

Lanthanide Salts Solutions: Representation of Osmotic Coefficients within the Binding Mean Spherical Approximation

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Osmotic coefficients of aqueous solutions of lanthanide salts are described using the binding mean spherical approximation (BIMSA) model based on the Wertheim formalism for association. The lanthanide(III) cation and the co-ion are allowed to form a 1–1 ion pair. Hydration is taken into account by introducing concentration-dependent cation size and solution permittivity. An expression for the osmotic coefficient, derived within the BIMSA, is used to fit data for a wide variety of lanthanide pure salt aqueous solutions at 25 °C. A total of 38 lanthanide salts have been treated, including perchlorates, nitrates, and chlorides. For most solutions, good fits could be obtained up to high ionic strengths. The relevance of the fitted parameters has been discussed, and a comparison with literature values has been made (especially the association constants) when available.

Introduction

It is well-known that solutions of lanthanide(III) and actinide(III) exhibit remarkable thermodynamical features in their properties when one goes along their series in the periodic table.¹ Both series follow a similar trend, which can be explained by lanthanides and actinides similarity regarding many microscopic properties (e.g., electronic structure and ionic radii). Hence, any theory suitable for the lanthanide(III) may be expected to give predictions for the actinide(III) salt [such as Am(NO₃)₃ and Cm(NO₃)₃] properties and to be a complement to their direct experimental acquisition. This approach is all of the more interesting because actinides can hardly be manipulated at high concentration because of their radioactivity, and actinide salts thermodynamical properties are of great interest for the improvement of spent fuel treatment. Furthermore, even if osmotic coefficient acquisition and theoretical concepts have been implemented for different actinide salts² (oxidation states +IV and +V), no values can be found for actinide(III) salts.

On the basis of this simple idea, we thought of describing by the BIMSA (binding mean spherical approximation), osmotic and activity coefficients for aqueous lanthanide(III) salts, as a starting point for a better understanding of osmotic and activity coefficients of actinide(III) salts.

The present paper is based on previous work,^{3–6} in which the mean spherical approximation (MSA)^{7–12} was used for the description of thermodynamic excess functions of solutions of strong^{3,4} and weak electrolytes⁵ and their mixtures.^{4,6} Here, we use this framework to describe departures from ideality for solutions of lanthanide perchlorates, nitrates, and chlorides.

Because lanthanide nitrates and chlorides are known to form weak complexes, in the present investigation, ionic association is explicitly and consistently taken into account for these salts.

Association has been discussed in the past by other authors^{13–16} who used the well-known chemical model of Bjerrum in conjunction with the MSA. In the present work, we use a more recent and convenient model for associating electrolytes.¹⁷ Unlike the classic chemical model for ion pairing, the effect of association is included in the computation of the MSA screening parameter Γ . Simple formulas for the thermodynamic excess properties have been obtained in terms of this parameter. One single parameter, the association constant, permits to take into account all association mechanisms (Coulombic and covalent). The treatment now includes the fraction of particles that are bonded, which is obtained by imposing the chemical equilibrium mass-action law. This formalism was shown to be very successful for ionic systems in both the hypernetted chain (HNC) approximation and the MSA.^{18–22}

In the first section, we give a short summary of the theory and derive corrections that account for the concentration variation of the physical parameters. The second section is dedicated to a discussion of the experimental results.

Theory

The expressions used in this work, issued from the BIMSA theory, are mainly taken from ref 5. However, for clarity, we recall the main formulas. As for the MSA, the BIMSA resolution takes into account hard-core repulsion and Coulombic potential, with the essential difference being that the BIMSA also considers a short-range potential, responsible for ion pairing.

A slightly modified expression was used here for the mass-action law (eq 1 below) as compared to the one used in ref 5. The influence of this feature on the osmotic and activity coefficients is calculated explicitly. All expressions are given in the international SI (MKS) unit system.

We consider a two-component electrolyte in which only one + ion and one – ion can form a pair. A pair is defined as two ions + and – being in contact. The valences, diameters, and

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total number densities of the ions are z_+ , z_- , σ_+ , σ_- , ρ_+ , and ρ_- , respectively. We denote by α_+ and α_- the unbound ion fractions.

In this work, the mass-action law (MAL) is written as

$$K_0 \equiv \frac{\rho_P}{(\rho_+ \alpha_+)(\rho_- \alpha_-)} = K g_c^{\text{HS}} \exp \left[-2\lambda \frac{z'_+ z'_-}{\sigma_P} + 2\lambda_0 \frac{z_+ z_-}{\sigma_{P,0}} \right] \quad (1)$$

in which K is the equilibrium thermodynamic constant, K_0 is the apparent equilibrium constant, $\rho_i \alpha_i$ is the density of unbound species i , ρ_P is the pair number density, g_c^{HS} is the contact hard-sphere radial distribution function whose expression is given below, and

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

$$\lambda \equiv \beta e^2 / (4\pi \epsilon_0 \epsilon) \quad (3)$$

$$\sigma_P \equiv \sigma_+ + \sigma_- \quad (4)$$

η and Γ are classical MSA parameters;^{7–12} ϵ_0 is the permittivity of a vacuum; and ϵ is the relative permittivity of solution. In eq 1, λ_0 and $\sigma_{P,0}$ are λ and σ_P , respectively, for infinitely diluted solution.

As mentioned above, eq 1 slightly differs from the expression for K given in ref 5 and $\sigma_{P,0}$ is taken instead of σ_P in the term corresponding to infinite dilution. This result has been shown in ref 23.

The pair density ρ_P and the MSA parameters η and Γ verify the same equations as in ref 5 that can be solved easily by numerical iterations.

The excess MSA Helmholtz energy A per volume unit is given by

$$\beta \Delta A^{\text{MSA}} = \beta \Delta U^{\text{MSA}} + \frac{\Gamma^3}{3\pi} + \beta \Delta A^{\text{MAL}} - 2\lambda \frac{\rho_P}{\sigma_P} z'_+ z'_- \quad (5)$$

where the excess electrostatic MSA internal energy per volume unit is

$$\beta \Delta U^{\text{MSA}} = \beta \Delta U_0^{\text{MSA}} + \lambda \frac{\rho_P}{\sigma_P} \left(\frac{z'_+ z'_-}{1 + \Gamma \sigma_+} + \frac{z_- z'_+}{1 + \Gamma \sigma_-} \right) \quad (6)$$

with

$$\beta \Delta U_0^{\text{MSA}} = -\lambda \sum_{i=+,-} \frac{\Gamma z_i + \eta \sigma_i}{\rho_i z_i (1 + \Gamma \sigma_i)} \quad (7)$$

The MAL contribution is given by

$$\beta \Delta A^{\text{MAL}} = \sum_{k=+,-} \rho_k \ln \alpha_k + \rho_P \quad (8)$$

With the cation size and solution permittivity being concentration-dependent, the osmotic coefficient is written as

$$\Delta \Phi^{\text{MSA}} = \Delta \Phi_0^{\text{MSA}} + \Delta \Phi_{\sigma_+} + \Delta \Phi_{\epsilon} \quad (9)$$

where

$$\Delta \Phi_0^{\text{MSA}} = \Delta \Phi_0^{\text{el}} + \Delta \Phi_0^{\text{MAL}} \quad (10)$$

$$\Delta \Phi_0^{\text{el}} = -\frac{\Gamma^3}{3\pi \rho_t} - \frac{\lambda}{\rho_t} \frac{2}{\pi} \eta^2 \quad (11)$$

$$\Delta \Phi_0^{\text{MAL}} = -\frac{\rho_P}{\rho_t} \left(1 + \rho_t \frac{\partial \ln g_c^{\text{HS}}}{\partial \rho_t} \right) \quad (12)$$

and

$$\Delta \Phi_{\sigma_+} = \frac{1}{\rho_t} \left[\frac{\partial \beta \Delta A^{\text{MSA}}}{\partial \sigma_+} \right]_{\Gamma} D(\sigma_+) \quad (13)$$

$$\Delta \Phi_{\epsilon} = \frac{1}{\rho_t} \left[\frac{\partial \beta \Delta A^{\text{MSA}}}{\partial \epsilon^{-1}} \right]_{\Gamma} D(\epsilon^{-1}) \quad (14)$$

with

$$D \equiv C_S \frac{\partial}{\partial C_S} \quad (15)$$

in which C_S is the electrolyte molar concentration.

One has⁵

$$\Delta \Phi_{\epsilon} = \frac{\beta \Delta E^{\text{MSA}}}{\rho_t} \epsilon D(\epsilon^{-1}) \quad (16)$$

as in refs 3 and 4 and

$$\left[\frac{\partial \beta \Delta A^{\text{MSA}}}{\partial \sigma_+} \right]_{\Gamma} = \left[\frac{\partial \beta \Delta U^{\text{MSA}}}{\partial \sigma_+} \right]_{\Gamma, \rho_P} - \rho_P \left[\frac{\partial \ln g_c^{\text{HS}}}{\partial \sigma_+} + 2 \frac{\lambda z'_+ z'_-}{\sigma_P^2} \right] \quad (17)$$

with

$$\left[\frac{\partial \beta \Delta U^{\text{MSA}}}{\partial \sigma_+} \right]_{\Gamma, \rho_P} = \lambda \rho_+ \frac{z'_+ [\Gamma^2 (z_+ + \eta \sigma_+^2) - 2\eta]}{1 + \Gamma \sigma_+} - \lambda \frac{2\rho_P}{\sigma_P} \frac{\Gamma (z_+ + \eta \sigma_+^2) + 2\eta \sigma_+}{(1 + \Gamma \sigma_+)^2} z'_- \quad (18)$$

Equation 17 differs from its counterpart in ref 5 because it accounts for eq 1 in the present work.

The expression for g_c^{HS} and its derivative with respect to σ_+ for use in eq 17 is given in ref 5. Its derivative with respect to ρ_t , needed in eq 12, may be calculated by using the relation

$$\frac{\partial g_c^{\text{HS}}}{\partial \rho_t} = \frac{X_2}{\rho_t} \frac{\partial g_c^{\text{HS}}}{\partial X_2} + \frac{X_3}{\rho_t} \frac{\partial g_c^{\text{HS}}}{\partial X_3} \quad (19)$$

where

$$X_i = \frac{\pi}{6} \sum_{j=+,-} \rho_j \sigma_j^i \quad (20)$$

Finally, the excess MSA mean activity coefficient can be obtained simply from the thermodynamic formula

$$\Delta \ln \gamma_{\pm}^{\text{MSA}} = \frac{\beta \Delta A^{\text{MSA}}}{\rho_t} + \Delta \Phi^{\text{MSA}} \quad (21)$$

and the total osmotic coefficient is

$$\Phi = 1 + \Delta \Phi^{\text{MSA}} + \Delta \Phi^{\text{HS}} \quad (22)$$

in which $\Delta \Phi^{\text{HS}}$ is the hard-sphere contribution that can be calculated from the Carnahan–Starling expression, as described in ref 3.

In this work, as in ref 5, the anion size is kept constant (equal to its crystallographic value or adjusted so as to yield an optimum fit) and the diameter of the cation σ_+ and ϵ^{-1} was chosen as a linear function of the concentration

$$\sigma_+ = \sigma_+^{(0)} + \sigma^{(1)} C_S \quad (23)$$

$$\epsilon^{-1} = \epsilon_W^{-1} (1 + \alpha C_S) \quad (24)$$

with ϵ_W being the relative permittivity of the pure solvent ($\epsilon_W = 78.3$ for water). Equations 23 and 24 introduce two adjustable parameters $\sigma^{(1)}$ and α that are characteristic of the electrolyte, while $\sigma_+^{(0)}$ is characteristic of the considered cation only. Therefore⁴

$$D(\sigma_+) = \sigma_+ - \sigma_+^{(0)} \quad (25)$$

$$\epsilon D(\epsilon^{-1}) = 1 - \epsilon/\epsilon_W \quad (26)$$

Besides, eqs 23 and 24 used in eqs 3 and 4

$$\lambda_0 \equiv \beta e^2 / (4\pi \epsilon_0 \epsilon_W) \quad (27)$$

$$\sigma_{P,0} \equiv \sigma_+^{(0)} + \sigma_- \quad (28)$$

In the different formulas presented in this section, issued from the BMSA theory, if the condition $K = 0$ is satisfied, we have $\rho_P = 0$ and, as expected, we recover all of the MSA relations, which do not take into account ion pairing.³⁻⁴

Results and Discussion

For lanthanide salts, osmotic coefficients have been subject to numerous experimental acquisition, contrary to activity coefficients, which were essentially calculated using the osmotic coefficient results.²⁴⁻³⁰ Therefore, we chose to fit osmotic coefficient data, for concentrations above 0.1 mol kg⁻¹. These data were raw values obtained from isopiestic equilibrium measurements,²⁴⁻³⁰ for a number of concentrated lanthanide chloride, nitrate, and perchlorate salts. EMF data^{24,25} at very low concentrations for some lanthanide salts were not used. However, after adjustment, the calculated osmotic coefficient values below 0.1 mol kg⁻¹ turned out to be in very good agreement with the EMF measurements.

To fit the closest way for all of the lanthanide salts, we had to use comparable maximum concentration for each system, when one goes from one salt to another. This could be done by choosing maximum concentrations related to the same X_3 value (eq 20). In the present case, the maximum concentrations were related to an X_3 value equal to 0.4. It is important to underline that the higher the X_3 values are, the less the approximations made in the MSA are satisfied. Therefore, fitting for an X_3 value up to 0.4 was considered as a compromise between fitting up to high concentrations and fitting in a concentration range where approximations made in the MSA are well-satisfied.

The fits were made with a FORTRAN program that can be run on a microcomputer. The procedure consisted of a least-square algorithm of the Marquardt type, in which the sum of the squares of the relative deviations was minimized.

It was checked numerically that the calculated osmotic and activity coefficients obtained from eq 12 and 23 accurately satisfy the Gibbs–Duhem relation.

For comparison with experimental data, these quantities were converted from the McMillan–Mayer to the Lewis–Randall (experimental) reference system by using the procedure de-

TABLE 1: Hydrated Lanthanide Diameter at Infinite Dilution, $\sigma_+^{(0)}$, Obtained from Fitting Osmotic Coefficients of Lanthanide Perchlorate Solutions

cation	$\sigma_+^{(0)a}$	cation	$\sigma_+^{(0)a}$	cation	$\sigma_+^{(0)a}$	cation	$\sigma_+^{(0)a}$
La ³⁺	0.877	Sm ³⁺	0.858	Dy ³⁺	0.951	Tm ³⁺	0.942
Pr ³⁺	0.865	Gd ³⁺	0.870	Ho ³⁺	0.944	Yb ³⁺	0.943
Nd ³⁺	0.864	Tb ³⁺	0.956	Er ³⁺	0.943	Lu ³⁺	0.942

^a Value in nanometers.

scribed in ref 4. Solution density values, taken from refs 29 and 31–33, were necessary for this transformation and for molal scale to molar scale conversion. In the case of Tm(NO₃)₃ solutions, for which no data could be found, we interpolated between Er(NO₃)₃ and Yb(NO₃)₃ solution densities.

The diameters of the anions were kept constant with the following values taken from previous work:⁴ Cl⁻ (0.362 nm), NO₃⁻ (0.340 nm), and ClO₄⁻ (0.453 nm). The diameters of the lanthanide(III) cations were adjusted using eq 25. In this relation, a consequence of the model is that the diameter of a given cation, at infinite dilution, $\sigma_+^{(0)}$, must have a common value for all (chloride, nitrate, and perchlorate) salts containing this cation. In practice, this constitutes one of the difficulties of the fitting procedure.

It is generally admitted that perchlorate and lanthanide ions hardly interact in water and that no significant influence of ion pairs can be expected below 2.5 molal.³⁴ Furthermore, this lack of noticeable interaction has been shown by X-ray-scattering measurements.³⁵ Likewise, the solutions of lanthanide perchlorates were treated by assuming that lanthanides and perchlorates do not associate (i.e., $K = 0$).

The corresponding diameter values, $\sigma_+^{(0)}$, obtained from a fit of lanthanide perchlorate experimental osmotic coefficients, are given in Table 1.

It is worth noting that the radii values corresponding to Table 1, which range from 0.438 to 0.471 nm, are close to the lanthanide–water molecule distances for the second coordination sphere as obtained from X-ray-scattering measurements,^{35,36} which range from 0.452 to 0.470 nm. The corresponding values for the first coordination sphere obtained by the same authors range from 0.237 to 0.257 nm. Therefore, our results agree with the generally admitted picture that lanthanide cations are surrounded by more than one hydration layer.

However, these values do not allow a very good representation of the chloride and nitrate salt osmotic coefficients. This could be done by slightly diminishing the $\sigma_+^{(0)}$ values shown in Table 1 by 6%. For a given lanthanide, this procedure led to satisfactory fits for the three salts (perchlorate, chloride, and nitrate). With this common $\sigma_+^{(0)}$ taken as a constant, we calculated the three remaining parameters ($\sigma^{(1)}$, α , and K) separately for each salt. The final results are given in Table 2.

Figure 1 compares the experimental and calculated osmotic coefficients for two salts, Lu(ClO₄)₃, which has the lowest AARD value for the solutions studied here, and LaCl₃, which has the highest AARD value. We can see that, even for LaCl₃, the discrepancy is acceptable and comparable with experimental uncertainty. Figure 2 compares experimental and calculated osmotic coefficients for three salts of a same cation: TmCl₃, Tm(NO₃)₃, and Tm(ClO₄)₃.

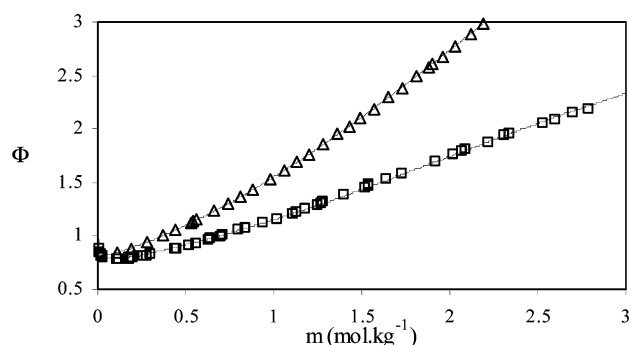
Figure 3 shows the variation of the $\sigma_+^{(0)}$ value along the lanthanide series.

Our $\sigma_+^{(0)}$ values are close to the values proposed by David and Fourest³⁷ (aquo-ion diameters of 0.922 and 0.95 nm for Pr³⁺ and Er³⁺, respectively), calculated from experimental

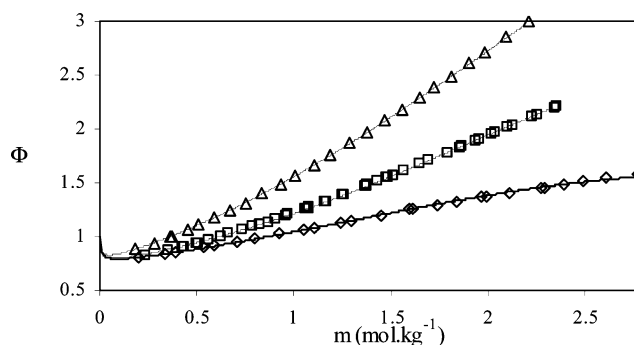
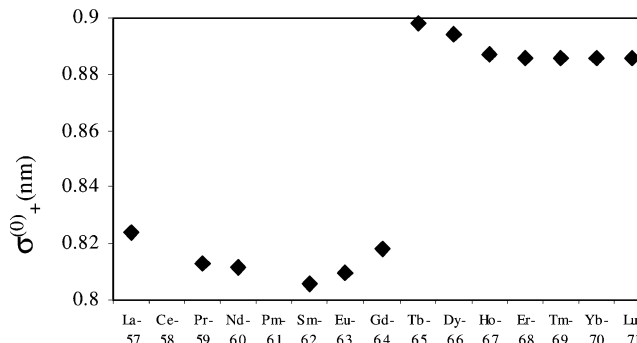
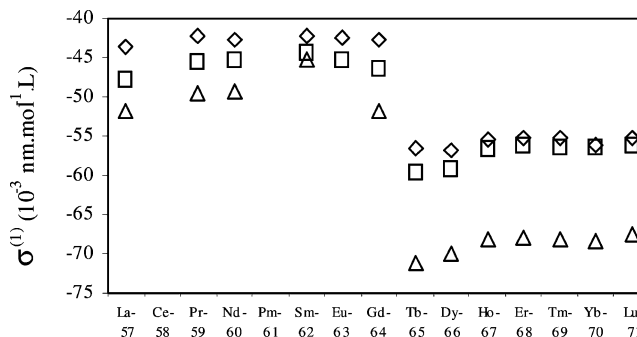
TABLE 2: Parameter Values Retained to Reproduce Lanthanide Chloride, Nitrate, and Perchlorate Osmotic Coefficient Values

salt	maximum m^a	$\sigma_+^{(0)b}$	$10^3\sigma^{(1)c}$	$10^2\alpha^d$	K^d	AARD (%) ^e
LaCl ₃	3.0	0.824	-47.8	10.2	3.05	0.8
La(NO ₃) ₃	3.5		-43.7	20.2	2.31	0.7
La(ClO ₄) ₃	2.5		-51.9	14.9	0	0.3
PrCl ₃	3.0	0.813	-45.5	9.8	2.55	0.5
Pr(NO ₃) ₃	3.6		-42.4	17.4	3.03	0.7
Pr(ClO ₄) ₃	2.6		-49.5	13.9	0	0.4
NdCl ₃	3.0	0.812	-45.2	9.6	2.59	0.6
Nd(NO ₃) ₃	3.8		-42.7	15.9	4.15	0.8
Nd(ClO ₄) ₃	2.6		-49.3	13.8	0	0.4
SmCl ₃	3.1	0.806	-44.4	8.5	2.48	0.6
Sm(NO ₃) ₃	3.8		-42.2	13.1	6.39	0.6
Sm(ClO ₄) ₃	2.5		-45.1	12.1	0	0.3
EuCl ₃	3.1	0.810	-45.2	8.1	2.55	0.6
Eu(NO ₃) ₃	3.8		-42.4	13.2	5.75	0.6
GdCl ₃	3.1	0.818	-46.3	8.6	2.26	0.7
Gd(NO ₃) ₃	3.6		-42.7	15.2	3.21	0.5
Gd(ClO ₄) ₃	2.6		-51.7	12.1	0	0.3
TbCl ₃	2.3	0.898	-59.5	18.5	2.25	0.4
Tb(NO ₃) ₃	2.6		-56.6	24.6	2.15	0.6
Tb(ClO ₄) ₃	2.2		-71.2	25.0	0	0.3
DyCl ₃	2.4	0.894	-59.0	17.6	2.39	0.6
Dy(NO ₃) ₃	2.8		-56.9	22.5	2.14	0.6
Dy(ClO ₄) ₃	2.2		-70.0	23.7	0	0.3
HoCl ₃	2.4	0.887	-56.6	17.5	1.94	0.4
Ho(NO ₃) ₃	2.8		-55.4	21.7	1.54	0.6
Ho(ClO ₄) ₃	2.2		-68.3	22.7	0	0.2
ErCl ₃	2.4	0.886	-56.2	17.3	2.10	0.5
Er(NO ₃) ₃	2.7		-55.3	20.8	1.32	0.5
Er(ClO ₄) ₃	2.2		-68.0	22.3	0	0.2
TmCl ₃	2.4	0.886	-56.3	17.2	2.11	0.4
Tm(NO ₃) ₃	2.8		-55.3	20.2	1.21	0.4
Tm(ClO ₄) ₃	2.2		-68.2	22.3	0	0.2
YbCl ₃	2.4	0.886	-56.3	17.1	2.20	0.4
Yb(NO ₃) ₃	2.6		-56.1	18.7	1.66	0.5
Yb(ClO ₄) ₃	2.2		-68.4	22.2	0	0.2
LuCl ₃	2.4	0.886	-56.2	17.5	2.08	0.4
Lu(NO ₃) ₃	2.8		-55.2	17.9	1.97	0.4
Lu(ClO ₄) ₃	2.2		-67.6	23.2	0	0.1

^a Given in mol kg⁻¹. ^b Value in nanometers. ^c Given in nm mol⁻¹ L. ^d Given in mol⁻¹ 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.

**Figure 1.** Calculated (—) and experimental LaCl₃ (□) and Lu(ClO₄)₃ (Δ) osmotic coefficient.

diffusion coefficient and ionic mobility values, using the Stokes–Einstein equation. Our hydrated cation diameter values and the ones found by David and Fourest follow the same trend: the diameter of a hydrated cation is lower for the lighter lanthanides (La–Sm) than for the heavier lanthanides (Dy–Lu). This can be explained by the fact that heavier lanthanides have a lower coordination number, thus fewer water molecules in their first hydration sphere, which means a higher charge

**Figure 2.** Calculated (—) and experimental TmCl₃ (□), Tm(NO₃)₃ (◇), and Tm(ClO₄)₃ (Δ) osmotic coefficient.**Figure 3.** Hydrated cation diameter at infinite dilution along the lanthanide series.**Figure 4.** Variation of the $\sigma^{(1)}$ parameter along the lanthanide series for, respectively, lanthanide chloride (□), nitrate (◇), and perchlorate (Δ) salts.

density on this primary sphere and more water molecules interacting with it in the outer layer. This results in a higher volume for the second hydration sphere and the hydrated cation when one compares a “light” lanthanide to a “heavy” one.³⁷ A significant gap is observed in the middle of the series, which may be attributed to this change in the coordination number of lanthanide +III occurring around the gadolinium element.

Figures 4 and 5 show the variation of the $\sigma^{(1)}$ and α value along the lanthanide series.

We observe that, in all cases, the expected conditions $\sigma^{(1)} \leq 0$ and $\alpha \geq 0$ are satisfied (the solvation number and the local solution permittivity are expected to decrease with the concentration). As for the variation of $\sigma_+^{(0)}$, a gap is observed for $\sigma^{(1)}$ and α in the middle of the series. $\sigma^{(1)}$ increases in absolute value with the size of the anion. This result agrees with the simple picture in which the effective cation size conveys the degree of hydration of the ion: the bigger the anion, the faster the cation size decreases with the concentration.

As seen in Figure 6, representing the effects of the concentration on hydrated lanthanide diameters according to our approximations (eqs 25), our $\sigma^{(1)}$ values cause the different

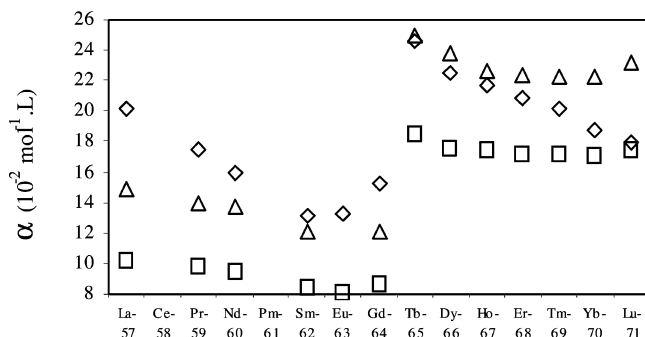


Figure 5. Variation of the parameter α along the lanthanide series for lanthanide chloride, nitrate, and perchlorate salts, same caption as Figure 4.

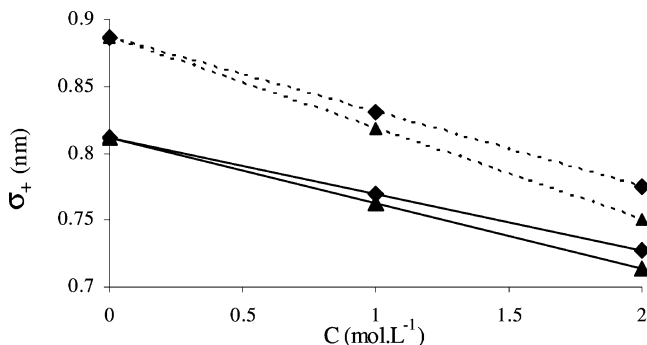


Figure 6. Hydrated cation diameter for $\text{Nd}(\text{NO}_3)_3$ (—◆—), $\text{Nd}(\text{ClO}_4)_3$ (—▲—), $\text{Er}(\text{NO}_3)_3$ (---◆---), and $\text{Er}(\text{ClO}_4)_3$ (---▲---).

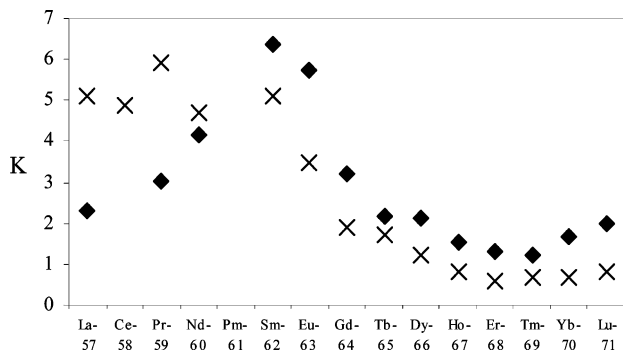


Figure 7. Variation of the lanthanide–nitrate association constant along the lanthanide series. (x) Experimental values.³⁸ (◆) Our results.

diameter differences decrease. However, we observe that, for a same counterion, heavy lanthanides have a higher hydrated cation diameter than light lanthanides, even at “high” concentration (2 or 3 mol kg^{-1}).

Lanthanide nitrate or chloride association has been the subject of numerous studies. However, these results are very scattered, probably because of the difficulty of assessing complexation with the use of weak ligands. Figure 7 shows the dependence of our calculated association constant for lanthanide nitrates, compared with extrapolation experimental values obtained by Bonal et al.³⁸ from microcalorimetric measurements.

It is noticed that the two sets of results are always of the same order of magnitude. Above samarium, the two curves exhibit noticeable parallel variation. Increasing K values when going from La to Sm and then decreasing values from Sm to Lu have already been observed experimentally by Peppard et al.³⁹ (liquid–liquid extraction method) and Anagnostopoulos et al.⁴⁰ (spectrophotometry method). The change in the coordination numbers in the aquo complexes of the lanthanides might be an essential factor explaining the nonmonotonic variation

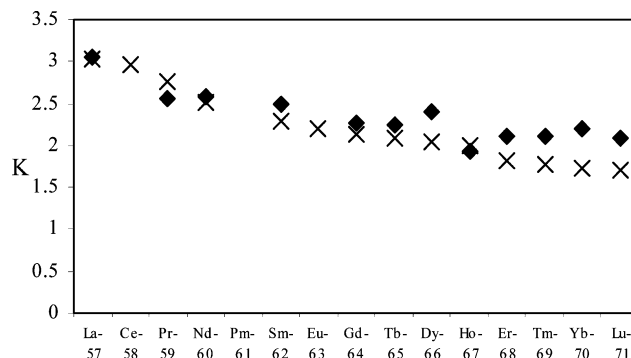
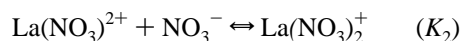


Figure 8. Variation of the lanthanide–chloride association constant along the lanthanide series. (x) Experimental values.⁴¹ (◆) Our results.

of the stability constants of nitrate complexes and in particular the sharp decrease in the constants as one goes from samarium to terbium.

Regarding lanthanide–chloride association, our calculated values can be compared with the data of Mironov et al.,⁴¹ both sets of data being surprisingly close (Figure 8). The variation of the association constant for lanthanide–chloride complexes seems to be less significant than with lanthanide–nitrate. Nevertheless, we can notice a slight decrease along the series. Analysis of apparent association constants obtained by Kozachenko and Batyaev⁴² and Peppard et al.³⁹ led to the same observations.

It must be emphasized that our model does not allow the formation of 1–2 or 1–3 complexes (i.e., LnX_2^+ and LnX_3). The existence of such species has been the subject of much controversy. For instance, using UV–visible spectroscopy and Raman spectroscopy, several authors only detected 1–1 nitrate complexes,^{40,43,44} whereas ultrasonic absorption measurements seem to show a noticeable amount of 1–2 lanthanide–nitrate complexes.⁴⁵ Furthermore, even in solutions of electrolyte, which are expected to be “simple”, evidence of triple species or aggregated species at high concentration has been obtained.⁴⁶ To test the different hypotheses within our model, we made an attempt to fit the experimental lanthanum nitrate osmotic coefficient data by assuming the equilibrium



and neglecting the presence of nonassociated La^{3+} . The calculations were performed in the “high” concentration region, between 1 and 3 mol kg^{-1} , where this equilibrium would be expected to be dominant. However, this procedure gave poor results, with a negative value for α and K values lower than 0.3. This fact might be regarded as a justification for assuming that the formation of 1–2 complexes is not a dominant phenomenon.

Conclusion

The inclusion of chemical association, combined with a Bjerrum-like exponential closure, to correctly represent low-density behavior, has been shown to allow good representation of the thermodynamic properties of associating electrolytes such as the lanthanide nitrates and chlorides.

All of the studied solutions of lanthanide perchlorate, chloride, and nitrate salts could be treated successfully up to high concentrations with the use of parameters that have microscopic physical meaning. These parameters are found to have reasonable and plausible adjusted values. Therefore, association constants are in amazingly good agreement with the experi-

mental values, in the interval between samarium and lutetium in the case of lanthanide–nitrate and in the whole series in the case of lanthanide–chloride. These satisfying results were obtained without taking into account an association of a higher order than 1–1. Nevertheless, we hope to come back to this point in the future and properly take into account the effect of higher order species on the osmotic coefficients.

Also, in future work, we will try to use this model as a predictive tool for properties of concentrated actinide solutions that are difficult to study experimentally, because of their radiotoxicity.

References and Notes

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