

Thermodynamics of the system $\text{HNO}_3\text{--UO}_2(\text{NO}_3)_2\text{--H}_2\text{O}$ at 298.15 K

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In order to predict extraction equilibria for uranyl nitrate and nitric acid between aqueous and tributyl phosphate (TBP)-hydrocarbon diluent solutions, activity coefficient equations for the three components in the system $\text{HNO}_3\text{--UO}_2(\text{NO}_3)_2\text{--H}_2\text{O}$ were derived and the general equation for excess Gibbs energy, proposed by Clegg and Pitzer, simplified. The activity coefficient equations comprise a Debye-Hückel term and a Margules expansion carried out to the four suffix level, where the higher order electrostatic contribution was neglected. The binary parameter was determined from the thermodynamic properties of the two relevant aqueous solutions. The three mixing parameters were obtained by correlating data for the partial pressure of nitric acid over $\text{HNO}_3\text{--UO}_2(\text{NO}_3)_2\text{--H}_2\text{O}$ solutions at 298.15 K. By using the mixing parameters, the activity coefficients of the ternary system can be calculated with good accuracy, and the solubility of uranyl nitrate in aqueous nitric acid with concentration up to 14 mol/kg can be satisfactorily predicted.

Introduction

Solvent extraction with tributyl phosphate (TBP) is a primary separation process for recovering uranium from irradiated nuclear fuel. It is essential to give a thermodynamic description of the distribution of water, nitric acid, uranyl nitrate, and fission products between their aqueous solution and 30 vol% TBP in a hydrocarbon diluent, because it permits the calculation of optimum conditions for this solvent extraction process operations.¹ In this system the components whose concentrations primarily affect interphase distribution are uranyl nitrate and nitric acid.² In this work, activity coefficient equations for uranyl nitrate and nitric acid in aqueous phase are established and compared with the experimental data.

For the thermodynamic properties of the $\text{HNO}_3\text{--UO}_2(\text{NO}_3)_2\text{--H}_2\text{O}$ ternary system, the densities and apparent molar volumes were measured by YU et al.³ using an Anto-Paar DMA60/602 digital densimeter⁴ thermostated at 298.15 ± 0.01 K. The experimental data were correlated and predicted with good accuracy using PITZER ion-interaction model.^{5,6} SHIN et al.⁷ also proposed a model based on Stokes-Robinson application of Brunauer-Emmett-Teller adsorption isotherm and activity equations given by GOLDBERG et al.² to evaluate the excess volume for this system. DAVIS et al.¹ measured partial pressures of water and nitric acid over 43 different $\text{HNO}_3\text{--UO}_2(\text{NO}_3)_2\text{--H}_2\text{O}$ ternary solutions for concentrations of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in the range of 0.10~2.3 mol/kg and HNO_3 1~15 mol/kg. The solubility data of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in $\text{HNO}_3\text{--H}_2\text{O}$ were also reported in the paper of DAVIS et al.¹ The expressions for activities of HNO_3 , $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and H_2O were given, but the activity equation for HNO_3 is not suitable at lower concentrations.²

It is well known that PITZER ion-interaction model^{5,6} can not be used to predict activity of electrolyte solutions at saturation. The modified primitive mean spherical approximation (MSA)⁸ gives activity coefficients of single electrolyte solutions with high accuracy up to saturation, but for mixed electrolyte solutions, it is valid only at low concentration because no additional mixing parameters are included. Recently, CLEGG and PITZER^{9,10} developed a generalized expression of the excess Gibbs energy on a mole fraction basis for mixtures containing an indefinite number of ions of arbitrary charge, over the entire concentration range. It has been tested using activity coefficient and salt solubility data for several systems.¹⁰ The only shortage of this equation is its complexity. This equation has been modified and simplified to predict vapor-liquid equilibria for the ternary mixed solvent systems.¹¹

In present work, the expression for excess Gibbs energy developed by CLEGG and PITZER^{9,10} was simplified by neglecting the quaternary interactions and other terms. The mean ionic activity coefficient equations for the three components in $\text{HNO}_3\text{--UO}_2(\text{NO}_3)_2\text{--H}_2\text{O}$ system were derived. The obtained equations with three mixing parameters were used to analyze the partial pressure of HNO_3 over in $\text{HNO}_3\text{--UO}_2(\text{NO}_3)_2\text{--H}_2\text{O}$ solutions and the solubility data of $\text{UO}_2(\text{NO}_3)_2$ in aqueous nitric acid solutions.

Theory

General equation for excess Gibbs energy

In the mole-fraction-based thermodynamic model developed by CLEGG and PITZER,^{9,10} the excess Gibbs

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energy per mole (g^E) is assumed to consist of short-range force (g^S) and total long-range force (g^{DHT}) components:

$$g^E = g^{\text{DHT}} + g^S \quad (1)$$

where the unit of g is J/mol. The total long-range force contribution to the excess Gibbs energy can be expressed as

$$g^{\text{DHT}} = g^{\text{DH}} + g^{\text{HOE}} \quad (2)$$

where g^{DH} is the Debye-Hückel contribution and g^{HOE} is the higher order electrostatic contribution. g^{HOE} can be calculated from the approximating equation given by PITZER.¹² It has a little effect on the activity coefficient for $\text{HNO}_3\text{-UO}_2(\text{NO}_3)_2\text{-H}_2\text{O}$ ternary system and was neglected in this work. CLEGG and PITZER⁹ adopted the following expression for Debye-Hückel contribution to the excess Gibbs energy

$$g^{\text{DH}} / RT = -(4 A_x I_x / b) \ln(1 + bI_x^{1/2}) + \sum_c \sum_a x_c x_a B_{ca} g(\alpha I_x^{1/2}) \quad (3)$$

where

$$g(x) = 2[1 - (1+x)\exp(-x)] / x^2 \quad (4)$$

$$I_x = \sum_i x_i z_i^2 / 2 \quad (5)$$

A_x is the Debye-Hückel parameter on a mole fraction basis (2.917 for water at 298.15 K), $R = 8.3144$ J/(mol·K), T is the absolute temperature (K), z_i is the magnitude of the charge on ion i , x_c and x_a are the mole fractions for cations and anions, respectively. The parameter B_{ca} is specific to each electrolyte ca , while parameter α and b are constants, and $\alpha = b = 13.0$ was adopted in this work.

The generalized expression of g^S for a mixture containing cations (c), anions (a) and neutral species (n) is

$$\begin{aligned} \frac{g^S}{RT} = & \sum_a E_a \sum_c \sum_{c'} x_c x_{c'} W_{cc'a} + \sum_c E_c \sum_a \sum_{a'} x_a x_{a'} W_{aa'c} + \\ & + \sum_a E_a \sum_c \sum_{c'} x_c x_{c'} (x_c / \nu_{c(a)} - x_{c'} / \nu_{c'(a)}) U_{cc'a} + \\ & + \sum_c E_c \sum_a \sum_{a'} x_a x_{a'} (x_a / \nu_{a(c)} - x_{a'} / \nu_{a'(c)}) U_{aa'c} + \\ & + \sum_n (x_n / F) \sum_c \sum_a E_c E_a (z_c + z_a) / (z_c z_a) W_{nca} + \\ & + \sum_n x_n \sum_c \sum_a x_c x_a (z_c + z_a)^2 / (z_c z_a) U_{nca} + \\ & + 4 \sum_n x_n^2 \sum_c \sum_a x_c x_a V_{nca} + 2 \sum_n x_n \sum_a E_a \sum_c \sum_{c'} x_c x_{c'} Q_{ncc'a} + \\ & + 2 \sum_n x_n \sum_c E_c \sum_a \sum_{a'} x_a x_{a'} Q_{naa'c} \end{aligned} \quad (6)$$

where W_{ijk} , U_{ijk} , V_{ijk} and Q_{nijk} are parameters for each system, and the summations are limited to distinguishable combinations of species present in the mixture (that is $c \neq c'$, $a \neq a'$). In Eq. (6) quaternary interactions are neglected except for $Q_{naa'c}$ and $Q_{ncc'a}$. Equivalent fractions E_c and E_a are defined as

$$E_c = x_c z_c / \left(\sum_c x_c z_c \right) \quad (7a)$$

$$E_a = x_a z_a / \left(\sum_a x_a z_a \right) \quad (7b)$$

and

$$F = 2 / \left(\sum_c x_c z_c + \sum_a x_a z_a \right) \quad (8)$$

$$\nu_{c(a)} = z_a / (z_c + z_a) \quad (9a)$$

$$\nu_{a(c)} = z_c / (z_a + z_c) \quad (9b)$$

Activity coefficient equations for single electrolyte solutions

Activity coefficients f_i on mole fraction scale are related to the excess Gibbs energy by

$$\ln f_i = \frac{1}{RT} \left[\partial \left(\sum_i n_i g^E \right) / \partial n_i \right]_{T,p} \quad (10)$$

For an aqueous solution of a single electrolyte $M_v + X_{v-}$, the activity coefficients of cation M , anion X , and water were obtained by differentiation of Eqs (3) and (6). The activity coefficient equation for water can be expressed as

$$\ln f_1 = 2 A_x I_x^{3/2} / (1 + bI_x^{1/2}) + x_M x_X B_{MX} \exp(-\alpha I_x^{1/2}) + x_1^2 (W_{1MX} + (x_1 - x_1) U_{1MX}) + 4 x_1 x_M x_X (2 - 3x_1) V_{1MX} \quad (11)$$

The mean ionic activity coefficient $\ln f_{\pm MX}^*$ is given by

$$\begin{aligned} \ln f_{\pm MX}^* = & -z_M z_X A_x \left[\frac{2}{b} \ln(1 + bI_x^{1/2}) + \frac{I_x^{1/2} (1 - 2I_x / z_M z_X)}{1 + bI_x^{1/2}} \right] - \\ & - x_M x_X B_{MX} \left[\frac{z_M z_X g(\alpha I_x^{1/2})}{2I_x} + \left(1 - \frac{z_M z_X}{2I_x} \right) \exp(-\alpha I_x^{1/2}) \right] + \\ & + \frac{2z_M z_X x_1 B_{MX} g(\alpha I_x^{1/2})}{(z_M + z_X)^2} + x_1^2 W_{1MX} + 2x_1^2 x_1 U_{1MX} + \\ & + 4x_1^2 x_1 (2 - 3x_1) \frac{z_M z_X}{(z_M + z_X)^2} V_{1MX} - W_{1MX} \end{aligned} \quad (12)$$

where $x_1 = x_M + x_X = 1 - x_1$, the superscript * indicates that the standard state is infinite dilution, and the subscript 1

refers to water. In the above equations, the long-range parameter is B_{MX} , and the short-range parameters are W_{1MX} , U_{1MX} and V_{1MX} . For a single electrolyte solution, there are four parameters to be determined.

Activity coefficient equations for ternary ion solutions

For mixed electrolyte solutions of type $\text{MX-NX}_2\text{-H}_2\text{O}$, the activity coefficient equations for the three components were derived in this work. The activity coefficient for the solute water is:

$$\begin{aligned} \ln f_1 = & \frac{2A_x I_x^{3/2}}{1+bI_x^{1/2}} + x_X(x_M B_{MX} + x_N B_{NX}) \exp(-aI_x^{1/2}) + \\ & + (1-x_1)(2E_M W_{1MX} + 1.5E_N W_{1NX}) / F + \\ & + (1-2x_1)x_X[4x_M U_{1MX} + 4.5x_N U_{1NX}] + \\ & + 4x_1(2-3x_1)x_X(x_M V_{1MX} + x_N V_{1NX}) - \\ & - 2x_M x_N W_{MNX} - 4x_M x_N(2x_M - 3x_N)U_{MNX} + \\ & + 4(1-2x_1)x_M x_N Q_{1MNX} \end{aligned} \quad (13)$$

The mean ionic activity coefficient of electrolyte MX can be expressed as

$$\begin{aligned} \ln f_{\pm MX}^* = & -A_x \left[\frac{2}{b} \ln(1+bI_x^{1/2}) + \frac{(1-2I_x)I_x^{1/2}}{(1+bI_x^{1/2})} \right] + \\ & + \left[\frac{x_M + x_X}{2} g(aI_x^{1/2}) - x_M x_X G_{MX}(I_x) \right] B_{MX} + \\ & + \left[(x_N / 2) g(aI_x^{1/2}) - x_N x_X G_{MX}(I_x) \right] B_{NX} + \\ & + x_1(1-2E_M / F)W_{1MX} - (3x_1 E_N / 2F)W_{1NX} + \\ & + [2x_1 x_X(1-2x_M) + 2x_1 x_M(1-2x_X)]U_{1MX} + \\ & + 9x_1 x_N(0.25 - x_X)U_{1NX} + 2x_1^2 x_N(1-6x_X)V_{1NX} + \\ & + 2x_1^2(x_M + x_X - 6x_M x_X)V_{1MX} + x_N(1-2x_M)W_{MNX} + \\ & + [x_N(4x_M - 3x_N) - 4x_M x_N(2x_M - 3x_N)]U_{MNX} + \\ & + 2x_1 x_N(1-4x_M)Q_{1MNX} - W_{1MX} \end{aligned} \quad (14)$$

where

$$E_M = x_M / (x_M + 2x_N), \quad E_N = 1 - E_M,$$

$$F = 2 / (x_M + 2x_N + x_X)$$

$$G_{MX}(I_x) = \frac{g(aI_x^{1/2})}{2I_x} + \left(1 - \frac{1}{2I_x} \right) \exp(-aI_x^{1/2})$$

The mean activity coefficient of electrolyte NX_2 is given by

$$\begin{aligned} \ln f_{\pm NX_2}^* = & -2A_x \left[\frac{2}{b} \ln(1+bI_x^{1/2}) + \frac{(1-I_x)I_x^{1/2}}{(1+bI_x^{1/2})} \right] + \\ & + \left[\frac{2x_N + x_X}{3} g(aI_x^{1/2}) - x_N x_X G_{NX}(I_x) \right] B_{NX} + \\ & + \left[(2x_M / 3) g(aI_x^{1/2}) - x_M x_X G_{NX}(I_x) \right] B_{MX} + \\ & + x_1(1-3E_N / 2F)W_{1NX} - (2x_1 E_M / 2F)W_{1MX} + \\ & + [3x_1 x_X(0.5 - x_N) + 3x_1 x_N(1-2x_X)]U_{1NX} + \\ & + 8x_1 x_M \left(\frac{1}{3} - x_X \right) U_{1MX} + \frac{4}{3} x_1^2 x_M(2-9x_X)V_{1MX} + \\ & + \frac{4}{3} x_1^2(2x_N + x_X - 9x_N x_X)V_{1NX} + \frac{2}{3} x_M(1-3x_N)W_{MNX} + \\ & + \left[\frac{4}{3} x_M(x_M - 3x_N) - 4x_M x_N(3x_N - 2x_M) \right] U_{MNX} + \\ & + \frac{4}{3} x_1 x_M(1-6x_N)Q_{1MNX} - W_{1NX} \end{aligned} \quad (15)$$

where

$$G_{NX}(I_x) = \frac{g(aI_x^{1/2})}{I_x} + \left(1 - \frac{1}{I_x} \right) \exp(-aI_x^{1/2})$$

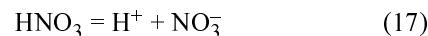
For $\text{HNO}_3\text{-UO}_2(\text{NO}_3)_2\text{-H}_2\text{O}$ system, $M = \text{H}^+$, $N = \text{UO}_2^{2+}$, and $X = \text{NO}_3^-$. There are three mixing parameters W_{MNX} , U_{MNX} and Q_{1MNX} to be determined in the above equations. In order to simplify the calculations, the unsymmetrical mixing terms were not included in the activity coefficient equations because the inclusion of them gives a small improvement.

Relation between the partial pressures of nitric acid and activity coefficients

Assuming an idea vapor phase and neglecting the Poynting correction, the partial pressure p_2 of HNO_3 can be written

$$p_2 = x_2 f_2 p_2^0 \quad (16)$$

where x_2 is the mole fraction of HNO_3 , p_2^0 is the vapor pressure of pure HNO_3 ($p_2^0 = 62.5$ mmHg at 298.15 K). f_2 is the mole fraction activity coefficient of HNO_3 with pure liquid as the standard state. Considering the dissociation equilibrium:



the criterion for equilibrium is:

$$\mu_2 = \mu_{\text{H}^+} + \mu_{\text{NO}_3^-} \quad (18)$$

where μ_2 , μ_{H^+} and $\mu_{\text{NO}_3^-}$ are the chemical potentials of HNO_3 , H^+ and NO_3^- , respectively.

They can be expressed as

$$\mu_2 = \mu_2^0(T) + RT \ln(x_2 f_2) \quad (19a)$$

$$\mu_{\text{H}^+} = \mu_{\text{H}^+}^0(T) + RT \ln(x_{\text{H}^+} f_{\text{H}^+}) \quad (19b)$$

$$\mu_{\text{NO}_3^-} = \mu_{\text{NO}_3^-}^0(T) + RT \ln(x_{\text{NO}_3^-} f_{\text{NO}_3^-}) \quad (19c)$$

where f_{H^+} and $f_{\text{NO}_3^-}$ are the activity coefficients with pure liquid as the standard state for H^+ and NO_3^- , respectively. In the pure HNO_3 , $x_2 f_2 = 1$, $f_{\text{H}^+} = f_{\text{NO}_3^-} = 1$, and $x_{\text{H}^+} = x_{\text{NO}_3^-} = 1/2$, where HNO_3 was assumed to be dissociated completely. From Eqs (18) and (19a)~(19c), the following equation can be obtained:

$$\mu_2^0(T) = \mu_{\text{H}^+}^0(T) + \mu_{\text{NO}_3^-}^0(T) + 2RT \ln(1/2) \quad (20)$$

Using Eqs (19a)~(19c), Eq. (18) can be written as

$$\begin{aligned} \mu_2^0(T) + RT \ln(x_2 f_2) &= \mu_{\text{H}^+}^0(T) + \mu_{\text{NO}_3^-}^0(T) + \\ &+ RT \ln(x_{\text{H}^+} x_{\text{NO}_3^-} f_{\text{H}^+} f_{\text{NO}_3^-}) \end{aligned} \quad (21)$$

Combining Eq. (21) with Eq. (20), the activity of HNO_3 was obtained

$$x_2 f_2 = x_{\text{H}^+} x_{\text{NO}_3^-} f_{\text{H}^+} f_{\text{NO}_3^-} / 4 = x_{\text{H}^+} x_{\text{NO}_3^-} f_{\pm, \text{HNO}_3}^2 / 4 \quad (22)$$

The relation between activity coefficients with the two different standard state¹³ is

$$f_{\pm} = f_{\pm}^* / f_{\pm}^{*0} \quad (23)$$

where f_{\pm} is the activity coefficient with pure liquid as the standard state, f_{\pm}^* is the activity coefficient with infinite dilution as the standard state, f_{\pm}^{*0} is the pure liquid activity coefficient with infinite dilution as the standard state. The activity coefficient on mole fraction scale is related to the corresponding molar value (y_{\pm}) by¹³

$$f_{\pm}^* = y_{\pm} \left[\rho + 0.001 \left(M_1 \sum \nu c - \sum c M_B \right) \right] / \rho_0 \quad (24)$$

where the summations are to be made over all the solute species, M_1 is the molecular weight (g/mol) of solvent, M_B is the molecular weight (g/mol) of solute, ν is the number of moles of ions formed by the ionization of one mole of solute, c is the molar concentration (mol/l) of solute, ρ and ρ_0 are the densities (g/cm³) of solution and solvent, respectively. For pure HNO_3 ,

$$f_{\pm, \text{HNO}_3}^{*0} = 0.001 \nu M_1 c_2^0 y_{\pm, \text{HNO}_3}^0 / \rho_0 \quad (25)$$

where c_2^0 and y_{\pm, HNO_3}^0 are the molar concentration and molar activity coefficient of pure HNO_3 , respectively.

At 298.15 K, $\rho_0 = 0.9971$ g/cm³, $c_2^0 = 23.867$ mol/l, and $y_{\pm, \text{HNO}_3}^0 = 21.0$, as derived by DAVIS and DEBRUIN¹⁴ for the $\text{HNO}_3\text{-H}_2\text{O}$ system.

From Eqs (16), (22), (23) and (25), the relation between the partial pressures of HNO_3 and the mole fraction activity coefficients can be obtained

$$p_2 = p_2^0 x_{\text{H}^+} x_{\text{NO}_3^-} \left(\frac{f_{\pm, \text{HNO}_3}^* \rho_0}{0.001 M_1 c_2^0 y_{\pm, \text{HNO}_3}^0} \right)^2 \quad (26)$$

Activities in aqueous solution are commonly represented in molal units, and for convenience a number of conversions to the corresponding mole fraction quantities are also given here. The conversion formula is¹³

$$f_{\pm}^* = y_{\pm} \left(1 + 0.001 M_1 \sum \nu m \right) \quad (27)$$

where y_{\pm} is the activity coefficient on molal scale, and m is the molal concentration (mol/kg) of the solute.

Results and discussion

Parameters for the binary aqueous solutions

There are four sets of vapor-liquid equilibrium data¹⁴⁻¹⁷ available for $\text{HNO}_3\text{-H}_2\text{O}$ system which are very consistent. The data of DAVIS and DEBRUIN¹⁴ are very accurate at low concentration, while the data of POTIER¹⁵ and HASSE et al.¹⁶ are reliable at higher concentration. The data of POTIER¹⁵ provide values of the partial pressure of HNO_3 that are progressively lower than those of DAVIS and DEBRUIN,¹⁴ and of VANDONI and LAUDY.¹⁷ The four sets of vapor-liquid equilibrium data were used to determine the parameters in the activity coefficient equations for $\text{HNO}_3\text{-H}_2\text{O}$ system at 298.15 K. The parameters were regressed by minimizing the variance of the partial pressures of HNO_3 over its aqueous solution with the concentrations up to $x_1 = 0.67$. Only one point in the data of HASSE et al.¹⁶ at low concentration was neglected in the regression because its deviation from that of DAVIS and DEBRUIN¹⁴ is very large (about 80%). The values of the parameters and of the absolute average relative deviation (AAD) were listed in Table 1. The activities of HNO_3 in $\text{HNO}_3\text{-H}_2\text{O}$ solutions were plotted against the composition in Fig. 1 at 298.15 K. It shows that the correlated results are in good agreement with the four sets of experimental data.

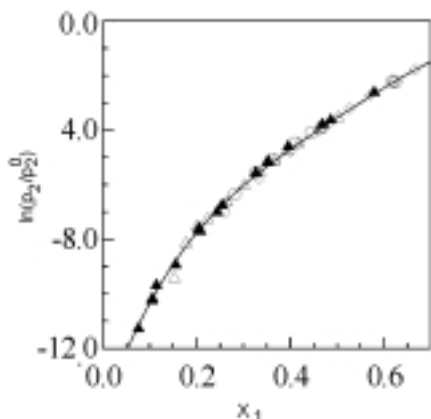


Fig. 1. Activities of HNO_3 in $\text{HNO}_3(2)\text{-H}_2\text{O}(1)$ solutions at 298.15 K; (\blacktriangle DAVIS and DE BRUIN,¹⁴ \diamond POTIER,¹⁵ \triangle HAASE et al.,¹⁶ \circ VANDONI and LAUDY,¹⁷ — correlated result)

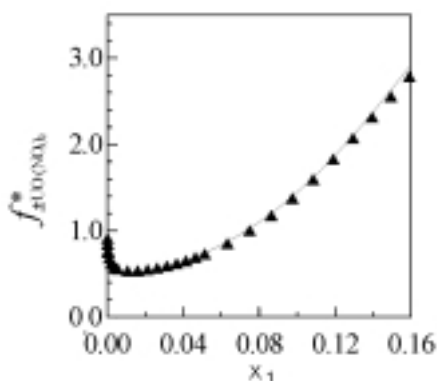


Fig. 2. Activity coefficient of $\text{UO}_2(\text{NO}_3)_2$ in binary system $\text{UO}_2(\text{NO}_3)_2\text{-H}_2\text{O}$ at 298.15 K. (\blacktriangle data of GOLDBERG,¹⁸ — calculated value)

GOLDBERG¹⁸ summarized the activity coefficients for $\text{UO}_2(\text{NO}_3)_2\text{-H}_2\text{O}$ system at 298.15 K. These data were directly used to obtain the parameters in the activity coefficient equations for $\text{UO}_2(\text{NO}_3)_2\text{-H}_2\text{O}$ system. The activity coefficients for $\text{UO}_2(\text{NO}_3)_2$ between the calculated and that of GOLDBERG¹⁸ were compared in Fig. 2. The parameters along with the AAD of activity coefficient for $\text{UO}_2(\text{NO}_3)_2$ were also included in Table 1.

$\text{HNO}_3\text{-UO}_2(\text{NO}_3)_2\text{-H}_2\text{O}$ ternary system

The partial pressures of HNO_3 over different $\text{HNO}_3\text{-UO}_2(\text{NO}_3)_2\text{-H}_2\text{O}$ ternary solutions measured by DAVIS et al.¹ were fitted to Eq. (26) by using Marquardt method. Following GOLDBERG et al.,² Experiment 52-0 was omitted in the regression because the partial

pressure appeared too high for the relatively low $\text{UO}_2(\text{NO}_3)_2$ molality, compared with Experimental 53-0. The fit yielded the three mixing parameters $W_{MNX}=50.977$, $U_{MNX}=-13.569$, and $Q_{1MNX}=-20.418$. Table 2 compared values of the partial pressure calculated from Eq. (26), using the mixing parameters obtained above, with the experimental data measured by DAVIS et al.¹ The results of GOLDBERG et al.² were also listed in Table 2. The calculated partial pressures from the experimental data of DAVIS et al.¹ were presented as relative deviations in Fig. 3.

From Table 2 and Fig. 3, one can see that the present results are slightly better than that of GOLDBERG et al.² The activity coefficient equations derived in this work are superior to the activity equations given by GOLDBERG et al.,² because only three mixing parameters are needed in this work, whereas the equations of GOLDBERG et al.² contain six mixing parameters.

In order to test suitability of the activity coefficient equations for high concentration solutions, the solubilities of $\text{UO}_2(\text{NO}_3)_2$ in aqueous HNO_3 solutions were predicted using the parameters obtained in this work. For solutions saturated with respect to the solid phase $\text{UO}_2(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, the activity product is constant. The molal concentration of saturated $\text{UO}_2(\text{NO}_3)_2\text{-H}_2\text{O}$ solution is 3.24 mol/kg at 298.15 K. The activity product of $\text{UO}_2(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ was calculated using the binary aqueous solution parameters listed in Table 1. The obtained value of activity product for $\text{UO}_2(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ is

$$\ln\left(x_{\text{UO}_3^+}x_{\text{NO}_3^-}^2f_{\pm\text{UO}_2(\text{NO}_3)_2}^*a_1^6\right)=-6.6855 \quad (28)$$

where a_1 is the activity of water.

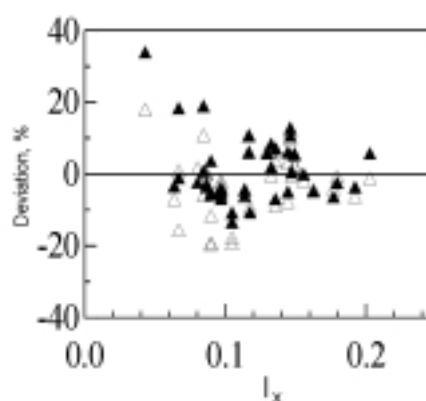


Fig. 3. Relative deviations of partial pressures of HNO_3 for $\text{HNO}_3\text{-UO}_2(\text{NO}_3)_2\text{-H}_2\text{O}$ system at 298.15 K (\blacktriangle result of GOLDBERG et al.,² \triangle present result)

Table 1. Parameters of the binary aqueous solutions at 298.15 K

Electrolyte	B_{MX}	W_{1MX}	U_{1MX}	V_{1MX}	Max. x_I	NP	AAD, %	Reference
HNO ₃	-34.627	-4.526	-2.302	3.904	0.16	50	7.78 ^a	14-17
UO ₂ (NO ₃) ₂	81.175	22.500	71.223	-43.852	0.67	38	1.65 ^b	18

^a AAD = $(100/NP)\Sigma(p_2^{\text{cal}} - p_2^{\text{exp}})/p_2^{\text{exp}}$, where p_2 is the partial pressure of HNO₃ and NP is the number of experimental points.

^b AAD = $(100/NP)\Sigma(f_{\pm}^{\text{cal}} - f_{\pm}^{\text{exp}})/f_{\pm}^{\text{exp}}$, where f_{\pm} is the activity coefficient of UO₂(NO₃)₂.

Table 2. Partial pressure of HNO₃ over HNO₃(2)-UO₂(NO₃)₂(3)-H₂O(1) solution at 298.15 K

m_2 , mol/kg	m_3 , mol/kg	Exptl ^b	Partial pressure of HNO ₃ , mmHg		Deviation, ^a %	
			GOLDBERG ^c	Present	GOLDBERG ^c	Present
1.046	0.499	0.000288	0.000384	0.000338	+33.4	+17.44
1.046	0.499	0.000288	0.000384	0.000338	+33.4	+17.44
1.054	1.000	0.000725	0.000854	0.000728	+17.8	+0.43
1.054	1.000	0.000868	0.000854	0.000728	-1.6	-16.12
1.056	1.509	0.00159	0.00164	0.001397	+3.1	-12.16
1.056	1.509	0.00174	0.00164	0.001397	-5.7	-19.73
1.056	1.509	0.00175	0.00164	0.001397	-6.3	-20.19
2.438	0.501	0.00232	0.00223	0.002143	-3.9	-7.64
2.414	0.978	0.00332	0.00393	0.003663	+18.4	+10.32
2.414	0.978	0.00392	0.00393	0.003663	+0.3	-6.57
2.395	1.462	0.00724	0.00642	0.005921	-11.3	-18.22
2.395	1.462	0.00739	0.00642	0.005921	-14.0	-19.88
4.983	0.100	0.0104	0.0101	0.01050	-2.9	+1.12
4.991	0.250	0.0121	0.0117	0.01211	-3.3	-0.29
4.991	0.250	0.0122	0.0117	0.01211	-4.1	-0.78
5.000	0.500	0.0156	0.0148	0.01512	-5.1	-3.09
5.000	0.500	0.0155	0.0148	0.01512	-4.5	-2.46
5.000	0.500	0.0158	0.0148	0.01512	-6.3	-4.32
5.000	0.500	0.0160	0.0148	0.01512	-7.5	-5.51
4.805	0.984	0.0210	0.0200	0.01995	-4.8	-5.02
4.805	0.984	0.0214	0.0200	0.01995	-6.5	-6.80
5.002	1.001	0.0213	0.0225	0.02243	+5.6	+5.33
5.002	1.001	0.0204	0.0225	0.02243	+10.3	+9.97
4.818	1.471	0.0286	0.0290	0.02831	+1.4	-1.01
4.818	1.471	0.0269	0.0290	0.02831	+7.8	+5.24
5.000	1.501	0.0348	0.0322	0.03149	-7.5	-9.53
4.834	1.790	0.0379	0.0358	0.03477	-5.5	-8.26
4.834	1.790	0.0339	0.0358	0.03477	+5.6	+2.56
5.000	1.870	0.0384	0.0404	0.03920	+5.2	+2.07
5.000	1.870	0.0385	0.0404	0.03920	+4.9	+1.81
6.230	0.667	0.0358	0.0318	0.03229	-11.2	-9.80
7.941	0.507	0.0558	0.0587	0.05910	+5.2	+5.91
9.908	0.131	0.0924	0.0984	0.09525	+6.5	+3.09
10.378	0.335	0.122	0.122	0.1201	+0.0	-1.18
9.647	0.506	0.0953	0.105	0.1042	+10.2	+9.29
9.647	0.506	0.0935	0.105	0.1042	+12.3	+11.39
10.836	0.688	0.163	0.154	0.1551	-5.4	-4.88
11.380	1.088	0.201	0.195	0.1986	-3.0	-1.21
11.512	1.480	0.240	0.230	0.2235	-4.2	-6.89
11.299	0.346	0.159	0.158	0.1551	-0.6	-2.46
12.236	0.778	0.232	0.216	0.2212	-6.9	-4.64
12.667	1.563	0.287	0.302	0.2819	+5.2	-1.77
Absolute average relative deviation, %					7.30	7.23

^a Deviation = 100 (calculated value-experimental value)/experimental value.

^b Experimental data are from DAVIS et al.¹

^c Calculated values of GOLDBERG et al.²

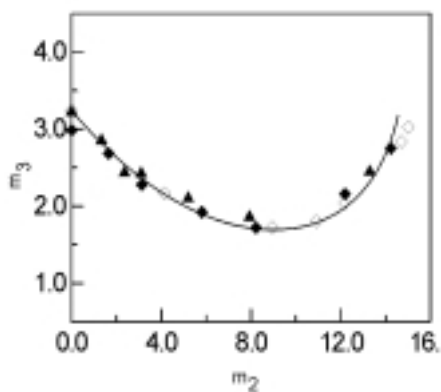


Fig. 4. Solubility of $\text{UO}_2(\text{NO}_3)_2(3)$ in $\text{HNO}_3(2)\text{-H}_2\text{O}(1)$ solution at 298.15 K. (The equilibrium solid phase is $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; \blacklozenge DAVIS et al.,¹ \blacktriangle YAKIMOV and MISHIN,¹⁹ \diamond COLANI,²⁰ — predicted result)

The experimental solubility data and the predicted values were compared in Fig. 4 at 298.15 K. The solubilities of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in aqueous HNO_3 solutions are satisfactorily represented by the equations given in this work up to the HNO_3 molal concentration of 14 mol/kg. When the molal concentration of HNO_3 is higher than 14 mol/kg, the equations overestimate the solubility of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. It should be pointed out that the stable hydrate will be $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ if the molal concentration of HNO_3 exceeds about 15 mol/kg.

Conclusions

The activity coefficient equations for ternary ion solutions were derived and the general equation for the excess Gibbs energy, reported by CLEGG and PITZER^{9,10} was simplified. The parameters in the activity coefficient equations were determined for the two relevant binary aqueous solutions. The partial pressures of HNO_3 over $\text{HNO}_3\text{-UO}_2(\text{NO}_3)_2\text{-H}_2\text{O}$ ternary solutions at 298.15 K

were correlated using the derived equations having three mixing parameters. The average absolute relative deviation of the partial pressures of HNO_3 between the correlated and the experimental data was 7.23%. The results have been compared with that of GOLDBERG et al.² By using the obtained mixing parameters, the solubilities of $\text{UO}_2(\text{NO}_3)_2$ in aqueous HNO_3 solutions at 298.15 K, where the equilibrium solid phase is $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, can be satisfactorily predicted.

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