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THERMODYNAMIC POTENTIALS OF SYMMETRICAL ELECTROLYTES

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The classical treatment of the thermodynamic properties of electrolytic solutions by Debye and Hückel¹ leads to the now familiar limiting square-root law which has been amply confirmed by experiment. At nonzero concentrations, however, positive deviations from the limiting law appear; there has been considerable speculation about their physical origin since 1923. The purpose of this communication is to show, by means of a more detailed study of the ionic potentials, that the properties of electrolytic solutions, specific for each electrolyte at nonzero concentrations, do not appear to be derivable by extension of the limiting solution of the Poisson-Boltzmann equation to higher concentrations, but rather must be sought in the projection of a theory of fused salts into and through the region of concentrated solutions.

We shall use the conventional model of charged spheres of diameter a in a dielectric continuum to represent the solution. Let there be n_i ions of charge ϵ_i in a

total volume V . Restriction to the case of simple electrolytes then requires that

$$n_1\epsilon_1 + n_2\epsilon_2 = 0 \quad (1)$$

where $n_1 = n_2 = n$ and $\epsilon_1 = \epsilon = -\epsilon_2$, with ϵ equal to the elementary charge times the valence. The Poisson-Boltzmann equation for the potential ψ_j of an ion of species j then takes the form

$$\Delta\psi_j = (\kappa^2\epsilon/D\beta) \sinh(\epsilon\psi_j/kT), \quad (2)$$

where

$$\kappa^2 = 8\pi n\epsilon^2/DkT \text{ cm}^{-2} \quad (3)$$

and

$$\beta = \epsilon^2/DkT \text{ cm} \quad (4)$$

By expansion of the hyperbolic sine as a series and neglect of all but the leading term, (2) is linearized and has the well-known solution

$$\psi_j = \epsilon_j e^{-\kappa r} e^{\kappa a} / rD(1 + \kappa a) \quad (5)$$

when the boundary conditions $\psi_j(\infty) = 0$ and continuity of potential and field strength at $r = a$ are satisfied.

Reduction of (2) to a linear equation implies that $\epsilon\psi/kT$ may be considered so small compared to unity that the cubic and higher terms in the series expansion may be neglected. For hypothetical solvents of very high dielectric constant and for distances $r \gg a$ in general, this approximation is justified, but *at ionic contact*, even in water ($D = 78.54$), the procedure appears hazardous: in this case, $\epsilon\psi/kT \approx \epsilon^2/aDkT = 2$ for $a = 3.57 \times 10^{-8}$ cm and $\sinh 2 = 3.63$.

It has been clearly established that the screening term $e^{-\kappa r}$ correctly accounts for the long-range interactions of ions, but the high-energy short-range electrostatic interactions have been too casually rejected as negligible fluctuation terms. Bjerrum,² by his *ad hoc* hypothesis of ion association, made the most successful approach to the problem of dealing with the effects of pairwise contacts of ions of opposite charge, and a substantial body of experimental observations has justified the fundamental soundness of explicitly including these effects in a general description of the properties of electrolytic solutions. Our treatment of the problem is in effect a re-integration of the Poisson-Boltzmann equation, using boundary conditions which permit the reference ion to control the electrostatic situation in its immediate vicinity, while still allowing for the atmosphere screening at large distances.

The distinction between "large" and "small" distances will be made on the basis of a criterion originally proposed by Bjerrum. It will be recalled that the probability that an anion and a cation will be found at a distance r from each other has in general³⁻⁶ a minimum near the distance $r = \beta/2$. For short distances, where, by hypothesis, $r \leq \beta/2$, we set

$$\psi_s = \epsilon/Dr + \varphi(r) \quad (6)$$

where ϵ/Dr is the potential at a distance r from an isolated ion and $\varphi(r)$ is the perturbation in the Coulomb potential produced by nearby ions in a real solution. (Even in dilute solutions, short-range approaches will occasionally occur.) Substitution in (2) gives

$$\Delta\varphi = (\kappa^2\epsilon/2D\beta)e^{\beta/r}e^{\epsilon\varphi/kT}[1 - \exp\{-(2\beta/r + 2\epsilon\varphi/kT)\}]. \quad (7)$$

The exponential term in the brackets is in any practical case negligible compared to unity; as a first approximation, we shall also neglect $\epsilon\varphi/kT$ compared to β/r in the exponent of the coefficient (*i.e.*, approximate $e^{\epsilon\varphi/kT}$ by unity), thereby reducing (7) to the equation

$$\Delta\varphi = (\kappa^2\epsilon/2D\beta)e^{\beta/r}. \quad (8)$$

Integration and substitution in (6) gives

$$\psi_S = \epsilon/Dr + (\kappa^2\beta\epsilon/2D)[A\beta/r + B + F_1(r)], \quad (9)$$

where A and B are coefficients of the solutions of the homogeneous equation and $F_1(r)$ is the particular integral of (8):

$$F_1(r) = e^{\beta/r}(r^2/6\beta^2 + r/3\beta - 1/6) + (\beta/6r - 1/2)\text{Ei}(\beta/r). \quad (10)$$

In (10), $\text{Ei}(x)$ is the positive exponential integral

$$\text{Ei}(x) = \int_{-\infty}^x (e^u/u)du. \quad (11)$$

For distances $r \geq \beta/2$, the long-range potential is obtained by integrating the appropriate approximation of (2):

$$\psi_L = (\kappa^2\epsilon/D\beta)[\epsilon\psi/kT + 1/6(\epsilon\psi/kT)^3], \quad (12)$$

which has the solution

$$\psi_L = Ce^{-\kappa r}/r + (\kappa^2\epsilon\beta/2D)(2\beta e^{\kappa r}E_4/3r - \beta e^{-\kappa r}E_2/3r) \quad (13)$$

where E_n is the negative exponential integral

$$E_n = \overline{\text{Ei}}(n\kappa r) = \int_{n\kappa r}^{\infty} (e^{-u}u^n)du. \quad (14)$$

(In (13), we have of course dropped the homogeneous solution $e^{\kappa r}/r$ in order to satisfy the boundary condition $\psi_L(\infty) = 0$.)

We now have (9) for the potential near the reference ion and (13) for the potential at distances beyond $\beta/2$; the integration constants must next be evaluated. The first can be determined from the condition of electroneutrality

$$-\epsilon = \int_a^{\infty} 4\pi\rho r^2 dr; \quad (15)$$

that is, the integrated space charge must exactly balance the charge on the reference ion. The other two constants can be evaluated by using the fact that potential and field strength are continuous for $a \leq r \leq \infty$ and specifically at $r = \beta/2$:

$$\psi_S(\beta/2 - 0) = \psi_L(\beta/2 + 0) \quad (16)$$

and

$$(d\psi_S/dr)_{\beta/2-0} = (d\psi_L/dr)_{\beta/2+0}. \quad (17)$$

Substitution of the Poisson relation between potential and density in (15) gives

$$\epsilon = D \int_a^{\infty} r^2 \Delta\psi dr, \quad (18)$$

and integration, with the Laplacian operator in spherical coordinates, immediately gives

$$\epsilon = D \left[r^2 \frac{d\psi_S}{dr} \right]_a^{\beta/2} + D \left[r^2 \frac{d\psi_L}{dr} \right]_{\beta/2}^{\infty}, \quad (19)$$

whence, using (17),

$$(d\psi_S/dr)_a = -\epsilon/Da^2, \quad (20)$$

Differentiation of (9) and substitution of (20) in the result evaluates A :

$$bA = (e^b/6b^2)(2 + b + b^2) - (b/6)\text{Ei}(b), \quad (21)$$

where b is the Bjerrum parameter

$$b = \epsilon^2/aDkT. \quad (22)$$

Elimination of C from (16) and (17) and substitution of

$$A = F_2(b)/b \quad (23)$$

from (21) evaluates B :

$$B = (1 + \tau)^{-1}[-1/\tau - G_3(\tau) - F_2(2) - (1 + \tau)F_1(2) - 2\tau F_2(b)/b], \quad (24)$$

where

$$G_3(\tau) = 2e^{-3\tau}/3 - 8\tau e^{\tau} \overline{\text{Ei}}(4\tau)/3 \quad (25)$$

and

$$\tau = \beta\kappa/2 = 4.2016 \times 10^6 c^{1/2}/(DT)^{3/2}. \quad (26)$$

In order to calculate the electrostatic contribution G_e to the free energy, we first isolate the potential ψ^* at the reference ion due to the presence of the other ions, where

$$\psi^* = \psi_S(a) - \epsilon/Da. \quad (27)$$

Substitution of $r = a$ and the values given by (23) and (24) for A and B in (9) yields

$$\psi^* = [\kappa^2\beta\epsilon/2D(1 + \tau)][-1/\tau - G_3(\tau) - H(b,2) - \tau L(b,2)] \quad (28)$$

$$= [\kappa^2\beta\epsilon/2D(1 + \tau)][-1/\tau - f(b,\tau)], \quad (29)$$

where

$$H(b,2) = 1/2\text{Ei}(b) - 1/2\text{Ei}(2) - e^b(1 + b)/2b^2 + 3e^2/8 \quad (30)$$

and

$$L(b,2) = 1/6\text{Ei}(b) - 1/6\text{Ei}(2) - e^b(b^2 + b - 4)/6b^3 + e^2/24. \quad (31)$$

Then the relations

$$G_e = 1/2 \sum_j n_j \epsilon_j \psi_j^* \quad (32)$$

and

$$kT \ln f_j = \partial G_e / \partial n_j \quad (33)$$

give for the activity coefficient

$$-\ln f_j = \tau/(1 + \tau) + [\tau^2/(1 + \tau)][G_3(\tau) + H(b,2) + \tau L(b,2)]. \quad (34)$$

While the leading term of (33) is independent of the charging process used to derive G_e , the detailed form of the higher terms will depend on the process chosen⁷; these details are not pertinent to the present discussion.

Let us first examine the limiting form of (34) for very low concentrations, where terms of order τ^2 (proportional to concentration c) in the second term of (34) may be disregarded:

$$-\ln f_j = \tau/(1 + \tau). \quad (35)$$

This equation states that the limiting law for the activity coefficient for ions of finite size is *independent of ion size*; the corresponding Debye-Hückel relation is

$$-\ln f_j = \tau/(1 + \kappa a). \quad (36)$$

A comparison of the two results with experiment is shown in Figures 1 and 2, where

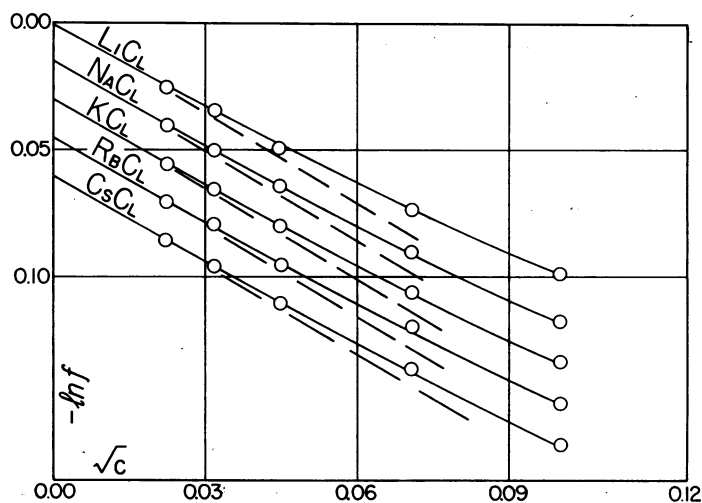


Fig. 1.—Comparison of experimental results with (36).

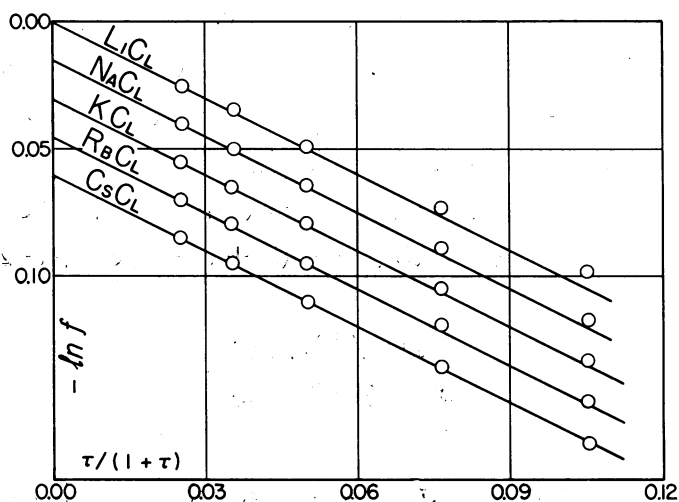


Fig. 2.—Comparison of experimental results with (35).

data⁸ for the alkali halides in water are plotted; in Figure 1, $(-\ln f)$ is plotted against square root of concentration and in Figure 2 against $\tau/(1 + \tau)$ where $\tau = 1.1725c^{1/2}$ for water at 25°. (Successive plots for the various halides are displaced vertically by constant amounts to avoid confusion.) It will be seen that the experimental values begin to show positive deviations from the limiting tangents (dashed lines of Fig. 1) at quite low concentrations; by inclusion of the term in κa , the deviations can, of course, be reduced, but at the price of using an arbitrary constant a . Equation (35), on the other hand, not only predicts the limiting tangent, but gives the first-order deviations. The difference between (35) and (36) is simply the appearance of the Bjerrum radius $\beta/2$ in the denominator of (35) in place of the ionic contact distance a in (36). Functions of this form for the activity

coefficient have also been proposed by Grunwald⁹ and by Kortüm¹⁰ on the basis of heuristic arguments; the present derivation shows that (34) is a direct consequence of the Poisson-Boltzmann equation alone, plus the continuity and neutrality conditions, without an added hypothesis regarding ion pair formation.

We next consider the higher terms¹¹ of (34). These are of two kinds: those depending only on τ and those depending on both a and τ . We note first that the former further decrease $\ln f$. We have carried out the integration of (2), retaining the next highest term in the series. The corresponding contribution G_5 to $\ln f$ likewise decreases this quantity; furthermore, G_5 is considerably smaller than G_3 as shown in the accompanying table of numerical values.

TABLE 1
VALUES OF $G_3(\tau)$ AND $G_5(\tau)$

τ	0.0	0.2	0.4	0.6	0.8	1.0
G_3	0.6667	0.2454	0.0952	0.0409	0.0186	0.0087
G_5	0.0444	0.0122	0.0074	0.0062	0.0047	0.0031

These terms represent volume effects in the sense that they arise from the fields of ions distant from the reference ion at the origin. The experimental observation is that activity coefficients usually go through a minimum with increasing concentration, eventually exceeding unity. The above analysis strongly suggests that the observed positive deviations from the limiting law cannot find their origin in the inclusion of further terms of the Poisson-Boltzmann equation, which, as we have just seen, work in the opposite direction. Furthermore, the positive deviations are characteristic of a given electrolyte, and one cannot expect long-range volume effects to produce specific differences from electrolyte to electrolyte. We therefore must conclude that the observed positive deviations are due to persistence into the moderately dilute range of concentrations of the distribution functions which characterize the fused salt and which obviously must depend on size and geometry of the ions in a highly specific way. As we remarked in the introduction, we therefore believe that a final theory of electrolytic solutions must proceed from a theory of the fused salt.

Next, we consider the other higher terms of (34), represented by the functions $H(b,2)$ and $L(b,2)$. The second is of order $c^{3/2}$ and may be disregarded for present purposes. The first takes the suggestive form

$$\tau^2 H / (1 + \tau) \approx 6\pi N a^3 e^2 c / 3000 \quad (37)$$

for large values of b . This term in the thermodynamic potential has its origin in configurations involving pairs of ions in contact, *via* the explicit appearance of a , and is precisely the expression which would have appeared if we had used the Debye-Hückel limiting law for the "free" ions and then grafted on, as did Bjerrum, the *ad hoc* hypothesis that short-range contacts can be accounted for by considering the ions involved as "associated" to pairs and not contributing to the atmosphere of any ion. Furthermore, the coefficient of c in the asymptotic expansion (37) is, within a numerical factor of $2/3$, the value calculated by Fuoss¹² for the association constant K_A . We thus see that the effects which have been ascribed to ion pairs are simply the expected consequences of a more rigorous integration of the Poisson-Boltzmann equation in which these contacts are explicitly included.

One significant practical difference between (35) and (36) calls for comment. If (35) is accepted, then clearly "ion sizes" computed from (36) plus an added empirical term Bc lose all physical meaning whatsoever, and we must consider new empirical interpolation formulas for the representation of activity coefficients at finite concentrations. Since theory so far offers no help in suggesting the form of the function, any convenient functions, such as $c \log c$ or $c^{1/3}$ may be used, *provided* they are introduced in such a way that they do not conflict with the limiting square-root law, $\ln f \sim \tau$.

We have also reconsidered the conductance problem from the present point of view. Briefly summarized, the results are as follows: (1) a universal reduced conductance equation in terms of the rational variable τ and a hydrodynamic constant proportional to viscosity is obtained; (2) in addition to the decrease in mobility due to volume effects (electrophoresis, and relaxation and velocity fields), a further decrease in conductance appears which is the explicit consequence of ions approaching to contact. The functional form of the latter has exactly the form which would appear as a consequence of hypothesizing ionic association; moreover, the coefficient contains the expected exponential term e^{θ} . These results are being prepared for publication.

The description of electrolytic properties in terms of a single universal dimensionless variable τ for all simple electrolytes appears to be fundamentally significant. This variable is the ratio of two distances, $\beta/2$ which in effect states the limit up to which the central ion has control, and $1/\kappa$ which is the parameter characteristic of the long-range screening of the reference ion by the ionic atmosphere. Dimensional analysis shows that τ should indeed be the rational independent variable for the description of electrolytic solutions: we are dealing with electrostatic interactions between ions at average distances proportional to $V^{1/3}$ with corresponding energies $\epsilon^2 c^{1/3}/D$. The order which the electrostatic forces attempt to maintain is opposed by Brownian motion; the ratio $\epsilon^2 c^{1/3}/DkT$ therefore logically appears; we would expect the description of the system to be in the form $f(c^{1/3}/DT)$, and indeed τ is proportional to $(c^{1/3}/DT)^{3/2}$. There thus appears to be some element of justification for the arguments that the cube root of concentration should appear in the theory of electrolytes, and there are in fact many reasons to believe that at moderate and high concentrations, electrolytic properties do become simple functions of $c^{1/3}$. As Debye pointed out,¹ the fallacy in the Ghosh¹³ model was the disregard of kT and the consequent attempt to extrapolate to zero concentration on a $c^{1/3}$ scale. In the fused salt and in highly concentrated solutions, however, interionic distances are necessarily of the order of $c^{-1/3}$; here of course the dielectric constant presents some serious problems. But it seems reasonable to predict that the goal of electrolyte theory will be the elucidation of the functions in expressions of the form

$$P = f_1(\tau)(1 - g) + f_2(\tau)g(V_s/V) \quad (38)$$

where P is a property of the solution, V_s is the volume of solute in a total volume V , and g is a partition function, possibly of the form proposed by Eyring,¹⁴ such that $g(1) = 1$ and $g(0) = 0$. Our present thesis is that the limiting form of f_1 is given by (35) when P is the thermodynamic potential and by other explicit functions of τ when P describes one of the irreversible processes such as conductance or diffusion.

* Contribution No. 1660.

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THE NET HYDRATION OF DEOXYRIBONUCLEIC ACID*†

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In 1954, Jacobson *et al.*¹ presented evidence for the extensive hydration of DNA from studies of the proton magnetic resonance in aqueous solutions of sodium DNA. The following year Wang² concluded that DNA was hydrated to the extent of only 0.35 gm water/gm dry deoxynucleate from self-diffusion measurements of water in NaDNA solutions. This paper presents evidence for a net hydration of 0.2 to 2 gm water/gm CsDNA in certain buoyant solvents.

The hydration of T-4 bacteriophage DNA³ has been studied in density gradient systems at sedimentation equilibrium in the ultracentrifuge.⁵ Williams *et al.*⁶ showed that the buoyant density is that of the solvated species. The buoyant density ρ_0 is defined by the following thermodynamic equations:

$$\frac{1}{\rho_0} = \frac{M_3\bar{v}_3 + \Gamma M_1\bar{v}_1}{M_3 + \Gamma M_1},$$

where 1 refers to water, 3 to the unhydrated polymer, and

$$\Gamma = - \left(\frac{\partial \mu_1}{\partial m_3} \right)_{T,P,m_1} / \left(\frac{\partial \mu_1}{\partial m_1} \right)_{T,P,m_3} = \left(\frac{\partial m_1}{\partial m_3} \right)_{T,P,\mu}$$

M , \bar{v} , μ , and m are molecular weights, partial specific volumes, chemical potentials, and molalities respectively. Molalities for this equation are expressed in moles per unit weight of salt. The unusual definition of molality is necessary so that Γ , the net solvation, remains a positive quantity.⁷

The net solvation of DNA is shown here to be a monotonic function of water