HAL
open science

Thermodynamic modeling of neodymium and cerium oxalates reactive precipitation in concentrated nitric acid media

Isaac Rodríguez-Ruiz, Sébastien Teychené, Youen Vitry, Béatrice Biscans, Sophie Charton

To cite this version:

Isaac Rodríguez-Ruiz, Sébastien Teychené, Youen Vitry, Béatrice Biscans, Sophie Charton. Thermodynamic modeling of neodymium and cerium oxalates reactive precipitation in concentrated nitric acid media. Chemical Engineering Science, 2018, 183, pp.20-25. 10.1016/j.ces.2018.03.007 . hal-01951511

HAL Id: hal-01951511

https://hal.science/hal-01951511v1

Submitted on 11 Dec 2018

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Open Archive Toulouse Archive Ouverte (OATAO)

OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible

This is an author's version published in: http://oatao.univ-toulouse.fr/21099

Official URL: https://doi.org/10.1016/j.ces.2018.03.007

To cite this version:

Rodríguez-Ruiz, Isaac and Teychené, Sébastien and Vitry, Youen and Biscans, Béatrice and Charton, Sophie *Thermodynamic modeling of neodymium and cerium oxalates reactive precipitation in concentrated nitric acid media.* (2018) Chemical Engineering Science, 183. 20-25. ISSN 0009-2509

Any correspondence concerning this service should be sent to the repository administrator: tech-oatao@listes-diff.inp-toulouse.fr

Thermodynamic modeling of neodymium and cerium oxalates reactive precipitation in concentrated nitric acid media

Isaac Rodríguez-Ruiz [a], Sébastien Teychené [b], Youen Vitry [b], Béatrice Biscans [b], Sophie Charton [a,*]

[a] CEA, DEN, Research Department of Mining and Fuel Recycling Processes, SA2I, F-30207 Bagnols-sur-Cèze, France
[b] Laboratoire de Génie Chimique, UMR 5503, 4 allée Emile Monso, Toulouse, France

HIGHLIGHTS

- A Pitzer thermodynamic model for Ce and Nd oxalate precipitation was developed.
- New data on Ce(NO3)3 water activity in HNO3 media is reported to complete the model.
- The model demonstrated to be valid over a wide range of pH and concentrations.

ARTICLE INFO

Keywords:
Cerium oxalate
Neodymium oxalate
Reactive precipitation
Thermodynamic model
Pitzer

ABSTRACT

Rare earth oxalates precipitation is extendedly used in hydrometallurgical processes related to rare earth recycling methods and treatment of radioactive liquid wastes, where rare earth elements are separated from other fission products. For a deeper comprehension of this reactive precipitation process, the thermodynamic modeling of the oxalate-rare earth systems in nitric acid aqueous media is presented for neodymium and cerium systems, due to their distinctive relevance among the rare earth elements. A Pitzer model was selected for the modeling, which was developed using the implementation present within PHREEQC software. Calculations were launched through a COM interface with Matlab® and PHREEQC database was complemented by adjustment of the individual Pitzer coefficients for each species interaction to experimental data reported in literature and own experimental water activity measurements required to complete the study. The implemented model is able to accurately predict oxalate-rare earth solubility in a wide range of rare earth and nitric acid concentrations up to >10 m.

1. Introduction

Reactive precipitation, together with liquid-liquid extraction methods are key operations involved in hydrometallurgical processes for rare earth extraction (Ellis et al., 1994; Bounds, 1994) and recycling processes for nuclear waste treatment (Forsberg, 1980). Here, alloys to be recycled are dissolved in strong mineral acids and subsequently, the rare earths are precipitated as double sulfates, oxalates or fluoride salts. Special attention is paid in the abovementioned context to oxalate precipitates from trivalent rare earth ions due to their low solubility in aqueous media. Thus, oxalates precipitation is extendedly used for the separation of rare earths from non-lanthanide impurities, not only at laboratory scale in analytical chemistry but also for the treatment of high-level liquid wastes, where rare earth elements are separated from other fission products (Forsberg, 1980).

Additionally, this precipitation procedure is widely used in other hydrometallurgical recycling processes, such as the recycling of permanent magnets, lamp phosphors and LED light sources, rechargeable batteries or catalysts (Binnemans et al., 2013). In the abovementioned context, the accurate determination of reaction kinetic data is essential for the modeling and development of new and more efficient chemical processes. While a vast number of routes have been proposed in literature at laboratory scale, large scale processes, envisaged to be of high importance for rare earth elements recovery in the near future, are still in an early stage of development (Binnemans et al., 2013). Given this background, for a deeper comprehension and an optimal control of supersaturation leading to rare earths precipitation, the understanding of the thermodynamics of these processes is a must.

The calculation of the activities of the different ions present in solution can be achieved using various thermodynamic models, ranging from fundamental equations (Debye-Hückel (Hückel and

* Corresponding author.
E-mail address: sophie.charton@cea.fr (S. Charton).

https://doi.org/10.1016/j.ces.2018.03.007

Debye, 1923) to more complex and largely empirical approaches (Pitzer (Pitzer, 1991). The use of such a model must permit an accurate calculation of ion activities, but additionally, these calculations must be valid over the widest possible range of ionic strength, covering the experimental conditions which are intended to be modeled. Hence, in this work, the thermodynamic modeling of the oxalate-nitrate-rare earth systems in acidic aqueous media is presented for neodymium (considered to be a mid-term critical element in view of its extraction rate and expected demand during the next 20 years (Binnemans et al., 2013) and cerium (of special interest due to the role of cerium oxalates as catalyst precursors (Palmqvist et al., 1999; Zhang et al., 1995) and models to understand actinide precipitation (Charton et al., 2013) systems due to their distinctive relevance among the rare earth elements.

2. Materials and methods

2.1. Reagents and solutions

Oxalic acid (>99.9% purity, ACS reagent), nitric acid (70%, ACS reagent), and both cerium and neodymium nitrates hexahydrate (>99.9% purity, ACS reagent) were purchased from Sigma-Aldrich.

Ternary Ce solutions (from Ce 0.1 to 2.5 m and from 0 to 1 m HNO_3) were prepared using 50 mL flasks using DI water. The desired HNO_3 and H_2O amounts were added first and weighted into the same flasks. Then the Nd or Ce salt is added and also weighted into the more-soluble acidic solution. Flasks were stirred until complete salt dissolution, aged for at least 48 h and filtered afterwards using Micropore 0.4 μm syringe membrane filters, prior to any water activity measurement.

2.2. Water activity measurements

Water activity determination was carried out using a LabMaster-aw equipment (Novasina, Switzerland) using "eVC-100" acid fume pre-filters which allow water activity measurements of high-concentration nitric acid solutions. Prior to any measurement, the water activity meter was calibrated at 25.0 ± 0.2 °C using the reference standards provided by the manufacturer. Afterwards, 10 mL of the different ternary solutions were pipetted in the measurement cell and the water activity meter was closed for temperature regulation at 25.0 ± 0.2 °C. Water activity values were determined after complete stabilization of temperature, and measurements in each solution were performed in continuous mode until values were found to be constant for at least 10 min. Experiments lasted between 30 and 60 min, corresponding to the vapor-liquid equilibration time.

2.3. Thermodynamic model

Three different and widely used modeling approaches were under consideration for the abovementioned systems of study, prior to the development of the modeling here presented. First, the Bromley model (Bromley, 1973), although easy to implement, was excluded because it is restricted to low ionic strength (I < 6 mol·kg^{-1}). The SIT model (Guggenheim and Turgeon, 1955) was dismissed too, as beyond an ionic strength of 3 mol·kg^{-1} it presents a significant deviation from experimental values (Elizalde and Aparicio, 1995). Finally, the Pitzer approach was selected because it allows the accurate calculation of ion activities for a wide range of pH (from pH < 1 to pH > 10) and ionic strength (I ~ 10 mol·kg^{-1}) (Qafoku and Felmy, 2007). It has moreover already been used for thermodynamic modeling of actinides in aqueous media (Felmy and Rai, 1999). Pitzer model results from an expansion of activity virial coefficients (Eq. (1)):

$$\ln \gamma_i = \ln \gamma_i^{DH} + \sum_j \beta_{ij}(I) m_j + \sum_j \sum_l C_{ijk} m_j m_k + \dots \quad (1)$$

where m is the molality, γ_i^{DH} an activity coefficient derived from a modified model of Debye-Hückel function of ionic strength, I, β_{ij} and C_{ijk} correspond to interactions between each specific ion and are dependent on the ionic strength: β_{ij}, phenomenologically explained by Pitzer (Pitzer, 1991), describes the binary interactions between two ions of opposite charge and ionic strength dependence; C_{ijk} is meanwhile describing the interaction between 3 ions and is considered independent of the ionic strength. Forms of Eq. (1) and its application for predicting compounds solubility in different systems at high ionic strengths can be found in the literature (Harvie et al., 1984; Felmy and Weare, 1986). To model the data for both Ce and Nd systems, in this work we have used the Pitzer model implemented in PHREEQC (Parkhurst and Appelo, 1999). Calculations were launched through a COM interface with Matlab®, and parameters of interactions were determined by identification with either data extracted from the literature (when available) or from in-house experimental water activity measurements (for non-previously reported data) using the digital "fminsearch' Matlab® optimization function.

The modeled system consists in the mixture of two initial solutions: i) a Nd (resp. Ce) nitrate and nitric acid mixture diluted in water and ii) an oxalic acid solution. The mixture of these two solutions at a given concentration leads to the generation of supersaturation with respect to the rare earth element's oxalate solid phase and consequently to precipitation. Supersaturation can therefore be expressed as:

$$S = \left(\frac{a^2_{RE^{3+}} + a^3_{C_2O_4^{2-}}}{Ps} \right)^{1/5} = \gamma_c^{+/-} \left(\frac{C^2_{RE^{3+}} + C^3_{C_2O_4^{2-}}}{Ps} \right)^{1/5} \quad (2)$$

where RE refers to the rare earth (Nd or Ce), a is the ion activity, Ps is the solubility product for their corresponding oxalate salt, $\gamma_c^{+/-}$ is the average activity coefficient for the ion pair, and C is the ion concentration in solution. All the possible subspecies of the different species involved must be taken into account in order to obtain a complete an accurate model. The inventory of the ions present in the solutions of study, and the corresponding dissociation equations describing their speciation, are the following:

$$HNO_3 \Longleftrightarrow H^+ + NO_3^- \quad (3)$$

$$RE^{3+} + 3NO_3^- \Longleftrightarrow RE(NO_3)_{3solid} \quad (4)$$

$$H_2C_2O_{4solid} \Longleftrightarrow H_2C_2O_{4aq} \quad (5)$$

$$HC_2O_4^- + H^+ \overset{k1}{\Longleftrightarrow} H_2C_2O_{4aq} \quad (6)$$

$$C_2O_4^{2-} + H^+ \overset{k2}{\Longleftrightarrow} HC_2O_4^- \quad (7)$$

$$RE_2(C_2O_4)_{3solid} \Longleftrightarrow 2RE^{3+} + 3C_2O_4^{2-} \quad (8)$$

$$RE^{3+} + C_2O_4^{2-} \overset{k_I}{\Longleftrightarrow} RE(C_2O_4)^+ \quad (9)$$

$$RE^{3+} + 2C_2O_4^{2-} \overset{k_{II}}{\Longleftrightarrow} RE(C_2O_4)_2^- \quad (10)$$

$$RE^{3+} + 3C_2O_4^{2-} \overset{k_{III}}{\Longleftrightarrow} RE(C_2O_4)_3^{3-} \quad (11)$$

The calculation of ion activity in both Ce and Nd solutions requires a priori to model all the interaction coefficients referring to binary, ternary, and quaternary interactions among ionic species, as well as the solubility products and dissociation constants

for oxalic acid, RE oxalates and RE nitrates. A thorough literature search was conducted in order to find the necessary information for these calculations, and in this regard, it is noteworthy mentioning the difficulty of finding information on the main reactants of the study (neodymium and cerium) due to the few data present in literature. Moreover, the available data need to be sorted and in some cases excluded due to their lack of reliability and relevance. For example, data prior to 1950 concerning neodymium and cerium have been excluded from this study because the purity of reagents used at the time was not sufficient to ensure accurate results. (Parkhurst and Appelo, 1999) Unless otherwise indicated, all of the interaction coefficients have been determined from thermodynamic data obtained at a temperature of 25 °C.

3. Results and discussion

3.1. Binary interactions

3.1.1. HNO_3-H_2O

Nitric acid is a strong acid of $pKa = -1.37$, which dissociates in water into H^+ and NO_3^- ions. The determination of the binary interaction coefficients between these two ions was achieved through the experimental measurements of Charrin and coworkers (Charrin et al., 1999). In order to obtain accurate data, these authors used two different measuring techniques depending on the concentration of nitric acid. They measured the activity of water for solutions of nitric acid ranging from 1.585 to 11.996 mol·kg^{-1} and the $\gamma^{\pm}$ for solutions ranging from 0.001 to 6 mol·kg^{-1}. To enable the model to properly approximate experimental data, six interaction parameters were determined whose values are given in Table 1. The first three parameters (β_0, β_1, C_0) are the classical Pitzer parameters characterizing the binary interactions between ions H^+ and NO_3^-. The three following parameters (λ, λ, μ) stand for the characterization of interactions with the protonated form of nitric acid present in solution at high ionic strength.

Fig. 1 compares the experimental data with our modeling results. The last experimental point in the series of $\gamma^{\pm}$ values (marked in Fig. 1a with a red[1] arrow) clearly seems to be erroneous and was therefore excluded from the modeling. The model reproduces the experimental data with an error lower than 1% on average.

Table 1
Binary interaction coefficients, HNO_3-H_2O.

β_0 (H^+, NO_3^-)	$12.49 \cdot 10^{-2}$
β_1 (H^+, NO_3^-)	$27.64 \cdot 10^{-2}$
C_0 (H^+, NO_3^-)	$-0.51 \cdot 10^{-2}$
λ (HNO_3, H^+)	$9.86 \cdot 10^{-2}$
λ (HNO_3, HNO_3)	$27.31 \cdot 10^{-2}$
μ (HNO_3, HNO_3, HNO_3)	$4.36 \cdot 10^{-2}$

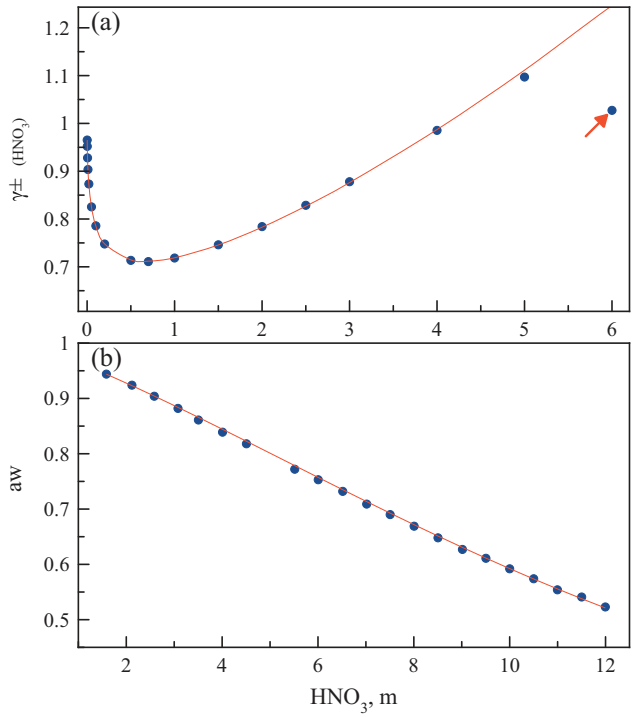

Fig. 1. HNO_3-H_2O binary interaction modeling (lines) and comparison with experimental results (dots) reported by Charrin and coworkers (Harvie et al., 1984; Felmy and Weare, 1986). (a) Average activity coefficient for the ion pair determination and (b) water activity measurements as a function of the nitric acid content.

3.1.2. $H_2C_2O_4$-H_2O

Oxalic acid is a weak acid dissociating in two species in water: $HC_2O_4^-$ and $C_2O_4^{2-}$. It has therefore two dissociation constants for which different values can be found in literature (Kettler et al., 1991). Accounting for the two dissociation constants is important, as oxalic acid speciation in solution is pH dependent. Indeed, in low acidic media, oxalic acid is completely dissociated, while in strongly acidic media oxalic acid does not dissociate, being present in the form of $H_2C_2O_4$. Due to the differences found among the reported dissociation constants values, Partanen and coworkers recently re-measured both constants at temperatures ranging from 0 °C to 60 °C. (Partanen et al., 2009) At 25 °C they measured the following values for $k_1 = 1.77 \cdot 10^1$ and $k_2 = 1.82 \cdot 10^4$, that we used in this work. To verify the ability of the model to predict the activity of oxalate ions, simulations were compared to water activity measurements reported by Maffia and Meirelles (Maffia and Meirelles, 2001), and Peng and coworkers (Peng et al., 2001), for solutions of oxalic acid in water of concentration up to 1.56 mol·kg^{-1} and 1.23 mol·kg^{-1} respectively. Fig. 2 compares our simulation results with experimental data.

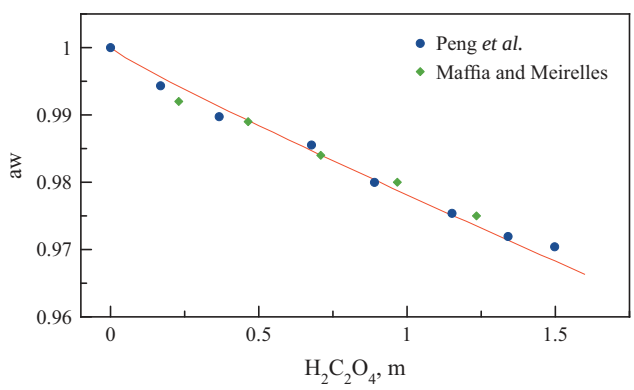

Fig. 2. Comparison of numerical results (line) and experimental water activity measurements for $H_2C_2O_4$-H_2O binary system reported by Maffia and Meirelles (2001) and Peng et al. (2001).

The model allows to accurately represent experimental data with an error below 1%, and without including interaction parameters. However, these data do not allow the calculation of oxalic acid solubility in water, which will be determined hereafter.

[1] For interpretation of color in Fig. 1, the reader is referred to the web version of this article.

Table 2
Water activity measurements for the ternary mixture. HNO_3-$Ce(NO3)_3$-H_2O.

HNO_3, m	$Ce(NO3)_3$, m	aw ($\times 10^2$)	HNO_3, m	$Ce(NO3)_3$, m	Aw ($\times 10^2$)
0	0.1	99.10	0.5	0.1	97.63
0	0.5	97.00	0.5	0.5	94.97
0	1	93.80	0.5	1	91.87
0	1.5	89.90	0.5	1.5	87.97
0	5	86.07	0.5	5	84.03
0	2.5	81.93	0.5	2.5	79.70
0	3	76.95	0.5	3	74.90
0.1	0.1	98.73	1	0.1	96.10
0.1	0.5	96.57	1	0.5	93.57
0.1	1	93.60	1	1	89.17
0.1	1.5	89.70	1	1.5	85.97
0.1	5	85.63	1	5	81.90
0.1	2.5	80.83	1	2.5	77.20
0.1	3	75.45	1	3	73.10

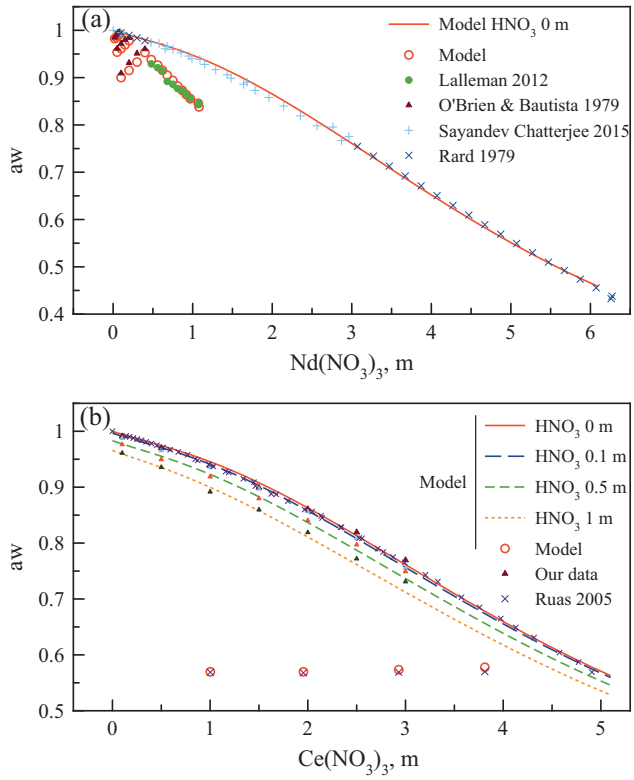

Fig. 3. Comparison of numerical results and experimental water activity determination for (a) Nd and (b) Ce nitrates binary and ternary systems in presence of HNO_3 media.

3.2. Ternary interactions

3.2.1. HNO_3-$RE(NO_3)_3$-H_2O

Ternary interactions occur between the RE^{+3}, H^+ and NO_3^- ions present in solution. Neodymium and cerium nitrates are salts which dissociate in water and in nitric acid solutions forming NO_3^- and Nd^{3+}/Ce^{3+}. Their solubility product is defined as follows:

$$pS_{RE(NO_3)_3} = \frac{a^1_{RE^{3+}_{eq}} a^3_{NO^-_{3eq}}}{a_{RE(NO_3)_{3_{solid}}}} \quad (12)$$

pS values at 25 °C for $Nd(NO_3)_3$ and for $Ce(NO_3)_3$ are reported elsewhere (Siekierski et al., 1983), and are respectively equal to $1.22 \cdot 10^4$ for $Nd(NO_3)_3$, and $2.26 \cdot 10^4$ for $Ce(NO_3)_3$.

In the case of neodymium, identification of the interaction parameters between the different ions was carried out using the experimental data reported by Rard et al. (1979) (in pure water), Chatterjee et al. (2015) and from the study conducted by O'Brien and Bautista (1979), who measured the saturation vapor pressure as a function of ionic force for various HNO_3-$Nd(NO_3)_3$-H_2O solutions. The values were transformed into water activity in order to compare them to the model. Additional water activity measurement data for different compositions of HNO_3-$Nd(NO_3)_3$-H_2O solutions were reported by Lalleman et al. (2012).

For cerium, we used the data reported by Ruas et al. (2005) (in pure water) and Torres-Arenas et al. (2010) (in HNO_3). Due to the small amount of results available for $Ce(NO_3)_3$, and in order to model the latter with sufficient precision, complementary experimental data were measured for HNO_3 concentrations ranging from 0 (so to obtain data of the binary mixture $Ce(NO_3)_3$-H_2O, which could be compared to those existing in literature (Ruas et al., 2005) to 1 m, and $Ce(NO_3)_3$ concentrations ranging from 0.1 to 3 m. The obtained water activity results are reported in Table 2.

The experimental water activity measurements are compared to our simulation results in Fig. 3a and b for the two RE systems. The best fit of the experimental and literature data was achieved with the coefficients reported in Table 3. In each case, the first three parameters correspond to the classical parameters of binary interactions (Nd^{3+}/Ce^{3+}, NO_3^-). These 3 parameters allow to correctly describe the experimental data measured in pure water, with a deviation below 1% on average. The additional use of the last parameter, θ (which stand for the ternary interactions between the RE^{+3}, H^+ and NO_3^- ions present in solution), allows to correctly represent the all set of available data, including those reported by of O'Brien and Bautista and Lalleman and coworkers, with an error lower than 1% and 2% respectively.

Table 3
Binary and ternary interaction coefficients for HNO_3-$RE(NO_3)_3$-H_2O.

	Nd	Ce
β_0 (RE^{3+}, NO_3^-)	$30.79 \cdot 10^{-2}$	$30.88 \cdot 10^{-2}$
β_1 (RE^{3+}, NO_3^-)	$601.37 \cdot 10^{-2}$	$1307.62 \cdot 10^{-2}$
C_0 (RE^{3+}, NO_3^-)	$-01.19 \cdot 10^{-2}$	$-1.38 \cdot 10^{-2}$
θ (H^+, RE^{3+})	$51.32 \cdot 10^{-2}$	$17.63 \cdot 10^{-2}$

Table 4
Ternary interaction coefficients, HNO_3-$H_2C_2O_4$-H_2O.

$pS_{H_2C_2O_4} = \frac{a^2_{H^+_{eq}} a^1_{C_2O^{2-}_{4_{eq}}}}{a_{H_2C_2O_{4_{solid}}}}$	$3.59 \cdot 10^{-6}$
θ (NO_3^-, $C_2O_4^{2-}$)	$-69.06 \cdot 10^{-2}$
λ ($H_2C_2O_4$, NO_3^-)	$2.67 \cdot 10^{-2}$

3.2.2. HNO_3-$H_2C_2O_4$-H_2O

Finally, the last ion triplet to study is formed by a mixture of nitric acid and oxalic acid in water. Ternary interactions take place between $C_2O_4^{2-}/HC_2O_4^-$, H^+ and NO_3^- ions present in solution. The only experimental data available regarding the solubility measurement of oxalic acid at different concentrations in nitric acid were reported by Masson (Masson, 1912). Oxalic acid solubility was studied in the nitric acid concentration range from 0 to 33 mol·kg^{-1} and at a temperature of 30 °C. This temperature difference should not have any influence on our model since the interaction parameters do not depend on the temperature in this range (25–30 °C).

To correctly fit the model to the experimental data, three parameters (presented in Table 4) were determined. The calculated solubility product for oxalic acid was found to be in good agreement with other values reported in literature ($pS = 2.95 \cdot 10^{-6}$, Qafoku and Felmy (2007). The two remaining parameters

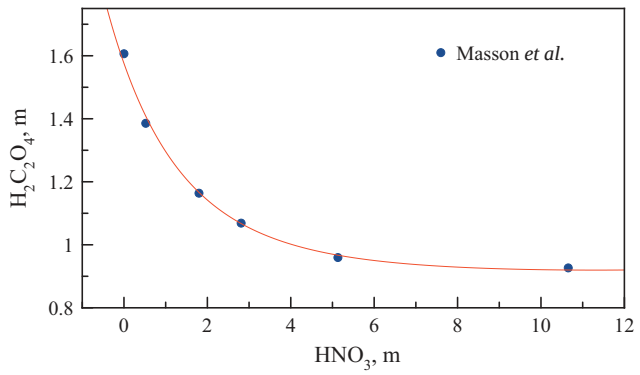

Fig. 4. Comparison of numerical results and experimental oxalic acid solubility determination as a function of nitric acid concentration.

correspond to ternary interaction coefficients. Contrary to previous studies, where its value was set to 0 (Qafoku and Felmy, 2007; Harvie et al., 1984), here we determined the value of the anionic interaction coefficient θ (NO_3^-, $C_2O_4^{2-}$). The second coefficient, λ ($H_2C_2O_4$, NO_3^-), allows to take into account the interactions between the fully protonated form of oxalic acid and NO_3^- ion. Indeed, as previously mentioned, in strongly acidic media, oxalic acid dissociates very little and remains mostly in its completely protonated form: $H_2C_2O_4$.

Fig. 4 presents the model's prediction compared to the experimental data reported by Masson. An excellent agreement is observed. However, the model was unable to predict the solubility of oxalic acid for nitric acid concentrations higher than 11 mol·kg^{-1}.

3.3. Precipitation solution

Finally, the solubility of neodymium and cerium oxalates were determined from the previous results related to both RE nitrates solutions and oxalic acid solutions. The solubility measurements of neodymium oxalate reported by Chung et al. (1996), and the solubility measurements for cerium oxalate reported by Crouthamel and Martin,(1951) were used for comparison in order to assess the model validity. In addition to the data from Chung et al., Pontisso et al. (2011) had also reported several solubility values for neodymium oxalate in different systems (water, oxalic mother liquor, nitric acid). However, these values have not been taken into account for our calculations, as they present a very high intrinsic variability.

Modeling results, considering neodymium and cerium oxalate solubility, and their corresponding dissociation constants are presented in Table 5 and compared to experimental values reported in the literature. Regarding Nd, our results are consistent with the previously reported data. For Ce however, the number of experimental values is not sufficient to efficiently achieve the optimization procedure (8 points vs. 6 parameters to fit), and it was not possible to determine any value of the dissociation k_{III} for trioxalate complex $RE(C_2O_4)_3^{3-}$, at which the simulation results were not sensitive. Therefore, we decided to impose the value of k_{III} reported by Crouthamel and Martin (1951). As illustrated in Fig. 5, with this assumption and the set of parameters reported in Table 5 ("our calculations"), a very good agreement was achieved between the experimental and the simulated solubility data for both Ce and Nd.

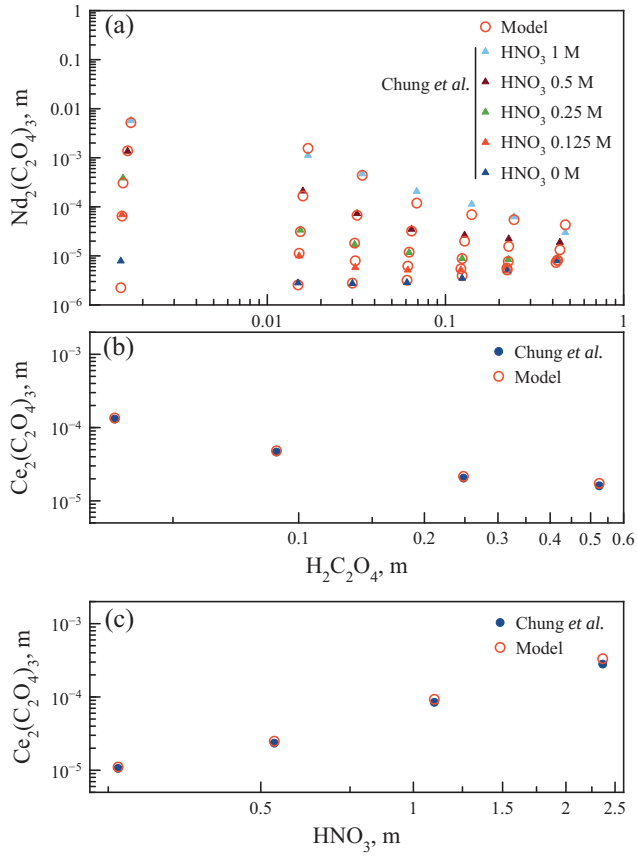

Fig. 5. Solubility plots of RE oxalates, comparison between literature data (Chung et al.) and model's prediction. (a) Neodymium oxalate at various HNO_3 concentration; (b) Cerium oxalate as a function of $H_2C_2O_4$, at HNO_3 0.5M; (c) Cerium oxalate as a function of HNO_3 concentration at $H_2C_2O_4$ 0.31 M.

Plots of the predicted solubility data compared to the experimental ones reported by Chung et al. (1998) are presented in Fig. 5a for neodymium oxalate as a function of oxalic acid concentration, and in Fig. 5b–d for cerium oxalate, respectively as a function of oxalic acid and nitric acid concentration for the data. The modeled results are in good agreement with experimental data.

Table 5
Summary of calculated equilibrium constants.

	Our calculations		Values reported in literature	
	Nd	Ce	Nd	Ce
$RE_2(C_2O_4)_{3solid} \Longleftrightarrow 2RE^{3+} + 3C_2O_4^{2-}$	$pS = 1.68 \cdot 10^{-31}$	$pS = 1.84 \cdot 10^{-28}$	$^{29}pS = 7.7 \cdot 10^{-32}$ $^{28}pS = 1.3 \cdot 10^{-31}$	$^{29}pS = 5.9 \cdot 10^{-30}$ $^{28}pS = 4 \cdot 10^{-31}$
$RE^{3+} + C_2O_4^{2-} \overset{kI}{\Longleftrightarrow} RE(C_2O_4)^+$	$k_I = 2.52 \cdot 10^7$	$k_I = 7.13 \cdot 10^5$	$^{29}k_I = 1.61 \cdot 10^7$ $^{28}k_I = 4.6 \cdot 10^7$	$^{29}k_I = 3.33 \cdot 10^6$ $^{28}k_I = 4.7 \cdot 10^7$
$RE^{3+} + 2C_2O_4^{2-} \overset{kII}{\Longleftrightarrow} RE(C_2O_4)_2^-$	$k_{II} = 2.01 \cdot 10^{11}$	$k_{II} = 7.31 \cdot 10^{10}$	$^{29}k_{II} = 3.23 \cdot 10^{11}$	$^{29}k_{II} = 3.03 \cdot 10^{10}$
$RE^{3+} + 3C_2O_4^{2-} \overset{kIII}{\Longleftrightarrow} RE(C_2O_4)_3^{3-}$	$k_{III} = 4.66 \cdot 10^{14}$	Same as (Crouthamel and Martin, 1951)	$^{29}k_{III} = 3.58 \cdot 10^9$	$^{29}k_{III} = 2.02 \cdot 10^{11}$

4. Conclusions

A thermodynamic study of neodymium and cerium oxalate precipitation in acidic media was conducted by means of a Pitzer model. The model implementation present within PHREEQC software was used for this purpose and calculations were launched through a COM interface with Matlab®. PHREEQC database was complemented by adjustment of the individual Pitzer coefficients for each species interaction to experimental data reported in literature and own experimental data required to complete the study. The model was found to be valid over a wide range of pH and concentration (corresponding to HNO_3 concentrations up to 10 $mol \cdot kg^{-1}$) and obtained numerical results were found to be in good agreement with the experimental results.

Besides the precision improvement for equilibrium data, and therefrom for the determination of improved nucleation and growth kinetic models which it permits, the possibility to control PHREEQC via a COM interface should allow the integration of ion activity calculations within a hydrodynamic simulation code, which is of special importance for the chemistry-transport coupling in the simulation of industrial precipitation processes.

Acknowledgement

This work was supported by the Nuclear Energy Division of CEA (DISN/PAREC). The authors thank Dr. Johanne Teychené and Kevin Vinh Phan for their assistance in the water activity measurements. IR-R acknowledges the CEA-Enhanced Eurotalents Program for his Incoming CEA postdoctoral fellowship.

Notes

Declarations of interest: none.

Contributions

IR-R and ST participated in the experimental campaign. YV and IR-R performed the bibliographic research. YV, SC and ST implemented the model and performed the simulations. IR-R, SC, BB and ST contributed to the article preparation. All authors have approved the final article.

References

Binnemans, K., Jones, P.T., Blanpain, B., Van Gerven, T., Yang, Y., Walton, A., Buchert, M., 2013. Recycling of rare earths: a critical review. J. Cleaner Prod. 51, 1–22.

Bounds, C., 1994. The recycle of sintered magnet swarf. Metals Mater. Waste Reduct. Recov. Remediat., 173–186

Bromley, L.A., 1973. Thermodynamic properties of strong electrolytes in aqueous solutions. AIChE J. 19 (2), 313–320.

Charrin, N., Moisy, P., Garcia-Argote, S., Blanc, P., 1999. Thermodynamic study of the ternary system Th (NO3) 4/HNO3/H2O. Radiochim. Acta 86 (3–4), 143–150.

Charton, S., Kacem, A., Amokrane, A., Borda, G., Puel, F., Klein, J.-P., 2013. Actinides oxalate precipitation in emulsion modeling: from the drop scale to the industrial process. Chem. Eng. Res. Des. 91 (4), 660–669.

Chatterjee, S., Campbell, E.L., Neiner, D., Pence, N.K., Robinson, T.A., Levitskaia, T.G., 2015. Aqueous binary lanthanide (III) nitrate Ln (NO3) 3 electrolytes revisited: extended pitzer and bromley treatments. J. Chem. Eng. Data 60 (10), 2974–2988.

Chung, D.-Y., Kim, E.-H., Shin, Y.-J., Yoo, J.-H., Kim, J.-D., 1996. Solubility of neodymium oxalate in nitric acid and oxalic acid media. J. – Kor. Inst. Chem. Eng. 34, 451–454.

Chung, D.Y., Kim, E.H., Lee, E.H., Yoo, J.H., 1998. Solubility of rare earth oxalate in oxalic and nitric acid media. J. Ind. Eng. Chem. 4 (4), 277–284.

Crouthamel, C.E., Martin Jr, D.S., 1951. Solubility of the rare earth oxalates and complex ion formation in oxalate solution. II. Neodymium and cerium (III) 1. J. Am. Chem. Soc. 73 (2), 569–573.

Elizalde, M., Aparicio, J., 1995. Current theories in the calculation of activity coefficients—II. Specific interaction theories applied to some equilibria studies in solution chemistry. Talanta 42 (3), 395–400.

Ellis, T., Schmidt, F., Jones, L., 1994. Methods and Opportunities in the Recycling of Rare Earth Based Materials. Ames Lab, IA (United States).

Felmy, A.R., Rai, D., 1999. Application of Pitzer's equations for modeling the aqueous thermodynamics of actinide species in natural waters: a review. J. Solut. Chem. 28 (5), 533–553.

Felmy, A.R., Weare, J.H., 1986. The prediction of borate mineral equilibria in natural waters: application to Searles Lake, California. Geochimica et Cosmochimica Acta 50 (12), 2771–2783.

Forsberg, C.W., 1980. Separation of americium, curium, and trivalent lanthanides from high-level wastes by oxalate precipitation: experiments with synthetic waste solutions. Nucl. Technol. 49 (2), 243–252.

Guggenheim, E., Turgeon, J., 1955. Specific interaction of ions. Trans. Faraday Soc. 51, 747–761.

Harvie, C.E., Møller, N., Weare, J.H., 1984. The prediction of mineral solubilities in natural waters: the Na-K-Mg-Ca-H-Cl-SO4-OH-HCO3-CO3-CO2-H2O system to high ionic strengths at 25 C. Geochim. Cosmochim. Acta 48 (4), 723–751.

Hückel, E., Debye, P., 1923. The theory of electrolytes: I. lowering of freezing point and related phenomena. Phys. Z., 24

Kettler, R.M., Palmer, D.A., Wesolowski, D.J., 1991. Dissociation quotients of oxalic acid in aqueous sodium chloride media to 175 C. J Solut. Chem. 20 (9), 905–927.

Lalleman, S., Bertrand, M., Plasari, E., Sorel, C., Moisy, P., 2012. Determination of the Bromley contributions to estimate the activity coefficient of neodymium electrolytes. Chem. Eng. Sci. 77, 189–195.

Maffia, M.C., Meirelles, A.J., 2001. Water activity and pH in aqueous polycarboxylic acid systems. J. Chem. Eng. Data 46 (3), 582–587.

Masson, J.I.O., 1912. XI.—The solubility of electrolytes in aqueous solutions. Part II. Solubility of oxalic acid in other acids. J. chem. Soc. Trans. 101, 103–108.

O'Brien, W.G., Bautista, R.G., 1979. The excess gibbs free energy and the activity coefficients of the Nd (NO3) 3—HNO3—H2O System at 25 °C. In: Thermodynamic Behavior of Electrolytes in Mixed Solvents-II: Advances in Chemistry. American Chemical Society, pp. 299–321.

Palmqvist, A., Wirde, M., Gelius, U., Muhammed, M., 1999. Surfaces of doped nanophase cerium oxide catalysts. Nanostruct. Mater. 11 (8), 995–1007.

Parkhurst, D.L., Appelo, C., 1999. User's guide to PHREEQC (Version 2): A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations.

Partanen, J.I., Juusola, P.M., Covington, A.K., 2009. Re-evaluation of the first and second stoichiometric dissociation constants of oxalic acid at temperatures from 0 to 60 °C in aqueous oxalate buffer solutions with or without sodium or potassium chloride. J. Solut. Chem. 38 (11), 1385–1416.

Peng, C., Chan, M.N., Chan, C.K., 2001. The hygroscopic properties of dicarboxylic and multifunctional acids: Measurements and UNIFAC predictions. Environ. Sci. Technol. 35 (22), 4495–4501.

Pitzer, K.S., 1991. Activity Coefficients in Electrolyte Solutions. CRC Press.

Pontisso, E.-A., Borda, G., Charton, S., Teychéné, S., Biscans, B., 2011. Precipitation en emulsion: mise en evidence et etude du rôle de l'interface sur la cinétique. Récents Progrès en Génie des Procédés 101 (SFGP, Paris).

Qafoku, O., Felmy, A.R., 2007. Development of accurate chemical equilibrium models for oxalate species to high ionic strength in the system: Na—Ba—Ca—Mn—Sr—Cl—NO3—PO4—SO4—H2O at 25 C. J. Solut. Chem. 36 (1), 81–95.

Rard, J.A., Miller, D.G., Spedding, F.H., 1979. Isopiestic determination of the activity coefficients of some aqueous rare earth electrolyte solutions at 25. degree. C. 4. Lanthanumnitrate, praseodymium nitrate, and neodymium nitrate. J. Chem. Eng. Data 24 (4), 348–354.

Ruas, A., Simonin, J.-P., Turq, P., Moisy, P., 2005. 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. J. Phys. Chem. B 109 (48), 23043–23050.

Siekierski, S., Mioduski, T., Salomon, M., 1983. Solubility Data Series Vol. 13: Scandium, Yttrium, Lanthanum, and Lanthanide Nitrates. Pergamon Press.

Torres-Arenas, J., Simonin, J.-P., Bernard, O., Ruas, A., Moisy, P., 2010. Thermodynamics of binary and ternary solutions of multivalent electrolytes with formation of 1: 1 and 1: 2 complexes, within the mean spherical approximation. Ind. Eng. Chem. Res. 49 (4), 1937–1946.

Zhang, Y., Andersson, S., Muhammed, M., 1995. Nanophase catalytic oxides: I. Synthesis of doped cerium oxides as oxygen storage promoters. Appl. Catal. B 6 (4), 325–337.