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Modeling Actinide Solution Densities with the Pitzer Method

C. F. Weber and C. M. Hopper

Oak Ridge National Laboratory,*
P.O. Box 2008,
Oak Ridge, TN 37831-6370, USA

webercf@ornl.gov   hoppercm@ornl.gov
(865) 576-4475   (865) 576-8617

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INTRODUCTION

In assessing the criticality of actinide solutions, highly accurate calculation of the solution density is essential. This is fairly simple for binary solutions where ample data are available, however it becomes much more difficult if solutions contain many components and are at temperatures other than 25°C. Empirical models usually include nonlinear terms in concentration and temperature, and may be quite effective within the range of the data used in fitting the empirical parameters. They become increasingly complicated if used for more than 1 or 2 components in solution, and cannot be reliably extended to include additional components. Recently, Charrin and coworkers have implemented the method of simple solutions to calculate densities in multi-component solutions.[1] This method can be extended to any number of solution components, and requires density data only from binary solutions of the individual salts. However, it also requires the water activities of solutions, and so has been applied only at 25°C. It is not generally applicable to solutions where complexation, ion association, or hydrolysis occur strongly, although it has been applied to solutions of Pu(IV) in HNO_3, where such behavior is likely to occur. A third approach is the method of Pitzer, which has been applied at 25°C to solutions of uranyl nitrate in nitric acid. [2]

THE PITZER METHOD

Pitzer and his co-workers developed the ion-interaction approach to modeling electrolyte solution thermodynamics [3], which has enjoyed remarkable success. It is especially popular with geochemists, waste chemists, and engineers for prediction of mineral solubilities and phase equilibria. The method extends the Debye-Huckel theory with a virial (i.e., polynomial) expansion of the Gibbs energy in the concentrations of each solution component. The second virial coefficients are shown to depend on the ionic strength of the solution through theoretical development (i.e., statistical mechanics). However, this dependence is then approximated using a special functional form involving two parameters: $\beta^{(0)}$ and $\beta^{(1)}$; hence, the method is often termed semi-empirical. Together with a third virial coefficient C (constant with respect to all concentrations), most binary systems (i.e., a single salt in water) can be modeled to quite high concentrations. For systems involving other ions, two additional mixing terms θ and ψ describe, respectively, interactions of like charged ions (cation-cation or anion-anion) and 3-body interactions where not all ions have the same charge (cation-cation-anion or cation-anion-anion). The method has shown remarkable ability to accurately model solutions containing many ions (literally dozens) using only these ion-interaction parameters.

In the Pitzer approach, the apparent molar volume is determined in a straightforward manner, and this quantity is then used to calculate solution density. The apparent molar volume is obtained by differentiating the excess Gibbs energy with respect to pressure. Hence, the parameters of interest are actually the pressure derivatives of those mentioned in the previous paragraph, and are denoted with a subscript "v": $\beta_v^{(0)} = \partial\beta^{(0)}/\partial P$, similarly for $\beta_v^{(1)}$, C_v, θ_v, and ψ_v. In practice, these quantities are obtained directly from regression of density data. In addition, they are given temperature dependence by fitting the following equation to each parameter:

$$f(T) = A + B(T - T_0) + C(1/T_0 - 1/T),$$
$$T_0 = 298.15 \text{ K}. \qquad (1)$$

APPLICATION TO ACTINIDE SOLUTIONS

The Pitzer method has been used to build a model for calculating solution densities involving nitric acid and the nitrate salts of UO_2^{2+}, Th^{4+}, and Pu^{4+}. Model parameters are given in Table 1, and were regressed using data in the temperature and concentration ranges shown in the table. Calculations of the model for

the system UO_2-H-NO_3-H_2O agree well with data, as shown in Fig. 1. In general, agreement is below 1% relative error. This pattern is also true of most binary systems. The maximum relative error for other ternary systems may be 2-3%, although error for most points is below 1%. Often this error is due to data scatter or systematic error, especially when more than one source of data is involved.
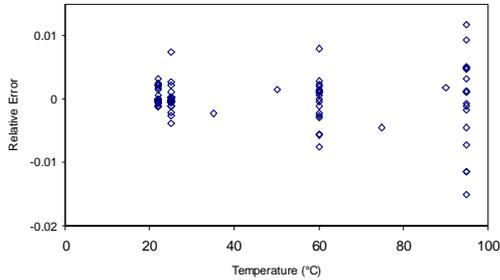

Fig. 1. Error in calculation of density for HNO_3-$UO_2(NO_3)_2$ solutions.

The present model is applicable to any solution involving U(VI), Th(IV), or Pu(IV) in nitric acid. All three actinides could be present. While the model is not proven beyond the ranges of concentration and temperature given in Table 1, some extrapolation in temperature (15-20% of the listed range) may be acceptable. It is anticipated that future development will extend these ranges, as new data become available. In addition, the model will include additional actinides and actinide salts involving other anions (e.g., fluoride, sulfate) and additional Pu oxidation states. The ultimate goal is a comprehensive model involving many actinide cations, all relevant anions, and a wide range for temperature.

REFERENCES

1. N. CHARRIN et al., "Contribution of the concept of simple solutions to calculation of the density of ternary and quaternary solutions of thorium(IV) or plutonium(IV) nitrate," *Radiochim. Acta* **88**, 445 (2000).
2. Y.-X. YU et al., "Densities and apparent molar volumes for aqueous solutions of HNO_3-$UO_2(NO_3)_2$ at 298.15 K," *J. Radioanal. Nucl. Chem.* **241**(2), 373 (1999).
3. K. S. PITZER, "Ion Interaction Approach: Theory and Data Correlation," in K.S. Pitzer, ed. *Activity Coefficients in Electrolyte Solutions*, 2nd Ed., CRC Press (1991).

Table 1. Parameter values for density model of actinide solutions

Parameter	Ions			Values of parameters in Eq. (1)			Ranges of applicability		
				$A \times 10^5$	$B \times 10^5$	C	T (°C)	acid (M)	actinide (M)
$\beta_v^{(0)}$	H^+	NO_3^-		5.9594	0	0.011793	0-100	0-10	
$\beta_v^{(1)}$	H^+	NO_3^-		123.63	0	-3.8189	0-100	0-10	
C_v	H^+	NO_3^-		-0.11772	0	-0.00113	0-100	0-10	
$\beta_v^{(0)}$	UO_2^{2+}	NO_3^-		-33.406	7.0534	0	0-100		0-0.8
$\beta_v^{(1)}$	UO_2^{2+}	NO_3^-		309.44	-68.776	0	0-100		0-0.8
C_v	UO_2^{2+}	NO_3^-		2.2263	-0.79601	0	0-100		0-0.8
$\beta_v^{(0)}$	Th^{4+}	NO_3^-		45.631	0	-1.1388	15-60		0.1-2.4
$\beta_v^{(1)}$	Th^{4+}	NO_3^-		4346.8	0	-482.29	15-60		0.1-2.4
C_v	Th^{4+}	NO_3^-		-1.7426	0	0.05406	15-60		0.1-2.4
$\beta_v^{(0)}$	Pu^{4+}	NO_3^-		-38.42	0	-0.06742	25-60	0.5-6	0.1-1.5
$\beta_v^{(1)}$	Pu^{4+}	NO_3^-		-4550.1	0	-47.908	25-60	0.5-6	0.1-1.5
C_v	Pu^{4+}	NO_3^-		3.2503	0	-0.00353	25-60	0.5-6	0.1-1.5
θ_v	H^+	UO_2^{2+}		36.774	-4.0529	0	20-95	2-6	0.5-1.2
ψ_v	H^+	UO_2^{2+}	NO_3^-	-3.8275	1.579	0	20-95	2-6	0.5-1.2
θ_v	H^+	Th^{4+}		-103.78	0	4.0488	25-50	1-14	1-3
ψ_v	H^+	Th^{4+}	NO_3^-	8.4562	0	-0.17523	25-50	1-14	1-3
θ_v	H^+	Pu^{4+}		240.61	0	0	25	0.5-6	0.1-1.5
ψ_v	H^+	Pu^{4+}	NO_3^-	-23.98	0	0	25	0.5-6	0.1-1.5