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Densities and apparent molar volumes for aqueous solutions of HNO_3-$UO_2(NO_3)_2$ at 298.15 K

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In order to obtain the exact information of atomic number density in the ternary system of HNO_3-$UO_2(NO_3)_2$-H_2O, the densities were measured with an Anton-Paar DMA60/602 digital density meter thermostated at 298.15±0.01 K. The apparent molal volumes for the systems were calculated from the experimental data. The present measured apparent molar volumes have been fitted to the Pitzer ion-interaction model, which provides an adequate representation of the experimental data for mixed aqueous electrolyte solutions up to 6.2 mol/kg ionic strength. This fit yields θ^V, and ψ^V, which are the first derivatives with respect to pressure of the mixing interaction parameters for the excess free energy. With the mixing parameters θ^V, and ψ^V, the densities and apparent molar volumes of the ternary system studied in this work can be calculated with good accuracy, as shown by the standard deviations.

Introduction

Atomic number densities of nuclide in the solvents, such as water, are necessary to generate critical parameters of nuclear fuel solution systems, and they could be calculated from the density data of the solution. In addition, the volumetric properties of aqueous HNO_3-$UO_2(NO_3)_2$ solution is an important factor in critical nuclear safety analysis for a wet-type uranium reconversion process of the nuclear fuel production.[1]

For the HNO_3-$UO_2(NO_3)_2$-H_2O ternary system, MOEKEN[2] had proposed a density equation based on poor and limited data (only nine points). MIN et al.[3] measured the densities of HNO_3-$UO_2(NO_3)_2$-H_2O mixtures using a pycnometer at 25±0.1 °C, which leads to a precision in densities of 10^{-3} g/cm³. This precision is not sufficient to determine reliable excess volumes.

Although the primitive mean spherical approximation modified by LU et al.[4] gives activity coefficients of aqueous electrolyte solutions with high accuracy up to saturation, it is not convenient to calculate volumetric properties by using that theory. SHIN et al.[1] proposed a model based on the Stokes-Robinson application of the Brunauer-Emmett-Teller adsorption isotherm and activity equations given by GOLDBERG et al.[5] to evaluate the excess volume of HNO_3-$UO_2(NO_3)_2$-H_2O ternary system. PITZER ion-interaction model[6,7] proved to be a very powerful working tool for reproducing various thermodynamic properties such as activities, osmotic coefficients, enthalpies and heat capacities for single and mixed aqueous electrolyte solutions. PITZER equation has been tested on the volumetric properties of some mixed aqueous electrolyte solutions at various concentrations. KUMAR[8,9] have recently shown the applicability of PITZER equation in predicting the apparent molar

volumes of aqueous electrolyte solutions, in which the ternary mixing terms have not been considered. It is noticed that the values of the mixing parameters greatly depend on the chosen data. The determination of binary mixing parameter θ^V and ternary mixing parameter ψ^V requires density data at sufficiently high concentrations and with high accuracy.

In present work, density measurements were carried out with samples of concentrations of $UO_2(NO_3)_2$ in the range of 0~0.48 mol/kg and HNO_3 0~4.8 mol/kg with a high precision digital density meter at 298.15 K. The PITZER formalism including mixing parameters θ^V and ψ^V is used to analyze the densities and apparent molar volumes of the aqueous solutions studied in this work.

Experimental

Sample preparation

The HNO_3 used was G.R. grade, subjected to no further purification and the $UO_2(NO_3)_2 \cdot 6H_2O$ was analytical grade. Two kinds of concentrated aqueous solutions, HNO_3 and $UO_2(NO_3)_2$, were prepared by dissolving each chemicals with the twice-distilled, deionized water. Their concentrations in the binary solutions were determined by Davis-Gray method and alkalimetric titration, respectively. The ternary solutions were prepared by using a Mettler balance and air-tight stoppered bottles. The standard HNO_3 solution was directly put into the bottle. The charged bottle was closed and weighed. Then the standard $UO_2(NO_3)_2$ solution was poured into the bottle. The prepared solutions were protected from moisture as far as possible. This hindered any vapor loss and contamination.

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Density measurement

An Anton Paar DMA60 vibrating tube density meter (Graz, Austria), in combination with one DMA602 remote cell, was used to measure densities of aqueous $HNO_3-UO_2(NO_3)_2$ solutions at 298.15 K. The temperature of the U-shaped tube was checked continuously using a calibrated digital thermometer (Anton Paar DT100-20) with an accuracy of ±0.01 K. An external Hetotherm bath circulator (Heto, type CB7) was used with a temperature control interval of ±0.005 K.

The density determination is based on measuring the period of oscillation of a vibrating U-shaped sample tube, which is filled with sample solution. The measurement procedures have been described by YU and LI.[10] The relationship between the period τ and the density ρ is

$$\rho = A(\tau^2 - B) \qquad (1)$$

where A and B are instrument constants which are determined by calibration with pure water (twice distilled and deionized) and dry air. Characteristic vibration period τ of the instrument a dry air and pure water were checked after every first and third measurements, respectively. The uncertainty in the measured vibration period τ is $\pm 1 \cdot 10^{-6}$ seconds, which leads to a precision in densities of $\pm 5 \cdot 10^{-5}$ g/cm^3.

Calculation of the apparent molal volume

The measured densities of the mixed aqueous electrolyte solutions were used to calculate the apparent molar volumes according to

$$\phi_V = \frac{1000(\rho_W - \rho)}{\rho_W \rho \sum_i m_i} + \frac{\sum_i m_i M_i}{\rho \sum_i m_i} \qquad (2)$$

where ϕ_V is the apparent molar volume (cm^3/mol), m_i is the molarity (mol/kg) of electrolyte i, M_i is the molar mass (g/mol) of electrolyte i, ρ_W and ρ are the density (g/cm^3) of water and solution, respectively.

The molarities, densities and apparent molar volumes for $HNO_3-UO_2(NO_3)_2-H_2O$ system at 298.15 K are listed in Table 1.

PITZER ion-interaction model

The apparent molar volume is defined as

$$\phi_V = \frac{V - n_W V_W}{\sum_i n_i} \qquad (3)$$

where V is the total volume (cm^3) of solution, n_W and n_i are the mole number of water and electrolyte i, respectively.

Table 1. Densities and apparent molar volumes for $HNO_3-UO_2(NO_3)_2-H_2O$ system at 298.15 K

m_1, mol/kg	m_2, mol/kg	ρ, g/cm^3	ϕ_V, cm^3/mol	m_1, mol/kg	m_2, mol/kg	ρ, g/cm^3	ϕ_V, cm^3/mol
0.9950	0.1336	1.07063	34.374	1.6404	0.3148	1.14426	35.645
1.0978	0.1341	1.07385	34.001	1.7487	0.3157	1.14740	35.369
1.6213	0.1361	1.08968	32.834	1.8578	0.3188	1.15104	35.214
1.7280	0.1365	1.09280	32.701	2.1884	0.3198	1.15975	34.622
1.9437	0.1375	1.09911	32.473	2.3001	0.3209	1.16292	34.452
2.0525	0.1379	1.10257	32.227	2.4127	0.3220	1.16605	34.308
2.1623	0.1383	1.10597	32.029	2.5260	0.3231	1.16920	34.164
1.3103	0.1934	1.09853	34.494	2.7554	0.3252	1.17538	33.940
1.6277	0.1951	1.10808	33.703	2.8712	0.3264	1.17850	33.843
1.7348	0.1958	1.11125	33.519	2.9881	0.3275	1.18169	33.724
1.8427	0.1964	1.11421	33.441	3.1058	0.3287	1.18488	33.621
1.9513	0.1971	1.11743	33.272	2.0908	0.4421	1.19250	36.388
2.0606	0.1977	1.12062	33.110	2.3196	0.4450	1.19875	35.966
2.1708	0.1983	1.12381	32.969	2.7790	0.4512	1.21130	35.271
2.2864	0.1994	1.12727	32.839	3.0137	0.4543	1.21752	34.997
2.3931	0.1997	1.13029	32.702	3.4946	0.4609	1.22984	34.600
2.5055	0.2004	1.13359	32.565	3.7408	0.4644	1.23600	34.445
1.9591	0.2572	1.13561	34.093	3.9911	0.4680	1.24226	34.291
2.0688	0.2579	1.13886	33.865	4.2458	0.4716	1.24841	34.171
2.1795	0.2588	1.14186	33.783	4.5047	0.4754	1.25452	34.082
2.2914	0.2597	1.14502	33.651	4.7688	0.4792	1.26041	34.040

For a molar aqueous solution containing 1 kg of water and $\sum_i n_i$ moles of electrolytes, the total volume is

$$V = n_W V_W + \sum_i n_i \overline{V_i}^0 + V^E \qquad (4)$$

where V^E is the excess volume (cm^3), $\overline{V_i}^0$ is the partial molar volume (cm^3/mol) of electrolyte i at infinite dilution. From Eqs (3) and (4), we can obtain

$$\phi V = \left(\sum_i n_i \overline{V_i}^0 + V^E \right) / \sum_i n_i \qquad (5)$$

The relationship between the excess volume and the excess free energy of a multi-component system is

$$V^E = \left(\frac{\partial G^E}{\partial P} \right)_{T,n_j} \qquad (6)$$

where G^E is the excess Gibbs energy (J), P is the pressure (MPa), and T is the absolute temperature (K).

The general equation for the excess Gibbs energy of a multi-component electrolyte solution proposed by PITZER[6,7] is

$$G^E / w_W RT = -\frac{4A_\phi I}{b} \ln(1 + bI^{1/2}) +$$

$$+2 \sum_c \sum_a m_c m_a [B_{ca} + (\sum mZ) C_{ca}] +$$

$$+ \sum_c \sum_{c'} m_c m_{c'} [\theta_{cc'} + \sum_a m_a \psi_{cc'a} / 2] +$$

$$+ \sum_a \sum_{a'} (\theta_{aa'} + \sum_c m_c \psi_{aa'c} / 2) \qquad (7)$$

where w_W is the mass (kg) of water in the solution, I is the ionic strength (mol/kg), θ is the binary interaction parameter (kg^2/mol^2), ψ is the ternary interaction parameter (kg^3/mol^3), subscript c and a represent cation and anion, respectively, and A_ϕ is the Debye-Hückel slope for the osmotic coefficient, $R = 8.3144$ cm^3·MPa/(mol·K), $b = 1.2$ kg$^{1/2}$/mol$^{1/2}$, B_{ca} is the ionic strength dependent second virial coefficient

$$B_{ca} = \beta_{ca}^0 + \beta_{ca}^1 [1 - (1 + 2I^{1/2}) \exp(-2I^{1/2})] / 2I \qquad (8)$$

$$\sum mZ = \sum_a m_a |z_a| = \sum_c m_c |z_c| \qquad (9)$$

where β_{ca}^0, β_{ca}^1 and C_{ca} are temperature- and pressure-dependent PITZER parameters reported in the literature.[6,7] Substituting Eqs (6) and (7) into Eq. (5), we obtain

$$\phi V = \frac{1}{\sum_j m_j} \left\{ \sum_j m_j \overline{V_j}^0 + \frac{A_V I}{b} \ln(1 + bI^{1/2}) + \right.$$

$$+ 2RT \sum_c \sum_a m_c m_a [B_{ca}^V + (\sum mZ) C_{ca}^V] +$$

$$+ RT \sum_c \sum_{c'} m_c m_{c'} [2\theta_{cc'}^V + \sum_a m_a \psi_{cc'a}^V] +$$

$$+ RT \sum_a \sum_{a'} m_a m_{a'} [2\theta_{aa'}^V + \sum_c m_c \psi_{aa'c}^V] \qquad (10)$$

where B_{ca}^V, C_{ca}^V, θ^V and ψ^V are the first derivatives with respect to pressure of B_{ca}, C_{ca}, θ and ψ at constant temperature, $A_V = 1.875$ cm^3·kg$^{1/2}$/mol$^{3/2}$. According to Eq. (7), B_{ca}^V can be expressed as

$$B_{ca}^V = \beta_{ca}^{0V} + \beta_{ca}^{1V} [1 - (1 + 2I^{1/2}) \exp(-2I^{1/2})] / 2I \qquad (11)$$

where β_{ca}^{0V} and β_{ca}^{1V} are the first derivatives with respect to pressure of β_{ca}^0 and β_{ca}^1 at constant temperature. The values of $\overline{V}_{ca}^0$, β_{ca}^{0V}, β_{ca}^{1V}, and C_{ca}^V for each single electrolyte solution can be determined by minimizing the standard deviation of the fit of the apparent molar volumes of the solution under consideration. Mixing parameters θ^V and ψ^V can be regressed from experimental apparent molar volumes for mixed aqueous electrolyte solutions.

The density of the solution can be expressed with

$$\rho = \frac{1000 / \rho_W + \sum_i m_i \phi V}{1000 + \sum_i m_i M_i} \qquad (12)$$

Results and discussion

Volumetric ion interaction parameters for binary systems

By using Pitzer's ion interaction approach to calculate volumetric characteristics of mixed electrolyte solutions, we need the set of respective volumetric ion interaction parameters $\overline{V}_{ca}^0$, β_{ca}^{0V}, β_{ca}^{1V}, and C_{ca}^V for all relevant single electrolyte solutions. The volumetric ion interaction parameters computed from unreliable experimental density data would lead to large errors. Recently, KRUMGALZ et al.[11] evaluated the volumetric ion interaction parameters at 298.15 K for 102 electrolytes by using exact density and apparent molar volume data, in a wide range of concentrations.

Table 2. PITZER volumetric ion interaction parameters for binary solutions at 298.15 K

Electrolyte	$\bar{V}^0$, $cm^3 \cdot mol^{-1}$	$10^4\beta^{0V}$, $kg/(mol \cdot MPa)$	$10^4\beta^{1V}$, $kg/(mol \cdot MPa)$	10^5C^V $kg^2/(mol^2 \cdot MPa)$
HNO_3^a	29.872	0.16514	–7.81857	0.13076
$UO_2(NO_3)_2^b$	80.294	6.13769	–149.733	–3.6018

[a] The parameters were regressed from the density data of LOBO.[12]
[b] The parameters were regressed from the density data of NOVOTNY and SOHNEL.[13]

Table 3. Predicted and correlated results for
HNO_3–$UO_2(NO_3)_2$–H_2O system

θ^V, $kg \cdot mol^{-1} \cdot MPa^{-1}$	ψ^V, $kg^2 \cdot mol^{-2} \cdot MPa^{-1}$	σ_V, cm^3/mol	σ_ρ, g/cm^3
0	0	0.114	0.00037
$-7.3959 \cdot 10^{-5}$	$3.1175 \cdot 10^{-6}$	0.064	0.00014

Unfortunately, the volumetric ion interaction parameters for aqueous HNO_3 and $UO_2(NO_3)_2$ binary solutions were not available in their paper. The volumetric ion interaction parameters for the two relevant single electrolyte solutions used in this work were evaluated by the least-squares regress method from the literature data[12,13] and are listed in Table 2.

Correlation and prediction of apparent volume and density

The apparent molar volume data for HNO_3–UO_2 $(NO_3)_2$–H_2O ternary systems were fitted to Eq. (10) by using a least-squares regress technique (Marquardt method). The fitted values of binary mixing parameter (θ^V) and ternary mixing parameter (ψ^V) along with the standard deviations are listed in Table 3. When we set $\theta^V = \psi^V = 0$, Eq. (10) can be used to predict the apparent volume of ternary system with the data of the relevant binary solutions. To examine the prediction ability of the PITZER ion interaction approach, the standard deviations of apparent molar volume (σ_V) and density (σ_ρ) in the case of $\theta^V = \psi^V = 0$ were also listed in Table 3.

From Table 3 we can see that the PITZER equation can be used to predict the apparent molar volumes and densities of the HNO_3–$UO_2(NO_3)_2$–H_2O system with better accuracy, but the inclusion of binary and ternary mixing parameters considerably reduces the standard deviations between the calculated and observed values.

The correlated and predicted results from experimental data measured in this work are presented as residuals $\Delta^\phi V = (^\phi V_{cal} - {}^\phi V_{exp})$ and $\Delta\rho = (\rho_{cal} - \rho_{exp})$ in Figs 1 and 2. As shown in Fig. 1, most of predicted results for apparent molar volumes are represented within ± 0.16 cm^3/mol and correlated results within ± 0.10 cm^3/mol. For the densities, most observed values

are predicted and correlated within ± 0.0006 g/cm^3 and ± 0.0002 g/cm^3, respectively, as demonstrated in Fig. 2.
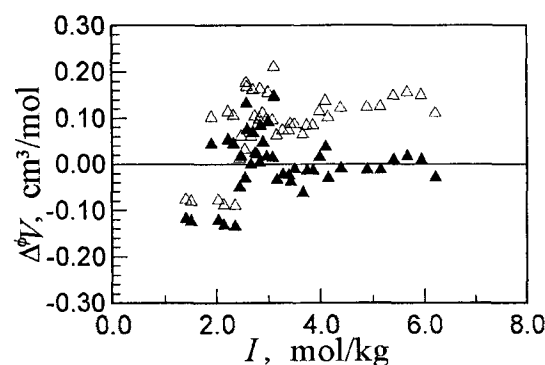
Fig. 1. Residual apparent molar volumes for HNO_3–$UO_2(NO_3)_2$–H_2O system ($\triangle$ predicted result; $\blacktriangle$ correlated result)
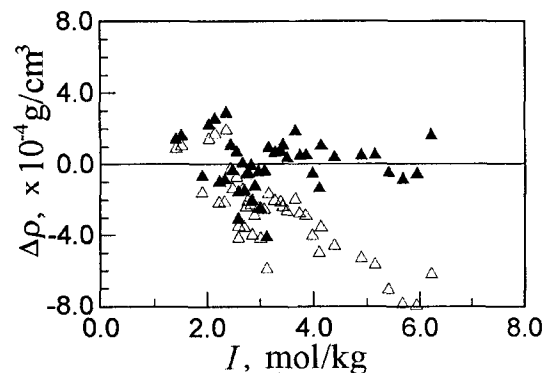
Fig. 2. Residual densities for HNO_3–$UO_2(NO_3)_2$–H_2O system ($\triangle$ predicted result; $\blacktriangle$ correlated result)

Conclusions

Densities of HNO_3–$UO_2(NO_3)_2$–H_2O ternary system were determined by using a vibrating density meter at 298.15 K. The experimental data were predicted and correlated by using PITZER ion-interaction model without or with the inclusion of the mixing parameter θ^V and ψ^V. By using obtained mixing parameters for volumetric properties, the densities and apparent molar volumes of the mixed aqueous HNO_3–$UO_2(NO_3)_2$ solutions can be calculated with good accuracy.

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