Table VI. High-Pressure Critical Line Data for the System DME/H_2O

temp, °C	press., MPa	DME mole fraction	temp, °C	press., MPa	DME mole fraction
100.11	50.8	0.35	180.15	21.4	0.28
121.06	45.1	0.34	200.45	17.6	0.27
140.86	35.3	0.31	220.01	15.5	0.26
154.25	28.7	0.30	(374.13)[a]	22.09	0.00
160.05	26.3	0.29			

[a] Pure-water critical point. Value obtained from the literature (*8*).

6c. The negative slope in the isotherm, just above the maximum in composition, indicates a rapid increase in the solubility of liquid water in supercritical DME with increasing pressure. This nose remains pronounced at temperatures as high as 60 °C above the upper critical end point, indicating enhanced solubility of the condensed phase (H_2O) in the supercritical solvent (DME) over an extended temperature range. This enhanced solubility, associated with the presence of an upper critical end point near the solvent critical point, is important in supercritical extraction; the effect is exaggerated here, because the condensed phase (H_2O) is itself volatile, but it illustrates the phenomenological relationship between critical end points and enhanced solubility in a supercritical fluid.

Registry No. $(CH_3)_2O$, 115-10-6.

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Osmotic Coefficients of Water for Thorium Nitrate Solutions at 25, 37, and 50 °C[†]

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Vapor pressure osmometry was used to measure osmotic coefficients of water for thorium nitrate solutions at 25, 37, and 50 °C and at molalities up to 0.2 mol·kg^{-1}. The data were fitted to three- and four-parameter equations containing limiting-law terms for a 4:1 electrolyte. The variation of the osmotic coefficients as a function of temperature was found to be small. The results are compared to published values for the osmotic coefficients.

Introduction

To analyze the data from experiments determining activities in the $Th(NO_3)_4$–HNO_3–H_2O system at 25 and 50 °C (*1*, *2*), osmotic coefficients were required for the $Th(NO_3)_4$–H_2O system. For 25 °C and low concentrations of thorium nitrate, osmotic coefficients have been reported by Apelblat et al. (*3*) from vapor pressure osmometry and by Robinson and Levien (*4*) from isopiestic measurements. Apelblat et al. (*3*) reported limited sets of osmotic coefficients at 37 and 50 °C, and these values are essentially identical for the two temperatures. Osmotic coefficients can also be calculated for ~0 °C from the freezing point experiments of this same group (*5*). The results of all these experiments (see Figure 1) show no clear pattern in the variation of the osmotic coefficient with temperature. Also, as noted by Apelblat (*3*), the two sets of 25 °C results do not agree well, thus complicating the calculation of thermodynamic properties for Th^{4+}(aq) (*6*, *7*). Therefore, we have reexamined the osmotic coefficients of water for $Th(NO_3)_4$ solutions at 25, 37, and 50 °C by using our modern vapor pressure osmometer.

Experimental Section

Thorium nitrate hydrate was recrystallized from concentrated aqueous solution by the addition of freshly prepared, anhydrous nitric acid. The precipitate was collected, washed with dilute nitric acid, and dried for several weeks under vacuum over anhydrous sodium carbonate. Stock solutions were prepared from this material and from the original, reagent-grade thorium nitrate hydrate. The two solutions were analyzed by titration with standard EDTA solution, and the concentrations were found to be 1.77 ± 0.01 and 2.11 ± 0.01 mol·dm^{-3}, respectively. Aliquots of both stock solutions were diluted to prepare the solutions for the osmotic coefficient measurements. The results obtained by using the reagent-grade thorium nitrate and the recrystallized salt were consistent within the error limits of the osmometric measurements.

Osmotic coefficients were measured at 25, 37, and 50 °C by using a Corona/Wescan Model 232A vapor pressure osmometer. In this instrument, the steady-state temperature difference is measured between a drop of pure water and a drop of solution, both being maintained in a chamber saturated with water vapor. Thermistors are used as temperature sensors, and the difference in the voltage developed across each of the two thermistors, ΔV, is measured at a constant bridge current. The operation of this instrument has been described by Burge (*8*).

At each temperature, the instrument was calibrated by using solutions of mannitol (ACS reagent grade) in water as standards. The voltage difference, ΔV, was divided by the mannitol

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[†] Issued as AECL-8089.

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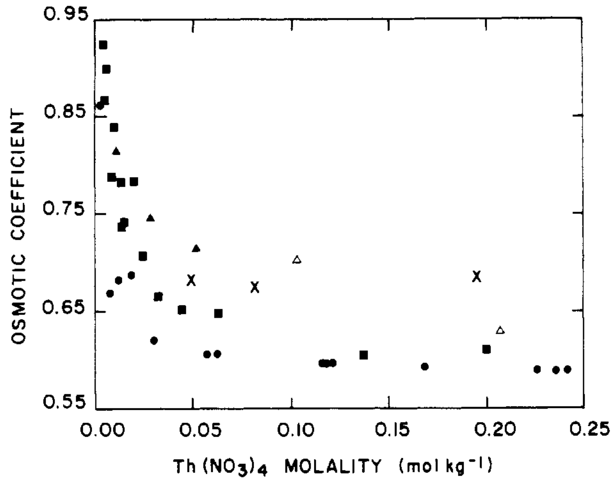

Figure 1. Experimental values from the literature for osmotic coefficients (ϕ) as a function of $Th(NO_3)_4$ molality (m): (●) 25 °C, ref *3*; (X) 25 °C, ref *4*; (■) ~0 °C, ref *5*; (△) 37 °C, ref *3*; (▲) 37 and 50 °C, ref *3*.

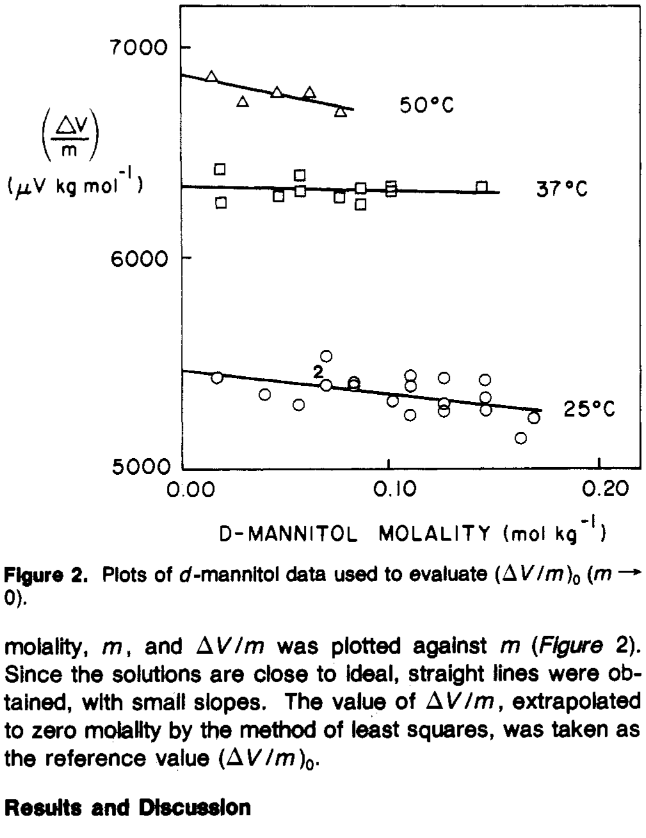

Figure 2. Plots of *d*-mannitol data used to evaluate $(\Delta V/m)_0$ ($m \to 0$).

molality, m, and $\Delta V/m$ was plotted against m (*Figure* 2). Since the solutions are close to ideal, straight lines were obtained, with small slopes. The value of $\Delta V/m$, extrapolated to zero molality by the method of least squares, was taken as the reference value $(\Delta V/m)_0$.

Results and Discussion

The voltage differences (ΔV) and the calculated values of the osmotic coefficients (ϕ), based on thorium nitrate behaving as a 4:1 electrolyte, are given in the supplementary material (see paragraph at end of text regarding supplementary material). The data were fitted by the method of least squares to the expression (*9*)

$$\Delta V = 5\left(\frac{\Delta V}{m}\right)_0 m \left\{1 + \frac{4}{3}SI^{1/2} - \sigma(P_1 I^{1/2}) + \frac{4}{5}Bm + \frac{16}{15}Cm^2 - \frac{1000}{5mM_1R}\left[\frac{T_R - T}{TT_R}\bar{L}_1 - \left\{\frac{T_R - T}{T} - \ln\left(\frac{T_R}{T}\right)\right\}\bar{J}_1\right]\right\} \quad (1)$$

$$\phi = \Delta V(5m(\Delta V/m)_0) \quad (2)$$

The reference temperature (T_R) was chosen to be 298.15 K.

Table I. Parameters for Eq 1 Derived from Experimental Osmotic Coefficient Data

no. of parameters	P_1	B	C	$\partial B/\partial T$	SD
3	2.35	−1.87	5.32		0.028_5
4	2.36	−1.87	5.35	−0.000 11	0.028_6

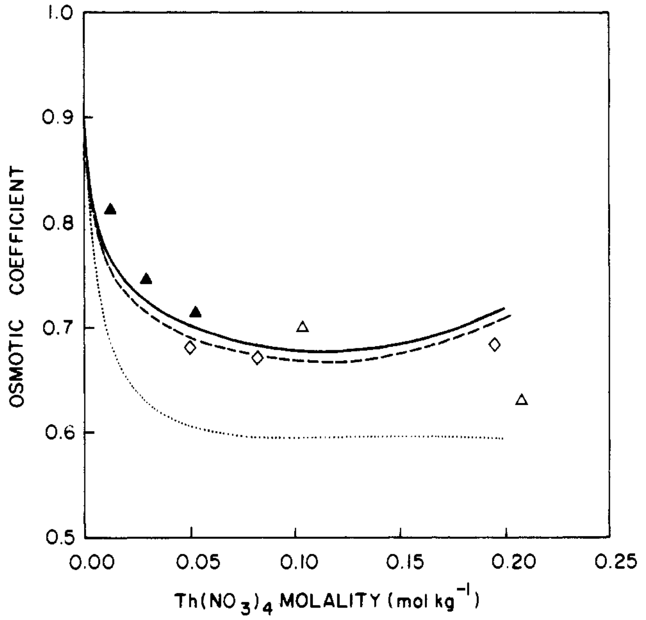

Figure 3. Comparison of osmotic coefficients with literature values. Lines from fitting data to eq 2: (---) this work, 25 °C; (—) this work, 50 °C; (···) ref *3*, 25 °C (fit to 25 °C data only). Experimental data: (△) ref *3*, 37 °C; (▲) ref *3*, 37 and 50 °C; (◇) ref *4*, 25 °C.

In eq 1 T is the temperature at which ϕ was measured, m is the molal concentration of the thorium nitrate solution (nominal ionic strength $I = 10\ m$), R is the gas constant, $S = -1.1762$ is the Debye–Hückel parameter for 298.15 K, $1000/M_1$ is the number of moles of water per kilogram of water. $\bar{L}_1$ and $\bar{J}_1$ are the values for the reference temperture, T_R, and are defined by the expressions given in Appendix 4 of Lewis and Randall (*9*), but using $\sigma(P_1 I^{1/2})$ rather than $\sigma(I^{1/2})$ and taking $\partial B/\partial T$ to be temperature independent. The four fitting parameters considered were, therefore, P_1, B, C, and $\partial B/\partial T$. Our parameters B, C, and $\partial B/\partial T$ differ from those in ref 9 by a factor of ln 10.

The ΔVs were weighted by assuming errors of 2% of the measured voltage difference. The values of the fitting parameters are given in Table I. As shown, the fit to the experimental data was essentially unchanged if $\partial B/\partial T$ was set to zero. Application of the F_x test (*10*) indicated a less than 50% probability that the four-parameter fit should be chosen. It appears, however, that the value of $\partial B/\partial T$ is small.

The standard deviations in the fitted values of ϕ (~±0.03) are greater than the 2% expected from the estimated errors in ΔV. The difference may, in part, result from hydrolysis of thorium nitrate, which, therefore, does not behave strictly as a 4:1 electrolyte. It should be emphasized that the equation used does not allow for hydrolysis effects at low salt concentrations (*11*) and is, hence, merely a fitting equation. Other experimental errors besides those estimated for ΔV may also be important.

As can be seen from Figure 3, our values for ϕ vary little over the temperature range 25–50 °C. Within the experimental errors, these values agree with those of Robinson and Levien (*4*) at 25 °C and those of Apelblat et al. (*3*) at 37 and 50 °C. For thorium nitrate concentrations less than 0.05 m, osmotic coefficients from freezing point data (*5*) are also consistent with values calculated by using eq 1 and 2 and the parameters from

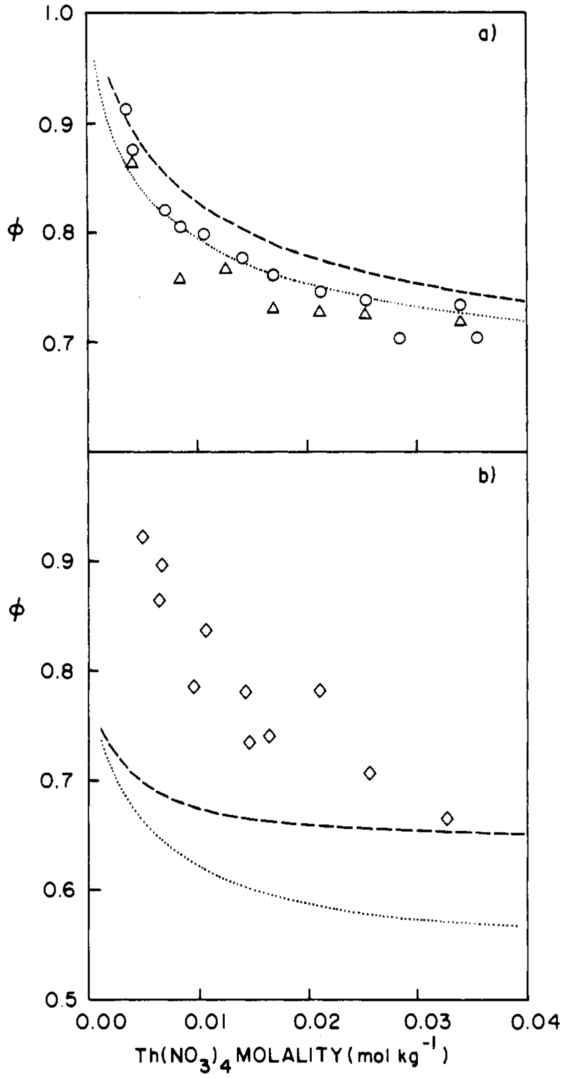

Figure 4. Calculations using $\bar{L}_1$ and $\bar{J}_1$ from ref *12*. (a) Values of the osmotic coefficient ϕ at 37 and 50 °C from the 25 °C data in this paper: (···) 37 °C, calculated; (---) 50 °C, calculated; (△) 37 °C, experimental; (○) 50 °C, experimental. (b) Values of ϕ at 0 °C: (---) from the 25 °C data in this paper; (···) from the 25 °C data in ref *3*; (◇) from experimental freezing point data, ref *5*.

Table I. However, at higher concentrations, the osmotic coefficients from the freezing point measurements are considerably lower than the calculated values.

Apelblat and Sahar (*12*) have measured heats of dilution ($m < 0.04$ mol·kg^{-1}) and apparent molal heat capacities for thorium nitrate solutions. Combining their values for $\bar{J}_1$ and $\bar{L}_1$ (using Table I of ref *12*, i.e., values for solutions not containing added HNO_3) with our 25 °C osmotic coefficient measurements generates values of ϕ for 37 and 50 °C that are in fair agreement with our experimental values at these low concentrations (see Figure 4a). However, neither our 25 °C osmotic coefficients nor those of Apelblat et al. (*3*) can be combined with $\bar{L}_1$ and $\bar{J}_1$ from ref *12* to give osmotic coefficients at 0 °C that agree with those from the freezing point data (*5*) (see Figure 4b).

In view of their lack of agreement with our experiments, Robinson's data, and the freezing point data, we conclude that the 25 °C osmotic coefficient values for $Th(NO_3)_4$ given by Apelblat et al. (*3*) are too low. This is somewhat surprising in light of the agreement of Apelblat's 25 °C osmometry and vapor pressure measurements for $Th(NO_3)_4$ concentrations between 0.20 and 0.25 mol·dm^{-3} and suggests that the source of the difference may be the thorium nitrate solutions themselves, not the osmometry measurements. Furthermore, it would appear that the freezing point data of Apelblat et al. (*5*), or their relative partial molal enthalpy values (*12*), are incorrect. The alternative is that even our values for ϕ at 25 °C are too low. As is the case for the enthalpies of dilution (*12*, *13*), values of the osmotic coefficients may be affected by acidic or basic impurities through hydrolysis. The scatter in our data is too great to make good estimates of $\bar{L}_l$ and $\bar{J}_l$, but rough calculations indicate that, near 0.03 m, the absolute values for $\bar{L}_l$ are smaller than indicated by Apelblat and Sahar's data, and $\bar{L}_1$ is negative, not positive.

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Supplementary Material Available: All the original voltage differences and osmotic coefficients at 25, 37, and 50 °C are listed (5 pages). Ordering information is given on any current masthead page.