

Solubility and thermodynamics of the Eu(III)-Na/Mg-NO₃-H₂O systems

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Considerable nitrate quantities are part of waste inventory (ILW-LL) in some repository concepts for radioactive waste disposal. Thus, understanding solution chemistry and the behavior of radionuclides in aqueous nitrate systems is important for long-term safety assessment in a saline plume environment. The inactive and under the given conditions redox-stable Eu(III) is considered as analogue of trivalent actinides due to shared charge, similar ionic radii and aqueous speciation. This work presents an investigation of Eu(III)-Na/Mg-NO₃-H₂O systems at T=(22±2) °C, including undersaturation solubility experiments, iso-water activity (IWA)/dynamic vapor sorption (DVS) measurements, time resolved laser fluorescence spectroscopy (TRLFS), X-ray powder diffraction, and Schreinemakers' method.

Solubility investigations for Eu(III)-Na-NO₃-H₂O result in solubility curves of Eu(NO₃)₃·6 H₂O and NaNO₃ with an invariant point at 2.7 mol NaNO₃/kg H₂O. The formation of 2 Eu(NO₃)₃·3 Mg(NO₃)₂·24 H₂O was observed for Eu(III)-Mg-NO₃-H₂O at 3.8 mol Mg(NO₃)₂/kg H₂O. IWA and DVS experiments provide osmotic coefficients and iso-water activity curves at 50-80 % relative humidity. TRLFS studies on Eu(III) show systematic intensity changes with increasing nitrate concentration, which evidences the formation of aqueous Eu(III)-NO₃ species (Fig. 1).

These results, combined with literature data, were used to develop parameter sets for thermodynamic Pitzer¹ and SIT² models. Full and partial dissociation approaches were comparatively conducted. The parametrization routine included the geochemical calculation codes PhreeqC and PhreeSCALE combined with the parameter estimation software PEST. Databases used are ThermoChimic^{3,4} (SIT) and PhreeSCALE⁵ (Pitzer).

The full dissociation Pitzer model describes solubility (Fig. 2) and iso-water activity data in good agreement. The partial dissociation models consider EuNO₃²⁺ and Eu(NO₃)₂⁺ species. Their advantages and limitations are comparatively discussed.

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References

- (1) Pitzer *J. Phys. Chem.* **1973**, 77 (2), 268–277.
- (2) Guggenheim *Phil. Mag.* **1935**, 19 (127), 588–643.
- (3) Giffaut et al. *Appl. Geochem.* **2014**, 49, 225–236.
- (4) Madé et al. *Appl. Geochem.* **2025**, 180, 106273.
- (5) André et al. PHREESCALE.DAT Version 1.0. **2020**.
- (6) Rard *J. Ch. Thermodyn.* **1984**, 16 (10), 921–925.
- (7) Eysseltová et al. *J. Phys. Chem. Ref. Data* **2017**, 46 (1), 013103.

