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Molar Volume of Ions

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A formula based on the scaled particle theory of fluids has been derived for the intrinsic volume of ions. Validity ranges of earlier semiempirical formulas are discussed in the light of the formula. Using the theoretical values of the intrinsic volumes of ions, values of volume contraction caused by ion-water interactions are estimated.

The partial molar volume of ions at infinite dilution, $\bar{V}_{\rm ion}$, has turned out to be one of the most important quantities for elucidating the structure and properties of aqueous solutions of electrolytes. $\bar{V}_{\rm ion}$ is given by

$$\bar{V}_{\rm ion} = \bar{V}_{\rm int} + \Delta\bar{V}, \tag{1}$$

where $\bar{V}_{\rm int}$ is the inrinsic volume of ions, and $\Delta\bar{V}$ is the volume contraction caused by ion-solvent interactions. Intrinsic volume is defined as *the volume of spherical cavities in which ions are contained,*[1] *or non-hydrated partial molar volume of ions.*[2]

Studies have been carried out to estimate the magnitude of $\bar{V}_{\rm ion}$, $\bar{V}_{\rm int}$ and $\Delta\bar{V}$.[1–10] Hepler gave the following equation.[1]

$$\bar{V}_{\rm ion} = Ar_{\rm X}^3 - B/r_{\rm X}, \tag{2}$$

where $Ar_{\rm X}^3$ and $-B/r_{\rm X}$ correspond to $\bar{V}_{\rm int}$ and $\Delta\bar{V}$, respectively, and $r_{\rm X}$ is the crystal radius of an ion. From Eq. (2) and observed values of the partial molar volume, A and B were determined empirically. The values of $Ar_{\rm X}^3$ given by Hepler were about twice as much as $4\pi r_{\rm X}^3 N_{\rm A}/3 (=2.52\, r_{\rm X}^3)$, where $N_{\rm A}$ is Avogadro's number, $r_{\rm X}$ being given in Å.

Since the studies on $\bar{V}_{\rm ion}$ by Stokes and Robinson[3] and by Hepler,[1] a number of studies have been carried out but with only partial success. For theoretical estimation of $\bar{V}_{\rm ion}$, it is important to calculate the values of $\bar{V}_{\rm int}$. Attempts were carried out to find expressions for $\bar{V}_{\rm int}$. They are summarized as follows.[2]

$$\bar{V}_{\rm int} = Ar_{\rm X}^3 \tag{3}$$

$$= 2.52 r_{\rm X}^3 + A' r_{\rm X}^2 \tag{4}$$

$$= 2.52 (r_{\rm X} + a)^3. \tag{5}$$

In Eq. (3) A is positive and larger than 2.52.[1,3–7] In Eq. (4) the contribution from a surface effect of ions in addition to the crystal volume, $2.52\, r_{\rm X}^3$ is taken into consideration.[7,8,10] In Eq. (5), $\bar{V}_{\rm int}$ is expressed with the assumption that the ionic radius is larger than that in crystals by an amount a. Assuming that "the dead space" in packing of hard spheres "corresponds to a hollow sphere of constant thickness", Glueckauf estimated the magnitude of an additive term to the crystal radius, a.[9] Since Eqs. (3), (4), and (5) are based on semiempirical and intuitive considerations, there remains an arbitrariness for estimating the values of $\bar{V}_{\rm int}$. The expressions are found to be inconsistent with each other, their applicability being restricted. Thus, it is necessary to remove the uncertainty in the estimation of $\bar{V}_{\rm int}$.

It is the purpose of this report to give a theoretical expression for the intrinsic volume of ions on the basis of the scaled particl theory of liquids[11] in order to make clear the physical meanings of the semiempirical expressions, and to investigate ion-water interactions through a discussion on $\Delta\bar{V}$.

Application of the Scaled Particle Theory

The Scaled Particle Theory.[11–13] The theory is based on the consideration of the properties of a new distribution function $G(r)$, where "$\rho G(r)$ is defined as the local concentration of molecular centers adjacent to a spherical cavity of radius r from which all molecular centers are excluded".[11] ρ is the number density of the fluid. The *key relation* of the theory is

$$G(d) = g(d), \tag{6}$$

where $g(r)$ is the radial distribution function at a separation r and d is a rigid sphere diameter. Noting that Eq. (6) is an exact relation for hard sphere fluids, Reiss *et al.* arrived at an approximate analytical expression for $G(r)$ by combining the packing of hard spheres with the thermodynamical consideration for the formation of spherical cavities. They derived an equation of state for hard sphere fluids, which is identical with the equation derived by Wertheim[14] as an analytical solution of Percus-Yevick equation for hard sphere fluids. It was proved that the equation is useful for various real fluids.[15,16] The theory is not only rigorous to the same extent as the Percus-Yevick equation, but also intuitive like a model theory.

The Partial Molar Volume of Solute. Pierotti made use of the theory to obtain the expression for solubility

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of non-polar gases in water.[17] The partial molar volume of solute at infinite dilution $\bar{V}_2$ is obtained as a partial derivative of chemical potential of the solute in a very dilute solution. The resulting equation is

$$\bar{V}_2 = (\partial\bar{G}_c/\partial p)_{N,T} + (\partial\bar{G}_i/\partial p)_{N,T} + RT\beta_T \quad (7)$$

$$= \bar{V}_c + \bar{V}_i + RT\beta_T \quad (8)$$

where β_T is the isothermal compressibility of the solvent. $\bar{V}_c$ and $\bar{V}_i$ appear since the process of introduction of a solute molecule into the solvent is considered to take place in two steps. The first step is "the creation of a cavity in the solvent of a suitable size to accomodate the solute molecule".[17] The reversible work required for the process is $\bar{G}_c$, which is given by the scaled particle theory as follows.

$$\bar{G}_c = K_0 + K_1 d_{12} + K_2 d_{12}^2 + K_3 d_{12}^3, \quad (9)$$

where d_{12} is $(d_1+d_2)/2$, and d_1 and d_2 are diameters for solvent and solute molecules, respectively. The second step is "the introduction into the cavity of a solute molecule which interacts with the solvent according to some potential law".[17] The reversible work required is $\bar{G}_c$. The K values in Eq. (9) were evaluated from the scaled particle theory[13] to be

$$\begin{aligned}
K_0 &= RT\{-\ln(1-y) + (9/2)[y/(1-y)]^2\} - (\pi p d_1^3)/6 \\
K_1 &= -(RT/d_1)\{[6y/(1-y)] + 18[y/(1-y)]^2\} + \pi p d_1^2 \\
K_2 &= (RT/d_1^2)\{[12y/(1-y)] + 18[y/(1-y)]^2\} - 2\pi p d_1 \\
K_3 &= (4/3)\pi p,
\end{aligned} \quad (10)$$

where $y=(\pi d_1^3 \rho)/6$, ρ is the number density of solvent molecules, p pressure, R gas constant and T absolute temperature. The last term on the right-hand side of Eq. (9) is the work expended in creating a cavity of volume, $4\pi d_{12}^3/3$. The third and second terms are surface work and additive terms accounting for the curvature dependence of surface tension, respectively. The first term is a function of density and temperature.

Equations (7)—(10) are now applied to ionic solutions. By neglecting the term $RT\beta_T$, Eq. (8) is reduced to Eq. (1). $\bar{V}_{\text{ion}}$, $\bar{V}_{\text{int}}$, and $\Delta\bar{V}$ in Eq. (1) correspond to $\bar{V}_2$, $\bar{V}_c$, and $\bar{V}_i$ in Eq. (8), respectively. Thus, using the ionic radius r_X, $\bar{V}_c$ $(\equiv \bar{V}_{\text{int}})$ is expressed as follows, after sine calculations.

$$\bar{V}_c \equiv \bar{V}_{\text{int}} = 2.52 r_X^3 + A' r_X^2 + A'' r_X + A''' \quad (11)$$

A', A'', and A''' are expressed as

$$\begin{aligned}
A' &= RT\beta_T\{12y/(1-y)^2 + 36y^2/(1-y)^3\}/d_1^2 \\
A'' &= RT\beta_T\{6y/(1-y)^2\}/d_1 \\
A''' &= RT\beta_T\{y/(1-y)\}.
\end{aligned} \quad (12)$$

Validity and Interpretation of Various Semiempirical Equations

The physical meaning and validity of semiempirical Eqs. (3), (4), and (5) are interpreted on the basis of Eqs. (11) and (12). Equation (3) by Hepler, and Stokes and Robinson includes only the cubic term, the value of A being determined empirically and intuitively. Formally, Eq. (3) is seen to drop out the second, third and fourth terms in Eq. (11). Equation (4) by Conway *et al.* and other workers includes cubic and square terms, A' being determined empirically. Equation (4) is seen formally to drop out the third and fourth terms in Eq. (11). Equation (5) has a cubic polynomial form similar to Eq. (11). Concerning Eq. (5), the value a was determined by Glueckauf as follows.

$$a = (3\phi_w/4\pi N)^{1/3} - r_w = (18.02/2.52)^{1/3} - 1.38$$

$$= 0.55,$$

where ϕ_W is the molar volume of water, r_W the radius of water molecule.[18] This intuitive consideration by Glueckauf is explained theoretically by means of Eqs. (11) and (12).

The values of coefficients A', A'', and A''' calculated by means of Eq. (12) are given in Table 1. The values of a', a'', and a''' are determined by comparing Eq. (5) with Eqs. (11) and (12). Equation (5) is expanded as follows.

TABLE 1. VALUES A', A'', A''' CALCULATED BY Eq. (12) AND VALUES a', a'', a''' BY COMPARING Eq. (5′) WITH Eq. (11)[a]

Temperature (°C)	A'	A''	A'''	a'	a''	a'''
0	4.527	2.291	0.662	0.60	0.55	0.64
25	4.310	2.187	0.639	0.57	0.54	0.64
50	4.434	2.270	0.666	0.59	0.55	0.64
75	4.735	2.454	0.727	0.63	0.57	0.66

a) In calculating A and a, r_X in Eqs. (11), (12), and (5) is represented in Å.

$$\bar{V}_{\text{int}} = 2.52 r_X^3 + 7.56 a r_X^2 + 7.56 a^2 r_X + 2.52 a^3. \quad (5')$$

The coefficients of the second, third and fourth term in Eq. (5′) correspond to A', A'', and A''' in Eq. (11), respectively. The values of a obtained using the values of A', A'', and A''' in Table 1 are denoted by a', a'', and a'''. From the fact that the values of a' and a'' remain nearly constant and equal to Glueckauf's value 0.55, and from the formal agreement of the formula with Eq. (11), Glueckauf's equation is found to be the most reasonable of Eqs. (3)—(5). On the other hand, disagreement of a''' indicates that a representation such as Eq. (5) is an over-simplification.

For the sake of comparison, the values of A' and a obtained by various methods are shown in Table 2,

TABLE 2. VALUES OF A' AND a OBTAINED BY VARIOUS METHODS

	A' (from Eq. (4))	a (from Eq. (5))
B. E. Conway *et al.*[8]	3.15	
R. Noyes[7]	4.09	0.45
M. Panckhurst[10]	4.03	0.436
E. Glueckauf[9]		0.55
F. J. Millero[19]	4.0	0.45

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[17] R. A. Pierotti, *J. Phys. Chem.*, **67**, 1840 (1963), *ibid.*, **69**, 281 (1965).

[18] $\phi_w = (4/3)\pi N(r+a)^3$. The value of a was used as a constant increment over the crystal radius of ions in solutions.

[19] F. J. Millero, *J. Phys. Chem.*, **73**, 2417 (1969).

A' from Eq. (4) and a from Eq. (5). It turns out that values of A' and a determined by semiempirical and intuitive methods are all underestimated when compared with those in Table 1.

Estimation of $\varDelta\bar{V}$

The values of the volume contraction caused by ion-water interactions are calculated by means of Eqs. (1), (11), (12) and the experimental values of $\bar{V}_{\text{ion}}$. The assignment of $\bar{V}_{\text{ion}}$ to each ion from the observed values of $\bar{V}$ for electrolytes has attracted the interest of workers in this field, many conventional methods having been presented.[2] For the partial molar volume of H^+, the value $\bar{V}_{H^+}=0$ has been used conventionally. We adopt here the value $-5.0\ \text{cm}^3$ for $\bar{V}_{H^+}$ as the most adequate.[2] $\bar{V}_{\text{ion}}$ of other ions are obtained from the conventional values of partial molar volume of ions $\bar{V}_{\text{conv}}$ which have been estimated assuming that $\bar{V}_{H^+}=0$. The values of $\bar{V}_{\text{conv}}$ were tabulated by Millero.[2] The values $\varDelta\bar{V}$ calculated from the values of $\bar{V}_{\text{int}}$ determined with the use of Eqs. (11) and (12) and those of $\bar{V}_{\text{ion}}$, are shown in Table 3 for various univalent ions. Pauling's crystal radii are used as ionic radii r_X in the calculation.

In alkali and halogen ions, the magnitudes of $|\varDelta\bar{V}|$ are seen to decrease with the increase of ionic radii, except for Li^+ ion. The behavior is interpreted as an electrostatic aspect in ion-water interactions. However, it should be remarked that the obtained results depend on the choice of the value of $\bar{V}_{H^+}$ used here.[1,4]

The magnitude of $|\varDelta\bar{V}|$ of the tetraalkylammonium ions increases with increasing ionic size. This behavior cannot be interpreted only in the light of electrostatic interactions between ions and water molecules but by the iceberg formation around the ions. We have shown recently by an ultrasonic study that icebergs formed around tetraalkylammonium ions have a dense and hard structure, and the trend of iceberg formation increases with the ionic size.[20] The behavior of $\varDelta\bar{V}$ in tetraalkylammonium ions given in Table 3 is consistent with the conclusion of the ultrasonic study. It is interesting to compare the difference between the values of $\varDelta\bar{V}$ of two subsequent ions, such as Me_4N^+ and Et_4N^+. The values of $(\varDelta\bar{V}_{Et_4N^+}-\varDelta\bar{V}_{Me_4N^+})$, $(\varDelta\bar{V}_{Pr_4N^+}-\varDelta\bar{V}_{Et_4N^+})$ and $(\varDelta\bar{V}_{Bu_4N^+}-\varDelta\bar{V}_{Pr_4N^+})$ at 25 °C are −14.7, −26.3, and −27.9 cm³/mol, respectively. This supports our conclusion that the trend of iceberg formation seems to be appreciable at Pr_4N^+.[20]

TABLE 3. THE VALUES OF $\varDelta\bar{V}$ $(=\bar{V}_{\text{ion}}{}^{a)}-\bar{V}_{\text{int}}{}^{b)})$ (cm³/mol)

Ion	r_X(Å)	0 °C	25 °C	50 °C	75 °C
H^+		−5.0	−5.0	−5.0	−5.0
Li^+	0.60	−9.7	−9.9	−10.4	−11.3
Na^+	0.95	−17.6	−15.0	−14.3	−13.7
K^+	1.33	−15.5	−13.1	−12.9	−13.0
Rb^+	1.48	−14.8	−12.4	−12.2	
Cs^+	1.69	−15.0	−12.5	−12.1	−12.4
F^-	1.36	−15.7	−14.1	−15.6	−17.3
Cl^-	1.81	−13.1	−10.8	−11.2	−13.2
Br^-	1.95	−13.0	−10.3	−10.2	−12.1
I^-	2.16	−13.6	−9.7	−9.1	−11.3
Me_4N^+	3.47	−84.8	−80.8	−81.0	−80.7
Et_4N^+	4.00	−101.1	−95.5	−95.4	−93.3
Pr_4N^+	4.52	−128.7	−121.8	−119.7	−118.8
Bu_4N^+	4.94	−160.1	−149.8	−143.9	−133.1
Am_4N^+	5.29		−171.7		

a) The values are obtained from the conventional values of partial molar volume of ions $\bar{V}_{\text{conv}}$ which have been estimated assuming that $\bar{V}_{H^+}=0$. That is, $\bar{V}_{\text{ion}}=\bar{V}_{\text{conv}}\pm 5.0\ \text{cm}^3/\text{mol}$ (+for anions, −for cations). The values of $\bar{V}_{\text{conv}}$ are those compiled by Millero.[2]

b) The values are calculated by Eqs. (11) and (12).

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