Polyelectrolyte Excluded Volume Paradox

M. Fixman* and J. Skolnick

Department of Chemistry, Yale University, New Haven, Connecticut 06520.

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ABSTRACT: Straightforward application of the Debye–Hückel screened Coulomb interaction to the excluded volume effect in polyelectrolytes is known to give estimates of the segment–segment excluded volume that may be too large by several orders of magnitude. It is argued that the major defect in this application lies in a conventional assumption of excluded volume theory that does not apply to charge interactions, rather than in the electrostatic potential itself. This assumption is that the cooperative interaction of neighboring segment pairs is unimportant because the interaction is weak. An attempt is made to restore the applicability of this assumption through the choice of a segment that incorporates many monomer units. The segment is modeled as a rod and is required to be longer than the Debye screening length. A numerical value has to be chosen for the linear charge density but not for the contour length of the rod. The present work reproduces the conventional formula for the excluded volume if the charge density is very low, but much smaller values are found for practical applications. An illustrative application is made to poly(acrylic acid), for which the charge density is chosen to be about twice the structural value for the extended configuration, in agreement with previous work. The Debye–Hückel interaction is found to work quite well.

I. Introduction

The expansion of polyelectrolyte chains due to repulsion between backbone charges is much less than most theories predict. The evidence and theories have been reviewed by Nagasawa et al.[1,2] It seems fair to conclude that those theories which do agree with experiment do so only at high charge densities and at the expense of ad hoc assumptions of uncertain merit. We certainly do not exclude from this comment a contribution by one of us.[3] What seems especially paradoxical is the apparent failure of Debye–Hückel theory to give even a qualitative explanation of the degree of expansion as a function of salt concentration. We propose to show here that the Debye–Hückel theory actually works reasonably well, and that its apparent failure in the usual method of application is due to other approximations made in conventional excluded volume theory. Our focus is on the paradox, and there are many aspects of the problem that we treat superficially, especially the charge condensation and internal conformations of a segment. So we still fall short of a conclusive theory.

One aspect of a complete theory, in the context of a worm model, is the variation of persistence length with ionic strength and linear charge density (real or effective). This has been considered elsewhere by ourselves and others.[4-8] We allow this variation here only to the limited extent that the length of a segment is allowed to depend adjustably on the charge density, but not on the ionic strength. A more careful treatment is omitted for several reasons. (1) The qualitative failure of Debye–Hückel theory is so striking as to require consideration separate from relatively minor corrections. (2) We are not content with the current theory of electrostatic effects on the persistence length (in regard to the applicability of the worm model, the effect of polymer dielectric constant and salt exclusion on the charge interactions,[9] and the nature of the effective charge correction). (3) Within the limits of current theory, the effect of a variable persistence length on excluded volume theory has already been analyzed clearly by Odijk and Houwaart.[8]

Several calculations of the electrostatic potential of rods and cylinders[10-14] indicate that the linearized Poisson–Boltzmann equation gives the correct potential out in the solvent if an effective charge density is used to describe the backbone. For fully charged native DNA the effective charge may be only a fourth of the actual charge, but for chain polymers the fraction will be higher, and for poly(acrylic acid) a maximum decrease of one-half should be about right. And at a degree of ionization of one-half the correction would vanish. But the failure of the Debye–Hückel interaction in excluded volume theory is still gross and we therefore conclude, with Nagasawa and Takahashi,[1] that something has gone wrong in its application.

The simplest use of the Debye–Hückel interaction adequately shows the problem. In this use the interaction is substituted into the theory of uncharged polymers, for which the degree of expansion is a function of z. This parameter will be considered fully below. For the present it suffices that z is proportional to $M^{1/2}$, where M is the molecular weight, and to X, where X is the excluded volume that two segments of the chain present to each other. Since the whole theory of the excluded volume effect for nonelectrolytes, and especially its modern versions based on scaling and renormalization, has considered the limits where M is large and X is small, it is natural to suppose that a segment is a single monomer unit, and that the interaction between two segments is just the screened Coulomb or Debye–Hückel interaction. For large Debye screening lengths this at once makes X inversely proportional to the salt concentration C, and $z \propto M^{1/2}/C$. But experiment indicates that z is proportional to $[M/C]^{1/2}$, which is, of course, a qualitatively different scaling.

The observed proportionality of z to the Debye length has motivated, we presume, certain plausible recalculations[8,15] of X that in effect replace the segment by a long cylinder of effective exclusion radius proportional to the Debye length. This model may seem reasonable enough at high charge densities, but requires ad hoc adjustments for low charge densities. Moreover, the only work known to us that comes close to a justification of the model is Onsager's calculation of the osmotic second virial coefficient for charged colloidal particles,[16] and that work we find insufficient to our needs for several reasons. First, the electrostatic part of the calculation was based on the interaction between infinite charged planes. Second, the modification made to that interaction to make it applicable to thin rods was ad hoc (but correct of course!), and left unspecified as a basic multiplicative constant for the interaction energy. And third, the calculation yields no insight into the apparent failure of Debye–Hückel theory for the excluded volume effect.

The present treatment begins with a division of the chain into segments which consist of many monomer units,

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and with an excluded volume potential that is simply the sum of all screened Coulomb interactions between backbone charges. The use of a large segment makes the application of conventional excluded volume theory[17] somewhat questionable, because of the implied limits of large M and small X. Unfortunately, it is not possible to observe these limits for any polyelectrolyte as the value of X computed for even a single pair of discrete charges may become large. That is, X may become comparable to or larger than the cube of the distance between adjacent backbone charges. Hence, an assumption of excluded volume theory that a segment has negligible interaction with its immediate neighbors and interacts only with segments distant along the backbone is no longer valid. To salvage the validity of this assumption, which seems quite essential in the two-parameter (or "scaled") excluded volume theory, we choose very large segments and hope that any new problems thereby incurred are not too serious. One of these problems is that the enlarged segment has a conformational distribution that can depend on the degree of ionization and salt concentration. Here we shall simply make a bald simplification that has much precedence in polyelectrolyte theory. We take the segment to be, more or less, a stiff rod with an adjustable length, and see whether lengths inferred from previous thermodynamic applications of the same model can be transferred to the current problem. In time, of course, this neglect of conformational fluctuations could be remedied. However, it seemed reasonable to us to deal first with the basic question concerning the Debye–Hückel theory.

In section II the values of X and z are computed for the given model, and it is shown that the usual result, $X \propto 1/C$, is recovered exactly for very low charge densities. However, an application to experiment in section III shows that the actual charge densities, even at a degree of ionization of one-tenth, are so large that the usual result is inapplicable. Although the electrostatic potential at any point may be small enough in practice to justify the Debye–Hückel approximation, the total interaction between segments is too large to be linearized in the calculation of X. Of course, for this remark to be meaningful it is necessary, as in the rest of the calculation, that the segments are small enough to be modeled as rods. A certain amount of bending would not be serious, but even so a few persistence lengths is all one would wish to allow. In fact we must use somewhat longer segments for chains with low degrees of ionization. Although it is never necessary to specify their exact length, they must be a bit longer than the Debye length to justify neglect of interactions between neighbors.

II. The Segment Excluded Volume

The excluded volume parameter X is the effective volume of exclusion that one segment presents to another, and has the general form

$$X = \int \langle 1 - e^{-v} \rangle \, d\mathbf{r} \tag{II.1}$$

where v is the interaction potential in units of kT, $\mathbf{r}$ is the difference between center of mass positions, and the angle brackets represent an average over internal coordinates. The complete potential is conveniently divided into contributions

$$v = v_c + v_a + v_e \tag{II.2}$$

from a core potential v_c, an attractive potential v_a, and a screened Coulomb potential v_e. The core potential is infinite or zero and may be used immediately to separate off a positive core contribution X_c,

$$X = X_c + \int{}' \langle 1 - \exp[-(v_a + v_e)] \rangle \, d\mathbf{r} \tag{II.3}$$

where the primed integral sign designates an integral over those values of the relative coordinates that do not violate the region of exclusion. An additional formal subdivision of X gives

$$X = X_c + X_e + X_a \tag{II.4}$$

where

$$X_e = \int{}' \langle 1 - e^{-v_e} \rangle \, d\mathbf{r} \tag{II.5}$$

and

$$X_a = \int{}' \langle e^{-v_e}(1 - e^{-v_a}) \rangle \, d\mathbf{r} \tag{II.6}$$

In practice X_e, the purely electrostatic part of X, will swamp other contributions at low salt concentrations unless the backbone charge is very low. The attractive part X_a is formally dependent on salt concentration, since v_e is dependent, but at the short distances where v_a is significant this dependence is not large, and X_a may be taken independent of salt concentration in first approximation. Our work is consequently restricted to a calculation of X_e.

A. The Electrostatic Interaction. For the calculation of v_e and X_e a rather schematic model is adopted. The segment is treated as a rigid rod of length L, and L is assumed to be much larger than the Debye screening length. We may argue, following Onsager,[16] that the results should also apply to flexible segments, if L is taken to be somewhat less than the contour length, unless the flexibility is so great or the segments so long that several close contacts between a given segment pair are allowed. But even if this possibility is allowed by chain flexibility, we expect it to be excluded by energetic factors except at low degrees of ionization I, and there the additional contributions will be minimized by a coefficient I^2. Consequently the model may serve, at least as a rough approximation, for any I.

A uniform charge distribution along the axis of each segment, or rod, gives

$$v_e = \int \int u(r_{ij}) \, di \, dj \tag{II.7}$$

where

$$u(r) = \beta^2 a_0 r^{-1} e^{-\kappa r} \tag{II.8}$$

In these expressions di and dj are elements of length measured along the two rods, and a_0 = 7.136 Å for an aqueous solution at 25 °C. β is the number of electron charges per unit length and has units (length)$^{-1}$. It is convenient for the evaluation of the integral[16] to set up a coordinate system in which the first rod is oriented along the z axis and centered on the origin, and the second rod makes a polar angle θ with the z axis. The value of the other orientational angle turns out to be irrelevant. The projection of the second rod on the xy plane will have length $L \sin \theta$. We define p to be the perpendicular distance from this projection to the origin, and require $|p| \geq d$, where d is the diameter of either rod. However, it is helpful in visualization and consistent with the model to regard p as infinitesimal on the scale of L. If the perpendicular intersects the projection outside its end points, the two rods are taken to have neglible interaction. Then

$$v_e = \int_{-\infty}^{\infty} \int u([p^2 + i^2 + j^2 - 2ij \cos \theta]^{1/2}) \, di \, dj \tag{II.9}$$

Extension of the limits to infinity is justified by the as-

Table I
Numerical Values of the Integral $R(y)$ Are Given and Compared with the Asymptotic Formula for Large y

y	$R(y)/y$	y	$R(y)$	$R(y)$ (asymptotic)
0.1	0.9633	1.5	0.9795	0.9235
0.2	0.9301	2.0	1.1754	1.1494
0.3	0.8996	2.5	1.3373	1.3247
0.4	0.8714	3.0	1.4742	1.4679
0.6	0.8205	3.5	1.5922	1.5890
0.8	0.7757	4.0	1.6955	1.6938
1.0	0.7359	5.0	1.8696	1.8691

sumption that L is much greater than the Debye length. Introduction of polar coordinates for i and j and completion of the integrals gives

$$v_e = 2\pi\beta^2 a_0(\kappa \sin\theta)^{-1} \exp(-\kappa|p|) \qquad \text{(II.10)}$$

This is the result put forward by Onsager, except for a proportionality constant previously left unspecified.[16]

B. The Excluded Volume. For the computation of X there remains an integration over relative center of mass coordinates and an average over the angle θ. The three orthogonal displacements for the center of mass of rod 2 are taken along the axis of p, along the z axis, and along a third orthogonal axis. The latter two displacements are restricted to values that do not eliminate the intersection defined above, and do not alter v_e within their allowed range. Their integrals give factors L and $L \sin\theta$, respectively. Then

$$X_e = 2L^2\left\langle \sin\theta \int_d^\infty (1 - e^{-v_e})\, dp \right\rangle \qquad \text{(II.11)}$$

The factor of 2 accounts for negative p; the average over θ must be taken with weight $\sin\theta$.

The remaining integrations in eq II.11 cannot be completed in closed form. The simplest expression seems to be

$$X_e = (2L^2/\kappa)R(w); \quad w \equiv 2\pi\beta^2 a_0 \kappa^{-1} e^{-\kappa d} \qquad \text{(II.12)}$$

where

$$R(y) \equiv \int_0^{\pi/2} d\theta \sin^2\theta \int_0^{y/\sin\theta} x^{-1}(1 - e^{-x})\, dx \qquad \text{(II.13)}$$

or[18]

$$R(y) = \int_0^{\pi/2} d\theta \sin^2\theta [E_1(y/\sin\theta) + \ln(y/\sin\theta) + \gamma] \qquad \text{(II.14)}$$

A numerical tabulation of $R(y)$ is given in Table I, and limiting forms are easily obtained. For small y

$$\lim_{y\to 0} y^{-1}R(y) = 1 \qquad \text{(II.15)}$$

and for large y the asymptotic form,

$$R(y) \sim (\pi/4)(\ln y + \gamma - \tfrac{1}{2} + \ln 2) \qquad \text{(II.16)}$$

is accurate to within 2% for $y > 2$, and to within 0.5% for $y > 3$. In the work of Odijk and Houwaart,[8] $R(y)$ is replaced by a constant.

C. The Low Charge Limit. We now wish to verify that our results are consistent with conventional ones for chains of very low charge density. Of course there is no point in a direct comparison of values for X_e, because the usual calculation implies a somewhat different "segment" than used here. However, if a two-parameter theory is to be used, corresponding values of

$$z = (3/2\pi h_0^2)^{3/2} n^2 X \qquad \text{(II.17)}$$

can be compared. Here h_0 is the root-mean-square end-to-end distance and is to be considered an experimentally determined quantity. So the comparison of electrostatic contributions to z comes down to n^2X_e. The same quantity, along with z, enters the theory of the osmotic second virial coefficient.

In the usual calculation, reduced to its essentials, there are n_0 small segments which can be identified with individual monomer units. Each has excluded volume X_0 calculated from

$$X_0 = \beta_0^2 a_0 \int r^{-1} e^{-\kappa r}\, d\mathbf{r} = 4\pi a_0 \beta_0^2/\kappa^2 \qquad \text{(II.18)}$$

where β_0 is the charge on a segment. That is, one assumes, as was discussed in the Introduction, a weak potential and linearizes the Boltzmann expression. Comparison of $n_0^2X_0$ with n^2X_e under conditions of low charge density, where $R(w)$ can be replaced by w, shows that agreement is found if $n_0\beta_0 = nL\beta$. Since each of these quantities is an expression for the total charge, agreement is indeed found.

III. Comparison with Experiment

Disclaimers regarding the finality of this comparison have already been entered in the Introduction. We repeat that our object is to resolve the fundamental paradox, and not to deal with every ramification.

A. Intrinsic Viscosity. The intrinsic viscosity data of Noda et al.[2] will serve to illustrate the theory. They analyzed their data on the basis of

$$[\eta]/M^{1/2} = K_0 + 0.51\Phi_0 B M^{1/2} \qquad \text{(III.1)}$$

where $\Phi_0 = 2.87 \times 10^{21}$, K_0 is a constant related to h_0 but of no present interest, and B is inferred from the data. The origin of this equation will be quite briefly reviewed. It relies on the assumption that the chain is nondraining and on a semiempirical form for the expansion

$$[\eta] = \Phi_0 h_0^3 \alpha_\eta^3/M \qquad \text{(III.2)}$$

$$\alpha_\eta^3 = 1 + A_\eta z \qquad \text{(III.3)}$$

where A_η is a coefficient inferred from an excluded volume perturbation theory. To the somewhat questionable extent that eq III.2 and III.3 provide an adequate basis for an understanding of eq III.1, they imply, together with the definition of z, eq II.17, that the electrostatic part of B is

$$B_e = aX_e/m_s^2 = A_\eta(3/2\pi)^{3/2}X_e/0.51m_s^2 \qquad \text{(III.4)}$$

$$m_s = M/n$$

where the value of a is to be inferred from A_η, and m_s is the molecular weight of a segment. Noda et al. chose $A_\eta = 1.55$, on the basis of theoretical estimates available at the time for nonelectrolyte polymers. More recent estimates[19] put A_η in the vicinity of 1.1, for nonelectrolytes, and as light-scattering data on polyelectrolytes suggest a still smaller value, we have used $a = 0.5$, corresponding to $A_\eta = 0.775$.

Equation II.12 now gives

$$B_e = (L^2/m_s^2\kappa)R(w) = R(w)/m_l^2\kappa \qquad \text{(III.5)}$$

where m_l is the molecular weight (i.e., the mass in Daltons), per unit length. In what follows m_l and β will be referred to a single monomer of effective length l,

$$m_l = m_s/L = m_0/l \qquad \beta = I/l \qquad \text{(III.6)}$$

where m_0 is the molecular weight of a monomer unit and I is the mean number of elementary charges on a monomer unit, i.e., I is the degree of ionization. An effective charge

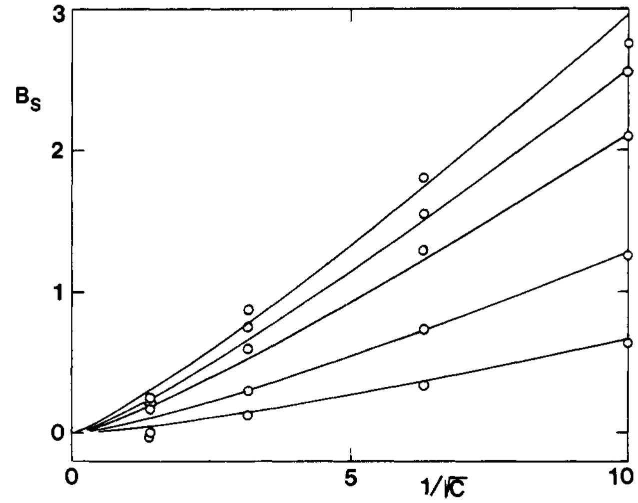

Figure 1. The scaled excluded volume parameter, $B_s = 10^{26}B_e$, vs. $1/C^{1/2}$, where C is the salt concentration in mol/L. Points are experimental results of Noda et al.[2] and the curves are theoretical. The values of (I,l), where I is the degree of ionization and l is the effective length of a monomer unit in ångströms, are, from bottom to top: (0.103, 0.8), (0.2, 1.0), (0.4, 1.15), (0.6, 1.2), (1.0, 1.2).

can be used if one wishes, but it would have little effect because of the logarithmic dependence on I through most of the relevant range of w. Then

$$B_e = (l^2/\kappa m_0^2)R(w) \tag{III.7}$$

where

$$w = (2\pi a_0 I^2/l^2\kappa)e^{-\kappa d} \simeq 136.4I^2/l^2C^{1/2}$$

$$\kappa^{-1} \simeq 3.043\ \text{Å}/C^{1/2} \tag{III.8}$$

and l is expressed in Å, C in mol/L. The numerical expressions involving C apply to a 1–1 salt and imply the neglect of κd.

Equation III.7 is compared with the data of Noda et al.[2] in Figure 1. A value $m_0 = 94$ g/mol has been used, and the value of l has been allowed to vary somewhat from its structural value of 2.51 Å. For $I = 1$ the value chosen, $l = 1.2$ Å, is close to the value inferred from titration and thermodynamic studies.[20,21] We have used values, listed in the caption for Figure 1, down to 0.8 Å for $I = 0.1$. The largest value of w occurs at $I = 1$ and $C = 0.01$ where $w = 947$, $R(w)/w = 0.006$. In other words, the actual segment excluded volume is 0.6% of the usual result given by eq II.18. For $I = 0.1$ at $C = 0.01$, $w = 4.58$ and $R(w)/w = 0.39$.

The agreement between theory and experiment seems good enough to justify the fairly modest conclusion put forward in the Introduction, that the Debye–Hückel approximation is reasonably adequate for the study of excluded volume problems, instead of being paradoxically bad.

B. Osmotic Second Virial Coefficient. The osmotic second virial coefficient is given by theory[17] as

$$A_2 = (N_{AV}n^2X/2M^2)h(\bar{z}) = N_{AV}R(w)h(\bar{z})/\kappa m_1^2 \tag{III.9}$$

where X has again been approximated by X_e, the latter to be obtained from eq II.12, and $h(z)$ is a decreasing function of z that is still, like α or α_η, not known exactly. However, for our present purposes, we may refer to the discussion of Nagasawa and Takahashi,[1] where it is shown that $h(\bar{z})$ decreases rather rapidly from unity to ca. 0.5 as z increases, and thereafter decreases quite slowly, or perhaps even levels off, depending on which theoretical formula is used to fit the data. We have simply put $h(\bar{z}) = 0.5$. The parameter w is calculated from eq III.8.

Table II
Experimental Osmotic Second Virial Coefficients from Orofino and Flory[16] Compared with Theoretical Results

I	C	10^4A_2 (exptl)	l	10^4A_2 (theory)
0.102	0.10	5.95	0.8	7.6
0.335	0.10	22.2	1.1	23.6
0.344	0.01	69.5	1.1	94.5
0.947	1.00	10.0	1.2	10.4
0.959	0.10	43.9	1.2	40.3
0.994	0.01	196	1.2	152.0

A comparison with the data of Orofino and Flory[22] for poly(acrylic acid) is given in Table II. The agreement between theory and experiment is about as good as the intrinsic viscosity comparison.

IV. Discussion

A referee has complained of our "overly casual attitude toward the numerical values" of I and l and insisted that there is only one correct choice consistent with a "thorough assimilation of the total polyelectrolyte literature". This choice is said to be $l = 2.5$ Å, the structural value, and $I = 0.35$, or the actual degree of ionization, whichever is less. These values are asserted to be consistent with an application of Manning's theory to titration and thermodynamic data on poly(acrylic acid). The referee further remarks that B_e(calcd)/B_e(obsd) = 2.4 for the fully charged chain in 0.01 M salt.

We think it appropriate again to refer the reader to Odijk and Houwaart[8] for calculations in which these refinements are included. Their use of an effective exclusion radius proportional to the Debye length is equivalent to replacing $R(y)$ by a constant, in comparison to our $R(y) \sim \ln y$. Our "casual" attitude to parameters will be excused, we hope, by two points: (a) the limited purpose of our work, which is to explain why $R(y) = y$ is inadequate even at fairly low degrees of ionization, and (b) our feeling that a conceptually acceptable quantitative theory requires a better account of chain curvature under all circumstances, and also, for large I, a better account of the potential than we are currently able to give. We accept the referee's warning against "the opinion that for any quantity x that appears in a polyelectrolyte theory, x has the range $-\infty < x < \infty$", and have confined our adjustments of l to the positive axis.

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Charge Interactions in Cylindrical Polyelectrolytes

J. Skolnick and M. Fixman*

Department of Chemistry, Yale University, New Haven, Connecticut 06520.

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ABSTRACT: The Debye–Hückel equation is solved for the electrostatic interaction of point charges on the surface of a dielectric cylinder immersed in salt water. Numerical results are given for the potential as a function of axial separation for charges on the same side and on opposite sides of the cylinder, and for two values of the Debye screening length: infinity and unity, in units of the cylinder radius. Major deviations from the interaction in bulk solvent are found. The analytical results are also applied to the self-energy of a helical distribution of charge, and that part $\Delta\Psi$ of the self-energy which depends on salt concentration is isolated. The deviation of $\Delta\Psi$ from its value for a uniformly charged cylinder is evaluated as a function of screening length. The deviation is small for DNA, and smaller for the α helix. The deviation from a line of charge self-energy is much more significant, but all expressions for $\Delta\Psi$ agree if the salt concentration is low.

I. Introduction

Although linear polyelectrolytes have been extensively studied for many years, the influence of the low dielectric constant backbone on the potential of mean force between a charge on the polymer and another ion is not well understood. We have studied this potential on the basis of classical electrostatic theory, which is supplemented by Debye–Hückel screening. One would like to know under what conditions, if any, the backbone behaves as if it were electrostatically invisible.

We cannot hope to summarize the vast body of polyelectrolyte literature which in one way or another models the low dielectric constant effect; rather a brief review emphasizing the ideas that influenced the present work will be undertaken.

An early consideration of the effect of a local dielectric constant appears in the work of Kirkwood and Westheimer[1,2] on the electrostatic influence of substituents on the dissociation constants of organic acids. The organic acid is treated as a spherical, and subsequently ellipsoidal, low dielectric constant region within which an arbitrary discrete collection of charges is located. The molecule is assumed to be immersed in salt-free, bulk solvent. Kirkwood and Westheimer express the electrostatic free energy in two parts: one part represents the Coulomb interaction of charges immersed in an infinite medium of dielectric constant characteristic of the molecule, and the other part gives boundary corrections. Buff et al.[3] and Beveridge et al.[4] have recently noted many related problems and devised several solutions for spherical boundaries. Harris and Rice[5] considered spheres permeated by salt solution and included appropriate screening.

A wide class of polyelectrolytes is more appropriately modeled by cylindrical rather than spherical domains. Hill[6] has solved the linearized Poisson–Boltzmann, or Debye–Hückel equation, for a uniformly charged cylinder immersed in bulk solvent. The result appears in terms of modified Bessel functions, and will be displayed later. It is of interest to observe that the potential outside the cylinder is independent of the dielectric constant inside, as is the charging free energy. But there is no reason to assume a priori that the potential for a more realistic charge distribution will remain independent of the interior dielectric constant. Indeed, the latter turns out to have large effects on the potential of discrete charge distributions.

For discussions of charge condensation, we refer to the literature.[7,8] Evidence exists that the linearized Poisson–Boltzmann equation describes the electrostatic potential outside the layer of condensed ions, and our use of that equation may therefore be consistent with condensation. But this work is concerned with a solution of the linearized equation, and not with its domain of application.

In section II the linearized Poisson–Boltzmann equation is solved for a discrete source charge located on the surface of a dielectric cylinder. The more general case is considered elsewhere.[9] The cylinder is supposed impermeable to the salt solution in which it is immersed and to have a dielectric constant D_0 different from the bulk value D. The solution to this problem is equivalent to a determination of the interaction free energy between two charges, one of which is on the cylinder. Numerical results are given for the special case that both charges are on the surface of the cylinder, either on the same or on opposite sides, and separated by an axial distance z.

In section III helical charge distributions of arbitrary pitch are considered. The solution to this problem is relevant to the calculation of colligative properties, and

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