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# THE RELATIONSHIP BETWEEN THE POISSON–BOLTZMANN MODEL AND THE CONDENSATION HYPOTHESIS: AN ANALYSIS BASED ON THE LOW SALT FORM OF THE DONNAN COEFFICIENT

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Two common models for the interaction of counterions with cylindrical polyions are considered in the context of the Donnan membrane equilibrium. General analytic expressions are obtained from the Poisson–Boltzmann equation for the Donnan coefficient in terms of the potential at the surface of the polyion or the local concentration of unbound ions at the surface. Analysis based on these expressions shows that if, and only if, the polyion charge density exceeds a certain critical value a large local concentration of ions will persist near the polyion surface at low ionic strengths. We therefore conclude that this principal hypothesis of the condensation model is consistent with the characteristics of the Poisson–Boltzmann potential at the surface of the polyion.

## 1. Introduction

### *1.1. Introductory comments*

Over the past decade the condensation model has provided a simple and powerful approach to the interpretation and quantitative analysis of those properties of polyelectrolyte solutions which are sensitive to the interactions of small counterions with rod-like polyions. These applications have been thoroughly discussed in several recent reviews [1–4]. The extent to which the counterion condensation model can be defined from, or is consistent with, the Poisson–Boltzmann (or Gouy–Chapman) model for cylindrical polyions has been a subject of interest, and some controversy [5,6]. Manning's earliest paper on the condensation theory [7] included reinterpretations of certain characteristics of the colligative properties of polyelectrolyte solutions, which had previously been derived from or accounted for in terms of the Poisson–Boltzmann theory. In particular, Manning showed that the hypothesis of counterion condensation can explain the characteristic dependence of the Donnan salt exclusion coefficient upon the charge density of the polyion at low ionic strengths. This dependence had been established by Gross and Strauss [8] using numerical solutions of the Poisson–Boltzmann equation.

The relationship between the condensation theory and the MacMillan–Mayer theory of polyelectrolyte solutions was investigated by Manning [9] in the limit of infinite dilution, and by Bailey [10] for ionic strengths up to 0.1M. Recently Fixman [11] used functional expansion techniques to examine the statistical mechanical foundation of the Poisson–Boltzmann approximation, as applied to polyelectrolyte solutions containing added salt. He found that the solution of the Poisson–Boltzmann equation retains its theoretical validity up to an ionic strength of 0.1M. In addition, Fixman derived a general condensation model for the description of ion-polyion interactions based on an approximation to the rigorous Poisson–Boltzmann equation. The goal of our paper is to consider the relationship between the conventional cylindrical Poisson–Boltzmann model, as it has been applied (for example) by Stigter [12], and the condensation model, as it has been reformulated by Manning in terms of molecular thermodynamics [1,2,13]. Some qualitative aspects of the relationship between the two models are developed below from an analysis of the low-salt limiting behavior of the Donnan coefficient. More quantitative comparisons will be presented in a subsequent paper [14].

The remainder of this section is devoted to a brief review of the Donnan coefficient, and summary of the results obtained by Gross and Strauss [8]. In section 2 the conventional Poisson–Boltzmann model is used to derive expressions relating the Donnan coefficient to the Poisson–Boltzmann potential at the surface of the polyion or, equivalently, to the local concentration of small ions at the surface. These expressions are valid at any ionic strength. In section 3, they are used to discuss the physical significance of the low-salt expressions for the Donnan coefficient established by Gross and Strauss. *Our principal conclusion is that the magnitude of the polyion charge density plays a crucial role in determining the asymptotic salt-dependence of the surface Poisson–Boltzmann potential, which in turn determines whether or not a substantial concentration of counterions persists near the surface of the polyion at very low ionic strengths.* The parameter which characterizes the polyion charge density is designated:

$$\lambda \equiv \alpha\xi \equiv \alpha q^2/\epsilon kTb\ , \qquad (1.1)$$

where $q$ is the protonic charge; $\epsilon$, the bulk dielectric constant; $b$, the mean axial length per structural polyion charge; and $\alpha$ accounts for the possibility that these structural charges may be neutralized by site-binding ($0 < \alpha \leqslant 1$). It is demonstrated in section 3 that even at low ionic strength a high concentration of mobile counterions remains close to the surface of any polyion for which $\lambda > 1$; but if $\lambda \leqslant 1$, no local concentration is retained at low salt. Thus, the central significance assigned to the parameter $\lambda$ in the condensation theories can be justified in terms of the conventional Poisson–Boltzmann model.

### *1.2. The Donnan salt-exclusion coefficient*

The Donnan membrane equilibrium has proved exceedingly useful in both the theoretical analysis and experimental determination of the interactions between small ions and polyelectrolytes in solutions containing excess added salt. In its simplest form the experiment involves the use of a semipermeable membrane to equilibrate a polyelectrolyte solution with a solution containing a single type of simple salt, one of whose ions is identical to the counterion of the polyelectrolyte. Since the polyion cannot pass through the membrane, the establishment of equilibrium requires that coions are excluded from the solution containing the polyion. The Donnan coefficient, $\Gamma$, is the experimental parameter which characterizes the extent to which the concentration of simple electrolyte differs in the two compartments:

$$\Gamma \equiv \lim_{m_2 \to 0} (m_3' - m_3)/m_2\ , \qquad (1.2)$$

where $m_3'$ and $m_3$ are the molar concentrations of simple salt (or, equivalently, coions) in the polyion-free and polyion-containing compartments, respectively; and $m_2$ is the molar concentration of polyion monomers. The physical reasons for the exclusion of coions are electrostatic repulsion and the finite size of the polyion and small ions.

Gross and Strauss [8] formulated the Donnan exclusion effect for penetrable and impenetrable polyion cylinders in terms of definite integrals involving the coion radial distribution function. These integrals were evaluated numerically from potentials obtained by numerical solutions of the cylindrical Poisson–Boltzmann equation. On the basis of resulting values for $\Gamma$ at low ionic strengths Gross and Strauss deduced that the value of $\lambda$ relative to unity determines the functional dependence of the low salt asymptote of $\Gamma$ on $\alpha$ and $\xi$. The focus of our paper is on the implications of this effect with regard to the interrelation of the condensation and Poisson–Boltzmann models. Recent theoretical discussions and calculations of the virial coefficient $A_1$, which is directly related to $\Gamma$, have been published by Schellman and Stigter [15], Stigter [5,12,16], and Fixman [11].

## 2. The Poisson–Boltzmann formulation of the Donnan salt exclusion coefficient

The rod-like polyion is modeled as an impenetrable cylinder whose surface charge distribution is assumed to be uniform and continuous. The cylinder is assumed to be sufficiently long that end effects can be neglected, but not infinitely long. The magnitude of the polyion charge density parameter $\lambda$ (1.1) is determined by $\xi$, the number of structural charged groups per unit length along the axis, and by $\alpha$, the fraction of structural charges which are not neutralized by counterion binding to specific sites. The model polyelectrolyte solution also contains an excess of one kind of simple salt. The radial distributions of counterions and coions with respect to the polyion axis are represented as a continuum of charge density extending from bulk solution to the distance $a$ from the polyion axis, which marks the distance of closest approach of the mobile, hydrated ions. From the conventional Poisson–Boltzmann equation for this model system two expressions for the Donnan coefficient, $\Gamma$, are derived in this section. These expressions relate $\Gamma$ analytically either to the Poisson–Boltzmann potential at the polyion surface or to the surface concentrations of small, mobile ions. The statistical thermodynamic approaches taken by Gross and Strauss [8] and, more recently, by Stigter [5,12] involve numerical solutions of the Poisson–Boltzmann equation to evaluate the appropriate coion radial distribution functions.

The validity of the following expressions for $\Gamma$ is not restricted to the limit of vanishingly small salt concentrations. In fact a lower limit on the ionic strength of the solution is imposed by the requirement that the characteristic Debye length of the polyion-salt solution must be much less than the length of the polyion. Otherwise, interpolyion interactions and departures from cylindrical symmetry would alter the form of the Poisson–Boltzmann equation. The following derivation does incorporate the condition of "excess salt". Alexandrowicz and Katchalsky [17] concluded that if the ratio of added salt to polyion monomer concentration, $m_3/m_2$, is at least ten, then the Debye length for the polyion containing compartment can be simply expressed in terms of $m_3'$ the salt concentration in the polyion free compartment. In the limit required by the definition of $\Gamma$(1.2), the condition of excess salt is naturally fulfilled.

The following brief outline of the conventional Poisson–Boltzmann analysis of the cell model for polyelectrolyte solutions will introduce our notation and provide a framework for the subsequent derivation.

The appropriate form of the Poisson equation, which relates the electrostatic potential $\psi(r)$ at the distance $r$ from the polyion axis to $\rho(r)$, the mobile ion charge density at that point is:

$$\frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r}\left(r\frac{\mathrm{d}y}{\mathrm{d}r}\right)=\frac{4\pi q}{\epsilon kT}|\rho(r)|\,,$$

where $y \equiv q|\psi|/kT$. For simplicity both counterions and coions are taken to be univalent, so that the absolute value of the charge density is:

$$|\rho(r)| = 10^{-3}Nq[m_\mathrm{g}(r) - m_\mathrm{n}(r)]\,,$$

where $N$ is Avogrado's number and $m_\mathrm{g}(r)$ and $m_\mathrm{n}(r)$ are the *local* molar concentrations of counterions (g) and coions (n). The fundamental assumption of the conventional Poisson–Boltzmann model is that these concentrations are related to the reference concentrations $m_\mathrm{g}^\mathrm{R}$ and $m_\mathrm{n}^\mathrm{R}$ by Boltzmann factors involving the electrostatic potential $y(r)$:

$$m_\mathrm{g}(r) = m_\mathrm{g}^\mathrm{R}\exp(y)\,,\qquad m_\mathrm{n}(r) = m_\mathrm{n}^\mathrm{R}\exp(-y)\,.$$

The superscript R denotes the ion concentration at $r = R$, half the mean interpolyion separation, at which $y = 0$. Because the condition of excess salt has been assumed,

$$m_\mathrm{g}^\mathrm{R} = m_\mathrm{n}^\mathrm{R} = m_3'\,.$$

Hence, the appropriate Debye parameter for the polyion-salt compartment can be expressed:

$$\kappa^2 = \frac{8\pi Nq^2m_3'}{10^3\epsilon kT} = 8\pi b\xi\left(\frac{N}{10^3}\,m_3'\right)\,. \qquad (2.1)$$

Then in terms of the dimensionless radial distance $x \equiv \kappa r$, the Poisson–Boltzmann equation for the polyelectrolyte solution is:

$$\frac{1}{x}\frac{\mathrm{d}}{\mathrm{d}x}\left(x\frac{\mathrm{d}y}{\mathrm{d}x}\right) = \tfrac{1}{2}\,[\exp(y) - \exp(-y)]\,. \qquad (2.2)$$

The two boundary conditions which are incorporated into the solution of this equation are:

A. The gradient of the potential vanishes at $x_R \equiv \kappa R$:

$$x_R(\mathrm{d}y/\mathrm{d}x)|_{x_R} = 0\,. \qquad (2.3)$$

B. Gauss' Law applies at the polyion-solution interface $x_a \equiv \kappa a$:

$$x_a(\mathrm{d}y/\mathrm{d}x)|_{x_a} = -2\lambda\,. \qquad (2.4)$$

Although the Poisson–Boltzmann equation has not been solved analytically, a variety of numerical solutions is available [18–20,8,12]. The following derivation is completely analytic.

The Poisson–Boltzmann equation, (2.2) may be rearranged and integrated directly to give:

$$x\frac{\mathrm{d}y}{\mathrm{d}x} + C_1 = \tfrac{1}{2}\int[\exp(y) - \exp(-y)]x\,\mathrm{d}x\,. \qquad (2.5)$$

A second useful integral equation is obtained by multiplying equation (2.2) by $x^2\mathrm{d}y/\mathrm{d}x$ and integrating:

$$\tfrac{1}{2}(x\,\mathrm{d}y/\mathrm{d}x)^2 + C_2 = \tfrac{1}{2}x^2\,[\exp(y) + \exp(-y)] - \int[\exp(y) + \exp(-y)]x\,\mathrm{d}x\,. \qquad (2.6)$$

Eqs. (2.5) and (2.6) can be combined to yield:

$$(x\,\mathrm{d}y/\mathrm{d}x + 2)^2 - 4C = x^2 \exp(y)$$
$$+ \left[x^2 \exp(-y) - 4\int x \exp(-y)\mathrm{d}x\right] . \qquad (2.7)$$

Eq. (2.7) is the precise analogue of an important intermediate expression in the derivation, due to Fuoss, Katchalsky and Lifson [21], of an analytic form for the Poisson–Boltzmann potential surrounding a cylindrical polyion in salt-free solution. (Refer to eq. (7) of ref. [21].) The two terms in brackets on the right of (2.7) arise from the distribution of coions around the polyion, and complicate adaptation of the approach of Fuoss, Katchalsky and Lifson toward analytic solution for the Poisson–Boltzmann potential in a polyion solution containing added salt. Nevertheless, eq. (2.7) can be employed to obtain a useful equation for Γ.

Rearrangement of (2.7) produces an expression for the integral which is proportional to the number of coions per polyion charge in the annular volume extending from a to the distance $r$ from the polyion axis:

$$\int_{x_a}^{x} x \exp(-y)\,\mathrm{d}x = -x\frac{\mathrm{d}y}{\mathrm{d}x} - 2\lambda - \tfrac{1}{4}x^2\left(\frac{\mathrm{d}y}{\mathrm{d}x}\right)^2 + \lambda^2$$
$$+ \tfrac{1}{4}x^2[\exp(y) + \exp(-y)]$$
$$- \tfrac{1}{4}x_a^2[\exp(y_a) + \exp(-y_a)] . \qquad (2.8)$$

The boundary condition (2.4) at $x = x_a$ has been incorporated. The total number of coions per polyion charge is obtained by setting the upper limit of the integral $x = x_R$, incorporating the boundary condition (2.3), and noting that $y_R = 0$:

$$\int_{x_a}^{x_R} x \exp(-y)\mathrm{d}x$$
$$= -2\lambda + \lambda^2 + \tfrac{1}{2}x_R^2 - \tfrac{1}{4}x_a^2[\exp(y_a) + \exp(-y_a)] . \qquad (2.9)$$

An analogous expression can be derived for the counterion distribution; the only difference from (2.9) is that the sign of the term (–2λ) changes.

The integral in (2.9) is proportional to the total concentration of coions (and hence, of added salt) in the compartment containing of polyion:

$$m_3 \int_0^R r\,\mathrm{d}r = m_n^R \kappa^{-2} \int_{x_a}^{x_R} x \exp(-y)\,\mathrm{d}x . \qquad (2.10)$$

By the condition of excess salt, $m_n^R = m_3'$, and (2.1) can be introduced to simplify (2.10):

$$m_3 = \frac{m_2}{4\xi}\int_{x_a}^{x_R} x \exp(-y)\,\mathrm{d}x . \qquad (2.11)$$

This expression incorporates the fact that the molar concentration of structural polyion charged groups $m_2 = 10^3/N\pi bR^2$. Since $x_R^2 = 8\xi(m_3'/m_2)$, (2.9) may be introduced into (2.11) to obtain an expression for the salt exclusion coefficient, Γ:

$$\frac{m_3' - m_3}{m_2} = \tfrac{1}{2}\alpha - \tfrac{1}{4}\alpha^2\xi + \frac{1}{16\xi}x_a^2[\exp(y_a) + \exp(-y_a)] . \qquad (2.12)$$

The terms on the right of (2.12) do not depend on the polyion monomer concentration, because the condition of excess salt ensures that the Debye parameter for the polyion containing compartment depends only on $m_3'$ the salt concentration in the polyion free compartment. Hence, (2.12) is a valid expression for the parameter Γ defined by the limit (1.2).

By introducing the excluded volume per mole of polyion charges, $\bar{V}_2 = 10^{-3}N\pi ba^2$, the third term in (2.12) may be expressed in a more physically instructive form. Since $x_a^2 = 8\xi\bar{V}_2 m_3'$, equation (2.12) may be rearranged to:

$$2\Gamma = \alpha - \tfrac{1}{2}\alpha^2\xi + [m_g(a) + m_n(a)]\,\bar{V}_2 . \qquad (2.13)$$

A thermodynamic interpretation of the terms in this expression will be presented in a following paper. The third term in (2.13) is proportional to the *local* concentration of mobile ions at $r = a$, the distance of closest approach to the polyion axis. In the limit of high ionic strength, the local concentration, $\tfrac{1}{2}[m_g(a) + m_n(a)]$, approaches the reference concentration $m_3'$ because $y_a \to 0$. Since the bulk salt concentration $m_3$ in the compartment containing the polyion is approximately equal to $m_3'$, the high salt limit of Γ can be obtained from (2.13):

$$\lim_{m_3\to\infty} \Gamma = m_3\bar{V}_2 . \qquad (2.14)$$

Under these conditions Γ is dominated by the physical exclusion of coions from the volume occupied by the polyion. The molar excluded volume is usually less than

$10^2\,(\mathrm{cm})^3$; for helical DNA, a rigid polyion with an exceptionally large hydrated radius, $a \approx 12$ Å, and $\bar{V}_2 \approx 460\,(\mathrm{cm})^3/\mathrm{mole}$.

Whenever the third term in (2.12) or (2.13) is non-negligible, the Donnan salt exclusion coefficient, a bulk thermodynamic variable, can provide a measure of the Poisson–Boltzmann potential and the concentration of mobile ions at the polyion-solution interface. As long as the concentration of added salt exceeds that of the polyion monomer by at least a factor of ten, (2.12) and (2.13) are valid for any ionic strengths at which the conventional Poisson–Boltzmann model itself retains validity. Thus, these expressions may afford a means of analyzing the experimental salt-dependence of $\Gamma$ over a range of salt concentrations to determine the corresponding variations of $y_a$ and $\frac{1}{2}[m_g(a)+m_n(a)]$ with ionic strength.

## 3. Analysis of Γ in the limit of low salt

In this section the implications of the low salt expressions for $\Gamma$ determined by Gross and Strauss [8] are developed by means of the exact relationships for $\Gamma$ derived in the preceding section. Using numerical solutions of the Poisson–Boltzmann equation (2.2) it was found that for ionic strengths such that $x_a \lesssim 10^{-3}$, $\Gamma$ approaches either of two asymptotic forms, whose dependence upon $\alpha$ and $\xi$ is determined completely by the magnitude of $\lambda$. These results of Gross and Strauss can be expressed:

$$\text{if } \lambda \leqslant 1, \quad \Gamma = [1-(\lambda-1)^2+\sigma_1]/4\xi\,, \tag{3.1}$$

$$\text{if } \lambda \geqslant 1, \quad \Gamma = [1+\sigma_2]/4\xi\,, \tag{3.2}$$

where $\sigma_1$ and $\sigma_2$ are small, positive quantities of indefinite magnitude, approaching zero at sufficiently low ionic strength. (If $\lambda = 1$, $\sigma_1 = \sigma_2$.) In the following analysis these expressions for $\Gamma$ are combined with (2.12) or (2.13) to determine the corresponding low salt asymptotic forms of $y_a$ and $\frac{1}{2}[m_g(a)+m_n(a)]$. It is demonstrated that for highly charged polyions ($\lambda > 1$), a high local concentration of counterions persists near the polyion surface, even at very low ionic strengths. Thus, it can be deduced that the phenomenon of counterion condensation is derivable from the $\lambda$-dependence of the conventional Poisson–Boltzmann potential, at low but finite concentrations of excess added salt.

### 3.1. *The Poisson–Boltzmann potential, $y_a$, at low ionic strengths*

Expressions (3.1) and (3.2) for $\Gamma$ in the limit of low salt can be substituted into (2.12) to produce two low-salt expressions for the quantity $S_a$:

$$S_a \equiv \tfrac{1}{4}x_a^2\,[\exp(y_a)+\exp(-y_a)]\,, \tag{3.3}$$

$$\text{if } \lambda \leqslant 1, \quad S_a = \sigma_1\,, \tag{3.4}$$

$$\text{if } \lambda \geqslant 1, \quad S_a = (\lambda-1)^2+\sigma_2\,. \tag{3.5}$$

Since it can be anticipated that $\exp(y_a) \gg \exp(-y_a)$, the corresponding low salt expressions for the potential are:

$$\text{if } \lambda \leqslant 1, \quad y_a = -2\ln x_a + \ln(4\sigma_1)\,, \tag{3.6}$$

$$\text{if } \lambda \geqslant 1, \quad y_a = -2\ln x_a + \ln[4(\lambda-1)^2+4\sigma_2]\,. \tag{3.7}$$

Since $\sigma_1$ and $\sigma_2$ become arbitrarily small as $x_a$ becomes less than $10^{-3}$, their asymptotic salt-dependence can be represented empirically as:

$$\sigma_1 \sim s_1 x_a^{p_1}\,; \qquad \sigma_2 \sim s_2 x_a^{p_2}\,, \tag{3.8}$$

where $s_1$, $s_2$, $p_1$, and $p_2$ are positive numbers, whose values are expected to depend upon $\lambda$. (If $\lambda = 1$, $s_1 = s_2$ and $p_1 = p_2$.) Introduction of these asymptotic forms into (3.6) and (3.7) demonstrates that at low ionic strengths, the corresponding asymptotic dependences of the potential on the Debye parameter $\kappa$ are determined by $\lambda$ in the following way:

$$\text{if } \lambda \leqslant 1, \quad y_a \sim -(2-p_1)\ln\kappa\,, \tag{3.9}$$

$$\text{if } \lambda > 1, \quad y_a \sim -2\ln\kappa\,. \tag{3.10}$$

MacGillivray and Winkleman [19] used singular perturbation theory to obtain a formal asymptotic expansion for the solution of the Poisson–Boltzmann equation (2.2) pertaining to "moderately charged" cylinders, for which $\lambda < 1$. They deduced that in the limit of infinite dilution, the solution of the linearized (or "Debye–Hückel") form of the cylindrical Poisson–Boltzmann equation is a uniformly valid approximation to the true Poisson–Boltzmann potential, so that, in the present notation:

$$\text{if } \lambda < 1, \quad y_a \sim -2\lambda\ln\kappa \quad \text{as} \quad \kappa \to 0\,. \tag{3.11}$$

This asymptotic form of the potential is evidently consistent with (3.9), provided that $p_1 = 2(1-\lambda)$. Recent numerical work has cast some doubt on the validity of

(3.11) at low, but finite ionic strengths [5,11]. Although it is not feasible to evaluate $p_1$ from the curves published by Gross and Strauss [8], their results unequivocally show that for polyions having $\lambda \leqslant 1$. The Poisson–Boltzmann potential at $r = a$ does not increase as strongly as $-2 \ln \kappa$ with decreasing $\kappa$.

From (3.10) it can be concluded that the low-salt Poisson–Boltzmann potential at the surface of *any* polyion for which $\lambda$ exceeds unity varies exactly as $-2 \ln \kappa$. Thus, if the polyion is sufficiently highly charged, its actual charge density ceases to be relevant in determining the asymptotic salt-dependence of the Poisson–Boltzmann potential at its surface. This asymptotic salt-dependence, (3.10), can be obtained from the "Debye–Hückel" potential by assigning $\lambda$ in (3.11) the effective value of unity. In some theoretical applications this "reduced" form of the Debye–Hückel potential can be used at the surface of a highly charged polyion, since it does have the correct asymptotic salt-dependence at low ionic strengths. Nevertheless, under these conditions the Poisson–Boltzmann equation cannot be linearized, so that in this sense the Debye–Hückel approximation fails.

The fact that the asymptotic salt-dependence of the Poisson–Boltzmann potential becomes independent of $\lambda$ for $\lambda > 1$ was deduced by MacGillivray in the limit of infinite dilution from the mathematical properties of the Poisson–Boltzmann equation, and from earlier formal asymptotic results for the case $\lambda < 1$ [19]. (Compare (3.10) above with (44) of [22]; further development may be found in [23].) The analysis presented here serves to support the validity of (3.10) outside the strict limit of infinite dilution, which can only be applied to a polyion of infinite length. The asymptotic expressions for $\Gamma$, (3.1) and (3.2), determined by Gross and Strauss [8] from numerical solutions of the Poisson–Boltzmann equation, have been used to show that at low but finite salt, the $\lambda$-dependence of the asymptotic form of $y_a$ is "saturated" at the value $\lambda = 1$. This characteristic feature of the Poisson–Boltzmann potential will now be correlated with the persistence at low ionic strength of a high counterion concentration near the surface of any polyion for which $\lambda > 1$.

### *3.2. The local counterion concentration, $m_g(a)$, at low ionic strengths*

Introducing the two numerically determined low salt values of $\Gamma$, (3.1) and (3.2), into (2.13) gives the corresponding values of the total concentration of mobile ions at $r = a$.

$$\text{if } \lambda \leqslant 1, \quad m_g(a) + m_n(a) = \sigma_1 / 2\xi \bar{V}_2 \,, \tag{3.12}$$

$$\text{if } \lambda \geqslant 1, \quad m_g(a) + m_n(a) = [(\lambda - 1)^2 + \sigma_2] / 2\xi \bar{V}_2 \,. \tag{3.13}$$

In view of (3.10) and the restriction $x_a \lesssim 10^{-3}$, the ratio $(m_n(a)/m_g(a)) = \exp(-2y_a) \lesssim 10^{-12}$, so that the presence of coions near the polyion surface is completely negligible. At high dilution, the dissociation of counterions from the region surrounding the polyion is strongly entropically favored. For the moderately charged polyion, (3.12) indicates that $m_g(a) \to 0$ with decreasing ionic strength. Thus, even though (3.9) shows that $y_a$ becomes very large at low salt, no local counterion concentration can persist near any polyion having $\lambda \leqslant 1$. In striking contrast, if $\lambda > 1$, (3.13) indicates that $m_g(a)$ remains finite; the attractive potential (3.10) effectively countervails the entropy to be gained by dissociation.

Equation (3.13) can be rewritten in a more informative way by incorporating the definition of $\bar{V}_2$ and the fact that $\xi b = 7.14$ Å for aqueous polyelectrolyte solutions near 25°C. (see (1.1)). For such systems, if the polyion is sufficiently highly charged, the molar concentration of monovalent counterions at $r = a$ (in Å) is:

$$m_g(a) = 37.0 (\lambda - 1)^2 / a^2 \quad (\lambda \geqslant 1) \,. \tag{3.14}$$

The validity of this expression is restricted to *low salt* ($x_a \lesssim 10^{-3}$), but *not* to the limit of "infinite dilution". To provide an illustration of the magnitude of the local counterion concentration at low salt: $m_g(a) = 2.6$M for helical DNA, whose structural parameters are: $a = 12$ Å, $\lambda = 4.2$, in the absence of site-binding. From (3.14) it can be concluded that for most polyions whose counterion-binding in excess salt has been studied, $m_g(a)$ is of the order 1M, and usually higher.

Even at the low ionic strengths to which (3.14) is restricted, $m_g(a)$ is only a crude (but absolute) upper bound estimate for the number of counterions per unit volume in an annular region of *finite* dimension surrounding the polyion. Manning's recent molecular thermodynamic theory of condensation, [1,2], predicts that the molar concentration of monovalent counterions that are "condensed" close to a highly charged polyion is, in aqueous solution at 25°C:

$$c_{\mathrm{loc}} = 3.4/b^2, \quad b(\text{Å}) \leqslant 7.14\,\text{Å}. \tag{3.15}$$

The quantity $a$ does not appear because this expression is analogous to an integrated form of (3.14). For helical DNA, $c_{\mathrm{loc}} = 1.2$M. [After our paper was accepted for publication, Guéron and Weissbuch [24] published extensive numerical calculations of the small ion radial distribution functions as predicted by the conventional Poisson–Boltzmann equation for highly charged polyions. They compared their computed local counterion concentrations in the vicinity of the polyion with values of $c_{\mathrm{loc}}$ predicted by (3.15). The low salt limiting values which they computed for "C1V" ($m_g$(a) in our notation) corroborate the validity of our analytic expression (3.14)].

Some reservations about the quantitative reliability of (3.14) may arise because the continuum model employed here does not recognize the finite size of the small mobile ions or the discreteness of the actual distribution of the polyion [15,25]. Theoretical refinements derived from these considerations are unlikely to alter qualitative inferences based on (3.12) and (3.13). The preceding analysis of $\Gamma$ in terms of the conventional Poisson–Boltzmann model has led to a conclusion entirely consistent with the principal hypothesis of the condensation model. If, and only if, the axial charge density $\lambda$ exceeds unity, a high local concentration of *unbound* counterions persists near the polyion surface at very low ionic strength.

The critical nature of the value $\lambda = 1$ was recognized by Oosawa [26] some time ago in his original formulation of the counterion condensation theory. Gross and Strauss [8] appreciated the significance of $\lambda$ in determining the value of $\Gamma$ at low ionic strengths and based their interpretation of this effect on an earlier model for diffuse counterion binding developed from the Poisson–Boltzmann equation by Kotin and Nagasawa [18]. By means of a thermodynamic approach, Manning showed that the low salt dependence of $\Gamma$ on $\xi$ can be nicely accounted for in terms of the condensation hypothesis [7]. The analysis of the low-salt forms of the Donnan coefficient presented here establishes a relationship between the $\lambda$-dependence of the Poisson–Boltzmann potential ((3.9), (3.10)) and the concentration of mobile ions close to the surface of a rod-like polyion ((3.12), (3.13)). It can be inferred that the (conventional) Poisson–Boltzmann potential does give rise to the phenomenon of counterion condensation at low, but finite, ionic strengths. The thermodynamic consequences of the characteristic $\lambda$ dependence of $S_a$, both in the low salt limit, (3.4), (3.5), and at arbitrary ionic strengths, will be developed in a subsequent paper [27].

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