ON THE THEORY OF IONIC SOLUTIONS

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ABSTRACT One of the purposes of this paper is to assess the degree of applicability of the nonlinear Poisson-Boltzmann equation. In order to do this we compare the thermodynamic properties calculated through this equation with Monte Carlo data on 1-1 and 2-2 electrolytes described by the restricted primitive model, in which the ions are modeled by hard spheres with a coulombic potential and the solvent is modeled as a continuum dielectric medium of uniform dielectric constant ϵ. We choose Monte Carlo data rather than real experimental data since all parameters are completely specified and there is no liberty for "adjustment." Thus this serves as a definitive test. In addition, we present a simple but numerically accurate alternative approximation scheme which is not only numerically superior to the Poisson-Boltzmann equation but avoids the necessity of solving a nonlinear partial differential equation which is approximate in the first place. The new approximation scheme that is presented here is suggested by recent developments in the statistical mechanical theories of ionic solutions which are reviewed in the Introduction. Although these theories themselves yield exceedingly good comparison with experimental (Monte Carlo) data, they involve fairly advanced theoretical and mathematical techniques and do not appear to be readily solvable for other than very simple geometries. The two approximations suggested here require only the solution of the linear Debye-Hückel equation, which has been solved for a variety of systems. These two approximations are simple to apply and yield good thermodynamic properties up to concentrations of 2 M for the restricted primitive model. In addition, they have a sound theoretical foundation and are offered as a substitute for the difficult-to-solve nonlinear Poisson-Boltzmann equation.

INTRODUCTION

The first successful molecular theory of electrolyte solutions was the well-known theory developed by Debye and Hückel in 1923 (1). Briefly, they combined Poisson's equation of electrostatics with the Boltzmann factor of statistical mechanics to derive a (nonlinear) partial differential equation for the electrostatic potential about a central ion in solution. The partial differential equation is now known as the (nonlinear) Poisson-Boltzmann equation. A key step in the Debye-Hückel treatment is the linearization of this nonlinear equation. This step yields a linear partial differential equation which is readily solved and straightforwardly leads to simple expressions for the thermodynamic properties of electrolyte solutions. It was subsequently shown by Fowler (2), Onsager (3), and others that the Debye-Hückel theory is *exact* in the limit of small concentration, and hence we have the expression "Debye-Hückel limiting law," emphasizing that the thermodynamic properties of all electrolyte solutions must approach the Debye-Hückel expressions as the concentration goes to zero. Extensive comparison with experimental data has substantiated the Debye-Hückel theory as a limiting law; but also shows that the practical region of its applicability is limited to concentrations less than approximately 0.01 mol/liter for aqueous 1-1 electrolytes and less for others. Thus, although the Debye-Hückel theory is a fundamental limiting law, it is not a theory for the calculation of the thermodynamic properties of other than very dilute solutions. It, in fact, has been stated facetiously that its validity is limited to slightly contaminated distilled water (4).

It is important to realize that the small concentration limit of the Debye-Hückel theory is not simply due to the linearization of the Poisson-Boltzmann equation. In fact, it has been clearly demonstrated theoretically by many authors (cf. e.g., Kirkwood and Poirier [5]) that the nonlinear Poisson-Boltzmann equation itself is rigorously valid *only* in the limit in which linearization becomes possible, i.e. in the limit of zero ionic strength. Nevertheless this equation has seen much use in the biophysical and physiological literature and its limitations or approximate nature are seldom discussed. One of the purposes of this paper is to study the numerical limitations of this equation for several specific cases by comparing the results of this approximate equation to rigorous calculations or to "experimental data."

We shall also present and discuss an alternative approach which is not only easier to use than the nonlinear Poisson-Boltzmann equation but is numerically superior, at least for all the cases for which definitive comparisons can be made. This new approach is based upon some recent advances in the statistical mechanical calculation of the properties of electrolyte solutions, which we shall review below.

There was little improvement made over the Debye-Hückel theory until 1950, when Mayer (6) reformulated his cluster expansion theory of nonideal gases to solutions of electrolytes. The end result of his analysis is a virial-type expansion of the thermodynamic properties of ionic solutions. He was able to show that the Debye-Hückel theory results from the lowest order in the concentration. Detailed calculations and tabulations were made for the first correction to the limiting law, yielding results that compare favorably with experiment up to 0.1 M for 1-1 electrolytes (7, 8).

The Mayer theory remained the most successful theory of ionic solutions until the late 1960s when several significant advances appeared simultaneously in the statistical mechanical literature. These recent theories, to be described shortly, and reviewed also by Rasaiah (9), are able to treat the coulombic interactions essentially exactly to concentrations exceeding 2 M. It thus became necessary to formalize the model upon which the Debye-Hückel theory and most all subsequent theories are based. In this model, known now as the restricted primitive model, the ions are treated as hard spheres of diameter R, with charges located at their centers, immersed in a continuous dielectric medium of uniform dielectric constant ϵ. Very recent work has begun to extend this primitive model (9-11) but the model is believed to represent the essential features of interionic interactions.

The first of these "modern" statistical mechanical theories of ionic solutions was presented by Rasaiah and Friedman in 1968 (12–15). Instead of formulating the statistical thermodynamics in terms of a virial-type expansion as Mayer had done, Rasaiah and Friedman utilized techniques that had been developed in the theory of liquids. These techniques consist of deriving integral equations for the radial distribution function, which in the case of ionic solutions represent the distribution of ions about one another. The solution of these integral equations requires a fairly elaborate numerical procedure, but once this is done, the thermodynamic properties of the solution follow by straightforward statistical thermodynamics. They find that one of this class of integral equations, called the hypernetted chain (*HNC*) equation, gives the best results for ionic solutions.

Shortly later, Waisman and Lebowitz (16, 17) introduced a new integral equation called the mean spherical model, which they were able to solve analytically for the restricted primitive model. For example, they find the following simple expression for the mean ionic activity coefficient for a z–z electrolyte

$$\ln \gamma_{\pm} = \ln \gamma^{HS} + \ln \gamma_{\pm}^{el}, \tag{1}$$

where

$$\ln \gamma_{\pm}^{el} = (1/24\xi)[x(1 + 2x)^{1/2} - x - x^2]. \tag{2}$$

$x = \kappa R$, where R is the effective ionic diameter, $1/\kappa$ is the Debye-Hückel screening parameter, $\kappa^2 = (4\pi e^2/\epsilon kT)\Sigma_i c_i z_i^2$, e is the magnitude of the electronic charge, k is the Boltzmann constant, T is the absolute temperature, ϵ is the dielectric constant of the solvent, z_i and c_i are the valence and the bulk number concentration (particles per unit volume) of species i, respectively. For a z–z electrolyte

$$\begin{aligned} x^2 &= 24\,B\xi \\ B &= e^2\,|\,z_+z_-\,|\,/\epsilon kTR \\ \xi &= (\pi/6)cR^3 \\ c &= \sum_i c_i \end{aligned} \tag{3}$$

and $\ln \gamma^{HS}$ is the hard sphere contribution. Carnahan and Starling (18) proposed an approximation for the thermodynamics of hard spheres that is essentially exact; one can derive:

$$\ln \gamma^{HS} = \xi(8 - 9\xi + 3\xi^2)/(1 - \xi)^2. \tag{4}$$

In spite of the beautiful simplicity of this theory, Tables I–V show that its results compare quite well with the extensive numerical calculations of Rasaiah and Friedman. A disadvantage of the mean spherical model, however, is that it has been solved so far only for the simplest cases. It has not yet been solved for the case of ions of different size hard-sphere cores, for example, or for other than spherical geometry.

Tables I–V introduce another important recent contribution to the theory of concentrated ionic solutions. Card and Valleau (19, 20) (J. Valleau, private communication) have undertaken a program of using Monte Carlo techniques to evaluate directly the statistical mechanical partition function of a restricted primitive model consisting of several hundred ions. This is extremely important work since it provides numerical data on the restricted primitive model. Since, of course, real experimental systems are only modeled by the restricted primitive model, such Monte Carlo calculations can be considered as the analog of experimental data. These "data" are indispensable in comparing competitive theories since the intermolecular (or interionic) model is completely specified. Thus, discrepancies are due to inadequacies of the theory and cannot be dismissed by an adjustment of parameters. Quality Monte Carlo calculations have appeared for 1–1 and 2–2 electrolytes (19, 20) in the restricted primitive model and we shall use these below.

The latest, and in a sense the most complete, of the recent developments is due to Andersen and Chandler (21–23). In a series of papers, they first developed a convergent expansion for the Helmholtz free energy by transforming the partition function into Fourier transform space. The first term in this expansion corresponds to the so-called random phase approximation (*RPA*). A faster converging expansion is obtained when a certain optimization of the long-range interaction potential *within* the hard core radius is performed. As a result of this optimization, inclusion of only the first term in the expansion, referred to as the optimized random phase approximation (*ORPA*), is found to be identical to the mean spherical model. The approximation obtained by inclusion of the second term in this expansion, called the optimized random phase approximation + the second mode ($ORPA + a_2$), gives excellent agreement with the Monte Carlo calculations of Card and Valleau.

This successful initial approach, also referred to as the *MEX* method (cf. Tables I–IV), was followed by an even more successful approach (24–27) which arises through a somewhat complicated topological reduction of the graphs that occur in the Mayer theory and the same optimization of the long-range interaction potential within the hard-core radius. This theory is called the optimized random phase approximation plus "virial correction," $ORPA + B_2$, the results of which are essentially identical to those obtained by Rasaiah and Friedman for a 1–1 electrolyte. An important result of this work is the so-called exponential approximation for the interionic radial distribution, an approximation which Andersen, Chandler and others (24–27) show is almost exact if formulated according to their prescription. Unfortunately, this requires that one solve the mean spherical model first. A second goal of this paper, in addition to a numerical assessment of the nonlinear Poisson-Boltzmann equation, is to present a modification of the exponential approximation which is extremely easy to use and yet yields quite satisfactory agreement with Monte Carlo results.

In the next section we shall review the relevant general statistical mechanical equations. Then we shall introduce the principal approximation of this paper and present a detailed numerical comparison of two easily used approximations to the more exact, but also more demanding, theories. In order to try to assess their merits for various cases, we shall discuss comparisons for 1-1 and 2–2 electrolytes.

GENERAL THEORY

Consider the restricted primitive model of an ionic solution, i.e. consider a system of charged hard spheres of diameter R with a charge located at the center and dissolved in a continuous medium of uniform dielectric constant ϵ. According to Poisson's equation, the average electrostatic potential $\psi_j(r)$ at a distance r from the center of an ion of type j is given by

$$\nabla^2\psi_j(r) = -(4\pi/\epsilon)n_j(r), \tag{5}$$

where $n_j(r)$ is the local charge density about the central j ion. This quantity can be written rigorously as

$$n_j(r) = \sum_i z_i e c_i g_{ij}(r), \tag{6}$$

where z_i and c_i are the valence and bulk concentration (particles per unit volume, N_i/V) of ionic species i, respectively, e is the magnitude of the electronic charge, and $g_{ij}(r)$ is the radial distribution function of ions of species i about a central j ion. The interionic radial distribution function is defined such that $c_i g_{ij}(r)$ is the *local* concentration if i-type ions about a central j ion. This function plays a central role in modern statistical mechanical theories of ionic solutions since all thermodynamic quantities can be expressed in terms of it. For example, the excess thermodynamic energy and excess (osmotic) pressure are given by (9, 12):

$$\frac{E^{ex}}{NkT} \equiv \frac{E}{NkT} - \frac{3}{2} = \frac{1}{2ckT}\sum_{ij} c_i c_j \int_0^\infty u_{ij} g_{ij}(r) 4\pi r^2 \mathrm{d}r, \tag{7}$$

and

$$p_v^{ex} \equiv p - ckT = -\frac{1}{6}\sum_{ij} c_i c_j \int_0^\infty r\frac{\partial u_{ij}}{\partial r} g_{ij}(r) 4\pi r^2 \mathrm{d}r, \tag{8}$$

where $c = \Sigma c_j$, $N = \Sigma N_j$, and u_{ij} is the interionic potential. The summations here are over all ionic species.

The subscript v in Eq. 8 comes about as follows. Eq. 8 is only one of three exact, independent expressions that one can derive for the excess osmotic pressure. One of these is a multicomponent generalization of an equation that relates the compressibility to the radial distribution function (12) and the other is derived from the expression $p^{ex} = -(\partial A^{ex}/\partial V)_T$, where A^{ex} is obtained by applying the Gibbs-Helmholtz equation, $E = (\partial[A/T]/\partial[1/T])_V$, to Eq. 7. Of course, since each of these equations is exact, the same value of the excess pressure is obtained *provided the exact interionic dis-*

tribution function is used. On the other hand, if, as is usually the case, an approximate interionic distribution function is used, each of these three equations will yield a different value for p^{ex}. Consequently we shall label p^{ex} to indicate through which equation it is calculated. Since Eq. 8 is closely related to the virial equation of imperfect gas theory, the excess pressure calculated from it will be denoted by p_v^{ex}. Similarly, the excess pressure calculated from the generalization of the compressibility equation will be denoted by p_c^{ex} (12) and that calculated through the energy equation and the Gibbs-Helmholtz equation will be denoted by p_E^{ex}.

In the restricted primitive model, the interionic potential is taken to be the sum of a hard sphere and an electrostatic potential. Thus we write

$$u_{ij}(r) = u_{ij}^{HS}(r) + u_{ij}^{\text{elec}}(r) \tag{9A}$$

where

$$u_{ij}^{HS}(r) = \begin{cases} \infty & r < R \\ 0 & r > R \end{cases} \tag{9B}$$

and

$$u_{ij}^{\text{elec}}(r) = z_i z_j e^2/\epsilon r \qquad r > R \tag{9C}$$

Note that the electrostatic potential need not be specified in the region $r < R$ since $u_{ij}^{HS} = \infty$ there. This fact will be discussed below. With this form for $u_{ij}(r)$, Eqs. 7 and 8 become

$$\frac{E^{ex}}{NkT} = \frac{2\pi e^2}{c\epsilon kT}\sum_{i,j} c_i c_j z_i z_j \int_R^\infty g_{ij}(r) r\,\mathrm{d}r, \tag{10}$$

and

$$p_v^{ex} = \frac{e^2}{6\epsilon}\sum_{i,j} c_i c_j z_i z_j \int_R^\infty g_{ij}(r) 4\pi r\,\mathrm{d}r + \frac{2\pi kTR^3}{3}\sum_{i,j} c_i c_j g_{ij}(R+), \tag{11}$$

where $g_{ij}(R+) = \lim g_{ij}(R + \alpha)$ as $\alpha \to 0$ for $\alpha > 0$.

It is customary to define the osmotic coefficient ϕ through

$$\phi = p/ckT. \tag{12}$$

If we use Eq. 11 for p_v, we have

$$\phi_v = 1 + \frac{E^{ex}}{3NkT} + \frac{2\pi R^3}{3c}\sum_{i,j} c_i c_j g_{ij}(R+), \tag{13}$$

where we have subscripted ϕ to indicate that we have used the virial expression for

p or p^{ex}. Clearly we also have the quantities ϕ_c and ϕ_E, which would all be identical if the exact $g_{ij}(r)$ were used, but not necessarily otherwise.

By using the Gibbs-Duhem equation, one can express the mean electrostatic activity coefficient $\gamma_\pm$ in terms of ϕ (12–15)

$$\ln \gamma_\pm = \phi(m) - 1 + \int_0^m (\phi(m') - 1)\, d \ln m', \tag{14}$$

where m is the molar salt concentration. Again we shall have the quantities $\ln \gamma_\pm^v$, $\ln \gamma_\pm^c$, and $\ln \gamma_\pm^E$.

The radial distribution function can be formally expressed in terms of the potential of mean force $w_{ij}(r)$ through

$$g_{ij}(r) = e^{-w_{ij}(r)/kT}. \tag{15}$$

The potential of mean force is the potential associated with the force between two ions *with the N-2 other ions canonically averaged over all positions.* Consequently it is a function of concentration and temperature. Using Eq. 15 for $g_{ij}(r)$, Eq. 5 becomes

$$\nabla^2 \psi_j(r) = -\frac{4\pi e}{\epsilon} \sum_i z_i c_i e^{-w_{ij}(r)/kT}. \tag{16}$$

This equation is exact. In the limit of low values of $B = | z_i z_j | e^2/\epsilon kTR$ and low concentrations, one can expand the exponential in Eq. 15 and keep the first two terms:

$$e^{-w_{ij}/kT} \approx 1 - w_{ij}/kT. \tag{17}$$

Consistent with this approximation is the assumption that the potential of mean force is given by

$$w_{ij}(r) \approx z_i e \psi_j(r) \qquad r > R \tag{18}$$

outside the hard core.

Eq. 16, together with approximations 17 and 18, becomes after invoking electroneutrallity

$$\begin{aligned} \nabla^2 \psi_j(r) &= 0 & r < R \\ &= \kappa^2 \psi_j(r) & r > R \end{aligned} \tag{19}$$

where

$$\kappa^2 = \frac{4\pi e^2}{\epsilon k T} \sum_j c_j z_j^2. \tag{20}$$

This is the linearized Poisson-Boltzmann equation, first obtained by Debye and

Hückel. The well-known solution to this equation for spherically symmetric ions is

$$\psi_j^{DH}(r) = (z_j e/\epsilon r)[e^{-\kappa(r-R)}/(1 + \kappa R)] \qquad r > R \tag{21}$$

This leads directly to the famous Debye-Hückel expression for $\ln \gamma_{\pm}$:

$$\ln \gamma_{\pm} = -\frac{|z_+ z_-| e^2}{2\epsilon kT} \frac{\kappa}{1 + \kappa R} \tag{22}$$

Strictly speaking, one should ignore the term in κR in this result since the theory is valid only in the $\kappa \rightarrow 0$ limit, but for practical reasons (cf. ref. 28, p. 401), Eq. 22 is often used and is referred to as the extended Debye-Hückel theory.

If the exponential in Eq. 15 is not linearized but approximation 18 is still used, one obtains the nonlinear Poisson-Boltzmann equation for $\psi_j(r)$:

$$\nabla^2 \psi_j(r) = -\frac{4\pi e}{\epsilon} \sum_i z_i c_i e^{-z_i e \psi_j(r)/kT} \qquad r > R \tag{23}$$

Since this equation is not exact, one obtains different expressions for thermodynamic properties whether one charges one ion (say the central one) against the others fully charged or charges all N ions simultaneously. The first is called the Güntelberg charging process and the second is called the Debye charging process. In addition the use of Eqs. 10–14 yields results differing from those obtained using either charging process.

For a symmetrical electrolyte, $|z_i| = |z_j| = z$, and Eq. 23 becomes

$$(1/\rho)(d^2/d\rho^2)(\rho y) = \sinh y \qquad \rho > \rho_0 \tag{24}$$

where $y = |z| e\psi/kT$, $\rho = \kappa r$ and $\rho_0 = \kappa R$. The appropriate boundary conditions are

$$y \rightarrow 0, \ dy/d\rho \rightarrow 0 \qquad (\rho \rightarrow \infty)$$

and

$$dy/d\rho = -B/\rho \qquad \text{at } \rho = \rho_0. \tag{25}$$

The Debye-Hückel theory results from replacing $\sinh y$ by y.

Eq. 24, being nonlinear, is difficult to solve. Numerical solutions have been obtained by Guggenheim (29, 30) and Gardner and Glueckauf (31) using the numerical method proposed by Müller (32). Some values of the thermodynamic properties of 1–1 and 2–2 electrolytes have been reported by Burley et al. (33). We have extended these results by using a variational technique due to Arthurs and Robinson (34, 35) and used recently by Brenner and Roberts for the case of a spherical colloidal particle (36). The details of the calculations are outlined in the Appendix and the results will be discussed below.

A NEW SIMPLE APPROXIMATION

Of the recent statistical mechanical theories of ionic solutions, the exponential approximation of Andersen and Chandler (21–24) is of particular interest here. The predicted thermodynamic properties of up to 2 M solutions are essentially exact when compared with the Monte Carlo data of Card and Valleau. One of the final results of their development is to write the interionic radial distribution function as

$$g_{ij}(r) = g_{ij}^{HS}(r)\exp\zeta_{ij}(r), \tag{26}$$

where $g_{ij}^{HS}(r)$ is the radial distribution function of a hard sphere system and $\zeta_{ij}(r)$ is a renormalized potential defined by a sum of certain kinds of diagrams. We shall discuss each of these in turn.

The quantity $g_{ij}^{HS}(r)$ is now a standard numerical function in statistical mechanics and there exist programs to evaluate it for any density of hard spheres (38).[1] On the other hand, even a 2 M solution is a dilute hard-sphere system (compared to a dense fluid) and so one can use the analytic expression (39)

$$\begin{aligned} g_{ij}^{HS}(r) &= 0 && r < R \\ &= 1 + \frac{4\pi}{3}cR^3\left[1 - \frac{3}{4}\frac{r}{R} + \frac{1}{16}\frac{r^3}{R^3}\right] && R < r < 2R \\ &= 1 && r > 2R \end{aligned} \tag{27}$$

When $\zeta_{ij}(r)$ is evaluated for a symmetric restricted primitive z-z electrolyte, it is given by

$$\zeta_{ij}(r) = \frac{(-1)^{i+j}}{(2\pi)^3}\int e^{i\mathbf{k}\cdot\mathbf{r}}\hat{v}(k)\mathrm{d}\mathbf{k}, \tag{28}$$

where

$$\hat{v}(k) = -\beta\hat{u}(k)/(1 + c\beta\hat{u}(k)). \tag{29}$$

$\beta = 1/kT$, and $\hat{u}(k)$ is the Fourier transform of the potential $u(r)$:

$$\hat{u}(k) = \int u(r)e^{-i\mathbf{k}\cdot\mathbf{r}}\mathrm{d}\mathbf{r} \tag{30}$$

where $u(r)$ is given by a coulombic potential for $r > R$, i.e.

$$u(r) = z^2e^2/\epsilon r \qquad r > R \tag{31}$$

but is arbitrary inside the hard core region, $r < R$, where the hard sphere potential is infinite. The key point of the exponential approximation is to find the form of the

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[1] We used a Fortran package kindly made available by D. Henderson; a listing of this program will appear in Appendix D of McQuarrie (39).

potential inside the hard core that makes the sum of diagrams converge fast and thus makes Eq. 26 a good approximation.

Chandler and Andersen (24–27) have formulated a functional differentiation optimization prescription for $u(r)$ inside the hard core, but if one assumes simply that $u(r)$ is given by Eq. 31 for all values of r, $\zeta_{ij}(r)$ can be obtained analytically, although the convergence is not fast. It is interesting that in this case, $\zeta_{ij}(r)$ is given by

$$\zeta_{ij}(r) = -(-1)^{i+j}(z^2e^2/\epsilon kT)(e^{-\kappa r}/r), \tag{32}$$

that is, the potential predicted by the Debye-Hückel limiting law.

This suggests the use of some form of the well-known extended form of the Debye-Hückel expression for $\zeta_{ij}(r)$, viz., something similar to

$$\zeta_{ij}(r) = -\frac{z_iz_je^2}{\epsilon kT(1+\kappa R)}\frac{e^{-\kappa(r-R)}}{r}. \tag{32}$$

One can use this directly and write

$$g_{ij}(r) = g_{ij}^{HS}(r)\exp\left\{-\frac{z_iz_je^2}{\epsilon kT(1+\kappa R)}\frac{e^{-\kappa(r-R)}}{r}\right\}, \tag{33}$$

which is equivalent to assuming that the potential of mean force is approximated by

$$w_{ij}(r) \approx w_{ij}^{HS}(r) + z_ie\psi_j^{DH}(r), \tag{34}$$

where $\psi_j^{DH}(r)$ is the solution of the linearized Poisson-Boltzmann equation given by Eq. 21 and $w_{ij}^{HS}(r)$ is the hard sphere poential of mean force, i.e., $g_{ij}^{HS}(r) = \exp\{-\beta w_{ij}^{HS}(r)\}$. For 1-1 electrolytes this approximation is found to give very good results, but as the charge on the ions, i.e. the value of B, increases, the results deteriorate. Furthermore, $g_{ij}(r)$ given by Eq. 33 does not satisfy the condition of electroneutrality. It is interesting to note that Rasaiah and Friedman (12) found similar results in their $g(\Lambda)$ approximation.

We have investigated two alternative approximations which are essentially parametrized forms of Eq. 32 in which the parameter is chosen to satisfy electroneutrality. For the first one we assume that $\zeta_{ij}(r)$ is given by Eq. 32 but with an *effective* concentration. Thus we write this as

$$\zeta_{ij}(r) = -[z_iz_je^2/\epsilon kT(1+p\kappa R)][e^{-p\kappa(r-R)}/r]. \tag{35}$$

Given the assumption of Eq. 35, we can choose the constant p by requiring that $g_{ij}(r)$ satisfy the condition of electroneutrality, viz., that the total charge surrounding a central ion must be opposite the charge on that ion. Mathematically, we write

$$\int_R^\infty \sum_j z_jec_jg_{ij}(r)4\pi r^2\mathrm{d}r = -z_ie.$$

By multiplying this relation by $z_i c_i e$ and summing over i we get

$$S_0 \equiv \sum_{i=1}^{\sigma} \sum_{j=1}^{\sigma} c_i c_j z_i z_j e^2 \int_R^{\infty} g_{ij}(r) 4\pi r^2 \mathrm{d}r = -\kappa^2 \epsilon kT/4\pi. \tag{36}$$

as an expression of electroneutrality. Substitution of Eqs. 26 and 35 into Eq. 36 gives an algorithm for finding p and hence $g_{ij}(r)$ through

$$g_{ij}(r) = g_{ij}^{HS}(r) \exp\left\{-\frac{z_i z_j e^2}{\epsilon kT(1 + p\kappa R)} \frac{e^{-p\kappa(r-R)}}{r}\right\}. \tag{37}$$

In particular, for a z-z electrolyte, the condition giving p is

$$\int_R^{\infty} g^{HS}(r) \sinh\left\{\frac{z^2 e^2}{\epsilon kT(1 + p\kappa R)} \frac{e^{-p\kappa(r-R)}}{r}\right\} r^2 \mathrm{d}r = (4\pi c)^{-1}, \tag{38}$$

where $c = 2c_1 = 2c_2$. For dilute solutions, sinh x may be linearized and $g^{HS}(r)$ taken equal to 1 to get $p = 1$, which is the extended Debye-Hückel theory result, Eq. 32. It turns out that for small values of z^2 (say $z^2 < 4$), $p = 1$ almost satisfies Eq. 38 for concentrations up to $\kappa R = 1$ (~ 1 M).

Once p is determined through condition Eq. 38, $g_{ij}(r)$ is specified through Eq. 37 and the thermodynamic properties are specified through Eqs. 10–14. These are given by the columns labeled exp(DH) in Tables I–VI.

We also have investigated another approximation for $\zeta_{ij}(r)$ that is suggested from the work of Hoskin (40), who obtained numerical solutions to the (nonlinear) Poisson-Boltzmann equation for the potential distribution in the double layer of a single spherical colloidal particle. After modifying Hoskin's expression for ψ for the case of a fixed surface charge density rather than a fixed surface potential, we write

$$\zeta_{ij}(r) = -\frac{z_i z_j e^2}{\epsilon kT(1 + \kappa R)} \frac{e^{-\kappa(r-R)}}{r} \left(\frac{1 + qe^{-2\kappa(r-R)}}{1 + q\alpha}\right), \tag{39}$$

where $\alpha = (1 + 3\kappa R)/(1 + \kappa R)$. We have used this expression in particular since it was used by Stigter and Hill (41) in the calculation of the osmotic pressure and of the salt distribution in a Donnan system with highly charged colloidal particles, or i.e. for a system not unlike our anticipated applications to protein solutions and charged membranes. The parameter q is determined by requiring that electroneutrality is satisfied when Eq. 39 is substituted into Eq. 26 and this in turn into Eq. 36. The results of this approximation are given by the columns labeled exp(H) in Tables I–VI.

NUMERICAL RESULTS

The excess thermodynamic energy, osmotic coefficient, and the logarithm of the mean ionic activity coefficient calculated through both the virial and compressibility routes

TABLE I

THE REDUCED CONFIGURATIONAL ENERGY $-E^{ex}/NkT$ FOR A 1-1 RESTRICTED PRIMITIVE MODEL AQUEOUS ELECTROLYTE SOLUTION

The ionic diameter is 4.25 Å, the dielectric constant is 78.5, and the temperature is 298.0°K. *PB* designates the Poisson-Boltzmann result, *MSM* is the mean spherical model, exp(*DH*) and exp(*H*) refer to approximations on Eqs. 37 and 39, *MEX* is the optimized mode expansion result, *HNC* is the hypernetted chain integral equation, and *MC* is the Monte Carlo data.

Molarity	*PB*	*MSM*	exp(*DH*)	exp(*H*)	*MEX*	*HNC*	*MC*
0.00911	0.101	0.0993	0.1015	0.1014	0.0993	0.1014	0.1029 ± 0.0013
0.10376	0.266	0.2675	0.2679	0.2669	0.2678	0.2714	0.2739 ± 0.0014
0.42502	0.405	0.4265	0.4099	0.4079	0.4285	0.4295	0.4341 ± 0.0017
1.0001	0.493	0.5406	0.5038	0.5002	0.5472	0.5447	0.5516 ± 0.0016
1.9676	0.559	0.6363	0.5802	0.5734	0.6519	0.6460	0.6511 ± 0.0020

are listed in Tables I–V. The first three tables are the results for 1–1 electrolytes and the second two are for 2–2 electrolytes. One can see from Table I, where the excess thermodynamic energy is presented, that the more rigorous statistical mechanical theories are in excellent agreement with the Monte Carlo data and that the nonlinear Poisson-Boltzmann equation and the two simple approximations presented above are comparable and agree with the Monte Carlo data to within 10% or so. It is important to emphasize, however, that both the exp(*DH*) and exp(*H*) approximations require the solution only to the *linearized* Poisson-Boltzmann equation and hence are much easier to apply. The nonlinear equation was solved by the variational technique described in the Appendix, i.e. by minimizing the difference between the upper and lower bounds.

Table II shows the numerical results for the osmotic coefficient. One sees from this table that all of the various theories appear to be able to calculate this quantity well, but again we point out the simplicity of the exp(*DH*) and exp(*H*) approximations.

Table III shows the mean ionic activity coefficient vs. *m*. The comments for this table are similar to those of the first two. We point out that the column labeled PB_{GCP} shows the $\ln \gamma_{\pm}$ predicted by the Poisson-Boltzmann equation calculated by means of the Güntelberg charging process as described by Gardner and Glueckauf (31). The standard procedure in the literature is to use the Debye or Güntelberg charging process. This procedure, however, gives only the electrostatic part of $\ln \gamma_{\pm}$ and, due to the lack of statistical foundation of the nonlinear equation, it is not clear how the non-electrostatic contribution should be introduced.

Some of these results are presented graphically in Fig. 1. The mode expansion results are in almost exact agreement with the Monte Carlo data. It should be emphasized by the curve labeled *PB*(*GCP*) is the standard result of the non-linear Poisson-Boltzmann (31), whereas that labeled PB_v represents the (nonstandard) incorporation of the Poisson-Boltzmann result into the statistical mechanical framework, viz. Eqs. 10–14. Nevertheless, one sees from the figure that both exp approximations are superior, even though the PB_v represents, in a sense, an optimum presentation of that

TABLE II

THE OSMOTIC COEFFICIENT FOR A 1-1 RESTRICTED PRIMITIVE MODEL AQUEOUS ELECTROLYTE SOLUTION

The parameters and notation are the same as in Table I. Here the subscripts v, c, and E specify whether the virial, compressibility, or energy equation was used, respectively.

Molarity	PB_v	MSM_v	MSM_E	$\exp(DH)_v$	$\exp(H)_v$	MEX_E	HNC_v	HNC_c	MC_v
0.00911	0.970	0.9687	0.9706	0.9703	0.9703	0.9706	0.9703	0.9705	0.9701 ± 0.0008
0.10376	0.946	0.9312	0.9454	0.9462	0.9464	0.9451	0.9453	0.9458	0.9445 ± 0.0012
0.42502	0.981	0.9446	0.9807	0.9854	0.9856	0.9786	0.9796	0.9800	0.9774 ± 0.0046
1.0001	1.08	1.039	1.0972	1.1062	1.1059	1.0906	1.0926	1.0906	1.094 ± 0.005
1.9676	1.26	1.2757	1.3595	1.3729	1.3713	1.3426	1.3514	1.3404	1.346 ± 0.009

TABLE III

THE LOGARITHM OF THE MEAN ACTIVITY COEFFICIENT, $\ln \gamma_{\pm}$

Values for the same system as Tables I and II. Here PB_{GCP} is the result of the Poisson-Boltzmann equation usually obtained by the Güntelberg charging process.

Molarity	PB_{GCP}	PB_v	MSM_v	MSM_E	$\exp(DH)_v$	$\exp(DH)_c$	$\exp(H)_v$	$\exp(H)_c$	MEX_E	MC_v
0.00911	−0.100	−0.0965	−0.0998	−0.0957	−0.0968	−0.0904	−0.0968	−0.0902	−0.0957	−0.0973
0.10376	−0.264	−0.227	−0.2587	−0.2269	−0.2271	−0.2170	−0.2265	−0.2155	−0.2273	−0.2311
0.42502	−0.403	−0.255	−0.3425	−0.2552	−0.2478	−0.2373	−0.2470	−0.2339	−0.2587	−0.2643
1.0001	−0.492	−0.139	−0.2634	−0.1149	−0.0975	−0.1022	−0.0971	−0.0964	−0.1263	−0.1265
1.9676	−0.559	0.146	0.069	0.286	0.317	0.282	0.316	0.294	0.259	0.254

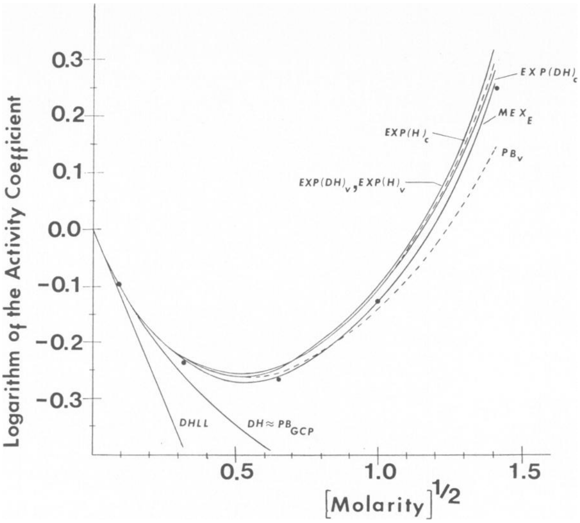

FIGURE 1 The logarithm of the mean activity coefficient $\ln \gamma_{\pm}$, for a 1-1 restricted primitive model aqueous electrolyte solution as a function of the square root of the molar concentration. As in Tables I-III, $R = 4.25$ Å, $T = 298.0°K$, and $\epsilon = 78.5$. The dots are the Monte Carlo "experimental" points.

theory. One sees clearly from the figure that the Debye-Hückel theory (*DHLL*) is truly a limiting law, but is valid as a quantitiative theory only at very low concentrations. The extended Debye-Hückel theory (*DH*), which includes the factors of κR (cf. Eq. 22) does little to improve the agreement.

Difficulties in the evaluation of thermodynamic functions increase as one goes to higher valence electrolytes. For 2–2 electrolytes the parameter $B = z^2e^2/\epsilon kTR$ is four times larger than that corresponding to a 1–1 electrolyte for the same values for ϵ, T, and R. This has the same effect of reducing the absolute temperature four times. Table IV lists the excess thermodynamic energies for 2–2 electrolytes. Again, the more rigorous theories agree well with the Monte Carlo data, whereas the nonlinear Poisson-

TABLE IV

THE REDUCED CONFIGURATIONAL ENERGY $-E^{ex}/NkT$ FOR A 2–2 RESTRICTED PRIMITIVE MODEL AQUEOUS ELECTROLYTE SOLUTION AT 298.16°K

In this model the ionic diameter is 4.2 Å and the dielectric constant is 78.358. The column *ORPA* + B_2 denotes the optimized random phase + B_2 approximation. The notation is the same as in Table I.

Molarity	*PB*	*MSM*	exp(*DH*)	exp(*H*)	*MEX*	*ORPA* + B_2	*HNC*	*MC*
0.0625	1.67	1.455	1.877	1.726	1.456	2.062	1.737	1.893 ± 0.017
0.25	2.14	2.178	2.255	2.165	2.184	2.55	2.365	2.473 ± 0.019
0.5625	2.40	2.645	2.479	2.420	2.661	2.916	2.757	2.822 ± 0.008
1.000	2.57	2.980	2.640	2.593	3.013	3.19	3.041	3.091 ± 0.01
2.000	2.75	3.380	2.833	2.788	3.465	3.579	3.396	3.509 ± 0.01

TABLE V

THE OSMOTIC COEFFICIENT ϕ FOR A 2-2 RESTRICTED PRIMITIVE MODEL AQUEOUS ELECTROLYTE SOLUTION

The parameters and symbols are the same as in Table IV.

Molarity	PB_v	MSM_v	MSM_E	$\exp(DH)_v$	$\exp(H)_v$	$(ORPA + B_2)_E$	HNC_v	MC_v
0.0625	0.627	0.527	0.630	0.609	0.635	0.643	0.645	0.667 ± 0.04
0.25	0.578	0.322	0.554	0.559	0.590	—	0.588	0.628 ± 0.04
0.5625	0.598	0.231	0.573	0.587	0.618	0.595	0.603	0.604 ± 0.06
1.000	0.659	0.218	0.652	0.664	0.697	—	0.667	0.673 ± 0.05
2.000	0.826	0.352	0.911	0.902	0.947	0.857	0.887	0.954 ± 0.06

Boltzmann equation and the $\exp(DH)$ and $\exp(H)$ approximations are comparable. Table V, which lists the various calculated osmotic coefficients for 2–2 electrolytes, is similar to Table II insofar as all of the theories seem to agree reasonably well. Since Monte Carlo data for $\ln \gamma_\pm$ have not been reported for 2–2 electrolytes, we have not presented a table of these values.

The radial distribution function itself is of particular interest. The local concentration of ith type of ions at a distance r from a charged species j, $c_i(r)$, is given by $c_i(r) = c_i g_{ij}(r)$, hence $c_i g_{ij}(r)$, as a function of r, describes the concentration profile of ions of type i about the j type. A similar description of concentration profiles in terms of distribution functions is valid for any other geometry. If one considers for instance a charged membrane immersed in an electrolytic solution, the concentration of ions of type i at a distance x from the membrane is given by

$$c_i(x) = c_i g_{is}(x) = c_i e^{-w_{is}(x)/kT}, \tag{40}$$

where $g_{is}(x)$ and $w_{is}(x)$ are, respectively, the appropriate distribution function and potential of mean force at that point, and *only in the approximation* $w_{is}(x) \cong z_i e \Psi_s(x)$ is $c_i(x)$ given by a Boltzmann factor. The use of a Boltzmann factor is the standard approximation in the literature as can be seen for example in the work of Ciani, Eisenman, and Szabo on the transport of ions across artificial membranes (42). To test this approximation we present in Table VI the potential of mean force at the point of closest approach $w_{ij}(R^+)$ for the restricted primitive model of the electrolyte as predicted for various theories.

The Boltzmann factor in the Poisson-Boltzmann equation does not differentiate, except for the sign, between the potential of mean force of different or identically charged ions, i.e. $w_{+-}^{PB} = -w_{++}^{PB}$. This difference becomes particularly great at high concentrations. This is mainly due to the poor representation of the hard sphere interactions, the hard sphere exclusion volume term $w^{HS}(R)$ contributes about 30% in the exponential approximation at 2 M. The $\exp(DH)$ and $\exp(H)$ give better agreement with the Monte Carlo data.

TABLE VI

THE POTENTIAL OF MEAN FORCE $w_{ij}(r)$ AT CONTACT, $r = R$, FOR A SYMMETRIC RESTRICTED PRIMITIVE MODEL AQUEOUS ELECTROLYTE SOLUTION

The values of T, R, and ϵ are given in Tables I and IV, where the notation is defined. $w^{HS}(R)$ is the hard-sphere contribution to the potential of mean force.

Valence type	Molarity	$\frac{w^{HS}(R)}{kT}$	$\frac{w^{PB}_{+-}(R)}{kT}$	$\frac{w^{\exp(DH)}_{+-}(R)}{kT}$	$\frac{w^{\exp(H)}_{+-}(R)}{kT}$	$\frac{w^{HNC}_{+-}(R)}{kT}$	$\frac{w^{MC}_{+-}(R)}{kT}$	$\frac{w^{\exp(DH)}_{++}(R)}{kT}$	$\frac{w^{\exp(H)}_{++}(R)}{kT}$	$\frac{w^{MC}_{++}(R)}{kT}$
1-1	0.00911	-0.0103	-1.479	-1.484	-1.482	-1.484	-1.635	1.482	1.480	1.309
1-1	0.10376	-0.013	-1.149	-1.169	-1.163	-1.179	-1.179	1.144	1.139	1.143
1-1	0.42502	-0.052	-0.871	-0.928	-0.920	-0.948	-0.963	0.822	0.816	0.872
1-1	1.0001	-0.124	-0.695	-0.816	-0.805	-0.842	-0.802	0.568	0.559	0.683
1-1	1.9676	-0.252	-0.563	-0.802	-0.789	-0.837	-0.867	0.299	0.285	0.348
2-2	0.0625	-0.007	-3.46	-3.77	-3.58	-3.64	-3.94	3.77	3.58	—
2-2	0.25	-0.0294	-2.52	-2.70	-2.59	-2.77	-2.94	2.65	2.52	2.37
2-2	0.5625	-0.067	-2.01	-2.14	-2.07	-2.28	-2.33	2.02	1.94	2.24
2-2	1.000	-0.120	-1.67	-1.82	-1.75	-1.97	-2.00	1.58	1.51	—
2-2	2.000	-0.247	-1.31	-1.52	-1.46	-1.66	-1.77	1.02	0.97	1.60

DISCUSSION

One of the purposes of this paper is to assess the degree of applicability of the nonlinear Poisson-Boltzmann equation. In order to do this we have compared the thermodynamic properties calculated through this equation to Monte Carlo data on 1–1 and 2–2 electrolytes described by the restricted primitive model, in which the ions are modeled by hard spheres with a coulombic potential and the solvent is modeled as a continuum dielectric medium of uniform dielectric constant ϵ. We have chosen Monte Carlo data rather than real experimental data since all parameters are completely specified and there is no liberty for "adjustment." Thus, this serves as a definitive test.

In addition, we have presented a simple but numerically accurate alternative approximation scheme which is not only numerically superior to the Poisson-Boltzmann equation but avoids the necessity of solving a nonlinear partial differential equation which is approximate in the first place. This new approximation scheme that is presented here is suggested by recent developments in the statistical mechanical theories of ionic solutions which are discussed in the Introduction. Although these theories themselves yield exceedingly good comparison with experimental (Monte Carlo) data, they involve fairly advanced theoretical and mathematical techniques and do not appear to be readily solvable for other than very simple geometries. The approximations suggested here require only the solution of the linear Debye-Hückel equation, which has been solved for a variety of systems (43).

The essence of each of these approximations is first to formulate the thermodynamic properties in terms of the interionic radial distribution functions $g_{ij}(r)$ (Eqs. 10–14); to write $g_{ij}(r)$ as (24–27)

$$g_{ij}(r) = g_{ij}^{HS}(r)\exp(\zeta_{ij}(r)), \tag{41}$$

where $g_{ij}^{HS}(r)$ is the well-known hard-sphere radial distribution function (39), and $\zeta_{ij}(r)$ is a renormalized potential defined in a somewhat formal and complicated manner, but which for low concentrations becomes

$$\zeta_{ij}(r) \rightarrow (-z_i z_j e^2/\epsilon kT)(e^{-\kappa r}/r); \tag{42}$$

to assume that $\zeta_{ij}(r)$ for all concentrations has the functional form given by Eq. 35 or 39 and to determine the parameters p or q by requiring the resultant $g_{ij}(r)$ to satisfy the condition of electroneutrality (Eq. 36).

The therymodynamic results predicted from this approximate prescription are presented in Tables I–VI and Fig. 1. It can be seen that both the $\exp(DH)$ and $\exp(H)$ give excellent values even at the higher concentrations not only for the standard thermodynamic functions but for the values of the distribution functions at contact as well.

The notation $\exp(DH)$ or $\exp(H)$ emphasizes that we have used the exponential approximation of Andersen and Chandler and the exact condition of electroneutrality. The condition of electroneutrality, however, is the first of a family of moment conditions. The second was first formulated by Stillinger and Lovett (44) and reads

$$S_2 = \sum_{i=1}^{\sigma} \sum_{i=1}^{\sigma} c_i c_j z_i z_j \int_0^{\infty} g_{ij}(r) 4\pi r^4 \mathrm{d}r = -\frac{3\epsilon kT}{2\pi}. \tag{43}$$

This allows one to approximate $\zeta_{ij}(r)$ by a two-parameter function and to determine these two parameters by using the two moment conditions, Eqs. 36 and 43. This presumably would yield even better results but we did not choose to add this extension here.

In summary, then, the approximations we have presented here are simple to apply and yield good thermodynamic properties up to concentrations of 2 M for the restricted primitive model. In addition, they are suggested by recent advances in statistical mechanics and are offered as a substitute for the difficult-to-solve nonlinear Poisson-Boltzmann equation. At present, we are applying this approximation scheme to the electrical double layer problem (45), the titration of proteins (43), and to polyelectrolyte solutions (46).

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APPENDIX

Arthurs and Robinson (34, 35) have developed a method for finding upper and lower bounds (complementary variational principal) for the solution of a certain class of non linear differential equations of which the Poisson-Boltzmann equation is a member. Following their work, it can be shown that if ϕ is the exact solution and $\tilde{\phi}$ is any approximate solution to the Poisson-Boltzmann equation then the functionals $G[\tilde{\phi}]$, $I[\phi]$, and $J[\tilde{\phi}]$, defined below, satisfy the relationship

$$G[\tilde{\phi}] \leq I[\phi] \leq J[\tilde{\phi}], \tag{44}$$

where

$$J[\tilde{\phi}] = \int_{\rho_0}^{\infty} \left\{ \frac{1}{2}\left(\frac{\mathrm{d}\tilde{\phi}}{\mathrm{d}\rho}\right)^2 + \cosh\tilde{\phi} - 1 \right\} \rho^2 \mathrm{d}\rho - \rho_0 B \tilde{\phi}(\rho_0), \tag{45}$$

$$G[\tilde{\phi}] = \int_{\rho_0}^{\infty} \left\{ -\frac{1}{2}\left(\frac{\mathrm{d}\tilde{\phi}}{\mathrm{d}\rho}\right)^2 - \chi \operatorname{arc\,sinh} \chi + (1 + \chi^2)^{1/2} - 1 \right\} \rho^2 \mathrm{d}\rho, \tag{46}$$

$$I[\phi] = J[\tilde{\phi} = \phi] = G[\tilde{\phi} = \phi], \tag{47}$$

$$\chi = \nabla^2 \tilde{\phi},$$

where $\rho = \kappa r$, $\rho_0 = \kappa R$, and ∇^2 is the Laplacian with respect to ρ. That is, $J[\tilde{\phi}]$ and $G[\tilde{\phi}]$ form

TABLE VII

THE CONFIGURATIONAL EXCESS ENERGY AS A FUNCTION OF CONCENTRATION PREDICTED BY THE POISSON-BOLTZMANN EQUATION

The column labeled $-E_v^{ex}/NkT$ shows the results of the variational technique and the column labeled $-E_{BHO}^{ex}/NkT$ shows the numerical solution as reported by Burley et al. (33). p is the variational parameter in the trial function.

Molarity	p	$-E_v^{ex}/NkT$	$-E_{BHO}^{ex}/NkT$
0.00911	0.014837	0.1015	0.101
0.10376	0.16884	0.2668	0.266
0.42502	0.012047	0.4056	0.405
1.001	0.008326	0.4932	0.493
1.9676	0.005767	0.5587	0.559

upper and lower bounds, respectively, to the exact functional $I[\phi]$. The optimum approximation is that one that minimizes the upper bound $J[\tilde{\phi}]$ and maximizes the lower bound or, alternatively, minimizes the difference $\Delta[\tilde{\phi}] = J[\tilde{\phi}] - G[\tilde{\phi}]$.

The first term on the upper bound $J[\phi]$ was shown by Levine (45) to be proportional to the free energy associated with the Poisson-Boltzmann equation. Hence the optimization procedure minimizes the associated free energy.

The work of Hoskin (40) suggests the trial function

$$\phi(\rho) = \phi^{DH}(\rho)C(\rho), \tag{48}$$

where

$$\phi^{DH}(\rho) = B[\rho_0/(1 + \rho_0)](e^{-(\rho-\rho_0)}/\rho), \tag{49}$$

$$C(\rho) = (1 + pe^{-2(\rho-\rho_0)})/(1 + \alpha p), \tag{50}$$

$$\alpha = (1 + 3\rho_0)/(1 + \rho_0),$$

$$B = z^2e^2/\epsilon kTR.$$

Here p is the only variational parameter. Note that $p = 0$ gives the Debye-Hückel potential, i.e. the solution of the linearized Poisson-Boltzmann equation.

The results for the configurational excess energy of a 1-1 electrolyte predicted by the nonlinear Poisson-Boltzmann equation are shown in Table VII. E_v^{ex}/NkT is the reduced excess energy obtained from the variational solution, E_{BHO}^{ex}/NkT corresponds to the solution of the Poisson-Boltzmann equation reported by Burley et al. (33) using a more sophisticated numerical technique. The parameter p is shown in Table VII. p is a measure of the deviation of the nonlinear Poisson-Boltzmann solution from the linear Debye-Hückel solution. The agreement shown in Table VII is excellent. For higher valence electrolytes very satisfactory results are obtained using this variational technique. The numerical complications involved in this method are trivial compared to those found in standard methods. Essentially no computer time is used. A simpler trial function

$$\tilde{\phi}(\rho) = [B\rho_0/(1 + p\rho_0)](e^{-p(\rho-\rho_0)}/\rho)$$

gives good results for 1-1 electrolytes.

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