THEORIES OF CONCENTRATED ELECTROLYTES

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The kinetic theory of electrolytes aims to account quantitatively for the thermodynamic and other properties of electrolytic solutions from reasonable assumptions about the forces between the ions. The approximate theory developed by Debye and Hückel for the effects of Coulomb forces is generally recognized as sound, and the consequent theoretical limiting laws for low concentrations of ions have been amply verified by experiments. For the extension of this theory to concentrated solutions, more accurate computations of the Coulomb forces are needed; in addition, it becomes necessary to make more specific assumptions about the non-Coulomb forces, which are important for small distances between the ions. This theory of concentrated electrolytes has met with many difficulties; in part, conflicting results have been deduced.

GENERAL STATISTICAL METHODS

Before we examine the different contributions to the field, we shall review briefly some of the common methods for computing thermodynamic functions from molecular mechanical models, and show the connection with the fundamental principles of statistical mechanics.

The "adiabate principle," which will be our main tool, takes its simplest form for a thermally isolated system, namely, the following relation between the energy E and the "reversible work" δW:

$$\delta E = \delta W = -\overline{K}\,\delta a = \overline{\partial E/\partial a}\,\delta a \tag{1}$$

where δa denotes the change of any parameter a (e.g., volume, molecular size, electric charge, etc.), and the average of the corresponding force K is taken over all phases of the molecular motion.

If a system is not thermally isolated but, instead, is kept at a constant temperature T, we must replace E by the "free energy"

$$F = E - TS$$

where S is the entropy, now variable, and the relation given by 1 is replaced by

$$\delta F = \delta W = -\overline{K}\,\delta a = \overline{\partial E/\partial a}\,\delta a \tag{2}$$

For averages taken at a given temperature T, it is legitimate to employ the "canonical ensemble" of Gibbs. The "phase-space" Ω

$$d\Omega = dq_1\,dq_2 \ldots dq_f\,dp_1\,dp_2 \ldots dp_f$$

(q = coördinate, p = impulse) is occupied with the local density

$$\exp\,((F - \epsilon)/kT) \tag{3}$$

where the energy ϵ is now a function of the coördinates and impulses:

$$\epsilon = \epsilon\,(q_1, \ldots q_f;\ p_1, \ldots p_f)$$

This function determines the mechanical properties of the system. The free energy F itself is determined directly by the condition

$$\int \exp\,((F - \epsilon)/kT)\,d\Omega = 1 \tag{4}$$

As a rule, certain conventional factors involving numbers of particles, Planck's constant, etc., are added to equation 4; these will be constant throughout our considerations and so need not concern us.

For a given temperature T, we want to know how F depends on parameters a_1, a_2, ... ,which enter into the function

$$\epsilon = \epsilon(q_1, \ldots q_f;\ p_1, \ldots p_f;\ a_1, a_2, \ldots)$$

According to equation 4, for constant T,

$$\int [\delta F - \delta\epsilon]\,\exp\,((F - \epsilon)/kT)\,d\Omega = 0$$

or

$$\delta F = \int \left[\frac{\partial\epsilon}{\partial a_1}\,\delta a_1 + \frac{\partial\epsilon}{\partial a_2}\,\delta a_2 + \ldots\right] \exp\,((F-\epsilon)/kT)\,d\Omega = -\overline{K_1}\,\delta a_1 - \overline{K_2}\,\delta a_2 - \ldots \tag{5}$$

which amounts to a verification of the formula 4 for F in terms of the canonical distribution ("phase integral"). However, besides verifying the statistical representation of macroscopic reversible work, our derivation also shows that, if the general premises of the statistical theory are correct, similar reasoning may be applied with equal confidence to the purely fictitious operation of changing any molecular parameter.

The canonical distribution is a generalization of the Maxwell-Boltzmann distribution law to the entire phase-space. We shall show next how the Maxwell-Boltzmann formula can be generalized, for a reduced number of degrees of freedom, to the case of fluctuating forces. That is, we consider a subspace, for example dq_1, of the entire phase-space

$$d\Omega = dq_1\, d\Omega'$$

(we may of course equally well take out several factors: dq_1, dq_2, ... of $d\Omega$), and we want to compute the probability for finding q_1 in the range $q_1' < q_1 < q_1' + \Delta\, q_1$. This probability we denote by

$$f(q_1')\,\Delta q_1 = \exp(-\,w(q_1')/kT)\,\Delta q_1$$

and according to equation 3,

$$f(q_1) = \int \exp\,((F - \epsilon)/kT)\,d\Omega' = \exp\,(-\,w(q_1)/kT) \tag{6}$$

where now

$$\int \exp\,(\,(F + w(q_1) - \epsilon(q, p, a)\,)/kT)\,d\Omega' = 1 \tag{7}$$

In these integrations, q_1 is kept constant, otherwise every formula is analogous to the case of the entire phase integral. In effect, we are now treating q_1 like a parameter (a); the advantage of this treatment is that the analog of equation 5 still holds. As before

$$\frac{\partial}{\partial a}\,(F + w(q_1)\,) = \overline{\partial\epsilon/\partial a}' \tag{8}$$

for any parameter a, while as regards q_1 itself, it does not enter into F, so that

$$\partial w/\partial q_1 = \partial(F + w(q_1)\,)/\partial q_1 = \overline{\partial\epsilon/\partial q_1}' \tag{9}$$

Here we have shown that the potential $w(q_1)$, which (for the case of fluctuating forces) replaces the energy in the Maxwell-Boltzmann distribution, is *the potential of the average force.* This result was used by Einstein and Smoluchowski in the theory of fluctuations.

At times it may be convenient to consider some of the parameters a as variables in the computation of $w(q_1)$. The procedure is straightforward: Since F depends only on a, we have

$$w(q_1'',a') - w(q_1',a') = [F(a') + w(q_1'',a')] - [F(a') + w(q_1',a')] =$$

$$= \int_{(q_1',\, a')}^{(q_1'',\, a')} [\,(\overline{\partial\epsilon/\partial a})\,\delta a + (\overline{\partial\epsilon/\partial q_1})\,\delta q_1] \tag{10}$$

THE COMPUTATION OF THE COULOMB ENERGY

By the methods outlined in the preceding section, it is fundamentally possible to calculate the deviations from the laws of ideal solutions whenever adequate information about the forces between the *solute* molecules is available. Certain rather trivial distinctions between the "free energies" at constant pressure *viz.* volume etc. should be observed; the complications in question, which recur everywhere in the kinetic theory of real solutions, are more tedious than important, and we shall content ourselves here with a reference to Bjerrum's discussion (1) of the corresponding thermodynamic distinctions.

The electrostatic contribution to the free energy of an electrolyte can be computed if the average potential $\psi^*(\eta)$ due to other ions at the point of an ion of charge η is known (as a function of η and of the composition of the solution), because then, on the basis of the preceding general considerations,

$$F_{\mathrm{el}} = \sum_{i=1}^{N} \int_{\eta=0}^{\eta=e_i} \psi^*(\eta)\,\mathrm{d}\eta \tag{11}$$

where the sum is extended over all the ions present. The function $\psi^*(\eta)$ depends on the instantaneous composition of the solution, which changes during the charging process, and on the momentary charge η of a selected ion. The ions may be charged simultaneously or one at a time, in arbitrary sequence; the result should be independent of any such choice of the charging process, provided that the functions $\psi^*(\eta)$ are correct, or at least consistent. It was pointed out by Güntelberg (2) that the work of charging one ion in a given solution yields directly the electrostatic contribution to the thermodynamic potential (partial free energy) of that ion:

$$\mu_{i\mathrm{el}} = \partial F_{\mathrm{el}}/\partial N_i \int_0^{e_i} \psi^* (\eta)\, d\eta \tag{12}$$

The derivation from equation 11 is obvious. Only one precaution must be observed in using either equation 11 or 12: The electrostatic free energy F_{el} may not represent the entire deviation from the laws of ideal solutions, because non-Coulomb forces may also cause a contribution to F (and to μ_i).

The main problem in the theory of strong electrolytes is the calculation of $\psi^*(\eta)$. Debye and Hückel (3) worked out the first successful method of attack, and up to the present no fundamental improvement has been introduced. They assume that the average concentration $n_{ji}(r)$ of ions of the species i at a distance r from a given ion of the kind j is related to the mean potential $\psi_j(r)$ at this distance from the j ion by Boltzmann's equation

$$n_{ji}(r) = n_i \exp\,(-\, e_i\psi_j/kT) \tag{13}$$

and with the aid of Poisson's equation

$$\mathrm{div\ grad}\ \psi_j = -\frac{4\pi}{D} \sum_i n_{ji}e_i \tag{14}$$

obtain an equation for ψ_j alone

$$\mathrm{div\ grad}\ \psi_j = -\frac{4\pi}{D} \sum_i n_i e_i \exp(-\, e_i\psi_j/kT) \tag{15}$$

This "Poisson-Boltzmann" equation was not solved completely by Debye and Hückel; they were content with the approximation

$$\exp\,(-\, e_i\psi_j/kT) \sim 1 - (e_i\psi_j/kT) \tag{16}$$

which leads to the approximate equation

$$\operatorname{div}\operatorname{grad}\psi_j = \kappa^2\psi_j \tag{17}$$

$$\kappa^2 = \frac{4\pi}{DkT}\sum_i n_i e_i^2$$

and its solution

$$\psi_j = \frac{e_j}{D(1+\kappa a)}\,\frac{\exp\left(\kappa(a-r)\right)}{r} \tag{18}$$

where a denotes the least distance of approach of (any) two ions. The potential of interaction becomes proportional to the charge:

$$\psi^*(\eta) = -\kappa\eta/D(1+\kappa a) \tag{19}$$

The approximation of formula 16 is poor for small distances r (because $\psi \sim 1/r$), and the efforts of later workers have largely been directed towards the elimination of this error.

Partly for this purpose, and partly in order to consider strong and weak electrolytes from a common point of view, Bjerrum (4) improved formula 16 by separate consideration of the cases where two ions (of opposite charges) come closer than a certain distance q:

$$q = -e_j e_i/2DkT > a > 0$$

Such couples of ions Bjerrum treats as undissociated molecules, *viz.*, particles of charge $(e_j + e_i)$, and he corrects the concentrations n_1, n_2, ... of "free" ions accordingly. For distances $r > q$, he retains the approximate equation 17, with k given by the corrected ion concentrations. In terms of Gibbs' phase integral (formula 4), one may say that Bjerrum applies different approximations to different regions of the space in evaluating the integral. Bjerrum was able to represent a more extensive range of experimental data than was possible with equation 19 as used by Debye and Hückel. For example, in order to describe the behavior of certain (relatively weak) electrolytes by equation 19, impossible values of a (<0) are required; but the adaptation of Bjerrum's theory leads to reasonable ionic diameters a.

H. Müller (7, 8) and Gronwall, La Mer, and Sandved (9) undertook the task that neither Debye and Hückel nor Bjerrum had attempted, of solving the complete Poisson-Boltzmann equation, after Gronwall (5) and La Mer and Mason (6) had made some advances in this direction. Recently, the computations for asymmetrical electrolytes have been completed by La Mer, Gronwall, and Greiff (10). Numerical integration or some method of successive approximation must be used; the preference is merely a matter of convenience.

While all these computations are based on the same equation and each one is sound, nevertheless one point of controversy remains. H. Müller computed the thermodynamic functions from the potentials by the easiest method, that is the Güntelberg principle, equation 12. Gronwall, La Mer, and Sandved (9) preferred the charging process used by Debye and Hückel, and pointed out that the Güntelberg method leads to somewhat different results; thereupon Müller (8) accepted their criticism and estimated his own "error," which turned out to be fairly small.

In view of the general results derived in section I, we must take a different view of Müller's "error," namely that either charging process is legitimate, but the Poisson-Boltzmann equation 15 is not entirely self-consistent. The requirement of consistency implied by equation 11 is that

$$\psi^*(e_1)\,\delta e_1 + \psi^*(e_2)\,\delta e_2 + \dots + \psi^*(e_N)\,\delta e_N = \sum_i n_i\psi^*(e_i)\,\delta e_i = \delta F_{\mathrm{el}}$$

should be a total differential, which involves reciprocal relations of the type

$$n_1\,\partial\psi^*\,(e_1)/\partial e_2 = n_2\,\partial\psi^*\,(e_2)/\partial e_1 \tag{20}$$

(The actual differential quotients and relations are complicated by the restriction $\Sigma n_i e_i = 0$, but only in a trivial fashion.)

The Poisson-Boltzmann equation 15 is not exact, because the underlying equation 13 is only an approximation. According to equations 6 and 9, we know that

$$n_{ji}(r) = n_i \exp(-\,w_{ji}\,(r)/kT) \tag{21}$$

where $w_{ji}(r)$ denotes the work expended (against the average force) in bringing two ions i and j from infinity to the distance r. Incidentally, we note that whenever a j ion is at the distance r from an ion of the kind i, then *vice versa*, whence

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

and, as one might expect

$$w_{ji}(r) = w_{ij}(r) \tag{22}$$

Equation 13, the fundamental assumption involved in the Poisson-Boltzmann equation, is obtained from equation 21 above by the approximation

$$w_{ji}(r) \sim e_i\psi_j(r) \tag{23}$$

applied to the "atmosphere" of the j ion in computing $\psi_j(r)$, while $\psi_i(r)$ is computed from the assumption.

$$w_{ji}(r) \sim e_j\psi_i(r) \tag{24}$$

We have to expect

$$e_i\psi_j(r) \neq e_j\psi_i(\mathrm{r}) \tag{25}$$

except in very symmetrical cases. Therefore we have found here, deep in the foundations of the theory, a discrepancy that reminds one quite strikingly of the discrepancy between different charging processes, when the condition for consistency of the latter is expressed by equation 20.

The approximate character of the Poisson-Boltzmann equation was recognized by Fowler (11) and by myself (12) some time before the question about the Güntelberg principle was raised. While my own reasoning was substantially that outlined above, Fowler (11) followed a different line of attack, and derived certain corrections to equation 15, which he expressed by the fluctuations of the forces on the ions, but did not actually compute. It will be shown in the Appendix to this article, that Fowler's "fluctuation-terms" are of the same order of magnitude as the maximum of the main terms in equation 15, but they are nearly cancelled (at least in some significant cases) by a supplementary term, which he omitted through an oversight. Since I do not see any way to exploit Fowler's method, I shall refer the reader to the Appendix for details.

The formulas 23 and 24 would hold exactly[1] if the mean distribution of charge in the neighborhood of a pair of ions i and j, at a distance r from each other, were always the sum of the charges induced by the two ions separately; because then the average force acting on either ion in the given configuration would correspond to the average electric field at the distance r from the other,—the force from its own atmosphere vanishes due to symmetry. This could not be true unless

$$\psi_1/e_1 = \psi_2/e_2 = \dots \tag{26}$$

for all the ions in the solution, considering that both the formulas 23 and 24 must be valid. For low concentrations, small charges, and large ionic diameters, equation 26 is indeed very nearly fulfilled; the approximate formula 18 conforms exactly to this condition. However, as soon as the higher terms in the Poisson-Boltzmann equation become important, we can no longer expect the ionic atmospheres to be additive, and then the Poisson-Boltzmann equation itself becomes unreliable.

Unfortunately, it is a very complicated task to improve this equation. I shall render here, in more definite form than before, a suggestion made by Fuoss and myself (13), which seems sound, although it would involve much tedious labor. We consider a more general distribution-function than that of equation 13, namely

$$\begin{aligned} &f_{i_1,i_2,\dots,i_\nu}(P_1, P_2, \dots, P_\nu) = \\ &= n_{i_1} n_{i_2} \dots n_{i_\nu} \varphi_\nu (P_1, e_{i_1}; P_2, e_{i_2}; \dots ; P_\nu, e_{i_\nu}) \end{aligned} \tag{27}$$

so defined that

$$f_{i_1,i_2,\dots,i_\nu} \, \mathrm{d}V_1 \, \mathrm{d}V_2 \dots \mathrm{d}V_\nu$$

equals the probability for finding ions of the species i_1, i_2, . . ., i_ν, (some of which may be identical) in volume elements dV_1,

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[1] Except for a slight modification due to short range forces (*v. i.*).

$dV_2, \ldots, dV_\nu$ surrounding the points $P_1, P_2, \ldots, P_\nu$, respectively. Moreover, let the electric field due to these ions in these positions, together with the charges which they induce in their environment possess at the point P an average potential

$$\psi_{i_1, i_2, \ldots, i_\nu}(P_1, P_2, \ldots, P_\nu; P) = \\ = \xi_\nu(P_1, e_{i_1}; P_2, e_{i_2}; \ldots ; P_\nu, e_{i_\nu}; P) \tag{28}$$

For simplicity, we assume that all the ions have the same diameter a, so that the functions f and ψ (which always refer to a given electrolyte) depend only on the points $P_1, \ldots P_\nu$ and on the charges $e_{i_1}, \ldots, e_{i_\nu}$, as indicated by the equations 27 and 28. We now focus our attention upon the functions φ_ν and ξ_ν and let these functions be defined, not only for all configurations $(P_1, \ldots, P_\nu)$, but also for any set of charges $(\eta_i, \ldots, \eta_\nu)$, whether the concentrations of ions with these particular charges be finite or zero. The Poisson equation takes the form

$$\operatorname{div}\operatorname{grad} \xi_\nu(P_1, \eta_1; P_2, \eta_2; \ldots ; P_\nu, \eta_\nu) = \\ = -\frac{4\pi}{D}\sum_i n_i e_i \frac{\varphi_{\nu+1}(P_1, \eta_1; P_2, \eta_2; \ldots ; P_\nu, \eta_\nu; P, e_i)}{\varphi_\nu(P_1, \eta_1; P_2, \eta_2; \ldots ; P_\nu, \eta_\nu)} \tag{29}$$

The main difficulty is to find a suitable generalization of the Boltzmann equation. For this purpose, we adapt our equation 10 as follows: The change of φ_ν due to a change of, say, the charge η_k of the ion at the point P_k, can be computed from the work expended in discharging that ion at some point far away from $P_1, \ldots, P_\nu$, and recharging it at the point P_k. This consideration leads to

$$-kT\frac{\partial}{\partial \eta_k}\log \varphi_\nu(P_1, \eta_1; \ldots ; P_k, \eta_k; \ldots ; P_\nu, \eta_\nu) = \\ = \partial w/\partial \eta_k = \lim_{P = P_k}\left(\xi_\nu(P_1, \eta_1; \ldots ; P_k, \eta_k; \ldots ; P_\nu, \eta_\nu; P) - \xi_1(P_k, \eta_k; P)\right) \tag{30}$$

where the definition by a limiting process is necessary on account of the self-potential η_k/Dr of the ion. The integration-constant in equation 30 will be nearly equal to

$$\prod_{i,k}\left(1 - \delta(P_i, P_k)\right) \sim \varphi_\nu(P_1, 0; P_2, 0; \ldots ; P_\nu, 0) \tag{31}$$

where

$$\delta(P_i, P_k) = \begin{cases} 1, \text{ for } r_{ik} < a \\ 0, \text{ for } r_{ik} > a \end{cases} \tag{32}$$

but on account of deviations from random arrangement due to Coulomb forces as well as short range repulsion (expressed by the diameter a), equation 31 will only be an approximation, although probably a good one. We shall leave this question aside, and return to the system formed by the equations 29, 30, 31. As it stands, this system is not determinate, but suppose that we expand φ_ν and ξ_ν in power series of $\eta_1, \eta_2, \ldots, \eta_\nu$, whereby the coefficients will be functions of the configuration $(P_1, P_2, \ldots, P_\nu)$. Next, in ξ_ν we neglect all powers of order higher than ν (in all the charges $\eta_1, \eta_2, \ldots, \eta_\nu$ together); then $\xi_{\nu+1}$ will contain only the same types of terms that are already contained in ξ_ν, and the difference between the coefficients of corresponding powers in ξ_ν and in $\xi_{\nu+1}$ will probably be small. If we may neglect this difference, we can obtain a determinate system of equations. However, it remains to investigate how the power series for the functions φ_ν should be abbreviated, if at all, in order to obtain good approximations and consistent results; (the integral of the differential equation 30 should be independent of the path of integration). Also, it seems likely that the approximation expressed by formula 31 will give rise to similar questions. These problems have not been analyzed, and I do not expect to take them up in the near future. Incidentally, the above scheme for abbreviating the power series expansions of φ_ν and ξ_ν may not be the most suitable.

I have made a few tentative computations of the corrections to be applied to equation 15, by the method outlined here. These computations indicate that as long as the difference between equation 15 and the approximate equation 17 may be regarded as a correction to the latter, *the corrections to equation 15 are of a higher order*, involving higher powers of the concentrations as well as the charges. In such cases the Poisson-Boltzmann equation 15 is probably a very good approximation.

It is worth pointing out that Bjerrum's method of computation takes into account the reduction of the effective ion concentration due to pair-wise association, perhaps the most important among the effects that are neglected by the Poisson-Boltzmann approximation. Therefore, while one may expect that the latter will be the more accurate for relatively strong electrolytes, it seems probable that Bjerrum's method will give better results in cases where the majority of the ions are present in the form of neutral pairs (corresponding to higher powers in the expansion of the Boltzmann formula).

SHORT RANGE FORCES

The fact that the electrostatic energy of the ions is finite proves that repulsive forces are superimposed on the Coulomb forces for molecular distances. So far, we have represented these repulsive forces by a minimum distance of approach, the "diameter" a, and we have considered their effects only to the extent that they limit the electrostatic energy. Now, whether there are Coulomb forces (ions) or not (molecules), repulsive forces will cause a direct contribution of their own to the free energy of any system. Incidentally, we have reasons to believe that the repulsive forces between the molecules decrease quite rapidly with the distance, even faster than the forces of ordinary cohesion. If so, then these forces can be represented for most purposes by a large discontinuity of the potential energy at some distance $r = a$, and the corresponding contribution to the free energy can be computed in terms of the excluded volume, per particle

$$\Lambda\mu_s = kT\,(\Sigma\,\frac{4\pi}{3}\,a^3/V) \tag{33}$$

where V is the total volume of the system. Van der Waals (14) derived the equivalent of this formula while dealing with intermolecular forces in gases (the well-known "b" in his equation). Boltzmann and others computed certain corrections due to the overlapping of "excluded spheres," but we shall not enter into such refinements.

The activity coefficients exp ($\Delta\mu\ kT$) of the strongest electrolytes in water increase for high concentrations and exceed unity, which means that the effect of the repulsive forces, as expressed by formula 33, outweighs that of the Coulomb attraction. The magnitude of the effect requires appreciably greater diameters *a* for the ions in solutions than in crystals; the difference must of course be ascribed to the attraction between the ions and the solvent. The *a* values derived from formula 33 need not agree exactly with those that are used in computing the Coulomb energy, because the picture of "hard billiard balls" is certainly too simple. Nevertheless, there seems to be a fairly close correspondence. A more complete study of this question might be worth while; it would show to what extent the thermodynamic functions of different electrolytes form a one-parameter family in regard to their dependence on the concentration, and give us more detailed information about the short range forces.

The assumption of short range repulsion is necessary and sufficient to explain the increase of the activity coefficients at high concentrations. The magnitude of the effect is primarily a measure for the range of the forces, as we have shown above, and the variation with the concentration is apt to be linear, no matter what the nature of the forces is. Hückel (15) suggested that the dielectric constant of electrolytes ought to decrease with increasing concentration, and he was able to show that his assumption would lead to an effect of the observed type. While this agreement is of little discriminatory value, Hückel's explanation is certainly plausible, and it seems difficult to account for the effect by any very different picture. As regards the direct evidence for the decrease of the dielectric constant, the measured variations turned out to be much larger (16) than those predicted by Hückel; but the data scatter so widely that they cannot be said to contradict a very small actual effect. A theoretical computation of the decrease in the dielectric constant to be expected from the saturation of the solvent dipoles has been made by Sack (17); again, the computed variation of the dielectric constant was much greater than what Hückel had inferred from the properties of electrolytes. My own opinion is that Hückel's relation between the dielectric constant and the thermodynamic properties of electrolytes ought to give the correct order of magnitude. If so, then it is difficult to reconcile Sack's conclusions with the observed behavior of electrolytes. Incidentally, such properties of ions as their mobilities also seem to contradict Sack's theory.

We may expect that all the various kinds of forces that are responsible for the cohesion of matter may take part in the short range interaction of ions. The forces which have been discussed here deserve special interest because they are peculiar to electrolytes, and also because they may be of somewhat greater range than ordinary molecular repulsive forces. Probably a better understanding of this phenomenon must be sought in connection with an improved theory of polar liquids. Certain properties of electrolytes seem to indicate that the electric moments of the solvent molecules are in many instances greater than is assumed by the present dipole theory.

APPENDIX

Critique of Fowler's fluctuation theory

Fowler (11) defines a function $W_{\alpha\beta}$ (r), equal to the potential of the average force acting on a pair of ions α and β at a distance r in the electrolyte. By differentiation of the Gibbs phase integral he correctly derives his equation 15, which may be written

$$\text{div}_\beta \, \text{grad}_\beta \, W_{\alpha\beta} - \frac{1}{kT} \text{grad}_\beta{}^2 \, W_{\alpha\beta} = \overline{\text{div}_\beta \, \text{grad}_\beta \, W} - \frac{1}{kT} \overline{\text{grad}_\beta{}^2 \, W} \qquad (15F)$$

Here, W denotes the potential energy of the entire collection of ions, that is, a function of the coördinates of all the ions in the system; the differentiations corresponding to grad_β, etc., are carried out with respect to the coördinates of the particular ion β, and the averages are taken for fixed positions of the two particular ions α and β.

Fowler now assumes that the only forces acting are Coulomb forces; this invites trouble, because then the phase integral does not converge. In order to make the phase integral convergent, one must introduce additional repulsive forces for small distances (*v. i.*).

For the moment, we grant Fowler's assumption; then the potential W of the forces obeys the relation

$$\mathrm{div}_\beta\, \mathrm{grad}_\beta\, \overline{W} = -(4\pi/D)\, \bar{\rho}\, e_\beta \tag{16F}$$

where $\bar{\rho}$ is an appropriate average of the charge density. Fowler obtains accordingly

$$\mathrm{div}_\beta\, \mathrm{grad}_\beta\, W_{\alpha\beta} + (4\pi/D)\, \bar{\rho}_\alpha\, e_\beta = \frac{1}{kT}\,(\mathrm{grad}_{\beta}{}^{2}\, W_{\alpha\beta} - \mathrm{grad}_{\beta}{}^{2}\, W) \tag{17F}$$

where $\bar{\rho}_\alpha$ denotes the mean charge density at the distance $r_{\alpha\beta}$ from the α ion.

We shall show that equation 16F cannot be correct. Consider the limiting case when the ions α and β are far apart; then

$$W_{\alpha\beta} = 0$$

together with its gradient etc., and the charge density $\bar{\rho}_\alpha$ induced by the α ion also vanishes, so that equation 16F may be written

$$0 = -\overline{\mathrm{grad}_{\beta}{}^{2}\, W} \tag{34}$$

This equation states that there are *no forces whatever* acting on the β ion.

In order to estimate the order of magnitude of the discrepancy, we recall that, assuming electrostatic forces only,

$$-\mathrm{grad}_\beta\, W = E_\beta\, e_\beta$$

where E_β denotes the electric field strength (due to other ions) at the point of the ion β. The density of other ions in the neighborhood of a given ion β is certainly comparable to the mean density in the solution—probably greater—and the same holds for the mean square field. That leads us to

$$\frac{1}{kT}\,\overline{\mathrm{grad}_{\beta}{}^{2}\, W} = \frac{e_\beta{}^2}{kT}\,\overline{E_\beta{}^2} \sim \frac{e_\beta{}^2}{kT}\,\overline{E^2} = \frac{e_\beta{}^2}{kT}\,\frac{1}{V}\int E^2\, \mathrm{d}V =$$

$$= \frac{e_\beta{}^2}{DkT}\,\frac{8\pi U_{e_1}}{V} \sim \frac{e_\beta{}^2}{DkT}\cdot 4\pi \sum_\gamma \frac{e_\gamma{}^2}{Da_{\beta\gamma}}$$

The integration is performed, for a representative configuration of the other ions, over all places that are accessible to a β ion,

($r_{\beta\gamma} > a_{\beta\gamma}$), and U_{el} is the total electrostatic energy (mainly self-energy) of a system of charged spheres of radius $a_{\beta\gamma}$. Taking all $a_{\beta\gamma} = a$ we obtain, in terms of the Debye-Hückel κ,

$$\frac{1}{kT}\,\overline{\mathrm{grad}_\beta^2\, W} \sim \kappa^2\, e_\beta^2/Da \tag{35}$$

which is (according to Debye and Hückel) of the same order of magnitude as the maximum of either term in the left member of equation 17F.

If we introduce repulsive forces of short range ($= a$), so as to make the phase integral converge, we may expect reasonable results. In this case equation 16F will contain an additional term

$$\overline{\mathrm{div}_\beta\, \mathrm{grad}_\beta\, W_s} \tag{36}$$

where W_s is the potential of the repulsive forces, and in general, W now contains W_s in addition to the electrostatic energy. It may be worth while to show more clearly the significance of the term given by formula 36; for this purpose, we chose a procedure that is very similar to Fowler's. Consider a given ion β in the field of N fixed ions, and let the energy of interaction between β and the other ions be

$$u = \sum_{\nu=1}^{N} \frac{e_\beta e_\nu}{r_{\beta\nu}} + u_s$$

where the function u_s is chosen in such a manner that $u = +\infty$ at all singularities and boundaries. The Coulomb energy obeys the Laplace equation; hence

$$\mathrm{div}\,\mathrm{grad}\, u = \mathrm{div}\,\mathrm{grad}\, u_s$$

We shall compute the time-average of this function on the assumption that the ion β will distribute itself among all positions according to the Maxwell-Boltzmann law. Write

$$Q = \int \exp(-u/kT)\,\mathrm{d}V$$

then

$$
\begin{aligned}
&Q\,\overline{\mathrm{div\ grad}\ u_s} = Q\,\overline{\mathrm{div\ grad}\ u} = \int \exp(-\,u/kT)\ \mathrm{div\ grad}\ u\ \mathrm{d}V = \\
&= -\int (\mathrm{grad}\ u, \mathrm{grad}\ (\exp\,(-\,u/kT))\,)\ \mathrm{d}V = (1/kT) \int \exp(-\,u/kT)\ \mathrm{grad}^2\,u\,\mathrm{d}V = \\
&= Q\,(1/kT)\ \overline{\mathrm{grad}^2\ u}
\end{aligned}
$$

The difference from equation 15F is that here we have extended the averaging over the coördinates of the β ion, while in equation 15F the ions α and β are kept fixed. This difference is immaterial when α and β are far apart, because then the position of the ion β does not matter anyway; in other words, we have shown that the terms in the right member of equation 15F actually do cancel each other when $r_{\alpha\beta} = \infty$.

The above evaluation of the right-hand member of equation 15F for the trivial case $r_{\alpha\beta} = \infty$ amounts to a reversal of Fowler's derivation, and does not bring us any nearer to the real problem of computing the same quantity for finite distances $r_{\alpha\beta}$. While it is impossible to foresee what results Fowler's method might yield with the aid of new devices, its value has not been demonstrated so far.

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