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Gilles F Montavon, M. Bouby, Sandrine Huclier-Markai, Bernd Grambow, H. Geckeis, et al.. Quantitative description and local structures of trivalent metal ions Eu(III) and Cm(III) complexed with polyacrylic acid. *Journal of Colloid and Interface Science*, 2008, 327, pp.324-332. 10.1016/j.jcis.2008.08.037 . in2p3-00339580

HAL Id: in2p3-00339580

<https://hal.in2p3.fr/in2p3-00339580>

Submitted on 2 Dec 2008

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Quantitative description and local structures of trivalent metal ions Eu(III) and Cm(III) complexed with Polyacrylic Acid

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ABSTRACT

The trivalent metal ion (M(III)=Cm, Eu) / polyacrylic acid (PAA) system was studied in the pH range between 3 and 5.5 for a molar PAA-to-metal ratio above 1. The interaction was studied for a wide range of PAA (0.05 mg.L⁻¹ – 50 g.L⁻¹) and metal ion concentrations (2.10⁻⁹ – 10⁻³ M). This work aimed at 3 goals i) to determine the stoichiometry of M(III)-PAA complexes, ii) to determine the number of complexed species and the local environment of the metal ion and iii) to quantify the reaction processes. Asymmetric flow-field-flow fractionation (AsFIFFF) coupled to ICP-MS evidenced that size distributions of Eu-PAA complexes and PAA were identical, suggesting that Eu bound to only one PAA chain. Time-Resolved Laser

Fluorescence Spectroscopy (TRLFS) measurements performed with Eu and Cm showed a continuous shift of the spectra with increasing pH. The environment of complexed metal ions obviously changes with pH. Most probably, spectral variations arose from conformational changes within the M(III)-PAA complex due to pH variation. Complexation data describing the distribution of complexed and free metal ion were measured with Cm by TRLFS. They could be quantitatively described in the whole pH-range studied by considering the existence of only a single complexed species. This indicates that the slight changes in M(III) speciation with pH observed at the molecular level do not significantly affect the intrinsic binding constant. The interaction constant obtained from the modelling must be considered as a mean interaction constant.

INTRODUCTION

The complexation of polycarboxylic acids with metal ions is of interest in the context of the assessment of heavy / radionuclide mobility in contaminated soils as well as for the safety of nuclear waste repositories. In the past 10 years, the interaction of trivalent metal ions (lanthanides and actinides) with polyacrylic acid (PAA) was extensively studied [1-8]. Some authors intended to describe the coordination of polymer chain bound metal ions using spectroscopic tools [3-7] while the goal of some other was to quantify the processes¹⁻³ by macroscopic batch titration experiments. The coordination environment of M(III) bound to PAA was notably studied by Time Resolved Laser Fluorescence Spectroscopy (TRLFS) with Eu as a fluorescent probe.

Between pH 3 and 5.5, two species were evidenced [8]. By analogy with simple reference ligands like acetate, 1:1 and 1:2 species were proposed where M(III) interacts in a bidentate coordination mode with one and two carboxylate groups, respectively. Recent Extended X-ray

Absorption Fine Structure (EXAFS) spectra measured with Eu at pH 5 showed that such a simple reference system is not applicable for Eu-PAA [4-5], i.e. the bidentate coordination could not be evidenced. This was explained by the degree of freedom of the carboxylate groups which is constrained by the flexibility of the methylene chain. In the pH range 5.6-10, one species dominates the Eu speciation. According to [6-7], the metal ion is coordinated in the first coordination sphere by three carboxylate group and 3 hydration water molecules whereas Yoon et al. [8] came to the conclusion that Eu is bound to two carboxylate groups and 4 water molecules. Finally, above pH 10, ternary complexes with OH⁻ are expected [6-7]. The complexation reaction was quantified indirectly by either separating free and PAA bound metal ions [2] or by using displacement methods in the liquid/liquid [1] or solid/liquid [3] system. The description was done with empirical models. The data could be well described at a given pH value considering the existence of a single complexed species. Depending on the methods used, the conditional complexation constant varies by more than two orders of magnitude [1-3]. A change in the Eu coordination was proposed to explain the variation of the conditional complexation constants with pH [1]. However, the authors did not take any electrostatic effect into account in their interpretation and no reliable conclusion can be derived from the study.

In conclusion, some spectroscopic results appear contradictory and none of the results of the macroscopic study can be related to those of the spectroscopic study, i.e. the possible coexistence of two species for a given pH value in the range 3-6 and the existence of three distinct species in the pH range 3-12. It is worth noting that an important parameter is different in batch and spectroscopic studies: the molar PAA-to-metal ratios. For the spectroscopic studies, one polymer chain binds more than one metal ion whereas most of the data for the macroscopic batch studies were measured at trace metal ion concentrations, i.e. under conditions where the ratio of polymer chains to metal ion concentration is high.

The objective of this work is to obtain a coherent description of M(III)/PAA interaction by using available published data with new complementary data measured both at the microscopic and macroscopic levels under well controlled experimental conditions. The pH range investigated was chosen between 3 and 5.5. This pH range was particularly studied in order to avoid the possible formation of ternary complexes [6-7]. The study was performed under conditions where the M(III)-PAA complex is soluble and not more than one metal ion is in average complexed per polymer chain. With this approach (i) possible lateral interactions between complexed metal ions in the modelling and (ii) a possible effect of metal ion loading on the speciation can be excluded.

The interaction was studied for a wide range of PAA (0.05 mg.L^{-1} – 50 g.L^{-1}) and metal ion concentrations ($2 \cdot 10^{-9}$ – 10^{-3} M). The quantification of M(III) distribution between the bulk solution and the polymer phase was done with TRLFS using Cm as fluorescent metal ion. The method has the advantage to be a “direct” speciation method as compared to other procedures described in the literature, where the metal ion speciation is derived indirectly. The characterization of the interaction at the molecular scale was studied by two approaches:

- the stoichiometry of the complex, i.e. the number of PAA chains interacting with Eu is analysed by Electrospray ionization mass spectrometry (ESI-MS) and by Asymmetric Flow Field Flow Fractionation coupled with either ICP-MS (AsFIFFF-ICP-MS for Eu detection) or Ultra-violet detection, (AsFIFFF-UV for PAA detection).
- The number and nature of complexed species, i.e the number of carboxylate groups bound (N_c), the mode of binding (bidentate, monodentate) and the number of hydration water molecules bound (q) were assessed by TRLFS.

EXPERIMENTAL SECTION

Chemicals

Commercially available sodium perchlorate monohydrate (Fluka, purum), Europium oxide (Prolabo, RECTAPUR™), sodium acetate (Ac) (Prolabo), polyacrylic acid (PAA) at $M_w=5000$ and $M_w=2000$ Da (Aldrich), DCl (99%, CE Saclay, Euriso Top), NaOD (99%, CE Saclay, Euriso Top) and D_2O (99.97%, CE Saclay, Euriso Top) were used as received. ^{248}Cm stock solution was obtained by dissolution and separation from a 30 years old Cf-252 neutron source.

Experimental methods and analysis

All the solutions were prepared with ultrapure water and all the analyses were done at room temperature. PAA with a molecular weight of 2000 Da was used to prepare the samples for TRLFS measurements in D_2O . For all other experiments, 5000 Da PAA was used. Based on literature data [6-7], it is assumed that PAA with $M_w=2000$ Da and 5000 Da have similar complexation properties for Eu.

Sample preparation: M(III)/PAA and M(III)/Ac samples were prepared by mixing aliquots of M and PAA, Ac (acetate) stock solutions. The pH value was then adjusted with aliquots of H(D)Cl or NaO(D)H. For the samples prepared in D_2O , experiments were performed in a glove box flushed with N_2 (31% relative humidity). For Ac, and PAA concentrations $> 1 \text{ mg.L}^{-1}$, the time to reach equilibrium was shown to be rapid, i.e. below five minutes. For PAA at concentrations $< 1 \text{ mg.L}^{-1}$, contact times varying from 1 and 7 days were necessary for equilibration. Eu, Cm and PAA, Ac concentrations were checked using a PQ-Excel ICP-MS (VG-Elemental), by liquid scintillation counting (Packard 2550 TR/AB Liquid Scintillation analyzer) and by Total Organic Carbon (TOC) measurements (Shimadzu TOC 5000A analyzer), respectively.

Sample description: Parameters for the M(III)/Ac system are: pH=6, $[Cm]_{tot}=10^{-7}$ M, $[Eu]_{tot}=10^{-3}$ M; acetate concentration was varied from $3 \cdot 10^{-3}$ to 5.8 M. For the M(III)/PAA system, the pH was varied from 3 to 5.5, the PAA concentration from 50 g.L^{-1} to 0.05 mg.L^{-1} and the metal ion concentration from 10^{-3} to $2 \cdot 10^{-9}$ M. In this study, experimental conditions were chosen so that in average not more than one metal ion is complexed per polymer chain (considering that only one PAA chain can interact with M). A list of the sample characteristics is given in the supplementary informations.

The experimental data for the M(III)/PAA system are divided into two series. For the first one (series I, SI), conditions were chosen in order to have 100 % of the metal ion complexed. The goal was to avoid the presence of free M and to analyse selectively the M(III)-PAA complex. According to the method used and the conditions studied, either Eu (TRLFS, AsFIFFF, ESI-MS) or Cm (TRLFS) were used as probes. For the second series (series II, SII), M(III) and M(III)-PAA species coexist in solution. These data were used for the determination of the parameters characterizing M(III)/PAA interaction. Only Cm was used for this series.

It is assumed that Eu and Cm have similar interaction properties for PAA, which is reasonable based on a multitude of studies reported in the literature.

TRLFS

Spectroscopic information:

1/ Emission decay rates of ${}^6D_{7/2}'$ (Cm) and 5D_0 (Eu) levels. The decay rate constants, k_{obs} , and the corresponding lifetimes, $\tau=k_{obs}^{-1}$, are sensitive to the number of coordinated water molecules, q , in the first coordination sphere [9-10].

2/ ${}^6D_{7/2}' \rightarrow {}^8S_{7/2}'$ emission spectra of Cm. The peak position of the emission spectra is known to be sensitive to the first coordination sphere around Cm [11].

2/ ${}^7F_0 \rightarrow {}^5D_0$ excitation spectra of Eu. The transition is entirely non-degenerated. Therefore, the appearance of multiple bands indicated the presence of different species. The deconvolution of the excitation spectra was performed considering that peak(s) exhibit Lorentzian and Gaussian shape [12] expressed by:

$$y = I \frac{\exp(-0.5 * (\frac{x-w}{L})^2)}{(\frac{x-w}{L})^2 + 1} \quad (1)$$

where I, w and L are the intensity, peak position, and line width, respectively.

In conclusion, each complexed species was characterized by its lifetime and the peak positions of ${}^6D'_{7/2} \rightarrow {}^8S'_{7/2}$ emission (Cm) and ${}^7F_0 \rightarrow {}^5D_0$ (Eu) excitation spectra. These information was used to assess the local environment of M using the M(III)/Ac system as a reference ⁸.

Interpretation of decay curves: where more than two species are present and if their chemical exchange rates are lower than the luminescence decay of the two species, lifetime values of the two species are obtained considering the simplified equation:

$$\tau_{\text{obs}}^{-1} = \sum_i X_i \tau_i^{-1} \quad (2)$$

with τ_{obs}^{-1} being the observed luminescence decay rate, τ_i the lifetime of excited species i, and X_i its mole fraction if the fluorescence yields for all species are identical [13]. X_i is calculated using the equilibrium constants while τ_i^{-1} are fitting parameters.

Measurements: Details concerning the spectroscopic device as well as details on how spectroscopic data were obtained can be found elsewhere [14,15]. If not stated otherwise, Eu and Cm species were excited at the 5D_2 (466 nm) and F (396.6 nm) levels, respectively. For

decay curve measurements, fluorescence emission peaks at about 616 nm (${}^5D_0 \rightarrow {}^7F_2$) and 595 nm (${}^5D_0 \rightarrow {}^7F_1$) for Eu, and 600 nm (${}^6D'_{7/2} \rightarrow {}^8S'_{7/2}$) for Cm were integrated. Lifetime measurements were started from the longest delay time down to 1 μ s. For excitation spectra of Eu, the excitation wavelength was varied from 578 to 580 with an interval of 0.05nm. The excitation spectra were determined by integration, for a given excitation wavelength, of the fluorescence intensity of the emission peak at about 616 nm (${}^5D_0 \rightarrow {}^7F_2$). The laser energy was fixed to (2.5 \pm 0.5) mJ. Under these conditions, no photodegradation of PAA could be observed. This was checked by monitoring PAA UV-absorption spectra before and after TRLFS measurements.

Quantitative analysis: All fittings carried out in this work were made using the fitting procedure of SigmaPlot software using the Marquardt-Levenberg algorithm (version 2.0, Jandel Co.). Based on repetitive experiments, errors were estimated at 5% and 0.2nm for lifetime values and peak position of emission spectra (Cm), respectively.

AsFIFFF coupled to UV-Visible spectrophotometer or ICP-MS detector

The equipment used in this work has been described in [16]. The AsFIFFF system (HRFFF 10.000 AF4) is from Postnova Analytics (Landsberg, (Germany)). The injected sample volume is 100 μ L. The fractionation channel comprises an accumulation wall consisting of an ultrafiltration membrane (regenerated cellulose; Cutoff: 5 kDa; Postnova Analytics (Landsberg, Germany)). The trapezoidal polytetrafluoroethylene (PTFE) spacer delimiting the channel where the fractionation took place has a height of 500 μ m. The carrier solution (eluent) consists of ultra pure water at pH 5.7. The carrier is degassed prior to use by a vacuum degasser (HP 1100, Model G 1322A, Agilent (Waldbronn, Germany)). After fractionation, the effluent is directed through an UV detector (LambdaMax LC Modell 481,

Waters (Milford, USA)) for monitoring the PAA light absorption at 225 nm. The laminar outflow rate is adjusted nominally to $0.8 \text{ mL}\cdot\text{min}^{-1}$ while the cross flow rate decreases exponentially from $3.2 \text{ mL}\cdot\text{min}^{-1}$ at the beginning down to $0 \text{ mL}\cdot\text{min}^{-1}$ after 30 min. For Eu analysis, the effluent is then mixed via a T-piece with 6 % nitric acid containing $50 \mu\text{g}\cdot\text{L}^{-1}$ Rh taken as an internal standard and introduced into an ICP-Mass Spectrometer (ELAN 6000, Perkin-Elmer (Rodgau - Jügesheim, Germany)) at a constant rate ($0.5 \text{ mL}\cdot\text{min}^{-1}$) via a peristaltic pump (Minipuls3 ABIMED, Gilson (Villiers le Bel, France. A series of polystyrene sulfonate (PSS) reference standards (Polysciences (Eppelheim, Germany)) of different molecular weights (1.29, 4.4, 15.2, 29 and 81.8) kDalton and a series of carboxylated polystyrene reference particles (Magsphere Inc., (Pasadena, California, USA)) of different sizes (24 nm, 105 nm, 207 nm) were used for size calibration. Dispersions were freshly prepared before injection in carrier solution.

ESI-MS experiments: PAA solutions were prepared at $0.25 \text{ g}\cdot\text{L}^{-1}$ in ultra pure water since the NaClO_4 solution induced interferences in the spectra. Either a QUATTRO LC triple stage quadrupole (Thermon Finningan) or a Q-TOF (Perkin Elmer) mass spectrometers were used. The samples were introduced directly into the source with a syringe pump at a flow rate of $6 \mu\text{L}/\text{min}$. Myoglobin ($m/z = 808$) was used for mass calibration checks. The MS spectra for PAA were recorded in negative ion mode ESI(-) with a source temperature of 150°C and a cone voltage of 36V. Conditions optimised for sensitivity use an ESI capillary voltage of $\pm 3300\text{V}$. Nitrogen was employed as both the drying and the nebulization gas.

Modeling

In the present paper, the model proposed by Miyajima et al. is used [17]. The theory is briefly described below.

At equilibrium, M is distributed between the bulk solution phase and PAA. This macroscopic binding equilibrium is characterized by the formation of a 1:1 M:PAA complex and an apparent binding constant, K_{app} , which can be simplified for low metal ions loadings as:

$$K_{app}(M) = \frac{[MP]}{[M]\alpha C_p} \quad (3)$$

where $[MP]$, $[M]$, and α represent the concentration of the complex (in mol/L), the concentration of free M and the degree of dissociation, respectively. C_p corresponds to the concentration of proton exchanging sites (in mol/L) and values are taken from [2]. For $pH \geq 3.5$, α values were experimentally determined by potentiometric titration using the procedure given in (1); i.e. $\alpha=0.06, 0.11, 0.17, 0.2, 0.25, 0.38$ for $pH=3.5, 3.7, 4, 4.25, 4.5$ and 5 , respectively. For $pH < 3.5$, they were calculated using the pka value of acetic acid [18] considering that the electrostatic term can be neglected in this pH range where α tends to 0 [17], i.e. $\alpha=0.049$ and 0.028 for $pH=3.25$ and 3 . For a given α value, $K_{app}(M)$ was determined by TRLFS with C_m using titration experiments, i.e. the distribution of C_m between solution and PAA was studied as a function of PAA concentration.

The apparent complexation constant takes the electrostatic term into account as well as the intrinsic interaction. This latter interaction describes the formation of the PAA complex and is characterized by an intrinsic binding constant K_0 . The electrostatic effect for each pH value is characterized by the difference between apparent ($K_{app}(H)$) and intrinsic ($K_0(H)$) acid dissociation constants of PAA sites:

$$\Delta pK = pK_{app}(H) - pK_0(H) \quad (4)$$

Using the Donnan concept [19], Miyajima et al. [17] came to the conclusion that in case a single complexed species was formed, $K_{app}(M)$ could be related to the intrinsic binding constant using the relation:

$$\log(K_{app}(M)) = Z\Delta pK + \log(K_0(M)) \quad (5)$$

with Z being the charge of the metal ion. In this case, a graphical analysis of $\log(K_{app}(M))$ as a function of ΔpK validates the model if the slope of the curve equals to $Z=3$ and the y-axis intercept gives the value of the intrinsic binding constant.

The Mineql+ program [20] was used to determine the apparent constants. The same program was used to calculate the speciation diagram of M in the presence of the acetate ion. The ionic strength correction was done using the Davies equation [21].

RESULTS

Complex stoichiometry

By analyzing the ESI-MS spectra of PAA (nominal $M_w= 5,000$ Da) (Figure 1), 2 main features could be observed. Firstly, only mono charged ion peaks were observed and main peaks were separated by $m/z = 72$, which was in good agreement with data from Leenheer et al. [22]. This ratio can be attributed to the PAA monomer. Secondly, the Gaussian distribution of the masses is centred at $m/z=473$. This means that the range of transmitted ions does not correspond to the nominal and expected PAA mass of 5000 Da. The same study was performed in positive electro spray ionisation mode leading to the same observation. One has to conclude that the relatively high number of ionised groups per chain leads to a fragmentation in the spray leading to the detection of the smaller fragments. Results obtained in the presence of Eu(III) were not sensitive enough to allow a characterization of the Eu:PAA stoichiometry.

The AsFFFF results are presented in Figure 2. Four successive injections of the 5000 Da PAA solution (10 mg.L^{-1}) lead to very reproducible UV-fractograms with a peak maximum at 119 s, in agreement with the elution of 2000 Da PSS standard arriving at 114 s. The PAA recovery yield amounts to $(60\pm 10)\%$ whereas it was weak for Eu (around 1%). Obviously Eu dissociates from the PAA complex during fractionation as the complexation equilibrium is

disturbed and the Eu aquo ion passes through membrane pores or is sorbed to the membrane surface. As indicated by the Eu-ICP-MS-fractogram in Figure 2B, the Eu size distribution follows the PAA one with an identical peak position. This means that the Eu-PAA complex formation has no effect on the PAA size, according to the size resolution achieved in the present experimental conditions. These results suggest that Eu is bound to only one PAA chain.

Number of complexed species

The number of complexed species was determined by examining Cm emission and Eu excitation spectra.

Series I (100% complexation): Neither the PAA concentration nor the PAA/metal ratio affected the Cm emission spectra measured at a given pH value. Fluorescence emission bands slightly shifted to higher wavelengths when the pH was increased (Figure 3A). The shape of emission spectra, i.e. the peak width remained identical for all experimental conditions (Figure 3B). It was thus not possible to identify different species by peak deconvolution. Similar results were obtained when looking at Eu excitation spectra (Figure 4):

- The shape of excitation spectra were nearly identical, with a line width of around 0.39 nm (Figure 4 caption);
- One component was sufficient to describe the spectrum at a given pH;
- A shift of the peak position but no peak broadening was observed as the pH varies.

Series II (less than 100% complexation): Cm emission spectra were deconvoluted using the spectrum of the free Cm and the shape of Cm-PAA spectrum as obtained from series I experiments. The Cm/Cm-PAA species distribution as well as the peak position of the Cm-PAA emission band were the fitting parameters. Peak positions correspond to those determined for series I (filled symbols in Figure 3A).

The continuous shift of spectra with pH not accompanied by a peak broadening suggests that there is only one distinct CmPAA species prevailing in the investigated pH range with, however, pH dependent conformation. The species distribution for Cm(Eu)PAA is identical for series I and II.

Nature of the complexed species

Analysis of decay curves determined by TRIFS

For given experimental conditions and for both metal ions, a single lifetime of the complex is sufficient for describing the decay curves. The lifetime values for the CmPAA complex in series II experiments (presence of both Cm and Cm-PAA) were determined using the method described in the “experimental methods and analysis” section. In the fitting procedures, the lifetime of Cm aquo ion was fixed to 64 μ s [11]. A typical experiment is presented in Figure 5A and τ values obtained for series I and II appear identical. For both ions, a continuous increase in lifetime is observed as the pH increases. This result confirms the continuous change in speciation already concluded from emission and excitation spectra analysis. The observed decay constant, k_{obs} , is given by:

$$k_{\text{obs}} = k_{\text{nat}} + k_{\text{nonrad}} + k_{\text{H}_2\text{O}} \quad (6)$$

where k_{nat} is the natural rate constant, k_{nonrad} is the rate constant for radiationless relaxation processes, and $k_{\text{H}_2\text{O}}$ is the rate constant for the transfer of energy to the O-H vibrations of coordinated water. To assess whether OH is the only quenching group, k values were measured in D₂O for Eu-PAA system (pH=3.2-5.3) in order to suppress the quenching effect of coordinated H₂O. In this case, $k_{\text{obs}}^{\text{D}_2\text{O}}$ is equal to $k_{\text{nat}}+k_{\text{nonrad}}$. Rate constants are invariant with pD and amount to $0.42\pm 0.02 \text{ ms}^{-1}$ (grey symbols, Figure 5B). Measured decay rates for the aquo ion in D₂O range from 0.38 to 0.53 ms^{-1} [9]. This suggests that coordinated PAA does not have a significant quenching impact and that k in H₂O is only related to coordinated

water molecules. The increase in τ (Figure 5B) may be therefore explained by a decrease of the number of H₂O molecules coordinated in the first coordination sphere. q can be determined using $k_{obs}^{D2O} - k_{obs}^{H2O}$ [9] (grey symbols in Figure 5C) or using directly k_{obs}^{H2O} (dark symbols in Figure 5C) based on the empirical law of Kimura et al [10]. Values are identical irrespective to the calculation method. The empirical law was also used for Cm. As expected, similar results are obtained for Cm and Eu. In conclusion, about 4-5 water molecules are excluded from the Eu/Cm hydration sphere upon complexation to PAA when varying the pH from 3 to 5.

Determination of Nc (number of coordinating carboxylate groups) using TRLFS

According to the TRLFS results, the change of speciation observed with varying pH is explained by a change of q . This change should then be accompanied by a concomitant change of Nc to maintain the octadentate/nonadentate coordination sphere of Eu/Cm(III).

The number of coordinating carboxylate groups may be assessed by comparing peak positions of Cm emission and Eu excitation spectra in M(III)/PAA and M(III)/Ac systems [8]. In this case, one assumes a bidentate mode of coordination, i.e. two water molecules are expelled from the first coordination sphere for one carboxylic group bound [6,8]. Considering the octadentate coordination determined by EXAFS [5], i.e. $N_{tot}=8$, and the variation of q values determined by TRLFS, two complexed species are expected in the pH range investigated, i.e. $\text{Eu}(\text{CH}_3\text{COO})_2 \cdot 6\text{H}_2\text{O}$ and $\text{Eu}(\text{CH}_3\text{COO})_3 \cdot 4\text{H}_2\text{O}$.

The characteristics of excitation spectra for Eu and Eu/Ac complexes can be found in the literature [8,23] and are given in Table 1. The Cm acetate emission spectrum for the 1:3 complex was obtained at $[\text{Ac}]=5.8 \text{ M}$ (see Figure 6). Eu as well exists only as 1:3 complex at this acetate concentration, and the excitation spectrum (not shown here) could be well described by eq. (1) using the parameters given in Table 1. 1:1 and 1:2 Cm acetate complexes

were obtained by deconvolution of emission spectra measured for acetate concentrations varying between $3 \cdot 10^{-3}$ M and $3 \cdot 10^{-2}$ M (Figure 6). From the measured species distribution one can calculate logK values of 3 and 4.2 for the 1:1 and 1:2 species, respectively (see Figure 5 caption). These values agree with those reported in the literature for Cm (2.9 and 4.4 for the 1:1 and 1:2 species after ionic strength correction) [18]. The results also indicate that the presence of the 1:3 complex can be neglected unless very high acetate concentrations are present. logK for the 1:3 complex is estimated to be ≤ 5.2 . No acetate complexation constant is given for Cm in the literature. For Am, which can be considered as chemically very similar to Cm, logK=5.5 (after ionic strength correction) [18].

Table 1 summarizes the spectroscopic results and a comparison is made between M(III)/PAA and M(III)/Ac systems. For Eu, there are some spectroscopic similarities for model Eu/Ac and Eu/PAA systems; 1:1 and 1:2 Eu:COO⁻ complexes can be expected at pH=3 and 5, respectively (similar peak positions). This is in agreement with the work of Yoon et al. [8] and in agreement with our starting assumption. However, this result cannot be confirmed with Cm; the peak position for the Cm-PAA complex varies with pH and lies close to the peak position of the 1:2 Cm:Ac complex. In conclusion, the Eu/Ac system appears not to be a good reference system and does not allow to derive structural parameters for the Eu/PAA system, in agreement with recent results obtained by EXAFS [5,4].

Based on dynamic molecular calculations [5], one water molecule is rather replaced by one carboxylate group bound in a monodentate fashion. This would lead to the possible existence of four different species in the pH range investigated, i.e. $\text{Eu}(\text{CH}_3\text{COO}) \cdot 7\text{H}_2\text{O}$, $\text{Eu}(\text{CH}_3\text{COO})_2 \cdot 6\text{H}_2\text{O}$, $\text{Eu}(\text{CH}_3\text{COO})_3 \cdot 5\text{H}_2\text{O}$ and $\text{Eu}(\text{CH}_3\text{COO})_4 \cdot 4\text{H}_2\text{O}$. The last species was proposed by Rothe et al. [5] from EXAFS spectra analysis. The consideration of the occurrence of distinctly different species at our experimental conditions remains however questionable regarding the excitation and emission spectra. One would then expect a mixture

of the different species as the pH value varies, and therefore a change in the shape of the fluorescence spectra with pH. As said before, this was not experimentally observed.

Most probably, the coordination sphere around M (q , N_c , N_{tot}) remains globally unchanged as the pH varies, and the TRLFS modifications arise from conformational changes within the M(III)-PAA complex due to pH variation. In this pH range, considering the change in α value, a strong conformational change is expected [24]. The increase of the lifetime with pH would then be explained by a slight change of the distance between M and coordinated water molecules rather than by a change in q value.

Quantitative description of complexation data

In agreement with AsFIFFF results, the model considers the formation of a 1:1 M:PAA complex (eq. (1)). The complexation data obtained for series II experiments at different pH values can be well described based on eq. (3) (Figure 7A) considering only one species as observed by Kubota et al. [18]. The conditional constant obtained at pH 5 ($\log K_{app}=6.65$) is comparable with the values given in the literature and determined using the anionic exchange separation method ($\log K_{app}=6.23$) [2] or the displacement method based on a liquid/liquid separation procedure ($\log K_{app}=7.06$) [1]. The one deduced from the displacement method using a solid/liquid separation methodology appears therefore underestimated ($\log K_{app}=5.24$) [3].

According to the model, to ensure balanced charges within the gel phase, three positive charges need to be compensated by three negative charges. It was experimentally shown that at saturation, the number of bound metal ions corresponds to the number of deprotonated carboxylic groups determined by potentiometric titration [2,7]. This appears coherent with an ion exchange model. However, this 1:3 Eu:COO⁻ stoichiometry cannot be evidenced by the spectroscopic techniques. This indicates that the neutralisation within the gel phase does not

imply that all carboxylate groups participate at the first coordination sphere of the metal ion. $\log K_{app}$ values obtained by TRLFS and those reported in [1] are presented in Figure 7B as a function of pH. As indicated by the solid line, the model of Miyajima et al. [17] allows to describe the data, i.e. a straight line with a slope of 3.1 ± 0.2 is obtained (eq. (5)). This indicates that the increase of $\log K_{app}$ with the pH is explained by an electrostatic effect and that only one complexed species exists in the pH range considered (3.1-5.5). It is characterized by an intrinsic binding constant of 3.7 ± 0.3 . This result is coherent with the conclusion derived from the microscopic study, i.e. the coordination sphere around M (q, Nc, N_{tot}) remains globally unchanged as the pH varies. The change in speciation observed by TRLFS with pH value is therefore not significant enough to allow a drastic change in the intrinsic binding constant. This latter value should be considered as a mean interaction constant.

Acknowledgements

The work was included in the EC Network Of Excellence Actinet (PAA project 02-15). The financial support given for mobility measurements is gratefully acknowledged. The authors are grateful to Pr. E. Simoni and G. Lagarde (Institut de Physique Nucléaire, Orsay) to allow us to use the apparatus of TRLFS.

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Table 1: TRLFS results. Comparison between M(III)/Ac and M(III)/PAA systems.

ligand	species	Cm	Eu
		peak position of excitation spectra (in nm)	peak position of emission spectra (in nm)
	M	593.9±0.2	578.83 [23]
acetate	1:1 complex	597.3±0.2	579.04 [8]
	1:2 complex	599.5±0.2	579.27 [8]
	1:3 complex	603.2±0.2	579.55 [8]
PAA	M(III)-PAA	599.2-601.6	579.06-579.2

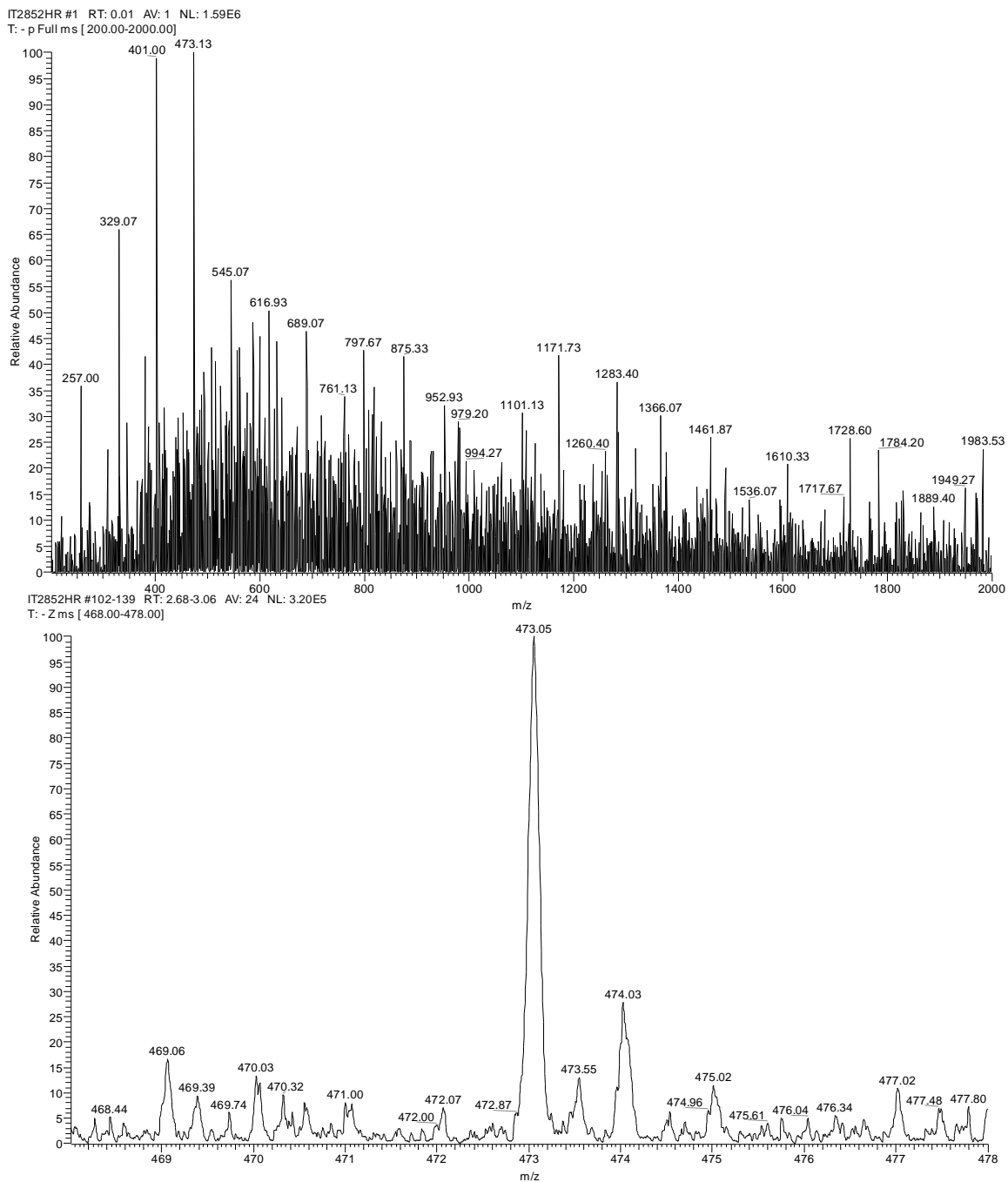


Figure 1 : ESI-MS spectrum of 5000 Da PAA at 0.25g.L^{-1} in ultrapure water recorded in negative electrospray. (A) global spectrum and (B) zoom on the peak of $m/z=473$ as a single charged peak.

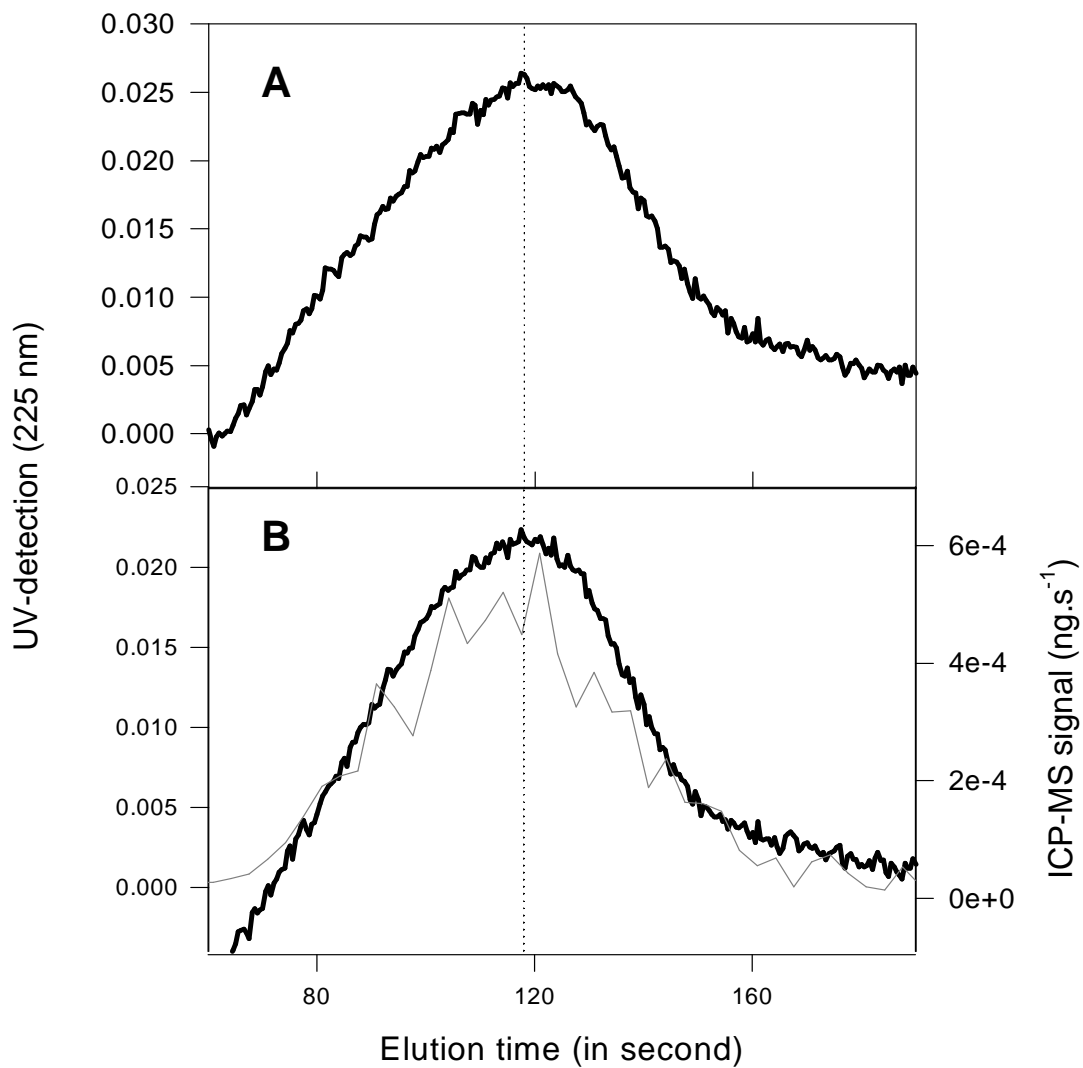


Figure 2: AsFIFFF results obtained with PAA (A) and Eu-PAA complex (B). Dark and grey lines correspond to UV- and ICP-MS fractograms, respectively. $[Eu]_{tot}=1.3 \cdot 10^{-7}$ M, (PAA)=10 $mg \cdot L^{-1}$, pH=5.

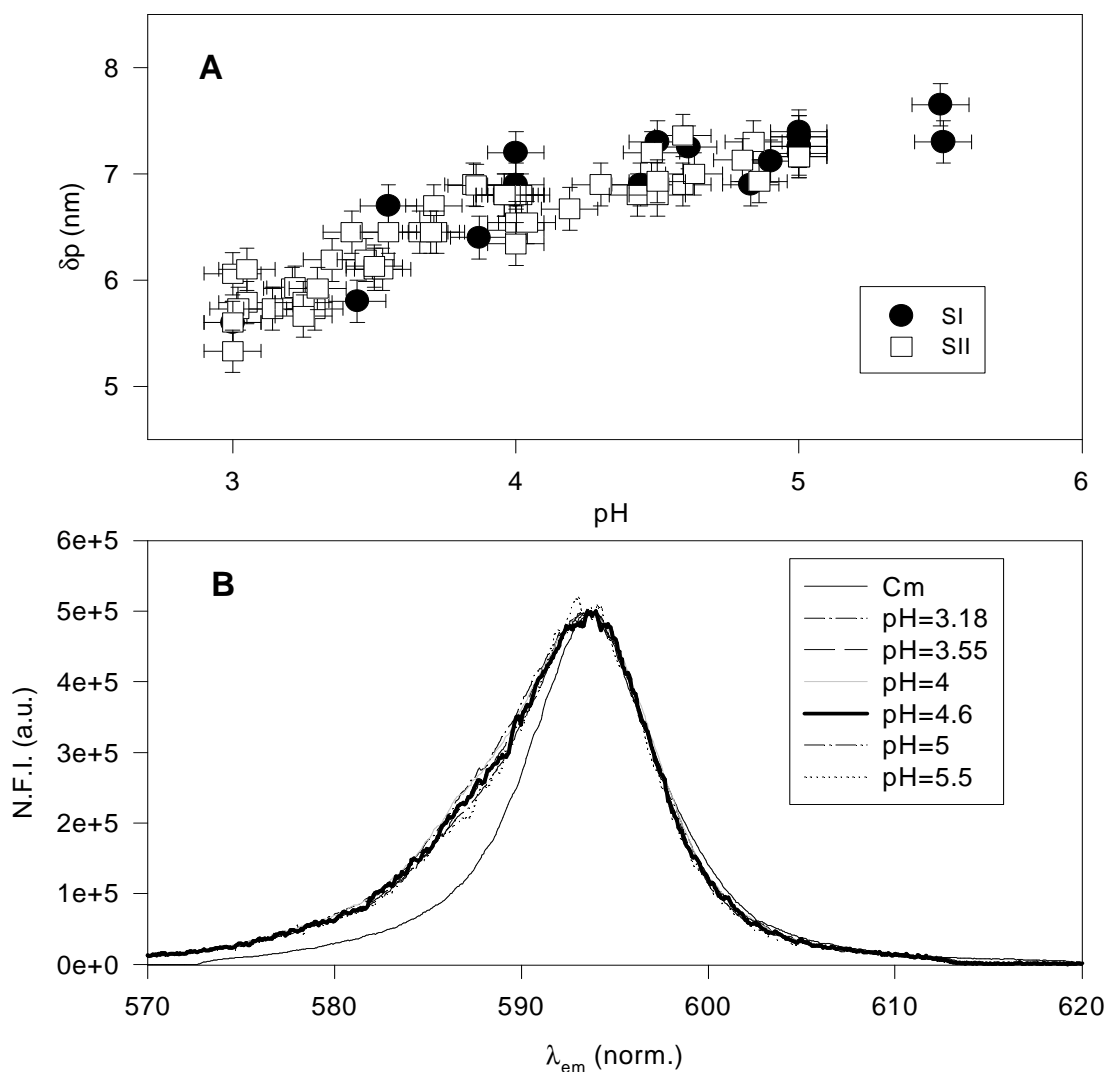


Figure 3: Emission spectra of Cm in the presence of PAA. (A) Variation of the peak position, as compared to that of free Cm, as a function of the pH for various experimental conditions (see supplementary informations). (B) Comparison of the shape of emission spectra obtained as a function of the pH with or without PAA. The spectra are normalized with respect to the peak height and peak position.

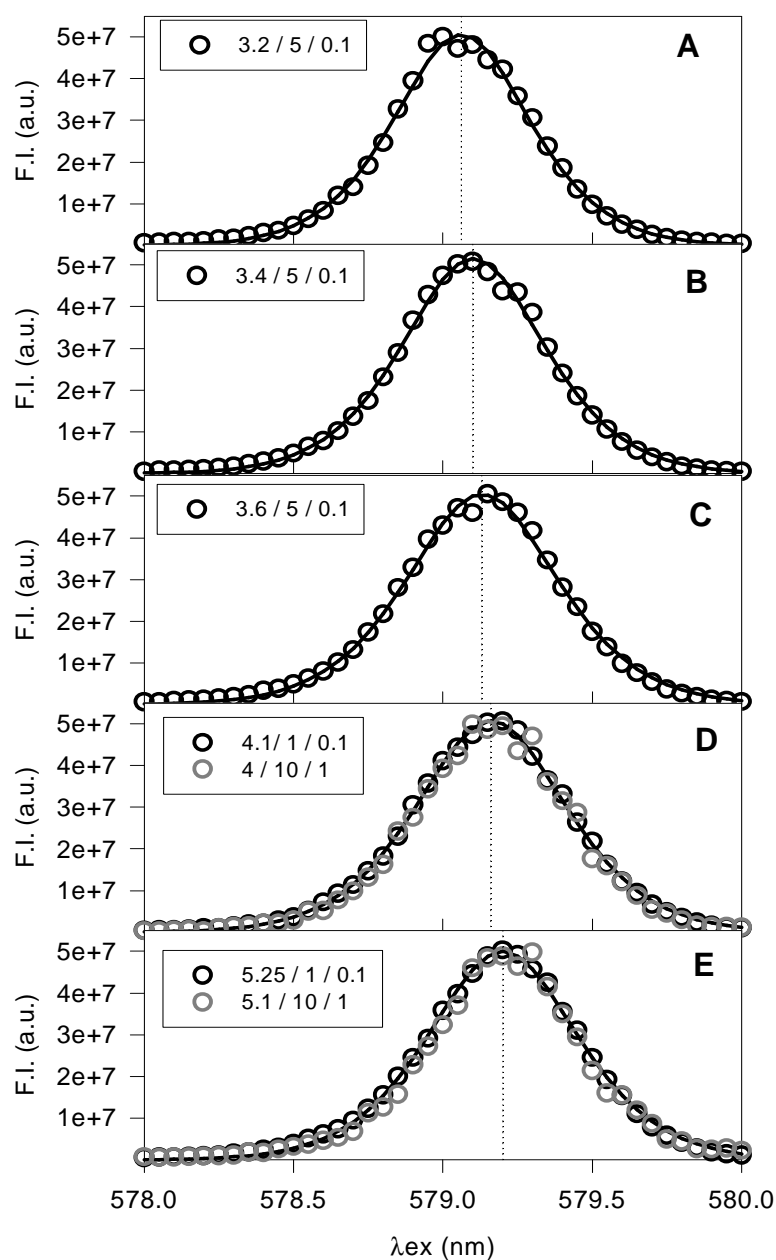
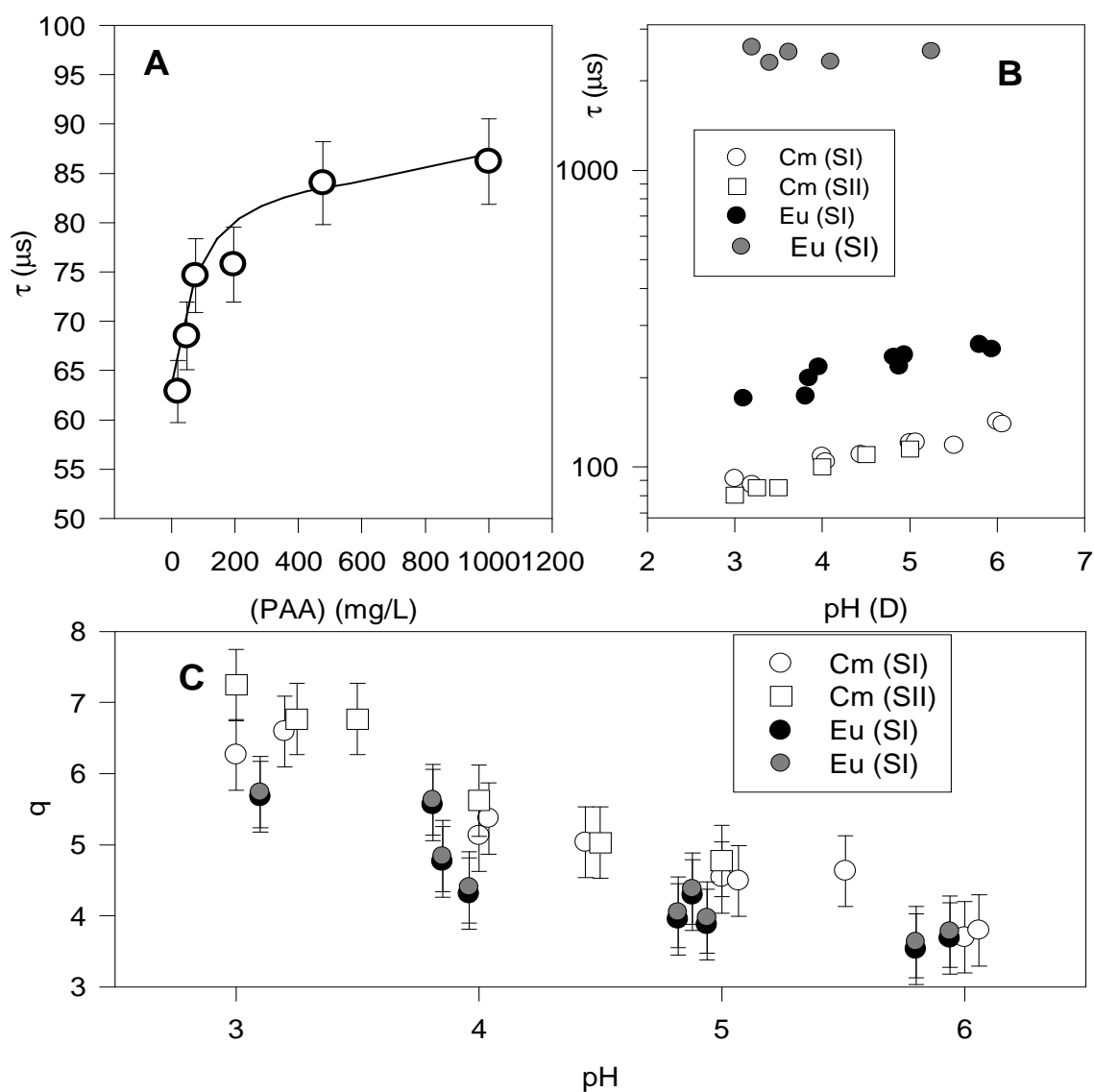


Figure 4 : Excitation spectra measured for Eu/PAA system for different experimental conditions (pH / (PAA) in $\text{g}\cdot\text{L}^{-1}$ / $[\text{Eu}]_{\text{tot}}$ (in mM)). The lines are the curves calculated according to eq. (1) considering the existence of one complexed species. (A) $w=579.06$, $L=0.37$; (B) $w=579.10$, $L=0.39$; (C) $w=579.13$, $L=0.40$; (D) $w=579.16$, $L=0.4$; (E) $w=579.20$, $L=0.4$.

Figure 5: Fluorescence decay curves. (A) An example for the determination of the decay constant for Cm-PAA obtained in series (II) experiments; pH=3.5, [Cm]= 10^{-7} M. The line corresponds to the calculation made according to eq. (2) with $\tau=87\mu\text{s}$; the species distribution (M/M(III)-PAA) is calculated with the parameters given in Figure 7. (B) Decay constants measured in D₂O (grey symbols) or H₂O (white + dark symbols) as a function of pD and pH, respectively. (C) q (number of coordinated water molecules) for the CmPAA complex using Horrocks (gray symbols) [9] or Kimura's (white + dark symbols) law [10]. The experimental conditions are given in the supplementary informations.



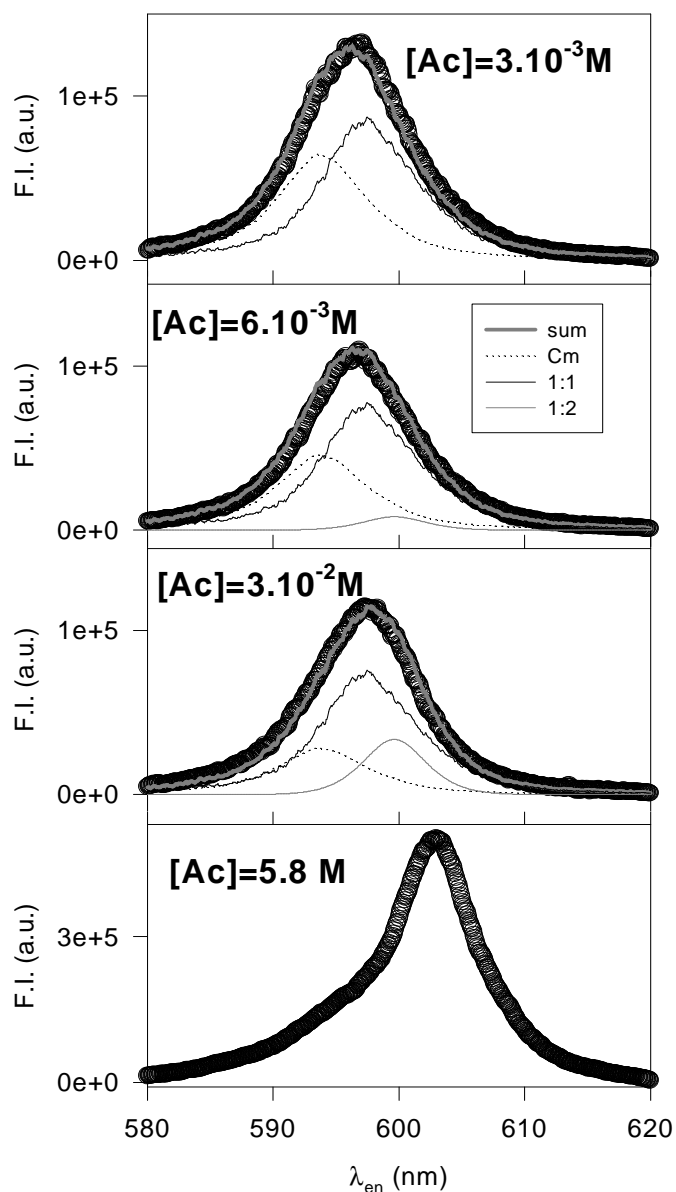


Figure 6: Emission spectra measured for Cm as a function of acetate concentration. The spectra deconvolution for $[Ac] < 0.03$ M is done considering a fluorescence intensity factor of 1 for all species with the species distribution (in %) Cm / 1:1 / 1:2 of 20 (30) / 80 (68) / 0 (2), 17 (18) / 80 (76) / 3 (6) and 12 (6) / 76 (74) / 12 (20) for $[Ac] = 0.003$, 0.006 and 0.03 M, respectively. The values in parenthesis are the calculated values with the complexation constants reported in the text.

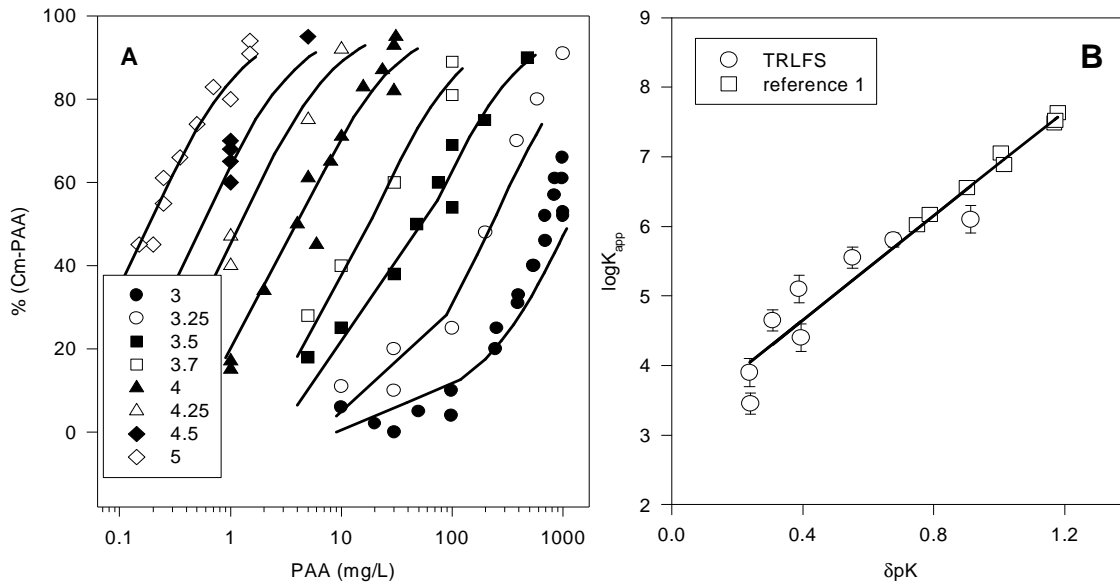


Figure 7: Complexation study for Cm/PAA system (series II) by TRLFS as a function of pH. (A) fraction of the Cm complexed by PAA (%) as a function of PAA concentration. The lines correspond to the calculation made with the apparent constants given in figure 7B. (B) Presentation of $\log K_{app}$ values obtained by TRLFS and given in [1] according to the method of Miyama et al [17].