THE INTERACTION ENERGY OF AN ISOLATED MONOVALENT ION

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Summary

The interaction energy of a monovalent ion in an aqueous medium at 25°C is determined. It is also found that the water molecules in the first hydration shell of the ion have a mean dipole moment far in excess of their permanent dipole moments. Thus, for example, the increase in the dipole moment of the attached water molecules due to the presence of an ion is about 60% for the small four-coordinated Li⁺ ion and about 30% for the larger four-coordinated I⁻ ion. Calculations are also carried out on the assumption that the ions are six coordinated.

I. INTRODUCTION

A formula for the Gibb's free energy of hydration of an isolated ion in an aqueous solution was first obtained by Born (1920). He assumed that the ion could be replaced by an empty spherical cavity containing a point charge at its centre with the surrounding medium having the macroscopic dielectric constant of water. This model has been used by many authors, including Webb (1926), Latimer, Pitzer, and Slansky (1939), and Noyes (1962), to mention but a few. Nevertheless the continuum model has met with much criticism since, for example, according to Powell and Latimer (1951), Cobble (1953), and Connick and Powell (1953), it cannot be used to calculate the hydration energies of other than monovalent ions. Laidler (1956) does not agree with their argument. In any case it is clear that this mathematical model is fairly crude and that a refinement should take some account of the discrete nature of the water molecules. It is with this fact in mind that we shall develop a discrete model here.

As a guide we can refer to the papers of Bernal and Fowler (1933), Verwey (1941, 1942), Rowlinson (1951), Buckingham (1957), Vaslow (1963), Ross (1968a), and Ross and Levine (1968). All but the last two papers omitted the polarizability of the water molecules, and in each case the water molecule was replaced by a point dipole (and sometimes a point quadrupole as well). In fact Ross (1968a) showed that, at 25°C, a good approximation can be obtained by replacing the polarizable water dipoles of the first hydration shell in the position of minimum electrostatic energy with the water outside this shell replaced by a dielectric continuum.

Now Bernal and Fowler (1933) indicated that the most likely coordination number of a monovalent ion is four, whereas Verwey (1941, 1942), who took into consideration the geometrical constraints in the second hydration shell, suggested that it is six or even eight. In the present paper we shall deal only with coordination number four or six, the former being the most probable. Similar calculations were

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carried out by Buckingham (1957) but he did not take full account of the polarizability of the water molecules near the strong field of the ion. Instead he found a formula for the electrostatic energy of formation of four solvent molecules tetrahedrally disposed and of six solvent molecules octahedrally disposed about a spherical ion in vacuo. These formulae are used here and the effects of polarization and the surrounding dielectric are included.

It is not the purpose of this paper to calculate the free energy of hydration of an ion because this has been done successfully by Randles (1956), Noyes (1962, 1964), and others. Rather, this discrete model is used to determine the zero energy level of a 10-coordinated ion pair with the hope that it will be possible to include it with the calculations of Ross and Levine (1968) in a later paper. In that case the interaction energy is taken as the difference between the energies at finite and infinite separations. This definition of interaction energy was used by Levine and Wrigley (1957), Levine and Bell (1962), Levine and Rosenthal (1966), and Ross (1968). It is thought to be a satisfactory one in determining the Gibb’s free energy of hydration, although it differs from the hypothetical five stage cycle of change proposed by Eley and Evans (1938). Those authors had great success in determining the hydration energy and the heat of solvation of ions in water. However, the aim of the present work is to find a discrete model that predicts these quantities as well as the mean coordination number and the induced dipole moment of the attached water molecules.

II. FURTHER DISCUSSIONS OF THE PHYSICAL MODEL

In order to study the energy of hydration of an ion in water it is necessary to know the spatial locations of each of the sets of electrical charges within the molecules themselves. Models for the charge distribution inside the water molecule have been obtained by theoretical and empirical means. Thus, Duncan and Pople (1953) were able to calculate the contribution to the dipole and quadrupole moments of the water molecule from the lone pair electrons and from the binding electrons and the protons; while Rowlinson (1951) determined the dipole and quadrupole moments of the water molecule by comparing the experimental values of the second virial coefficient of water vapour with values calculated on the basis of an assumed intermolecular potential. Unfortunately there is a large difference between the quadrupole moments of the water molecule obtained by these two methods (see McWeeny and Ohno 1960; Stogryn and Stogryn 1966, 1967). Campbell (1952) examined various point-charge models of the water molecule and showed that in ice the higher order multipole moments through the fifth are important. Furthermore the energy of interaction depends upon the assumed relative orientations not only of neighbouring molecules but also of more distant ones. The problems that this involves are extremely complicated and so we shall begin by replacing each water molecule by a point dipole \( \mu_w = 1 \cdot 84 \) debye at the centre of a sphere of radius \( r_w = 1 \cdot 38 \) Å. This seems the best that we can do at this stage for there is still considerable doubt about the values of the quadrupole and higher multipole moments of the charge distribution inside the water molecule. A tentative calculation involving the quadrupole moments will, however, be included.
With the exception of Verwey (1942) and Vaslow (1963), it has generally been supposed that in an aqueous solution of electrolytes the dipole of a water molecule adjacent to a small or highly charged ion points directly at the centre of the ion. In such a model the attached water molecules form a symmetrical tetrahedron or octahedron as the primary hydration shell and, moreover, there is then no induced dipole or quadrupole moment of the ion itself. The evidence for this type of structure is not experimental but present theories are not inconsistent with this possibility (cf. Vaslow 1963). We shall follow the model proposed by Buckingham (1957) and others and suppose that, for both positive and negative ions, the water dipoles point directly away from or towards the ion centre (see Outhwaite 1967). As regards the quadrupole moment, it is supposed that the charge distribution of each water molecule is axially symmetric about its dipole axis. Then on changing the sign of the ionic charge, while keeping the radius fixed, the ion–quadrupole energy term must change sign. It is positive for a cation and negative for an anion.

Now the most important contributions to the interaction energy of a single ion complex in vacuo as given by Muirhead-Gould and Laidler (1966) are associated with (1) ion–dipole forces, (2) ion-induced dipole forces, (3) ion–quadrupole forces, (4) ion-induced quadrupole forces (nothing whatever is known about the magnitude of these and so they will be neglected here), (5) dipole–dipole forces, (6) dipole-induced dipole forces, (7) dipole–quadrupole forces, (8) dispersion forces (these, according to Buckingham (1957), are relatively small, for if they were not the inert gases would be soluble in liquids like water and this is in disagreement with the results of Slater and Kirkwood (1931), Eley (1939), and Frank and Evans (1945)), and (9) charge-transfer forces (see Mulliken 1952a, 1952b; Eusuf and Laidler 1963; Kortüm 1965). In the following calculations only the forces (1), (2), (3), (5), (6), and (7) are considered; in any case, if we calculate the difference between the energy of an ion pair at separation $R$ and that at infinite separation the dispersive and charge-transfer forces are small and tend to cancel out.

III. The Ion and its Attached Water Molecules in Vacuo

As a first step we shall calculate the interaction energy for a single monovalent ion complex in vacuo for both four- and six-coordinated ions. In each case the water molecules are in contact with the ion to which they belong and the effect of polarization is neglected in the first instance. Thus, for an ion of radius $r_1$ and coordination number $m$ the ion–water molecule interaction energy is

$$U_m = -\frac{m\mu_w}{(r_1+r_w)^2} + \frac{zem\Theta}{(r_1+r_w)^3},$$

(1)

where $z = 1$ for a cation and $-1$ for an anion. Here $\mu_w$ and $\Theta (=\frac{1}{2}(\Theta_a+\Theta_b)$ in the notation of Buckingham 1957) are the permanent dipole and quadrupole moments of the water molecules respectively.

To determine the interaction energy between the $m$ coordination water molecules it is necessary to calculate the field at the centre of the typical water molecule and therefore to choose a model to describe the relative positions of the water molecule.
Thus, in the tetrahedral structure \((m = 4)\) the water molecules are placed at alternate vertices of a cube of sides \(2(r_1+r_\mu)/\sqrt{3}\) and a z axis is so chosen that it contains one water dipole and passes through the ion centre. For the octahedral structure \((m = 6)\) the water molecules are placed on either side of the ion centre on three mutually perpendicular lines (one of which is taken as the z axis) that intersect at the ion centre.

The field at the centre of the water molecules is radial and given by

\[
F_w = \frac{e}{(r_1+r_\mu)^3} - \frac{15\sqrt{6}\mu_w}{32(r_1+r_\mu)^3} + \frac{45\sqrt{6}z\Theta}{128(r_1+r_\mu)^4}
\]

when \(m = 4\), and by

\[
F_w = \frac{e}{(r_1+r_\mu)^2} - \frac{(1+6\sqrt{2})\mu_w}{4(r_1+r_\mu)^3} + \frac{3(1+6\sqrt{2})z\Theta}{16(r_1+r_\mu)^4}
\]

when \(m = 6\).

Now the electrostatic energy \(V_m\) of the ion complex in \textit{vacuo} can be determined by using the Güntelberg–Müller-type charging process (see Kirkwood 1934). In that case

\[
V_m = \frac{e}{2}\phi_0 - \frac{1}{2} \sum F_w \mu_w - \frac{1}{2} \sum \left(\frac{1}{2} \frac{\partial F_w}{\partial \Theta}\right),
\]

where the summations are carried out over the \(m\) water molecules, and the potential at the ion centre is given by

\[
\phi_0 = -\frac{m\mu_w}{(r_1+r_\mu)^2} + \frac{mz\Theta}{(r_1+r_\mu)^3}.
\]

On combining equations (2)–(5) we see that

\[
V_m = U_m + U_m^*,
\]

where

\[
U_4^* = \frac{15\sqrt{6}\mu_w^2}{16(r_1+r_\mu)^2} - \frac{45\sqrt{6}z\mu_w\Theta}{32(r_1+r_\mu)^4} + \frac{45\sqrt{6}\Theta^2}{64(r_1+r_\mu)^5}
\]

and

\[
U_6^* = \frac{3(1+6\sqrt{2})\mu_w^2}{4(r_1+r_\mu)^3} - \frac{9(1+6\sqrt{2})z\mu_w\Theta}{8(r_1+r_\mu)^4} + \frac{9(1+6\sqrt{2})\Theta^2}{16(r_1+r_\mu)^5}.
\]

Thus the electrostatic energy can be written as the sum of two terms \(U_m\), the interaction of the ion with the attached water molecules, and \(U_m^*\), the interaction energy between them.

The above equations are the same as those obtained by Buckingham (1957) but he omitted the quadrupole–quadrupole term, which turns out to be extremely small. Table 1 shows the relative magnitudes of the energy terms for some monatomic ions for both the tetrahedral and octahedral configurations. The ionic radii \(r_1\) are those given by Pauling (1927).
We are now in a position to calculate the induced dipole moment $\mu_{\text{w}1}$ by making use of the relation

$$\mu_{\text{w}1} = \alpha_w F_w,$$  \hspace{1cm} (9)

where $F_w$ is obtained from (2) or (3), as the case may be, by replacing the dipole moment $\mu_w$ by $\mu_w + \mu_{\text{w}1}$ and substituting it in equation (9). This enables us to calculate the energy terms given in Table 1 and to take into account the induced dipole moment.

### Table 1
**FIELD AT CENTRE OF TYPICAL WATER MOLECULE AND VARIOUS ENERGY TERMS FOR MONOVALENT IONS IN VACUUM AT 298°K**

<table>
<thead>
<tr>
<th>Ion</th>
<th>$r_i$ (Å)</th>
<th>$E_{\text{id}}$</th>
<th>$E_{\text{iq}}$</th>
<th>$E_{\text{dd}}$</th>
<th>$E_{\text{dq}}$</th>
<th>$E_{\text{qq}}$</th>
<th>$F_w \times 10^{-6}$ (e.s.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$^+$</td>
<td>0.78</td>
<td>$-7.575$</td>
<td>0.572</td>
<td>0.771</td>
<td>0.087</td>
<td>0.003</td>
<td>0.831</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$-11.363$</td>
<td>0.858</td>
<td>2.390</td>
<td>0.271</td>
<td>0.010</td>
<td>0.621</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>0.98</td>
<td>$-6.346$</td>
<td>0.438</td>
<td>0.591</td>
<td>0.061</td>
<td>0.002</td>
<td>0.710</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$-9.518$</td>
<td>0.658</td>
<td>1.832</td>
<td>0.190</td>
<td>0.007</td>
<td>0.547</td>
</tr>
<tr>
<td>K$^+$</td>
<td>1.33</td>
<td>$-4.812$</td>
<td>0.290</td>
<td>0.391</td>
<td>0.035</td>
<td>0.001</td>
<td>0.552</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$-7.219$</td>
<td>0.434</td>
<td>1.210</td>
<td>0.109</td>
<td>0.003</td>
<td>0.445</td>
</tr>
<tr>
<td>Rb$^+$</td>
<td>1.49</td>
<td>$-4.291$</td>
<td>0.244</td>
<td>0.329</td>
<td>0.028</td>
<td>0.001</td>
<td>0.497</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$-6.436$</td>
<td>0.366</td>
<td>1.019</td>
<td>0.087</td>
<td>0.002</td>
<td>0.406</td>
</tr>
<tr>
<td>Cs$^+$</td>
<td>1.65</td>
<td>$-3.850$</td>
<td>0.207</td>
<td>0.279</td>
<td>0.023</td>
<td>0.001</td>
<td>0.450</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$-5.774$</td>
<td>0.311</td>
<td>0.886</td>
<td>0.070</td>
<td>0.002</td>
<td>0.373</td>
</tr>
<tr>
<td>F$^-$</td>
<td>1.33</td>
<td>$-4.812$</td>
<td>$-0.290$</td>
<td>0.391</td>
<td>$-0.035$</td>
<td>0.001</td>
<td>0.543</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$-7.219$</td>
<td>$-0.434$</td>
<td>1.210</td>
<td>$-0.109$</td>
<td>0.003</td>
<td>0.425</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>1.81</td>
<td>$-3.473$</td>
<td>$-0.178$</td>
<td>0.240</td>
<td>$-0.018$</td>
<td>0.000</td>
<td>0.404</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$-5.210$</td>
<td>$-0.266$</td>
<td>0.742</td>
<td>$-0.057$</td>
<td>0.001</td>
<td>0.332</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>1.96</td>
<td>$-3.188$</td>
<td>$-0.155$</td>
<td>0.209</td>
<td>$-0.015$</td>
<td>0.000</td>
<td>0.371</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$-4.752$</td>
<td>$-0.232$</td>
<td>0.646</td>
<td>$-0.047$</td>
<td>0.001</td>
<td>0.309</td>
</tr>
<tr>
<td>I$^-$</td>
<td>2.19</td>
<td>$-2.773$</td>
<td>$-0.127$</td>
<td>0.171</td>
<td>$-0.012$</td>
<td>0.000</td>
<td>0.329</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$-4.160$</td>
<td>$-0.190$</td>
<td>0.529</td>
<td>$-0.036$</td>
<td>0.001</td>
<td>0.278</td>
</tr>
</tbody>
</table>

Thus, the ion–(dipole + induced dipole) energy is

$$E_{\text{id}} = -me(\mu_w + \mu_{\text{w}1})(r_1 + r_w)^2 + \frac{1}{2}me\mu_{\text{w}1}(r_1 + r_w)^2,$$  \hspace{1cm} (10)

where the first term is the electrostatic interaction energy and the second term is the change in the internal energy of the induced dipoles due to the proton charge $+e$. Similarly, $E_{\text{dd}} + E_{\text{dq}}$ can be deduced from equation (7) (and (8)) by replacing the factor $\mu_w$ by $\mu_w + \frac{1}{2}\mu_{\text{w}1}$ and the factor $\mu_w^2$ by $\mu_w(\mu_w + \mu_{\text{w}1})$ and neglecting the quadrupole–quadrupole contribution. Table 2 shows the amended values of $E_{\text{id}}$, $E_{\text{dd}}$, $E_{\text{dq}}$, and $F_w$ and gives the value of the induced dipole moment $\mu_{\text{w}1}$.  

0.5
As expected, a comparison of Tables 1 and 2 shows that the field intensity \( F_w \) is smaller when (1) the coordination number is larger, and (2) the induced dipole moment is taken into account. Also, it is seen that the dipole–dipole interaction energy is a little larger than the ion–quadrupole term and can be as much as 20% of the ion–dipole interaction. This alone does not invalidate the assumption made by Levine and Wrigley (1957) that “as a first approximation the interaction between adjacent water molecules inside a hydration shell may be neglected compared with that between the ion and a hydration molecule” since, in their calculations, it is only the change in the dipole–dipole energy associated with the reaction field that matters.

**Table 2**

**FIELD \( F_w \) AND ENERGY TERMS \( E_{id}, E_{dd}, \) AND \( E_{dq} \) IN VACUO AT 298°K FOR CASE WHERE INDUCED DIPOLE MOMENT \( \mu_{wl} \) IS INCLUDED IN CALCULATIONS**

<table>
<thead>
<tr>
<th>Ion</th>
<th>Energy Terms (10^{-12} erg/ion)</th>
<th>( \mu_{wl} ) (debye)</th>
<th>( F_w \times 10^{-6} ) (e.s.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li+</td>
<td>-9·989 1·263 0·115 1·172 0·706 0·445</td>
<td>0·699 0·619 0·420</td>
<td>0·699 0·619 0·420</td>
</tr>
<tr>
<td>Na+</td>
<td>-8·139 0·926 0·079 1·040 0·706 0·445</td>
<td>0·619 0·420</td>
<td>0·619 0·420</td>
</tr>
<tr>
<td>K+</td>
<td>-5·919 0·570 0·043 0·846 0·622 0·370</td>
<td>0·504 0·370</td>
<td>0·504 0·370</td>
</tr>
<tr>
<td>Rb+</td>
<td>-5·192 0·467 0·034 0·773 0·584 0·348</td>
<td>0·460 0·348</td>
<td>0·460 0·348</td>
</tr>
<tr>
<td>Cs+</td>
<td>-7·458 1·342 0·101 0·584 0·348</td>
<td>0·421 0·348</td>
<td>0·421 0·348</td>
</tr>
<tr>
<td>F−</td>
<td>-6·633 1·123 0·080 0·547 0·326</td>
<td>0·495 0·326</td>
<td>0·495 0·326</td>
</tr>
<tr>
<td>Cl−</td>
<td>-8·385 1·601 0·127 0·595 0·354</td>
<td>0·405 0·354</td>
<td>0·405 0·354</td>
</tr>
<tr>
<td>Br−</td>
<td>-5·914 0·942 0·065 0·497 0·296</td>
<td>0·354 0·296</td>
<td>0·354 0·296</td>
</tr>
<tr>
<td>I−</td>
<td>-3·172 0·220 0·013 0·530 0·315</td>
<td>0·255</td>
<td>0·255</td>
</tr>
</tbody>
</table>

In what follows the quadrupole moment of the water molecules will be neglected, since to include it in the calculation of the reaction field due to the aqueous medium would raise a number of new problems regarding the orientation of the water molecules about their dipole axes. This is a very complicated analysis (something along the lines followed by Vaslow 1963) and requires an accurate knowledge of the quadrupole tensor. In any case, it is felt that its contribution is small.

**IV. THE ION AND ITS ATTACHED WATER MOLECULES EMBEDDED IN A DIELECTRIC MEDIUM**

Since the ion complex is actually surrounded by an aqueous medium, other terms have to be considered. So far we have determined the interaction energy \( V_m \) in vacuo. We shall now calculate the work that has to be done to bring up the
aqueous medium. According to Böttcher (1952) this is given by

\[ W_m = -\frac{\varepsilon - 1}{8\pi} \int_V E_0 \cdot E \, dV, \]  

(11)

where \( V \) is the volume of the dielectric, \( E_0 \) the electric field at any point in the volume \( V \) before it is filled with the dielectric, and \( E \) the corresponding field in the dielectric medium \( \varepsilon = 78.30 \) after this operation. Following Levine and Rosenthal (1966) this work done can be written

\[ W_m = -\frac{\varepsilon - 1}{8\pi} \int_S \psi_0 \frac{\partial \Psi_0}{\partial n} \, dS, \]  

(12)

where \( S \) is the surface bounding the volume \( V \) of the dielectric, \( \partial \)/\( \partial n \) denotes differentiation along the normal to \( S \) drawn outwards from \( V \), and the potentials \( \psi_0 \) and \( \Psi_0 \) are such that \( E_0 = -\nabla \psi_0 \) and \( E = -\nabla \Psi_0 \). If we apply the usual boundary conditions to this problem then, since the integral (12) vanishes on the outer boundary \( V \), we see that

\[ W_m = -\frac{1 - \varepsilon^{-1}}{8\pi} \int_{S^*} \psi_1 \frac{\partial \Psi_1}{\partial n} \, dS, \]  

(13)

where \( S^* \) is the surface of the spherical cavity and \( \psi_1 \) and \( \Psi_1 \) are the potentials inside corresponding to \( \psi_0 \) and \( \Psi_0 \) outside.

Now the potential in the cavity of radius \( a_0 = r_1 + 2r_w \) may be written in the form

\[ \Psi_1 = \sum_k e_k \frac{1}{r - r_k} + \frac{1}{a_0} \sum_{n=0}^{\infty} \sum_{l=-n}^{n} B_{n,l} \left( \frac{a_0}{r} \right)^{n+1} \frac{\partial}{\partial n} P_n^l(\cos \theta) \exp(il\phi), \]  

(14)

where the first term is the potential due to the set of charges \( e_k \) placed at \( r = r_k \) and the second term is the reaction field \( \psi_R \) due to the presence of the outside medium. Hence the \( P_n^l(\cos \theta) \) represent the associated Legendre functions of the first kind and \( B_{n,l} \) are a set of constants determined by the boundary conditions.

Using some of the results of Kirkwood (1934), Linderstrøm-Lang (1953), and Tanford and Kirkwood (1957) we find that, for \( \max |r_k| < r < a_0 \),

\[ \sum_k \frac{e_k}{r - r_k} = \frac{1}{a_0} \sum_{n=0}^{\infty} \sum_{l=-n}^{n} E_{n,l} \left( \frac{a_0}{r} \right)^{n+1} P_n^l(\cos \theta) \exp(il\phi), \]  

(15)

where

\[ E_{n,l} = \sum_k e_k (r_k/a_0)^n (-1)^l P_n^{-l}(\cos \theta_k) \exp(-il\phi_k), \]  

(16)

and also that

\[ B_{0,0} = -e(1 - \varepsilon^{-1}) \]  

(17)

and

\[ B_{n,l} = \frac{(n+1)e}{(n+1)e + n}(1 - \varepsilon^{-1}) E_{n,l}. \]  

(18)
The contribution to the interaction energy from the aqueous medium must be a real quantity and so it is sufficient to consider only the values of \( E_{n,l} \) for which \( l \geq 0 \). To begin with we have

\[
E_{0,0} = B_{0,0}
\]

and, for the tetrahedral structure, the numbers \( E_{n,l} \) (with \( n \geq 1 \)) are given by

\[
E_{n,l} = \begin{cases} 
\frac{n \mu_w}{a_0} \left( \frac{r_1 + r_w}{a_0} \right)^{n-1} (-1)^l \{ \begin{array}{l}
P_n^l(1) + 3P_n^l(-\frac{1}{2}) \quad \text{if} \quad l = 3, 6, 9, \ldots \\0 \quad \text{otherwise},
\end{array} \} 
\end{cases}
\]

where

\[
\mu_w^* = \mu_w + \mu_{w1},
\]

while, for the octahedral structure, the numbers \( E_{n,l} \) (with \( n \geq 1 \)) are given by

\[
E_{n,l} = \begin{cases} 
\frac{n \mu_w}{a_0} \left( \frac{r_1 + r_w}{a_0} \right)^{n-1} (-1)^l \{ \begin{array}{l}
2P_n^l(1) + 4P_n^l(0) \quad \text{if} \quad n \text{ even and} \\
0 \quad \text{otherwise},
\end{array} \} 
\end{cases}
\]

Now the potential \( \psi_1 \) before the volume \( V \) is filled with dielectric is given by

\[
\psi_1 = \sum_k e_k / |r - r_k|
\]

and so, on substitution of equations (14)–(22) into (13) and making use of the usual addition formula for the Legendre polynomials, we find that

\[
W_4 = -\frac{1}{2} e^2 (1 - \epsilon^{-1}) / a_0
\]

\[
-\frac{1}{2} (1 - \epsilon^{-1}) \sum_{n=1}^{\infty} \frac{n^2 (n+1) \epsilon^{(2n)} / a_0^3} {(n+1) \epsilon + n} \left( \frac{r_1 + r_w}{a_0} \right)^{2n-2} \left( 4 + 12P_n(-\frac{1}{2}) \right),
\]

where the first term is the Born energy of the ion of radius \( a_0 \) and the second term represents the interaction of the water dipoles with their "images" in the aqueous medium. Similarly,

\[
W_6 = -\frac{1}{2} e^2 (1 - \epsilon^{-1}) / a_0
\]

\[
-\frac{1}{2} (1 - \epsilon^{-1}) \sum_{n=1}^{\infty} \frac{n^2 (n+1) \epsilon^{(2n)} / a_0^3} {(n+1) \epsilon + n} \left( \frac{r_1 + r_w}{a_0} \right)^{2n-2} \left( 6(1 + (1)^n) + 24P_n(0) \right).
\]

Now it turns out that

\[
W_m = \frac{1}{2} e \phi_r - \frac{1}{2} \sum \mu_w \cdot F_r,
\]

where \( \phi_r \) and \( F_r \) are respectively the contributions to the potential at the ion centre and to the field at the typical water molecule from the aqueous medium. It follows that \( W_m \) is the energy of charging up the ion and the dipoles against their respective reaction fields. Now the change in internal energy of the induced dipole is given by
\[ \frac{1}{2} \sum \mu_w \cdot F_r \] and so the total electrostatic energy is obtained from \( V_m + W_m \) by replacing the factor \( \mu_w \) by \( \mu_w + \frac{1}{2} \mu_{wl} \) and the factor \( \mu_w^2 \) (and \( \mu_w^2 \) in \( W_m \)) by \( \mu_w (\mu_w + \mu_{wl}) \).

The data in Table 3 show that the reaction field \( F_r \) of the ion complex plays a significant part in the determination of the free energy of hydration of an ion complex. (Some further calculations were carried out and it was found that, for \( m = 4, \Theta = 0 \) and (1) \( a_0 = 3 \cdot 09 \text{ Å}, \frac{1}{2} \sum \mu_w \cdot F_r = 31 \cdot 98, \) (2) \( a_0 = 3 \cdot 59 \text{ Å}, \frac{1}{2} \sum \mu_w \cdot F_r = 2 \cdot 69, \) and (3) \( a_0 = 4 \cdot 09 \text{ Å}, \frac{1}{2} \sum \mu_w \cdot F_r = 0 \cdot 68 \) in units of \( 10^{-12} \) erg/ion.) All of the

**Table 3**

**FIELD INTENSITY \( F_w + F_r \) AT CENTRE OF TYPICAL WATER MOLECULE, INDUCED DIPOLE MOMENT \( \mu_{wl} \), AND ENERGY TERMS \( E_{1d}, E_{dd}, E_{aq}, \) AND \( W_{m1} \)

\( W_{m1} \) is the energy of charging the dipoles and quadrupoles against their reaction field.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Born Energy</th>
<th>( E_{1d} )</th>
<th>( E_{dd} )</th>
<th>( E_{aq} )</th>
<th>( W_{m1} )</th>
<th>( \mu_{wl} ) (debye)</th>
<th>( (F_w + F_r) \times 10^{-6} ) (o.s.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li+</td>
<td>-3.215</td>
<td>-10.961</td>
<td>1.461</td>
<td>0.126</td>
<td>-2.334</td>
<td>1.645</td>
<td>0.979</td>
</tr>
<tr>
<td>Na+</td>
<td>-3.043</td>
<td>-14.448</td>
<td>3.688</td>
<td>0.344</td>
<td>-1.782</td>
<td>0.999</td>
<td>0.585</td>
</tr>
<tr>
<td>K+</td>
<td>-2.783</td>
<td>-8.978</td>
<td>1.082</td>
<td>0.087</td>
<td>-2.236</td>
<td>1.526</td>
<td>0.909</td>
</tr>
<tr>
<td>Rb+</td>
<td>-2.678</td>
<td>-12.088</td>
<td>2.822</td>
<td>0.241</td>
<td>-1.898</td>
<td>0.994</td>
<td>0.591</td>
</tr>
<tr>
<td>Cs+</td>
<td>-2.581</td>
<td>-5.105</td>
<td>1.462</td>
<td>0.030</td>
<td>-1.906</td>
<td>1.200</td>
<td>0.714</td>
</tr>
<tr>
<td>F-</td>
<td>-2.783</td>
<td>-7.205</td>
<td>1.295</td>
<td>0.087</td>
<td>-2.047</td>
<td>0.912</td>
<td>0.543</td>
</tr>
<tr>
<td>Cl-</td>
<td>-2.491</td>
<td>-6.544</td>
<td>0.672</td>
<td>0.048</td>
<td>-2.034</td>
<td>1.324</td>
<td>0.788</td>
</tr>
<tr>
<td>Br-</td>
<td>-2.412</td>
<td>-6.441</td>
<td>1.093</td>
<td>0.070</td>
<td>-2.023</td>
<td>0.870</td>
<td>0.518</td>
</tr>
<tr>
<td>I-</td>
<td>-2.299</td>
<td>-5.085</td>
<td>0.765</td>
<td>0.044</td>
<td>-2.015</td>
<td>0.819</td>
<td>0.488</td>
</tr>
</tbody>
</table>

Authors mentioned previously have omitted this term, have taken as the radius of the ion complex \( a_0 = r_1 + 2r_w \), and have compensated for the difference between the theoretical and experimental results in a number of rather arbitrary ways. Thus, for example, Bernal and Fowler (1933) used a large energy of making a hole in the water, Latimer, Pitzer, and Slansky (1939) added an arbitrary length to the ionic radii, and Buckingham (1957) accounted for the difference by introducing a rather large quadrupole moment for the attached water molecules. However, Coulson and Eisenberg (1966) took into account a large number of water molecules and, for an ice structure, estimated the contribution to the electric field and to the induced dipole moment at the centre of an ice molecule from 85 nearest neighbours. These contributions are of the same order of magnitude as those given here in the presence of an ion in solution and show the importance of taking into account the induced dipole moment.
The total electrostatic energy $V_{el}$ of the four-(or six-)coordinated ion complexes is given by

$$V_{el} = E_{1d} + E_{1q} + E_{dd} + E_{dq} + E_{qq} + W_{m1} \mu_w/\mu_w^* - \frac{1}{2} e^2 (1-\epsilon^{-1})/a_0$$  \hspace{1cm} (26)

and is listed in Table 4.

The energy of hydration of an ion depends on the choice of a zero energy level. Thus, for example, Eley and Evans (1938) considered a hypothetical series of steps leading to the transfer of an ion from a dilute gas to a dilute aqueous solution, while Noyes (1962, 1964) discharged the gaseous ion, hydrated the resulting neutral species (i.e. monatomic inert species of the same radius as the ion of interest), and then recharged it. In an alternative treatment, Stokes (1964) used a simple electrostatic model in which he made use of the crystal radii of the ions when in water and the van der Waals radii calculated from those of the iso-electronic noble gases by the quantum mechanical scaling principle when in the gas phase. He used these to compare the experimental free energies of hydration of ions of noble gas structure with the values calculated from the electrostatic model. In this model Stokes used a technique developed by Hasted, Ritson, and Collie (1948) in which he assumed that the effective dielectric constant ranged from 5 at the ion to > 78 over one or two layers (each 2·8 Å thick) depending on the charge. His results (as are those of Noyes 1962, 1964) are in good agreement with the known data.

Now, according to Eley and Evans (1938), the energy of reorientation of the water molecules near a positive ion is 8 kcal/mole and near a negative ion is 20 kcal/mole. If we accept these values here and add them to the electrostatic energy $V_{el}$ listed in Table 4 then we can obtain a good estimate of the free energy of hydration of both cations and anions by adding on 64 kcal/mole.

One of the main differences between the calculations on the discrete model and those of most other authors is the appearance of the term $W_{m1} \mu_w/\mu_w^*$, which is the work done in bringing up the aqueous medium plus the corresponding change in the internal energy of the attached water dipoles. The importance of this term was
pointed out by Böttcher (1952), Levine and Wrigley (1957), and Levine and Rosenthal (1966). It follows that both the radius of the ion, here taken to be the Pauling (1927) radius, and the size of the cavity are critical. Thus, for example, in the hypothetical cycle discussed by Eley and Evans (1938) this energy is omitted and, as it happens, it would tend to cancel out round the cycle. In essence, they say that the difference between the energy of bringing up the dielectric to the tetrahedral group of five water dipoles and to the ion with its four attached water dipoles is small since the change in the size of the hole into which the groups fit is negligible. This is only an approximation and in a more refined treatment this energy and the effects of the induced dipole moment should be taken into account.

Recently, Fumi and Tosi (1964) suggested that the actual radii of the monovalent ions are different from those proposed by Pauling (1927); however, since there is no known method of calculating the cavity size (see Linder and Hoernschemeyer 1967), there is little point in using these values at such an early stage in the theory.

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