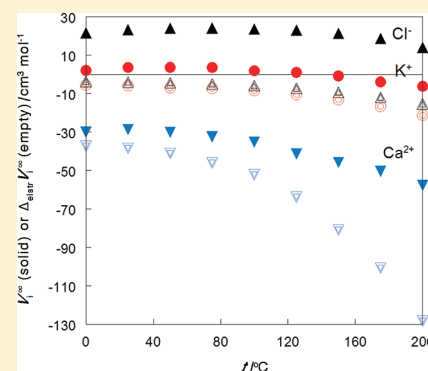


The Standard Partial Molar Volumes of Ions in Solution. Part 5. Ionic Volumes in Water at 125–200 °C

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ABSTRACT: The standard partial molar volumes, $V^\infty(i,T)$, of 12 univalent ions (alkali metal, ammonium, halide, nitrate, and perchlorate) and five divalent ions (alkaline earth and sulfate) in water at 125, 150, 175, and 200 °C and at 2 MPa were derived from the data of Ellis. Similar data for NH_4^+ and NO_3^- at 0–100 °C, not included in Part 4, were added, derived from his data too. The (negative) electrostrictive volumes, $\Delta V_{\text{elstr}}(i,T)$, of these ions at infinite dilution were 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 of the water around the ion and the electrical field strength at it. The expanded volumes of the ions, defined as $V_{\text{Expan}}(i,T) = V^\infty(i,T) - \Delta V_{\text{elstr}}(i,T)$, were then derived and compared with their intrinsic volumes, calculated according to Glueckauf. The calculation yields also the spatial extension of the dielectrically saturated region around the ions. The numbers of water molecules, the molar volume of which is affected by the ions at infinite dilution, were estimated from the ratio of $\Delta V_{\text{elstr}}(i,T)$ and $V_{\text{wel}}(T)$, the latter being the average molar electrostriction of the water in the vicinity of the ions.



1. INTRODUCTION

Some 40 years ago, Ellis published a set of papers in which the standard partial molar volumes of numerous aqueous salts up to 200 °C (at 20 atm pressure) were reported.^{1–3} Most of the data up to 100 °C were treated in Part 4 of the present series,⁴ but the higher temperature data, at 125, 150, 175, and 200 °C, did not receive the attention due to them. One of the reasons for this was the scarcity of the required properties of the solvent, water, at these temperatures, which, although available in principle in the literature, had to be recalculated in a proper manner. This was done for the present paper. A great stumbling block on this road was the relation of the permittivity of the water with the ionic field strength (the nonlinear dielectric effect) at temperatures above 100 °C, which was overcome by calculations made by Danielewicz-Ferchmin and Ferchmin.⁵

Other authors reported standard partial molar volumes of aqueous electrolytes at elevated temperatures but at considerably larger pressures than that (2.0265 MPa (20 atm)) used by Ellis:^{1–3} 10 and 30 MPa for Na_2SO_4 and K_2SO_4 ,^{6,7} and for MgCl_2 ,⁸ 10 and 28 MPa for NH_4Cl ,⁹ 16 and 32 MPa for LiCl ¹⁰ and NaBr ,¹¹ 20 and 40 MPa for NaCl ¹² and CaCl_2 ,¹³ and 17.7 MPa for NaCl .¹⁴ However, the intent in the present paper was not to explore the effects of the external pressure on the standard partial molar volumes of the electrolytes and ions, but to remain as close as possible to the saturation line (for which data at ≤ 100 °C are available). Therefore the paper deals only with the consistent set of the data of Ellis^{1–3} at 2.0265 MPa, with the assumption that the small pressure difference from the saturation pressures (see Table 2 below) does not affect the standard partial molar volumes outside the experimental errors

in these data and those inherent in the estimation of the individual ionic values (see below).

Conventional ionic standard partial molar volumes, $V^{\text{conv}}(i)$, were derived from the above-mentioned data^{1–3} by means of the Ellis and McFadden data for aqueous hydrochloric acid at the relevant temperatures¹⁵ on setting $V^{\text{conv}}(\text{H}^+, \text{aq}) = 0$. This provides values for $V^{\text{conv}}(\text{Cl}^-, \text{aq})$, and application of the ionic additivity principle at infinite dilution then yields the conventional values for the other ions treated. Millero¹⁶ provided estimates for the absolute standard partial molar volumes of the hydrogen ion, $V^\infty(\text{H}^+, \text{aq})/\text{cm}^3 \cdot \text{mol}^{-1}$, at the relevant temperatures: -8.8 at 125 °C, -10.1 at 150 °C, -11.7 at 175 °C, and -13.5 at 200 °C, implicitly at or near the saturation pressure. These values, obtained from the partial molar expansibilities, differ somewhat from those suggested by Ellis and McFadden¹⁵ on the basis of correspondence plots. Use of the Millero values¹⁶ then yields the absolute ionic standard partial molar volumes $V^\infty(i)$:

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

where z_i is the (algebraic) ionic charge number. The resulting values of $V^{\text{conv}}(i)$ and $V^\infty(i)$ are shown in Table 1 for 100, 125, 150, 175, and 200 °C (the 100 °C values are from Part 4 for comparison⁴). For ammonium and nitrate ions, the corresponding values at 0, 25, 50, and 75 °C, not included in Part 4,⁴ are also shown there.

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Table 1. Conventional Molar Ionic Volumes, V^{conv} , Absolute Molar Ionic Volumes, $V^{\infty}(i,T)$, and Molar Volume Decrements on Electrostriction, $\Delta V_{\text{elstr}}(i,T)$, of Aqueous Ions at Various Temperatures^a

Volumes/cm ³ ·mol ⁻¹	100 °C	125 °C	150 °C	175 °C	200 °C
			H+		
V^{conv}	0	0	0	0	0
$V^{\infty}(i,T)^{16}$	-7.6	-8.8	-10.1	-11.7	-13.5
			Li ⁺ (0.8)		
V^{conv}	-2.7	-3.6	-4.7	-7.0	-8.1
$V^{\infty}(i,T)$	-10.3	-12.4	-14.8	-18.7	-21.6
$\Delta V_{\text{elstr}}(i,T)$	-17.5	-21.3	-27.2	-33.8	-42.9
			Na ⁺ (2.7)		
V^{conv}	0.8	0.9	1.2	0.5	-0.1
$V^{\infty}(i,T)$	-6.8	-7.9	-8.9	-11.2	-13.6
$\Delta V_{\text{elstr}}(i,T)$	-11.9	-14.4	-18.5	-23.1	-29.6
			K ⁺ (6.6)		
V^{conv}	9.5(10.2) ^b	9.4(10.1) ^b	9.3(9.8) ^b	7.8(9.3) ^b	7.3(8.6) ^b
$V^{\infty}(i,T)$	1.9	1.0	-0.8	-3.9	-6.2
$\Delta V_{\text{elstr}}(i,T)$	-8.4	-10.5	-13.2	-16.7	-21.3
			Rb ⁺ (8.3)		
V^{conv}	14.9 ^b	14.8 ^b	14.6 ^b	14.1 ^b	13.6 ^b
$V^{\infty}(i,T)$	8.3	6.0	4.5	2.4	0.1
$\Delta V_{\text{elstr}}(i,T)$	-7.6	-9.3	-13.1	-15.2	-19.5
			Cs ⁺ (12.4)		
V^{conv}	23.0	23.2	23.5	22.3	22.1
$V^{\infty}(i,T)$	15.4	14.4	13.4	10.6	8.6
$\Delta V_{\text{elstr}}(i,T)$	-5.6	-7.8	-10.2	-12.9	-16.7
			NH ₄ ⁺ (8.28)		
V^{conv}	19.5	19.3	19.1	18.8	20.0
$V^{\infty}(i,T)$	11.9	10.5	9.0	7.1	6.5
$\Delta V_{\text{elstr}}(i,T)$	-7.5	-9.5	-12.2	-15.3	-19.7
			Mg ²⁺ (0.9)		
V^{conv}	-23.4	-26.0	-29.0	-34.0	-37.0
$V^{\infty}(i,T)$	-38.6	-43.6	-49.2	-57.4	-64.0
$\Delta V_{\text{elstr}}(i,T)$	-71.1	-86.9	-109.8	-136.2	-173.0
			Ca ²⁺ (2.5)		
V^{conv}	-20.0	-23.7	-25.7	-27.0	-30.7
	(-19.6) ^b	(-21.3) ^b	(-23.8) ^b	(-28.4) ^b	(-33.0) ^b
$V^{\infty}(i,T)$	-35.2	-41.3	-45.9	-50.4	-57.7
$\Delta V_{\text{elstr}}(i,T)$	-52.3	-63.9	-81.0	-100.8	-128.3
			Sr ²⁺ (3.6)		
V^{conv}	-17.4	-19.8	-22.4	-25.5	-29.0
$V^{\infty}(i,T)$	-32.6	-37.4	-42.6	-48.9	-56.0
$\Delta V_{\text{elstr}}(i,T)$	46.2	-56.6	-71.7	-89.4	-114.0
			Ba ²⁺ (6.3)		
V^{conv}	-83.1	-10.5	-11.9	-15.0	-17.0
$V^{\infty}(i,T)$	-23.3	-28.1	-32.1	-38.4	-44.0
$\Delta V_{\text{elstr}}(i,T)$	-37.8	-46.5	-59.3	-74.0	-94.0
			F ⁻ (5.9)		
V^{conv}	-3.7	-6.4	-10.3	-14.4	-21.3
$V^{\infty}(i,T)$	3.9	2.4	-0.2	-2.7	-7.8
$\Delta V_{\text{elstr}}(i,T)$	-8.8	-10.5	-13.8	-17.3	-22.2
			Cl ⁻ (15.0)		
V^{conv}	16.0(16.1) ^b	14.1(14.2) ^b	11.2(11.1) ^b	7.0(6.2) ^b	0.5(-0.2) ^b
$V^{\infty}(i,T)$	23.6	22.9	21.3	18.7	14.0
$\Delta V_{\text{elstr}}(i,T)$	-5.9	-7.2	-9.3	-11.9	-15.3
			Br ⁻ (19.0)		
V^{conv}	24.9	23.9	21.5	19.2	13.0
$V^{\infty}(i,T)$	32.5	32.7	31.6	30.9	26.5
$\Delta V_{\text{elstr}}(i,T)$	-5.2	-6.4	-8.4	-10.7	-13.8
			I ⁻ (26.9)		
V^{conv}	38.7	37.5	35.8	34.6	30.2
$V^{\infty}(i,T)$	46.3	46.36	45.9	46.3	43.7
$\Delta V_{\text{elstr}}(i,T)$	-4.4	-5.4	-7.1	-9.0	-11.9

Table 1. continued

Volumes/cm ³ ·mol ⁻¹	100 °C	125 °C	150 °C	175 °C	200 °C
			NO ₃ ⁻ (20.2)		
V ^{conv}	31.9	31.6	30.0	28.2	22.3
V [∞] (i,T)	39.5	40.4	40.1	39.9	35.8
ΔV _{elstr} (i,T)	-4.9	-6.2	-8.2	-10.4	-13.5
			ClO ₄ ⁻ (34.9)		
V ^{conv}	47.9	48.6	48.2	46.5	43.0
V [∞] (i,T)	55.5	57.4	58.3	58.2	56.5
ΔV _{elstr} (i,T)	-3.8	-4.6	-6.2	-8.0	-10.4
			SO ₄ ²⁻ (30.7)		
V ^{conv}	11.5	6.2	-0.7	-10.3	-22.9
V [∞] (i,T)	26.7	23.8	19.5	13.1	4.1
ΔV _{elstr} (i,T)	-20.0	-24.6	-31.8	-40.2	-51.9
volumes/cm ³ ·mol ⁻¹	0 °C	25 °C	50 °C	75 °C	
			NH ₄ ⁺		
V ^{conv}	17.5	17.9	19.2	19.5	
V [∞] (i,T)	12.4	12.5	13.3	12.9	
ΔV _{elstr} (i,T)	-3.8	-4.5	-5.2	-6.2	
			NO ₃ ⁻		
V ^{conv}	26.6	29.0	30.3	30.7	
V [∞] (i,T)	31.7	34.4	36.2	37.3	
ΔV _{elstr} (i,T)	-2.3	-2.7	-3.3	-4.0	

^aThe numbers in parentheses after the symbols of the ions are the “bare” ionic volume, $V_{\text{bare}}(i)/\text{cm}^3\cdot\text{mol}^{-1}$. ^bValues from ref 27.

2. CALCULATIONS

The electrostriction volume, $\Delta V_{\text{elstr}}(i,T)$, for the ions listed in Table 1 were calculated from the shell-by-shell method proposed by Marcus and Hefter.¹⁷ The working expression for this calculation is:

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

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 expression 2, $r(0) = r_c(i)$, the radius of the bare ion, $\Delta r = r(j) - r(j-1) = 0.005$ nm was used for convenience, $\epsilon(j) = \epsilon(j,T,E)$ is the temperature- and electric field-dependent relative permittivity in the j th shell, and $E(j) = E(j,\epsilon,T)$ is the electric field strength in this shell. The other symbols have their usual meaning, and the values of $(\partial \epsilon / \partial P)_T$ and κ_T are temperature dependent but are taken to be independent of $E(j)$, implicitly assumed by Frank in his seminal paper¹⁸ as suggested by Wood and Quint¹⁹ (but see the discussion). The relevant values for water are shown in Table 2 for 100 to 200 °C, interpolated in the tables of $\epsilon(P,T,\rho)$ of Fernandez et al.²⁰

An iterative calculation is required because the field strength E and the permittivity ϵ in any shell j are mutually dependent. At the periphery of a small ion, E is huge, on the order of 10^{11} V·m⁻¹, a field strength that is not artificially attainable in the laboratory.²¹

$$E(\epsilon, r) = |ze| / (4\pi\epsilon_0) \epsilon(E, r) \cdot r^2 \quad (3)$$

As the distance r from the center of the ion increases, E diminishes rapidly as the second power of r . As long as the field strength is $>10^8$ V·m⁻¹, the permittivity of water is saturated and has values only somewhat larger than n_∞^2 , the square of the infinite frequency refractive index. The iterative calculation thus proceeds until $r(j)$ in eq 3 is sufficiently large and $E(j)$ is sufficiently low for the relative permittivity to reach its bulk

Table 2. The Relevant Properties of Water

property	100 °C	125 °C	150 °C	175 °C	200 °C
P/MPa^a	0.1013	0.2320	0.4757	0.8926	1.5551
ϵ^b	55.53	49.44	44.04	39.18	34.76
$(\partial \epsilon / \partial P)_T / \text{GPa}^{-1}{}^b$	34.69	35.28	37.76	40.16	43.77
$(\partial^2 \epsilon / \partial P^2)_T / \text{GPa}^{-2}{}^b$	-86.70	-106.8	-131.4	-155.4	-193.9
$\kappa_T / \text{GPa}^{-1}{}^c$	0.4902	0.5225	0.5960	0.7085	0.8780
$(\partial \kappa_T / \partial P)_T / \text{GPa}^{-2}{}^c$	-1.58	-2.28	-3.15	-4.10	-5.32
n_∞^{2d}	1.9125	1.8920	1.8705	1.8451	1.8187
$10^{17}b / (\text{GV}\cdot\text{m}^{-1})^2{}^e$	-2.01	-2.27	-2.56	-2.89	-3.28
$V_W / \text{cm}^3\cdot\text{mol}^{-1}{}^f$	18.80	19.18	19.64	20.14	20.83
$\Delta V_{\text{Wd}} / \text{cm}^3\cdot\text{mol}^{-1}{}^g$	-2.44	-2.31	-2.32	-2.45	-2.60

^aFrom Sengers and Kamgar-Parsi²⁹ (interpolated where necessary).

^bFrom Fernandez et al.²⁰ (interpolated as necessary). ^cCalculated from data of Kell and Whalley³⁰ up to 150 °C, and from data of Schmidt³¹ up to 200 °C (interpolated as necessary). ^dFrom Harvey et al.²⁵ ^eCalculated from data supplied by Danielewicz-Ferchmin and Ferchmin.^{5f}Calculated from data of Schmidt.³¹ ^gCalculated from eq 7.

(field-free) value, $\epsilon(0)$, at which distance the incremental change in $\Delta V_{\text{elstr}}(i,T)$ becomes negligible.

The field-dependent relative permittivity, the nonlinear dielectric effect, was reviewed by several authors (e.g., refs 22 and 23) and since it cannot be measured experimentally for fields $>10^7$ V·m⁻¹,²¹ it has to be calculated theoretically. A good approximation is the Booth expression (ignoring the difference between the integral and the differential value) as presented by Grahame and as suggested by Liszi et al.²²

$$\epsilon(E) = n_\infty^2 + (\epsilon(0) - n_\infty^2) / (1 + bE^2) \quad (4)$$

However, values of the coefficient b have been reported only for near ambient conditions; they could be deduced from the values of $E(\epsilon,T)$ for $273 \leq T/\text{K} \leq 373$ reported by Danielewicz-Ferchmin and Ferchmin²⁴ and were used in Part 4.⁴ Values of $E(\epsilon,T)$ communicated by them to the present author for higher temperatures⁵ were employed in the present study. The square of the refractive index of water at infinite

frequency at these temperatures, n_{∞}^2 , is not known, but can be approximated well as $n_{\infty}^2 \approx 1.1n_D(T)^2$, where $n_D(T)$ is the refractive index at the sodium D line, at 589 nm.²⁵ The n_{∞}^2 and b values for 100–200 °C are shown in Table 2.

The expanded volume, $V_{\text{Expan}}(i, T)$, was calculated from

$$V_{\text{Expan}}(i, T) = V^{\infty}(i, T) - \Delta V_{\text{elstr}}(i, T) \quad (5)$$

(Note the change in naming this quantity from “intrinsic volume” used in Part 4.⁴) It includes the volume of the bare ion, the volume of voids between the ion and water molecules and among the latter, as well as certain regions of water associated with the ion.⁴ The shell-by-shell method also provides the spatial extension of the region around the ion where dielectric saturation occurs, as it depends on the charge and size of the ion and the temperature.

The average molar contraction of the water, $\Delta V_{\text{Wel}}(T)$, over the temperature range considered here was calculated according to Marcus.²⁶ It leads to the number of water molecules, the molar volume of which is affected by the ions at infinite dilution, $h^{\infty}(i, T)$:

$$h^{\infty}(i, T) = \Delta V_{\text{elstr}}(i, T) / \Delta V_{\text{Wel}}(T) \quad (6)$$

These may be construed as operationally defined hydration numbers. The average molar contraction of the volume of water due to electrostriction was given by Marcus²⁶ as

$$\Delta V_{\text{Wel}} = \{2X/[X^2 - 2(\partial X/\partial P)_T]\} \kappa_T V_W \quad (7)$$

Here the auxiliary variable is $X = 3(\partial \ln \epsilon/\partial P)_T - \kappa_T$, and V_W is the molar volume of water. The derivative of X with respect to the pressure requires the second pressure derivatives of the permittivity and the density of water, again interpolated in the tables of $\epsilon(P, T, \rho)$ of Fernandez et al.²⁰ The data for water at 100–200 °C are shown in Table 2.

3. RESULTS

The calculated values of the electrostriction volume decrement, $\Delta V_{\text{elstr}}(i, T)$, from application of eqs 2–4 at 125, 150, 175, and 200 °C, are shown in Table 1, where also the values for 100 °C, taken from Part 4,⁴ are shown for comparison. Figure 1 shows both the $V^{\infty}(i, T)$ and the $\Delta V_{\text{elstr}}(i, T)$ values for K^+ , Cl^- , and Ca^{2+}

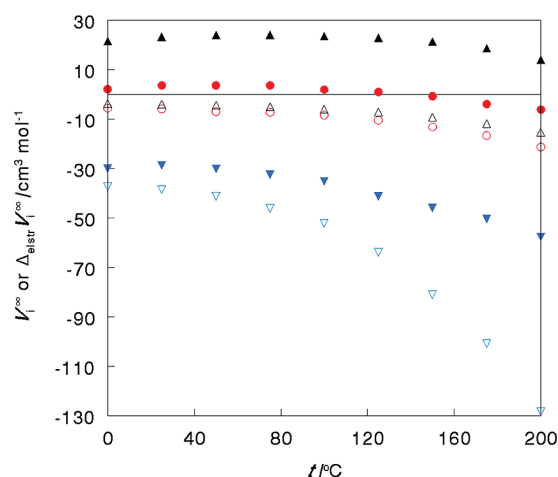


Figure 1. The standard partial ionic molar volumes V_i^{∞} (filled symbols) and the electrostriction volumes $\Delta_{\text{elstr}} V_i^{\infty}$ (open symbols) of aqueous K^+ (●, ○), Cl^- (▲, △), and Ca^{2+} (▼, ▽) at various temperatures along the saturation line.

as representative ions over the entire range, 0–200 °C. The conventional values, $V^{\text{conv}}(i, T)$, for these three ions, estimated by Tanger and Helgeson²⁷ from a revised equation of state, are also shown in Table 1. They agree quite well with the experimental values derived from Ellis^{1–4} for Cl^- , but somewhat less so for K^+ and Ca^{2+} . No data for $V^{\text{conv}}(\text{Rb}^+, T)$ were available from Ellis, hence the values from Tanger and Helgeson were used instead. Some irregularities in the derived quantities for Rb^+ may be ascribed to this.

The expanded volumes of the ions, $V_{\text{Expan}}(i, T)$, obtained from application of eq 5, are shown in Table 3, along with their intrinsic volumes, $V_{\text{intr}}(i, T)$, calculated as discussed below, with which they may be compared.

The widths of the regions of dielectric saturation, $\Delta r_{\text{elstr}}(i, T)$, obtained from the shell-by-shell calculation are the largest values of $r(j) - r(0)$ for $E(j) \geq 8 \text{ GV}\cdot\text{m}^{-1}$ to prevail. The cutoff value of $8 \text{ GV}\cdot\text{m}^{-1}$ was chosen because beyond it, $\epsilon(j)$ rises very steeply with increasing distances $r(j)$. These $\Delta r_{\text{elstr}}(i, T)$ values are shown in Table 3 and are considered to be accurate to within $\pm 0.005 \text{ nm}$, due to the step-size Δr used in the calculation according to eq 2. The values of $\Delta r_{\text{elstr}}(i, T)$ are systematic with respect to $r_c(i)$ (diminishing with increasing ion sizes) and T (increasing with the temperature). Most (>95%) of the electrostriction, ΔV_{elstr} , takes place within this region of dielectric saturation, Δr_{elstr} .

The water molecules in the dielectric saturation region are rotationally immobilized by the field of the ion and their volume is strongly compressed. The values of the average molar contraction of the water due to electrostriction, $\Delta V_{\text{Wel}}(T)$, calculated according to eq 7, are seen in Table 2 to have a maximum (minimum of the negative values) near 125 °C and are considered to have an uncertainty of $\pm 0.1 \text{ cm}^3 \text{ mol}^{-1}$. The ratio of $\Delta V_{\text{elstr}}(i, T)$, the molar solvent volume contraction around the ion per mole of ions, and $\Delta V_{\text{Wel}}(T)$ (both negative quantities), eq 6, should yield the number of water molecules per ion rotationally immobilized and the molar volumes of which is compressed by the ionic electric field. This may be construed as an operational definition²⁶ of the infinite dilution hydration number. The derived values of $h^{\infty}(i, T)$ are shown in Table 3 with an estimated uncertainty of ± 0.3 units. They are seen to vary systematically with respect to $r_c(i)$, diminishing with increasing ion sizes, and to increase with the temperature, T . These derived hydration numbers are commensurate with such numbers obtained by other methods²⁸ for univalent ions but at the elevated temperatures are much larger than those generally ascribed to the divalent cations.

4. DISCUSSION

The restricted primitive model of the aqueous solution of ions is employed here. The solvent, water, is considered to be a continuum with known dielectric, volumetric, and compressive properties (Table 2), and the ions are considered to be centrally charged conducting hard spheres of fixed sizes, their crystal ionic radii r_c (Table 3).²⁸ The values of r_c in crystals are temperature dependent, as shown by Krestov,³² but 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, $V_{\text{bare}}(i)$ (Table 1), are thus taken as temperature independent.

This paper deals with the standard partial molar volumes, i.e., those at infinite dilution, hence, the properties of pure water may be used in the calculations using the restricted primitive model of the solutions. The accuracy of the experimental $V^{\infty}(i, T)$

Table 3. The Ionic Expanded Molar Volumes, $V_{\text{Expan}}(i,T)$ (eq 5), the Ionic Intrinsic Molar Volumes, $V_{\text{intr}}(i,T)$ (eq 13), the Widths of the Rotationally Immobilized Water (Dielectric Saturation) Regions near Ions,^a $\Delta r_{\text{elstr}}(i,T)$, and Their Operationally Defined Hydration Numbers, $h^{\infty}(i,T)$ (eq 6)^b

	100 °C	125 °C	150 °C	175 °C	200 °C		100 °C	125 °C	150 °C	175 °C	200 °C
Li ⁺ (0.069, 1.5)						Ba ²⁺ (0.136, 11.3)					
$V_{\text{Expan}}(i,T)/\text{cm}^3\cdot\text{mol}^{-1}$	5.1	8.9	12.8	15.1	21.3	$\Delta r_{\text{elstr}}(i,T)/\text{nm}$	0.068	0.071	0.074	0.077	0.080
$V_{\text{intr}}(i,T)/\text{cm}^3\cdot\text{mol}^{-1}$	5.1	5.3	5.5	5.7	5.9	$h^{\infty}(i,T)$	15.5	20.1	25.6	30.2	36.1
$\Delta r_{\text{elstr}}(i,T)/\text{nm}$	0.051	0.053	0.056	0.059	0.062	F ⁻ (0.133, 10.6)					
$h^{\infty}(i,T)$	7.2	9.2	11.7	13.8	16.5	$V_{\text{Expan}}(i,T)/\text{cm}^3\cdot\text{mol}^{-1}$	12.7	12.9	13.6	14.6	14.4
Na ⁺ (0.102, 4.8)						$V_{\text{intr}}(i,T)/\text{cm}^3\cdot\text{mol}^{-1}$	17.4	17.8	18.2	18.7	19.3
$V_{\text{Expan}}(i,T)/\text{cm}^3\cdot\text{mol}^{-1}$	5.1	6.5	9.6	11.9	16.0	$\Delta r_{\text{elstr}}(i,T)/\text{nm}$	0.044	0.048	0.052	0.056	0.060
$V_{\text{intr}}(i,T)/\text{cm}^3\cdot\text{mol}^{-1}$	10.2	10.5	10.8	11.1	11.6	$h^{\infty}(i,T)$	3.6	4.6	6.0	7.1	8.5
$\Delta r_{\text{elstr}}(i,T)/\text{nm}$	0.048	0.051	0.054	0.058	0.061	Cl ⁻ (0.181, 26.7)					
$h^{\infty}(i,T)$	4.9	6.2	8.0	9.4	11.4	$V_{\text{Expan}}(i,T)/\text{cm}^3\cdot\text{mol}^{-1}$	29.5	30.1	30.6	30.6	29.3
K ⁺ (0.138, 11.8)						$V_{\text{intr}}(i,T)/\text{cm}^3\cdot\text{mol}^{-1}$	34.2	34.7	35.4	36.1	37.1
$V_{\text{Expan}}(i,T)/\text{cm}^3\cdot\text{mol}^{-1}$	10.3	11.5	12.4	12.8	15.1	$\Delta r_{\text{elstr}}(i,T)/\text{nm}$	0.040	0.042	0.044	0.046	0.048
$V_{\text{intr}}(i,T)/\text{cm}^3\cdot\text{mol}^{-1}$	18.8	19.2	19.6	20.1	20.8	$h^{\infty}(i,T)$	2.4	3.1	4.0	4.9	5.9
$\Delta r_{\text{elstr}}(i,T)/\text{nm}$	0.044	0.048	0.052	0.056	0.060	Br ⁻ (0.196, 33.9)					
$h^{\infty}(i,T)$	3.4	4.6	6.0	6.8	8.2	$V_{\text{Expan}}(i,T)/\text{cm}^3\cdot\text{mol}^{-1}$	37.7	43.7	40.0	41.3	40.3
Rb ⁺ (0.149, 14.9)						$V_{\text{intr}}(i,T)/\text{cm}^3\cdot\text{mol}^{-1}$	41.0	41.7	42.4	43.3	44.4
$V_{\text{Expan}}(i,T)/\text{cm}^3\cdot\text{mol}^{-1}$	15.9	15.3	17.6	17.6	19.6	$\Delta r_{\text{elstr}}(i,T)/\text{nm}$	0.038	0.041	0.043	0.046	0.048
$V_{\text{intr}}(i,T)/\text{cm}^3\cdot\text{mol}^{-1}$	22.2	22.6	23.1	23.7	24.4	$h^{\infty}(i,T)$	2.2	2.8	3.6	4.3	5.3
$\Delta r_{\text{elstr}}(i,T)/\text{nm}$	0.043	0.047	0.052	0.056	0.060	I ⁻ (0.220, 47.9)					
$h^{\infty}(i,T)$	3.5	4.1	5.7	6.2	7.5	$V_{\text{Expan}}(i,T)/\text{cm}^3\cdot\text{mol}^{-1}$	50.7	51.7	53.0	55.3	55.6
Cs ⁺ (0.170, 22.1)						$V_{\text{intr}}(i,T)/\text{cm}^3\cdot\text{mol}^{-1}$	53.8	54.6	55.5	56.5	58.3
$V_{\text{Expan}}(i,T)/\text{cm}^3\cdot\text{mol}^{-1}$	21.8	22.2	23.6	23.5	25.3	$\Delta r_{\text{elstr}}(i,T)/\text{nm}$	0.036	0.039	0.042	0.045	0.048
$V_{\text{intr}}(i,T)/\text{cm}^3\cdot\text{mol}^{-1}$	29.7	30.2	30.8	31.5	32.4	$h^{\infty}(i,T)$	1.8	2.4	3.0	3.7	4.5
$\Delta r_{\text{elstr}}(i,T)/\text{nm}$	0.041	0.045	0.050	0.054	0.058	NO ₃ ⁻ (0.200, 36.0)					
$h^{\infty}(i,T)$	2.9	3.3	4.4	5.3	6.4	$V_{\text{Expan}}(i,T)/\text{cm}^3\cdot\text{mol}^{-1}$	44.4	46.6	48.9	50.3	49.3
NH ₄ ⁺ (0.148, 14.6)						$V_{\text{intr}}(i,T)/\text{cm}^3\cdot\text{mol}^{-1}$	43.0	43.7	44.4	45.3	46.5
$V_{\text{Expan}}(i,T)/\text{cm}^3\cdot\text{mol}^{-1}$	19.4	20.0	21.2	22.4	26.2	$\Delta r_{\text{elstr}}(i,T)/\text{nm}$	0.036	0.039	0.042	0.045	0.048
$V_{\text{intr}}(i,T)/\text{cm}^3\cdot\text{mol}^{-1}$	21.9	22.3	22.8	23.3	24.1	$h^{\infty}(i,T)$	2.0	2.9	3.6	4.3	5.2
$\Delta r_{\text{elstr}}(i,T)/\text{nm}$	0.042	0.047	0.051	0.056	0.060	ClO ₄ ⁻ (0.240, 62.2)					
$h^{\infty}(i,T)$	3.4	4.1	5.2	6.3	7.6	$V_{\text{Expan}}(i,T)/\text{cm}^3\cdot\text{mol}^{-1}$	59.3	62.1	64.5	66.2	66.9
Mg ²⁺ (0.072, 1.7)						$V_{\text{intr}}(i,T)/\text{cm}^3\cdot\text{mol}^{-1}$	66.3	67.2	68.2	69.4	70.9
$V_{\text{Expan}}(i,T)/\text{cm}^3\cdot\text{mol}^{-1}$	32.5	43.3	90.6	78.8	109.0	$\Delta r_{\text{elstr}}(i,T)/\text{nm}$	0.034	0.038	0.041	0.045	0.048
$V_{\text{intr}}(i,T)/\text{cm}^3\cdot\text{mol}^{-1}$	5.5	5.6	5.8	6.1	6.4	$h^{\infty}(i,T)$	1.6	2.0	2.7	3.3	4.0
$\Delta r_{\text{elstr}}(i,T)/\text{nm}$	0.075	0.076	0.078	0.079	0.080	SO ₄ ²⁻ (0.230, 54.8)					
$h^{\infty}(i,T)$	29.1	37.6	47.3	55.6	66.5	$V_{\text{Expan}}(i,T)/\text{cm}^3\cdot\text{mol}^{-1}$	46.9	48.3	51.3	53.3	56.0
Ca ²⁺ (0.100, 4.5)						$V_{\text{intr}}(i,T)/\text{cm}^3\cdot\text{mol}^{-1}$	59.9	60.7	61.6	62.3	64.7
$V_{\text{Expan}}(i,T)/\text{cm}^3\cdot\text{mol}^{-1}$	17.1	22.0	36.0	50.4	70.6	$\Delta r_{\text{elstr}}(i,T)/\text{nm}$	0.059	0.064	0.070	0.075	0.080
$V_{\text{intr}}(i,T)/\text{cm}^3\cdot\text{mol}^{-1}$	9.8	10.1	10.4	10.7	11.1	$h^{\infty}(i,T)$	8.2	10.6	13.7	16.6	20.0
$\Delta r_{\text{elstr}}(i,T)/\text{nm}$	0.072	0.074	0.076	0.078	0.080						
$h^{\infty}(i,T)$	21.5	27.7	34.9	41.1	49.4						
Sr ²⁺ (0.113, 6.5)											
$V_{\text{Expan}}(i,T)/\text{cm}^3\cdot\text{mol}^{-1}$	13.6	19.2	29.1	40.5	58.0	$V_{\text{Expan}}(i,T)/\text{cm}^3\cdot\text{mol}^{-1}$	16.2	17.0	18.5	19.1	
$V_{\text{intr}}(i,T)/\text{cm}^3\cdot\text{mol}^{-1}$	12.5	12.8	13.1	13.5	14.2	$V_{\text{intr}}(i,T)/\text{cm}^3\cdot\text{mol}^{-1}$	20.9	21.0	21.2	21.5	
$\Delta r_{\text{elstr}}(i,T)/\text{nm}$	0.071	0.073	0.076	0.078	0.080	$\Delta r_{\text{elstr}}(i,T)/\text{nm}$	0.030	0.032	0.036	0.038	
$h^{\infty}(i,T)$	18.9	24.5	30.9	36.5	43.8	$h^{\infty}(i,T)$	1.1	1.5	2.0	2.6	
Ba ²⁺ (0.136, 11.3)											
$V_{\text{Expan}}(i,T)/\text{cm}^3\cdot\text{mol}^{-1}$	14.6	18.4	27.2	35.6	50.4	$V_{\text{Expan}}(i,T)/\text{cm}^3\cdot\text{mol}^{-1}$	34.0	37.1	39.5	41.3	
$V_{\text{intr}}(i,T)/\text{cm}^3\cdot\text{mol}^{-1}$	18.2	18.8	19.0	19.5	20.2	$V_{\text{intr}}(i,T)/\text{cm}^3\cdot\text{mol}^{-1}$	41.5	41.7	42.0	42.4	
						$\Delta r_{\text{elstr}}(i,T)/\text{nm}$	0.024	0.028	0.030	0.034	
						$h^{\infty}(i,T)$	0.6	0.9	1.3	1.7	

^aThe values of Δr_{elstr} need to be multiplied by 10. ^bThe numbers in parentheses after the symbols of the ions are the "bare" ionic radii, $r_c(i)/\text{nm}$, and the Mukerjee intrinsic volumes, $V_{\text{intr}}(i,T)/\text{cm}^3\cdot\text{mol}^{-1}$, eq 15.

values in Table 1 depends on the conversion from the conventional to the absolute values by means of eq 1, assuming that the conventional values $V^{\text{conv}}(i,T)$ are accurate. However, the extrapolation to infinite dilution of the Ellis data^{1–3} was made by Masson's empirical expression (plots against the square root of the molality) rather than by the appropriate use of the

theoretical (Debye–Hückel) limiting slopes (not known at the time). Possible ion pairing of the 1:2 or 2:1 electrolytes used for obtaining $V^{\text{conv}}(i,T)$ could also be a source for inaccuracies, in particular at elevated temperatures where the permittivity of water is only moderate. These problems could have led to somewhat faulty $V^{\text{conv}}(i,T)$ values. The agreement of the $V^{\text{conv}}(i,T)$ from

Ellis¹⁻⁴ at 2 MPa with those from Tanger and Helgeson at saturation pressures²⁷ (examples shown in Table 1 for K⁺, Ca²⁺, and Cl⁻) shows, at least up to 175 °C, no appreciable pressure effects outside the stated data uncertainties. Millero's $V^\infty(\text{H}^+, \text{aq})$ values are the result of the integration of the molar expansibility of the hydrogen ion, which has a mean uncertainty of $\pm 0.024 \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$ according to the figure shown.¹⁶ This would lead to an uncertainty of ± 2.4 to $\pm 4.8 \text{ cm}^3 \text{ mol}^{-1}$ in $V^\infty(i, T)$ at the relevant temperatures, but (multiplied by $|z(i)|$) would be systematic for all the ions. Millero¹⁶ did not state the pressure at which the derived $V^\infty(\text{H}^+, \text{aq})$ values were valid, but since these values were reported for the entire range of 0–200 °C, they should be valid at or near saturation pressures. They need not be valid at, say, 10 MPa, the lowest pressure for which data at the elevated temperatures were reported,⁶⁻¹⁴ other than those of Ellis,¹⁻³ and this is the reason why only the latter (at 2 MPa) were considered in the present paper. The pressure effects on the ionic molar volumes would be the subject of another study.

The primary result of the present approach is the electrostriction volumes, $\Delta V_{\text{elstr}}(i, T)$, of the ions calculated according to eqs 2–4. Other results, $V_{\text{Expan}}(i, T)$ and $h^\infty(i, T)$, are derived from them. No inherent differences between cations and anions are expected as a result of using the restricted primitive model, because the ion characteristics used in the calculations are $|z(i)|$ (but leading to $z(i)^2$ in $E(j)^2$; eq 3) and $r_c(i)$. The resulting electrostriction volumes (Table 1) are considerably more negative than expected from the Drude-Nernst-Born expression (eq 8):

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

using the field-independent relative permittivity ϵ_r . As pointed out by Desnoyers et al.³³ among others, the field-dependence of ϵ_r , leading to dielectric saturation near the ion, should be taken into account for obtaining proper values of the electrostriction. This was already noted for the 0–100 °C range in Part 4.⁴ As mentioned there, there are several approximations and assumptions involved in the present calculation of the electrostriction volume. The values of the parameter b of eq 4 shown in Table 2, evaluated from the $E(\epsilon, T)$ data furnished by Danielewicz-Ferchmin and Ferchmin,⁵ have an uncertainty of $\pm 20\%$, but this affects the resulting $\Delta V_{\text{elstr}}(i, T)$ by only $\pm 2\%$.

The values of $(\partial \epsilon / \partial P)_T$ and κ_T are temperature dependent but are taken to be independent of $E(j)$. The justification for this assumption was examined for the worst case (200 °C) and the ion with the largest electrical field (Mg^{2+}). The field at the middle of the first hydration shell, i.e., at $r_c(\text{Mg}^{2+}) + r_W = 0.072 + 0.138 \text{ nm} = 0.210 \text{ nm}$, where r_W is the radius of a water molecule, is obtained from the iterative calculation as $39.0 \text{ GV} \cdot \text{m}^{-1}$. This is indeed a huge electrical field, causing dielectric saturation and extreme compression of the water. The pressure at this site is obtained from Desnoyers et al.³³ according to their eq 11, with the expression in the square brackets on its right-hand side being multiplied by $4\pi\epsilon_0$ in order to keep to the correct dimensions (ϵ_0 is the permittivity of vacuum):

$$\log(1 + P/B) = (1 - C)^{-1} \log[1 + \epsilon_0 C(1 - C)n_\infty^2 E^2 / 2BD] \quad (9)$$

The parameters B , C , and D were obtained from the Tait–Gibson type expressions used by Desnoyers et al.,³³ namely:

$$\kappa_T = D/(B + P) \quad (10)$$

$$(\partial \ln \epsilon / \partial P)_{E,T} = A/(B + P) \quad (11)$$

$$(\partial \ln n_\infty^2 / \partial P)_{E,T} = C/(B + P) \quad (12)$$

The value of B was obtained from the expression given by Harned and Owen,³⁴ although valid for $25 \leq t/^\circ\text{C} \leq 85$, but used by them for extrapolation outside this range. The resulting value for 200 °C is $B = 2.9085 \text{ GPa}$. Given this value and $\kappa_T = 0.8780 \text{ GPa}^{-1}$ at 200 °C for low pressures (Table 2), the value $D = 2.617$ results from eq 10. The value of $C = 0.06034$ results from the data of Harvey et al.²⁵ for 200 °C. Insertion of these values in eq 9 yields $P = 0.2575 \text{ GPa}$ at the site under consideration. This large pressure is still small relative to the value of B , and causes $\kappa_T(E)$ and $(\partial \ln \epsilon / \partial P)_{E,T}$ to diminish only to 93% of the value at 2 MPa. For lower temperatures and smaller electric fields (other ions), the relative diminution of $\kappa_T(E)$ and $(\partial \ln \epsilon / \partial P)_{E,T}$ would be smaller, hence the assumption of their independence of E is a good working assumption.

The derived expanded molar volumes of the ions, $V_{\text{Expan}}(i, T)$, defined by eq 5, are shown in Table 3. They include the volumes of the bare ions and the void spaces between the packed spheres of different sizes: the ions and the water molecules (departing for now from the restricted primitive model). Therefore, the values of $V_{\text{Expan}}(i, T)$ are much larger than those of $V_{\text{bare}}(i)$ and may be compared with the intrinsic ionic volumes $V_{\text{intr}}(i, T)$.³⁵ Glueckauf³⁶ suggested that the void volumes contributing to $V_{\text{intr}}(i, T)$ can be accounted for by an addend, a , to the ionic radius $r_c(i)$ to yield

$$V_{\text{intr}}(i, T) = (4\pi N_A / 3) [r_c(i) + a(T)]^3 \quad (13)$$

The values of $a(T)$ are estimated from

$$a(T) = (3V_W(T) / 4\pi N_A)^{1/3} - r_W \quad (14)$$

where $V_W(T)$ is the temperature-dependent molar volume of water (Table 2). Over the temperature range from 100 to 200 °C, a varies from 0.0573 to 0.0641 nm, some 12%. The resulting values of $V_{\text{intr}}(i, T)$ are shown in Table 3, varying more than a for small ions due to the third power. The same expression (eq 13) was used also for the polyatomic ions NH_4^+ , NO_3^- , ClO_4^- , and SO_4^{2-} , although Glueckauf's method was not meant to apply to them,³⁷ but no better way was found. The tetrahedral ions are globular and approximate spheres, and for the nitrate ion this is certainly a rough estimate.

For large univalent ions ($r_c(i) \geq 0.11 \text{ nm}$), $V_{\text{Expan}}(i, T)$ is smaller than $V_{\text{intr}}(i, T)$ by 3–8 $\text{cm}^3 \cdot \text{mol}^{-1}$. Instead of Glueckauf's estimates of the intrinsic volumes, the temperature-independent estimate of Mukerjee,³⁸ applicable to the alkali metal and halide ions at room temperature, namely

$$V_{\text{intr}}(i, T) = (4\pi N_A / 3) k^3 r_c(i)^3 \quad (15)$$

with $k = 1.213$ could be used, as was done in Part 4.⁴ Then much better agreement of $V_{\text{Expan}}(i, T)$ with $V_{\text{intr}}(i, T)$ would be achieved for the large univalent ions. The mean deviations increasing from $1.0 \text{ cm}^3 \cdot \text{mol}^{-1}$ at 100 °C to $4.6 \text{ cm}^3 \cdot \text{mol}^{-1}$ at 200 °C. There could be several reasons for the deviations noted by the two methods. One reason is the overestimation of $V_{\text{intr}}(i, T)$ by Glueckauf's method of taking into account the void volumes. The systematic increase in the deviation according to Mukerjee's method, eq 15, could be avoided by letting k depend on the temperature. Another reason for the deviations may be the inaccuracy of the $V^\infty(i, T)$ values, leading to $V_{\text{Expan}}(i, T)$ by eq 5, the inaccuracy being ascribable to the uncertainty in $V^\infty(\text{H}^+, \text{aq}, T)$ mentioned

above. A third reason is the inaccuracy of the $\Delta V_{\text{elstr}}(i,T)$ values calculated according to eqs 2–4, leading again to $V_{\text{Expan}}(i,T)$ values by eq 5. Nevertheless, the values of $V_{\text{Expan}}(i,T)$ are commensurate with $V_{\text{intr}}(i,T)$ by Glueckauf's or Mukerjee's estimations within the stated experimental and estimation uncertainties, a fact that lends credence to the electrostriction calculations for the univalent ions of both signs having radii larger than 0.11 nm.

For the divalent cations and small univalent ones ($r_c(i) \leq 0.11$ nm), the deviations between $V_{\text{Expan}}(i,T)$ and $V_{\text{intr}}(i,T)$ are large and systematic with the temperature. $V_{\text{Expan}}(i,T) > V_{\text{intr}}(i,T)$ is caused by the electrostriction volume $\Delta V_{\text{elstr}}(i,T)$ becoming much more negative than the standard molar volume $V^\infty(i,T)$ with increasing temperatures, especially for the divalent cations (see Figure 1 for Ca^{2+}). Desnoyers et al.³³ calculated a value of $-7.8 \text{ cm}^3 \cdot \text{mol}^{-1}$ for the mean molar electrostrictive compression of the water, ΔV_{Wel} at a distance of 0.200 nm from the center of a tervalent ion at an unspecified temperature, presumably ambient, where the field is $6.06 \times 10^{10} \text{ V} \cdot \text{m}^{-1}$. The corresponding value for Mg^{2+} at 0.210 nm would according to their calculation be $\Delta V_{\text{Wel}} = -6.3 \text{ cm}^3 \cdot \text{mol}^{-1}$ at a field of $3.66 \times 10^{10} \text{ V} \cdot \text{m}^{-1}$, compressing the water to near its minimal volume, the van der Waals volume. The ΔV_{Wel} value should be multiplied by the amount of water affected by the ionic field to obtain the total electrostriction volume, $\Delta V_{\text{elstr}}(i,T)$. The electric field for such ions is still sufficiently strong for causing electrostriction where dielectric saturation takes place beyond the first shell (see next paragraph for $\Delta r_{\text{elstr}}(i,T)$) in Table 3. The permittivity in this region for multivalent small ions indeed increases less steeply with increasing distance than for univalent ions.

The widths of the dielectric saturation region around ions, $\Delta r_{\text{elstr}}(i,T)$ in Table 3 are systematic with respect to $r_c(i)$ (diminishing with increasing ion sizes) and T (increasing with the temperature). On reaching 200 °C, the values become essentially independent of the ionic size, becoming 0.60 nm for univalent cations, 0.48 nm for univalent anions, and 0.80 nm for divalent ions, i.e., nearly 3 times the diameter of a water molecule. Most (>95%) of the solvent electrostriction, ΔV_{elstr} takes place within this region of dielectric saturation, Δr_{elstr} .

It remains to discuss the numbers of water molecules at infinite dilution, $h^\infty(i,T)$, obtained from eq 6 and shown in Table 3. Whether or not hydration numbers obtained by any method have physical meaning, for the given operational definition they serve for comparison of different solutes at the same conditions. They measure the amount of water affected by the ionic field, not necessarily the "binding" of water molecules to the ions. They increase markedly with the temperature for all the ions examined, and reach values of many tens for small divalent cations. The numbers depend on the validity of the assumption that the mean molar electrostrictive compression of the water, $\Delta V_{\text{Wel}}(T)$, is independent of the ion in the hydration shell of which the hydration water resides and is constant over the entire $\Delta r_{\text{elstr}}(i,T)$ region. As shown in Part 4,⁴ the hydration numbers obtained by eq 6 at ambient conditions are compatible with those obtained by other methods. The large increase of the negative values of $\Delta V_{\text{elstr}}(i,T)$ at ≥ 100 °C are well supported by other approaches.²⁷ Therefore, the unexpected increase in $h^\infty(i,T)$ at >100 °C is either a true phenomenon or depends on an incorrect evaluation of $\Delta V_{\text{Wel}}(T)$ that varies only little (in the range $-2.4 \pm 0.2 \text{ cm}^3 \cdot \text{mol}^{-1}$) between 100 and 200 °C. In fact, Desnoyers et al.³³ estimated considerably larger negative ΔV_{Wel} values (see above). However, there is a clear limit to $\Delta V_{\text{Wel}}(T)$: it cannot

be more negative than the difference between V_{W} and the close-packed molar volume of water, i.e., not more negative than -4.9 to $-5.4 \text{ cm}^3 \cdot \text{mol}^{-1}$ at 100–200 °C. In this extreme case, the values of $h^\infty(i,T)$ would diminish by a factor of about ca. 2.2, and converge toward the values at ambient conditions. The author tends not to accept this conclusion.

Hardly any information on the temperature dependence of hydration numbers, defined in any manner, could be found in the literature, for the sake of comparison. Zavitsas³⁹ concluded from the colligative properties, in particular the vapor pressures, of aqueous CaCl_2 solutions up to 200 °C that the hydration number of Ca^{2+} diminishes with increasing temperatures. However, it is not clear why the hydration number is ascribed to the individual Ca^{2+} ions and not to the entire electrolyte, and why ion association at high concentrations of the 1:2 electrolyte at elevated temperatures with only moderate permittivities is disregarded. In particular, the derived hydration numbers do not pertain to infinite dilution as those estimated in Table 3, and hence cannot be compared. Driesner and Cummings⁴⁰ in molecular dynamics simulations of aqueous SrCl_2 solutions compared results at the two temperatures 300 and 600 K only, the higher temperature being outside the range in the present study, 473 K. Various water potential functions were compared, but all indicated a decrease of the coordination number of Sr^{2+} and an increase of that of Cl^- at the higher temperature relative to that at the lower one. However, the coordination number is not identical with the hydration number h^∞ derived in the present study. Furthermore, the 0.68 *m* solutions had appreciable contents of ion associates,⁴⁰ hence comparison with the present results is excluded.

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Notes

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