when $r > 1 - \xi^{-1}$ and $c_s \rightarrow 0$, the entire right-hand side of eq 31 vanishes, but of course the left-hand side cannot. On the other hand, the factor containing c_s diverges to infinity (in the limit $c_s \rightarrow 0$) when its exponent is negative, which occurs for $r < 1 - \xi^{-1}$. Thus, when $r < 1 - \xi^{-1}$ and $c_s \rightarrow 0$, the right-hand side of eq 31 diverges, but of course the left-hand side cannot. Thus, the only possible solution (in the limit $c_s \rightarrow 0$) is

$$r = 1 - \xi^{-1} \quad \text{when } \xi \geq 1.0 \qquad (33)$$

In this case, β is determined from the self-consistency condition that eq 31 be obeyed when eq 33 is substituted for r. This yields

$$\beta = \frac{(1 - \xi^{-1})m_0(Kbe)^2}{F(1 - \xi^{-1})} \quad \text{for } \xi \geq 1.0 \qquad (34)$$

Note that the molarity of solvent (m_0) drops out of the binding isotherm when this value of β is substituted into eq 30 or 31.

Equation 34 is just a modification of Manning's expression for the free volume that takes account of site binding and fluctuations in nearest-neighbor interactions and applies when $\xi \geq 1.0$. In general, $F(r)$ approaches 1.0 when $r \rightarrow 0$; hence $F(1 - \xi^{-1})$ approaches 1.0 when ξ *declines* toward 1.0 from above. Thus, from eq 34, one many conclude that β also approaches 0 as ξ declines toward 1.0 from above. We infer that, *for purely electrostatic binding*

$$\beta = 0 \quad \text{for } \xi \leq 1.0 \qquad (35)$$

How should one treat the circumstance when nonelectrostatic (more precisely nonionic) as well as electrostatic interactions contribute to the site binding of an ion? Let β_{ne} denote the *nonelectrostatic* binding constant. The solution for r in eqs 32 and 33 must still apply *in the limit* $c_s \rightarrow 0$, but β must be everywhere at least as large as β_{ne}. We propose that one should set β equal to β_{ne} for $\xi \leq 1.0$ and set β equal to the larger of β_{ne} or β in eq 34 when $\xi \geq 1.0$. The singularity in eq 31 in the limit $c_s \rightarrow 0$ is so strong that the solution for r can be made arbitrarily close to that in eq 33, *regardless of the value of* β, just by taking c_s sufficiently small. This indicates that the self-consistency criterion used to determine β is not rigorously binding and may actually admit some ambiguity. Nevertheless, we treat only the example of purely electrostatic binding in this work and retain the β value in eq 34, which represents the self-consistent solution of eq 31.

It is interesting to examine the value of β for the particular case when site binding is retained, but the effects of fluctuations in nearest-neighbor interactions are removed. In this case $H = 1$, $F(r) = 1 - r$, and the factor e in eq 34 is replaced by 1.0. Hence, eq 34 becomes $\beta = (1 - b/L_B)(8\pi L_B^2 b)m_0$, where $L_B = q^2/\epsilon kT$ is the Bjerrum length. The factor m_0 is a trivial consequence of the conversion from mole fraction to molar units. The remaining factor, $(1 - b/L_B)(8\pi L_B^2 b)$, might be interpreted to imply that each bound counterion occupies the volume of a cylinder with length b and radius $a = (8(1 - b/L_B))^{1/2}L_B$. With decreasing charge separation b, this radius rises

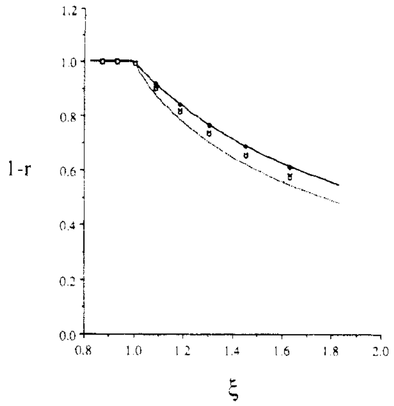

Figure 3. Fraction of the polyion charge $(1 - r)$ that is not compensated by counterion condensation vs the reduced charge density parameter (ξ) for straight-chain polyions. The parameters used for all of these curves are $b = 8.73$ Å and $T = 293$ K. The solid line is Manning's limiting law, $r = 1 - \xi^{-1}$. The solid diamonds are computed using the full straight-chain theory in eqs 30, 32, 34, and 36 with $c_s = 10^{-7}$ M. The dotted line at the bottom is also computed using the full straight-chain theory in eqs 30, 32, 34, and 36 with $c_s = 4$ mM. The crosses are calculated for the case when fluctuations in nearest-neighbor interactions are omitted but site binding is retained. This calculation uses eqs 30, 32, 34, and 36 with $c_s = 4$ mM, but the product of the last two factors in eq 30 is set to $1 - r$ and the factor $e^2/F(1 - \xi^{-1})$ in eq 34 is set to ξ. The circles are calculated for the case when both nearest-neighbor interactions and site binding are omitted, which corresponds to Manning's theory at finite c_s. This calculation uses eqs 30, 32, 34, and 36 with $c_s = 4$ mM, but the product of the last two factors in eq 30 is set to 1.0 and the factor $e^2/F(1 - \xi^{-1})$ in eq 34 is also set to 1.0.

monotonically from $a = 0$ at $b = L_B$ up to a maximum value $a = 8^{1/2}L_B$ at $b = 0$. In contrast, when the effects of both site binding and fluctuations in nearest-neighbor interactions are omitted, which corresponds to Manning's theory, eq 34 becomes $\beta = (1 - b/L_B)(8\pi L_B b^2)m_0$, which differs from the preceding value by the factor b/L_B. With decreasing charge separation b, the effective radius in this case, namely, $a = (8(1 - b/L_B)bL_B)^{1/2}$, rises from $a = 0$ at $b = L_B$ up to a maximum value $a = 2^{1/2}L_B$ at $b = L_B/2$ and then declines back to $a = 0$ at $b = 0$.

At realistic (nonvanishing) salt concentrations, one can solve eq 30 or eq 31 numerically for r. When the total concentration of polyion subunits, $Nm_P°$, is not negligible compared to the salt concentration, c_s, the conservation equation for counterions, namely

$$m_C = c_s + (1 - r)Nm_P° \qquad (36)$$

must be taken into account. This was done in the present calculations, even though the salt concentration substantially exceeds the subunit concentration (i.e., $c_s = 13.5Nm_P°$).

Effects of Fluctuations in Nearest-Neighbor Interactions. The present theory, manifested in eqs 30 and 34, contains the effects of both site binding and fluctuations in nearest-neighbor interactions. Nevertheless, the present theory yields the same binding ratio, r, as Manning's theory in the limit $c_s \to 0$. These limiting r values are given by eqs 32 and 33, and the resulting $(1 - r)$ values are plotted vs ξ in Figure 3, where they appear as the top curve. When c_s is finite, eqs 30 and 36 are solved numerically for r using the β value from eq 34, the given value of c_s, and a range of ξ values that brackets 1.0. In view of eq 35, no binding occurs (i.e., $r = 0$) for $\xi < 1.0$ even at finite c_s. The solutions for $\xi > 1.0$ are found by a one-dimensional grid search along the r coordinate. Such calculations are carried out for $c_s = 10^{-7}$ M and for $c_s = 4$ mM, and the resulting $(1 - r)$ values are plotted vs ξ in Figure 3. The $(1 - r)$ values for $c_s = 10^{-7}$ M essentially coincide with the limiting $(1 - r)$ values for $c_s \to 0$. The $(1 - r)$ values for $c_s = 4$ mM, which is the prevailing salt concentration in the experiments of Klein and Ware,[3] define the bottom curve in Figure 3. Although the combined effects of site binding, fluctuations in nearest-neighbor interactions, and the finite salt concentration act to increase r slightly above the limiting law values, these effects are clearly insufficient to account for the results of Klein and Ware,[3] which are shown in Figure 1.

When fluctuations in nearest-neighbor interactions are omitted, but site binding is retained, eqs 30 and 34 are modified in the following way. The factor $(\exp[e^{-\lambda b}])^{-2(1-r)\xi}F(r)$ is set to $(1 - r)$ on the right-hand side of eq 30, as noted above, and the factor $e^2/F(1 - \xi^{-1})$ is set to ξ in eq 34. This modified eq 30 and eq 36 are solved numerically for r using this modified eq 34, the same value of c_s (4 mM), and the same range of ξ values employed previously. The resulting $(1 - r)$ values are plotted vs ξ in Figure 3. Comparison of these points with the bottom curve described above indicates that fluctuations in the nearest-neighbor interactions cause only a small increase in binding ratio. This is just another example of how mean-field theories work rather well in Coulomb and screened Coulomb interactions.

When the effects of both site binding and fluctuations in nearest-neighbor interactions are omitted, the present theory goes over to Manning's theory. The r values predicted by Manning's theory for finite c_s (4 mM) are computed in the following way. As noted above, eq 30 is transformed to Manning's theory when the factor $(\exp[e^{-\lambda b}])^{-2(1-r)\xi}F(r)$ on its right-hand side is replaced by 1.0. Likewise, the factor $e^2/F(1 - \xi^{-1})$ on the right-hand side of eq 34 also must be replaced by 1.0. This modified eq 30 and eq 36 are solved numerically for r using this modified eq 34, the same value of c_s (4 mM), and the same range of ξ values as in the previous examples. The resulting $(1 - r)$ values are plotted vs ξ in Figure 3. As noted by Manning, the fraction r of bound counterions at $c_s = 4$ mM is not much larger than predicted by the limiting law.

A comparison of the two lowest "curves" with the limiting law in Figure 3 indicates that most of the difference between the present theory for $c_s = 4$ mM and the limiting law is actually due to the effect of the finite salt concentration, while the combined effects of site binding and fluctuations in nearest-neighbor interactions increase r by a smaller amount. Comparison of the two middle "curves" shows that the inclusion of site binding without taking fluctuations in nearest-neighbor interactions into account actually decreases r very slightly (or increases $(1 - r)$ very slightly) in comparison to the case when neither site binding nor fluctuations in nearest-neighbor interactions are taken into account. In other words, the restriction to site binding without taking nearest-neighbor interactions into account yields slightly less counterion binding than Manning's theory for $c_s = 4$ mM. However, incorporating both fluctuations in nearest-neighbor interactions and site binding yields slightly more counterion binding than Manning's theory for $c_s = 4$ mM.

General Remarks Concerning the Effects of Bending on Counterion Binding. We consider here only inextensible polyions whose contour length does not change upon bending. Spontaneous thermally excited bending of an intrinsically stiff polymer can influence its counterion binding in two different ways. (1) Polyion bending *directly* increases counterion binding by decreasing the spacing between all polyion charges except for nearest neighbors.[13,14] (The statement in a recent review[15] that counterion binding is not affected to second order in the bending angle is incorrect. The counterion binding is indeed altered to second order in the bending angle, but that has no effect on the electrostatic contribution to the bending rigidity through second order in the degree of bend or curvature.[16]) (2) Counterion binding reduces the electrostatic contribution to the bending rigidity and thereby increases the bending partition function and decreases the free energy associated with that. In other words, counterion binding enhances the configurational entropy of the bending degrees of freedom. The resulting decrease in bending free energy upon counterion binding acts *indirectly* to promote counterion binding. The *direct* and *indirect* effects of bending on counterion binding are discussed separately below.

Indirect Effect of Bending on Counterion Binding. When bending is allowed, the polyion is no longer straight, but can still be represented by a chain of contiguous bond vectors of equal length (b) connecting the charges. The bending rigidity (κ) is related to the bending torque constant (κ_b) between bond vectors by $\kappa = \kappa_b b$.[17] The internal configuration of a chain of N bond vectors is completely specified by the set of solid angles $(\phi_2,\beta_2;\phi_3,\beta_3;...,\phi_N,\beta_N)$, where ϕ_j,β_j are the polar coordinates of the jth bond vector in the "frame" of the $(j-1)$th bond vector. The coordinate frame of the jth bond vector is chosen so that $\hat{\mathbf{z}}_j$ lies along that bond vector and $\hat{\mathbf{x}}_j$ (perpendicular to $\hat{\mathbf{z}}_j$) lies in the plane containing $\hat{\mathbf{z}}_{j-1}$ and $\hat{\mathbf{z}}_j$. The configurational part of the bending partition function is

$$Z_b = \int ... \int \prod_{j=2}^{N} (\mathrm{d}\phi_j\, \mathrm{d}\beta_j \sin \beta_j) e^{-[\kappa_b/(2kT)]\Sigma_{l=2}{}^{N}\beta_l{}^2} = [\int_0^{2\pi} \mathrm{d}\phi \int_0^{\infty} \mathrm{d}\beta\, \beta e^{-[\kappa_b/(2kT)]\beta^2}]^{N-1} = \left[\frac{2\pi kT}{\kappa_b}\right]^{N-1} \quad (37)$$

In the evaluation of Z_b, it is assumed that the chain is sufficiently stiff that the β_j are restricted to small values for which $\sin \beta \cong \beta$ and the upper limit on the integral can be extended to ∞. In the large-N limit, the (configurational) free energy of bending is

$$A_b = -kT \ln Z_b = -NkT \ln \left(\frac{2\pi kT}{\kappa_b}\right) = -NkT \ln (2\pi b/P) \quad (38)$$

where $P = b\kappa_b/kT$ is the persistence length.

Typically P has both intrinsic (P_0) and electrostatic (P_{el}) contributions, such that[13,14,17]

$$P = P_0 + P_{el} \quad (39)$$

The electrostatic persistence length, $P_{el} = P_{el}(n_C)$, is here assumed to depend only on the number n_C of bound counterions, but not on their arrangement along the chain. In this sense, $P = P(n_C)$ and $A_b = A_b(n_C)$ are mean-field, or mean-occupation, results that depend only on n_C. We assume that eq 38 is a useful approximation even when P_{el} makes a substantial, or dominant, contribution to P. However, when $P_0 \ll \lambda^{-1}$, the bending potential can no longer be regarded as entirely local, and eq 38 may become inaccurate. Indeed, for some sufficiently small P_0, A_b should become the configurational free energy of a charged random coil with the appropriate excluded volume interactions. In any case, the configurational free energy of the bending degrees of freedom is generally decreased by counterion binding and therefore acts to promote that. Thus, eq 38 will yield qualitatively correct predictions in this regard.

In the presence of thermally excited bending the free-energy change for reaction 1 becomes

$$\mu_{D_J(n_C)}{}^\circ - \mu_P{}^\circ - n_C\mu_C{}^\circ = A^{el}(n_C,J) - A^{el}(0) + A_b(n_C) - A_b(0) + n_C\Delta A^\circ \quad (40)$$

in place of eq 5. The additional term $A_b(n_C) - A_b(0)$ accompanies $A^{el}(n_C,J) - A^{el}(0)$ in eqs 6, 7, and 11 as well. Equation 15 is modified to become

$$\frac{\bar{r}}{m_C} = \frac{\beta}{m_0} \exp\left[-\frac{\partial}{\partial n_C} A^{el}_{glo}(\bar{n}_C)/kT\right] \times \exp\left[-\frac{\partial}{\partial n_C} A_b(\bar{n}_C)/kT\right] F(\bar{r}) \quad (41)$$

The electrostatic persistence length is given by[13-16,18]

$$P_{el} = f^2 L_B/4\lambda^2 b^2 \quad (42)$$

wherein $L_B = q^2/\epsilon kT$ is the Bjerrum length and $f = (1 - r) = (1 - n_C/N)$ is the mean fractional charge on each subunit. The quantity b applies to the *straight* polyion under the same conditions. Substituting eqs 19a, 38, 39, and 42 into eq 41, taking the indicated derivatives, setting $\bar{r} = r$, and rearranging somewhat yields

$$\frac{r}{m_C} = \frac{\beta}{m_0}(1 - e^{-\lambda b})^{-2(1-r)\xi}(\exp[e^{-\lambda b}])^{-2(1-r)\xi} F(r) \times \exp\left[\frac{\dfrac{(1-r)\xi}{2\lambda^2 b}}{P_0 + \dfrac{(1-r)^2\xi}{4\lambda^2 b}}\right] \quad (43)$$

The last factor in eq 43 is the indirect contribution of the bending partition function to counterion binding. It should be noted that when $\xi < 1.0$, this last factor must be omitted, because in that case $f = 1.0$ is independent of n_C, so the derivative of P_{el} and A_b with respect to n_C vanishes. Since the argument in the exponent of the last factor is positive and $e > 1.0$, this factor is always greater than or equal to 1.0, so it acts to *enhance* counterion binding as expected. It is important to note that the parameters b and ξ *in the last (indirect bending) factor* must apply to the corresponding *straight* chain. Because it is the *straight-chain parameters* that govern both the bending rigidity (up to second order in the degree of bend) and the bending free energy $A_b(\bar{n}_C)$, the factor β in eq 43 also takes its straight-chain value. In other words, the straight-chain value of β applies to both the straight and (weakly) bent configurations in eq 43.

In the limit $c_s \to 0$, P_0 is negligible compared to P_{el} and can be ignored. In that case the last factor reduces to $\exp[+2/(1 - r)]$, which is independent of c_s. Hence, this factor does not affect the solution for $\bar{r}$ in the limit $c_s \to 0$. In other words, this indirect effect of bending does not change the nature of the singularity in the function $r(c_s)$ when $c_s \to 0$. The indirect effect of bending amounts simply to an extra contribution to β that depends on c_s away from the $c_s \to 0$ limit.

Direct Effect of Bending. A statically bent polyion exhibits a slightly smaller *effective* charge spacing b_c and a slightly larger *effective* linear charge-density parameter ξ_c, as shown below, which in turn cause a slightly larger binding ratio $r = r_0 + r'$ than the corresponding straight-chain value $r_0 = 1 - \xi^{-1}$. The detailed argument is as follows.

The polyion is represented by a smooth line of contour length Nb which lies in a plane where it is uniformly bent through an arc θ. The distances between nonadjacent charges are taken to be the appropriate chords of the arc.

For simplicity, the distances between nearest-neighbor charges are taken to be a constant independent of θ. This would actually be the case if the polyion consisted of single bond vectors connecting the charges. In any case, the error incurred by invoking this approximation is very small. The electrostatic free energy of such a uniformly bent polyion was evaluated previously to order θ^2.[13-16] It again consists of a global mean-field term

$$A_{\mathrm{glo}}^{\mathrm{el}}(n_{\mathrm{C}},\theta) = \frac{Nf^2q^2}{\epsilon b}\left[\ln(1-e^{-\lambda b}) - \frac{1}{24}\left(\frac{\theta}{N}\right)^2 \frac{e^{\lambda b}}{(e^{\lambda b}-1)^2} \times \left(1 + \frac{\lambda b(e^{\lambda b}+1)}{e^{\lambda b}-1}\right)\right] - \frac{Nf^2q^2}{\epsilon b}\exp[-\lambda b] \quad (44)$$

and the same local term $A_{\mathrm{loc}}^{\mathrm{el}}(n_{\mathrm{C}})$ as appears in eq 20a. In this approximation, only the global term depends upon θ. It was shown previously that the entire first term in $A_{\mathrm{glo}}^{\mathrm{el}}(n_{\mathrm{C}},\theta)$ in eq 44 can be written correct to order θ^2 in the same form as the first term in $A_{\mathrm{glo}}^{\mathrm{el}}(n_{\mathrm{C}})$ in eq 19a, provided that $\lambda b \ll 1.0$.[16] Using the result in the limit $\lambda b \ll 1.0$ yields

$$A_{\mathrm{glo}}^{\mathrm{el}}(n_{\mathrm{C}},\theta) = \frac{Nf^2q^2}{\epsilon b_{\mathrm{c}}}\ln(\lambda b_{\mathrm{c}}) - \frac{Nf^2q^2}{\epsilon b} \quad (45)$$

wherein the *effective* b value for the curved polyion is

$$b_{\mathrm{c}} = b + b' \quad (46)$$

and[16]

$$b' = -\frac{b}{8}\frac{1}{(1-\ln(\lambda b))(\lambda b)^2}\left(\frac{\theta}{N}\right)^2 \le 0 \quad (47)$$

The effect of bending is to decrease b by an amount ($|b'|$) proportional to $(\theta/N)^2$. Since b' depends on the salt concentration, it is not simply geometrical in origin but arises instead from rewriting the first term in eq 44 in the form of the first term in eq 45, which is precisely the form for a straight polyion with spacing b_{c} between charges. Incorporating eq 45 into eq 41, taking the indicated derivatives, setting $\bar{r} = r$, and rearranging somewhat yield

$$\frac{r}{m_{\mathrm{C}}} = \frac{\beta}{m_0}(\lambda b_{\mathrm{c}})^{-2(1-r)\xi_{\mathrm{c}}} e^{-2(1-r)\xi} F_0(r)\exp\left[\frac{\dfrac{(1-r)\xi}{2\lambda^2 b}}{P_0 + \dfrac{(1-r)^2\xi}{4\lambda^2 b}}\right] \quad (48)$$

wherein

$$\xi_{\mathrm{c}} = \frac{q^2}{\epsilon b_{\mathrm{c}} kT} = \xi\left(\frac{b}{b+b'}\right) \quad (49)$$

and $F_0(r)$ is evaluated using b and ξ instead of b_{c} and ξ_{c}. The only manifestation of the direct bending effect on the polyion is the appearance of ξ_{c} and b_{c} in place of ξ and b, respectively, in the second factor on the right side of eq 48. In any case, the direct effect of bending can be omitted simply by setting $b_{\mathrm{c}},\xi_{\mathrm{c}} \to b,\xi$, and the indirect effect of bending can be omitted by setting the last factor equal to 1.0.

The quantity $(\theta/N)^2$ in eqs 44–49 must be replaced by an appropriate mean-squared bending angle per bond vector $\langle(\theta/N)^2\rangle$ for relevant thermally excited arcs. An *upper bound* could be obtained by setting

$$\langle(\theta/N)^2\rangle = \langle\eta^2\rangle = 2b/P \quad (50)$$

where η is the polar angle between any two adjacent bond vectors. The well-known relation between $\langle\eta^2\rangle$ and the persistence length[17] is used to obtain the final equality in eq 50. However, a fluctuating filament does not bend uniformly, and the bending of successive bond vectors is not coherent or correlated as would be implied by the use of eq 50. That is, the bending between one pair of adjacent bond vectors is not sustained over an arc longer than two bond vectors. A better estimate of $\langle(\theta/N)^2\rangle$ would be the mean-squared bending angle per bond vector for a polyion *segment* with a length L such that the sum in the electrostatic potential (e.g., the first term in eq 16) is largely, but not entirely, converged. Such a segment length is $L = \lambda^{-1}$, which would contain $M = \lambda^{-1}/b$ subunits, or bond vectors. In this case we identify $\langle(\theta/N)^2\rangle$ with $\langle(\eta_{1M}/M)^2\rangle$, where $\langle(\eta_{1M})^2\rangle$ is the mean-squared polar angle of the Mth bond vector in the frame of the first. That is our best estimate of the mean-squared angle of arc for such a segment. $\langle(\eta_{1M})^2\rangle$ is evaluated by noting that for a weakly bending segment

$$\begin{aligned} 1 - \langle(\eta_{1M})^2\rangle/2 = \langle\cos\eta_{1M}\rangle &= \langle\cos\eta\rangle^{M-1} \\ &= (1-b/P)^{M-1} \\ &\cong 1-(M-1)b/P \end{aligned} \quad (51)$$

The first line is derived elsewhere,[17] and the well-known relation[17] $P = b/(1-\langle\cos\eta\rangle)$ is used to obtain the second line from the first. We now set

$$\left\langle\left(\frac{\theta}{N}\right)^2\right\rangle = \frac{\langle(\eta_{1M})^2\rangle}{M^2} = \frac{2(M-1)}{M^2}\frac{b}{P} \cong \frac{2}{M}\frac{b}{P} = 2\lambda\frac{b^2}{P} \quad (52)$$

Incorporating eq 52 into eq 47 yields finally

$$b' = -\frac{b}{8}\frac{1}{(1-\ln\lambda b)(\lambda b)^2}\left(2\lambda\frac{b^2}{P}\right) \quad (53)$$

Equation 53 is used to calculate b', which in turn is substituted into eqs 46 and 49 to calculate b_{c} and ξ_{c}, respectively, for use in eq 48. Although this procedure for estimating a suitable average value of $\langle(\theta/N)^2\rangle$ is somewhat ad hoc, it will be found that the direct effect of bending is small compared to the indirect effect of bending in any case.

It is interesting to examine the behavior of b' in the limit as $c_{\mathrm{s}} \to 0$. When $c_{\mathrm{s}} \to 0$, $P_{\mathrm{el}} \propto c_{\mathrm{s}}^{-1}$ diverges, so $P = P_0 + P_{\mathrm{el}}$ also diverges as c_{s}^{-1}. In addition, $\lambda \propto c_{\mathrm{s}}^{1/2}$. Hence, in the limit $c_{\mathrm{s}} \to 0$, one has $b' \propto (-)c_{\mathrm{s}}^{1/2}/(-\ln c_{\mathrm{s}}^{1/2}) \to 0$. Thus, in the limit $c_{\mathrm{s}} \to 0$, there is no decrease in effective charge spacing, because significant bending does not occur due to the infinite electrostatic persistence length. There is no direct effect of bending in the low salt limit, as might have been expected. In eq 48, then, one must replace $b_{\mathrm{c}},\xi_{\mathrm{c}}$ by b,ξ in the limit $c_{\mathrm{s}} \to 0$. Hence, direct bending also does not change the nature of the singularity in the function $r(c_{\mathrm{s}})$ or alter the limiting solution, $r_0 = 1 - \xi^{-1}$, as $c_{\mathrm{s}} \to 0$.

The final result of this work is eq 48, which contains both the direct and indirect effects of bending, as well as the effects of site binding and fluctuations in nearest-neighbor interactions. In the evaluation of eq 48 it is necessary to employ also eq 34 for β, eqs 46 and 53 for b_{c}, eq 49 for ξ_{c}, and the conservation equation (36) when that is necessary.

Comparison with Experimental Data. To evaluate eq 48 it is necessary to know the charge spacing b, the dielectric constant ϵ, and the intrinsic persistence length P. Klein and Ware give $b = 8.73$ Å for their 6,6-ionene polyion and give the Bjerrum length indirectly through the values of $\xi = e_0^2/\epsilon bkT$ but do not report a value for P_0 (or P).[3] In the absence of a firm estimate for P_0, binding curves are calculated for several arbitrary choices, $P_0 = 5$,

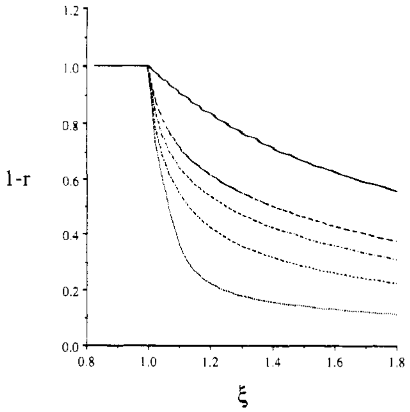

Figure 4. Fraction of the polyion charge $(1 - r)$ that is not compensated by counterion condensation vs reduced charge density parameter (ξ) for polyions with different intrinsic persistence lengths (P_0). All curves are calculated using $b = 8.73$ Å, $T = 293$ K, and $c_s = 4$ mM, except where noted. The topmost solid curve is the limiting law of Manning, which applies for $P_0 = \infty$ and $c_s = 0$. The other curves are calculated using eqs 32 and 48 together with eqs 34, 36, 49, and 53. The values of the intrinsic persistence length are (from top to bottom) $P_0 = 40$, 20, 10, and 5 Å.

10, 20, and 40 Å. These results are displayed in Figure 4 along with the limiting law of Manning given by eqs 32 and 33. With increasing ξ above 1.0, counterion condensation in all cases sets in much more rapidly when bending is taken into account than is predicted by any of the theories for straight polyions displayed in Figure 3. By performing calculations (not shown) in which either the indirect effect or the direct effect of bending was omitted, it could be ascertained that the enhancement of counterion binding is due almost entirely to the indirect effect of bending. The curve for $P_0 = 10$ Å is coplotted with the experimental data in Figure 1. Given the repeating subunit, $({}^+N(CH_3)_2CH_2CH_2CH_2CH_2CH_2CH_2)$, of the 6,6-ionene polymer, an intrinsic persistence length near 10 Å is at least plausible. This calculation predicts that the total persistence length decreases by approximately 5-fold from $P = 64$ Å at $\xi = 1.0$ to $P = 13$ Å at $\xi = 1.74$. Because the polyion coil is largely free drained in electrophoresis, the decrease in coil dimensions would *not* be sensitively manifested in the electrophoretic mobility but should be reflected in the diffusion coefficient. Under very favorable conditions the diffusion coefficient governs the width of the Doppler-shifted peak in the power spectrum of the heterodyne correlation function in electrophoretic light scattering experiments. Unfortunately, no information regarding that diffusion coefficient is available in this case.

The unusually good agreement between the theoretical curve and the experimental data in Figure 1 should be regarded cautiously for several reasons. First, the actual intrinsic persistence length of the polyion might differ significantly from the chosen value, $P_0 = 10$ Å. Second, the assumed value of P_0 is substantially smaller than the Debye screening length, λ^{-1}. Under such conditions, the validity of certain aspects of the theory becomes very questionable. For example, the average degree of bend of a contour length equal to λ^{-1} may become large enough that the second-order (in θ) contribution no longer provides an accurate account of the electrostatic free energy; hence the electrostatic contribution to the bending rigidity is no longer entirely local, and the validity of the bending partition function in eq 38 is no longer strictly valid. Also, the assumption implicit in eq 48 that all molecules exhibit the same uniform degree of counterion condensation along their length, regardless of variations in the local curvature, becomes increasingly inaccurate for large bending amplitudes. Unfortunately, we have no quantitative estimate of how much error is introduced by the breakdown of these assumptions. In any case, one would expect qualitatively similar behavior from a more complete theory. Finally, as discussed by Klein and Ware, the determination of the effective charge from the electrophoretic mobility is a somewhat inexact science. In any case, the relative change in $(1 - r)$ follows closely the measured relative change in electrophoretic mobility, which gives us some hope that we are fitting the right quantity.

The good agreement between theory and experiment suggests that the enhancement of counterion condensation by bending may be responsible for most of the rapid onset of condensation as ξ increases beyond 1.0 in the case of the 6,6-ionene polymer. For much stiffer polymers, such as DNA, and salt concentrations such that $P_{el} \ll P_0$, the counterion binding would be expected to follow more closely the straight-chain result, which is not much different from Manning's limiting law.

Different Ways to Vary ξ. At a given temperature ξ can be increased either by decreasing the dielectric constant ϵ, as done by Klein and Ware, or by decreasing the average polyion charge spacing b, for example, by titration. However, one may expect to see somewhat different effects on counterion binding depending on which parameter is varied and the prevailing conditions. For example, β varies with b, apart from ξ, as b^2. Thus, β will be smaller when ξ is increased by decreasing b than when ξ is increased by the same amount by decreasing ϵ. In the low-salt limit such that $P_{el} \gg P_0$, the indirect bending factor in eqs 43 and 48 becomes $\exp[2\xi] = \exp[2q^2/\epsilon bkT]$, which is affected equally by changes in ϵ or b. In the high-salt limit such that $P_0 \gg P_{el}$, the indirect bending factor is approximately 1.0 and independent of ϵ or b. Thus, under these conditions, namely, $P_0 \ll P_{el}$ or $P_0 \gg P_{el}$, and at finite salt concentration (where the value of β has some influence), a decrease in b will produce less counterion bending than the same relative decrease in ϵ. In the intermediate regime, when $P_{el} \sim P_0$, the indirect bending factor becomes $\exp[(\epsilon/b)g/(P_0 + (\epsilon/2b)(\epsilon bkT/q^2)g]$, where $g = kT/(16\pi q^2 c_s)$. In this intermediate regime, the indirect bending factor is increased more by a decrease in b than by the same relative decrease in ϵ, and this counteracts the smaller β value caused by the decrease in b. In this regime, then, the increase in counterion binding when ξ is increased by decreasing b should be more nearly comparable to that when ξ is increased by decreasing ϵ.

One may also find different effects on persistence length, depending on which parameter is varied. The electrostatic persistence length in eq 42 is evaluated in terms of elementary quantities using the limiting law $r = 1 - \xi^{-1}$ to give $P_{el} = \epsilon^2(kT)^4/(32\pi q^2 c_s) \propto \epsilon^2 b^0$ when $\xi \geq 1.0$. Thus, the electrostatic persistence length is independent of b but decreases rapidly when ϵ decreases. To the extent that P_{el} determines the envelope of the polyion coil, its hydrodynamic radius, and its diffusion coefficient in solution, those quantities will vary in strong response to changes in ϵ but not in response to changes in b. Hence, one does not expect to see any abrupt change in diffusion coefficient as ξ is increased beyond 1.0 by decreasing b. Thus, there is not necessarily any contradiction between the abrupt drop in electrophoretic mobility *with decreasing* ϵ (as ξ increases past 1.0) reported by Klein and Ware[3] and the smooth variation in diffusion coefficient *with decreasing* b (as ξ increases past 1.0) reported by Kowblansky and Zema.[19]

A Possible Explanation for Structural Transitions near $\xi = 1.0$. In a recent paper Manning[20] discussed discrepancies between counterion condensation theory and certain experimental data[21-26] in the region $\xi < 1.0$, at least some of which are linked to a structural transition from a more compact to a more extended conformation near $\xi = 1.0$. In those experiments, b and also ξ are varied either by copolymerization of charged and neutral residues or by titration. Manning suggested that the onset of counterion condensation may trigger an abrupt structural transition from a locally folded (possibly helical or even condensed) state that prevails for $\xi < 1.0$ to an extended state that prevails for $\xi > 1.0$. The present theory suggests a mechanism for such a relatively abrupt increase in relative stability of the extended state, namely, the rather abrupt decrease in its bending free energy due to the rather abrupt onset of counterion condensation and the consequent reduction of its persistence length and increase in its bending partition function as ξ increases past 1.0. To demonstrate such behavior, the counterion binding ratio r and the bending free energy per subunit ($-kT \ln (b/P)$) are calculated for an extended conformation of a linear polyion, which has an intrinsic subunit spacing $b_0 = 3.2$ Å and an intrinsic persistence length $P_0 = 10$ Å, and also for a locally contracted and stiffer state of the same polyion, which has an intrinsic subunit spacing $b_1 = 0.9 \times 3.2 = 2.88$ Å and an intrinsic persistence length $P_1 = 30$ Å. Both ξ and the mean spacing b between charges are varied by adjusting the relative fractions of charged and uncharged subunits, but the structural subunit spacings b_0 and b_1, which appear only in the respective bending partition functions in eq 38, remain constant. The binding ratios r of each state are calculated for the case when both site binding and the effects of fluctuations in nearest-neighbor interactions are omitted, so the factors $e^{-2(1-r)\xi}F(r)$ in eq 48 and $e^2/F(1 - \xi^{-1})$ in eq 34 are set to 1.0. The bending free energies per subunit are calculated for each state using eq 38 (divided by N) with b_0 or b_1 in place of b, together with eqs 39 and 42 with the variable mean charge spacing b. It is assumed throughout that the ratio of the average charge spacing of the locally contracted state to that of the extended conformation remains equal to 0.9 as ξ is varied. Hence, the reduced charge density parameter (ξ') of the locally contracted state is always related to that (ξ) of the extended conformation by $\xi' = \xi/0.9 = 1.11\xi$. The resulting bending free energies per subunit for both states are plotted vs the reduced charge density ξ *of the extended conformation* in Figure 5. An arbitrary constant has been added to the bending free energy per subunit of the locally contracted state to position it below the curve for the extended conformation over the region from $\xi = 0.6$ to $\xi = 1.17$. For this particular disposition of free energies, a relatively abrupt transition from the locally contracted state to the extended conformation is predicted to occur at $\xi = 1.17$. The swing in relative stability of these two states between $\xi = 0.9$ and $\xi = 1.6$ amounts to about 500 cal/mol subunit, which is comparable to the range of transition free energies inferred from titration data by Dubin and Strauss.[22] It is thus plausible that the onset of counterion condensation could "trigger" a structural transition from a locally contracted state to a more extended and more flexible conformation.

One could also imagine a situation in which the onset of counterion condensation triggers a structural transition from a globally condensed state to an extended conformation. In this scenario, a condensed state would remain stable with respect to a relatively stiff extended conformation that prevails for $\xi < 1.0$, but when ξ (for the extended conformation) increases past 1.0, counterion binding sets in rather abruptly, as shown in Figure 4, the persistence length decreases rather abruptly (provided the intrinsic value P_0 is not too large), and the bending free energy decreases accordingly. If the decrease in bending free energy of the extended conformation is sufficiently large, the free energy of the extended conformation will now lie below that of the compact state and the structural transition is "triggered". The reader is cautioned that these proposed scenarios for structural transitions are highly speculative and are predicated in any case on rather delicately balanced structural equilibria. However, as Manning points out,[20] it is time to begin thinking about the ways in which counterion condensation might act to trigger structural transitions near $\xi_{ext} = 1.0$.

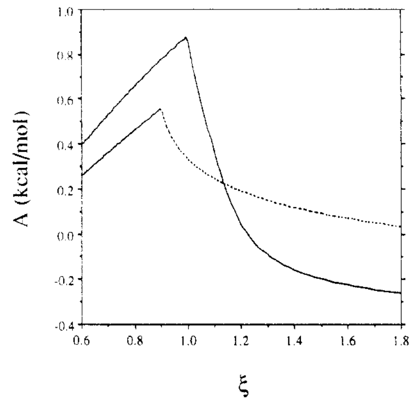

Figure 5. Bending free energy plus an arbitrary constant per mole of subunits (A) vs reduced charge density parameter of *the extended conformation* (ξ). The solid line is the bending free energy of the extended conformation of a linear polyion, which has an intrinsic subunit spacing $b_0 = 3.2$ Å and an intrinsic persistence length $P_0 = 10$ Å. The dashed line is a constant plus the bending free energy of a locally contracted and stiffer state of the same linear polyion, which has an intrinsic subunit spacing $b_1 = 0.9 \times 3.2 = 2.88$ Å and an intrinsic persistence length $P_1 = 30$ Å. ξ is varied by adjusting the relative fractions of charged and uncharged subunits. The ratio of the average charge spacing of the locally contracted state to that of the extended conformation remains equal to 0.9 as ξ is varied. The reduced charge density parameter of the locally contracted state (ξ') is always related to that of the extended conformation (ξ) by $\xi_1 = \xi/0.9 = 1.11\xi$. The binding ratios r for each state of the polyion are calculated for the case when both site binding and fluctuations in nearest-neighbor interactions are omitted. Hence, the factors $e^{-2(1-r)\xi}F(r)$ in eq 48 and $e^2/F(1 - \xi^{-1})$ in eq 34 are set to 1.0. The bending free energies are calculated using eqs 38 (divided by N), 39, and 42. A constant is added to the bending free energy of the contracted state so that it lies below that of the extended conformation between $\xi = 0.6$ and $\xi = 1.17$. In this case, the extended conformation becomes the stable conformation for $\xi > 1.17$ due to the considerably larger decrease in its bending free energy as ξ increases beyond 1.0.

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Appendix A. Binding Isotherm in the Absence of Global Interactions

We start from eqs 26 and 27 in the text. The characteristic equation for the matrix **M** is $(X - \Lambda)(H - \Lambda) - X = 0$. This gives

$$\Lambda^2 = \Lambda(H + X) - HX + X \tag{A1}$$

Equation 28 can be rewritten as

$$\frac{\bar{r}}{X} = \frac{\partial \ln (\Lambda^2)^{1/2}}{\partial X} = \frac{1}{2\Lambda^2}\frac{\partial \Lambda^2}{\partial X} \tag{A2}$$

Substituting (A1) into (A2), completing the derivative, and solving for X gives

$$X = -\frac{\bar{r}\Lambda H/2}{\bar{r}(\Lambda/2 - H + 1) - (1/2)(\Lambda - H + 1)} \qquad \text{(A3)}$$

Equation A3 gives X in terms of $\bar{r}$ and Λ. Dividing eq A1 by Λ yields an equation for Λ in terms of X

$$\Lambda = H + X + (1 - H)\frac{X}{\Lambda} \qquad \text{(A4)}$$

Substituting X in eq A3 into (A4) yields a relation between Λ and $\bar{r}$ alone, which can be solved to yield

$$\Lambda = \left\{-(1-\bar{r})(1-H) + \frac{1}{2} + \left[\left((1-\bar{r})(1-H) - \frac{1}{2}\right)^2 + \frac{4(1-\bar{r})^2}{4}H(1-H)\right]^{1/2}\right\} \Big/ (1-\bar{r}) \qquad \text{(A5)}$$

Now, rearranging eq A3 gives finally

$$\frac{\bar{r}}{m_{\mathrm{C}}} = \frac{\beta}{m_0}\frac{2}{\Lambda H}\left[\frac{\Lambda(1-\bar{r})}{2} - \left(\bar{r} - \frac{1}{2}\right)(1-H)\right] \qquad \text{(A6)}$$

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