ISOTOPE EFFECTS ON STANDARD AND PARTIAL MOLAR VOLUMES OF NACL, HCL AND NAOH MEASURED IN LIGHT AND HEAVY WATER AT 250 °C AND 300 °C

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Apparent molar volumes $V_{\phi,2}$ were measured for aqueous solutions of NaCl, HCl (DCl), and NaOH (NaOD) in light and heavy water at 250 °C and 300 °C and $p = 14$ MPa using a vibrating platinum u-tube densitometer in the molality range from $0.25 < m < 2.5$ mol kg^{-1}. Standard partial molar volumes of NaCl, DCl and NaOD in heavy water were determined for the first time above 100 °C as part of an ongoing project in our lab to determine thermodynamic properties of electrolytes and non-electrolytes in heavy water under CANDU-PHW reactor primary coolant conditions.

1. Introduction

D_2O is used in CANDU Pressurized Heavy Water reactors, at temperatures between 250 °C to 320 °C, to transfer heat from the reactor core to the steam generator system through the primary coolant loop. Chemical equilibrium models of corrosion product transport and pH control require an understanding of the isotope effect on chemical equilibrium constants under operating conditions. Present practice relies on room-temperature data and semi-empirical correlations to estimate deuterium isotope effects.

In this project, apparent molar volumes $V_{\phi,2}$ were measured for aqueous solutions of NaCl, HCl (DCl), and NaOH (NaOD) in light and heavy water at 250 °C and 300 °C and p = 14 MPa using a vibrating platinum u-tube densitometer in the molality range from $0.25 < m < 2.5$ mol kg^{-1}. Standard partial molar volumes of NaCl, DCl and NaOD in heavy water were determined for the first time above 100°C as part of a new program in our lab to determine thermodynamic properties of electrolytes and non-electrolytes in heavy water.

2. Experimental

All solutions were prepared from nanopure water (resistivity > 18MΩ cm^{-1}) and deuterium oxide (99.8 %). The mole percentage of deuterium in the deuterium oxide was determined by standard addition of glacial acetic acid to deuterium oxide and subsequent measurement of the deuterium/hydrogen exchange by ^{1}H NMR. In order to minimize proton exchange due to moisture in the air, deuterium oxide solutions were prepared in a moisture-free argon environment and stored under positive argon pressure. Solutions of NaCl (Fisher, ACS reagent grade) were prepared by mass after drying the NaCl at 393 K for a minimum of 24 hours. HCl (Fisher, 35 wt% certified ACS) and DCl (Aldrich, 35 wt% in D_2O, 99 atom% D) solutions were prepared by mass, and concentrations determined titrimetrically against standardized NaOH. NaOH (Fisher, carbonate free 50 wt%, certified ACS) and NaOD (Aldrich, carbonate free 40 wt% in D_2O, 99 atom% D) were used to prepare solutions by mass which were then titrated against potassium hydrogen phthalate (Fisher, certified ACS).

Volumetric measurements were made in a platinum u-tube vibrating densimeter described elsewhere (Xiao *et al.*, 1997; Clarke and Tremaine, 1999). Calibration was performed daily with 1.0780 mol kg^{-1} NaCl solution prepared by mass and reference values for densities of aqueous NaCl solutions from Archer (1992).

3. Results

Densities measured in a vibrating-tube densimeter can be related to the vibrational period through the following expression:

$$\rho_S = \rho_1^* + K(\tau_S^2 - \tau_1^2) \qquad (1)$$

Here, ρ_s and ρ^*_1 represent the densities of the solution and the pure solvent respectively, τ_s and τ_1 represent the vibrational period of the solution and the pure solvent respectively, and K is an instrumental constant determined by calibration between a standard 1.0780 mol kg^{-1} NaCl solution and pure water. In order to minimize instrument instability between light and heavy water measurements, electrolytes in light and heavy water were measured sequentially.

Apparent molar volumes can be obtained from the general expression:

$$V_{\phi,2} = \frac{V_S - n_1 V_1^*}{n_2} \tag{2}$$

where V_S and V^*_1 are volumes of the solution and the pure solvent respectively, n_1 is the moles of solvent, and n_2 is the moles of solute. In order to relate the densities of the solutions to the apparent molar volumes, the following expression can be used:

$$V_{\phi,2} = \frac{55.509 \cdot M_1 \cdot (\rho_1^* - \rho_S)}{m_{aq} \rho_S \rho_1^*} + \frac{M_2}{\rho_S} \tag{3}$$

where M_1 and M_2 are the molar masses of the solvent and solute respectively, and m_{aq} refers to the aqua-molality of the species in light or heavy water. Densities of light water were derived from Archer and Wang (1990) while heavy water densities were obtained from Hill (1990).

Apparent molar volumes, $V_{\phi,2}$, are satisfactorily represented by the extended Debye-Hückel equation (Hovey and Tremaine, 1986).

$$V_{\phi,2} = V_2^0 + A_V m_{aq}^{1/2} + B_V m_{aq} + C_V m_{aq}^2 \tag{4}$$

where V°_2 is the standard partial molar volume at infinite dilution, A_V is the Debye-Hückel limiting slope for volume, and B_V and C_V are adjustable parameters in the fitting equation. Values of A_V for light water were obtained from Archer and Wang (1990), while values for heavy water were calculated from the following equation:

$$A_V = \frac{2}{3} RT \left(\frac{2\pi N_A \rho^*}{1111.74} \right)^{1/2} \left(\frac{e^2}{4\pi \varepsilon_0 \varepsilon k T} \right)^{3/2} \left[3\left(\frac{\partial \ln \varepsilon}{\partial P} \right)_T + \left(\frac{\partial \ln V^*}{\partial P} \right)_T \right] \tag{5}$$

Here, N_A is Avogadro's number, ρ^* is the density of pure D_2O obtained from Hill's equation of state for heavy water (Hill, 1990), e is the charge on an electron, ε_0 is the permittivity of free space, ε is the dielectric constant of heavy water, R is the gas constant and k is the Boltzmann constant. The dielectric constant of heavy water, ε, was calculated from the Uematsu-Frank equation for the dielectric constant of light water (Uematsu and Franck, 1980) by following the suggestion of Okada *et al.* (1999) and using the numerical density as opposed to the mass density.

While it is well known that ionic species undergo association at high temperatures (>250 °C) (Simonson *et al.*, 1994), this simpler model was selected due to scope of the experiments, and the lack of experimental data on ionic association in heavy water.

Equation (4) was fitted to apparent molar volume values calculated from equation (3) using the least squares method. Plots of $V_{\phi,2}$ against aquamolality have been shown in Figure 1, Figure 2 and Figure 3 for both 250 °C and 300 °C. The apparent molar volumes decreased with temperature as the critical temperature of the solvent was approached, and increased at higher concentrations. The solvent isotope effect for a given electrolyte can be represented by $V_{\phi,2}$ (H_2O) – $V_{\phi,2}$ (D_2O), and increases with temperature. For NaCl and NaOD, the solvent isotope effect is very small at 250 °C, and increases to ~4-5 cm^3/mol at 300 °C.

4. Discussion

4.1 Partial Molar Volumes at Infinite Dilution

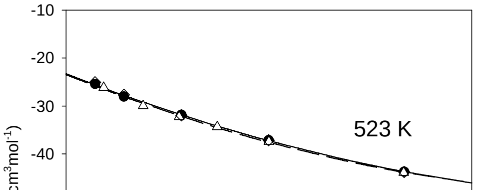
Standard partial molar volumes, $V°_2$, agree well with literature values to within ±2.5 cm^3/mol (Archer, 1992; Sharygin and Wood, 1997; Corti and Simonson, unpublished). Due to the increase in compressibility of the solvents as the critical temperature is approached, values of $V°_2$ decrease with increasing temperature as expected. The critical temperatures of H_2O and D_2O are T_c = 374.0 °C and T_c = 370.7 °C respectively. Hence as the temperature increases, the difference in compressibility becomes more significant which results in an increase in the solvent isotope effect. Wood *et al.* (1983) have suggested that the standard partial molar volume can be estimated from the Born equation, assuming the electrostatic contribution to the volume, V_ϕ^{el}, to be the dominant contribution.

$$V_2^0 \approx V_\phi^{el} = \frac{-K}{R^*}\left(\frac{\partial \varepsilon}{\partial P}\right)_T \varepsilon^{-2} \tag{6}$$

where

$$K = \frac{N_A e^2}{4\pi\varepsilon_0} \text{ and } \frac{1}{R^*} = \frac{(R_+^{-1} + R_-^{-1})}{2}$$

Here, R_+ and R_- represent the radii of the cation and anion respectively. Using equation (6), an expression predicting the solvent isotope effect can be deduced which is a function of the dielectric constants and their derivatives with pressure alone, by assuming the radii of the ions are equal in both solvents. The result is listed below as equation (7):



250 °C

300 °C

Figure 1: Experimental apparent molar volumes plotted against aquamolality for NaCl at 250 °C and 300 °C. (●) H_2O, (△) D_2O, (◇) NaCl taken from Archer (1992). Lines are calculated values from equation (4).

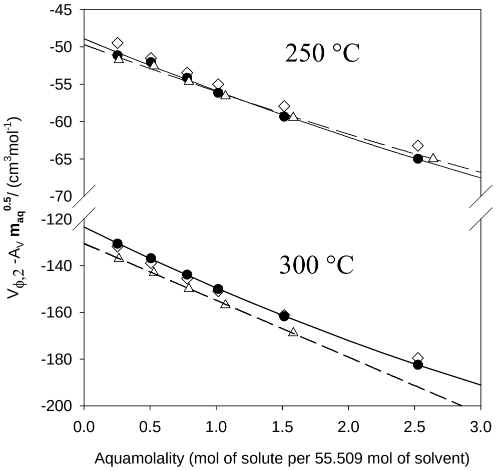


Figure 2: Experimental apparent molar volumes plotted against aquamolality for NaOH at 250 °C and 300 °C. (●) H_2O, (△) D_2O, (◇) NaOH taken from Corti and Simonson (Unpublished). Lines are calculated values from equation (4).

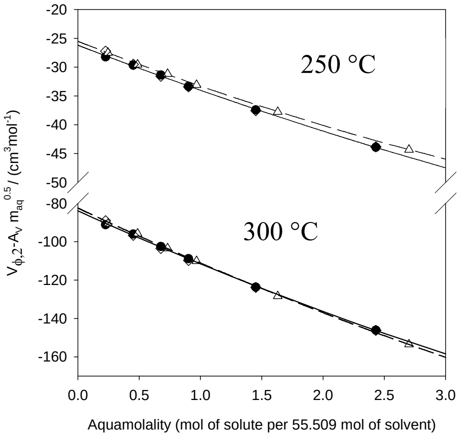


Figure 3: Experimental apparent molar volumes plotted against aquamolality for HCl at 250 °C and 300 °C. (●) H_2O, (△) D_2O, (◇) HCl taken from Sharygin and Wood (1997). Lines are calculated values from equation (4).

$$\Delta V_2^0 = V_2^0(H_2O) - V_2^0(D_2O) = V_2^0(H_2O)\left[1 - \frac{(\partial\varepsilon/\partial P)_{T,D_2O}}{(\partial\varepsilon/\partial P)_{T,H_2O}} \cdot \frac{{\varepsilon_{H_2O}}^2}{{\varepsilon_{D_2O}}^2}\right]$$

(7)

Using the Uematsu-Frank equation to calculate the dielectric constant of both solvents, the following results were obtained: Predicted values of $V°_2$ for NaCl are 0.8 cm^3/mol and 6.6 cm^3/mol at 250 and 300 °C respectively, which are in good agreement with the experimental results of 0.2 cm^3/mol and 4.5 cm^3/mol. Results for NaOH are also in good agreement, with predicted values of 1.7 cm^3/mol and 8.4 cm^3/mol at 250 °C and 300 °C respectively, and experimental values of 0.8 cm^3/mol and 7.1 cm^3/mol**.** The predicted values of HCl however, was 5.7 cm^3/mol at 300 °C while the experimental value obtained was -1.4 cm^3/mol. With the exception of HCl at 300 °C, this model predicts solvent isotope effects which are in good agreement with the experimentally obtained data.

This model works well at high temperatures where the electrostatic contributions, V_ϕ^{el}, dominate the volumes of ions in solution. At lower temperatures, this approximation is no longer valid as the solvent becomes more structured and chemical effects contribute significantly to the volume of ions in solution.

4.2 $\Delta V°$ for the Ionization of H_2O/D_2O

To calculate $\Delta V°$ for the ionization of water and heavy water, the standard partial molar volumes calculated from equation (4), $V°_2$, along with the molar volumes of the pure solvents, V^*_{H2O} and V^*_{D2O} must be combined. From the following reaction,

$$\mathrm{NaCl(aq.)} + \mathrm{H_2O(aq.)} \equiv \mathrm{NaOH\ (aq.)} + \mathrm{HCl\ (aq.)} \qquad (8)$$

the partial molar volume change for the ionization of water and heavy water, $\Delta V°_{ion}$, can be calculated from

$$\Delta V^0_{ion} = V^0_2(HCl/DCl) + V^0_2(NaOH/NaOD) - V^0_2(NaCl) - V^*_{H_2O/D_2O} \qquad (9)$$

From equation (9), the partial molar volume change for the ionization of water, $\Delta V°_{ion}$, was calculated to be -74.0 (±1.1) cm^3/mol and -137.8 (±2.5) cm^3/mol at 250 °C and 300 °C respectively. This data is in excellent agreement with values calculated from literature data on $V°_2$ for NaCl, NaOH and HCl in light water (Archer, 1992; Sharygin and Wood, 1997; Corti and Simonson; unpublished) which yield values of -74.7 (±1.5) cm^3/mol and -134.8 (±2.5) cm^3/mol at 250 °C and 300 °C respectively.

5. Conclusions

This work provides the first apparent and partial molar volumes for NaCl, NaOD and DCl in heavy water above 77 °C. $\Delta V°$ of ionization for water and heavy water have been calculated based on partial molar volumes of the studied electrolytes in water and heavy water, and the semi-empirical Born model has been used to describe the isotope effects on the partial molar volumes in heavy water based on data in light water. This study shows a tendency to more negative values for ΔV° of ionization as temperatures approach the critical point. Further experiments at high temperature may confirm these results.

At higher temperatures, ion-association can play a role in the volumetric measurements, and a part of this research program will be to determine the extent of ionic association using conductimetric measurements at high temperatures.

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