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# The speciation of protactinium since its discovery: a nightmare or a path of resilience

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## Abstract

This review concerns the speciation of protactinium in aqueous solution under its both oxidation states +IV and +V. Emphasis is placed on experimental data obtained at trace level but also in macroscopic amount leading to the determination of thermodynamic and structural data. Thus, the complexation of Pa(V) with mineral acids and organic acids, mainly polyamino carboxylic acids (IDA, NTA, EDTA and DTPA) are highlighted and compared. The review also includes the actual knowledge about the Pa(IV) aqueous chemistry pinpointing its spectroscopic features.

## 1. Introduction

The vacant place between Th and U for ekatantalum in the table of Mendeleev was filled in 1913 thanks to the discovery of the isotope <sup>234</sup>Pa independently by Fajans, Russell and Soddy applying radioactive displacement laws to uranium [1-3]. The same year, Fajans and Göhring identified the short-lived <sup>234m</sup>Pa and proposed brevium for the name of element 91 [4]. A few years later, processing pitchblende, Hahn and Meitner, simultaneously with Soddy and Cranston confirmed the existence of Pa through the identification of an isotope of longer half-life, parent of actinium, <sup>231</sup>Pa [5,6]. Initially named protoactinium, element 91 became protactinium in 1949 [7,8]. Although the names cited above have gone down in the history of protactinium discovery, the work of Crooks in 1900 must not be forgotten: he performed for the first time the separation of uranium from its daughters but failed in the identification of <sup>234</sup>Pa [9].

The first studies devoted to the chemical properties of Pa have been conducted by von Grosse at the end of the 1920's and in the 1930's. It is noticeable that this pioneering work has highlighted two features of Pa chemistry: the importance of fluoride (Von Grosse synthesized K<sub>2</sub>PaF<sub>7</sub> for the determination of the molar mass of <sup>231</sup>Pa) and the limited analogy between Pa and Ta in particular as regards the solubility of Pa/Ta<sub>2</sub>O<sub>5</sub> [10, 11]. It is mostly thanks to the isolation of 127g of <sup>231</sup>Pa from uranium refinery residues, made available for all interested laboratories by UKAEA in 1960's, that investigations could be made on the chemical properties of this element, at solid state and in solution [12].

Solution chemistry studies conducted in 1960's and 1970's involved <sup>231</sup>Pa mainly in macro-amount but also <sup>233</sup>Pa at tracer scale. The latter can be produced either by irradiation of <sup>232</sup>Th in thermal neutron flux as well as by purification of its parent <sup>237</sup>Np. Whatever the isotope, the preparation of Pa solution requires efficient separation procedures. For that purpose, different techniques such as co-precipitation, solvent extraction, ion exchange and extraction chromatography, and volatilisation have been used with a plethora of reagents. All these studies contributed to outline the features of the aqueous chemistry of Pa and the associated experimental difficulties leading to irreproducible behaviour. Several reviews dedicated to the analytical chemistry of protactinium are available in the literature [7, 8, 13-16].

After some decades rather poor in publications, a renewed interest in Pa chemistry is observed over the last twenty years, that reflects its possible application in various areas.

As the first actinide with 5f orbitals involved in bonding, Pa chemistry is of fundamental interest for a better understanding of 5f elements, especially the interplay of 6d and 5f orbitals [17]. In addition, with many applications of different Pa isotopes come the needs of a thorough knowledge of its chemical behaviour [18]. In nuclear technology, the use of thorium-based fuels leads to the formation of <sup>233</sup>Pa as an intermediate in the production of

51 the fissile  $^{233}\text{U}$ , and to the formation of  $^{231}\text{Pa}$  as a byproduct which contributes to the long-term radiotoxicity [19].  
52 The reprocessing and waste management of spent Th-fuel should take into account the fate of protactinium:  
53 separation steps and the guaranty of safety of radwaste disposal require reliable data on Pa chemistry. The ratio  
54  $^{231}\text{Pa}/^{235}\text{U}$  is used in geochronology as radiochronometer for young samples ( $< 200\ 000$  years), and in nuclear  
55 forensics to date 10-50 years old samples of enriched uranium [20, 21]. An accurate determination of this ratio  
56 requires the isolation of each radionuclide with high yield and high purity. Finally, a medical application of  $^{230}\text{U}$   
57 has been proposed recently for targeted alpha therapy or as generator of  $^{226}\text{Th}$  [22, 23]. The production of  $^{230}\text{U}$  can  
58 involve either  $^{230}\text{Pa}$  or  $^{231}\text{Pa}$  isotopes. The isotope  $^{230}\text{Pa}$ , parent of  $^{230}\text{U}$  is produced by proton or deuteron irradiation  
59 on natural Th. This uranium isotope can also be formed by irradiation of  $^{231}\text{Pa}$  with protons or deuterons. Whatever  
60 the way of production, efficient separations of Pa-U-Th are mandatory. All these applications require a thorough  
61 knowledge of Pa chemistry, that even today, remains mysterious.

62 The present review focuses on the speciation of protactinium (IV) and (V) in aqueous solution deduced from  
63 experimental studies performed at tracer scale as well as in macroscopic amount. Tracer scale experiments involve  
64 partition or diffusion methods combined with radiometric techniques or ICP-MS, which unfortunately provide  
65 little unequivocal information on species composition. The use of additional spectroscopic techniques (UV-Vis,  
66 IR, Raman, and more recently Time Resolved Laser Fluorescence spectroscopy and X-ray absorption  
67 spectroscopy) are needed for a complete characterization of the investigated systems. Theoretical calculations, in  
68 spite of their significant contribution in the understanding of protactinium chemistry, is out the scope of the present  
69 review.

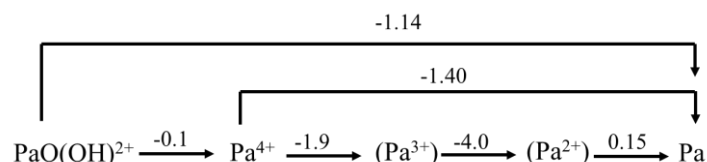
## 71 2.Redox properties

72  
73 In aqueous solution, protactinium can exist in oxidation states IV and V, the latter being the most stable like its  
74 analogs of group 5, Nb and Ta [7, 8, 24]. The first experimental determination of the standard potential  
75  $\text{Pa(V)}/\text{Pa(IV)}$  has been conducted by Fried et al. [25]. The quantitative oxidation by  $\text{Np(IV)}$  of a  $\text{Pa(IV)}$  solution  
76 obtained by dissolution of  $\text{PaCl}_4$  in deaerated 1 M HCl allowed the authors to conclude that  $E_{\text{Pa(V)}/\text{Pa(IV)}}$  is higher  
77 than  $E_{\text{Np(IV)}/\text{Np(III)}}$ , that is to say  $-0.14$  V. Moreover, the oxidation of  $\text{Pa(IV)}$  in sealed cell attributed to an oxidation  
78 by protons, has led Fried et al. to estimate  $E_{\text{Pa(V)}/\text{Pa(IV)}}$  to  $-0.1$  V/NHE. In 6 M HCl, Haissinsky et al. have conducted  
79 the reduction of  $\text{Pa(V)}$  at tracer scale using  $\text{Cr}^{2+}$  and  $\text{V}^{2+}$  [26]. The potential of the system was monitored with  
80 different ratio  $\text{Cr}^{2+}/\text{Cr}^{3+}$  and  $\text{V}^{2+}/\text{V}^{3+}$ , and the authors have estimated the apparent potential at  $-0.25$  V. Because of  
81 the uncertainty on the chemical form of the involved species and thus on the impact of acidity on the potential, the  
82 values of Fried et al. and Haissinsky et al. can only be considered as estimates.

83 Scarce direct measurements of  $\text{Pa(V)}/\text{Pa(IV)}$  potential have been performed using polarography [27-30]. One or  
84 two reduction waves have been observed, depending on the electrolyte and  $\text{Pa(V)}$  concentration; In neutral  $\text{NH}_4\text{F}$   
85 solutions, Ferreira et al. observed a variation of the half-wave potential of the first wave with fluoride  
86 concentration:  $E_{1/2}$  was found to vary between  $-1.43$  and  $-1.25$  V/SCE as fluoride concentration increased from  
87 1.02 to 7.94 M [28], but Schwochau et al. determined a single  $E_{1/2} = -1.42$  V/SCE with  $\text{NH}_4\text{F}$  ranging from 0.45  
88 to 4 M [29]. In both cases, the well-defined wave was proved to correspond to one electron transfer. In oxalate  
89 medium, Elson and Ferreira et al. observed the first wave at  $E_{1/2} = -1.75$  V/SCE [27, 28]. Whatever the electrolyte  
90 ( $\text{NH}_4\text{F}$ ,  $\text{K}_2\text{C}_2\text{O}_4$ ,  $\text{Na}_2(\text{SO}_4)$ ), this first wave has been attributed to the reduction of  $\text{Pa(V)}$  into  $\text{Pa(IV)}$  but authors  
91 disagree with regard to the reversibility of the process. The second wave has been related to catalytic reduction of  
92 protons or reduction to  $\text{Pa(III)}$ . However, the existence of this oxidation state in aqueous solution was not  
93 conclusively established.

94 The chemical reduction of  $\text{Pa(V)}$  has been performed in acidic media under Ar or  $\text{H}_2$  using several reagents:  $\text{Zn(Hg)}$   
95 [31-37],  $\text{Zn(Hg)}$  and  $\text{Cr(II)}$  [31, 38-45],  $\text{Zn(Hg)}$  and  $\text{Ti(III)}$  [38],  $\text{Zn(Hg)}$  and  $\text{Eu(II)}$  [46] and recently ronalite  
96 ( $\text{NaCH}_2\text{OHSO}_2$ ) [47]. Some authors indicated that the reduction with zinc amalgam alone is slow and does not  
97 proceed quantitatively, especially with solid amalgam and Pa at tracer scale. The use of additional reducing agent  
98 significantly improves kinetics and yield of  $\text{Pa(IV)}$  formation. The choice of reducing agent depends on the  
99 technique used for the investigation of  $\text{Pa(IV)}$  chemistry (see Part 4) in order to avoid any interference with the  
100 measured parameter.

101 Oxidation states lower than 4 have not been observed in aqueous solution. However, in chloride based melts,  
 102 Mikheev et al. described the reduction to Pa(III) and Pa(II) by cocrystallization with divalent lanthanides [48].  
 103 Standard redox potentials of each couple have been determined experimentally (Pa(V)/Pa(IV)), estimated using  
 104 stabilization/destabilization of electron configurations (Pa<sup>3+</sup>/Pa<sup>2+</sup>) or deduced from MCDF calculations of  
 105 ionization potentials [49, 50]. Figure 1 presents the Latimer's diagram of protactinium using standard potential  
 106 available in [50].  
 107



108  
 109  
 110 Figure 1: Latimer's diagram of protactinium according to [50]. In parentheses: species not found but estimation of  
 111 thermodynamic properties. Potential in V/SHE.  
 112

### 113 3. Protactinium(V)

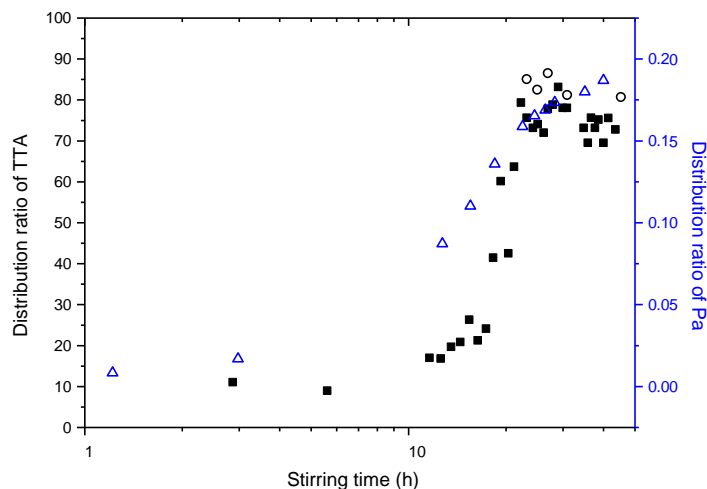
114  
 115 The main feature of Pa(V) aqueous chemistry is a strong tendency towards hydrolysis in non and low complexing  
 116 media (HClO<sub>4</sub>, HCl, HNO<sub>3</sub>) that leads to the formation of radiocolloids by condensation of monomeric hydrolysed  
 117 species, polymerisation and precipitation [7, 8, 13-15, 24]. The unstability of Pa solution is enhanced by an increase  
 118 in pH and protactinium concentration. According to Starik et al., colloids predominate at pH higher than 5 [51].  
 119 Experimentally, this unstability has been observed by a change in absorption spectra, a decrease in distribution  
 120 ratio with time, and a difference between direct and back extraction. It occurs with unpredictable induction time,  
 121 depends on the preparation method of Pa solution and also on its age. In non complexing media, stable solutions  
 122 are obtained only with Pa at tracer scale in highly acidic media. Although these conditions of concentration are  
 123 suitable for getting reliable data on Pa(V) in the absence of strong ligand, obviously a different behaviour is  
 124 expected with macroamount of Pa [7, 8, 24].

125 Another feature of Pa(V), as a result of its high sensitivity to hydrolysis, is its strong sorption on siliceous materials  
 126 (silica gel, glass, quartz). The sorption ratio reaches values as high as 90-95 % in 1-8 M HClO<sub>4</sub> and 1-10 M HNO<sub>3</sub>,  
 127 97-99% in perchlorate medium at pH = 1.8 [52]. Although plastic vials (polyethylene for example) seem more  
 128 suitable for studying Pa chemistry, glass vials have been used in solvent extraction experiments to ensure tightness  
 129 towards volatil organic solvent. In that case, walls have been chemically processed: Spitsyn et al. and Suzuki et al.  
 130 have saturated the walls of their containers with hydroxy species of protactinium leading to the formation of M-  
 131 O-Si.) [53, 54]. Silicone grease as well as « old » vials have also been used [55, 56]. More recently, surface coating  
 132 of glass walls has been performed with parylene C, a hydrophobic polymer [52, 57].  
 133

#### 134 3.1. Hydrolysis

135  
 136 The speciation of Pa(V) in non-complexing media, has been investigated mainly with Pa at tracer scale using  
 137 solvent extraction. The organic phase is either composed of beta-diketone (thenoyltrifluoroacetone-TTA,  
 138 acetylacetone-AA, dibenzoylmethane-DBM), or organophosphorous compounds (bis-(2-ethylhexyl)phosphate-  
 139 HDEHP, tributylphosphate-TBP) diluted in benzene, toluene or xylene [24]. The distribution of protactinium  
 140 between aqueous and organic phases reflects the competition between the formation of a neutral chelate or solvate  
 141 in organic phase, and hydrolysis (or complexation) in aqueous phase [58]. However, acid-base properties of beta  
 142 diketones could lead to significant amount of the anionic form in aqueous phase that can act as ligand. Some  
 143 formation constants of Pa(V) with ACA (pKa = 8.9) and TTA (pKa = 6.2) are available in the literature [59-62].  
 144 To prevent or limit these competitive reactions in aqueous phase, low concentration of extractant and pH much  
 145 lower than pKa are used. As regards the partition kinetics, it has been proved to be governed by the partition of

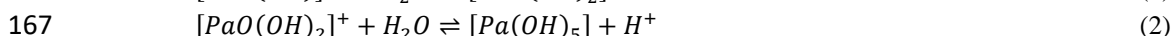
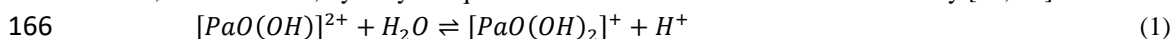
146 the extractant in the case of TTA, whatever the composition of the aqueous phase (complexing as well as non-  
 147 complexing medium) as illustrated in Figure 2.  
 148



149 Figure 2: Variation of the distribution ratio of TTA and of Pa(V) as function of the stirring time 25°C, ionic strength  
 150 3 M. Black symbols: 0.05 M TTA in toluene / 0.5 M [H<sup>+</sup>] / 0.15 M H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (■). 0.025 M TTA in toluene 0.25 M  
 151 [H<sup>+</sup>] / 5mM DTPA (○). Blue symbols: 0.05 M TTA in toluene / 0.25 M [H<sup>+</sup>] / 5mM DTPA in the presence of <sup>233</sup>Pa  
 152 (Δ).  
 153

154 Information on the ionic species of Pa(V) at tracer scale have been deduced mainly from the logarithmic variation  
 155 of the distribution ratio as function of extractant and free protons concentration. Slopes of these linear variations  
 156 allow one to determine the mean composition of the predominant species in each phase [58, 63]. The literature  
 157 tends to agree that Pa(V) predominates in the form of a 2-fold charged cation between 0.1-0.2 M and 6 M. The  
 158 less hydrolyzed form in these media should be written [PaO(OH)]<sup>2+</sup> instead of [Pa(OH)<sub>3</sub>]<sup>2+</sup>. The formulation with  
 159 one mono oxo bond has been preferred to pure hydroxo species because of an absorption band in UV domain in  
 160 the range 200-210 nm for fresh solutions of Pa ~10<sup>-5</sup> M in concentrated HClO<sub>4</sub>, also observed in other acids and  
 161 attributed to the Pa oxo bond [24, 64]. This has ruled out the formulation PaO<sub>2</sub><sup>+</sup> postulated by Welch from cation  
 162 exchange studies in perchloric acid [65]. However, this wavelength domain remains difficult to explore and  
 163 interferences with concentrated acids could occur [8].  
 164

165 Thus, at tracer scale, hydrolysis equilibria in true acidic solutions are most likely [56, 57]:



168 Writing the neutral species [Pa(OH)<sub>5</sub>] is arbitrary: it is equivalent to [PaO(OH)<sub>3</sub>] according to Rydberg's formalism  
 169 [66]. Hydrolysis constants  $K_1$  and  $K_2$  associated to equilibria (1) and (2) are shown in Table 1. The values of  $K_1^0$   
 170 and  $K_2^0$  extrapolated at zero ionic strength have been compared with standard data relative to other actinides  
 171 at different oxidation state available in OCDE-NEA data base [67, 68]. The first hydrolysis constant of Pa(V),  $K_1^0$  is  
 172 closer to those of An(IV) than of An(V). But the validity of such a comparison is questionable since Pa(V) species  
 173 is already hydrolyzed. A comparison with actinide aquo ions should involve an equilibrium between PaO<sup>3+</sup> and  
 174 [PaO(OH)]<sup>2+</sup> for which there is no available data in aqueous solution.

175 Both hydrolysis equilibria of Pa(V) have been found endothermic, with standard enthalpy variation of 5 kJ mol<sup>-1</sup>  
 176 and ~60 kJ mol<sup>-1</sup> for equilibria (1) and (2) respectively. No significant entropy variation has been associated to the  
 177 first hydrolysis equilibrium, whereas a moderate entropic contribution (around 80 J K<sup>-1</sup>mol<sup>-1</sup>) seems to be involved  
 178 in the second hydrolysis equilibrium [67]. Data about the temperature dependence on the hydrolysis of actinides  
 179 are rather scarce. The first hydrolysis of U<sup>4+</sup>, Pu<sup>4+</sup>, and PuO<sub>2</sub><sup>2+</sup> is also endothermic but with high entropic  
 180 contribution in the case of tetravalent actinides (> 100 J K<sup>-1</sup>mol<sup>-1</sup>). Obviously the hydrolysis of Pa(V) is not  
 181 comparable to that of other actinides.  
 182

183

Table 1: Hydrolysis constants of Pa(V) at 25°C (molal unit)

Medium and ionic strength (molal unit)	$[PaO(OH)]^{2+} + H_2O \rightleftharpoons [PaO(OH)_2]^+ + H^+$	$[PaO(OH)_2]^+ + H_2O \rightleftharpoons [Pa(OH)_5] + H^+$	Ref.
3.5 m (Li,H)ClO <sub>4</sub>	$-0.89 \pm 0.33$		[56]
3.5 m (Li,H)ClO <sub>4</sub>		$-4.7 \pm 0.4$	[69]
3.5 m (Li,H)ClO <sub>4</sub>		$-5.5$	[70]
6.6 m (Na,H)ClO <sub>4</sub>		$-5 \pm 1$	[71]
0.1 m (Na,H)ClO <sub>4</sub>	$-1.5 \pm 0.2$	$-7.0 \pm 0.3$	[57]
0.51 m (Na,H)ClO <sub>4</sub>	$-1.6 \pm 0.2$	$-6.9 \pm 0.6$	[52]
1.05 m (Na,H)ClO <sub>4</sub>	$-1.7 \pm 0.2$	$-6.9 \pm 0.6$	[57]
3.52 m (Na,H)ClO <sub>4</sub>	$-2.0 \pm 0.15$	$-5.8 \pm 0.3$	[57]

184

185 Literature devoted to the behaviour of Pa(V) in alkaline medium is rather scarce. The formation of an anionic  
 186 species was deduced from paper and anion exchange chromatography on samples prepared by alkaline fusion and  
 187 solubilisation of a small fraction of the melt in water [72, 73]. Using DBM in successive direct and back extractions  
 188 of Pa from aqueous solutions with  $7 < \text{pH} < 11.04$ , Guillaumont confirmed the existence of a protactinate ion that  
 189 should bear a charge  $-1$  and correspond to  $[Pa(OH)_6]^-$  [74]. No stability constant could be determined.

190

### 191 3.2. Complexation thermodynamics and structural information of known Pa(V) complexes: fluoride, 192 sulfate and oxalate

193

194 The complexation of Pa(V) in hydrofluoric, sulfuric and oxalic solutions have been investigated at tracer scale and  
 195 millimolar scale allowing the determination of both thermodynamic and structural data. Various techniques have  
 196 been used in this way with mainly solvent extraction and ion exchange at tracer scale, but also potentiometry,  
 197 conductimetry and spectrophotometry at higher concentration [7, 24, 75]. Structural data were often obtained by a  
 198 combination of X-ray absorption spectroscopy and theoretical calculations. In that case, the concentration of  
 199 protactinium needs to be increased (mM scale) and thus, only complexes with higher stoichiometry could be  
 200 studied. Because the behaviour of Pa(V) in those media has now already been extensively related, the known data  
 201 will be briefly summarized and compared according to the media.

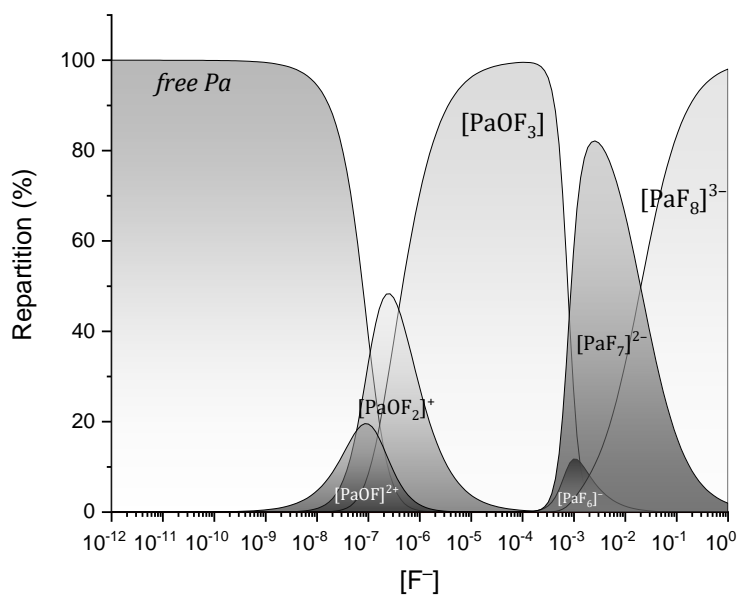
202

#### 203 3.2.1. Thermodynamic aspects

204 Fluoride, and sulfate or hydrogenosulfate media are among the most commonly used complexing media for the  
 205 study of protactinium in solution. Indeed, their complexing power allows to stabilize the protactinium at the + V  
 206 oxidation state and to ensure a reproducibility of the results. Thus, a high solubility of Pa(V) is observed in  
 207 hydrofluoric and sulfuric acids, and the complexes formed possess the highest stability in solution. However,  
 208 different behaviours are observed with each medium, leading to either the formation of oxo and  
 209 hydroxocomplexes, or the absence of oxo complexes. In each case, the protactinium speciation can be described  
 210 by two parameters, pH and ligands concentration.

211 In fluoride media, several species can occur in solution according to the pH and the fluorine content. However, the  
 212 widest range is observed for  $[PaF_7]^{2-}$ . Thus, complexes of stoichiometry from 1:1 to 1:8 are expected, with  
 213 homoleptic complexes from 1:5 to 1:8 and oxo/hydroxo complexes at lower stoichiometry.  $[PaF_7]^{2-}$  is present in  
 214 solution when HF concentration is between  $10^{-3}$  M and 4-8 M, whereas  $[PaF_8]^{3-}$  appears in highly concentrated  
 215 fluoride medium ( $> 0.5$  M) but at low acid conditions ( $10^{-7}$  M  $< [H^+] < 10^{-2}$  M) [76]. Otherwise, at hydrofluoric  
 216 acid concentration lower than  $10^{-3}$  M, oxo and hydroxyfluoro complexes become predominant [24]. The figure 3  
 217 depicts the distribution diagram of Pa(V)-fluoride species. It is worth noting the missing species  $[PaF_4]^+$  and  
 218  $[PaOF_4]^-$ . These species have never been detected experimentally. Recent theoretical calculations performed to  
 219 attempt in elucidating this missing suggest that  $[PaF_4]^+$  is more stable than  $[PaOF_4]^-$  [76]. However, it seems that  
 220  $[PaF_4]^+$  reacts with one water molecule present in the first hydration sphere to form  $[PaF_4OH]$ .

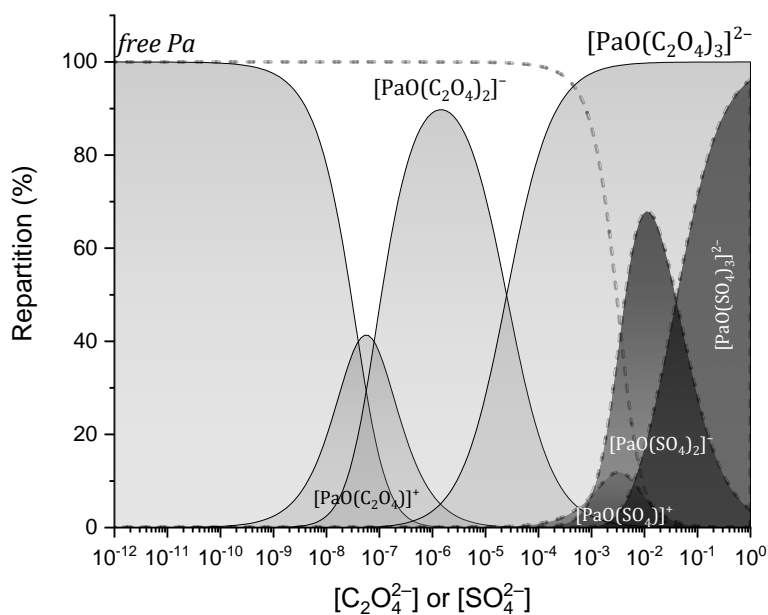
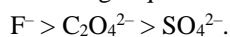
221



222  
 223 Figure 3: Distribution diagram of Pa-fluoride species at  $I = 3$  M. The species  $[\text{PaF}_4]^+$  and  $[\text{PaOF}_4]^-$  have never  
 224 been detected experimentally.  $[\text{PaF}_5]$  is a minor species ( $< 0.5\%$ ).  
 225

226 In oxalic medium, literature is scarcer and more controversial. Various complexes, from 1:1 to 1:4 were observed  
 227 with and without mono-oxo or/and hydroxyl groups. However, the corresponding formation constants are not  
 228 always correlated to a suitable equilibrium [24]. Only, the first two complexation constants are consistent between  
 229 all studies. More recently, three oxalate complexes were determined with their stability constants, leading in each  
 230 case to the presence of the mono oxo bond:  $[\text{PaO}(\text{C}_2\text{O}_4)]^+$ ,  $[\text{PaO}(\text{C}_2\text{O}_4)_2]^-$  and  $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{2-}$  [77].

231 In sulfuric medium, the presence of this mono-oxo bond was also identified in complexes of stoichiometry 1:1 to  
 232 1:3. The associated formation constants have been determined at different values of ionic strength and temperature.  
 233 [24, 78, 79]. In the Figure 4 are merged the speciation diagram of Pa(V)- oxalate and sulfate species. It highlights  
 234 the relative strength of both ligands. According to Table 2, the relative capability of these three ligands to form  
 235 complexes with Pa(V) varies according to the following sequence:



237  
 238 Figure 4: Speciation diagram of Pa(V)- oxalate and sulfate species at  $I = 1-3$  M. Remark: the two repartitions are  
 239 independent, i.e. they have been merged to highlight the difference of strength between ligands.

240  
241

Table 2: Complexation constants of fluoro-, oxalato- and sulfato-complexes of Pa(V) at 25°C  
(ligand in totally deprotonated form)

Complex (Ionic strength)	Proposed complex	Formation constant
Fluoro-complexes (3 M) [56]		
	$[\text{PaOF}]^{2+}$	$\log \beta_1 = 6.70$
	$[\text{PaOF}_2]^+$	$\log \beta_2 = 13.93 \pm 0.10$
	$[\text{PaOF}_3]$	$\log \beta_3 = 20.34 \pm 0.20$
Fluoro-complexes (1 M) [76]		
	$[\text{Pa}(\text{OH})_x\text{F}]^{(4-x)+}$	$\log \beta_1 = 5.4 \pm 0.5$
	$[\text{Pa}(\text{OH})_x\text{F}_2]^{(3-x)+}$	$\log \beta_2 = 10.4 \pm 1.0$
	$[\text{Pa}(\text{OH})_x\text{F}_3]^{(2-x)+}$	$\log \beta_3 = 15.3 \pm 1.4$
	-	$\log \beta_4 = 20.1 \pm 1.7$
	$[\text{PaF}_5]$	$\log \beta_5 = 24.6 \pm 1.9$
	$[\text{PaF}_6]^-$	$\log \beta_6 = 29.0 \pm 2.1$
	$[\text{PaF}_7]^{2-}$	$\log \beta_7 = 32.7 \pm 2.3$
	$[\text{PaF}_8]^{3-}$	$\log \beta_8 = 34.4 \pm 2.8$
Oxalato-complexes (3 M) [77]		
	$[\text{PaO}(\text{C}_2\text{O}_4)]^+$	$\log \beta_1 = 7.4 \pm 0.3$
	$[\text{PaO}(\text{C}_2\text{O}_4)_2]^-$	$\log \beta_2 = 14.5 \pm 0.8$
	$[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$	$\log \beta_3 = 19.1 \pm 0.7$
Sulfato-complex (1 M) [78]		
	$[\text{PaO}(\text{SO}_4)]^+$	$\log \beta_1 = 1.9 \pm 0.2$
	$[\text{Pa}(\text{SO}_4)_2]^-$	$\log \beta_2 = 4.9 \pm 0.5$
	$[\text{Pa}(\text{SO}_4)_3]^{3-}$	$\log \beta_3 = 6.3 \pm 0.3$

242

### 243 3.2.2. Structural data

244 The presence or not of the mono-oxo bond in the protactinium(V) complexes has been verified mainly in  
245 complexes with higher stoichiometry, using X-ray absorption spectroscopy at the Pa L<sub>III</sub> edge [77, 80, 81]. This  
246 technique is suitable to determine the local structure of actinide in solution, however presents some limitation,  
247 especially using protactinium. Unlike other actinides, the XANES at the L<sub>III</sub> edge does not allow to distinguish  
248 complexes with a mono-oxo bond from a complex that does not possess one, due to the absence of the characteristic  
249 linear transdioxo moiety for Pa(V) compared to other An(V). Thus, the speciation can only be determined from  
250 EXAFS measurements, which required the use of protactinium in macro-concentration increasing polymerization  
251 phenomenon if the complexation is not strong enough. For these reasons, the experimental structural studies of  
252 Pa(V) complexes in solution are rather scarce. Despite these limitations, EXAFS experiments have been conducted  
253 in HF, H<sub>2</sub>SO<sub>4</sub> and oxalic media [77, 80, 81]. For instance,  $[\text{PaF}_7]^{2-}$  has been characterized by an EXAFS spectrum  
254 depicting a monotonic sinusoidal signal that features a single contribution from seven fluoride ligands located at  
255 2.15 Å. For both oxalic and sulfuric medium, EXAFS spectra indicated the presence of a short mono-oxo bond at  
256 1.75 and 1.72 Å. The structure of the  $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$  has been proposed as a complex with three oxalates  
257 coordinated to Pa in a bidentate fashion (side-on arrangement) [77]. Unlike the oxalate complex, the structure of  
258 the sulfate complex remains uncertain but the protactinium seems to be coordinated to sulfates in both monodentate  
259 and bidentate fashion [80].

260

### 261 3.3 Complexation with polyamino carboxylic acids

262

263 Polyaminocarboxylic acids (PACs) are composed of several nitrogen and oxygen atoms connected to two or more  
264 carboxyl groups. Because of their chelating properties, these ligands form strong complexes with metals including  
265 actinides. The speciation of PACs depends strongly on the acidity. For example, DTPA is involved in 8 acid  
266 dissociation equilibria starting from  $[\text{H}_8\text{DTPA}]^{3+}$ . The lack of knowledge of the dissociation constants of PACs at  
267 different values of ionic strength and temperature complicates the identification of complexes (protonation state)  
268 and may affect the accuracy of complexation constants.



269 Literature data about the complexation of protactinium(V) with aminopolycarboxylic acids are rather scarce. Until  
 270 now, only five studies have been dedicated to four of them (Figure 5): ethylenediaminetetraacetic acid (EDTA),  
 271 diethylenetriaminepentaacetic acid (DTPA), nitrilotriacetic acid (NTA) and iminodiacetic acid (IDA) [82-86]. In  
 272 all studies, the Pa(V) complexation has been studied at tracer scale ( $C_{Pa} < 10^{-8}$  M) using mainly solvent extraction  
 273 and/or ion exchange.  
 274

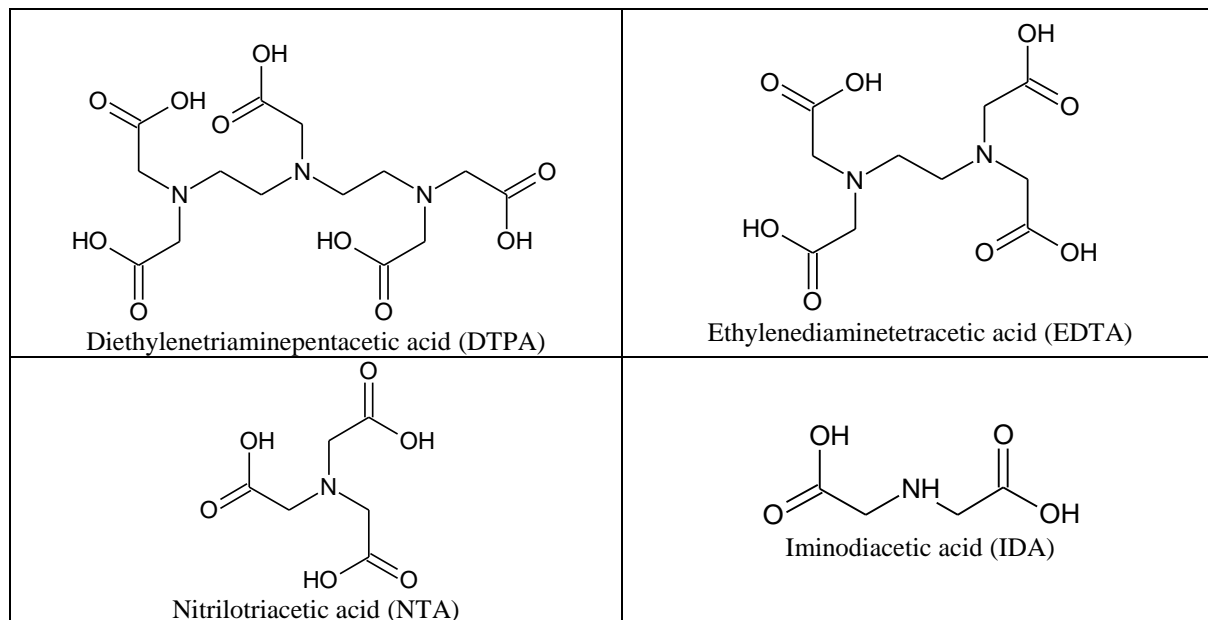


Figure 5: Polyaminocarboxylic acids used as complexing agents of Pa(V)

275  
 276  
 277

### EDTA

278 From cation and anion exchange chromatography experiments in batch mode, Galateanu concluded that Pa(V)  
 279 forms complex of stoichiometry 1:1 with EDTA. Despite of the narrow range of pH used (2.4-2.7), different  
 280 complexes according to different protonation states have been proposed: cationic, anionic and neutral, but no  
 281 associated constant. In contrast, Shiokawa et al. and Ishibashi et al. deduced quantitative information from solvent  
 282 extraction experiments from HCl, resp. HClO<sub>4</sub> with TTA in benzene, resp. xylene [83, 84]. In both cases, the  
 283 speciation of Pa(V) in absence of ligand is questionable: on one side, [Pa(OH)<sub>2</sub>]<sup>3+</sup> and on the other side a mixture  
 284 of [PaO(OH)]<sup>2+</sup> and [PaO(OH)<sub>3</sub>], a speciation that is, considering the pH used, not consistent with the hydrolysis  
 285 constants available in the literature. Concerning the complex, Ishibashi et al. proposed the formulation  
 286 [PaO(OH)(EDTA)]<sup>2-</sup> but did not exclude the non hydrolyzed species [PaO(EDTA)] and [Pa(EDTA)]. Despite a  
 287 discrepancy in the speciation, the stability constant obtained in both studies are very close:  $\log \beta = 22.1 \pm 0.1$  and  
 288  $21.54 \pm 0.03$ , considering the totally deprotonated form of EDTA. This confirms a strong complexation between  
 289 Pa(V) and EDTA.

290

### DTPA

292 Compared to EDTA, DTPA possesses one additionnel amine group and two additional carboxylic groups (Figure  
 293 4). Mendes et al. have studied the complexation of Pa(V) with DTPA combining solvent extraction and capillary  
 294 electrophoresis coupled to ICP-MS (CE-ICP-MS) at tracer scale [85]. From solvent extraction experiments  
 295 performed at constant ionic strength (0.1-3 M) and temperature (25-50 °C), they deduced the formation of a 1:1  
 296 complex in presence of DTPA. The authors also used CE-ICP-MS to determine the mean charge of the complex  
 297 of maximum stoichiometry and thus demonstrated the formation of a neutral complex. The use of DFT calculations  
 298 reduced the possibility to either [Pa(DTPA)], or [PaO(H<sub>2</sub>DTPA)], as the complex formula. Mendes et al. proposed  
 299 the stability constant  $\log \beta = 25.34 \pm 0.12$  for the following equilibrium, at 25°C and with an ionic strength equal  
 300 to 1 M (Na,H)ClO<sub>4</sub>.



302 However, the technique used does not allow one to preclude the presence of the oxo bond corresponding to the  
 303 formulation [PaO(H<sub>2</sub>DTPA)].

304

305 **NTA**

306 Compared to DTPA and EDTA, NTA is a smaller ligand that presents only one amine function with three  
 307 carboxylates groups, however NTA is known for still being a good chelating agent. A thermodynamic study has  
 308 been performed recently on the complexation of Pa(V) with NTA using solvent extraction at tracer scale and CE-  
 309 ICP-MS [86]. Luchini et al., observed with this smaller ligand not only the 1:1 complex but also the 1:2. Coupling  
 310 this result to the study of the mean charge of the complex of maximum stoichiometry obtained by CE-ICP-MS,  
 311 they could propose the successive complexes as [PaO(NTA)] and [PaO(NTA)<sub>2</sub>]<sup>3-</sup> with stability constants of 15.16  
 312 ± 0.06 and 28.46 ± 0.06, respectively.

313

314 **IDA**

315 The iminodiacetic acid is the smallest aminopolycarboxylic ligand that has been investigated with Pa(V). Its  
 316 structure differs from that of the NTA molecule only by the substitution of a carboxylic function by a hydrogen  
 317 atom. Like NTA, the maximum stoichiometry of the complexes deduced from partition data with Pa at tracer scale  
 318 was found equal 2 [87]. As expected, the associated stability constants were smaller than for NTA (Table 3).

319

320

Table 3: Complex formation constant of Pa(V) with aminopolycarboxylic acids

Equilibrium	log β <sub>i</sub>	conditions	Ref.
$[PaO(OH)]^{2+} + DTPA^{5-} + 3H^+ \rightleftharpoons "[Pa - DTPA]"$	log β = 25.34 ± 0.12	I = 1 M (Na, H)ClO <sub>4</sub> , T = 25°C	[85]
$[PaO(OH)]^{2+} + EDTA^{4-} \rightleftharpoons "[Pa - (EDTA)]"$	log β = 22.1 ± 0.1	I = 1 M (Na,H)Cl, T = 25°C	[83]
$[PaO(OH)]^{2+} + EDTA^{4-} \rightleftharpoons [PaO(OH)(EDTA)]^{2-} + 2H_2O$	log β = 21.54 ± 0.03	I = 1 M HClO <sub>4</sub> , T = 25°C	[84]
$[PaO(OH)]^{2+} + NTA^{3-} + H^+ \rightleftharpoons [PaO(NTA)] + 2H_2O$	log β <sub>1</sub> = 15.16 ± 0.06	I = 1 M (Na, H)ClO <sub>4</sub> , T = 25°C	[86]
$[PaO(OH)]^{2+} + 2NTA^{3-} + H^+ \rightleftharpoons [PaO(NTA)_2]^{3-} + H_2O$	log β <sub>2</sub> = 28.46 ± 0.06		
$[PaO(OH)]^{2+} + IDA^{2-} + H^+ \rightleftharpoons [PaO(IDA)]^+ + H_2O$	log β <sub>1</sub> = 10.11 ± 0.07	I = 1 M (Na, H)ClO <sub>4</sub> , T = 25°C	[87]
$[PaO(OH)]^{2+} + 2IDA^{2-} + H^+ \rightleftharpoons [PaO(IDA)_2]^- + H_2O$	log β <sub>2</sub> = 19.17 ± 0.15		

321

322 The values of the complex formation constants of Pa(V) with the different aminopolycarboxylic acids decreases  
 323 with the size and the number of chelating groups. Thus, as expected, Pa(V)-DTPA form a more stable complex  
 324 than Pa(V)-EDTA, Pa(V)-NTA and Pa(V)-IDA. Moreover, in presence of the smallest ligands (NTA and IDA),  
 325 the complex of maximum stoichiometry 1:2 can also be formed. Until now, no experimental structural data have  
 326 confirmed the speciation proposed for those complexes. Speciation techniques, such as EXAFS or FTIR combined  
 327 to theoretical calculations would lead to verify those equilibria.

328

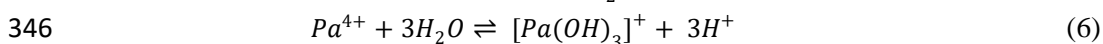
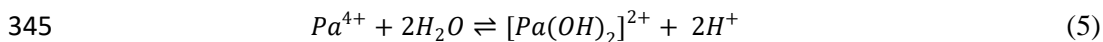
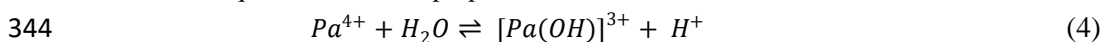
329 **4.Protactinium(IV)**

330

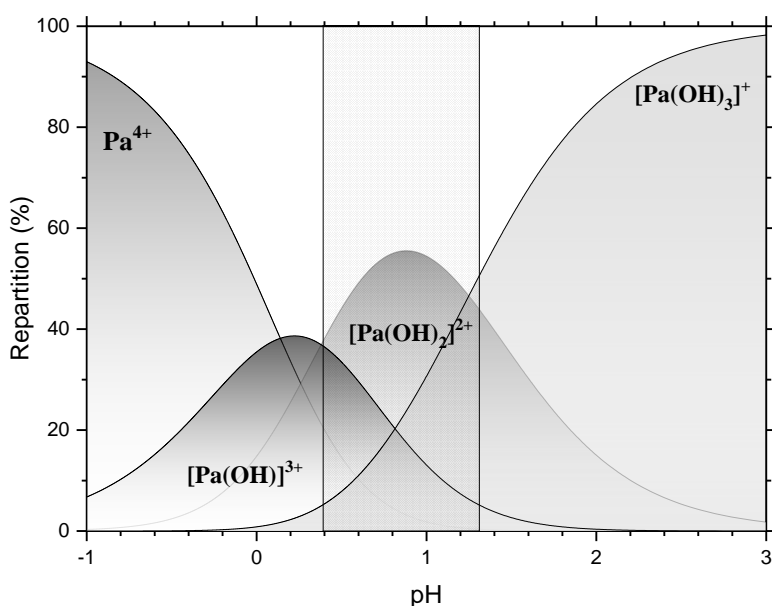
331 Studying the chemical properties of Pa(IV) in aqueous solutions represents a great challenge because of unstability  
 332 of this oxidation state. Oxidation to Pa(V) occurs more or less rapidly and like other actinides (IV), its high  
 333 reactivity results in strong tendency to precipitation for example with fluoride or phosphate. In most of the studies,  
 334 Pa(IV) has been prepared by chemical reduction of Pa(V) under inert atmosphere leading sometimes to interference  
 335 with the property investigated. In solvent extraction experiments involving Pa at tracer scale, the reducing agent  
 336 Cr(II) has been found to be co-extracted with Pa in the TTA-benzene phase [41, 42, 44], but the formation of the  
 337 complexes between Cr and extractant can be limited by a judicious choice of pH and extractant concentration. No  
 338 impact of Eu or Ti(III) has been observed [38, 46]. With Pa at millimolar scale, the presence of chloro complexes

339 of  $\text{Hg}^{2+}$  or  $\text{Zn}^{2+}$ , as well as rongalite, a powerful reducing agent used recently interfere with UV absorption bands  
 340 of Pa(IV), but fortunately not with fluorescence emission.

341 Only one publication provides quantitative information on Pa(IV) hydrolysis at tracer scale [41]. According to  
 342 Guillaumont, the aquo ion  $\text{Pa}^{4+}$  would predominate for protons concentration higher than 3 M. The following  
 343 successive equilibria were then proposed:



347 characterized by  $\log \beta_1 = -0.14$ ,  $\log \beta_2 = -0.52$  and  $\log \beta_3 = -1.77$ . Since species differing from water molecules  
 348 cannot be distinguished, the species  $[\text{Pa}(\text{OH})_2]^{2+}$  and  $[\text{Pa}(\text{OH})_3]^+$  are equivalent to  $\text{PaO}^{2+}$  and  $[\text{PaO}(\text{OH})]^+$ . The  
 349 corresponding speciation diagram is illustrated in Figure 6.



350  
 351 Figure 6: Distribution diagram of hydrolyzed species of Pa(IV) at tracer scale using data in [41]. The box area  
 352 represents the predominance of  $[\text{Pa}(\text{OH})_2]^{2+}$  according to Mitsuji [43].  
 353

354 In non complexing media, polymerisation of Pa(IV) has been found to occur as soon as Pa concentration reaches  
 355  $10^{-6}$  M. Due to the low solubility of Pa(IV) in perchloric media, UV-Vis spectrum has been registered on sample  
 356 prepared by dissolution of  $\text{PaCl}_4$  in  $\text{HClO}_4$  [89]. Three bands have been observed at 225, 256 and 277 nm in 1.5  
 357 M  $\text{HClO}_4$  ( $C_{\text{Pa}} = 1.1 \cdot 10^{-3}$  M).

358 In 3 M  $\text{HClO}_4/\text{HCl}$  mixture and with Pa at tracer scale, the existence of complexes of stoichiometry 1:1 and 1:2  
 359 have been deduced from solvent extraction data [56]. The related constants are presented Table 4. In concentrated  
 360 HCl, the complex  $[\text{PaCl}_6]^{2-}$  should be formed according to Muxart et al. However, this is in contradiction with the  
 361 results of Pluchet et al. deduced from anion exchange chromatography experiments performed in concentrated  
 362 HCl (6-12 M) [39]. Changes in UV-Vis absorption spectra with HCl concentration have been attributed to the  
 363 formation of chloro complexes corresponding to the general formula  $[\text{PaCl}_x]^{(4-x)}$  without any information about the  
 364 maximum value of  $x$ . Moreover, spectra depend on the preparation method of Pa(IV). The presence of chloro  
 365 complexes of  $\text{Zn}^{2+}$  or  $\text{Hg}^{2+}$  [36, 90] might interfere with the absorption band of Pa(IV) at the lowest wavelength.  
 366 This interference is not observed in samples prepared by dissolution of  $\text{PaCl}_4$  [36, 89].

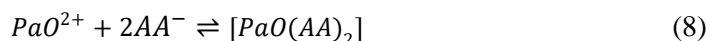
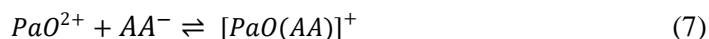
367 In presence of sulphate species, Pa(IV) forms complexes of stoichiometry 1:1 and 1:2 in the form  $[\text{Pa}(\text{SO}_4)_x]^{(5-2x)}$   
 368 in strong acidic medium (3 M). Only a complex of stoichiometry 1:1 containing hydroxo group has been observed  
 369 at higher pH (Table 4). Absorption spectra are characterized by three bands whose position varies slightly with  
 370 sulphuric acid and free sulphate concentration. For example, absorption maxima are observed at 232.5, 265 and  
 371 287.5 nm in 1.4-4 M  $\text{H}_2\text{SO}_4$ , and at 237, 273 and 297 nm in 9 M  $\text{H}_2\text{SO}_4$  [24, 34, 90].

372 At tracer scale, the fluoro-complexes  $[PaF]^{3+}$  and  $[PaF_2]^{2+}$  have been proposed by Guillaumont in  $HClO_4$  3 M and  
 373 fluoride concentration lower than  $10^{-6}$  M. The very low solubility of  $PaF_4$  hinders the study of successive  
 374 complexation and thus the characterization of complexes of higher stoichiometry using solvent extraction.  
 375 However, solubility of  $PaF_4$  (2 mM) in ammonium fluoride and tetramethylammonium fluoride has been observed  
 376 allowing absorption spectra to be registered [35, 91]. As compared to spectra in other mineral acids, spectra of  
 377 Pa(IV) in fluoride media display only two well-defined absorption bands at 250 and 352.5 nm in 15 M  $NH_4F$ , the  
 378 third being a shoulder at around 220 nm [91]. These bands are observed at 323 and 344, with the shoulder at 230  
 379 nm in  $(CH_3)_4NF$ . The band at the highest wavelength may correspond the the species  $[PaF_8]^{4-}$ .

380  
 381 Table 4: Formation constants of Pa(IV) complexes deduced from solvent extraction experiments with Pa at tracer  
 382 scale

Conditions	Equilibrium	Constant	Ref.
Chloride			
HClO <sub>4</sub> 3 M	$Pa^{4+} + HCl \rightleftharpoons [PaCl]^{3+} + H^+$	$\log \beta_1 < 0$	[56]
	$Pa^{4+} + 2HCl \rightleftharpoons [PaCl_2]^{2+} + 2H^+$	$\log \beta_1 = 0$	
Sulphate			
HClO <sub>4</sub> 3 M	$Pa^{4+} + HSO_4^- \rightleftharpoons [PaSO_4]^{2+} + H^+$	$\log \beta_1 = 1.6$	[56, 69]
	$Pa^{4+} + 2HSO_4^- \rightleftharpoons [Pa(SO_4)_2] + 2H^+$	$\log \beta_2 = 2.2$	
0.5 M, 10°C, pH 0.4-1.1	$[Pa(OH)_2]^{2+} + HSO_4^- \rightleftharpoons [Pa(OH)SO_4]^+ + H_2O$	$\log \beta = 2.5$	[43]
(Na,H)ClO <sub>4</sub> , pH 0.6-2.7	$[Pa(OH)_2]^{2+} + HSO_4^- \rightleftharpoons [Pa(OH)SO_4]^+ + H_2O$	$\log \beta = 2.8 \pm 0.1$	[92]
Fluoride			
HClO <sub>4</sub> 3 M	$Pa^{4+} + HF \rightleftharpoons [PaF]^{3+} + H^+$	$\log \beta_1 = 4.7$	[56]
	$Pa^{4+} + 2HF \rightleftharpoons [PaF_2]^{2+} + 2H^+$	$\log \beta_2 = 8.3$	

383  
 384 Studies of the complexation of Pa(IV) with chelating agents used as extractants have been performed only with  
 385 the element at tracer scale [45, 92-94]. Surprisingly, the extraction mechanism has been proved to depend on the  
 386  $\beta$ -diketone: Pa(IV) is extracted with 4 TTA and 4 BA (benzoylacetone) molecules and only 2 AA molecules from  
 387 (Li or Na, H)ClO<sub>4</sub> aqueous solutions [42, 45, 93]. Lundqvist, considering Pa(IV) in the form of  $PaO^{2+}$  (equivalent  
 388 to  $[Pa(OH)_2]^{2+}$ ) as predominant species in aqueous phase, determined the constants associated to the following  
 389 equilibria:



392 with  $\log \log \beta_1 = 6.1$  (Eq. 7) and  $\log \beta_2 = 13.15 \pm 0.13$  (Eq. 8) [45].

393 In their study of the complexation of Pa(IV) with EDTA in the system AA/Benzene/(Na,H)ClO<sub>4</sub>, Lundqvist et al.  
 394 have shown the formation of complexes of 1:1 stoichiometry with different protonation states. The complexation  
 395 constant of  $PaO^{2+}$  with EDTA (totally deprotonated form) was found equal  $10^{19.2}$  [94].

396 Fluorescence spectroscopy has been used several times in order to study the  $5f^1 \rightarrow 6d^1$  transition of Pa(IV), but  
 397 only in solid matrix until 2004. Those studies have demonstrated the Pa(IV) capacity to fluoresce leading to several  
 398 transitions from the lowest 6d level of  $Pa^{4+}$  to the different 5f levels [95].

399 The first fluorescence spectroscopy study has been reported in the literature in 2004 by Marquardt et al. [37]. They  
 400 analyzed Pa(IV) solution using Time Resolved Laser Fluorescence spectroscopy with several mineral acids such  
 401 as perchloric, hydrochloric and sulfuric acids. Thus, a laser excitation into the 6d levels, leads, in aqueous solution,  
 402 to a single broad band around 460 nm. By comparing the fluorescence emission spectra obtained in the various  
 403 acids, at different pH, they confirmed the use of TRFLS to study the speciation of Pa(IV) in solution. In  $HClO_4$ , a  
 404 weakly complexing ligand, the emission band is observed at 465 nm, whereas with more complexing acids (HCl  
 405 and  $H_2SO_4$ ), the emission band was blue-shifted up to 455 nm. Moreover, this hypsochromic shift, corresponding  
 406 to a complexation phenomenon, was more intense as the concentration of the acid increased. However, no  
 407 significant changes have been observed on the half-width and the lifetime (15-20 ns).

408 Recently, these results were combined to the first EXAFS analysis performed on  $Pa^{4+}$  in solution at the Pa L<sub>III</sub>  
 409 edge. Thus, Banik et al. have determined from these data and thanks to quantum calculations the hydration

410 structure of Pa<sup>4+</sup> [47]. The difficulty of the measurement is mainly due to the stability of Pa(IV) that can undergo  
411 photo-oxidation under the beam. By using rongalite as the reducing agent, and in a 6 M HCl, the first EXAFS  
412 spectrum has been recorded. The white line is observed at 16737.3 eV, which is 4.2 eV below the white line of  
413 Pa(V). From the EXAFS fitting, Pa<sup>4+</sup> aquo ion has been found coordinated to nine water molecules with a Pa-O  
414 distance around 2.43 Å. This distance follows the same trend than the early tetravalent actinides according to their  
415 ionic radii. Thus, Pa<sup>4+</sup>, unlike Pa(V), act as the other tetravalent early actinides (from Th<sup>4+</sup> to Bk<sup>4+</sup>).  
416

## 417 **5. Conclusion**

418 The chemistry of protactinium is considered “capricious”. From the moment it was discovered, it tested analytical  
419 chemistry as a whole and forced chemists to use ingenuity to confirm the nature of its chemical species. Whether  
420 at trace scale or macro-concentration, information remains often limited. Even today, the new methods recently  
421 used (CE-ICPMS, EXAFS) fail to give unequivocal information about the speciation of Pa. The researchers  
422 therefore developed complementary multi-technical strategies for extracting information. Today theoretical  
423 chemistry seems to be one of the keys, not necessarily the only key, to help greatly in elucidating its behavior.

424 Unlike Pa(V), Pa(IV) appears to behave like a tetravalent actinide. As the first in the series of tetravalent actinides,  
425 obtaining basic data is important. Spectroscopic techniques are available for this oxidation state and recent work  
426 using for example Time-Resolved Laser Fluorescence Spectroscopy or Extended X-Ray Absorption Fine Structure  
427 spectroscopy seems promising [37, 47].

428 The path is still long to master its behaviour in solution while predictive calculations of theoretical chemistry still  
429 require experimental data. Even today, analytical chemistry is still the most important tool for acquiring all missing  
430 data.

431

432

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