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The Contraction of Water in the Hydration Shell

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Synopsis. In the aqueous solutions of some sulfates, the contraction of water molecules in a hydration shell and the hydration number were estimated by using the data of the limiting equivalent conductance of the ion and the partial molal volume of electrolytes at an infinite dilution.

In a previous paper,[1] we estimated the partial molal volumes of the ion pairs of some sulfates in aqueous solutions by using the data obtained from the molar conductances obtained under high pressures and discussed the tendency of the metal ion to form an outer-sphere ion pair with the sulfate ion. The partial molal volumes of the electrolytes and the volume changes of the dissociation of the ion pairs in the aqueous solutions at an infinite dilution were always negative. This may be mainly ascribed to the contraction of water molecules in the hydration shell with ions so that the density of water in the neighborhood of an ion may be higher than that of the bulk water.

From the conductance data, the volume of the hydration shell of an ion or electrolyte and the hydration number can be found by applying the Stokes law and the Robinson and Stokes method[2] as follows:

$$r_s = \frac{0.820|z|}{\lambda^\circ \cdot \eta}, \qquad (1)$$

where λ° is the limiting equivalent conductance of an ion with the Stokes radius of r_s and an absolute charge, $|z|$, and where η is the viscosity of pure water. r_s is corrected to the effective radius, r_e, by means of the Robinson-Stokes correction factor, f,

$$r_e = r_s \cdot f. \qquad (2)$$

Then, the volume of the hydration shell in the neighborhood of the ion, V_H, can be represented by this equation

$$V_H = \frac{4}{3}\pi L(r_e^3 - r_c^3), \qquad (3)$$

where L is Avogadro's number, and r_c, the crystallographic radius of the ion. The hydration number, h, is given by this equation

$$h = \frac{V_H}{V_E}, \qquad (4)$$

where V_E is the molar volume of water in the hydration shell in the neighborhood of the ion. In most cases, V_E was assumed to be equal to the molar volume of the bulk water, V_B,[2,3] so the hydration number may be underestimated.

As has been mentioned above, the contraction of water molecules surrounding an ion may occur upon a change in the states of the water molecules from the bulk to the hydration during the dissolution and dissociation of electrolyte. It has been shown by Padova[4] that the average theoretical contraction due to the electrostriction per mole of water is $\Delta V = -2.1$ cm^3/mol. Millero *et al.*[5] have determined $\Delta V = V_E - V_B = -3.0$ cm^3/mol from the isothermal compressibility data of aqueous solutions of various salts. Recently, Millero *et al.*[6] have determined the amount of water lost in the ion-pairing process of an aqueous $CaSO_4$ solution by using the value of $V_E - V_B = -3.8$ cm^3/mol.

The partial molal volume of an electrolyte at an infinite dilution, $\bar{V}^\circ(M^{2+}) + \bar{V}^\circ(SO_4^{2-})$, may be represented by the sum of the two major components resulting from the simple model for hydration[7]

$$\bar{V}^\circ(M^{2+}) + \bar{V}^\circ(SO_4^{2-}) = \bar{V}^\circ(\text{int}) + \bar{V}^\circ(\text{elect}), \qquad (5)$$

and

$$\bar{V}^\circ(\text{int}) = \frac{4}{3}\pi L[r_c(M^{2+})^3 + r_c(SO_4^{2-})^3], \qquad (6)$$

where $\bar{V}^\circ(\text{int})$ is the intrinsic partial molal volume of the electrolyte, and $\bar{V}^\circ(\text{elect})$, the electrostriction partial molal volume. Then, the electrostriction partial molal volume of the electrolyte can be estimated by using the partial molal volume of the electrolyte at an infinite dilution and related to the hydration number of the electrolyte, n_H, by this equation

$$\bar{V}^\circ(\text{elect}) = n_H(V_E - V_B). \qquad (7)$$

[4,7,8]

We assume that n_H in Eq. 7 is equal to the sum of $h(M^{2+})$ and $h(SO_4^{2-})$ in Eq. 4 as a first approximation, though the hydration numbers obtained by the various methods do not always coincide with each other. From Eqs. 4 and 7, we obtain this equation,

$$\frac{V_H(M^{2+}) + V_H(SO_4^{2-})}{V_E} = \frac{V_H(M^{2+}) + V_H(SO_4^{2-})}{V_B + (V_E - V_B)} = \frac{\bar{V}^\circ(\text{elect})}{V_E - V_B}. \qquad (8)$$

$V_E - V_B$ for each electrolyte was estimated by means of Eq. 8 with the values of $V_H(M^{2+}) + V_H(SO_4^{2-})$ and $\bar{V}^\circ(\text{elect})$ in Tables 1 and 2, and with $V_B = 18.05$ cm^3/mol at 25 °C. These results are also shown in Table 2. The mean value of $V_E - V_B$ is found to be

TABLE 1. LIMITING EQUIVALENT CONDUCTANCE, STOKES, EFFECTIVE, AND CRYSTALLOGRAPHIC RADII, HYDRATION VOLUME, AND HYDRATION NUMBER AT 25 °C

Ion	λ°	$\frac{r_s}{\text{nm}}$	$\frac{r_e}{\text{nm}}$	$\frac{r_c^{9)}}{\text{nm}}$	$\frac{V_H}{\text{cm}^3\,\text{mol}^{-1}}$	h
Mg^{2+}	53.1	0.345	0.431	0.065	201.2	13.6
Mn^{2+}	53.2	0.345	0.431	0.080	200.6	13.6
Co^{2+}	55.7	0.330	0.426	0.072	194.0	13.1
Ni^{2+}	54.4	0.337	0.426	0.070	194.1	13.1
Cu^{2+}	54.3	0.338	0.427	0.072	195.4	13.2
Zn^{2+}	53.4	0.344	0.430	0.074	199.5	13.5
SO_4^{2-}	80.0	0.229	0.366	0.273[10]	72.3	4.9

Table 2. Partial molal volumes, hydration number of electrolyte, and contraction volume of water at 25 °C

Electrolyte	$\bar{V}^\circ(M^{2+})+\bar{V}^\circ(SO_4^{2-})$ cm^3 mol^{-1}	$\bar{V}^\circ$(elect) cm^3 mol^{-1}	n_H	V_E-V_B cm^3 mol^{-1}
$MgSO_4$	−7.2[7]	−59.2	17.9	−3.2
$MnSO_4$	−3.7	−56.3	17.1	−3.1
$CoSO_4$	−9.5	−61.7	18.7	−3.4
$NiSO_4$	−10.0[7]	−62.2	18.8	−3.4
$CuSO_4$	−8.1	−60.3	18.3	−3.3
$ZnSO_4$	−8.0	−60.3	18.3	−3.3

−3.3 cm^3/mol. This value is in good agreement with those estimated by Padova[4] and Millero *et al.*[5,6] V_E is about 14.8 cm^3/mol, and the density of the water in the hydration shell in the neighborhood of the ions is estimated to be about 1.22 g/cm^3, comparable to the densities of ice III and/or V under high pressures. The hydration number of the ion, h, is also shown in Table 1. These values are in reasonable agreement with those estimated by Padova[4] and suggest that, especially in a metal ion, the hydration shell may contain the water molecules not only in the first layer, but also in the second and the outer layers.

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