Europium(III), Colloidal α-Al2O3 and Humic acid interactions

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Europium(III), Colloidal α-Al_2O_3 and Humic Acid Interactions

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Context

Interactions between Natural Organic Matter (NOM) and minerals modify mobility and bioavailability of trace elements. A better description of these ternary metal/NOM/mineral surface systems is needed to improve the understanding of radionuclides transfer from a repository site to the geosphere. This study is focused on Europium(III) speciation in presence of aluminum oxide α-Al_2O_3 and Purified Aldrich Humic Acid (PAHA) as a surrogate of NOM. In case of lanthanides, one way to obtain both macroscopic and spectroscopic information on metal sorption onto mineral surfaces is through Time-Resolved Laser-induced Luminescence Spectroscopy (TRLS), which allows to have a direct insight on speciation of ions in solution at relevant environmental metal concentration. Macroscopic and spectroscopic experiments have been carried out to see the influence of pH on the evolution of the different binary Eu(III)/α-Al_2O_3 and Eu(III)/PAHA and ternary Eu(III)/PAHA/α-Al_2O_3 systems.

Conclusions and Perspectives

✓ Eu(III) in the ternary system is mostly bound to sorbed humic acid in the whole pH range

✓ Modification of HA reactivity due to adsorption onto the mineral must be taken into account for modeling

✓ At high pH in the ternary system, Eu(III) complexation to the mineral surface becomes predominant

→ Same approach is conducted to evidence the influence of HA concentration and ionic strength on Eu(III) speciation

I. Methodology

▪Description of experiments

- Contact time: 3 days
- Ultracentrifugation: 2h, 60,000 rpm
- PAHA concentration: DOC measurements
- Eu(III) concentration: TRLS (standard addition method)
- [Eu(III)] = 10^{-6} mol/L
- [α-Al_2O_3] = 1 g/L
- [PAHA] = 28 mg_{HA}/L
- I = 0.1M $NaClO_4$

▪Time-Resolved Laser Induced Luminescence Spectroscopy *(Fig. 1 and 2)*

- Eu(III) complexation (asymmetry ratio $^7F_2/^7F_1$)
- Symmetry of Eu(III) environment ($^7F_0$)
- Quenching groups in the first coordination sphere (Luminescence lifetime)

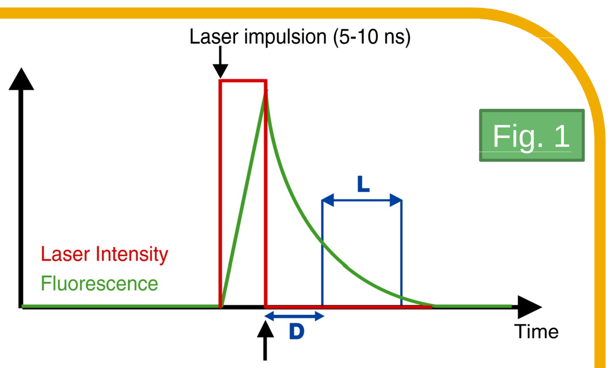


Fig. 1

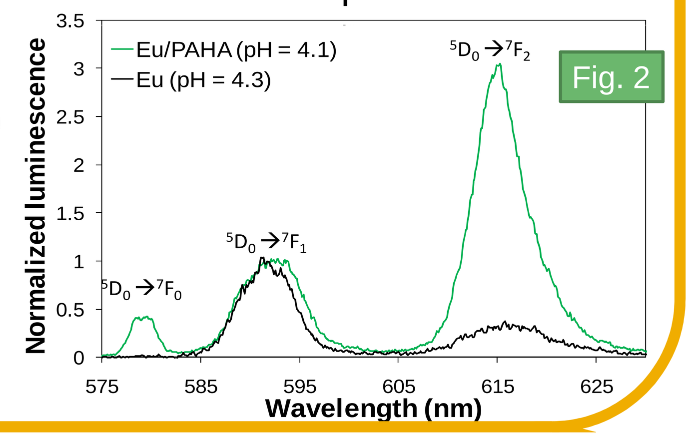


Fig. 2

II. Results of macroscopic measurements

PAHA sorption onto α-Al_2O_3 (Fig. 3)

▪ Binary PAHA/α-Al_2O_3
Sorption decreases with increasing pH (from 76 to 37%)

▪Ternary Eu(III)/PAHA/α-Al2O3
Presence of Eu(III) homogeneously increases the humic sorption in the whole pH range (from 88 to 38%)

Eu(III) sorption onto α-Al_2O_3 (Fig. 4)

▪ Binary Eu(III)/α-Al_2O_3
pH-edge around 7, typical of Eu(III)

▪Ternary Eu(III)/PAHA/α-Al_2O_3
- pH<6, increase of Eu(III) uptake
- pH>7, decrease of sorption due to decrease of PAHA sorption
- pH>8, increase of sorption due to Eu(III)-α-Al_2O_3 complexation

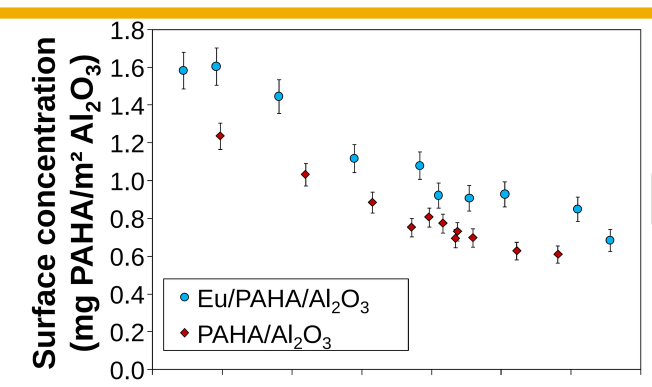


Fig. 3

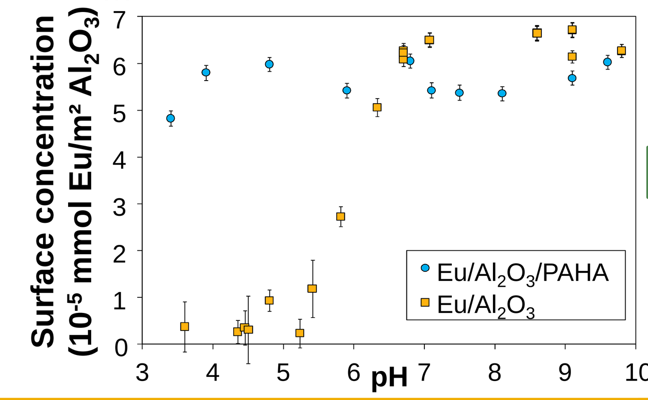


Fig. 4

III. Spectroscopic results

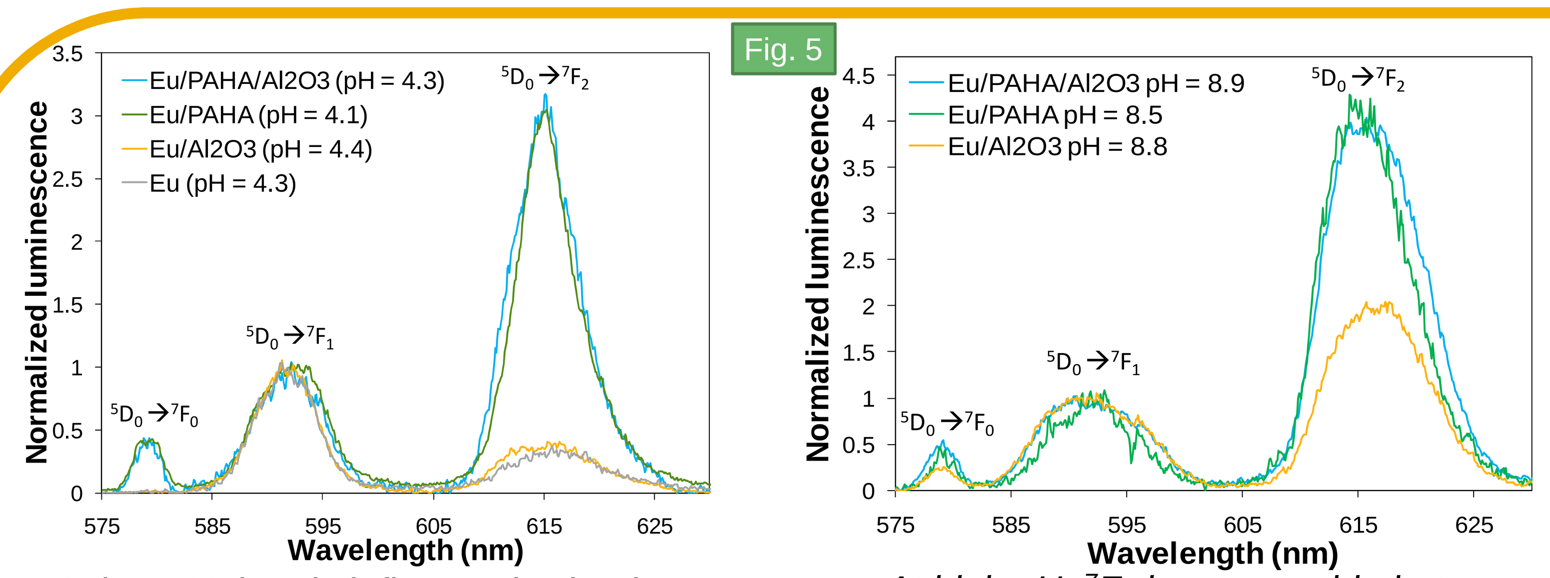


Fig. 5

At low pH, humic influence is clearly seen in Eu(III) spectra of ternary system

At high pH, $^7F_1$ is comparable between binary Eu(III)/α-Al_2O_3 and ternary systems

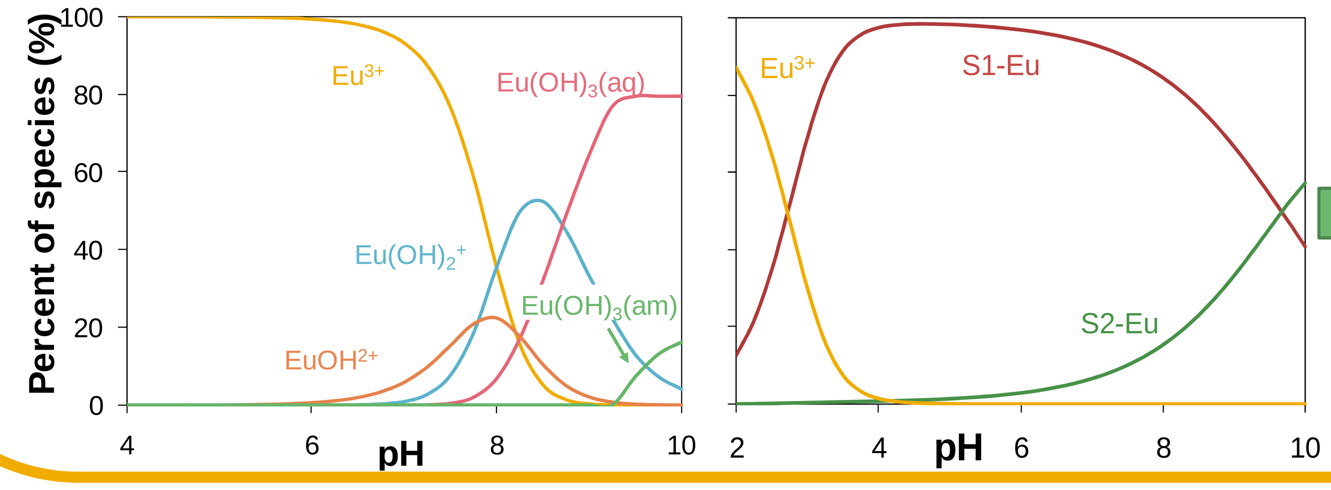


Fig. 6

Binary Eu(III)/α-Al_2O_3 system

- **$^7F_0$ transition** appears at pH > 5.5 *(Fig. 5)*
- **$^7F_2/^7F_1$ increases with pH** and formation of inner-sphere surface complexes *(Fig. 7)*
- **Monoexponential decay time τ** increases with pH *(Fig. 8)*

Binary Eu(III)/PAHA system

- **$^7F_2/^7F_1$ increases with pH**

  $^7F_2/^7F_1$ > 1 and $^7F_0$ always present: Eu(III) is always complexed to PAHA *(Fig. 5, 6, 7)*
- **Biexponential decay time** *(Fig. 8)*
  - Short τ_1 < $\tau_{free\ Eu}$ characteristic from humic binding
  - τ_2 increases with pH

Ternary Eu(III)/α-Al_2O_3/PAHA system

- **$^7F_2/^7F_1$ increases with pH** = evolution of chemical environment of Eu(III) *(Fig. 5 and 7)*
  - pH < 7 : similar environment to Eu(III)/PAHA
  - pH > 7.5 : shift of maxima and change of peaks shapes
- **Biexponential decay time** *(Fig. 8)*
  - τ_1 presence: Eu(III) always bound to PAHA
  - τ_2 longer than τ_2 of binary systems : more constrained environment, but of the same symmetry than in binary Eu(III)/PAHA system (comparable spectra)
  - τ_2 decreases when pH increases : Eu(III) more exposed to quenching groups; progressive change in structure of Eu(III)/PAHA complexes onto the surface

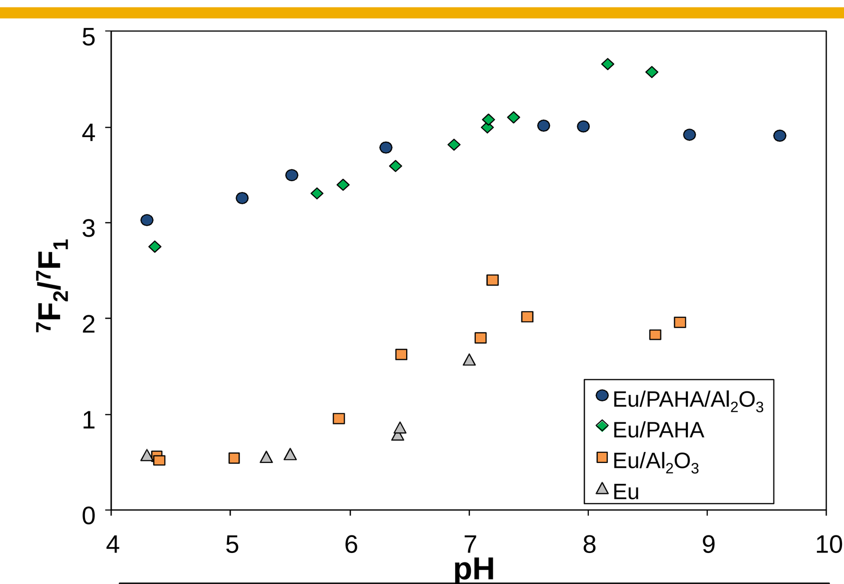


Fig. 7

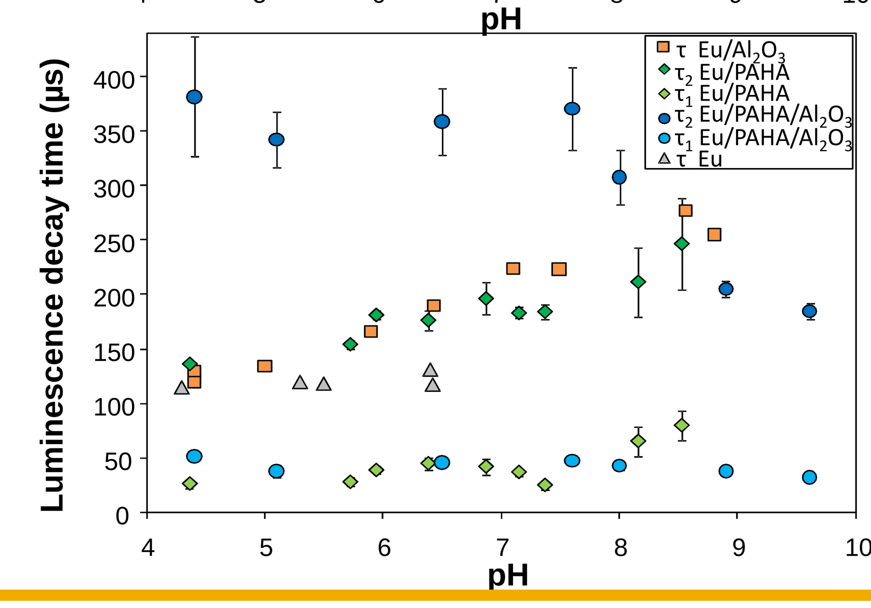
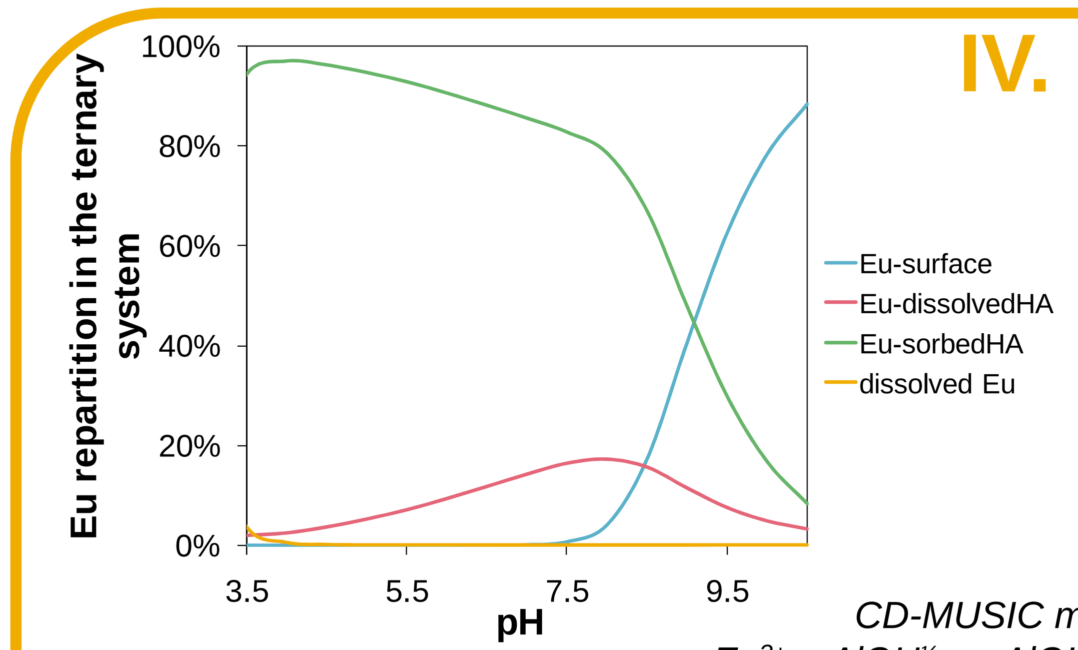
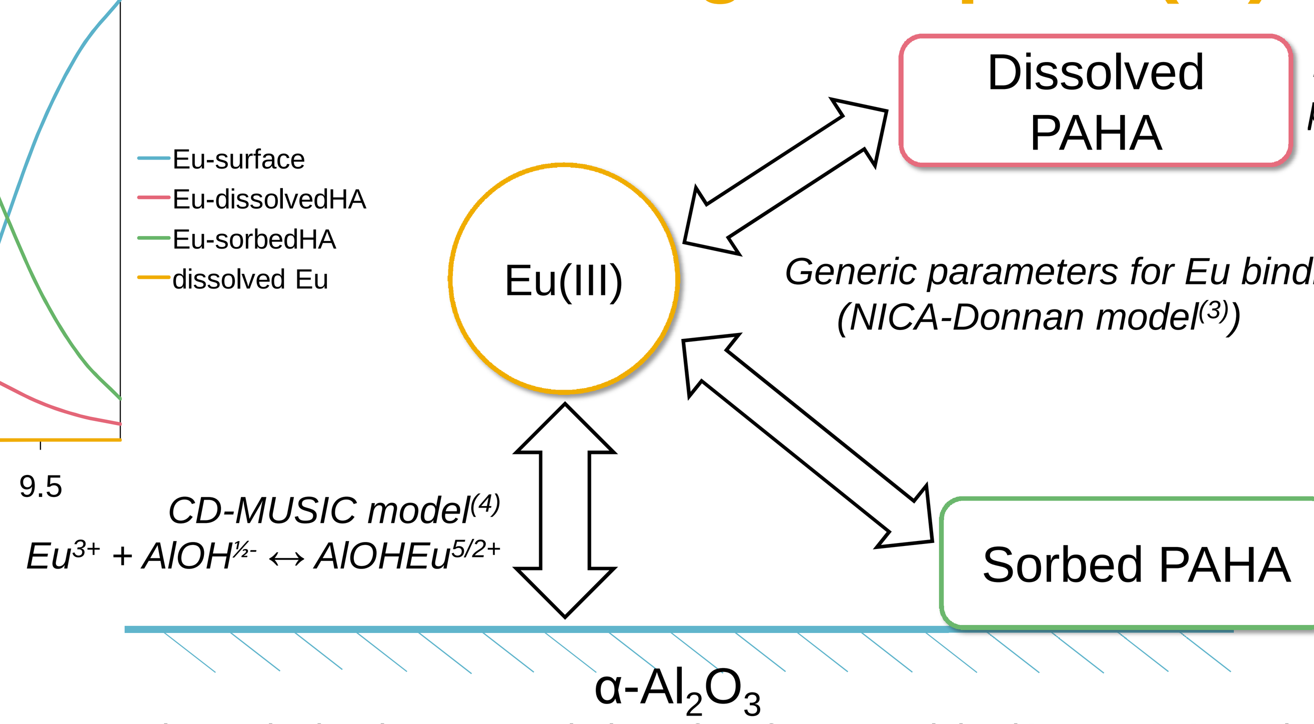


Fig. 8

IV. Modeling Europium(III) speciation in ternary systems





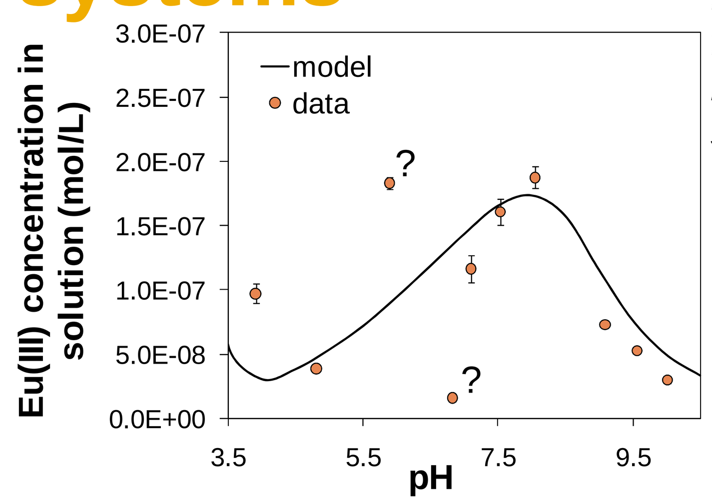
Proton-binding parameters from spectro-photometric titrations of supernatant from retention experiments[1]

Generic parameters for Eu binding[2] (NICA-Donnan model[3])

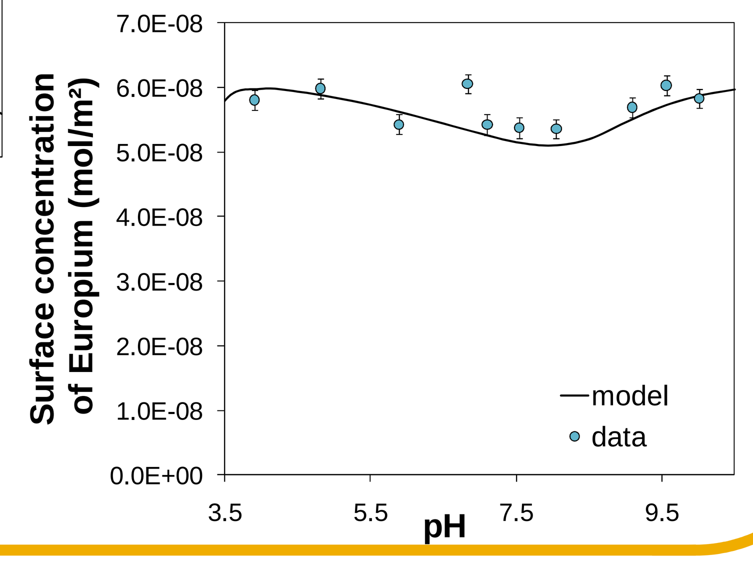
CD-MUSIC model[4]
Eu^{3+} + $AlOH^{½-}$ ↔ $AlOHEu^{5/2+}$

Potentiometric titrations: Description of surface reactivity (NICA-Donnan model[3])

Potentiometric titrations: Description of surface reactivity (CD-MUSIC model[4])



Europium-binding parameters of dissolved fraction of PAHA may be modified in order to better describe the amount of Eu(III) left in solution in the ternary system



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