Supporting Information

Thermodynamics of the Eu(III)–Mg–SO_4–H_2O and Eu(III)–Na–SO_4–H_2O systems. Part II: spectroscopy experiments, complexation and Pitzer/SIT models

P. F. dos Santos[1,*], X. Gaona[1,*], A. Lassin[2], A. Skerencak[1], D. Fellhauer[1], M. Altmaier[1] and B. Madé[3]

[1]*Institute for Nuclear Waste Disposal, Karlsruhe Institute of Technology, Karlsruhe, Germany*
[2]*Water, Environment, Process Development and Analysis Division, BRGM, Orléans, France*
[3]*Research and Development Division, ANDRA, Châtenay-Malabry, France*
corresponding author(s): pedro.santos@kit.edu; xavier.gaona@kit.edu

Table SI-1 summarizes all the results and experimental conditions of the systems investigated by TRLFS, including normalized intensities and pH measurements. The proton concentration, pH_m were obtained from the measured values of pH_{exp} considering $pH_m = pH_{exp} + A_m$, where A_m is a correction factor that involves the H^+ activity coefficient and the liquid junction potential of the electrode at a given concentration of background electrolyte. A_m values for Na_2SO_4 systems were used as reported in Duckworth et al[1] (work performed between 0.1–1.75 mol·Kg^{-1} Na_2SO_4). All values pH_m are close to 5, which supports the absence of any significant Eu(III) hydrolysis species or HSO_4^- (< 1%).

Table SI-1 – Measured and modelled normalized fluorescence intensity of Eu(III)–Na^+–SO_4^{2-} aqueous solutions at room temperature.

$[Na^+]$(mol·Kg^{-1})	$Log_{10}[SO_4^{2-}]$	pH_{exp}	pH_m	$I_{norm}^{R,exp}$	$I_{norm}^{R,SIT}$	$I_{norm}^{R,Pitzer}$
0.00	-5.49	5.7 ± 0.1	-	1.00 ± 0.05	1.08	1.08
8.50E-04	-3.07	5.8 ± 0.1	-	1.46 ± 0.07	1.27	1.28
1.97E-03	-2.70	5.6 ± 0.1	-	1.65 ± 0.08	1.41	1.42
6.62E-03	-2.18	5.5 ± 0.1	-	1.74 ± 0.09	1.68	1.69
9.77E-03	-2.01	5.6 ± 0.1	-	1.72 ± 0.09	1.76	1.78
1.19E-02	-1.93	5.6 ± 0.1	-	1.82 ± 0.09	1.80	1.82
4.74E-02	-1.32	5.7 ± 0.1	-	2.02 ± 0.10	2.05	2.08
7.70E-02	-1.11	5.6 ± 0.1	-	2.11 ± 0.11	2.14	2.17
0.11	-0.96	5.5 ± 0.1	5.1 ± 0.1	2.16 ± 0.11	2.20	2.23
0.16	-0.81	5.6 ± 0.1	5.2 ± 0.1	2.33 ± 0.12	2.29	2.31
0.20	-0.70	5.5 ± 0.1	5.1 ± 0.1	2.35 ± 0.12	2.36	2.38
0.26	-0.59	5.5 ± 0.1	5.1 ± 0.1	2.43 ± 0.12	2.43	2.45
0.31	-0.50	5.4 ± 0.1	5.0 ± 0.1	2.52 ± 0.13	2.51	2.52
0.36	-0.45	5.4 ± 0.1	5.0 ± 0.1	2.58 ± 0.13	2.56	2.56
0.45	-0.35	5.4 ± 0.1	5.0 ± 0.1	2.81 ± 0.14	2.67	2.66
0.51	-0.29	5.5 ± 0.1	5.1 ± 0.1	2.83 ± 0.14	2.73	2.72
0.61	-0.22	5.4 ± 0.1	5.0 ± 0.1	2.79 ± 0.14	2.82	2.81
0.70	-0.15	5.4 ± 0.1	4.9 ± 0.1	2.89 ± 0.14	2.90	2.89
0.82	-0.09	5.3 ± 0.1	4.8 ± 0.1	2.93 ± 0.15	2.98	2.97
0.90	-0.05	5.3 ± 0.1	4.9 ± 0.1	2.98 ± 0.15	3.04	3.03
1.00	0.00	5.3 ± 0.1	4.9 ± 0.1	2.95 ± 0.15	3.11	3.10
1.20	0.08	5.4 ± 0.1	5.0 ± 0.1	3.11 ± 0.16	3.22	3.20
1.46	0.16	5.2 ± 0.1	4.9 ± 0.1	3.39 ± 0.17	3.34	3.32
1.55	0.19	5.2 ± 0.1	4.9 ± 0.1	3.36 ± 0.17	3.38	3.36
1.82	0.26	5.2 ± 0.1	-	3.54 ± 0.18	3.48	3.44
2.03	0.31	5.1 ± 0.1	-	3.64 ± 0.18	3.54	3.49

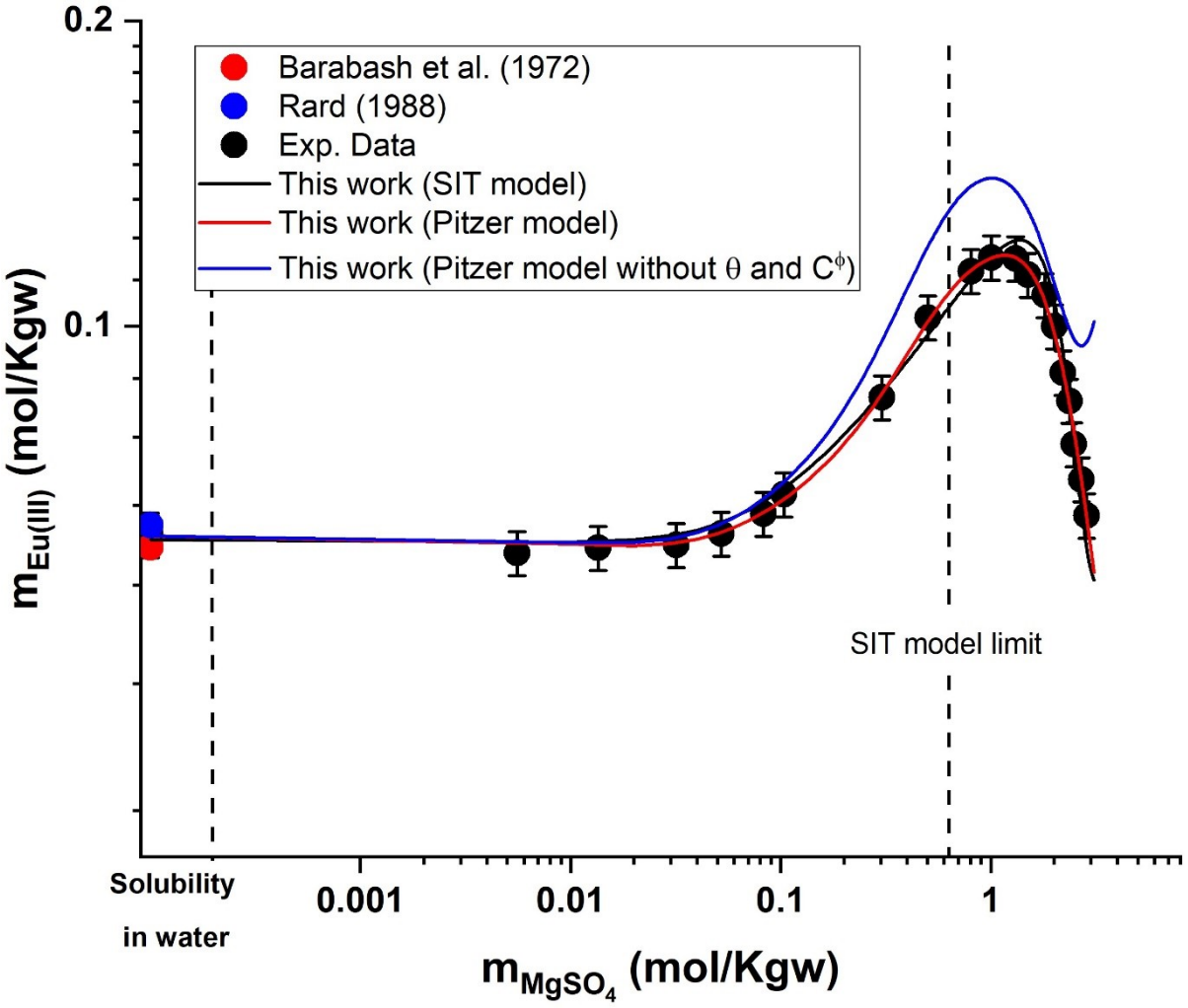

Figure SI-1 – Solubility in the system $Eu_2(SO_4)_3$–$MgSO_4$–H_2O at room temperature in logarithmic scale, according to SIT (black line), Pitzer (red line) models. The blue line corresponds to the Pitzer excluding $\theta_{Mg^{2+},Eu(SO_4)^+}$, $C^{\phi}_{Mg^{2+},Eu(SO_4)_2^-}$ and $C^{\phi}_{Mg^{2+},Eu(SO_4)_3^{3-}}$ as fitting parameters (see main text). Symbols: experimental data as reported in Part I of this work or in the literature[2].

REFERENCES

1 S. B. Duckworth, X. Gaona, A. Baumann, K. Dardenne, J. Rothe, D. Schild, M. Altmaier and H. Geckeis, *Radiochim. Acta*, 2021, **109**, 681–697.

2 P. F. dos Santos, A. Lassin, X. Gaona, K. Garbev, M. Altmaier and B. Madé, *Dalt. Trans.*