

THE INTERACTION ENERGY OF AN ION PAIR WITH OVERLAPPING HYDRATION SHELLS

I. A TRUNCATED SPHERES MODEL

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[*Manuscript received February 22, 1968*]

Summary

The energy of interaction of two univalent ions of opposite charge with overlapping hydration shells and in an aqueous medium is discussed in terms of a truncated spherical cavity model. The general trend of the effective dielectric constant considered as a function of the separation between the ion centres is found to be in agreement with some earlier results on a spheroidal cavity model. The present investigation has the advantage that the boundary of the ion pair varies continuously with separation and hence that no matching of a two-sphere model onto a spherical cavity model is required. It is found that the effective dielectric constant has a maximum value at very small ion overlap.

I. INTRODUCTION

A monovalent ion in an aqueous medium consists of a central charge surrounded by layers of water molecules in thermal motion. In the first hydration or coordination shell these molecules are strongly bound to the ion centre, while in subsequent layers the water molecules are more or less free to move about. Frank and Wen (1957) have discussed this idea in more detail. For a single ion many authors have introduced a spherical hydration shell of oriented water molecules and have treated the water outside this shell as a continuous dielectric medium. In one such model (Bernal and Fowler 1933; Eley and Evans 1938; Everett and Coulson 1940; Verwey 1941, 1942; Rowlinson 1951; Buckingham 1957; Vaslow 1963) the molecular configuration of the water inside the hydration shell is considered and the electrical and short-range interactions between the ions and these molecules are examined in detail. In a simplified variant of this model (Born 1920; Webb 1926; Latimer, Pitzer, and Slansky 1939; Noyes 1962, see also 1964) the inner shell is treated as a spherical cavity of low dielectric constant to account for the dielectric saturation that is due to a very intense electric field. For a pair of ions the situation is much more complicated; nevertheless, Levine and Wrigley (1957), Levine and Bell (1962), and Levine and Rosenthal (1966) have developed several two-sphere models for non-overlapping hydration shells. (These papers will henceforth be referred to as L.W., L.B., and L.R. respectively.) At small separations, where the coordination shell overlaps, Levine and Rosenthal used a spheroidal cavity model but they found considerable difficulty in treating the transition between the non-overlapping and overlapping stages.

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It is the purpose of the present paper to extend the work of Levine and co-authors to the case of overlapping hydration shells by using a truncated spheres model in which the radius of the spheres increases with decrease in the separation between the ion centres in such a way that the volume of the two cavities remains constant. With this model there is no difficulty associated with the abrupt change in the shape of the cavity. Several variations are considered but calculations are only carried out for the K^+ and F^- ions in water at 25°C.

In problems of electrostatics and hydrodynamics relating to two truncated spheres, so-called peripolar coordinates were found useful by a number of authors, including Snow (1949), Morse and Feshbach (1953), Payne and Pell (1960), Pell and Payne (1960*a*, 1960*b*), Lebedev (1965), and Ranger (1965). However, in the present paper these coordinates are not used because of the different nature of the conditions at the boundary of the cavity. We therefore use spherical harmonic expansions and, by adopting a least-squares technique, find that a finite number of terms (< 8) in such an expansion satisfies the appropriate boundary conditions to a high degree of accuracy provided that the separation between the ions is not less than about 90% of the diameter of a single ion complex. (For brevity an ion with its attached water molecules will be referred to as an ion complex.) Actually the method used here leads to an infinite set of equations for which it is important to prove the existence of a unique solution. The validity of the expansions can be proved as in Mitra (1944).

Now one purpose of the present investigation is to confirm the general trend of the effective dielectric constant ϵ_{eff} defined by the relation

$$V(R) = e^2/\epsilon_{\text{eff}} R, \quad (1)$$

where $V(R)$ is the interaction energy corresponding to the separation R between the ion centres. In particular, we show that ϵ_{eff} has a maximum at very small overlap. An explanation is also given for the large discontinuity in the electric field at the ion centres, as found in the L.R. spheroidal cavity model at the transition stage from one model to the other. In view of the complexity of the problem, we shall begin with the simplified model of two point charges at the centre of the truncated spheres, which are treated as a continuous medium of low dielectric constant. This is an extension to overlapping spheres of the model considered in L.B. The next step is to place the two ions in a cavity of dielectric constant 1, containing the appropriate distribution of water molecules (see L.W. for this approach). We find that the determination of the interaction energy with such a distribution is very difficult and, since this will be considered in a following paper, only some preliminary results are given here.

II. POTENTIAL PROBLEMS FOR TWO INTERSECTING SPHERES

In order to estimate the interaction energy of two ion complexes in close proximity we can use as a model two intersecting spheres, S_1 containing the positive charge $+e$ and S_2 containing the negative charge $-e$, of equal radius a and dielectric constant ϵ' (which may or may not be unity). Each sphere represents an ion and its attached water dipoles and encloses the charge distribution which, for the sake of

simplicity, is taken to be symmetrical about the line of centres and which lies at the centre of the sphere to which it belongs. The whole system is embedded in a continuous medium of dielectric constant ϵ .

The potential inside the dielectric spheres is harmonic except at those points where there is an electric charge. We shall assume that the charge distribution is confined to two spherical neighbourhoods each of radius b ($b < \min(a, \frac{1}{2}R)$) centred at O_1 and O_2 , for then the potential outside these neighbourhoods can be represented by a set of multipoles lying at the centres of the spheres so that the potential inside the overlapping spheres can be written in the form

$$\Psi_1 = \Psi_R + \frac{e}{\epsilon'} \left(\frac{1}{r_1} - \frac{1}{r_2} \right) + \sum_{n=1}^{\infty} \left(\frac{a_n P_n(\cos \theta_1)}{r_1^{n+1}} + \frac{b_n P_n(\cos \theta_2)}{r_2^{n+1}} \right), \quad (2)$$

where Ψ_R is harmonic inside the whole region bounded by the overlapping spheres and the second term on the right-hand side represents the potential due to an equivalent multipole distribution situated at O_1 and O_2 , with (r_1, θ_1, ϕ_1) and (r_2, θ_2, ϕ_2) as the spherical polar coordinates referred to the ion centres and P_n denoting the Legendre polynomials of order n . These coordinates are so defined that $(r_1, \theta_1, \phi_1) = (r_2, \theta_2, \phi_2)$ for any point P on the median plane. This geometry is illustrated in Figure 1.

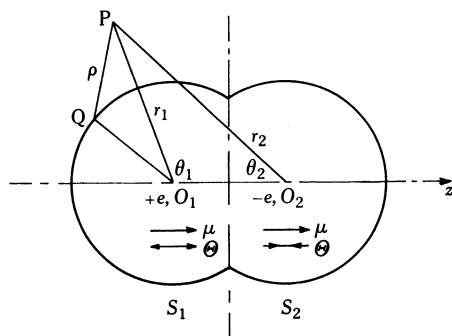


Fig. 1.—Model of two truncated spherical cavities containing point charges $+e$ and $-e$, induced dipoles μ , and induced quadrupoles Θ at the centres. This model is taken to represent overlapping hydration ions.

Since the charge distribution is antisymmetric with respect to the median plane perpendicular to the line joining the ion centres, it is sufficient to determine the potential Ψ_R inside one sphere S_1 . Let Q be any point on the boundary of the two spheres with spherical polar coordinates $(a, \theta_1^*, \phi_1^*)$ when on S_1 and $(a, \theta_2^*, \phi_2^*)$ when on S_2 . Then, using Green's theorem at any point P interior to the spheres, we get

$$\Psi_R(P) = \frac{1}{4\pi} \int_{S_1+S_2} \left\{ \Psi_R \frac{\partial}{\partial n} \left(\frac{1}{\rho} \right) - \frac{1}{\rho} \frac{\partial \Psi_R}{\partial n} \right\} dS, \quad (3)$$

where $\rho = PQ$ and $\partial/\partial n$ denotes differentiation along the outward normal \mathbf{n} . When Q is a point on the surface S_1 and $r_1 < a$, we introduce the expansion

$$\frac{1}{\rho} = \frac{1}{(r_1^2 + a^2 - 2ar_1 \cos \gamma_1)^{1/2}} = \frac{1}{a} \sum_{n=0}^{\infty} \left(\frac{r_1}{a} \right)^n P_n(\cos \gamma_1), \quad (4)$$

with

$$\cos \gamma_1 = \cos \theta_1 \cos \theta_1^* + \sin \theta_1 \sin \theta_1^* \cos(\phi_1 - \phi_1^*),$$

and, when Q is on the surface S_2 and $r_2 > a$, the expansion

$$\frac{1}{\rho} = \frac{1}{(r_2^2 + a^2 - 2ar_2 \cos \gamma_2)^{\frac{1}{2}}} = \frac{1}{a} \sum_{n=0}^{\infty} \left(\frac{a}{r_2}\right)^{n+1} P_n(\cos \gamma_2), \quad (5)$$

with

$$\cos \gamma_2 = \cos \theta_2 \cos \theta_2^* + \sin \theta_2 \sin \theta_2^* \cos(\phi_2 - \phi_2^*).$$

By a well-known addition formula for the Legendre polynomials (see Hobson 1931) we may write the function $P_n(\cos \gamma_i)$ as a sum of terms of the type

$$P_n^m(\cos \theta) P_n^m(\cos \theta^*) \cos m(\phi - \phi^*). \quad (6)$$

On each surface S_1 and S_2 , $\partial/\partial n$ becomes $\partial/\partial r_1$ and $\partial/\partial r_2$ respectively, so that the final result should be axially symmetric, and, in the region $r_1 < a < r_2$, $\Psi_R(P)$ takes on the form

$$\sum_{n=0}^{\infty} \left(c_n r_1^n P_n(\cos \theta_1) + d_n r_2^{-n-1} P_n(\cos \theta_2) \right). \quad (7)$$

On expanding each term in (r_2, θ_2) in terms of (r_1, θ_1) the expression (7) becomes

$$\sum_{n=0}^{\infty} \left(c_n r_1^n P_n(\cos \theta_1) + (d_n/R^{n+1}) \sum_{m=0}^{\infty} \binom{m+n}{n} (r_1/R)^m P_m(\cos \theta_1) \right), \quad (8)$$

valid in the region $r_1 < a < R$. Here the second term is a double power series in (r_1/R) and (a/R) and so is absolutely convergent inside the radius of convergence. It follows that we can interchange the order of the summation and so, with the aid of (2) and (8), we obtain an expression for the potential Ψ_1 inside the sphere S_1 as a sum of a reaction field potential Ψ_R and a "self-potential" Ψ_s . Thus

$$\Psi_1 = \Psi_R + \Psi_s, \quad (9)$$

where

$$\Psi_R = (e/a) \left(B_0 + \sum_{n=1}^{\infty} B_n (r_1/a)^n P_n(\cos \theta_1) \right), \quad (10)$$

valid in the whole interior of the sphere S_1 and

$$\Psi_s = (e/a) \left(a/\epsilon' r_1 + \sum_{n=1}^{\infty} W_n (a/r_1)^{n+1} P_n(\cos \theta_1) \right), \quad (11)$$

valid for $b < r_1 < a$. Here the reaction field Ψ_R is precisely the Taylor series expansion of the potential inside S_1 with a set of coefficients B_n which are related to the sequence of numbers c_j and d_j of (8) and which are determined by the appropriate boundary conditions. On the other hand, the self-potential Ψ_s is expressed in terms of the dimensionless quantities $W_n = p_n/ea^n$, where p_n is the moment of the point multipole of order n situated at the centre of each sphere.

The potential outside the two spheres may be written in the form

$$\Psi_0 = \frac{e}{\epsilon a} \left(\frac{a}{r_1} - \frac{a}{r_2} \right) + \psi_0(P), \quad (12)$$

where $\psi_0(P)$ is harmonic outside the two spheres. An expression for $\Psi_0(P)$ can then

be found by using Green's theorem once again and setting

$$\frac{1}{\rho} = \frac{1}{a} \sum_{n=0}^{\infty} \left(\frac{a}{r_i}\right)^{n+1} P_n(\cos \gamma_i), \quad (13)$$

with $i = 1$ when Q is on S_1 and $i = 2$ when on S_2 . On each surface S_1 and S_2 , \mathbf{n} is the unit inward normal and $\partial/\partial n$ becomes $-\partial/\partial r_1$ and $-\partial/\partial r_2$ respectively. It follows that, since the potential is antisymmetric with respect to the median plane (S_m),

$$\Psi_0 = \frac{e}{\epsilon a} \left(\frac{a}{r_1} - \frac{a}{r_2} \right) + \frac{e}{a} \sum_{n=0}^{\infty} A_n \left(\frac{P_n(\cos \theta_1) a^{n+1}}{r_1^{n+1}} - \frac{P_n(\cos \theta_2) a^{n+1}}{r_2^{n+1}} \right), \quad (14)$$

where the constants A_n depend on the potential on the surface of the two spheres and are determined from the boundary conditions appropriate to this problem; namely

$$\left. \begin{aligned} \Psi_0 &= \Psi_1, & \epsilon \partial \Psi_0 / \partial r_1 &= \epsilon' \partial \Psi_1 / \partial r_1 & \text{on } S_1, \\ \text{with} & & \Psi_1 &= 0 & \text{on } S_m. \end{aligned} \right\} \quad (15)$$

Since the boundary conditions at the surface of the sphere S_1 and on the median plane S_m will be used to obtain formulae involving the coefficients A_n , it is necessary to express the potential Ψ_0 in terms of (r_1, θ_1) . In that case equation (14) becomes

$$\begin{aligned} \Psi_0 &= \frac{e}{\epsilon a} \left(\frac{a}{r_1} - \frac{a}{r_2} \right) - \frac{e}{a} \sum_{m=0}^{\infty} \frac{A_m a^{m+1}}{R^{m+1}} \\ &+ \frac{e}{a} \sum_{n=0}^{\infty} \left[\frac{A_n a^{n+1}}{r_1^{n+1}} - \left(\frac{a^{n+1}}{\epsilon R^{n+1}} + \sum_{m=0}^{\infty} \binom{m+n}{n} \frac{A_m a^{m+n+1}}{R^{m+n+1}} \right) \right] \left(\frac{r_1}{a} \right)^n P_n(\cos \theta_1), \end{aligned} \quad (16)$$

valid for $\frac{1}{2}R < r_1 < R$.

We now assume that the potential inside the sphere S_1 may be represented sufficiently accurately by the first N coefficients B_n of the series in equations (9)–(12) and that the potential outside S_1 , but near the boundary, may be represented by the first N coefficients A_n of the series in (16). This assumption seems reasonable since the potential must be continuous on the whole of the boundary. Now equation (10) shows that the contribution to the potential inside one of the spheres from the reaction field Ψ_R can be written as a Taylor series in r_1 with coefficients that depend on θ_1 . Thus, once the multipole moments of the charge distribution inside the spheres are known, the set of constants B_n is uniquely determined by the values of the potential Ψ_1 on the boundary. However, the same argument does not apply to the potential on the outside for there exists an expansion of the form

$$\sum_{n=0}^{\infty} A_n^* \left(\frac{P_n(\cos \theta_1)}{r_1^{n+1}} - \frac{P_n(\cos \theta_2)}{r_2^{n+1}} \right) \quad (17)$$

which is identically zero everywhere outside the two spheres. One such identity can be obtained by expressing the function r^{-1} , where r is the radial distance measured from the origin O , in terms of Legendre series in (r_1, θ_1) and subtracting from it a similar series in (r_2, θ_2) . In that case $A_n^* = (\frac{1}{2}R)^n$. At first sight it seems as if the non-uniqueness of the coefficients A_n would lead to further complications but, as it happens, the equations that determine the B_n (equations (20) and (21);

see below) do not depend on the individual values of these constants but rather on the potential Ψ_0 and on its derivative $\partial\Psi_0/\partial r_1$. Hence, it is clear that the inclusion of terms like (17) cannot affect the determination of the set of constants B_n . This state of affairs is verified by checking that the final result is unaltered when the number of terms in the series is increased from $N = 8$ to 40.

For spheres that do not overlap we may equate the coefficients of the Legendre polynomials that arise when substituting equations (9)–(11) and (16) in the boundary conditions (15), because these polynomials are orthogonal in the range $-\pi < \theta_1 < \pi$; however, when there is overlap the orthogonality condition does not hold and we are not justified in merely equating coefficients because this would take no account of the last condition in (15).

If we look at the case of small overlap then we might expect a least-squares procedure to give reasonable answers. Such an approach has the advantage that it is continuously connected with the non-overlap case. Suppose that the potential is known in the region exterior to the two spheres. We can then determine the B_n 's which minimize the integrals

$$\Delta_1 = \int_{S_1} (\Psi_1 - \Psi_0)^2 dS_1 + \int_{S_m} \Psi_1^2 dS_m \quad (18)$$

and

$$\Delta_2 = \int_{S_1} (\epsilon \partial\Psi_0/\partial r_1 - \epsilon' \partial\Psi_1/\partial r_1) dS_1. \quad (19)$$

This leads to the set of simultaneous equations

$$\int_{S_1} (\Psi_1 - \Psi_0) r_1^n P_n(\cos \theta_1) dS_1 + \int_{S_m} \Psi_1 r_1^n P_n(\cos \theta_1) dS_m = 0 \quad (20)$$

and

$$\int_{S_1} (\epsilon \partial\Psi_0/\partial r_1 - \epsilon' \partial\Psi_1/\partial r_1) r_1^n P_{n+1}(\cos \theta_1) dS_1 = 0 \quad (21)$$

for $n = 0, 1, 2, \dots$

For convenience we shall now define a new set of constants E_n and F_n by the relations

$$\Psi_1 - \Psi_0 = (e/a) \sum_{n=0}^{\infty} E_n P_n(\cos \theta_1) \quad \text{on } S_1 \quad (22)$$

and

$$\partial\Psi_1/\partial r_1 - (\epsilon/\epsilon') \partial\Psi_0/\partial r_1 = (e/a^2) \sum_{n=1}^{\infty} F_n P_n(\cos \theta_1) \quad \text{on } S_1. \quad (23)$$

By comparison with equations (9)–(11) and (16) we see that

$$E_n = B_n + W_n + (\tfrac{1}{2}x)^{n+1}/\epsilon - A_n + \sum_{m=0}^{\infty} \binom{m+n}{n} A_m (\tfrac{1}{2}x)^{m+n+1} \quad (24)$$

for $n = 0, 1, 2, \dots$ and that

$$F_n = nB_n - (n+1)W_n + n(\tfrac{1}{2}x)^{n+1}/\epsilon' + (n+1)A_n \epsilon/\epsilon' + \sum_{m=0}^{\infty} \binom{m+n}{n} n A_m (\tfrac{1}{2}x)^{m+n+1} \epsilon/\epsilon' \quad (25)$$

for $n = 1, 2, 3, \dots$, where we define $W_0 = 1/\epsilon' - 1/\epsilon$, $A_0 = 0$, and $x = 2a/R$. If we

substitute these expressions into (20) and (21) we obtain

$$F_n = 0 \text{ for } n = 1, 2, 3, \dots \quad \text{and} \quad G_n = 0 \text{ for } n = 0, 1, 2, \dots, \quad (26)$$

where

$$G_n = \sum_{m=0}^{\infty} \{E_m I_{m,n} + B_m J_{m,n} x^{-m-n-2} + W_m K_{m,n} x^{m-n-1}\}, \quad (27)$$

with

$$I_{m,n} = \int_{-1}^{\cos \alpha^*} P_m(t) P_n(t) dt, \quad (28)$$

$$J_{m,n} = \int_{-1}^{\cos \alpha^*} P_m(t) P_n(t) t^{-m-n-3} dt, \quad (29)$$

$$K_{m,n} = \int_{-1}^{\cos \alpha^*} P_m(t) P_n(t) t^{m-n-2} dt, \quad (30)$$

and

$$\cos \alpha^* = \left. \begin{array}{ll} 1/x, & \text{if } x > 1, \\ 1, & \text{if } x \leq 1. \end{array} \right\} \quad (31)$$

In order to complete the discussion we must consider the charge distribution in each ion complex. We shall use the model of L.W., where it was supposed that there are four water molecules in each hydration shell forming a tetrahedral configuration. (A detailed discussion of this model is given in Section IV.) At infinite separation of the ion complexes the water dipoles point directly towards a negative ion and away from a positive ion and hence the equivalent dipole and quadrupole moments of the ion complexes at their centres vanish, that is, $p_1 = 0 = p_2$. However, at finite separations, the reaction field that one ion complex and the surrounding dielectric medium produce inside the other ion complex will induce dipole and quadrupole moments. These induced dipole and quadrupole moments situated at O_1 are taken as

$$\mu = p_1 = -\alpha d\Psi_R/dz, \quad \Theta = p_2 = -\gamma d^2\Psi_R/dz^2, \quad (32)$$

where α and γ are the dipole and quadrupole polarizabilities respectively and depend on the arrangement of the water molecules in the first hydration shell (see L.W. with a correction in L.R.). In nondimensional forms the induced multipole moments can be expressed as

$$\mu' = W_1 = -\alpha' B_1, \quad \Theta' = W_2 = -\gamma' B_2, \quad (33)$$

where

$$\alpha' = \alpha/a^3, \quad \gamma' = \gamma/a^5. \quad (34)$$

In L.R. higher order terms in μ' and Θ' were introduced to describe field gradient polarizabilities and hyperpolarizabilities. However, it was found that even at contact of the two spheres their contributions to the interaction energy was less than 0.01%. Furthermore, the inclusion of such terms raises new problems, such as the loss of axial symmetry, and at this stage of the theory there is little point in considering such refinements. So if we now neglect the higher order multipole moments we

have a complete set of nonlinear equations in terms of the parameter x representing the ion separation. Once these equations have been solved for A_n and B_n we can substitute these values into the integrals (18) and (19) and so obtain an estimate of the accuracy of this least-squares method. In fact the second integral vanishes identically and the first integral is given by

$$\begin{aligned} \Delta_1 = 2\pi e^2 \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} (E_m E_n I_{m,n} + B_m B_n J_{m,n} x^{-m-n-2} + 2B_m W_n K_{n,m} x^{n-m-1} \\ + W_m W_n L_{m,n} x^{m+n}), \end{aligned} \quad (35)$$

where

$$L_{m,n} = \int_{\cos \alpha^*}^1 P_m(t) P_n(t) t^{m+n-1} dt. \quad (36)$$

To solve these simultaneous equations we can use the following procedure. First assume that the dipole and quadrupole moments are known and then rewrite (27) in terms of the column matrix $x_i = (B_0, A_1, A_2, A_3, \dots)'$ by eliminating the other unknown B_n 's from (24) and (25). This leaves the set of linear equations

$$a_{i,j} x_i = y_j, \quad a_{i,1} = -I_{0,i-1} - J_{0,i-1} x^{i-1}, \quad (37)$$

where

$$\begin{aligned} a_{i,j+1} = I_{j,i-1} \{1 + (1+j^{-1})\epsilon/\epsilon'\} + J_{j,i-1} (1+j^{-1}) x^{i-j-1} \epsilon/\epsilon' \\ + \sum_{m=0}^{\infty} \binom{m+j}{j} \left(\frac{1}{2}x\right)^{m+j+1} \{I_{m,i-1}(\epsilon/\epsilon' - 1) + J_{m,i-1} x^{m-i-1} \epsilon/\epsilon'\} \end{aligned} \quad (38)$$

and the y_j 's are determined by setting the column matrix x_i equal to zero in (24) and (25) and then substituting into (27) once again. Hence

$$y_{j+1} = \sum_{r=0}^{\infty} (E_r^* I_{r,j} + B_r^* J_{r,j} x^{-r-j-2} + W_r K_{r,j} x^{r-j-1}), \quad (39)$$

where

$$B_0^* = 0, \quad B_n^* = (1+n^{-1})W_n - (\tfrac{1}{2}x)^{n+1}/\epsilon' \quad (40)$$

and

$$E_0^* = 1/\epsilon' - 1/\epsilon - \tfrac{1}{2}x/\epsilon, \quad E_n^* = B_n + W_n + (\tfrac{1}{2}x)^{n+1}/\epsilon. \quad (41)$$

We now solve (37) by using a matrix inversion and then make use of (25) to determine the B_n 's. This in turn enables us to calculate the induced dipole and quadrupole moments from equations (33). This process is repeated in order to evaluate μ' and Θ' by successive approximations.

III. INTERACTION ENERGY FOR INTERSECTING SPHERE MODEL

To determine the interaction energy $V(R)$ for the ion complexes we can use a Güntelberg-Müller-type charging process (Kirkwood 1934), i.e. we calculate the work that has to be done to bring the point charges from infinity in infinitesimal increments to separation R , the energy needed to produce the dipole and quadrupole moments, and the change in the internal energy associated with their formation.

Now the potential at the positive charge due to the presence of the negative ion is given by

$$\Psi_R^* = \lim_{r_1 \rightarrow 0} \left(\Psi_1 - \Psi_s - \lim_{R \rightarrow \infty} \left(\Psi_1 - \frac{e}{\epsilon' r_1} \right) \right) = \frac{e}{a} \left(B_0 + \frac{a}{a_0} \left(\frac{1}{\epsilon'} - \frac{1}{\epsilon} \right) \right), \quad (42)$$

because the induced multipole moments must vanish at infinity. Here a_0 is the radius of the ion complex at infinite separation. If we imagine that the two ion complexes are charged simultaneously (i.e. that each ion centre and each multipole moment is charged at the same rate) and denote by the fraction λ the stage in the charging process, then at any stage $\lambda < 1$ the potential against which the ion complexes are being formed is $\lambda \Psi_R^*$ and hence the difference between the work done in charging the ion centres at separation R and that at infinite separation is

$$V_e(R) = 2 \int_0^1 \lambda \Psi_R^* d(\lambda e) = \frac{e^2}{a} \left(B_0 + \frac{a}{a_0} \left(\frac{1}{\epsilon'} - \frac{1}{\epsilon} \right) \right). \quad (43)$$

To calculate the contribution to the interaction energy from the induced dipole moments we may consider each dipole as a doublet of length L' and moment $\mu = e'L'$ situated at the ion centre and pointing in the appropriate sense along the z axis. At any stage λ the corresponding potential is again $\lambda \Psi_R^*$ and hence the energy of charging the dipole is obtained by contracting these charges in such a way that $\mu = e'L'$. Thus

$$\begin{aligned} V_\mu(R) &= \lim_{L' \rightarrow 0} 2 \int_0^1 \lambda \{ (\Psi_R^*)_{L'} - (\Psi_R^*)_0 \} d(\lambda e') \\ &= e^2 B_1 \mu' / a. \end{aligned} \quad (44)$$

In a similar manner we can find the energy of charging the quadrupoles. This time we imagine three point charges e'' , $-2e''$, and e'' situated at distances of 0, L'' , and $2L''$ from the ion centres and along the z axis. Then, by contracting these charges in such a way that $\Theta = 2e''L''^2$, we obtain an expression for the energy of charging the quadrupole, namely

$$V_\Theta(R) = e^2 B_2 \Theta' / a. \quad (45)$$

Finally, we have to include in the interaction energy the change in the internal energy associated with the formation of the dipole and quadrupole. If the reaction field is regarded as an external field then, according to Böttcher (1952), the work done by this external field when μ changes by an amount $\delta\mu$ and Θ changes by an amount $\delta\Theta$ is

$$-(\partial \Psi_R^* / \partial z) \delta\mu - \frac{1}{2} (\partial^2 \Psi_R^* / \partial z^2) \delta\Theta \quad (46)$$

and, since this is equal to the work done on the internal field, it follows that the change in the internal energy associated with the formation of the dipole and quadrupole is

$$-2(e^2/a) \int_0^{\mu'} B_1 d\mu' - 2(e^2/a) \int_0^{\Theta'} B_2 d\Theta', \quad (47)$$

which, in view of equations (33), becomes $-(e^2/a)(B_1 \mu' + B_2 \Theta')$. The interaction

energy is now obtained by adding the above-mentioned contributions. It is given by

$$V(R) = (e^2/a)\{B_0 + (a/a_0)(1/\epsilon' - 1/\epsilon)\}. \quad (48)$$

We note that the interaction energy does not contain terms linear in the field or field gradient. A similar result, but involving only the dipole moment, was obtained by Mandel and Mazur (1958).

In the model of the ion complexes to be considered here we shall assume that the ion complexes have radius a_0 as long as their coordination shells do not overlap; however, in order that the radius of the complexes may change with separation in the case of overlap (e.g. so as to keep the volume of the two cavities constant), we shall define a volume factor f by the relation

$$4\pi a_0^3 f/3 = \pi \int_{-a}^{\frac{1}{2}R} (a^2 - t^2) dt. \quad (49)$$

It will be found convenient to make $R/2a$ the subject of this equation, in which case

$$R/2a = \{c + c(1-c)^{\frac{1}{2}}\}^{\frac{1}{2}} + \{c - c(1-c)^{\frac{1}{2}}\}^{\frac{1}{2}}, \quad (50)$$

with

$$c = \{1 + 4f(R/2a_0)^3\}^{-1}. \quad (51)$$

IV. INDUCED MULTIPOLE MOMENTS FOR A TETRAHEDRAL CONFIGURATION

In this work we are primarily interested in potassium fluoride solution where the K^+ and F^- ions have equal radius $r_i = 1.33 \text{ \AA}$ and where, for the sake of simplicity, we choose them to have the same polarizability $\alpha_i = 0.93 \times 10^{-24} \text{ cm}^3$ (the mean of their actual polarizabilities). For the water molecule we take $r_w = 1.38 \text{ \AA}$, $\alpha_w = 1.68 \times 10^{-24} \text{ cm}^3$, and the permanent dipole moment $\mu_w = 1.84$ debye. An upper estimate for the radius of the ion complex a_0 is $r_i + 2r_w = 4.09 \text{ \AA}$ while, for the case of a tetrahedral water structure, a lower estimate is 3.09 \AA , which is the radius of the sphere touching the nearest molecules that are not in contact with the ion. We shall use the mean value $a_0 = 3.59 \text{ \AA}$ to be consistent with the papers of Levine and co-authors.

To begin we can follow the method of L.W. and imagine that the ion complexes lie in a cavity (or two cavities if $R > 7.18 \text{ \AA}$) that contains four water molecules per ion. Each arrangement of four water molecules is assumed to be situated at the alternate vertices of a cube of sides $2(r_i + r_w)/\sqrt{3} = 3.13 \text{ \AA}$ with the ion at the centre. For this model the distance of nearest approach of the ion centres is 2.86 \AA . At ion separations less than $2(r_i + r_w) = 5.42 \text{ \AA}$ the Taylor series expansions (9)–(11) for the potential inside the cavity are no longer valid and so there is no point in pushing this model to smaller separations. In any case water molecules cannot be treated as point dipoles when the potential at intermolecular distances is calculated.

The polarizabilities of the ion complexes are now estimated by neglecting the interaction of adjacent water molecules inside the same hydration shell and determining the orientation of the water dipoles so as to make the potential energy of the water dipoles in the field of the other ion and of the reaction field a minimum.

The dipole moment of the ion complex is then given by

$$\alpha = \alpha_0 + 4\alpha_w + \alpha_i, \quad (52)$$

with

$$\alpha_0 = \mu_w \{ (r_i + r_w)^2 / e \} \sum (1 - \cos^2 \theta_1), \quad (53)$$

where α_w and α_i are the polarizabilities of the water molecule and the ion respectively, θ_1 is the angle between a typical water dipole of the ion complex O_1 and the z axis at infinite separation, and the summation is carried out over the positions of the attached water molecules. This is only the leading approximation since higher order terms in the reaction field are neglected and the rotation of the water dipoles from the line joining the centre of the water molecule to the centre of the ion to which it belongs is assumed to be small. Thus, if θ_1 becomes $(\theta_1 - \beta)$ due to the reaction field at finite separation R , we need $|\beta| \ll 1$. Of course, this assumption is not valid for small ion separations R , in which case the dipole-dipole interactions become more significant and the region between the ions has a coordination rather like that for a divalent ion.

Now a feature of this model is that $\sum (1 - \cos^2 \theta_1) = 8/3$ is independent of the positions of the water molecules. Similarly, L.R. showed that for an arrangement of six water molecules placed in an octahedral structure the same result holds except that the 4 in equation (52) is replaced by a 6 and that $\sum (1 - \cos^2 \theta_1) = 4$. No calculations on this model are included here since their general characteristics are the same as that of the four-coordinated ions.

The quadrupole moments of the tetrahedral and octahedral structures were calculated by L.R. They obtained an expression for the quadrupole polarizability; namely

$$\gamma = \frac{1}{2} m \alpha_w (r_i + r_w)^2 + 2 \cdot 25 \{ \mu_w (r_i + r_w)^4 / e \} \sum (\cos^2 \theta_1 - \cos^4 \theta_1), \quad (54)$$

with $\sum (\cos^2 \theta_1 - \cos^4 \theta_1) = 2m/9$ when the coordination number m is 4 or 6. The first term in (54) is the contribution to the quadrupole moment from the induced dipoles in the attached water molecules while the second term is due to the change in the orientation of the water dipoles of fixed moment μ_w , caused by the reaction field. The results of the calculations on the tetrahedral structure are shown in Table 1.

These data show that ϵ_{eff} has a maximum at very small overlap and that it is there greater than the dielectric constant of the aqueous medium. This is no cause for concern since ϵ_{eff} is only a dielectric constant by convention. At large separations it is clear that the value of ϵ_{eff} approaches that of the aqueous medium ϵ while at very small separations it tends to the internal molecular dielectric constant ϵ' .

The calculations also show that the induced dipole and quadrupole moments are very small when the coordination shells do not overlap and that these moments increase rapidly as the separation between the ions decreases from the contact value $R = 2a_0$. The smallness of the induced multipole moments at larger separations is related to the shielding effect of one ion complex from the other by the aqueous medium. Thus, as $\epsilon'/\epsilon \rightarrow \infty$ the ions behave like conducting spheres and so cannot influence each other or be affected by the surrounding aqueous medium. On the

other hand, once overlap occurs the amount of shielding is much reduced and the ions interact with each other much more strongly. This illustrates the importance of choosing a realistic model to describe the ion complexes, particularly in the case where overlap of the coordination shells begins. A further point to note is that the positions of the attached water molecules will have to be known even at moderate overlap because there will be a significant contribution to the potential energy from the dipole-dipole interactions of water molecules that belong to the same ion complex. Furthermore, the thermal motions of the water molecules will be increasingly important because there will now be certain geometrical constraints to consider.

TABLE 1

EFFECTIVE DIELECTRIC CONSTANT (ϵ_{eff}), INDUCED DIPOLE (μ) AND QUADRUPOLE (Θ) MOMENTS, AND FIELD INTENSITY (E) FOR THE TWO SPHERES CAVITY MODEL ($\epsilon' = 1$) WITH EIGHT ATTACHED WATER MOLECULES PLACED IN TWO TETRAHEDRAL CONFIGURATIONS

$a_0 = 3.59 \text{ \AA}$, $\alpha = 15.15 \times 10^{-24} \text{ cm}^3$, $\gamma = 66.01 \times 10^{-40} \text{ cm}^5$. For $N = 8, 20$ the ratio Δ_1/e^2B_0 has the maximum value 10^{-22} when $R/2a_0 \geq 1$ and ranges from 10^{-5} at $R/2a_0 = 1$ to 10^{-4} at $R/2a_0 = 0.9$

$R/2a_0$	ϵ_{eff}	μ (debye)	$\Theta \times 10^{26}$ (e.s.u.)	$E \times 10^{-6}$ (e.s.u.)
1.60	79.61	0.0149	0.0106	0.0010
1.40	80.34	0.0191	0.0153	0.0013
1.20	81.61	0.0250	0.0226	0.0017
1.00	84.23	0.0332	0.0332	0.0022
0.99	83.16	0.0363	0.0427	0.0024
0.98	80.18	0.0449	0.0713	0.0030
0.96	69.35	0.0819	0.1948	0.0054
0.94	55.47	0.1486	0.4166	0.0098
0.92	42.24	0.2457	0.7390	0.0162
0.90	31.42	0.3773	1.1763	0.0249

These will have the effect of introducing into the cavity permanent dipole, quadrupole, and other moments associated with these molecules. Moreover, at small separations the water molecules can no longer be treated as point dipoles and a much more detailed knowledge of the charge distribution of these molecules is needed than is at present available. The above results show that the field intensity E at each ion centre increases very quickly with increase in the amount of overlap.

There are certainly quite a number of problems associated with choosing a detailed molecular structure for the ion complexes. Thus, as an alternative, we can follow Marcus (1963*a*, 1963*b*) and separate the "electronic" polarizability of an ion complex from its "orientation" polarizability, which is due to the permanent charge distribution of the two ions and their attached water molecules. We imagine that the point charges and multipoles are placed at the ion centres in a dielectric medium for which $\epsilon' = n^2$, where n is its optical refractive index. However, since no data are available for this problem we follow Kirkwood and Westheimer (1938) and Hill (1944), who chose a small value for this dielectric constant to account for the dielectric saturation associated with the strong field between the ions. We shall

use $\epsilon' = 2.5$ and halve the polarizabilities α and γ . Table 2 shows the results of this calculation.

In order to make a comparison of the above two sets of calculations it is found useful to assign the value 5 to the dielectric constant ϵ' and thereby replace the induced multipole moments altogether. These results are also shown in Table 2.

We see from the calculations that, when the ion complexes are treated as a cavity ($\epsilon' = 1$) containing the charge distribution associated with the coordination water molecules, the effective dielectric constant is found to change rather abruptly near contact separation. On the other hand, if we use the dielectric spheres model ($\epsilon' = 5$) then this change is much more gradual. Of course, it is unlikely that such

TABLE 2

VARIATION IN EFFECTIVE DIELECTRIC CONSTANT (ϵ_{eff}) AND FIELD INTENSITY (E), AT THE ION CENTRES, WITH IONIC SEPARATION FOR THE CASES $\epsilon' = 5$ WITH $\mu = \Theta = 0$ AND $\epsilon' = 2.5$ WITH POLARIZABILITIES HALF THE PREVIOUS VALUES

For $N = 8, 20$ and $\epsilon' = 2.5$ or 5 the ratio A_1/e^2B_0 has the maximum value 10^{-23} when $R/2a_0 \geq 1$ and ranges from 10^{-7} at $R/2a_0 = 1$ to 10^{-5} at $R/2a_0 = 0.9$

$R/2a_0$	$\epsilon' = 5$		$\epsilon' = 2.5$			
	ϵ_{eff}	$E \times 10^{-6}$ (e.s.u.)	ϵ_{eff}	$E \times 10^{-6}$ (e.s.u.)	μ (debye)	$\Theta \times 10^{26}$ (e.s.u.)
1.60	79.52	0.0007	79.56	0.0008	0.0060	0.0046
1.40	80.17	0.0008	80.23	0.0010	0.0076	0.0066
1.20	81.38	0.0011	81.48	0.0013	0.0100	0.0098
1.00	83.78	0.0015	83.95	0.0018	0.0133	0.0145
0.99	83.73	0.0016	83.64	0.0018	0.0139	0.0163
0.98	83.22	0.0016	82.48	0.0020	0.0153	0.0211
0.96	80.76	0.0019	77.60	0.0028	0.0209	0.0401
0.94	76.46	0.0025	69.88	0.0041	0.0307	0.0733
0.92	70.61	0.0033	60.50	0.0060	0.0455	0.1228
0.90	63.71	0.0045	50.79	0.0088	0.0664	0.1914

a crude macroscopic theory of dielectric saturation is applicable to the water molecules in the first coordination shell, but, by a comparison of these results with the third model ($\epsilon' = 2.5$), the trends become clearer. It appears that the effective dielectric constant reaches a maximum at very small overlap and then begins to decrease fairly rapidly with decrease in ion separation.

A comparison of the field intensities at the ion centres reveals that E is small and hence that $|\beta| \ll 1$; it follows that the approximations regarding the tetrahedral structure that are used here and in L.W. and L.R. are acceptable. On examination of the cases where $\epsilon' = 1$ and 5 we see that the field intensity is smaller when the dielectric constant of the cavity is larger, in other words, the induced multipole moments are not completely accounted for by the introduction of a dielectric cavity model with $\epsilon' = 5$, although the trends in the two cases are clearly the same. For the case where $\epsilon' = 2.5$ the field intensities lie between those for the other two models considered above, but the induced dipole moment is much smaller

(approximately 40% at contact) and it increases with decrease in separation at only about half the rate observed in the cavity model ($\epsilon' = 1$). This is a satisfactory result for it shows a measure of success in replacing an induced dipole moment by a dielectric medium.

To represent the cavity as two truncated spheres is by no means the only possibility. Thus, Kirkwood and Westheimer (1938) estimated the dissociation constants of two similarly constituted acids by using a spheroidal cavity model to calculate the electrostatic work necessary to transfer a proton from the first acid to the ion of the second. They showed the importance not only of the charges present and the distance between them, but also of the shape of the molecule and the positions of the charges. Later Tanford (1957) proved that the interaction energy is critically dependent on the depth of the charges below the surface of the cavity and that this depth is a much more important variable than is the size or shape of the molecule. He suggested that this depth can be interpreted as a measure of the distance of nearest approach of the solvent to the charge or dipolar site and that it increases with increase in temperature.

The success of Kirkwood's model with organic ions suggests that we might try the same model here at small ion separations. Preliminary calculations made in L.R. show the extreme difficulty of matching the interaction energy and, at the same time, the force between the ions for the two spheres at contact separation onto the spheroidal cavity model. However, it may be possible to choose a spheroidal cavity so that there is continuity in the interaction energy and field intensity at each ion centre at some smaller ion separation. Of course, it is not clear which is the better cavity shape to use once the hydration shells overlap or even when they are nearly in contact, since then there is considerable distortion associated with the strong electrical field between the ions. A comparison of the two models is given in the following paper (Part II, pp. 587-95 of the present issue).

V. ACKNOWLEDGMENTS

The authors wish to thank Mr. F. Forti for preparing the diagram.

The calculations were carried out with the kind permission of the Manchester University Computing Service on their Atlas electronic computer.

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