IONIC HYDRATION

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In applying the general theory of intermolecular forces to the complicated problem of ionic solvation, the minimum requirements are an exact knowledge of (1) the force laws governing the interaction of two isolated solvent molecules as a function of their separation and the various angles of mutual inclination, (2) the force laws governing the interaction of an ion with one solvent molecule, also as a function of their distance apart and of their mutual inclinations, (3) the average disposition of solvent molecules in the pure liquid and (4) the disposition of the solvent molecules in the force field of the ion, particularly in its immediate vicinity. None of these theoretical requirements is available for systems of practical interest. The established laws of intermolecular force are those relating to spherically symmetrical fields, applied to gases (J. E. Lennard-Jones; see (1)), in which the molecular arrangements are random, and to crystals (M. Born (2)), in which the arrangements are orderly. In seeking to extend these laws to liquids and solutions, we are hampered at the start by our ignorance of directional forces in general and of the degree of disorder prevailing in condensed fluid systems. What is attempted here is a simplification of the problem of applying intermolecular force theory to ionic hydration by the introduction of assumptions which can claim some experimental warrant. How far the introduction of these assumptions may swamp other factors must remain an open question. At any rate, the attempt removes many anomalies, and allows of the absolute calculation of ionic dimensions in aqueous solution from intermolecular force constants determined without reference to the condensed states of matter.

Theoretical attempts at interpreting the heats of solvation of ions have been dominated by the conception (3) of reversible electrical charging in a medium of uniform dielectric constant. On this basis, the decrease in free energy attending the dissolution of an ion of charge ze and radius r in a solvent of dielectric constant D is given directly by electrostatic theory as

$$-\Delta G = \frac{z^2\epsilon^2}{2r}\left(1-\frac{1}{D}\right). \tag{1}$$

If r in this expression is identified with the ionic radius of elementary ions in crystals, the resulting value of $-\Delta G$ is found to be larger than the experimental value. This conclusion is inevitable whether we accept the original assignment of individual heats of hydration (4) or any of the later assignments which in principle are not less plausible. Qualitatively, the equation is satisfactory, for it is known that the smaller ions have the larger heats of hydration. Quantitatively, however, it is inconsistent with the facts (5). Its particular inadequacy to explain the specific heats of aqueous ions has been demonstrated in a variety of ways (6), (7), (8). The original conception has accordingly been modified by many investigators.

Most modifications of the original theory aim at discovering increments of distance which, when added to the crystals radii, r_i, make equation (1) fit the facts. The theory of

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electrostriction assesses this increment as 0·53 A. (9). An empirical value, found by plotting the reciprocal of ΔG against the crystal radius, is 0·65 A. (10). A similar treatment, applied separately to univalent cations and anions (11), indicates that the increment is 0·85 A. in the former case and 0·1 A. in the latter.

A more radical modification has resulted by discarding the idea of water as a uniform dielectric, and by stressing the quartz-like arrangement of its molecules (12). Additional energy terms are then necessary to account for the interaction of the ion with the dipole of the solvent medium, and for the intermolecular repulsion which arises from the new orientation of the solvent dipole in the immediate vicinity of the ion. The difficulties of the problem do not allow of its quantitative solution, and the application of the revised theory to the determination of heats of hydration proceeds by semi-empirical methods. For our purpose, the relevant aspect of Bernal and Fowler's theory is that the principal component of the energy of solvation is still given by equation (1), and that r, now referred to as the radius of the coordination sphere, is still determinable only by experiment. Bernal and Fowler's device of estimating the principal electrostatic energies by means of fractional charges has been employed in a kindred attempt (13) to estimate ionic entropies—a problem much simplified by assuming that r is the sum of the crystal radius and the radius of the water molecule.

It is the object of this paper to discover how far it is possible completely to account for the energy of hydration of elementary ions in terms of known intermolecular forces, without appealing to the concepts of electrical charging or ionic radii. The method consists in the *a priori* calculation of the average internuclear distances between ion and solvent molecule, and the computation of the potential energy, u_0, of the ion and its solvent neighbours in their most stable state in terms of the corresponding internuclear distance, a_0. The only unknown factor arising is a product, bc, where b is the distance between the centres of the solvent molecule and its dipole, and c is the coordination number. For its evaluation, one thermal datum is required.

The ion in solution is assumed to be surrounded by c equidistant solvent molecules, which it repels with a force varying inversely as the tenth power of the distance, a, from its centre. At equilibrium, this force is balanced chiefly by inductive and electrostatic forces. The energy of interaction of a single cation with its environment is then

$$u = c\left[Aa^{-9} - Ba^{-4}\left(1 - 4\frac{b}{a}\right) - Ca^{-2}\left(1 - 2\frac{b}{a}\right) + Da^{-3}\right] - \frac{4\pi nB}{a+\sigma}, \qquad (2)$$

where A = the specific energy constant of the repulsive field,

$B = \frac{1}{2}\alpha(z\epsilon)^2$,

$C = z\epsilon\mu$,

$D = (3/2\sqrt{2})\mu^2$,

α = the polarizability of the solvent molecule,

z = the valency of the ion,

ϵ = the electronic charge,

μ = the dipole moment of the solvent molecule,

n = the number of solvent molecules per c.c.,

and σ = the average distance between the centres of two neighbouring solvent molecules in the pure liquid.

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According to this model, the dipoles are radially situated, and there are two dipole-dipole interactions for each ion-dipole interaction. The nearest actual model is that of the rock-salt lattice, for which c is 6. To a sufficient degree of approximation, however, the equation is also applicable to a diamond lattice, for which c is 4. The term outside the bracket allows for the attraction of the ion for solvent molecules outside the first coordination shell, where only the induction forces need be considered. It has been obtained by integrating the expression $-4\pi nB\int\frac{dr}{r^2}$ from $a+\sigma$ to infinity.

The condition of equilibrium yields the following relation between the energy constants and the minimum internuclear distance, a_0:

$$A = \tfrac{4}{9}Ba_0^5\left(1-5\frac{b}{a_0}\right)+\tfrac{2}{9}Ca_0^7\left(1-3\frac{b}{a_0}\right)-\tfrac{1}{3}Da_0^6+\frac{4\pi nBa_0^{10}}{9c(a_0+\sigma)}. \quad (3)$$

The corresponding energy is

$$-u_0 = c\left[\tfrac{5}{9}Ba_0^{-4}\left(1-\frac{16}{5}\frac{b}{a_0}\right)+\tfrac{7}{9}Ca_0^{-2}\left(1-\frac{12}{7}\frac{b}{a_0}\right)-\tfrac{2}{3}Da_0^{-3}\right]+\frac{4\pi nB}{a_0+\sigma}\left[1-\frac{a_0}{9(a_0+\sigma)}\right]. \quad (4)$$

Attention is confined in this paper to ions in water, for which

$$\alpha = 1{\cdot}444\times10^{-24}\text{ c.c./molecule},$$
$$\mu = 1{\cdot}834\times10^{-18}\text{ e.s.u.},$$
$$n = 3{\cdot}36\times10^{22}\text{ molecules/c.c.},$$

and

$$\sigma = 2{\cdot}68\times10^{-8}\text{ cm.}$$

Three of the energy constants are, therefore,

$$B = z^2\times1{\cdot}643\times10^{-43}\text{ erg-cm.}^4,$$
$$C = z\times8{\cdot}76\times10^{-28}\text{ erg-cm.}^2,$$

and

$$D = 3{\cdot}57\times10^{-36}\text{ erg-cm.}^3$$

Univalent cations. Because the end of the water molecule facing the cations so closely resembles the fluorine ion, we propose the adoption of the repulsion constants known to prevail between the fluorine ion and the various cations. These have been determined from the properties of gases and crystals (J. E. Lennard-Jones; see (1)), and are reproduced in Table 1. By the method of successive approximations, based on equation (3), it is then found that the nearest integral value of c is 6, and that $b = 0{\cdot}274$ A. A comparison of the observed heats of hydration with the values of $-u_0$ calculated by means of equation (4) shows an agreement which in view of the absolute nature of the computation is reasonable. If we accept the experimental heats of hydration,

Table 1. *Univalent cations*

Ion	$A\times10^{82}$ (erg-cm.^{9})	$a_0\times10^8$ (cm.) calc.	$-u_0$ (kcal.) calc.	$-\Delta H_0$ (kcal.) obs.	$a_0\times10^8$ (cm.)	$A\times10^{82}$ (erg-cm.^{9})
Na^+	6·3	2·40	100·8	94·6	2·50	8·5
K^+	28·4	2·92	74·8	75·8	2·90	26·5
Rb^+	49·4	3·15	66·3	69·2	3·09	42·5
Cs^+	90·3	3·42	58·7	62·0	3·38	82·5

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a_0 may be calculated from equation (4), and A from equation (3); the results are shown in the last two columns of Table 1.

Univalent anions. Because hydrogen atoms come between the water molecules and the ions in these cases, it is not legitimate to use the repulsion constants adopted for the cations. We may, however, accept the experimental heats of hydration, and evaluate a_0 therefrom, taking b to have the same magnitude as for the cations, but with opposite sign. The results (Table 2) lead to a_0 values which are greater than those for the corresponding cations by an average value of 0·18 A.

Table 2. *Univalent anions*

Ion	$-\Delta H$ (kcal.) obs.	$a_0 \times 10^8$ (cm.) cal.
F^-	122·6	2·60
Cl^-	88·7	3·16
Br^-	81·4	3·31
I^-	72·1	3·55

Divalent cations. The treatment here is as for univalent cations, except that z is 2. The values of a_0 obtained from the heats of hydration (Table 3) exceed the crystal 'radii' by an average of 1·05 A. The calculated values of the repulsion constants agree as well as can be expected with those found to be the most convenient for interpreting data on crystals, which are given in brackets.

Table 3. *Divalent cations*

Ion	$-\Delta H$ (kcal.) (obs.)	$a_0 \times 10^8$ (cm.) (equation (4))	$A \times 10^{82}$ (erg-cm.^{9}) (equation (3))
Mg^{++}	456	1·84	2·9 (4·0)
Ca^{++}	370	2·08	7·2 (16·8)
Sr^{++}	336	2·19	10·5 (30·1)
Ba^{++}	306	2·32	16·2 (55·6)
Zn^{++}	484	1·80	2·4
Cd^{++}	429	1·91	4·0
Hg^{++}	442	1·88	3·5
Pb^{++}	355	2·37	19·0

A comparison of the two theories. The energy of hydration according to equation (1) is expressed in terms of a radius, r, which is independent of the nature of the solvent, is empirically related to the radius of the ion in crystals and can be evaluated only by assuming the equation to be true. The energy of hydration, according to equation (4), is expressed in terms of the minimum internuclear distance, a_0, between ion and solvent, is a function of the polarizability and dipole moment of the solvent molecule, and can be evaluated explicitly in terms of known force constants. As both are attempts at explaining the same thing we can equate the two expressions. We are merely interested in indicating the formal relation between r and a_0. To do so, it will suffice to ignore the dipole-dipole repulsions between solvent molecules and induction effects outside

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the coordination shell, as these to some extent cancel each other. For simplicity, we may take b as zero, and thus ignore the difference known to exist between isoelectronic ions of opposite signs. We thus have

$$\frac{1}{r} = \frac{c}{9a_0}\left(\frac{5\alpha}{a_0^3} + \frac{14\mu}{z\epsilon a_0}\right). \tag{5}$$

On taking c as 6, and using the values of α and μ appropriate for water, the a_0 values computed in Table 1 lead to r values in satisfactory agreement with those empirically employed.

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