

Uranyl(VI) Nitrate Salts: Modeling Thermodynamic Properties Using the Binding Mean Spherical Approximation Theory and Determination of “Fictive” Binary Data

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This work is aimed at a description of the thermodynamic properties of highly concentrated aqueous solutions of uranyl nitrate at 25 °C. A new resolution of the binding mean spherical approximation (BIMSA) theory, taking into account 1–1 and also 1–2 complex formation, is developed and used to reproduce, from a simple procedure, experimental uranyl nitrate osmotic coefficient variation with concentration. For better consistency of the theory, binary uranyl perchlorate and chloride osmotic coefficients are also calculated. Comparison of calculated and experimental values is made. The possibility of regarding the ternary system $\text{UO}_2(\text{NO}_3)_2/\text{HNO}_3/\text{H}_2\text{O}$ as a “simple” solution (in the sense of Zdanovskii, Stokes, and Robinson) is examined from water activity and density measurements. Also, an analysis of existing uranyl nitrate binary data is proposed and compared with our obtained data. On the basis of the concept of “simple” solution, values for density and water activity for the binary system $\text{UO}_2(\text{NO}_3)_2/\text{H}_2\text{O}$ are proposed in a concentration range on which uranyl nitrate precipitates from measurements on concentrated solutions of the ternary system $\text{UO}_2(\text{NO}_3)_2/\text{HNO}_3/\text{H}_2\text{O}$. This new set of binary data is “fictive” in the sense that the real binary system is not stable chemically. Finally, a new, interesting predictive capability of the BIMSA theory is shown.

Introduction

Uranyl(VI) nitrate is the most abundant salt that can be found in the reprocessing of spent nuclear fuel. Thus, its aqueous solutions thermodynamic data are of great interest, for example, for the optimization of its treatment by means of liquid–liquid extraction.

We have seen that binary data of salt solutions can be useful for thermodynamic calculations.^{1–3} As an example, the knowledge of binary data of given compounds, combined with the use of the concept of “simple” solutions, can be a convenient way for predicting properties of mixtures (ternary or quaternary systems) containing these compounds, over a wide range of concentration. Nevertheless, the use of this concept for mixtures of low water activity requires the knowledge of binary data of a given compound of the mixture for low water activities as well, sometimes lower than the one corresponding to the solubility limit of the binary solution. In other words, in many cases, “fictive binary data” may be necessary.

In the past, Charrin et al. determined “fictive binary data” for the $\text{Pu}(\text{NO}_3)_4/\text{H}_2\text{O}$ and $\text{U}(\text{NO}_3)_4/\text{H}_2\text{O}$ systems,⁴ and later, Kappenstein et al. determined “fictive binary data” for $\text{NpO}_2\text{-NO}_3/\text{H}_2\text{O}$.⁵ All the authors calculated these data from the concept of “simple” solutions and the use of the “inverse” Zdanovskii rule after measurements on low water activity ternary and quaternary mixtures. But, we hope, by means of a suitable

microscopic theory, to deduce “fictive binary data” in a more straightforward way as well, from extrapolation of binary data under the solubility limit.

Regarding binary uranyl nitrate osmotic coefficients, some studies have been made up to high concentration and were compiled by Goldberg⁶ whose data is mostly taken from isopiestic measurements by Robinson, Wilson, and Ayling⁷ (0.0930–2.0350 mol·kg^{−1} concentration range) and Robinson and Lim⁸ (0.1010–5.511 mol·kg^{−1} concentration range). More recently, Apelblat et al. also conducted osmotic coefficients measurements.⁹ To our knowledge, Robinson and Lim are the only authors to propose osmotic coefficients for oversaturated $\text{UO}_2(\text{NO}_3)_2$ solutions.⁸ Surprisingly, these authors do not mention the fact that several of their studied solutions are in a concentration range widely above the solubility limit, which is 3.24 mol·kg^{−1} according to OECD¹⁰ reports.

Other authors have measured densities for uranyl nitrate solutions,^{11–18} especially Kapustinsky and Lipilina who provided 12 density values at low concentration¹³ and 20 density values up to 2.79 mol·kg^{−1}.¹⁵ Nevertheless, in the range of 2.00–2.79 mol·kg^{−1}, the values obtained are scarce and the various authors are in disagreement.

Besides, for the reasons previously mentioned, reliable uranyl(VI) nitrate “fictive” binary data (above its solubility limit) are necessary for the prediction of a wide range of mixture properties containing this salt. Also, studies of the uranyl(VI) nitrate system are of great importance because of its similarity with other actinide(VI) nitrate salts (such as $\text{PuO}_2(\text{NO}_3)_2$), which are difficult to study, especially at high concentration, due to higher radioactivity and unstable +VI oxidation state for actinides other than uranium.¹⁹ However, the prediction of a

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given actinide(VI) nitrate's properties from those for uranyl(VI) nitrate requires the use of a suitable theory.

In view of these aspects, the purpose of this paper is twofold.

The first aim of the present work was, with the use of existing binary data on the uranyl(VI) salts (perchlorate, chloride, and nitrate), to test the applicability of the BIMSAs (binding mean spherical approximation) theory on the actinyl(VI) salts binary systems. The BIMSAs theory, based on the Wertheim formalism, can reproduce osmotic and activity coefficients, up to high concentration and for a wide variety of aqueous salts^{20–22} including the lanthanide(III) salts.²³ The BIMSAs theory was studied for several uranyl salts in previous works,^{21,22} where we have seen that it could provide satisfying results. Considering that uranyl(VI) as other actinyl(VI) is expected to form 1–2 complexes with many ligands,¹⁰ including weak ligands such as nitrates,²⁴ a BIMSAs theory taking into account 1–1 but also 1–2 complexes was used to reproduce obtained osmotic coefficients or water activities up to high concentration. The constants of formation of 1–1 and 1–2 complexes were taken from the data selected from OECD¹⁰ when available. The second aim was to assess the capability of the BIMSAs theory to extrapolate osmotic coefficients to higher concentrations, more precisely to deduce, from osmotic coefficient values of the binary $\text{UO}_2(\text{NO}_3)_2$ under the solubility limit, “fictive” values of the same binary system.

For this purpose, in continuation to previous work on $\text{Pu}(\text{NO}_3)_4$, $\text{U}(\text{NO}_3)_4$, and NpO_2NO_3 salts,^{4,5} a set of “fictive binary data” for $\text{UO}_2(\text{NO}_3)_2$ salts was established from the concept of “simple” solutions and measurements on uranyl nitrate–nitric acid mixtures.

More precisely, it was necessary, in a first step, to check whether the ternary system $\text{UO}_2(\text{NO}_3)_2/\text{HNO}_3/\text{H}_2\text{O}$ exhibits “simple” behavior. In practice, one says that a ternary mixture $\text{S}_1/\text{S}_2/\text{H}_2\text{O}$ satisfies the “simple” behavior criterion if, when mixing solutions of equal water activity, the water activity of the resulting $\text{S}_1/\text{S}_2/\text{H}_2\text{O}$ mixture is unchanged, regardless of the proportions of the two binaries $\text{S}_1/\text{H}_2\text{O}$ and $\text{S}_2/\text{H}_2\text{O}$ in the mixture.²⁵

Then, to validate our procedure, binary data of the system $\text{UO}_2(\text{NO}_3)_2/\text{H}_2\text{O}$ under the solubility limit, was calculated from measured data of the ternary system $\text{UO}_2(\text{NO}_3)_2/\text{HNO}_3/\text{H}_2\text{O}$. These data were compared to “directly” experimentally measured binary data of $\text{UO}_2(\text{NO}_3)_2/\text{H}_2\text{O}$ and also to binary data in the literature under the solubility limit.

Finally, “fictive binary data”, in other words, above the solubility limit, was proposed. This $\text{UO}_2(\text{NO}_3)_2/\text{H}_2\text{O}$ “fictive binary data”, obtained from measurements on the ternary system $\text{UO}_2(\text{NO}_3)_2/\text{HNO}_3/\text{H}_2\text{O}$ and the use of the concept of “simple” solutions, was compared to “fictive” osmotic coefficients of the binary system $\text{UO}_2(\text{NO}_3)_2/\text{H}_2\text{O}$ deduced from the BIMSAs theory, using microscopic parameters optimized on $\text{UO}_2(\text{NO}_3)_2/\text{H}_2\text{O}$ binary data under the solubility limit.

Experimental Protocol

The density (d) and water activity (a_w) were measured using an Anton-Paar DMA 602 tuning-fork density transducer and a Novasina AW-Center water activity meter, respectively. These two devices were found to provide reliable data for different actinide solutions and to be adapted to highly acidic media measurements.^{1,4,5,26,27}

The density meter was calibrated at a temperature of 25.00 ± 0.02 °C, according to a previously described protocol,² over the range of 990–1970 $\text{kg}\cdot\text{m}^{-3}$.

The AW-Center water activity meter has sensors, located above the analyzed liquid sample. They are made of a hygroscopic material sensitive to the relative humidity of the vapor phase in equilibrium with the liquid phase. The water activity of solution may be deduced from this measurement. One experiment lasts between 30 and 90 min, corresponding to the vapor–liquid equilibration time.²⁷ The water activity meter was calibrated at 25.0 ± 0.2 °C. The calibration was conducted as described in ref 2 by using different lithium nitrate solutions, for which data (density and water activity variation with concentration) is well established.²⁸ The measurement or calculation of water activities, a_w , of a given binary system (UO_2X_2 , H_2O) leads to the calculation of the osmotic coefficient Φ by the following relation

$$\Phi = - \frac{\ln a_w}{M_{\text{H}_2\text{O}} \nu m_{\text{UO}_2\text{X}_2}^{\text{bi}}} \quad (1)$$

where ν is the total number of ions formed by the complete dissociation of one molecule of the salt ($\nu = 3$ in the case of UO_2X_2), $m_{\text{UO}_2\text{X}_2}^{\text{bi}}$ is the salt concentration (in $\text{mol}\cdot\text{kg}^{-1}$), and $M_{\text{H}_2\text{O}}$ is the molar mass of water ($18.015 \cdot 10^{-3} \text{ kg}\cdot\text{mol}^{-1}$).

Prolabo normapur hexahydrate uranium nitrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), whose isotopic composition is known (²³⁴U 0.001%, ²³⁵U 0.237%, and ²³⁸U 99.762%) and Prolabo titrinorm nitric acid reactants were used. Deionized water was added to the nitric acid solution to prepare diluted nitric acid solutions.

Different binary $\text{UO}_2(\text{NO}_3)_2/\text{H}_2\text{O}$ and $\text{HNO}_3/\text{H}_2\text{O}$ stock solutions were prepared. The molality of $\text{UO}_2(\text{NO}_3)_2$ was calculated from mass measurements of the initially dissolved solid ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) compound. The molality of HNO_3 was deduced from density measurements and nitric acid data from Charrin et al.²⁶

These binary stock solutions were mixed in different proportions to constitute ternary solutions $\text{UO}_2(\text{NO}_3)_2/\text{HNO}_3/\text{H}_2\text{O}$. Therefore, from mass measurements, we were able to calculate the molalities involved in the ternary systems.

Theory

1. BIMSAs Theory. In this section, we shortly recall the theoretical ingredients used in this work. We focus on the changes made in comparison to previous forms,^{23,27} by taking into account not only 1–1 but also 1–2 complex formation.

The BIMSAs theory is one of the several derivatives of the mean spherical approximation (MSA).^{30–35} As for the MSA, the BIMSAs takes into account, at a microscopic scale, hard-core repulsion and Coulombic interaction.

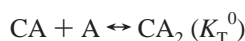
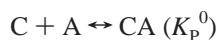
The main difference is that the BIMSAs includes a short-range potential, responsible for ion pairing. In earlier work,^{23,27} the formation of dimers (1–1 complexes) was taken into account. Here, we consider that short-range potential can also lead to the formation of 1–2 complexes (one cation and two anions, hereafter called trimers).

The effect of association is included in the computation of the MSA screening parameter Γ .³⁶ The resulting thermodynamic excess properties can be expressed in a simple way in terms of Γ when using the Wertheim formalism,³⁶ in which the thermodynamic formation constants K_F^0 and K_T^0 , permit us to take into account all associating mechanisms (Coulombic, covalent). This formalism was shown to be successful for ionic systems in both the hypernetted chain approximation and the MSA.^{37–41}

The expressions given in the SI unit system presented in this section are based on ref 42. Bernard and Blum established expressions for the MSA classical parameters, Γ and η , and

also for the excess free energy in the case of the flexible trimer with three different ions.⁴² These latter relations were modified so as to take into account 1–2 complex formation. In this work, we also take into account the fact that the cation size and the permittivity may be concentration dependent.⁴³ As in refs 20–23, the anion diameter σ_- is kept constant.

So, we consider a two-component electrolyte (CA) in which the cation (C) can form either a pair (CA) or a trimer (CA₂) with the anion (A). As in previous work, a pair is defined as two ions being in contact. A trimer is defined as three ions (two A ions and one C ion) in contact, the trimer being centered on the C ion. Then, we have the two following chemical equilibria between the ions A and C



The valences, diameters, and total number densities of the ions are z_+ , z_- , σ_+ , σ_- , ρ_+ , and ρ_- , respectively. Furthermore, we denote by $\alpha_- \rho_-$ the density of unbound A ions, $\alpha_+ \rho_+$ the density of unbound C ions, ρ_P the density of pair ions CA, and ρ_T the density of trimers CA₂. We set

$$K_P = \frac{\rho_P}{(\alpha_- \rho_-)(\alpha_+ \rho_+)} = K_P^0 G_P \quad (2)$$

$$K_T = \frac{\rho_T}{(\alpha_- \rho_-)\rho_P} K_T^0 G_T \quad (3)$$

with the proportion of unbound ions

$$\alpha_- = 1 - \frac{\rho_P}{\rho_-} - 2 \frac{\rho_T}{\rho_-} \quad (4)$$

$$\alpha_+ = 1 - \frac{\rho_P}{\rho_+} - \frac{\rho_T}{\rho_+} \quad (5)$$

In eqs 2 and 3, G_P (respectively, G_T) expresses the departure of the apparent equilibrium constant K_P (respectively, K_T) from the thermodynamic equilibrium constant K_P^0 (respectively, K_T^0). In other words, G_P (respectively, $G_P \cdot G_T$) defines the difference between the chemical potential of a pair (respectively, a trimer) and the chemical potential of the two ions constituting the pair (respectively, the three ions constituting the trimer) at infinite dilution in unbound states

$$G_P = g_C^{\text{HS}} \exp \left(-2\lambda \frac{z_- z'_+}{\sigma_- + \sigma_+} + 2\lambda_0 \frac{z_- z_+}{\sigma_- + \sigma_+^{(0)}} \right) \quad (6)$$

$$G_T = G_P \exp \left(-2\lambda \frac{(z'_-)^2}{(2\sigma_- + \sigma_+)(1 + \Gamma\sigma_+)} + 2\lambda_0 \frac{z_-^2}{(2\sigma_- + \sigma_+^{(0)})} \right) \quad (7)$$

and

$$z'_i = (z_i - \eta\sigma_i^2)/(1 + \Gamma\sigma_i) \quad (8)$$

$$\lambda = \beta e^2 / (4\pi\epsilon_0\epsilon) \quad (9)$$

with ϵ_0 being the permittivity of a vacuum and ϵ the relative

permittivity of solution. λ_0 and $\sigma_i^{(0)}$ are λ and σ_i , respectively, for an infinitely diluted solution. We recall that the diameter of an anion is assumed as constant with concentration: $\sigma_- = \sigma_-^{(0)}$.

In comparison to previous work,²² the MSA parameters η and Γ are noticeably modified when one takes into account trimer formation. After some algebra whose principles are detailed in ref 42, one finds

$$\frac{\Gamma^2}{\pi\lambda} = \sum_{k=-,+} \rho_k z'_k{}^2 + 2 \frac{\rho_P + 2\rho_T}{\sigma_- + \sigma_+} z'_- z'_+ \sum_{k=-,+} \frac{\sigma_k}{1 + \Gamma\sigma_k} + 2 \frac{\rho_T}{(2\sigma_- + \sigma_+)(1 + \Gamma\sigma_+)} \left(\frac{2\sigma_-}{1 + \Gamma\sigma_-} + \frac{\sigma_+}{1 + \Gamma\sigma_+} \right) (z'_-)^2 \quad (10)$$

$$\eta = \frac{\pi}{2\Delta\Omega} \left[\sum_{k=-,+} \rho_k \frac{z_k \sigma_k}{1 + \Gamma\sigma_k} + \frac{\rho_P + 2\rho_T}{\sigma_- + \sigma_+} \frac{z_- \sigma_+^2 + z_+ \sigma_-^2}{(1 + \Gamma\sigma_-)(1 + \Gamma\sigma_+)} + 2 \frac{\rho_T}{(2\sigma_- + \sigma_+)(1 + \Gamma\sigma_+)} \frac{z_- \sigma_-^2}{(1 + \Gamma\sigma_-)^2} \right] \quad (11)$$

with

$$\Omega = 1 + \frac{\pi}{2\Delta} \left[\sum_{k=-,+} \rho_k \frac{\sigma_k^3}{1 + \Gamma\sigma_k} + 2 \frac{\rho_P + 2\rho_T}{\sigma_- + \sigma_+} \frac{\sigma_-^2 \sigma_+^2}{(1 + \Gamma\sigma_-)(1 + \Gamma\sigma_+)} + 2 \frac{\rho_T}{(2\sigma_- + \sigma_+)(1 + \Gamma\sigma_+)} \frac{\sigma_-^4}{(1 + \Gamma\sigma_-)^2} \right] \quad (12)$$

and

$$\Delta = 1 - X_3 \quad (13)$$

$$X_n = \frac{\pi}{6} \sum_{k=-,+} \rho_k \sigma_k^n \quad (14)$$

Ω and η are parameters which take into account the dissymmetry of the electrolyte. As in previous work,^{20–22} the modified MSA screening parameter Γ verifies the condition $\Gamma \sim \kappa/2$ at infinite dilution, κ being the Debye screening parameter.

As for the case of ion-pair formation, eqs 10, 11, and 12 are solved by numerical iterations. At each step, we use eqs 2 and 3 for given values of K_P^0 and K_T^0 , and the mass action law (MAL) is solved. Nevertheless, contrary to the ion-pair case where a simple formula can solve the MAL, a subroutine is needed, so that for given K_P , K_T , ρ_- , and ρ_+ values, the concentration of each fraction $\alpha_- \rho_-$, $\alpha_+ \rho_+$, ρ_P , and ρ_T can be calculated.

After convergence, the obtained values are used to calculate the different thermodynamic functions.

The excess MSA Helmholtz energy per volume unit ΔA^{MSA} is the excess Helmholtz energy in comparison to a system of uncharged hard-spheres. Uncharged hard-spheres excess energy per volume unit (ΔA^{HS}) can be found in ref 20. ΔA^{MSA} satisfies

$$\beta\Delta A^{\text{MSA}} = \beta\Delta U^{\text{MSA}} + \frac{\Gamma^3}{3\pi} + \beta\Delta A^{\text{MAL}} - \rho_{\text{P}} \left(\frac{\partial\beta\Delta U^{\text{MSA}}}{\partial\rho_{\text{P}}} \right)_{\Gamma} - \rho_{\text{T}} \left(\frac{\partial\beta\Delta U^{\text{MSA}}}{\partial\rho_{\text{T}}} \right)_{\Gamma} \quad (15)$$

where the excess electrostatic MSA internal energy per volume unit is now

$$\beta\Delta U^{\text{MSA}} = \beta\Delta U_0^{\text{MSA}} + \lambda \frac{\rho_{\text{P}} + 2\rho_{\text{T}}}{\sigma_{-} + \sigma_{+}} \left(\frac{z_{-}z'_{+}}{1 + \Gamma\sigma_{-}} + \frac{z_{+}z'_{-}}{1 + \Gamma\sigma_{+}} \right) + 2\lambda \frac{\rho_{\text{T}}}{(2\sigma_{-} + \sigma_{+})(1 + \Gamma\sigma_{+})} \frac{z_{-}z'_{-}}{1 + \Gamma\sigma_{-}} \quad (16)$$

with ΔU_0^{MSA} given by

$$\beta\Delta U_0^{\text{MSA}} = -\lambda \sum_{k=-,+} \rho_k z_k \frac{\Gamma z_k + \eta\sigma_k}{1 + \Gamma\sigma_k} \quad (17)$$

The MAL contribution is modified as

$$\beta\Delta A^{\text{MAL}} = \sum_{k=-,+} \rho_k \ln \alpha_k + \rho_{\text{P}} + 2\rho_{\text{T}} \quad (18)$$

The two derivatives of ΔU^{MSA} used for the calculation of ΔA^{MSA} verify

$$\left[\frac{\partial\beta\Delta U^{\text{MSA}}}{\partial\rho_{\text{P}}} \right]_{\Gamma} = \frac{2\lambda}{\sigma_{-} + \sigma_{+}} z'_{-}z'_{+} \quad (19)$$

$$\left[\frac{\partial\beta\Delta U^{\text{MSA}}}{\partial\rho_{\text{T}}} \right]_{\Gamma} = 2 \left[\frac{\partial\beta\Delta U^{\text{MSA}}}{\partial\rho_{\text{P}}} \right]_{\Gamma} + \frac{2\lambda}{2\sigma_{-} + \sigma_{+}} \frac{(z'_{-})^2}{1 + \Gamma\sigma_{+}} \quad (20)$$

As in previous work, with the cation size and solution permittivity being concentration-dependent, the osmotic coefficient is written as²³

$$\Delta\Phi^{\text{MSA}} = \Delta\Phi_0^{\text{MSA}} + \Delta\Phi_{\sigma_{+}} + \Delta\Phi_{\epsilon} \quad (21)$$

where

$$\Delta\Phi_0^{\text{MSA}} = \Delta\Phi_0^{\text{el}} + \Delta\Phi_0^{\text{MAL}} \quad (22)$$

The expression of $\Delta\Phi_0^{\text{el}}$ is as given in earlier work,²³ with ρ being the total ion concentration: $\rho = \rho_{-} + \rho_{+}$

$$\Delta\Phi_0^{\text{el}} = -\frac{\Gamma^3}{3\pi\rho} - \frac{\lambda}{\rho} \frac{2}{\pi} \eta^2 \quad (23)$$

whereas $\Delta\Phi_0^{\text{MAL}}$ is modified due to trimer formation.

$$\Delta\Phi_0^{\text{MAL}} = -\frac{\rho_{\text{P}} + 2\rho_{\text{T}}}{\rho} \left(1 + \rho \frac{\partial \ln g_{\text{C}}^{\text{HS}}}{\partial\rho} \right) \quad (24)$$

with the expression of the contact probability g_{C}^{HS} and its derivative with respect to ρ being given elsewhere.^{22,23}

The effect of the concentration-dependent cation size and solution permittivity is as before^{22,23} given by

$$\Delta\Phi_{\sigma_{+}} = \frac{1}{\rho} \left[\frac{\partial\beta\Delta A^{\text{MSA}}}{\partial\sigma_{+}} \right]_{\Gamma} D(\sigma_{+}) \quad (25)$$

$$\Delta\Phi_{\epsilon} = \frac{1}{\rho} \left[\frac{\partial\beta\Delta A^{\text{MSA}}}{\partial\epsilon^{-1}} \right]_{\Gamma} D(\epsilon^{-1}) \quad (26)$$

with

$$D \equiv C_{\text{S}} \frac{\partial}{\partial C_{\text{S}}} \quad (27)$$

The value of $\Delta\Phi_{\sigma_{+}}$ was performed by numerical differentiation of ΔA^{MSA} . Regarding the calculation of $\Delta\Phi_{\epsilon}$, we have

$$\Delta\Phi_{\epsilon} = \frac{\beta\Delta U^{\text{MSA}}}{\rho} \epsilon D(\epsilon^{-1}) \quad (28)$$

The total osmotic coefficient is

$$\Phi = 1 + \Delta\Phi^{\text{MSA}} + \Delta\Phi^{\text{HS}} \quad (29)$$

in which $\Delta\Phi^{\text{HS}}$ is the hard-sphere contribution that can be calculated from the Carnahan–Starling expression, as described in ref 20.

The mean activity coefficient can be expressed as

$$\ln \gamma = \Delta \ln \gamma_{\pm}^{\text{MSA}} + \Delta \ln \gamma_{\pm}^{\text{HS}} \quad (30)$$

with $\Delta \ln \gamma_{\pm}^{\text{HS}}$ given in previous work²¹ and

$$\Delta \ln \gamma_{\pm}^{\text{MSA}} = \frac{\beta\Delta A^{\text{MSA}}}{\rho} + \Delta\Phi^{\text{MSA}} \quad (31)$$

In this work, as in refs 21–23, the anion size is kept constant and the diameter of the cation σ_{+} and the inverse of the relative permittivity of the solution ϵ^{-1} were chosen as linear functions of the salt molar concentration

$$\sigma_{+} = \sigma_{+}^{(0)} + \sigma^{(1)} C_{\text{S}} \quad (32)$$

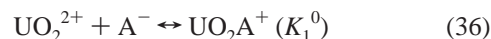
$$\epsilon^{-1} = \epsilon_{\text{W}}^{-1} (1 + \alpha C_{\text{S}}) \quad (33)$$

with ϵ_{W} the relative permittivity of pure solvent ($\epsilon_{\text{W}} = 78.3$ for water). Equations 32 and 33 introduce two adjustable parameters $\sigma^{(1)}$ and α that are characteristic of the electrolyte, while $\sigma_{+}^{(0)}$, the cation diameter at infinite solution, is characteristic of the considered cation only. It must have a common value for all salts (perchlorate, chloride, and nitrate salts in the present work) containing the same cation (uranyl, in the present work). Therefore^{21–23}

$$D(\sigma_{+}) = \sigma_{+} - \sigma_{+}^{(0)} \quad (34)$$

$$\epsilon D(\epsilon^{-1}) = 1 - \epsilon/\epsilon_{\text{W}} \quad (35)$$

In the present work, the considered equilibria are



The anions (A^{-}) studied in the present work are the perchlorates, chlorides, and nitrates. The corresponding anion diameters, σ_{-} , were used previously for a wide variety of salts,^{22,23} and their values are taken from previous work:²¹ 0.453 nm for ClO_4^{-} , 0.362 nm for Cl^{-} , and 0.340 nm for NO_3^{-} .

The results obtained by means of the BMSA theory were calculated using a FORTRAN program that can be run on a

microcomputer. To optimize the different parameters, and minimize the difference between our calculated osmotic coefficients values and those existing in the literature,⁶ a least-squares algorithm of the Marquardt type was used.

$\sigma_+^{(0)}$ was refined in a first step. As done in previous work,^{21–23} $\sigma_+^{(0)}$ was refined by fitting the perchlorate salt osmotic coefficient (uranyl perchlorate in the present work). This procedure is justified by the fact that most perchlorate salts, commonly regarded as strong electrolytes, are the simplest systems to study. The resulting $\sigma_+^{(0)}$ value for the uranyl cation was used as an input parameter for fitting chloride and nitrate uranyl salts osmotic coefficients.

2. “Simple” Solution Concept. The “simple” solution model was utilized. The following equation, known as the Zdanovskii–Stokes–Robinson (ZSR) relation and verified for “simple” mixtures, was discovered empirically by Zdanovskii²⁵ and derived later by Stokes and Robinson⁴⁴

$$\sum_{i=1}^n \frac{m_i}{m_i^{\text{bi}}} = 1 \quad (38)$$

and

$$a_w = \text{constant}$$

where m_i is the molality of electrolyte i in the mixture, and m_i^{bi} is the molality of the electrolyte i in a binary solution of the same solvent activity as the mixture, a_w . Therefore, the ZSR relationship is expressed in terms of the properties of solutions of individual binaries constituting the mixture.

Vdovenko and Rjazanov demonstrated that, for a given mixture satisfying the “simple” solution criterion, binary data such as density may easily be deduced from data for the ternary or quaternary systems⁴⁵ and vice versa. For example, for a ternary mixture $S_1/S_2/H_2O$ satisfying the “simple” behavior, the density depends on the binary density data of the electrolytes constituting the mixture and indirectly on the water activity of the system through the relation

$$d = \frac{M_1 m_1 + M_2 m_2 + 1}{\frac{m_1}{m_1^{\text{bi}}} \frac{M_1 m_1^{\text{bi}} + 1}{d_1^{\text{bi}}} + \frac{m_2}{m_2^{\text{bi}}} \frac{M_2 m_2^{\text{bi}} + 1}{d_2^{\text{bi}}}} \quad (39)$$

where M_i is the molar mass of salt S_i ($\text{kg} \cdot \text{mol}^{-1}$), d is the density of the mixture, and d_i^{bi} is the density of S_i solution in binary solutions with the same water activity as the ternary mixture.

“Simplicity” of solutions has been used and discussed for various ternary and quaternary electrolyte and nonelectrolyte systems^{3,44–48} and also on mixtures including actinide salts.^{1,4,26}

Results and Discussion

1. Application of the BIMSA Theory to Uranyl Binary Salts. This part is aimed at the treatment from the BIMSA of binary data of uranyl nitrate under the solubility limit that can be found in the literature.

Uranyl nitrate binary osmotic coefficients were calculated from the BIMSA theory using optimized microscopic parameters. To ensure the consistency of the BIMSA parameters, especially regarding the $\sigma_+^{(0)}$ parameter which must have a common value for all the salts containing the same cation, uranyl chloride and uranyl perchlorate osmotic coefficients were also fitted. Uranyl perchlorate, chloride, and nitrate osmotic coefficients were taken from Goldberg selection, considering Rob-

TABLE 1: Parameter and Input Data Values of the BIMSA, Retained to Reproduce Uranyl Perchlorate, Chloride, and Nitrate Osmotic Coefficient

salt	max m^a	$\sigma_+^{(0)b}$	$10^3 \sigma^{(1)c}$	$10^2 \alpha^d$	$K_1^0 d$	$K_2^0 d$	AARD (%) ^e
UO ₂ (ClO ₄) ₂	5.5	0.8390	−46.07	18.24	0	0	0.26
UO ₂ Cl ₂	3.0		−49.41	15.76	1.479	0.054	0.73
UO ₂ (NO ₃) ₂	3.2		−48.06	2.76	1.995	0.070	0.36

^a Given in $\text{mol} \cdot \text{kg}^{-1}$. ^b Value in nm. ^c In $\text{nm} \cdot \text{mol}^{-1} \cdot \text{L}$. ^d In $\text{mol}^{-1} \cdot \text{L}$. ^e AARD is the relative deviation for the calculated osmotic coefficients: $\text{AARD}(\%) = (100/N) \sum_{k=1}^N |\Phi_{\text{cal}}(k) - \Phi_{\text{com}}(k)| / \Phi_{\text{com}}(k)$, with N being the number of data points, Φ_{cal} are the calculated osmotic coefficients from the BIMSA, and Φ_{com} are the osmotic coefficients compiled by Goldberg.⁶

inson et al. measurements^{7,8} (up to $3.24 \text{ mol} \cdot \text{kg}^{-1}$ for UO₂(NO₃)₂) but also the most reliable values from other authors.⁴⁹ According to experimental and theoretical results,⁵⁰ for uranyl perchlorate, we assumed that no complexes are formed: $K_1^0 = K_2^0 = 0$.

For comparison of the osmotic coefficients calculated using the BIMSA model with experimental data, the calculated quantities were converted from the McMillan–Mayer to the Lewis–Randall (experimental) reference system⁵¹ by using the procedure described in ref 21. Solution density values were necessary for this transformation and for molal scale to molar scale conversion. Uranyl nitrate density was taken from our selection (part 2). Uranyl chloride density data was taken from Robinson et al.,⁸ who are, to our knowledge, the only authors proposing experimental densities at high concentration for this system. In the case of uranyl perchlorate, densities were empirically estimated from uranyl chloride⁸

$$d = d_0 + 371 \frac{C}{C_0} - 6 \left(\frac{C}{C_0} \right)^{3/2} \quad (40)$$

where $C_0 = 1 \text{ mol} \cdot \text{L}^{-1}$ and d_0 is the density of water at 25 °C ($d_0 = 997.075 \text{ kg} \cdot \text{m}^{-3}$).

First, the uranyl perchlorate osmotic coefficient was fitted up to the maximum concentration proposed by Goldberg.⁶ Considering our assumptions ($K_1^0 = K_2^0 = 0$), the fit was made with only three adjustable parameters ($\sigma_+^{(0)}$, $\sigma^{(1)}$, and α) and led to very satisfying results: the relative deviation (AARD) was very low (0.26%) and the fit was made up to $5.5 \text{ mol} \cdot \text{kg}^{-1}$. The resulting $\sigma_+^{(0)}$ value reported in Table 1, without any further modification, was used as an input parameter for the uranyl nitrate and chloride osmotic coefficients.

For the associating salt UO₂Cl₂, constants K_1^0 and K_2^0 selected from OECD¹⁰ were used as an input data: $K_1^0 = 1.479 \text{ mol}^{-1} \cdot \text{L}$ and $K_2^0 = 0.054 \text{ mol}^{-1} \cdot \text{L}$. This procedure minimizes the number of adjustable parameters: a two-parameter fit ($\sigma^{(1)}$ and α) leads to a satisfying AARD of 0.73% up to a concentration of $2.6 \text{ mol} \cdot \text{L}^{-1}$ (corresponding to a molality of $3.0 \text{ mol} \cdot \text{kg}^{-1}$), close to the maximum concentration tabulated by Goldberg.⁶

Finally, for uranyl nitrate UO₂(NO₃)₂, $K_1^0 = 1.995 \text{ mol}^{-1} \cdot \text{L}$ selected from OECD¹⁰ was used as an input parameter (as $\sigma_+^{(0)}$). The formation of 1–2 uranyl nitrate complexes is expected.^{24,52} Besides, according to the OECD, no reliable K_2^0 value for uranyl nitrate has been retained. For our calculation, we observed that fixing a K_2^0 value comprised between 0.0 and $0.2 \text{ mol}^{-1} \cdot \text{L}$ leads to good results (AARD close to 0.36%).

The optimized BIMSA parameters and deviation between calculated and osmotic coefficients compiled by Goldberg⁶ are shown in Table 1 and Figure 1. Regarding uranyl nitrate, results obtained by fixing a K_2^0 value of $0.070 \text{ mol}^{-1} \cdot \text{L}$ are reported.

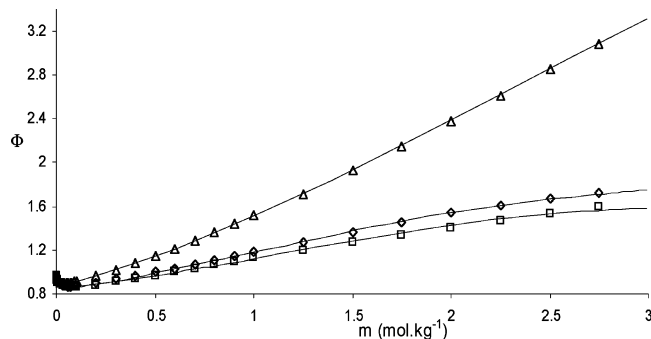


Figure 1. Osmotic coefficients calculated from the BMSA (—, this work) and data compiled by Goldberg⁶ (Δ , $\text{UO}_2(\text{ClO}_4)_2$, \square , UO_2Cl_2 , and \diamond , $\text{UO}_2(\text{NO}_3)_2$).

TABLE 2: Water Activities of $\text{UO}_2(\text{NO}_3)_2/\text{HNO}_3/\text{H}_2\text{O}$ Solutions C Resulting from the Mixture of A ($\text{UO}_2(\text{NO}_3)_2/\text{HNO}_3/\text{H}_2\text{O}$, $m_{\text{UO}_2(\text{NO}_3)_2} = 2.746 \text{ mol}\cdot\text{kg}^{-1}$, and $m_{\text{HNO}_3} = 1.744 \text{ mol}\cdot\text{kg}^{-1}$) and B ($\text{HNO}_3/\text{H}_2\text{O}$ and $m_{\text{HNO}_3} = 7.097 \text{ mol}\cdot\text{kg}^{-1}$)

X_A^a	$a_w (\pm 0.003)$
0	0.706
0.333	0.704
0.5	0.705
0.667	0.705
0.75	0.706
0.8	0.704
1	0.705

^a X_A is the volume ratio of A in the final mixture.

We see that the osmotic coefficients calculated from the BMSA provide satisfying results, very close to the ones compiled by Goldberg,⁶ up to high concentration. The parameters $\sigma^{(1)}$ and α satisfy the expected conditions: $\sigma^{(1)} < 0$ and $\alpha > 0$.²⁰

It is worth noting that these promising results were obtained with a restricted number of adjustable parameters (only two in the case of uranyl chloride), a common $\sigma_+^{(0)}$ value and a simple procedure. The BMSA theory, when taking into account 1–2 complex formation, is therefore compatible with presumably reliable association constants found in the literature.

2. “Real” and “Fictive” $\text{UO}_2(\text{NO}_3)_2/\text{H}_2\text{O}$ Binary Data. We checked that, for a given concentration range, the ternary system $\text{UO}_2(\text{NO}_3)_2/\text{HNO}_3/\text{H}_2\text{O}$ satisfies the “simple” solution concept.

“Simplicity” of other mixtures containing uranyl nitrate has been studied by Kirgintsev et al.⁴⁶ It was reported that some of them, such as $\text{UO}_2(\text{NO}_3)_2/\text{RbNO}_3/\text{H}_2\text{O}$, even at moderate concentration, do not satisfy the “simple” criterion. In such a system, the ZSR relationship cannot be used: instead, a modified ZSR using an empirical parameter is required.⁴⁶

The “simplicity” of the ternary system $\text{UO}_2(\text{NO}_3)_2/\text{HNO}_3/\text{H}_2\text{O}$ was examined for a water activity lower than its value at the $\text{UO}_2(\text{NO}_3)_2/\text{H}_2\text{O}$ solubility limit (estimated from ref 6). More precisely, a given $\text{UO}_2(\text{NO}_3)_2/\text{HNO}_3/\text{H}_2\text{O}$ system (A), in which the concentrations were $m_{\text{UO}_2(\text{NO}_3)_2} = 2.746 \text{ mol}\cdot\text{kg}^{-1}$ and $m_{\text{HNO}_3} = 1.744 \text{ mol}\cdot\text{kg}^{-1}$, was prepared and its water activity was measured, giving $a_w = 0.705 \pm 0.003$. This ternary system was mixed with $\text{HNO}_3/\text{H}_2\text{O}$ solutions (B) of very close water activity: for $m_{\text{HNO}_3} = 7.097 \text{ mol}\cdot\text{kg}^{-1}$, we found $a_w = 0.706 \pm 0.003$.

The measured water activities of the resulting ternary solutions (C) are shown in Table 2, as a function of the volume ratio of initially introduced (A) and (B) in the mixture. Regardless of the proportion and considering our experimental uncertainty (which is ± 0.003), the water activity is constant.

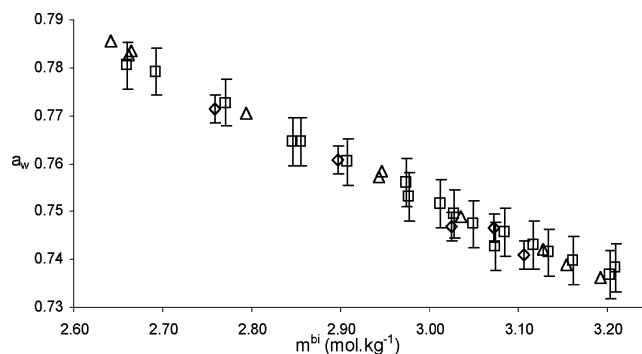


Figure 2. Water activities for $\text{UO}_2(\text{NO}_3)_2$: \diamond , this work, from measurements on the binary system $\text{UO}_2(\text{NO}_3)_2/\text{H}_2\text{O}$; \square , this work, calculated from measurements on the ternary system $\text{UO}_2(\text{NO}_3)_2/\text{HNO}_3/\text{H}_2\text{O}$; Δ , Robinson et al. values.⁸

These results show that, even for high-concentration ternary mixtures and low water activity (around 0.705), the ternary system $\text{UO}_2(\text{NO}_3)_2/\text{HNO}_3/\text{H}_2\text{O}$ obeys the Zdanovskii–Stokes–Robinson rule.

Since the chemical behavior of the ternary system $\text{UO}_2(\text{NO}_3)_2/\text{HNO}_3/\text{H}_2\text{O}$ is very close to the chemical behavior of another ternary system containing an actinyl(VI) ion $\text{AnO}_2(\text{NO}_3)_2/\text{HNO}_3/\text{H}_2\text{O}$, such ternary systems are expected to exhibit a “simple” behavior up to high concentration. In other words, the ZSR relation is expected to be respected on actinyl(VI) mixtures $\text{AnO}_2(\text{NO}_3)_2/\text{HNO}_3/\text{H}_2\text{O}$, without use of empirical parameters. This aspect could be important to consider and could simplify noticeably future work on actinyl(VI) other than uranyl. The ternary system $\text{UO}_2(\text{NO}_3)_2/\text{HNO}_3/\text{H}_2\text{O}$ satisfying the “simple” criterion down to low water activity, the validation of the method, consisting of obtaining “fictive” binary data from ternary data, was continued.

In a second step, we checked whether our binary $\text{UO}_2(\text{NO}_3)_2/\text{H}_2\text{O}$ water activity values were in agreement with the water activities selected by Goldberg.⁶ As previously mentioned, his selected data was mostly based on Robinson et al. measurements.^{7,8} We especially focused on the water activity range 0.74–0.77 corresponding to a binary solution $\text{UO}_2(\text{NO}_3)_2/\text{H}_2\text{O}$ close to its solubility limit. Our binary water activities were issued from direct measurements or from measurements on the ternary system $\text{UO}_2(\text{NO}_3)_2/\text{HNO}_3/\text{H}_2\text{O}$. In the latter case, as a consequence of the “simplicity” which was verified in the first step, the “inverse” Zdanovskii relation derived from eq 38 was used to obtain from ternary data and binary data of the same water activity

$$m_{\text{UO}_2(\text{NO}_3)_2}^{\text{bi}} = \frac{m_{\text{UO}_2(\text{NO}_3)_2}}{1 - \frac{m_{\text{HNO}_3}}{m_{\text{HNO}_3}^{\text{bi}}}} \quad (41)$$

As in eq 38, m_i is the molality of electrolyte i in the mixture and m_i^{bi} is the molality of the electrolyte i in a binary solution of the same water activity as the mixture, a_w . The quantity $m_{\text{HNO}_3}^{\text{bi}}$, necessary for the calculation of $m_{\text{UO}_2(\text{NO}_3)_2}^{\text{bi}}$, is taken from ref 26.

Results obtained from our measurements are shown in Table S1.

Figure 2 compares our binary data with water activities calculated from Robinson et al. osmotic coefficients measurements⁸ using eq 1, in a restricted concentration range for better clarity.

Our measured water activities are in very good agreement with Robinson et al. values⁸ if we take into consideration our experimental uncertainty (which is ± 0.003 , for water activities obtained from measurements on binary systems and which can be assessed as ± 0.005 for water activities calculated from measurements on ternary systems) from 1.9 mol·kg⁻¹, up to the saturation limit (3.24 mol·kg⁻¹). Apelblat et al. made a single water activity measurement at 25 °C at a concentration of 3.323 mol·kg⁻¹, considered by the authors as the saturation limit.⁹ These authors obtained $a_w = 0.698$. Apelblat et al.'s water activity and their proposed saturation limit value seem inaccurate.

The results shown in this part confirm the “simplicity” of the ternary $\text{UO}_2(\text{NO}_3)_2/\text{HNO}_3/\text{H}_2\text{O}$ system. The procedure consisting of obtaining binary data from water activities of the ternary system $\text{UO}_2(\text{NO}_3)_2/\text{HNO}_3/\text{H}_2\text{O}$ seems to provide results close to those reported by Robinson et al.⁸

Most of the ternary $\text{UO}_2(\text{NO}_3)_2/\text{HNO}_3/\text{H}_2\text{O}$ and the binary $\text{UO}_2(\text{NO}_3)_2/\text{H}_2\text{O}$ solutions prepared in the previous part were used for density measurements at high concentration. This also permitted us to provide data in a concentration range where density data is scarce.

The results are shown in Table S1. In the case of binary densities calculated from ternary densities, eq 39 could be used, since HNO_3 density variation with concentration can be found in ref 26 as HNO_3 water activity varies with concentration. The molar masses necessary for using eq 39 are $M_{\text{UO}_2(\text{NO}_3)_2} = 394.04 \times 10^{-3} \text{ kg}\cdot\text{mol}^{-1}$ and $M_{\text{HNO}_3} = 63.01 \times 10^{-3} \text{ kg}\cdot\text{mol}^{-1}$.

Comparison of our binary data from direct measurements and binary data calculated from ternary measurements using eq 39 with literature was made (Figure S1).

Although somewhat inaccurate and scattered, due to the likely conjunction of various uncertainties, the binary densities obtained from measurements on the ternary system provide satisfying results that are compatible with “directly” measured densities from the $\text{UO}_2(\text{NO}_3)_2/\text{H}_2\text{O}$ binary system. These results can be regarded as a justification for using the concept of “simple” solutions for density calculations of the $\text{UO}_2(\text{NO}_3)_2/\text{HNO}_3/\text{H}_2\text{O}$ system.

As regards directly measured binary uranyl nitrate densities, our measurements and the values from different authors provide compatible results (with relative deviations always less than 1%). Nevertheless, some discrepancies seem to exist between all the existing values, when one takes into account the very low uncertainty of direct binary density measurements.

Three authors propose values at high concentration (higher than 1 mol·kg⁻¹). Values from Krigen¹⁶ at high concentration are very close to our densities. It has also been noticed that Burger¹⁴ values are scattered. The data of Kapustinsky and Lipilina^{13,15} are referred.^{53–55} However, their values seem overestimated at concentrations higher than 2.0 mol·kg⁻¹. As a consequence, we did not take into account in our selected values Kapustinsky and Lipilina measurements for concentrations higher than 2.0 mol·kg⁻¹.

Our selected data under the solubility limit, including our densities measured on the binary system $\text{UO}_2(\text{NO}_3)_2/\text{H}_2\text{O}$, were fitted according to the following relation

$$d = d_0 + A_1 \frac{m}{m_0} + A_2 \left(\frac{m}{m_0} \right)^2 + A_3 \left(\frac{m}{m_0} \right) + A_4 \left(\frac{m}{m_0} \right)^4 + A_5 \left(\frac{m}{m_0} \right)^5 \quad (42)$$

with m being the concentration in mol·kg⁻¹, $m_0 = 1 \text{ mol}\cdot\text{kg}^{-1}$,

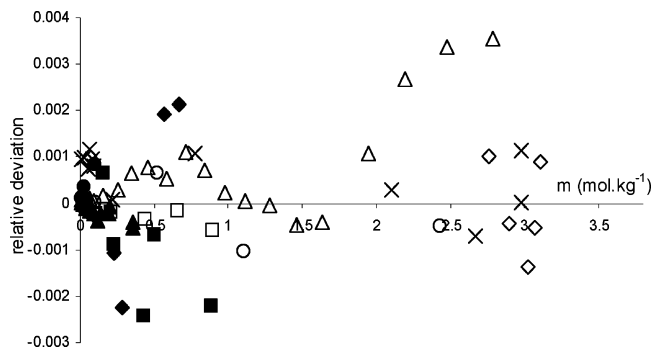


Figure 3. Relative deviation of experimental binary densities of $\text{UO}_2(\text{NO}_3)_2$ with fitted densities: \diamond , this work, from measurements on the system $\text{UO}_2(\text{NO}_3)_2/\text{H}_2\text{O}$; \triangle , Kapustinsky and Lipilina;¹⁵ \blacktriangle , Kapustinsky and Lipilina;¹³ \circ , Burger et al.;¹⁴ \times , Krigen;¹⁶ \bullet , Gomez et al.;¹¹ \blacksquare , Grant et al.;¹² \square , Brown et al.;¹⁷ \blacklozenge , Alem et al.¹⁸

d_0 being the density of water at 25 °C, $d_0 = 997.075 \text{ kg}\cdot\text{m}^{-3}$, and the density parameters for eq 9: $A_1 = 3.26595 \times 10^2$, $A_2 = -3.91187 \times 10^1$, $A_3 = 2.14874 \times 10^1$, $A_4 = -1.01142 \times 10^1$, and $A_5 = 1.58137$.

Figure 3 shows the relative deviations of our retained values, with our fitted density (the selected values were chosen so that the absolute value of the relative deviations were lower than 0.25%). This figure shows also all the densities from Kapustinsky and Lipilina,^{13,15} including the nonselected values at concentrations higher than 2.0 mol·kg⁻¹.

The previous results showed that the procedure consisting of assuming simplicity of the ternary system $\text{UO}_2(\text{NO}_3)_2/\text{HNO}_3/\text{H}_2\text{O}$ and obtaining $\text{UO}_2(\text{NO}_3)_2/\text{H}_2\text{O}$ binary data from the ternary system provided reliable water activities and densities.

Therefore, measurements were made on ternary solutions of lower water activities than the one corresponding to $\text{UO}_2(\text{NO}_3)_2/\text{H}_2\text{O}$ at saturation in order to provide “fictive” binary data, by using eq 41.

Also, ternary $\text{UO}_2(\text{NO}_3)_2/\text{HNO}_3/\text{H}_2\text{O}$ solutions densities were measured. As previously, binary densities were calculated from ternary densities by using eq 39. The main difference is that, in the present case, the binary densities are “fictive”.

For a given range of water activity, to provide more reliable “fictive” binary data, it was necessary to prepare ternary solutions close to the solubility limit. Actually, this procedure allows one to have the highest $m_{\text{UO}_2(\text{NO}_3)_2}/m_{\text{HNO}_3}$ ratio, resulting in a more reliable calculated molality (mol·kg⁻¹) of $\text{UO}_2(\text{NO}_3)_2$ in the “fictive” binary solution of the same activity as the ternary mixture, $m_{\text{UO}_2(\text{NO}_3)_2}^{\text{bi}}$. In practice, conducting experiments on solutions close to the solubility limit was one of the difficulties of this part.

The low value of the $m_{\text{UO}_2(\text{NO}_3)_2}/m_{\text{HNO}_3}$ ratio when working with low water activity solutions has the consequence that the highest water activity solutions provide more reliable “fictive” data than the lowest water activity solutions.

Results obtained from our measurements for “fictive” binary data from 3.240 mol·kg⁻¹ to 6.867 mol·kg⁻¹ are shown in Table S2.

As quoted above, Robinson and Lim do not mention the fact that their most concentrated solutions (up to 5.511 mol·kg⁻¹)⁸ were highly above the solubility limit (3.24 mol·kg⁻¹). Even if the isopiestic technique used by the authors has already provided oversaturated solutions,¹⁰ their data for oversaturated uranyl solutions cannot be considered as thermodynamic data of stable solutions. Furthermore, it is important to note that Robinson and Lim⁸ made two series of measurements including sets of data in which concentration was higher than the solubility limit.

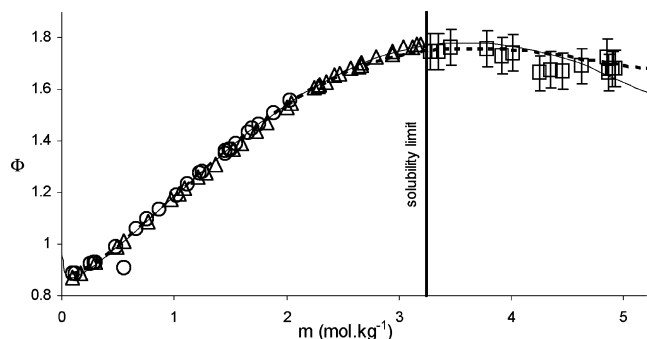


Figure 4. Uranyl nitrate osmotic coefficients: full line, calculated from the BMSA; dotted line, calculated from the NIST equation; Δ , experimental, Robinson, and Lim⁸ for $m < 3.24 \text{ mol}\cdot\text{kg}^{-1}$; \circ , experimental, Robinson, Wilson, and Ayling;⁷ \square , “fictive” from experimental water activities, this work.

One of these two series, which included two oversaturated measurements ($3.401 \text{ mol}\cdot\text{kg}^{-1}$ and $3.587 \text{ mol}\cdot\text{kg}^{-1}$), led to values that are different from those of the other series (from $2.245 \text{ mol}\cdot\text{kg}^{-1}$ to $5.511 \text{ mol}\cdot\text{kg}^{-1}$). This fact suggests that the supersaturated data from Robinson and Lim should be considered with caution.

A fit of the binary $\text{UO}_2(\text{NO}_3)_2$ osmotic coefficients from Robinson et al.^{7,8} was performed for $m < 3.24 \text{ mol}\cdot\text{kg}^{-1}$ and from our “fictive” water activities converted to osmotic coefficients using eq 1 for higher concentration. Osmotic coefficient variation with concentration can be expressed according to eq 43 recommended by the NIST

$$\Phi = 1 - \left\{ \frac{1.7625 \cdot 2}{\left(\frac{I}{m_0}\right) a^3} \left[\left(1 + a \sqrt{\frac{I}{m_0}}\right) - 2 \ln \left(1 + a \sqrt{\frac{I}{m_0}}\right) - \frac{1}{1 + a \sqrt{\frac{I}{m_0}}} \right] - \frac{1}{2} b \frac{m}{m_0} - \frac{2}{3} c \left(\frac{m}{m_0}\right)^2 - \frac{3}{4} d \left(\frac{m}{m_0}\right)^3 - \frac{4}{5} e \left(\frac{m}{m_0}\right)^4 - \frac{5}{6} f \left(\frac{m}{m_0}\right)^5 \right\} \quad (43)$$

with m being the concentration in $\text{mol}\cdot\text{kg}^{-1}$, $m_0 = 1 \text{ mol}\cdot\text{kg}^{-1}$, I the ionic strength of the binary solution, and the osmotic coefficient parameters for eq 43: $a = 2.18364$, $b = 2.17731 \times 10^{-1}$, $c = 4.33070 \times 10^{-1}$, $d = -1.68928 \times 10^{-1}$, $e = 2.41498 \times 10^{-2}$, and $f = -1.20740 \times 10^{-3}$.

Osmotic coefficients fitted from the NIST equation are plotted in Figure 4.

Considering this part, we have binary uranyl nitrate water activities from 1 down to 0.58, which are essential for calculating mixtures of uranyl nitrate properties. We have also densities from 997 to $2354 \text{ kg}\cdot\text{m}^{-3}$ which can be used as an example, for molar and molal scales conversion.

3. Capability of the BMSA Theory for Extrapolating Binary Uranyl Nitrate Osmotic Coefficients. Uranyl nitrate osmotic coefficients or water activities were calculated from the BMSA theory up to concentrations higher than the solubility limit ($3.24 \text{ mol}\cdot\text{kg}^{-1}$) using the parameter values ($\sigma_+^{(0)}$, K_1^0 , K_2^0 , $\sigma^{(1)}$, and α) for uranyl nitrate shown in Table 1, optimized only under the solubility limit. We noticed that, above the solubility limit and up to $5 \text{ mol}\cdot\text{kg}^{-1}$, with the use of the input data values corresponding to Table 1, our “fictive” binary water activities were reproduced within reasonable accuracy (Figure 4). Actually, BMSA parameters optimized below the solubility

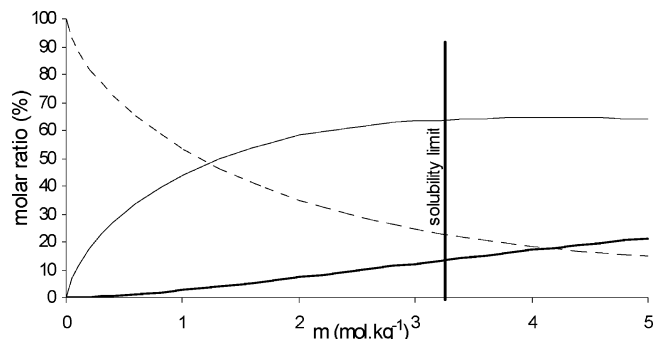


Figure 5. Proportion calculated from the BMSA of free (---), 1–1 complex (—), and 1–2 complex (···) uranyl in a $\text{UO}_2(\text{NO}_3)_2/\text{H}_2\text{O}$ binary system. Calculations were made with the selected parameters from Table 1.

limit ($m < 3.24 \text{ mol}\cdot\text{kg}^{-1}$) were appropriate for osmotic coefficients calculation above this value. The agreement was equivalent to the empirical equation of the NIST form (eq 43) fitted in the whole “fictive” concentration range (Figure 4). This result shows that osmotic coefficients obtained from the BMSA model optimized in a given concentration range may be extrapolated to higher concentrations. This capability of extrapolation of the BMSA model constitutes a very interesting and seemingly uncommon feature of this theory. This feature can be attributed to the fact that 1–1 and 1–2 complex formation is correctly taken into account by the model, which is of great importance for $\text{UO}_2(\text{NO}_3)_2$ highly concentrated or “fictive” solutions, considering the expected high proportion of associated species. Figure 5, showing the ratio of complexed and uncomplexed uranyl for uranyl nitrate using the parameters shown in Table 1, confirms the fact that 1–2 complexes are formed in appreciable proportions at high concentration, despite a low K_2^0 value.

If we consider the anion–cation proportion in uranyl chloride and nitrate binary solutions, and the fact that the association constant of the 1–3 complex should be weaker than K_2^0 ,⁵² it does not seem necessary to take into account such complexes for the modeling of these binary solutions.

For molalities higher than $5 \text{ mol}\cdot\text{kg}^{-1}$, deviation between osmotic coefficients predicted from the BMSA and osmotic coefficients issued from our “fictive” binary data is highly pronounced. It seems that the different approximations made within the model or the concept of “simple” solutions are not verified for very high concentrations.

Conclusion

The present work shows that the convenient concept of “simple” solutions is applicable to the ternary system $\text{UO}_2(\text{NO}_3)_2/\text{HNO}_3/\text{H}_2\text{O}$ over a wide range of water activity. As a consequence, from $\text{UO}_2(\text{NO}_3)_2/\text{HNO}_3/\text{H}_2\text{O}$ water activity and density measurements in a seldom studied concentration range, “fictive” binary data of the system $\text{UO}_2(\text{NO}_3)_2/\text{H}_2\text{O}$ was established. These data provide useful information for many thermodynamic studies of mixtures containing uranyl nitrate of water activity lower than 0.74. Furthermore, literature binary data for uranyl nitrate salts solutions under and above the solubility limit have been checked with accuracy, and it seems that some usually referred density and osmotic coefficient values should be considered with caution.

Also, the BMSA theory taking into account 1–1 and also 1–2 stoichiometry complexes was used to reproduce experimental binary uranyl nitrate and also perchlorate and chloride salts osmotic coefficients up to high concentration, with the use

of self-consistent parameters that have some microscopic physical meaning. Calculations were performed with the use of a restricted number of adjustable parameters: most of the association constants used as input parameters were taken from OECD selected data when available. This procedure led to a very small discrepancy between experimentally measured data and those deduced from the BIMSA. Therefore the theory, by properly taking into account 1–1 and 1–2 complex formation, could be considered as a tool suited for binary actinyl(VI) salts solutions studies.

The capability of the BIMSA to extrapolate osmotic coefficients to higher concentration has also been shown: from microscopic parameters optimized on Goldberg uranyl salts osmotic coefficients under solubility limit, our previously obtained “fictive” binary uranyl nitrate osmotic coefficients were recovered. This feature is interesting considering the difficulty of obtaining high concentration actinides solutions. As a consequence, in further work, we expect to use the BIMSA theory for predicting from binary water activities of uranyl nitrate, binary water activities of another actinyl(VI) nitrate, even for “fictive” or highly concentrated solutions.

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Supporting Information Available: Figure showing binary densities of $\text{UO}_2(\text{NO}_3)_2$, and tables showing water activities and densities of binary $\text{UO}_2(\text{NO}_3)_2/\text{H}_2\text{O}$ and ternary $\text{UO}_2(\text{NO}_3)_2/\text{HNO}_3/\text{H}_2\text{O}$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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