

tions in the potential energy of an α -particle as it moves from one point to another, and these increase without limit as $c^{(B)}$ becomes large.

Further Development

There are several questions which arise in connection with the results of this paper. First of all, if the α - and β -species are solutes in a liquid solvent, then hydrodynamic interactions between diffusing particles (the electrophoretic effect in electrolyte conduction) must not be ignored. Such interactions can be fitted into the variational treatment, but lead, inevitably, to more complicated expressions for the upper bound on $u - u_0$, expressions which involve four-particle distribution functions. We shall treat this point in a separate publication.

Next, we may ask whether it is possible to bound $u - u_0$ from below as well as from above. Such bounds have been derived in related problems⁸ and can also

(8) Z. Hashin and S. Shtrikman, *J. Appl. Phys.*, **33**, 3125 (1962); J. L. Jackson and S. R. Coriell, *J. Chem. Phys.*, **38**, 959 (1963); D. M. Schrader and S. Prager, *ibid.*, **37**, 1456 (1962); S. Prager and J. O. Hirschfelder, *ibid.*, **39**, 3289 (1963).

be obtained here. Once again, however, the calculations turn out to involve four-particle distribution functions or worse. Moreover, when the interparticle potentials can become infinite, which is all too likely in view of the short range repulsive forces that are usually present, the lower bound on u simply vanishes, leaving us with a rather trivial result.

Finally, it is evident that the variational approach is not restricted to the interdiffusion problem of the present paper. For example, a similar treatment can be developed for the viscosity of solutions in which the solute particles interact with one another.⁹ A rather different type of situation involving the Brownian movement of interacting particles is offered by a diffusion-controlled reaction; here it is possible to obtain bounds on the reaction rate, and some work along these lines has been published.¹⁰

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(9) S. Prager, *Physica*, **29**, 129 (1963).

(10) S. Prager, *Chem. Eng. Sci.*, **18**, 227 (1963).

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A Correction to the Poisson-Boltzmann Equation for Unsymmetrical Electrolytes

BY LARS ONSAGER

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The lowest order correction term to the Poisson-Boltzmann equation for unsymmetrical electrolytes is computed; the logical symmetry of the distribution functions obviates any need to consider greater sets than pairs of ions for this purpose. The dominant part of the correction is proportional to the first power of the concentration, with a coefficient which depends only on the Coulomb interaction. The effect may be interpreted as a scale-dependent activity correction to the effective ionic strength.

Debye and Hückel¹ computed the mutual shielding of Coulomb forces between the ions in solution on the assumption that the concentration $n_{ji}(r)$ of species i near species j is given according to the Boltzmann principle by the charge e_i of the former and the average potential $\psi_j(r)$ near the latter

$$n_{ji}(r) = n_i \exp(-e_i\psi_j(r)/kT) \quad (1)$$

This combined with the Poisson relations

$$\begin{aligned} \Delta^2\psi_j &= -(4\pi/D)\rho_j \\ &= -(4\pi/D)\sum e_i n_{ji}(r) \quad (2) \\ &\quad (r > a) \end{aligned}$$

$$a^2\psi_j'(a) = -e_j/D \quad (3)$$

to obtain the Poisson-Boltzmann equation

$$\Delta^2\psi_j = -(4\pi/D)\sum n_i e_i \exp(-e_i\psi_j/kT) \quad (4)$$

The solution of (4) with the boundary condition (3) yields the potential $\psi_j(e_j, a)$ at the ion as a function of the charge e_j and of the concentrations and charges of other ions, and the electrostatic contributions to the free energy can be computed as the work involved in an idealized charging process.

On general principles, such idealization is quite legitimate, and if the potentials described were known ac-

curately, one should obtain the same result whether the ions are charged one at a time² or together in proportion.³ However, these two methods yield somewhat different results when applied to the solutions of the Poisson-Boltzmann equation. Consistent results are obtained when the linear approximation

$$n_{ji}(r) \approx n_i(1 - (e_i\psi_j/kT)) \quad (5)$$

is substituted for the Boltzmann formula, whence

$$\Delta^2\psi = \kappa^2\psi \quad (6)$$

$$\kappa^2 = \left(\frac{4\pi}{DkT}\right) \sum_i n_i e_i^2$$

Discrepancies appear as soon as any additional terms are retained in the power series of the exponential function in eq. 1

$$\Delta^2\psi_j - \kappa^2\psi_j = -\kappa^2(n_i/2kT)\psi_j^2 + O(\psi_j^3) \quad (7)$$

$$\eta_2 = \sum n_i e_i^3 / \sum n_i e_i^2$$

for electrolytes of unsymmetrical valence type, and

$$\Delta^2\psi_j - \kappa^2\psi_j = (n_2/6(kT)^2)\psi_j^3 + O(\psi_j^5) \quad (8)$$

$$\eta_2 = \sum n_i e_i^4 / \sum n_i e_i^2$$

for binary electrolytes or mixtures of any symmetric type.

(2) H. Mueller, *ibid.*, **28**, 324 (1927); **29**, 78 (1928).

(3) T. R. Gronwall, K. Sandved, and V. K. La Mer, *ibid.*, **29**, 358 (1928).

(1) P. Debye and E. Hückel, *Physik. Z.*, **24**, 185 (1923).

These discrepancies are related to the fact that eq. 1 yields results inconsistent with the logical requirement

$$n_j n_{ji}(r) = n_i n_{ij}(r)$$

for the solutions of eq. 7 whenever the $e_j \neq e_i$, and for the solutions of eq. 8 whenever $e_j^2 \neq e_i^2$. Accordingly, the superposition principle assumed in eq. 1 cannot be exact.⁴

A deeper analysis is needed to estimate the corrections. The problem is none too attractive because it requires a series of increasing efforts to produce refinements of decreasing importance, and as soon as terms proportional to the first power of the concentration are reached, the result depends in any case on the specific short range forces between pairs of ions. Moreover, it is practically certain that for binary electrolytes the corrections to eq. 1 will not modify the interpretation of the coefficient B in an expansion of the form

$$\mu = \mu_0 + kT \log c - Ac^{1/2} + Bc + O(c^{3/2} \log c) \quad (9)$$

in terms of short range forces, which involves essentially integrals of the form

$$-B^*/kT = 4\pi \int (e^{-w/kT} - 1)r^2 dr \quad (10)$$

where w denotes the potential of the (average) forces between two ions, and proper cut-off procedures can be determined from the solutions of eq. 4.

We shall see presently that a different situation prevails for unsymmetrical electrolytes. The pertinent correction to eq. 1 corresponds to the leading term in the right member of eq. 7, and it contributes to the coefficient B_1 in the asymptotic formula

$$\mu = \mu_0 + kT \log c - Ac^{1/2} + (-B_0 \log c + B_1)c + \varphi(c^{3/2} \log c) \quad (11)$$

valid for unsymmetrical electrolytes.

For this purpose we shall use a scheme of approximation which was suggested and described in some detail many years ago,^{4,5} a few years after the first system for the computation of short range effects by way of cluster expansion had been developed.⁶

For simplicity we assume short range forces of the "hard sphere" type and equal sizes for all ions, not that this assumption affects the result to the desired order.

We next assume that the distribution functions for pairs, triples, etc., of ions as well as the potentials near finite sets of ions in specific configurations can be developed in power series of the charges.

Thus, we describe the distribution functions as follows

$$f_{ji}(\mathbf{r}_1, \mathbf{r}_2) = n_j n_{ji}(|\mathbf{r}_2 - \mathbf{r}_1|) = n_i n_{ij}(|\mathbf{r}_1 - \mathbf{r}_2|) = n_j n_i \{ F_{00}(\mathbf{r}_2 - \mathbf{r}_1) + (e_j + e_i) F_{01}(\mathbf{r}_2 - \mathbf{r}_1) + e_j e_i F_{11}(|\mathbf{r}_2 - \mathbf{r}_1|) + (e_j^2 e_j + e_j e_i^2) F_{12}(|\mathbf{r}_2 - \mathbf{r}_1|) + \dots \} \quad (12)$$

and $f_{jik}(r_1, r_2, r_3)$, etc., in similar fashion by more elaborate series. By the approximations

(4) L. Onsager, *Chem. Rev.*, **18**, 73 (1933).

(5) L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

(6) H. D. Ursell, *Proc. Cambridge Phil. Soc.*, **23**, 685 (1927).

$$\begin{aligned} F_{00}(r) &= 0 \quad (r < a) \\ F_{00}(r) &= 1 \quad (r > a) \\ F_{01}(r) &= 0 \end{aligned} \quad (13)$$

we disregard complications which arise from cluster sums of order three or higher; the error so incurred is negligible for the purpose in hand. Thus, eq. 12 takes the simpler form

$$f_{ji}(\mathbf{r}_1, \mathbf{r}_2) = n_j n_i \{ 1 + e_j e_i F_{11}(|\mathbf{r}_2 - \mathbf{r}_1|) + (e_j^2 e_i + e_j e_i^2) F_{12}(|\mathbf{r}_2 - \mathbf{r}_1|) + \dots \} \quad (|\mathbf{r}_2 - \mathbf{r}_1| > a) \quad (14)$$

For the potential at a point \mathbf{r} somewhere in the vicinity of ions j, i situated at \mathbf{r}_1 and \mathbf{r}_2 we assume similarly

$$\psi_{ji}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}) = e_j \Psi_1(|\mathbf{r} - \mathbf{r}_1|) + e_i \Psi_1(|\mathbf{r} - \mathbf{r}_2|) + e_j^2 \Psi_2(|\mathbf{r} - \mathbf{r}_1|) + e_i^2 \Psi_2(|\mathbf{r} - \mathbf{r}_2|) + e_j e_i \Psi_{11}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}) \quad (15)$$

At this point the Boltzmann equation is replaced by the substantially exact relation⁴

$$-kT \partial \log f_{ji}(\mathbf{r}_1, \mathbf{r}_2) / \partial e_i = \lim_{(r=0)} (\psi_{ji}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_2 + \mathbf{r}) - \psi_i(\mathbf{r})) \quad (16)$$

A comparison of coefficients yields the symmetry relation

$$2\Psi_{11}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_2) = \Psi_2(\mathbf{r}_2, \mathbf{r}_1) \quad (17)$$

so that we obtain a closed set of equations for Ψ_1 and Ψ_2 when we combine eq. 16 with the Poisson relation described by eq. 2 and discard higher powers beyond Ψ_1^2 and Ψ_2 , as follows

$$(\Delta^2 - \kappa^2)\Psi_1 = \kappa^2 \eta_1 \Psi_2 \quad (18a)$$

$$(\Delta^2 - \kappa^2)\Psi_2 = -(\eta_1/kT) \kappa^2 \Psi_1^2 \quad (18b)$$

$$\Psi_1'(a) = -1/a^2 D; \quad \Psi_2(a) = 0 \quad (18c)$$

The well-known first approximation¹

$$\Psi_1 = (1/D(1 + \kappa a)) e^{\kappa(a-r)}/r \quad (19)$$

is obtained by disregarding the right member of (18a). This inserted in (18b) yields the result first obtained by La Mer and Mason⁷

$$\Psi_2(r) = \frac{\kappa \eta_1 e^{2\kappa a}}{2D^2 kT (1 + \kappa a)^2} \left\{ \frac{e^{\kappa r}}{r} E(3\kappa r) - \frac{e^{-\kappa r}}{r} \left(E(\kappa r) - E(\kappa a) - \frac{(1 - \kappa a)}{(1 + \kappa a)} e^{2\kappa a} E(3\kappa a) \right) \right\} \quad (20)$$

where $E(x) = \int_x^\infty e^{-t} dt/t$

The solution of (18a) with the result (20) substituted for Ψ_2 yields a correction to the first approximation (19) as follows

$$\begin{aligned} \Psi_1(r) - e^{\kappa(a-r)}/Dr(1 + \kappa a) = \\ -(\eta_1^2 \kappa / 4D^2 kT) e^{2\kappa a} (1 + \kappa a)^{-2} \times \\ \left\{ \phi(r) + Ce^{-\kappa r} + Be^{-\kappa r}(r) \right\} \quad (21a) \end{aligned}$$

(7) V. K. La Mer and C. F. Mason, *J. Am. Chem. Soc.*, **49**, 410 (1927).

where

$$r\phi(r) = (4/3)e^{-2\kappa r} - (1 + \kappa r)e^{-\kappa r}E(\kappa r) - (1 - \kappa r)e^{\kappa r}E(3\kappa r) \quad (21b)$$

$$C = -\kappa E(\kappa a) + \kappa(1 - \kappa a)(1 + \kappa a)^{-1}e^{2\kappa a}E(3\kappa a) \quad (21c)$$

$$(1 + \kappa a)^2 B e^{\kappa a} = -(2/3)(1 + \kappa a)(2 + \kappa a) + (1 + \kappa a)^2 E(\kappa a) - (1 - \kappa^2 a^2 + 2\kappa^3 a^3)e^{2\kappa a}E(3\kappa a) \quad (21d)$$

We shall be content with the approximate solutions described by eq. 20 and 21, because the system (18) is itself hardly accurate enough to justify further refinement. The corresponding electrostatic corrections to the thermodynamic potentials of the ions are accordingly

$$\begin{aligned} \Delta\mu_j &= \int_{\eta=0}^{\eta=e_j} ((\Psi_1(a) - (1/Da))\eta + \Psi_2(a)\eta^2) d\eta \\ &= (1/2)(\Psi_1(a) - (1/Da))e_j^2 + (1/3)\Psi_2(a)e_j^3 \quad (22) \end{aligned}$$

where according to eq. 20 and 21

$$\Psi_2(a) = (\kappa^2\eta_1/D^2kT)e^{3\kappa a}(1 + \kappa a)^{-3}E(3\kappa a) \quad (23)$$

as first found by La Mer and Mason, and

$$\begin{aligned} \Psi_1(a) - (1/Da) &= -(\kappa/2DkT)(1 + \kappa a)^{-1} + \\ &(\kappa^2\eta_1^2/12D^2kT)[(1 + \kappa a)^{-3} - \\ &\kappa a(1 + \kappa a)^{-4}e^{3\kappa a}E(3\kappa a)] \quad (24) \end{aligned}$$

The terms proportional to η_1^2 represent corrections to the Poisson-Boltzmann equation, which would actually contribute other terms of comparable to $\kappa^3 E(3\kappa a)$ when treated more accurately. We note that the term of order κ^2 has a fairly small coefficient, which is independent of the parameter a . Moreover, its effect differs trivially from that of replacing κ^2 in the original Debye-Hückel formula by

$$\kappa^2(1 + (\kappa\eta_1^2/3DkT)) \quad (25)$$

This means simply that the opportunities for correlation among the ions are slightly enhanced by the immersion of a charge, provided that the resultant polarization tends to distribute the ionic strength unevenly. In a symmetrical electrolyte there is no first-order effect of this sort, and the correction vanishes.

It seems likely that further corrections to Ψ_1 , corresponding by reciprocity to Ψ_3 , etc., will represent *reductions* of the effective ionic strength. As was recognized by Bjerrum, pairs of ions close together will not contribute much to the shielding of electrostatic forces.

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Theoretical Activity Coefficients of an Ideal Debye-Hückel Electrolyte¹

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A previous⁴ approximate integration of the Poisson-Boltzmann equation leads to a chemical potential which contains two major terms at low but nonzero concentrations. The first is the classical square root term due to long range electrostatic forces, and the second (linear in concentration) is due to short range interactions. It is shown that the net chemical potential is substantially independent of the distance chosen for the transition from the short to the long range approximation of the electrostatic potential. Also, it is shown that the deviations from the limiting law which derive from the Poisson-Boltzmann equation are in the opposite direction from those observed in real electrolytic solutions. The calculated activity coefficient for an idealized dilute electrolyte, defined as one whose properties are described by the Poisson-Boltzmann equation, is the product of two terms: the Debye-Hückel activity coefficient for point charge electrolytes times the fraction of ions which contribute to long range interaction (the "free" ions in the Bjerrum sense).

Debye's fundamental contribution to the theory of electrolytes was the introduction of the space charge model, which permitted statement of the mathematical problems in the form of differential equations. For the thermodynamic properties, a solution of the Poisson-Boltzmann equation was required; an approximate solution, valid at low concentrations, was obtained through the familiar series expansion of the Boltzmann factor. The classical limiting law (proportionality between logarithm of activity coefficient and square root of ionic strength) followed immediately. Most subsequent treatments have been empirical and/or theoretical attempts to increase the con-

centration range of the calculated activity functions. Here we shall discuss a solution so dilute that only long range interactions and *pairwise* ionic contacts need be considered; this is an idealized model which will show the magnitude and direction of those deviations from the limiting law which are inherent in the nonlinearity of the Poisson-Boltzmann equation. It is a fictitious system of charged spheres in a continuum, whose properties are described by the differential equation; of interest is how its properties differ from those of a real electrolytic solution. It is agreed that the limiting behavior at extremely low concentrations is the same for both. It will be found that the ideal and real systems diverge from the limiting tangent in *opposite* directions.

Another approximate integration of the Poisson-Boltzmann equation

$$\Delta\psi_j = (\kappa^2\epsilon/D\beta) \sinh(\epsilon\psi_j/kT) \quad (1)$$

was recently⁴ made in which special attention was

(1) This paper is based on part of a thesis submitted by James F. Skinner to the Graduate School of Yale University in June, 1964, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Sterling Research Fellow, 1963-1964.

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(4) R. M. Fuoss and L. Onsager, *Proc. Natl. Acad. Sci. U. S. A.*, **47**, 818 (1961).