

The Standard Partial Molar Volumes of Ions in Solution. Part 4. Ionic Volumes in Water at 0–100 °C

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The standard partial molar volumes of 10 univalent and 5 divalent ions in water over the temperature range of its existence as a liquid at ambient pressure (0–100 °C) are fitted as the sum of their (negative) electrostrictive volumes and intrinsic volumes, including disordered water. The former are obtained from the shell-by-shell calculation of the electrostriction according to Marcus and Hefter that takes into account the mutual dependence of the relative permittivity and the electrical field strength of the water around the ion. This calculation yields also the spatial extension of the dielectrically saturated region around the ions. The average molar electrostriction of the water in the vicinity of the ions is also calculated and leads to estimated hydration numbers.

1. Introduction

The standard partial molar volumes of many electrolytes, $V^\infty(\text{salt})$, are known for aqueous solutions over the temperature range where water is liquid under ambient pressures, 0–100 °C. These data give rise to conventional ionic values $V^{\text{conv}}(\text{i})$ on application of the additivity principle and setting $V^{\text{conv}}(\text{H}^+, \text{aq}) = 0$ at all temperatures, as listed by Millero.¹ Estimates of the absolute ionic values, $V^\infty(\text{i})$, are obtained on application of an appropriate extra-thermodynamic assumption. The absolute value for the hydrogen ion, $V^\infty(\text{H}^+, \text{aq})$, is generally employed for this purpose:

$$V^\infty(\text{i}) = V^{\text{conv}}(\text{i}) + zV^\infty(\text{H}^+, \text{aq}) \quad (1)$$

where z is the algebraic charge number of the ion. For aqueous solutions the expression

$$V^\infty(\text{H}^+, \text{aq})/\text{cm}^3 \cdot \text{mol}^{-1} = -5.1 - 0.008(t/^\circ\text{C}) - 1.7 \times 10^{-4}(t/^\circ\text{C})^2 \quad (2)$$

was derived by Millero.^{1,2} Hence, the absolute standard partial molar ionic volumes of the 16 ions shown in Table 1 are obtained. For most of the ions $V^\infty(\text{i})$ exhibits a small maximum at intermediate temperatures in this range, 0–100 °C, as shown for some ions in Figure 1.

It is generally accepted (see refs 1–3 and 5–7 among many others) that the standard molar ionic volumes, $V^\infty(\text{i})$, of the ions, monatomic, or if polyatomic then nearly spherical and not hydrophobic, can be described as the sum of two terms. One of these describes the intrinsic volume of the ions and the second describes the (negative) volume change due to the electrostriction of the solvent by the electric field of the ion, as suggested by Drude and Nernst over 100 years ago.⁴

$$V^\infty(\text{i}) = V_{\text{intr}}(\text{i}) + \Delta V_{\text{elstr}}(\text{i}) \quad (3)$$

The opposite natures of these contributions and their variation with the temperature lead to the nearly parabolic curves in Figure 1.

Various authors presented different estimates of the two terms making up $V^\infty(\text{i})$. Hepler³ showed that the first term of the rhs of eq 3 should be proportional to the cube of the (crystal) ionic radius, $r_c(\text{i})^3$, and the second to $z(\text{i})^2/r_c(\text{i})$, on the basis of the pressure derivative of the Born expression for the Gibbs energy of hydration of the ion (recharging in water the ion discharged in vacuum). However, the coefficients of $r_c(\text{i})^3$ and $z(\text{i})^2/r_c(\text{i})$ needed to fit the data at 25 °C were empirical and different for cations and anions.

The simplest estimate of the intrinsic ionic volume is, according to Benson and Copeland,⁵ just the volume of the bare (unhydrated) ions per mole of ions:

$$V_{\text{intr}}(\text{i}) = V_{\text{bare}}(\text{i}) = (4\pi N_A/3)r_c(\text{i})^3 = 2522.5r_c(\text{i})^3 \quad (4)$$

where the numerical coefficient is valid for $V_{\text{intr}}(\text{i})$ in $\text{cm}^3 \text{mol}^{-1}$ and $r_c(\text{i})$ in nm. The electrostriction is obtained⁵ from:

$$\Delta V_{\text{elstr}}(\text{i}) = -[N_A e^2/8\pi\epsilon_0]z(\text{i})^2r_c(\text{i})^{-1}\epsilon^{-2}(\partial\epsilon/\partial P)_T \quad (5)$$

where e is the elementary charge, ϵ is the relative permittivity of water, ϵ_0 is the permittivity of vacuum, and P and T are the pressure and temperature. Thus, although r_c and hence $V_{\text{intr}}(\text{i})$ were taken to be independent of the temperature, $\Delta V_{\text{elstr}}(\text{i})$ should be temperature dependent due to both $\epsilon = f(T)$ and $(\partial\epsilon/\partial P)_T = f(T)$. At 25 °C the coefficient of $z(\text{i})^2r_c(\text{i})^{-1}$ in eq 5 for water should be 4.73, but with the values of $V_{\text{intr}}(\text{i})$ from eq 4 the data could not be fitted well, nor was the temperature dependence explored by Benson and Copeland.⁵

Mukerjee⁶ and Glueckauf⁷ argued that the values for $V_{\text{intr}}(\text{i})$ need to take into account the void space between closely packed spheres (assigning spherical shape to the water molecules). Both advocated a modified form of eq 4; Mukerjee⁶ suggested a factor of 1.213 for r_c that yields a void fraction of $1 - 1/1.213^3 = 0.440$ (it should be 0.4203 for randomly close packed spheres, due to purely geometrical reasons, i.e., slightly smaller).

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TABLE 1: Conventional Molar Ionic Volumes, V^{conv} , Absolute Molar Ionic Volumes, $V^{\infty}(\text{i}, T)$, Molar Volume Decrements on Electrostriction, $\Delta V_{\text{elstr}}(\text{i}, T)$, and Resulting Intrinsic Molar Ionic Volumes $V_{\text{intr}}(\text{i}, T)$, at Various Temperatures^a

volumes/cm ³ mol ⁻¹	0 °C	25 °C	50 °C	75 °C	100 °C	volumes/cm ³ mol ⁻¹	0 °C	25 °C	50 °C	75 °C	100 °C
H⁺						Sr²⁺ (3.64, 6.28)					
V^{conv}	0	0	0	0	0	V^{conv}	-20.77	-18.16	-17.69	-16.8	-17.4
$V^{\infty}(\text{i}, T)$	-5.10	-5.41	-5.93	-6.7	-7.6	$V^{\infty}(\text{i}, T)$	-30.97	-29.18	-29.55	-30.2	-32.6
Li⁺ (0.83, 1.43)						$\Delta V_{\text{elstr}}(\text{i}, T)$	-32.78	-33.90	-36.30	-40.70	-46.22
V^{conv}	-0.45	-0.88	-1.24	-1.8	-2.7	$V_{\text{intr}}(\text{i}, T)$	1.81	4.72	6.75	10.5	13.6
$V^{\infty}(\text{i}, T)$	-5.55	-6.29	-7.17	-8.5	-10.3	Ba²⁺ (6.34, 10.95)					
$\Delta V_{\text{elstr}}(\text{i}, T)$	-12.45	-12.87	-13.78	-15.42	-17.52	V^{conv}	-15.79	-12.47	-11.73	-7.7	-8.1
$V_{\text{intr}}(\text{i}, T)$	6.90	6.60	6.61	6.9	7.2	$V^{\infty}(\text{i}, T)$	-25.99	-23.29	-23.59	-21.1	-23.3
Na⁺ (2.68, 4.62)						$\Delta V_{\text{elstr}}(\text{i}, T)$	-26.54	-27.54	-29.64	-33.30	-37.92
V^{conv}	-3.51	-1.21	-0.30	0.8	0.8	$V_{\text{intr}}(\text{i}, T)$	0.75	4.25	6.10	12.2	14.6
$V^{\infty}(\text{i}, T)$	-8.61	-6.62	-6.23	-5.9	-6.8	F⁻ (5.93, 10.24)					
$\Delta V_{\text{elstr}}(\text{i}, T)$	-8.22	-8.56	-9.22	-10.39	-11.87	V^{conv}	-2.21	-1.16	-1.4	-3.1	-3.7
$V_{\text{intr}}(\text{i}, T)$	-0.4	1.94	2.99	4.5	5.1	$V^{\infty}(\text{i}, T)$	2.89	4.25	4.53	3.6	3.9
K⁺ (6.63, 11.44)						$\Delta V_{\text{elstr}}(\text{i}, T)$	-5.90	-6.20	-6.73	-7.64	-8.76
V^{conv}	7.17	9.02	9.57	10.3	9.5	$V_{\text{intr}}(\text{i}, T)$	8.79	10.45	11.26	12.2	12.7
$V^{\infty}(\text{i}, T)$	2.07	3.61	3.64	3.6	1.9	Cl⁻ (14.96, 25.80)					
$\Delta V_{\text{elstr}}(\text{i}, T)$	-5.59	-5.89	-6.96	-7.28	-8.39	V^{conv}	16.45	17.83	18.00	17.4	16.0
$V_{\text{intr}}(\text{i}, T)$	7.66	9.50	10.60	10.9	10.3	$V^{\infty}(\text{i}, T)$	21.55	23.24	23.93	24.1	23.6
Rb⁺ (8.34, 14.39)						$\Delta V_{\text{elstr}}(\text{i}, T)$	-3.71	-3.97	-4.39	-5.04	-5.88
V^{conv}	12.31	14.07	17.71	[21.2]	[24/7]	$V_{\text{intr}}(\text{i}, T)$	25.26	27.21	28.32	29.1	29.5
$V^{\infty}(\text{i}, T)$	7.21	8.66	8.78	[7.9]	[9.5]	Br⁻ (18.99, 32.76)					
$\Delta V_{\text{elstr}}(\text{i}, T)$	-5.02	-5.30	-5.79	-6.60	-7.63	V^{conv}	23.06	24.71	25.49	25.1	24.9
$V_{\text{intr}}(\text{i}, T)$	13.23	13.96	14.57	[14.5]	[17.1]	$V^{\infty}(\text{i}, T)$	28.16	30.12	31.42	31.8	32.5
Cs⁺ (12.39, 21.38)						$\Delta V_{\text{elstr}}(\text{i}, T)$	-3.25	-3.47	-3.85	-4.47	-5.23
V^{conv}	19.68	21.34	22.22	23.2	23.0	$V_{\text{intr}}(\text{i}, T)$	31.41	33.59	35.27	36.3	37.7
$V^{\infty}(\text{i}, T)$	14.58	15.93	16.29	16.5	15.4	I⁻ (26.86, 46.33)					
$\Delta V_{\text{elstr}}(\text{i}, T)$	-4.11	-4.38	-4.81	-5.52	-6.41	V^{conv}	33.57	36.22	37.52	37.2	38.7
$V_{\text{intr}}(\text{i}, T)$	18.69	20.31	21.10	22.0	21.8	$V^{\infty}(\text{i}, T)$	38.67	41.63	43.45	43.9	46.3
Mg²⁺ (0.94, 1.62)						$\Delta V_{\text{elstr}}(\text{i}, T)$	-2.59	-2.83	-3.18	-3.70	-4.38
V^{conv}	-21.81	-21.17	-20.90	-21.7	-23.4	$V_{\text{intr}}(\text{i}, T)$	41.26	44.46	46.63	47.6	50.7
$V^{\infty}(\text{i}, T)$	-32.01	-31.99	-32.76	-35.1	-38.6	ClO₄⁻ (34.87, 60.15)					
$\Delta V_{\text{elstr}}(\text{i}, T)$	-51.54	-52.53	-56.40	-62.94	-71.14	V^{conv}	40.7	44.12	45.1	46.9	47.9
$V_{\text{intr}}(\text{i}, T)$	19.53	20.97	23.64	27.8	32.5	$V^{\infty}(\text{i}, T)$	45.8	49.53	51.03	53.6	55.5
Ca²⁺ (2.52, 4.35)						$\Delta V_{\text{elstr}}(\text{i}, T)$	-2.15	-2.38	-2.70	-3.18	-3.79
V^{conv}	-19.84	-17.85	-18.22	-19.1	-20.0	$V_{\text{intr}}(\text{i}, T)$	47.95	51.91	53.73	56.8	59.3
$V^{\infty}(\text{i}, T)$	-30.04	-28.67	-30.08	-32.5	-35.2	SO₄²⁻ (30.69, 52.94)					
$\Delta V_{\text{elstr}}(\text{i}, T)$	-37.34	-38.52	-41.16	-46.10	-52.26	V^{conv}	11.11	13.98	16.03	13.8	11.5
$V_{\text{intr}}(\text{i}, T)$	7.30	9.85	11.08	13.6	17.1	$V^{\infty}(\text{i}, T)$	21.30	24.80	27.89	27.2	26.7
						$\Delta V_{\text{elstr}}(\text{i}, T)$	-13.08	-13.84	-15.14	-17.32	-20.02
						$V_{\text{intr}}(\text{i}, T)$	34.38	38.64	43.03	44.5	46.9

^a The numbers after the symbol of the ions in parentheses are the “bare” ionic volume, $V_{\text{bare}}(\text{i})$, and the expanded intrinsic volume, taking into account close packing of spheres. All volumes are in cm³ mol⁻¹.

Glueckauf⁷ preferred an addend, a , to be added to the ionic radius $r_c(\text{i})$ to yield $V_{\text{intr}}(\text{i}) = (4\pi N_A/3)[r_c(\text{i}) + a]^3$. The value of a was estimated from:

$$a = (3V_W(T)/4\pi N_A)^{1/3} - r_W \quad (6)$$

where $V_W(T)$ is the temperature-dependent molar volume of water, and $r_W = 0.138$ nm is the radius of a water molecule. Over the temperature range 0–100 °C, a varies some 5%, from 0.0546 to 0.0573 nm. A numerical consequence of the addition of a to r_c is that $V_{\text{intr}}(\text{i})$ depends not only on the third power of r_c but also on the second power, corresponding to the surface of the bare ion (and first and zeroth powers too, of course), as demanded by the void space of closely packed spheres.⁷ This large expansion of the intrinsic volume requires a correspondingly large (negative) electrostriction volume in order to fit the experimental standard molar ionic volumes according to eq 3.

This needs a larger coefficient of $z(\text{i})^2 r_c(\text{i})^{-1}$ than the Drude–Nernst–Born treatment can provide.

Other views regarding the nature of the intrinsic volume have been expressed and summarized by Millero.^{1,2} The intrinsic volume was taken as the sum of the (molar) volume of the bare ion, give by eq 4, and the molar volume of disordered water, V_{dis} , not necessarily the void volume described above. Several semiempirical expressions were reviewed there.

It is the purpose of the present paper to calculate the electrostriction volume, $\Delta V_{\text{elstr}}(\text{i}, T)$, for the ions listed in Table 1 from the shell-by-shell method proposed by Marcus and Hefter,⁸ rather than from modifications of the Born expression (eq 5). This approach has the advantage that it takes the dielectric saturation in the vicinity of the ions into account as well as the field dependence of the permittivity (the nonlinear dielectric effect). Given the electrostrictive volume, $\Delta V_{\text{elstr}}(\text{i}, T)$, the intrinsic volume, $V_{\text{intr}}(\text{i}, T)$, can be deduced from eq 3 and rationalized.

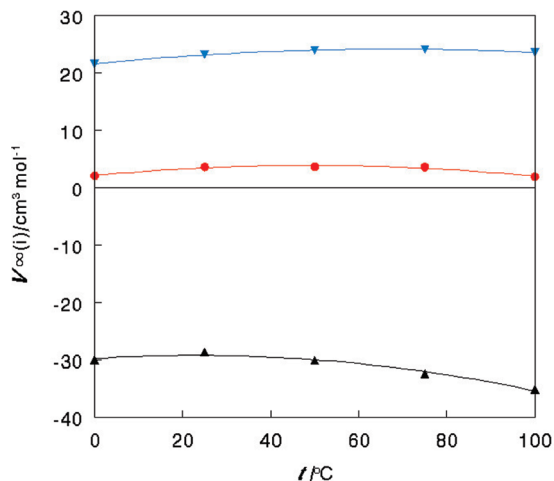


Figure 1. The standard molar ionic volumes $V_{\infty}(i, T)/\text{cm}^3 \text{mol}^{-1}$ of Cl^- (▼), K^+ (●), and Ca^{2+} (▲) at various temperatures.

This calculation also provides the spatial extension of the region around the ion in the infinitely dilute solution where dielectric saturation takes place, as it depends on the charge and size of the ion and the temperature. The average molar contraction of the water, $\Delta V_{\text{w,el}}(T)$, over the temperature range considered here was calculated according to Marcus.⁹ It leads to operationally defined hydration numbers of the ions at infinite dilution, $h^{\infty}(i, T)$.

2. Calculations

The working expression for the calculation of the electrostrictive volume derived by Marcus and Hefter⁸ is the summation of incremental values over sequentially increasing concentric shells around the ion:

$$\Delta V_{\text{elstr}}(i, T) = -(8\pi^2 N_A \epsilon_0) \sum_j [r(j)^3 - r(j-1)^3] \times \{\epsilon(j)[(\partial \ln \epsilon / \partial P)_T - \kappa_T] + \kappa_T\} E(j)^2 \quad (7)$$

The summation extends over the shell numbers j from 1 up to such a value that the incremental change in $\Delta V_{\text{elstr}}(i, T)$ is negligible. In eq 7, $r(0) = r_c(i)$, $\Delta r = r(j) - r(j-1)$ is fixed at some small value, say 0.005 nm, $\epsilon(j) = \epsilon(j, T, E)$ is the temperature- and electric field-dependent (hence pressure-dependent) relative permittivity in the j th shell, $(\partial \ln \epsilon / \partial P)_T$ is $\epsilon(j)^{-1}$ times the pressure dependence of the relative permittivity, κ_T is the isothermal compressibility of water, and $E(j) = E(j, \epsilon, T)$ is the electric field strength in the j th shell. The values of $(\partial \epsilon / \partial P)_T$ and κ_T are temperature dependent but are taken to be independent of $E(j)$.

The field strength E and the permittivity ϵ in any shell j are mutually dependent, so that an iterative calculation is required. As shown, for example, by Padova,¹⁰ the field-dependent relative permittivity is given by the Booth expression, still considered valid years later:

$$\epsilon(E) = n_{\infty}^2 + (\epsilon(0) - n_{\infty}^2)/(1 + bE^2) \quad (8)$$

Here $n_{\infty}^2 \approx 1.1n_D^2$, where $n_D(T)$ is the refractive index at the sodium D line, is the square of the infinite frequency refractive index of water, representing the saturated permittivity. The nonlinear dielectric effect $\beta = [\epsilon(E) - \epsilon(0)]/E^2$ in water is $\beta/(V^2$

$\text{m}^{-2}) = -1.080 \times 10^{-15}$, practically temperature-independent at very high fields as shown by Danielewicz-Ferchmin and Ferchmin¹¹ and is taken from Marcus and Hefter.⁸ Therefore, the coefficient $b \approx -\beta/[\epsilon(0) - 1.1n_D^2]$ in eq 8, depends on the temperature and $b/(V^2 \text{m}^{-2})$ decreases practically linearly from -1.255×10^{-17} at 0 °C to -2.006×10^{-17} at 100 °C.

The electric field strength at the periphery of a small ion is huge, on the order of 10^{11}V m^{-1} , and not readily attainable in the laboratory. It decreases rapidly with increasing distances from the ion, diminishing according to the reciprocal square of the distance from the center of the ion:

$$E(\epsilon, r) = |ze|e/(4\pi\epsilon_0)\epsilon(E, r)r^2 \quad (9)$$

As long as the field strength is $>10^8 \text{V m}^{-1}$, the permittivity of water is saturated and has values only somewhat larger than n_{∞}^2 . The iterative calculation thus combines eqs 8 and 9 until $r(j)$ in eq 7 is sufficiently large and $E(j)$ is sufficiently low for the relative permittivity to reach its bulk (field-free) value, $\epsilon(0)$.

The data for the ion required for the calculation of $\Delta V_{\text{elstr}}(i, T)$ from eqs 7–9 are the charge number $z(i)$ and the radius $r_c(i)$,¹² recorded in Table 2. For water at temperatures from 0 to 100 °C the needed data are the relative permittivity $\epsilon(T)$, its pressure derivative, $(\partial \epsilon / \partial P)_T(T)$, the isothermal compressibility $\kappa_T(T)$ from Fernandez et al.,¹³ and the refractive index $n_D(T)$,¹¹ which are recorded in Table 3. For fields $\geq 10^9 \text{V m}^{-1}$ the values of $\epsilon(E)$ become practically independent of the temperature¹¹ (n_D^2 changes by only -2.4% from 0 to 100 °C), but for lower fields its variation with T is significant, as the values of $b/(V^2 \text{m}^{-2})$ shown above indicate.

The working expression for the calculation of the average molar electrostrictive volume contraction of water given by Marcus⁹ is:

$$\Delta V_{\text{w,el}} = (S_V/S_K)\kappa_T V_W = \{2X/[X^2 - 2(\partial X / \partial P)_T]\}\kappa_T V_W \quad (10)$$

Here S_V and S_K are the limiting slopes of the Debye–Hückel expressions for the apparent molar volume and apparent molar compressibility of the ions in solution, and the auxiliary variable is $X = 3(\partial \ln \epsilon / \partial P)_T - \kappa_T$. The derivative of X with respect to the pressure requires the second pressure derivatives of the permittivity and the density of water, and these were taken from the compilations of Fernandez et al.,¹³ as shown in Table 3.

3. Results

The calculated values of $\Delta V_{\text{elstr}}(i, T)$ at 0, 25, 50, 75, and 100 °C are shown in Table 1 for 15 ions. The overall uncertainty in ΔV_{elstr} from all the sources (see Section 4) is estimated at $\pm 0.5 \text{cm}^3 \text{mol}^{-1}$. Also shown there are the values of $V_{\text{intr}}(i, T) = V^{\infty}(i, T) - \Delta V_{\text{elstr}}(i, T)$ obtained from eq 3, with a similar uncertainty, assuming the $V^{\infty}(i, T)$ values to be accurate (for some reservations regarding this assumption see the end of Section 4). These derived $V_{\text{intr}}(i, T)$ values are generally larger than those based on eq 4: $V_{\text{bare}}(i) = 2522.5(r_c(i)/\text{nm})^3$. The exceptions are Na^+ at 0 and 25 °C, Sr^{2+} at 0 °C, and Ba^{2+} at 0, 25, and 50 °C. The derived $V_{\text{intr}}(i, T)$ do not conform, at least for most ions at the lower temperatures, to the expanded volumes required by the random close packing of spheres, $1.725 \times 2522.5(r_c(i)/\text{nm})^3$, shown in Table 1.

Table 2 shows the widths of the regions of dielectric saturation, $\Delta r_{\text{elstr}}(i, T)$ (Figure 2), obtained from the shell-by-

TABLE 2: Extents in nm of the Electrostricted Region, $\Delta r_{\text{elstr}}(i,T)$, and of the Disordered/Structured Region, $\Delta r_{\text{dis}}(i,T)$, around Ions and Their Operationally Defined Hydration Numbers at Various Temperatures^a

	0 °C	25 °C	50 °C	75 °C	100 °C
Li⁺ (0.069)					
$\Delta r_{\text{elstr}}(i,T)$	0.038	0.041	0.044	0.047	0.051
$\Delta r_{\text{dis}}(i,T)$	0.047	0.044	0.042	0.042	0.042
$h^{\infty}(i,T)$	3.49	4.42	5.40	6.59	7.96
Na⁺ (0.102)					
$\Delta r_{\text{elstr}}(i,T)$	0.035	0.038	0.041	0.044	0.048
$\Delta r_{\text{dis}}(i,T)$			0.002	0.011	0.013
$h^{\infty}(i,T)$	2.30	2.94	3.62	4.44	5.40
K⁺ (0.138)					
$\Delta r_{\text{elstr}}(i,T)$	0.031	0.034	0.037	0.040	0.044
$\Delta r_{\text{dis}}(i,T)$	0.005	0.012	0.016	0.016	0.014
$h^{\infty}(i,T)$	1.57	2.02	2.73	3.11	3.81
Rb⁺ (0.149)					
$\Delta r_{\text{elstr}}(i,T)$	0.030	0.033	0.036	0.039	0.043
$\Delta r_{\text{dis}}(i,T)$	0.018	0.020	0.021	[0.022]	[0.024]
$h^{\infty}(i,T)$	1.41	1.82	2.27	2.82	3.47
Cs⁺ (0.170)					
$\Delta r_{\text{elstr}}(i,T)$	0.028	0.031	0.034	0.037	0.041
$\Delta r_{\text{dis}}(i,T)$	0.019	0.023	0.025	0.026	0.025
$h^{\infty}(i,T)$	1.15	1.51	1.89	2.36	2.91
Mg²⁺ (0.072)					
$\Delta r_{\text{elstr}}(i,T)$	0.057	0.061	0.065	0.070	0.075
$\Delta r_{\text{dis}}(i,T)$	0.085	0.085	0.089	0.096	0.103
$h^{\infty}(i,T)$	14.44	18.05	22.12	26.90	32.34
Ca²⁺ (0.100)					
$\Delta r_{\text{elstr}}(i,T)$	0.054	0.058	0.062	0.067	0.072
$\Delta r_{\text{dis}}(i,T)$	0.023	0.032	0.035	0.041	0.050
$h^{\infty}(i,T)$	10.46	13.24	16.14	19.70	23.75
Sr²⁺ (0.113)					
$\Delta r_{\text{elstr}}(i,T)$	0.053	0.057	0.061	0.066	0.071
$\Delta r_{\text{dis}}(i,T)$		0.005	0.013	0.025	0.043
$h^{\infty}(i,T)$	9.18	11.65	14.24	17.39	21.01
Ba²⁺ (0.136)					
$\Delta r_{\text{elstr}}(i,T)$	0.050	0.054	0.059	0.063	0.068
$\Delta r_{\text{dis}}(i,T)$				0.018	0.023
$h^{\infty}(i,T)$	7.43	9.46	11.62	14.23	17.24
F⁻ (0.133)					
$\Delta r_{\text{elstr}}(i,T)$	0.032	0.035	0.038	0.041	0.044
$\Delta r_{\text{dis}}(i,T)$	0.013	0.019	0.021	0.024	0.025
$h^{\infty}(i,T)$	1.65	2.13	3.64	3.26	3.98
Cl⁻ (0.181)					
$\Delta r_{\text{elstr}}(i,T)$	0.027	0.030	0.033	0.036	0.040
$\Delta r_{\text{dis}}(i,T)$	0.028	0.031	0.033	0.035	0.034
$h^{\infty}(i,T)$	1.04	1.36	1.72	2.25	2.67
Br⁻ (0.196)					
$\Delta r_{\text{elstr}}(i,T)$	0.026	0.028	0.031	0.035	0.038
$\Delta r_{\text{dis}}(i,T)$	0.029	0.033	0.036	0.037	0.038
$h^{\infty}(i,T)$	0.91	1.19	1.51	1.91	2.38
I⁻ (0.220)					
$\Delta r_{\text{elstr}}(i,T)$	0.023	0.026	0.029	0.032	0.036
$\Delta r_{\text{dis}}(i,T)$	0.029	0.034	0.037	0.037	0.041
$h^{\infty}(i,T)$	0.73	0.97	1.25	1.58	1.99
ClO₄⁻ (0.240)					
$\Delta r_{\text{elstr}}(i,T)$	0.021	0.024	0.027	0.030	0.034
$\Delta r_{\text{dis}}(i,T)$	0.023	0.029	0.031	0.035	0.038
$h^{\infty}(i,T)$	0.60	0.82	1.06	1.36	1.72
SO₄²⁻ (0.230)					
$\Delta r_{\text{elstr}}(i,T)$	0.041	0.045	0.049	0.054	0.059
$\Delta r_{\text{dis}}(i,T)$	0.006	0.013	0.020	0.021	0.024
$h^{\infty}(i,T)$	3.66	4.76	5.94	7.40	9.10

^a The numbers after the symbol of the ions in parentheses are r_c (nm).

shell calculation as the largest $r(j) - r(0)$ for $\varepsilon(j) \leq 3$ to prevail. These values are considered accurate to within ± 0.005 nm, due to the step-size Δr used in the calculation according to eq 7. The cutoff value of 3 (some 1.5 times n_{∞}^2) was chosen because beyond it $\varepsilon(j)$ rises very steeply with increasing distances $r(j)$, see Figure 2. The values of $\Delta r_{\text{elstr}}(i,T)$ are systematic with respect to r_c (diminishing with increasing ion

TABLE 3: Properties of Water at Various Temperatures: the Relative Permittivity, ε , Its First and Second Pressure Derivatives, $(\partial\varepsilon/\partial P)_T$ and $(\partial^2\varepsilon/\partial P^2)_T$, the Isothermal Compressibility κ_T and Its Pressure Derivative, $(\partial\kappa_T/\partial P)_T$, the Molar Volume, V_w , and the Average Molar Electrostriction Volume, $\Delta V_{w,\text{el}}$

$t/^{\circ}\text{C}$	0	25	50	75	100
$\varepsilon(0)$	87.98	78.41	69.93	62.42	55.75
$(\partial\varepsilon/\partial P)_T/\text{GPa}^{-1}$	41.90	37.88	35.45	34.69	34.39
$(\partial^2\varepsilon/\partial P^2)_T/\text{GPa}^{-2}$	-55.98	-59.87	-65.10	-73.44	-86.70
κ_T/GPa^{-1}	0.5088	0.4525	0.4418	0.4562	0.4902
$(\partial\kappa_T/\partial P)_T/\text{GPa}^{-2}$	-0.1425	-0.1152	-0.1171	-0.1324	-0.1580
$V_w/\text{cm}^3 \text{ mol}^{-1}$	18.02	18.07	18.23	18.48	18.80
$\Delta V_{w,\text{el}}/\text{cm}^3 \text{ mol}^{-1}$	-3.57	-2.91	-2.55	-2.34	-2.20

sizes) and T (increasing with the temperature). Most (>95%) of the solvent electrostriction, ΔV_{elstr} , takes place within this region of dielectric saturation, Δr_{elstr} .

The present approach considers the intrinsic molar volume to be the sum of the molar volume of the bare ion, $V_{\text{bare}}(i) = (4\pi N_A/3)r_c(i)^3$ and the volume of disordered water, V_{dis} , due to the presence of the ion:

$$V_{\text{intr}}(i,T) = V^{\infty}(i,T) - \Delta V_{\text{elstr}}(i,T) = V_{\text{bare}}(i) + V_{\text{dis}}(i,T) \quad (11)$$

The expansion of $V_{\text{intr}}(i,T)$ with respect to the volume of the bare ion is expressed as the width, Δr_{dis} , of the annular shell of disordered water (Figure 2) around the tight region near the ion of width Δr_{elstr} , where dielectric saturation takes place:

$$\Delta r_{\text{dis}} = [(V_{\text{intr}} - V_{\text{bare}})/(4\pi N_A/3) + (r_c + \Delta r_{\text{elstr}})^3]^{1/3} - (r_c + \Delta r_{\text{elstr}}) \quad (12)$$

The first term in eq 12 describes the distance from the center of the ion to the outer edge of the region where the disordered water exists. This is the cubic root of its molar volume per ion (divided by $4\pi/3$). The second term is the similar distance to the end of the electrostricted water layer. These values of Δr_{dis} are shown in Table 2. For cations with $r_c > 0.100$ nm (i.e., all those considered here except Li^+ , Mg^{2+} , and Ca^{2+}) the width of the disordered water region increases linearly with the temperature and is proportional to r_c :

$$\Delta r_{\text{dis}}(\text{cations})/\text{nm} = [0.115 + 0.42 \times 10^{-3}(t/^{\circ}\text{C})](r_c/\text{nm}) \quad (13a)$$

The temperature dependence for the anions appears to be better expressed as quadratic:

$$\Delta r_{\text{dis}}(\text{anions})/\text{nm} = [0.115 + 1.31 \times 10^{-3}(t/^{\circ}\text{C}) - 6 \times 10^{-6}(t/^{\circ}\text{C})^2](r_c/\text{nm})/|z| \quad (13b)$$

The division by $|z|$ in eq 13b accommodates the sulfate anion with the other anions. The fitting eqs 13a generally express the values of Δr_{dis} from eq 12 within ± 0.005 nm, the accuracy of the Δr_{elstr} values. Application of eq 13a to Rb^+ at 75 and 100 °C, for which no V^{conv} data were provided by Millero,¹ permits their estimation as shown in the bracketed values in Table 1.

The values of the average molar contraction of the water due to electrostriction, $\Delta V_{w,\text{el}}(T)$, calculated according to eq 10, are

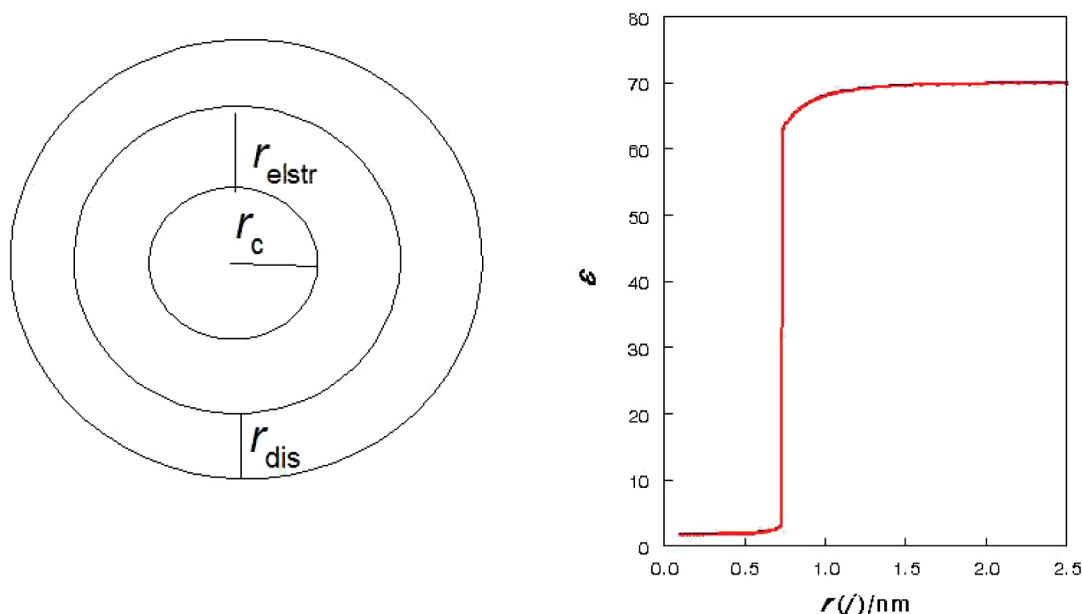


Figure 2. Left panel: two-dimensional schematic representation of the Frank and Wen²⁰ model of concentric shells around an ion in aqueous solutions. The circle marked with r_c is the bare ion, the ring marked with r_{elstr} is the electrostricted water region ($\epsilon \leq 3$) of width Δr_{elstr} ; the ring marked r_{dis} is the disordered (for structure-breaking ions) or structured (for structure-making ions) region of width Δr_{dis} ; and outside this the bulk permittivity $\epsilon(E=0)$ prevails. Right panel: schematic representation of the permittivity of water ϵ as a function of the distance from the center of an ion.

shown in Table 3. The uncertainty of these values is estimated at $\pm 0.1 \text{ cm}^3 \text{ mol}^{-1}$. The ratio of the solvent volume contraction around the ion at infinite dilution of the ions per mole of ions, $\Delta V_{\text{elstr}}(i, T)$, and $\Delta V_{\text{wel}}(T)$ (both negative quantities) should yield the number of water molecules per ion affected by its electric field. This is an operational definition⁹ of the infinite dilution hydration number:

$$h^\infty(i, T) = \Delta V_{\text{elstr}}(i, T) / \Delta V_{\text{wel}}(T) \quad (14)$$

The derived values of $h^\infty(i, T)$ are shown in Table 2 with an estimated uncertainty of ± 0.3 . They are seen to vary systematically with respect to r_c , diminishing with increasing ion sizes and increasing with the temperature, T . These derived hydration numbers are commensurate with such numbers obtained by other methods,¹² but merit some discussion.

4. Discussion

The present treatment, calculating the electrostriction according to the shell-by-shell method of Marcus and Hefter,⁸ essentially employs the restricted primitive model of the aqueous solution of ions. The ions are considered as centrally charged conducting hard spheres of fixed sizes, r_c , and the solvent, water, as a continuum with known dielectric, volumetric, and compressive properties.

The crystal ionic radii of the ions are relevant for aqueous solutions because the distances between the centers of ions and of the nearest water molecules, as measured by X-ray and neutron diffraction,^{14,15} are represented well by the sums of the r_c and the radius of a water molecule, 0.138 nm. No advance appears to have been made regarding the temperature dependence of ionic radii in solution since the statement of Ohtaki and Radnai¹⁵ that the effects of temperature on the ion–water bond lengths are very small and not detectable within the accuracies of the then available techniques. Although the values of r_c in crystals are temperature dependent as shown by

Krestov,¹⁶ they change by only $\leq 0.5\%$ over the 100 °C range considered here, so that this variation may be neglected. The molar volumes of the bare ions, $V_{\text{bare}}(i)$, are thus taken as temperature independent.

The primary result of the present approach is the electrostriction volumes, $\Delta V_{\text{elstr}}(i, T)$, calculated according to eq 7, the other results: $V_{\text{intr}}(i, T)$, $\Delta r_{\text{dis}}(i, T)$, and $h^\infty(i, T)$, being derived from them. The ion characteristics used in this calculation are $|z(i)|$ (eq 9) and $r_c(i)$, so no inherent differences between cations and anions are expected (but see below), a result of the restricted primitive model employed.

The resulting electrostriction volumes (Table 1) are considerably more negative than expected from the Drude–Nernst–Born expression (eq 5). For a univalent ion with a radius of 0.1 nm the latter values are $-\Delta V_{\text{elstr}}/\text{cm}^3 \text{ mol}^{-1} = 3.76, 4.28, 5.03, 6.18, \text{ and } 7.69$ at 0, 25, 50, 75, and 100 °C, respectively, compared with the values from eq 7 for Na^+ ($r_c = 0.102 \text{ nm}$) of 8.22, 8.56, 9.22, 10.39, and 11.87, respectively.

There are several approximations and assumptions involved in the employment of eq 7 for the calculation of the electrostriction volume. The values of $(\partial\epsilon/\partial P)_T$ and κ_T are temperature dependent but are taken to be independent of $E(j)$. As a better approximation, the known pressure derivatives of these two quantities could have been used, with pressures estimated from the field strength according to Desnoyers et al.¹⁷ or Bockris and Saluja,¹⁸ but this refinement was not employed at the present stage. The value of the nonlinear dielectric effect $\beta = -1.080 \times 10^{-15} \text{ V}^2 \text{ m}^{-2}$ was taken⁸ as a mean of values for 20–25 °C and in view of the very high field independence¹¹ of $\epsilon(E, T)$ from T was taken also as invariant in the entire range 0–100 °C. A change from this value of β to a less negative value, $-0.900 \times 10^{-15} \text{ V}^2 \text{ m}^{-2}$ as reported by Liszi et al.¹⁹ for 25 °C, changed both ΔV_{elstr} and Δr_{elstr} by $<1\%$. The temperature dependence of the coefficient b in eq 8 results therefore mainly from that of $\epsilon(0)$.

Given the values of $\Delta V_{\text{elstr}}(i, T)$, the responsibility for yielding from them values for $V^\infty(i, T)$, the standard partial molar ionic

volume, in agreement with experiment is, thus, transferred to the intrinsic molar volumes, derived by difference from eq 3. The accuracy of the experimental $V^\infty(i,T)$ values in Table 1 depends on the conversion from the conventional to the absolute values by means of eqs 1 and 2, assuming, for the present purposes, that the conventional values $V^{\text{conv}}(i,T)$ are accurate. Millero's eq 2 is the result of the unweighted means of estimates by 11 methods involving different extra-thermodynamic assumptions for the range 0–200 °C.² These are anchored at the estimate of Zana and Yeager²⁰ for 22 °C from vibration potentials, $V^\infty(\text{H}^+, \text{aq})/\text{cm}^3 \text{ mol}^{-1} = -5.4$, having a root-mean-square deviation of $0.2 \text{ cm}^3 \cdot \text{mol}^{-1}$ for its derivation from different electrolytes. The temperature derivative of these means the aqueous hydrogen ion expansivity is linear with the temperature, with its standard deviation being $0.02 \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$.² This leads to a quite large (but unstated) standard deviation of the integral expression, eq 2. If attention is limited to the range of 0–100 °C and to only the five sources^{6,21–24} yielding estimated $V^\infty(\text{H}^+, \text{aq})$ values in good agreement among themselves, the resulting expression is linear with the temperature:

$$V^\infty(\text{H}^+, \text{aq})/\text{cm}^3 \text{ mol}^{-1} = (-4.09 \pm 0.12) - (0.0266 \pm 0.0020)(t/^\circ\text{C}) \quad (15)$$

The standard deviation of the fit is $0.16 \text{ cm}^3 \text{ mol}^{-1}$, and the resulting values over the 0–100 °C range are, on the average, $0.7 \text{ cm}^3 \text{ mol}^{-1}$ less negative than those from eq 2. It cannot be claimed, however, that eq 15 is on the whole superior to eq 2, so that the conversion from the conventional $V^{\text{conv}}(i,T)$ to the absolute values $V^\infty(i,T)$ was made according to eq 2.

As said, the intrinsic volumes, $V_{\text{intr}}(i,T)$, were not calculated a priori from independent considerations but were fitted to the experimental values, albeit according to a plausible model. The model follows the classical concentric hydration shells view of Frank and Wen.²⁵ Because the model is based on the restricted primitive solution concept, it does not recognize the random packing of spheres of different sizes and hence does not allow for void spaces between the spheres. The disordered water exists in a concentric shell around the electrostricted shell (Figure 2), the width of which, Δr_{elstr} , should not be related to the irrelevant radius of a water molecule. The width of the disordered water shell, Δr_{dis} , increases with the size of the ion, eq 13a for ions with $r_c > 0.100 \text{ nm}$, a result that is compatible with the increasing water structure breaking effects of such ions.²⁶ It also increases with the temperature, which is not an obvious result from the purported two-state nature of water,^{27,28} according to which the relative amount of disordered water increases anyway with increasing temperatures.

Smaller ions, those with $r_c \leq 0.100 \text{ nm}$, that is, Li^+ , Mg^{2+} , and Ca^{2+} , have considerably larger Δr_{dis} values than derived from eq 13a. Furthermore, Δr_{dis} decreases with the increasing sizes of the divalent cations. This also includes Sr^{2+} and Ba^{2+} at the higher temperatures as far as the reported $V^\infty(i,T)$ and the derived V_{intr} values permit to judge, that is, not yielding values less than V_{bare} . These ions are water structure makers,²⁶ so that the annular shell of width Δr_{dis} specified as “disordered water” should rather be called “structured water”, Δr_{struc} , albeit not necessarily having the structure of bulk water. The rate of change of Δr_{struc} with the temperature is much larger than for the univalent cations, eq 13a:

$$\Delta r_{\text{struc}} = [A + 3.47 \times 10^{-3}(t/^\circ\text{C})](r_c/\text{nm}) \quad (16)$$

TABLE 4: Hydration Numbers of Ions at $T = 25^\circ\text{C}$: $h^\infty(i,T)$ from Equation 14, $h_{\text{Stokes}}^\infty(i,T)$ from Equation 16, and $h_{\text{compr}}^\infty(i,T)$ from Bockris and Saluja¹⁸

ion	$h^\infty(i,T)$	$h_{\text{Stokes}}^\infty(i,T)$	$h_{\text{compr}}^\infty(i,T)$
Li^+	4.4	4.3	4.0
Na^+	2.9	3.5	4.5
K^+	2.0	2.2	3.5
Rb^+	1.8	1.8	3.0
Cs^+	1.5	1.4	2.5
Mg^{2+}	18.1	18.9	10.0
Ca^{2+}	13.2	17.2	9.0
Sr^{2+}	11.7		9.0
Ba^{2+}	9.5	15.5	11.0
F^-	2.1		4.9
Cl^-	1.4	1.0	2.0
Br^-	1.2	0.6	1.8
I^-	1.0	0.0	1.5
ClO_4^-	0.8		
SO_4^{2-}	4.6	3.6	

The temperature-independent term A equals 1.083 for Mg^{2+} , 0.0185 for Ca^{2+} , and -0.035 for Sr^{2+} , rather than a size-independent value as for the univalent cations (Mg^{2+} at 0°C and Sr^{2+} at 100°C are outliers). For Li^+ $A = 0.664$, but the temperature coefficient is slightly negative: $-0.692 \times 10^{-3}(t/^\circ\text{C})$. No ready explanation for these results was found. A very short ion–water center-to-center distance, 0.223 nm , was presumed by Danielewicz-Ferchmin and Ferchmin²⁹ to hold for aqueous Sr^{2+} , being responsible for anomalies in the water structure around this ion (possibly leading to $V_{\text{intr}} < V_{\text{bare}}$ at low temperatures). However, this center-to-center distance, from the same experimental source, was not corroborated in the review by Ohtaki and Radnai.¹⁴

It remains to discuss the ionic hydration numbers at infinite dilution, $h^\infty(i,T)$, obtained from eq 14 and shown in Table 2. They increase markedly with the temperature, but hardly any information on the temperature dependence of hydration numbers, defined in any manner, could be found in the literature. The only relevant information is the Stokes radii of aqueous ions $r_{\text{Stokes}}(i,T)$, obtained by Krumgalz³⁰ from their limiting ionic molar conductivities in water and the viscosity of water at temperatures from 5 to 300°C . The validity of Stokes' law was assumed and the numerical values assumed ideal slipping conditions (if ideal sticking were assumed, the values would be increased by the factor $6/4$). Ionic hydration numbers at infinite dilution can be derived¹² from the Stokes radii via the operational expression:

$$h_{\text{Stokes}}^\infty(i,T) = z^2[kN_A(4\pi/3)\{0.214 + 0.427(r_{\text{Stokes}}(i,T)/\text{nm})\}^3/V_w(i,T)] \quad (17)$$

where $k = 0.888$ is a packing factor and the values in curled brackets are corrected Stokes radii introduced by Nightingale³¹ to make the “raw” Stokes radii compatible with the sizes of hydrated ions, a correction assumed to be independent of the temperature. The values of $h_{\text{Stokes}}^\infty(i,T)$ for the ions studied here increase mildly with increasing temperatures. Agreement of $h_{\text{Stokes}}^\infty(i,T)$ with the values of $h^\infty(i,T)$ obtained via eq 14 for 25°C is seen in Table 4, but the temperature dependence of the former is much smaller than that of the latter, possibly due to the assumed independence of the Nightingale correction from the temperature. Therefore, at 100°C the $h^\infty(i,T)$ are considerably larger than the hydration numbers obtained from the Stokes radii of Krumgalz via eq 17. However, no further hydration

numbers for temperatures other than 20 or 25 °C appear to have been reported.

A host of other operational definitions of hydration numbers, hence of their numerical values, have been reported in the literature, and as an example for their variety the comparison made by Bockris and Saluja¹⁸ may be quoted. In view of the operational definition and derivation of the present $h^\infty(i,T)$ values (Table 4), they are most akin to those obtained from compressibility data rather than ones derived from transport data (i.e., Stokes radii). Therefore, also shown in Table 4 are the compressibility-derived values, $h_{\text{compr}}^\infty(i,T)$, reported by Bockris and Saluja.¹⁸ These were obtained, for complete electrolytes, according to Passinskii's method,³² assuming that the ion itself and the electrostricted water surrounding it are not further compressible by the application of external pressure. The electrolyte data (sum of cation and anion values) were split¹⁸ into the ionic values from the vibration potential data of Zana and Yeager²⁰ (difference between cation and anion values) that are essentially transport properties.

A final word is due the anomaly presented by the sodium cation. Nonconformation of the small cations Li^+ and Mg^{2+} to the behavior expected from the restricted primitive model employed here is readily rationalized in terms of crowding of water molecules around the former and strong coordinative bonds in the first hydration shell of the latter. However, in the case of Na^+ such rationalization cannot be suggested. The experimental standard partial molar volumes $V^\infty(i,T)$ of aqueous Na^+ ions that are at 0 and 25 °C more negative than those of Li^+ ions are well established. On the other hand, the electrostriction of the water around the larger of these two ions, Na^+ , should be less than around the smaller one, Li^+ (Table 1). The result is an apparent intrinsic molar volume $V_{\text{intr}}(\text{Na}^+, 0 \text{ and } 25 \text{ }^\circ\text{C})$ that is smaller than the molar volume of the bare ion, $V_{\text{bare}}(\text{Na}^+)$ shown in Table 1. No ready explanation of these facts could be provided. Note that $V_{\text{intr}} < V_{\text{bare}}$ also resulted for Sr^{2+} and Ba^{2+} at the lower temperatures, but there it is suspected that the $V^\infty(i,T)$ or $V^\infty(\text{salt},T)$ are at fault. In the case of Sr^{2+} at 0 °C, the value of $V^{\text{conv}} = -20.77 \text{ cm}^3 \text{ mol}^{-1}$ from Millero¹ is ca. $3 \text{ cm}^3 \text{ mol}^{-1}$ more negative than the value estimated by Tanger and Helgeson,³³ -17.85 , whereas the latter estimates for 25 and 50 °C agree considerably better with the values Millero's review.¹ The data for Ba^{2+} remain puzzling, but the extrapolation to infinite dilution of most of the data compiled by Millero^{1,2} for temperatures other than 25 °C was made by Masson's empirical expression³⁴ rather than by the appropriate use of the theoretical (Debye–Hückel) limiting slopes according to Redlich and Meyer,³⁵ a fact that may lead to faulty $V^{\text{conv}}(i,T)$ values.

In particular, possible ion pairing of the 1:2 or 2:1 electrolytes used for obtaining $V^{\text{conv}}(i,T)$ could be a source for inaccuracies, in particular at elevated temperatures where the permittivity of water is only moderate. On the other hand, competition of the

strong hydration of divalent ions with the electrostatic interaction leading to ion pairing must also be taken into account, with the latter diminishing with decreasing concentrations. The data for the alkaline earths used are for the chlorides and are for sulfate for the sodium (or potassium) salts.² Data for calcium chloride, for instance, at moderate temperatures show association constants <1 ,³⁶ that is, hardly any ion pairing in dilute solutions. Specifically, no formation of CaCl^+ could be detected at 100 °C.³⁷ The same is true for NaSO_4^- formation, with an association constant <1 .³⁸ Thus, ion pairing may be discounted as a source of inaccurate $V^{\text{conv}}(i,T)$ values below 100 °C.

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