ISOTOPE EFFECTS ON APPARENT AND PARTIAL MOLAR VOLUMES OF HCl, LiCl, AND NaCl MEASURED IN H_2O AND D_2O FROM 250 ^oC TO 350 ^oC AND 14 MPa TO 19 MPa

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Abstract

Apparent molar volumes have been measured for solutions of HCl (DCl), LiCl, and NaCl in H_2O and D_2O over the temperature range T = 250 ^oC to T = 350 ^oC and p = 14 MPa to p = 19 MPa using a high-temperature, high-pressure vibrating tube densimeter in the molality range $0.05 < m < 3.50$ $mol{\cdot}kg^{-1}$. The experimental results have been represented using an extended Debye-Huckel equation to describe the molality dependence of the apparent molar volumes. The Born model and Krichevskii model have been used to describe solvent isotope effects. The results will contribute to developing models for predicting pD under CANDU reactor primary coolant conditions.

1. Introduction

Heavy water (D_2O) is used as a heat transfer medium between the reactor core and steam generator in CANDU pressurized heavy water reactors, reaching temperatures between 250 ^oC and 320 ^oC. In order to minimize feeder thinning, an accurate understanding of heavy-water solvent isotope effects (SIEs) is required to optimize pD under primary coolant operating conditions.

With the exception of phosphoric acid [1] and our own recent work [2, 3], experimental investigation of SIEs on ionization constants have been restricted to temperatures below 100 ^oC. The first of these studies reported deuterium isotope effects for two model systems, boric acid and β-naphthoic acid, at 250 ^oC and 300 ^oC [2]. The results are plotted in Figure 1, which shows values of $\Delta pK = [pK(D_2O)\text{-}pK(H_2O)]$ for $D_2PO_4^-$ [1], β-naphthoic acid, $B(OD)_3$, and CH_3COOD [2], as a function of temperature.

Standard partial molar volumes, V_2^o, are of interest in this context, both because they are a key parameter used to develop predictive models of solvation effects, and because the pressure dependence of ΔpK is determined by the relationship:

$$\left(\frac{\partial[pK(D_2O)-pK(H_2O)]}{\partial p}\right)_T = \frac{\Delta_{ion}V_2^o(D_2O)-\Delta_{ion}V_2^o(H_2O)}{RT}, \tag{1}$$

where $\Delta_{ion}V_2^o$ is the standard partial molar volume change of the ionization reaction. Our second study [3] reported apparent molar volumes, $V_{\phi,2}$, and the corresponding standard partial molar volumes, of aqueous NaCl, DCl and NaOD in D_2O at temperatures up to 300 °C. These are the first values reported for the SIEs of standard partial molar volumes above 100 °C. Models based on both the Born equation [4] and the generalized Krischevskii equation [5] were successful in predicting these effects.

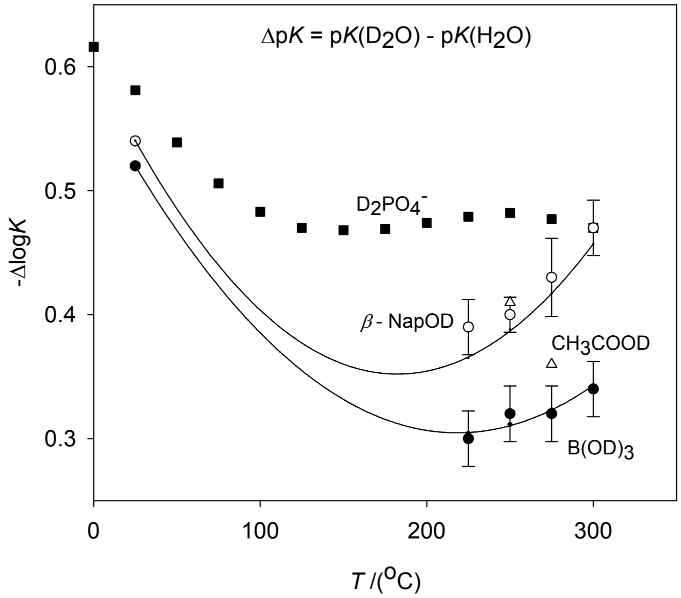

Figure 1 Values of ΔpK ($pK(D_2O) - pK(H_2O)$) for $D_2PO_4^-$ (■) [1], β-naphthoic acid (○) [2], $B(OD)_3$ (●) [2], and CH_3COOD (△) (preliminary work in our group) as a function of temperature

The objective of the present study is to extend these measurements made in our laboratory to higher temperatures and to more systems, so that detailed predictive models for deuterium isotope effects on coolant chemistry can be developed. The systems under investigation include aqueous HCl (DCl), NaCl, and LiCl. This paper reports measurements of apparent and standard partial molar volumes of LiCl, NaCl, and HCl (DCl) in H_2O and D_2O at temperatures from $T = 250$ °C to $T = 350$ °C, at pressures of $p = 14$ MPa to $p = 19$ MPa. These results have been used to test the success of the Born and Krichevskii models under more extreme conditions.

2. Experimental methods

The reagents were used as received from commercial sources. Standard stock solutions of NaCl (Fisher Scientific, ACS reagent grade) and LiCl (Aldrich, ACS reagent grade) were prepared by mass after drying the salts at $T = 120$ °C for at least 7 days. 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. %, Fisher Certified ACS) and standardized by titration against standard NaOH solutions. Nanopure water (resistivity 18 MΩ·cm) and deuterium oxide (99.6 mol %D) were used to prepare corresponding solutions, in the approximate molality range $0.05 < m < 3.50$ mol·kg^{-1}, from the stock solutions by mass. The deuterium content in the D_2O was determined using ^{1}H NMR, where standard additions of variable amounts of 99.99+% glacial acetic acid (Aldrich) were added to D_2O as an internal reference. The solutions in D_2O were prepared in a glove-bag flushed with argon, which was continually kept under positive argon pressure. These solutions were maintained under an atmosphere of argon. All concentrations of solutions are given in terms of aquamolality, m_{aq}, defined as mol of solute per 55.509 mol of solvent.

The volumetric measurements were made using a high-temperature, high-pressure platinum vibrating tube densimeter [6]. The instrument was calibrated several times daily with H_2O and D_2O based on Hill's equations of state for water [7] and heavy water [8]. The validity of the calibration was confirmed using a standard solution of 1.9999 mol·kg^{-1} NaCl in light water, using density values compiled by Archer for aqueous NaCl [9]. At temperatures up to 325 $^{\circ}$C, the overall uncertainty in the measured relative densities (due to the sensitivity limits of the instrument and the accuracy of the NaCl reference data) is estimated to be ∀ 0.0002 g·cm^{-3}, while its precision is ∀ 0.00002 g·cm^{-3}.

The experimental design involved sequential injections of D_2O, the NaCl(aq) standard solution, and solutions of interest in H_2O and D_2O, at constant temperature and constant pressure, using H_2O as a reference, so that differences in the density of the solutes and D_2O relative to H_2O could be measured directly. At higher temperatures, the absolute accuracy was lower because the uncertainties in both Hill's equation of state for D_2O, and Archer's model for the excess properties of aqueous NaCl are both estimated to be ∀ 1x10^{-4} g·cm^{-3} [8, 9].

3. Data Treatment

The relative densities of a solution with respect to H_2O, $\rho - \rho_1$, were determined from the expression:

$$\rho - \rho_1 = K\left(\tau^2 - \tau_1^{\,2}\right), \tag{2}$$

where ρ_1 is the density of pure H_2O, while τ and τ_1 are the periods of vibration of the densimeter tube containing the solution of interest and pure water, respectively. K is the calibration constant of the densimeter, determined from measurements on H_2O and D_2O using the literature compiled by Hill [7] and Hill *et al.* [8].

Apparent molar volumes were calculated through the following expression:

$$V_{\phi,2} = \frac{(V_{so\ln} - n_1 V_1{}^*)}{n_2}, \tag{3}$$

where V_{soln} is the volume of the solution of interest, V_1* is the apparent molar volume of the solvent (H_2O or D_2O), n_2 represents the number of moles of the solute, n_1 represents the number of moles of solvent, and $V_{\phi,2}$ is the apparent molar volume of the solution. The equation that relates the apparent molar volumes to the densities and total aquamolality is:

$$V_{\phi,2} = 55.509\frac{M_1(\rho_1 - \rho)}{m_{aq}\rho_1\rho} + \frac{M_2}{\rho}, \tag{4}$$

where M_1 and M_2 are the molar masses of the solvent and solute, respectively.

The extended Debye-Hückel expression [10]:

$$V_{\phi,2} = V_2^{o} + A_v m_{aq}^{1/2} + B_v m_{aq} + C_v m_{aq}^{3/2}, \tag{5}$$

was used to describe the molality dependence upon the apparent molar volumes of NaCl, LiCl, and HCl (DCl) in H_2O and D_2O over the temperature pressure ranges indicated above. In equation (5), B_v and C_v are adjustable parameters. A_v is the Debye-Hückel limiting slope, values of which have been tabulated by Archer and Wang for H_2O [11]. The values for A_v in D_2O were calculated using equation (6):

$$A_v = (2/3)RT\left[\frac{(2\pi N_A \rho_{1,D})}{1111.7}\right]^{1/2}\left[\frac{e^2}{(4\pi\varepsilon_o \varepsilon k_B T)}\right]^{3/2}\left[3\left(\frac{\partial \ln \varepsilon}{\partial p}\right)_T + \left(\frac{\partial \ln V_{1,D}}{\partial p}\right)_T\right], \tag{6}$$

where R is the gas constant (R = 8.31451 $J \cdot K^{-1} \cdot mol^{-1}$); T is the temperature (in Kelvin); e is the charge on an electron (e = 1.60218 x 10^{-19} C); ε_o is the permittivity of a vacuum (ε_o = 8.85419x10^{-12} $C^2 \cdot N^{-1} \cdot m^{-2}$); ε is the dielectric constant of D_2O (calculated using the Uematsu-Franck equation [12]); k_B is Boltzmann's constant (k_B = 1.38065 x 10^{-23} $J \cdot K^{-1}$); N_A is Avagadro's number (N_A = 6.02214x10^{-23} mol^{-1}); $V_{1,D}$ is the molar volume of D_2O, and $\rho_{1,D}$ is its density. The factor of 1111.7 is due to the difference in conversion from m_{aq} to ions per cubic centimetre in H_2O and D_2O.

4. Results and Discussion

Fits of equation (5) to the apparent molar volume data for solutes in H_2O and D_2O have been compared in order to see the overall SIE effect as a function of molality for solutes at each temperature and pressure condition. Figure 2 below shows one specific example, for HCl and DCl at T = 300 °C and p = 14 MPa.

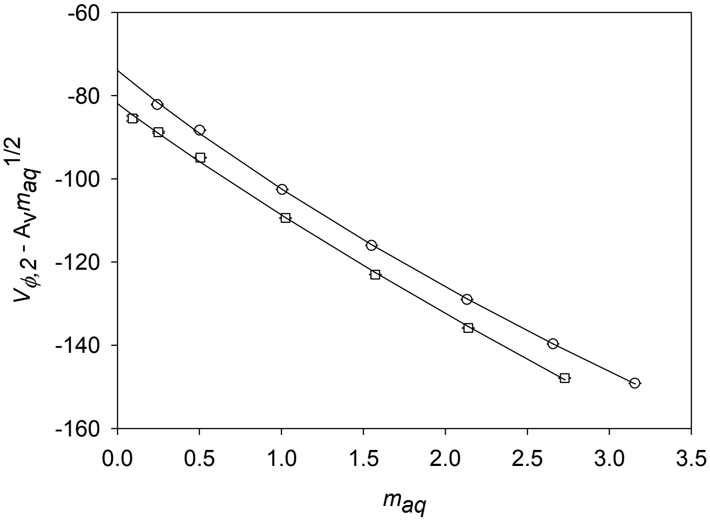

Figure 2 Comparison of equation (4) fits (solid lines) for HCl (□) in H_2O and DCl (○) in D_2O at $T = 300$ °C and $p = 14$ MPa

Differences in $V_{\phi,2}$ for solutes in H_2O and D_2O ($\Delta V_{\phi,2} = V_{\phi,2}(D_2O) - V_{\phi,2}(H_2O)$) have been calculated for each system at each temperature and pressure. These have been used to experimental establish trends in $\Delta V_{\phi,2}$ as a function of m_{aq}. Prediction of the SIE on partial molar volumes (ΔV_2^o) have been calculated using the Born model [4] (equation (7)) and the Krichevskii model [5] (equation (8)) for each system at each temperature and pressure condition:

$$\Delta V_2^o = V_{2,D}{}^o \left\{ 1 - \left[\left[\frac{(\partial \varepsilon / \partial p)_{T,H}}{(\varepsilon_H)^2} \right] / \left[\frac{(\partial \varepsilon / \partial p)_{T,D}}{(\varepsilon_D)^2} \right] \right] \right\}, \tag{7}$$

$$\Delta V_2{}^o = RT\left[\kappa_D A_{12}{}^o \rho_{r,D} - k_H A_{12}{}^o \rho_{r,H}\right], \tag{8}$$

where "D" and "H" refer to D_2O and H_2O, respectively, ρ_r is the reduced density of the solvent, κ is the isothermal compressibility coefficient of the solvent, and A_{12}^o is the dimensionless Krichevskii term ($A_{12}^o = V_2^o/(\kappa RT)$).

Figures 3 to 5 show comparisons of our experimental values of $\Delta V_{\phi,2}$ with values of ΔV_2^o predicted from the Born and Krichveskii models for LiCl (at $T = 300$ °C and $p = 14$ MPa, $T = 325$ °C and $p = 14$ MPa, and $T = 350$ °C and $p = 19$ MPa, respectively). Figure 6 shows comparisons of experimental ΔV_2^o values for NaCl (at $T = 250$ °C and $p = 14$ MPa, and $T = 300$ °C, and $p = 14$ MPa) with those values previously reported [3], and those predicted from the Born and Krichveskii models.

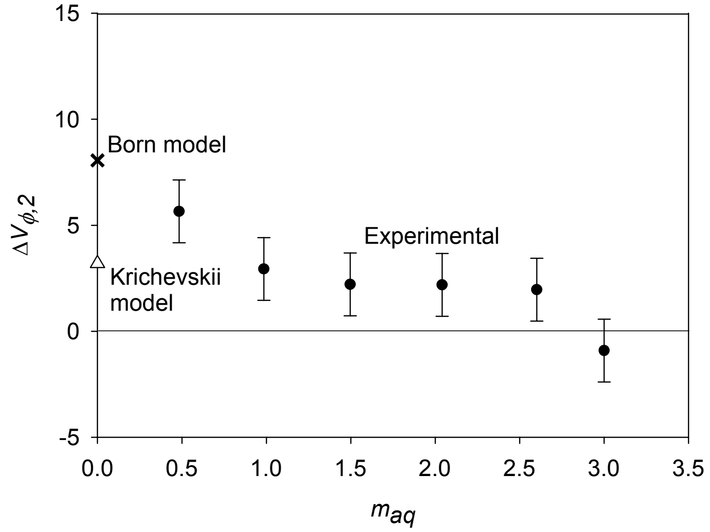

Figure 3 Comparison of experimental $\Delta V_{\phi,2}$ values with those ΔV_2^o values predicted by the Born model (**X**) and Krichevskii model (△)for LiCl at T = 300 °C and p = 14 MPa.

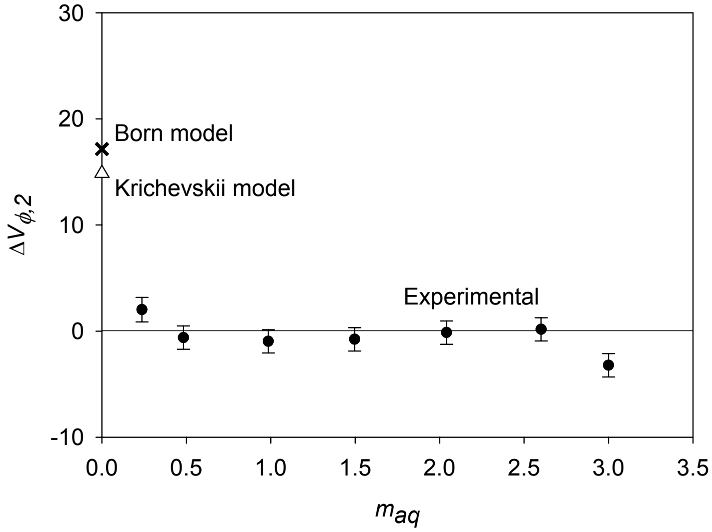

Figure 4 Comparison of experimental $\Delta V_{\phi,2}$ values with those ΔV_2^o values predicted by the Born model (**X**) and Krichevskii model (△)for LiCl at T = 325 °C and p = 14 MPa

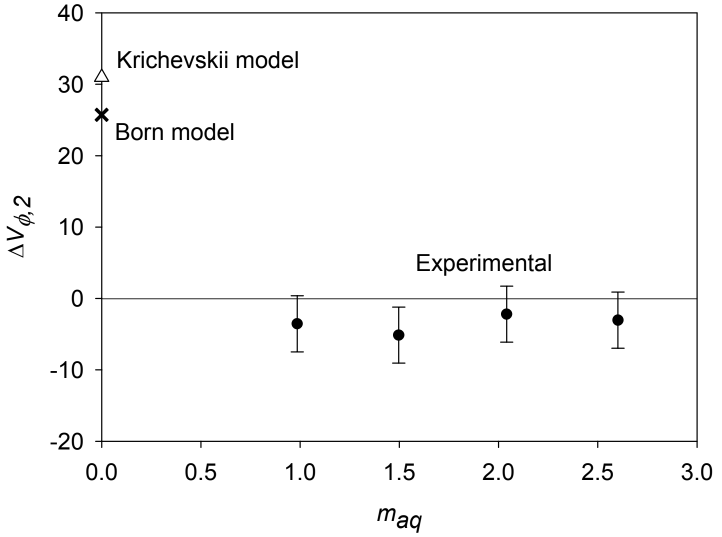

Figure 5 Comparison of experimental $\Delta V_{\phi,2}$ values with those ΔV_2^o values predicted by the Born model (✕) and Krichevskii model (△)for LiCl at T = 350 °C and p = 19 MPa

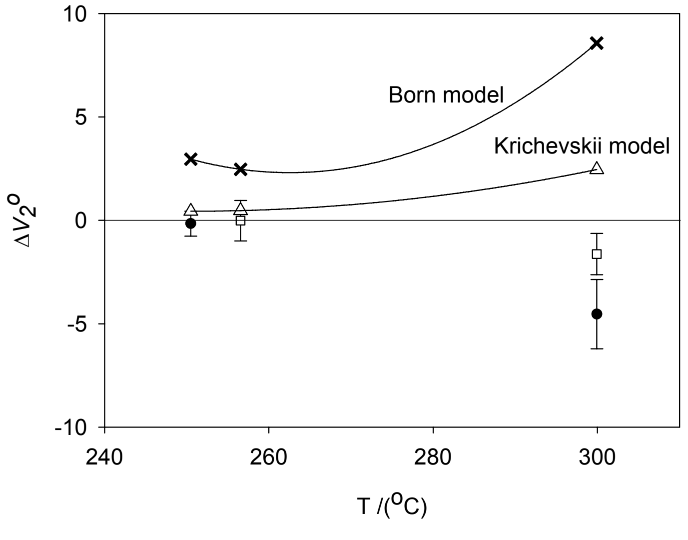

Figure 6 Comparison of experimental ΔV_2^o values (□) with those predicted by the Born model (✕) and Krichevskii model (△), as well as those experimental (●) ΔV_2^o values reported previously [3], for NaCl at T = 250 °C and p = 14 MPa, and T = 300 °C and p = 14 MPa.

Based on these preliminary results, it appears that, at T = 300 °C, the Krichevskii model allows us to predict the ΔV_2^o value for LiCl(aq) to within the experimental uncertainties, whereas the Born model is less accurate. However, at T = 325 °C and T = 350 °C, neither the Born model nor the Krichevskii model appears to yield accurate predictions of the deuterium isotope effect. The sign and magnitude of the deviation from the Krichevskii model is similar for both LiCl(aq) and NaCl(aq). Conductimetric studies [13-15] have shown that ion association occurs in aqueous solutions of HCl and LiCl above T = 300 °C, and that ion association occurs in solutions of NaCl above T = 330 °C. In this work, we have not yet considered the effect of ion association in any of these modeling techniques. Therefore, further investigation concerning the effects of ion association on ΔV_2^o values may result in more accurate SIE predictions. This is not a concern for application of these methods to CANDU-6 primary coolant chemistry, since the reactors operate at temperatures below 320 °C.

5. Conclusion

This study is a continuation of previous work done in our laboratory. Apparent molar volumes have been measured for NaCl, LiCl, and HCl (DCl) in H_2O and D_2O. These apparent molar volumes have been successfully modeled, as a function of molality, using an extended Debye-Hückel equation to obtain partial molar volume ΔV_2^o SIE values. In addition, we have confirmed our earlier finding that the Born and Krichevskii models can be used to predict ΔV_2^o values for simple salt systems at temperatures up to T = 300 °C, with the Krichevskii model yielding more accurate results.

Conductimetric studies have confirmed that these salt systems display ion association behavior at high temperatures. Further investigation is required in order to accurately model the effects of ion association of these aqueous species, and to extend the results to LiOH (LiOD) and other solutes. Future work will extend this study, to include 2+ metal cations, oxyanions, acids and their conjugate bases in order to develop predictive models for oxide solubility and chemistry control additives. These volumetric studies are interesting in their own right, and will provide complementary information to high-temperature, high-pressure conductance and Raman SIE measurements that are currently underway in our laboratory.

6. References

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