Evaluation of the Counterion Condensation Theory of Polyelectrolytes

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ABSTRACT We compare free energies of counterion distributions in polyelectrolyte solutions predicted from the cylindrical Poisson-Boltzmann (PB) model and from the counterion condensation theories of Manning: CC1 (Manning, 1969a, b), which assumes an infinitely thin region of condensed counterions, and CC2 (Manning, 1977), which assumes a region of finite thickness. We consider rods of finite radius with the linear charge density of B-DNA in 1-1 valent and 2-2 valent salt solutions. We find that under all conditions considered here the free energy of the CC1 and the CC2 models is higher than that of the PB model. We argue that counterion condensation theory imposes nonphysical constraints and is, therefore, a poorer approximation to the underlying physics based on continuum dielectrics, point-charge small ions, Poisson electrostatics, and Boltzmann distributions. The errors in counterion condensation theory diminish with increasing distance from, or radius of, the polyion.

INTRODUCTION

One of the main theoretical tools for predicting the distributions of small, mobile ions around polymers, colloids, biomembranes, and biomolecules in solution has been the Poisson-Boltzmann (PB) theory, which originated in the early part of this century. For the subclass of solution electrostatics problems that involve charged rods, a popular alternative has been the Manning theory of counterion condensation (CC) (Manning, 1969a, b, 1977).

The counterion condensation theory arose in response to mathematical difficulties in the PB theory. The two theories treat essentially the same physical model. Which is more correct? This question has not been answered satisfactorily in the past in part because CC and PB both rest on questionable, but different, approximations. Here we compare the theories by using a free energy test. We reason that whichever model gives the small ion distribution with the lower free energy is the model with the least artificial constraint. In all of the cases we tested, we found that the PB theory gives the lower free energy and, hence, the more stable ion distribution.

Although the PB theory is now widely used in solution electrostatics, it fell out of favor for a considerable period of time when it was found that its mean-field approximation does not suitably treat ion fluctuations, and that this is important for small multivalent ions. Early treatments of electrostatic effects in polyelectrolyte—salt solutions were based on a PB description of the distribution of the small, mobile ions, by Hermans and Overbeek (1948) for a porous sphere model, and by Katchalsky and others (Fuoss et al., 1951; Alfrey et al., 1951) for a charged rod model of polyelectrolyte molecules. In view of the high local potential near polyelectrolyte chains, the full (nonlinear) PB equation was preferred to the linearized Debye-Hückel approximation. The full PB equation was solved analytically for a cell model of the charged rod (Fuoss et al., 1951; Alfrey et al., 1951) and numerically for the single charged rod in a salt solution (Kotin and Nagasawa, 1962; Sugai and Nitta, 1973; Stigter, 1975). But Kirkwood (1934) showed that the PB equation ignores the distinction between two different types of averages of the potential, which causes serious errors in the Debye-Hückel theory of strong electrolytes, except at low concentrations where the linearized PB equation is adequate. This difficulty discouraged use of the nonlinear PB equation in biophysics for many years.

But progress on the theory of charged rods was reinvigorated by Manning's development of the counterion condensation theory (Manning, 1969a, b, 1977). This approach treats the distribution of counterions around highly charged polyelectrolytes in terms of the linear charge density parameter $\xi = l_B/b$, where $l_B = e^2/4\pi\epsilon_0\epsilon kT$ is the Bjerrum length ($l_B = 7.13$ Å at 25°C in water), and b is the axial distance between successive charges fixed to the polyelectrolyte chain. Manning considered highly charged polyelectrolytes, $\xi > 1$, and counterions with valency z_i. He argued that the PB ion atmosphere around the polyion is unstable for $\xi > 1/z_i$ and proposed that, as a result, the fraction $1 - 1/z_i\xi$ of the fixed charges on the rod becomes completely neutralized by counterions that condense onto them, effectively reducing the density of the fixed charges on the rod from ξ to the value $1/z_i$. Counterion condensation theory then assumes that the noncondensed counterions are distributed according to the linearized PB equation. It is partly the nature of Manning's arguments that has made his condensation theories controversial.

There are two counterion condensation theories. The first condensation treatment (CC1) (Manning, 1969a, b) modeled the polyelectrolyte chain as a charged rod (having finite thickness) or a line charge (infinitely thin), with counterions condensing onto the rod surface or onto the line charge as a radial δ-function. In the second condensation treatment (CC2) (Manning, 1977), the polyion was represented as a

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linear array of point charges, with a finite cylindrical volume around it, V_p per point charge, in which the condensed counterions are uniformly distributed as a radial step function.

One virtue of CC theory is its simplicity. And the CC theory has been rather successful in explaining colligative properties of polyelectrolyte solutions (Manning, 1969a, b, 1977). It has been widely used (Manning, 1972, 1975, 1978, 1981, 1984; Devore and Manning, 1974; Record et al., 1976, 1978; De Gennes et al., 1976; Fenley et al., 1990; Dewey, 1990; Severin, 1993; Cantor and Schimmel, 1980), often in preference to the PB theory. Several comparisons of CC with the PB theory have been made, some emphasizing the differences (Stigter, 1978; Gueron and Weisbuch, 1980), others showing the close correspondence (Anderson and Record, 1980; Klein et al., 1981; Le Bret and Zimm, 1984) between them. In particular, Le Bret and Zimm (1984) have found that the PB equation predicts that a polyelectrolyte ion associates closer with the "condensed" than with the "uncondensed" fraction of its counterions. Fixman (1979) has studied a two-phase or condensation model akin to CC1 as an approximation to the PB equation, mainly for the purpose of simplifying PB theory for systems with complicated geometry.

Supporters hold that CC theory improves on PB because CC does not use the nonlinear equation, which is where the self-consistency problem in the PB equation arises; it uses only the linearized equation, which is known to be satisfactory. In this view, counterion condensation is a physical process caused by the instability of a highly charged polyion (Manning, 1969a, b, 1977). But opponents hold that the CC theory is only an ad hoc model that: 1) does not confront the question of the fluctuations—it just neglects them in a different way; and 2) does not have the same depth of underlying physical justification of the PB theory. This paper does not argue the absolute merit of either approach, but focuses on comparing the relative free energies of the ion distributions. We develop a way to test them on equal footing, and we find that the CC theory is an approximation to the PB theory insofar as it gives higher free energies and, thus, predicts counterion distributions that are unstable relative to the PB theory.

The relative stabilities of CC and PB distributions have not been studied directly by a free energy comparison, perhaps for two reasons. 1) The CC1 and PB models for an infinitely long line charge yield infinitely large free energies per unit length. 2) A ranking of free energies gives relative stabilities only for comparable models; it is difficult to treat the linear array of point charges of CC2 with PB theory. In this paper, we sidestep these difficulties and compare the models on equal footing by concentrating on charged rods with a PB double layer or, for the CC models, with a step function for the condensed counterions. The model has three variables: the salt concentration M_{salt}, the radius a of the rod, and the outer radius c of the condensation region. We compute the free energy *differences*, ΔF, between the CC and PB models down to $M_{\text{salt}} = 0.001$, $a = 0.1$ Å, and $c = a + 0.001$ Å for extrapolation to the limiting cases of CC1 and CC2. The important difference between CC and PB theory is not the particular polyion model, but the distribution of small ions around it. In computing free energy *differences*, we focus on the difference of the small ion distributions in PB and CC theory; the influence of the polyion model is neglected in this comparison. This neglect is completely justified in the limiting case of low salt solutions because for $M_{\text{salt}} \rightarrow 0$ and $a \rightarrow 0$ the difference between the ion distributions around our line charge model and around the linear array of point charges of CC2 vanishes. Therefore, the trends of ΔF with the three variables allow conclusions about the sign of ΔF in the limiting cases of CC1 and CC2. Thus, we calculate free energy differences between models, as shown in the next two sections. The interpretation of a free energy difference in terms of the relative stability of the ion distributions, using a variational argument, is given in a section headed the Relative Stability of Small Ion Distributions.

The electrostatic free energy

We consider a charged rod surrounded by an atmosphere of small ions in a strong electrolyte solution. The rod has radius a, a uniform surface charge, totalling ξe per Bjerrum length. The surface potential of the rod, denoted ψ_a, the volume charge density in the ion atmosphere, ρ, and the potential at axial distance r from the rod, $\psi(r)$, depend on the small ion distributions. In all cases, the potential at $r = \infty$, in the bulk solution, is $\psi = 0$. We neglect end effects of the rod. The ion atmosphere has n_i ions of type i and n_w water molecules per unit volume. In dilute solutions, the respective mole fractions are $x_i \approx n_i/n_w$ and $x_w = 1 - \Sigma_i x_i$. Bulk values are denoted n_{i0}, $n_{w0} \approx n_w$, x_{i0}, and x_{w0}, respectively.

There are various equivalent expressions for the electrostatic free energy of ionic double-layer systems (Overbeek, 1990). Here we calculate the electrical energy and entropy separately and combine them later to get the free energy. The electrostatic energy of a charge distribution is the sum of the pair interactions between the charges. This sum can be expressed as the product of charge and local potential summed over all charges, and divided by two to avoid double counting (Feynman et al., 1964). For the rod, we have a term for the surface charge, $\xi e/l_B$ per unit length, and an integral for the space charge $\rho(r)$ in the ionic atmosphere. The general expression for the electrostatic energy, E_{el} per unit length of the rod, is for all models discussed below:

$$E_{el} = \frac{1}{2l_B}\xi e\psi_a + \frac{1}{2}\int_a^\infty \rho(r)\psi(r)\,2\pi r\,dr \tag{1}$$

The potential ψ in Eq. 1 may depend on a temperature-dependent dielectric constant. In that case, Eq. 1 does not yield a pure energy, but involves also an entropy.

The difference in composition between the ion atmosphere and the bulk solution gives rise to the entropy of the ionic double layer, S_{el} per unit rod length. The electrostatic interactions between ions are already in Eq. 1. Now treating the solution everywhere as an ideal mixture of ions and water molecules yields for the entropy (Overbeek, 1990; Guggenheim, 1957):

$$S_{el} = -k\int_a^{\infty}\left(\sum_i n_i \ln\frac{x_i}{x_{i0}} + n_w \ln\frac{x_w}{x_{w0}}\right) 2\pi r\,dr \tag{2}$$

The integrand in Eq. 2 is the ideal entropy of mixing of a single, uniform phase. Because in the ionic atmosphere the solution composition varies with the radial distance r, we can regard Eq. 2 as giving the entropy of a succession of microphases with increasing r. For nonhomogeneous mixtures, Debye (1959) has derived extra contributions to the free energy due to the nonhomogeneity. Debye's treatment suggests that such extra contributions vanish for ideal mixtures, as assumed in Eq. 2. Moreover, for the electrostatic interactions Eq. 1 is valid for nonhomogeneous mixtures. The free energy derived with eqs 1 and 4 is consistent with the assumptions in the PB eq, see Eq. 9 below. With approximations for dilute solutions

$$\begin{aligned} n_w \ln\frac{x_w}{x_{w0}} &= n_w \ln\frac{1-\sum_i x_i}{1-\sum_i x_{i0}} \\ &\approx n_w\left(-\sum_i x_i + \sum_i x_{i0}\right) \\ &\approx \sum_i(-n_i + n_{i0}) \end{aligned} \tag{3}$$

Equation 2 becomes

$$S_{el} = -k\int_a^{\infty}\sum_i\left(n_i \ln\frac{n_i}{n_{i0}} - n_i + n_{i0}\right) 2\pi r\,dr \tag{4}$$

We first apply Eqs. 1 and 4 to the PB model. We apply the Boltzmann relation using the dimensionless potential $\phi = e\psi/kT$ for ions with charge $z_i e$:

$$n_i = n_{i0}e^{-z_i\phi} \tag{5}$$

With Eq. 5, Eq. 4 becomes (Overbeek, 1990)

$$S_{el} = k\int_a^{\infty}\sum_i n_{i0}(z_i\phi e^{-z_i\phi} + e^{-z_i\phi} - 1)\, 2\pi r\,dr \tag{6}$$

The potential ϕ is obtained by solving the PB equation. For cylindrical symmetry and a single z-z electrolyte with bulk concentration $n_{i0} = n_0$, the PB equation is

$$\frac{d^2(z\phi)}{dr^2} + \frac{1}{r}\frac{d(z\phi)}{dr} = \kappa^2 \sinh(z\phi) \tag{7}$$

and the Debye length $1/\kappa$ is

$$\kappa^2 = \frac{2z^2e^2n_0}{\epsilon_0\epsilon kT} \tag{8}$$

where ϵ is the dielectric constant of the solution and ϵ_0 is the permittivity of free space.

We have computed $\phi(r)$ by the numerical integration of Eq. 7, as described previously (Stigter, 1975). Using these results, we obtain the desired free energy $F_{el} = E_{el} - TS_{el}$ with the help of Eqs. 1 and 6. Following Overbeek (1990), with Eqs. 1, 6, and 7, the free energy may be converted into a different form that represents the work of charging the polyelectrolyte per unit length:

$$F_{el} = \frac{1}{l_B}\int_0^{\xi} e\psi_a(\xi')d\xi' \tag{9}$$

As a test of our numerical procedures, we have compared the two methods of computing F_{el} and found agreement to 1 part in 10^4, as expected from the numerical integration errors.

We now discuss the CC models. We start again with the infinitely long rod with radius a and charge $\xi e/l_B$ per unit length. Of this fixed charge, the portion $e/(z_il_B)$ is neutralized by a Debye-Hückel type of ionic atmosphere. The remaining counterions are distributed uniformly between the rod surface at $r = a$ and the cylindrical "condensation" surface at $r = c$ in the solution. In the limit $a \to 0$, the condensed counterions have the stepwise distribution of the CC2 model, provided that c is chosen such that the condensation volume is V_p per fixed charge. That is,

$$\pi(c^2 - a^2)l_B = \xi V_p \tag{10}$$

On the other hand, when both $a \to 0$ and $c \to 0$ we have the CC1 model with $V_P = 0$, the line charge with the δ-function of condensed counterions.

In the CC models, the potential is assumed to be the sum of two parts

$$\psi(r) = \psi_1(r) + \psi_2(r) \tag{11}$$

The first part is the DH potential around the rod (Stigter, 1975) with fixed charge $e/(z_il_B)$ per unit length:

$$\frac{e\psi_1(r)}{kT} = \phi_1(r) = \frac{2K_0(\kappa r)}{z_i\kappa a K_1(\kappa a)} \quad \text{for} \quad r > a \tag{12}$$

where K_0 and K_1 are zero-order and first-order modified Bessel functions (Abramowitz and Stegun, 1965), and κ follows from Eq. 8 with $z_i = z$.

The potential $\psi_2(r)$ is generated by the remaining fixed charge and the condensed charge with density

$$\rho_c = -\frac{(\xi - 1/z_i)e}{\pi(c^2 - a^2)l_B} \quad \text{for} \quad a < r < c \tag{13}$$

and $\rho_c = 0$ elsewhere. Integrating Poisson's equation,

$$\frac{1}{r}\frac{d}{dr}\left(r\frac{d\psi_2}{dr}\right) = -\frac{\rho_c}{\epsilon_0\epsilon} \quad \text{for} \quad a < r < c \tag{14}$$

with Gauss' boundary condition, $d\psi_2/dr = 0$ at $r = c$, and setting $\psi_2 = 0$ for $r > c$, we obtain with Eq. 13 for ρ_c:

$$\frac{e\psi_2(r)}{kT} = \phi_2(r) = \left(\frac{\xi - 1/z_i}{c^2 - a^2}\right)\left(2c^2 \ln\frac{c}{r} - c^2 + r^2\right) \qquad (15)$$

$$\text{for} \quad a < r < c$$

The ion concentrations near the rod follow from Eq. 13 and from the Boltzmann equation with Eq. 12 for ϕ_1. For the co-ions, with $i = 1$ and charge ze, we have

$$n_1 = n_0 e^{-z\phi_1} \quad \text{for} \quad r > a \qquad (16)$$

and for the counterions, with $i = 2$ and charge $-ze$,

$$n_2 = n_0 e^{z\phi_1} + \frac{\xi - 1/z}{\pi(c^2 - a^2) l_B z} \quad \text{for} \quad a < r < c \qquad (17)$$

$$= n_0 e^{z\phi_1} \quad \text{for} \quad r > c$$

With the charge density in the ionic atmosphere

$$\rho = (n_1 - n_2)ze \qquad (18)$$

and Eqs. 11, 12, and 15 for ψ, numerical integration in Eq. 1 yields E_{el}. Furthermore, with Eqs. 16 and 17 for n_1 and n_2 the integral in Eq. 4 for S_{el} can be evaluated, thus obtaining $F_{el} = E_{el} - TS_{el}$.

Numerical comparison of the PB and CC free energies

For all results in this section, we have assumed the linear charge density of B-DNA, $\xi = 2\, l_B/3.37 = 4.23$ in water at 25°C. The radius a of the rod is varied from 10 Å (Fig. 2) or 100 Å (Figs. 3 and 7) down to $a = 0.1$ Å, to provide information on the line charge, $a = 0$, by extrapolation. In the computations pertaining to the CC2 model (step function of counterions), c is chosen such that the volume of the condensed ion region is constant, $c = \sqrt{(a^2 + 14.6^2)}$ Å, giving the radius $c = 14.6$ Å by extrapolation to the line charge, $a = 0$, in 1-1 salt solutions, and $c = \sqrt{(a^2 + 25.1^2)}$ Å in 2-2 salt solutions, in accordance with Eq. 10 and with Manning's (1977) radii of the condensation regions. Computations were carried out for various concentrations, M_{salt}, of 1-1 and 2-2 electrolyte. Because we are interested in *relative* stabilities, the quantities of interest are the free energy *differences* between the CC and the PB models, F_{el} (CC) − F_{el} (PB) per Å of rod.

We first present results for 1-1 electrolytes, in Figs. 1–6. The counterion concentrations of the PB and the CC2 models are compared in Fig. 1 for a radius $a = 5$ Å of the rod and for $M_{salt} = 0.01$ M. It is obvious that the differences between the models are significant in the area close to the rod, but not in the outer part of the ionic atmosphere. For the CC2 model, Fig. 2 shows free energy differences, in units of kT, vs. $\log(M_{salt})$ for different radii a of the rod. We find that for constant a the free energy difference increases approximately linearly with decreasing $\log(M_{salt})$. The same data are replotted in Fig. 3 for constant M_{salt} as a function of $\log a$. This shows that the errors in the CC theory are greatest for rods of the smallest radii. Here the difference F(CC2) − F(PB) increases almost linearly with decreasing $\log a$. The main reason is that, for constant ξ, thinner rods have a higher surface potential and, hence, a higher electrostatic free energy. From a physical point of view, a rod with radius $a = 0.1$ Å is very close to a line charge. Figs. 2 and 3 show that for $M_{salt} = 10^{-3}$ M and $a = 0.1$ Å the CC model has a higher free energy than the PB distribution. There is no reason to believe that this would be different for $M_{salt} < 10^{-3}$ M and/or $a < 0.1$ Å in the CC2 model. For larger rod radii, around $a = 10$ Å in Fig. 3, the difference F(CC2) − F(PB) has a minimum for constant salt concentration, but for all radii F(CC2) > F(PB).

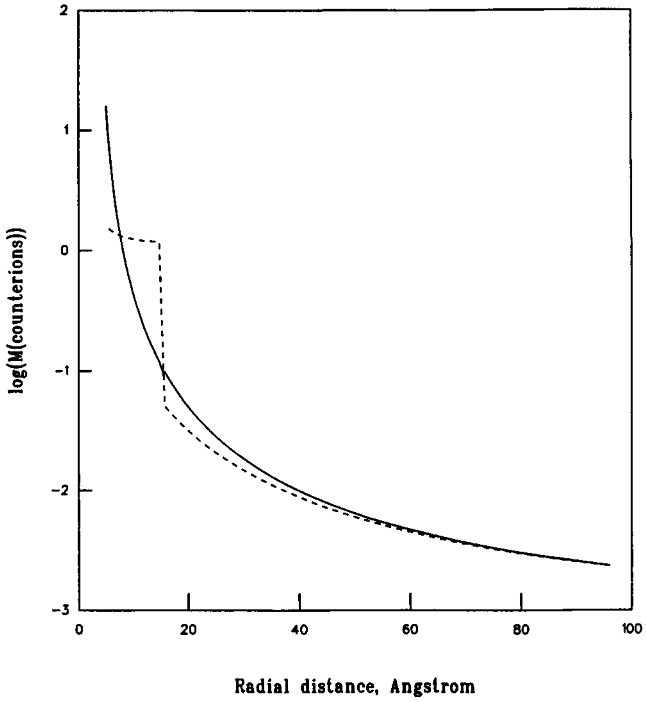

FIGURE 1 Counterion concentration (log molarity) versus radial distance, r Å, around infinitely long rod with radius $a = 5$ Å and linear charge density of B-DNA ($\xi = 4.23$ electronic charges per Bjerrum length $l_B = 7.13$ Å) in 0.01 M 1-1 electrolyte. (——) Poisson-Boltzmann model (PB). (- - - -) Second counterion condensation model (CC2) (Manning, 1977).

Whereas Fig. 3 shows the dependence on rod radius a, now we consider the dependence on condensation radius c. Figs. 4–6 show the relative stability of CC1, for constant radius of the rod, $a = 0.1$ Å. The radius c of the condensed region is varied from the value $c = 14.6$ Å for the CC2 model (see above) down to $c = a + 0.001$ Å. The differences in free energy, energy, and entropy between the CC and the PB models are plotted versus $\log(c - a)$ at constant M_{salt}. Because results for the PB model depend on a but not on c, the curves in Figs. 4–6 reflect changes in the CC model.

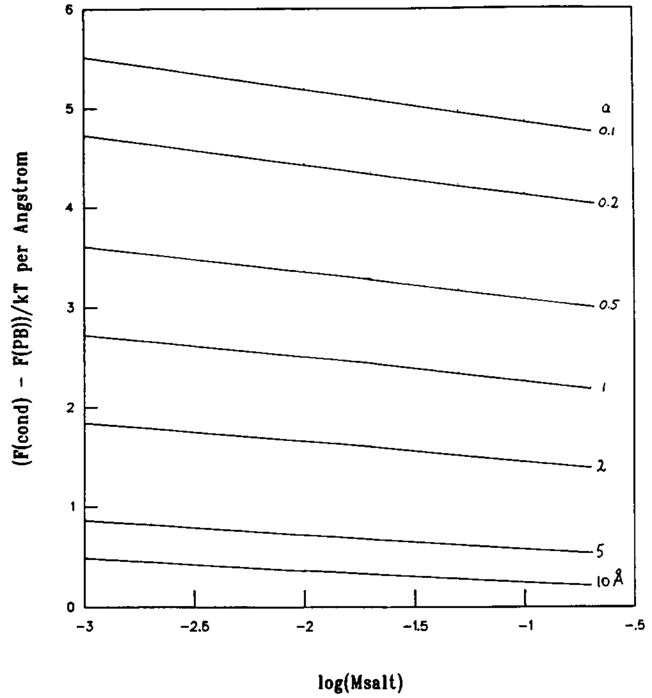

FIGURE 2 Difference of free energy, in units of kT per Å, between CC2 model (step function) and PB model versus 1-1 electrolyte molarity for rod radii $a = 0.1$ Å to $a = 10$ Å, as indicated in the figure.

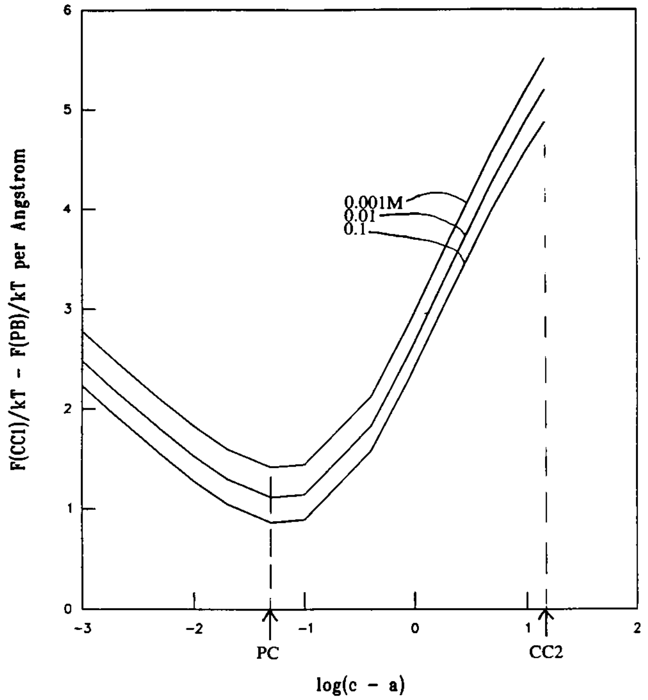

FIGURE 4 Difference of free energy, in units of kT per Å, between CC and PB models with rod radius $a = 0.1$ Å versus thickness of condensation layer, c–a Å, for 1-1 electrolyte molarities as indicated in the figure.

Fig. 4 shows that CC2 is most reliable around c–a = 0.05 Å, and becomes worse either for larger or smaller "condensation regions." Fig. 5 shows energy differences of the CC2 and PB models. For thin condensation regions, the CC2 model energy approaches a constant value because the condensed counterions cancel part of the central line charge. For wider condensation regions, the polyion-counterion attraction weakens, giving higher E_{cl}.

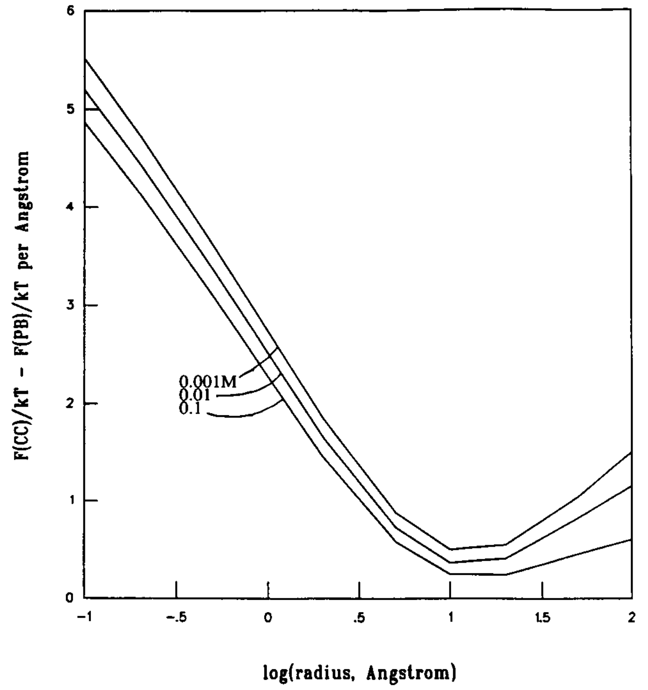

FIGURE 3 Difference of free energy, in units of kT per Å, between CC2 model and PB model versus rod radius a Å for 1-1 electrolyte molarities as indicated in the figure.

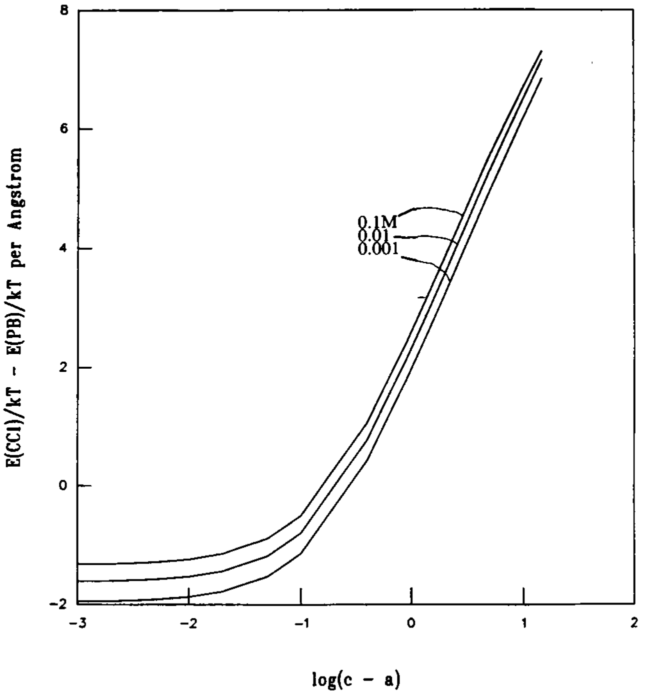

FIGURE 5 Energy differences for models of Fig. 4.

On the other hand, Fig. 6 shows that the entropy S of the condensed ions decreases steadily with diminishing thickness of the condensation region, c–a. This is because of the "ordering" of these counterions that are crowded into a diminishing volume of solution. The combined behavior of E and S explains the minimum in the free energy $F = E - TS$ in the curves of Fig. 4. Even at the minima, we find $F(\mathrm{CC}) > F(\mathrm{PB})$, the difference rising with decreasing salt concentration. On the basis of Fig. 4, we conclude that both the CC1 (for $c - a = 0$) and the CC2 models have higher free energy than the corresponding PB ion distribution.

Results for 2-2 electrolytes are presented in Figs. 7 and 8 for the conditions of Figs. 3 and 4, respectively. The behavior in 2-2 salt solutions is qualitatively the same as in 1-1 salt solutions. Minima occur in the difference curves of Figs. 7 and 8 for the same reasons as given above for 1-1 salt solutions. The data show that also for 2-2 salts the CC2 model (Fig. 7, for $a \rightarrow 0$) and the CC1 model (Fig. 8, for $c - a \rightarrow 0$) both have higher free energy than the PB model.

Relative stability of small ion distributions

The relation between free energy and stability is not always simple, in particular when two theories are compared that are both defective. Improvement of a theory may well increase the free energy. An example is the protein model of Linderstrøm-Lang (1924), a charged sphere with radius R and a charge free shell around it, between R and R_{ex}, whose thickness equals the radius of the counterions. Neglecting ionic radii by setting the exclusion radius of the protein $R_{\mathrm{ex}} = R$ does not improve the theory, although it lowers the free energy. This is so because we have changed the physics of the model by neglecting the size of the small ions.

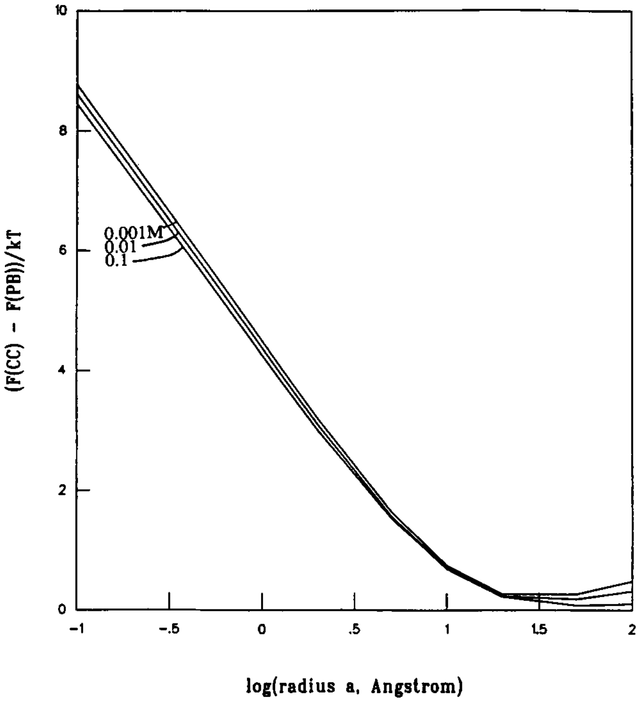

FIGURE 7 Free energy differences in 2-2 electrolyte solutions for models of Fig. 3.

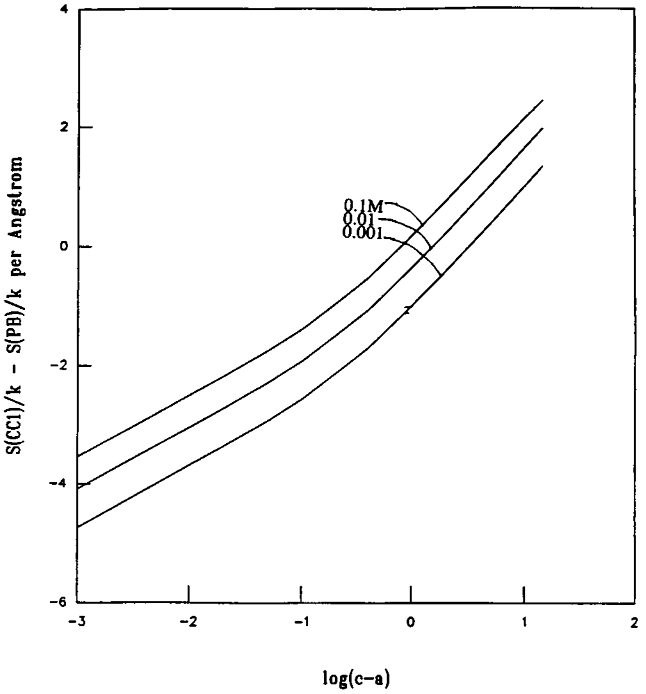

FIGURE 6 Entropy differences for models of Fig. 4.

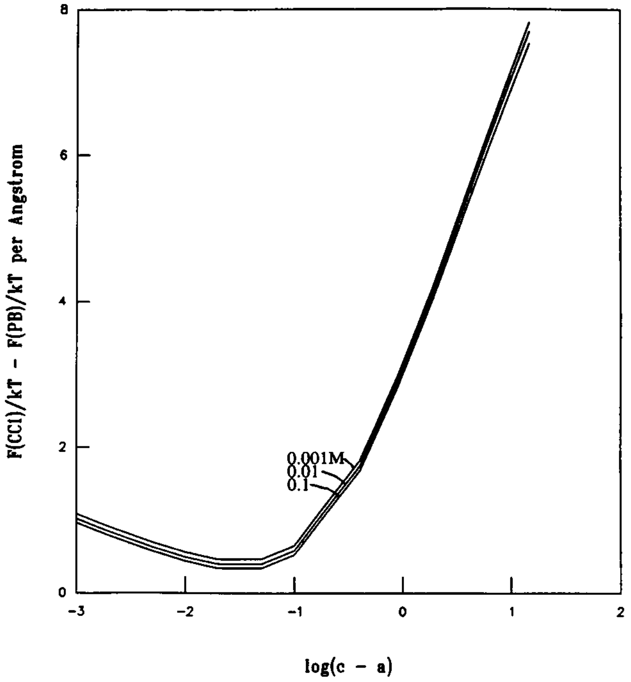

FIGURE 8 Free energy differences in 2-2 electrolyte solutions for models of Fig. 4.

PB and counterion condensation theories, however, are based on the same physical assumptions: continuum dielectric and small ions as point charges everywhere in the solution. This is obvious, e.g., from expressions such as Eqs. 19 and 20 below used in condensation theory. Here we argue that the step function of condensed counterions in CC2 theory is an artificial constraint on the Boltzmann distribution, leading to a higher free energy. A further increase of the free energy is due to the neglect of the electrostatic interaction between polyelectrolyte and condensed counterions in CC2 theory.

As mentioned earlier, in Fig. 4 the free energy of the PB model is independent of the radius c of the condensation region. Therefore, Fig. 4 shows free energy changes of the CC model as a function of the condensation radius c for the three salt concentrations. Why are the minima in the three curves, marked PC in Fig. 4, located at so much lower c than the values $c \sim 14.5$ Å reported for the CC2 model (Table 3 of Manning, 1977), marked CC2 in Fig. 4?

CC2 theory (Manning, 1977) models the polyelectrolyte chain as a linear array of point charges e with spacing b. A fraction r of the counterions is condensed in a cylindrical region with radius c around the linear array. In this theory, the electrostatic free energy is derived for the array with charge $(1 - r)e$ per site in the array. This set of effective fixed charges and the corresponding counter charge, is treated with the linearized PB equation in a solution with Debye length $1/\kappa$. The potential at a site, ψ_{site}, due to all the other charged sites at distance $b, 2b, \ldots ib, \ldots$ is

$$\psi_{\text{site}} = \frac{(1-r)e}{4\pi\epsilon_0\epsilon}\sum_{i=1}^{\infty}\frac{2e^{-\kappa ib}}{ib} = \frac{2(1-r)e}{4\pi\epsilon_0\epsilon b}\ln(1-e^{-\kappa b}) \quad (19)$$

Using the Bjerrum length $l_B = e^2/(4\pi\epsilon_0\epsilon kT)$, the electrical free energy per site with charge $(1 - r)e$ is in units of kT

$$\frac{F_{\text{site}}}{kT} = \frac{1}{2}(1-r)e\psi_{\text{site}} = \frac{(1-r)^2 l_B}{b}\ln(1-e^{-\kappa b}) \quad (20)$$

In the further derivation, Manning (1977) assumes that "... all electrostatic interactions among associated counterions and between polyion and associated counterions are adequately built into [Eq. 20] ..."

The above summary shows that, instead of using Eq. 15 above for ψ_2, Manning (1977) approximates $\psi_2 = 0$. The free energy is then minimized to find the fraction r and the condensation radius c (denoted a in Table 3 of Manning, 1977). So the difference in equilibrium values of c between PC and CC2 in Fig. 4 is caused mainly by different approximations to the electrostatic free energy. As the present treatment is more complete, we conclude that Fig. 4 gives a better value, PC, for the condensation radius c and that the CC2 theory (Manning, 1977) does not give a reliable equilibrium value of c for the condensation model.

Let us call the present CC treatment, with Eq. 15 for ψ_2, the Poisson-condensation (PC) model. Then we have for the PC value of c in Fig. 4 the free energy comparison of two different small ion distributions. In both cases, the potentials are evaluated with Poisson's equation and the free energies with Eqs. 1 and 4. It is generally accepted that an equilibrium distribution of small, mobile ions obeys Boltzmann's law, that is, the local ion concentration relates to the local ion potential through Boltzmann's equation. For example, if Poisson's equation is used for the potential calculation, the solution of the PB equation, with appropriate boundary conditions, gives the ion distribution with, through Eqs. 1, 4, and 5, the minimum free energy. This has been confirmed by variational treatments (Reiner and Radke, 1990; Sharp and Honig, 1990). In this context, we may consider the PC ion distribution as an approximation of the PB distribution. For example, dividing the ionic atmosphere into radial sections, we can construct a trial function by mixing the PC and the PB ion distributions with the coefficients in the section as unknowns, subject to overall electroneutrality. Then the free energy minimization with Eqs. 1 and 4 yields the PB ion distribution. Alternately, if we constrain the final ion distribution such that the condensed counterions ($\xi > 1$) are distributed uniformly in a condensation region, free energy minimization, with Eqs. 1 and 4 on the same ion density functional as above, produces the PC ion distribution, as given by Eqs. 16 and 17 with the PC condensation radius c of Fig. 4, and with a higher free energy than the PB model, as shown in Fig. 4. In summary, counterion condensation is an artificial constraint that raises the free energy and, hence, reduces the stability of the ion distribution. Because we see no physical justification for introducing such a constraint, or for assuming $\psi_2 = 0$ in the condensation region, we consider CC theory a nonphysical approximation to the PB theory.

DISCUSSION

The two parameters of CC theory are the effective charge, $\xi_{\text{eff}} = 1/z_i$, and the outer radius, c, of the condensation region. In many applications, ξ_{eff} is the only attribute of the theory and the parameter c is not even considered. One might well ask why CC theory agrees so often with experiment. There are two features of electrical double layers that help explain this remarkable fact. First, the outer part of ionic double layers is mostly determined by the contacting salt solution, in particular its Debye length $1/\kappa$. As demonstrated in Fig. 1, the tail end of the counterion distribution and, therefore, of the potential-distance curve, is quite close for PB and CC2 theory. So for properties that depend mostly on the distant regions of the double layer, predictions by PB and CC theory are expected to be quite close. An example is the salt distribution in a Donnan equilibrium. Second, some properties depend more on the overall electroneutrality of the double layer than on its particular structure. An example is the binding of ionic ligands to polyelectrolytes, in particular the dependence of such binding on ionic strength.

Above we have used a variational argument to show that CC ion distributions are more artificially constrained and, therefore, less stable than the PB model. We now present a different view of the deficiencies of CC theory. For specified boundary conditions, the PB equation uniquely determines the small ion distribution in the ionic atmosphere around the polyion. It follows that, because the CC distribution is different, CC theory cannot everywhere satisfy both the Poisson and the Boltzmann laws, as shown more specifically by the following arguments.

The first condensation theory (Manning, 1969a, b) discusses the counterion distribution around a polyelectrolyte rod with radius a in a salt solution with Debye length $1/\kappa$. The central argument of CC1 theory (Manning, 1969a) is that in the limit $\kappa a = 0$ (line charge, $a = 0$, in salt solution or rod in saltfree solution, $\kappa = 0$), the attraction between the central rod or line charge and a counterion causes divergence of the phase integral for $\xi = 1/z_i$. This divergence is avoided by assuming an *effective* charge density $<1/z_i$ of the polyelectrolyte by the condensation of counterions on it. Although the derivation produces a limiting law, to mend a defect for $\kappa a = 0$, this limiting law is assumed to have validity also for finite κa. Our view is that the application at finite κa of counterion condensation is not warranted. For finite κa, the electrostatic potential at and near the model rod remains finite and, therefore, Boltzmann's law predicts a finite counterion concentration at the surface of the rod. However, CC1 theory assumes a δ-function of condensed counterions, that is, an *infinitely high* surface concentration of counterions, for $\kappa a > 0$ in equilibrium with a *finite* surface potential. Therefore, for finite κa the behavior of the condensed ions in CC1 theory is inconsistent with Boltzmann's law.

In CC2 theory, only the uncondensed counterions are accounted for completely in the free energy, through Eq. 20. For the condensed counterions and the corresponding polyion charge, on the other hand, the electrostatic interaction is omitted. This omission implies that the condensed counterions can be separated from the fixed polyion charge without doing any work, that is, all charges remain in a region of the same electrostatic potential. However, to assume a constant potential, that is, a potential field without curvature in the charged condensation volume, does not agree with Poisson's law.

It might be argued that violation of the Poisson or Boltzmann law as shown above is irrelevant, because at or near a highly charged interface the PB equation is in error anyway. For flat double layers, such errors were addressed by Stern already in 1924. He proposed Langmuir adsorption to the charged surface of small ions modeled as charged spheres of finite size with an electrostatic adsorption potential, and a PB atmosphere of point-charge ions outside such an ionic monolayer. This Stern-PB double-layer model explains experimental data for the mercury/water interface quite well (Kruyt, 1952; Hunter, 1987). A similar Langmuir adsorption with electrostatic corrections is also consistent with size effects of counterions on the electrophoretic mobility of B-DNA (Schellman and Stigter, 1977). PB theory predicts counterion concentrations at or near highly charged surfaces that are far too high (see, e.g., Fig. 1). Stern theory reduces these high concentrations by introducing the excluded volume effect of small ions. CC theory ignores excluded volume, as does PB theory, but treats the counterion concentration in quite a different way. CC1 theory exacerbates the error of PB theory at the charged surface with a further increase of the local ion concentration (in a δ-function of condensed counterions). CC2 theory overcompensates for the error of PB theory by assuming a condensation layer of thickness 14 Å for monovalent or 25 Å for divalent counterions, instead of a thickness of 4 or 5 Å for a monolayer of counterions. Therefore, we do not consider CC theory an improvement of PB theory.

TABLE 1 Free energy ratio of DH and PB double layers of rod with one charge e per Bjerrum length l_B = 7.13 Å as a function of ratio κa of radius and Debye length

κa	F(DH)/F(PB)
16.	1.00026
8.	1.00105
4.	1.00350
2.	1.01005
1.	1.02353
0.5	1.04340
0.25	1.06426
0.125	1.08028
0.0625	1.08934
0.03125	1.09223
0.015625	1.09165

It is well known (Kirkwood, 1934) that for low potentials the PB equation may be linearized and becomes self consistent, that is, when $\sinh(z\phi) = z\phi$, and the Debye-Hückel approximation is valid:

$$\nabla^2\phi = \kappa^2\phi \tag{21}$$

As shown analytically for flat double layers (Verwey and Overbeek, 1948; Overbeek and Stigter, 1956) and numerically for colloidal spheres (Overbeek and Stigter, 1956) and rods (Stigter, 1975) with constant surface charge, linearization of the PB equation for higher potentials always leads to an increase of the free energy. This is demonstrated in Table 1, which shows for $\xi = 1$ in 1-1 electrolyte the ratio F(DH)/F(PB) as a function of κa. Therefore, except for sufficiently low potentials, DH ion distributions are always unstable compared with (nonlinear) PB ion distributions. In summary, for high charge densities there is no simple way to rectify the inconsistency of the PB equation: both the Debye-Hückel approximation and the condensation of counterions introduce larger errors.

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