THE ELEVATION OF BOILING POINTS IN H$_2$O AND D$_2$O ELECTROLYTES

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ABSTRACT

The excess enthalpy effect in cold fusion experiments for Pd/D$_2$O + LiOD systems is subject to positive feedback, i.e., increasing the cell temperature increases the excess enthalpy. Therefore, the largest excess enthalpy effects are often observed near or at the boiling point corresponding to that of the electrolyte solution in the cell. The exact boiling temperatures at different electrolyte concentrations are needed for cold fusion experiments. These studies of LiOH in H$_2$O and LiOD in D$_2$O both show boiling point elevations at higher concentrations that are significantly lower than theoretical calculations based on ideal solutions. Activity coefficients of LiOD in D$_2$O at the boiling point of D$_2$O (101.42°C) are also reported. These boiling point measurements suggest a purity problem with heavy water samples that may contribute to the reproducibility problem for excess enthalpy.

INTRODUCTION

In cold fusion experiments involving D$_2$O + LiOD, the actual boiling temperature increases as the D$_2$O evaporates and the LiOD concentration increases toward saturation. As an approximation, it may be assumed for dilute solutions that this temperature correction is given by the equation for an ideal solutions, $\Delta T = -(R/L)(T \cdot T^*) \ln X_1$, where X_1 is the mole fraction of the solvent (D$_2$O) in the electrolyte, L is the heat of vaporization (41.673 kJ/mol) of D$_2$O, T^* is the boiling point of D$_2$O (374.57 K), and T is the boiling point of the LiOD electrolyte solution. The purpose of this project will be to compare experimental values of ΔT obtained using electrolyte solutions of H$_2$O+LiOH and D$_2$O+LiOD with theoretical values of ΔT calculated by assuming ideal solutions. It is expected that the behavior in D$_2$O electrolytes will be similar to the effects measured in H$_2$O electrolytes. There are no known literature values for the boiling point elevation of either LiOH in H$_2$O or LiOD in D$_2$O.[1]

EXPERIMENTAL

Solutions were prepared using LiOH•H$_2$O (Aldrich, Reagent) and distilled water or anhydrous LiOH (Fisher, Laboratory grade) and D$_2$O (Cambridge Isotope Laboratories, 99.9% D, 100 g bottles). At the highest concentration (7 m, saturated), the D$_2$O solution, therefore, will contain about 7 mol% H. Assuming linear behavior, this would lower the measured temperature by only 0.10°C. Boiling point measurements were made both by using glass thermometers and a thermistor unit (Cole-Palmer Mod. 8502-16). The glass thermometers and thermistors were calibrated by measurements on distilled H$_2$O and on a saturated NaCl solution (bp = 108.66°C at 760 Torr). [1]

Measurements were carried out by adding the solution to a test tube that was placed in a hot saturated NaCl bath solution for even heating. Boiling chips were always used to minimize superheating in the solution.[2] The atmospheric pressure was monitored in the laboratory during these experiments to within ±0.1 Torr and was always in the range of 743 to 757 Torr. The theoretical pressure correction for the boiling point (dT/dP) is 0.03743 K/Torr for H$_2$O and 0.03680 K/Torr for D$_2$O.[2]

RESULTS

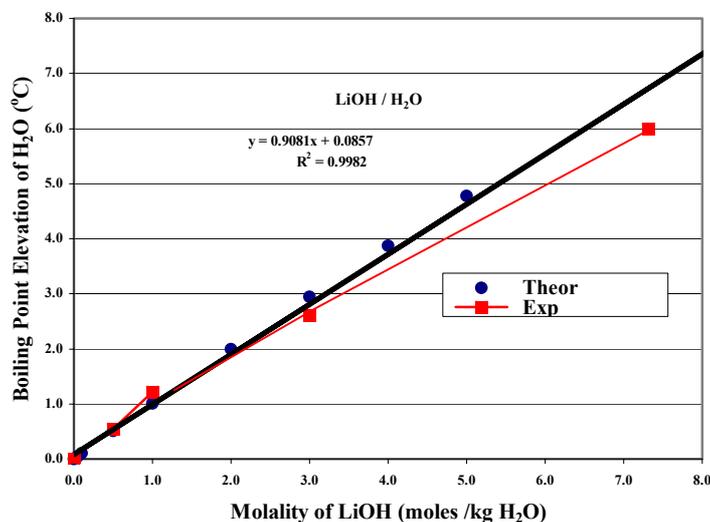The experimental and theoretical boiling point elevations for LiOH solutions in H_2O are given in Fig. 1.

Fig. 1. Theoretical and experimental boiling point elevations for LiOH solutions in H_2O.

The measured boiling point elevations (ΔT_b) are within experimental error of the theoretical values for concentrations up to about 1.0 m LiOH. At higher concentrations the experimental ΔT_b values become significantly less than the theoretical value. The reported solubility of LiOH in H_2O at 100°C is 17.5 g per 100 cm^3 H_2O or 7.31 m.

Figure 2 presents the experimental and theoretical boiling point elevations for LiOD solutions in D_2O.
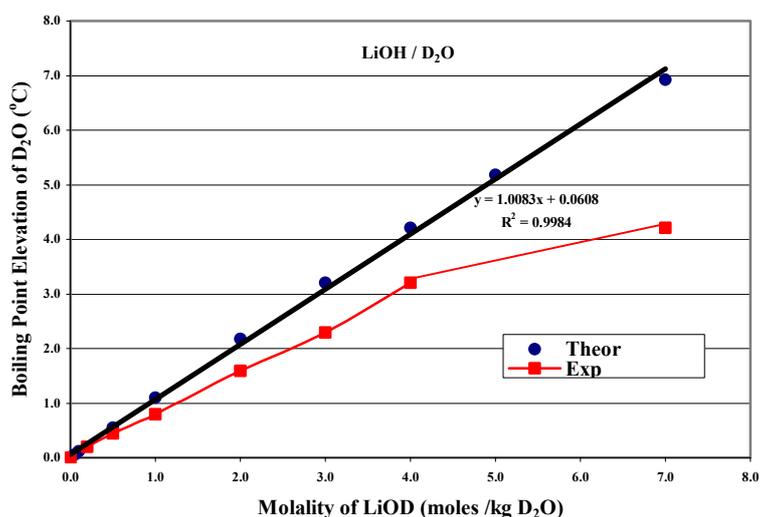

Fig. 2 Theoretical and experimental boiling point elevations for LiOD solutions in D_2O.

The experimental ΔT_b values are significantly less than the theoretical values at LiOD concentrations of 0.5 m and higher. The departure from the theoretical values are obviously much larger for LiOD in

D_2O than for LiOH in H_2O. It was assumed that the solubility limit of LiOD in D_2O was 7.0 m. A smoother curve would be obtained for Fig. 2 if the actual solubility limit is closer to 6.0 m. Theoretically, the boiling point elevations for any solute in D_2O is larger than for that same concentration in H_2O as shown in Table 1.

Table 1.   Theoretical boiling point elevations in H_2O and D_2O

Molality (m)	ΔT_b (H_2O) (°C)	ΔT_b (D_2O) (°C)
0.010	0.0103	0.0112
0.050	0.0513	0.0560
0.100	0.102	0.112
0.500	0.509	0.556
1.000	1.011	1.103
2.000	1.992	2.170
3.000	2.946	3.204
4.000	3.873	4.206
5.000	4.78	5.18
10.0	8.97	9.67

The mean activity coefficient of electrolytes can be determined from boiling point elevation measurements.[3,4]   These calculations were made for LiOD in D_2O using experimental ΔT_b values along with estimated values at lower concentrations. The mean activity coefficients of LiOD in D_2O at 101.42°C are shown in Fig. 3.
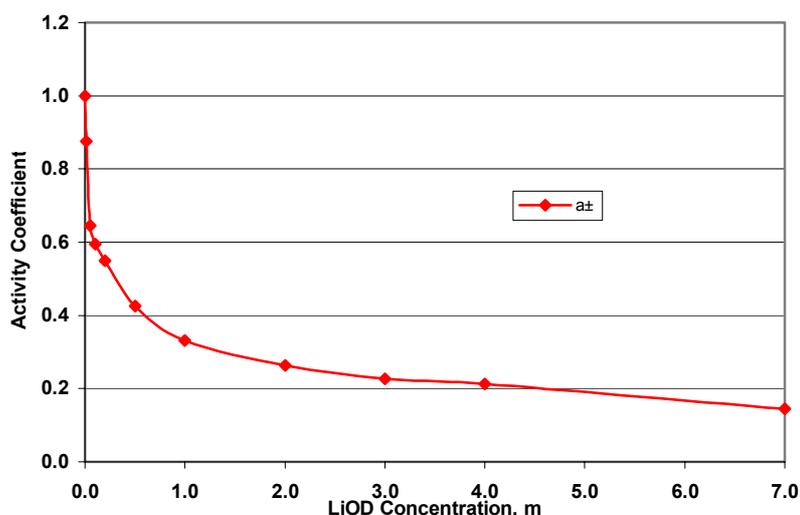

Fig. 3 Mean activity coefficients of LiOD in D_2O at 101.42°C.

These activity coefficients show a reasonably smooth curve that continues to decrease with increasing LiOD concentration up to saturation.

DISCUSSION

The major experimental problem for measurements in heavy water was the variation in the boiling point of D_2O from one sample bottle to another. Typically, the measured boiling point of the D_2O used was 0.2 to 0.3°C higher than the expected value of 101.42°C at 760 Torr. This suggests a significant impurity concentration that increases the boiling point. Previous cold fusion studies have shown that some bottles of D_2O create serious foaming problems during electrolysis.[5] Inorganic and

organic contamination as well as bacteria contamination have been reported in ordinary heavy water. [6] These contamination problems are a likely contributor to reproducibility problems in cold fusion experiments.

Boiling point elevations and freezing point depressions in water solutions of electrolytes show an upward curvature (larger than theoretical) for salts such as LiCl, NaBr, and KI.[7] These apparent large deviations from ideal behavior are eliminated by taking account of the number of H_2O molecules binding sufficiently strongly as to be removed from the "bulk" solvent.[7] In contrast, electrolytes containing polyatomic anions such as OH^-, NO_3^-, $CO_3^=$, $SO_4^=$ and $PO_4^{\equiv}$ often show downward curvature of boiling point elevations and freezing point depressions.[7] This downward curvature was found in the present studies for LiOH in H_2O (Fig. 1) and LiOD in D_2O (Fig. 2). However, NaOH in H_2O and KOH in H_2O both show ΔT_b values larger than theoretical.[1] It is difficult to find a simple explanation for all the observed boiling point elevations of various electrolytes. Recent work suggests that quantum electrodynamics (QED) is needed for the modeling of electrolyte solutions.[8]

The largest excess enthalpy effects in cold fusion experiments are often observed near or at the boiling point corresponding to the electrolyte solution in the cell.[9-11] Therefore, electrolytes yielding higher boiling points than D_2O + LiOD solutions should be investigated. Suggested possibilities are D_2O + LiCl, D_2O + NaOD, and D_2O + KOD. These salts exhibit exceptionally high solubilities in H_2O, and the reported ΔT_b values are 66°C for 35 m LiCl + H_2O, 176°C for 500 m NaOH + H_2O and 236°C for 110 m KOH + H_2O. Even higher temperatures are possible using molten salts such as LiOH-NaOH (25-75 mol%) that melts at 210°C.

ACKNOWLEDGEMENTS

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