

Apparent and Standard Partial Molar Volumes of NaCl, NaOH, and HCl in Water and Heavy Water at $T = 523$ K and 573 K at $p = 14$ MPa

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Received: June 19, 2006; In Final Form: November 27, 2006

Apparent molar volumes, $V_{\phi,2}$, of aqueous NaCl, NaOH, NaOD, HCl, and DCl in water and heavy water were determined at $T = 523$ and 573 K and $p = 14$ MPa with a high-temperature platinum vibrating-tube densimeter in the aquamolality range $0.25 \leq m_{\text{aq}} \leq 2.5 \text{ mol} \cdot (55.509 \text{ mol solvent})^{-1}$. The experimental results have been represented with an extended Debye–Hückel equation to describe the concentration dependence of $V_{\phi,2}$ and to derive standard partial molar volumes of these electrolytes in light and heavy water, $V_{2,\text{H}}^\circ$ and $V_{2,\text{D}}^\circ$, respectively. For NaCl and NaOH, the D_2O isotope effect at infinite dilution, $[V_{2,\text{H}}^\circ - V_{2,\text{D}}^\circ]$, increases from 0.2 and $0.8 \text{ cm}^3 \text{ mol}^{-1}$ to 4.5 and $7.1 \text{ cm}^3 \text{ mol}^{-1}$, respectively, when the temperature is increased from 523 to 573 K. For HCl and DCl, the effect is smaller and the sign is reversed, $[V_{2,\text{H}}^\circ - V_{2,\text{D}}^\circ] = -0.7 \text{ cm}^3 \text{ mol}^{-1}$ at 523 K and $-1.4 \text{ cm}^3 \text{ mol}^{-1}$ at 573 K. When the effect of ion association is included, the deuterium isotope effect for HCl becomes positive, $[V_{2,\text{H}}^\circ - V_{2,\text{D}}^\circ] \approx 17 \text{ cm}^3 \text{ mol}^{-1}$ at 573 K, consistent with NaCl and NaOH. Two models are proposed to describe the solvent isotope effect on the infinite dilution limit, one based on the Born equation and the other on the dimensionless Krichevskii parameter. The experimental values of $V_{2,\text{D}}^\circ$ also have been used to calculate the first reported values for the pressure dependence of the ionization constant of D_2O at temperatures higher than 313 K.

1. Introduction

Heavy water (D_2O) is used as the heat-transfer medium in the current generation of CANDU-pressurized heavy water nuclear reactors. CANDU-PHW reactors operate at temperatures from $523 \leq T \leq 600$ K. A detailed understanding of deuterium isotope effects on chemical equilibria under these conditions is of interest, both for optimizing chemistry control strategies and as a contribution to basic research on ionic solvation in high-temperature water.

Previous work on the $\text{D}_2\text{O}/\text{H}_2\text{O}$ solvent isotope effect for partial molar properties of electrolyte solutions has been restricted to temperatures below 350 K where “structural” or “chemical” hydration effects dominate.^{1–5} During the past few decades, there has been very active research to develop techniques for determining the properties of aqueous solutes at much higher temperatures and pressures, up to and including the critical point, as a means of probing the hydration of ions and nonelectrolytes under conditions where long-range polarization effects are much more important.^{6–9} Recently, the dielectric constant of D_2O has been determined at liquid-like densities well into the super-critical region, $T \leq 770$ K and $p \leq 59$ MPa,⁶ so that a theoretically correct extrapolation of experimental apparent molar volumes to infinite dilution can now be made under extreme conditions.

In this study, we describe measurements of apparent and standard partial molar volumes of NaCl, HCl, DCl, NaOH, and NaOD in H_2O and D_2O at temperatures of 523 and 573 K and a pressure of 14 MPa. Volumetric properties of these electrolytes in H_2O are well known up to temperatures near the critical point of the solvent^{10–15} and thus serve as a check on the quality of

our results. In addition, our laboratory is carrying out conductivity measurements to determine ionization and association constants of simple acids, bases, and salts for which solution densities are required.

We have analyzed various approaches to describe the experimental results and found that the solvent isotope effect on standard partial molar volumes, $V_{2,\text{H}}^\circ$, can be accurately described by a simple Born equation.^{16,17} Because this model becomes less accurate in describing standard partial molar properties under near-critical conditions,^{18,19} we also have chosen to describe $V_{2,\text{H}}^\circ$ in terms of the dimensionless Krichevskii parameter, $A_{12}^\circ = V_{2,\text{H}}^\circ/\kappa_1 RT$.^{20–24} The mean spherical approximation (MSA)/hard sphere (HS) model^{22,25–26} is shown to provide a semiquantitative description of the concentration dependence of excess partial molar volumes in D_2O .

The experimental and calculated standard partial molar volumes of NaCl, HCl, and NaOH in H_2O and NaCl, DCl, and NaOD in D_2O were combined with solvent molar volume data to calculate the standard partial molar volumes of ionization of H_2O and D_2O , so that the pressure dependence of the ionization constants of light and heavy water under hydrothermal conditions can be compared for the first time.

2. Experimental Methods

All reagents were used as received from commercial sources. Standard solutions of NaCl (Fisher Scientific, ACS reagent grade) were prepared by mass after drying the salt at 393 K for at least 24 h. Stock solutions of NaOH (carbonate free 50% solutions, Fisher Certified ACS) and NaOD (Aldrich, 40 wt.% solution in D_2O , 99+ atom %D) were prepared by mass and standardized by titration against potassium hydrogen phthalate. Stock solutions of DCl and HCl were prepared by mass from DCl (Aldrich, 35 wt.% in D_2O , 99 atom %D) and HCl (35 wt.

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%, Fisher Certified ACS) and standardized by titration against standard NaOH solutions. Nanopure water (resistivity 18 MΩ.cm) and deuterium oxide (99.8 mol %D) were used to prepare the solutions. The determination of deuterium content in D₂O was carried out by NMR, using standard additions of variable amounts of 99.99+% glacial acetic acid (Aldrich) to D₂O as an internal reference. D₂O solutions were prepared in a glovebag flushed with argon and kept under positive argon pressure. Solutions were maintained under an atmosphere of argon and stored in a desiccator. All concentrations are given in terms of aquamolality, m_{aq} , defined as mol of solute per 55.509 mol of solvent.

High-temperature volumetric measurements were made in a platinum U-tube densimeter, constructed according to the design of Albert and Wood,²⁷ as modified by Corti et al.¹⁴ A detailed description of the densimeter has been given by Xiao et al.²⁸ and Clarke and Tremaine.²⁹ The instrument was calibrated daily with D₂O and a standard solution of 1.078 mol kg⁻¹ NaCl in light water, based on Hill's equation of state for heavy water³⁰ and density values compiled by Archer for aqueous NaCl.¹¹ The overall uncertainty in the measured densities due to the sensitivity limits of the instrument itself and the accuracy of the NaCl reference data is estimated to be $\pm 0.0002 \text{ g cm}^{-3}$, while its precision is $\pm 0.00002 \text{ g cm}^{-3}$. The experimental design, described below, involves sequential measurements of the density of flowing H₂O, D₂O, and similar solutions in light and heavy water at constant temperature and pressure over a short period of time, so that differences in the volumetric properties of solutes in the two solvents can be measured directly.

3. Results

The relative density of each solution was determined from the expression

$$(\rho - \rho_1^*) = K(\tau^2 - \tau_1^2) \quad (1)$$

where ρ and ρ_1^* are the densities of the solution and water, respectively, τ and τ_1 are the resonance periods of the solution and water in the vibrating-tube densimeter, respectively, and K is a characteristic constant determined by calibration with the solvent H₂O and a standard solution. To ensure a high level of precision, our calibrations were done by averaging results from both the standard solution of 1.078 mol kg⁻¹ NaCl and D₂O, before and after each set of measurements, while H₂O was used as a baseline for the measurement on every solution. Tabulated values for D₂O from Hill³⁰ were used in the calculations without taking into account the small 0.2% contribution of HOD. The densimeter constant is therefore the result of four calibrations: two at the beginning and two at the end of each set of measurements.

The densities of water and heavy water solutions for a given electrolyte were sequentially measured against water to minimize introducing any error because of any instability in the instrument. Water was adopted as baseline in both cases to reduce the use of heavy water. The apparent molar properties were calculated through the expression

$$V_{\phi,2} = \{V(\text{sln}) - n_1 V_1^*\}/n_2 \quad (2)$$

where $V(\text{sln})$ is the volume of solution, V_1^* is the volume of pure solvent (H₂O or D₂O), and n_1 and n_2 are the number of moles of solvent and solute, respectively. The equation that

relates the apparent molar volumes, $V_{\phi,2}$, to the densities and total molality is

$$V_{\phi,2} = (55.509)M_1(\rho_1^* - \rho)/(m_{\text{aq}} \rho \rho_1^*) + M_2/\rho \quad (3)$$

where ρ_1^* is the density of pure water from ref 31 or heavy water from ref 30 corresponding to measurement in light and heavy water, respectively, ρ is the density of the solution, m_{aq} is the aquamolality of the solution, and M_1 and M_2 are the molar masses of the solvent and solute, respectively. The experimental relative densities $(\rho - \rho_1^*)$, the apparent molar volumes for NaCl, NaOH, and HCl in water, and the apparent molar volumes for NaCl, NaOD, and DCl in heavy water are listed in Table 1 for temperatures $T = 523$ and 573 K .

We chose to use a simple extended Debye–Hückel expression to describe the concentration dependence of the apparent molar volumes at 523 and 573 K, recognizing that some degree of ion association takes place at 573 K.^{10,12,15} Because there are no data for ion association constants in heavy water, our model selection was based on the best fit to experimental data. The apparent molar volumes $V_{\phi,2}$ in Table 1 were well represented by the extended Debye–Hückel equation³²

$$V_{\phi,2} = V^\circ_2 + A_V(m_{\text{aq}}/m^\circ_{\text{aq}})^{1/2} + B_V(m_{\text{aq}}/m^\circ_{\text{aq}}) + C_V(m_{\text{aq}}/m^\circ_{\text{aq}})^2 \quad (4)$$

where V°_2 is the standard partial molar volume at infinite dilution, A_V is the Debye–Hückel limiting slope for apparent molar volumes, B_V and C_V are adjustable parameters, and $m^\circ_{\text{aq}} = 1 \text{ mol of solute per } 55.509 \text{ mol of solvent}$. For water, the A_V values were taken from the compilation of Archer and Wang.³¹ The A_V values for heavy water were calculated using eq 5

$$A_V = (2/3)RT[(2\pi N_A \rho_{1,D}^*) / 1111.7]^{1/2} [e^2 / (4\pi \epsilon_0 \epsilon k_B T)]^{3/2} [3(\partial \ln \epsilon / \partial p)_T + (\partial \ln V_1^* / \partial p)_T] \quad (5)$$

Here N_A is Avogadro's number, R is the gas constant, e is the charge of the electron, ϵ_0 is the permittivity of a vacuum, and k_B is Boltzmann's constant. The factor 1111.7 is due to the difference between light and heavy water in the conversion from aquamolality to concentration of ions per cubic centimeter. The terms V_1^* , ϵ , and $\rho_{1,D}^*$ are the molar volume, static dielectric constant, and density of heavy water, respectively. The volumetric properties of heavy water required to calculate A_V at each temperature were taken from Hill's equation of state.³⁰ Static dielectric constants for D₂O at elevated temperatures have been measured by Okada et al.,⁶ who reported that the values of ϵ in both solvents are the same at the same number density of water molecules. On the basis of this result, we chose to calculate values of ϵ and $(\partial \epsilon / \partial p)_T$ for use in eq 5 from a version of the Uematsu–Franck equation for the dielectric constant of water³³ in which the mass density was replaced by the number density of the solvent molecules.

Equation 4 was fitted to the apparent molar volumes of the solutions at each temperature by the method of least-squares. The resulting values of V°_2 , B_V , and C_V for each system together with their standard deviation are presented in Table 2. Plots of the fitted results for $V_{\phi,2}$ against aquamolality at both temperatures are compared with the experimental data in Figures 1–3. Apparent molar volumes for the reference systems NaCl, HCl, and NaOH in H₂O from refs 11, 10, and 15, respectively, are included for comparison. Figures 1–3 also include plots on an expanded scale, showing the difference between the experimental values for each electrolyte in H₂O and D₂O, relative to

TABLE 1: Apparent Molar Volumes, $V_{\phi,2}$, for NaCl, NaOH (NaOD), and HCl (DCl) in H_2O and D_2O at $T = 523$ and 573 K and $p = 14$ MPa

T/K	p/MPa	$\rho_{1,\text{H}}^*$ / g cm^{-3}	m_{aq}	$(\rho - \rho_{1,\text{H}}^*)$ / g cm^{-3}	$V_{\phi,2,\text{H}}$ / $\text{cm}^3 \text{mol}^{-1}$	$\rho_{1,\text{D}}^*$ / g cm^{-3}	m_{aq}	$(\rho - \rho_{1,\text{H}}^*)$ / g cm^{-3}	$V_{\phi,2,\text{D}}$ / $\text{cm}^3 \text{mol}^{-1}$
$\text{H}_2\text{O}-\text{NaCl}$					$\text{D}_2\text{O}-\text{NaCl}$				
523.63	13.96	0.80938	0.2146	0.01180	-11.54	0.89552	0.2783	0.10139	-10.55
523.66	13.97	0.80935	0.4283	0.02269	-8.45	0.89547	0.5707	0.11623	-7.63
523.70	13.97	0.80929	0.8529	0.04280	-4.19	0.89542	0.8362	0.12876	-5.18
523.67	13.97					0.89547	1.1183	0.14139	-3.05
523.64	13.97	0.80938	1.4990	0.07141	-0.47	0.89552	1.5003	0.15815	-1.18
523.67	13.96	0.80932	2.5010	0.11148	3.66	0.89546	2.4970	0.19788	2.86
$\text{H}_2\text{O}-\text{HCl}$					$\text{D}_2\text{O}-\text{DCl}$				
523.61	13.97	0.809422	0.2263	0.00877	-13.98	0.89557	0.2454	0.09586	-12.86
523.60	13.97	0.809436	0.4525	0.01623	-9.52	0.89558	0.4877	0.10406	-8.90
523.62	13.96	0.809397	0.6778	0.02307	-6.72	0.89555	0.7320	0.11143	-5.88
523.61	13.96	0.809411	0.9030	0.02966	-4.91	0.89556	0.9680	0.11825	-3.98
523.63	13.97	0.809393	1.4517	0.04421	-1.36	0.89554	1.6308	0.13536	-0.001
523.65	13.97	0.809363	2.4316	0.06698	2.77	0.89550	2.7012	0.15867	4.27
$\text{H}_2\text{O}-\text{NaOH}$					$\text{D}_2\text{O}-\text{NaOD}$				
523.11	13.99	0.81017	0.2542	0.01438	-36.20	0.89641	0.2645	0.10213	-36.70
523.11	14.00	0.81018	0.5073	0.02708	-30.94	0.89643	0.5291	0.11612	-31.30
523.11	14.00	0.81018	0.7808	0.04033	-27.97	0.89643	0.7937	0.12970	-28.61
523.13	14.00	0.81015	1.0150	0.05150	-26.30	0.89639	1.0702	0.14326	-26.29
523.13	14.00	0.81015	1.5140	0.07382	-22.86	0.89639	1.5829	0.16678	-22.63
523.15	14.00	0.81012	2.5251	0.11559	-17.86	0.89641	2.6405	0.21147	-17.42
$\text{H}_2\text{O}-\text{NaCl}$					$\text{D}_2\text{O}-\text{NaCl}$				
573.07	13.88	0.72364	0.2146	0.01597	-60.00	0.79797	0.2783	0.09577	-59.69
573.10	13.94	0.72370	0.4283	0.03013	-51.42	0.79802	0.5707	0.11546	-50.01
573.07	13.89	0.72366	0.8529	0.05558	-40.55	0.79797	0.8362	0.13073	-41.61
573.01	13.89					0.79813	1.1183	0.14770	-37.80
573.08	13.98	0.72382	1.4990	0.08967	-29.75	0.79817	1.5003	0.16858	-32.53
573.09	13.98	0.72370	2.5010	0.13626	-19.58	0.79814	2.4970	0.21560	-21.66
$\text{H}_2\text{O}-\text{HCl}$					$\text{D}_2\text{O}-\text{DCl}$				
573.09	14.00	0.72384	0.2263	0.01188	-49.01	0.79818	0.2454	0.08737	-44.97
573.11	14.00	0.72380	0.4525	0.02082	-36.39	0.79814	0.4877	0.09647	-31.37
573.09	14.00	0.72384	0.6778	0.02880	-29.55	0.79819	0.7320	0.10472	-24.52
573.11	14.01	0.72380	0.9030	0.03607	-24.64	0.79815	0.9680	0.11162	-19.33
573.12	14.00	0.72377	1.4517	0.05208	-16.89	0.79811	1.6308	0.12873	-10.55
573.15	14.00	0.72371	2.4316	0.07518	-7.83	0.79804	2.7012	0.15004	-1.80
$\text{H}_2\text{O}-\text{NaOH}$					$\text{D}_2\text{O}-\text{NaOD}$				
573.14	14.0	0.72381	0.2542	0.01910	-85.94	0.79815	0.2645	0.09607	-89.60
573.15	14.0	0.72379	0.5073	0.03522	-73.72	0.79813	0.5291	0.11411	-76.01
573.11	14.0	0.72387	0.7808	0.05132	-65.57	0.79823	0.7937	0.13072	-67.75
573.14	14.0	0.72381	1.0150	0.06455	-60.75	0.79815	1.0702	0.14697	-61.47
573.13	14.0	0.72383	1.5140	0.09082	-52.66	0.79818	1.5829	0.17490	-52.83
573.15	14.0	0.72379	2.5251	0.13868	-41.63				

TABLE 2: Regression Parameters of Eq 4 for the Apparent Molar Volumes, $V_{\phi,2}$, of NaCl, HCl, DCl, NaOH, and NaOD in H_2O and D_2O at Averaged Temperatures and Pressures

solute	solvent	T/K	p/MPa	V_2^{c} / $\text{cm}^3 \text{mol}^{-1}$	A_V / $\text{cm}^3 \text{mol}^{-1}$	B_V / $\text{cm}^3 \text{mol}^{-1}$	C_V / $\text{cm}^3 \text{mol}^{-1}$
NaCl	H_2O	523.66	13.97	-23.30 (± 0.28)	29.958	-11.005 (± 0.547)	1.140 (± 0.195)
		573.09	13.94	-94.39 (± 1.15)	88.788	-35.444 (± 2.268)	3.712 (± 0.809)
NaCl	D_2O	523.66	13.97	-23.46 (± 0.54)	29.596	-11.340 (± 0.929)	1.272 (± 0.319)
		573.07	13.93	-98.93 (± 1.22)	92.404	-36.660 (± 2.118)	3.658 (± 0.728)
HCl	H_2O	523.62	13.97	-26.20 (± 0.26)	29.937	-8.171 (± 0.500)	0.359 (± 0.180)
		573.11	14.00	-83.93 (± 0.93)	88.676	-29.007 (± 1.815)	1.386 (± 0.654)
DCl	D_2O	523.62	13.97	-25.53 (± 0.13)	29.572	-8.259 (± 0.233)	0.479 (± 0.076)
		573.11	14.00	-82.52 (± 1.05)	92.284	-29.935 (± 1.881)	1.335 (± 0.613)
NaOH	H_2O	523.12	14.00	-48.91 (± 0.54)	29.657	-7.347 (± 0.966)	0.379 (± 0.332)
		573.14	14.04	-123.40 (± 0.35)	88.626	-27.919 (± 0.621)	1.785 (± 0.214)
NaOD	D_2O	523.12	14.00	-49.71 (± 0.47)	29.286	-6.586 (± 0.819)	0.295 (± 0.270)
		573.13	14.04	-130.53 (± 0.26)	92.235	-24.327 (± 0.275)	

the corresponding light-water calculated values from equations in refs 10, 11, and 15.

As is the case for other aqueous electrolyte solutions, the apparent molar volumes of these solutes in both H_2O and D_2O increase with concentration and decrease with temperature toward more negative values as the critical temperature of the solvent is approached. At 523 K, the values of $V_{\phi,2}$ for all three

solutes at the same aquamolality in D_2O and H_2O are in agreement to within the combined experimental uncertainties. However, the values for $V_{\phi,2,\text{D}}$ (NaCl) and $V_{\phi,2,\text{D}}$ (NaOD) at 573 K, plotted in Figures 1 and 2, are more negative than the corresponding values of $V_{\phi,2,\text{H}}$ (NaCl) and $V_{\phi,2,\text{H}}$ (NaOH). As a result, the solvent isotope effect [$V_{\phi,2,\text{H}} - V_{\phi,2,\text{D}}$], which is very small at 523 K, increases with temperature to ~ 2 and $\sim 4 \text{ cm}^3$

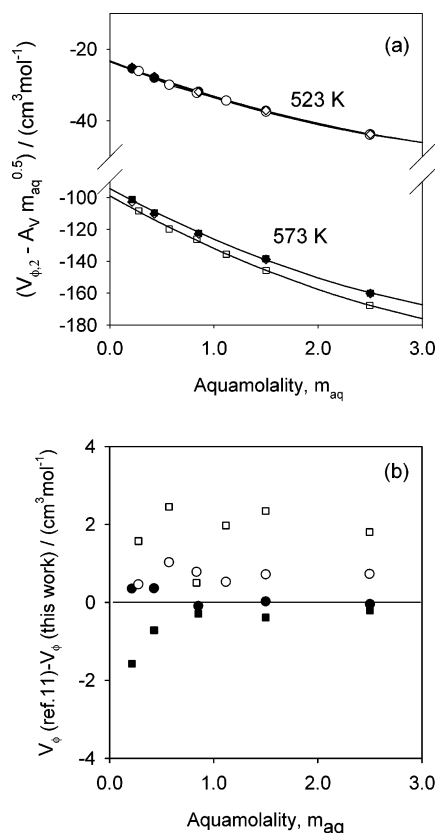


Figure 1. (a) Experimental apparent molar volumes $V_{\phi,2}$ of NaCl plotted against aquamolality at 523 and 573 K: (●) H_2O and (○) D_2O at 523 K; (■) H_2O and (□) D_2O at 573 K; (◇) values for NaCl in H_2O taken from ref 11. Solid lines were calculated from eq 4 and parameters reported in Table 2. (b) Difference plots of the same data expressed as $[V_{\phi,2}(\text{ref. 11}) - V_{\phi,2}(\text{this work})]$. Symbols have the same meaning as those in (a).

mol^{-1} at 573 K for NaCl and NaOH, respectively. As we will demonstrate below, this effect is consistent with differences in the compressibility of D_2O and H_2O , which become more pronounced at higher temperatures. It is clear from Figure 3 that the system HCl/DCl displays quite different behavior.

4. Discussion

4.1. Standard Partial Molar Volumes. Despite the fairly small number of measured densities in the low concentration region and the use of a different function to extrapolate $V_{\phi,2}$ to infinite dilution, the extrapolated standard partial molar volumes, V°_2 , for the three electrolytes in H_2O are in agreement with literature values reported for HCl, NaCl, and NaOH by Sharygin and Wood,¹⁰ Archer,¹¹ and Corti and Simonson,¹⁵ respectively, to within $\pm 2.5 \text{ cm}^3 \text{mol}^{-1}$, as shown in Table 4. The exception is HCl at 573 K for which the difference is $\sim 4 \text{ cm}^3 \text{mol}^{-1}$.

Several authors^{17,20,34} have shown that ionic species are characterized by values of V°_2 that decrease with temperature toward a negative discontinuity at the critical point of water, and that this effect is associated with the increasing compressibility of the solvent as the critical temperature and pressure are approached. The critical point of heavy water is lower than that of light water, $[T_c(\text{D}_2\text{O}) = 643.9 \text{ K}, p_c(\text{D}_2\text{O}) = 21.67 \text{ MPa}]$ and $T_c(\text{H}_2\text{O}) = 647.1 \text{ K}, p_c(\text{H}_2\text{O}) = 22.06 \text{ MPa}]$, so that D_2O is more compressible than H_2O at the same temperature and pressure in the subcritical region. As a result, the solvent isotope effect $[V_{\phi,2,\text{H}} - V_{\phi,2,\text{D}}]$ would be expected to shift to more positive values with increasing temperature, as the difference between the isothermal compressibilities of H_2O and D_2O

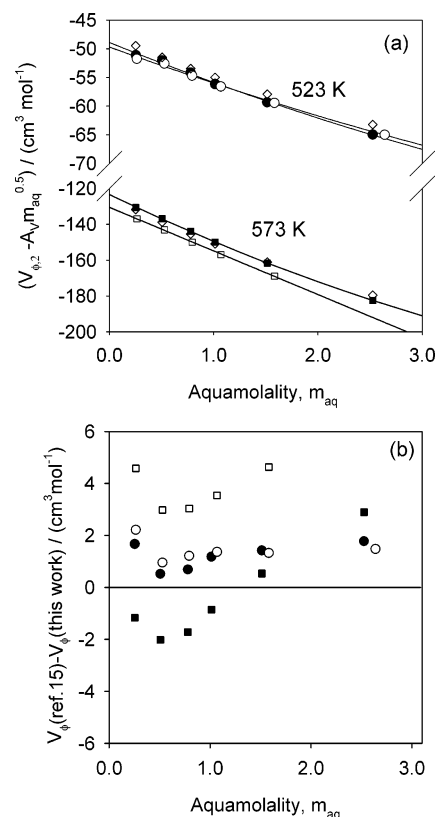


Figure 2. (a) Experimental apparent molar volumes $V_{\phi,2}$ of NaOH plotted against aquamolality at 523 and 573 K: (●) H_2O and (○) D_2O at 523 K; (■) H_2O and (□) D_2O at 573 K; (◇) values for NaOH in H_2O taken from ref 15. Solid lines were calculated from eq 4 and parameters reported in Table 2. (b) Difference plots of the same data expressed as $[V_{\phi,2}(\text{ref. 15}) - V_{\phi,2}(\text{this work})]$. Symbols have the same meaning as those in (a).

increases. This is entirely consistent with the results for NaCl, NaOH, and NaOD. In the analysis that follows, we will show that the negative solvent isotope effect for $V_{\phi,2,\text{D}}$ (DCl) and $V_{\phi,2,\text{H}}$ (HCl) at 573 K in Figure 3 is consistent with the effect of ionic association, which is known to be significant for HCl at this temperature.^{35,36}

Wood et al.¹⁷ have used the Born equation¹⁶ with a single adjustable radius to describe the standard partial molar volume of NaCl at temperatures approaching the critical point in which the electrostatic contribution to the volume is large and ion–solvent interactions are largely due to Coulombic forces. The Born expression that describes the partial molar volumes at infinite dilution is

$$V^\circ_2 = - (K/R) (\partial\epsilon/\partial p)_T / \epsilon^2 \quad (6)$$

where $K = N_A e^2 / 4\pi\epsilon_0$ and $1/R = (R_+^{-1} + R_-^{-1})/2$.¹⁷ The solvent isotope effect on the standard partial molar volumes can be estimated from eq 6 by assuming the size of the solvated ions to be identical in H_2O and D_2O , so that

$$\Delta V^\circ_2 = [V^\circ_{2,\text{H}} - V^\circ_{2,\text{D}}] = V^\circ_{2,\text{H}} \{1 - [(\partial\epsilon/\partial p)_{T,\text{D}_2\text{O}} / \epsilon_{\text{D}_2\text{O}}^2] / [(\partial\epsilon/\partial p)_{T,\text{H}_2\text{O}} / \epsilon_{\text{H}_2\text{O}}^2]\} \quad (7)$$

Values of $[V^\circ_{2,\text{H}} - V^\circ_{2,\text{D}}]$ for NaCl, NaOH/NaOD, and HCl/DCl have been calculated from eq 7 using the solvent number-density form of the Uematsu–Franck equation^{6,33} to calculate the dielectric constants of water and heavy water and their derivatives. The model predicts values for NaCl of $\Delta_{\text{H-D}} V^\circ_2 =$

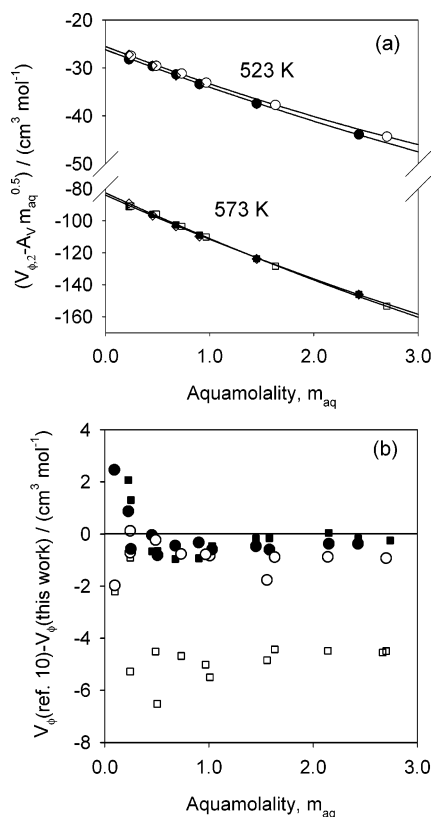


Figure 3. (a) Experimental apparent molar volumes $V_{\phi,2}$ of HCl plotted against aquamolality at 523 and 573 K: (●) H₂O and (○) D₂O at 523 K; (■) H₂O and (□) D₂O at 573 K; (◇) values for HCl in H₂O taken from ref 10. Solid lines were calculated from eq 4 and parameters reported in Table 2. (b) Difference plots of the same data expressed as $[V_{\phi,2}(\text{ref 10}) - V_{\phi,2}(\text{this work})]$. Symbols have the same meaning as those in (a).

TABLE 3: Fitting Parameters for A_{12}° from Eq 8 as a Function of Reduced Density for NaCl, NaOH, and HCl

system	a	b	c
Model I ^a			
NaCl	-7.3851 (± 0.2279)	0.1654 (± 0.0273)	1.4061 (± 0.0477)
NaOH	-8.1553 (± 0.4438)	0.7955 (± 0.2951)	0.7505 (± 0.0914)
HCl	-4.5136 (± 0.1083)	0.0062 (± 0.0013)	2.3788 (± 0.0637)
Model II ^b			
NaCl	-7.3351 (± 0.0408)	0.1594 (± 0.0008)	1.4168
NaOH	-6.0442 (± 0.0611)	0.0677 (± 0.0011)	1.4168
HCl	-7.001 (± 0.1550)	0.1472 (± 0.0030)	1.4168

^a $A_{12}^{\circ} = 1 + \rho_{r,1}^* \{a + b [\exp(c \cdot \rho_{r,1}^*) - 1]\}$. ^b $A_{12}^{\circ} = 1 + \rho_{r,1}^* \{a + b [\exp(1.4168 \cdot \rho_{r,1}^*) - 1]\}$

$0.8 \text{ cm}^3 \text{mol}^{-1}$ and $\Delta_{\text{H-D}}V_{\phi,2}^{\circ} = 6.6 \text{ cm}^3 \text{mol}^{-1}$ at 523 and 573 K, respectively, which is in good agreement with the experimental results of $0.2 \text{ cm}^3 \text{mol}^{-1}$ and $4.5 \text{ cm}^3 \text{mol}^{-1}$. Similarly, for NaOH/NaOD the predicted values, $\Delta_{\text{H-D}}V_{\phi,2}^{\circ} = 1.7 \text{ cm}^3 \text{mol}^{-1}$ and $\Delta_{\text{H-D}}V_{\phi,2}^{\circ} = 8.4 \text{ cm}^3 \text{mol}^{-1}$, agree well with those obtained in this study, $\Delta_{\text{H-D}}V_{\phi,2}^{\circ} = 0.8 \text{ cm}^3 \text{mol}^{-1}$ and $\Delta_{\text{H-D}}V_{\phi,2}^{\circ} = 7.1 \text{ cm}^3 \text{mol}^{-1}$ at 523 and 573 K, respectively. The results for HCl/DCI are less successful. The predicted isotope effect for HCl/DCI at 573 K is large and positive ($\Delta_{\text{H-D}}V_{\phi,2}^{\circ} = 5.7 \text{ cm}^3 \text{mol}^{-1}$) while the experimental isotope effect is small and negative ($\Delta_{\text{H-D}}V_{\phi,2}^{\circ} = -1.4 \text{ cm}^3 \text{mol}^{-1}$). Although the overall agreement between the data and the model is good, the Born equation becomes inaccurate as temperature approaches the

TABLE 4: Experimental and Calculated Standard Partial Molar Volumes for NaCl, NaOH, and HCl in H₂O and NaCl, NaOD, and DCI in D₂O at 523.15 and 573.15 K and 14.0 MPa^a

System	$V_{2,\text{H}}^{\circ} / \text{cm}^3\text{mol}^{-1}$		$V_{2,\text{D}}^{\circ} / \text{cm}^3\text{mol}^{-1}$		$\Delta_{\text{H-D}}V_{2}^{\circ} / \text{cm}^3\text{mol}^{-1}$	
	523 K	573 K	523 K	573 K	523 K	573 K
Experimental Values from Table 2						
NaCl	-23.3	-94.4	-23.5	-98.9	0.2	4.5
NaOH	-48.9	-123.4	-49.7	-130.5	0.8	7.1
HCl	-26.2	-83.9	-25.5	-82.5	-0.7	-1.4
Experimental Values, Corrected for Ion Association						
HCl	-96		-113		17	
Calculated Values from References 10, 11, and 15 ^b						
NaCl	-21.1	-92.9				
NaOH	-46.8	-122.9				
HCl	-24.1	-79.9				
Model I ^b						
NaCl	-20.7	-93.8	-22.5	-101.1	1.8	7.3
NaOH	-46.6	-123.1	-48.3	-130.6	1.7	7.5
HCl	-23.4	-81.2	-24.9	-86.6	1.5	5.4
Model II ^b						
NaCl	-20.7	-93.6	-22.5	-100.9	1.8	7.3
NaOH	-46.9	-118.0	-48.6	-124.7	1.6	6.7
HCl	-21.9	-92.1	-23.6	-99.1	1.7	7.0

^a Solvent isotope effect, $\Delta_{\text{H-D}}V_{\phi,2}^{\circ} = V_{\phi,2,\text{H}}^{\circ} - V_{\phi,2,\text{D}}^{\circ} = RT [\kappa_{1,\text{H}} A_{12}^{\circ}(\rho_{r,\text{H}}) - \kappa_{1,\text{D}} A_{12}^{\circ}(\rho_{r,\text{D}})]$. ^b Calculated without ion association.

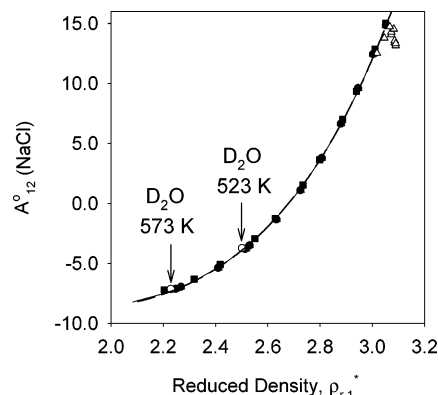


Figure 4. A_{12}° parameters plotted as a function of the reduced density ($\rho_{r,1}^* = \rho_1^* / \rho_{c,1}^*$). Calculated values for NaCl in H₂O from data in ref 11 at (■) saturation pressure, (●) 14 MPa, and (▲) 25 MPa. A_{12}° values for NaCl in D₂O: (△) calculated from data in references 3 and 5 at 0.1 MPa and (○) this work at 14 MPa. Lines were calculated from eq 8 and parameters reported in Table 3: (----) Model I and (---) Model II.

critical point because of compressibility effects.^{18,19} In an attempt to address this limitation, we also have developed an alternative semiempirical treatment for modeling the results.

Cooney and O'Connell,²⁰ O'Connell et al.,²¹ and Sedlbauer and Wood²² have used the dimensionless Krichevskii parameter, $A_{12}^{\circ} = V_{\phi,2}^{\circ} / \kappa_1 RT$, to describe the properties of both electrolytes and nonelectrolytes over a wide range of conditions. A_{12}° is related to the solute-solvent direct correlation function and is a function of the standard partial molar volume of the solute, $V_{\phi,2}^{\circ}$, the pure solvent isothermal compressibility, κ_1 , the gas constant, R , and the temperature, T . Although the Krichevskii parameter depends strongly on water density, it is nearly independent of temperature at temperatures above $\sim 323 \text{ K}$.^{20,23} This behavior is illustrated in Figures 4 and 5, where the values for A_{12}° corresponding to our experimental results NaCl, NaOH/NaOD, and HCl/DCI at $T = 523$ and 573 K are plotted as a function of reduced density, $\rho_{r,1}^* = \rho_1^* / \rho_{c,1}^*$, where $\rho_{c,1}^*$ is

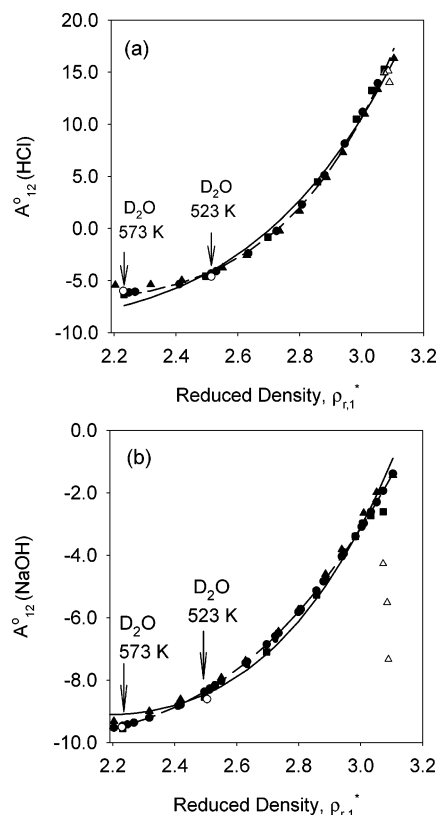


Figure 5. A_{12}° parameters plotted as a function of the reduced density ($\rho_{r,1}^* = \rho_i^*/\rho_{c,1}^*$) for (a) NaOH/NaOD and (b) HCl/DCl. Calculated data for NaOH in H₂O from ref 15 and for HCl in H₂O from ref 10 at (■) saturation pressure, (●) 14 MPa, and (▲) 25 MPa. A_{12}° values for DCl and NaOD in D₂O: (△) calculated from data in ref 3 at 0.1 MPa and (○) this work at 14 MPa. Lines were calculated from eq 8 and parameters reported in Table 3: (---) Model I and (—) Model II.

the critical density of H₂O or D₂O ($\rho_{c,1,H}^* = 0.3220 \text{ g cm}^{-3}$ and $\rho_{c,1,D}^* = 0.35799 \text{ g cm}^{-3}$, respectively).⁹

Several correlations have been proposed in the literature to describe the dependence of the Krichevskii parameter on solvent density. In this work, we have found that exponential correlations, similar to those proposed by O'Connell and his co-workers,^{20,21} accurately represent the experimental results in both light and heavy water. Moreover, as illustrated in Figures 4 and 5, only one set of fitting parameters is required to represent the data in both solvents, if the A_{12}° values are represented in terms of the reduced density. Consequently we have adopted the following correlation

$$A_{12}^\circ = 1 + \rho_{r,1}^* \{a + b[\exp(c\rho_{r,1}^*) - 1]\} = V_2^\circ/\kappa_1 RT \quad (8)$$

where a , b , and c are fitting parameters. O'Connell et al.²¹ have found that the exponential parameter, c , is nearly constant with a value of $0.0044 \text{ m}^3 \text{ kg}^{-1}$. We have arbitrarily chosen three sets of representative V_2° values for HCl, NaCl, and NaOH from references 10, 11, and 15, respectively; one is at saturation pressure and other two are at $p = 14 \text{ MPa}$ and $p = 25 \text{ MPa}$ for temperatures between 340 and 573 K. As expected, the three sets of values for A_{12}° lie on a single curve (see Figures 4 and 5) along with our experimental values for the same electrolytes in D₂O at elevated temperatures.

Equation 8 was fitted to the A_{12}° values for the electrolytes in H₂O by the least-squares method. Two models have been analyzed, one in which c is assumed to be an adjustable parameter to improve accuracy (Model I) and another in which the value of the exponential parameter proposed by O'Connell et al.,²¹ $c = (0.0044 \text{ m}^3 \text{ kg}^{-1}) \rho_{c,1,H}^*$, was assumed to be constant (Model II). Fitting parameters and the predicted values of V_2° for NaCl, HCl, and NaOH in H₂O and in D₂O are listed in Tables 3 and 4, respectively. Both models correctly predict the volume isotope effects for NaCl and NaOH/NaOD; however, the model with three adjustable parameters more accurately reproduces the experimental standard partial molar volumes. The exception is the HCl/DCl system at $T = 573 \text{ K}$ for which a treatment including ion association is required.

4.2. Excess Partial Molar Volumes. Partial molar volumes at finite concentrations $V_{m,2}$ were determined from the expression

$$V_{m,2} = V_{\phi,2} + m_{\text{aq}} (\partial V_{\phi,2} / \partial m_{\text{aq}})_{T,p} \quad (9)$$

using eq 4 with the coefficients given in Table 2 to calculate the apparent molar volume terms. Excess partial molar volumes, V_2^{ex} , (sometimes called relative partial molar volumes) are the difference between the partial molar volumes at finite concentration and the standard partial molar volume, $V_2^{\text{ex}} = (V_{m,2} - V_2^\circ) = 3/2 A_V(m_{\text{aq}}/m_{\text{aq}}^\circ)^{1/2} + 2 B_V(m_{\text{aq}}/m_{\text{aq}}^\circ) + 3 C_V(m_{\text{aq}}/m_{\text{aq}}^\circ)^2$.

We have adopted the MSA/HS model to describe the short-range ion–ion interaction effects that contribute to V_2^{ex} . MSA is an analytical solution of the Ornstein–Zernike equation³⁷ that has been used extensively to describe the thermodynamic properties of electrolyte solutions. The expressions required to calculate the excess partial molar volumes for the unrestricted version of the MSA and the hard sphere contribution have been presented by Corti,²⁵ and they will be reproduced here for clarity.

In this model, the excess partial molar volume, eq 10, has three contributions: the MSA term, a hard-sphere contribution, and a correction term to account for the different reference systems (i.e. the Lewis–Randall reference state (constant pressure) and the MacMillan–Mayer reference state (constant chemical potential of the solvent))

$$V_2^{\text{ex}} = V_2^{\text{ex,MSA}} + V_2^{\text{ex,HS}} + \Delta V_2^{\text{LRMM}} \quad (10)$$

To calculate the excess partial molar volume, V_2^{ex} , Corti²⁵ adopted an approach in which the solution compressibility was assumed to be equal to that of the solvent and in which the correction term, ΔV_2^{LRMM} , is omitted and incorporated in the adjustable parameter as the diameter of either the cation or the anion. These assumptions yield the expressions

$$V_2^{\text{ex,MSA}} = - (3/2) \nu RT \ln \gamma_{\pm} (\partial \ln \epsilon / \partial p)_T - RT \kappa_1 \{ [(\alpha^2 P_n^2) / (4\rho_2 \Delta^3 \Omega)] + [(\rho_2 \Phi^2) / (4\pi \psi)] \} \quad (11)$$

$$\ln \gamma_{\pm} = - [(\alpha^2 \Gamma) / (4\pi \nu)] \sum_i [\nu_i z_i^2 / (1 + \sigma_i \Gamma)] - [\alpha^2 / (8\nu \rho_2)] [(P_n^2 \Omega / \Delta) + (P_n^2 / \Delta^2)] \quad (12)$$

Here, Γ is the screening parameter, equivalent to the reciprocal screening distance, κ_D , in the Debye–Hückel theory

$$4 \Gamma^2 = \alpha^2 \sum_i [(\rho_i a_i^2) / (1 + \sigma_i \Gamma)^2] \quad (13)$$

Other parameters in eqs 11 and 12 are as follows:

$$\alpha^2 = [(4\pi e^2)/(\epsilon k_B T)] \quad (14)$$

$$a_i = z_i - (\pi/2\Delta) P_n \sigma_i^2 \quad (15)$$

$$P_n = (1/\Omega) \sum_i [(\rho_i \sigma_i z_i)/(1 + \sigma_i \Gamma)] \quad (16)$$

$$\Omega = 1 + (\pi/2\Delta) \sum_i [(\rho_i \sigma_i^3)/(1 + \sigma_i \Gamma)] \quad (17)$$

$$\Delta = 1 - \xi_3 \quad (18)$$

$$\Phi = (4 \Gamma^2 / \rho_2) - [(\pi \alpha^2 P_n) / (\Delta^2 \Omega)] \sum_i [(\nu_i a_i \sigma_i^2) / (1 + \sigma_i \Gamma)^2] \quad (19)$$

$$\psi = 8\Gamma + 2\alpha^2 \left\{ \sum_i [(\rho_i \sigma_i a_i^2) / (1 + \sigma_i \Gamma)^3] \right\} - [(\pi \alpha^2) / (\Delta \Omega)] \left\{ \sum_i [(\rho_i a_i \sigma_i^2) / (1 + \sigma_i \Gamma)^2] \right\}^2 \quad (20)$$

The hard-sphere contribution, $V_2^{\text{ex,HS}}$, is obtained from the equation by Mansoori et al.³⁸ for the pressure of a hard sphere mixture ($V_i/\kappa_T = (\partial p/\partial \rho_i)_T$)

$$V_2^{\text{ex,HS}} = \sum_i V_i^{\text{ex,HS}} = RT\kappa_1 \sum_i (1/\Delta) + [\sigma_i(\xi_0 \sigma_i^2 + 3\xi_1 \sigma_i + 3\xi_2)/\Delta^2] + [\xi_2 \sigma_i^2(6\xi_1 \sigma_i + 9\xi_2 - \xi_2^2 \sigma_i - 3\xi_2 \xi_3)/\Delta^3] + [\xi_2^3 \sigma_i^3(9 - 3\xi_3)/\Delta^4] \quad (21)$$

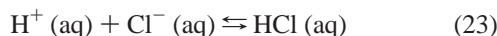
with

$$\xi_k = (\pi/6) \sum_i \rho_i \sigma_i^k \quad (22)$$

We have chosen to fix the ionic diameters to their crystallographic values: $\sigma(\text{Cl}^-) = 3.6 \text{ \AA}$, $\sigma(\text{OD}^-) = 2.8 \text{ \AA}$, $\sigma(\text{Na}^+) = 1.9 \text{ \AA}$, $\sigma(\text{D}^+) = 2.8 \text{ \AA}$ and the same ionic diameter for a given ion was used throughout the calculations. The model and the experimental excess partial molar volumes are plotted in Figure 6. As shown in Figure 6, the concentration dependence of the experimental excess partial molar volumes at 523 K is well represented by the MSA/HS model for the three electrolytes in heavy water with differences that are all below $3 \text{ cm}^3 \text{ mol}^{-1}$. At 573 K, the agreement is good at low concentrations, but the model over-predicts the experimental excess volumes at high concentrations. These deviations may be due to ion-association reactions which have not been taken into account in the model.^{10,15}

4.3. The Effects of Ion Association. An estimate of the effect of ion-association reactions on the extrapolation to infinite dilution could help to resolve the differences in behavior between NaCl and HCl at 573 K. Previous studies³⁹ indicate that, above 523 K, the degree of ionic association of aqueous HCl is significantly greater than that for NaCl.

The association reaction and corresponding expression for the association constant, K_{assoc} , are given below



$$K_{\text{assoc}} = (\alpha_{\text{ass}} \gamma_{\text{ip}}) / ((1 - \alpha_{\text{ass}})^2 m \gamma_{\pm}^2) \quad (24)$$

where α_{ass} is the degree of association, m is the molality of the acid, γ_{ip} is the activity coefficient of the neutral species

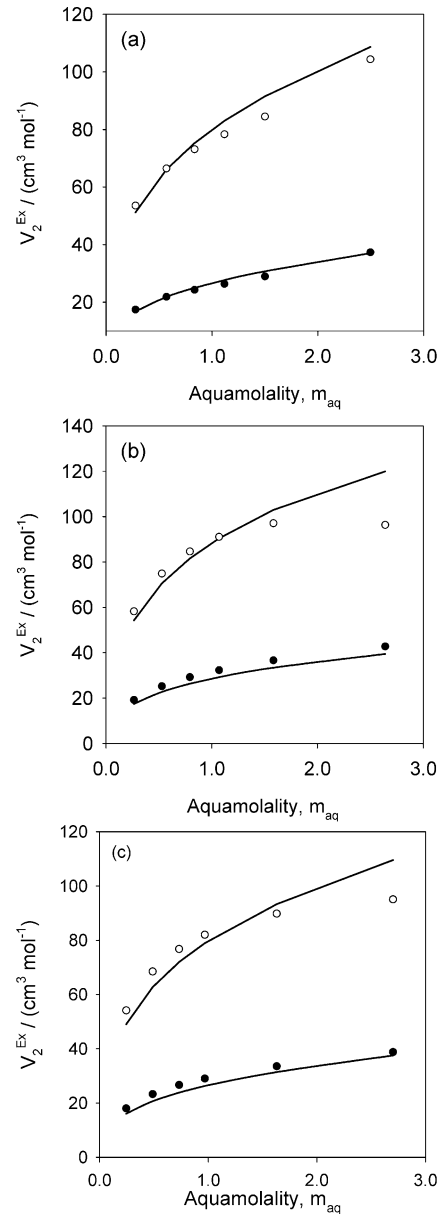


Figure 6. Excess partial molar volumes for (a) NaCl, (b) NaOD, and (c) DCl in D_2O as a function of concentration at (●) 523 K and (○) 573 K. Solid lines correspond to the MSA/hard sphere model with $\sigma(\text{Na}^+) = 1.9 \text{ \AA}$, $\sigma(\text{Cl}^-) = 3.6 \text{ \AA}$, $\sigma(\text{D}^+) = 2.8 \text{ \AA}$, and $\sigma(\text{OD}^-) = 2.8 \text{ \AA}$.

(ion pair), and γ_{\pm} is the mean activity coefficient of the electrolyte (free ions).

Association constants for aqueous HCl have been determined by conductance^{40,41} and by heat of dilution measurements.⁴² We have chosen to use the association model developed for HCl by Simonson et al.,³⁶ which incorporates the conductance data of Frantz and Marshall,⁴¹ instead of the more recent conductance data and model by Ho et al.,⁴⁰ which is restricted to lower concentrations. The Simonson model is based on the ion interaction treatment of Pitzer,⁴³ and takes the form

$$\ln K_{\text{assoc}} = 12.45 - (8923.9/T) - 13.93 \ln(\rho_1^*/\rho^\circ) \quad (25)$$

with $\rho^\circ = 1 \text{ g cm}^{-3}$. The association constant value obtained with eq 25 at 573.11 K and 14.0 MPa is equal to $K_{\text{assoc}} = 3.98$. This is in excellent agreement with the value obtained from the equation reported by Fuangswandi et al.⁴² from heat-of-dilution studies but lower than the value $K_{\text{assoc}} = 11.5$, which is retrieved from the equation by Ho et al.⁴⁰

The degree of association, α_{ass} , required to estimate the standard partial molar volume of the free ions was found to change from approximately 0.1 to 0.2 over the range of compositions for aqueous HCl listed in Table 1. These values were calculated by an iterative procedure using the semiempirical association–interaction parameters given by Simonson et al.³⁶

$$\ln \gamma_{\pm} = -(A_{\phi}/1.2) [2 \ln(1 + 1.2I^{1/2}) + 1.2I^{1/2}/(1 + 1.2I^{1/2})] + m_i B^{\gamma} + m_i^2 C^{\gamma} \quad (26)$$

with

$$B^{\gamma} = 2\beta^{(o)} + 2\beta^{(1)} [1 - (1 + 2I^{1/2} - 2I) \exp(-2I^{1/2})/4I]$$

and

$$C^{\gamma} = 1.5 C^{\phi}$$

The coefficients and expressions used for calculating B^{γ} and C^{γ} at each temperature are listed in ref 36 and are not reproduced here.

The apparent molar volume of the partially dissociated HCl electrolyte can be described by adopting the approach by Majer and Wood for describing volumetric properties of aqueous 1–1 electrolytes near and above the critical point of water.⁴⁴ In our treatment, the apparent molar volume of the electrolyte, eq 27, is expressed in terms of the degree of association, α_{ass} , the aquamolality of the free ions, $m_{i,\text{aq}} = (1 - \alpha_{\text{ass}})m_{\text{aq}}$, the standard partial molar volume of the free ions, $V_{\pm,2}^{\circ}$, and the change in standard partial molar volume for the ion pair formation reaction, $\Delta_r V^{\circ}$. The model assumes the deviation from nonideality is due only to the ions ($V_{\phi,\text{ip}} = V_{\text{ip}}^{\circ}$), and the interaction between ions is described by the Pitzer ion interaction model,⁴³

$$V_{\phi,2} = V_{\pm,2}^{\circ} + \alpha_{\text{ass}} \Delta_r V^{\circ} + (1 - \alpha_{\text{ass}}) \{ (A_{\phi}/1.2) \ln(1 + 1.2(m_{i,\text{aq}}/m^{\circ}_{\text{aq}})^{1/2}) + 2RT(m_{i,\text{aq}}/m^{\circ}_{\text{aq}})(B_V^{\gamma} + (m_{i,\text{aq}}/m^{\circ}_{\text{aq}})C_V^{\gamma}) \} \quad (27)$$

The change in standard partial molar volume for the ion pair formation reaction in eq 27 is given by

$$\Delta_r V^{\circ} = V_{\text{ip}}^{\circ} - V_{\pm}^{\circ} \quad (28)$$

and it can be calculated from the density dependence of $\ln K_{\text{assoc}}$ ⁴⁵

$$\Delta_r V^{\circ} = -RT\kappa_1(\partial \ln K_{\text{assoc}}/\partial \ln \rho_1^*) \quad (29)$$

The Pitzer interaction parameters, B_V^{γ} and C_V^{γ} , are given by

$$B_V^{\gamma} = 2\beta^{(o)V} + 2\beta^{(1)V}f(I) \quad (30)$$

and

$$C_V^{\gamma} = (\partial C^{\gamma}/\partial p)_T$$

The V_{ϕ} values in this study were found to be best represented by assuming $\beta^{(1)V} = 0$. The calculated $\Delta_r V^{\circ}$ values (eq 29) along with the $V_{\pm,2}^{\circ}$, B_V^{γ} , and C_V^{γ} values obtained from least-squares fitting to the experimental results at 573 K are tabulated in Table 5. The standard partial molar volume of the electrolyte, $V_{\pm,2}^{\circ} = -93.5 \pm 1.5 \text{ cm}^3 \text{ mol}^{-1}$, was also calculated with B_V^{γ} and C_V^{γ} derived from the interaction parameters of Simonson et al.³⁶ after assuming $\beta^{(1)V} = 0$. The agreement is excellent, particularly because the interaction parameters in ref 36 were obtained from

TABLE 5: Regression Parameters of Eq 27 for the Apparent Molar Volumes of HCl/DCl in H₂O and D₂O at 573.11 K and 14.0 MPa

system	$\Delta_r V^{\circ}$ /cm ³ mol ⁻¹	V_{\pm}° /cm ³ mol ⁻¹	$B_V^{\gamma} \times 10^5$ /MPa ⁻¹	$C_V^{\gamma} \times 10^5$ /MPa ⁻¹	σ /cm ³ mol ⁻¹
HCl/H ₂ O	181.2 ^a	-96 ± 1	-45.2	-9.65	0.8
DCl/D ₂ O	181.2	-113	-41.0	-23.5	0.6

^a From eq 29: $\Delta_r V^{\circ} = -RT\kappa_1 (\partial \ln K_{\text{assoc}}/\partial \ln \rho_1^*)$.

pressure-dependent heat of dilution data rather than volumetric measurements.

The value $V_{\pm,2}^{\circ} = -96 \text{ cm}^3 \text{ mol}^{-1}$ for the free ions is more negative by $\sim 12 \text{ cm}^3 \text{ mol}^{-1}$ than that obtained by neglecting ion-association. The value $\Delta_r V^{\circ} = 181 \text{ cm}^3 \text{ mol}^{-1}$ for the association reaction in water is in relatively good agreement with the value $\Delta_r V^{\circ} = 132 \text{ cm}^3 \text{ mol}^{-1}$, adopted by Majer and Wood⁴⁴ for NaCl under similar conditions, but is much larger than the value $\Delta_r V^{\circ} \sim 63 \text{ cm}^3 \text{ mol}^{-1}$ given by Sedlbauer et al.⁴⁵ For that reason, we have not included the partial molar volumes at infinite dilution for the neutral ion pairs, V_{ip}° , as these are strongly dependent on the value used for $\Delta_r V^{\circ}$.

The same treatment was adopted for analyzing the apparent molar volumes for DCl in D₂O at 573 K, although in this case we were forced to make several additional assumptions:

(i) The association constant in heavy water was assumed to follow the trend observed for the ionization of several weak acids at low temperature,⁴⁶ $\text{p}K_{\text{assoc,D}_2\text{O}} = \text{p}K_{\text{assoc,H}_2\text{O}} + 0.45$, on a molality scale. This is in good agreement with the difference observed by Mesmer and Herting⁴⁷ for the association of D_2PO_4^- at 598.15 K, $\text{p}K_{\text{assoc,D}_2\text{O}} = \text{p}K_{\text{assoc,H}_2\text{O}} + 0.47$. Values for the ionization constant of heavy water from ref 48 are consistent with earlier results from Shoesmith and Lee.⁴⁸

(ii) The isotope effect on the activity coefficient of the free ions was assumed to be small so that values for HCl in H₂O could be used to calculate the degree of association in D₂O. The assumption is supported by low-temperature data for the ionization of water. For example, at 50 °C and $I = 0.2$, $\log(\gamma_{\text{H}^+}\gamma_{\text{OH}^-}/\gamma_{\text{D}^+}\gamma_{\text{OD}^-}) = 0.03$.⁴⁷

(iii) The effect of pressure on the solvent isotope effect for the association constant was assumed to be negligible.⁴⁹ Consequently, the standard volume change for the association reaction is the same in both solvents.

Although $V_{\pm,2}^{\circ}$, B_V^{γ} , and C_V^{γ} were obtained from nonlinear least-square fitting to the experimental results on the aquamolality scale, for simplicity the degree of association was estimated on a molality basis. The relatively large increase in the value of the association constant when going from H₂O to D₂O causes the degree of association in heavy water to be significantly higher than that in water. For instance, for the same concentration range, the degree of association of DCl in D₂O varied from 0.25 to 0.43 over the range of our measurements, while the degree of association for HCl in water over the same molality range was only 0.11 to 0.23.

As shown in Table 5, the standard partial molar volumes for the free ions in D₂O, $V_{\pm,2}^{\circ}$, are more negative than in water, resulting in a solvent isotope effect consistent with the behavior observed for NaCl, although the effect is larger ($17 \text{ cm}^3 \text{ mol}^{-1}$). Similar corrections should be carried out for NaOH (NaOD), which also undergoes significant ion pairing, and the similarity in its uncorrected deuterium isotope effect with that of NaCl may be fortuitous. Further measurements of deuterium isotope effects on association constants, apparent molar volumes, and activity coefficients at 300 °C are needed to refine this analysis.

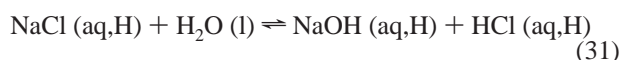
TABLE 6: $\Delta_{\text{ion}}V^\circ$ for the Ionization of H_2O and D_2O at $T = 523$ and 573 K and $p = 14$ MPa

System	$\Delta_{\text{ion}}V^\circ / \text{cm}^3 \text{mol}^{-1}$ Experimental ^a		$\Delta_{\text{ion}}V^\circ / \text{cm}^3 \text{mol}^{-1}$ Calculated ^{a,b}		$\Delta_{\text{ion}}V^\circ / \text{cm}^3 \text{mol}^{-1}$ Predicted ^{a,c}	
	523 K	573 K	523.15 K	573.15 K	523.15 K	573.15 K
Without Correction for Ion-Association						
H_2O	-74 (± 1)	-138 (± 3)	-72 (± 2)	-135 (± 2)	-72	-135
D_2O	-74 (± 1)	-139 (± 3)			-73	-141
Ion - Interaction Association Model						
H_2O		-150 (± 10)				
D_2O		-170 (± 20)				

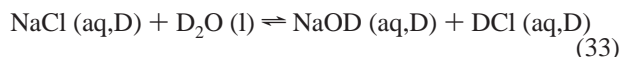
^a $V_{1,\text{H}}^* = 22.242 \text{ cm}^3 \text{mol}^{-1}$ and $24.897 \text{ cm}^3 \text{mol}^{-1}$ and $V_{1,\text{D}}^* = 22.343 \text{ cm}^3 \text{mol}^{-1}$ and $25.096 \text{ cm}^3 \text{mol}^{-1}$ at 523.15 and 573.15 K and 14 MPa, respectively. ^b Standard partial molar volumes for HCl, NaCl, and NaOH taken from refs 10, 11, and 15, respectively. ^c $\Delta_{\text{ion}}V^\circ = [(A_{12}^\circ(\text{HCl}) + A_{12}^\circ(\text{NaOH}) - A_{12}^\circ(\text{NaCl}))\kappa_1 RT - V_1^*]$. A_{12}° values calculated from the estimated regression parameters for eq 8 reported in Table 3 for Model I.

Association constants for DCl and NaOD in D_2O , as a function of temperature, pressure, and composition, are required to provide experimental values for the necessary corrections for ion association so that we can confirm these results. These measurements are currently underway in our laboratory.

4.4. ΔV° for the Ionization of H_2O and D_2O . The standard partial molar volumes in Table 2 were combined with molar volumes for water, $V_{1,\text{H}}^*$, and heavy water, $V_{1,\text{D}}^*$, to calculate the standard partial molar volume change, $\Delta_{\text{ion}}V^\circ$, for the ionization of H_2O and D_2O reactions 31 and 33, respectively, using the expressions



$$\Delta_{\text{ion}}V^\circ_{\text{H}} = V^\circ_{2,\text{H}}(\text{HCl}) + V^\circ_{2,\text{H}}(\text{NaOH}) - V^\circ_{2,\text{H}}(\text{NaCl}) - V_{1,\text{H}}^* \quad (32)$$



$$\Delta_{\text{ion}}V^\circ_{\text{D}} = V^\circ_{2,\text{D}}(\text{DCl}) + V^\circ_{2,\text{D}}(\text{NaOD}) - V^\circ_{2,\text{D}}(\text{NaCl}) - V_{1,\text{D}}^* \quad (34)$$

The values calculated for $\Delta_{\text{ion}}V^\circ$ at $T = 523$ K and $T = 573$ K, using eqs 32 and 34, are listed in Table 6. The tabulated error estimates for the data without corrections for ion association were calculated from the standard errors reported in Table 2. These do not include the systematic errors in the molar volume of water or a correction for the small differences in temperature and pressure between runs. The results in Table 6 appear to show a small $\text{D}_2\text{O}/\text{H}_2\text{O}$ solvent effect on $\Delta_{\text{ion}}V^\circ$ of water at 573 K; however, our values lie within the combined experimental uncertainties. The uncertainties in the values for $\Delta_{\text{ion}}V^\circ$ calculated from the ion-associated model are a “best guess” estimate based on the assumptions used in the analysis. When the effects of ion-pairing are included, there is a difference of $20 \text{ cm}^3 \text{mol}^{-1}$ in the values of $\Delta_{\text{ion}}V^\circ$, however the difference also lies within the combined uncertainties.

The quality of our results must be evaluated by comparing the experimental values for the ionization of H_2O (our reference system) with those obtained from the global fitting equations for HCl, NaCl, and NaOH in references 10, 11, and 15, respectively. As shown, there is an excellent agreement between both sets of data within the combined estimated error limits. These new values for the ionization of H_2O also compare reasonably well with those reported by Sweeton et al.⁵⁰ for the dissociation of water at saturation pressure in KCl media, $\Delta_{\text{ion}}V^\circ = (-76.4 \pm 5.1) \text{ cm}^3 \text{mol}^{-1}$ and $\Delta_{\text{ion}}V^\circ = (-166.1 \pm 18.3) \text{ cm}^3 \text{mol}^{-1}$ at $T = 523$ and 573 K, respectively.

We have used eqs 32 and 34 to estimate the $\Delta_{\text{ion}}V^\circ$ for water and heavy water with the A_{12}° values calculated from eq 8 using the parameters in Table 3 for our more accurate model (Model I)

$$\Delta_{\text{ion}}V^\circ = [A_{12}^\circ(\text{HCl, aq}) + A_{12}^\circ(\text{NaOH, aq}) - A_{12}^\circ(\text{NaCl, aq})]\kappa_1 RT - V_1^* \quad (35)$$

Here, κ_1 and V_1^* are the isothermal compressibility and molar volume of water or heavy water, as appropriate. As shown in Table 6, the predicted values of $\Delta_{\text{ion}}V^\circ$ are in reasonable agreement with the experimental data for the self-ionization of both water and heavy water.

When association effects are included, the value for light water, $\Delta_{\text{ion}}V^\circ = (-150 \pm 10) \text{ cm}^3 \text{mol}^{-1}$ at $T = 573$ K, is in good agreement with those calculated by Sweeton et al.⁵⁰ from the pressure dependence of $\log K_w$, $\Delta_{\text{ion}}V^\circ = (-166.1 \pm 18.3) \text{ cm}^3 \text{mol}^{-1}$. Unfortunately, similar pressure-dependent studies were not carried out for the ionization constants of heavy water^{47,48} and there are no literature results for comparison.

5. Conclusions

These are the first apparent and partial molar volumes reported for NaCl, NaOD, and DCl in D_2O at temperatures higher than 350 K. Despite the limited scope of this study (see Note Added in Proof), we have found two semiempirical equations, one based on the Born model and the other on the dimensionless Krichevskii parameter, A_{12}° , that can be used for predicting standard partial molar volumes of electrolytes in D_2O based on available data for aqueous (H_2O) solutions. Also for the first time, values for the standard partial molar volume of ionization of D_2O , $\Delta_{\text{ion}}V^\circ$, have been determined under hydrothermal conditions at $T = 523$ and 573 K so that the pressure dependence of the ionization constant can be calculated.

Note Added in Proof. To illustrate the consistency and precision of these measurements, several additional new data points from a related follow-up study have been added to Figure 3(b).

Acknowledgment. The authors thank Dr. H. R. Corti for help with the MSA computer program and for fruitful discussions. We also thank Ms. Sarah Moore for permission to use unpublished data in Figure 3(b). This work was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC), the University Network of Excellent in Nuclear Engineering (UNENE), and the University of Guelph. Heavy water was provided by Ontario Power Generation Ltd.

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