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

Claire Le Naour¹, Melody Maloubier¹ and Jean Aupiais²

¹Université Paris-Saclay, CNRS/IN2P3, IJCLab, 91405 Orsay, France

²CEA, DAM, DIF, 91297 Arpajon, France

Corresponding author: Claire Le Naour, E-mail claire.le-naour@ijclab.in2p3.fr

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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 ²³⁴Pa independently by Fajans, Russell and Soddy applying radioactive displacement laws to uranium [1-3]. The same year, Fajans and Göhring identified the short-lived ^{234m}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, ²³¹Pa [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 ²³⁴Pa [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 K₂PaF₇ for the determination of the molar mass of ²³¹Pa) and the limited analogy between Pa and Ta in particular as regards the solubility of Pa/Ta₂O₅ [10, 11]. It is mostly thanks to the isolation of 127g of ²³¹Pa 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 ²³¹Pa mainly in macro-amount but also ²³³Pa at tracer scale. The latter can be produced either by irradiation of ²³²Th in thermal neutron flux as well as by purification of its parent ²³⁷Np. 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 ²³³Pa as an intermediate in the production of

51 the fissile ^{233}U , and to the formation of ^{231}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}U
57 has been proposed recently for targeted alpha therapy or as generator of ^{226}Th [22, 23]. The production of ^{230}U can
58 involve either ^{230}Pa or ^{231}Pa isotopes. The isotope ^{230}Pa , parent of ^{230}U is produced by proton or deuteron irradiation
59 on natural Th. This uranium isotope can also be formed by irradiation of ^{231}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.

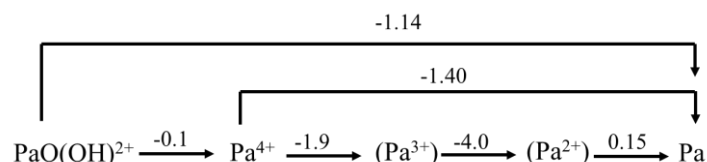
71 2.Redox properties

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 Np(IV) of a Pa(IV) solution
76 obtained by dissolution of 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 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 Pa(V) at tracer scale using Cr^{2+} and 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 Pa(V) concentration; In neutral NH_4F
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 NH_4F 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 (NH_4F , $\text{K}_2\text{C}_2\text{O}_4$, $\text{Na}_2(\text{SO}_4)$), this first wave has been attributed to the reduction of Pa(V) into 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 Pa(III) . However, the existence of this oxidation state in aqueous solution was not
93 conclusively established.

94 The chemical reduction of Pa(V) has been performed in acidic media under Ar or H_2 using several reagents: Zn(Hg)
95 [31-37], Zn(Hg) and Cr(II) [31, 38-45], Zn(Hg) and Ti(III) [38], Zn(Hg) and 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 Pa(IV) formation. The choice of reducing agent depends on the
99 technique used for the investigation of 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 (Pa³⁺/Pa²⁺) 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)

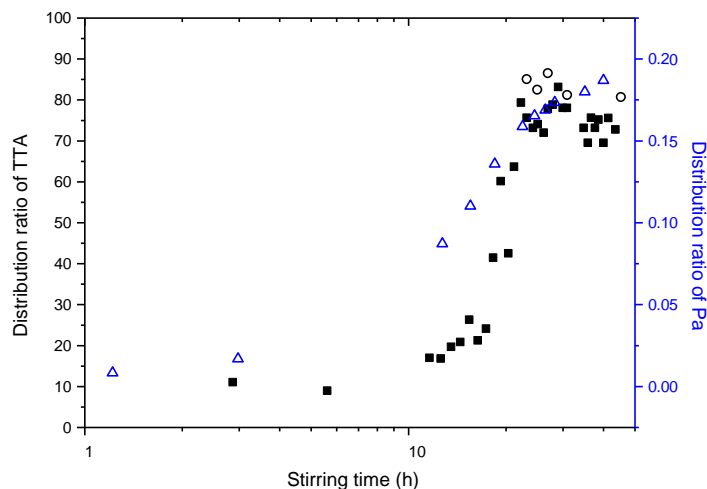
114
 115 The main feature of Pa(V) aqueous chemistry is a strong tendency towards hydrolysis in non and low complexing
 116 media (HClO₄, HCl, HNO₃) that leads to the formation of radiocolloids by condensation of monomeric hydrolysed
 117 species, polymerisation and precipitation [7, 8, 13-15, 24]. The 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 HClO₄ and 1-10 M HNO₃,
 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

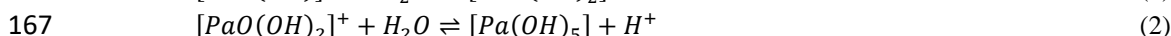
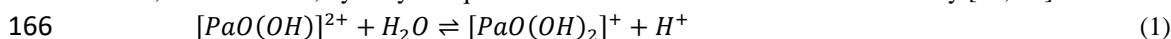
146 the extractant in the case of TTA, whatever the composition of the aqueous phase (complexing as well as non-
 147 complexing medium) as illustrated in Figure 2.
 148



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⁺] / 0.15 M H₂C₂O₄ (■). 0.025 M TTA in toluene 0.25 M
 151 [H⁺] / 5mM DTPA (○). Blue symbols: 0.05 M TTA in toluene / 0.25 M [H⁺] / 5mM DTPA in the presence of ²³³Pa
 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)]²⁺ instead of [Pa(OH)₃]²⁺. 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 ~10⁻⁵ M in concentrated HClO₄, also observed in other acids and
 161 attributed to the Pa oxo bond [24, 64]. This has ruled out the formulation PaO₂⁺ 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)₅] is arbitrary: it is equivalent to [PaO(OH)₃] 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 PaO³⁺ and
 174 [PaO(OH)]²⁺ 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⁻¹
 176 and ~60 kJ mol⁻¹ 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⁻¹mol⁻¹) 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 U⁴⁺, Pu⁴⁺, and PuO₂²⁺ is also endothermic but with high entropic
 180 contribution in the case of tetravalent actinides (> 100 J K⁻¹mol⁻¹). 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 ₄	-0.89 ± 0.33		[56]
3.5 m (Li,H)ClO ₄		-4.7 ± 0.4	[69]
3.5 m (Li,H)ClO ₄		-5.5	[70]
6.6 m (Na,H)ClO ₄		-5 ± 1	[71]
0.1 m (Na,H)ClO ₄	-1.5 ± 0.2	-7.0 ± 0.3	[57]
0.51 m (Na,H)ClO ₄	-1.6 ± 0.2	-6.9 ± 0.6	[52]
1.05 m (Na,H)ClO ₄	-1.7 ± 0.2	-6.9 ± 0.6	[57]
3.52 m (Na,H)ClO ₄	-2.0 ± 0.15	-5.8 ± 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.

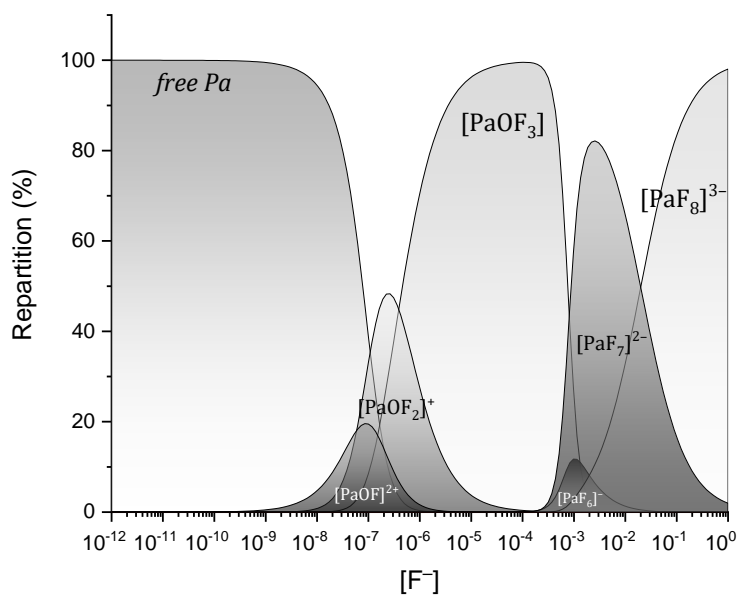
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203 3.2.1. Thermodynamic aspects

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 $[PaF_4OH]$.

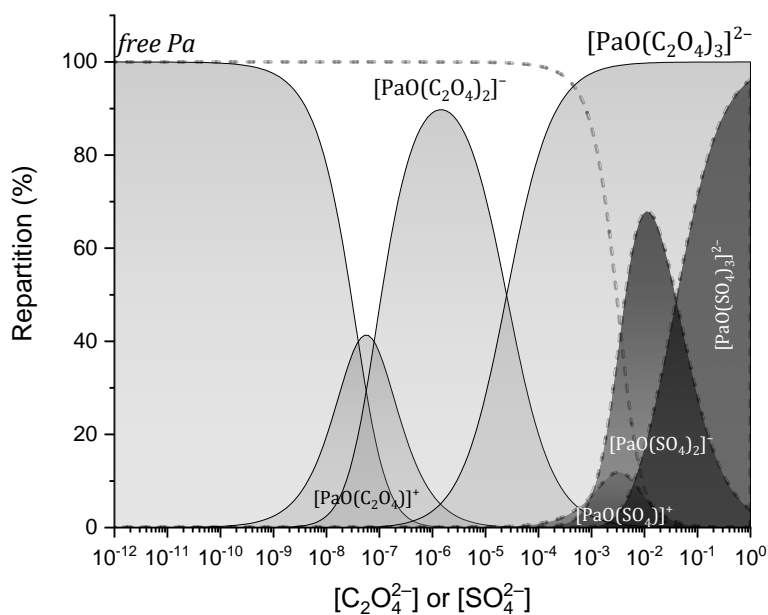
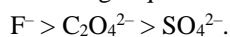
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222
 223 Figure 3: Distribution diagram of Pa-fluoride species at $I = 3$ M. The species $[\text{PaF}_4]^+$ and $[\text{PaOF}_4]^-$ have never
 224 been detected experimentally. $[\text{PaF}_5]$ is a minor species ($< 0.5\%$).
 225

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_{III} 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_{III} 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, H₂SO₄ 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

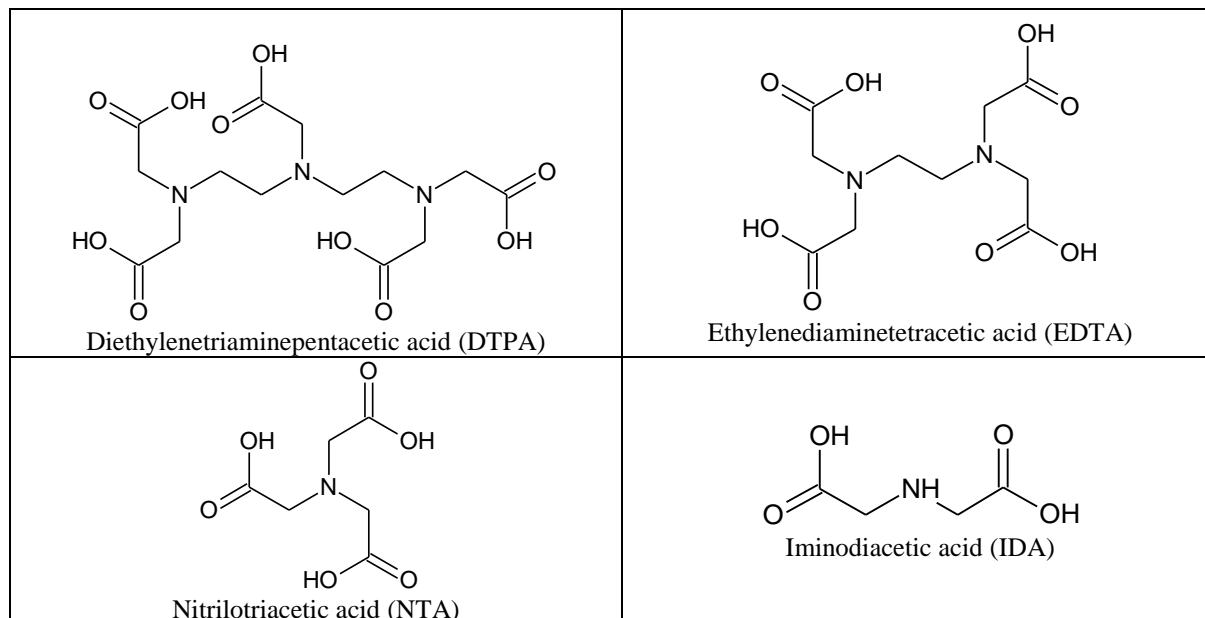


Figure 5: Polyaminocarboxylic acids used as complexing agents of Pa(V)

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. HClO₄ 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)₂]³⁺ and on the other side a mixture
 284 of [PaO(OH)]²⁺ and [PaO(OH)₃], 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)]²⁻ 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 ± 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(H₂DTPA)], 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)ClO₄.



302 However, the technique used does not allow one to preclude the presence of the oxo bond corresponding to the
 303 formulation [PaO(H₂DTPA)].

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)₂]³⁻ 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	$\log \beta_i$	conditions	Ref.
$[PaO(OH)]^{2+} + DTPA^{5-} + 3H^+ \rightleftharpoons "[Pa - DTPA]"$	$\log \beta = 25.34 \pm 0.12$	I = 1 M (Na, H)ClO ₄ , T = 25°C	[85]
$[PaO(OH)]^{2+} + EDTA^{4-} \rightleftharpoons "[Pa - (EDTA)]"$	$\log \beta = 22.1 \pm 0.1$	I = 1 M (Na,H)Cl, T = 25°C	[83]
$[PaO(OH)]^{2+} + EDTA^{4-} \rightleftharpoons [PaO(OH)(EDTA)]^{2-} + 2H_2O$	$\log \beta = 21.54 \pm 0.03$	I = 1 M HClO ₄ , T = 25°C	[84]
$[PaO(OH)]^{2+} + NTA^{3-} + H^+ \rightleftharpoons [PaO(NTA)] + 2H_2O$	$\log \beta_1 = 15.16 \pm 0.06$	I = 1 M (Na, H)ClO ₄ , T = 25°C	[86]
$[PaO(OH)]^{2+} + 2NTA^{3-} + H^+ \rightleftharpoons [PaO(NTA)_2]^{3-} + H_2O$	$\log \beta_2 = 28.46 \pm 0.06$		
$[PaO(OH)]^{2+} + IDA^{2-} + H^+ \rightleftharpoons [PaO(IDA)]^+ + H_2O$	$\log \beta_1 = 10.11 \pm 0.07$	I = 1 M (Na, H)ClO ₄ , T = 25°C	[87]
$[PaO(OH)]^{2+} + 2IDA^{2-} + H^+ \rightleftharpoons [PaO(IDA)_2]^- + H_2O$	$\log \beta_2 = 19.17 \pm 0.15$		

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

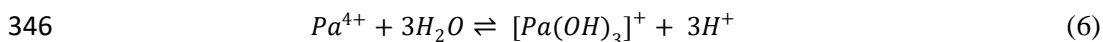
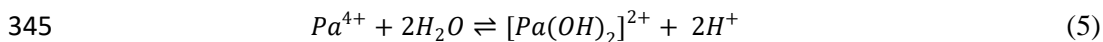
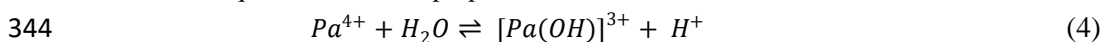
329 4. Protactinium(IV)

330

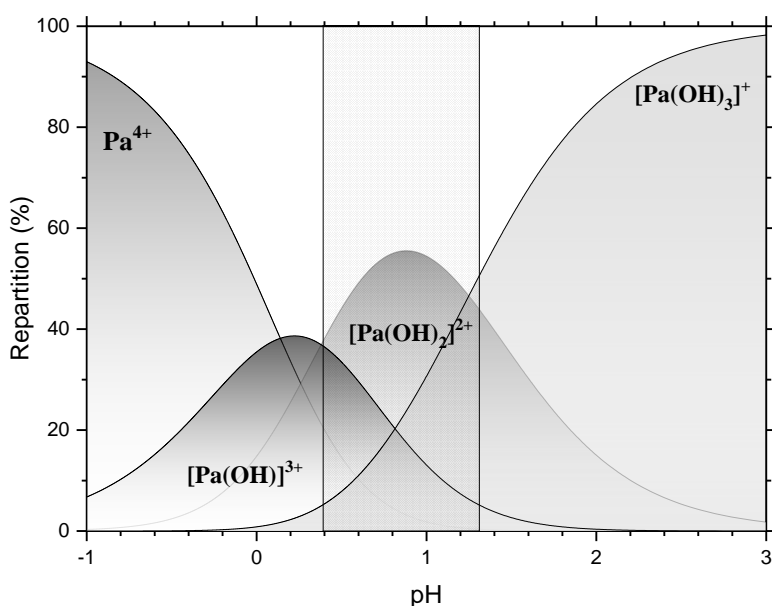
331 Studying the chemical properties of Pa(IV) in aqueous solutions represents a great challenge because of unstability
 332 of this oxidation state. Oxidation to Pa(V) occurs more or less rapidly and like other actinides (IV), its high
 333 reactivity results in strong tendency to precipitation for 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 Hg^{2+} or 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 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 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 PaCl_4 in HClO_4 [89]. Three bands have been observed at 225, 256 and 277 nm in 1.5
 357 M HClO_4 ($C_{\text{Pa}} = 1.1 \cdot 10^{-3}$ M).

358 In 3 M HClO_4/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 Zn^{2+} or 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 PaCl_4 [36, 89].

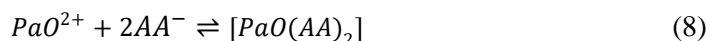
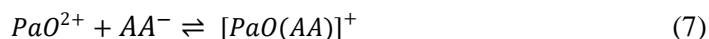
367 In presence of sulphate species, Pa(IV) forms complexes of stoichiometry 1:1 and 1:2 in the form $[\text{Pa}(\text{SO}_4)_x]^{(5-2x)}$
 368 in strong acidic medium (3 M). Only a complex of stoichiometry 1:1 containing hydroxo group has been observed
 369 at higher pH (Table 4). Absorption spectra 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 H_2SO_4 , and at 237, 273 and 297 nm in 9 M H_2SO_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 ₄ 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 ₄ 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 ₄ , 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 ₄ 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 β -diketone: Pa(IV) is extracted with 4 TTA and 4 BA (benzoylacetone) molecules and only 2 AA molecules from
 387 (Li or Na, H)ClO₄ 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)ClO₄, 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_{III}
 409 edge. Thus, Banik et al. have determined from these data and thanks to quantum calculations the hydration

410 structure of Pa⁴⁺ [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, Pa⁴⁺ 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, Pa⁴⁺, unlike Pa(V), act as the other tetravalent early actinides (from Th⁴⁺ to Bk⁴⁺).
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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