

Study of the reversibility of the interaction between Eu(III) and polyacrylic acids

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Humic substances are known to be a potential vector for the transport of trivalent metal ions in the environment due to non-reversible interactions. The goal of the present paper is to understand the origin of this non-reversibility using polyacrylic acid, PAA, as model substance and Eu(III). The reversibility of the interaction between Eu(III) and two polyacrylic acids (5000 and 50 000 Da) is investigated by comparing the interaction constants deduced from complexation and dissociation experiments in the presence of the chelex resin. The work is done at pH = 5 in 0.1 mol L⁻¹ NaClO₄. Fluorescence spectroscopy is used as a speciation method to characterize the mode of interaction between Eu(III) and PAA functional groups. The results show that Eu(III), in a first step, interacts rapidly with polyacrylic acid functional groups, probably by electrostatic forces. This process is followed by a rearrangement of the polymer chain to form an inner sphere site where Eu(III) is probably coordinated with three carboxylate groups. The interaction between Eu(III) and polyacrylic acid is shown to be reversible: the parameters deduced from complexation and dissociation experiments are identical. This result differs from that previously reported for the model system composed of synthetic polycarboxylic acids and Th(IV). This discrepancy is explained by the difference in the nature of the metal ion studied and/or by the difference in the range of ligand-to-metal ratios investigated. The difference in complexation behavior of Eu(III) with natural and synthetic polyelectrolytes is ascribed to their different structures.

Introduction

In the context of the safety of nuclear waste repositories as well as for the assessment of radionuclide mobility in contaminated soils, the interaction between metal ions, M, and humic substances, HS, has been the subject of an important number of studies.^{1,2} Studies have been carried out notably with trivalent actinides (Cm, Am) and homologs [*i.e.*, Eu(III)] as their solution behavior in the environment is known to be dominated by organic macromolecules.³ The results show that humic substances are strong complexants for these metal ions^{4–8} and various models can satisfactorily quantify their equilibrium properties.⁹

Several papers on humic substances, and particularly on humic acids, HA, have shown that after equilibration of the distribution between free and complexed trivalent metal ion in solution, a modification of the binding site of M within the humic acid structure occurs. This was shown either indirectly by studying the dissociation of the M–HS complex in the presence of a competing complexing agent^{10–13} or directly by time-resolved laser-induced fluorescence spectroscopy (TRLFS).¹⁴ This modification was shown to be strongly dependent on the contact time between M and HS.

As a consequence, classical equilibration models can be used only with well-defined limitations to predict the effect of humic substances on the migration of trivalent metal ions in the environment. A mixed kinetic and equilibrium approach was shown to be more appropriate.¹⁵ This latter implies two distinct interaction sites: an exchangeable site allowing rapid ion exchange equilibration and a site with slow interaction kinetics.

The origin of the change in site occupation with contact time remains unclear. An understanding is difficult because the

M–HS interaction is affected and controlled by the heterogeneous and polyelectrolyte nature of natural organic matter. To study the polyelectrolyte effect separately, Choppin *et al.*¹⁶ have studied the kinetics of dissociation of Th(IV) bound to polycarboxylic acids of the polymaleic acid (PMA) family. Polycarboxylic acids are linear weak polyelectrolytes whose conformational behavior in solution is represented by the random coil model, as is also the case for humic substances.¹⁷ They contain carboxylic functions that are responsible for the strong interaction¹⁸ between metal ions and humic substances in weakly acidic media. Choppin *et al.* observed, as for HA,¹⁹ a modification in the speciation of Th with contact time (below 2 days). This modification was interpreted in terms of conformational changes upon complexation, leading to the passage of Th bound to freely accessible binding sites towards a “hydrophobic” cage in which the ion is “hidden” from interaction with the aqueous media and becomes “irreversibly” bound. This explanation is also given to explain the behavior of metal ions with humic substances.^{11,12}

The goal of this paper is to gain further insight into this interpretation for trivalent metal ions using polyacrylic acid, PAA, as the model substance and Eu(III). The reversibility of the interaction between Eu(III) and PAA is investigated by comparing the interaction constants between Eu(III) and PAA deduced from complexation and dissociation experiments. The equilibrium constant between Eu(III) and PAA is determined by an ion exchange equilibrium method²⁰ in the presence of the chelex resin. The resin is also used to promote dissociation of Eu(III) from the Eu–PAA complex.²¹ Experiments are carried out at pH = 5 in the presence of 0.1 mol L⁻¹ NaClO₄. Two polymers of 5000 Da (PAA1) and 50 000 Da (PAA2) are used to represent the typical distribution in molecular weights of humic acids.¹⁷

In the first part of this paper, reference data on the complexation of Eu(III) with PAA and the chelex resin are presented. The interaction data are quantified by a Langmuir-type isotherm.⁹ Fluorescence spectroscopy is used as a speciation technique to characterize the mode of interaction between Eu(III) and PAA functional groups. In the second part of this paper, the dissociation experiments of the Eu–PAA complex in the presence of the chelex resin are presented. In the final section, the data will be discussed and compared with those measured in the model system Th(IV)/PMA¹⁶ and Eu(III) with natural polyelectrolytes.^{12,13}

Experimental

All of the experiments were conducted in polyethylene tubes and all of the solutions were prepared with Milli-Q water.

Chemicals

Commercially available sodium perchlorate monohydrate (Fluka, purum) was used as received. An Eu(III) stock solution at 0.1 mol L⁻¹ was prepared from Eu₂O₃ (Prolabo, RECTA-PURTM) after dissolution, evaporation and redissolution in perchloric acid (Fluka, purum). From this stock solution, solutions of concentration ranging from 1 × 10⁻² to 1 × 10⁻⁶ mol L⁻¹ were prepared by dilution in 1 × 10⁻³ mol L⁻¹ HClO₄ with calibrated pipettes. A ¹⁵²Eu tracer solution was provided by CEA/DAMRI and a stock solution was prepared in 1 × 10⁻³ mol L⁻¹ HClO₄. The Eu and tracer solutions were used to prepare the solution/suspension for the experiments. The amount of ¹⁵²Eu added as a tracer is considered in the total europium concentration for the experiments carried out at low Eu concentrations (below 1 × 10⁻⁸ mol L⁻¹).

The two synthetic organic polymers were purchased from Aldrich Chemical Company (MW = 5000 Da, PAA1) and Polysciences, Inc. (MW = 50000 Da, PAA2). Some characteristics of these polymers are given in Table 1. PAA stock solutions at pH = 5 in 0.1 mol L⁻¹ NaClO₄ were stored for a maximum of 1 month.

The chelex resin (chelex 100, 50–100 mesh) was provided in the sodium form by Sigma Chemical Company. It presents at its surface iminodiacetic acid groups. Before use, the resin was equilibrated at pH = 5 in 0.1 M NaClO₄. For the experiments, the resin was filtered from the equilibrated suspension and a weighted aliquot was added to the solution to get the desired concentration. In the following, the chelex resin is denoted “R”.

Experimental procedures

(A) Number of available sites on PAA1 and PAA2. The number of available sites for Eu(III) complexation on a polymer chain was assessed from complexation experiments carried out close to metal ion saturation where Eu–PAA complex starts to precipitate.⁹ PAA and Eu(III) concentrations were varied from 30 to 100 mg L⁻¹ and from 1 × 10⁻⁴ to 4 × 10⁻³ M, respectively. The solutions were prepared by mixing aliquots of the stock solutions of the components. Then, pH values were readjusted to 5 by addition of aliquots of NaOH. After equilibration, the complexed Eu(III) was separated from the

aquo ion by centrifugation for 15 min at 36 000 *g*. Aliquots of the supernatant were finally analyzed to determine the free Eu(III) concentration in solution.

(B) Complexation kinetics of Eu(III) by PAA. The rate of complex formation was measured either by fluorescence spectroscopy or with a stopped-flow apparatus with optical detection. In the first case, the intensity in fluorescence emission was recorded as a function of time at 616 nm with a Perkin–Elmer LS-50B spectrofluorimeter. In the second case, the absorbance change due to complex formation was followed with a Biologic SFM-3 stopped-flow apparatus (Grenoble, France), totally computer-controlled (Tandon PC ASL/486-110) with Biokine Software. Both experiments were conducted at 25.0 ± 0.2 °C. The excitation wavelength was fixed at 250 nm. This allows to detect selectively complexed Eu(III) because free Eu(III) does not adsorb and thus does not fluoresce under the conditions of the study. The experiments were carried out for PAA1 at 1 g L⁻¹ in the presence of Eu(III) at 2 × 10⁻⁴ M. The molar absorption coefficient of the Eu–PAA1 complex at 250 nm was found to be 466 ± 29 L mol⁻¹ cm⁻¹.

(C) Complexation studies at equilibrium. All complexation studies were performed at room temperature under batch conditions. For the Eu(III)/R system, the isotherm was measured by varying R and Eu(III) concentrations from 0.5 to 3 g L⁻¹ and from 1 × 10⁻⁸ to 3 × 10⁻³ mol L⁻¹, respectively. For the Eu(III)/PAA/R system, PAA, R and Eu(III) concentrations were varied from 10 to 100 mg L⁻¹, 0.5 to 2 g L⁻¹ and 1 × 10⁻⁶ to 1 × 10⁻⁷ mol L⁻¹, respectively. The suspensions of Eu(III)/R and Eu(III)/PAA/R were allowed to equilibrate for at least 1 day and 1 week, respectively. For the Eu(III)/PAA/R system, the order of addition of the reagents was varied: in the first case, Eu(III) was equilibrated with PAA before the addition of R and in the second case, Eu(III) was equilibrated with R before the addition of PAA. After equilibration, the Eu(III) concentration in solution was deduced from the measurement of an aliquot of the supernatant after centrifugation at 1800 *g* for 5 min.

(D) Kinetic studies in the presence of the chelex resin. These experiments concern the complexation kinetics of Eu(III) with R and the dissociation kinetics of Eu–PAA complexes. The Eu(III)/R system was studied by varying Eu(III) concentration from 1 × 10⁻⁷ to 1 × 10⁻⁵ mol L⁻¹ and R from 2 to 10 g L⁻¹. For the dissociation experiments, Eu(III) concentration was fixed to 1 × 10⁻⁷ mol L⁻¹. Experiments were performed either with one polycarboxylic acid or with a mixture of PAA1 and PAA2. For the Eu(III)/PAA/R system, PAA and R concentrations were varied from 30 to 100 mg L⁻¹ and 3 to 40 g L⁻¹, respectively. For the Eu(III)/PAA1 + PAA2/R system, PAA1, PAA2 and R concentrations were fixed to 0.015, 0.015 and 20 g L⁻¹, respectively. The kinetics experiments were carried out by a batch technique in a thermostated cell at (21.0 ± 0.1) °C. The resin was added to a solution containing either Eu(III) or Eu–PAA at time *t* = 0. The suspension was then stirred at 200 rpm with a magnetic stirrer. Aliquots were taken under agitation as a function of time. The sampling was homogeneous, that is the R concentration remained constant in the cell. After sampling at time *t*, the resin in the aliquot was allowed to sedimentate for a few seconds (Δ*t*). Then, a fraction of the supernatant was taken for analysis to determine the distribution of Eu(III) between solid and liquid phases at time *t* + Δ*t*.

For the Eu(III)/PAA/R systems, it was observed that PAA does not sorb on R in the range of time, R, PAA and Eu(III) concentrations studied.

(E) Speciation experiments. The fluorescence data measured, sensitive to the chemical environment of Eu(III), are

Table 1 Characteristics of the PAA used in this work.

	<i>M_w</i> /kDa	Polydispersity	PEC ^a /mequiv g ⁻¹
PAA1	6	1.75	11.3 ± 0.4
PAA2	51.4	1.6	11.6 ± 0.4

^a Proton exchange capacity determined by potentiometric titration.²⁹

the fluorescence lifetimes, τ , and the ratio ($R_{616/592}$) of the fluorescence intensity at 616 nm ($^5D_0 \rightarrow ^7F_2$ transition) over the one at 592 nm ($^5D_0 \rightarrow ^7F_1$ transition).^{22,23} Measurements were performed for samples with Eu(III) and PAA concentrations varying from 5×10^{-5} to 1.5×10^{-4} mol L⁻¹ and from 0.15 to 2.65 g L⁻¹, respectively. Under these conditions, about 100% of the Eu(III) is complexed by PAA and Eu-PAA does not precipitate. Fluorescence measurements were recorded by excitation at 250 nm at $25 \pm 0.2^\circ\text{C}$ with a Perkin-Elmer LS-50B spectrofluorimeter. The source was a pulsed xenon flash lamp with a pulsewidth at half peak height $< 10 \mu\text{s}$ and a power equivalent to 20 kW. Flashes were produced with a 20 ms cycle time. The fluorescence emission was measured in the range of 580–640 nm. Complexed Eu(III) lifetimes, τ , were recorded only for PAA1.

The metal ion loading parameter varied in the experiments is characterized by the ligand-to-metal ratio defined by:²⁴

$$r = \frac{[\text{PAA}]_{\text{tot}}}{[\text{Eu}]_{\text{tot}}} \quad (1)$$

with $[\text{Eu}]_{\text{tot}}$ being the total concentration of Eu(III) in solution and $[\text{PAA}]_{\text{tot}}$ the total concentration of carboxylate groups in mol L⁻¹ with

$$[\text{PAA}]_{\text{tot}} = (\text{PAA}) \cdot \text{PEC} \quad (2)$$

(PAA) is the PAA concentration in g L⁻¹ and PEC its proton exchange capacity in mequiv g⁻¹ (see Table 1).

Analysis

The concentration of PAA was analyzed by total organic carbon (TOC) measurements using a Shimadzu TOC 5000A analyzer and Eu(III) analysis was performed by liquid scintillation counting using a Packard 2550 TR/AB Liquid Scintillation analyzer. The scintillation cocktail was ULTIMA GOLD ABTM (Packard). The pH electrode was calibrated using NBS standard solutions.

The number-average (M_n) and weight-average (M_w) molecular weights for PAA1 and PAA2 were determined by using the method of Carr *et al.*²⁵ The measurements were realized at pH = 2.5 in 0.1 M of NaClO₄ for PAA concentrations ranging from 1 to 20 g L⁻¹. A DMA 48 Auto Paar densimeter and a Schmidt-Haensch DUR-W2 ($\lambda = 589.3$ nm) refractometer were used to determine the specific polarizability and the refractive index of PAA. Light scattering measurements were performed with a Spectra Physics laser emitting vertically polarized light at 514.5 nm. The diffused light was detected at different angles varying from 30° to 120° .

Quantitative treatment

(A) Complexation studies. The complexation data between Eu(III) and the polycarboxylic acids and the ion exchanger are quantitatively described by a Langmuir-type isotherm.⁹ In the following, both components are considered as polyelectrolytes and the abbreviation “P” is used to denote both PAA and R. Schematically, it assumes the formation of 1:1 complexes between the metal ion and the polyelectrolyte P, following the reaction:



Within the polyelectrolyte, Eu(III) may interact with different sites that are distinguished one from the other by the number of COO⁻ groups interacting with Eu(III). Each site, i , is described by a complexation constant $^{\text{P}}K_i$:

$$^{\text{P}}K_i = \frac{[\text{EuP}]_i}{[\text{Eu}]_{\text{sol}}[\text{P}]_i} \quad (4)$$

and the number of active binding sites per unit mass of P, $^{\text{P}}S_i$ (mol g⁻¹). The total concentration of available binding sites for Eu(III) concentration per unit volume of solution is given by:

$$[\text{P}]_{\text{tot,a}} = (\text{P}) \sum_i ^{\text{P}}S_i = \sum_i [\text{P}]_i + [\text{EuP}]_i \quad (5)$$

with (P) being the concentration of the polyelectrolyte in g L⁻¹.

The global interaction constant between Eu(III) and PAA, $^{\text{P}}K$, is defined as:

$$^{\text{P}}K = \frac{[\text{EuP}]}{[\text{Eu}]_{\text{sol}}[\text{P}]} = \frac{\sum_i [\text{EuP}]_i}{[\text{Eu}]_{\text{sol}} \sum_i [\text{P}]_i} \quad (6)$$

The parameters $^{\text{P}}K_i$ and $^{\text{P}}S_i$ can be extracted from the isotherm $^{\text{c}}K = f([\text{Eu}]_{\text{sol}})$ following the expression:

$$^{\text{c}}K = \frac{[\text{EuP}]}{[\text{Eu}]_{\text{sol}}(\text{P})} = \sum_i \frac{^{\text{P}}K_i}{1 + ^{\text{P}}K_i[\text{Eu}]_{\text{sol}}} ^{\text{P}}S_i \quad (7)$$

(B) Kinetics of complexation between Eu(III), R and PAA.

For all the experiments, an excess of R and PAA was used to get nearly 100% complexation at equilibrium ($[\text{R}, \text{PAA}]_{\text{tot,a}} \gg [\text{Eu}]_{\text{tot}}$).

The kinetics of complexation of Eu(III) with R is described by a global reaction order of 2 and of partial order of 1 with respect to the reagents Eu(III) and R:



After integration, and considering only one site for Eu(III) on the resin, the following equation is used:²⁶

$$\frac{[\text{EuR}]_t}{[\text{Eu}]_{\text{tot}}} = A[1 - \exp(-Bt)] \quad (9)$$

with

$$A = \frac{[\text{EuR}]_{\text{eq}}}{[\text{Eu}]_{\text{tot}}} = \frac{{}^{\text{R}}k_+[\text{R}]_{\text{tot,a}}}{{}^{\text{R}}k_+[\text{R}]_{\text{tot,a}} + {}^{\text{R}}k_-} \quad (10)$$

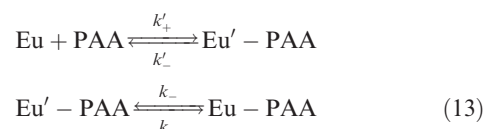
and

$$B = {}^{\text{R}}k_+[\text{R}]_{\text{tot,a}} + {}^{\text{R}}k_- \quad (11)$$

with $[\text{EuR}]_{\text{eq}}$ being the concentration of the complex at equilibrium. As A is close to one, ${}^{\text{R}}k_+[\text{R}]_{\text{tot,a}} \gg {}^{\text{R}}k_-$ and eqn. (11) may be simplified to:

$$B = {}^{\text{R}}k_+[\text{R}]_{\text{tot,a}} \quad (12)$$

For the Eu(III)/PAA system, the complexation kinetics are described by the two elementary reactions:



In this reaction mechanism, Eu(III) is in interaction with outer-sphere and inner-sphere sites in Eu'-PAA and Eu-PAA complexes, respectively. Applying the steady-state assumption for the Eu'-PAA concentration and considering that Eu(III), PAA and Eu'-PAA are rapidly equilibrated, the following equation can be obtained:²⁶

$$\frac{d[\text{EuPAA}]}{dt} = \frac{k'_+k_+}{k'_-} [\text{Eu}][\text{PAA}] - k_-[\text{EuPAA}] \quad (14)$$

This may be simplified by considering the following reversible reaction:



with:

$$\text{PAA}k_+ = \frac{k'_+k_+}{k'_-} \quad (16)$$

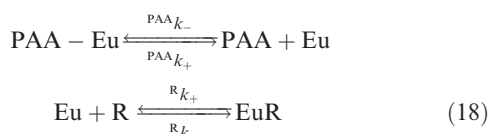
and

$$\text{PAA}k_- = k_- \quad (17)$$

In this paper, the $\text{PAA}k_+$ and $\text{PAA}k_-$ constants are treated as global parameters and no attempt was made to extract individual k_+ , k'_+ and k_- values. Based on these considerations, kinetic complexation data for the Eu(III)/PAA systems can be described, as for the Eu(III)/R system, by eqns. (9)–(12).

(C) Kinetics of dissociation. For the dissociation experiments of the Eu–PAA complex, an excess of PAA is used with respect to Eu(III) to get nearly 100% of Eu(III) complexed ($[\text{PAA}]_{\text{tot,a}} \gg [\text{Eu}]_{\text{tot}}$) and an excess of R is used with respect to PAA to get at equilibrium nearly 100% of Eu(III) sorbed on the chelex resin ($[\text{R}]_{\text{tot,a}} \gg [\text{PAA}]_{\text{tot,a}}$).

For the Eu/PAA/R system, the reaction mechanism is considered as the addition of the two following elementary reactions:



Applying the steady-state assumption to the Eu(III) concentration and considering only one site for Eu(III) on R and PAA (and recalling that in our conditions $[\text{R}]_{\text{tot,a}} \gg [\text{Eu}]_{\text{tot}}$ and $[\text{PAA}]_{\text{tot,a}} \gg [\text{Eu}]_{\text{tot}}$), one finds that:

$$\frac{[\text{EuR}]_{(t)}}{[\text{Eu}]_{\text{tot}}} = A[1 - \exp(-Bt)] \quad (19)$$

with

$$A = \frac{[\text{EuR}]_{\text{eq}}}{[\text{Eu}]_{\text{tot}}} = \frac{[\text{R}]_{\text{tot,a}} \text{R}k_+ \text{PAA}k_-}{[\text{R}]_{\text{tot,a}} \text{R}k_+ \text{PAA}k_- + [\text{PAA}]_{\text{tot,a}} \text{R}k_- \text{PAA}k_+} \quad (20)$$

and

$$B = \frac{[\text{R}]_{\text{tot,a}} \text{R}k_+ \text{PAA}k_- + [\text{PAA}]_{\text{tot,a}} \text{R}k_- \text{PAA}k_+}{\text{PAA}k_+ [\text{PAA}]_{\text{tot,a}} + \text{R}k_+ [\text{R}]_{\text{tot,a}}} \quad (21)$$

with $[\text{EuR}]_{\text{eq}}$ being the concentration of the Eu–R complex at equilibrium.

As A is close to one in the kinetic experiments, $[\text{R}]_{\text{tot,a}} \text{R}k_+ \text{PAA}k_- \gg [\text{PAA}]_{\text{tot,a}} \text{R}k_- \text{PAA}k_+$. Therefore, eqn. (21) may be simplified to:

$$B = \left[\frac{\text{PAA}K[\text{PAA}]_{\text{tot,a}}}{[\text{R}]_{\text{tot,a}} \text{R}k_+} + \frac{1}{\text{PAA}k_-} \right]^{-1} \quad (22)$$

with

$$\text{PAA}K = \frac{\text{PAA}k_+}{\text{PAA}k_-} \quad (23)$$

For the Eu(III)/PAA1 + PAA2/R system, dissociation curves of Eu–PAA complexes in the presence of R were simulated with the program MAKSIMA²⁷ considering the reaction

mechanism as an addition of three elementary reactions as in eqn. (18) with PAA corresponding to PAA1 and PAA2.

All fittings performed in this work were realized with the fitting procedure in SigmaPlot software using the Marquardt–Levenberg algorithm (version 2.0, Jandel Co.). All kinetic and fluorescence decay curves could be fitted by a mono-exponential function. Total uncertainties were estimated to be in the range of $\pm 10\%$ and $\pm 5\%$ for the $R_{616/592}$ and τ values, respectively. Calculations of the Eu(III) distribution at equilibrium in the Eu(III)/PAA/R system were carried out with the program MINEQL⁺ (version 3.0).²⁸

Results

Complexation studies

(A) Eu(III)/R system. Results of the kinetic of complexation are reported in Fig. 1(A) and Table 2. In agreement with eqn. (12), the exponential term B varies linearly with R concentration. Considering the uncertainties of the data, it cannot be entirely ruled out that Eu(III) concentration has a slight effect on the slopes of the curves. This effect is not expected according to eqn. (12). It could be explained by the effect of metal ion loading on the values of the rate and conditional $^{\text{R}}K$ constants for either electrostatic or steric reasons.²⁶ This effect is not considered in the model because it appears to be weak under the conditions of the study. As shown by the solid line in Fig. 1(A), the quantitative description of the experimental data with the simple model appears to be satisfactory. The deduced rate constant $^{\text{R}}k_+$ is $(7.0 \pm 1.7) \times 10^3 \text{ L mol}^{-1} \text{ h}^{-1}$. The isotherm for the Eu(III)/R system is reported in Fig. 1(B). It can be described by the interaction of Eu(III) with only one site. The associated parameters $^{\text{R}}K$ and $^{\text{R}}S$ are given in Table 2.

(B) Eu(III)/PAA system. Fluorescence spectroscopy was used in a first approach to assess the number and the nature of the binding sites for Eu(III) on the polymer chain. The data are reported in Fig. 2 as a function of the ligand-to-metal ratio together with the lifetimes measured at pH = 5 for Eu(III) complexed with PAA1 (5000 Da) in the region where Eu–PAA precipitates²⁹ and for Eu(III) complexed with PAA (2000 and 250 000 Da).^{24,30} Decay curves could be quantitatively described by a mono-exponential function. Furthermore, $R_{616/592}$ and τ values do not vary with metal ion loading and are identical for all polyacrylic acids. Both results indicate the presence of only one dominant binding site for Eu(III) on the polymer chain, which is the same irrespective of metal ion loading (r varying from 10 to 320), polymer weight and Eu–PAA chemical state (soluble or precipitate). The latter is characterized by $\tau = (270 \pm 14) \mu\text{s}$ and $R = 3.8 \pm 0.2$. From the lifetime value, using the empirical relationship between τ and the hydration data of Kimura *et al.*,³¹ Takahashi *et al.* proposed that Eu(III) was bound in the site by three carboxylate groups in a bidentate mode of coordination.²⁴ This 1:3 Eu:COO[−] coordination was also evidenced for the Eu(III)/PAA system at pH = 5.6 by studying the effect of metal ion loading on the variation of the luminescence intensity of the $^5\text{D}_0 \leftarrow ^7\text{F}_0$ excitation spectra.³²

Fluorescence spectroscopy was also used in a first approach to study the complexation kinetics of Eu(III) with PAA at high metal ion loading ($r = 57$). After decreasing for 40 s, the fluorescence intensity value becomes constant [Fig. 3(A)]. This indicates a rapid kinetic interaction. In a second approach, the stopped-flow technique was used. The results are reported in Fig. 3(B). The absorbance at 250 nm increases within the dead time of the apparatus (1.5 ms) from 0 to a maximum value of 0.17 and then decreases exponentially to 0.096. This latter value corresponds to the absorbance of the Eu(III)–PAA

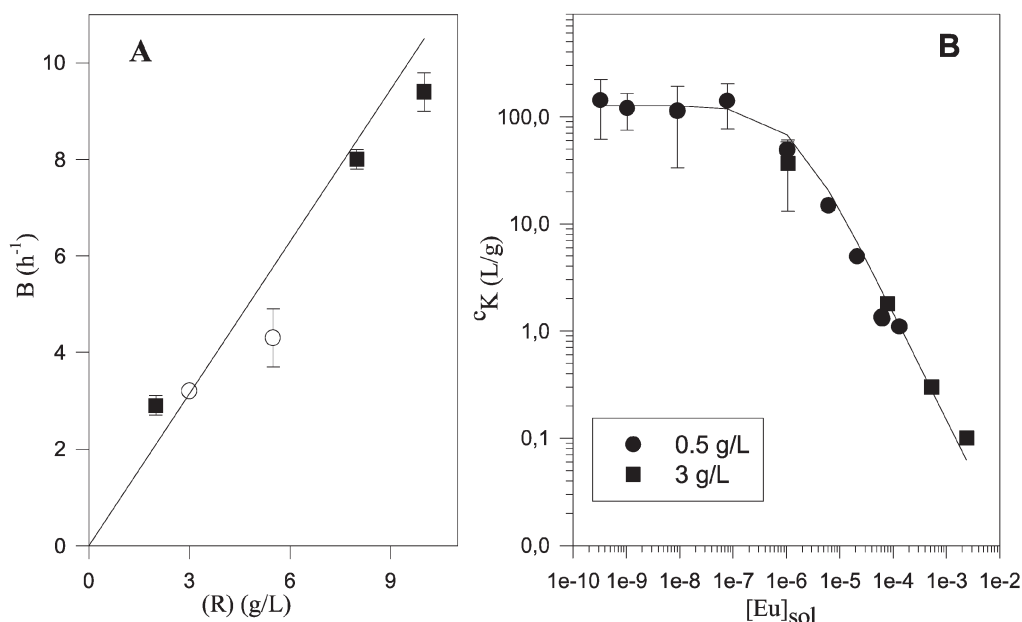


Fig. 1 Complexation studies on the Eu(III)/R system at pH = 5 in 0.1 M NaClO₄. (A) Complexation kinetics of Eu(III) on R. Dependence of B as a function of Eu(III) and R concentrations. $[Eu]_{tot} = 1 \times 10^{-7}$ M (■) and 1×10^{-5} M (○). The line is calculated according to eqn. (12) with the parameter $^Rk_+$ given in Table 2. (B) Sorption isotherms of Eu(III) on R. The line corresponds to the calculation made according to eqn. (7) with the parameters given in Table 2.

complex at equilibrium. The decrease in absorbance with time is in agreement with the decrease in fluorescence intensity shown in Fig. 3(A) and follows a mono-exponential decay function (see Fig. 3 caption). The deduced term B can be associated to the rate constant of the Eu–PAA interaction according to eqns. (12) and (15) (see also Table 2).

The interaction constant between Eu(III) and PAA was determined by the ion exchange equilibrium method²⁰ considering the existence of one site as observed by fluorescence spectroscopy. It is based on the competition between PAA and the resin R for Eu(III). The ^{PAA}K constant can be obtained from the experimental data measured at equilibrium [Fig. 4(A)], knowing the RS , RK and ^{PAA}S values. The number of available binding sites for Eu(III) on PAA is determined in this study from the Eu(III)/PAA isotherm measured close to saturation. In this region, eqn. (7) reduces to:⁹

$$^cK = \frac{1}{[Eu]_{sol}} ^{PAA}S \quad (24)$$

Therefore, cK no longer depends on the parameter ^{PAA}K but is determined by ^{PAA}S . The experimental results are presented in Fig. 4(B). In agreement with eqn. (24), $\log ^cK$ decreases with increasing $\log [Eu]_{sol}$ with a slope of -1 . The ^{PAA}S values deduced from the curves are given in Table 2. The number of available sites is higher by a factor of about 3 for PAA2 than for PAA1.

Based on these data and the RK and RS values, the ^{PAA}K constant associated to the binding site has been determined

by fitting the experimental data. The results correspond to the lines and the ^{PAA}K constants are given in Table 2. ^{PAA1}K and ^{PAA2}K constants are similar, in agreement with fluorescence measurements that have shown that the binding site is identical for both polymer chains.

In the following, PS values will be considered fixed to those deduced from the complexation experiments and given in Table 2.

Dissociation experiments

(A) Determination of ^{PAA}K constants. In these experiments, to avoid an eventual change in speciation of Eu(III), the contact time between Eu(III) and PAA was set to less than 3 min. Typical dissociation experiments are reported in Fig. 5 for PAA1 and PAA2. These data, measured for similar PAA and R concentrations in $g L^{-1}$, show that the Eu–PAA1 complex dissociates more rapidly than the Eu–PAA2 complex. Parameters ^{PAA}K and $^{PAA}k_-$ have been fitted according to eqn. (22) from the experimental curves $B = f([R]_{tot,a})$ and $B = f([PAA]_{tot,a})$ given in Figs. 6(A) and 6(B), respectively. As can be seen from the lines, the reaction mechanism proposed describes the experimental data, that is an increase in B with R concentration and a decrease in B with PAA concentration. The parameters obtained are given in Table 2.

(B) Effect of aging. The variation of the contact time between Eu(III) and PAA up to 1 month has been studied for

Table 2 Results of the quantitative treatment. The abbreviation P refers to the polyelectrolytes R and PAA

P	Complexation experiments			Dissociation experiments			Nature of the site
	Kinetic parameters	Equilibrium parameters		Kinetic parameters		Equilibrium parameters ^a	
	$10^5 \cdot ^Pk_+/L \text{ mol}^{-1} \text{ h}^{-1}$	$\log ^PK$	$^PS/\text{mmol g}^{-1}$	$10^5 \cdot ^Pk_+/L \text{ mol}^{-1} \text{ h}^{-1}$	$^Pk_-/\text{h}^{-1}$	$\log ^PK$	
R	0.07 ± 0.02	5.93 ± 0.12	0.15 ± 0.05	—	—	—	—
PAA1	7.52 ± 0.05	5.24 ± 0.16	1.30 ± 0.07	12.8 ± 5.7^b	19 ± 6	4.83 ± 0.12	Eu(COO) ₃ (H ₂ O) ₃
PAA2	—	4.93 ± 0.09	3.56 ± 0.36	8.7 ± 6.6^b	11 ± 7	4.90 ± 0.15	

^a ^{PAA}S is fixed to the value deduced from the complexation experiments. ^b Calculated according to eqn. (23)

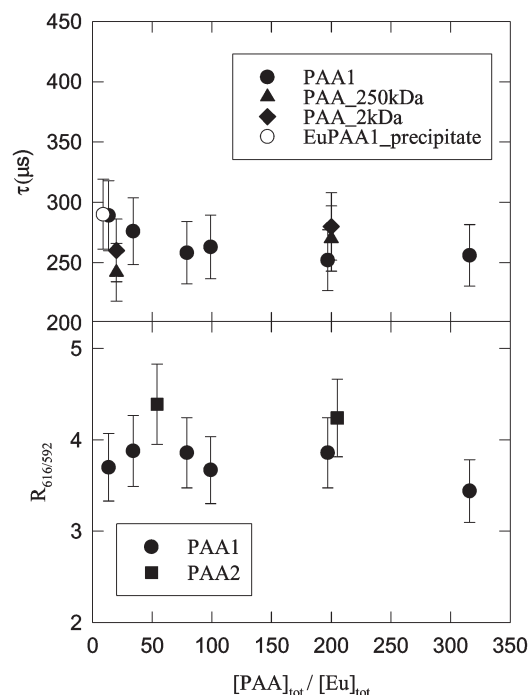


Fig. 2 Evolution of lifetime and $R_{616/592}$ values measured at pH = 5 in the presence of NaClO_4 as a function of the metal ion loading for PAA1 (●), PAA2 (■), 250 kDa PAA (▲)³⁰ and 2 kDa PAA (◆).²⁴ For 250 kDa PAA and 2 kDa PAA, a laser source is used (395 nm). For (○), the Eu–PAA1 complex is in precipitate form.²⁹

both PAA [data shown for PAA2 in Fig. 7(A)]. No variation in B values was observed.

(C) Effect of the degree of polydispersity. In this series of experiments, PAA1 and PAA2 were mixed in the presence of Eu(III) , before the addition of the chelex resin. Under the conditions chosen, according to the complexation parameters given in Table 2, there is a mixture of 38% and 51% of the Eu–PAA1 and Eu–PAA2 complexes, respectively.

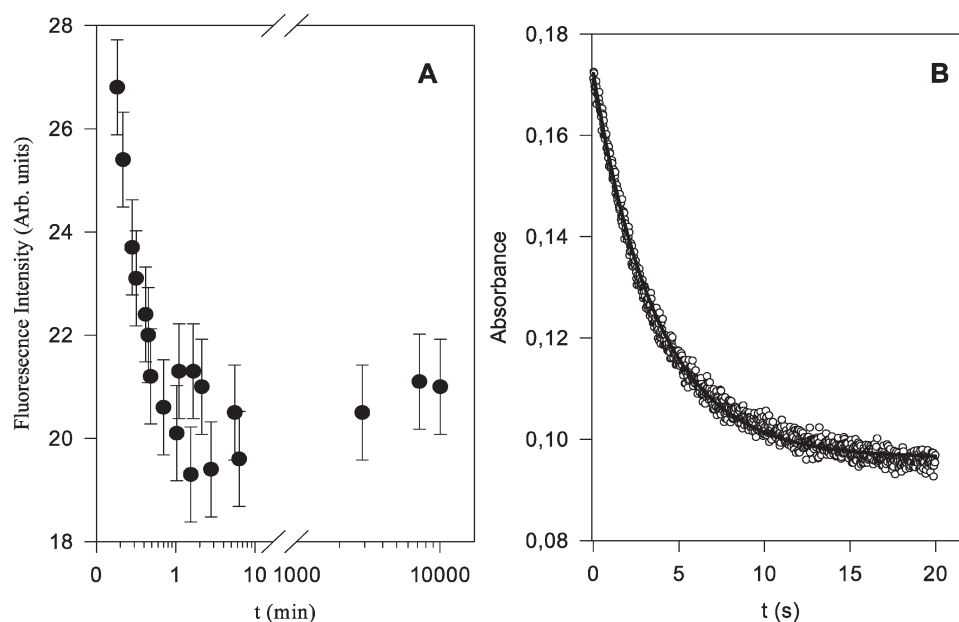


Fig. 3 Complexation kinetics of Eu(III) on PAA1 at pH = 5 in 0.1 M NaClO_4 . (A) Variation in the fluorescence intensity at 616 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition) as a function of the contact time. (B) Variation in the absorbance as a function of contact time with the stopped-flow apparatus. ($\text{PAA1} = 1 \text{ g L}^{-1}$ and $[\text{Eu}]_{\text{tot}} = 2 \times 10^{-4} \text{ mol L}^{-1}$). The line is calculated according to the following relation for the absorbance: $A = X + Y \cdot \exp(-Bt)$ with $X = 0.096 \pm 0.001$, $Y = 0.076 \pm 0.001$ and $B = 0.272 \pm 0.001 \text{ s}^{-1}$.

Dissociation experiments are presented in Fig. 7(B) as a function of the contact time. The simulation made with the program MAKSIMA²⁷ [solid line in Fig. 7(B)] is in good agreement with the experimental data. On the other hand, no modification in the kinetic curve is observed when the contact time is increased.

Discussion and conclusion

The complexation kinetics of Eu(III) with PAA are rapid and seem to be realized in two successive steps (Fig. 3). This may be interpreted by two successive processes: an electrostatic interaction between Eu(III) and ionized PAA functional groups followed by a rearrangement of the binding groups around Eu(III) to form an inner-sphere site [see eqn. (13)]. In this site, according to fluorescence spectroscopy measurements, polyacrylic acid would interact with Eu(III) through 3 carboxylate groups.^{24,32} The interaction constant associated to the site is similar for both polyacrylic acids of 5000 and 50 000 Da. However, the interaction strength of PAA2 towards Eu(III) , which can be characterized by the product $^{\text{PAA}}K \cdot ^{\text{PAA}}S$, is higher than that of PAA1. This is due to the fact that PAA2 presents a number of available sites about three times higher than that furnished by PAA1.

The dissociation experimental curves of Eu–PAA complexes in the presence of R could be fitted by a mono-exponential function as expected with only one binding site for Eu(III) within the polymer chain [see eqn. (19)]. The associated $^{\text{PAA}}K$ and $^{\text{PAA}}k_{-}$ parameters deduced from these experiments are similar for PAA1 and PAA2. The difference in the kinetic curves observed in Fig. 5 can be explained quantitatively according to eqn. (22) by the difference in the number of sites between PAA1 and PAA2. The $^{\text{PAA}}K$ constant values and the rate constant value $^{\text{PAA1}}k_{+}$ deduced from dissociation experiments are in agreement with those obtained from the complexation experiments. Furthermore, the kinetic parameters $^{\text{P}}k_{+}$ and $^{\text{P}}k_{-}$ deduced from the $\text{Eu(III)}/\text{R}$ and $\text{Eu(III)}/\text{PAA}/\text{R}$ systems allow a description of the dissociation experiments carried out in the mixed $\text{Eu}/\text{PAA1} + \text{PAA2}/\text{R}$ system [solid line in Fig. 7(B)]. This shows that the interaction between Eu(III) and PAA is reversible.

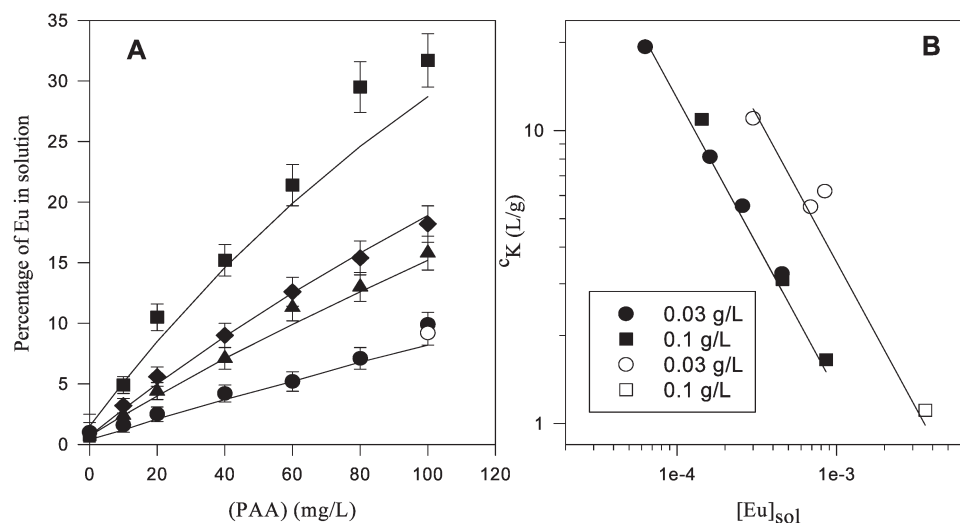


Fig. 4 Complexation studies for Eu(III)/PAA systems. (A) Distribution of Eu(III) between solid and liquid phases at equilibrium in the presence of PAA and R as a function of PAA concentration. (■) PAA1, (R) = 0.5 g L⁻¹ and $[Eu]_{tot} = 1 \times 10^{-7}$ M; (◆) PAA2, (R) = 1 g L⁻¹ and $[Eu]_{tot} = 1 \times 10^{-7}$ M; (▲) PAA1, (R) = 1 g L⁻¹ and $[Eu]_{tot} = 1 \times 10^{-6}$ M; (●,○) PAA1, (R) = 2 g L⁻¹ and $[Eu]_{tot} = 1 \times 10^{-6}$ M. For (○) Eu(III) is equilibrated with R before the addition of PAA. In the other experiments Eu(III) is equilibrated with PAA before the addition of R. The lines correspond to the calculations carried out with the ^{PAA}K , ^{PAA}S , RS and RK values taken from Table 2. (B) Sorption isotherm of Eu(III) on PAA close to metal ion saturation. PAA1 (filled symbols) and PAA2 (open symbols). The lines are calculated according to eqn. (24) with the ^{PAA}S values given in Table 2.

The dissociation curves [Fig. 7(A)] performed for high ligand-to-metal ratios (r ranging from 3400 to 11 600) do not vary when the aging time between Eu(III) and PAA increases. This indicates that there is no change in the speciation of Eu(III) with contact time within the polymer chain. This is not surprising considering the nature of the assumed binding site where Eu(III) is well coordinated to 3 carboxylate groups. From dissociation experiments of Eu(III) in interaction with humic (HA) and fulvic (FA) acids performed in the presence of Dowex resin under similar experimental conditions to those of the present study (pH = 4.5 in 0.1 mol L⁻¹ NaClO₄, high ligand-to-metal ratios varying from $r = 500$ to 2600),¹³ three rate constants were reported. The first two rate constants were about 13.2 and 0.43 h⁻¹ for FA and were considered to be associated to binding sites in which Eu(III) was exchangeable.¹³

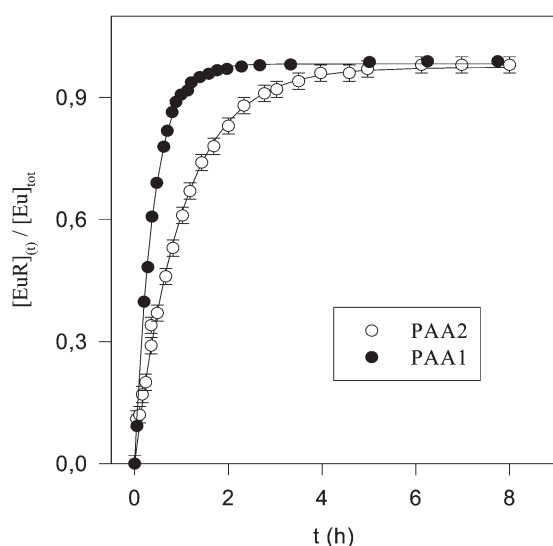


Fig. 5 Dissociation of Eu-PAA complexes as a function of time in the presence of the chelate resin R: pH = 5, $[NaClO_4] = 0.1$ mol L⁻¹, (R) = 10 g L⁻¹ and (PAA) = 0.03 g L⁻¹. The lines correspond to the fit carried out according to eqn. (19) with $A = 0.98$ and $B = 2.54$ h⁻¹ for (●) and $A = 0.97$ and $B = 1.0$ h⁻¹ for (○).

The values are on the order of magnitude with those obtained in our model system. The third constant measured was about 4.3×10^{-3} h⁻¹ for the Eu(III)/FA and Eu(III)/HA systems and was associated to the fraction of metal ion held in a kinetically hindered site. It was shown that this fraction increased with contact time. This fraction was not observed in our model system.

A change in site occupation with contact time was also evidenced by luminescence spectroscopy¹² for the Eu(III)/HA system for a low ligand-to-metal ratio ($r = 12$). The experiments, performed at pH = 5 in 0.1 mol L⁻¹ NaClO₄, showed a variation in the fluorescence intensity of the $^7F_0 \rightarrow ^5D_0$ transition as a function of the contact time between Eu(III) and HA. Such an effect was not observed in our model system for $r = 53$. Once the equilibrium was reached, no variation in the fluorescence intensity of the $^5D_0 \rightarrow ^7F_2$ transition was observed [see Fig. 3(A)]. As the $^5D_0 \rightarrow ^7F_2$ radiative transition probability is very sensitive to the detailed nature of the Eu(III) environment (symmetry and coordination number),²³ this result indicates no change in Eu(III) speciation as the contact time increases.

In conclusion, no change in site occupation is observed in the model system after equilibrium, irrespective of the ligand-to-metal ratio. Therefore, polycarboxylic acids are not suitable as model substances for humic substances when regarding the irreversible binding properties of the latter towards Eu(III). Thus, the interpretation of a simple change in polyelectrolyte configuration upon complexation to explain the change in site occupation after equilibrium for Eu/HS systems appears to be not totally satisfactory for trivalent metal ions. Another mechanism should be operative and it may be related to the more complicated structure of the natural polyelectrolytes.

On the other hand, the result of this study appears to be in disagreement with the result obtained for the Th(IV)/PMA model system:¹⁶ Choppin *et al.* observed from dissociation experiments, as for humic acid,¹⁹ a modification in the site occupation with contact time (between 1 min to 48 h). Differences between their and our studies concern the degree of polydispersity of the synthetic polyelectrolytes, the nature of the model polymer used, the range in ligand-to-metal ratio investigated and finally the ion studied. Each of these points is discussed separately in the following.

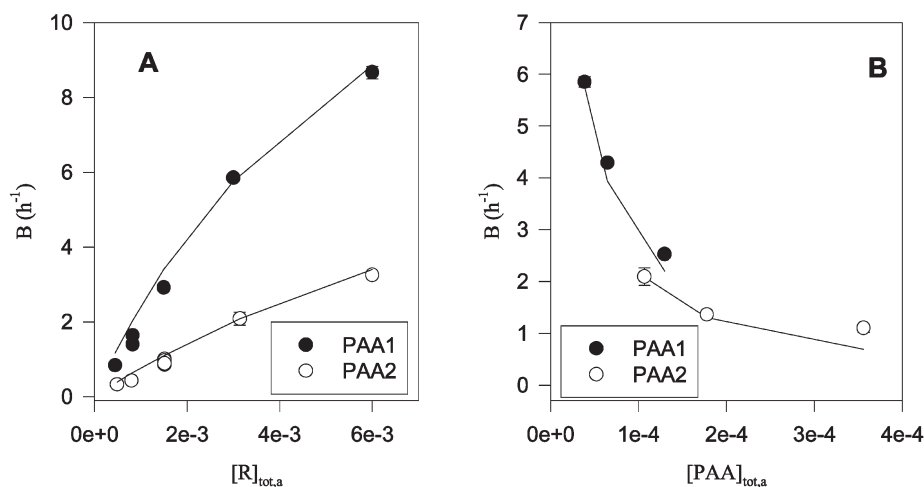


Fig. 6 Dissociation experiments of Eu-PAA complexes. (A) Dependence of B with R concentration. $[Eu]_{tot} = 1 \times 10^{-7}$ M and $(PAA) = 0.03$ g L⁻¹. (B) Dependence of B on total available PAA concentration. $[Eu]_{tot} = 1 \times 10^{-7}$ M and $(R) = 20$ g L⁻¹. The lines are calculated according to eqn. (22) with the parameters given in Table 2.

Regarding the degree of polydispersity, Choppin *et al.*¹⁶ used a mixture of polyelectrolytes ranging from 5000 to 40 000 Da. As shown in Fig. 7(B), PAA1 and PAA2 mixing induces no change in Eu speciation after equilibrium.

In a previous study,³³ the dissociation of Eu(III) associated to polymaleic acid of 1900 Da was studied in the presence of the chelex resin in the experimental conditions of this study (pH = 5, $[NaClO_4] = 0.1$ M and high ligand-to-metal ratios). As for PAA, no change in site occupation with contact time was observed. Therefore, providing that polymer length has no effect as it is the case for PAA, the difference in the nature of the polymer cannot explain the discrepancy.

Dissociation experiments with Th(IV) have been performed for a ligand-to-metal ratio ($r = 20$) less important than that used with Eu(III) (r ranging from 3400 to 11 600 for the dissociation experiments and $r = 53$ for the experiment followed by fluorescence spectroscopy). According to Choppin *et al.*,¹⁶ the modification in speciation observed for Th(IV) within the polymer chain after equilibrium is explained by a modification in polymer configuration. This change was explained by the metal ion complexation, which modifies the net polyelectrolyte anionic charge and induces a relocation of the cations from “territorial” to “interior” binding sites.

Therefore, the metal ion loading is expected to affect the configuration change and thus the distribution between the different binding sites for Th(IV). This was observed for the Eu(III)/FA and Eu(III)/HA systems: as the metal ion loading increased, the content of the non-exchangeable fraction for a given contact time was shown to increase.^{13b}

The difference between Eu(III) and Th(IV) concerns the metal ion speciation in solution and affinity for the polyelectrolyte. Using the thermodynamic database of the geochemical program EQ3/6,³⁴ and without taking into account the formation of the hydrolysis species $Eu_2(OH)_2^{4+}$,³⁵ it is found that Eu(III) exists 99% as the aquo Eu^{3+} ion under the conditions of the study. For Th(IV), using the selected database given in ref. 36, it appears that Th(IV) exists in solution, under the conditions of the study and between pH = 4.2 and 6, as mononuclear $[Th(OH)_n]^{+(4-n)}$ with $n = 1-4$ and polynuclear $[Th_4(OH)_{12}]^{4+}$ hydrolysis species. The polymer hydrolysis species become dominant above pH = 5. Considering the rapid time to reach equilibrium between free and complexed Th(IV),¹⁶ one cannot exclude a rapid interaction between the different kinds of cationic hydrolysis species and the polyelectrolyte. This will lead to several binding sites of different stability within the polymer structure, depending on the charge and nuclearity of the

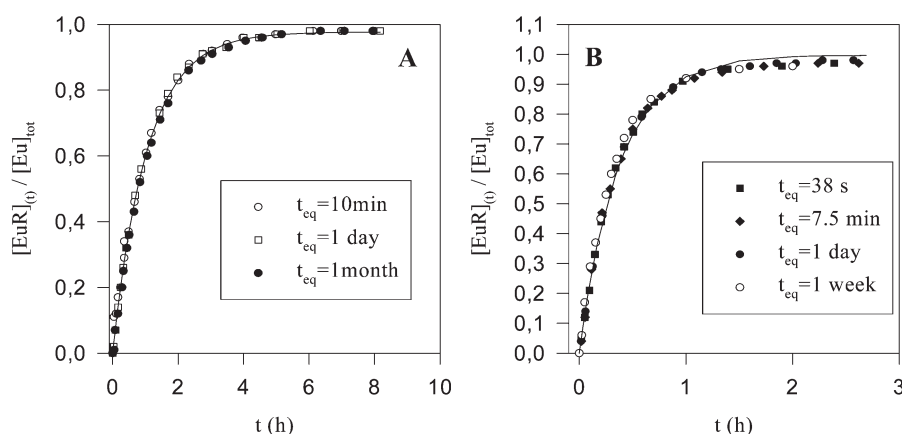


Fig. 7 Study of the dissociation of Eu-PAA complexes in the presence of R as a function of the contact time. (A) Eu(III)/PAA2/R system. $[Eu]_{tot} = 1 \times 10^{-7}$ M, $(R) = 10.1$ g L⁻¹ and $(PAA2) = 0.03$ g L⁻¹. The line is calculated according to eqn. (19) with $A = 0.98 \pm 0.01$ and $B = 0.95 \pm 0.01$ h⁻¹. (B) Eu(III)/PAA1 + PAA2/R system. $[Eu]_{tot} = 1 \times 10^{-7}$ M, $(R) = 20$ g L⁻¹ and $(PAA) = 0.03$ g L⁻¹ with 0.015 g L⁻¹ each of PAA1 and PAA2. The line corresponds to the simulation carried out with the MAKSIMA program²⁷ considering an equilibrium in the Eu/PAA1 + PAA2 system before the addition of R and using the Pk_+ and Pk_- kinetic parameters given in Table 2 (the $PAA1k_+$ value is fixed to the value deduced from the dissociation experiments).

species. This is in agreement with the fact that the analysis of the Th–PMA dissociation has to be described by the addition of several first-order terms.¹⁶ Therefore, both Eu(III)/PAA and Th(IV)/PMA systems appear different as far as the nature of the binding sites are concerned.

Based on these considerations, the difference in ligand-to-metal ratio and/or metal ion studied between both model systems should be at the origin of the difference in behavior observed for PAA and PMA with respect to Eu and Th(IV), respectively.

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