CHEMICAL THERMODYNAMICS AND THERMOCHEMISTRY

Thermodynamic Modeling of Multicomponent Rare Earth Nitrates Aqueous Systems

A. V. Dzuban^{a,*}, A. A. Galstyan^b, N. A. Kovalenko^a, and I. A. Uspenskaya^a

^a Department of Chemistry, Moscow State University, Moscow, 119991 Russia

^b Department of Materials Science, Moscow State University, Moscow, 119991 Russia

*e-mail: dzuban@td.chem.msu.ru

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Abstract— Solubility constants of rare earth (RE) nitrates crystalline hydrates are determined in a wide temperature range (–30 to 120°C), salts solubilities and phase diagrams of water–RE nitrate systems are calculated. For multicomponent ($n > 5$) solutions of RE nitrates the assessment of solution properties as well as phase diagrams are shown to be feasible within experimental uncertainty. In case of mixtures of RE nitrates with similar hydrodynamic radii of ions, the parameters of RE1–RE2 interparticle interaction can be ignored without losing accuracy of thermodynamic modeling.

Keywords: thermodynamic modeling, electrolyte solutions, RE nitrates, electrolyte generalized local composition model (eGLCM)

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INTRODUCTION

The production and consumption of rare earth (RE) elements in different areas of science and technology are key economic indicators of industrial countries. High-purity RE elements are of particular interest due to their active use as catalysts in oil refinement, luminescence activators, components of high-temperature superconductors, permanent magnets, laser crystals, etc. The available production capacities are nevertheless gradually becoming insufficient to satisfy the growing demand for high-purity RE elements. The technology of liquid-phase extraction from acidic water–organic solutions with subsequent deposition of the product from the raffinate or aqueous re-extract is currently mostly used [1]. Yet, the conditions for these multistep processes are generally adjusted empirically by obtaining huge experimental datasets for certain stocks, that is obviously quite challenging. Thermodynamic modeling can be a reasonable alternative which allows to reduce considerably the time and labor for optimization of the separation process. The aim of this work was therefore to construct a thermodynamic model for describing the properties of phases and their equilibria in multicomponent systems of water and RE nitrates in a wide range of temperatures.

Binary systems (aqueous solutions of nitrates of particular RE nitrate) have been extensively investigated in a number of studies [2–10] where the osmotic coefficient and solvent activity were mostly determined isopiesticly (relative to potassium and cal-

cium chlorides) at 25°C. For yttrium, cerium, samarium, europium, gadolinium, terbium, dysprosium, holmium, thulium, and lutecium nitrates, the operating range of salt molality reached saturated solutions (~4 to 5 mol/kg). For lanthanum, praseodymium, neodymium, erbium, and ytterbium, even supersaturated mixtures we studied. The calorimetric properties of aqueous lanthanide nitrate solutions were considered in [11, 12]. Spedding et al. [11] measured the heats of dilution and then proposed the dependences of components partial enthalpies vs. solution composition and ionic radii of the RE element. The most comprehensive review of the experimental data on the solubility of RE nitrates in a wide range of temperatures (–25 to 120°C) and the formation of their crystalline hydrates was presented in [13] (Tables 1 and 2). The authors of [14] performed differential scanning calorimetry (DSC) measurements of the liquidus temperature for aqueous solutions of yttrium nitrate, complementing existing data on the solid–liquid equilibria in this system.

The ice liquidus was additionally studied in [15–17], as well as the boiling temperatures were determined for the systems water–nitrates of lanthanum, cerium, praseodymium, neodymium, samarium, and europium. The existence range of crystalline hydrates were also examined and compared to early results. In [18], it was shown that experimental investigations of the solubility of RE nitrates penta- and tetrahydrates are not always possible, since they are metastable towards the hexahydrate. Using these data, phase dia-

Table 1. Confirmed crystalline hydrates in the $n\text{H}_2\text{O}$ – $\text{RE}(\text{NO}_3)_3$ systems

n	Y	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Yb	Lu
4	+	–	+	+	–	–	–	+	+	+
5	+	+	+	+	+	–	–	+	+	+
6	+	+	+	+	+	+	+	+	+	+

Hydrates with composition $\text{RE}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ ($n = 3$ – 6) are known for $\text{RE} = \text{La}, \text{Ce}, \text{Pr}, \text{Er}, \text{and Tm}$.

Table 2. Experimental data for water–RE nitrate systems

System	ϕ (25°C), mol/kg	ΔT , °C [13, 14]
H_2O – $\text{Y}(\text{NO}_3)_3$	0.991–5.156 [9]	–20 to 120
H_2O – $\text{La}(\text{NO}_3)_3$	0.125–4.537 [10]	–26 to 122
H_2O – $\text{Ce}(\text{NO}_3)_3$	0.991–5.156 [8]	–20 to 110
H_2O – $\text{Pr}(\text{NO}_3)_3$	0.126–4.977 [10]	–30 to 127
H_2O – $\text{Nd}(\text{NO}_3)_3$	0.126–4.977 [10]	–28 to 90
H_2O – $\text{Sm}(\text{NO}_3)_3$	0.005–4.277 [9]	–34 to 135
H_2O – $\text{Eu}(\text{NO}_3)_3$	1.099–4.063 [9]	–28 to 90
H_2O – $\text{Gd}(\text{NO}_3)_3$	0.005–4.370 [2]	0–50
H_2O – $\text{Tb}(\text{NO}_3)_3$	0.005–4.532 [2]	0–50
H_2O – $\text{Dy}(\text{NO}_3)_3$	0.185–4.664 [6]	0–50
H_2O – $\text{Ho}(\text{NO}_3)_3$	0.184–5.020 [6]	25
H_2O – $\text{Er}(\text{NO}_3)_3$	0.005–5.358 [2]	0–50
H_2O – $\text{Tm}(\text{NO}_3)_3$	0.005–5.953 [2]	25
H_2O – $\text{Yb}(\text{NO}_3)_3$	0.005–6.561 [2]	0–50
H_2O – $\text{Lu}(\text{NO}_3)_3$	0.182–6.717 [6]	25

ϕ is the osmotic coefficient, and ΔT is the temperature range of salt solubility.

grams of water–RE nitrate systems ($\text{RE} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{and Eu}$) were plotted from the eutectic temperature to the boiling point. A summary of the literature experimental data for the H_2O – $\text{RE}(\text{NO}_3)_3$ binary systems is presented in Table 2.

Published efforts of thermodynamical modeling of H_2O – $\text{RE}(\text{NO}_3)_3$ systems where $\text{RE} = \text{Y}, \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}, \text{and Lu}$, have been based mainly on vapor–liquid equilibria and employed the Pitzer model [20]. The authors of [2–4] managed to describe their results with acceptable accuracy only for a narrow range of concentrations with a maximum at 1.9 mol/kg. Employing a modified Pitzer model allowed to expand it. Pérez-Villaseñor et al. [19] succeeded in describing the properties of H_2O – $\text{RE}(\text{NO}_3)_3$ systems up to a salt content of 6 mol/kg with an accuracy better than 1%. In [20], a five-parameter version of the Pitzer model was used to calculate not only the osmotic coefficients above the saturation point but the solubility of salt at 25°C as well. The molar Gibbs energies of $\text{RE}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ crystalline hydrate formation, where $n = 5$ and 6, were

estimated simultaneously. The complete dissociation of RE nitrates in water without the formation of intermediate species or associates was assumed in [2, 19, 20].

Dealing with the same, Chatterjee et al. [21] wrongly assumed that the Pitzer model describes osmotic coefficients well but not the mean ionic activity coefficients at ionic strengths greater than 4 mol/kg. It was nevertheless shown in [22] that an error was made in the calculations of [21] (the dependence of parameter C_{ex} of the Pitzer model on concentration was not considered). Introducing it allows to describe the activity coefficients up to an ionic strength of 20 mol/kg. In addition, a correlation between the Pitzer model parameters and the ionic radius of the RE element was revealed in [21] that can be used to estimate unknown parameters of the H_2O – $\text{Pm}(\text{NO}_3)_3$ system.

Modeling RE solutions is not limited to the Pitzer model. For the comparison, Chatterjee et al. [21] employed an expanded version of the semiempirical Bromley model [23]. The electrolyte generalized local composition model (eGLCM) developed at the Laboratory of Chemical Thermodynamics of the Chemistry Department of Lomonosov Moscow State University, which accurately describes binary and multicomponent systems in a wide range of temperatures and concentrations, was used in [24].

Experimental data on *ternary systems* water–RE nitrate 1–RE nitrate 2 are nonsystematic (Table 3). Mutual solubilities of several RE nitrates were given in [13] for the following combinations at 20°C: La^{3+} – Pr^{3+} – NO_3^- – H_2O , La^{3+} – Nd^{3+} – NO_3^- – H_2O , La^{3+} – Sm^{3+} – NO_3^- – H_2O , Pr^{3+} – Nd^{3+} – NO_3^- – H_2O , and Nd^{3+} – Sm^{3+} – NO_3^- – H_2O . It was also shown that equilibrium solids are solutions $(\text{RE}_1\text{RE}_2)_{1-x}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, with only several of them $((\text{Pr}_x\text{Nd}_{1-x})(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O})$ and $(\text{Nd}_x\text{Sm}_{1-x})(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ being continuous.

Thermodynamic properties of ternary systems containing a nitrate anion and two RE cations were studied in [25–27]: H_2O – $\text{Y}(\text{NO}_3)_3$ – $\text{La}(\text{NO}_3)_3$, H_2O – $\text{Y}(\text{NO}_3)_3$ – $\text{Pr}(\text{NO}_3)_3$, H_2O – $\text{Y}(\text{NO}_3)_3$ – $\text{Nd}(\text{NO}_3)_3$, H_2O – $\text{La}(\text{NO}_3)_3$ – $\text{Pr}(\text{NO}_3)_3$, H_2O – $\text{La}(\text{NO}_3)_3$ – $\text{Nd}(\text{NO}_3)_3$, H_2O – $\text{Pr}(\text{NO}_3)_3$ – $\text{Nd}(\text{NO}_3)_3$, H_2O – $\text{Er}(\text{NO}_3)_3$ – $\text{La}(\text{NO}_3)_3$, H_2O – $\text{Er}(\text{NO}_3)_3$ – $\text{Pr}(\text{NO}_3)_3$, H_2O – $\text{Er}(\text{NO}_3)_3$ – $\text{Nd}(\text{NO}_3)_3$, and H_2O – $\text{Er}(\text{NO}_3)_3$ – $\text{Y}(\text{NO}_3)_3$. The isopiestic osmotic coefficients were determined experimentally at 25°C in a wide range of concentrations, from infinitely dilute solutions to saturated. A similar situation was also observed for *quaternary* and *quinary systems* of water–RE nitrates with Y^{3+} , La^{3+} , Pr^{3+} , Nd^{3+} , and Er^{3+} cations [27–29] (Table 4). It was noted in [25] that the absence of interaction between salts makes the empirical Zdanovskii rule [30–33] applicable with quite high accuracy. The authors of [25–29] used a seven-

parameter Pitzer model with a modified parameter C for more rigorous modeling.

Investigating the properties of multicomponent aqueous solutions of RE nitrates is therefore generally limited to a temperature of 25°C (with the exception of binary systems). The main type of data are osmotic coefficients, salts solubility, and (rarely) thermochemical properties. Thermodynamic modeling is generally performed at one temperature only (25°C) using different versions of the Pitzer model.

CALCULATION PROCEDURE

eGLCM model [24] was used for thermodynamic modeling of the properties of aqueous solutions of RE nitrates and phase equilibria in the considered systems. It has proven its reliability with respect to extraction systems, as it allowed to calculate the binary diagram of the water–tributyl phosphate system (the extracting agent), which was unsuccessful with any other models [34].

THERMODYNAMIC MODEL OF THE LIQUID PHASE

The expression for the molar excess Gibbs energy in the eGLCM model contains three terms:

$$G^{\text{ex}} = G_{\text{LR}}^{\text{ex}} + G_{\text{MR}}^{\text{ex}} + G_{\text{SR}}^{\text{ex}},$$

where $G_{\text{LR}}^{\text{ex}}$ is the contribution of long-range interactions, $G_{\text{MR}}^{\text{ex}}$ is the contribution of middle-range interactions, and $G_{\text{SR}}^{\text{ex}}$ is the contribution of short-range interactions.

A symmetric reference state was used to normalize the properties, and the concentration was in mole fractions. Activity coefficient $\gamma_k \rightarrow 1$ when $x_k \rightarrow 1$ for any species in a solution (such state is hypothetical for ions). The dissociation of electrolytes in a solution was assumed to be complete.

The mole fraction of the k th species can be calculated as

$$x_k = \frac{n_k}{\sum_i n_i},$$

where summation is made over all species in the solution.

In the eGLCM model, the Pitzer–Debye–Hückel equation is used to consider *long-range* interactions in a symmetric reference state for each component:

$$\frac{G_{\text{LR}}^{\text{ex}}}{RT \sum_i n_i} = -\frac{4A_x I_x}{\rho} \ln \left(\frac{1 + \rho I_x^{1/2}}{\sum_i (x_i [1 + \rho (I_{x,i}^0)^{1/2}])} \right),$$

Table 3. Experimental data for ternary systems containing water and two RE nitrates

Salt 1	Salt 2	$a_{\text{H}_2\text{O}}(25^\circ\text{C})$	Solid solution boundaries at 20°C
			solubility [13]
Y(NO ₃) ₃	La(NO ₃) ₃	[25]	—
	Pr(NO ₃) ₃	[25]	—
	Nd(NO ₃) ₃	[25]	—
	Er(NO ₃) ₃	[26]	—
La(NO ₃) ₃	Pr(NO ₃) ₃	[25]	9–55
	Nd(NO ₃) ₃	[25]	14.7–87.8
	Sm(NO ₃) ₃	—	14.1–97
	Er(NO ₃) ₃	[26]	—
Pr(NO ₃) ₃	Nd(NO ₃) ₃	[25]	Continuous solid solution
	Er(NO ₃) ₃	[26]	—
Nd(NO ₃) ₃	Sm(NO ₃) ₃	—	Continuous solid solution
	Er(NO ₃) ₃	[26]	—

Ranges of existence of the solid solutions are indicated in mol % of salt 1.

Table 4. Experimental data on the osmotic coefficients of multicomponent aqueous RE nitrate solutions at 25°C

Salt 1	Salt 2	Salt 3	Reference
Quaternary systems			
Y(NO ₃) ₃	La(NO ₃) ₃	Pr(NO ₃) ₃	[27]
		Nd(NO ₃) ₃	[27]
		Er(NO ₃) ₃	[26]
	Pr(NO ₃) ₃	Nd(NO ₃) ₃	[27]
		Er(NO ₃) ₃	[26]
		Nd(NO ₃) ₃	Er(NO ₃) ₃
La(NO ₃) ₃	Pr(NO ₃) ₃	Er(NO ₃) ₃	[28]
	Nd(NO ₃) ₃	Er(NO ₃) ₃	[28]
	Pr(NO ₃) ₃	Nd(NO ₃) ₃	Er(NO ₃) ₃
Quinary system			
Y(NO ₃) ₃ –La(NO ₃) ₃ –Pr(NO ₃) ₃ –Nd(NO ₃) ₃ –H ₂ O			[29]

where $I_x = \frac{1}{2} \sum_i x_i z_i^2$ is the ionic strength expressed in the scale of mole fractions; $I_{x,i}^0 = z_i^2/2$ is the ionic strength in a hypothetical single-component system consisting of an i -th component; and ρ is a parameter of the closest approach of ions with diameter $a = 5.4671 \times 10^{-10}$ m:

$$\rho = a \sqrt{\frac{2e^2 N_A d_s}{M_s \epsilon_0 \epsilon_s k_B T}}.$$

Debye–Hückel parameter A_x is

$$A_x = \frac{1}{2} \left(\frac{2\pi N_A d_s}{M_s} \right)^{1/2} \left(\frac{e^2}{4\pi\epsilon_0\epsilon_s k_B T} \right)^{3/2},$$

where $N_A = 6.022141 \times 10^{23} \text{ mol}^{-1}$ is the Avogadro number; $e = 1.602177 \times 10^{-19} \text{ C}$ is the elementary charge; $\epsilon_0 = 8.8541878 \times 10^{-12} \text{ F/m}$ is the permittivity of a vacuum; $k_B = 1.38065 \times 10^{-23} \text{ J/K}$ is the Boltzmann constant; T is temperature [K]; d_s is the density of the solution [kg/m^3]; M_s is the molar weight of the solution [kg/mol]; and ϵ_s is the dielectric permittivity of the solution [F/m].

The density and dielectric permittivity of a dilute solution are normally assumed to be equal to the corresponding values of the solvent; in this study, however, the indicated values were determined using empirical equations (mixing rules) to achieve a better description:

$$d_s = \sum_i v_i' d_i,$$

$$\epsilon_s = \sum_i v_i' \epsilon_i,$$

where $v_i' = \frac{x_i v_i}{\sum_j x_j v_j}$, $v_i = \frac{M_i}{d_i}$ is the molar volume of the components [m^3/mol].

The molar weight of a solution is calculated from molar weight of its components:

$$M_s = \sum_i x_i M_i,$$

where x_i and M_i are the molar fraction and molar weight of the i th component, respectively.

The contribution from long-range interactions to the activity coefficient is expressed as

$$\begin{aligned} \ln \gamma_k^{\text{LR}} = & -\frac{4A_x I_x}{\rho} \ln \left(\frac{1 + \rho I_x^{1/2}}{\sum_i (x_i [1 + \rho(I_{x,i}^0)^{1/2}])} \right) \\ & \times ((\ln A_x)_k' - (\ln \rho)_k') - \frac{2A_x z_k^2}{\rho} \\ & \times \ln \left(\frac{1 + \rho I_x^{1/2}}{\sum_i (x_i [1 + \rho(I_{x,i}^0)^{1/2}])} \right) - \frac{A_x I_x^{1/2} (z_k^2 - 2I_x)}{1 + \rho I_x^{1/2}} \\ & - \frac{4A_x I_x^{3/2}}{1 + \rho I_x^{1/2}} (\ln \rho)_k' + \frac{4A_x I_x}{\sum_i (x_i [1 + \rho(I_{x,i}^0)^{1/2}])} \\ & \times \left(((\ln \rho)_k' - 1) \sum_i (x_i (I_{x,i}^0)^{1/2}) + (I_{x,k}^0)^{1/2} \right), \end{aligned}$$

where

$$(\ln \rho)_k' = \frac{1}{2} \left(\frac{(d_s)_k'}{d_s} - \frac{(M_s)_k'}{M_s} - \frac{(\epsilon_s)_k'}{\epsilon_s} \right),$$

$$(\ln A_x)_k' = \frac{1}{2} \left(\frac{(d_s)_k'}{d_s} - \frac{(M_s)_k'}{M_s} - \frac{3(\epsilon_s)_k'}{\epsilon_s} \right),$$

$$(M_s)_k' = M_k - M_s, \quad (d_s)_k' = \frac{v_k(d_k - d_s)}{\sum_i x_i v_i},$$

$$(\epsilon_s)_k' = \frac{v_k(\epsilon_k - \epsilon_s)}{\sum_i x_i v_i}.$$

Middle-range interactions in the eGLCM model are those involving charged species and which are not considered in the Pitzer–Debye–Hückel theory. Corresponding excess Gibbs energy is expressed as

$$\frac{G_{\text{MR}}^{\text{ex}}}{RT \sum_i n_i} = \sum_i \sum_j x_i x_j B_{ij}(I_x),$$

where $B_{ij}(I_x)$ is the interaction parameter between the i -th and j -th species. It depends on the ionic strength and has the form of a symmetric matrix: $B_{ij}(I_x) = B_{ji}(I_x)$ and $B_{ii}(I_x) = B_{jj}(I_x) = 0$. $B_{ij} = 0$, since the i th and j th species are uncharged. Parameter $B_{ij}(I_x)$ is fitted with the empirical dependence

$$B_{ij}(I_x) = b_{ij} + c_{ij} \exp(\alpha_1 \sqrt{I_x} + \alpha_2 I_x),$$

where b_{ij} and c_{ij} are the matrices of interaction between the components, $\alpha_1 = -1.2$ for interaction between uncharged species and -1 for interaction between ions, and $\alpha_2 = 0.13$.

The expression for the corresponding contribution to the activity coefficient has the form

$$\begin{aligned} \ln \gamma_k^{\text{MR}} = & 2 \sum_i x_i B_{ik}(I_x) - \sum_i \sum_j x_i x_j B_{ij}(I_x) \\ & + \sum_i \sum_j x_i x_j (B_{ij})_k', \end{aligned}$$

where

$$(B_{ij})_k' = c_{ij} \exp(a_1 \sqrt{I_x} + a_2 I_x) \left(\frac{a_1}{2\sqrt{I_x}} + a_2 \right) \left(\frac{z_k^2}{2} - I_x \right).$$

The excess Gibbs energy for *short-range* interactions in the eGLCM model are written as

$$\begin{aligned} \frac{G_{\text{SR}}^{\text{ex}}}{RT \sum_i n_i} = & \sum_i x_i \ln \frac{\Phi_i}{x_i} + \frac{z}{2} \sum_i q_i x_i \ln \frac{\theta_i}{\Phi_i} \\ & - \sum_i q_i x_i \ln \left(\sum_j \theta_j \tau_{ji} \right) + \sum_i x_i \ln \left(\sum_j x_j \rho_{ji} \right), \end{aligned}$$

where

$$\theta_i = \frac{x_i q_i}{\sum_j x_j q_j}, \quad \phi_i = \frac{x_i r_i}{\sum_j x_j r_j},$$

$$\tau_{ij} = \rho_{ij} \exp\left(-\frac{a_{ij}}{T}\right),$$

where q_j and r_i are structural parameters (the relative surface area and van der Waals volume) of the i -th species; a_{ij} and ρ_{ij} are temperature-dependent parameters of binary interactions between the i -th and j -th species ($a_{ij} \neq a_{ji}$, $\rho_{ij} \neq \rho_{ji}$, $a_{ii} = 0$, and $\rho_{ii} = 1$).

The contribution from short-range interactions to the activity coefficient takes the form

$$\ln \gamma_k^{\text{SR}} = 1 - \frac{\phi_k}{x_k} + \ln \frac{\phi_k}{x_k} - \frac{z q_k}{2} \left(1 - \frac{\phi_k}{\theta_k} + \ln \left(\frac{\phi_k}{\theta_k} \right) \right)$$

$$+ q_k \left(1 - \ln \left(\sum_i \theta_i \tau_{ik} \right) - \sum_i \frac{\theta_i \tau_{ki}}{\sum_j \theta_j \tau_{kj}} \right)$$

$$- \left(1 - \ln \left(\sum_i x_i \rho_{ik} \right) - \sum_i \frac{x_i \rho_{ki}}{\sum_j x_j \rho_{ji}} \right).$$

The properties of pure water were taken from [35, 36]; structural parameters q and r , from [24] (Table 5).

OPTIMIZING MODEL PARAMETERS AND CALCULATING THE PHASE DIAGRAMS OF BINARY AND MULTICOMPONENT SYSTEMS

Parameters of the eGLCM model were optimized using the Levenberg–Marquardt algorithm [37] in the MATLAB® R2017a programming environment. The sum of squared deviations between experimental and analytical data was minimized. The general form of the target function was

$$\sum_{i=1}^n f_i^2 = \sum_{i=1}^n \left(\frac{x_i^{\text{calc}}(a) - x_i^{\text{exp}}}{x_i^{\text{exp}}} \right)^2,$$

where x_i^{exp} is the experimental value, x_i^{calc} is the value calculated using the model, a is the vector of model parameters, and n is the number of experimental points. The standard error of regression was estimated as

$$\sigma^2 = \frac{1}{n - m} \sum_{i=1}^n f_i^2,$$

where n is the number of experimental points, and m is the number of the model parameters.

Table 5. Individual parameters of species for the water–RE nitrate systems [24, 35, 36]

Component	$M \times 10^3$, kg/mol	$d \times 10^3$, kg/m ³	ε	r	q
H ₂ O	18.016	0.997048	78.38	0.92	1.40
NO ₃ [−]	62	2.468	12.17	0.9222	0.9485
Y ³⁺	88.906	44.453	3.34	0.1518	0.2848
La ³⁺	138.91	21.437	3.92	0.2464	0.3934
Ce ³⁺	140.12	26.741	3.99	0.2596	0.4074
Pr ³⁺	140.91	21.36	3.96	0.2529	0.4004
Nd ³⁺	144.24	31.086	3.72	0.2095	0.3531
Sm ³⁺	150.36	63.983	3.65	0.1981	0.3402
Eu ³⁺	151.96	101.307	3.65	0.1981	0.3402
Gd ³⁺	157.25	137.939	3.44	0.1663	0.3027
Tb ³⁺	158.93	131.347	3.48	0.1713	0.3088
Dy ³⁺	162.5	120.37	3.37	0.1565	0.2908
Ho ³⁺	164.93	79.293	3.37	0.1565	0.2908
Er ³⁺	167.26	49.194	3.34	0.1518	0.2848
Tm ³⁺	168.93	71.885	3.34	0.1518	0.2848
Yb ³⁺	173.05	30.792	3.3	0.1471	0.2970
Lu ³⁺	174.97	29.606	3.27	0.1426	0.2732

Standard deviations of the model parameters were calculated by the formula

$$s_p^2 = \sigma^2 \text{diag}[(J^T J)^{-1}]; \quad J_{ij} = \frac{\partial x_i^{\text{calc}}(a)}{\partial a_j},$$

where diag is the main diagonal, and J is the Jacobian matrix.

Binary Water–RE Nitrate Systems

The parameters of middle-range interactions b_{ij} and c_{ij} were optimized in [24] for a temperature of 25°C and combinations of species RE³⁺–H₂O, H₂O–NO₃[−], and RE³⁺–NO₃[−] (Table 6). They are used here without changes.

When calculating solid–liquid equilibria, the dissolution of RE crystalline hydrate is regarded as the reaction

where (s) is the solid phase, (liq) is the liquid, and (aq) is the aqueous solution. This reaction has the equilibrium constant

$$K = a_{\text{RE}^{3+}} a_{\text{NO}_3^{-}}^3 a_{\text{H}_2\text{O}}^n.$$

The properties of ions are commonly determined relative to an infinitely dilute solution, so $a_{\text{RE}^{3+}}$ and $a_{\text{NO}_3^{-}}$

Table 6. Parameters of the eGLCM model for a water–RE nitrate binary system at 25°C [24]

RE ³⁺	$c_{ij} = c_{ji}$	$b_{ij} = b_{ji}$	$c_{ij} = c_{ji}$
	H ₂ O–RE ³⁺	RE ³⁺ –NO ₃ [–]	
Y ³⁺	–2.49822	24.35075	–77.33070
La ³⁺	–2.33658	18.95212	–80.475570
Ce ³⁺	0	17.51729	–68.19000
Pr ³⁺	–3.52711	23.60510	–92.33609
Nd ³⁺	–3.80824	24.58369	–94.61446
Sm ³⁺	–0.28875	20.31439	–69.86688
Eu ³⁺	0	21.28268	–69.58433
Gd ³⁺	–1.45599	25.39504	–81.70711
Tb ³⁺	–2.49447	26.76369	–87.30551
Dy ³⁺	–2.64580	25.34267	–83.98603
Ho ³⁺	–2.52565	23.65161	–78.91915
Er ³⁺	–1.59695	20.86985	–67.93636
Tm ³⁺	0	17.04240	–52.56535
Yb ³⁺	2.40368	13.03395	–33.65642
Lu ³⁺	4.18675	10.23258	–20.01694

For H₂O–NO₃[–] interaction, $c_{ij} = c_{ji} = 0$, $b_{ij} = b_{ji} = -4.80115$; for H₂O–RE³⁺ interaction, $b_{ij} = b_{ji} = 0$. Values are given with an excess number of significant digits to reproduce the calculation results. The errors of the parameters are listed in [24].

are hypothetical activities of RE and nitrate ions in a non-symmetric reference state, and $a_{\text{H}_2\text{O}}$ is the activity of water in a symmetric reference state. Since the eGLCM model deals with a symmetric one by default, the following expression was used to determine the activities at infinite dilution ($\gamma_k \rightarrow 1$ at $x_k \rightarrow 0$):

$$\ln \gamma_k^* = \ln \gamma_k - (\ln \gamma_k)_{x_k \rightarrow 0, x_{\text{H}_2\text{O}} \rightarrow 1},$$

where γ_k^* is the activity coefficient of the k th component in the non-symmetric reference state; γ_k is the activity coefficient of the k th component in the symmetric reference state; and $(\gamma_k)_{x_k \rightarrow 0, x_{\text{H}_2\text{O}} \rightarrow 1}$ is the activity coefficient in the symmetric reference state at infinite dilution of component k in water (i.e., $x_{\text{H}_2\text{O}} = 1$ when $x_k = 0$).

The dissociation constants of the salt crystalline hydrates were described by three-parameter empirical dependences in the form

$$\ln K = A + \frac{B}{T} + C \ln T,$$

where A , B , and C are coefficients determined from least squares, based on deviations of the liquidus points measured experimentally and calculated by the eGLCM model.

The corresponding equilibrium constant for ice was determined using the known stability parameters of pure water:

$$-RT \ln K = \Delta_m G = \Delta_m H + \Delta_m C_p (T - T_m) - T \left(\frac{\Delta_m H}{T_m} + \Delta_m C_p \ln \frac{T}{T_m} \right),$$

where $\Delta_m H = 6010$ J/mol and $T_m = 273.15$ K are the enthalpy and temperature of melting of water, and $\Delta_m C_p = 38.21$ J/(mol K) is the change in the heat capacity of water at the temperature of melting [38].

Multicomponent Systems

According to [13], solid solutions of two or more RE nitrates are precipitated from aqueous solutions, instead of pure crystalline hydrates. Depending on the combination of the nitrates, such solid solutions can be either continuous or limited. The former were considered to be ideal, and the latter were described using the Margules formalism. For a solid solution with composition $(\text{RE}_1)_x(\text{RE}_2)_{1-x}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$, the Gibbs energy takes the form

$$G = (1-x)\Delta G_{s1} + x\Delta G_{s2} + RT(x \ln x + (1-x) \ln(1-x)) + x(1-x)(g_0 + g_1x),$$

where G_{s1} and G_{s2} are the stability parameters of crystalline hydrates of individual REs; n is the amount of water in a crystalline hydrate; x denotes mole fractions; and g_0 and g_1 are parameters of the Margules model.

The stability parameters of the crystalline hydrate were determined as the Gibbs energy of dissociation:

$$\text{RE}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}_{(s)} = \text{RE}_{(\text{aq})}^{3+} + 3\text{NO}_{3(\text{aq})}^- + n\text{H}_2\text{O}_{(\text{liq})},$$

$$\Delta G_s^0 = -RT \ln K = -RT(\ln a_{\text{RE}^{3+}} + 3 \ln a_{\text{NO}_3^-} + n \ln a_{\text{H}_2\text{O}}),$$

where $a_{\text{RE}^{3+}}$, $a_{\text{NO}_3^-}$, and $a_{\text{H}_2\text{O}}$ are the activities of RE ions, nitrate ions, and water.

The parameters of the Margules model were calculated by solving a set of equations with known values of equilibrium temperature T , and the limits of existence of solutions x_{s1} and x_{s2} :

$$\begin{cases} RT \ln \frac{1-x_{s1}}{1-x_{s2}} = RT \ln \gamma_{1,s2} - RT \ln \gamma_{1,s1} \\ = x_{s2}^2(g_0 - (2x_{s2} - 1)g_1) - x_{s1}^2(g_0 - (2x_{s1} - 1)g_1) \\ RT \ln \frac{x_{s1}}{x_{s2}} = RT \ln \gamma_{2,s2} - RT \ln \gamma_{2,s1} \\ = (1-x_{s2})^2(g_0 + 2x_{s2}g_1) - (1-x_{s1})^2(g_0 + 2x_{s1}g_1). \end{cases}$$

The calculations and construction of the phase diagrams sections were done using the TernAPI program developed at Lomonosov Moscow State University's Laboratory of Chemical Thermodynamics [39].

RESULTS AND DISCUSSION

Two-Component Systems

The dissociation constants of RE crystalline hydrates were assessed using literature data on their solubilities. Obtained parameters of the temperature dependences are given in Table 7. The values of the constants at 25°C coincide with those listed in [24]. Binary systems containing Ho, Tm, and Lu were not considered, since there were no measurements for them at temperatures other than 25°C. Further in the text, we consider only those investigated multicomponent systems that were studied most comprehensively (i.e., those containing Y, La, Pr, Nd, and Sm [13–16]) (Figs. 1a–1e).

Note that we were able to describe the available experimental data by introducing a temperature dependence only for dissociation constants of RE crystalline hydrates while keeping parameters b_{ij} and c_{ij} of the eGLCM model constant. Since experimental studies were performed only for the osmotic coefficients, heats of dilution, and heat capacities of the solutions at 25°C, we considered it unnecessary to make b_{ij} and c_{ij} temperature dependent, which also increased the number of optimized parameters considerably.

Looking on the ice liquidus, one can notice that the calculated curve is a bit steeper than the experimental one in almost all cases. Any efforts to introduce the temperature dependence for b_{ij} and c_{ij} made no noticeable improvements here either. We associate this deviation with the features of differential thermal analysis (DTA) used by the authors of [15–17]. The incomplete deconvolution of the DTA signal can lead in particular to the increased results for the melting point, mostly due to the delay in the recorded system response. Additional experiments are nevertheless required to clarify the reasons.

Note also that there are almost no solubility data for lower RE crystalline hydrates, probably because of the high equilibrium temperatures. In cases where the metastable solubility is known, the eGLCM model with the optimized parameters describes it very well (dashed lines in Figs. 1a–1e).

Three-Component Systems

A thermodynamic model of ternary systems containing water and two RE nitrates (Y, La, Pr, Nd, Er, and Sm) was constructed on the basis of binary subsystems with earlier determined parameters b_{ij} and c_{ij} . Parameters of $\text{RE}_1^{3+}-\text{RE}_2^{3+}$ interparticle interaction

Table 7. Calculated values of the stability parameters of RE crystalline hydrates ($\ln K = A + B/T + C \ln T$)

Crystalline hydrates	A	$B/300$	C
$\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	-318.2 ± 30	31.4 ± 4	49 ± 5
$\text{Y}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	-104 ± 12	15 ± 2	15 ± 2
$\text{Y}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$	33 ± 8	-14 ± 2	-4 ± 1
$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	-321 ± 60	32 ± 9	50 ± 9
$\text{La}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	2500 ± 500	372 ± 70	370 ± 70
$\text{La}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$	6 ± 1	25 ± 4	2 ± 0.2
$\text{La}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$	1 ± 0.2	8 ± 1	0.4 ± 0.03
$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	-389 ± 40	42 ± 5	60 ± 6
$\text{Ce}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	-1212 ± 170	177 ± 27	181 ± 26
$\text{Ce}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$	-1757 ± 260	267 ± 40	181 ± 20
$\text{Ce}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$	-1633 ± 450	250 ± 80	243 ± 60
$\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	-391 ± 40	41.7 ± 6	59 ± 6
$\text{Pr}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	-497 ± 240	60.6 ± 40	75 ± 40
$\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	-428 ± 40	46 ± 6	65 ± 6
$\text{Nd}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	-1710 ± 270	242 ± 40	255 ± 40
$\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	-437 ± 26	48.6 ± 4	67 ± 4
$\text{Sm}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	-347 ± 180	35.9 ± 28	54 ± 26
$\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	-487 ± 160	56 ± 22	75 ± 24
$\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	-1361 ± 190	192 ± 30	204 ± 28
$\text{Eu}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$	-2530 ± 1000	400 ± 260	370 ± 130
$\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	-417 ± 80	46 ± 12	64 ± 11
$\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	-368 ± 80	40 ± 12	56 ± 12
$\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	0	-16 ± 12	0
$\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	-317 ± 24	30 ± 3	50 ± 4
$\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	-220 ± 90	17 ± 12	36 ± 16

Values are given with an excess number of significant digits. The parameters correlate in between due to features of the eGLCM model, so correct rounding can result in a much worse description of the experimental data.

were optimized using experimental data on the water activity. They proved to be statistically significant in cases of $\text{H}_2\text{O}-\text{Y}(\text{NO}_3)_3-\text{La}(\text{NO}_3)_3$, $\text{H}_2\text{O}-\text{Er}(\text{NO}_3)_3-\text{La}(\text{NO}_3)_3$, $\text{H}_2\text{O}-\text{Nd}(\text{NO}_3)_3-\text{Er}(\text{NO}_3)_3$, $\text{H}_2\text{O}-\text{Pr}(\text{NO}_3)_3-\text{Er}(\text{NO}_3)_3$, and $\text{H}_2\text{O}-\text{Y}(\text{NO}_3)_3-\text{Pr}(\text{NO}_3)_3$, and allowed to describe better the properties of solutions (Figs. 2a and 2b). Their necessity is likely due to the strong difference between the hydrodynamic radii of RE^{3+} ions (the average distance between an ion and the center of the nearest water molecule) [40].

Table 8 lists the optimized values of the parameters for all of the studied systems. In all cases, $c_{23} = 0$, which can be considered as the independence of $\text{RE}_1^{3+}-\text{RE}_2^{3+}$ interparticle interactions on a solution's ionic strength. Differences between the calculated and the experimentally measured water activities are listed

Fig. 1. Results of the thermodynamic modeling of the $\text{H}_2\text{O}-\text{RE}(\text{NO}_3)_3$ binary systems ($\text{RE} = \text{Y}, \text{La}, \text{Pr}, \text{Nd}, \text{Sm}$). Symbols denote experimental data, lines represent calculations.

in Table 9. The root-mean-square error does not exceed 0.25%, and in most cases it does not go beyond the limit of 0.09%.

The mutual solubilities of RE nitrates were predicted using optimized values of binary and ternary

parameters of interparticle interactions. Since there are no data for phase equilibria between the lower RE crystalline hydrates, in this work we confined to constructing the phase diagrams sections only up to ~70 wt % salts. Results are presented in Fig. 2. Param-

Fig. 2. Sections of the (a) $\text{H}_2\text{O}-\text{Pr}(\text{NO}_3)_3-\text{Nd}(\text{NO}_3)_3$ and (b) $\text{H}_2\text{O}-\text{La}(\text{NO}_3)_3-\text{Pr}(\text{NO}_3)_3$ phase diagrams at 20°C . Symbols denote experimental data [13], continuous lines represent calculations. L is a liquid solution; ss is a continuous solid solution with composition $(\text{Pr}_{1-x}\text{Nd}_x)(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$; and I and II are $(\text{La}_{1-x}\text{Pr}_x)(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ solid solutions with $x > 0.91$ and $x < 0.45$, respectively.

eters of the Margules model for nonideal solid solutions are given in Table 10. In other cases, an ideal solid solution approximation (e.g., in the $\text{H}_2\text{O}-\text{Pr}(\text{NO}_3)_3-\text{Nd}(\text{NO}_3)_3$ system) (Fig. 2a) in combination with the eGLCM model shows its high predictive ability.

Multicomponent Systems

For calculations in multicomponent systems we used the model parameters determined at the previous step, assuming there were no higher order interactions in the solutions of several salts or they could be ignored relative to others. Unfortunately, there is no informa-

tion on liquid–solid equilibria in multicomponent aqueous mixtures of RE nitrates. Still the water activity in *quaternary* and *quinary* systems is quite predictable,

Table 9. Resulting accuracy of describing the activity of water in RE nitrate solutions using the eGLCM model (δ is the root-mean-square error)

System	δ , %
$\text{H}_2\text{O}-\text{La}(\text{NO}_3)_3-\text{Er}(\text{NO}_3)_3$ [26]	0.18
$\text{H}_2\text{O}-\text{La}(\text{NO}_3)_3-\text{Nd}(\text{NO}_3)_3$ [25]	0.20
$\text{H}_2\text{O}-\text{La}(\text{NO}_3)_3-\text{Pr}(\text{NO}_3)_3$ [25]	0.09
$\text{H}_2\text{O}-\text{Nd}(\text{NO}_3)_3-\text{Er}(\text{NO}_3)_3$ [26]	0.25
$\text{H}_2\text{O}-\text{Pr}(\text{NO}_3)_3-\text{Er}(\text{NO}_3)_3$ [26]	0.16
$\text{H}_2\text{O}-\text{Pr}(\text{NO}_3)_3-\text{Nd}(\text{NO}_3)_3$ [25]	0.11
$\text{H}_2\text{O}-\text{Y}(\text{NO}_3)_3-\text{La}(\text{NO}_3)_3$ [25]	0.07
$\text{H}_2\text{O}-\text{Y}(\text{NO}_3)_3-\text{Nd}(\text{NO}_3)_3$ [25]	0.08
$\text{H}_2\text{O}-\text{Y}(\text{NO}_3)_3-\text{Er}(\text{NO}_3)_3$ [25]	0.05
$\text{H}_2\text{O}-\text{Y}(\text{NO}_3)_3-\text{Pr}(\text{NO}_3)_3$ [25]	0.06
$\text{H}_2\text{O}-\text{Y}(\text{NO}_3)_3-\text{Pr}(\text{NO}_3)_3-\text{Nd}(\text{NO}_3)_3$ [27]	0.08
$\text{H}_2\text{O}-\text{Y}(\text{NO}_3)_3-\text{La}(\text{NO}_3)_3-\text{Pr}(\text{NO}_3)_3$ [27]	0.08
$\text{H}_2\text{O}-\text{Y}(\text{NO}_3)_3-\text{La}(\text{NO}_3)_3-\text{Nd}(\text{NO}_3)_3$ [27]	0.09
$\text{H}_2\text{O}-\text{Y}(\text{NO}_3)_3-\text{La}(\text{NO}_3)_3-\text{Er}(\text{NO}_3)_3$ [26]	0.06
$\text{H}_2\text{O}-\text{Y}(\text{NO}_3)_3-\text{Pr}(\text{NO}_3)_3-\text{Er}(\text{NO}_3)_3$ [26]	0.05
$\text{H}_2\text{O}-\text{Y}(\text{NO}_3)_3-\text{Nd}(\text{NO}_3)_3-\text{Er}(\text{NO}_3)_3$ [26]	0.08
$\text{H}_2\text{O}-\text{La}(\text{NO}_3)_3-\text{Nd}(\text{NO}_3)_3-\text{Er}(\text{NO}_3)_3$ [28]	0.08
$\text{H}_2\text{O}-\text{Pr}(\text{NO}_3)_3-\text{Nd}(\text{NO}_3)_3-\text{Er}(\text{NO}_3)_3$ [28]	0.08
$\text{H}_2\text{O}-\text{Y}(\text{NO}_3)_3-\text{La}(\text{NO}_3)_3-\text{Pr}(\text{NO}_3)_3-\text{Nd}(\text{NO}_3)_3$ [29]	0.08

Table 8. Calculated parameters of interparticle interaction in the eGLCM model for $\text{H}_2\text{O}-\text{RE}_1(\text{NO}_3)_3-\text{RE}_2(\text{NO}_3)_3$ ternary systems

RE_1	RE_2	$b_{23}(\text{RE}_1^{3+}-\text{RE}_2^{3+})$
La	Er	-2.26938 ± 1.4
La	Nd	0
La	Pr	0
Nd	Er	-4.54651 ± 1.9
Pr	Er	-1.46467 ± 1.1
Pr	Nd	0
Y	La	-1.86966 ± 0.6
Y	Nd	0
Y	Er	0
Y	Pr	-0.81177 ± 0.5

Values are given with an excess number of significant digits.

Table 10. Parameters of the Margules model for solid solutions in the $\text{H}_2\text{O}-\text{La}(\text{NO}_3)_3-\text{RE}(\text{NO}_3)_3$ ternary systems

RE	g_0	g_1
Pr	1457	−5113
Nd	6391	−998
Sm	9116	−3653

confirming the quality of constructed eGLCM model. As was expected, the accuracy of describing the properties of a system rises along with its dimension. The comparison of calculation results with the experimental data for the studied systems are given in Table 9. The root-mean-square error does not exceed 0.09%.

CONCLUSIONS

Constructed eGLCM model for multicomponent RE nitrates solutions describes highly accurate the different types of phase equilibria as well as the properties of aqueous solutions of RE nitrates from -30 to 120°C within the experimental error using a fairly small set of parameters. Accounting the binary interactions only allows to extend the eGLCM model's range of applicability to systems containing three or more RE elements. In case of the mixtures of RE nitrates with similar sizes of ions in the solution, parameters of $\text{RE}_1^{3+}-\text{RE}_2^{3+}$ interaction can be ignored without losing in accuracy of modeling.

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