Supporting Information

Thermodynamics of the Eu(III)–Mg–SO$_4$–H$_2$O and Eu(III)–Na–SO$_4$–H$_2$O systems. Part I: solubility experiments and full dissociation Pitzer model

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A brief summary of the Pitzer equations

The Pitzer model developed in 1973 by Kenneth Pitzer is an extention of the Debye-Hückel theory[1–3]. It is widely used for calculating activity coefficients and has shown very good ability to describe both low and high ionic strength experimental data, up to at least 20 mol/Kg[4,5]. The activity coefficient describes the non-ideality of thermodynamic systems and can be calculated for each compound i of the studied mixture[6]. Theoretically, it depends on the pressure, the temperature and the composition of the aqueous phase because it represents the derivative of the excess Gibbs free energy of the system with respect to the mole content of compound i. Pitzer's model is semi-empirical, based on ion-specific interaction theory, and incorporates short-range interactions, that represent physical and chemical interactions between contacting solutes, and long-range interactions, related to electrostatic forces between electrically charged particles in solution[2,3]. The Pitzer model relies on the viral expansion of the excess Gibbs free energy (G^E) of the real solution mixture:

$$\frac{G^E}{W_{solv}RT} = f(I) + \sum_i \sum_j \lambda_{i,j}(I)m_im_j + \sum_i \sum_j \sum_k \mu_{i,j,k}m_im_jm_k \tag{A-1}$$

W_{solv} is the mass of the solvent, m_i is the molality of species i. $\lambda_{i,j}(I)$ and $\mu_{i,j,k}$ are respectively the second and third coefficients of the virial, they take into account the potential forces at short range. $f(I)$ is a Debye-Hückel type function that takes into account long-range electrostatic forces. It is also a function of the temperature and of the volumetric and dielectric properties of the solvent:

$$f(I) = -A_\varphi(T)\frac{4I}{b_0}\ln(1 + b_0\sqrt{I}) \tag{A-2}$$

Where b_0 is a universal parameter equal to 1.2 Kg$^{0.5}$/mol$^{0.5}$ [7] and A_φ is the usual Debye-Hückel constant and determined from the parameter $A(T)$ of Debye-Hückel law:

$$A_\varphi = \frac{2.303A(T)}{3} \tag{A-3}$$

The derivative of the excess Gibbs free energy equation (Eq. A-1) with respect to the molality of a given solute gives the expressions of the activity coefficients for anions (A, a and a'), cations (C, c and c') and neutral species (N). The activity coefficients in a system with n_c cations and n_a anions calculated by the Pitzer model are described as follows. These equations assume that interactions between a charged species and neutral species do not affect the activity coefficient of the charged species. This is our case; more general equations include these additional second-order interaction terms[8]:

$$\ln \gamma_A$$

$$= \vartheta_A^2 F + \sum_{c=1}^{n_c} m_c [2B_{cA} + ZC_{cA}] + \sum_{a=1}^{n_a} m_a \left[2\Phi_{Aa} + \sum_{c=1}^{n_c} \right. \quad \text{(A-4)}$$

$$\ln \gamma_C$$

$$= \vartheta_C^2 F + \sum_{a=1}^{n_a} m_a [2B_{Ca} + ZC_{Ca}] + \sum_{c=1}^{n_c} m_c \left[2\Phi_{Cc} + \sum_{a=1}^{n_a} \right. \quad \text{(A-5)}$$

$$\ln \gamma_N = \sum_{c=1}^{n_c} 2m_c \lambda_{N,c} + \sum_{a=1}^{n_a} 2m_a \lambda_{N,a} + \sum_{c=1}^{n_c} \sum_{a=1}^{n_a} m_c m_a \zeta_{N,c,a} \quad \text{(A-6)}$$

Where:

$$Z = \sum_{i=1}^{N} m_i |\vartheta_i| \quad \text{(A-7)}$$

$$C_{ca} = \frac{C_{ca}^{\Phi}}{2\sqrt{|\vartheta_c \vartheta_a|}} \quad \text{(A-8)}$$

$$\Phi_{ij} = \theta_{ij} + E_{\theta_{ij}}(I) \quad \text{(A-9)}$$

$$F = \frac{df(I)}{dI} + \sum_{c=1}^{n_c} \sum_{a=1}^{n_a} m_c m_a B'_{ca} + \sum_{c=1}^{n_c-1} \sum_{c'=2}^{n_c} m_c m_{c'} \Phi'_{cc'} + \sum_{a=1}^{n_a-1} \sum_{a'=2}^{n_a} m_a m_{a'} \Phi'_{aa'} \quad \text{(A-10)}$$

$$\frac{df(I)}{dI} = - A_\Phi \left[\frac{\sqrt{I}}{1 + b_0\sqrt{I}} + \frac{2}{b_0} \ln\left(1 + b_0\sqrt{I}\right) \right] \quad \text{(A-11)}$$

$$\Phi'_{ij} = E_{\theta'_{ij}}(I) \quad \text{(A-12)}$$

With:

γ_i: Species activity coefficient i (-);

n_i: Number of moles of species i (mol);

m_i: Molality of species i (mol/Kg of solvent);

ϑ_i: Charge of species i (-);

I: Ionic strength of the solution (mol/Kg). Calculated by $I = \frac{1}{2} \sum_{i=1}^{n} m_i \vartheta_i^2$;

F: Function that represents the contribution of the Debye-Hückel law;

$\lambda_{N,i}$: Binary interaction parameter between the neutral species N and an ion i (-);

$\zeta_{N,i,j}$: Ternary interaction parameter between the neutral species N and two ions i and j of charges of different signs (-);

$\Psi_{i,j,k}$: Ternary interaction parameters between three different ions i, j and k. Two with charges of the same sign;

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Φ_{ij}: Binary interaction parameter of two ions i and j with charges of identical signs (θ_{ij} and $E_{\theta_{ij}}(I)$). $E_{\theta_{ij}}(I)$ represents asymmetric mixing effects and depends on the ionic strength of the solution[2,7].

Φ'_{ij}: Binary cation-cation (or anion-anion) interaction parameter;

C_{ca}: Binary cation-anion interaction parameter, which is a function of the binary interaction parameter C_{ca}^{Φ} and the electric charges of the cations ϑ_c and anions ϑ_a;

The parameters B_{ij} and B'_{ij} are described by the following expressions:

$$B_{ca} = \beta_{ca}^{(0)} + \frac{2\beta_{ca}^{(1)}}{\alpha_1^2 I}\left[1 - (1 + \alpha_1\sqrt{I})exp(-\alpha_1\sqrt{I})\right] + \frac{2\beta_{ca}^{(2)}}{\alpha_2^2 I}\left[1 - (1 + \alpha_2\sqrt{I})exp(-\alpha_2\sqrt{I})\right] \qquad \textbf{(A-13)}$$

$$B'_{ca} = -\frac{2}{\alpha_1^2 I^2}\left[\beta_{ca}^{(1)}\left(1 - \left(1 + \alpha_1\sqrt{I} + \frac{\alpha_1^2 I}{2}\right)exp\left(-\alpha_1\sqrt{I}\right)\right)\right] - \frac{2}{\alpha_2^2 I^2}\left[\beta_{ca}^{(2)}\left(1 - \left(1 + \alpha_2\sqrt{I} + \frac{\alpha_2^2 I}{2}\right)exp\left(-a\right)\right)\right.$$ **(A-14)**

$\beta_{ca}^{(0)}$, $\beta_{ca}^{(1)}$ and $\beta_{ca}^{(2)}$ are adjustable symmetric anion-cation binary interaction parameters. The fact that they are symmetrical means that they have the following property: $\beta_{ij} = \beta_{ji}$ and $\beta_{ii} = \beta_{jj} = 0$. α_1 and α_2 parameters (Kg$^{0.5}$/mol$^{0.5}$) are associated with $\beta_{ca}^{(1)}$ and $\beta_{ca}^{(2)}$, respectively. In the classical use of the Pitzer equations, $\alpha_1 = 2$ and $\alpha_2 = 0$ for 1:1, 2:1, 3:1, and 4:1 type electrolytes [2,7]. In the present work, it is assumed that $\alpha_2 = 0$.

Experimental solubility results

Table 1 – Summary of Experimental Data of Eu(III) Solubility in Magnesium Sulfate and Sodium Sulfate Solutions at T = (22 ± 2)°C.

mMgSO$_4$ (mol·Kg^{-1})	mEu(III) (mol·Kg^{-1})	pH$_{exp}$	pH$_m$[c]	Solid[d]
0.0056[a] ± 1.00E-04	0.0598 ± 2.99E-03	3.7 ± 0.1	-	EuS
0.0135[a] ± 1.00E-04	0.0605 ± 3.03E-03	3.5 ± 0.1	-	EuS
0.0318[a] ± 1.00E-04	0.0609 ± 3.04E-03	3.5 ± 0.1	-	EuS
0.0521[a] ± 1.00E-04	0.0625 ± 3.12E-03	3.5 ± 0.1	-	EuS
0.0827[a] ± 1.00E-04	0.0653 ± 3.27E-03	3.5 ± 0.1	-	EuS
0.1034[a] ± 1.00E-04	0.0683 ± 3.41E-03	3.9 ± 0.1	-	EuS
0.3033[a] ± 1.00E-04	0.0851 ± 4.26E-03	3.9 ± 0.1	-	EuS
0.5024[a] ± 1.00E-04	0.1020 ± 5.10E-03	3.9 ± 0.1	-	EuS
0.8045[a] ± 1.00E-04	0.1133 ± 5.67E-03	3.9 ± 0.1	-	EuS
1.0081[a] ± 1.00E-04	0.1169 ± 5.84E-03	3.8 ± 0.1	-	EuS
1.3101[a] ± 1.00E-04	0.1167 ± 5.83E-03	3.9 ± 0.1	-	EuS
1.5038[a] ± 1.00E-04	0.1124 ± 5.62E-03	3.8 ± 0.1	-	EuS
1.8094[a] ± 1.00E-04	0.1073 ± 5.37E-03	3.8 ± 0.1	-	EuS
2.0125[a] ± 1.00E-04	0.1000 ± 5.00E-03	3.8 ± 0.1	-	EuS
2.2060[a] ± 1.00E-04	0.0900 ± 4.50E-03	3.8 ± 0.1	-	EuS
2.3683[a] ± 1.00E-04	0.0845 ± 4.22E-03	3.7 ± 0.1	-	EuS
2.4897[a] ± 1.00E-04	0.0765 ± 3.83E-03	3.7 ± 0.1	-	EuS
2.6948[a] ± 1.00E-04	0.0707 ± 3.53E-03	3.6 ± 0.1	-	EuS
2.8537[a] ± 1.00E-04	0.0651 ± 3.26E-03	3.6 ± 0.1	-	EuS
mNa$_2$SO$_4$ (mol·Kg^{-1})	mEu(III) (mol·Kg^{-1})	pH$_{exp}$	pH$_m$[c]	Solid[d]
0.0000[a]	0.0623 ± 3.12E-03	2.9 ± 0.1	-	EuS
0.0020[a] ± 1.00E-04	0.0618 ± 3.09E-03	3.6 ± 0.1	-	EuS
0.0031[a] ± 1.00E-04	0.0625 ± 3.12E-03	3.6 ± 0.1	-	EuS
0.0072[a] ± 1.00E-04	0.0605 ± 3.03E-03	3.6 ± 0.1	-	EuS
0.0084[a] ± 1.00E-04	0.0610 ± 3.05E-03	3.6 ± 0.1	-	EuS
0.0104[a] ± 1.00E-04	0.0608 ± 3.04E-03	3.6 ± 0.1	-	EuS
0.0152[b] ± 1.00E-04	0.0130 ± 6.51E-04	4.9 ± 0.1	-	NaEuS
0.0348[b] ± 1.00E-04	0.0068 ± 3.41E-04	4.9 ± 0.1	-	NaEuS
0.0596[b] ± 1.00E-04	0.0038 ± 1.92E-04	5.0 ± 0.1	-	NaEuS
0.0811[b] ± 1.00E-04	0.0030 ± 1.52E-04	5.0 ± 0.1	-	NaEuS
0.1004[a] ± 1.00E-04	0.0038 ± 1.92E-04	4.1 ± 0.1	3.7 ± 0.1	NaEuS
0.1200[b] ± 1.00E-04	0.0023 ± 1.13E-04	4.7 ± 0.1	4.3 ± 0.1	NaEuS
0.1225[b] ± 1.00E-04	0.0031 ± 1.53E-04	4.1 ± 0.1	3.7 ± 0.1	NaEuS
0.1355[a] ± 1.00E-04	0.0033 ± 1.65E-04	4.7 ± 0.1	4.3 ± 0.1	NaEuS
0.1962[a] ± 1.00E-04	0.0015 ± 7.28E-05	5.1 ± 0.1	4.6 ± 0.1	NaEuS
0.2060[a] ± 1.00E-04	0.0017 ± 8.70E-05	4.2 ± 0.1	3.8 ± 0.1	NaEuS
0.2485[a] ± 1.00E-04	0.0015 ± 7.39E-05	4.3 ± 0.1	3.9 ± 0.1	NaEuS
0.3054[a] ± 1.00E-04	0.0015 ± 7.73E-05	4.4 ± 0.1	4.0 ± 0.1	NaEuS
0.4642[a] ± 1.00E-04	0.0014 ± 6.99E-05	4.8 ± 0.1	4.3 ± 0.1	NaEuS
0.6425[a] ± 1.00E-04	0.0009 ± 4.57E-05	4.9 ± 0.1	4.4 ± 0.1	NaEuS + NaS[e]
0.8014[a] ± 1.00E-04	0.0009 ± 4.33E-05	4.5 ± 0.1	4.0 ± 0.1	NaEuS + NaS[e]

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$0.8419^a \pm$ 1.00E-04	$0.0012 \pm$ 5.78E-05	$4.9 \pm$ 0.1	$4.4 \pm$ 0.1	NaEuS + NaS[e]
$0.9931^a \pm$ 1.00E-04	$0.0009 \pm$ 4.57E-05	$4.9 \pm$ 0.1	$4.4 \pm$ 0.1	NaEuS + NaS[e]
$1.0260^a \pm$ 1.00E-04	$0.0011 \pm$ 5.27E-05	$5.0 \pm$ 0.1	$4.6 \pm$ 0.1	NaEuS + NaS[e]
$1.5595^a \pm$ 1.00E-04	$0.0011 \pm$ 5.54E-05	$5.0 \pm$ 0.1	$4.7 \pm$ 0.1	NaEuS + NaS[e]
$1.7817^a \pm$ 1.00E-04	$0.0013 \pm$ 6.60E-05	$4.9 \pm$ 0.1	-	NaEuS + NaS[e]

[a]Samples generated from $Eu_2(SO_4)_3 \cdot 8H_2O(cr)$. [b]Samples generated from $Na_2Eu_2(SO_4)_4 \cdot 2H_2O(cr)$. [c]Defined in *2.1.2*. [d]EuS = $Eu_2(SO_4)_3 \cdot 8H_2O(cr)$, NaEuS = $Na_2Eu_2(SO_4)_4 \cdot 2H_2O(cr)$, NaS = Na_2SO_4. The solubility limit of Na_2SO_4 (2 mol·Kg^{-1}) is well above the highest salt concentration considered in this work. The presence of Na_2SO_4 observed by XRD is thus attributed to the insufficient washing of the solid before characterization.

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