Summary and Future Directions

As we have tried to indicate, the study of noncovalent complexes involves a fruitful interplay between theory and experiment. We have concentrated our attention mainly on the structure and binding energy of such complexes; much theoretical and experimental work has concerned itself with spectroscopic properties (NMR, UV, IR), but we have not had space here to discuss these.[7,41]

It is an important theme of our work that the "electrostatic" properties of molecules are a key to the structure and energy of their interactions, and we have tried to put all noncovalent bonding into a single picture. We do not feel there is anything intrinsically special about hydrogen bonding, van der Waals complexes, charge-transfer interactions, or ionic interactions but feel all are, to first order, electrostatic interactions. The other energy components are important, and we have tried to show specific examples of this. However, it is our opinion that the approach outlined above is the most sensible way to think about the directionality and relative energies of most noncovalent interactions.[55] Not only does it give a simple way to semiquantitatively systematize a large body of known facts but it also is consistent with more quantitative empirical potential function approaches to study intermolecular interactions.

It is also worth stressing that the directionality of electrophilicity and nucleophilicity predicted from our simple model is often the same as that predicted by a simple HOMO–LEMO picture. For example, the direction of the most positive electrostatic potential and the site of the largest LEMO coefficient in SO_2 coincide (above the molecular plane, approximately over the sulfur). Thus, it is likely that some of the features of our charge distributions can be used to rationalize chemical reactivity as well as noncovalent interactions. For the purpose of noncovalent interactions, we have stressed the electrostatic aspects, rather than the HOMO–LEMO aspects, of the charge distributions because of the many examples discussed above in which the electrostatic component has been the dominant determinant of directionality.

We have concentrated in this Account on intermolecular effects, but there have been a number of ab initio studies on intramolecular interactions. These indicate that electrostatic effects, after factoring out the intramolecular geometry constraints and the energetic contributions from eclipsed bonds and other types of "strain", can provide a qualitative prediction of strength and directionality of many intramolecular noncovalent interactions.[56]

(55) With the obvious exception of rare gas–rare gas and hydrocarbon–hydrocarbon interactions, which are likely to be mainly dispersion dominated.

(56) P. Kollman and G. L. Kenyon, *J. Am. Chem. Soc.*, 99, 1892 (1977); S. Dietrich, P. Kollman, E. C. Jorgensen, and S. Rothenberg, *ibid.*, 98, 8310 (1976).

Electrolyte Theory—Improvements since Debye and Hückel

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In 1923 Debye and Hückel[1] provided, in a simple theory, the correct equation for the behavior of electrolyte solutions in the limit of very low concentration. This eliminated an anomaly that had troubled physical chemists and allowed a great advance in the semiempirical, semitheoretical treatment of dilute electrolytes at finite concentrations. While the severe approximations of Debye and Hückel were found not to affect the limiting law, great uncertainty[2] remained concerning any higher order terms.

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There were many intermediate advances[3] through the years, especially in the work of Mayer, Kirkwood, Poirier, and Friedman. However, a really sound and fruitful theory for electrolytes at substantial concentration has only emerged in the last decade. While these contributions have been summarized in reviews[4,5] addressed to specialists in statistical mechanics and electrolyte theory, it seemed desirable to call this advance to the attention of physical chemists and solution chemists more generally. This more recent theory may be too complex for use or for presentation in some cases, but even then it should be realized that a rigorous

(1) P. Debye and E. Hückel, *Phys. Z.*, 24, 185, 334 (1923); 25, 97 (1924).
(2) H. S. Frank and P. T. Thompson, *J. Chem. Phys.*, 31, 1086 (1959).
(3) This work is reviewed by H. L. Friedman, "Ionic Solution Theory", Wiley-Interscience, New York, N.Y., 1962.
(4) H. C. Andersen, *Mod. Aspects Electrochem.*, No. 11, 1 (1975).
(5) J. C. Rasaiah, *J. Solution Chem.*, 2, 301 (1973).

theory now exists. Thus one should evaluate the accuracy of the traditional Debye–Hückel theory by comparison with the rigorous theory for the same model.

It is also possible to extend the Debye–Hückel theory in a simple manner to yield a relatively simple equation which is an excellent approximation.[6] The recent theory suggests new forms of semiempirical equations which have proven to be remarkably successful in representing experimental results and in thermodynamic calculations.

In reviewing and summarizing the recent development it is desirable to divide the complete theory into three parts. This division is equally applicable to Debye–Hückel theory; hence, we can discuss the improvements in each part. The three parts are: (1) the selection of the molecular model, i.e., the interionic potentials of mean force, (2) the calculation of the interionic radial distribution functions from this model, and (3) the calculation of thermodynamic functions from the potentials and the radial distribution functions.

Interionic Potentials

In principle one would like to have an adequate theoretical treatment for water and to use it together with the properties of the ions to derive[7] the interionic potentials of mean (or average) force in water. But there is not yet an adequate model for water. Hence one must start with a model for the interionic potentials of mean force.

The potential of mean force is defined in a manner such that its derivative gives the force on the selected particle averaged over the motion of other particles in the system.[8] Thus the familiar equation for the electrostatic potential in the presence of a dielectric is a potential of mean force; its derivative gives the force on a charged particle averaged over the motion of the particles constituting the dielectric.

Any plausible model can be described by the interionic potential equation

$$u_{ij}(r) = u_{ij}^*(r) + z_i z_j e^2 / Dr \qquad (1)$$

where $z_i e$ is the charge on the ith ion, r is the distance between the i and j ions, D is the dielectric constant of the solvent, and $u^*(r)$ is a short-range function giving the difference between the true interionic potential of mean force and the electrostatic term.

There is no question concerning the effect of the dielectric constant of the solvent in yielding the last term in eq 1 for sufficiently large interionic separation. All effects yielding departures from this electrostatic term are combined in $u_{ij}^*(r)$. These include at intermediate distances a variety of effects related to the molecular nature of the solvent (solvation, dielectric saturation, etc.) as well as dispersion forces between the ions and at shorter distances the direct repulsion of ions as their electron shells begin to overlap.

The simplest assumption for u^*, used by Debye and Hückel and frequently called the primitive model, is

$$u_{ij}^* = +\infty, \, r < a$$
$$u_{ij}^* = 0, \, r > a \qquad (2)$$

where the hard-core diameter a is the same for all ions. A first improvement is to make the hard core distance in (2) the sum of radii which may differ for the positive and negative ions in a salt. Further improvements are continuous functions reflecting the softness of the direct interionic repulsion and the short-range effects of the solvent. Since there has been a major advance in the correct solution of the primitive model, we will proceed at once in describing that theory. But we will describe equations valid for other forms of u^* and will eventually discuss some results for another model.

While improvements in part 2, the calculation of the radial distribution function, were important, the most critical advance was for part 3; hence we discuss part 3 next. Debye and Hückel were unable to include the direct effect of the short-range potential u^* on thermodynamic properties; they included only the indirect effect of u^* on the electrostatic term (and even that only partially).

Equations Yielding Thermodynamic Functions

An adequate theory relating intermolecular potentials and radial distribution functions to thermodynamic functions was first developed for simple fluids such as argon. For the energy content the result is rather easily derived:

$$\frac{E}{N} = \frac{3}{2} kT + \frac{1}{2} \frac{N}{V} \int_0^\infty u(r)g(r)4\pi r^2 dr \qquad (3)$$

where $g(r)$ is the radial distribution function and $u(r)$ is the intermolecular potential. It is considerably more difficult to obtain a useful relationship for free energy, but somewhat indirect approaches were successful. The most direct and useful gives the pressure

$$\frac{PV}{NkT} = 1 - \frac{N}{6VkT} \int_0^\infty r \frac{\partial u}{\partial r} g(r)(4\pi r^2) dr \qquad (4)$$

Given the pressure as a function of volume, other functions can be calculated from thermodynamic relationships. There is also an equation for the compressibility which provides a useful check, but the pressure equation is ordinarily the most convenient.

This theory for simple fluids can be found in a number of books on statistical mechanics; for example, Fowler[9] and Henderson and Davison[10] give derivations based on the virial theorem. A different and relatively simple derivation based on the volume derivative of the partition function is given by Davidson[11] and by Hill.[12] Still another derivation has been given by Hill.[13]

The generalization of these equations to multicomponent fluids is relatively straightforward. But we can hardly deal in detail with all of the solvent molecules as well as the solute; hence some method of averaging over solvent effects is essential. This was provided by McMillan and Mayer[14] who considered a solution in

(6) K. S. Pitzer, *J. Phys. Chem.*, **77**, 268 (1973).

(7) An interesting approach toward the derivation of interionic potentials of mean force is given by G. N. Patey and J. P. Valleau, *J. Chem. Phys.*, **63**, 2334 (1975).

(8) T. L. Hill, "An Introduction to Statistical Thermodynamics", Addison-Wesley, Reading, Mass., 1960, p 313.

(9) R. H. Fowler, "Statistical Mechanics", Cambridge University Press, Cambridge, England, 1936, p 286.

(10) D. Henderson and S. G. Davison, in "Physical Chemistry, an Advanced Treatise", Vol. II, H. Eyring, Ed., Academic Press, New York, N.Y., 1967, p 359.

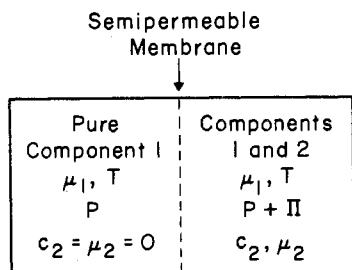(11) N. Davidson, "Statistical Mechanics", McGraw-Hill, New York, N.Y., 1962, p 473.

(12) T. L. Hill, "Statistical Mechanics", McGraw-Hill, New York, N.Y., 1956, p 190.

(13) Reference 8, p 304.

Figure 1. Osmotic equilibrium for the McMillan–Mayer theory. The solute is component 2 and the total pressure on the solution in the right side is $P + \pi$.

osmotic equilibrium with pure solvent through a solvent-permeable, solute-impermeable membrane; see Figure 1. They showed that the entire array of equations for molecules in imperfect gases (fluids) applied to the solute in this system provided one used potentials of mean force at infinite dilution in the solvent and interpreted the pressure as the osmotic pressure. There are some questions of convergence for long-range electrical forces, but these have been answered.

Hill[15] gives both a simplified and a more rigorous account of the McMillan–Mayer theory.

Rasaiah and Friedman[16] were the first to take full advantage of this theory for application to electrolytes. The pressure equation now yields the osmotic coefficient for the solution

$$\phi - 1 = (\Pi/ckT) - 1$$

$$= -(6ckT)^{-1} \sum_i \sum_j c_i c_j \int_0^\infty r \frac{\partial u_{ij}}{\partial r} g_{ij}(r)(4\pi r^2)dr \quad (5)$$

where c_i is the concentration of the ith ion and c is the total concentration of solute species, $c = \sum c_i$. Once ϕ is known as a function of concentration, the activity coefficient can be calculated from the Gibbs–Duhem equation.

It should be noted (see Figure 1) that these functions apply to the solution under a pressure equal to its own osmotic pressure plus the pressure on the pure solvent rather than to the usual standard pressure of 1 atm. Friedman[17] has discussed the conversion between these states and provides the needed equations. The differences are negligible for our purposes.

Rasaiah and Friedman[16] also derived the analogue of the compressibility equation for the electrolyte system and used it to verify certain calculations.

Although the complete theory underlying eq 5 is complex and lengthy, it is rigorous and provides a valid means to obtain thermodynamic properties provided both the potentials of mean force and the radial distribution functions are available.

Radial Distribution Functions

We turn now to the problem of obtaining the radial distribution functions from the potentials. The basic equation of statistical mechanics[18] for the radial dis-
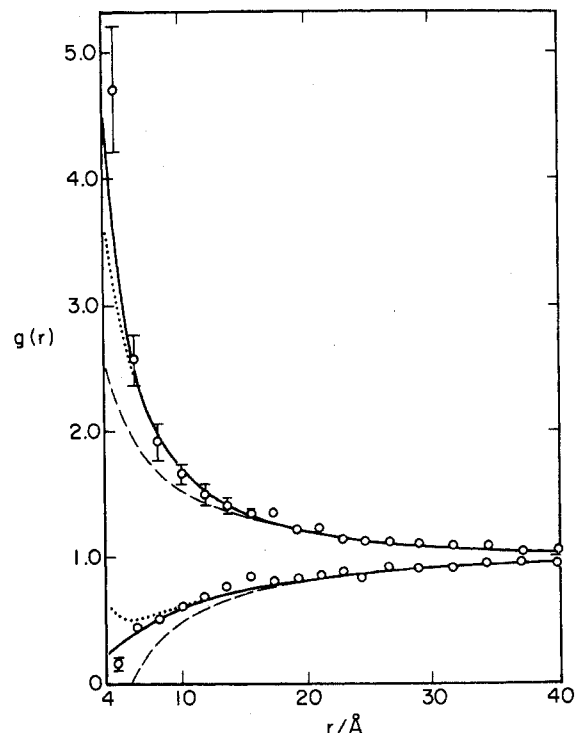
Figure 2. The radial distribution functions (g_{+-} above, $g_{++} = g_{--}$ below) for 0.00911 M aqueous solution (1–1 type, $a = 4.25$ Å). The points are Monte Carlo calculations, the solid curve is the exponential D–H expression, the dotted and dashed curves are, respectively, the three-term and two-term D–H expressions.

tribution function (or pair correlation function) yields for a pair of like ions in a binary electrolyte

$$g_{ii}(r) =$$

$$V^2 \frac{\int \ldots \int \exp(-\Phi/kT)dr_{i3} \ldots dr_{iN} dr_{j1} \ldots dr_{jN}}{\int \ldots \int \exp(-\Phi/kT)dr_{i1} \ldots dr_{iN} dr_{j1} \ldots dr_{jN}} \quad (6)$$

where Φ is the total potential energy for all pairs of ions interacting in accordance with the potentials $u_{ij}(r)$ of eq 1. Note that the numerator differs only in that the first two coordinates for the ith type of ions are not integrated.

For the radial distribution function for a pair of unlike ions the analogous equation is

$$g_{ij}(r) =$$

$$V^2 \frac{\int \ldots \int \exp(-\Phi/kT)dr_{i2} \ldots dr_{iN} dr_{j2} \ldots dr_{jN}}{\int \ldots \int \exp(-\Phi/kT)dr_{i1} \ldots dr_{iN} dr_{j1} \ldots dr_{jN}} \quad (7)$$

where now the integral in the numerator omits the integration over the coordinates of one ion of each type.

These basic equations may be evaluated directly by Monte Carlo methods.[19] Such calculations involve numerical approximations and various technical features, but they may be made as accurate as desired with the expenditure of sufficient care and computer time. Vorontsov-Veliaminov et al.[20,21] and Card and Valleau[22] have made significant Monte Carlo calculations for electrolytes. We shall present the results of Card and

(14) W. G. McMillan and J. E. Mayer, *J. Chem. Phys.*, **13**, 276 (1945).

(15) T. L. Hill, ref 8, p 341, is the simplified account of McMillan–Mayer theory. A more rigorous account is in ref 12, p 262. See also Andersen, ref 4, p 7.

(16) J. C. Rasaiah and H. L. Friedman, *J. Chem. Phys.*, **48**, 2742 (1968); **50**, 3965 (1969).

(17) H. L. Friedman, *J. Chem. Phys.*, **32**, 1351 (1960); see also the appendix in ref 29 and ref 3, p 207.
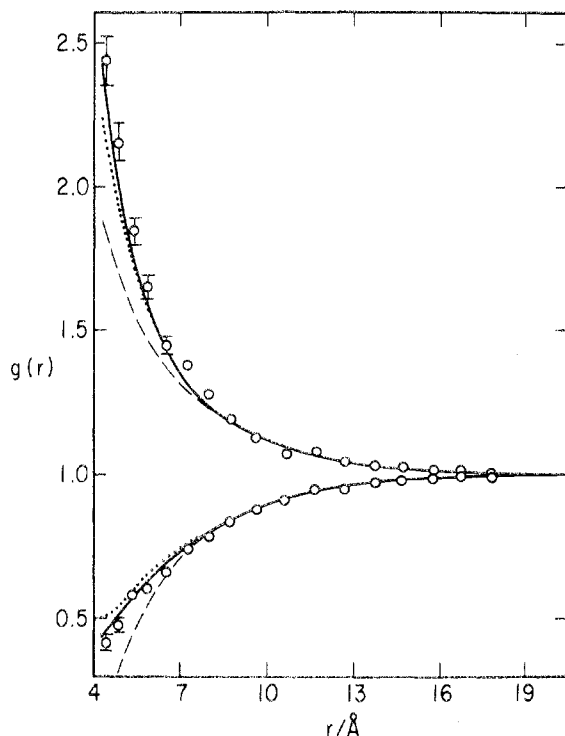
(18) See Davidson, ref 11, Chapter 2, or Hill, ref 8, Section 17-4.

(19) J. A. Barker and D. Henderson, *Rev. Mod. Phys.*, **48**, 587 (1976).

(20) P. N. Vorontsov-Veliaminov, A. M. Eliashevich, and A. K. Kron, *Elektrokhimaya*, **2**, 708 (1966).

(21) P. N. Vorontsov-Veliaminov and A. M. Eliashevich, *Elektrokhimaya*, **4**, 1430 (1968); *Strukt. Rol. Vody. Zhivom. Org.*, **2**, 99 (1968).

(22) D. N. Card and J. P. Valleau, *J. Chem. Phys.*, **52**, 6232 (1970).

Figure 3. The radial distribution functions for 0.425 M solution; other aspects the same as in Figure 2.

Valleau which are based on the primitive model appropriate for aqueous solutions at room temperature and for a uni-univalent solute with $a = 4.25$ Å. The results are shown as points on Figures 2 and 3.

In addition to the combination of Monte Carlo calculations with eq 5 to obtain thermodynamic quantities, the method of "molecular dynamics" would also provide a rigorous numerical solution for an electrolyte within the McMillan–Mayer solution theory framework. In this method[19] the motions of a number of particles are followed by integration of the equations of motion subject to the potentials assumed. Then the desired quantities are determined from averages over the motion. It has been successfully applied to nonelectrolyte fluids with results comparable to those of the Monte Carlo method, and an exploratory calculation has just been reported for an electrolyte.[23]

While we shall presently mention some other recent theories, let us first compare results which can be derived from the Debye–Hückel treatment with the Monte Carlo results.

In the conventional Debye–Hückel treatment[24] the concentration of ionic species i near an ion of species j is given by the Boltzmann expression

$$c_i' = c_i \exp(-z_i e \psi_j/kT) \tag{8}$$

where c_i is the average concentration and $\psi_j(r)$ is an electrostatic potential associated with the ion j. This implies a radial distribution function

$$g_{ij}(r) = \exp(-z_i e \psi_j(r)/kT) \tag{9}$$

The Debye–Hückel treatment then combines the concentrations of all charged species to yield the charge density

(23) P. Turq, F. Lantelme, and H. L. Friedman, *J. Chem. Phys.*, **66**, 3039 (1977).
(24) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions", Butterworths, London, 1955; revised 1959, Chapter 4.

$$\rho_j(r) = \sum_i z_i e c_i'$$

$$= \sum_i z_i e c_i \exp(-z_i e \psi_j/kT) \tag{10}$$

The exponentials are expanded, yielding

$$\rho_j(r) = e\sum_i z_i c_i - (e^2 \psi_j/kT) \sum_i z_i^2 c_i +$$

$$(e^3 \psi_j^2/2k^2 T^2)\sum_i z_i^3 c_i. \ldots \tag{11}$$

From electrical neutrality the first term on the right is zero. The second term is clearly nonzero and is the only term used for ρ in the usual treatment, where the Poisson equation now takes a linear form

$$\nabla^2 \psi = -(4\pi/D)\rho$$

$$= \kappa^2 \psi \tag{12}$$

Appropriate boundary conditions then yield

$$\psi_j(r) = \frac{z_j e \exp(\kappa a)}{D(1 + \kappa a)} \frac{\exp(-\kappa r)}{r} \tag{13}$$

where

$$\kappa^2 = (4\pi e^2/DkT)\sum_i z_i^2 c_i \tag{14}$$

and a is the diameter of the hard core in eq 2.

Let us return to the distribution function which now becomes

$$g_{ij} = \exp(-q_{ij}) \tag{15}$$

$$q_{ij} = \frac{z_i z_j e^2 \exp(\kappa a)}{DkT(1 + \kappa a)} \frac{\exp(-\kappa r)}{r} \tag{16}$$

Clearly the required symmetry to exchange of i and j is present. However, for the Poisson equation the exponentials in ρ were expanded[25] and only the second term was used. Thus it can be argued that it is inconsistent to retain the exponential form for g_{ij}. Since this entire treatment is approximate, this objection has limited significance. Alternatively one may note that the third term in the expanded form for the charge density is zero for a symmetrical electrolyte. Thus, without any inconsistency for symmetrical electrolytes, one may retain the third term in the expansion and the corresponding expression for the radial distribution function is

$$g_{ij}(r) = 1 - q_{ij} + q_{ij}^2/2 \tag{17}$$

The original Debye–Hückel approximation can be regarded as the first two terms

$$g_{ij}(r) = 1 - q_{ij} \tag{18}$$

In Figures 2 and 3 we compare the exponential form (15), the three-term form (17), and the two-term form (18) for g_{ij} with the "exact" results of the Monte Carlo calculations for the case $a = 4.25$ Å and solvent properties for water at 25 °C. For the dilute solution, 0.00911 M, in Figure 2 one notes that the exponential form is, indeed, an excellent approximation which agrees with the Monte Carlo results essentially within the computational uncertainty of the latter. The three-term "extended D–H" approximation agrees very well except for r values just above a. Here g_{+-} is a little too small and g_{++} shows a false increase as r decreases below 6 Å.

(25) There is an extended literature on solution of the Poisson equation without the linear approximation; see D. M. Burley, V. C. L. Hutson, and C. W. Outhwaite, *Mol. Phys.*, **23**, 867 (1972), and references cited therein.

The two-term approximation is satisfactory for large r but deviates considerably at small r. The function for like ions even goes negative below about 6 Å; this is quite unacceptable. Since the three-term formula involves no inconsistency with the original derivation (for symmetrical electrolytes), there would appear to be no reason for further use of the much poorer two-term approximation.

Figure 3 gives the same functions for a moderately concentrated solution, 0.425 M. The same comments apply as for the dilute solution, although the differences in the various D–H approximations are somewhat reduced.

We can now bypass the many objections[2] to the formulation of D–H theory by noting that it yields good agreement with the correct radial distribution function, particularly in the exponential form.

In applying any of these radial distribution functions with hard-core potentials to eq 5, one faces an anomaly in the integral at $r = a$ where $\partial u / \partial r$ is infinite. This has been resolved mathematically and yields[26] for the osmotic coefficient

$$\phi - 1 = (\Pi/ckT) - 1$$

$$= (6ckT)^{-1} \sum_i \sum_j c_i c_j \int_a^\infty r \frac{\partial u_{ij}}{\partial r} g_{ij}(4\pi r^2)dr$$

$$+ \frac{2\pi a^3}{3c} \sum_i \sum_j c_i c_j g_{ij}(a) \tag{19}$$

where $g_{ij}(a)$ is the value of $g_{ij}(r)$ for r infinitesimally greater than a.

For the Monte Carlo calculations $g_{ij}(r)$ must be extrapolated to $r = a$; this adds some numerical uncertainty. The various D–H expressions are unambiguous for $g_{ij}(a)$; hence, there is no difficulty in evaluating the expressions in eq 19. Also there is some cancellation of the errors of the $g(a)$ values for the three-term approximation. For the exponential form, the integral can be evaluated only numerically, but for the two- or three-term approximations, eq 18 and 17, the integration yields simple functions. The latter result is

$$\phi - 1 = \frac{-\kappa^3}{24\pi c(1 + \kappa a)} +$$

$$c\left[\frac{2\pi a^3}{3} + \frac{\kappa^4 a}{48\pi c^2(1 + \kappa a)^2}\right] \tag{20}$$

It is convenient to define

$$w = \sum_i z_i^2(c_i/c)$$

which is an average value of z_i^2 and becomes z^2 for a symmetrical electrolyte. Then

$$\phi - 1 = \frac{-wl\kappa}{6(1 + \kappa a)} +$$

$$c\left[\frac{2\pi a^3}{3} + \frac{\pi a w^2 l^2}{3(1 + \kappa a)^2}\right] \tag{22}$$

where $l = e^2/DkT$ and $\kappa^2 = 4\pi lwc$. In both eq 20 and 22 the first term, which contains the D–H limiting law, arises from the second term in the expansion of g_{ij}. This is the term that leads to nonzero charge density; it can be thought of as the primary electrostatic term. The
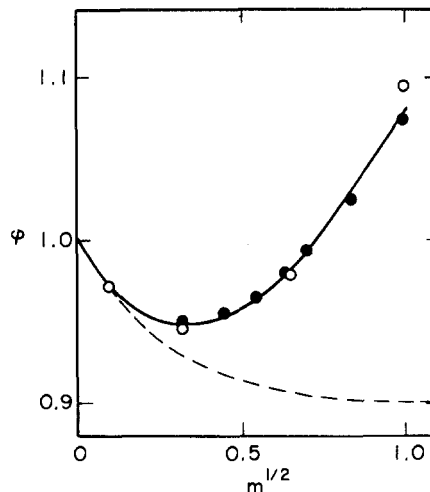
(26) See Barker and Henderson, ref 19, p 591.

Figure 4. The osmotic coefficient for a 1–1 type aqueous electrolyte at 25 °C. Solid circles are experimental values for HBr. Open circles are calculated by the Monte Carlo method ($a = 4.25$ Å). The solid curve is based on the three-term D–H expression and the "pressure" equation while the dashed curve is the traditional D–H expression based on the "charging process".

first term, unity, in the expressions for g_{ij} yields the term $c(2\pi a^3/3)$ which would be the kinetic effect of the hard core in the absence of electrical effects. The last term in (20) and (22) arises from the third term in the expressions for g_{ij} and would be absent if only the D–H two-term expression were used. This term gives the increased hard-core repulsive effect caused by the electrical interactions.

Figure 4 shows, for the case $a = 4.25$ Å and a 1–1 aqueous electrolyte, the osmotic coefficient from the Monte Carlo calculations, that from the three-term D–H approximation of eq 22, and that from the original D–H formula which was derived by a charging process

$$\phi - 1 = -(\kappa^3/24\pi c)\sigma(\kappa a) \tag{23}$$

where

$$\sigma(x) = (3/x^3)[1 + x - (1 + x)^{-1} - 2\ln(1 + x)] \tag{24}$$

This model fits the observed data for HBr very well, and the experimental osmotic coefficients for HBr are also shown on Figure 4. The three-term D–H expression is an excellent approximation. The original D–H equation is a useful approximation, however, only below 0.01 M. The three-term D–H expression for g_{ij} had been recognized earlier[24] as a good approximation, but so long as the charging process was used to calculate thermodynamic properties it did not yield any improvement over the two-term expression.

Thermodynamic equations may be used to transform eq 22 to the forms for the activity coefficient and the excess Gibbs energy. With the assumption that concentration is proportional to molality, the results are

$$\ln \gamma_{\pm} = -\left(\frac{wl}{6}\right)\left[\frac{2\kappa}{1 + \kappa a} + \frac{1}{a}\ln(1 + \kappa a)\right] +$$

$$c\left[\frac{4\pi a^3}{3} + \frac{\pi a w^2 l^2}{3(1 + \kappa a)^2}\right] \tag{25}$$

$$G^{ex}/ckT = -\frac{lw}{6}\left[\frac{\kappa}{1 + \kappa a} + \frac{1}{a}\ln(1 + \kappa a)\right] +$$

$$c\left(\frac{2\pi a^3}{3}\right) \tag{26}$$
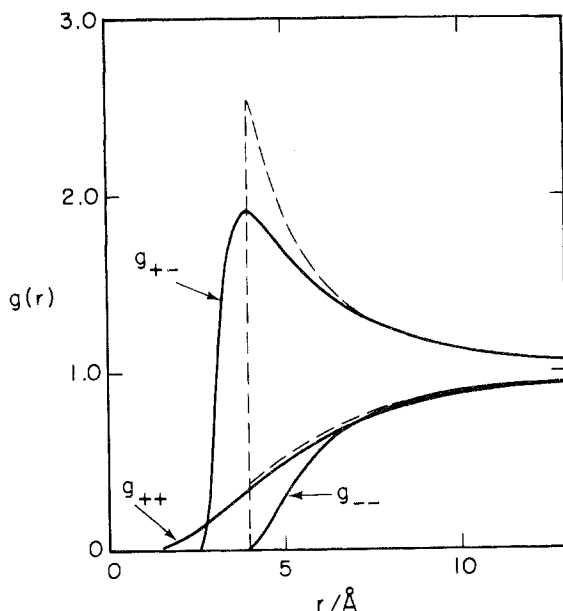
Figure 5. Radial distribution functions for LiBr at 0.4 M. The solid curves are based on a refined model, see text; the dashed curves on the primitive model.

In addition to the Monte Carlo method, which is exact in principle, a number of approximate equations or methods[27] have been proposed and applied recently to the calculation of the radial distribution functions for electrolytes. While these yield equations which usually require less computation than the Monte Carlo method, their derivation is more complex and the evaluation of possible errors from the approximations is even more complex. Indeed, now that Monte Carlo solutions are available, these other methods are tested[28] by comparison with the Monte Carlo results for identical potential models.

The principal advantage of these other methods arises from the possibility of exploring a variety of interionic potentials with less computational cost than the Monte Carlo method would require. This has been done by Friedman and Rasaiah and collaborators.[29,30] They used the "hypernetted chain equation" and tested its accuracy in various ways, including comparison with Monte Carlo results.[28] We shall not discuss these results in detail but show in Figure 5 the radial distribution function for LiBr obtained by Ramanathan and Friedman.[29,31] They assumed the bare-ion repulsive potentials obtained in studies of ionic crystals and adjusted the potentials at intermediate distances to obtain agreement with experiment. The final potentials are smooth functions of radius. It was found that the selection of the three potentials (Li^+–Li^+, Li^+–Br^-, and Br^-–Br^-) at intermediate distances was not unique; many alternatives fitted the osmotic coefficients equally well.

For comparison, the D–H exponential radial distribution functions are also shown in Figure 5 for a value of $a = 4.0$ Å which fits the experimental data for LiBr reasonably well. There are Monte Carlo results[21] for

$a = 4.0$ Å but not at the molality 0.4 of the other curves in Figure 5. The Monte Carlo results at other concentrations, however, show agreement with the D–H exponential functions.

Equations for Use in Chemical Thermodynamics

For chemical thermodynamic calculations for electrolytes it is usually preferable to use semiempirical equations rather than purely theoretical equations since the latter are either very complex or contain significant approximations. Also at present any theoretical equation is based on a model whose accuracy is subject to argument. The semiempirical equations include the D–H limiting law and such other features taken from theory as seem useful.

The traditional D–H result, eq 23 for ϕ or the more familiar

$$\ln \gamma_\pm = -w l \kappa / 2(1 + \kappa a) \qquad (27)$$

is seen from Figure 4 to become inadequate even at very low concentration. Equation 27 is commonly extended with a term analogous to the second term in eq 20 and 22. After rearrangement and for a symmetrical electrolyte, this becomes

$$\ln \gamma_\pm = -\frac{z^2 A_\gamma I^{1/2}}{(1 + \rho I^{1/2})} + 2\beta m \qquad (28)$$

where A_γ is the traditional D–H parameter, m is the molality, and I is the ionic strength. Also $\rho = \kappa a / I^{1/2}$ and β are parameters generally related to the diameter of the ions. The corresponding form for the osmotic coefficient is

$$\phi - 1 = -z^2 A_\phi I^{1/2} \sigma(\rho I^{1/2}) + \beta m \qquad (29)$$

Guggenheim[32] proposed taking $\rho = 1$ for all solutes and letting the specific properties of each solute appear in β. This system has been widely used[33] with considerable success. But with β a constant, this equation still does not fit the better quality data within experimental accuracy over a substantial range in m.

The needed improvement[6] is suggested by the last term in eq 20, 22, and 25. One notes that this term which decreases with increasing ionic strength (increasing κ) is added to the constant term, $2\pi a^3/3$, in (22) to yield the quantity equivalent to β in eq 28 and 29. A directly analogous form would be

$$\beta = \beta^{(0)} + [\beta^{(1)}/(1 + \alpha I^{1/2})^2] \qquad (30)$$

while a somewhat simpler form with similar properties is

$$\beta = \beta^{(0)} + \beta^{(1)} \exp(-\alpha I^{1/2}) \qquad (31)$$

These forms were tested[6] with a wide range of accurate osmotic coefficient data, and the second (eq 31) was found to be slightly better. In each case $\beta^{(0)}$ and $\beta^{(1)}$ were freely adjusted for each electrolyte while α was optimized but to a single value for all solutes. Similarly the two forms for the electrostatic term, in eq 22 and 23, were compared[6] and the more recent (eq 22) was slightly superior. The resulting practical equation for

(27) See ref 16; also several cited in ref 4 and 5.
(28) J. C. Rasaiah, D. N. Card, and J. P. Valleau, *J. Chem. Phys.*, **56**, 248 (1972).
(29) P. S. Ramanathan and H. L. Friedman, *J. Chem. Phys.*, **54**, 1086 (1971).
(30) J. C. Rasaiah, *J. Chem. Phys.*, **52**, 704 (1970).
(31) Numerical values of the distribution functions supplied by Professor H. L. Friedman.

(32) E. A. Guggenheim, *Phil. Mag.*, [7] **19**, 588 (1935); E. A. Guggenheim and J. C. Turgeon, *Trans. Faraday Soc.*, **51**, 747 (1955).
(33) K. S. Pitzer and L. Brewer, revised edition of "Thermodynamics" by G. N. Lewis and M. Randall, McGraw-Hill, New York, N.Y., 1961.

the osmotic coefficient of a single symmetrical electrolyte is

$$\phi - 1 = -z^2 A_\phi I^{1/2}/(1 + bI^{1/2}) + m[\beta^{(0)}{}_{MX} + \beta^{(1)}{}_{MX} \exp(-\alpha I^{1/2})] + m^2 C^\phi{}_{MX} \tag{32}$$

where b is kept the same for all solutes with a best value of 1.2, α is 2.0 for all 1–1 and many other electrolytes, and an additional term in m^2 has been added to extend the equation to very high concentrations. Equation 32 fits the experimental osmotic coefficients for over 200 pure aqueous electrolytes essentially within experimental accuracy.[34]

The corresponding equation for the activity coefficient is

$$\ln \gamma_{\pm} = -z^2 A_\phi [I^{1/2}/(1 + bI^{1/2}) + (2/b) \ln (1 + bI^{1/2})] + m\{2\beta^{(0)}{}_{MX} + (2\beta^{(1)}{}_{MX}/\alpha^2 I)[1 - (1 + \alpha I^{1/2} - \alpha^2 I/2) \exp(-\alpha I^{1/2})]\} + m^2(3C^\phi{}_{MX}/2) \tag{33}$$

These equations become only a little more complex for unsymmetrical solutes. Even for mixed electrolytes[35] the corresponding equations are relatively simple, and all of the more important parameters are determined from the data on single solutes. The result is an extremely general and compact representation of the known properties of aqueous electrolytes which also has the capacity of prediction of properties of mixtures to useful accuracy.

Summary

First we recall that there is not yet an adequate theory for water (or for other ionizing solvents); hence any theory must start with assumptions concerning the interionic potentials of mean force in the solvent. From that point, however, we now have an exact theory which can be applied numerically to obtain as accurately as desired the interionic radial distribution functions and thermodynamic properties.

There is no longer any need to speculate about the net inaccuracies in the Debye–Hückel theory, or extensions thereof, or of other approximate theories. These questions can be answered by comparison with calculations based on exact theories. The original D–H expression which contained no contribution from the direct effects of short-range forces is seriously inadequate outside of the range of the limiting law. But the D–H calculation of interionic distribution functions is found to be surprisingly accurate in either the exponential or three-term expansion form (at least for the model for aqueous 1–1 electrolytes with ionic diameters near 4 Å). The three-term expansion form of these distributions can be used in the "pressure" equation to yield a simple but relatively accurate expression for the osmotic coefficient up to about 1 M for this model.

It is now feasible also to investigate more realistic interionic potentials. This should be very valuable in the future, although the requirement of fitting osmotic and activity coefficient data is not likely to yield a unique determination of the short-range potential.

The recent theory suggested important improvements in the form of semiempirical equations. Reasonably simple equations are now available which fit within experimental accuracy a wide variety of data on pure and mixed electrolytes. Also, since the more important parameters are determined from the single solutes, the equations allow prediction of the properties of mixtures.

(34) K. S. Pitzer and G. Mayorga, *J. Phys. Chem.*, **77**, 2300 (1973); *J. Soln. Chem.*, **3**, 539 (1974).
(35) K. S. Pitzer and J. J. Kim, *J. Am. Chem. Soc.*, **96**, 5701 (1974).