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Abstract

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O. A. Osipov and I. K. Shelomov

On the Question of the Hydration of Ions in Aqueous Solutions

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In the works of J. Bernal and R. Fowler (1) and O. Ya. Samoilov (2), it has been shown that in aqueous solutions different ions affect the translational motion of the water molecules nearest to them in different ways. Multicharged and small singly charged ions weaken this motion, whereas large ions strengthen it; that is, small ions increase the orientation of dipoles in water, while large ions, on the contrary, cause their disorientation. This phenomenon is customarily called "orientational hydration." It can be interpreted on the basis of the electrostatic theory of the liquid state (3,4).

We have shown (3) that at any point in the volume of a polar liquid there acts an internal field E, which may be approximately expressed as follows:

$$E = \frac{4}{3}\pi N \frac{d}{M}\mu, \tag{1}$$

where M is the molecular weight of the polar liquid under study, d is the density, μ is the dipole moment, and N is Avogadro' s number. Since water molecules are associated through hydrogen bonding, the dipole moment of water in the liquid state differs significantly from that in gases and, when calculated by Syrkin' s formulas (5) or by the formula proposed by one of us (6), is approximately equal to 3 debye. Calculation shows that at room temperature

$$E \approx 4.2 \cdot 10^5 \text{ CGSE}.$$

When one water molecule is replaced by an ion, the energetic state of the liquid will remain unchanged only in the case where the force with which the ion acts on the surrounding molecules is equal to the force with which the molecules surrounding it—of course, without changing the degree of their orientation—will act on the ion; that is, when we have equilibrium of forces. In other words, the field strength created by the ion at the centers of the nearest molecules must be equal to the field strength created by the liquid molecules at the center of the ion, i.e., to the internal field:

$$E_{\mathrm{i}} = E, \tag{2}$$

where E_{i} is the field of the ion.

For $E_{\mathrm{i}} > E$, we shall observe a weakening of the translational motion of the water molecules nearest to the ion, i.e., positive hydration, and, conversely, for $E_{\mathrm{i}} < E$, an increase in the mobility of the molecules—negative hydration.

According to the laws of electrostatics,

$$E_{\mathrm{i}} = \frac{Ze}{\left(r_{\mathrm{i}} + r_{\mathrm{H_2O}}\right)^2}, \tag{3}$$

where r_i is the ion radius, $r_{\mathrm{H_2O}}$ is the effective radius of the water molecule. Obviously, the difference $E_i - E = \Delta E$ determines the sign of ion hydration. From the condition $\Delta E = 0$ one can determine the critical radius of the ion at which positive hydration changes into negative hydration:

$$\frac{Ze}{\left(r_i^{\mathrm{cr}} + r_{\mathrm{H_2O}}\right)^2} - \frac{4}{3}\pi N \frac{d}{M}\mu = 0, \tag{4}$$

whence

$$r_i^{\mathrm{cr}} = \sqrt{\frac{Ze}{\frac{4}{3}\pi N \frac{d}{M}\mu}} - r_{\mathrm{H_2O}}. \tag{5}$$

Assigning, approximately, a spherical form to the water molecule, we find its effective radius from the formula

$$r_{\mathrm{H_2O}} = \sqrt[3]{\frac{3M}{4\pi N d}} = 1.93\ \text{Å}.$$

For monovalent ions the critical radius is equal to 1.45 Å ($r_i^{\mathrm{cr}} = 3.38 - 1.95 = 1.45$), and for divalent ions to 2.05 Å.

According to the data of J. Bernal and R. Fowler, the nonhydrating ions should include ions beginning with rubidium, for which $r_i = 1.49$ Å, which is in good agreement with the results of our calculations. E. H. Frischman (^{6}) comes to an analogous conclusion on the basis of a study of the spectra of aqueous solutions. O. Ya. Samoilov gives a somewhat lower value for r_i^{cr}, including potassium among the negatively hydrating ions.

Let us calculate the additional orientation energy that the ion imparts to the nearest water molecules. An associated liquid may be regarded as a system of molecules located in potential minima with barrier height u. When a field ΔE is applied, according to Ya. I. Frenkel (^{7}), the potential barriers of the molecules surrounding the ion decrease in the direction of the field by Δu and increase against the field likewise by Δu. Obviously, the work of the field will be equal to

$$A = 2n \cdot \Delta u, \tag{6}$$

Table 1

Ion	r_i, Å	$\Delta u_{\text{calc.}}$, kcal/mol	$\Delta u_{\text{exp.}}$, kcal/mol
Li^+	0.78	+0.63	+0.63
Na^+	0.98	+0.39	+0.34
Ag^+	1.15	+0.23	+0.14
K^+	1.33	+0.08	−0.07
Tl^+	1.50	−0.04	−0.15
Cs^+	1.65	−0.12	−0.24
Cl^-	1.81	−0.21	−0.25
Br^-	1.96	−0.28	−0.3
J^-	2.20	−0.37	−0.37

where n is the coordination number of the ion in solution. On the other hand, according to literature data (^{8}),

$$A = \frac{\Delta E \mu}{2}, \tag{7}$$

where μ is the dipole moment of the water molecule. From equations (6) and (7) we obtain

$$\Delta u = \frac{\Delta E \mu}{4n}. \tag{8}$$

But Δu is the additional energy of orientation of the molecule in the field of the ion. As was shown by O. Ya. Samoilov (^{10,11}), the coordination number n for dilute solutions may be taken equal to four. Then

$$\Delta u = \frac{\mu \cdot \Delta \varepsilon}{16}. \tag{9}$$

Table 1 gives, for several ions, the values of Δu calculated by formula (9), compared with the data for Δu obtained by O. Ya. Samoilov from ion mobility values (^{2}). The data presented show that the values of Δu calculated by us are in good agreement with the experimental data, especially if one takes into account that in Samoilov' s data the second significant figure for Δu has only computational significance.

Rostov-on-Don
State University

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