

Experimental Determination of Water Activity for Binary Aqueous Cerium(III) Ionic Solutions: Application to an Assessment of the Predictive Capability of the Binding Mean Spherical Approximation Model

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This work is aimed at a description of the thermodynamic properties of actinide salt solutions at high concentration. The predictive capability of the binding mean spherical approximation (BIMSA) theory to describe the thermodynamic properties of electrolytes is assessed in the case of aqueous solutions of lanthanide(III) nitrate and chloride salts. Osmotic coefficients of cerium(III) nitrate and chloride were calculated from other lanthanide(III) salts properties. In parallel, concentrated binary solutions of cerium nitrate were prepared in order to measure experimentally its water activity and density as a function of concentration, at 25 °C. Water activities of several binary solutions of cerium chloride were also measured to check existing data on this salt. Then, the properties of cerium chloride and cerium nitrate solutions were compared within the BIMSA model. Osmotic coefficient values for promethium nitrate and promethium chloride given by this theory are proposed. Finally, water activity measurements were made to examine the fact that the ternary system $\text{Ce}(\text{NO}_3)_3/\text{HNO}_3/\text{H}_2\text{O}$ and the quaternary system $\text{Ce}(\text{NO}_3)_3/\text{HNO}_3/\text{N}_2\text{H}_5\text{NO}_3/\text{H}_2\text{O}$ may be regarded as “simple solutions” (in the sense of Zdanovskii and Mikulin).

Introduction

Since aqueous solutions of lanthanides(III) and actinides(III) exhibit close thermodynamic properties,¹ any theory suitable for the former may be expected to give predictions for the properties of the latter. This approach is all the more interesting since actinides, for example, americium(III) and curium(III) nitrate solutions, can be hardly manipulated at high concentration due to their radioactivity. Furthermore, the thermodynamic properties of the two salts at high concentration are of great interest for the improvement of spent fuel treatment by means of liquid–liquid extraction.

Besides, with the use of appropriate protective equipment, plutonium(III) nitrate salt, due to a moderate radioactivity of ²³⁹Pu or ²⁴²Pu isotopes as compared to americium or curium isotopes, can be studied experimentally up to high concentration. This means that plutonium(III) nitrate salt solutions are the closest systems to americium(III) or curium(III) nitrate salts solutions that can be experimentally studied, if one is interested in the properties of the latter two salts in concentrated media. However, to avoid plutonium(III) hydrolysis and oxidation, an appreciable amount of nitric acid and reduction agent (typically hydrazinium nitrate) must be introduced in the medium. Therefore, plutonium(III) nitrate binary data cannot be measured directly. Instead, measurements must be made for a quaternary mixture such as $\text{Pu}(\text{NO}_3)_3/\text{HNO}_3/\text{N}_2\text{H}_5\text{NO}_3/\text{H}_2\text{O}$. Nevertheless, “fictive” binary data for an aqueous solution of $\text{Pu}(\text{NO}_3)_3$ may be deduced from the quaternary system data, for example, by using the model of “simple” solutions of Zdanovskii and

Mikulin,^{2–4} as was done previously for other actinide(IV) mixtures.⁵

We have seen that the BIMSA (binding mean spherical approximation), based on the Wertheim formalism, can very well reproduce osmotic and activity coefficients, up to high concentration, for a wide variety of aqueous lanthanide(III) salts.⁶ Thus, it was shown to be a potentially powerful tool for predicting osmotic and activity coefficients of actinide(III) salts. In terms of ionic size, the lanthanide(III) salts that are the analogues of the more interesting actinide(III) salts for nuclear spent fuel treatment (i.e., americium(III), curium(III), and plutonium(III) salts) are located at the beginning of the series as shown in Table 1. Therefore, within the lanthanide series, we especially focus on the lanthanides situated between lanthanum and samarium.

Even if osmotic coefficients have been accurately measured by Rard et al. and Spedding et al.^{8–15} for many solutions of nitrate, chloride, and perchlorate lanthanide(III) salts, there is a lack of data in the beginning of the series. As a radioelement with only short-lived isotopes, data for promethium solutions are almost impossible to obtain. Amazingly, values related to cerium salts are also very scarce. To our knowledge, the only cerium salt osmotic coefficients and density measurements were made by Mason^{16,17} for cerium(III) chloride. No cerium(III) nitrate osmotic coefficient, nor density, could be found. Regarding cerium(III) chloride experimental results, surprisingly, according to Mason, some values seem to be shifted in the lanthanide series at several concentrations: osmotic coefficients (respectively, water activities) are significantly higher (respectively, lower) than the praseodymium(III) chloride osmotic coefficient (respectively, water activity), which is opposite to the general trend observed within the lanthanide series. On the

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TABLE 1: Ionic Radii of Lanthanides(III) and Actinides(III)^a

M ³⁺ ion	ionic radii (pm)	M ³⁺ ion	ionic radii (pm)
La ³⁺	103.2	Ac ³⁺	112
Ce ³⁺	101.0	Th ³⁺	
Pr ³⁺	99.0	Pa ³⁺	104.0
Nd ³⁺	98.3	U ³⁺	102.5
Pm ³⁺	97.0	Np ³⁺	101.0
Sm ³⁺	95.8	Pu ³⁺	100.0
Eu ³⁺	94.7	Am ³⁺	97.5
Gd ³⁺	93.8	Cm ³⁺	97
Tb ³⁺	92.3	Bk ³⁺	96.0
Dy ³⁺	91.2	Cf ³⁺	95.0
Ho ³⁺	90.1	Es ³⁺	
Er ³⁺	89.0	Fm ³⁺	
Tm ³⁺	88.0	Md ³⁺	
Yb ³⁺	86.8	No ³⁺	
Lu ³⁺	86.1	Lr ³⁺	

^a Data are from ref 7.

other hand, no difference has been observed when comparing the thermodynamic properties of cerium(III) solutions ($Z = 58$) with those of the closest lanthanides (lanthanum salts, $Z = 57$ and praseodymium salts, $Z = 59$)^{18–20} at moderate concentration.

The purpose of this paper is 3-fold.

The first aim of this work was to examine whether cerium(III) solutions exhibit abnormal behavior within the lanthanide series. As a consequence, we made experimental acquisition of the cerium nitrate solution density and water activity over a wide range of concentrations (from 0.84 to 4.91 mol·kg⁻¹). Also, the water activity of cerium(III) chloride solutions was studied in the concentration range where experimental values found in the literature^{16,17} seemed to be noticeably different from the “expected” values.

The second aim of this work was to study the predictive capability of the BIMSA model, by comparing the water activities for cerium(III) solutions obtained from the BIMSA theory using model parameters for elements close to cerium, with the experimental activities measured in this work. This may be regarded as a preliminary test before considering the case of actinide(III) solutions. Once the predictive capability of BIMSA theory was demonstrated, we proposed osmotic coefficient values for promethium nitrate and promethium chloride as its first application.

Finally, because in the future we plan to estimate plutonium(III) nitrate “fictive” binary data from data for plutonium(III) quaternary mixtures, as a first approach of the problem, “simplicity” of the ternary system Ce(NO₃)₃/HNO₃/H₂O and of the quaternary system Ce(NO₃)₃/HNO₃/N₂H₅NO₃/H₂O was studied from water activity measurements on these systems. In practice, one says that a ternary mixture S₁/S₂/H₂O satisfies “simple” behavior if, when mixing the binary solutions S₁/H₂O and S₂/H₂O of equal water activity, the water activity of the mixture is unchanged, regardless of the proportions of the two binaries in the mixture. This principle may be extended to the case of quaternary solutions and so on.

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.^{5,21–24}

The density meter was calibrated at a temperature of 25.00 ± 0.02 °C, according to a previously described protocol,²¹ over the range 990–1970 kg·m⁻³.

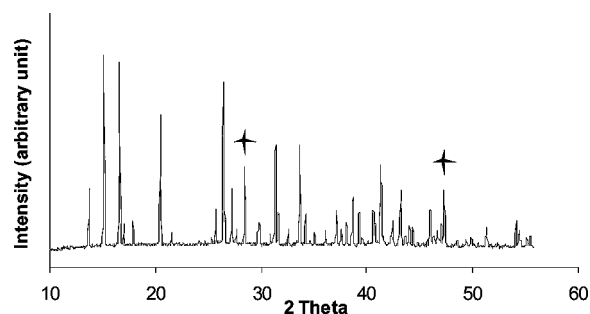


Figure 1. X-ray diffraction plot of a solid cerium nitrate sample before dissolution: (+) denotes diffraction lines from silicon reference material.

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.²¹ The sensors include “eVC-100” acid fume prefilters that allow water activity measurements of high-concentration nitric acid solutions.²¹ The water activity meter was calibrated at 25.0 ± 0.2 °C, considering that the investigation range for a_w was between 0.95 and 0.56. In a first step, the calibration was conducted by using different lithium nitrate solutions as described in ref 21. To minimize the uncertainty of our measurements, the calibration was supplemented by measurements of Pr(NO₃)₃ solutions (Rectapur Prolabo salt) because the data for Pr(NO₃)₃ solutions is well established^{11,25} and its physical-chemical behavior is expected to be close to that of cerium salt solutions.

The measurement of water activities, a_w , of a given binary system (CeX₃, H₂O) leads to the calculation of osmotic coefficient Φ using the relation

$$\Phi = - \frac{1000 \ln a_w}{M_{H_2O} \nu m_{CeX_3}^{bi}} \quad (1)$$

where ν is the total number of ions formed by the complete dissociation of one molecule of the salt, $m_{CeX_3}^{bi}$ is the salt concentration (in mol·kg⁻¹), and M_{H_2O} is the molar mass of water (in g·mol⁻¹).

Merck extra pure cerium(III) nitrate, Prolabo recta pure cerium(III) chloride, and Prolabo titrinorm nitric acid reagents were used. Deionized water was added to the nitric acid solution to prepare diluted nitric acid solutions.

The commercial cerium(III) nitrate pentahydrate (Ce(NO₃)₃·5H₂O) salt was dried for two days under vacuum (0.06 bar) at 50 °C in the presence of silicagel. Immediately after this treatment, the salt was weighed and then it was dissolved by adding a weighed amount of the aqueous diluted nitric acid solution. The cerium nitrate stock solution concentration was $m = 4.908$ mol·kg⁻¹. To confirm the stoichiometry of the solid compound, used to obtain this calculated value, the salt was studied using X-ray diffraction after treatment. The obtained diffraction curve corresponded to the salt in the pentahydrated form,²⁶ satisfying our assumptions (Figure 1). This hydration number could be expected because Mironov et al. showed that, for a given hydrated cerium nitrate crystal, the bonding of the sixth water molecule is weak compared to the bonding of the fifth water molecule.²⁶ Next, several dilutions of the stock solution were implemented by adding a weighed amount of 10⁻³ mol·L⁻¹ nitric acid or 10⁻⁴ mol·L⁻¹ nitric acid when the

concentration of cerium was below $1 \text{ mol}\cdot\text{kg}^{-1}$. It was checked by simple calculations that the nitric acid, introduced in order to maintain a slightly acidic pH value (in the range of 3–4) and to avoid cerium hydrolysis, was sufficiently diluted compared to cerium nitrate so as not to modify concentration, water activity, or density values, within the respective experimental uncertainties. Therefore, the assumption that the prepared cerium nitrate solutions were binary $\text{Ce}(\text{NO}_3)_3/\text{H}_2\text{O}$ solutions was verified.

The variation of cerium(III) nitrate density with salt concentration was established by measuring the densities of 39 solutions of known molalities (calculated from weight measurements). These data were used subsequently in the water activity measurements: the water activities of 20 solutions were determined experimentally and their densities were used to determine their molality. Concentrated cerium(III) chloride solutions were prepared by dissolving a commercial (Prolabo Rectapur) hydrated ($\text{CeCl}_3 \cdot x\text{H}_2\text{O}$) salt. For each solution, density was measured and its concentration was deduced by using density variation as a function of concentration proposed by Mason.¹⁶ It is important to note that, as may be expected, the solution density values obtained by Mason lie between that of praseodymium(III) chloride and that of lanthanum(III) chloride obtained by Spedding et al.,²⁷ with the three density variations being very close.

The “simplicity” of the ternary system $\text{Ce}(\text{NO}_3)_3/\text{HNO}_3/\text{H}_2\text{O}$ and of the quaternary system $\text{Ce}(\text{NO}_3)_3/\text{HNO}_3/\text{N}_2\text{H}_5\text{NO}_3/\text{H}_2\text{O}$ was inspected by mixing, in different proportions, solutions of very close water activity. The concentrations in $\text{mol}\cdot\text{kg}^{-1}$ of the mixed solutions were calculated from the mass measurements of the added solutions and the densities of the initial binary systems.^{21,28}

The study of the ternary system $\text{Ce}(\text{NO}_3)_3/\text{HNO}_3/\text{H}_2\text{O}$ was made by mixing the binary systems $\text{Ce}(\text{NO}_3)_3/\text{H}_2\text{O}$ and $\text{HNO}_3/\text{H}_2\text{O}$. More precisely, once the properties of the binary cerium nitrate stock solution were established, we prepared a nitric acid solution whose water activity was expected to be very close to that of our cerium nitrate stock solution. The molal concentrations of the solutions were estimated from their densities.²¹

For the quaternary system, a ternary system $\text{Ce}(\text{NO}_3)_3/\text{N}_2\text{H}_5\text{NO}_3/\text{H}_2\text{O}$ was prepared and its water activity measured. Another ternary mixture $\text{HNO}_3/\text{N}_2\text{H}_5\text{NO}_3/\text{H}_2\text{O}$ was prepared, and carefully diluted several times, until the measured water activity was very close to the $\text{Ce}(\text{NO}_3)_3/\text{N}_2\text{H}_5\text{NO}_3/\text{H}_2\text{O}$ ternary system. After that, the two considered ternary systems were mixed in different proportions to constitute the quaternary system $\text{Ce}(\text{NO}_3)_3/\text{HNO}_3/\text{N}_2\text{H}_5\text{NO}_3/\text{H}_2\text{O}$.

Theory

In this section, we shortly recall the theoretical aspects used in this work.

The BIMSA theory is one of the several derivatives of the mean spherical approximation (MSA).^{29–34} As for the MSA, the BIMSA takes into account, on a microscopic scale, hard-core repulsion and Coulombic interaction.

The main difference is that BIMSA also considers a short-range potential, responsible for ion pairing. The effect of association is included in the computation of the MSA screening parameter Γ ³⁵. The resulting thermodynamic excess properties can be expressed in a simple way in terms of Γ when using the Wertheim formalism³⁵, in which the thermodynamic association constant K , allows us to take into account all associating mechanisms (Coulombic, covalent). In the present model, one cation and one anion can form a pair, a pair being defined as

two ions of opposite charge being in contact, the proportion of ion pairs and free ions being calculated from K . This formalism was shown to be successful for ionic systems in both the hypernetted chain approximation and the MSA.^{36–40}

The results obtained by means of the BIMSA 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,^{8,9,11–15} a least-squares algorithm of the Marquardt type was used.

The program includes expressions that can be found in refs 6 and 41–43.

As in refs 6 and 41–43, the anion diameter σ_- was kept constant, with values taken from previous work and used for a wide variety of salts: 0.3620 nm for Cl^- and 0.3400 nm for NO_3^- . The diameter of the cation σ_+ and the inverse of the relative permittivity of solution ϵ^{-1} were taken as a linear function of the salt concentration C_s (in $\text{mol}\cdot\text{L}^{-1}$)

$$\sigma_+ = \sigma_+^{(0)} + \sigma^{(1)} C_s \quad (2)$$

$$\epsilon^{-1} = \epsilon_w^{-1} (1 + \alpha C_s) \quad (3)$$

with ϵ_w the relative permittivity of pure solvent ($\epsilon_w = 78.3$ for water). These equations introduce two adjustable parameters $\sigma^{(1)}$ and α that are characteristic of the electrolyte, while $\sigma_+^{(0)}$, the cation diameter at infinite dilution, is characteristic of the considered cation. It must have a common value for all salts (in the present work chloride and nitrate) containing the same cation. As in ref 6, $\sigma_+^{(0)}$ was refined in a first step. Then, to have a more accurate set of parameters, the association constant K was refined. Finally $\sigma^{(1)}$ and α were adjusted using the Marquardt least-squares algorithm to fit existing experimental osmotic coefficients.

Besides, the simple solution model was utilized. A basic equation in this model is the Zdanovskii–Stokes–Robinson relation (ZSR rule) connecting the concentrations of the constituent electrolytes with their concentrations in the binary solutions of the same water activity⁴⁴

$$\sum_{i=1}^n \frac{m_i}{m_i^{\text{bi}}} = 1 \quad (4)$$

$$a_w = \text{constant}$$

where m_i is the molality (in $\text{mol}\cdot\text{kg}^{-1}$) of electrolyte i in the mixture and m_i^{bi} is the molality ($\text{mol}\cdot\text{kg}^{-1}$) of electrolyte i in a binary solution of the same water activity as the mixture, a_w .

Ryazanov and Vdovenko demonstrated that, for a given mixture satisfying the simple solution criterium, binary data such as density and water activity can easily be deduced from data for the ternary or quaternary systems.²¹ “Simplicity” of solutions has been used and discussed for different ternary and quaternary actinide systems.^{5,21–23}

Results and Discussion

1. Density of Cerium Nitrate Solutions. Two different series of measurements led to the values given in Table S1.

The densities of the samples were measured to within $\pm 8 \times 10^{-2} \text{ kg}\cdot\text{m}^{-3}$. Our density values satisfied the generally admitted idea that the heavier the lanthanide(III) nitrate salt, the higher the density and, for a given concentration, the relations $d(\text{La}(\text{NO}_3)_3) < d(\text{Ce}(\text{NO}_3)_3) < d(\text{Pr}(\text{NO}_3)_3)$ were satisfied within the uncertainty of our measurements (despite a very small

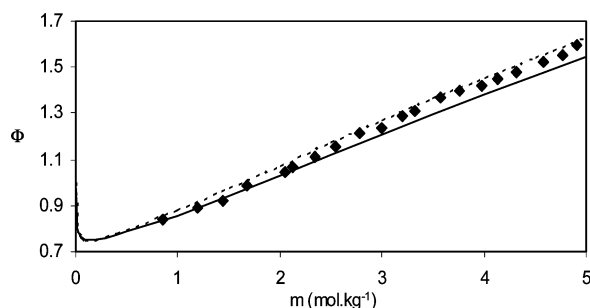


Figure 2. Osmotic coefficient for $\text{Ce}(\text{NO}_3)_3$ (◆, experimental, our values), $\text{La}(\text{NO}_3)_3$ (—), fitted values from Rard and Spedding¹⁴, and $\text{Pr}(\text{NO}_3)_3$ (---), fitted values from Rard¹⁵.

difference between the densities of lanthanum nitrate and praseodymium nitrate solutions).

This set of data was fitted to an empirical equation of the same form as in ref 25 for lanthanide nitrate salts, namely

$$d = d_0 + A_1 \frac{m}{m_0} + A_2 \left(\frac{m}{m_0} \right)^{3/2} + A_3 \left(\frac{m}{m_0} \right)^2 + A_4 \left(\frac{m}{m_0} \right)^{5/2} + A_5 \left(\frac{m}{m_0} \right)^3 + A_6 \left(\frac{m}{m_0} \right)^{7/2} \quad (5)$$

m being the concentration in $\text{mol} \cdot \text{kg}^{-1}$, $m_0 = 1 \text{ mol} \cdot \text{kg}^{-1}$, 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 5: $A_1 = 285.73503$, $A_2 = -51.379538$, $A_3 = 45.036724$, $A_4 = -50.432307$, $A_5 = 19.379740$, and $A_6 = -2.5770791$.

This fit was used for calculating, from density measurements, the molality of the solutions used in the next section.

2. Water Activity of Cerium Nitrate Solutions. The results are given in Table S2, which gives the water activities of the studied solutions, their density, and the corresponding concentration; the uncertainty on water activity measurements is generally of the order of ± 0.003 , but higher (± 0.004) for activity measurements above $a_w = 0.90$, due to water saturation of our apparatus. For the same reason, no measurement was made for water activity higher than 0.95.

For a given concentration, the expected relations $a_w(\text{La}(\text{NO}_3)_3) > a_w(\text{Ce}(\text{NO}_3)_3) > a_w(\text{Pr}(\text{NO}_3)_3)$ were satisfied within experimental uncertainty.

The water activities could be converted to osmotic coefficient values using eq 1. Figure 2 compares, in the studied concentration range, osmotic coefficients deduced from our experimental values with fitted osmotic coefficient values from^{14,15} the closest salts to cerium nitrate: lanthanum and praseodymium nitrates. Cerium nitrate osmotic coefficient values seem slightly closer to lanthanum nitrate than to praseodymium nitrate at concentrations lower than $2.5 \text{ mol} \cdot \text{kg}^{-1}$ and vice versa at higher concentrations. However, this observation has to be considered with caution if one takes into account the uncertainty of our measurements.

3. Water Activity of Cerium Chloride Solutions. The fact that our cerium nitrate binary data satisfied the expected relation $a_w(\text{La}(\text{NO}_3)_3) > a_w(\text{Ce}(\text{NO}_3)_3) > a_w(\text{Pr}(\text{NO}_3)_3)$ prompted us to reconsider the data of Mason^{16,17} regarding cerium chloride. As explained before, osmotic coefficients found by Mason for cerium chloride showed an unexpected behavior in comparison to the two closest lanthanide salts, lanthanum chloride and praseodymium chloride. For concentrations higher than $1.5 \text{ mol} \cdot \text{kg}^{-1}$ and up to $2.2 \text{ mol} \cdot \text{kg}^{-1}$, the cerium chloride osmotic coefficients of Mason were significantly higher than those for praseodymium chloride (obtained by Spedding et al.⁹). It is

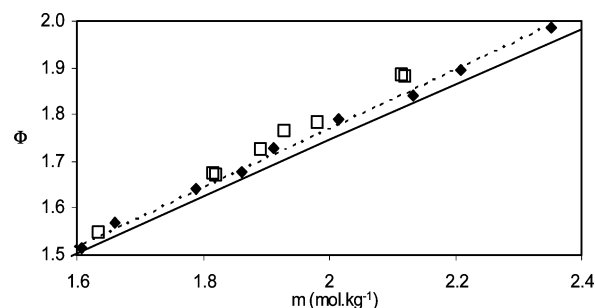


Figure 3. Osmotic coefficient for CeCl_3 (◆, experimental (this work), □, experimental, Mason values),¹⁶ LaCl_3 (---), fitted values from Spedding et al.⁹, and PrCl_3 (---), fitted values from Spedding et al.⁹.

important to note that the same observation was made by comparing Mason's cerium chloride osmotic coefficients with praseodymium chloride osmotic coefficients obtained by the same author.^{16,17} Our measurements were made in order to cover the range of concentration in which Mason's osmotic coefficients appeared to be high.

Cerium chloride density values proposed by Mason¹⁶ were fitted with an empirical equation similar to eq 5, of the same form as in ref 27 for lanthanide chloride salts

$$d = d_0 + B_1 \frac{m}{m_0} + B_2 \left(\frac{m}{m_0} \right)^{3/2} + B_3 \left(\frac{m}{m_0} \right)^2 + B_4 \left(\frac{m}{m_0} \right)^{5/2} + B_5 \left(\frac{m}{m_0} \right)^3 \quad (6)$$

In this case, the density parameters for eq 6 are $B_1 = 253.31579$, $B_2 = -127.24443$, $B_3 = 190.86879$, $B_4 = -134.75979$, and $B_5 = 32.149478$.

Table S3 gives the measured density and water activity, and calculated concentration from density measurement and using eq 6.

Our obtained water activity values for cerium chloride solutions were converted to osmotic coefficients, using eq 1 and were compared to experimental osmotic coefficients obtained by Mason.^{16,17} We also compared our cerium chloride osmotic coefficients with fitted osmotic coefficients obtained by Spedding⁹ for lanthanum and praseodymium chlorides. Our calculated osmotic coefficients are in very good agreement with the results obtained by Spedding et al. for lanthanum chloride and praseodymium chloride. If we take into consideration our experimental uncertainty compared to the very small discrepancy between LaCl_3 and PrCl_3 osmotic coefficients obtained by Spedding et al., our results satisfy the expected relation: $\Phi(\text{LaCl}_3) < \Phi(\text{CeCl}_3) < \Phi(\text{PrCl}_3)$. On the other hand, differences between our osmotic coefficients values and those of Mason for the same cerium chloride salts are noticeable at concentrations higher than $1.6 \text{ mol} \cdot \text{kg}^{-1}$, as shown in Figure 3.

4. Comparison of Experimental Cerium Salts Data with Predicted Data Obtained from the BIMSA Theory. In previous work, the BIMSA theory has been used to reproduce successfully, up to high concentration, osmotic coefficients for a wide range of lanthanide salts. The parameters used for this purpose were found to have plausible adjusted values.⁶ The studied salts included several analogues of the most interesting actinide(III) salts for nuclear spent fuel treatment (in the beginning of the lanthanide series). The adjusted parameters are $\sigma_+^{(0)}$, the hydrated lanthanide(III) diameter at infinite dilution, $\sigma^{(1)}$, reflecting the (hydrated) cation diameter change with concentration, α , reflecting the permittivity change with concentration, and K , the cation–anion association constant. They

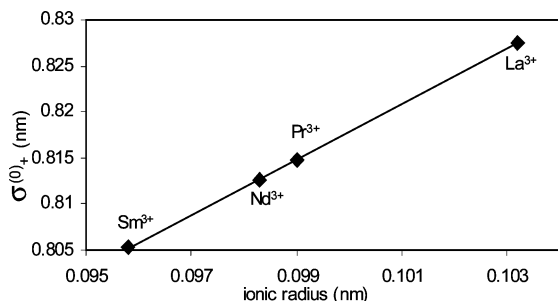


Figure 4. Chosen hydrated cation diameter at infinite dilution from lanthanum to samarium.

exhibit general tendencies within the lanthanide series. In particular, a gap in the properties is observed between lanthanides in the beginning of the series and lanthanides in the end of the series. Besides, in this earlier study, no attempt was made to predict properties of a given salt with use of parameters for other salts.

In this work, the previously proposed parameter values⁶ were slightly modified for lanthanum, praseodymium, neodymium and samarium chloride, and nitrate salts. First, it has been observed that the previously adjusted $\sigma_+^{(0)}$ values vary roughly linearly with the ionic radius of the cation. Therefore, in the present study, the $\sigma_+^{(0)}$ values (in nanometers) were slightly modified so as to better satisfy this feature (Figure 4), which led to the following empirical equation

$$\sigma_+^{(0)} = 3.00573r_i + 0.517260 \quad (7)$$

with r_i being the ionic radius (in nanometers) of the considered cation (La^{3+} , Pr^{3+} , Nd^{3+} , or Sm^{3+}) as given by Shannon.⁷ In a second step, with this $\sigma_+^{(0)}$ value taken for these cations, we fitted the three remaining parameters ($\sigma^{(1)}$, α , and K) to experimental osmotic coefficients.^{8,9,11–15} We observed empirically that the variation of K with ionic radius could be correlated with the cation radius by using simple analytical functions. Therefore, the K values were modified so as to better satisfy the equations

$$K = 1.9701611 \times 10^{-13} r_i^{-13.218335} \quad (8)$$

for the lanthanide nitrate salts and

$$K = 11484.59r_i^2 - 2211.044r_i + 108.9075 \quad (9)$$

for the lanthanide chloride salts.

Finally, with $\sigma_+^{(0)}$ and K taken as constants, we fitted the two remaining parameters ($\sigma^{(1)}$, α). With no further modification, $\sigma^{(1)}$ ($\text{nm} \cdot \text{mol}^{-1} \cdot \text{L}$) and α ($\text{mol}^{-1} \cdot \text{L}$) accurately satisfied the empirical equations

$$\sigma^{(1)} = 15.66885r_i^2 - 3.422549r_i + 0.1422279 \quad (10)$$

$$\alpha = -192.4043r_i^2 + 48.39191r_i - 2.736670 \quad (11)$$

for the nitrate salts and

$$\sigma^{(1)} = -30.46386r_i^2 + 5.507868r_i - 0.2923933 \quad (12)$$

$$\alpha = -466.4431r_i^2 + 95.8218r_i - 4.814917 \quad (13)$$

for the chloride salts.

This procedure allowed us to outline the slight change of properties from lanthanum to samarium salts. As an example,

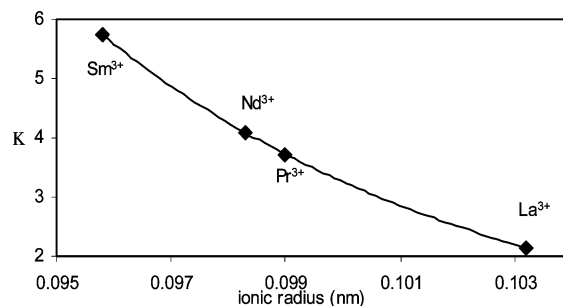


Figure 5. Chosen lanthanide–nitrate association constant from lanthanum to samarium.

TABLE 2: Parameter Values Retained to Reproduce Lanthanide Chloride and Nitrate Osmotic Coefficient Values

salt	maximum m^a	$\sigma_+^{(0)} b$	$10^3 \sigma^{(1)} c$	$10^2 \alpha^d$	K^d	AARD (%) ^e
LaCl_3	3.0	0.8275	−48.42	10.62	3.041	0.8
$\text{La}(\text{NO}_3)_3$	3.5		−44.10	20.82	2.148	0.7
PrCl_3	3.0	0.8148	−45.77	10.00	2.575	0.5
$\text{Pr}(\text{NO}_3)_3$	3.6		−43.07	16.91	3.720	0.8
NdCl_3	3.0	0.8126	−45.26	9.70	2.536	0.6
$\text{Nd}(\text{NO}_3)_3$	3.8		−42.76	16.03	4.086	0.8
SmCl_3	3.1	0.8053	−44.34	8.40	2.491	0.6
$\text{Sm}(\text{NO}_3)_3$	3.8		−41.86	13.36	5.743	0.6

^a Given in $\text{mol} \cdot \text{kg}^{-1}$. ^b Value in nanometers. ^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: $\text{AARD} (\%) = (100/N) \sum_{k=1}^N |\Phi_{\text{cal}}(k) - \Phi_{\text{exp}}(k)| / \Phi_{\text{exp}}(k)$, with N being the number of data points.

TABLE 3: Parameter Values for Cerium Chloride and Cerium Nitrate, Interpolated from the Other Lanthanide Salts

salt	$\sigma_+^{(0)} a$	$10^3 \sigma^{(1)} b$	$10^2 \alpha^c$	K^c
CeCl_3	0.8208	−46.86	10.49	2.746
$\text{Ce}(\text{NO}_3)_3$		−43.61	18.82	2.856

^a Given in nanometers. ^b In $\text{nm} \cdot \text{mol}^{-1} \cdot \text{L}$. ^c In $\text{mol}^{-1} \cdot \text{L}$.

Figure 5 shows the variation of the selected K values for lanthanide nitrates. The modified parameter values are given in Table 2, in which we show, for the studied concentration region, the discrepancy between the resulting osmotic coefficient calculated by the BIMSA theory and the available experimental data.^{8,9,11–15}

In practice, the modifications of the initial parameters shown in ref 6 were so small that they did not appreciably worsen the agreement between the calculated and experimental osmotic coefficients from refs 8,9, and 11–15.

From the ionic radius of cerium(III)⁷ (Table 1) and variation of all the parameters with the ionic radius from lanthanum nitrate (respectively, chloride) to samarium nitrate (respectively, chloride) (eqs 7–13), we recalculated and proposed a set of these parameters for the cerium nitrate (respectively, chloride) salt (Table 3).

The osmotic coefficient variation with concentration, resulting from the BIMSA theory with use of these parameters, was calculated. Cerium salt solutions density values were necessary for the transformation from the molar to molal scale. The calculated osmotic coefficients were converted to water activity, using eq 1, and could be compared with our experimental values. Figures 6 and 7 reflect this comparison, in narrow concentration regions for better clarity.

For cerium nitrate, the obtained BIMSA osmotic coefficient variation was compatible with our experimental water activity variation according to the different uncertainties in the 0.8–

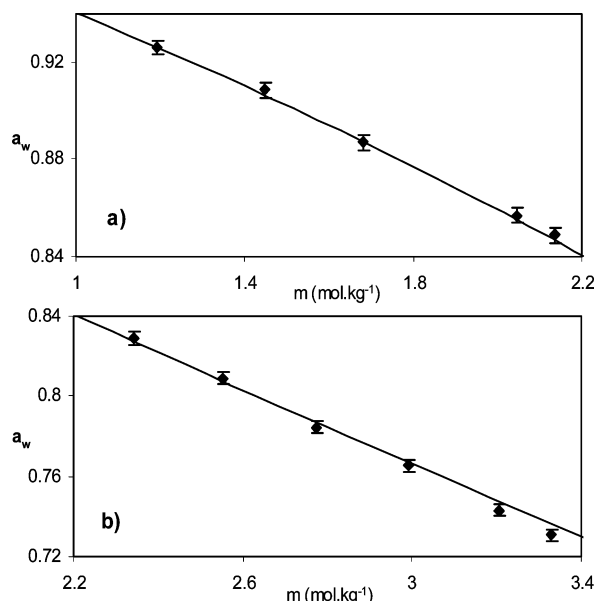


Figure 6. (a and b) Water activity for $\text{Ce}(\text{NO}_3)_3$ (◆, experimental, our water activity measurements, (—), result from the BIMSA theory interpolated to cerium nitrate).

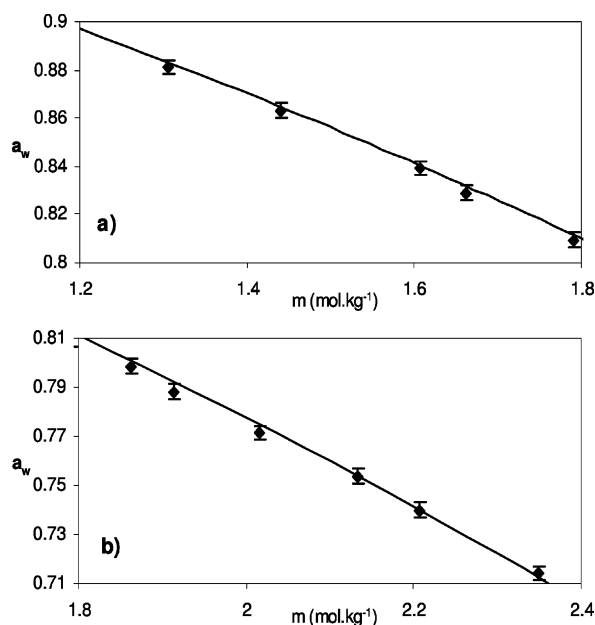


Figure 7. (a and b) Water activity for CeCl_3 (◆, experimental (this work), (—) deduced from the BIMSA theory interpolated to cerium chloride).

$3.0 \text{ mol}\cdot\text{kg}^{-1}$ concentration range: the average deviation ($\Delta a_w = 0.0013$) was very low in this concentration range. Above $3 \text{ mol}\cdot\text{kg}^{-1}$, the osmotic coefficient proposed by BIMSA seemed to have systematically low values compared with the osmotic coefficient deduced from experimental acquisition. This can be explained by the fact that, at very high concentration, the MSA equations are seldom verified.

Regarding cerium chloride, the obtained BIMSA osmotic coefficient variation was compatible with our experimental water activity variation over the entire experimentally studied concentration range ($1.3\text{--}2.4 \text{ mol}\cdot\text{kg}^{-1}$). In this range, as for cerium nitrate, the discrepancy for cerium chloride was very low ($\Delta a_w = 0.0017$).

For concentrations lower than $0.8 \text{ mol}\cdot\text{kg}^{-1}$, water activities deduced from the BIMSA theory for cerium nitrate may be reliable but this assertion needs experimental confirmation

TABLE 4: Parameter Values for Promethium Chloride and Promethium Nitrate, Interpolated from the Other Lanthanide Salts

salt	$\sigma_+^{(0) a}$	$10^3 \sigma^{(1) b}$	$10^2 \alpha^c$	K^c
PmCl_3	0.8088	−44.77	9.10	2.495
$\text{Pm}(\text{NO}_3)_3$		−42.33	14.70	4.872

^a Given in nanometers. ^b In $\text{nm}\cdot\text{mol}^{-1}\cdot\text{L}$. ^c In $\text{mol}^{-1}\cdot\text{L}$.

because our Novasina AW-Center water activity meter is not adapted to measure water activity greater than 0.95.

5. Prediction of Thermodynamic Data for Promethium Nitrate and Promethium Chloride Solutions. The previous part suggests that the BIMSA theory may be used for predicting osmotic coefficients of lanthanide salts of the beginning of the series. Since osmotic coefficients calculated from the BIMSA theory have shown to be reliable for the $0.8\text{--}3.0 \text{ mol}\cdot\text{kg}^{-1}$ (respectively, $1.3\text{--}2.4 \text{ mol}\cdot\text{kg}^{-1}$) concentration region for cerium nitrate (respectively, cerium chloride), we propose predicted values for promethium nitrate (respectively, promethium chloride) for these concentration regions. We also propose osmotic coefficients for promethium chloride in the $0.8\text{--}1.3 \text{ mol}\cdot\text{kg}^{-1}$ concentration region where we do not expect strong deviation.

Therefore, according to the variation of the four parameters ($\sigma_+^{(0)}$, $\sigma^{(1)}$, α , K) with the ionic radius (Table 2, Figures 4 and 5, eqs 7–13) for the first lanthanides of the series, we proposed values for promethium nitrate and promethium chloride (Table 4), as was done for cerium. As a radioelement with only very short-lived isotopes, no data about promethium density could be found. So, promethium nitrate (respectively, chloride) solution densities were interpolated between neodymium and samarium nitrate densities²⁵ (respectively, chloride densities²⁷). This procedure led to reliable values considering the very small differences between neodymium and samarium salts densities. The predicted values for promethium nitrate and chloride osmotic coefficients are shown in Tables S4 and S5, for the selected concentration range.

As a “soft” β -emitter, promethium 147 is an interesting isotope for radioactive source fabrication. For this purpose, its separation from other elements from ion exchange is necessary.⁴⁵ Data such as activity coefficient that can be deduced from osmotic coefficients is useful for a better control of thermodynamic equilibria involved in ion exchange.

6. Study of the Ternary System $\text{Ce}(\text{NO}_3)_3/\text{HNO}_3/\text{H}_2\text{O}$ and the Quaternary System $\text{Ce}(\text{NO}_3)_3/\text{HNO}_3/\text{N}_2\text{H}_5\text{NO}_3/\text{H}_2\text{O}$. In this part, we checked from water activity measurements that, in the chosen concentration range, the solutions satisfied the simple solution concept. For this, same water activity solutions were mixed and water activity measured according to the protocol detailed in the experimental section.

Regarding the studies on the ternary system, $\text{Ce}(\text{NO}_3)_3/\text{HNO}_3/\text{H}_2\text{O}$ composition of the different solutions and measured water activity are shown in Table 5. These results show that, even for very concentrated ternary mixtures and low water activity, the ternary system $\text{Ce}(\text{NO}_3)_3/\text{HNO}_3/\text{H}_2\text{O}$ obeys the Zdanovskii–Stokes–Robinson rule.

Since the chemical behavior of the ternary system $\text{Ce}(\text{NO}_3)_3/\text{HNO}_3/\text{H}_2\text{O}$ is very close to the chemical behavior of a ternary system containing an actinide(III) ion $\text{An}(\text{NO}_3)_3/\text{HNO}_3/\text{H}_2\text{O}$, the latter ternary system is expected to exhibit simple behavior up to high concentration. This aspect will be important for future work on actinides(III).

Contrary to the previously studied ternary system, it has been shown that the ternary system containing hydrazinium nitrate

TABLE 5: Experimental Water Activity Values for Ternary $\text{Ce}(\text{NO}_3)_3/\text{HNO}_3/\text{H}_2\text{O}$, Binary $\text{Ce}(\text{NO}_3)_3/\text{H}_2\text{O}$, and Binary $\text{HNO}_3/\text{H}_2\text{O}$ Solutions at 25 °C

solutions	$m_{\text{Ce}(\text{NO}_3)_3}$ (mol·kg ⁻¹)	m_{HNO_3} (mol·kg ⁻¹)	a_w
$\text{Ce}(\text{NO}_3)_3/\text{H}_2\text{O}$	4.908	0.000	0.569
$\text{HNO}_3/\text{H}_2\text{O}$	0.000	10.522	0.572
ternary solution 1	3.812	2.350	0.570
ternary solution 2	2.931	4.238	0.569
ternary solution 3	1.955	6.331	0.568
ternary solution 4	1.002	8.375	0.569

TABLE 6: Experimental Water Activity Values for Quaternary $\text{Ce}(\text{NO}_3)_3/\text{HNO}_3/\text{N}_2\text{H}_5\text{NO}_3/\text{H}_2\text{O}$, Ternary $\text{Ce}(\text{NO}_3)_3/\text{N}_2\text{H}_5\text{NO}_3/\text{H}_2\text{O}$, and Ternary $\text{HNO}_3/\text{N}_2\text{H}_5\text{NO}_3/\text{H}_2\text{O}$ Solutions at 25 °C

solutions	$m_{\text{Ce}(\text{NO}_3)_3}$ (mol·kg ⁻¹)	m_{HNO_3} (mol·kg ⁻¹)	$m_{\text{N}_2\text{H}_5\text{NO}_3}$ (mol·kg ⁻¹)	a_w
$\text{Ce}(\text{NO}_3)_3/\text{N}_2\text{H}_5\text{NO}_3/\text{H}_2\text{O}$	2.24	0.00	0.20	0.832
$\text{HNO}_3/\text{N}_2\text{H}_5\text{NO}_3/\text{H}_2\text{O}$	0.00	4.23	0.12	0.830
quaternary solution 1	1.79	0.84	0.18	0.831
quaternary solution 2	1.35	1.68	0.17	0.830
quaternary solution 3	0.90	2.53	0.15	0.828
quaternary solution 4	0.71	2.89	0.14	0.830
quaternary solution 5	0.44	3.40	0.13	0.830

($\text{N}_2\text{H}_5\text{NO}_3$), $\text{HNO}_3/\text{N}_2\text{H}_5\text{NO}_3/\text{H}_2\text{O}$, does not exhibit simple behavior, even up to high water activity (0.917).²⁸ This observation can be attributed to an acid–base equilibrium involving N_2H_5^+ and $\text{N}_2\text{H}_6^{2+}$.²⁸

It is expected to be an issue since plutonium(III) in nitric acid aqueous solution requires the addition of hydrazinium nitrate to stabilize the +III oxidation state. In fact, as previously mentioned, the concept of simple solution is a convenient tool to establish, from ternary or quaternary systems (such as $\text{Pu}(\text{NO}_3)_3/\text{HNO}_3/\text{N}_2\text{H}_5\text{NO}_3/\text{H}_2\text{O}$) data, “fictive” binary system (such as $\text{Pu}(\text{NO}_3)_3/\text{H}_2\text{O}$) data. On the other hand, the concentration of hydrazinium nitrate can be low (0.1–0.2 mol·kg⁻¹, typically); thus, its impact on the nonsimplicity of the system is likely to be small. Same water activities $\text{Ce}(\text{NO}_3)_3/\text{N}_2\text{H}_5\text{NO}_3/\text{H}_2\text{O}$ and $\text{HNO}_3/\text{N}_2\text{H}_5\text{NO}_3/\text{H}_2\text{O}$ solutions prepared according to the experimental protocol were mixed, and the water activity of the resulting solutions was measured. Table 6 shows the water activity of these different quaternary systems containing a low amount of hydrazinium nitrate.

According to Table 6, a moderate concentration of hydrazinium nitrate (0.1–0.2 mol·kg⁻¹) does not impact the simplicity of the concentrated ternary mixtures. Therefore, for the same concentration of hydrazinium nitrate and lower water activity (from 0.83 and as low as 0.57), where the ratios $m_{\text{N}_2\text{H}_5\text{NO}_3}/m_{\text{HNO}_3}$ and $m_{\text{N}_2\text{H}_5\text{NO}_3}/m_{\text{Ce}(\text{NO}_3)_3}$ are expected to be lower than those in Table 6, and where simplicity of the ternary system was verified, the simplicity of the quaternary system should be satisfied.

Considering the relatively close properties of lanthanide(III) salts and actinide(III) salts and considering the simplicity of different mixtures containing cerium, we expect a similar system ($\text{Pu}(\text{NO}_3)_3/\text{N}_2\text{H}_5\text{NO}_3/\text{HNO}_3/\text{H}_2\text{O}$ containing a relatively small concentration of hydrazinium nitrate) to follow the Zdanovskii–Stokes–Robinson relation.

Conclusion

Studies in the present work provided a reliable set of binary data for cerium nitrate and cerium chloride and filled in the lack of data for concentrated cerium salts. Furthermore, existing data of cerium chloride were revised in the 1.5–2.2 mol·kg⁻¹ concentration range.

Also, BIMSAs parameters, that have some microscopic physical meaning, were refined from lanthanide salts other than cerium, so as to reproduce experimentally obtained cerium water activity. The very small discrepancy between our experimentally measured data and the ones deduced from the BIMSAs theory over wide concentration ranges (0.8–3.0 mol·kg⁻¹ for cerium nitrate and 1.3–2.4 mol·kg⁻¹ for cerium chloride) shows that, from correlating the BIMSAs parameters with the cation(III) radius, the theory may be used in a predictive way. Thus, we can consider the theory as a valuable tool for establishing properties of actinide salts that are difficult to study experimentally, because of their high radioactivity. More precisely, we expect to deduce, from plutonium(III) nitrate salts “fictive” binary data, those for americium(III) nitrate and curium(III) nitrate. Such an extrapolation might be obtained from a correlation between actinide(III) or lanthanide(III) radii and the values of the BIMSAs parameters.

The applicability of the concept of simple solutions to the systems $\text{Ce}(\text{NO}_3)_3/\text{HNO}_3/\text{H}_2\text{O}$ and $\text{Ce}(\text{NO}_3)_3/\text{HNO}_3/\text{N}_2\text{H}_5\text{NO}_3/\text{H}_2\text{O}$ showed that the same concept could be applied as a convenient tool for equivalent actinide(III) systems. We therefore expect to easily deduce the properties of the “fictive” binary $\text{Pu}(\text{NO}_3)_3/\text{H}_2\text{O}$ system from measurements on the real $\text{Pu}(\text{NO}_3)_3/\text{HNO}_3/\text{N}_2\text{H}_5\text{NO}_3/\text{H}_2\text{O}$ system containing a small amount of hydrazinium nitrate. Measurements on this quaternary system and calculation of the $\text{Pu}(\text{NO}_3)_3$ binary data will be the subject of future work.

We hope to enhance the concentration range where the BIMSAs theory may provide reliable thermodynamic data. This improvement may be implemented by properly taking into account the effect of higher order species than the 1:1 complex on the osmotic coefficients in our theory. Hence, the discrepancy found at very high concentration could be attributed to such complexes. Also, water activity measurements at low concentration by another device should be made, and comparison with values predicted from the BIMSAs theory could validate the predictive aspect at concentrations lower than 0.8 mol·kg⁻¹.

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Supporting Information Available: Tables containing information regarding the densities of cerium nitrate solutions, water activities of cerium nitrate and cerium chloride, and osmotic coefficients of promethium nitrate and promethium chloride. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) Katz, J. J.; Seaborg, G. T.; Morss, L. R. *The Chemistry of the Actinide Elements Second Edition*, 2nd ed.; Chapman and Hall Ltd: London, 1986.
- (2) Zdanovskii, A. B.; Tr. Solyanoi Lab. Vses. Inst. Galurgii, Akad. Nauk. SSSR **1936**, 6, 1.
- (3) Mikulin, G. I. *Abstracts of papers presented to the Symposium on Salting-In and Salting-Out Problems of Liquids from Solutions*; Kaunas, Lithuania, 1963, 17.
- (4) Stokes, R. H.; Robinson, R. A. *J. Phys. Chem.* **1966**, 70, 2126.
- (5) Charrin, N.; Moisy, Ph.; Blanc, P. *Radiochim. Acta* **2001**, 89, 579.
- (6) Ruas, A.; Moisy, Ph.; Simonin, J. P.; Bernard, O.; Dufre che, J. F.; Turq, P. *J. Phys. Chem. B* **2005**, 109, 5243.
- (7) Shannon, R. D. *Acta Crystallogr.* **1976**, A32, 751.
- (8) Rard, J. A.; Shiers, L. E.; Heiser, D. J.; Spedding, F. H. *J. Chem. Eng. Data* **1977**, 22, 337.

- (9) Spedding, F. H.; Weber, H. O.; Saeger, V. W.; Petheram, H. H.; Rard, J. A.; Habenschuss, A. *J. Chem. Eng. Data* **1976**, *21*, 341.
- (10) Rard, J. A.; Weber, H. O.; Spedding, F. H. *J. Chem. Eng. Data* **1977**, *22*, 187.
- (11) Rard, J. A.; Miller, D. G.; Spedding, F. H. *J. Chem. Eng. Data* **1979**, *24*, 348.
- (12) Rard, J. A.; Spedding, F. H. *J. Chem. Eng. Data* **1981**, *26*, 391.
- (13) Rard, J. A.; Spedding, F. H. *J. Chem. Eng. Data* **1982**, *27*, 454.
- (14) Rard, J. A.; Spedding, F. H. *J. Chem. Eng. Data* **1987**, *32*, 92.
- (15) Rard, J. A. *J. Chem. Eng. Data* **1987**, *32*, 334.
- (16) Mason, C. M. *J. Am. Chem. Soc.* **1938**, *60*, 1638.
- (17) Mason, C. M. *J. Am. Chem. Soc.* **1941**, *63*, 220.
- (18) David, F. H.; Fourest, B. *New J. Chem.* **1997**, *21*, 167.
- (19) Bonal, C.; Morel, J. P.; Morel-Desrosiers, N. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 1431.
- (20) Miguiditchian, M.; Guillauneux, D.; Guillaumont, D.; Moisy, Ph.; Madic, C.; Jensen, M. P.; Nash, K. L. *Inorg. Chem.* **2005**, *44*, 1404.
- (21) Charrin, N.; Moisy, Ph.; Garcia-Argote, S.; Blanc, P. *Radiochim. Acta* **1999**, *86*, 143.
- (22) Charrin, N.; Moisy, Ph.; Blanc, P. *Radiochim. Acta* **2000**, *88*, 25.
- (23) Charrin, N.; Moisy, Ph.; Blanc, P. *Radiochim. Acta* **2000**, *88*, 445.
- (24) Gregoire-Kappenstein, A. C.; Moisy, Ph.; Cote, G.; Blanc, P. *Radiochim. Acta* **2003**, *91*, 371.
- (25) Spedding, F. H.; Shiers, L. E.; Brown, M. A.; Baker, J. L.; Guitierrez, L.; McDowell, L. S.; Habenschuss, A. *J. Phys. Chem.* **1975**, *79*, 1087.
- (26) Mironov, K. E.; Popov, A. P.; Moroz, E. M. *Russ. J. Inorg. Chem.* **1969**, *14*, 165.
- (27) Spedding, F. H.; Saeger, V. W.; Gray, K. A.; Boneau, P. K.; Brown, M. A.; DeKock, C. W.; Baker, J. L.; Shiers, L. E.; Weber, H. O.; Habenschuss, A. *J. Chem. Eng. Data* **1975**, *20*, 72.
- (28) Kappenstein, A. C.; Moisy, Ph.; Cote, G.; Blanc, P. *Phys. Chem. Chem. Phys.* **2000**, *2*, 2725.
- (29) Percus, J. K.; Yevick, G. *Phys. Rev.* **1966**, *110*, 251.
- (30) Waisman, E.; Lebowitz, J. L. *J. Chem. Phys.* **1970**, *52*, 4307.
- (31) Blum, L. *Mol. Phys.* **1975**, *30*, 1529.
- (32) Blum, L.; Høye, J. S. *Mol. Phys.* **1974**, *61*, 2129.
- (33) Blum, L.; Høye, J. S. *J. Phys. Chem.* **1977**, *81*, 1311.
- (34) Hiroike, K. *Mol. Phys.* **1977**, *33*, 1195.
- (35) Bernard, O.; Blum, L. *J. Chem. Phys.* **1996**, *104*, 4746.
- (36) Kalyuzhnyi, Yu. V.; Holovko, M. F.; Haymet, A. D. J. *J. Chem. Phys.* **1991**, *95*, 9151.
- (37) Kalyuzhnyi, Yu. V.; Vlachy, V. *Chem. Phys. Lett.* **1993**, *215*, 518.
- (38) Kalyuzhnyi, Yu. V.; Holovko, M. F. *Mol. Phys.* **1993**, *80*, 1165.
- (39) Holovko, M. F.; Kalyuzhnyi, Yu. V. *Mol. Phys.* **1991**, *73*, 1145.
- (40) Blum, L.; Holovko, M. F.; Protsykevych, I. A. *J. Stat. Phys.* **1996**, *84*, 191.
- (41) Simonin, J. P.; Bernard, O.; Blum, L. *J. Phys. Chem. B* **1998**, *102*, 4411.
- (42) Simonin, J. P. *J. Phys. Chem. B* **1997**, *101*, 4313.
- (43) Simonin, J. P.; Blum, L.; Turq, P. *J. Phys. Chem.* **1996**, *100*, 7704.
- (44) Liu, Y. S.; Xu, C. M.; Hu, Y. F.; Yan, J. *Chin. J. Chem. Eng.* **2004**, *12*, 470 and literature therein.
- (45) Gelis, V. M.; Maslova, G. B. *Radiokhimiya* **1999**, *41*, 436.