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Thermodynamics of Binary and Ternary Solutions of Multivalent Electrolytes with Formation of 1:1 and 1:2 Complexes, within the Mean Spherical Approximation

José Torres-Arenas,^{*,†,‡} Jean-Pierre Simonin,^{*,†} Olivier Bernard,[†] Alexandre Ruas,[§] and Philippe Moisy[§]

Physicochimie des Electrolytes, Colloïdes et Sciences Analytiques (PECSA), CNRS-UMR 7195, UPMC Université Paris 06, Boite 51, 4 Place Jussieu, 75252 Paris, France, División de Ciencias e Ingenierías, Campus León, Universidad de Guanajuato, Loma del Bosque 103, Colonia Loma del Campestre, León, Guanajuato, 37150, México., Commissariat à l'Énergie Atomique/Marcoule/DEN/DRCP, BP 17171, 30207 Bagnols-sur-Ceze Cedex, France

The mean activity (γ_{\pm}) and osmotic (Φ) coefficients for binary and ternary aqueous solutions of trivalent electrolytes (mainly made up of lanthanide salts) are described in the framework of the primitive model of ionic solutions, using the binding mean spherical approximation (BiMSA). This model, based on the Wertheim formalism, accounts for (chemical or electrostatic) association of ions. In this work, the multivalent cation and the anion are allowed to form 1:1 (pairs) and 1:2 (trimers) complexes. Expressions for γ_{\pm} and Φ are given which satisfy the Gibbs–Duhem relation. The model involves concentration-dependent cation size and effective relative permittivity, variations that can be interpreted in terms of solvent effects. The theory is applied to aqueous solutions of binary and ternary mixtures at 25 °C with common anion.

Introduction

Lanthanides and actinides compose about one-third of the periodic table and are of particular importance from both theoretical and practical points of view.^{1–3}

It is well-known that lanthanides(III) and actinides(III) exhibit several similar properties along their series because of their similarity in external electron configuration and size. The effective radii of the lanthanide and actinide cations decrease across the series (the so-called lanthanide/actinide contraction), reaching ca. 20 and 15% in the case of lanthanide and actinide ions, respectively.⁴ This phenomenon causes an increase in the strength of cation–anion and cation–dipole interactions (with the dipole of water). Increased strength of ion–dipole interactions, in turn, implies that the heavy members of both series bind water more closely than the light members. Besides, the coordination numbers (CNs) of lanthanides(III) and actinides(III) in aqueous solutions decrease from 9 to 8 from the beginning to the end of both series,⁴ varying with the crystallographic radius as an S-shaped curve with a discontinuity around the europium–gadolinium and berkelium–californium cations, respectively.

Lanthanide and actinide salts are generally well-soluble in aqueous solutions, the high dielectric constant of water allowing dissociation of ionic species and the water producing an efficient solvation of cations. However, in the case of actinides, an acid is generally added to the solution in order to avoid hydrolysis of the metal cation. So, in the industry of reprocessing of nuclear wastes, nitric acid is used at concentrations in the range of 1–7 mol L^{−1}.

In these operations, the trivalent rare earth ions are difficult to separate from each other, but their highly unsymmetrical mixing and complex formation with 1–1 salting-out agents in

concentrated solutions can improve their separation. In addition, because of the strong similarity of the various lanthanide(III) and actinide(III) cations, any theory describing the properties of lanthanide(III) solutions may also be suitable for those containing trivalent actinide electrolytes.

In the past, we have applied the mean spherical approximation^{5–8} (MSA) to describe the thermodynamics of real ionic solutions.^{9–13} Aqueous solutions of pure salts and mixtures, possibly associating, were considered up to very high concentrations, generally to saturation at 25 °C. The model was developed at the McMillan–Mayer level of solutions in which the solvent is regarded as a continuum that manifests itself through its dielectric permittivity. In these studies, the formation of 1:1 complexes was taken into account within the binding MSA (BiMSA)¹⁴ also known as associative MSA (AMSA)¹⁵ or polymer MSA.¹⁶

In the BiMSA, the strong short-range attractive interaction is modeled by an orientationally averaged sticky interaction potential (sticky-electrolyte model) and the electrostatic interaction is described in the primitive MSA. The MSA is an analytic theory applicable to the primitive model of ionic solutions in which the solvent is regarded as a continuum, as well as to models with molecular solvent. One of the remarkable properties of the MSA for electrolytes is that its mathematical solution can be expressed in terms of a single screening parameter Γ , which plays a role similar to that of the Debye–Hückel screening parameter κ . In these solutions, ionic association may occur in two different ways: through ion pairing in which the clustering process is due to strong Coulomb interactions or via chemical association with the formation of a true chemical bond. The BiMSA theory can accommodate both of these mechanisms. Notice that the BiMSA naturally contains a mass action law for the ion association equilibrium.

Besides solutions of monovalent and divalent electrolytes, we have used the BiMSA in the case of trivalent lanthanide salt solutions up to high concentrations.¹⁷ The predictive capability of this approach was assessed in the case of aqueous

* To whom correspondence should be addressed. E-mail: jtorres@fisica.ugto.mx (J.T.-A.); jpsimonin@gmail.com (J.-P.S.).

[†] UPMC Université Paris 06.

[‡] Universidad de Guanajuato.

[§] Commissariat à l'Énergie Atomique/Marcoule/DEN/DRCP.

solutions of cerium(III) nitrate and chloride.¹⁸ The additional formation of a 1:2 complex was included to treat the case of aqueous solutions of uranyl nitrate and dysprosium chloride and nitrate at 25 °C in a more realistic way.¹⁹ The parameters used in the theoretical description were discussed in the light of experimental (UV–visible/near-IR, time-resolved laser-induced fluorescence spectroscopy) and simulation (molecular dynamics) results for dilute to concentrated solutions of DyCl₃ in water.²⁰

In the present work, the BiMSA theory accounting for 1:1 and 1:2 complexes is systematically applied to binary aqueous solutions of lanthanide and uranyl salts (perchlorate, chloride, and nitrate). A new procedure is proposed for the estimation of the BiMSA parameters, in particular for the choice of the sizes of the cations in the lanthanide series. Moreover, the description is extended to the case of aqueous ternary mixtures composed of a trivalent salt (mainly a lanthanide) and a monovalent electrolyte such as nitric acid. This description is a first step toward the modeling of chemical engineering processes developed in the nuclear industry in which concentrated nitric acid is present in the feed solutions of lanthanide and actinide ions.

The paper is organized as follows. The next section presents the theory for a ternary mixture within the BiMSA and the thermodynamic quantities that are used throughout. Then, the model is applied to represent experimental results for binary and ternary solutions of (mainly) trivalent electrolytes.

Theory

The BiMSA theory consistently combines the MSA and the Wertheim theory^{21–24} for a description of association between ions in solution. It accounts for the effect of electrostatic interactions on the binding process of ions in electrolyte solutions.

Within Wertheim theory, a pair (respectively a trimer) is defined as two ions (respectively three ions) being in contact. This view is in contrast with the classic chemical model^{25,26} in which a pair is a separate species. The BiMSA model provides a more realistic representation of the pair (constituted of two charged spheres in contact interacting with the surrounding ionic atmosphere) and, correlatively, a better account for electrostatic and excluded volume interactions. Moreover, unlike the classic chemical model, the effect of the pairing process is included in the computation of the MSA screening parameter.

We consider a ternary aqueous electrolyte solution with common anion. It contains three ionic components: C (the first cation, e.g., a lanthanide ion), A (the common anion, e.g., NO₃[−]), and D (the second cation, e.g., H⁺ or NH₄⁺), with the total number densities ρ_k ($k = C, A, D$), and charges ez_k . The ions are modeled as hard spheres of diameter σ_k . The (pure) water is regarded as a continuum of dielectric constant ϵ_w . The temperature of the system is T , Boltzmann's constant is k_B , and $\beta = 1/k_B T$. The system is electroneutral so that

$$\sum_k \rho_k z_k = 0 \quad (1)$$

The cation C is assumed to possess two sticky points, while components A and D have only one sticky point, all these binding sites being randomly positioned on the surface of the ions (see Figure 1). Only association between unlike ions is supposed to occur. This model therefore allows the formation of pairs, CA and DA, and of trimers, ACA ($\equiv CA_2$), also denoted as follows by T.

The various chemical equilibria involving the ions may be represented as follows, K_{CA}^0 , K_T^0 , and K_{DA}^0 being the thermodynamic



dynamic equilibrium constants associated with the respective reactions. We denote by α_k the fraction of unbound particles of type k , ρ_{CA} the density of CA pairs, ρ_{DA} the density of DA pairs, and ρ_T the density of ACA trimers. We set

$$K_{CA} \equiv \frac{\rho_{CA}}{(\alpha_C \rho_C)(\alpha_A \rho_A)} = K_{CA}^0 G_{CA} \quad (5)$$

$$K_T \equiv \frac{\rho_T}{(\alpha_A \rho_A) \rho_{CA}} = K_T^0 G_T \quad (6)$$

$$K_{DA} \equiv \frac{\rho_{DA}}{(\alpha_A \rho_A)(\alpha_D \rho_D)} = K_{DA}^0 G_{DA} \quad (7)$$

which represent the sometimes called “apparent” association constants.

The G functions appearing in eqs 5–7 express the departure of the apparent equilibrium constant from the thermodynamic equilibrium constant. In other words, they are associated with the difference between the chemical potential of a pair (respectively, trimer) and the chemical potential of the two (respectively, three) free ions constituting the pair (respectively, trimer). The G functions are given by^{19,27}

$$G_{CA} = g_{CA}^{HS} \exp \left(-2\lambda \frac{z'_C z'_A}{\sigma_C + \sigma_A} + 2\lambda_0 \frac{z_C z_A}{\sigma_C^{(0)} + \sigma_A} \right) \quad (8)$$

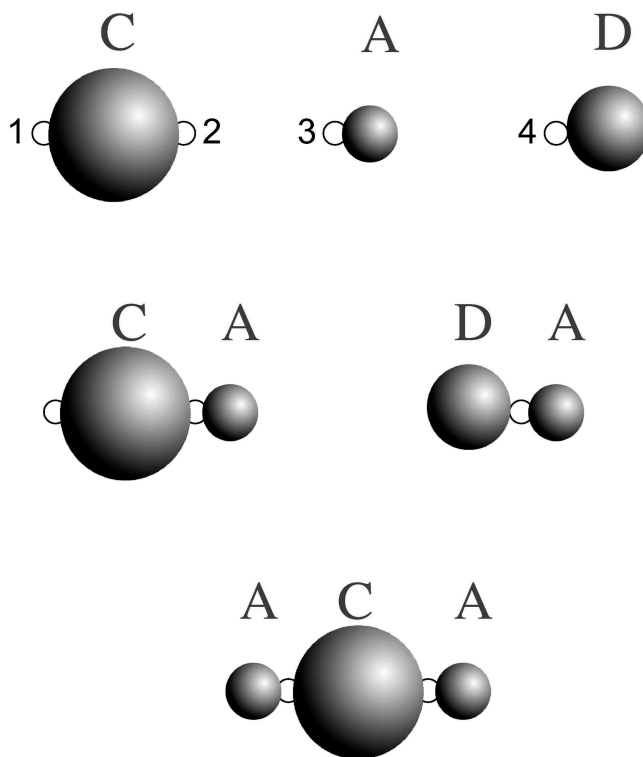


Figure 1. Schematic representation of the species: C (first cation), A (common anion), and D (second cation) with their binding sites (1, 2, 3, and 4) and the corresponding complexes, CA, DA, and T = CA₂.

$$G_T = G_{CA} \exp \left(-2\lambda \frac{(z'_A)^2}{(\sigma_C + 2\sigma_A)(1 + \Gamma\sigma_C)} + 2\lambda_0 \frac{(z_A)^2}{\sigma_C^{(0)} + 2\sigma_A} \right) \quad (9)$$

$$G_{DA} = g_{DA}^{HS} \exp \left(-2\lambda \frac{z_D z'_A}{\sigma_D + \sigma_A} + 2\lambda_0 \frac{z_D z_A}{\sigma_D^{(0)} + \sigma_A} \right) \quad (10)$$

and

$$z'_k = \frac{z_k - \eta \sigma_k^2}{1 + \Gamma \sigma_k} \quad (11)$$

$$\lambda = \frac{\beta e^2}{4\pi \epsilon_0 \epsilon} \quad (12)$$

with ϵ_0 being the permittivity of a vacuum, ϵ the relative permittivity of solution, and g_{ij}^{HS} is the hard sphere radial distribution function at contact between I and J, which can be calculated using the Boublik–Carnahan–Starling–Leland expression.^{28,29} Moreover, since ϵ and the cation diameters σ_k are commonly supposed to vary with the composition of solution, we denote by λ_0 and $\sigma_k^{(0)}$ the infinite dilution values of λ and σ_k , respectively.

The global conservation of the species containing C, A, and D clearly gives the following relations

$$\rho_C = \rho_C \alpha_C + \rho_{CA} + \rho_T \quad (13)$$

$$\rho_A = \rho_A \alpha_A + \rho_{CA} + \rho_{DA} + 2\rho_T \quad (14)$$

$$\rho_D = \rho_D \alpha_D + \rho_{DA} \quad (15)$$

By inserting the relations 5–7 into eqs 13–15, the densities of complexes can be substituted by their expressions as functions of the apparent equilibrium constants, which leads to the proportion of unbound ions in the following alternative forms,

$$\alpha_C = 1 - \frac{\rho_{CA}}{\rho_C} - \frac{\rho_T}{\rho_C} = [1 + \rho_A \alpha_A K_{CA} + (\rho_A \alpha_A)^2 K_{CA} K_T]^{-1} \quad (16)$$

$$\alpha_A = 1 - \frac{\rho_{CA}}{\rho_A} - \frac{\rho_{DA}}{\rho_A} - 2\frac{\rho_T}{\rho_A} = [1 + \rho_C \alpha_C K_{CA} + \rho_D \alpha_D K_{DA} + 2\rho_C \alpha_C \rho_A \alpha_A K_{CA} K_T]^{-1} \quad (17)$$

$$\alpha_D = 1 - \frac{\rho_{DA}}{\rho_D} = [1 + \rho_A \alpha_A K_{DA}]^{-1} \quad (18)$$

The BiMSA parameters Γ and η for this case are expressed by

$$\Gamma^2 = \pi \lambda \left[\sum_k \rho_k (z'_k)^2 + \frac{2\rho_{DA}}{\sigma_D + \sigma_A} \left(\frac{\sigma_D}{1 + \Gamma\sigma_D} + \frac{\sigma_A}{1 + \Gamma\sigma_A} \right) z'_A z'_D + \frac{2(\rho_{CA} + 2\rho_T)}{\sigma_C + \sigma_A} \left(\frac{\sigma_C}{1 + \Gamma\sigma_C} + \frac{\sigma_A}{1 + \Gamma\sigma_A} \right) z'_C z'_A + \frac{2\rho_T}{(\sigma_C + 2\sigma_A)(1 + \Gamma\sigma_C)} \times \left(\frac{\sigma_C}{1 + \Gamma\sigma_C} + \frac{2\sigma_A}{1 + \Gamma\sigma_A} \right) (z'_C)^2 \right] \quad (19)$$

with the quantities z'_k ($k = C, A, D$) given by eq 11 as a function of Γ and η , and

$$\eta = \frac{\pi}{2\Delta\Omega} \left[\sum_k \frac{\rho_k z_k \sigma_k}{1 + \Gamma\sigma_k} + \frac{\rho_{DA}(z_A \sigma_D^2 + z_D \sigma_A^2)}{(\sigma_A + \sigma_D)(1 + \Gamma\sigma_A)(1 + \Gamma\sigma_D)} + \frac{(\rho_{CA} + 2\rho_T)(z_C \sigma_A^2 + z_A \sigma_C^2)}{(\sigma_C + \sigma_A)(1 + \Gamma\sigma_C)(1 + \Gamma\sigma_A)} + \frac{2\rho_T z_A \sigma_A^2}{(\sigma_C + 2\sigma_A)(1 + \Gamma\sigma_C)(1 + \Gamma\sigma_A)^2} \right] \quad (20)$$

where

$$\Omega = 1 + \frac{\pi}{2\Delta} \left[\sum_k \frac{\rho_k \sigma_k^3}{1 + \Gamma\sigma_k} + \frac{2\rho_{DA} \sigma_D^2 \sigma_A^2}{(\sigma_D + \sigma_A)(1 + \Gamma\sigma_D)(1 + \Gamma\sigma_A)} + \frac{2(\rho_{CA} + 2\rho_T) \sigma_C^2 \sigma_A^2}{(\sigma_C + \sigma_A)(1 + \Gamma\sigma_C)(1 + \Gamma\sigma_A)} + \frac{2\rho_T \sigma_A^4}{(\sigma_C + 2\sigma_A)(1 + \Gamma\sigma_C)(1 + \Gamma\sigma_A)^2} \right] \quad (21)$$

$$\Delta = 1 - X_3 \quad (22)$$

$$X_3 = \frac{\pi}{6} \sum_k \rho_k \sigma_k^3 \quad (23)$$

The BiMSA screening parameter Γ satisfies the condition $\Gamma \approx \kappa/2$ at large dilution, κ being the Debye–Hückel screening parameter. Noting that α_C and α_D can be expressed as functions of α_A , the coupled system of eqs 17, 19, and 20 was solved using a numerical iterative procedure with the starting values $\Gamma_0 = \kappa/2$, $\eta_0 = \eta|_{\rho_{CA}=\rho_{DA}=\rho_T=0}$, and $\alpha_A = 0.01$.

By thermodynamic integration it is possible to get the excess MSA Helmholtz energy per volume unit, which reads^{14,19,27}

$$\beta \Delta A^{MSA} = \beta \Delta U^{MSA} + \frac{\Gamma^3}{3\pi} + \beta \Delta A^{MAL} - \sum_{M=C,A,T,DA} \rho_M \left(\frac{\partial \beta \Delta U^{MSA}}{\partial \rho_M} \right)_\Gamma \quad (24)$$

where $\beta \Delta U^{MSA}$ is the MSA internal energy contribution

$$\beta \Delta U^{MSA} = \lambda \left[- \sum_k \rho_k z_k \frac{\Gamma z_k + \eta \sigma_k}{1 + \Gamma\sigma_k} + \frac{\rho_{DA}}{\sigma_D + \sigma_A} \times \left(\frac{z_A z'_D}{1 + \Gamma\sigma_A} + \frac{z_D z'_A}{1 + \Gamma\sigma_D} \right) + \frac{(\rho_{CA} + 2\rho_T)}{\sigma_C + \sigma_A} \times \left(\frac{z_C z'_A}{1 + \Gamma\sigma_C} + \frac{z_A z'_C}{1 + \Gamma\sigma_A} \right) + 2 \frac{\rho_T}{\sigma_C + 2\sigma_A} \frac{z_A z'_A}{(1 + \Gamma\sigma_C)(1 + \Gamma\sigma_A)} \right] \quad (25)$$

The mass action law (MAL) contribution to the Helmholtz energy taking into account the 1:1 and 1:2 complexes is²⁷

$$\beta \Delta A^{MAL} = \sum_{k=C,A,D} \rho_k \ln \alpha_k + \rho_{CA} + \rho_{DA} + 2\rho_T \quad (26)$$

As compared to the case of binary solutions, eq 26 has an additional term corresponding to the presence of the DA pair, taking into account the 1:1 association of particles A and D.

In the last term of eq 24, the partial derivatives of the MSA internal energy with respect to the densities are related to the electrostatic part of the G functions defined previously. With the help of eq 25, it follows that

$$\left(\frac{\partial \beta \Delta U^{MSA}}{\partial \rho_{CA}} \right)_\Gamma = \frac{2\lambda}{\sigma_C + \sigma_A} z'_C z'_A \quad (27)$$

$$\left(\frac{\partial \beta \Delta U^{\text{MSA}}}{\partial \rho_{\text{T}}}\right)_{\Gamma} = 2 \left(\frac{\partial \beta \Delta U^{\text{MSA}}}{\partial \rho_{\text{CA}}}\right)_{\Gamma} + \frac{2\lambda}{(2\sigma_{\text{A}} + \sigma_{\text{C}})(1 + \Gamma\sigma_{\text{C}})} (z'_{\text{A}})^2 \quad (28)$$

$$\left(\frac{\partial \beta \Delta U^{\text{MSA}}}{\partial \rho_{\text{DA}}}\right)_{\Gamma} = \frac{2\lambda}{\sigma_{\text{D}} + \sigma_{\text{A}}} z'_{\text{D}} z'_{\text{A}} \quad (29)$$

The MSA excess osmotic coefficient is obtained from the Helmholtz energy as

$$\Delta \Phi^{\text{MSA}} = \rho_{\text{t}} \frac{\partial}{\partial \rho_{\text{t}}} \left[\frac{\beta \Delta A^{\text{MSA}}}{\rho_{\text{t}}} \right]_{\Gamma} \quad (30)$$

where the partial derivation is performed at constant Γ .^{9,30} Furthermore

$$\rho_{\text{t}} = \sum_{\text{k=C,A,D}} \rho_{\text{k}} \quad (31)$$

is the total number density of ions.

Using the chain rule, we get for the osmotic coefficient

$$\Delta \Phi^{\text{MSA}} = \Delta \Phi_0^{\text{MSA}} + \Delta \Phi_{\sigma_{+}} + \Delta \Phi_{\varepsilon} \quad (32)$$

where

$$\Delta \Phi_0^{\text{MSA}} = \Delta \Phi_0^{\text{el}} + \Delta \Phi_0^{\text{MAL}} \quad (33)$$

$$\Delta \Phi_0^{\text{el}} = -\frac{\Gamma^3}{3\pi\rho_{\text{t}}} - \frac{2\lambda\eta^2}{\pi\rho_{\text{t}}} \quad (34)$$

Starting from eq 26 for the MAL contribution to the Helmholtz energy and using the relation $\partial \ln \alpha_{\text{k}} / \partial \rho_{\text{t}} = -\alpha_{\text{k}} [\partial(1/\alpha_{\text{k}}) / \partial \rho_{\text{t}}]$ together with eqs 16–18, the following expression^{14,27} is obtained:

$$\rho_{\text{t}} \frac{\partial}{\partial \rho_{\text{t}}} \left[\frac{\beta \Delta A^{\text{MAL}}}{\rho_{\text{t}}} \right] = -\frac{\rho_{\text{CA}} + \rho_{\text{DA}} + 2\rho_{\text{T}}}{\rho_{\text{t}}} - \rho_{\text{CA}} \frac{\partial \ln K_{\text{CA}}}{\partial \rho_{\text{t}}} - \rho_{\text{T}} \frac{\partial \ln(K_{\text{CA}} K_{\text{T}})}{\partial \rho_{\text{t}}} - \rho_{\text{DA}} \frac{\partial \ln K_{\text{DA}}}{\partial \rho_{\text{t}}} \quad (35)$$

Now, using eqs 5–7 to express the apparent association constants K_{M} ($\text{M} = \text{CA}, \text{T}, \text{DA}$) appearing in eq 35 in terms of the G functions and then using eqs 8–10 to express the G functions in terms of their electrostatic and hard sphere contributions ($g_{\text{CA}}^{\text{HS}}$ or $g_{\text{DA}}^{\text{HS}}$), we obtained electrostatic terms that were introduced in $\Delta \Phi^{\text{el}}$ and, besides, terms containing the derivatives of the hard sphere distribution functions at contact. These latter terms constitute the MAL contribution to the osmotic coefficient, namely,

$$\Delta \Phi_0^{\text{MAL}} = -\frac{\rho_{\text{CA}} + 2\rho_{\text{T}}}{\rho_{\text{t}}} \left(1 + \rho_{\text{t}} \frac{\partial \ln g_{\text{CA}}^{\text{HS}}}{\partial \rho_{\text{t}}} \right) - \frac{\rho_{\text{DA}}}{\rho_{\text{t}}} \left(1 + \rho_{\text{t}} \frac{\partial \ln g_{\text{DA}}^{\text{HS}}}{\partial \rho_{\text{t}}} \right) \quad (36)$$

The effect of the concentration-dependent cation size and solution permittivity is given by¹¹

$$\Delta \Phi_{\sigma_{+}} = \frac{1}{\rho_{\text{t}}} \left[\frac{\partial \beta A^{\text{MSA}}}{\partial \sigma_{+}} \right] D(\sigma_{+}) \quad (37)$$

$$\Delta \Phi_{\varepsilon} = \frac{1}{\rho_{\text{t}}} \left[\frac{\partial \beta A^{\text{MSA}}}{\partial \varepsilon^{-1}} \right] D(\varepsilon^{-1}) \quad (38)$$

$$D \equiv \sum_{\text{k=C,A,D}} C_{\text{k}} \frac{\partial}{\partial C_{\text{k}}} \quad (39)$$

where C_{k} is the molar concentration of species k . As in ref 19, the value of $\Delta \Phi_{\sigma_{+}}$ was computed numerically.

As found in previous work,^{10,11,13,17,19} the contribution $\Delta \Phi_{\varepsilon}$ is obtained in closed form as

$$\Delta \Phi_{\varepsilon} = \frac{\beta \Delta U^{\text{MSA}}}{\rho_{\text{t}}} \varepsilon D(\varepsilon^{-1}) \quad (40)$$

The total osmotic coefficient is given by

$$\Phi = 1 + \Delta \Phi^{\text{HS}} + \Delta \Phi^{\text{MSA}} \quad (41)$$

in which $\Delta \Phi^{\text{HS}}$ represents the hard sphere contribution to the osmotic coefficient, which can be calculated using the Boublik–Carnahan–Starling–Leland expression.^{28,29}

The mean ionic activity coefficient is

$$\ln \gamma_{\pm} = \Delta \ln \gamma_{\pm}^{\text{HS}} + \Delta \ln \gamma_{\pm}^{\text{MSA}} \quad (42)$$

with⁹

$$\Delta \ln \gamma_{\pm}^{\text{MSA}} = \frac{\beta \Delta A^{\text{MSA}}}{\rho_{\text{t}}} + \Delta \Phi^{\text{MSA}} \quad (43)$$

Results and Discussion

The results of the previous section were applied to a representation of departures from ideality in various binary and ternary aqueous solutions containing trivalent electrolytes or uranyl salts.

First, it was checked numerically that the calculated osmotic and activity coefficients obtained from eqs 41 and 42 accurately satisfied the Gibbs–Duhem relation. This verification was done for both binary and ternary solutions. This not only shows thermodynamic consistency of the calculated activity and osmotic coefficients. It also provides support to the correctness of the expressions derived for these quantities, which result from tedious algebraic manipulations and differentiations. This precaution is necessary before going to the applications.

For comparison with experimental data, the theoretical activity and osmotic coefficients were converted from the McMillan–Mayer (MM) to the Lewis–Randall (LR) reference system (MM-to-LR conversion) by using the usual procedure.^{10,31} Solution density values were taken from the literature,^{32–37} except in the case of $\text{Tm}(\text{NO}_3)_3$ solutions for which it was interpolated between the densities of $\text{Er}(\text{NO}_3)_3$ and $\text{Yb}(\text{NO}_3)_3$, and in the case of $\text{UO}_2(\text{ClO}_4)_2$ whose density was estimated experimentally (see below). The densities of ternary solutions were assessed from those of the binary solutions as done earlier.^{10,38}

As in previous work^{9–12} the (hydrated) cation diameter σ_{k} and ε^{-1} were taken as linear functions of concentration. For binary mixtures we took

$$\sigma_{\text{k}} = \sigma_{\text{k}}^{(0)} + \sigma^{(1)} C \quad (44)$$

$$\varepsilon^{-1}/\varepsilon_{\text{W}}^{-1} = 1 + \alpha C \quad (45)$$

where C is the molar concentration of salt and ε_{W} is the dielectric constant of pure water.

The values of diameters at infinite dilution, $\sigma_k^{(0)}$, for the H^+ (5.04 Å) and NH_4^+ (3.33 Å) ions were taken from previous work.^{10,11} The diameters of the anions were kept constant with salt concentration because anions may be viewed as essentially unhydrated.^{39,40} The following values^{10,11} were used: Cl^- , 3.62 Å; NO_3^- , 3.40 Å; ClO_4^- , 4.53 Å.

We mention that the experimental value for the relative solution permittivity, $\varepsilon_{\text{expt}}$, a macroscopic quantity describing the interactions of ions at large separation, is not likely to be the quantity to be used in the MSA formulas.^{10,13,41} This is the reason why it is introduced as an adjustable parameter through eq 45. However, it is expected^{10,41} that $\varepsilon > \varepsilon_{\text{expt}}$. This condition was indeed found to be satisfied in cases where experimental data were available.¹⁰

For ternary solutions in which two salts A and B are dissolved in water, we used a natural extension^{10,12} of the previous relations, namely,

$$\sigma_k = \sigma_k^{(0)} + \sigma_A^{(1)}C_A + \sigma_{B \rightarrow A}^{(1)}C_B \quad (46)$$

$$\varepsilon^{-1}/\varepsilon_W^{-1} = 1 + \alpha_A C_A + \alpha_B C_B \quad (47)$$

with the introduction of a cross-term, $\sigma_{B \rightarrow A}^{(1)}$, in eq 46 to account for the effect of salt B on the size of cation k belonging to salt A. For a ternary solution, this introduces two new cross-parameters, $\sigma_{B \rightarrow A}^{(1)}$ and $\sigma_{A \rightarrow B}^{(1)}$. No cross-term is added in eq 47 to the relative permittivity, as done in earlier work.^{10,12}

Binary Solutions. (a) Trivalent Salts. Osmotic coefficient data for yttrium(III) and lanthanide(III) solutions were represented for concentrations above 0.1 mol kg⁻¹ and up to a maximum concentration corresponding to the ion volume fraction $X_3 = 0.4$. These data were obtained from isopiestic^{33,34,42–46} and water activity¹⁸ measurements.

To estimate the infinite dilution diameter values, $\sigma_{\pm}^{(0)}$, of the lanthanide(III) cations, we followed a procedure slightly different from the one used previously,¹⁷ in which they were obtained by fits in the case of perchlorate solutions, keeping the association constant equal to zero (perchlorates being assumed to behave as strong electrolytes). Here, the following trivalent lanthanides—lanthanum, terbium, erbium, and lutetium—were considered, and it was attempted to simultaneously represent the osmotic coefficients for the perchlorate, chloride, and nitrate solutions of these elements. This led to optimal values of $\sigma_{\pm}^{(0)}$: La^{3+} , 8.12 Å; Tb^{3+} , 8.37 Å; Er^{3+} , 8.43 Å; and Lu^{3+} , 8.62 Å.

Besides, it was observed that (i) the hydrodynamic Stokes diameter (dielectric friction effects⁴⁷ bringing a very slight correction) of the trivalent lanthanides, calculated using conductivity^{48,49} and diffusion⁵⁰ data, approximately varies linearly with the atomic number, Z , of the lanthanide; (ii) the above adjusted values of $\sigma_{\pm}^{(0)}$ for the four trivalent lanthanides, La, Tb, Er and Lu, closely obey a linear relationship. Both quantities are found to *increase* with Z , a behavior going in reverse order as compared to that of the ion radius (lanthanide/actinide contraction).

Thus, a similar behavior was assumed for the diameters of the whole series of the lanthanides, which led to

$$\sigma_{\pm}^{(0)}/\text{Å} = (6.186 + 3.37 \times 10^{-2}Z) \quad (48)$$

The $\sigma_{\pm}^{(0)}$ values for the trivalent lanthanide cations (calculated from the previous relation) are given in Table 1. In the case of yttrium(III), the value was deduced from a fit of the osmotic coefficient for the chloride and the nitrate, leading to a value close to that for lanthanum(III).

Table 1. Cation Sizes at Infinite Dilution, $\sigma_{\pm}^{(0)}$

ion	$\sigma_{\pm}^{(0)}$ (Å)	ion	$\sigma_{\pm}^{(0)}$ (Å)	ion	$\sigma_{\pm}^{(0)}$ (Å)
Y^{3+}	8.10	Eu^{3+}	8.31	Er^{3+}	8.48
La^{3+}	8.11	Gd^{3+}	8.34	Tm^{3+}	8.51
Ce^{3+}	8.14	Tb^{3+}	8.38	Yb^{3+}	8.55
Pr^{3+}	8.17	Dy^{3+}	8.41	Lu^{3+}	8.58
Nd^{3+}	8.21	Ho^{3+}	8.44	UO_2^{2+}	8.07
Sm^{3+}	8.28				

Osmotic coefficients for the lanthanide solutions containing a given anion (perchlorate, chloride, or nitrate) are very similar. For perchlorates there is almost no difference, chlorides exhibit a greater variation, and nitrates vary more than chlorides. For a given lanthanide, a general behavior is observed, $\Phi(NO_3^-) < \Phi(Cl^-) < \Phi(ClO_4^-)$. This tendency may be understood at low salt concentration where van't Hoff law applies and MM-to-LR corrections are small, by noting that ionic association in these solutions increases in the series $ClO_4^- < Cl^- < NO_3^-$, association reducing the effective number of particles and, consequently, the osmotic pressure of solution.

For the binary case, one has four parameters in the model— $\sigma^{(1)}$, α , K_{CA} , and K_T —except in the case of perchlorates which are regarded as strong electrolytes ($K_{CA} = K_T = 0$).

In Table 2 the results for the BiMSA parameters and the AARD are given for the binary solutions. It is worth noticing that in all cases the expected conditions $\sigma^{(1)} \leq 0$ and $\alpha \geq 0$ are fulfilled, meaning that, as usual, the hydrated cation size and permittivity decrease with salt concentration. This is a satisfying result.

A very good representation of experimental osmotic coefficients is found. The maximum AARD is for lanthanum nitrate (0.69%). However, it must be noticed that the fit is made to high concentration for this solution, viz., 3.5 mol kg⁻¹, which corresponds to an ionic strength of 21 mol kg⁻¹.

Chloride solutions were in general better described than perchlorate and nitrate solutions. It must be remembered that in the case of perchlorate solutions Φ was fitted using only two parameters, instead of four in the case of chloride and nitrate solutions. Besides, according to the results of Table 2, nitrates are found to undergo stronger association than chlorides.

To illustrate, the results for three lanthanides along the series, namely, praseodymium, dysprosium, and lutetium, are shown in Figures 2, 3, and 4, with plots of experimental and adjusted osmotic coefficients. The fits are very good on the whole concentration range. In Table 2, we observe that, for a given lanthanide,

$$|\sigma^{(1)}(NO_3^-)| < |\sigma^{(1)}(Cl^-)| < |\sigma^{(1)}(ClO_4^-)| \quad (49)$$

Furthermore it is seen in Figure 5 that $-\sigma^{(1)}$ is an overall increasing function of Z for a given anion. Remembering that the sizes of the anions are in the order $\sigma_A(ClO_4^-) > \sigma_A(Cl^-) > \sigma_A(NO_3^-)$ eq 49 is an expected result if one notices that the amount of water available for hydration of a given cation decreases with the size of the anion at given salt concentration. A similar reasoning may be applied concerning the effect of Z on $-\sigma^{(1)}$ by noting that the value of $\sigma_{\pm}^{(0)}$ increases with Z in the present description.

On the other hand, the α values lend themselves less clearly to a simple and direct interpretation. One just may say that the chlorides lead to the smaller values of α , and the perchlorates to the larger ones, meaning that for a given cation the permittivity would decrease more rapidly with salt concentration in the following order: $\varepsilon(ClO_4^-) < \varepsilon(NO_3^-) < \varepsilon(Cl^-)$. As compared to the discussion of the $\sigma^{(1)}$ values, the order for the α 's is reversed between nitrate and chloride. Besides, we are

Table 2. BiMSA Results for Binary Solutions

lanthanides	max m^a	$-10^2\sigma^{(1)b}$	$10^2\alpha^c$	$K_{CA}^0{}^c$	$K_T^0{}^c$	AARD ^d (%)
La(ClO ₄) ₃	2.6	49.2	12.6	0	0	0.57
Pr(ClO ₄) ₃	2.5	50.5	14.5	0	0	0.33
Nd(ClO ₄) ₃	2.4	51.4	15.2	0	0	0.31
Sm(ClO ₄) ₃	2.5	54.0	15.4	0	0	0.32
Gd(ClO ₄) ₃	2.4	55.6	14.6	0	0	0.24
Tb(ClO ₄) ₃	2.4	56.5	14.0	0	0	0.39
Dy(ClO ₄) ₃	2.4	57.0	14.1	0	0	0.40
Ho(ClO ₄) ₃	2.4	57.7	14.9	0	0	0.32
Er(ClO ₄) ₃	2.4	58.7	15.5	0	0	0.29
Tm(ClO ₄) ₃	2.3	59.0	16.3	0	0	0.26
Yb(ClO ₄) ₃	2.3	60.7	16.6	0	0	0.26
Lu(ClO ₄) ₃	2.3	60.7	18.0	0	0	0.13
UO ₂ (ClO ₄) ₂	3.0	39.7	11.9	0	0	0.17
YCl ₃	3.0	45.6	3.78	5.07	0.0255	0.25
LaCl ₃	3.1	48.1	5.74	6.10	0.0324	0.18
CeCl ₃	1.8	47.8	6.30	4.86	0.108	0.67
PrCl ₃	2.9	47.5	6.81	5.33	0.112	0.12
NdCl ₃	3.0	47.8	7.31	5.38	0.104	0.10
SmCl ₃	2.9	49.0	7.72	5.06	0.0873	0.09
EuCl ₃	2.8	49.6	6.69	5.29	0.167	0.11
GdCl ₃	2.8	50.0	6.96	5.04	0.0976	0.14
TbCl ₃	2.8	50.5	6.11	5.54	0.171	0.14
DyCl ₃	2.8	50.6	7.31	4.91	0.0767	0.10
HoCl ₃	2.7	50.5	7.32	4.63	0.158	0.17
ErCl ₃	2.6	51.1	7.56	5.07	0.167	0.09
TmCl ₃	2.6	51.5	6.98	5.40	0.301	0.11
YbCl ₃	2.6	52.2	7.00	5.54	0.378	0.10
LuCl ₃	2.6	52.3	9.11	4.74	0.195	0.13
UO ₂ Cl ₂	3.2	41.9	11.8	0.876	0.368	0.47
Y(NO ₃) ₃	3.5	40.8	10.5	1.16	0.553	0.22
La(NO ₃) ₃	3.5	42.5	13.4	4.49	0.729	0.69
Ce(NO ₃) ₃	3.3	40.1	17.1	2.42	0.534	0.63
Pr(NO ₃) ₃	3.5	43.0	13.8	4.60	0.588	0.61
Nd(NO ₃) ₃	3.5	44.2	12.7	5.81	0.646	0.67
Sm(NO ₃) ₃	3.4	45.6	11.5	8.26	0.608	0.52
Eu(NO ₃) ₃	3.4	46.0	11.6	7.35	0.634	0.54
Gd(NO ₃) ₃	3.2	45.2	13.3	4.80	0.422	0.36
Tb(NO ₃) ₃	3.2	45.0	14.9	2.59	0.411	0.34
Dy(NO ₃) ₃	3.1	46.4	14.0	2.45	0.411	0.33
Ho(NO ₃) ₃	3.1	46.8	13.7	2.00	0.481	0.38
Er(NO ₃) ₃	3.0	46.9	14.7	1.35	0.439	0.34
Tm(NO ₃) ₃	3.0	47.6	14.3	1.37	0.363	0.23
Yb(NO ₃) ₃	2.9	49.6	11.2	2.67	0.423	0.21
Lu(NO ₃) ₃	3.0	50.1	10.4	3.05	0.496	0.23
UO ₂ (NO ₃) ₂	4.0	43.8	0.0536	1.74	0.00819	0.23

^a In mol kg⁻¹. ^b In Å mol⁻¹ L. ^c In mol⁻¹ L. ^d AARD is the average relative deviation of the calculated osmotic coefficients: AARD(%) = $(100/N)\sum_i |\Phi_{\text{calc}}(k) - \Phi_{\text{exp}}(k)|/\Phi_{\text{exp}}(k)$, with N being the number of data points, $\Phi_{\text{calc}}(k)$ the calculated osmotic coefficients, and $\Phi_{\text{exp}}(k)$ are the experimental osmotic coefficients values.

not aware of experimental data concerning this quantity for lanthanide solutions.

The calculated distribution of associated species was examined as a function of salt concentration. Typical results for the proportion of CA pairs and CA₂ trimers (defined as the ratios to total C density) are plotted in Figure 6 in the case of praseodymium salt solutions. The results for other lanthanide salts are very similar. It was found that the proportion of pairs exhibits a maximum in the case of chlorides and nitrates, with maximum values of ca. 18 and 12%, respectively. This maximum may result from the competition between the formation of pairs and that of trimers. The proportion of pairs in the case of chlorides generally exceeds that for nitrates (for a given lanthanide). The opposite situation occurs for the proportion of trimers. The maximum values of the latter are of the order of 5% for the chloride and 10% for the nitrate. The relative association degrees of chlorides and nitrates are consistent with the values for the 1:1 and 1:2 association constants reported in Table 2.

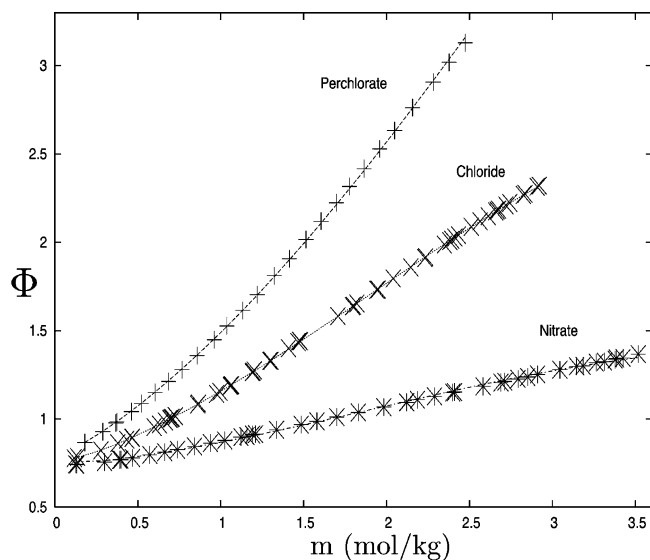


Figure 2. Experimental (symbols) and calculated (lines) osmotic coefficients values for praseodymium salts solutions.

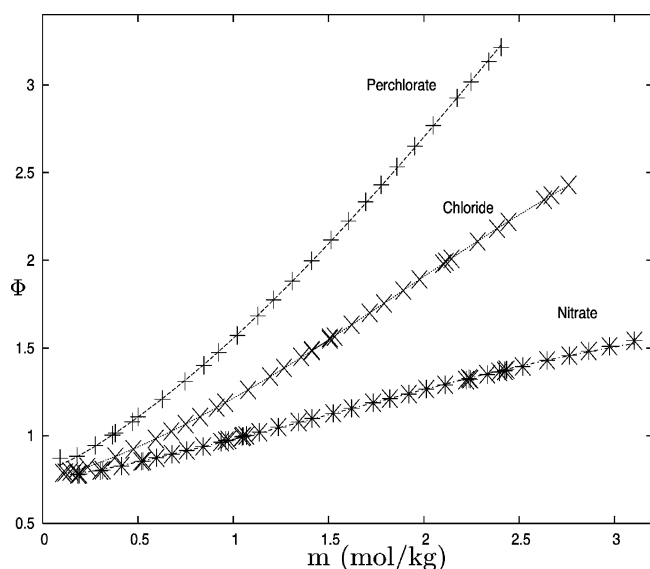


Figure 3. Experimental (symbols) and calculated (lines) osmotic coefficients values for dysprosium salts solutions.

Values for the 1:1 thermodynamic association constants have been reported in the literature for lanthanide chlorides and nitrates.^{51,52} They are compared with our present values in Figures 7 and 8 respectively for the chlorides and the nitrates. Overall the agreement is very good in the latter case, and in the former case our values are systematically ca. 2.5 times larger than those of Millero.⁵¹ However, discrepancies are not unexpected because the literature values were computed from data obtained using different techniques and another model, the Pitzer model, to describe the effect of activity coefficients on the measured apparent association constants. In the case of the chlorides, the 1:1 association constants are rather homogeneously distributed as a function of Z , while in the case of the nitrates a maximum is noted around the samarium and a minimum around the erbium. However, no explanation seems at hand for this phenomenon, which occurred also in the model with only 1:1 complexes.¹⁷ Constants for trimers show a more scattered pattern.

(b) Uranyl Ion. For the UO₂²⁺ (VI) uranyl ion, a divalent actinide oxide ion, an optimum $\sigma^{(0)}$ value was determined by a

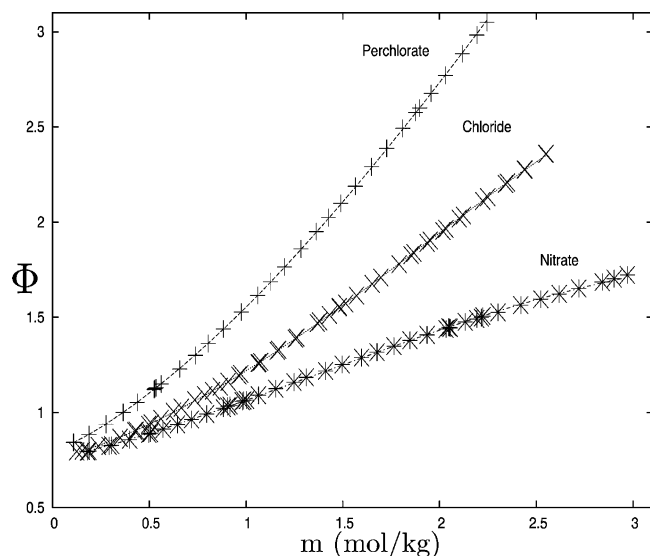


Figure 4. Experimental (symbols) and calculated (lines) osmotic coefficients values for lutetium salts solutions.

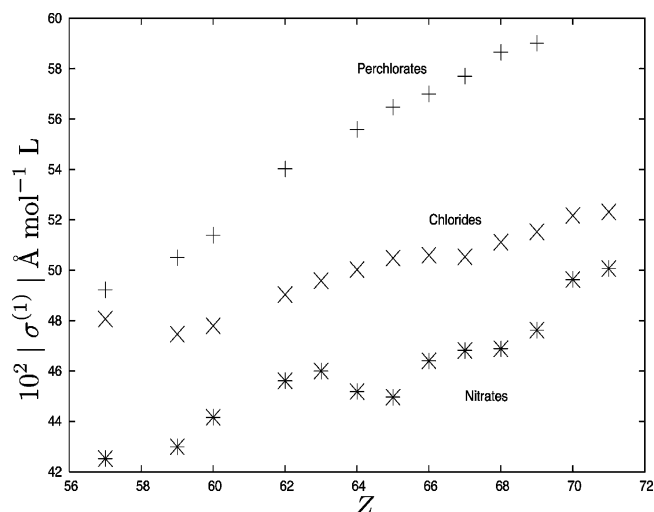


Figure 5. Values of the $\sigma^{(1)}$ BiMSA parameter (in absolute value) for solutions of lanthanide perchlorates, chlorides, and nitrates.

simultaneous fit of Φ for the uranyl perchlorate, chloride, and nitrate solutions.

In the case of $\text{UO}_2(\text{ClO}_4)_2$, the density of solution was evaluated from the experimental density measurement of the ternary mixture, $\text{UO}_2(\text{NO}_3)_2 + 2\text{HClO}_4$ (the concentration of HClO_4 being twice that of $\text{UO}_2(\text{NO}_3)_2$), which may be viewed alternately as the mixture $\text{UO}_2(\text{ClO}_4)_2 + 2\text{HNO}_3$. Knowing the density of the HNO_3 solution and applying the formula for ternary solutions,³⁸ a fit of these densities led to the following relationship, $d = d_w + 0.3918(C/C_0) - 0.01575(C/C_0)^{3/2}$ for $\text{UO}_2(\text{ClO}_4)_2$ solution, with d_w the density of pure water, $C_0 = 1 \text{ mol L}^{-1}$, and d and C being expressed in kg L^{-1} and mol L^{-1} , respectively.

The results of fit for the three salts are very satisfying, with a small AARD in each case. The adjusted value of $\sigma_{\text{F}}^{(0)}$ was 8.07 \AA (given in Table 1), which is slightly smaller than our previous value of 8.39 \AA .¹⁹

Values for the thermodynamic association constants have been proposed in the literature,⁵³ namely, $K_{\text{CA}}^0 \approx 1.48 \text{ mol}^{-1} \text{ L}$ and $K_{\text{T}}^0 = 0.054 \text{ mol}^{-1} \text{ L}$ for UO_2Cl_2 solution, and $K_{\text{CA}}^0 \approx 2.00 \text{ mol}^{-1} \text{ L}$ for $\text{UO}_2(\text{NO}_3)_2$ solution (no value was proposed for the 1:2 association constant). The latter value for K_{CA}^0 compares well

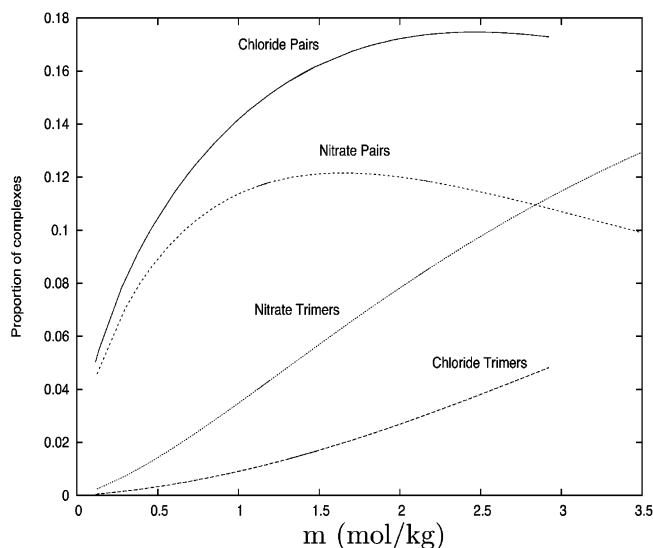


Figure 6. Calculated proportions of CA pairs and CA_2 trimers in the case of praseodymium salts solutions.

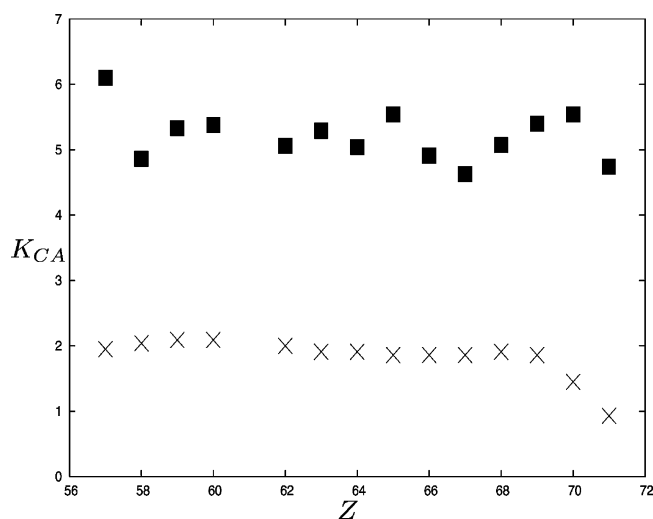


Figure 7. Lanthanide–chloride dimer association constant as a function of the lanthanide atomic number: (x) literature values;⁵¹ (■) BiMSA adjusted values.

with ours, $K_{\text{CA}}^0 = 1.74$. In the case of UO_2Cl_2 solution, the discrepancy is larger, although the order of magnitude (of the order of unity) is comparable. On the other hand, our value for the trimer association constant, $K_{\text{T}}^0 = 0.368$, is significantly greater than the literature value, $K_{\text{T}}^0 = 0.054$, by almost 1 order of magnitude. However, as in the previous section, a discrepancy is not surprising since the literature value was calculated from data obtained using different techniques and a different model, the specific interaction model (SIT), to account for nonideality effects. Moreover, large discrepancies may be expected in the estimation of thermodynamic constants for association orders beyond that of dimers.

Ternary Mixtures. Experimental data for aqueous ternary mixtures containing lanthanide or actinide salts are not plentiful.

Values for the experimental osmotic coefficient were found for mixtures of nitrate salts of Y(III), Pr(III), and Nd(III) with NH_4NO_3 ,⁵⁴ and mixtures of nitrate salts of Ce(III)¹⁸ and UO_2^{2+} (VI)¹⁹ with HNO_3 . High concentrations are reported in these references, up to ionic strengths $I = 20.9 \text{ mol kg}^{-1}$ for Y(III), $I = 25.2 \text{ mol/kg}$ for the lanthanides(III), and $I = 12.45 \text{ mol kg}^{-1}$ for the uranyl cation.

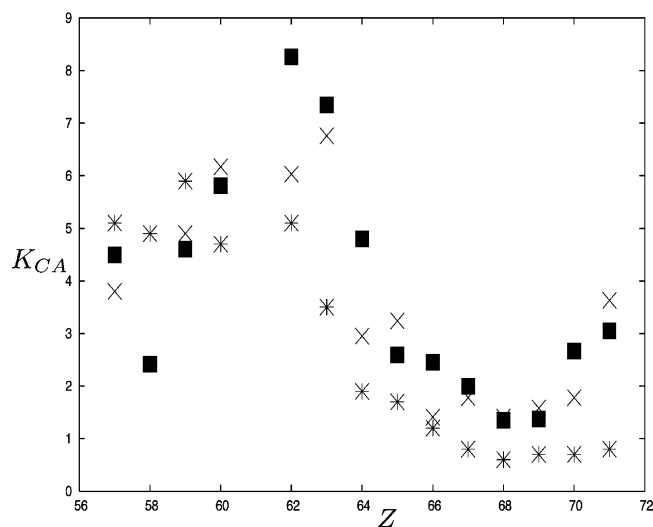


Figure 8. Lanthanide–nitrate dimer association constant as a function of the lanthanide atomic number: (x) literature values;⁵¹ (*) literature values;⁵² (■) BiMSA adjusted values.

Table 3. BiMSA Parameters for the Ternary Mixtures

salt A + salt B	ref	max I^a	$10^2 \sigma_{A-B}^{(1)c}$	$10^2 \sigma_{B-A}^{(1)b}$	AARD ^c (%)
Y(NO ₃) ₃ + NH ₄ NO ₃	54	20.9	−2.71	−13.2	0.88
Pr(NO ₃) ₃ + NH ₄ NO ₃	54	23.1	−25.5	−6.11	0.89
Nd(NO ₃) ₃ + NH ₄ NO ₃	54	23.1	−32.8	−4.19	1.1
Ce(NO ₃) ₃ + HNO ₃	18	21.8	−31.4	−7.75	0.12
UO ₂ (NO ₃) ₂ + HNO ₃	19	12.5	−23.0	−16.5	1.2

^a I is ionic strength: $I = (1/2)\sum z_i^2 m_i$, in mol kg^{−1}; ^b In Å mol^{−1} L.
^c Defined in Table 2.

In the adjustment procedure, similarly to the case of binary mixtures, it was checked that the condition on the volume fraction occupied by the ions, $X_3 \leq 0.4$, was satisfied.

The parameter values determined for the binary solutions (Table 2) were used for the ternary mixtures, together with the introduction in eq 46 of the two cross-parameters, $\sigma_{A-B}^{(1)}$ and $\sigma_{B-A}^{(1)}$ accounting for the effect of a salt on the cation size of the other salt.

Besides, new optimum parameters were regressed for binary HNO₃ and NH₄NO₃ solutions, using the expressions for associating 1:1 electrolytes derived in earlier work,¹⁷ that are consistent with the present model. This led to the following results: $K_{HNO_3}^0 = 0.0722$ mol^{−1} L, $\sigma_{HNO_3}^{(1)} = -0.0747$ Å mol^{−1} L, and $\alpha_{HNO_3} = 0.100$ mol^{−1} L for HNO₃ (with $\sigma_{H^+}^{(0)} = 5.04$ Å, a common value for all acids)¹⁰ and $K_{NH_4NO_3}^0 = 0.348$ mol^{−1} L, $\sigma_{NH_4NO_3}^{(1)} = -0.0192$ Å mol^{−1} L, and $\alpha_{NH_4NO_3} = 0.0597$ mol^{−1} L for NH₄NO₃ (with $\sigma_{NH_4^+}^{(0)} = 3.33$ Å). These fits were made up to high concentrations of 16 mol kg^{−1} for HNO₃ and 25 mol kg^{−1} for NH₄NO₃, compatible with the high ionic strengths of the ternary mixtures, with AARD's of 0.7 and 0.3%, respectively.

We denote by A the salt containing the multivalent cation and by B the other salt. Because of the larger size of the multivalent cation and of the greater total stoichiometric number of A, the following relation is expected

$$|\sigma_{A-B}^{(1)}| > |\sigma_{B-A}^{(1)}| \quad (50)$$

Table 3 gathers the parameter values obtained by a fit of the experimental data. It shows that, as expected, the two cross-parameters $\sigma_{A-B}^{(1)}$ and $\sigma_{B-A}^{(1)}$ are found to have negative values in all cases, similarly to the parameter $\sigma^{(1)}$. This is again a satisfying result. Moreover, it is seen in Table 3 that relation

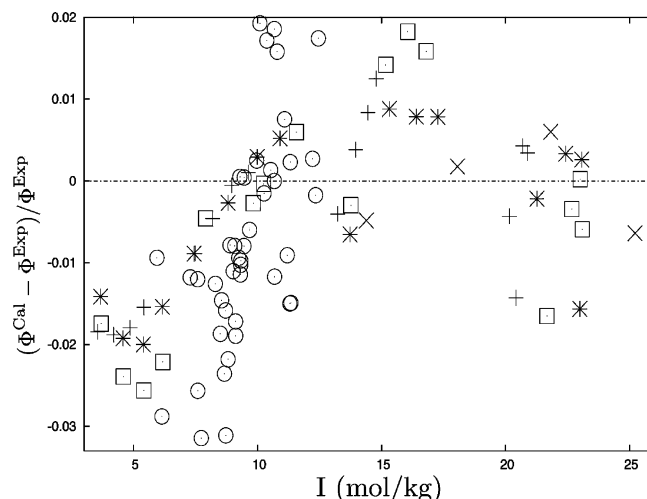


Figure 9. Relative deviation between experimental and calculated osmotic coefficients for the ternary mixtures: (+) Y(NO₃)₃–NH₄NO₃–H₂O, $I_{\max} = 20.9$ mol kg^{−1}; (x) Ce(NO₃)₃–HNO₃–H₂O, $I_{\max} = 25.2$ mol kg^{−1}; (*) Pr(NO₃)₃–NH₄NO₃–H₂O, $I_{\max} = 23.1$ mol kg^{−1}; (□) Nd(NO₃)₃–NH₄NO₃–H₂O, $I_{\max} = 23.1$ mol kg^{−1}; (○) UO₂(NO₃)₂–HNO₃–H₂O, $I_{\max} = 12.5$ mol kg^{−1}.

47 is satisfied by all mixtures except the one containing the Y³⁺ cation. It is observed besides that the AARD's for the ternary mixtures are slightly greater than for the binaries. As shown in Figure 9, the relative deviation between experimental and calculated osmotic coefficients is within the range of −2 to +2% for all the ternary mixtures, except in the case of the uranyl and neodymium mixtures where it can be between −3 and 2% at the lowest ionic strengths, below 10 mol kg^{−1}.

We mention finally that the ternary mixture Th(NO₃)₄–HNO₃–H₂O containing the tetravalent cation Th⁴⁺ was also studied. The adjusted BiMSA parameter values for the aqueous binary solution of Th(NO₃)₄ were as follows: $\sigma_{Th}^{(0)} = 12.1$ Å, $\sigma_{Th}^{(1)} = -1.67$ Å mol^{−1} L, $\alpha = 0.497$ mol^{−1} L, $K_{CA} = 77.9$ mol^{−1} L, and $K_T = 0.0223$ mol^{−1} L with an AARD of fit of 0.32%. With these values, a fit of the osmotic coefficient data⁵⁵ led to cross-parameter values, $\sigma_{A-B}^{(1)} = -33.8$ Å mol^{−1} L and $\sigma_{B-A}^{(1)} = -27.3$ Å mol^{−1} L, where A = Th(NO₃)₄ and B = HNO₃. However, the fit was not good, resulting in an AARD of 4.1%.

It may be put forward that considering 1:1 and 1:2 complexes in the model is not sufficient to satisfactorily describe this type of solution containing a cation of high valence. Indeed, in the case of the Th(IV) ion, a significantly higher degree of complexation, leading at least up to the 1:4 complex, has been reported experimentally.⁵⁶

Conclusion

In the nuclear industry, the reprocessing of spent fuel is a fundamental step, leading to the separation of the various elements for their eventual recycling or repository.⁵⁷ The concentrated solutions encountered in these processes are commonly composed of nitric acid and actinide and lanthanide ions. Actinides include uranyl and plutonium ions. Lanthanide ions represent half of the fission products.

The present study constitutes an additional step toward the modeling of the thermodynamic properties of such mixtures.

In subsequent work it will be attempted to include complexes of higher stoichiometry in the model and to describe multicomponent mixtures. Moreover, experimental data will be acquired

for ternary mixtures of lanthanides or actinides with nitric acid or ammonium nitrate.

Acknowledgment

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