

Supporting Information

Effect of different complexing ligands on Europium uptake form aqueous phase by kaolinite: batch sorption and fluorescence studies

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Experimental section

Kinetics of Eu(III) sorption

The $^{152,154}\text{Eu(III)}$ (10^{-6} M) sorption kinetics onto kaolinite (1 g/L) was studied at different conditions of pH (approximately 3, 5.5 and 7.5) and ionic strengths (0.01, 0.1 and 1 M NaClO_4). The weighted amount of kaolinite was added to MilliQ water to get the desired solid/liquid ratio. The ionic strength in different tubes was adjusted using the stock 1 M NaClO_4 solution for 0.01 and 0.1 M ionic strength. Weighted amount of NaClO_4 (**Caution: Hygroscopic solid must be kept in desiccators under vacuum!**) was added to reaction vial to maintain 1M NaClO_4 ionic strength. The kaolinite suspension at desired ionic strength was equilibrated for 24 hr, before addition of $^{152,154}\text{Eu(III)}$. The Zero time of kinetics was started at the time of addition of $^{152,154}\text{Eu(III)}$ to kaolinite suspension at different ionic strength. 1 ml of suspension was assayed for $^{154}\text{Eu(III)}$ just after the $^{152,154}\text{Eu(III)}$ addition to get the initial counts (to avoid pipetting errors) for all the tubes at different chemical conditions. The suspensions were centrifuged for 15 minutes at 20000rpm using a high speed centrifuge (Sigma3-30K) to separate the solid. The % sorption of $^{152,154}\text{Eu(III)}$ on the kaolinite suspension was determined by radiometric assay of 1 ml of the supernatant sample for 5 min after the equilibration with kaolinite at different time interval using following equation:

$$\% \text{ Sorption} = [(A_i - A_f) / A_i] / 100$$

Where A_i : initial counts (at $t=0$); A_f : Final counts (with varying time)

Photoluminescence studies of Eu(III) samples

Photoluminescence studies were performed on an Edinburgh unit provided with CD-920 controller and micro sec flash lap. The data acquisition and analysis were done by the F-900 software provided by Edinburgh Analytical Instruments, UK. For $\text{Eu(III)}_{\text{aq}}$ and Eu(III) -kaolinite suspension, the emission spectra were recorded at λ_{ex} 248 nm, charge transfer band, for all the samples. The suspension was shaken in between the measurements to take care of slow settling of suspension with time. The life time data was recorded at λ_{em} 617 at the same excitation wavelength. For the luminescence of supernatant and solid samples, the two were separated by high-speed centrifuge. The supernatant was measured as mentioned above. For solid, the slurry

was spread on glass slide and air dried, before the measurements. At least 5 scans were taken for all the samples. The fluorescence decay curves for all the samples were recorded on a 4 ms scale and fitted via an iterative method. The decay curves were fitted into mono, bi or tri exponential decay. The quality of fit was ascertained by chi squares (χ^2) values.

Result and Discussion

Table and Figures

The speciation of Eu(III) (10^{-6} M) was calculated using **Medusa** in aerobic condition. The equilibrium constants were listed in **Table S1**.

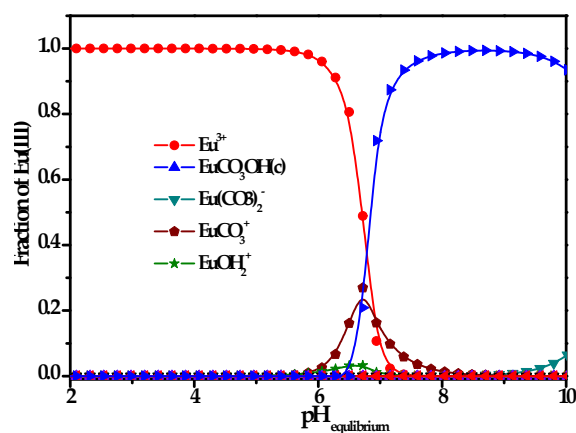


Fig. S1: Aqueous speciation of Eu(III) (10^{-6} M) with varying pH, $p\text{CO}_2 : 10^{-3.5}$

Table S1: Equilibrium constants used for the speciation plot of Eu(III) using **Medusa**

Species	Log β
$\text{Eu}(\text{CO}_3)_2^-$	-24.05
$\text{Eu}(\text{OH})_2^+$	-16.38
$\text{Eu}(\text{OH})_3$	-25.42
$\text{Eu}(\text{OH})_4^-$	-34.53
EuCO_3^+	-10.199
EuHCO_3^{2+}	-6.22
EuOH^{2+}	-7.9
EuCO_3OH	-10.34
H_2CO_3	-1.468
HCO_3^-	-7.82
OH^-	-14
CO_3^{2-}	-18.149

Surface speciation in ternary system of clay, metal ion and complexing ligands

The spectroscopic studies such as Extended X-ray Absorption Fine Structure (EXAFS) or fluorescence (in case of fluorescent metal ions) are used for the surface speciation studies. In present case fluorescence studies were preferred due to good luminescent properties of Eu(III). The surface speciation of sorbed metal ion in the presence of clay and complexing ligands can be of different types. **a)** The ligand is non-interacting and the metal ions can sorbed onto clay minerals depending on prevailing chemical condition (outer sphere at low pH in present studies); **b)** ligand bridge between metal and surface; **c)** metal bridge between ligand and surface and **d)** metal-ligands complex precipitation (**Fig. S2**).

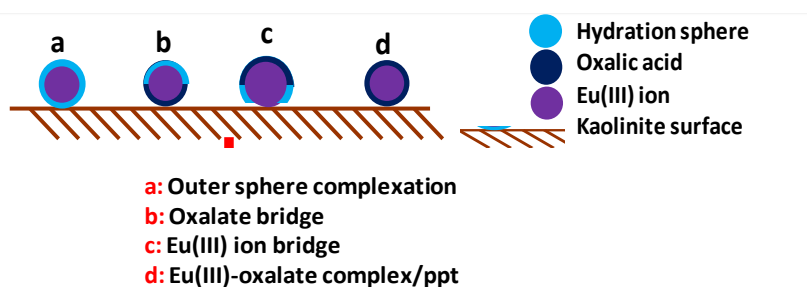


Fig.S2: Different mechanism/speciation in the case of ternary system of clay, metal ion (in this case Eu(III)) and complexing ligands (in this case oxalic acid)

Luminescence of ternary system of kaolinite-oxalic acid-Eu(III)

The luminescence studies were done as mentioned above. The emission spectra were analysed to compare the spectral features of $\text{Eu(III)}_{\text{aq}}$, binary system (Eu(III)-oxalate, Eu(III)-kaolinite) and ternary system (Eu(III)-kaolinite-oxalate). The fluorescence decay curves for all the samples were fitted into mono, bi or tri exponential decay. The quality of fit was ascertained by chi squares (χ^2) values. The life time data was also used for the calculation of number of water molecules in inner spheres of Eu(III) using equation 1, proposed by Barthelemy et. al.¹

$$N_{\text{H}_2\text{O}} = 1.05k - 0.7 \quad \dots\dots(1)$$

where $k = 1/\tau(\text{ms})$ and $N_{\text{H}_2\text{O}}$ is number of water molecules in inner sphere of Eu(III).

The complexation of Eu(III) with the complexing ligands can also modify the overall symmetry of the metal-ligand complex. Such modification in the symmetry leads to variation in the peak intensity on the emission spectra. The $^5\text{D}_0$ to $^7\text{F}_2$ ($\lambda=617 \text{ nm}$) is a hypersensitive transition for Eu(III) and is affected more by such structural perturbations when compared to other transitions. Asymmetric ratio is a parameter to quantify such perturbation in ligand induced system.² The asymmetric ratio is a ratio of intensity (or more accurately area under the peak) of 617 nm ($^5\text{D}_0$ to $^7\text{F}_2$) peak to 593 nm ($^5\text{D}_0$ to $^7\text{F}_1$) as given in equation 2.

$$\text{Asymmetric ratio} = \frac{\int_a^b \lambda_{617}}{\int_c^d \lambda_{593}} \quad \dots\dots 2$$

Where $\int_a^b \lambda_{617}$ is peak area under 617 nm peak (under integration limit a: 608 , b: 630) and $\int_c^d \lambda_{593}$ is peak area under 593 nm peak (under integration limit c:585 , d:603). The integration limits were kept same for the

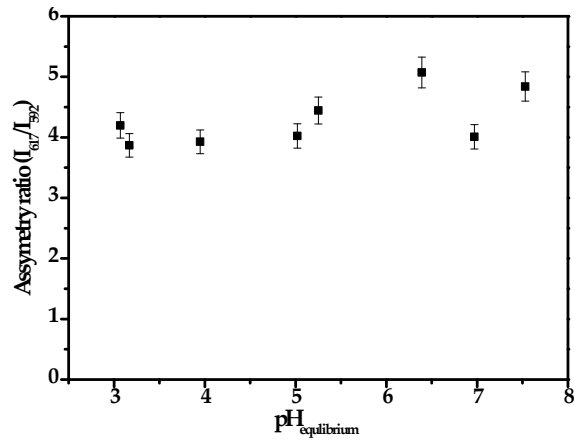


Fig.S3: Asymmetric ratio of Eu(III)-oxalate (10^{-4} M each) as a function of varying pH

calculation of area under the peak for all the samples except $\text{Eu(III)}_{\text{aq}}$ (under integration limit a: 601 , b:635 and c:580 , d:601). The asymmetric ratio was also calculated for the Eu(III)-oxalic acid system as a function of pH. The asymmetric ratio remains close to 4.0 ± 0.5 for all the samples with varying pH (**Fig. S4**).

$\text{Eu(III)}_{\text{aq}}$ at pH ~ 5 , was used as reference and was plotted in fig.S4.

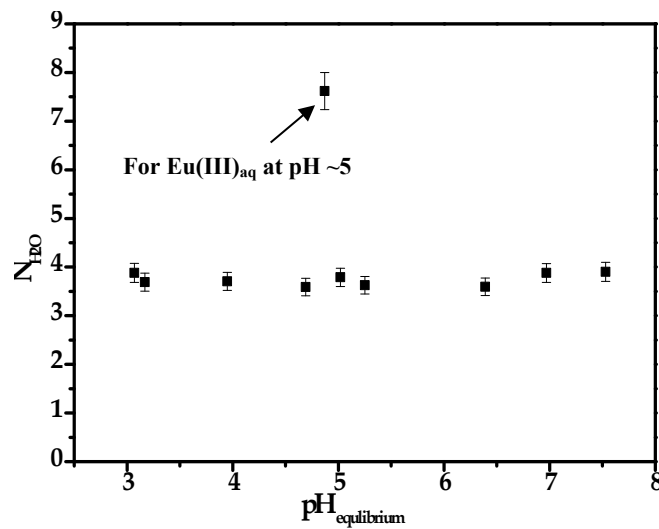


Fig.S4: Number of water molecules in binary system (Eu(III)-oxalate (10^{-4} M each)) as a function of varying pH

Luminescence under UV lamp for ternary system of kaolinite-oxalic acid-Eu(III)

UV chamber equipped with the UV-lamp (CAMAG, Anchrom, Switzerland) was used to see the luminescence in the UV chamber. **Caution: Use UV-protective glass, Do not see the lamp by naked eyes!**

The lamp has two excitation wavelengths 254 nm and 366 nm. The Eu(III)-oxalate spot onto glass plate and pure kaolinite slurry spread onto glass plate (air dried) was used as reference. To see the luminescence solid samples under UV lamp, the suspension was centrifuged with high-speed centrifuge. The supernatant and solid was separated. For solid, the slurry was spread on glass slide and air dried. The glass plate was then seen under UV lamp at 254 nm and 366 nm excitation. The red luminescence from the surface is seen only with 254 nm lamp, no colour with 366 nm lamp. The red luminescence at 254 nm conforms the presence of Eu(III) as Eu(III)-Ox complex onto the kaolinite surface.

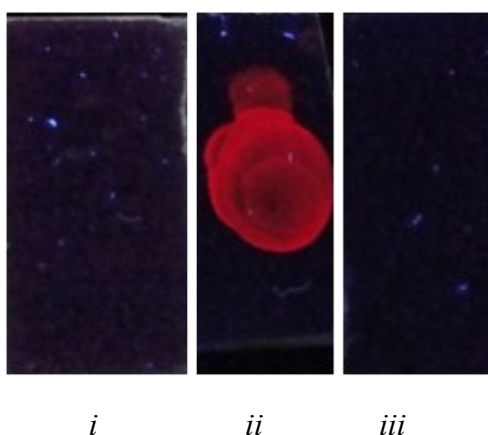


Fig. S5: Fluorescence under UV lamp (*i*: Eu-Kaolinite-Oxalate *ii*: Eu(III)-oxalate spot, *iii*: blank (only kaolinite)) (λ_{ex} : 254 nm), of Eu(III) (10^{-4}M) sorbed onto kaolinite (2.5g/L)

Notes and References

1. Barthelemy P.P.; Choppin G.R., *Inorg. Chem.*, **28**, 1989, 3354.
2. D. Janczewski, D. N. Reinhoudt, W. Verboom, E. Malinowska, M. Pietrzak, C. Hill and C. Allignole, *New J. Chem.*, **31**, 2007, 109.