Macromolecules **1980**, *13*, 335-338

(16) A similar equation was used to interpret intramolecular excimer formation by M. J. Goldenberg, J. Emert, and H. Morawetz, *J. Am. Chem. Soc.*, **100**, 7171 (1978).
(17) (a) G. Weill and J. des Cloizeaux, *J. Phys. (Paris)*, **40**, 100 (1979); (b) P. G. deGennes, *Macromolecules*, **9**, 587 (1976); (c) J. des Cloizeux, *J. Phys. (Paris), Colloq.*, **C2**, 135 (1978).
(18) J. L. Martin, M. S. Sykes, and F. T. Hioe, *J. Chem. Phys.*, **46**, 3478 (1967).
(19) P. H. Verdier and W. H. Stockmayer, *J. Chem. Phys.*, **36**, 227 (1962).

A Preliminary Examination of End Effects in Polyelectrolyte Theory: The Potential of a Line Segment of Charge

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ABSTRACT: The potential, ψ_T, of a line segment of charge is calculated in the Debye–Hückel approximation. We determine ψ_T as a function of segment length and the position of the test charge. If the test charge is near the line segment and the length of the line segment of charge is large relative to the screening length, ψ_T is well approximated by the electrostatic potential of an infinite line of charge. When the test charge is far from the line segment, ψ_T reduces to the point charge limit.

Recently, considerable attention has been devoted to elucidating the properties of the line of charge model of polyelectrolyte solutions.[1-6] The infinitely long line of charge model has been employed to calculate the colligative properties of dilute polyelectrolyte solutions,[1-3] the diffusion constant of a mobile ion in the presence of a polyelectrolyte,[4,5] and the expansion parameter, Z, of the excluded volume theory.[6] We note, however, that real polyions are of finite size; as such, it would be quite useful to determine the magnitude of end effects on the electrostatic potential arising from a finite line of charge. Hence, a partial motivation of the present work is to determine when the replacement of the potential of the line segment of charge by that of an infinite line is justified and when it is not. We also note that the line segment of charge may perhaps be a plausible model for low molecular weight DNA and helical poly(glutamic acid) at low to moderate ionic strengths. Thus, this paper is a preliminary step toward understanding the dependence of polyelectrolyte behavior on chain length.

If the length of the line segment of charge is large relative to the screening length and if the test charge is near the source, it seems intuitively reasonable that the electrostatic potential should be well approximated by the infinite line of charge result. However, when the test charge is far from the line segment of charge, the line segment should appear as a point charge. In the context of the Debye–Hückel approximation, verification of the above conjectures will be presented in what follows.

Consider a uniformly charged line segment of length L immersed in bulk solvent. It is assumed that each infinitesimal piece interacts with the test charge via a screened Coulomb potential. For discussions concerning the applicability of an effective charge density and counterion condensation, we refer to the literature.[1-3,7-9]

Let the line segment of charge lie on the z axis, in the cylindrical coordinate system (r,θ,z), and let one end of the line segment be located at $z = 0$. Whereupon, the potential, ψ_T, felt at a point $\mathbf{r} = (r,\theta,z)$ by a test charge is given by

$$\psi_T(\mathbf{r}) = \frac{\beta}{D_2}\int_0^L dz'\,\frac{\exp\{-\kappa[r^2 + (z - z')^2]^{1/2}\}}{[r^2 + (z - z')^2]^{1/2}} \qquad (1)$$

with $\beta \equiv$ charge per unit length of the line segment and $D_2 \equiv$ bulk dielectric constant. κ^{-1} is the Debye screening length and is defined by

$$\kappa^2 = \frac{4\pi e^2}{D_2 k_B T}\sum_i C_i \mu_i^2$$

Here, e is the protonic charge. The summation extends over all the ionic species "i" in solution; C_i is the concentration of species "i" in ions per cm^3; μ_i is the valence of the ith species. k_B is Boltzmann's constant, and T is the absolute temperature.

It is convenient to define the dimensionless interaction energy ψ_d; ψ_d is related to ψ_T through the relation $\psi_d = \xi^{-1} e\psi_T/k_B T$; $\xi = |e\beta|/k_B T D_2$.

The test charge can either be positioned between the two ends of the line segment, i.e., $0 \le z \le L$, or below or above an end of the segment, i.e., $z < 0$ or $z > L$. By symmetry, it is obvious that the two latter situations are physically equivalent.

Let $z'' = z - z'$, it then follows from eq 1 that

$$\psi_d(\mathbf{r}) = \int_{-z}^{L-z} dz''\,\frac{\exp\{-\kappa[r^2 + z''^2]^{1/2}\}}{[r^2 + z''^2]^{1/2}} \qquad (2)$$

If $0 \le z \le L$,

$$\psi_d = \int_0^{L-z} dz''\,\frac{\exp\{-\kappa[r^2 + z''^2]^{1/2}\}}{[r^2 + z''^2]^{1/2}} + \int_0^{z} dz''\,\frac{\exp\{-\kappa[r^2 + z''^2]^{1/2}\}}{[r^2 + z''^2]^{1/2}} \qquad (3)$$

Similarly when $z < 0$

$$\psi_d^{\,b} = \int_0^{L+|z|} dz''\,\frac{\exp\{-\kappa[r^2 + z''^2]^{1/2}\}}{[r^2 + z''^2]^{1/2}} - \int_0^{|z|} dz''\,\frac{\exp\{-\kappa[r^2 + z''^2]^{1/2}\}}{[r^2 + z''^2]^{1/2}} \qquad (4)$$

While it is apparent from eq 3 and 4 that the potential ψ_d must vary continuously from the $0 \le z \le L$ case to that when $z < 0$, we find it conceptually useful to examine the two situations separately. As the $0 \le z \le L$ configuration is most closely related to the infinite line result, it is treated first.

At this juncture, a few qualitative observations on certain limiting forms of ψ_d are necessary. First of all, it must

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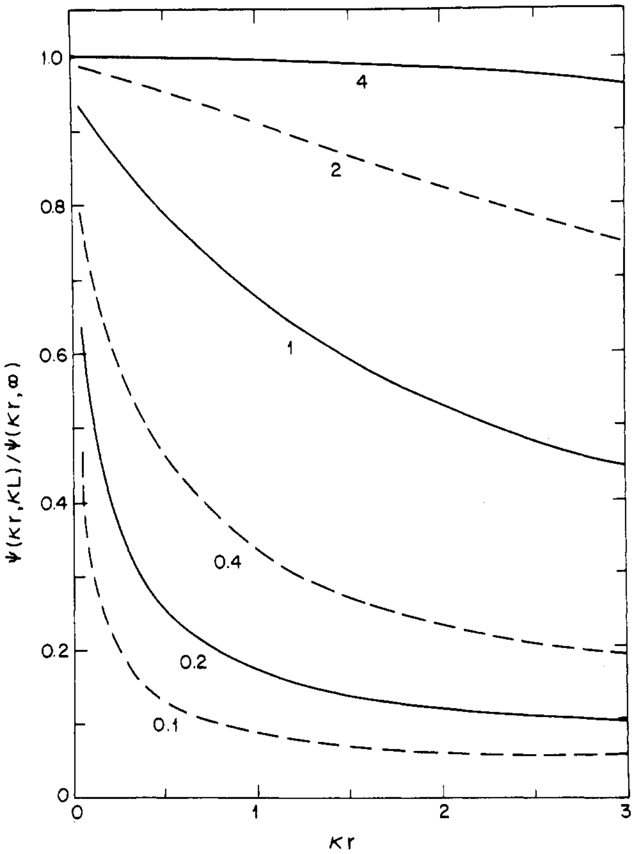

Figure 1. The ratio $\psi(\kappa r,\kappa L)/\psi(\kappa r,\infty)$ is plotted as a function of κr. κL is fixed along a given curve.

be recognized that there are two kinds of divergences in the potential of an infinite line of charge. One type arises only when $\kappa = 0$ and r is finite and is due to the long range nature of unscreened electrostatic interactions; i.e., at zero salt, a test charge interacts strongly with the entire infinite line of charge. Thus, there is a uniform, infinite background potential. This particular effect is eliminated at finite κ. The second kind of divergence is due to a short range effect and occurs as $r \to 0$. It is a result of the interaction of the test charge with those parts of the line of charge having z components of position near those of the test charge. The potential is proportional to $-\ln r$ and is independent of κ for sufficiently small r. It is precisely the short range part of the interaction energy that the line segment and infinite line of charge have in common. Parenthetically, we note that the "Gaussian Pillbox" method of electrostatics gives the short range part of the potential of an infinite line of charge in a salt free solution.[11] Consequently, we restrict our discussion to nonzero values of κ.

Provided that $\kappa \neq 0$, we can rewrite eq 3 as

$$\psi_{\mathrm{d}} = \psi(\kappa r,\kappa(L - z)) + \psi(\kappa r,\kappa z) \tag{5a}$$

where

$$\psi(\kappa r,\kappa L') = \int_0^{\kappa L'} \mathrm{d}z' \frac{\exp\{-[\kappa^2 r^2 + z'^2]^{1/2}\}}{\sqrt{\kappa^2 r^2 + z'^2}} \tag{5b}$$

As expected, there are three characteristic lengths that determine ψ_{d}: κr, $\kappa(L - z)$, and κz. Physically, $\psi(\kappa r,\kappa z)$ is the interaction energy of a test charge with that portion of the line segment of charge lying on the negative z axis. In a similar fashion, $\psi(\kappa r,\kappa(L - z))$ is the interaction energy of the test charge and the part of the line segment along the positive z axis. Since

$$\psi_{\mathrm{d}} = \psi(\kappa r,\kappa(L - z)) + \psi(\kappa r,\kappa z);\ 0 \leq z \leq L$$

we need merely elucidate the behavior of $\psi(\kappa r,\kappa L')$ to understand the properties of ψ_{d}. In what follows, the reported values of $\psi(\kappa r,\kappa L')$ were determined numerically.

If we let $\kappa L' \to \infty$ with κr fixed, eq 5b becomes

$$\psi(\kappa r,\infty) = \int_0^{\infty} \mathrm{d}z' \frac{\exp\{-[\kappa^2 r^2 + z'^2]^{1/2}\}}{[\kappa^2 r^2 + z'^2]^{1/2}} \tag{6a}$$

$$\psi(\kappa r,\infty) = K_0(\kappa r) \tag{6b}$$

Here, K_0 is a modified Bessel function of the second kind.[10] $\psi(\kappa r,\infty)$ is the dimensionless interaction energy of a test charge and half-line of charge.

In Figure 1 we plot $\psi(\kappa r,\kappa L)/\psi(\kappa r,\infty)$ as a function of κr; each curve represents a fixed value of κL. When $\psi(\kappa r,\kappa L)/\psi(\kappa r,\infty) = 1$, the interaction energy of the test charge and line segment of length L is equivalent to that of the half-line of charge. As the ratio $\psi(\kappa r,\kappa L)/\psi(\kappa r,\infty)$ decreases, the less the interaction energy resembles that of the half-line of charge. For a fixed value of κL, the smaller the ratio of r is to the screening length (i.e., small κr) the closer the ratio $\psi(\kappa r,\kappa L)/\psi(\kappa r,\infty)$ is to unity. Basically, as $r \to 0$ the test charge probes that part of the interaction energy, common to line segments and half-lines, responsible for the short range type of divergence discussed earlier. An analytical demonstration that

$$\lim_{\substack{\kappa r \to 0 \\ \kappa,L \text{ fixed}}} \psi(\kappa r,\kappa L)/\psi(\kappa r,\infty) = 1$$

is presented below.

Let us rewrite $\psi(\kappa r,\kappa L)$ in eq 5b by

$$\psi(\kappa r,\kappa L) = \int_0^{L} \mathrm{d}z' \frac{\exp\{-\kappa[r^2 + z'^2]^{1/2}\}}{[r^2 + z'^2]^{1/2}} \tag{7a}$$

Setting $t^2 = r^2 + z'^2$

$$\psi(\kappa r,\kappa L) = \int_r^{[r^2+L^2]^{1/2}} \mathrm{d}t \frac{\exp(-\kappa t)}{[t^2 - r^2]^{1/2}} \tag{7b}$$

$$\lim_{\substack{\kappa r \to 0 \\ \kappa,L \text{ fixed}}} \psi(\kappa r,\kappa L) \sim -\ln r \quad \text{(ref 12)} \tag{7c}$$

Moreover,[10]

$$\lim_{\substack{\kappa r \to 0 \\ \kappa \text{ fixed}}} K_0(\kappa r) \sim -\ln \kappa r \tag{8}$$

Consequently, it follows immediately from eq 7c, 6b, and 8 that

$$\lim_{\substack{\kappa r \to 0 \\ \kappa,L \text{ fixed}}} \psi(\kappa r,\kappa L)/\psi(\kappa r,\infty) = 1 \tag{9}$$

Note that for κr fixed, larger values of κL result in ratios of $\psi(\kappa r,\kappa L)/\psi(\kappa r,\infty)$ closer to unity; i.e., the longer the length of the line segment relative to the range of the interaction, the more closely the potential resembles that of the half-line of charge.

In the limit $\kappa r \to \infty$, it is trivially demonstrated that[10]

$$\lim_{\substack{\kappa r \to 0 \\ \kappa L \text{ fixed}}} \psi(\kappa r,\kappa L)/\psi(\kappa r,\infty) \sim \left(\frac{2}{\pi}\right)^{1/2} \frac{\kappa L}{(\kappa r)^{1/2}} \tag{10}$$

For the convenience of the reader, in Figure 2 we plot $K_0(\kappa r)$ as a function of κr.

Upon moving the test charge further and further away from the line segment of charge, ψ_{d}, defined in eq 5a,

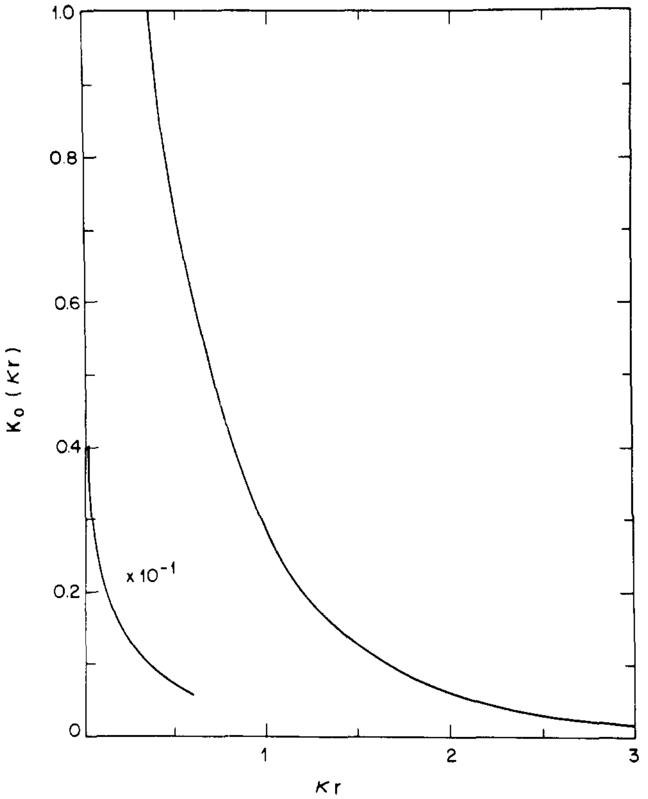

Figure 2. The modified Bessel function, $K_0(\kappa r)$, is plotted as a function of κr.

should approach the point charge limit.

Define ψ_r by

$$\psi_r = \lim_{\kappa r \to \infty} \psi_d / L \tag{11a}$$

$$\psi_r = \lim_{\kappa r \to \infty} \frac{1}{L} \int_0^L \mathrm{d}z' \, \frac{\exp\{-\kappa[r^2 + z'^2]^{1/2}\}}{[r^2 + z'^2]^{1/2}} \tag{11b}$$

By hypothesis $\kappa r \gg \kappa L$, thus we can neglect the variation of the integrand with z, therefore

$$\psi_r \sim e^{-\kappa r}/r \equiv \Phi(\kappa r) \tag{11c}$$

In Figure 3, $R_p = \psi_r/\Phi$ is plotted as a function of κr; κL is fixed along a given curve. Observe that $\psi_r/\Phi \leq 1$. The physical origin of this inequality is explained below. For a given total charge, the lines of flux from a point charge are more concentrated than those of the line segment of charge. As the charge density decreases as L increases for a fixed total charge, Q, one finds, at fixed κr and Q, the ratio R_p to be a decreasing function of κL. Finally, it is an immediate consequence of eq 7c and l'Hospital's rule that

$$\lim_{\substack{\kappa r \to 0 \\ \kappa, L \text{ fixed}}} \psi_r/\Phi \to 0$$

The behavior of the potential, $\psi_d^{\,b}$, given in eq 4, is qualitatively different if the test charge lies below (or above) an end of the line segment (the $z < 0$ or $z > L$ case). Notice that there is no singularity at $r = 0$; an essential feature of the line of charge is entirely absent. Moreover the potential more rapidly approaches the point charge limit than ψ_d (eq 3) does. This is clearly demonstrated in Figure 4 where we plot

$$R_0 = L^{-1}[\psi(\kappa r, \kappa(L + |z|)) - \psi(\kappa r, \kappa|z|)]/\Phi(\kappa[r^2 + z^2]^{1/2}) \tag{12}$$

as a function of κr. R_0 is the ratio of the potential of a line segment of charge to that of a point charge located at (0,0,z). It is easy to show that

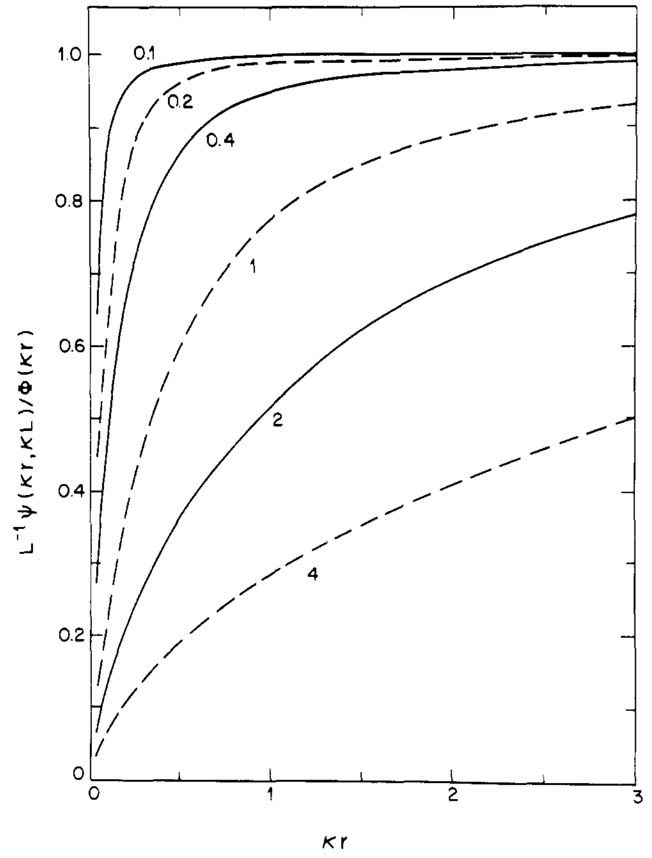

Figure 3. The ratio $L^{-1}\psi(\kappa r,\kappa L)/\Phi(\kappa r)$ is given as a function of κr. κL is constant along each curve.

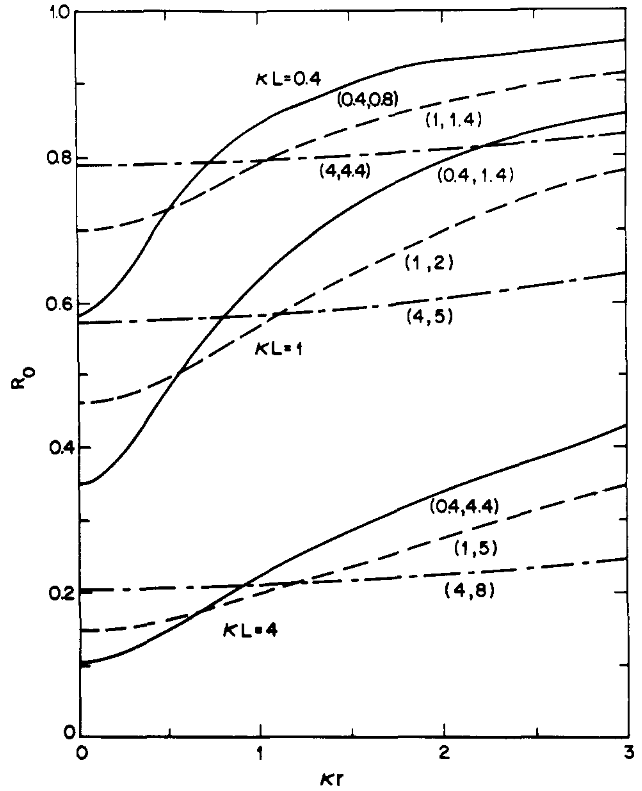

Figure 4. The quantity $R_0 = L^{-1}\{\psi(\kappa r,\kappa(L + |z|)) - \psi(\kappa r,\kappa|z|)\}/\Phi(\kappa(r^2 + z^2)^{1/2})$ is presented as a function of κr. On any particular curve, the values of κz and $\kappa(L + z)$ are constant and are denoted by the quantity $(\kappa|z|,\kappa(L + |z|))$.

$$\lim_{\kappa r \to \infty} R_0 = 1 \tag{13}$$

and

$$\lim_{\kappa r \to 0} R_0 = \frac{z}{L} e^{\kappa z} \{E_1(\kappa z) - E_1(\kappa(L + |z|))\} \tag{14}$$

where $E_1(x)$ is the exponential integral.[10]

In Figure 4, $\kappa z = 0.4$ on the solid lines, $\kappa z = 1.0$ on the dashed lines, and $\kappa z = 4.0$ on the dot-dashed lines. Along each curve, the value of κL is fixed. For a given κr and κz, the smaller κL is, the more point-like the line segment appears, i.e., R_0 is closer to unity. If κL is fixed, the behavior of the curves in Figure 4 is a consequence of the fact that R_0 must be a nondecreasing function of the distance between the test charge and the line segment. As the test charge moves further from the line segment, the more closely ψ_d^b resembles the potential of a point charge. Thus, when $\kappa r = 0$, if $\kappa z_2 > \kappa z_1$

$$R_0(\kappa r = 0, \kappa z_2) > R_0(\kappa r = 0, \kappa z_1) \text{ at fixed } \kappa L \tag{15}$$

In fact,

$$R_0(\kappa r = 0, \kappa z_1 = 0) = 0$$

Holding κL constant, a given radial displacement of the test charge results in a proportionately larger increase in the distance from the line segment when κz is small than when κz is large. This implies that if $\kappa z_1 < \kappa z_2$ and κL is fixed

$$\frac{\partial R_0(\kappa r, \kappa z_1)}{\partial \kappa r} \geq \frac{\partial R_0(\kappa r, \kappa z_2)}{\partial \kappa r} \geq 0 \text{ where } \kappa z_1 \leq \kappa z_2$$

Therefore, since the slope of the κz_1 curve is greater than or equal to the slope of the κz_2 curve, it follows from eq 15 that the two curves must cross once. This is clearly seen in Figure 4.

At this juncture, a few words concerning the utility of the numerical results are appropriate. We have examined the relationship of the Debye–Hückel potential of a line segment to the limiting cases of the line and point charge. Knowledge of both ψ_d (eq 3) and ψ_d^b (eq 4) is necessary in the calculation of the electrostatic part of the salt exclusion coefficient, A_1^e, for a solution containing both simple salt and line segments of charge.[13] Comparison of A_1^e for a line segment with those of the infinite line and point charge should yield the following result: At very low ionic strength, A_1^e for the line segment should be quite close to the equivalent point charge salt exclusion coefficient. At moderate ionic strengths, A_1^e of the line segment should be reasonably well approximated by the infinite line of charge salt exclusion coefficient.

The replacement of the actual polyelectrolyte by an infinite line of charge is central to the development of the Manning theory.[1] For line segments of charge in the Debye–Hückel approximation, our work shows where this replacement is justified and where it is not. Furthermore, it is a straightforward matter on the basis of eq 3 and eq 7a to calculate the colligative properties of a system consisting of line segments of charge in the presence of excess salt.

In the calculation of many polyelectrolyte properties, ψ_d is required. For example, the dependence on simple salt concentration of the surface potential of short segment DNA can be related to the variation of the $\lim_{r \to 0} \psi_d$ with κ. However, recent work by Soumpasis[14] and one of us[15] demonstrates the importance of the three-dimensional character of the charge distribution in the calculation of the potential. The presence of low dielectric, salt excluding regions may exert a comparable influence to that of end effects on the properties of linear charged molecules. Moreover, the use of the Debye–Hückel approximation may, in itself, lead to an incorrect treatment of end effects. We believe, however, that the qualitative conclusions of this work will emerge unscathed from a more exact treatment, the solution of the nonlinear Poisson–Boltzmann equation for a finite cylinder of charge. Such a study is planned in the near future.

Although the current work has in it all the limitations implicit in the Debye–Hückel theory, it is nevertheless a useful reference system and provides a preliminary step toward understanding the dependence of polyelectrolyte behavior on chain length. Clearly, much work remains to be done.

References and Notes

(1) G. Manning, *J. Chem. Phys.*, **51**, 924, 3249 (1969).
(2) G. Manning, *Biophys. Chem.*, **7**, 95 (1977).
(3) T. Odijk and M. Mandel, *Physica (Utrecht)*, **93A**, 298 (1978).
(4) J. L. Jackson and S. R. Coriell, *J. Math. Phys. (N.Y.)*, **5**, 1075 (1964).
(5) G. Manning, *J. Chem. Phys.*, **51**, 934 (1969).
(6) M. Fixman and J. Skolnick, *Macromolecules*, **11**, 863 (1978).
(7) D. Stigter, *J. Phys. Chem.*, **82**, 1602 (1978).
(8) M. Fixman, *J. Chem. Phys.*, **70**, 4995 (1979).
(9) M. T. Record, Jr., and T. M. Lohman, *Biopolymers*, **17**, 159 (1978).
(10) M. Abramowitz and I. A. Stegun, Ed., "Handbook of Mathematical Functions", National Bureau of Standards, U.S. Department of Commerce, 1964.
(11) R. P. Feynman, R. B. Leighton, and M. Sands, "The Feynman Lectures on Physics", Addison-Wesley Co., New York, 1964, p II-5-3.
(12) H. B. Dwight, "Tables of Integrals and Other Mathematical Data", Macmillan, New York, 1957, p 59.
(13) The quantity A_1^e is defined by the series $n_s/n_s^* = 1 + A_1 n_p^e$ that relates the salt concentration inside, n_s, and outside, n_s^*, the polyelectrolyte solution. n_p^e is the polyelectrolyte concentration in equivalents/volume. The electrostatic contribution to A_1 for a 1–1 salt having common counterions with the polymer is $A_1^{el} = n_s^*(e/q) \int d\mathbf{v}(e^{-e\psi_T/k_BT} - 1)$, with q as the total charge on the polymer and e as the protonic charge. Both e and q are assumed to be positive. See ref 8 and references cited therein.
(14) D. Soumpasis, *J. Chem. Phys.*, **69**, 3190 (1978).
(15) J. Skolnick, *Macromolecules*, **12**, 515 (1979).