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GRADUATE COLLEGE

A THEORY OF ELECTROLYTE SOLUTIONS

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

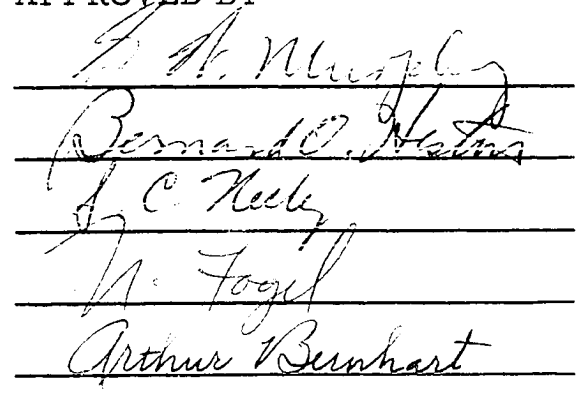
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Norman, Oklahoma

1967

A THEORY OF ELECTROLYTE SOLUTIONS

APPROVED BY



DISSERTATION COMMITTEE

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A THEORY OF ELECTROLYTE SOLUTIONS

CHAPTER I

INTRODUCTION

For many years the interionic attraction theory of Debye and Hückel (1) has provided the accepted description of the behavior of electrolyte solutions at low concentrations. Although preceded by the work of Milner (2), the complex nature of the result obtained in this earlier analysis obscured the concentration dependence of the solution properties, i. e. the solution properties dependent on a fractional power of the concentration at high dilution.

Details and discussions of the theory of Debye and Hückel are readily available, so only the most general considerations will be discussed here. Their model of a solution of a completely dissociated electrolyte consists of a system of rigid, spherical ions in a homogeneous, continuous medium whose dielectric constant is unaffected by the presence of ions. The disorder prevailing among the ions is modified by the spherically symmetrical electrical interactions with a chosen central ion. The Poisson equation of electrostatics is combined with the statistical

distribution function of Boltzmann to give an equation for the average electrostatic potential. The limiting form of the interionic attraction theory was obtained by retaining only the linear term in the expansion of the Poisson-Boltzmann equation. The assumptions and approximations involved in this development are covered in a number of sources, e. g. Kirkwood (3), Robinson and Stokes (4). In the years immediately following, a number of investigators including Gronwall (5), Gronwall, La Mer and Sandved (6) and Müller (7), undertook the solution of the complete Poisson-Boltzmann equation in order to extend the range of applicability of the interionic attraction theory. Evaluation of the complete equation by the method of Müller has been recently reexamined by Guggenheim (8) utilizing the capability of modern high-speed computers. However, the applicable concentration range has not been significantly extended by this approach, and, in fact, the internal consistency of the Poisson-Boltzmann equation at higher concentrations and for unsymmetrical electrolytes has been questioned by Robinson and Stokes (4). It is generally assumed that the applicable concentration range certainly cannot extend past 0.1M even for 1-1 electrolytes. The development and application of more rigorous statistical treatments (9-12) apparently confirm the limiting form of the Debye-Hückel theory.

A number of semi-empirical correction terms have been proposed to extend the range of validity of the interionic attraction theory. Several investigators have attempted to correct for the change in the

dielectric constant of the medium as the electrolyte concentration increased, e.g. Hückel (13) and Jones and Bickford (14). Shortly after the publication of the Debye-Hückel theory, Bjerrum (15) suggested that the higher order terms in the expansion could be considered as a correction arising from the formation of cation-anion pairs. This approach is a correction in the direction of weak electrolytes to the interionic attraction theory of strong electrolytes. Many workers, including Bjerrum (16), Scatchard (17), Robinson and Stokes (4) and Glueckauf (18), have proposed correction terms arising from ion hydration which serves to remove "free" solvent from the solution. Utilizing hydration number as an additional parameter, experimental data are fit to high concentrations. Excluded volume effects arising from the finite size of the ions (or hydrated ions) have been considered by Van Rysselberghe and Eisenberg (19) and Eigen and Wicke (20); the latter treatment has met with criticism on logical grounds (21).

It has long been observed that the properties of strong electrolyte solutions display a long segment of linear dependence on the cube root of concentration. In fact, Kohlrausch (22) used cube-root-of-concentration plots for conductance data for many years before adopting the square root dependence. Several years before the theory of Debye and Hückel, Bjerrum (23) proposed a cube-root-of-concentration dependence for dilute electrolyte solutions and later extended this to include concentrated solutions (16). More recently, Robinson and Stokes (4) have again

commented on the long linear segment in plots of log $y_{\pm}$ versus the cube root of concentration beginning at about 0.001M. Proceeding from these observations, Frank and Thompson (24) examined the theory of Debye and Hückel and concluded that the square-root-of-concentration dependence is limited to a range between zero and some critical value of the concentration where the assumptions are no longer valid. From their calculations they found this "breakdown" to occur in the vicinity of 0.001M for 1-1 electrolytes, and, at even lower concentrations, for electrolytes of higher valence. Based on these results, a "diffuse lattice" picture was postulated as a possible explanation for the observed $M^{1/3}$ dependence of electrolyte solution properties in the experimentally convenient concentration range. Fuoss and Onsager (26) have also discussed the possibility that the theory of electrolyte solutions should contain a term which would reflect the simple $M^{1/3}$ dependence of solutions of moderate to high concentrations. In 1918, Ghosh (25) attempted to describe electrolyte solutions in terms of an ionic lattice; however, his lack of consideration of the proper statistical treatment resulted in the invalidation of the approach (1). Unfortunately, the criticism of this treatment led to the exclusion of the cube-root-of-concentration dependence of electrolyte solution properties from theoretical investigation for many years.

The interionic attraction theory of Debye and Hückel was derived for dilute electrolyte solutions and, even in the most favorable case (1-1 electrolytes), the underlying assumptions become invalid at concentrations

higher than about 0.001 molar (24). At least in the range above this "critical" region to moderate concentrations, the colligative properties can be represented by an expression involving a simple cube-root-of-concentration dependence. By assuming a more restricted model for an electrolyte solution than was adopted by Debye and Hückel, mathematical expressions describing electrolyte solution properties can be derived which have a simple cube-root-of-concentration dependence at low electrolyte concentrations, while, in higher concentration regions, the properties are described by a series in ascending powers of the cube root of concentration. Smith (27) adopted a model wherein the counter ion (initially considering a symmetrical electrolyte) was restricted to a "cell" of radius R determined by the solute concentration ($4\pi R^3/3 = 1000/N_oM$), where N_o is Avogadro's number and M the molar concentration, and was able to approximate 1-1 electrolyte solution data over rather extensive concentration ranges. For electrolytes of the n-1 type, Smith assumed the counter ions to be equidistant from the central ion and from each other. Considering the much oversimplified nature of his model, the results were quite encouraging in the sense that approximate fits to experimental data were obtained over substantial concentration ranges, and the correct shape for activity coefficient curves was predicted. In the present approach, a rather less restricted model is chosen resulting in an increase in mathematical complexity but offering an excellent fit to experimental results over a surprisingly wide concentration range.

Recently, Murphy and Weissenböck (28), using the constant pressure (TPN) ensemble (29), have improved the statistical foundation of the pair distribution function obtained in this work. Their treatment considers a general potential energy function rather than the specific case of coulomb interaction used here.

CHAPTER II

MATHEMATICAL DEVELOPMENT

Development of the Unit Partition Function

The adopted model of an electrolyte solution assumes that, at any instant, the solute ions can be grouped into electrically-neutral, chemical formula units. The interactions between unit members are obtained by first choosing a central ion as the center of coordinates, with the restriction that $|z_c| \geq |z_g|$, where z_c is the charge of the central ion and z_g the individual charge of the counter ion(s). Considering only the interactions between oppositely charged ions, the pairing proceeds stepwise until all unit members have been included. Of course, for symmetrical electrolytes, there is a single pair of ions per chemical formula (and electrically-neutral) unit. For electrolytes of the n-1 type, there are n pairs of electrostatic interactions between oppositely charged species per unit. In the consideration of electrolyte solutions, the specific assumptions involved are:

(1) The statistical mechanical ensemble consists of electrically-neutral, chemical formula units of ions containing ν members (ν = the number of ions into which the electrolyte dissociates).

(2) The motion of the center of mass of these units can be treated independently of the relative motion of the constituent ions; electrostatic interactions are part of the latter treatment and are considered to be angularly independent (smearing approximation).

(3) Only pairwise interactions between oppositely charged ions are considered; for units containing more than a single counter ion, pairing proceeds in a stepwise manner from the chosen central ion ($|z_c| \geq |z_g|$).

(4) Other than electrostatic interaction, the only non-ideal gas contribution considered is hard core repulsion.

(5) The solvent is a structureless dielectric medium; the bulk dielectric constant of the pure solvent is used at all solute concentrations.

It is assumed that each pair (unit) is independent, i. e., there is no potential energy of interaction between units. The unit is thus describable in terms of a unit partition function q in much the same way as the molecules in an ideal gas. The unit partition function is related to the canonical partition function Q of the system by the equation

$$\ln Q = N[\ln(q/N) + 1] \tag{1}$$

where N is the number of units in the ensemble.

For symmetrical electrolytes the unit partition function is

$$\frac{q}{N} = \underbrace{\left[\frac{2\pi(m_+ + m_-)kT}{h^2}\right]^{3/2}}_{\text{center of mass translation}} \underbrace{\left[\frac{2\pi m_+ m_- kT}{(m_+ + m_-)h^2}\right]^{3/2}}_{\text{internal translations}} \zeta \tag{2}$$

where m_+ and m_- are the masses of the cation and anion, respectively, T is the absolute temperature, k is Boltzmann's constant and h is Planck's constant. Equation 2 can be simplified to yield

$$\frac{q}{N} = \left[\frac{2\pi m_{\pm} kT}{h^2}\right]^3 \zeta = \zeta/\Lambda^{3\nu} \tag{3}$$

using

$$m_{\pm} = (m_+^{\nu_+} m_-^{\nu_-})^{1/\nu} \tag{4}$$

and

$$\Lambda = (h^2/2\pi m_{\pm} kT)^{1/2} \tag{5}$$

The pair configuration integral is given by

$$\zeta = \overline{v}^f \int_a^{\infty} \exp\left[-\beta u(r) - \gamma v^f\right] 4\pi r^2 dr \tag{6}$$

where

$$\beta = 1/kT \tag{7}$$

$$\gamma = 1/\overline{v}^f \tag{8}$$

$$\overline{v}^f = \overline{v} - b = (1000/NM) - 4\pi a^3/3 \tag{9}$$

$$v^f = 4\pi(r^3 - a^3)/3 \tag{10}$$

a is the distance between centers, cation-anion contact.

M is the solute concentration in moles/liter,

and u(r) is the appropriate potential energy function. In essence, this derivation includes the constraint of constant free volume in addition to constant energy and constant number of independent pairs when treating pairwise interactions. This explicit inclusion of constant free volume

results in a modified Maxwell-Boltzmann distribution for independent pairs as given by the exponential terms in the integrand of Equation 6. That is, the second exponential, $\exp(-\gamma v^f)$, modifies the distribution of energy states given by the regular Maxwell-Boltzmann term, $\exp[-\beta u(r)]$, with the appropriate expression for the potential energy $u(r)$. Radial symmetry of a counter ion about a chosen central ion is assumed; therefore, the probability of a counter ion being between r and r+dr is proportional to the integrand in Equation 6.

Extension of the approach to describe units composed of more than a single pair requires careful consideration of the adopted model. For a three particle unit (corresponding to a 2-1 electrolyte such as $CaCl_2$), two individual pair interactions are involved, when including only those pairs made up of oppositely charged ions. Such a unit can be pictured as shown in Figure 1a. A doubly-charged cation is taken as the central ion and the remaining members of this independent, chemical formula unit are two counter ions. The pairing proceeds outwardly from the central ion. The interaction of the closest counter ion with the central ion constitutes what is termed an "inner ion pair"; the net electrostatic result is to give a virtual central ion with a charge corresponding to the charge of the central ion minus the charge of the "paired" counter ion. For a 2-1 electrolyte, the final pair, termed an "outer pair", is formed by interaction of the remaining counter ion with the virtual central ion, Figure 1b. The electrostatic result is to give an electrically

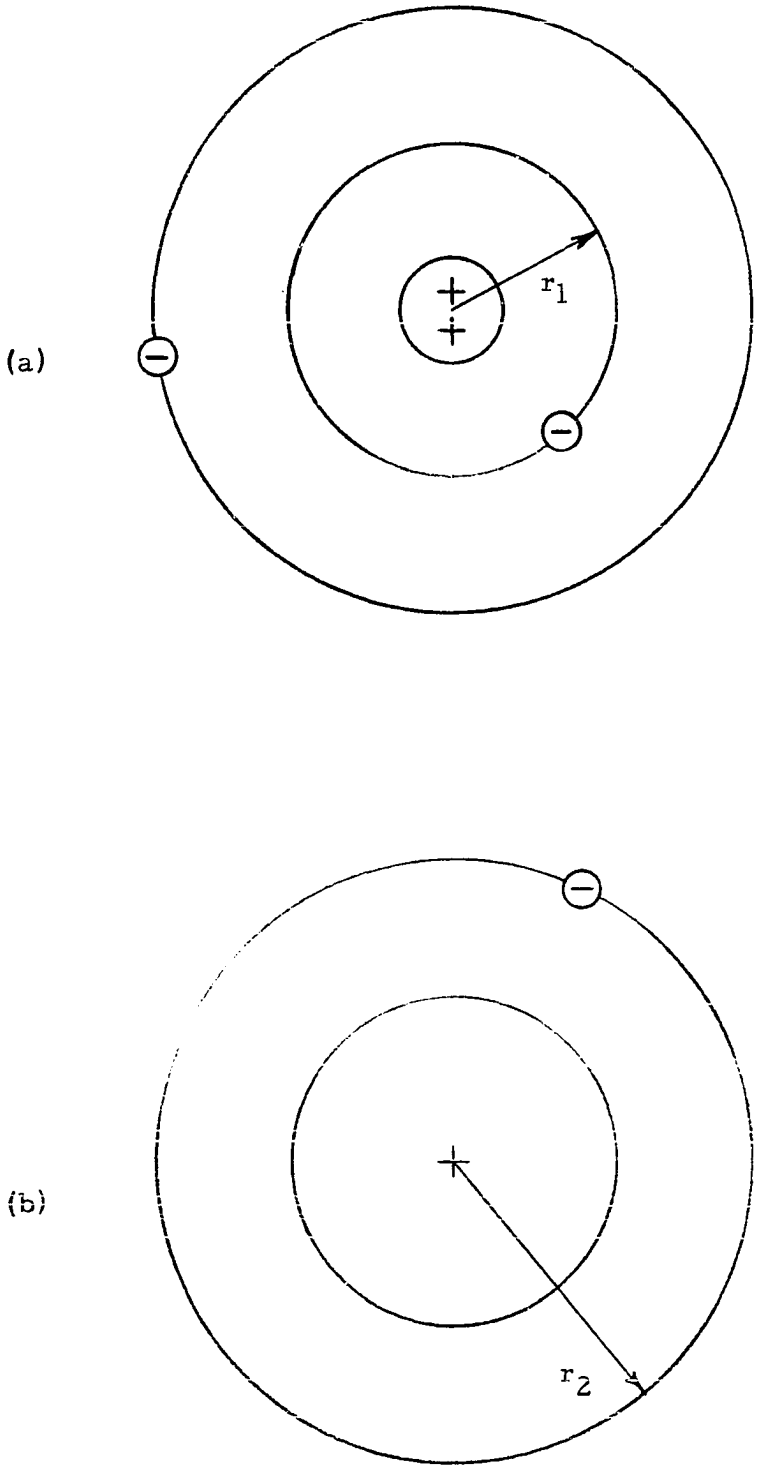


Figure 1. Pairing Sequence, 2-1 Electrolytes. (a) Inner ion pair formed from central ion and counter ion at r_1. (b) Outer ion pair formed from virtual central ion (of radius r_1) and counter ion at r_2.

neutral unit as seen by adjacent units.

The unit partition function for a 2-1 electrolyte is

$$\frac{q}{N} = \left[\frac{2\pi(m_+ + 2m_-)kT}{h^2}\right]^{3/2} \left[\frac{2\pi m_+ m_- kT}{(m_+ + m_-)h^2}\right]^{3/2} \left[\frac{2\pi(m_+ + m_-)m_- kT}{(m_+ + 2m_-)h^2}\right]^{3/2} \zeta_{12} \quad (11)$$

center of mass translation	internal translation, inner ion pair	internal translation, outer ion pair

with the unit configuration integral being given by

$$\zeta_{12} = \bar{v}^f \int_a^\infty \exp\left[-\beta u(r_1) - \gamma_1 v_1^f\right] 4\pi r_1^2 \, dr_1 \int_{r_1}^\infty \exp\left[-\beta u(r_2) - \gamma_2 v_2^f\right] 4\pi r_2^2 \, dr_2 \quad (12)$$

where $\bar{v}^f$ (given by Equation 9) is the free volume term associated with the contribution from the center of mass term, and

$$\gamma_1 = 1/\bar{v}_1^f \quad (13)$$

$$v_1^f = v_1 - b = 4\pi(r_1^3 - a^3)/3 \quad (14)$$

$$\bar{v}_1^f = \alpha\bar{v} - b \quad (15)$$

$$\gamma_2 = 1/\bar{v}_2^f \quad (16)$$

$$v_2^f = v_2 - v_1 = 4\pi(r_2^3 - r_1^3)/3 \quad (17)$$

$$\bar{v}_2^f = \bar{v}(1 - \alpha) \quad (18)$$

It is assumed that the average free volume of an inner ion pair is some fraction of the average volume available per unit. Since the fractional value at finite concentrations is as yet unknown, α is taken as a second

fitting parameter. A more rigorous treatment would attempt to express a as a function of concentration. Assuming a to be constant with concentration and using it as a fitting parameter gives a value, resulting from fitting experimental data, which is some type of average for this parameter over the concentration range which can be reproduced.

Using the definition employed for symmetrical electrolytes to give a simplified expression for the unit partition function, the partition function for a 2-1 electrolyte (Equation 11) becomes

$$q/N = \zeta_{12}/\Lambda^9 \tag{19}$$

Evaluation of the Configuration Integral

The pair configuration integrals, Equations 6 and 12, cannot be solved in closed form, but can be integrated numerically. The following dimensionless variables are adopted for transformation of the pair configuration integral for symmetrical electrolytes:

$$x = v/\bar{v}^f = 4\pi r^3/3\bar{v}^f \tag{20}$$

$$\Phi = b/\bar{v}^f \tag{21}$$

$$B = z_1 z_2 e^2 \Phi^{1/3}/DkTa \tag{22}$$

Substitution into Equation 6 yields

$$\zeta = (\bar{v}^f)^2 e^{\Phi} \int_{\Phi}^{\infty} \exp\left[(B/x^{1/3}) - x\right] dx = (\bar{v}^f)^2 e^{\Phi} I \tag{23}$$

The function in Equation 23 is transformed into a function of

$x^{1/3}$, which is more directly related to r, the distance of separation of pair members, to give

$$\zeta = (\bar{v}^{f})^{2} 3e^{\Phi} \int_{\Phi^{1/3}}^{\infty} \exp\left[(B/x^{1/3}) - x\right] x^{2/3} \, d(x^{1/3}) \qquad (24)$$

The integrand in Equation 24 is plotted vs $x^{1/3}$ in Figure 2 for a series of concentrations at a constant value of a, the ion size parameter. The lowest concentration considered corresponds approximately to the lower limit of the experimentally accessible region, i.e., 0.001M. In Figure 2, the lower limit of integration ($\Phi^{1/3}$) falls at separation distances above the location of the minimum in the function. Since the area under the curve between the lower limit and some value of $x^{1/3}$ is proportional to the probability of finding the counter ion at a distance $x^{1/3}$ (proportional to r) from the central ion, the plot for the lowest concentration in Figure 2 shows that there is a very small probability of the counter ion being located close to the central ion for an electrolyte displaying this a value (3.5A). This situation corresponds to the description of a strong electrolyte, i.e., complete dissociation. As the concentration increases, the minimum in the curve moves upward and gradually blends in with the maximum in the function corresponding to the increased probability of finding the counter ion close to the central ion.

For a constant low concentration, the function plotted in Figure 2 remains essentially unaffected as the a value decreases. The only effect is that the lower limit of integration ($\Phi^{1/3}$) moves to lower $x^{1/3}$

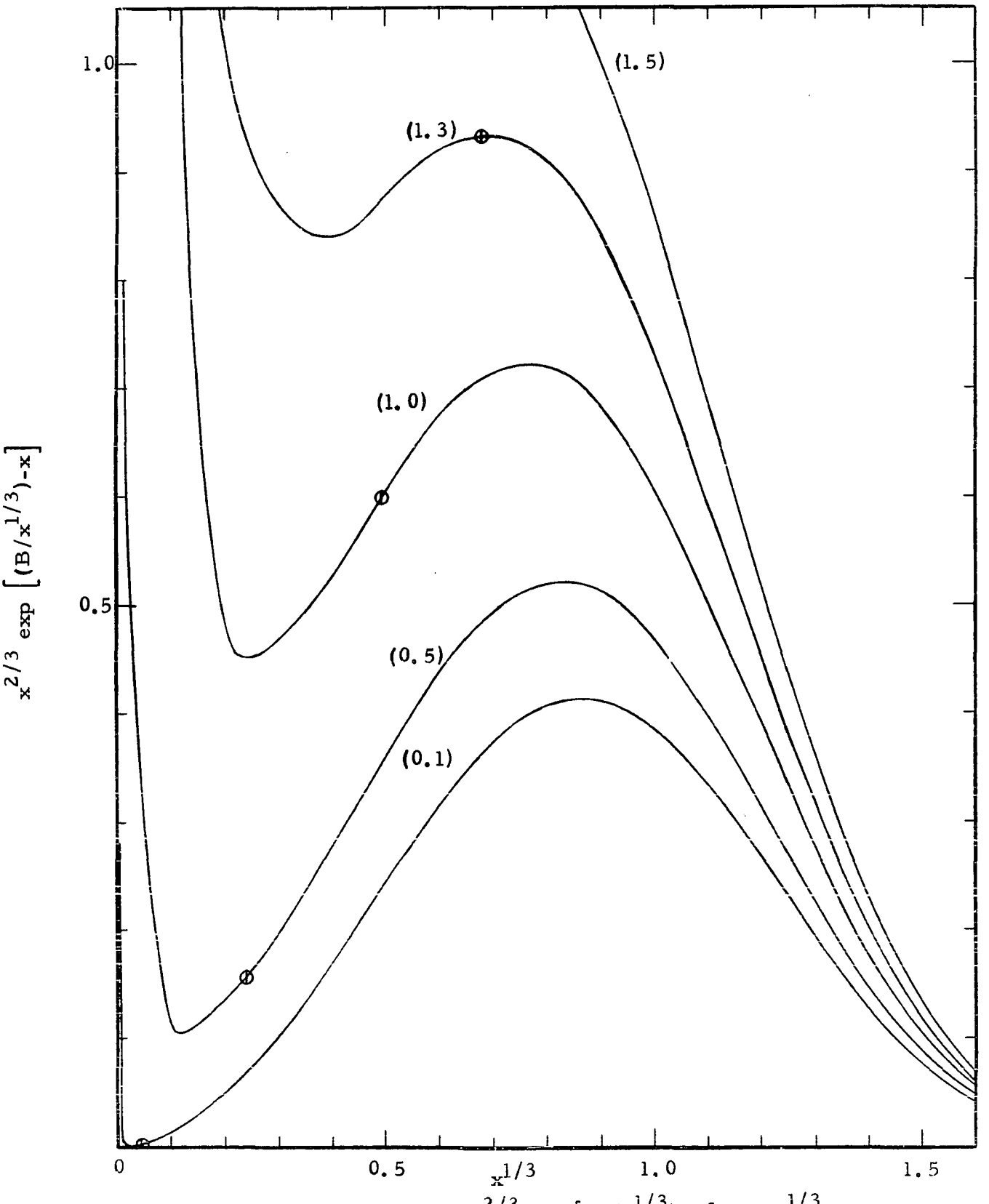


Figure 2. Family of Curves, $x^{2/3} \exp\left[(B/x^{1/3})-x\right]$ vs. $x^{1/3}$ for Various Values of the Concentration ($M^{1/3}$), a = 3.5Å. ⊘: the lower limit of the function for the particular a value and concentration.

values and, at sufficiently low a values, moves below the minimum into the region where the value of the function is rapidly increasing. Therefore, an electrolyte requiring a low a value for a fit of the calculated behavior to solution data, would be an electrolyte which has been termed classically as intermediate or weak, depending on the a value required. The increased area at low $x^{1/3}$ values for such types would correspond to an increased probability of the existence of ion-pairs in the sense of incomplete dissociation. All electrolyte types could be incorporated into the proposed approach; however, the ion size parameter would be related to actual ion, or solvated ion, radii only in the case of strong electrolytes where pair members are clearly separated. There is a smooth transition from "strong" to "weak" electrolytes.

The limiting behavior of Equation 23 can be determined by expanding the first exponential

$$\zeta = (\bar{v}^f)^2 e^{\Phi} \int_{\Phi}^{\infty} \left[1 + (B/x^{1/3}) + (B^2/2x^{2/3}) + \cdots\right] e^{-x} dx \qquad (25)$$

which gives, considering each term as $\Phi \to 0$,

$$\zeta/(\bar{v}^f)^2 = 1 + B\Gamma(2/3) + B^2\Gamma(1/3)/2 + \cdots \qquad (26)$$

where the second and third terms on the right are given by the appropriate gamma function.

The unit configuration integral for a 2-1 electrolyte, Equation 12, is transformed using the dimensionless variables

$$y = v_1/\bar{v}_1^f \qquad (27)$$

$$\Phi_1 = b/\bar{v}_1^f \tag{28}$$

$$B_1 = z_1 z_2 e^2 \Phi_1^{1/3}/DkTa \tag{29}$$

$$z = v_2/\bar{v}_2^f \tag{30}$$

$$\Phi_2 = b_2/\bar{v}_2^f \tag{31}$$

$$B_2 = z_{12} z_2 e^2 \Phi_2^{1/3}/DkTr_1 \tag{32}$$

where z_1 is the charge on the central ion, z_2 is the charge of a counter ion and z_{12} is the charge of the virtual central ion. These variables give

$$\zeta_{12} = \bar{v}^f \bar{v}_1^f e^{\Phi_1}\left[\int_{\Phi_1}^{\infty} \exp\left[(B_1/y^{1/3}) - y\right]dy\left(\bar{v}_2^f e^{\Phi_2}\int_{\Phi_2}^{\infty} \exp\left[(B_2/z^{1/3}) - z\right]dz\right)\right] \tag{33}$$

The limiting form of Equation 33 is obtained by expanding the first exponential term in each integrand to yield, as $M \to 0$,

$$\frac{\zeta_{12}}{\bar{v}^f \bar{v}_1^f \bar{v}_2^f} = \left[1 + B_1\Gamma(2/3) + \frac{B_1^2}{2}\Gamma(1/3) + \ldots\right] \times$$

$$\left[1 + B_2\int_A^{\infty} \frac{e^{-z}dz}{z^{1/3}} + \frac{B_2^2}{2}\int_A^{\infty} \frac{e^{-z}dz}{z^{2/3}} + \ldots\right] \tag{34}$$

with

$$A = a/(1 - a) \tag{35}$$

The limiting behavior for a 2-1 electrolyte is a function of the fraction

of the average volume available per unit which is occupied, on the average, by an inner ion pair. The integrals appearing in the second term of Equation 34 have been evaluated using a computer program given in the Appendix.

The unit configuration integrals, Equations 24 and 33, are evaluated by numerical integration using a high-speed computer. Equation 33 is transformed into a function of $y^{1/3}$ and $z^{1/3}$ for the numerical integration. Because of the infinite upper limits, the integrations are performed over subintervals (using Simpson's method) to a preselected level of precision. The complete computer programs are listed in the Appendix.

CHAPTER III

COMPARISON OF THEORY AND EXPERIMENT

Activity Coefficients

The Helmholtz free energy is given by the statistical thermodynamic expression

$$A = - RT \ln Q \tag{36}$$

In the later development by Murphy and Weissenbock (28) using the constant pressure ensemble, the partition function is related directly to the Gibbs free energy. For a non-ideal solution, the chemical potential of the solute is

$$\mu = \mu^{o} + RT \ln a_s \tag{37}$$

where μ^{o} is the chemical potential of the standard state and a_s the activity of the solute. Utilizing the good approximation that the Gibb's free energy can be replaced by the Helmholtz free energy for a solution, Equations 36 and 37 yield

$$- RT \ln (q/N) = \mu^{o} + \nu RT \ln a_{\pm}$$

where $a_{\pm}$ is the mean ionic activity of the solute ($a_s = a_{\pm}^{\nu}$). Assuming that the non-ideality displayed by an electrolyte solution arises solely from the coulomb interaction between pair members comprising a

formula unit, and including all concentration independent terms in μ^{o}, gives

$$1/y_{\pm}^{\nu} = (\zeta_{\pm}/\bar{v}_{\pm})^{\nu} \tag{38}$$

where

$$\zeta_{\pm}^{\nu} = \Lambda^{3\nu} \ (q/N) \tag{39}$$

$$a_{\pm} = M_{\pm} y_{\pm} \tag{40}$$

$$\bar{v}_{\pm} = 1/M_{\pm} = 1/WM = \bar{v}/W \tag{41}$$

$$W = (\nu_{+}^{\nu} + \nu_{-}^{\nu})^{1/\nu} \tag{42}$$

Using these relations with Equation 23, the activity coefficient for symmetrical electrolytes is given by

$$1/y_{\pm}^{2} = (1 + \Phi)^{-2} e^{\Phi_I} \tag{43}$$

Combination of the limiting expression for the pair configuration integral for symmetrical electrolytes (Equation 26) with Equation 43, gives the limiting relation for the activity coefficient:

$$\ln y_{\pm} = -0.6771 \frac{z^2e^2}{DkT} \left[\frac{4\pi NM}{3000}\right]^{1/3} - 0.6697 \left(\frac{z^2e^2}{DkT} \left[\frac{4\pi NM}{3000}\right]^{1/3}\right)^{2} - \ldots \tag{44}$$

The low concentration limiting slope depends only on the valence of the ions and, considering only the leading term, the cube root of the concentration. In the limit, there is no dependence on specific characteristics such as ion size. Conversion to common logarithms (considering the leading term only) yields, for the limiting slope of 1-1 electrolytes:

$$\log y_{\pm} = -0.286\, M^{1/3} \qquad (45)$$

The effect of varying a on log $y_{\pm}$ (for 1-1 electrolytes), as calculated using Equation 43, is depicted in Figure 3. The limiting line shows that electrolytes displaying an apparent negative deviation from the limiting slope at low concentrations could be reproduced using appropriate a values. The a values giving the best reproduction of experimental data for KCl (30, 31), NaCl (32, 33) and HCL (34) are shown in Figure 4. In all three cases the experimental data are predicted to high concentrations for reasonable values of a, and the theoretical limiting slope is consistent with the data at low concentrations. Although the expression for the limiting slope for 1-1 electrolytes (Equation 45) contains only the leading term, it describes these experimental data to relatively high concentrations. Theoretical curves are fit to activity coefficient data for HI (35), HBr and HNO_3 (36) in Figure 5; again, the experimental data are described, at least to the region of the minimum, using reasonable a values, as compared with the HCl results depicted in Figure 4. Tabulated data at round concentrations for LiCl, RbCl and CsCl (36), and low concentration data for CsCl (37), are fit with theoretical curves in Figure 6. For the rubidium and cesium chlorides, the a values required for a calculated fit are in the reverse order expected from their crystallographic radii. In addition, these are the only cases encountered where the theoretical curve appropriate for the low concentration data goes below the experimental data at the higher concentrations.

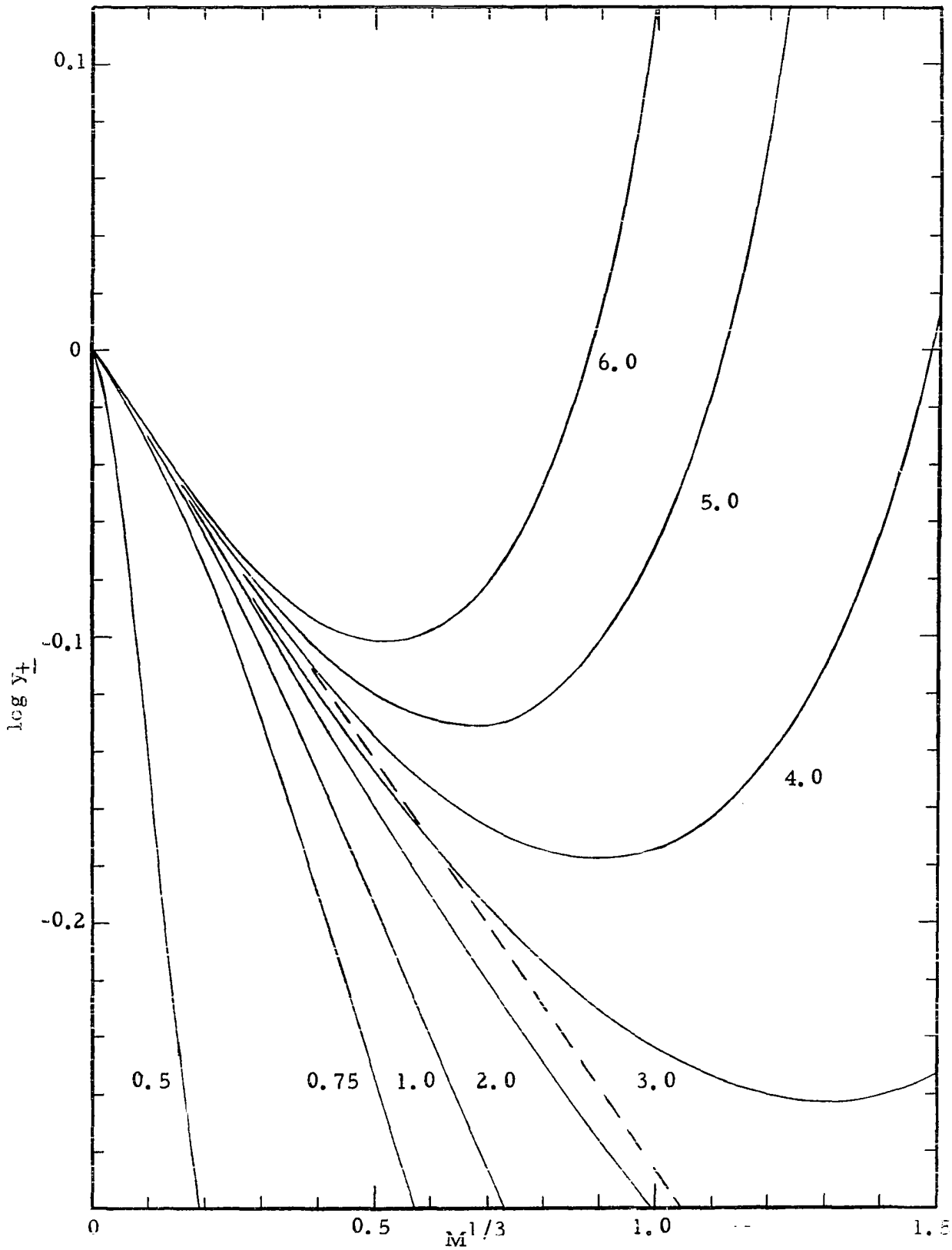


Figure 3. Theoretical Behavior of log $y_{\pm}$ for Various Values of the Ion Size Parameter (in angstroms), 1-1 Electrolytes, 25°. - - -: theoretical limiting behavior.

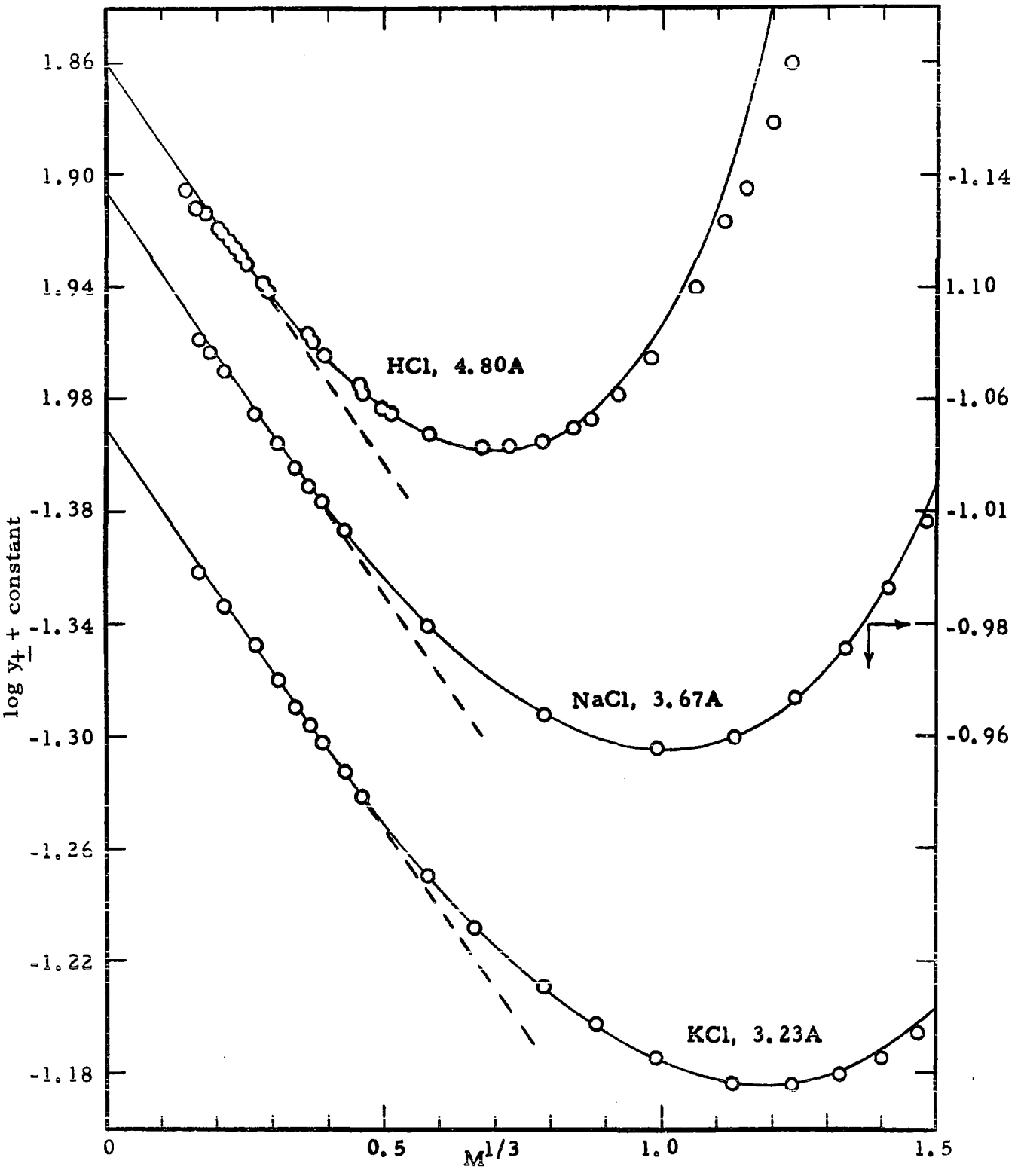


Figure 4. Activity Coefficient Data for Three 1-1 Chlorides Compared with Best-Fit Theoretical Curves, 25°. - - -: theoretical limiting behavior.

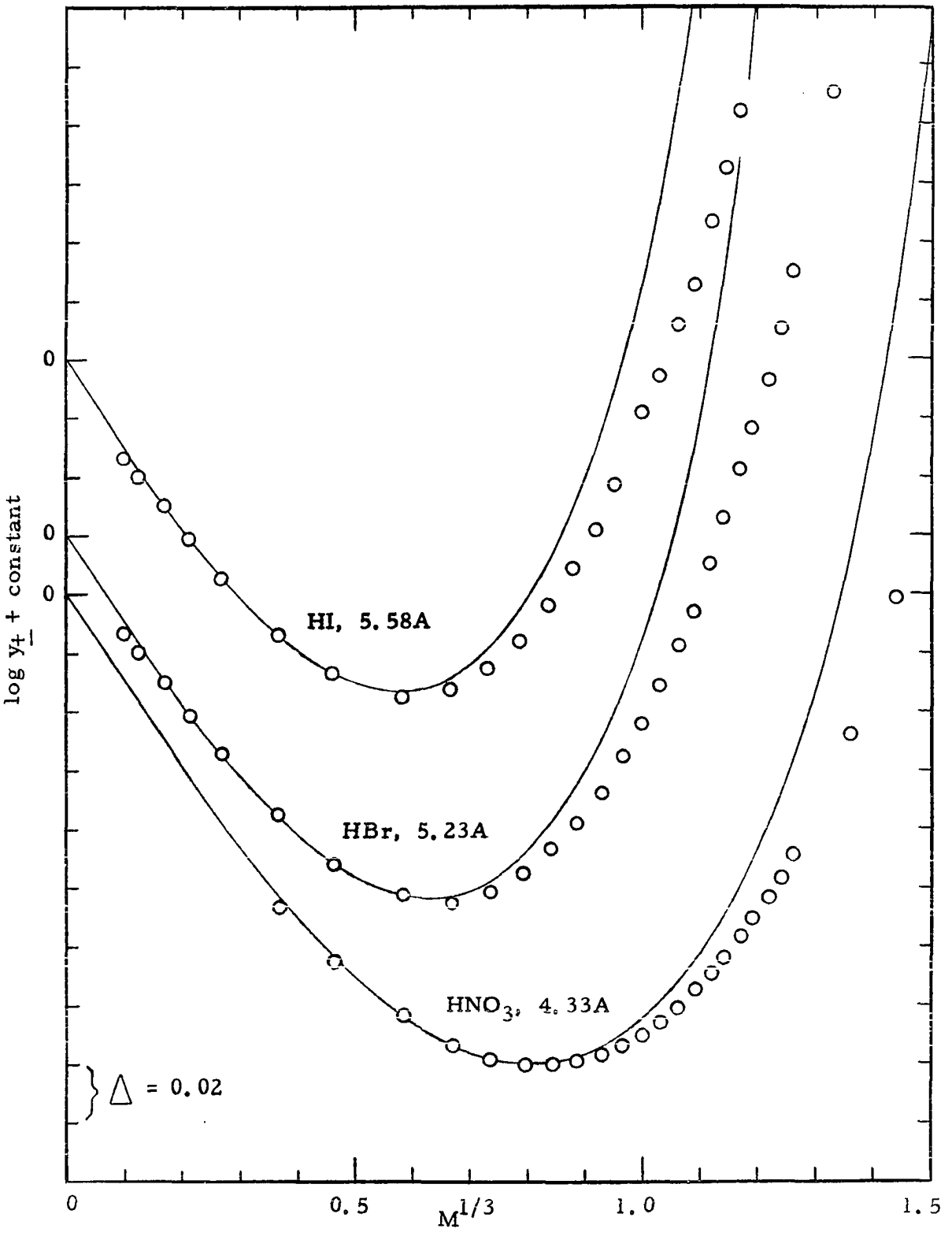


Figure 5. Activity Coefficient Data for Three Strong Acids Compared with Best-Fit Theoretical Curves, 25°.

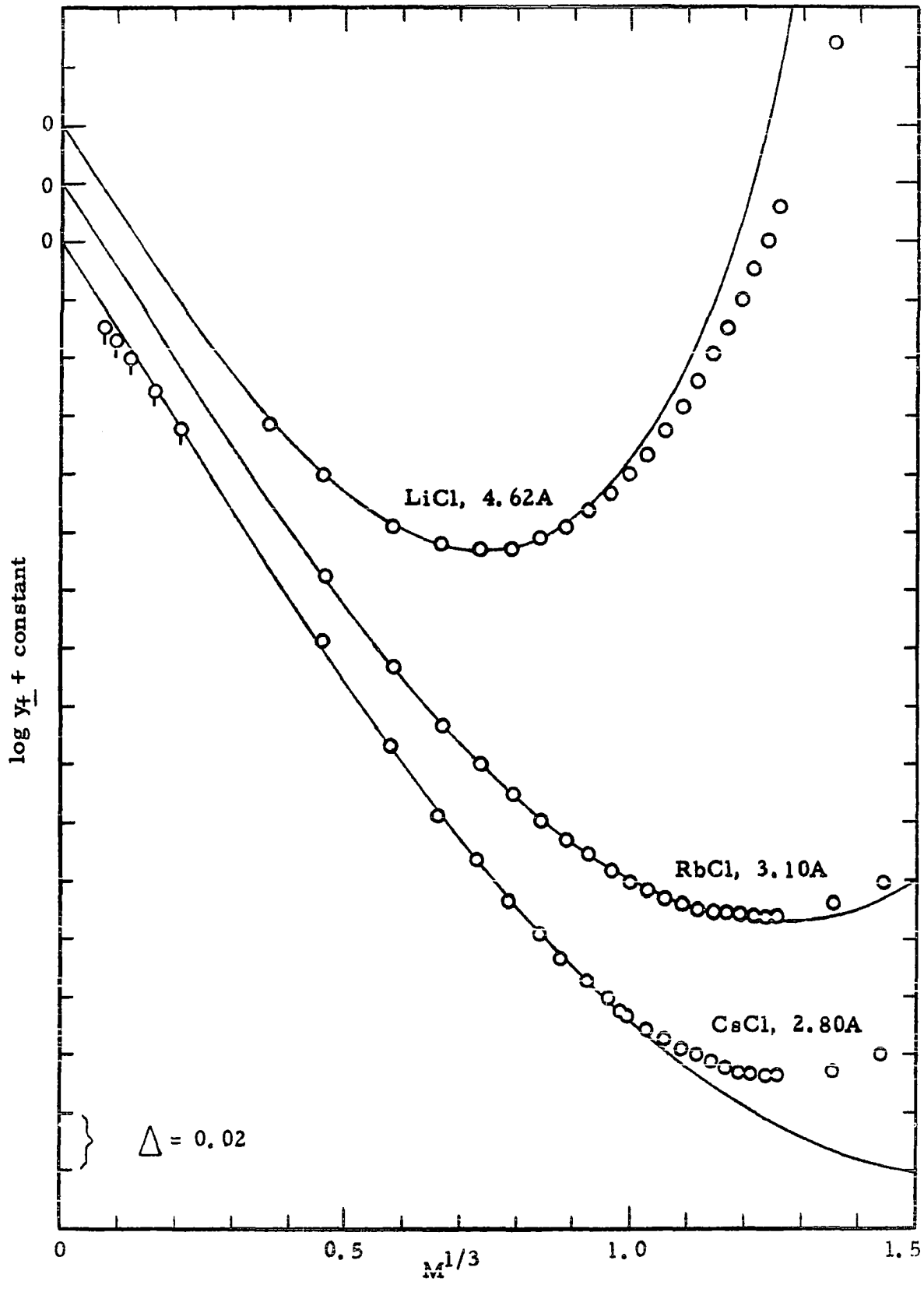


Figure 6. Activity Coefficient Data for Three Alkali Metal Chlorides Compared with Best-Fit Theoretical Curves, 25°.
♀: Diffusion data from Harned and Owen (37).

These observations are more fully discussed in the following chapter, but are consistent with the order obtained using extended forms of the Debye-Hückel theory (4). Experimental data at round concentrations for NaF and NaBr (36) and NaI (38) are compared with the best fit theoretical curves in Figure 7. The a values obtained for the sodium halides are in the order to be expected from the crystallographic radii. Similarly compiled data for $NaNO_3$ and NH_4Cl (36) and NaOH (39) are shown in Figure 8. As in previous cases, the experimental activity coefficient data are fit to relatively high concentrations. The isopiestic data of Bower and Robinson (40) and Lindenbaum and Boyd (41) for tetraethylammonium iodide have been converted to the molar scale using the density data tabulated in Conway (39), and are shown with the best fit theoretical curve in Figure 9. The very low activity coefficients displayed by this salt can be well represented by the present approach, but a very low a value is required.

Solutions of 2-2 electrolytes are described by the equations utilized for the 1-1 case with the appropriate change of the valency terms. The behavior of log $y_{\pm}$ vs $M^{1/3}$ for a series of a values is shown in Figure 10; included is the limiting behavior considering only the $M^{1/3}$ term. For this higher charge type of symmetrical electrolyte, terms of higher order than the cube root play a significant role at very low concentrations. Tabulated experimental data for $ZnSO_4$ (38, 42) are compared with the best fit theoretical curve and the limiting line

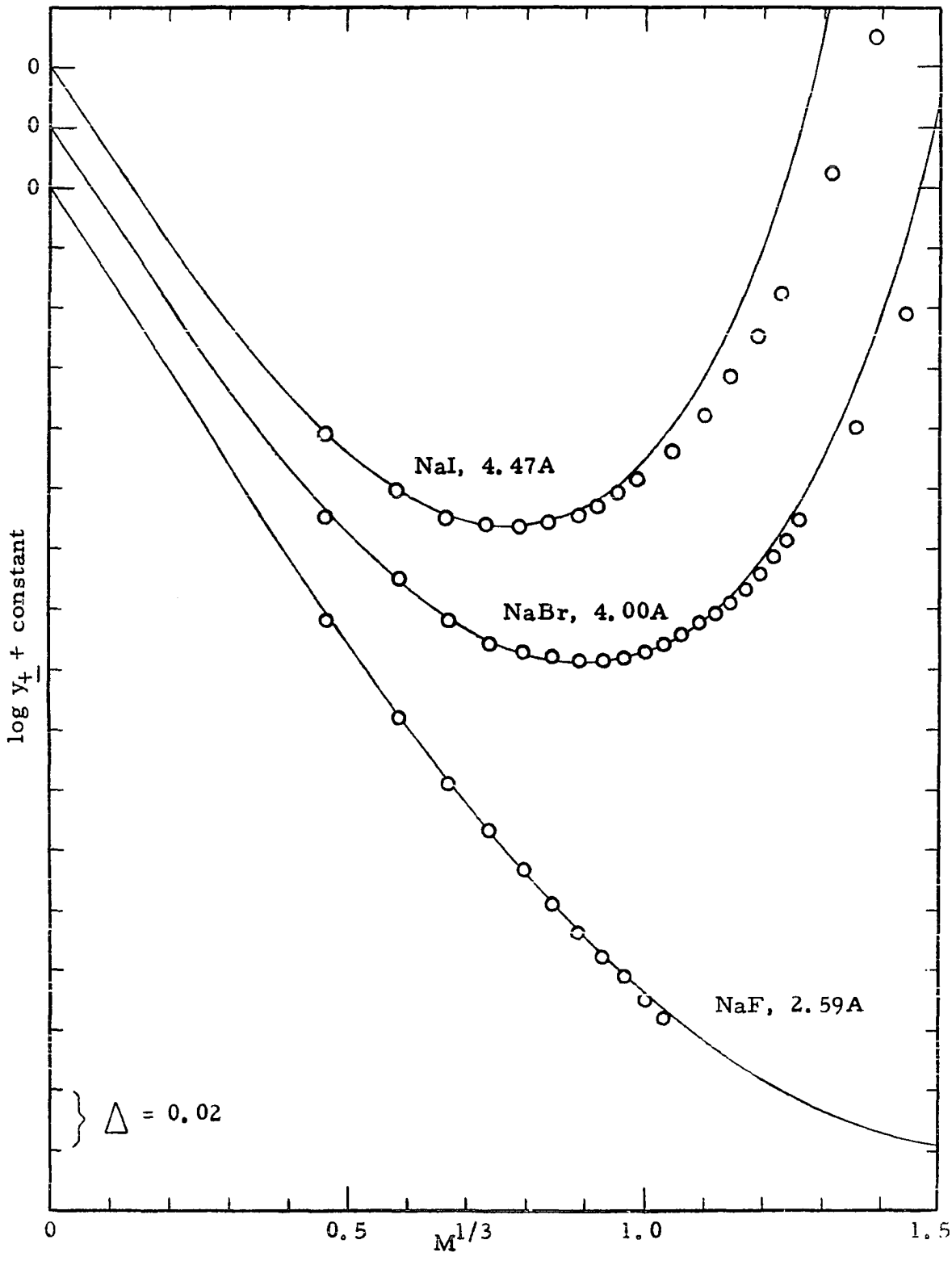


Figure 7. Activity Coefficient Data for Several Sodium Halides Compared with Best-Fit Theoretical Curves, 25°

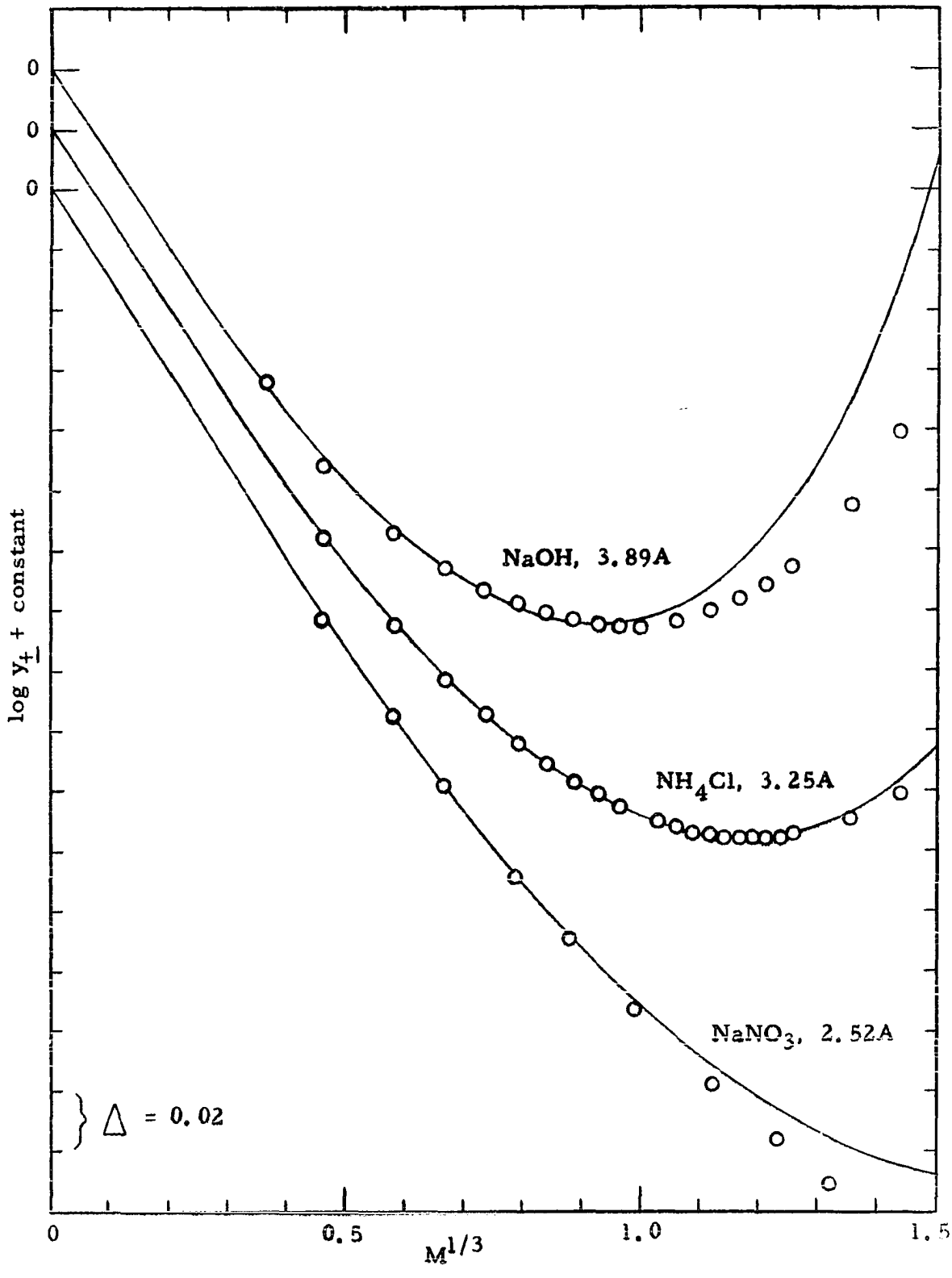


Figure 8. Activity Coefficient Data for Three 1-1 Electrolytes Compared with Best-Fit Theoretical Curves, 25°.

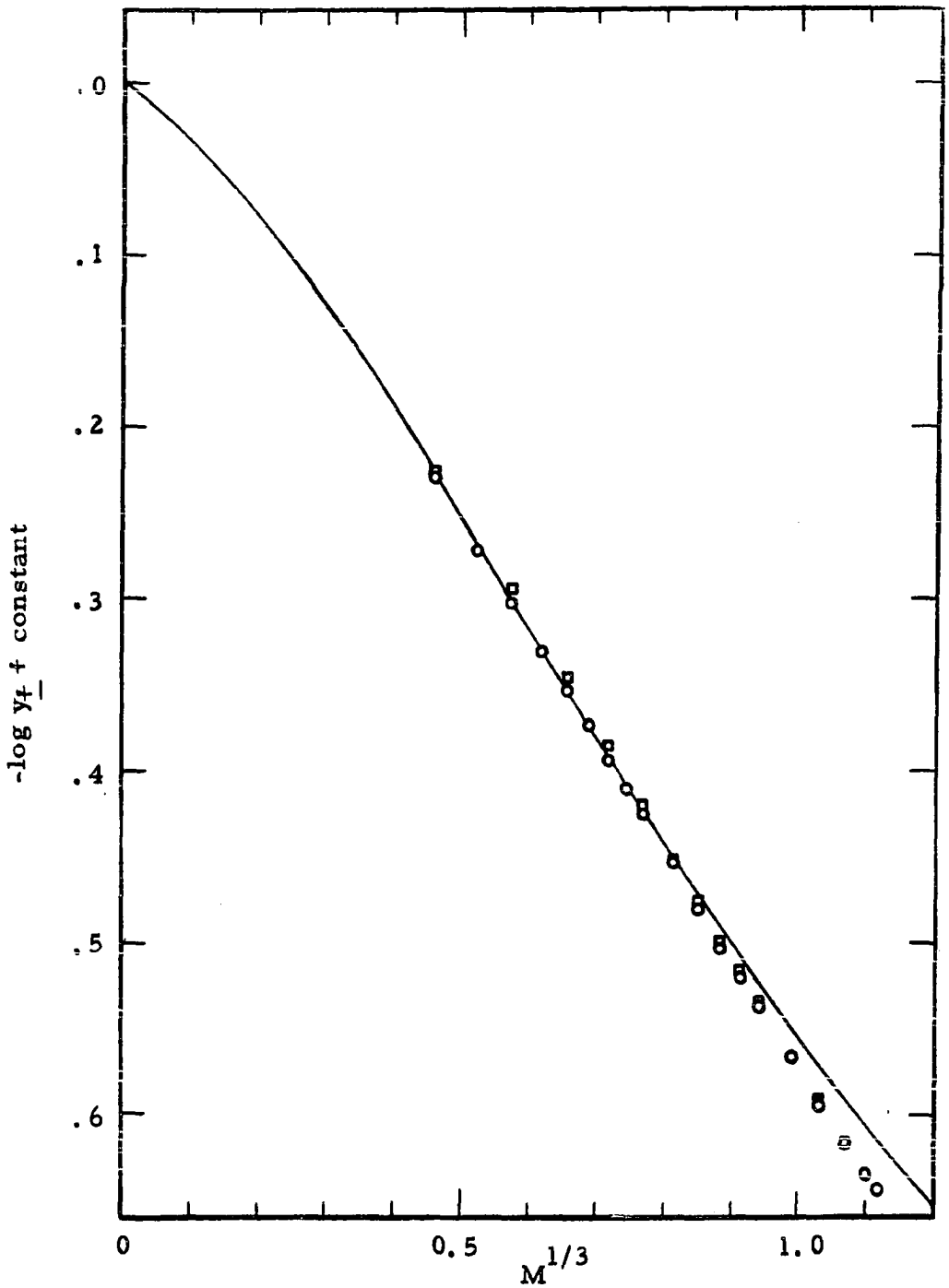


Figure 9. Activity Coefficient Data for Tetraethylammonium Iodide Compared with Best-Fit Theoretical Curve, 25°. O: data of Lindenbaum and Boyd (41); □: data of Bower and Robinson (40). a = 0.75A.

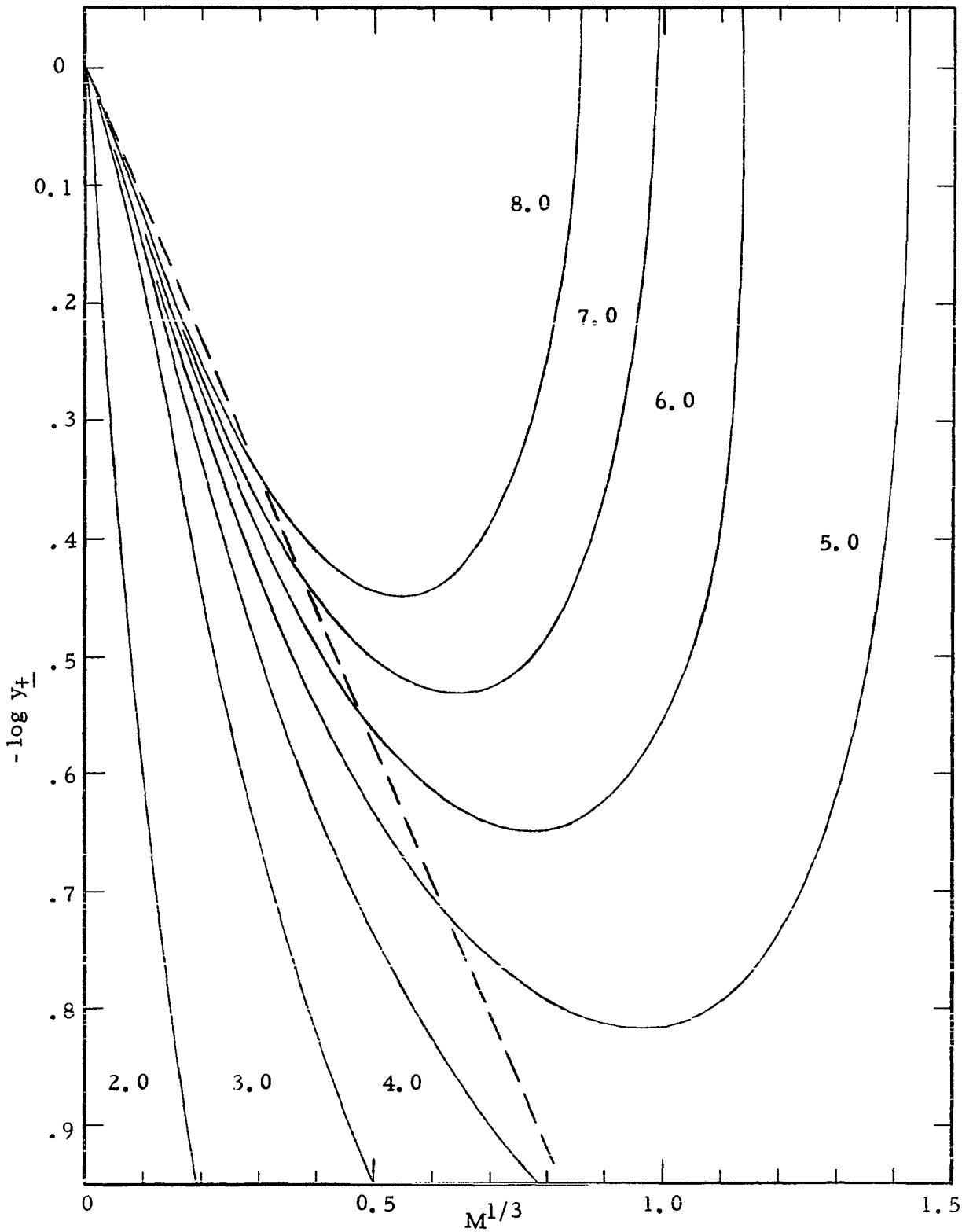


Figure 10. Theoretical Behavior of log $y_{\pm}$ for Various Values of the Ion Size Parameter (in angstroms), 2-2 Electrolytes, 25°. - - -: theoretical limiting behavior.

(considering only the $M^{1/3}$ term) for 2-2 electrolytes in Figure 11. The low concentration data fall on the theoretical curve corresponding to a reasonable a value. Deviation of the data from the theoretical curve at relatively low concentrations is not surprising because of the tendency of this salt to hydrolyze (43). The simple $M^{1/3}$ limiting line would reproduce experimental data only at vanishingly small concentrations. In the past few years a class of apparently well-behaved 2-2 electrolytes, the salts of benezenedisulfonic acids, has been investigated and the isopiestic data of Brubaker and Rasmussen (44) for the Mn(II), Cu(II) and Zn(II) salts are compared with theoretical curves in Figure 12. Unfortunately, no density data for these solutions could be found, so the molal activity coefficients reported by these workers have been corrected only by the solvent density for these plots. However, the low concentration data would be little affected by this correction error, and, as can be seen in Figure 12, these points are well reproduced by the theoretical curves. Once density data for these solutions become available, the a values required for the best fits over a wider concentration range can be determined.

For a 2-1 electrolyte, the mean ionic activity coefficient is given by

$$\left(\frac{1}{y_{\pm}}\right)^3 = \left(\frac{\zeta_{\pm}}{\bar{v}_{\pm}}\right)^3 = \left\{ \bar{v}\, \frac{f}{v_1}\, e^{\bar{\Phi}_1} \int_{\bar{\Phi}}^{\infty} \exp\left[\frac{B_1}{y^{1/3}} - y\right] dy \left(\frac{\bar{v}_2^f}{} e^{\bar{\Phi}_2} \int_{\bar{\Phi}_2}^{\infty} \exp\left[\frac{B_2}{z^{1/3}} - z\right] dz \right) \right\} \left(\frac{W}{\bar{v}}\right)^3 \quad (46)$$

utilizing Equation 33 and the relations given at the beginning of this

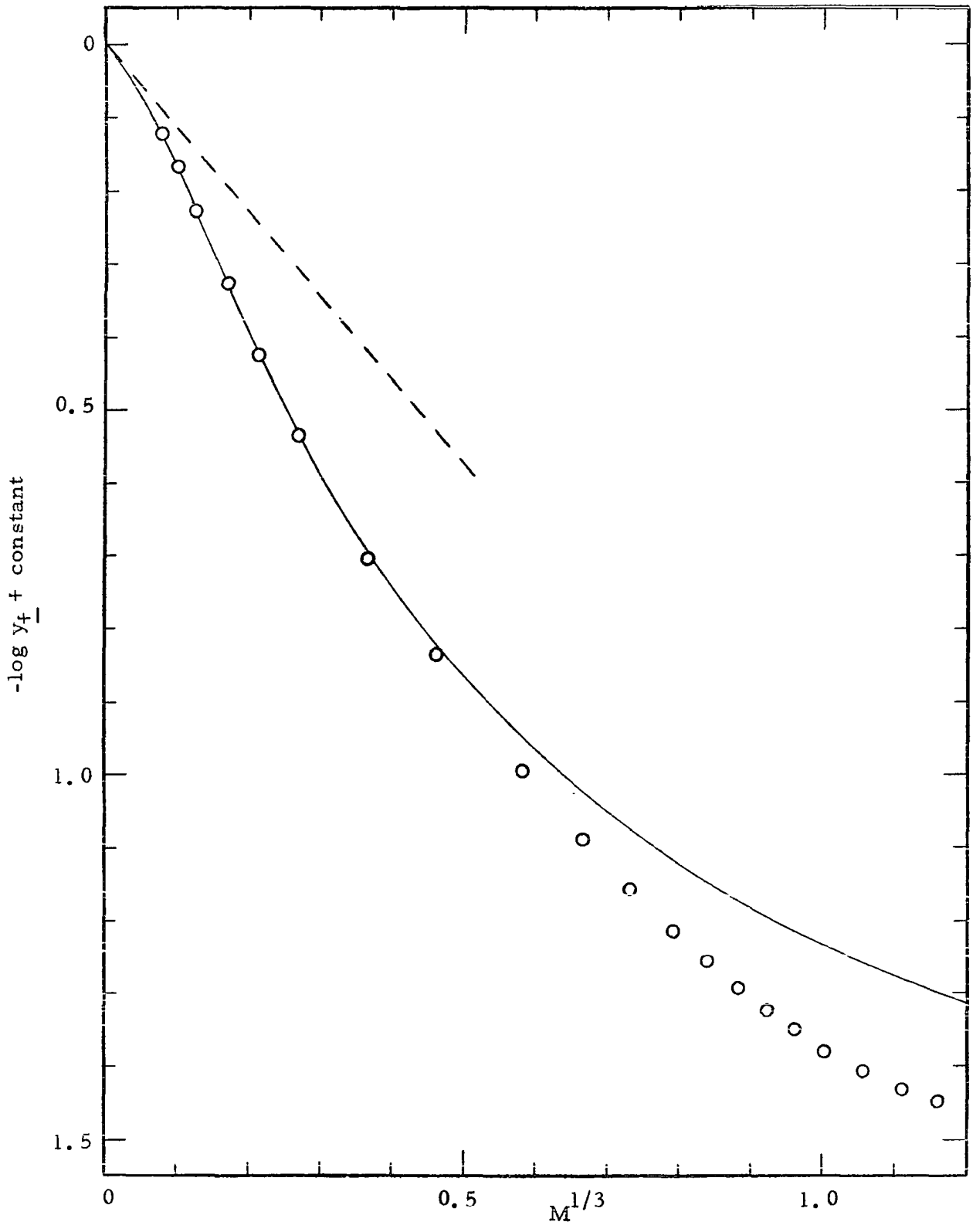


Figure 11. Activity Coefficient Data for Zinc Sulfate Compared with Best-Fit Theoretical Curve, 25°. - - -: theoretical limiting behavior. a = 3.30A.

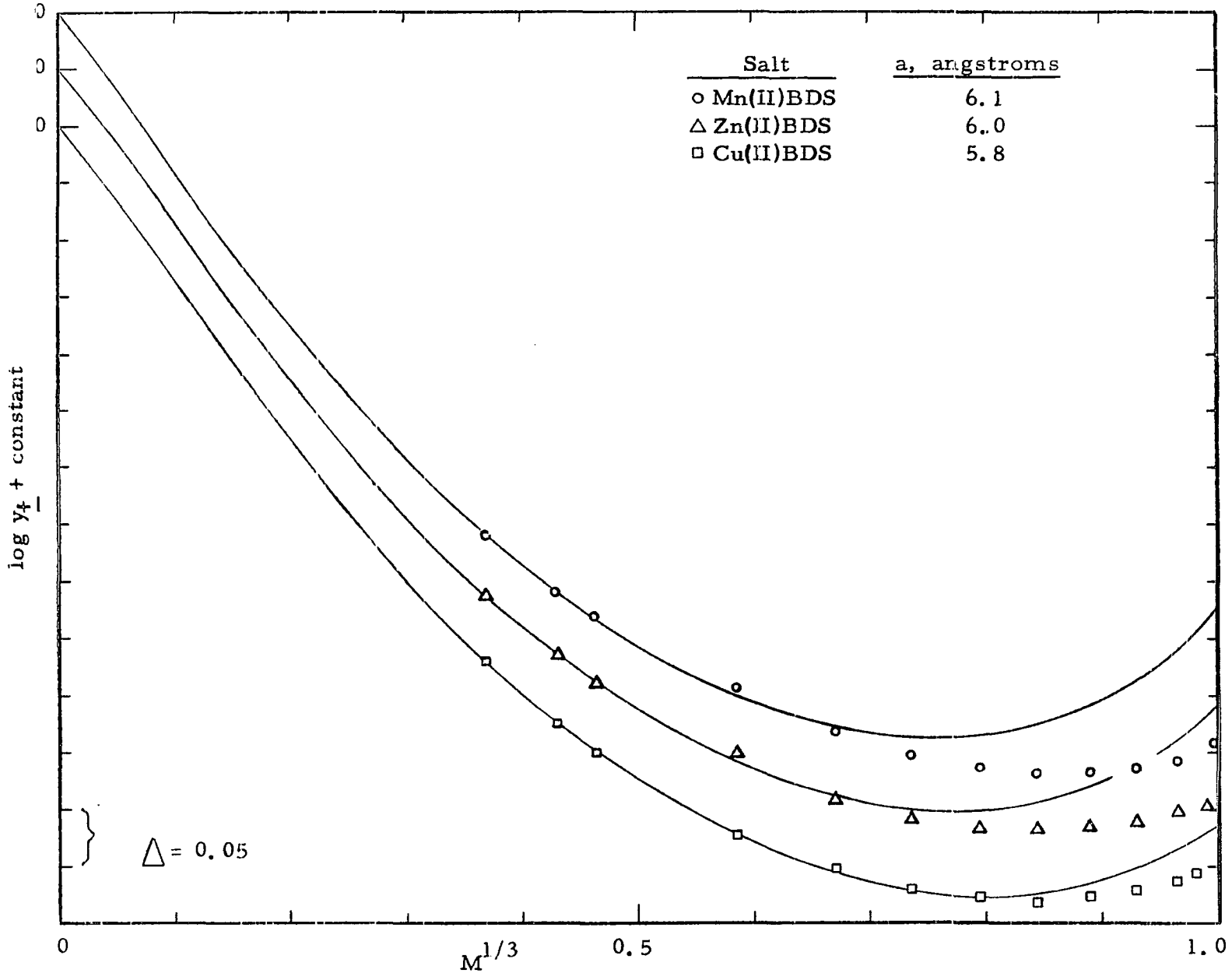


Figure 12. Activity Coefficient Data of Brubaker and Rasmussen (44) for Several m-Benzene Disulfonates (BDS) Compared with Theoretical Curves, 25°.

section. The limiting relation for the activity coefficient of a 2-1 electrolyte is obtained using the limiting expression (Equation 34) for the complete integral in Equation 46. Considering the cube root terms only, and normalizing so that the activity coefficient equals unity at infinite dilution, gives

$$\ln y_{\pm} = - \frac{0.4514\, z_1 z_2 e^2}{DkTa^{1/3}} \left[\frac{4\pi NM}{3000}\right]^{1/3} - \frac{0.3333\, z_{12} z_2 e^2}{DkT(1 - a)^{1/3}} \int_A^{\infty} \frac{e^A e^{-z} dz}{z^{1/3}} \qquad (47)$$

Because a is used as a fitting parameter in the present development, the limiting slopes of log $y_{\pm}$ for various a values are given in Table I. The

TABLE I

THEORETICAL LIMITING VALUES FOR 2-1 ELECTROLYTES AS A FUNCTION OF a

a	$\frac{-d \log y_{\pm}}{dM^{1/3}}$	$\frac{K \times 10^{-7},\ cm^{-1}}{M^{1/3}}$
0.2	0.810	3.919
.3	.722	3.495
.33	.703	3.403
.35	.691	3.347
.4	.665	3.217
.5	.626	3.032

integral appearing in the second term of Equation 47 is evaluated by expansion of the exponential and term-by-term integration. The program employed for this integration is given in the Appendix.

The behavior of Equation 46 for a series of a values, at a specific value of α, is shown in Figure 13; for a series of α values at a constant a value in Figure 14. The best fit theoretical curve for $CaCl_2$ experimental data (32, 45) is shown in Figure 15. There is a unique pair of a and α values (a = 4.85A, α = 0.33) which reproduces the experimental activity coefficient data through the observed minimum. The experimental data diverge from the theoretical limiting line (corresponding to the best-fit value of α) at the lowest concentrations for which activity coefficient data are available. This divergence shows that terms of higher order than $M^{1/3}$ and specific characteristics of the electrolyte become significant at much lower concentrations than is the case for 1-1 electrolytes.

Tabulated data for other alkaline earth chlorides have been examined, but the experimental data for $MgCl_2$ and $SrCl_2$ do not extend to sufficiently low concentrations to be considered. The tabulated data for $BaCl_2$ (36) are compared with the best-fit theoretical curve in Figure 16. The α and a values required to best reproduce these data are 0.27 and 4.26A, respectively. As was the case with the alkali metal chlorides, the a values obtained for these two alkaline earth chlorides are in the opposite order of the sum of their univalent radii. The scarcity of low concentration activity coefficient data for most of the alkaline earth salts (with univalent anions) makes it impossible to complete any sort of extensive comparison of theoretical predictions with experimental

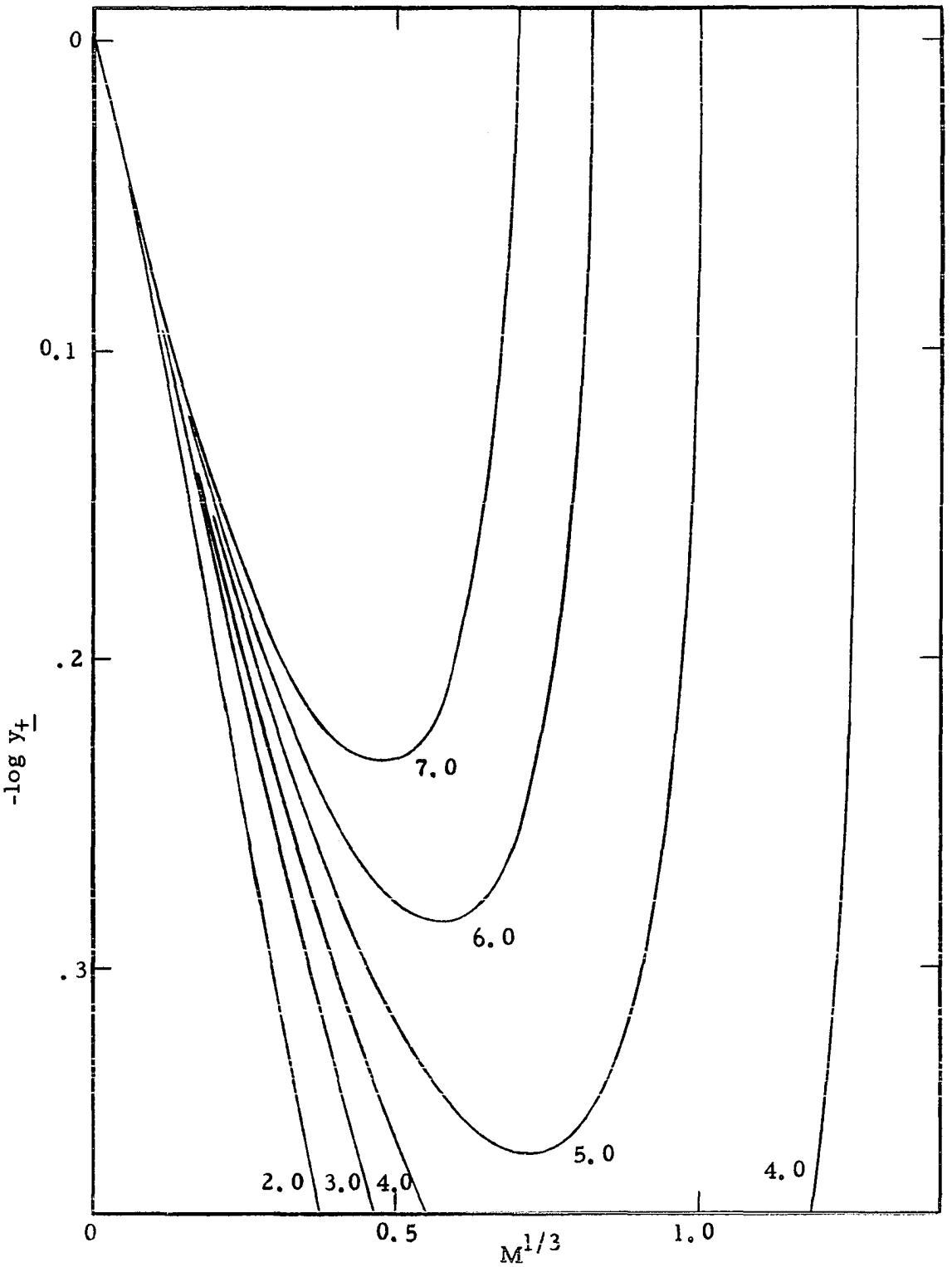


Figure 13. Theoretical Behavior of log $y_{\pm}$ for Various Values of the Ion Size Parameter (in angstroms), a = 0.33, 2-1 Electrolytes, 25°

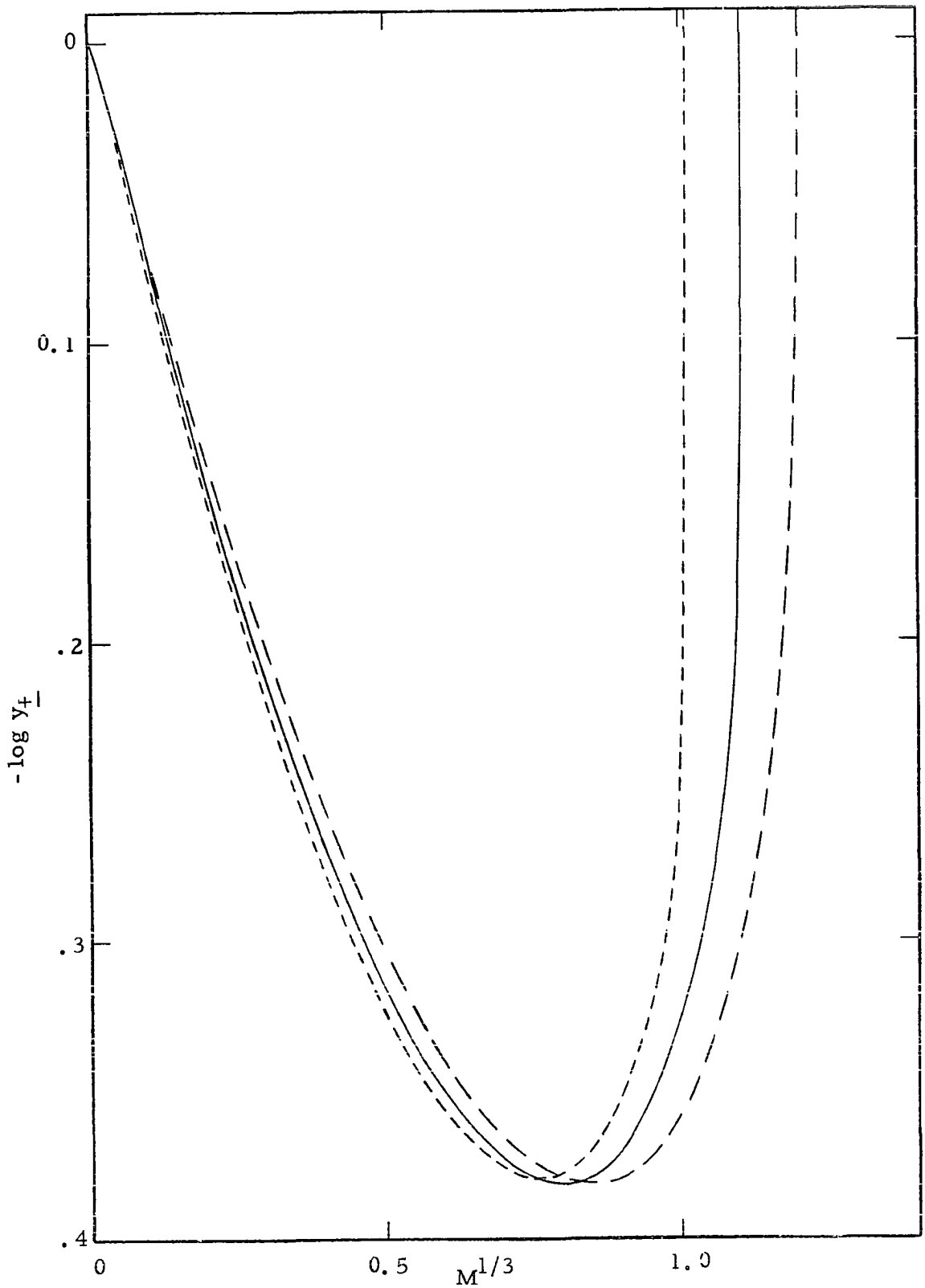


Figure 14. Theoretical Behavior of log $y_{\pm}$ for Various Values of a, a = 4.80A, 2-1 Electrolytes, 25°. - - -: a = 0.33; ——: a = 0.40; — — —: a = 0.50.

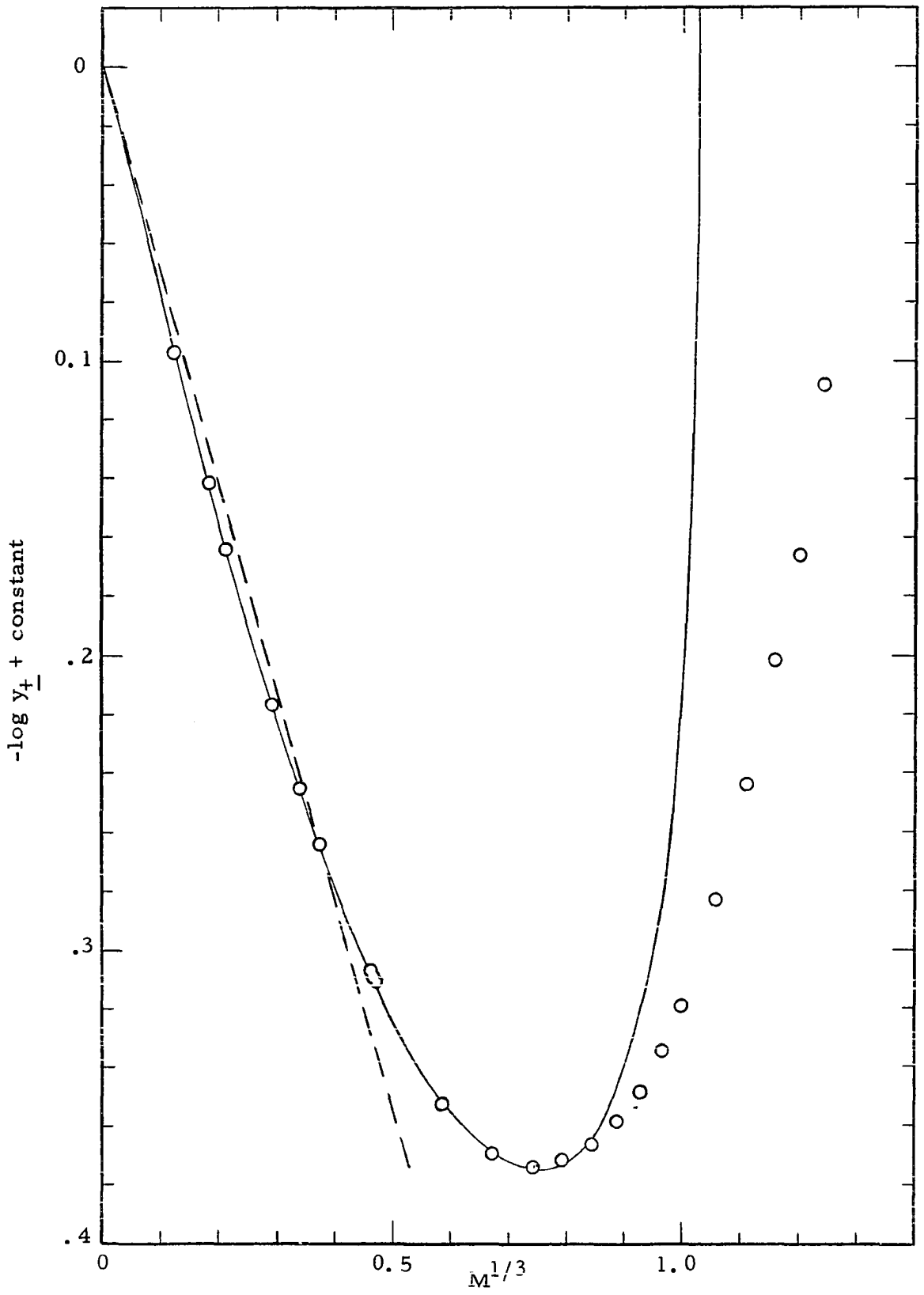


Figure 15. Activity Coefficient Data for Calcium Chloride Compared with Best-Fit Theoretical Curve (a = 4.85A, α = 0.33), 25°. - - -: theoretical limiting behavior, α = 0.33.

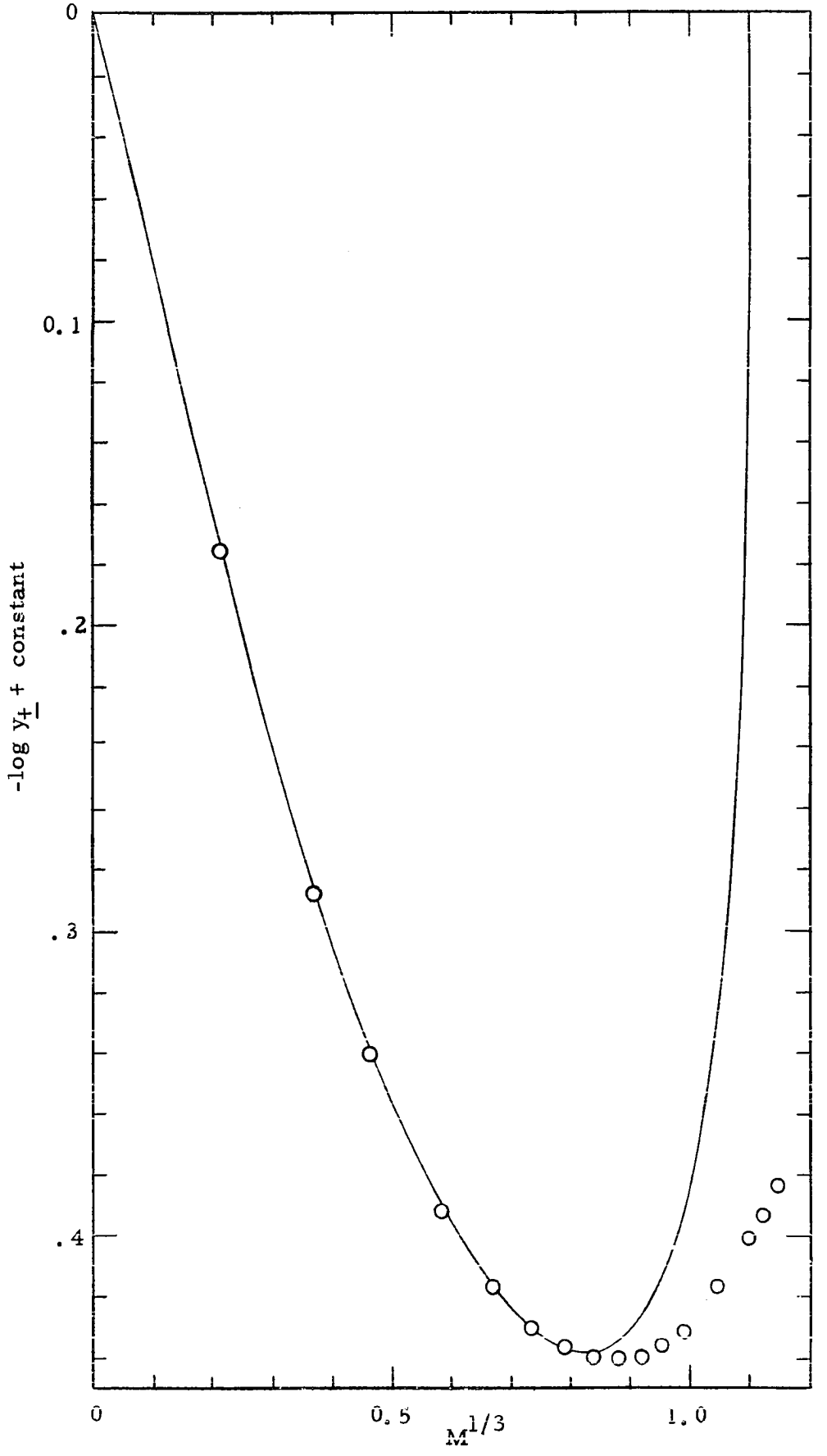


Figure 16. Activity Coefficient Data for Barium Chloride Compared with Best-Fit Theoretical Curve (a = 4.26A, α = 0.27), 25°.

data.

The calculated activity coefficient data for the various electrolytes which have been examined are tabulated in round values of the cube root of concentration (mole/liter) in the Appendix.

Conductance

In the limiting case, the average radius of the volume occupied by a unit can be calculated by equating the limiting expression for the activity coefficient to the coulombic energy. The average reciprocal radius (κ) can be determined from

$$\nu kT \ln y_{\pm} = - |z_1 z_2| e^2 \kappa / D \tag{48}$$

using the appropriate limiting expression for $\ln y_{\pm}$. The κ obtained in this manner can be related to the corresponding average reciprocal radius of the ion atmosphere (κ^*) arising from the Debye-Hückel treatment. Having determined this relationship, the Onsager equation for limiting conductance can be used to compare theoretical limiting lines from the present treatment with experimental conductance data.

The limiting expression for the rational activity coefficient, as given by the Debye-Hückel approach, is

$$\ln f_{\pm} = \frac{-|z_1 z_2| e^2}{2DkT} \frac{\kappa^*}{1 + \kappa^* a} \tag{49}$$

At low concentrations $y_{\pm} = f_{\pm}$ and $\kappa^* a \ll 1$, therefore, comparison of Equations 48 and 49 yields

$$\kappa^* / \kappa = 2/\nu \tag{50}$$

Using reliable values for the dielectric constant (46) and viscosity (47) of water at 25°C, the Onsager equation for limiting conductance becomes

$$\Lambda = \Lambda^{o} - \{7.1356 \times 10^{-8} |z_1 z_2| [q/(1 + q^{1/2})] \Lambda^{o}$$

$$+ 2.7634 \times 10^{-6} (|z_1| + |z_2|)\} K^{*}/3 \qquad (51)$$

where

$$q = \frac{|z_1 z_2|}{(|z_1| + |z_2|)(|z_2| t_1^{o} + |z_1| t_2^{o})}$$

and t_1^{o} and t_2^{o} are the limiting transference numbers of the respective ions. In the case of symmetrical electrolytes $q/(1 + q^{1/2}) = 0.2929$. For 1-1 electrolytes, Equation 51 becomes

$$\Lambda = \Lambda^{o} - (2.0900 \times 10^{-8} \Lambda^{o} + 5.5268 \times 10^{-6}) K^{*}/3 \qquad (52)$$

Using Equations 45 and 48, the value of K for 1-1 electrolytes is given by

$$K_{1-1}\,cm^{-1} = 1.8435 \times 10^{7}\, M^{1/3} \qquad (53)$$

The limiting conductance, as obtained from the Onsager equation using K as calculated from the present approach, is compared with experimental data for HCl (48) in Figure 17; the relation giving the best fit to the experimental data is

$$\Lambda_{HCl} = 431.0 - 89.3\, M^{1/3} \qquad (54)$$

Included in Figure 17 is the limiting conductance curve obtained using the Debye-Hückel treatment. The present approach gives the better

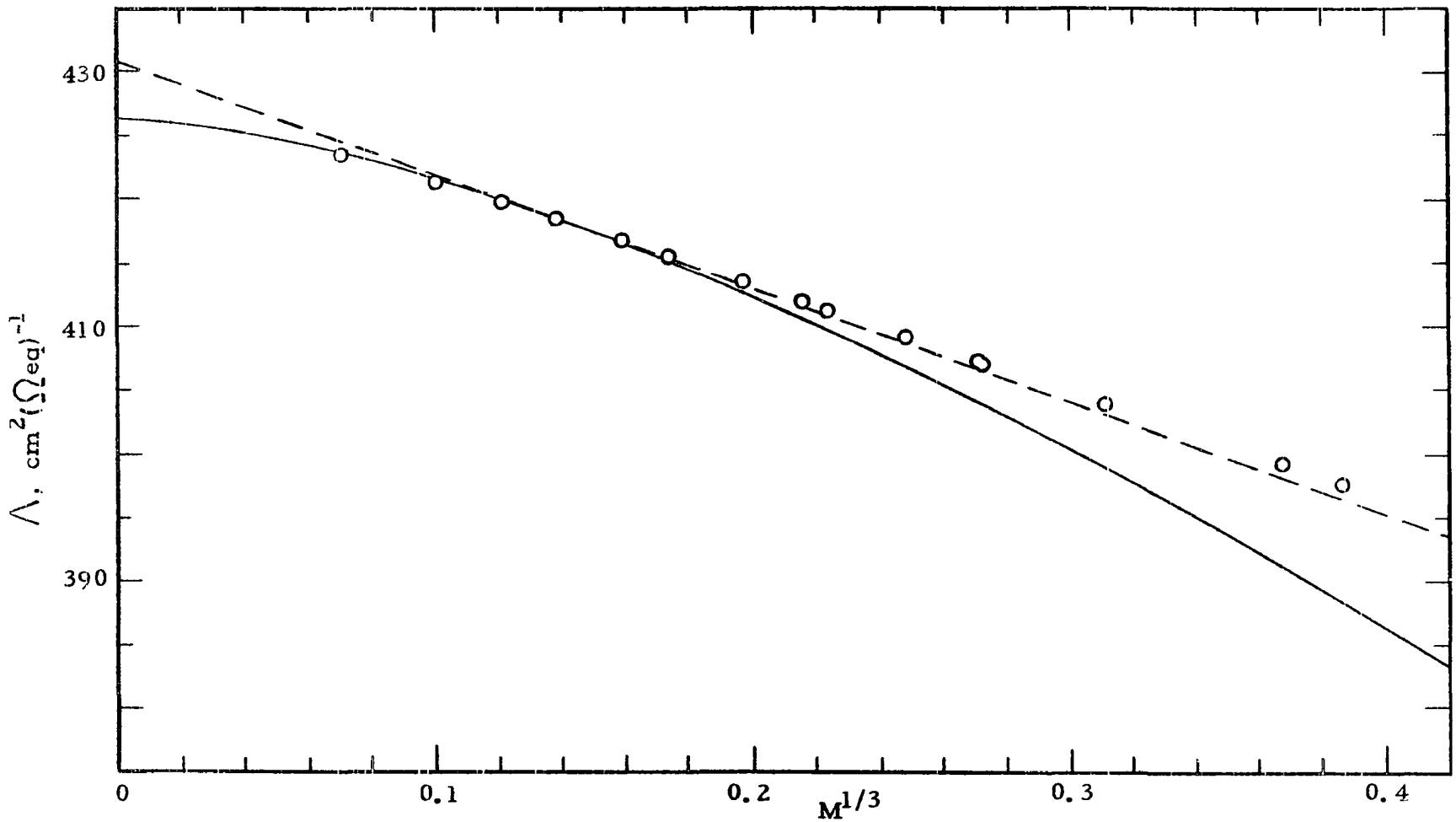


Figure 17. Equivalent Conductance Data for Hydrochloric Acid Compared with the Limiting Behavior Predicted by the Theory (- - -) and by the Debye-Hückel Treatment (——), 25°.

approximation of the experimental conductance data over a wider concentration range.

For 2-1 electrolytes the limiting expression for ln $y_{\pm}$ is dependent on a, therefore, K_{2-1} depends on the value of this parameter. In order to compare the limiting conductance predicted from the present approach to low concentration data, one can either use the value of a obtained from the best fit to activity coefficient data, or, a can be determined by fitting the conductance data. The best fit to the low concentration conductance data for $CaCl_2$ (49) is obtained with a = 0.5 (the corresponding value of K is given in Table I). For 2-1 electrolytes the Onsager equation for limiting conductance

$$\Lambda = \Lambda^{o} - (1.2283 \times 10^{-8}\Lambda^{o} + 2.7634 \times 10^{-6})K^{*} \qquad (55)$$

becomes, for $CaCl_2$ (with the K value for a = 0.5),

$$\Lambda_{CaCl_2} = 137.6 - 90.0\ M^{1/3} \qquad (56)$$

This relation is compared with the limiting equation from the Debye-Hückel treatment and the low concentration conductance data for $CaCl_2$ in Figure 18. Using the K value corresponding to the a which gave the best fit to $CaCl_2$ activity coefficient data gives

$$\Lambda_{CaCl_2} = 138.0 - 101.1\ M^{1/3}\ (a = 0.33) \qquad (57)$$

The two limiting conductance expressions, Equations 56 and 57, are compared with the Debye-Hückel limiting curve and the experimental data in Figure 19.

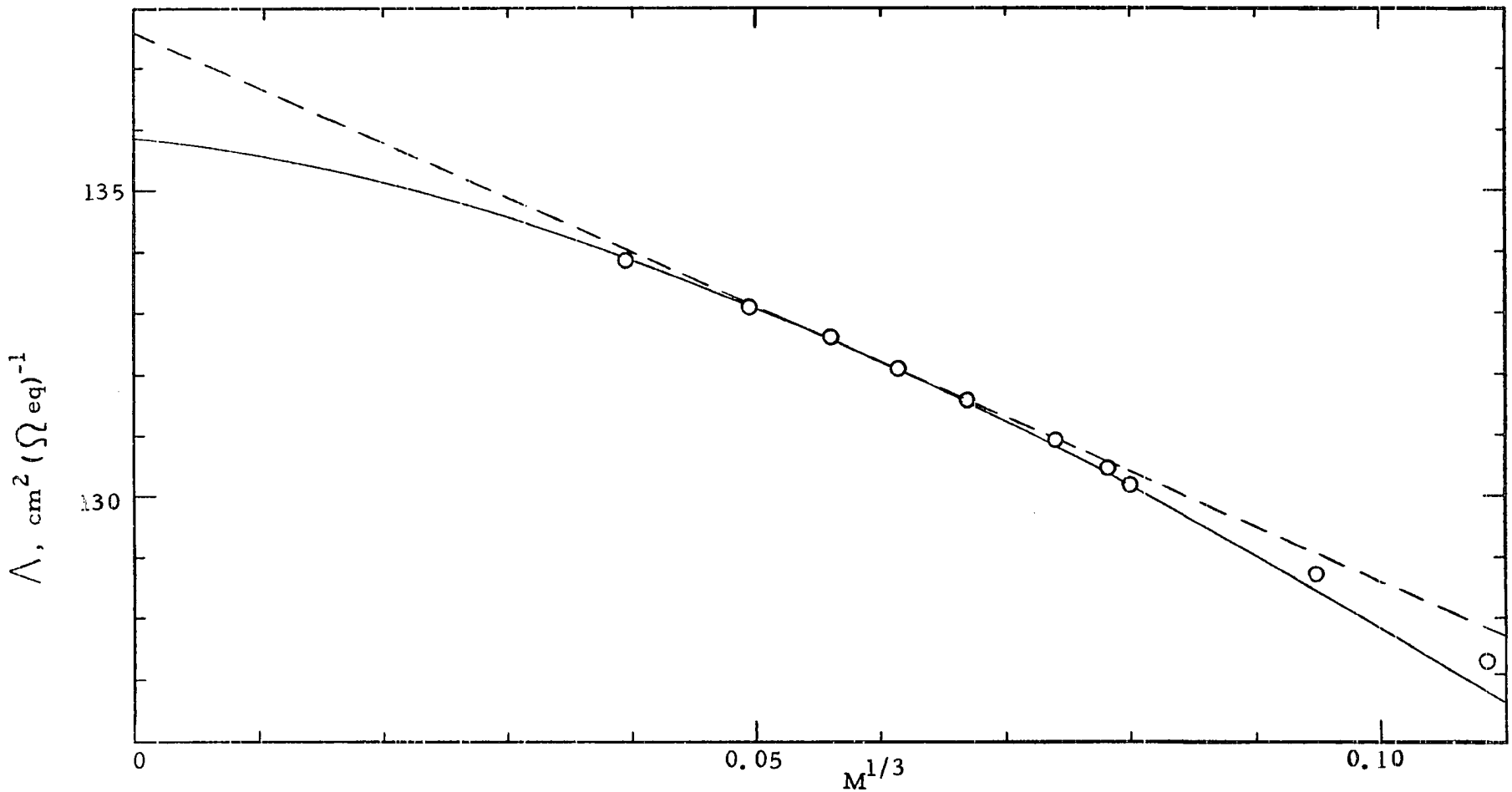


Figure 18. Low Concentration Equivalent Conductance Data for Calcium Chloride Compared with the Limiting Behavior Predicted by the Theory (- - -, a = 0.50) and by the Debye-Hückel Treatment (——), 25°.

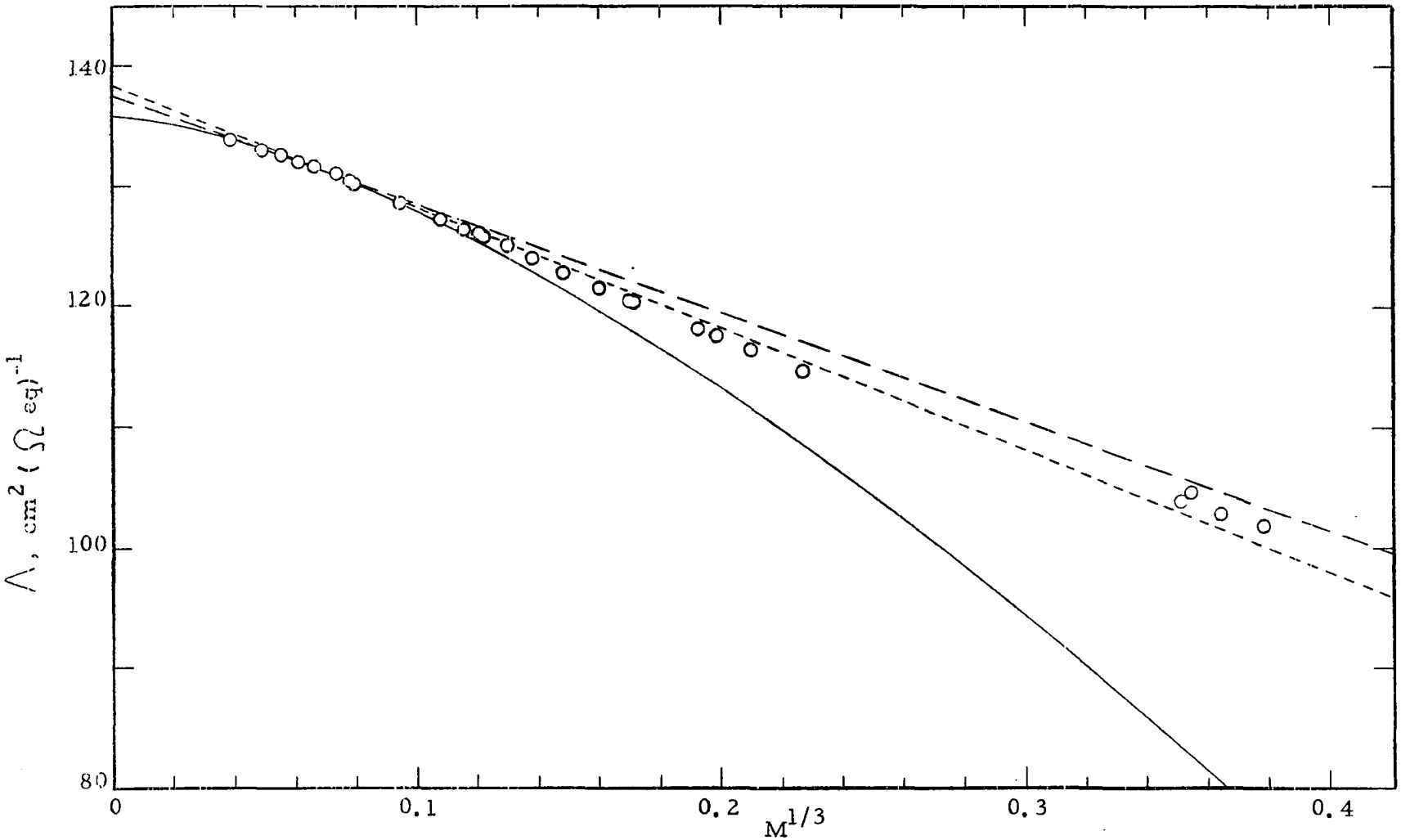


Figure 19. Equivalent Conductance Data for Calcium Chloride Compared with the Limiting Behavior Predicted by the Theory (— — —, a = 0.50; ----, a = 0.33) and by the Debye-Hückel Treatment (——), 25°.

Heat of Dilution

At present only the interpretation of low concentration limiting cases can be considered. The partial molar enthalpy of the electrolyte is given by

$$\bar{L}_2 = -\nu RT^2(\partial \ln y_\pm/\partial T) \tag{58}$$

where R is the gas constant. From the limiting expression for $\ln y_\pm$, Equation 58 becomes

$$\bar{L}_2 = -RT^2\{(\partial \ln V/\partial \ln T)/3 + (\partial \ln D/\partial \ln T) + 1\}(|z_1 z_2| e^2 K/DkT) \tag{59}$$

The relative apparent molar enthalpy, Φ_L, is more directly comparable with experimental data since it differs from the integral heat of dilution only by a constant. Φ_L can be obtained from $\bar{L}_2$ by the relation

$$\Phi_L = (1/M)\int_0^M \bar{L}_2 dM = (3/4)\,\bar{L}_2 \tag{60}$$

Use of the limiting expression for K and Equations 59 and 60 yields the theoretical expression for 1:1 electrolytes:

$$\Phi_L, \text{ cal/mole} = 198.5\, M^{1/3} \tag{61}$$

Values for the terms inside the brackets in Equation 59 were obtained from Harned and Owen (50). The theoretical line closely matches the limiting slope of the experimental data for NaCl (51), Figure 20, and approximates the data over a wide concentration range.

The relative apparent molar enthalpy for a 2-1 electrolyte is, using the value of K corresponding to $a = 0.5$,

$$\Phi_L, \text{ cal/mole} = 653.0\, M^{1/3} \tag{62}$$

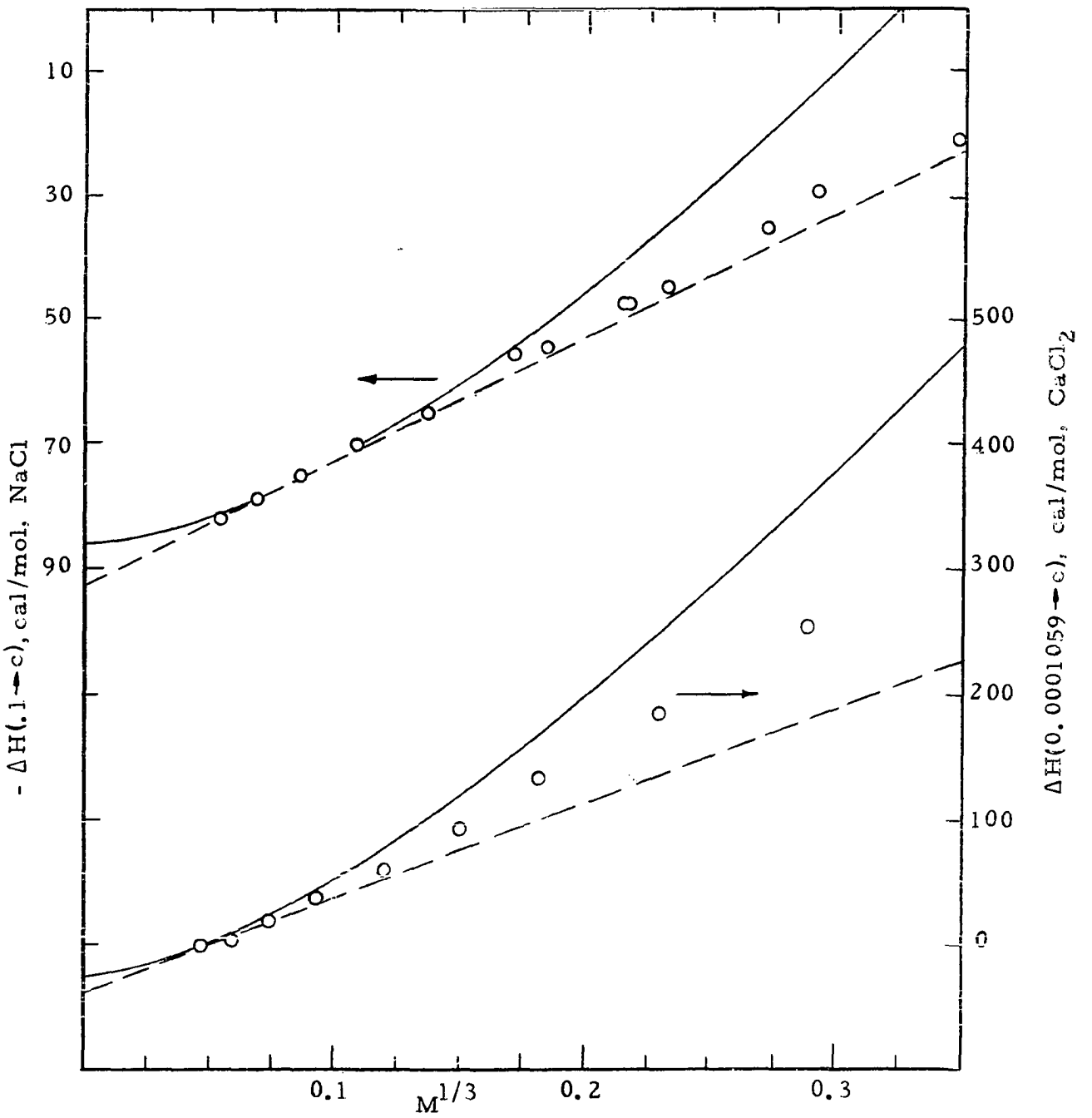


Figure 20. Low Concentration Heat of Dilution Data for Sodium Chloride and Calcium Chloride Compared with the Limiting Behavior Predicted by the Theory (- - -; a = 0.50 for $CaCl_2$) and by the Debye-Hückel Treatment (——), 25°.

The theoretical limiting behavior is compared with experimental heat of dilution data for $CaCl_2$ (52) in Figure 20. The theoretical line reproduces the experimental data at the lower concentrations. Because the experimental data at the lowest concentrations are too limited to distinguish between a values, only the value giving the best fit to low concentration conductance data is considered.

CHAPTER IV

DISCUSSION OF RESULTS

Activity Coefficients

For the numerous electrolytes examined in the preceding chapter, the theory discussed in Chapter II reproduces the experimental data to relatively high concentrations and predicts the correct behavior in the higher concentration region. A summary of the a values required to fit the experimental data is given in Table II; included are values obtained using modified forms of the Debye-Hückel treatment. One method involves the inclusion of terms of higher order in concentration than $M^{1/2}$ (53); the other considers hydration number as an additional parameter (18, 54). Table II also contains the sums of the various univalent radii as calculated from crystallographic data by Pauling (55), and the more recent experimental data of Gourary and Adrian (56).

Comparison of the a values for the strong acids obtained from the present approach with those from extended forms of the Debye-Hückel theory shows both rank the acids in the same order of the ion size parameter. In addition, the theory predicts the three halogen acids to be closer in size than is predicted by other approaches, i.e., various

TABLE II

ION SIZE PARAMETER VALUES REQUIRED TO FIT EXPERIMENTAL ACTIVITY COEFFICIENT DATA

1-1 Electrolytes, 25°

Electrolyte	a value, angstroms				
	This Theory	Debye-Hückel		$r_+ + r_-$	
		S and R[a]	R and H[b]	Pauling[c]	G and A[d]
HNO_3	4.33				
HCl	4.80	4.47	4.3		
HBr	5.23	5.18			
HI	5.58	5.69	5.5		
LiCl	4.62	4.32	4.25	2.41	2.58
NaCl	3.67	3.97	4.20	2.76	2.81
KCl	3.23	3.63	3.85	3.14	3.13
RbCl	3.10	3.49	3.2	3.29	3.27
CsCl	2.80		2.5	3.46	3.50
NaF	2.59			2.31	2.33
NaCl	3.67	3.97	4.2	2.76	2.81
NaBr	4.00	4.24	4.2	2.91	2.97
NaI	4.47	4.47	4.2	3.13	3.22
NaOH	3.89				
$NaNO_3$	2.52				
NH_4Cl	3.25			3.29	
$(C_2H_5)_4NI$	0.75				

[a]Extended form considering ion hydration, Stokes and Robinson (54).
[b]Extended form using higher order terms, Robinson and Harned (53).
[c]Tabulated univalent radii of Pauling (55).
[d]Experimental univalent radii of Gourary and Adrian (56).

forms of the Debye-Hückel treatment. Although the differences between the halide ions in these acids, as determined by the present theory, are larger than those calculated using Pauling's (univalent) radii, the a value differences obtained from the theory are closer to the univalent radii differences than those obtained from the extended forms of the Debye-Hückel equation. For the alkali metal chlorides, both general approaches order the salts in the opposite direction expected from their univalent radii. This can be explained by considering hydration to occur in the case of the smaller cations, lithium and sodium, while, for the largest cations, rubidium and cesium, their large area and small charge could allow interpenetration on contact leading to an a value smaller than the sum of their respective univalent radii. There is also the possibility that the rubidium and cesium chlorides might be associated to a very slight extent (53). The a value obtained for potassium chloride is quite close to the sum of the univalent radii.

Among the sodium halides, Table II, the order of the a values is as would be expected from the corresponding univalent radii. The value of the ion size parameter for sodium hydroxide is slightly larger than the a value for sodium chloride. This suggests that the hydroxyl ion cannot be extensively hydrated or entrapped in any water structure that might be present; this follows from estimations of ionic hydration discussed in later paragraphs. The relatively low a values obtained for sodium fluoride and nitrate could be the result of a small degree of

association in solution. In the case of sodium nitrate, the small a value might result from a significant number of close approaches of the planar nitrate ion in a specific orientation where the plane of the ion is more or less perpendicular to the cation-nitrogen line of centers.

The isopiestic activity coefficient data for ammonium chloride are well represented by the theory and the a value obtained is quite close to the sum of the univalent radii, Table II. The low concentration data for this salt, as determined by freezing point depression measurements (57), deviate from the Debye-Hückel limiting law in the negative direction. However, Frank (58) has shown that these data are linear in the cube root of concentration. The activity coefficient data for tetraethylammonium iodide also deviate in the negative direction from the Debye-Hückel limiting law, but can be reproduced with the present theory using a low value of the ion size parameter. The very low a value required, Table II, suggests that a significant amount of association is occurring; it is quite likely that high order aggregates of significant lifetime are being formed in such solutions. This explanation would be consistent with the relatively high viscosities displayed by these solutions (59). The low a value determined for tetraethylammonium iodide is consistent with the values found for several quaternary halides by Evans and Kay (60) using precise conductance data and an extended form of the Fuoss-Onsager conductance equation.

It is of particular interest to note that the a value obtained for

potassium chloride using the theory is quite close to the sum of the univalent radii. This suggests that the individual ions are essentially unhydrated; therefore, their individual radii could be used to estimate the degree of hydration of other electrolytes containing one of these ions. However, the individual univalent radii of K^+ and Cl^- as determined by Pauling do not appear to be consistent with limiting transference number data (38), assuming that both ions are essentially unhydrated. The limiting transference number data have been used, in conjunction with the a value determined by fitting activity coefficient data with the present theory, to determine the ionic radii. These results have been compared with the radii calculated from Stokes law using the limiting ionic mobilities of K^+ and Cl^-. However, Stokes law

$$u = 1/6\pi\eta r \qquad (63)$$

where u is the ionic mobility and η the viscosity of the solvent, was derived for the motion of a sphere through a continuous medium. This is obviously not the case for the motion of an ion through a solvent such as water. If the medium is not continuous, the constant in the denominator of Equation 63 is something less than 6π but its exact value is uncertain. In view of this complication, the results obtained using the ion size parameter are compared with results calculated using two different factors in the denominator of Equation 63. The univalent radii of Pauling and the more recent experimental determinations of Gourary and Adrian are included with the above results in Table III.

TABLE III

COMPARISON OF ION RADII, KCl

	From Transport Data	Stokes Law		Univalent Radii	
		6π	4π	Pauling[b]	G and A[c]
Radius of K^+, A	1.65	1.25	1.88	1.33	1.49
Radius of Cl^-, A	1.58	1.21	1.81	1.81	1.64

[a]Calculated using limiting transference numbers and a = 3.23A.
[b]Tabulated univalent radii of Pauling (55).
[c]Experimental data of Gourary and Adrian (56).

The results obtained using the ion size parameter value for KCl, as determined by the theory, with the limiting transference numbers, agree quite well with the univalent radii determined by Gourary and Adrian. The results are also consistent with a form of Stokes law containing a somewhat reduced value for the numerical constant in the denominator. The individual ionic radii do not conform to the values of Pauling; however, the more recent experimental values of Gourary and Adrian should be the more reliable for absolute comparisons.

The chloride ion radius, as determined from transport data and the ion size parameter, can be used to estimate the degree of hydration of other chloride-containing electrolytes, remembering the underlying assumption that the chloride ion is essentially unhydrated. Two specific examples have been calculated, sodium chloride and hydrochloric acid.

In calculating the hydration number of the sodium ion, it was assumed that its unhydrated radius was in the same proportion to its univalent radius (Pauling) as the ratio of the calculated radius of the potassium ion to its univalent radius, Table III. Pauling's radii were used in these calculations because of the more extensive tabulations which are available. Once the volume of the solvation shell is calculated, one must decide which value for the volume of a water molecule is to be adopted. Stokes and Robinson (54) and Glueckauf (18) used the value of 30 A^3 corresponding to the apparent volume occupied by each molecule in one mole of water. However, if one assumes a solvation sheath with a significant time of occupancy by specific molecules, then the value of 11.5A^3 adopted by Bernal and Fowler (61) appears to be the more appropriate. This volume corresponds to the actual volume of the water molecule as approximated from structure data. Upon the adoption of a value for the volume of a water molecule, the calculations are straightforward and lead to the results compiled in Table IV; included are the sodium ion radius and extent of hydration estimated using the limiting transference numbers of NaCl (38) in conjunction with the chloride ion radius determined from the potassium chloride data, Table III.

As regards the Na^+ data in Table IV, the bare ion radius is consistent with the results of Gourary and Adrian, and the apparent radius compares well with the value obtained using the limiting transference numbers of NaCl with the chloride ion radius determined from the KCl

TABLE IV

CALCULATION OF RADIUS AND EXTENT OF HYDRATION OF Na^+ and H^+

	Radius, angstroms						
	From Ion Size Parameter (ISP)		Transport No. and r_{Cl^-} from	Univalent		Hydration Number	
Ion	Bare	Apparent	KCl data (TN)	Pauling[a]	G and A[b]	ISP	TN
Na^+	1.18	2.09	2.37	0.95	1.17	2.8	4.2
H^+	-[c]	3.22	-[d]	-	-	12	-

[a]Tabulated univalent radii of Pauling (55).
[b]Values of Gourary and Adrian (56).
[c]Assumed the bare proton to be of insignificant size.
[d]Because of unusual transport mechanism of the proton, cannot use limiting transference numbers to estimate size.

data (Table II, first column). The hydration numbers vary according to the method of calculating the radius (apparent) of the sodium ion but are comparable to the value obtained by Glueckauf (18) for the hydration number of the molecule, i.e., 3.60. However, it must be remembered that Glueckauf did not assume that the chloride ion is unhydrated, and, the volume of the water molecule which he adopted for his calculations is much different than the value used in these determinations. Both the bare ion radius and the hydration number obtained using the ion size parameter from this theory are reasonable compared with the experimental univalent radius and various hydration numbers which have been reported (62) for the sodium ion.

The hydration number for the proton in solution (Table IV) is a maximum value with no consideration of the packing of water molecules about the bare proton. It is of interest to note that the volume corresponding to the apparent radius of the proton ($140A^3$) approximates the volume occupied by a regular pentagonal dodecahedron ($161A^3$) with an edge length of 2.76Å, the O-H $\cdots$ O bond distance in water, with no volume corrections for the atoms comprising the framework. The dodecahedral structure has been found for the crystalline clathrate compound chlorine hydrate (63). The postulated form of the proton in water, $H_9O_4^+$, might either be contained in such a clathrate structure or be the primary fragment of such a structure. The repeated forming and reforming of the structure to various degrees of perfection could account for the minor difference between the two volumes, i.e., the apparent volume of the proton obtained by fitting activity coefficient data with the theory and the volume of the regular pentagonal dodecahedron. Of course, there is always the possibility that a somewhat different polyhedron is the primary structure.

The same calculations could be applied to the other electrolytes containing the appropriate ions in order to estimate the extent of hydration. However, in the absence of good hydration number data for comparison, these calculations are at present superfluous.

The values of the ion size parameter required by the theory to fit experimental activity coefficient data for several 2-2 electrolytes are

summarized in Table V; included are a values obtained by other workers

TABLE V

ION SIZE PARAMETER VALUES REQUIRED TO FIT EXPERIMENTAL ACTIVITY COEFFICIENT DATA

2-2 Electrolytes, 25°

	a value, angstroms		
Electrolyte	This Theory	Debye-Hückel Modifications	$r_+ + r_-$, Pauling
$ZnSO_4$	3.30	3.64[b]	3.83 (max)
MnBDS[a]	6.1	5.71[c]	-
ZnBDS[a]	6.0	5.22[c]	-
CuBDS[a]	5.8	4.97[c]	-

[a]BDS: m-benzenedisulfonate
[b]Value obtained by Cowperthwaite and LaMer (64).
[c]Values obtained by Brubaker and Rasmussen (44).

using variations of the Debye-Hückel approach. At low concentrations, the data for zinc sulfate are reproduced by the theory with a reasonable a value, which is somewhat lower than the value determined by Cowperthwaite and LaMer using a form of the Debye-Hückel equation. Both a values determined by fitting activity coefficient data are lower than the maximum a value for zinc sulfate calculated using Pauling's univalent radii. The theoretical curve and the experimental data begin to diverge at relatively low concentrations, but this salt is known to hydrolyze (42).

The m-benzenedisulfonates appear to be very well-behaved 2-2 electrolytes which could be readily fit by the theory. However, the lack of accurate density data precludes fitting into the high concentration region at the present time. The a values obtained by the theory, considering only the low concentration data, are of comparable size with those determined by Brubaker and Rasmussen using an extended form of the Debye-Hückel equation. The present theory gives somewhat higher values of the ion size parameter and the range of values is less for the various disulfonates than reported by Brubaker and Rasmussen.

The a values for two 2-1 electrolytes obtained with this theory are compared with the results of other workers, using modified forms of the Debye-Hückel equation, and with the sum of their univalent radii, in Table VI. The theory ranks the ion size parameters of the two alkaline earth chlorides in the same order as the two forms of the Debye-Hückel approach, and, as was the case for the alkali metal chlorides, in the opposite order expected from the univalent radii. In both cases, the theory gives much larger a values than the sum of the univalent radii, thus showing the large extent of hydration of these small, doubly-charged cations. The span of a values obtained from the theory is slightly greater than the range displayed by the Debye-Hückel modification considering hydration, and somewhat smaller than the range resulting from the modification including higher order terms. The a values required for these fits, Table VI, vary according to the electrolyte, and increase with the

TABLE VI

ION SIZE PARAMETER VALUES REQUIRED TO FIT EXPERIMENTAL ACTIVITY COEFFICIENT DATA

2-1 Electrolytes, 25°

Electrolyte	a value, angstroms			
	This Theory	Debye-Hückel		$r_+ + r_-$, Pauling[c]
		S and R[a]	R and H[b]	
$CaCl_2$	4.85 (0.33)[d]	4.73	5.2	2.80
$BaCl_2$	4.26 (0.27)[d]	4.45	4.1	3.16

[a]Extended form considering ion hydration, Stokes and Robinson (54).
[b]Extended form using higher order terms, Robinson and Harned (53).
[c]Tabulated univalent radii of Pauling (55).
[d]The a value required for the best fit to experimental data.

a value. This may or may not be significant because there are insufficient low concentration data to give an unequivocal fit to a particular value of a. With presently available data, a can easily vary by as much as 0.02. A shortage of low concentration data prevents examination of most 2-1 electrolytes.

Conductance

Using the limiting form of the theoretical equation for 1-1 electrolytes, in combination with the Onsager equation for limiting conductance, results in a relation giving a good approximation of the experimental conductance data for HCl over a wide concentration range. At

the lowest concentrations, the experimental data appear to diverge from the theoretical limiting conductance in the direction of the Debye-Hückel prediction. The low concentration data are insufficient in number to definitely decide whether or not this divergence is real. In the case of 2-1 electrolytes, it is found that the low concentration data are best represented (for $CaCl_2$) by an a value of 0.5, while the activity coefficient data require a value of 0.33; the lower value also better approximates the conductance data over a wider concentration range. A value of 0.5 would be expected as the concentration approaches zero for then each pair would occupy one half of the unit volume. The lower value found for activity coefficient data is a result of fitting at higher concentrations. Being restricted to consideration of the limiting conductance at the present stage of development, only the two electrolytes have been examined.

Heat of Dilution

Only the limiting cases can be considered, but the heat of dilution data for sodium chloride are well approximated by the theory over a relatively wide concentration range. The lowest concentration data for calcium chloride are fit by the theory using an a value of 0.5. There are insufficient data to decide between a values.

General Considerations

In all cases, particularly for symmetrical electrolytes where

extensive data are available, the theory reproduces the data over a wide concentration range; the low concentration data are also generally well-represented. It must be remembered that, for symmetrical electrolytes, the theoretical equations contain a single adjustable parameter. However, there are some indications, considering both conductance and activity coefficient data, that the data at the lowest concentrations are deviating from the theoretical limiting line in the direction of the Debye-Hückel limiting curve (on an $M^{1/3}$ plot). Unfortunately, data at very low concentrations are not only scarce but the most imprecise, thus making a definite conclusion difficult. However, this possible deviation from linearity in the cube root of concentration in the direction of the Debye-Hückel square-root-of-concentration dependence at very low concentrations, would be consistent with the speculations of Frank and Thompson (24) and Frank (58). These investigators suggested that the theory of Debye and Hückel might transform into an $M^{1/3}$ dependence at finite concentrations. Their calculations showed that the Debye-Hückel assumptions and approximations are valid only at concentrations below 0.001M for 1-1 electrolytes (at still lower concentrations for higher charge types). This transition from a square-root- to a cube-root-of-concentration dependence might well correspond to the concentration where the two theoretical limiting curves coincide (Figures 17, 18, 20). Although this is interesting speculation, its confirmation awaits definitive low concentration data.

CHAPTER V

SUMMARY

By considering an electrolyte solution to be a system of chemical formula units whose members can be paired in a stepwise fashion to give an electrically neutral unit (as seen by neighboring units), a modified form of the Maxwell-Boltzmann equation is obtained which can be used to calculate solution properties. The theory predicts a linearity in the cube root of concentration for solution properties, e.g., the activity coefficient of the solute, at low concentrations.

Experimental activity coefficient data for a large number of electrolytes are reproduced by the theory to high concentrations (typically above 1 molar). For symmetrical electrolytes, a single parameter (a, the ion size parameter) is sufficient to describe solution behavior over an extensive concentration range. Two parameters are required for the description of the solution properties of 2-1 electrolytes, the ion size parameter and α, the fraction of the average unit volume occupied by the pair formed from the doubly-charged central ion and the innermost counter ion. In the case of well-behaved electrolytes, the ion size parameter appears to be physically significant and has been used to

estimate the extent of hydration of several ions.

The limiting expression for the appropriate unit configuration integral can be used to predict limiting conductance and heat of dilution data. These data are approximated to relatively high concentrations in the case of 1-1 electrolytes.

The theory, at its present stage of development, could be extended by consideration of such effects as a change in ion size with increasing concentration, the overlap of unit volumes at high concentrations, and the change in dielectric constant of the solution with increasing solute concentration. Derivation of an expression describing the change in a with concentration would allow the elimination of the second parameter in the fitting of 2-1 electrolyte data. At the present time, without an expression relating a with concentration, it would be quite difficult to consider higher charge types of electrolytes in view of the large amounts of computer time that would be required. Of course, the development of a computer program with much improved efficiency would change the situation concerning the higher charge types.

Fitting available experimental data with theoretically calculated curves has dramatically demonstrated the need for additional low concentration data of improved precision, and for experiments which will determine such parameters as ion size and hydration with increased surety.

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APPENDIX

COMPUTER PROGRAMS

All programs used in the course of this research were written in a modified form of Algol 60 for use on the OSAGE computer of the University of Oklahoma. Following are complete listings, and necessary documentation, for the three programs utilized.

```
Program 202;
Begin Comment Numerical evaluation of integral for 1:1 electrolytes using
Simpson's Method;
Real A, PREC, DELTA, THETA, VOL, C13, VE, INTGRL, SIMPSON, VA,
     PHI2, PHI213, FUNMULT, BETA, LOLIM, LOLIMSQ, LY16, MIN,
     MAX, DELCON;
Integer N, LOOPS;
Real Array F [0:3];
Format 01 (J7, F6.4, '=A', R5, '=PREC', F5.4, '=DELTA', F5.4, '=MIN',
     F5.4, '=MAX', F5.4, '=DELCON', 2(J1), S2, 'PHI2', S4, 'PHI213',
     S5, 'SIMPSON', S9, '12(2)', S5, 'LOG Y16', S3, 'C13', S3, 'LOOPS',
     J1), 02(J1, S5, 'VA IS NEGATIVE, 'C13=', F5.2),
```

```
        03(J1, 2(F9.6), R9.8, F9.6, F4.2, I4);
L5:     READPT(DECIMAL, A);
        If A=0 Then Goto L35;
        READPT(PREC, DELTA, MIN, MAX, DELCON);
        PRINT(01, A, PREC, DELTA, MIN, MAX, DELCON);
        THETA ← 7.135761/A;
        VOL ← 4.1887902*A*A*A*1D-24;
L12:    For C13 ← MIN Step DELCON Until MAX Do
        Begin
                        VE ← 1.65963D-21/(C13*C13*C13);
                        INTGRL ← SIMPSON ← 0.;
                        VA ← VE-VOL;
                        If VA≤ 0. Then Begin PRINT(02, C13);
        Goto L5 End;
                        PH12 ← VOL/VA;
                        PHI213 ← PH12 ↑.33333333333333↓;
                        FUNMULT ← (VA/VE) ↑2.↓ ;
                        BETA ← THETA*PHI213;
                        LOLIM ← PHI213-DELTA;
                        N ← 0; LOOPS ← 0;
Comment Calculation of Function values at three X values;
L15:    If N<3 Then Begin N ← N+1; LOLIM ← LOLIM + DELTA;
                        Goto L20 End;
```

```
                    Else Goto L25;
L20:                LOLIMSQ ← LOLIM * LOLIM;
    F[N]←LOLIMSQ*(EXP(BETA/LOLIM)-1.)*1./(EXP(LOLIMSQ*
    LOLIM));
                    Goto L15;
Comment Integration of Subinterval by Simpsons Method;
L25: SIMPSON← (DELTA/3.)*(F[1]+ 4.*F[2]+ F[3]);
    If SIMPSON <PREC Then Goto L30
            Else INTGRL ← INTGRL + SIMPSON;
    F[1]←F[3];
    N ←1;
    LOOPS ← LOOPS + 1;
    Goto L15;
L30: LY16 ← -.5*(LOG(FUNMULT+3.*(EXP)PHI2))*FUNMULT*INTGRL));
    PRINT(03, PHI2, PHI213, SIMPSON, INTGRL, LY16, C13, LOOPS)End
Comment Completion of evaluation for a given A value over the complete
concentration range;
    Goto L5;
L35: End Program 202;
```

Input:

A, the ion size parameter, in angstroms.

PREC, the desired level of precision in the integration

DELTA, the interval size used in the integration

MIN, the starting value of $M^{1/3}$

MAX, the uppermost $M^{1/3}$ value to be calculated

DELCON, the $M^{1/3}$ increment in advancing from MIN to MAX

Program 202 calculates the integral by evaluating subintervals of three points each. The results of the integration are used inside the program to calculate -log $y_{\pm}$ at the various concentrations. The program can be used for 2-2 electrolytes by simply multiplying the program variable BETA by 4. Calculation stopped by MAX or when the free volume term, VA, $\leqslant 0$.

The unit configuration integral for 2-1 electrolytes is evaluated by the following program:

```
Program 207;
Begin Comment Numerical evaluation of double integral for 2-1 electrolytes.
Real VOLMOL, PRETHET, A1, A2, PRECOUT, PRECIN, DELW, DELZ, DEL,
     INCON, DELCON, FINCON, CONCOR, PIMUL, CRPIMUL, WVOL,
     C13, TIME, VBAR, VBARFCM, VBARF1, ATOT, VBARF2, XPHI,
     WPHI, WMUL, B1, W, W2, R1, BTOT, RIVAR, R1A2, YPHI, ZPHI, B2
     Z, Z2, D, ZMUL, AVOL1, SUMW, SUMZ, DTOT, SUMZMAX, ZPHIOLD,
     LOGY213;
Integer DATE, PROGRAM, M, STEPS, N, J;
Real Array PREFUNW[0:3], FUNZ[0:3], FUNW[0:3];
Format 01(J7, F6.4, '=A1', F6.4, '=A2', R5, '=PRECOUT', R5, '=PRECIN',
     F5.4, '=DELW', 2(J1), F5.4, '=DELZ', F7.6, '=INCON', F7.6,
     '=DELCON', F7.6, '=FINCON', F5.4, '=AVOL1', 2(J1), F6.4,
```

```
        '=CONCOR', I6, '=DATE', I6, '=PROGRAM NO. ', 2(J1), S7, 'X-PHI',
        S7, 'OUT-INT', S6, 'LOGY213', S7, 'C1/3', S9, 'TIME', S5, 'STEPS',
        2(J1)),
        02(S5, 'VBARF1 IS NEGATIVE,  C1/3=', F7.5, J1),
        03(R6, S1, R8, S2, R8, F8.6, S5, F5.3, S2, I6, J1),
        04(S5, 'VBARF2 IS NEGATIVE,  STEPS=', I6, J1);
Real Procedure SIMPSON (B, C, D, E);
        Real B, C, D, E;
        Begin SIMPSON ← (B/3.)*(C+4.*D+E);End;
PIMUL ← 4.1887902047864;
VOLMOL ← 1000./6.02252D23;
PRETHET ← (4.80298D-10*4.80298D-10)/(78.54*1.38054D-16*298.16);
CRPIMUL ← CUBRT(PIMUL);
L5:     READPT(A1);
        If A1 = 0.  Then Goto L50;
        READPT(A2, PRECOUT, PRECIN, DELW, DELZ, INCON, DELCON,
                FINCON, AVOL1, CONCOR, DATE, PROGRAM);
        PRINT(01, A1, A2, PRECOUT, PRECIN, DELW, DELZ, INCON, DELCON,
                FINCON, AVOL1, CONCOR, DATE, PROGRAM);
A1 ← A1*1.D-8;
A2 ← A1*1.D-8;
WVOL ← PIMUL*A1*A1*A1;
L12:    For C13 ← INCON Step DELCON Until FINCON Do
```

```
Begin
                    TIME ← CLOCK;
                    VBAR ← VOLMOL/C13*C13*C13);
                    ATOT ← A1+ A2;
                    VBARFCM ← VBAR-PIMUL*(ATOT*ATOT*ATOT);
                    VBARF1 ←VBAR*AVOL1-WVOL;
                    If VBARF1 ⩽ 0.  Then Begin PRINT (02, C13);
                    Goto L5 End;
                    R1←CUBRT(VBAR*AVOL1)/CRPIMUL;
                    BTOT←R1 + A2;
                    VBARF2←VBAR-PIMUL*(BTOT*BTOT*BTOT);
                    If VBARF2⩽0.  Then Begin PRINT(04, C13);
                    Goto L5 End;
XPHI←WVOL/VBARF1;
WPHI←CUBRT(XPHI);
WMUL←3.*(EXP(XPHI))*(VBARFCM/VBAR)*(VBARF1/VBAR);
B1←(PRETHET/A1)*WPHI*2.;
Comment Initialization for integrations;
      STEPS←J←M←0;
      SUMW←0.;
      W←WPHI-DELW;
L15:  For M←M+1 Step 1 Until 3 Do Begin
      W←W+DELW;
```

```
        STEPS←STEPS + 1;
        W2←W*W;
        RIVAR←CUBRT(VBARF1)*W/CRPIMUL;
        R1A2←RIVAR + A2;
        YPHI←(PIMUL*R1A2*R1A2*R1A2)/VBARF2;
        ZPHI←CUBRT(YPHI);
        B2←PRETHET*CRPIMUL/CUBRT(VBARF2);
        PREFUNW[M]←W2*EXP(B1/W)*EXP(-W2*W);
        ZMUL←3.*VBARF2/VBAR;
If J=0 Then Begin DEL←DELZ;N←0;
        ZPHIOLD←ZPHI;
        Z←ZPHI-DEL;
        SUMZ←0.; Goto L25 End
        Else DEL←(ZPHI-ZPHIOLD)/2.;
        Z←ZPHIOLD-DEL;
        ZPHIOLD←ZPHI;
L25:    For N←N+1 Step 1 Until 3 Do Begin
        Z←Z + DEL;
        Z2←Z*Z;
        FUNZ[N]←Z2*EXP(B2/Z)*EXP(-Z2*Z) End;
        D←SIMPSON(DEL, FUNZ[1], FUNZ[2], FUNZ[3]);
        DTOT←ZMUL*D;
If J=0 Then Begin If PRECIN<DTOT Then Begin
```

```
        SUMZ ← SUMZ+ DTOT;
        FUNZ[1] ← [3];
        N ← 1;
        Goto L25 End
Else    SUMZMAX←SUMZ;J←1;N← 0;Goto L30;
                        End Else SUMZ ← SUMZMAX-DTOT
If ¬ SUMZ ⩽ 0.  Then Begin FUNZ[1] ← FUNZ[3];
        ZPHIOLD ← ZPHI;
        SUMZMAX ← SUMZ;
        N ← 1; End
        Else SUMZ ← 0;
        If 165. < YPHI Then PRINT (04, STEPS);
L30:    FUNW[M] ← PREFUNW[M] * SUMZ * EXP(YPHI) End;
        D ← SIMPSON(DELW, FUNW[1], FUNW[2], FUNW[3]);
        DTOT ← WMUL*D;
If PRECOUT < DTOT Then Begin
        SUMW ← SUMW+DTOT;
        FUNW[1] ← FUNW[3];
        M ← 1;
        Goto L15;
        End;
LOGY213 ← -LOG(SUMW*CONCOR)/3.;
TIME ← (CLOCK-TIME)/1000.;
```

PRINT(03, XPHI, SUMW, LOGY213, C13, TIME, STEPS);

End;

Goto L5;

L50; End Program 207;

Input*:

Ai, the ion size parameter for an inner ion pair, in angstroms

A2, the ion size parameter for an outer ion pair, in angstroms (not used as fitting parameter, always taken as zero)

PRECOUT, preselected level of precision for integration of outer function

PRECIN, preselected level of precision for integration of inner function, PRECIN<PRECOUT

DELW, step size, outer function

DELZ, step size, inner function

INCON, initial $M^{1/3}$ value to be calculated

DELCON, $M^{1/3}$ increment

FINCON, the maximum value of $M^{1/3}$ to be calculated

AVOL1, the value of the parameter a

CONCOR, the value of the normalization constant to give log $y_{\pm} \rightarrow 0$ as $M^{1/3} \rightarrow 0$; CONCOR = 1/a(1-a)

DATE

PROGRAM, the program number

*In the following variable definitions, outer integral denotes the integral

involving y and inner integral denotes the integral involving z in Equation 33, respectively.

The integrands in Equation 33 were transformed into functions of $y^{1/3}$ and $z^{1/3}$ before programming. The inner integral was evaluated for each value of $y^{1/3}$ and used to weight the value of $f(y^{1/3})$ for each point used to calculate the complete integral. The inner integral was evaluated over the complete range of integration for the minimum value of its lower limit and this value stored in the machine. For each subsequent step of $y^{1/3}$, the integral between the new $y^{1/3}$ and the previous $y^{1/3}$ was evaluated and this amount subtracted from the total value of the inner integral. This procedure minimized the computer time required since it obviated repeated integration of the inner function over the entire range. The calculations are stopped by having completed all desired computations or by having a free volume term equal zero or go negative.

The last program evaluates the integral containing $z^{-1/3}$ in Equation 34 to determine the limiting behavior of ζ_{12} for various values of a. The program is based on the following derivation:

$$\int_A^\infty \frac{e^{-z}dz}{z^{1/3}} = \int_0^\infty \frac{e^{-z}dz}{z^{1/3}} - \int_0^A \frac{e^{-z}dz}{z^{1/3}}$$

$$= \Gamma(2/3) - \sum_{n=0}^{\infty}(-1)^n \int_0^A \frac{z^n}{n!\, z^{1/3}}\, dz$$

$$= \Gamma(2/3) \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \int_0^A z^{n(1/3)} dz$$

$$= \Gamma(2/3) \sum_{n=0}^{\infty} \frac{(-1)^n}{n!\,(n+2/3)} A^{(n+(2/3))}$$

Program 211;

Begin Comment Series evaluation of second and third integrals appearing

in the expansion of the inner integral in the 2-1 electrolytes case.

Real GAMMA, LOLIM, FRAC, PREC, TEST, CONST, STEP, N, SUM, PRETERM,

TERM, INT;

Format 01(J7, J1, F6.4, '=GAMMA', F6.4, '=1-N', R5, '=PREC', 2(J1), S7

'LOLIM', S7, 'INT', S7, 'N', 2(J1)).

02(J2, R6, S1, R8, S10, F5.0);

L5: READPT(GAMMA);

If GAMMA=0. Then Goto L8;

READPT(LOLIM, FRAC, PRE, TEST, CONST, STEP);

PRINT(01, GAMMA, FRAC, PREC);

L8: N←0. SUM←0.;

PRETERM←LOLIM↑FRAC;

SUM←SUM+(1./CONST)*PRETERM;

L9: N←N+1.;

PRETERM←(-1.)*N*PRETERM*LOLIM;

TERM←(1./(N+CONST))*PRETERM;

```
        If |TERM| < PREC Then Goto L15;
        SUM←SUM+ TERM;
        Goto L9;
L15:    INT←GAMMA-SUM;
        PRINT(02, LOLIM, INT, N);
        If LOLIM< TEST Then Begin LOLIM←LOLIM+STEP;
                                  Goto L8 End;
        Goto L5;
L25:    End Program 211;
```

Input: GAMMA, the value of the appropriate gamma function

LOLIM, the lower limit of integration (A in preceding derivation)

FRAC, the complement of the exponent of Z in the integral to be evaluated

PREC, preselected precision level for terminating series

CONST, numerator of the fraction corresponding to the appropriate gamma function, e.g. for $\Gamma(2/3)$, CONST-2.

STEP, the value of the incremental change in LOLIM if the integral for a number of values of the lower limit is desired.

The program is written in such a manner that any integral involving a fractional exponent of z which is a multiple of -1/3 can be calculated. The results for the integrals involving $z^{-1/3}$ and $z^{-2/3}$ (for several values of the lower limit, A) are listed below.

Computer output for $\int_A^\infty \frac{e^{-z}dz}{z^{1/3}}$ = INT:

1.3541 = GAMMA .6666 = 1-N .10000D-9 = PREC

LOLIM	INT	N
.20	.87971924	8.
.22	.85243837	8.
.24	.82649725	8.
.26	.80176742	8.
.28	.77814169	8.
.30	.75552925	8.
.32	.73385216	9.
.34	.71304276	9.
.36	.69304176	9.
.38	.67379678	9.
.40	.65526113	9.
.42	.63739299	9.
.44	.62015461	10.
.46	.60351178	10.
.48	.58743332	10.
.50	.57189071	10.
.52	.55685771	10.
.54	.54231017	10.
.56	.52822570	10.
.58	.51458355	10.

LOLIM	INT	N
.60	.50136440	11.
.62	.48855021	11.
.64	.47612414	11.
.66	.46407037	11.
.68	.45237404	11.
.70	.44102120	11.
.72	.42999865	11.
.74	.41929396	11.
.76	.40889537	11.
.78	.39879171	12.
.80	.38897242	12.
.82	.37942745	12.
.84	.37014725	12.
.86	.36112273	12.
.88	.35234522	12.
.90	.34380647	12.
.92	.33549857	12.
.94	.32741398	12.
.96	.31954548	12.
.98	.31188618	13.
1.00	.30442944	13.

Computer output for $\int_A^\infty \frac{e^{-z}dz}{z^{2/3}}$ = INT:

2.6789 = GAMMA .3333 = 1-N .10000D-9 = PREC

LOLIM	INT	N
.20	1.0074610	8.
.22	.96154992	8.
.24	.91919944	8.
.26	.87993455	8.
.28	.84337384	8.
.30	.80920564	9.
.32	.77717150	9.
.34	.74705435	9.
.36	.71866980	9.
.38	.69185968	9.
.40	.66648716	9.
.42	.64243290	9.
.44	.61959212	10.
.46	.59787224	10.
.48	.57719097	10.
.50	.55747482	10.
.52	.53865783	10.
.54	.52068054	10.
.56	.50348916	10.
.58	.48703479	10.

LOLIM	INT	N
.60	.47127290	11.
.62	.45616276	11.
.64	.44166702	11.
.66	.42775135	11.
.68	.41438409	11.
.70	.40153600	11.
.72	.38917997	11.
.74	.37729088	11.
.76	.36584535	11.
.78	.35482159	12.
.80	.34419930	12.
.82	.33395947	12.
.84	.32408431	12.
.86	.31455715	12.
.88	.30536233	12.
.90	.29648513	12.
.92	.28791168	12.
.94	.27962893	12.
.96	.27162456	13.
.98	.26388691	13.
1.00	.25640498	13.

The rightmost column in the output listing denotes the number of terms in the series required to reach the listed level of precision.

TABLE A-I

CALCULATED ACTIVITY COEFFICIENT DATA, 1-1 ELECTROLYTES, 25°

$M^{1/3}$	-log $y_{\pm}$, various a values, angstroms							
	0.75	2.52	2.59	2.80	3.10	3.23	3.25	3.67
0.1	0.0326	0.0295	0.0295	0.0294	0.0294	0.0294	0.0294	0.0293
.2	.0748	.0603	.0602	.0600	.0597	.0594	.0595	.0591
.3	.1275	.0916	.0914	.0907	.0898	.0893	.0893	.0879
.4	.1885	.1225	.1220	.1206	.1186	.1177	.1176	.1147
.5	.2536	.1523	.1514	.1490	.1455	.1440	.1438	.1387
.6	.3193	.1803	.1791	.1753	.1700	.1676	.1672	.1594
.7	.3832	.2065	.2047	.1993	.1916	.1882	.1877	.1762
.8	.4442	.2304	.2280	.2207	.2103	.2056	.2049	.1888
.9	.5017	.2520	.2489	.2394	.2257	.2195	.2185	.1969
1.0	.5557	.2712	.2673	.2552	.2377	.2297	.2284	.1999
1.1	.6063	.2879	.2831	.2680	.2461	.2358	.2342	.1972
1.2	.6537	.3020	.2962	.2777	.2504	.2375	.2355	.1879
1.3	.6981	.3134	.3065	.2839	.2505	.2343	.2317	.1706
1.4	.7399	.3221	.3138	.2865	.2457	.2255	.2222	.1435
1.5	.7792	.3278	.3181	.2850	.2353	.2100	.2059	.1034
1.6	.8163	.3304	.3189	.2790	.2183	.1864	.1813	.0451
Electrolyte	$(C_2H_5)_4NI$	$NaNO_3$	NaF	CsCl	RbCl	KCl	NH_4Cl	NaCl

TABLE A-I--(Continued)

CALCULATED ACTIVITY COEFFICIENT DATA,
1-1 ELECTROLYTES, 25°

	-log $y_{\pm}$, various a values, angstroms							
$M^{1/3}$	3.89	4.00	4.33	4.47	4.62	4.80	5.23	5.58
0.1	0.0293	0.0292	0.0292	0.0292	0.0291	0.0291	0.0290	0.0289
.2	.0588	.0587	.0583	.0581	.0580	.0577	.0571	.0566
.3	.0872	.0868	.0856	.0851	.0846	.0839	.0821	.0805
.4	.1132	.1124	.1099	.1088	.1076	.1061	.1022	.0988
.5	.1360	.1346	.1301	.1281	.1259	.1232	.1162	.1099
.6	.1550	.1527	.1456	.1424	.1388	.1344	.1228	.1122
.7	.1697	.1664	.1556	.1508	.1454	.1386	.1205	.1039
.8	.1797	.1749	.1595	.1525	.1446	.1346	.1075	.0819
.9	.1843	.1779	.1563	.1463	.1351	.1207	.0806	.0415
1.0	.1830	.1743	.1446	.1307	.1149	.0941	.0347	-.0264
1.1	.1748	.1631	.1225	.1030	.0806	.0506	-.0401	-.1418
1.2	.1582	.1426	.0867	.0591	.0266	-.0182	-.1923	-.3668
1.3	.1312	.1102	.0317	-.0089	-.0581	-.1294	-.4180	
1.4	.0904	.0616	-.0532	-.1172	-.1993	-.3315		
1.5	.0298	-.0110	-.1932	-.3128				
1.6	-.0624	-.1242	-.4808					
Electrolyte	NaOH	NaBr	HNO_3	NaI	LiCl	HCl	HBr	HI

TABLE A-II

CALCULATED ACTIVITY COEFFICIENT DATA,
2-2 ELECTROLYTES, 25°

	-log $y_{\pm}$, various a values, angstroms			
$M^{1/3}$	3.30	5.80	6.00	6.10
0.1	0.1681	0.1328	0.1320	0.1317
.2	.3937	.2769	.2736	0.2721
.3	.5868	.4011	.3948	0.3919
.4	.7401	.5000	.4906	0.4860
.5	.8634	.5756	.5627	0.5565
.6	.9648	.6303	.6133	0.6049
.7	1.0494	.6649	.6426	0.6315
.8	1.1207	.6781	.6486	0.6334
.9	1.1810	.6656	.6247	0.6029
1.0	1.2319	.6163	.5549	0.5200
1.1	1.2743	.5006	.3894	0.3150
1.2	1.3088	.1944	-.2244	
1.3	1.3355			
1.4	1.3542			
1.5	1.3643			
1.6	1.3645			
Electrolyte	$ZnSO_4$	CuBDS[a]	ZnBDS[a]	MnBDS[a]

[a]BDS: m-benzenedisulfonate

TABLE A-III

CALCULATED ACTIVITY COEFFICIENT DATA,
2-1 ELECTROLYTES, 25°

$M^{1/3}$	$-\log y_{\pm}$, two a values, angstroms	
	4.26 (a = 0.27)	4.85 (a = 0.33)
0.05	0.0413	0.0379
.10	.0829	.0768
.15	.1250	.1157
.20	.1660	.1534
.25	.2048	.1889
.30	.2410	.2218
.35	.2743	.2517
.40	.3046	.2786
.45	.3319	.3024
.50	.3562	.3231
.55	.3777	.3406
.60	.3961	.3548
.65	.4116	.3656
.70	.4238	.3724
.75	.4326	.3748
.80	.4375	.3718
.85	.4375	.3615
.90	.4315	.3407
.95	.4167	.3015
1.00	.3873	.2173
1.05	.3265	
1.10	.0764	
Electrolyte	$BaCl_2$	$CaCl_2$