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

$$\Delta\mu_{\mathrm{j}} = \int_{\eta = 0}^{\eta = e\mathrm{j}} ((\Psi_1(a) - (1/Da))\eta + \Psi_2(a)\eta^2)\mathrm{d}\eta$$

$$= (^1/_2)(\Psi_1(a) - (1/Da))e_{\mathrm{j}}^2 + (^1/_3)\Psi_2(a)e_{\mathrm{j}}^3 \quad (22)$$

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

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

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.

[CONTRIBUTION NO. 1754 FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY, NEW HAVEN, CONNECTICUT]

Theoretical Activity Coefficients of an Ideal Debye–Hückel Electrolyte[1]

BY JAMES F. SKINNER[2] AND RAYMOND M. FUOSS[3]

RECEIVED MARCH 30, 1964

A previous[4] 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 concentration 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 recently[4] 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.

(3) Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

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

given to the electrostatic interaction of ions at short mutual distances.[5] These configurations are automatically excluded from consideration by the classical approximation of the hyperbolic sine in (1) by its argument, a step which linearizes the equation to the form

$$\Delta\psi_j = \kappa^2\psi_j \tag{2}$$

(Above, ψ_j is the potential at a distance r from a reference ion of species j of charge ϵ in a medium of dielectric constant D at temperature T; k is Boltzmann's constant and $\beta = \epsilon^2/DkT$. This discussion is limited to symmetrical electrolytes where $\epsilon^+ = -\epsilon^-$.) The procedure used was to represent the potential at short distances by the (linear) self-potential ϵ/Dr plus an unknown function $\phi(r)$

$$\psi_j = \epsilon_j/Dr + \phi(r) \tag{3}$$

Substitution of (3) into (1) gave a second-order nonlinear differential equation which determines $\phi(r)$

$$\Delta\phi = (\kappa^2\epsilon/2D\beta)\exp(\beta/r + \epsilon\phi/kT) \times [1 - \exp(-2\beta/r + 2\epsilon\phi/kT)] \tag{4}$$

By approximating the quantity in brackets by unity and neglecting $\epsilon\phi/kT$ compared to β/r, (4) reduced to the inhomogeneous equation

$$\Delta\phi = (\kappa^2\epsilon/2D\beta)e^{\beta/r} \tag{5}$$

which can be solved explicitly to give a potential ψ_s which is valid for small values of r. ("Small" and "large" distances are, respectively, distances of the order of ionic diameters and distances of the order of the radius κ^{-1} of the ionic atmosphere.) Two arbitrary constants are, of course, involved. One of these is evaluated using the condition that the field strength at $r = a$, the contact distance, must reduce to $(-\epsilon/Da^2)$. Then for large distances, the hyperbolic sine was approximated by the first two terms of its series in (1) to give the differential equation

$$\Delta\psi_L = (\kappa^2\epsilon/D\beta)[\epsilon\psi_L/kT + (\epsilon\psi_L/kT)^3/6] \tag{6}$$

which was solved to give ψ_L, the long range potential. Again, two constants of integration appear; one of these is zero by the condition that the field strength vanish at $r = \infty$.

In this way, two expressions, ψ_s and ψ_L, were obtained for the potential, the former describing the field near the ion where screening of the reference ion is negligible, and the latter serving in the region where the ionic atmosphere appreciably screens the charge of the central ion. Two arbitrary constants remain: they are evaluated by requiring that potential and field strength, which must be everywhere continuous, are in particular continuous at a value R of r. The value $\beta/2$, the Bjerrum radius, was chosen for R, because pairwise distribution functions[6-9] for ions generally have a minimum near $r = \beta/2$. Ion pairs for which $r > \beta/2$ are defined as free,[7] in the sense that no particular ion of the opposite charge is nearby; those pairs for which $r < \beta/2$ present essentially a dipole field to a distant observer. These ions are the ones for which the approximation $\sinh x \approx x$ is emphatically never justified, even in solvents of high dielectric constant, and for which the function $\phi(r)$ was introduced.

Using this value of R and the Güntelberg charging process, the following expression for the activity coefficient was found

$$-\ln f_j = \tau/(1 + \tau) + O(\tau^2) \tag{7}$$

where τ is the dimensionless variable

$$\tau = \beta\kappa/2 = 4.2016 \times 10^6 c^{1/2}/(DT)^{3/2} \tag{8}$$

For $\mathring{a} = 4.00$ and at 25°

$$c = 4.1285\tau^2/b^3 \tag{9}$$

where

$$b = \beta/a = \epsilon^2/DkTa \tag{10}$$

$$= 140.1/D_{25} \text{ for } \mathring{a} = 4.00 \tag{10'}$$

The limiting form of (7) for dilute solutions

$$f_j = e^{-\tau} \tag{11}$$

agrees exactly of course with the classical result of Debye and is independent of ion size and of the value R of r at which long and short range potentials and field strengths are matched.

Terms of order $\tau^2 \sim c$ (and higher), however, depend both on a and R. The general nature of the higher terms is to increase the numerical value of $\ln f_j$, *i.e.*, to *decrease* the activity coefficient. In other words, the empirical Bc term in $\ln f$ which approximately describes the frequently observed minimum in activity coefficients cannot possibly derive from (1); high concentration properties will require qualitatively different theoretical sources. The purpose of this paper is to consider the influence of the choice of R on the results and conclusions of the previous analysis.[4]

Theoretical

Before introducing a variable matching distance R, the approximations made in reducing (4) to (5) will be reconsidered. For r small, neglecting the term in $\exp(-2\beta/r)$ compared to unity in (4) is completely justified. The other approximation, $\exp(\epsilon\phi/kT) \approx 1$, can easily be improved, and since the result introduces the point-charge activity coefficient as a multiplier, the recalculation is worth doing. The first approximation[10] gives

$$\epsilon\phi/kT = 2\tau^2[B + A\beta/r + F_1(r)] \tag{12}$$

where

$$B \approx -1/(1 + \tau)\tau \tag{13}$$

is the leading term in the bracketed expression in (12). For small distances (which is the only range where ϕ is used), this term dominates the others, and increasingly so with decreasing concentration. We therefore use

$$\epsilon\phi/kT \approx -2\tau/(1 + \tau) \tag{14}$$

---

(5) The model used here to represent the electrolytic solution is charged rigid spheres in a dielectric continuum. The short range potential is $\psi = \infty$ for $r < a$. Ionic polarization and other short range effects are excluded by hypothesis.

(6) N. Bjerrum, *Kgl. Danske Videnskab. Selskab., Mat. fys. Medd.*, **7**, No. 9 (1926).

(7) (a) R. M. Fuoss, *Trans. Faraday Soc.*, **30**, 967 (1934); (b) R. M. Fuoss, *J. Am. Chem. Soc.*, **57**, 2604 (1935).

(8) H. Reiss, *J. Chem. Phys.*, **25**, 400 (1956).

(9) J. C. Poirier and J. H. de Lap, *ibid.*, **35**, 213 (1961).

(10) Ref. 3, eq. 9 and 24.

in (4), giving as the starting equation for $\phi(r)$

$$\Delta\phi = (\kappa^2\epsilon/2D\beta)e^{\beta/r}\exp[-2\tau/(1 + \tau)] \quad (15)$$

where

$$\exp[-2\tau/(1 + \tau)] = f_{\pm}^2 \quad (16)$$

is the square of the activity coefficient.

The solution of (15) is

$$\phi = (\kappa^2\epsilon\beta f_{\pm}^2/2D)[B' + A\beta/r + F_1(r)] \quad (17)$$

where A and $F_1(r)$ are the same as before,[11] but B' is left dependent on the choice of R. The long range solution ψ_L is, of course, also the same as before. On matching at $r = R$, we find

$$f_{\pm}^2B'(1 + \kappa R) = -1/\tau - G_3(\kappa R) + f_{\pm}^2[F_1(R) + F_2(R)] + O(\tau) \quad (18)$$

For the potential $\psi_j^*(a)$ at the reference ion due to the presence of other ions, combination of (3), (17), and (18) gives

$$\psi_j^*(a) = \psi_j - \epsilon_j/Da = (\tau\epsilon_j\kappa f_{\pm}^2/D)[B' + F_1(a) + F_2(a)] \quad (19)$$

Use of (19) to give the electrical part of the free energy, and differentiation of the latter with respect to n_j to give the activity coefficient, produces the equation

$$-\ln f_j = (1 + \kappa R)^{-1}[\tau + \tau^2G_3(\kappa R) + \tau^2f_{\pm}^2H(b,\beta/R)] \quad (20)$$

where terms of order τ^3 have been dropped, and the function H is defined by

$$2H(b,x) = E_p(b) - e^b(1 + b)/b^2 - E_p(x) + e^x(1 + x)/x^2 \quad (21)$$

The function $G_3(\kappa R)$ has its origin in the higher term (in ψ^3) which was retained in the differential equation for the long range potential. Its value, when multiplied by τ^2, is small compared to the other two terms in the brackets in (20) and rapidly decreases as its argument increases. Explicitly

$$G_3(x) = 2e^{-3x}/3 - 8xe^xE_n(4x)/3 \quad (22)$$

Numerical values are given in Table I. In order to simplify the calculation, $G_3(\kappa R)$ in (20) will be replaced by $G_3(\tau)$ in constructing Fig. 1 and 2. The error is practically invisible.

TABLE I

THE FUNCTION $G_3(x)$

x	$G_3(x)$	x	$G_3(x)$
0.02	0.5176	0.25	0.12712
.04	.4348	.30	.09999
.06	.3740	.35	.07936
.08	.3261	.40	.06346
.10	.2869	.45	.05104
.12	.2541	.50	.04125
.14	.2263	.55	.03349
.16	.2024	.60	.02728
.18	.1817	.65	.02230
.20	.1635	.70	.01828

In Table II are given the values of $H(b,x)$ which will be used later. The first column gives the values of x, and the headings of the H columns are the values of b. This function, which is defined by (21), has as its asymptotic expansion for $b > x >> 1$ the same form as the association constant for ion pairs[12]

TABLE II

THE FUNCTION $H(b,x)$

	b						
x	2	3	4	5	6	7	8
2	0.0000	0.7972	1.5781	2.5765	4.0644	6.5214	10.8786
1	1.4769	2.2741	3.0551	4.0535	5.5413	7.9984	.....
2/3	2.8741	3.6713	4.4522	5.4506	6.9385	9.3955	13.7527
1/2	4.4253	5.2225	6.0034	7.0018	8.4897	10.9467	.....
2/5	6.1806	6.9778	7.7587	8.7571	10.2450	12.7020	17.0592
$b/2$	1.4769	1.3426	1.5781	2.1570	3.2672	5.3475	9.3005
$b/3$	2.8741	2.2741	2.3660	2.9169	4.0644	6.2344	10.3310

$$\tau^2f^2H(b,x) \approx (6\pi Na^3e^b/3000)f^2c \quad (23)$$

Discussion

Two kinds of choices are available for R: a value which depends on the solvent *via* the Bjerrum radius $\beta/2 = \epsilon^2/2DkT$ and a value independent of dielectric constant. Examples of both will be considered. The chemical potential is most simply presented in terms of the dimensionless variable τ, defined by (8). It depends on both concentration and the DT product; two solutions which have equal values of τ are in corresponding electrostatic states. Concentration can be expressed also in terms of b and τ, as shown by (9). In the figures, a c-scale is given at the top and a τ-scale at the bottom of each panel. The Bjerrum parameter b depends on the contact distance a and on the DT product. For convenience, we shall choose the round value $\mathring{a} = 4.00$ and set $T = 298.2°$; values of dielectric constant corresponding to a given value of b are then easily obtained from (10′). It is clear that the approximations made in deriving (20) will limit consideration to dilute solutions; we shall use the same criterion as that used in the conductance problem[13]

$$\kappa a < 0.2 \quad (24)$$

This choice is based on both theoretical and practical grounds: (1) if $\kappa a > 0.2$, the maximum charge in the atmosphere is less than five diameters from the center of the reference ion; at shorter distances, fluctuation terms will soon become dominant and the approximation by a continuous space charge (which justifies the use of the Poisson equation) ceases to be realistic; (2) for $\kappa a > 0.2$, terms of order κ^3a^3 start to become visible, and the purely numerical approximations (such as dropping terms in τ^3) no longer are valid. Translating (24) into other terms, we restrict the discussion to the range of variables where

$$2\tau/b = \kappa a < 0.2 \quad (25)$$

i.e., to the range

$$\tau < b/10 \quad (26)$$

For convenience in discussion, we rewrite (20) in the form

$$-\ln f_j = T_1 + T_2 + T_3 = -\mu_j/kT \quad (27)$$

where T_1 is the leading term $\tau/(1 + \kappa R)$ in activity due to long range interionic forces, and T_3 is the term which explicitly depends on short range interactions. (As

---

(11) Ref. 3, eq. 9, 10, and 23.

(12) R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).

(13) R. M. Fuoss and L. Onsager, *J. Phys. Chem.*, **61**, 668, last two paragraphs of Section 11 (1957).

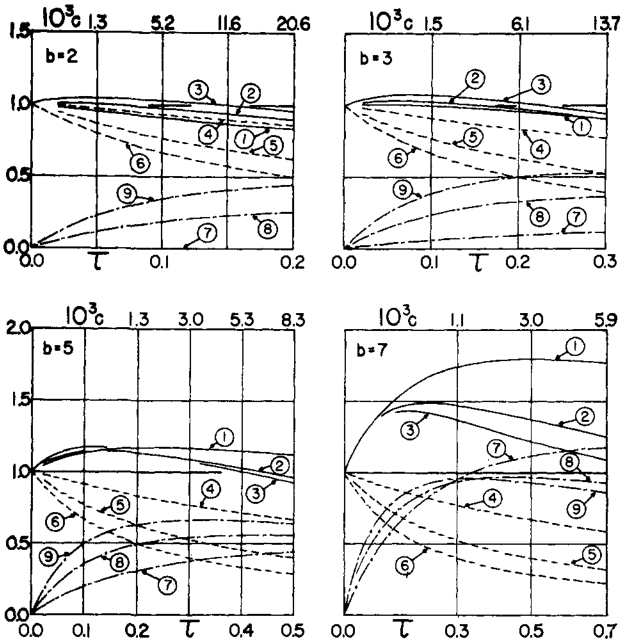

Fig. 1.—Potential functions for matching at multiples of the Bjerrum radius, $n\beta/2$. Code:

n	T_1/τ	T_3/τ	μ_j/μ_j^*
1	4	7	1
3	5	8	2
5	6	9	3

already mentioned, T_2 is small and calls for no further comment.)

In order to focus attention on the deviations from point-charge behavior, we shall consider the ratio μ_j/μ_j^*, where μ_j^* is the chemical potential for the model point-charge electrolyte, with activity coefficient f_j^*

$$-\ln f_j^* = -\mu_j^*/kT = \tau = \epsilon^2\kappa/2DkT \quad (28)$$

In the figures this ratio is shown as the solid curves; explicitly

$$\mu_j/\mu_j^* = T_1/\tau + T_2/\tau + T_3/\tau \quad (29)$$

When the solid curve falls below unity, the activity coefficient lies above the limiting tangent (*i.e.*, the calculated activity coefficient is nearer unity than the point charge value). The dashed curves represent the long range effects T_1/τ and the dot-dash curves the short range ones T_3/τ.

In Fig. 1, three values of R are represented: $\beta/2$, $3\beta/2$, and $5\beta/2$, where the code is given by the table in the caption. For $\mathring{a}$ = 4.00, the Bjerrum radius $\beta/2$ is numerically equal to $2b \times 10^{-8}$ cm. Consider first curves 1, 2, and 3 for b = 2, 3, and 5 ($D \approx 70$, 47, and 28). Curve 1 for b = 2 lies below the 1.00 line, because T_3 is zero: the upper and lower limits of the ion pair integral, a and $\beta/2$, coincide; the solutions are matched at the surface $r = a$. For this case, $\psi_s = \epsilon/Da$ at $r = a$ and $\psi = \psi_L$ for $r > a$. But for $b > 2$, the curves approach unity from above as τ goes to zero. There is, however, no startling departure: even for b = 5 at $c \times 10^{-3}$, $\ln f$ is -0.234 *vs.* the limiting law value of -0.200. But note that μ_j/μ_j^* is *greater* than unity; in words, the activity coefficient is *smaller* than the limiting value. We recall that activity coefficients of real solutions at nonzero concentrations generally are *larger* than the limiting values. For $b > 5$ (see, for example, $b = 7$), the positive deviations become rapidly more significant as more and more ions cluster as pairs. (The crossover of curves 1,2,3 as b increases is due to the term $(1 + \kappa R) = (1 + n\tau)$ in the denominator and the increasing permissible range of τ.)

To state the result in a different way, in the range of higher dielectric constants ($2 < b < 5$), the ratio μ_j/μ_j^* is not at all sensitive to the value chosen for R. This comes about by a compensation between T_1 and T_3 that has physical significance. We note that at $\tau = 0$, T_1 is unity and decreases with increasing τ, while T_3 starts at zero and increases; compare curves 4, 5, and 6 with 7, 8, and 9. If we choose a larger value of R, T_3 increases (at fixed τ); larger R means counting more ions as short range pairs and fewer as atmosphere ions. To compensate for this, T_1 decreases, and in such a way that the sum remains almost constant. Consequently, while details of the picture depend on the choice of R, the net chemical potential is substantially independent of R (until, of course, the dielectric constant becomes so small that the exponential nature of H starts to control).

The model to represent the solvent is a dielectric continuum, which certainly is not realistic for distances of the order of small multiples of a, however good it may be for distances large compared to a. There has been considerable speculation on the dependence of "effective" dielectric constant on distance from the reference ion.[14-16] In the examples of Fig. 1, the matching distance R depends on the dielectric constant through the Bjerrum radius; as already noted, this choice, for b = 2, automatically eliminates the ψ_s from the equations, and only absurd results can be obtained for systems for which $a > \beta/2$ (large quaternary ions in water, for example). Consequently we shall now consider some examples in which the matching distances are absolute. An undoubtedly interesting choice would be to match at $R = a + md$, where d is the diameter of a solvent molecule. A simpler choice, which is likewise a pure distance, is to match at $R = ma$, *i.e.*, multiples of the contact distance. These distances will be of the order of several layers of nearest neighbor solvent molecules, of course. In Fig. 2, plots of μ_j/μ_j^*, T_1, and T_3 for b = 2, 3, 5, and 7 are shown for $R = 2a$ and $3a$. Again, the decrease in T_1 and the increase in T_3 with increasing R appears, but now the compensation is nearly perfect; even at b = 7, curves 1 and 2 practically coincide. Varying the match point between ψ_s and ψ_L between 8 and 24 Å. has practically no effect on the calculated thermodynamic potential. The computation was also made for $R = 4a$, $5a$, and $6a$; the ratio μ_j/μ_j^* is strikingly insensitive to the choice of m, for a given value of b. Some numerical values of the ratio are shown in Table III. The result may be stated as follows: the chemical potential of an electrolyte which is described by our approximate solution of the nonlinear Poisson–Boltzmann equation contains two large terms, one arising from short range electrostatic interactions and one from averaged long range effects. As the distance at which short and long range solutions are matched is increased, the first term increases and the second term

---

[14] R. M. Fuoss, *Chem. Rev.*, **17**, 27, footnote 3 (1935).

[15] H. S. Frank, *J. Chem. Phys.*, **23**, 2023 (1955).

[16] J. Padova, *ibid.*, **39**, 1552 (1963).

decreases in such a way that the sum remains practically constant.

TABLE III

THE RATIO u_j/u_j^* FOR VARIABLE b AND m; $\tau = 0.2$

	b			
m	2	3	5	7
2	0.8888	0.9672	1.1567	1.6145
3	.9029	.9704	1.1699	1.6443
4	.9260	.9719	1.1629	1.6302
5	.9592	.9780	1.1526	1.6065
6	1.0009	.9895	1.1432	1.5810

Equation 20 can be rearranged into an interesting form which leads to the heuristic argument that calculation of the concentration of ion pairs by the mass action equation is arithmetically justified, even though the hypothesis of an equilibrium between free and paired ions is no longer needed. Dropping small terms which are not relevant, (20) can be approximated as

$$-\ln f_j = \tau + \tau^2 e^{-2\tau} H \tag{30}$$

whence

$$f_j = e^{-\tau} \exp(-\tau^2 e^{-2\tau} H) \tag{31}$$

For low concentrations, expansion of the second exponential function in (31) gives

$$f_j \approx e^{-\tau}(1 - \tau^2 e^{-2\tau} H) \tag{32}$$

and using (23)

$$f_j \approx e^{-\tau}(1 - K_A e^{-2\tau} c) \tag{33}$$

The mass action equation is

$$1 - \gamma = K_A c \gamma^2 e^{-2\tau} \tag{34}$$

where γ is the fraction of free ions. At low concentrations (34) becomes approximately

$$1 - \gamma \approx K_A c e^{-2\tau} \tag{35}$$

and combining this result with (33), we finally obtain

$$f_j = \gamma e^{-\tau} \tag{36}$$

To restate the result, the activity coefficient calculated from (20) is formally the product of $e^{-\tau}$, the coefficient for point charges, and γ, the fraction of ions outside $r = R$.

The approximation given by matching function and first derivative at $R = r$ is really quite close, as is shown by a consideration of the curvature at $r = R$. We show the result for $R = \beta/2$. Here the second derivatives are

$$\psi_s'' = (16\epsilon/D\beta^3)[1 + \tau^2 L_s(b)] \tag{37}$$

and

$$\psi_L'' = (16\epsilon/D\beta^3)[1 + \tau^2 L_L(b)] \tag{38}$$

where

$$L_s(b) = (2/b)F_2(b) + (1/3)E_p(2) - 5e^2/24 \tag{39}$$

$$L_L(b) = (2/b)F_2(b) + (1/3)E_p(2) + 1/2 - e^2/3 \tag{40}$$

and

$$F_2(b) = e^b(1 + b/2 + b^2/2)/3b^2 - (b/6)E_p(b) \tag{41}$$

Inserting numerical values

$$L_s(b) = (2/b)F_2(b) + 0.111 \tag{42}$$

and

$$L_L(b) = (2/b)F_2(b) - 0.315 \tag{43}$$

We see that the curvatures at the matching distance for $\psi_s(R - 0)$ and $\psi_L(R + 0)$ both equal $(16\epsilon/D\beta^3)$ plus terms of order τ^2 and higher, and that the coefficients of the τ^2-terms do not differ greatly. This close match in curvature means that the function goes very smoothly through the point $r = R$.

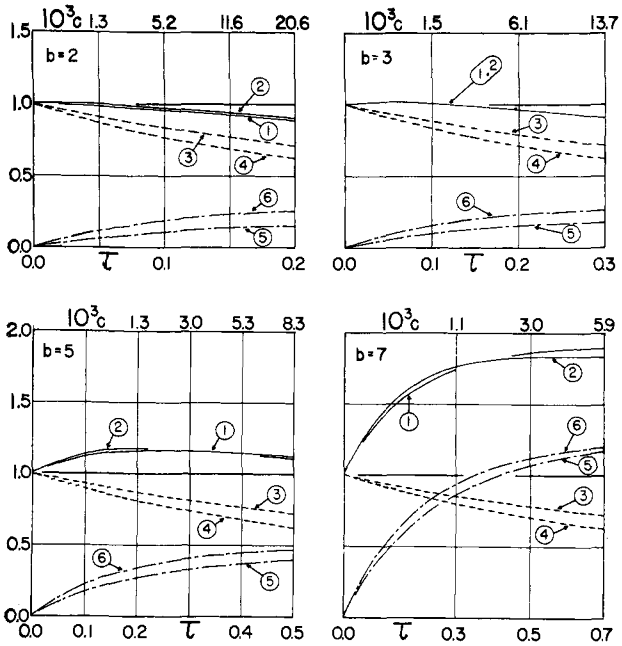

Fig. 2.—Potential functions for matching at multiples of the contact distance, ma. Code:

m	T_1/τ	T_3/τ	μ_j/μ_j^*
2	3	5	1
3	4	6	2