

Influence of adipic acid on the speciation of Eu(III): review of thermodynamic data in NaCl and NaClO₄ media, and a new determination of Eu-adipate complexation constant in 0.5 mol.kg_w⁻¹ NaClO₄ medium by time-resolved luminescence spectroscopy

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ABSTRACT

The complexation of Eu(III) by adipic acid — AdipH₂, hexane-1,6-dioic acid —, one of the major hydro-soluble degradation products (HDPs) from radio-oxidized polyesterurethane, is investigated by time-resolved luminescence spectroscopy (TRLS) in NaClO₄ ionic medium (0.5 mol.kg_w⁻¹). The solubility and deprotonation constants of adipic acid, as well as specific interaction theory (SIT) coefficients of aqueous AdipH₂(aq) and adipate ions (AdipH⁻ and Adip²⁻) were estimated using available literature data in NaCl and NaClO₄ ionic media. A 1:1 (EuAdip⁺) complex is evidenced in TRLS with $\log_{10}\beta(0.5\ m) = 2.09 \pm 0.16$. Using reaction constant at another NaClO₄ ionic strength from literature, the logarithm of reaction constant $\log_{10}\beta^{\circ} = 3.88 \pm 0.40$ at 0 ionic strength and specific ion parameter $\varepsilon(\text{EuAdip}^+, \text{ClO}_4^-) = (0.10 \pm 0.40) \text{ kg}_w \cdot \text{mol}^{-1}$ is estimated. This implies that adipic acid can control the Eu(III) speciation from mildly acidic to mildly basic conditions, but not in highly basic solutions characteristic of cementitious interstitial waters.

Keywords

Europium; hexane-1,6-dioic acid; adipic acid; hydro-soluble degradation products.

1. INTRODUCTION

The knowledge of interactions between radionuclides and organic contaminants issued from radio-oxidized polymer is crucial for assessing the mobility of radionuclides in different environments near potential nuclear waste geological repositories [1]. Polymer waste are generated during exploitation, maintenance, and dismantling of nuclear fuel cycle facilities [2], as *e.g.* gloves, filters, seals, cables, windows of glove-boxes, or ion exchange resins. These polymers are considered to be placed in intermediate level long-lived (ILW-LL) waste cemented packages where they will be degraded by radio-oxidation because of the presence of radionuclides and dioxygen. Consequently, studies on the characterization of the degradation products issued either from hydrolysed polymers [3-5] or from hydrolysed radio-oxidized polymers were led to identify the main constituents [6-9].

In the case of degradation products of cellulose, iso-saccharinic acid was recognized as a strong complexing agent — see references [10,11] and references therein. In the case of radio-oxidized ion exchange resins, oxalic acid was identified but a pool of unidentified ligand was also evidenced [6,7]. In the case of polyesterurethane, used in gloves for glove boxes, adipic acid — hexane-1,6-dioic acid, noted afterwards AdipH₂(aq), structure shown on Fig. 1 — was shown to be the main hydro-soluble degradation product (HDP). As ions from a dicarboxylic acid, adipate ions are able to complex trivalent f-transition elements [12] such as Eu(III) [13] — analogue of 5f actinides(III) such as Cm(III) and Am(III) for the complexation by oxygen containing molecules [14]. Eu(III) is showing interesting luminescent properties that makes it suitable for both complexation studies and chemical environment probing by time-resolved luminescence spectroscopy (TRLS), [13,15-20] including complex organic mixtures [21-23].

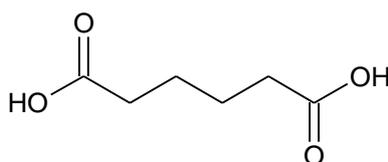


Fig. 1. Structure of AdipH₂.

The assessment of the extent of complex formation by the organic ligands identified in HDPs requires thermodynamic data both on protonation constants for these ligands, as well as on complexation with radionuclides, including the account of ionic strength in the case of cemented waste packages. The most advanced current state of knowledge on these constants and coefficients applied for the nuclear waste management is in the framework of the specific interaction theory [10,24], *i.e.* thermodynamic constants ($\log_{10}K^\circ$), as well as specific ion interaction coefficients $\varepsilon(M^+,X^-)$ — mostly considered constant with ionic strength —, and thermodynamic functions ($\Delta_f G^\circ_m$, $\Delta_f H^\circ_m$, $S_f^\circ_m$, and $C_p^\circ_m$). Up to now no specific ion interaction coefficients are available in the open literature for adipic acid protonation constants and Eu(III) complexation constants within the SIT formalism

proposed in Guillaumont *et al.* [24] and Hummel *et al.* [10]. Data on adipic acid deprotonation constant in NaClO₄ [25-29] or NaCl [30,31] ionic media are existing. Thermodynamic functions of reaction for K_n [32] and formation for adipic acid[31] has been proposed. Bretti *et al.* [33] proposed protonation constants in various ionic media including NaCl, N(CH₃)₄Cl, and N(C₂H₅)₄I in the framework of a SIT formalism, which considers that $\epsilon(M^+,X^-)$ values vary with ionic strength, and Pitzer model. Wang *et al.* [13] proposed complexation constants of Eu(Adip)_n⁽³⁻²ⁿ⁾⁺ only at 0.1 M NaClO₄. Thus, there is a need of a reinterpretation of the system, with addition of complexation constant determination at higher ionic strength within the SIT formalism proposed in Guillaumont *et al.* [24] and Hummel *et al.* [10].

The first part of this study will consist in literature data analysis for adipic acid solubility and acid-base equilibria — *i.e.*, $\log_{10}K_n^\circ$, and $\Delta_f G^\circ_m$, $\Delta_f H^\circ_m$, and $S_f^\circ_m$ — within the SIT framework providing specific ion interaction coefficients in NaCl and NaClO₄ ionic media — *i.e.*, $\epsilon(\text{Na}^+, \text{Adip}^{2-})$ and $\epsilon(\text{Na}^+, \text{AdipH}^-)$, and eventually $\epsilon(\text{AdipH}_2(\text{aq}), \text{NaCl})$ or $\epsilon(\text{AdipH}_2(\text{aq}), \text{NaClO}_4)$ as proposed in Hummel *et al.* [10]. Then, the determination of the complexation constant of Eu(III) by adipate ion using TRLS at 0.5 mol.kg_w⁻¹ (NaClO₄), and the extrapolation to zero ionic strength of the Eu(Adip)_n⁽³⁻²ⁿ⁾⁺ complex(es) formation constant and specific interaction parameter(s) will be done using existing literature data at 0.1 M (NaClO₄) [13], and our new determination. Luminescence spectra evolution will also be discussed. Finally, estimation of the role of adipate ion on the speciation of Eu(III) from slightly acidic to strongly basic solution will be discussed in the light of already available data of Eu complexation [34].

2. MATERIALS

2.1. Solutions preparation

Solutions of different adipic acid (99.5 %, Fluka) total concentration were prepared up to the solubility limit of 0.17 mol.kg_w⁻¹ [33]. In order to determine the complexation constant, the solutions were made following these conditions: (i) ionic strength was fixed to 0.5 mol.kg_w⁻¹ NaClO₄ (≥ 98 %, Sigma-Aldrich); (ii) Eu(III) concentrations were fixed at 10⁻⁵ mol.kg_w⁻¹ — the europium(III) stock solution was prepared by dissolving Eu₂O₃ (99.9 %, Alfa Aesar) into 0.1 mol.kg_w⁻¹ HClO₄ (60 %, Fisher Scientific) —; and (iii) pH values were fixed at 5.0 ± 0.05 by NaOH (99 %, Prolabo) solutions. The pH values were measured with a NaClO₄/NaCl combined microelectrode (pH InLab, Mettler Toledo) by redetermination of the potential/pH plot using commercial buffer solutions (4.01, 7.00, and 10.01). Uncertainties from the linear regression were typically in the range of 0.05 pH-units. Concentration of protons were calculated as

$$[\text{H}^+] = 10^{-\text{pH}} / \gamma_{\text{H}^+} \quad (1)$$

with

$$\log_{10}\gamma_{\text{H}^+} = -\frac{A\sqrt{I_m}}{1 + 1.5 \cdot \sqrt{I_m}} + \varepsilon(\text{H}^+, \text{ClO}_4^-) \cdot I_m \quad (2)$$

where $A = 0.509 \text{ kg}_w^{1/2} \cdot \text{mol}^{-1/2}$ — A should be $0.507 \text{ kg}_w^{1/2} \cdot \text{mol}^{-1/2}$ at 22°C , but we decided to neglect the effect of temperature difference in a first approximation— and $\varepsilon(\text{H}^+, \text{ClO}_4^-) = 0.14 \pm 0.02 \text{ kg}_w \cdot \text{mol}^{-1}$.

From thermodynamic constants for Eu(III) hydrolysis in Table 1, this pH range allowed considering that Eu^{3+} was predominant in the solution [34]. This pH range was also chosen to observe adipate ion Adip^{2-} in a significant amount in solution, according to previously proposed pK_a values of adipic acid [35].

2.2. TRLS parameters

The TRLS experimental set-up is slightly modified compared to the one already described elsewhere [19,21-23,36-38]. It is including a 355 nm tripled neodymium-doped yttrium aluminium garnet (Nd:YAG) laser (Surelite, Continuum) providing *ca.* 170 mJ, pulsed at 10 Hz with a 5 ns pulse. An optical parametric oscillator (OPO) (Horizon, Continuum) set at 393.8 nm, which corresponds to the ${}^5\text{L}_6 \leftarrow {}^7\text{F}_0$ transition [39], provided *ca.* 2 mJ of energy. The beam is focused in a quartz fluorescence cell (Hellma QS-111-10-40), which contains the analyte. The energy received by the analyte is monitored by a RJP-734 Joulemeter (Laser Probe Inc.). The emitted luminescence beam is collected at 90° and focussed into an Acton spectrometer (slit 1 nm), which only the 300 lines $\cdot\text{min}^{-1}$ grating is used. Emission spectra are recorded using the CCD sensor cooled down at -15°C by Peltier effect. All the described device is located in a $(22 \pm 1)^\circ\text{C}$ thermostated room. The emission signal is collected after a 10 μs delay (D) after the laser pulse, during a 300 μs gate width (W). The spectra presented in this work are obtained after 500 accumulations. For each spectrum, the background noise is subtracted and the luminescence is divided by the average of 100 laser shots energy after the acquisition.

The luminescence decay times are obtained as described elsewhere [19,21,37], fitting the decay to the following equation.

$$F = F^\circ \cdot \tau \cdot \exp\left(-\frac{D}{\tau}\right) \left(1 - \exp\left(-\frac{W}{\tau}\right)\right) \quad (3)$$

The initial luminescence F° and luminescence decay time τ are obtained from a nonlinear regression using Microsoft Excel Solver and uncertainties are calculated using the SolverAid Macro from de Levie [40].

2.3. Thermodynamic data and specific ion interaction coefficients

The different thermodynamic constants and functions used and calculated throughout this study are recalled in Table 1, 2, and 3; specific ion interaction coefficients are recalled in Table 4.

Table 1. Reactions and thermodynamic constants used in this work.

Reaction	$\log_{10}K^\circ (\pm 1\sigma)$	Reference
$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$	-14.00 ± 0.01	[24]
$\text{Adip}^{2-} + \text{H}^+ \rightleftharpoons \text{AdipH}^-$	5.49 ± 0.02	This work from [25-29] in NaClO_4 and [30,33] in NaCl
$\text{AdipH}^- + \text{H}^+ \rightleftharpoons \text{AdipH}_2(\text{aq})$	4.48 ± 0.01	This work from [25-29] in NaClO_4 and [30,33] in NaCl
$\text{Adip}^{2-} + 2\text{H}^+ \rightleftharpoons \text{AdipH}_2(\text{aq})$	9.97 ± 0.02	This work from [25-29] in NaClO_4 and [30,33] in NaCl
$\text{AdipH}_2(\text{s}) \rightleftharpoons \text{AdipH}_2(\text{aq})$	-0.77 ± 0.02	This work from [33] in NaCl
$\text{AdipH}_2(\text{s}) \rightleftharpoons \text{Adip}^{2-} + 2\text{H}^+$	-10.74 ± 0.02	This work from [33] in NaCl for solid and [25-29] in NaClO_4 and [30,33] in NaCl for Adip^{2-}
$\text{Eu}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{Eu}(\text{OH})^{2+} + \text{H}^+$	-7.64 ± 0.04	[34]
$\text{Eu}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Eu}(\text{OH})_2^+ + 2\text{H}^+$	-15.1 ± 0.2	[34]
$\text{Eu}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Eu}(\text{OH})_3(\text{aq}) + 3\text{H}^+$	-23.7 ± 0.1	[34]
$\text{Eu}^{3+} + \text{CO}_3^{2-} \rightleftharpoons \text{Eu}(\text{CO}_3)^+$	8.1 ± 0.2	[34]
$\text{Eu}^{3+} + 2\text{CO}_3^{2-} \rightleftharpoons \text{Eu}(\text{CO}_3)_2^-$	12.1 ± 0.3	[34]
$\text{Eu}^{3+} + 3\text{CO}_3^{2-} \rightleftharpoons \text{Eu}(\text{CO}_3)_3^{3-}$	13.8 ± 0.3	[41,42]
$\text{Eu}(\text{OH})_3(\text{am}) + 3\text{H}^+ \rightleftharpoons \text{Eu}^{3+} + 3\text{H}_2\text{O}$	-17.6 ± 0.8	[34]
$\text{Eu}_2(\text{CO}_3)_3(\text{cr}) \rightleftharpoons 2\text{Eu}^{3+} + 3\text{CO}_3^{2-}$	-35.0 ± 0.3	[34]
$\text{EuOHCO}_3(\text{cr}) \rightleftharpoons \text{Eu}^{3+} + \text{CO}_3^{2-} + \text{OH}^-$	-21.7 ± 0.1	[34]
$\text{EuOHCO}_3(\text{cr}) + \text{H}^+ \rightleftharpoons \text{Eu}^{3+} + \text{CO}_3^{2-} + \text{H}_2\text{O}$	-7.7 ± 0.1	[34]
$\text{Eu}^{3+} + 3\text{e}^- \rightleftharpoons \text{Eu}$	-1.983 V	[34]
$\text{Eu}^{3+} + \text{Adip}^{2-} \rightleftharpoons \text{EuAdip}^+$	3.88 ± 0.40	This study

Table 2. Thermodynamic constants and functions of reaction for the adipic acid system.

Reaction	$\Delta_r G_m^\circ$ kJ.mol ⁻¹	$\Delta_r H_m^\circ$ kJ.mol ⁻¹	$\Delta_r S_m^\circ$ J.mol ⁻¹ .K ⁻¹
Adip ²⁻ + H ⁺ ⇌ AdipH ⁻	-31.337 ± 0.114 ^a	-2.68 ± 0.21 ^b	-90.0 ^b
AdipH ⁻ + H ⁺ ⇌ AdipH ₂ (aq)	-25.572 ± 0.057 ^a	-1.26 ± 0.21 ^b	-112.5 ^b
Adip ²⁻ + 2H ⁺ ⇌ AdipH ₂ (aq)	-56.909 ± 0.114 ^a		
AdipH ₂ (s) ⇌ AdipH ₂ (aq)	4.395 ± 0.114 ^a		
AdipH ₂ (s) ⇌ Adip ²⁻ + 2H ⁺	61.304 ± 0.171 ^a		
Eu ³⁺ + Adip ²⁻ ⇌ EuAdip ⁺	-22.147 ± 2.169 ^a	n.a.	n.a.

^a present work

^b Christensen *et al.* [32]

n.a. not available

Table 3. Thermodynamic functions of formation calculated for the Eu(III)-adipate system calculated from literature values, and values from Table 2.

	$\Delta_f G_m^\circ$ kJ.mol ⁻¹	$\Delta_f H_m^\circ$ kJ.mol ⁻¹	S_m° J.mol ⁻¹ .K ⁻¹
Eu ³⁺	-551.1 ^a	-	-
AdipH ₂ (aq)	-722.953 ^b	-961.274 ^b	340.2 ^b
AdipH ⁻	-697.381 ^c	-962.534 ^c	250.2 ^c
Adip ²⁻	-666.044 ^c	-965.214 ^c	137.7 ^c
AdipH ₂ (s)	-727.348 ^c	-	-
EuAdip ⁺	-1 239.291 ^c	-	-

^aHummel *et al.* [34]

^b Shock [31]

^c present work

Table 4. Ion interaction coefficients used and determined in this work.

Ion interaction coefficient	Value ($\pm 1\sigma$)	Reference
$\varepsilon(\text{H}^+, \text{ClO}_4^-)$	0.14 ± 0.02	[24]
$\varepsilon(\text{H}^+, \text{Cl}^-)$	0.12 ± 0.01	[24]
$\varepsilon(\text{Na}^+, \text{OH}^-)$	0.04 ± 0.01	[24]
$\varepsilon(\text{Na}^+, \text{CO}_3^{2-})$	-0.08 ± 0.03	[24]
$\varepsilon(\text{Adip}^{2-}, \text{Na}^+)$	0.215 ± 0.006	estimated here from [25-29] in NaClO_4 and [30,33] in NaCl
$\varepsilon(\text{AdipH}^-, \text{Na}^+)$	0.135 ± 0.006	estimated here from [25-29] in NaClO_4 and [30,33] in NaCl
$\varepsilon(\text{AdipH}_2(\text{aq}), \text{NaClO}_4)$	0.037 ± 0.009	estimated here from [25-29] in NaClO_4 and [30,33] in NaCl
$\varepsilon(\text{AdipH}_2(\text{aq}), \text{NaCl})$	0.105 ± 0.005	estimated here from [33]
$\varepsilon(\text{Eu}^{3+}, \text{ClO}_4^-)$	0.49 ± 0.03	analogy with Am^{3+} [24]
$\varepsilon(\text{Eu}(\text{OH})^{2+}, \text{ClO}_4^-)$	0.39 ± 0.04	analogy with $\text{Am}(\text{OH})^{2+}$ [24]
$\varepsilon(\text{Eu}(\text{OH})_2^+, \text{ClO}_4^-)$	0.17 ± 0.04	analogy with $\text{Am}(\text{OH})_2^+$ [24]
$\varepsilon(\text{Eu}(\text{CO}_3)^+, \text{ClO}_4^-)$	0.17 ± 0.04	analogy with $\text{Am}(\text{CO}_3)^+$ [24]
$\varepsilon(\text{Eu}(\text{CO}_3)_2^-, \text{Na}^+)$	-0.05 ± 0.05	analogy with $\text{Am}(\text{CO}_3)_2^-$ [24]
$\varepsilon(\text{Eu}(\text{CO}_3)_3^{3-}, \text{Na}^+)$	-0.23 ± 0.07	analogy with $\text{Am}(\text{CO}_3)_3^{3-}$ [24]
$\varepsilon(\text{EuAdip}^+, \text{ClO}_4^-)$	0.10 ± 0.40	this study

3. RESULTS AND DISCUSSION

3.1. Literature analysis of the solubility, protonation constants and SIT coefficients of the adipic acid system

As stressed earlier, proposition of protonation constants of Adip^{2-} are available in the literature either in the framework of the Davies [43] correction for activity [35], or using SIT — slightly different from [10,24] — or Pitzer model [33]. Solubility of $\text{AdipH}_2(\text{s})$ was also proposed [33] in NaCl ionic medium. We have decided to reinterpret available data in NaClO_4 [25-29] and NaCl [30,33] from literature at 25°C to propose coherent data to be used in the framework of SIT [10,24].

3.1.1. Solubility of adipic acid

Bretti *et al.* [33] provided $\text{AdipH}_2(\text{s})$ solubility measurement at different ionic strength. The data were interpreted in the framework of the Setschenow equation [44]. Hummel *et al.* [10] proposed a SIT interpretation of the organic acid solubility implying the definition of a specific parameter $\varepsilon(\text{MH}_n(\text{aq}), \text{NX})$ between the neutral acid and the background salt N^+X^- .

$$\log_{10}S^{\circ}_m = \log_{10}K^{\circ}_s - \varepsilon(\text{AdipH}_2(\text{aq}),\text{NaCl}) \cdot I_m \quad (4)$$

Plotting the data from Bretti *et al.* [33] as a function of molal ionic strength — recalculated according to Novotny and Sohnel [45] — in Fig. 2 leads to $\log K^{\circ}_s = -0.77 \pm 0.02$ — *i.e.* $S^{\circ} = 0.171 \pm 0.003 \text{ mol.kg}_w^{-1}$, in agreement with other data with no salt added [46], and the specific interaction parameter $\varepsilon(\text{AdipH}_2(\text{aq}),\text{NaCl}) = 0.105 \pm 0.005 \text{ kg}_w.\text{mol}^{-1}$.

The data on solubility of $\text{AdipNa}_2(\text{s})$ are seldom in literature, *i.e.*, $3.52 \text{ mol.kg}_w^{-1}$ at 25°C in Rozaini and Brimblecombe [47], and will not be interpreted here. It seems that several phases are implied that has not been identified. This would need further studies.

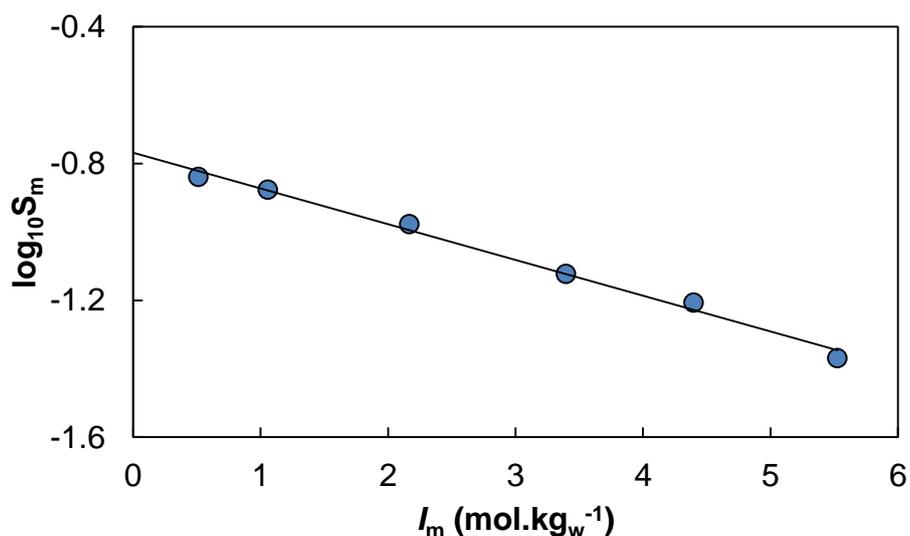


Fig. 2. Logarithm of the solubility of adipic acid vs. ionic strength (mol.kg_w^{-1}) in NaCl from Bretti *et al.* [33].

3.1.2. Protonation constants of Adip^{2-}

Protonation constants available in NaCl and NaClO_4 are recalled in Table 5. Ionic strength in molal scale is recalculated for data in NaClO_4 and NaCl when given in molar scale according to Novotny and Sohnel [45]. Plot of $\log_{10}K_2$ and $\log_{10}K_1K_2$ vs. ionic strength are reported in Fig. 3. It can be seen that $\log_{10}K_1$ and $\log_{10}K_2$ evolutions seemed to be slightly different at high ionic strength in NaClO_4 and NaCl, which would imply that knowing that $\varepsilon(\text{AdipH}_2(\text{aq}),\text{NaCl})$ seems not nil, the adjustment of $\varepsilon(\text{AdipH}_2(\text{aq}),\text{NaClO}_4)$ would be necessary.

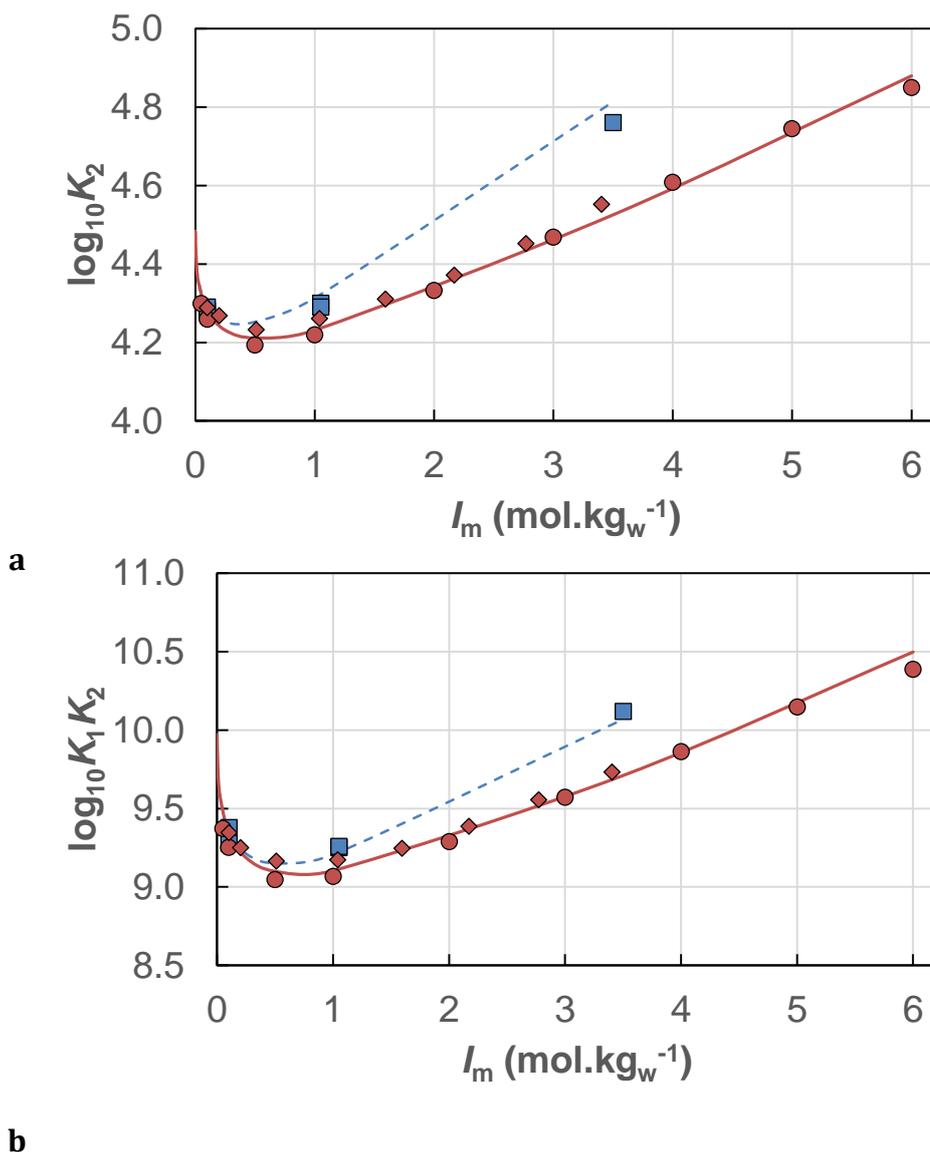


Fig. 3. Extrapolation of the protonation constants of Adip²⁻ at zero ionic strength by SIT from data in Table 5: diamonds [30] and circles [33] and plain lines in NaCl ionic medium, and squares and dashed lines in NaClO₄ ionic medium [25-29].

Performing the adjustment simultaneously on $\log_{10}K^{\circ}_1$, $\log_{10}K^{\circ}_2$, $\varepsilon(\text{AdipH}_2(\text{aq}), \text{NaClO}_4)$, $\varepsilon(\text{Adip}^{2-}, \text{Na}^+)$, and $\varepsilon(\text{AdipH}^-, \text{Na}^+)$ gives the evolutions in Fig. 3, and associated data in Table 1 and 2; correlation matrix is given in Table S2 of the SI. The choice of the non-linear regression instead of constrained linear regression in Hummel *et al.* [10] was done in order to have directly access to the standard deviation of all the constants and coefficients and not through propagation of errors. One can nevertheless admit that a linear representation allows verifying that constant values of specific ion interaction coefficients vs. ionic strength can be used.

The $\log_{10}K^{\circ}_1$ and $\log_{10}K^{\circ}_2$ values compare favourably well, even though slightly higher, with proposed values in NaCl by Bretti *et al.* [33]. Adjusted specific ion interaction coefficients $\varepsilon(\text{AdipH}_2(\text{aq}), \text{NaClO}_4)$, $\varepsilon(\text{AdipH}^-, \text{Na}^+)$, and $\varepsilon(\text{Adip}^{2-}, \text{Na}^+)$ are reported in

Table 4. From the correlation factor in Table S2 of the SI it can be seen that the different constants and coefficients are only weakly correlated. Thermodynamic functions of reaction from $\log_{10}K^n$ [32], and formation thermodynamic functions for adipic acid [31] can be proposed — see Table 2 and 3. They can be used to calculate thermodynamic functions of reactions and formation for adipate ions in Table 1 and 2.

A predominance diagram using thermodynamic constants from Table 1 and 2, and specific ion coefficients in Table 4 can be proposed in Fig. 4 in $0.5 \text{ mol.kg}_w^{-1}$ NaCl and NaClO₄. It can be seen that under these conditions of ionic strength fixed by either NaCl or NaClO₄, Adip²⁻ is the major species at pH above 5. Knowing the speciation of Eu(III), which first hydrolysis is *ca.* pH 7.5 (Table 1), a pH of 5 will be chosen for the complexation study.

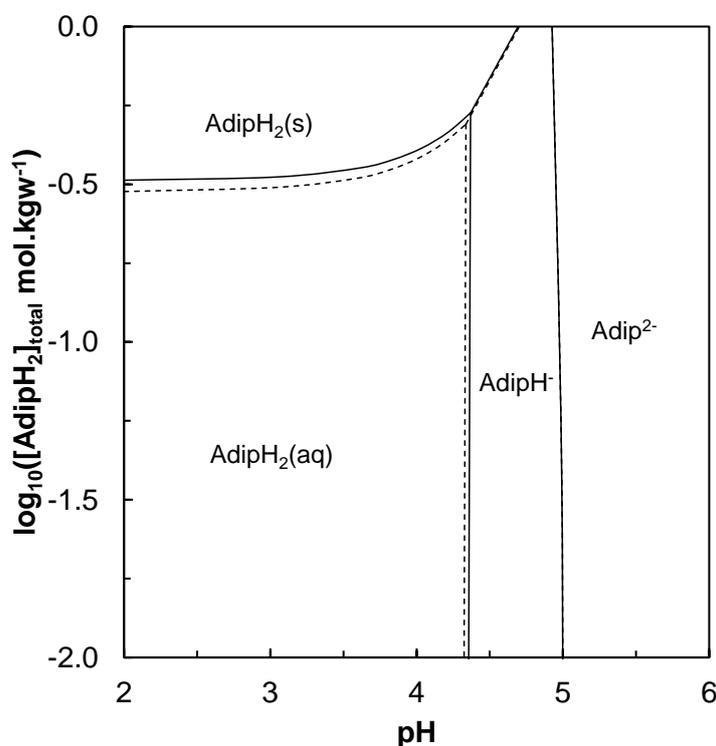


Fig. 4. Predominance diagram of adipic acid in $0.5 \text{ mol.kg}_w^{-1}$ NaCl (plain lines) and NaClO₄ (dashed lines) using thermodynamic constants in Table 1 and 2, and specific ion interaction coefficients in Table 4 — diagram obtained using Phreeplot software [48].

3.2. Europium-adipate complexation study

3.2.1. Luminescence spectra

The evolution of the TRLS spectra of Eu(III) with increasing adipic acid concentrations are shown in Fig. 5a and Fig. S1 of the SI. The spectra are normalized to the area of the ⁵D₀→⁷F₁ transition in Fig. 5a — trapezoid method between 582 and 603 nm — and to the total area of the spectra in Fig. S1 of the SI — 560 and 715 nm. The relative intensity of the ⁵D₀→⁷F₂ transition increases with the adipic acid concentration, which shows the progressive

complexation of Eu(III). The forbidden $^5D_0 \rightarrow ^7F_0$ transition is progressively increasing, which indicates a loss of the centro-symmetry of Eu(III) environment [49,50]. It seems that isosbestic points occurs in Fig. S1 of the SI, which indicates the progressive complexation implying two species. A progressive hypsochromic shift of the $^5D_0 \rightarrow ^7F_0$, $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$, and $^5D_0 \rightarrow ^7F_3$ transitions — more apparent in Fig. S1 of the SI — towards higher emission wavelength, and a broadening of the $^5D_0 \rightarrow ^7F_4$ transition can be observed. In the case of $^5D_0 \rightarrow ^7F_0$ transition this has been attributed to a nephelauxetic effect of the coordinated atoms [51,52] and evolution in the charge of the ligand [53].

The last two spectra are showing the highest hypsochromic shift. One can remind that the two corresponding concentrations are equal and above the theoretical solubility limit of adipic acid with no added background electrolyte. Therefore, these solutions will not be taken into account in the complexation constants determination.

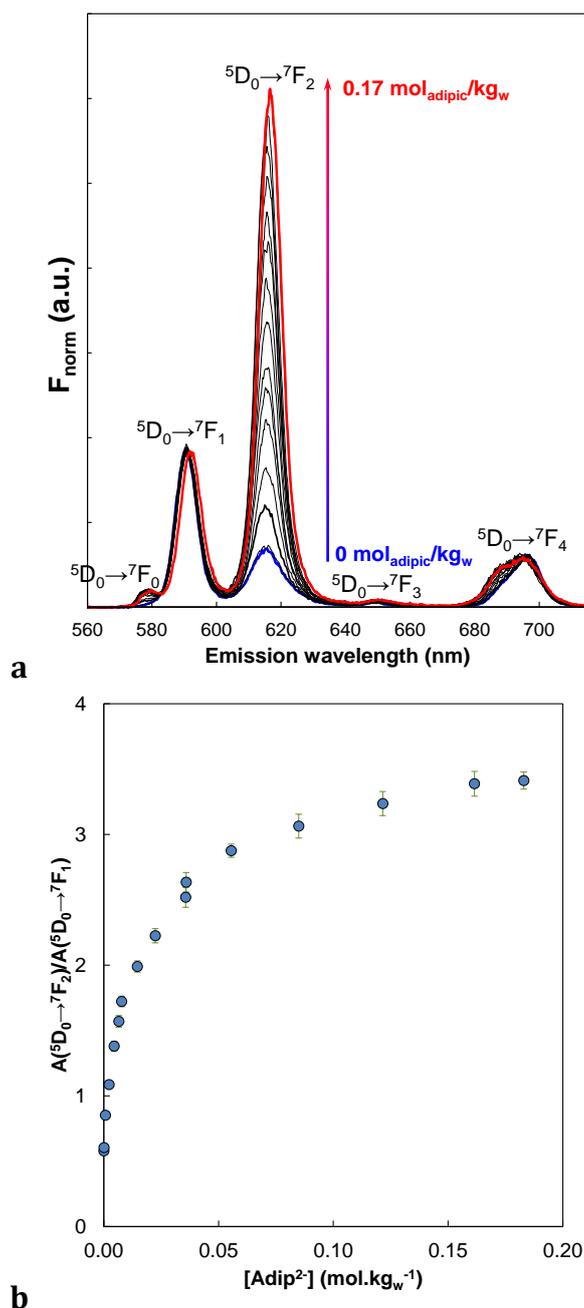
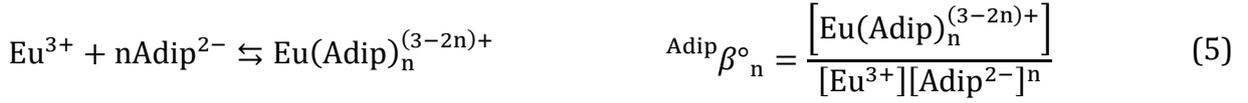


Fig. 5. Evolution of the luminescence spectrum of Eu(III) normalized to the area of the $^5D_0 \rightarrow ^7F_1$ transition in the presence of increasing adipic acid concentration (a), and the $^7F_2/7F_1$ area ratio in the presence of increasing adipate concentration (b): $[\text{Eu}] = 10^{-5} \text{ mol} \cdot \text{kg}_w^{-1}$, $[\text{NaClO}_4] = 0.5 \text{ mol} \cdot \text{kg}_w^{-1}$. $D = 10 \mu\text{s}$, $W = 300 \mu\text{s}$, $\lambda_{\text{exc}} = 393.8 \text{ nm}$. Error bars represent 2σ of the area ratio using the trapezoid method.

3.2.2. Complexation constant determination at $0.5 \text{ mol} \cdot \text{kg}_w^{-1} \text{ NaClO}_4$.

As the pH value is fixed *ca.* 5.0, Eu(III) is considered to be only under the form of free Eu^{3+} ion; the other hydroxo species can be neglected — see thermodynamic constants in Table 1 and specific ion interaction coefficients in Table 4. The reaction can be written as,



with $\text{Adip}\beta_n^\circ$ the cumulative reaction constants. The concentration of Adip^{2-} can be calculated using the $\log_{10}K_n^\circ$ of adipic acid estimated earlier (*vide supra*).

The luminescence spectra evolutions in Fig. 5b can be considered as complexometric titrations. The formation of $\text{Eu}(\text{Adip})_n^{(3-2n)+}$ is considered to be complete as the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2 / {}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ ratio — named hereafter ${}^7\text{F}_2 / {}^7\text{F}_1$ — is no longer modified after increasing the adipic acid concentration. Fig. 5b shows that this point is reached at $[\text{Adip}^{2-}] = 0.17 \text{ mol.kg}_w^{-1}$. As recalled in section 2 of the SI, the $[\text{Eu}(\text{Adip})_n^{(3-2n)+}] / [\text{Eu}^{3+}]$ ratio can be determined from the ${}^7\text{F}_2 / {}^7\text{F}_1$ ratio as a function of $\log_{10}([\text{Adip}^{2-}] / \text{mol.kg}_w^{-1})$ in Fig. 6. The linear regression shows a determination coefficient $r^2 = 0.9517$, with the slope corresponding to the stoichiometry of the complexation reaction ($n = 0.97 \pm 0.08$), which is close to unity. The y-intercept corresponds to $\log_{10}\text{Adip}\beta = 2.09 \pm 0.15$ (1σ) at $[\text{NaClO}_4] = 0.5 \text{ mol.kg}_w^{-1}$ — see section 2 in SI for more details. Unlike Wang *et al.* [13], who studied the Eu(III)-adipate system at $[\text{NaClO}_4] = 0.1 \text{ mol.L}^{-1} = 0.101 \text{ mol.kg}_w^{-1}$ [45] —, we did not observe a second complex formation with $n = 2$.

3.2.3. Estimation of complexation constant at infinite dilution

The SIT defined in Guillaumont *et al.* [24] was used to estimate the constant and ion interaction coefficients at zero ionic strength and 22°C,

$$\log_{10} \text{Adip}\beta - \Delta z^2 \cdot D = \log_{10} \text{Adip}\beta^\circ - \Delta\varepsilon \cdot I_m \quad (6)$$

with I_m the ionic strength in mol.kg_w^{-1} , $D = 0.509 \cdot \sqrt{I_m} / (1 + 1.5 \cdot \sqrt{I_m})$, and $\Delta\varepsilon$ the ion interaction parameter in $\text{kg}_w.\text{mol}^{-1}$. In the case of EuAdip^+ formation (equation 5), $\Delta z^2 = -12$ and $\Delta\varepsilon$ is expressed as follows.

$$\Delta\varepsilon = \varepsilon(\text{EuAdip}^+, \text{ClO}_4^-) - \varepsilon(\text{Adip}^{2-}, \text{Na}^+) - \varepsilon(\text{Eu}^{3+}, \text{ClO}_4^-) \quad (7)$$

Plotting $\log_{10} \text{Adip}\beta - \Delta z^2 \cdot D$ vs. I_m gives $-\Delta\varepsilon$ as the slope and $\log_{10} \text{Adip}\beta^\circ$ at the intercept.

Wang *et al.* [13] proposed the $\log_{10}\text{Adip}\beta(0.1 \text{ M}) = 2.59 \pm 0.01$, supposedly using the protonation constants from Choppin *et al.* [12] — the reference in Table 1 from Wang *et al.* [13] seems to be incorrectly attributed, and the protonation numbering is inverted in regards to ours —, which was taken from Martell and Smith [54], *i.e.*, $\log_{10}K_2(0.1 \text{ M}) = 4.26$ and $\log_{10}K_1(0.1 \text{ M}) = 5.03$. A correction for the protonation constants used can be done [55] as follows,

$$\log_{10}\beta_{\text{SIT}} = \log_{10}\beta_{\text{Davies}} + \left(\frac{\alpha_{\text{SIT}}}{\alpha_{\text{Davies}}} \right) \quad (8)$$

with α being the Ringböm [56] coefficient of adipic acid protonation.

$$\alpha = 1 + K_2\gamma_{H^+}[H^+] + K_1K_2\gamma_{H^+}^2[H^+]^2 \quad (9)$$

At pH = 5, $\alpha_{\text{Davies}} = 2.690$ can be calculated using Wang *et al.* [13] data and equation from Davies [43] for proton activity coefficient ($\log_{10}\gamma_{\pm} = -0.107$), and $\alpha_{\text{SIT}} = 2.966$ can be calculated back extrapolating thermodynamic constants from Table 1 using specific ionic data in Table 4 — $\log_{10}K_2(0.1 \text{ M}) = 4.29$ and $\log_{10}K_1(0.1 \text{ M}) = 5.07$, with $\log_{10}\gamma_{H^+} = -0.124$.

It can be commented that the uncertainty, or standard deviation, given by Wang *et al.* [13] is particularly low — i.e. 0.4%. As the experimental data of the Eu-Adip system are not directly given it seems awkward to propose an expert guess value of the uncertainty. One can remark that an uncertainty equivalent to the one proposed in this work would not greatly alter the propagation of errors.

Using SIT and the corrected complexation constant from the one proposed by Wang *et al.* [13], i.e. $\log_{10}^{\text{Adip}}\beta_{\text{SIT}}(0.101 \text{ mol.kg}_w^{-1}) = 2.63 \pm 0.01$, the complexation constant at zero ionic strength can only be estimated. The ion interaction coefficient values used for this estimation are reported in Table 4. The slope ($-\Delta\varepsilon$) is calculated using,

$$\Delta\varepsilon = -\frac{\left(\log_{10}^{\text{Adip}}\beta - \Delta z^2 \cdot D\right)_{0.5 \text{ m}} - \left(\log_{10}^{\text{Adip}}\beta - \Delta z^2 \cdot D\right)_{0.101 \text{ m}}}{0.5 - 0.101} \quad (10)$$

the y-intercept ($\log_{10}^{\text{Adip}}\beta^\circ$) is calculated using,

$$\log_{10}^{\text{Adip}}\beta^\circ = \left(\log_{10}^{\text{Adip}}\beta - \Delta z^2 \cdot D\right)_{I_m} + \Delta\varepsilon \cdot I_m \quad (11)$$

and the extrapolation is shown in Fig. 7. We obtained from these two points, $\Delta\varepsilon = -(0.61 \pm 0.40) \text{ kg}_w.\text{mol}^{-1}$ and $\log_{10}^{\text{Adip}}\beta^\circ = 3.88 \pm 0.40$, respectively — the standard deviations are the result of the propagation of errors. Using thermodynamic functions from literature [24,31,34] and the constants determined here (Table 1) the free energy of formation for EuAdip⁺ complex, i.e. $\Delta_f G_m^\circ(\text{EuAdip}^+) = -1\,239.291 \text{ kJ.mol}^{-1}$ is calculated (Table 3) — no uncertainty can be given as no standard deviation of $\Delta_f G_m^\circ(\text{Adip}^{2-})$ is available.

Finally, using the $\varepsilon(\text{Adip}^{2-}, \text{Na}^+)$ and $\varepsilon(\text{Eu}^{3+}, \text{ClO}_4^-)$ values in Table 4, $\varepsilon(\text{EuAdip}^+, \text{ClO}_4^-) = (0.10 \pm 0.40) \text{ kg}_w.\text{mol}^{-1}$ is calculated. This value compares favourably well to the specific ion parameter in NaClO₄ of an Am³⁺ complex with a di-basic ion, i.e. oxalate $\varepsilon(\text{AmOx}^+, \text{ClO}_4^-) = (0.08 \pm 0.10) \text{ kg}_w.\text{mol}^{-1}$ [10]. In view of the low number of points further works are clearly needed to ascertain this value with more determinations at other ionic strengths and background salts.

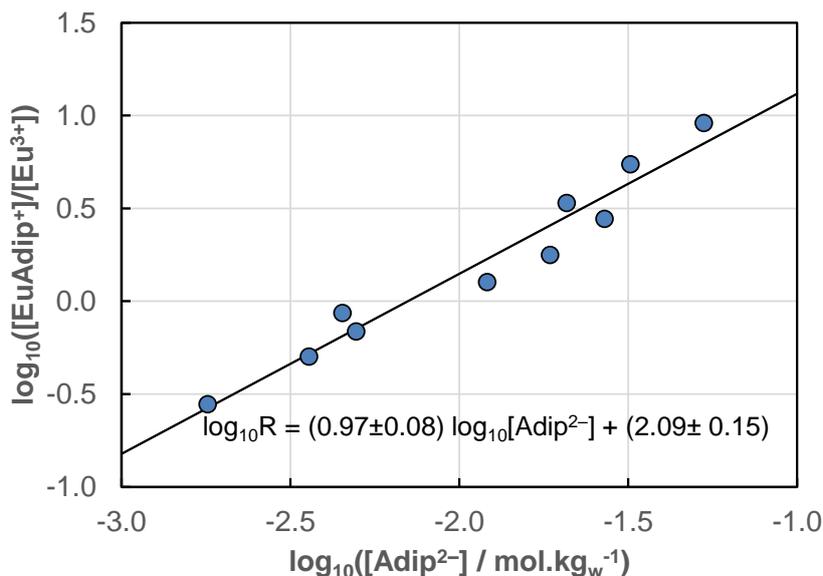


Fig. 6. Determination of the Eu(III)-adipate stoichiometry and the complexation constant from TRLS results from Fig. 5; the experimental data are represented by the symbols while the linear regression is represented as a plain line: $[Eu] = 10^{-5} \text{ mol.kg}_w^{-1}$, $[NaClO_4] = 0.5 \text{ mol.kg}_w^{-1}$, $D = 10 \text{ }\mu\text{s}$, $W = 300 \text{ }\mu\text{s}$, $\lambda_{exc} = 393.8 \text{ nm}$.

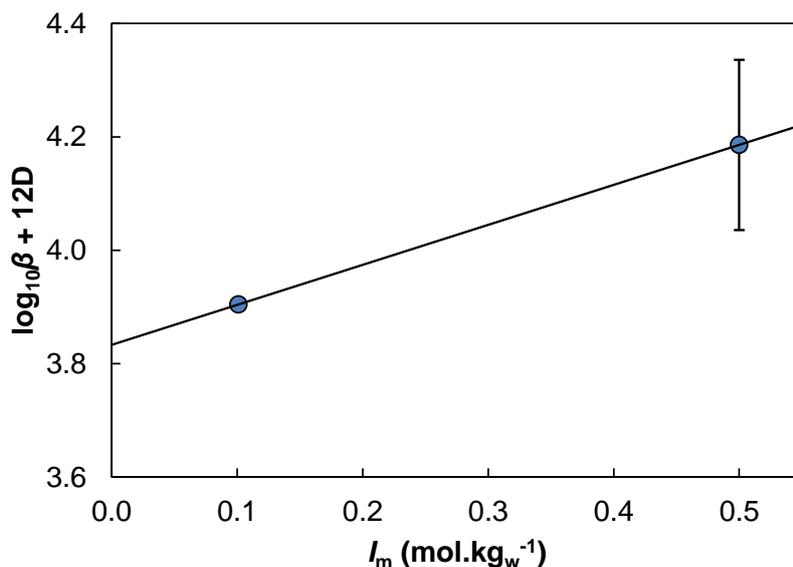


Fig. 7. Extrapolation of the complexation constant at zero ionic strength from the constant of this work at $I_m = 0.5 \text{ mol.kg}_w^{-1} \text{ NaClO}_4$, and the constant of Wang *et al.* [13] at $I_m = 0.101 \text{ mol.kg}_w^{-1} \text{ NaClO}_4$ using SIT. Error bars represent 1σ of the constant.

3.2.4. Luminescence decay evolution

The decay time evolution during the titration of the Eu^{3+} by Adip^{2-} (Fig. 8) is showing only mono-exponential decays, from $114 \text{ }\mu\text{s}$ — on the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition for Eu^{3+} — to $187 \text{ }\mu\text{s}$

— on the ${}^5D_0 \rightarrow {}^7F_2$ transition for the EuAdip^+ complex, *i.e.* $k_{\text{obs}} = 5.3 \text{ ms}^{-1}$. This means that the exchange between the two excited states is too fast to be observed.

The application of the equation from Kimura and Choppin [57],

$$n_{\text{H}_2\text{O}} = \frac{1.07}{\tau} + 0.62 \quad (12)$$

to our case would yield in 5 remaining molecules in the first hydration sphere of the EuAdip^+ complex. This is reminiscent of the results obtained by Wang *et al.* [13] at their highest adipic acid concentration. The authors attributed this decay time to a $\text{Eu}(\text{Adip})_2^-$ complex, which was not evidenced here.

This can be discussed as a 1:1 complex of with a diacid seems unlikely to form a strong bidentate complex involving the two acidic functions separated by a linear chain of 4 carbons. Choppin *et al.* [12] showed that 7 to 9 membered ring complexes — *i.e.*, succinate, glutarate, and adipate — are less prone to form chelate than lower 5 and 6 membered ring complexes — *i.e.* oxalate and malonate. A complete study in D_2O would be necessary [15,58], but was out of the framework of this study.

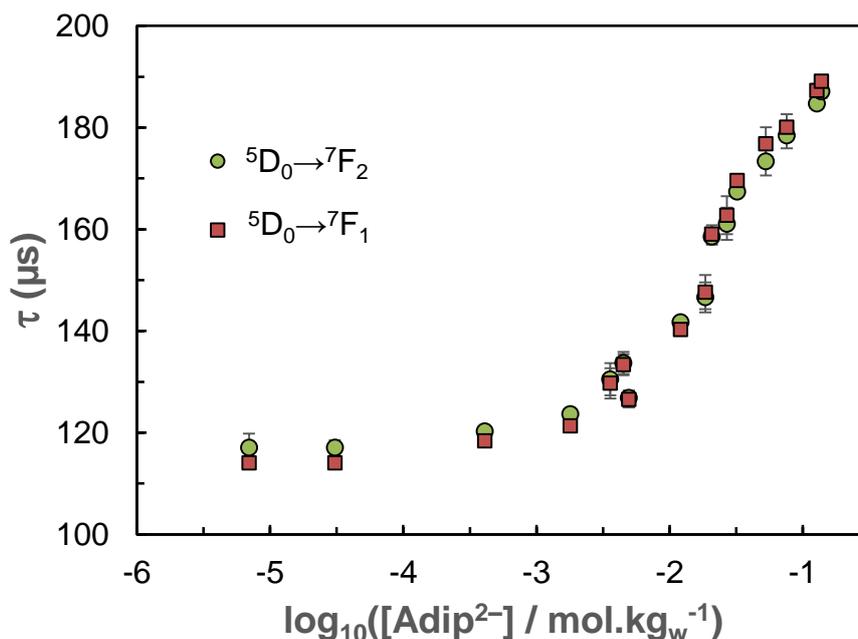


Fig. 8. Luminescence decay of the EuAdip^{2+} complex taken from the areas of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transitions: $[\text{Eu}] = 10^{-5} \text{ mol.kg}_w^{-1}$, $[\text{AdipH}_2]_{\text{total}} = 0.1 \text{ mol.kg}_w^{-1}$, $I_m = 0.5 \text{ mol.kg}_w^{-1} \text{ NaClO}_4$, $W = 300 \mu\text{s}$, $\lambda_{\text{exc}} = 393.8 \text{ nm}$.

3.3. Theoretical europium(III) speciation in adipate medium

Knowing the high concentration of adipate in HDPs of polyesterurethane [9,59], *i.e.* $0.3 \text{ mol.kg}_w^{-1}$, and the complexation constant with Eu(III) previously determined, the theoretical Eu(III) speciation in leachates can be shown in Fig. 9 fixing ionic strength with $0.5 \text{ mol.kg}_w^{-1} \text{ NaClO}_4$. Under these conditions, adipate ion seem to mainly control the Eu(III) speciation from mildly acidic to mildly basic media ($4 < \text{pH} < 9$). But, adipate do not seem to be able to complex Eu(III) in an alkaline medium — from pH 10, see Fig. 9a. At pH 13.3, which is the pH value of a CEM-I interstitial cement water [60] — consisting mainly of mixture of KOH and NaOH —, Eu(III) should predominantly be $\text{Eu}(\text{OH})_3(\text{aq})$ and/or amorphous solid $\text{Eu}(\text{OH})_3(\text{am})$. If Eu(III) is complexed by HDPs from radio-oxidized polyesterurethane, as it is case for the HDPs from a radio-oxidized PVC [38], other molecules than adipate from the ligand pool should be responsible.

One can argue that other types of adipate complexes might be existing under these conditions, *i.e.* supposedly mixed $\text{Eu}(\text{OH})_n\text{Adip}^{(3-2-n)+}$. But it must not be forgotten that in a previous work it has been shown that oxalate and glutarate — which are supposed to have greater complexation constants than adipate [13] — did not increase $\text{Eu}(\text{OH})_3(\text{s})$ solubility at pH 13.3 [38]. Even phthalic acid has not been shown to impact solubility of $\text{Eu}(\text{OH})_3(\text{s})$ [13].

The predominance of EuAdip^+ complex in absence of atmospheric CO_2 is shown in Fig. 10a fixing ionic strength at $0.1 \text{ mol.kg}_w^{-1} \text{ NaClO}_4$. It can be seen that the organic complex

predominance domain is limited to mildly acid and mildly basic solution and total adipic acid concentration higher than *ca.* $3 \cdot 10^{-3} \text{ mol.kg}_w^{-1}$, which means that it account for 10% *ca.* $3 \cdot 10^{-4} \text{ mol.kg}_w^{-1}$.

Fig. 9b is showing the Eu(III) speciation at $\log_{10}(P_{\text{CO}_2} / \text{atm}) = -3.5$ and $[\text{AdipH}_2]_{\text{total}} = 0.3 \text{ mol.kg}_w^{-1}$, in a lower pH span. The extent of EuAdip⁺ stability is comparable to the preceding case, however limited to pH 8 by the EuOHCO₃(cr) precipitation. The extent of the EuAdip⁺ predominance is shown in Fig. 10b. Similar calculation on the predominance of EuAdip⁺ complex can be made in the presence of atmospheric CO₂, but its impact is more limited in the mildly basic domain.

If the impact of adipic acid is proven to be very limited, if not negligible, in alkaline media representative of near-field environment from ILW-LL nuclear waste, its influence in the envisaged host rocks of radioactive wastes repositories remains to be clarified. Knowing the source term of adipate in PUR, the complexation of calcium [61,62] and, most likely, the precipitation of calcium adipate [63] can occur in cementitious equilibrium waters. As an anion it is likely to adsorb on cementitious minerals [64,65] and compete with anionic radionuclides [66]. In less alkaline media, the adsorption of adipate has recently been shown in the case of the Callovo-Oxfordian claystone in France [67]. Studies on the eventual impact on adsorption of Eu(III) in presence of adipic acid would then be desirable including the formation of ternary surface complex formation [23,68].

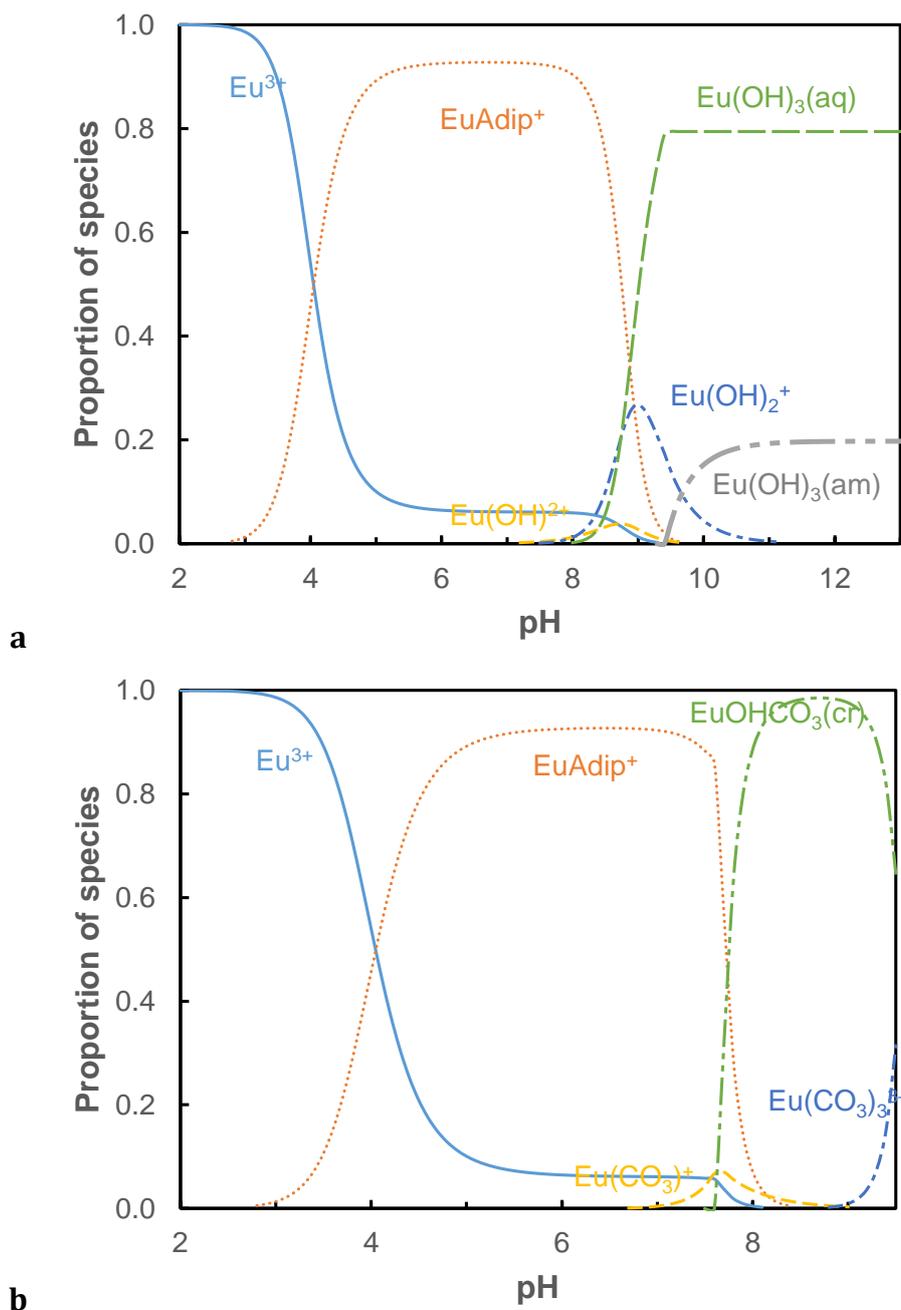


Fig. 9. Speciation of Eu(III) $10^{-6} \text{ mol.kg}_w^{-1}$ in $0.3 \text{ mol.kg}_w^{-1}$ adipic acid at $I = 0.5 \text{ mol.kg}_w^{-1}$ (NaClO_4), $P(\text{CO}_2) = 10^{-12} \text{ atm}$ (a) and $P(\text{CO}_2) = 10^{-3.5} \text{ atm}$ (b). The speciation was calculated using thermodynamic constants reported in Table 1 and 2, and specific ion interaction coefficients in Table 4. Species representing less than 5% in total are not plotted.

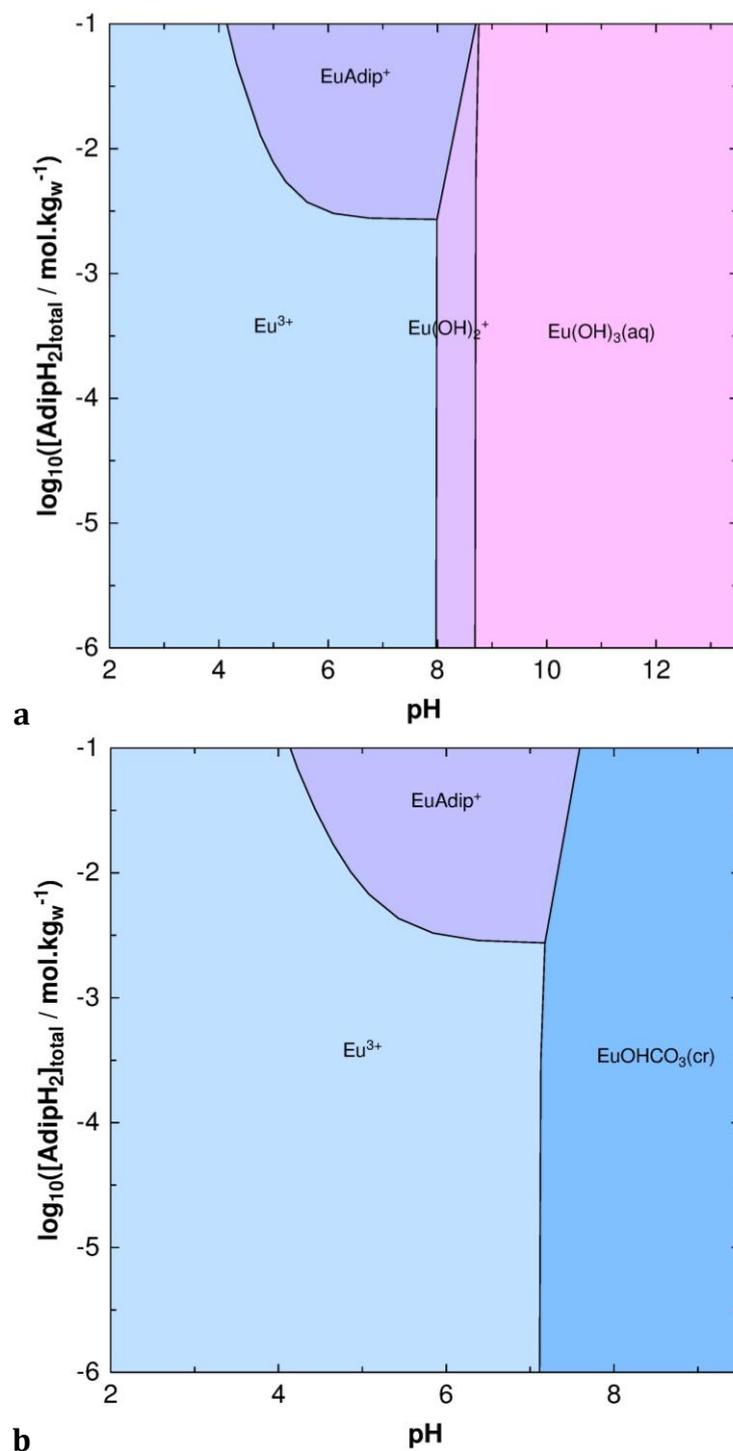


Fig. 10. Predominance diagrams of Eu(III) $10^{-6} \text{ mol.kg}_w^{-1}$ vs. pH with increasing total adipic acid concentration, $I = 0.1 \text{ mol.kg}_w^{-1}$ (NaClO_4) at $P(\text{CO}_2) = 10^{-12} \text{ atm}$ (a), and $P(\text{CO}_2) = 10^{-3.5} \text{ atm}$ (b). The speciation was calculated using thermodynamic constants reported in Table 1 and specific ion interaction coefficients in Table 4 — diagram obtained using Phreeplot software [48].

4. CONCLUSIONS

The aim of this work was to investigate the complexation of Eu(III) by adipate ion, a major HDP released from a polyesterurethane irradiated with gamma rays. First, the thermodynamic constants for protonation of adipate and solubility of adipic acid in NaCl and NaClO₄ ionic media were reviewed and extrapolated to zero ionic strength in the framework of the specific interaction theory: specific ion interaction coefficients of AdipH₂(aq), AdipH⁻, and Adip²⁻ were estimated. The formation of a 1:1 complex between Eu³⁺ and Adip²⁻ was confirmed and the complexation constant can be extrapolated to zero ionic strength $\log_{10}\beta^{\circ} = 3.88 \pm 0.40$, and the specific ion interaction coefficient was evaluated at $\epsilon(\text{EuAdip}^+, \text{ClO}_4^-) = (0.10 \pm 0.40) \text{ kg}_w \cdot \text{mol}^{-1}$.

If an important amount of polyesterurethane is radio-oxidized, the formation of a EuAdip⁺ complex cannot compete with hydrolysis in cementitious system, and can only occur at slight acidic to mildly basic pH values. The impact of this complex on the adsorption of radionuclides onto host rocks of radioactive nuclear waste repository should be evaluated.

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