

SOLUBILITY AND AQUEOUS SPECIATION OF Ln(III) AND An(III) IN DILUTE TO CONCENTRATED AQUEOUS NITRATE AND SULFATE SYSTEMS: PITZER AND SIT MODELS AT 25 °C

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Taking into account the similarities in ionic radii and equal charge, Eu(III) is commonly considered to be an inactive and redox-stable analogue of trivalent actinides (An) expected in nuclear waste. Thus, thermodynamic and activity models capable of describing the solubility and ionic interactions of Eu(III) in dilute to concentrated solutions of nitrate and sulfate can provide relevant information for the description of An(III) under relevant conditions for waste disposal [1]. In this work, comprehensive solubility experiments for the $\text{Eu}^{3+}\text{-Na}^+\text{-Mg}^{2+}\text{-SO}_4^{2-}\text{-NO}_3^-$ aqueous systems were combined with advanced spectroscopic techniques (TRLFS) and a multimethod approach for solid phase characterization in order to derive complete thermodynamic and (SIT, Pitzer) activity models for these systems.

Diluted to concentrated aqueous solutions containing Na_2SO_4 , NaNO_3 , MgSO_4 and $\text{Mg}(\text{NO}_3)_2$ were prepared and contacted with the binary, well characterized solid phases $\text{Eu}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}_{(\text{cr})}$ and $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}_{(\text{cr})}$. Batch undersaturation solubility samples under air conditions ($3.3 < \text{pH} < 5.8$) were continuously stirred, and the concentration of Eu(III) in the liquid phase was monitored by ICP-OES until attaining equilibrium conditions. Solid phases were characterized (XRD, Raman and TG-DTA) after terminating the solubility experiments. As reported for other lanthanides, the formation of the double salt $\text{Na}_2\text{Eu}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}_{(\text{cr})}$ was observed above $\sim 0.01 \text{ M Na}_2\text{SO}_4$.

The new solubility and spectroscopic experimental data obtained in this study for the $\text{Eu}^{3+}\text{-Na}^+\text{-Mg}^{2+}\text{-SO}_4^{2-}\text{-NO}_3^-$ aqueous system, in combination with previously reported solubility and isopiestic data, are considered to derive the thermodynamic and (SIT, Pitzer) activity models for these systems. The implemented optimization routine combines PEST, a parameter estimation software, PhreeqC [2] or PhreeSCALE [1] for chemical equilibria calculations, and the dedicated database. The ThermoChimie database is considered as basis for the development of the SIT models [3].

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References

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