



## Research paper

## Electrochemical, spectroscopic and theoretical studies on redox speciation of neptunium with phenylphosphonic acid

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## ABSTRACT

Neptunium (Np) is a key element of concern for the safety aspects regarding the reprocessing and handling of spent nuclear fuel owing to its long half life ( $t_{1/2} = 2.14 \times 10^6$  years). Np can exist in several oxidation states in aquatic environments depending on the surrounding conditions in which it exists. The +5 oxidation state of Np as  $\text{NpO}_2^+$  is the most stable and least binding moiety that can migrate in aquatic arena to far away positions from its source of origin. Humic acids, which are omnipresent in aquifers, are the major source of binding for the actinides including Np to facilitate their migration and transportation phenomenon. Probing the systematic knowledge of neptunium (Np), such as, speciation and coordination as function of its oxidation states in presence of chelating agents is essential aspect of its solution chemistry. The present study aimed at investigating the redox and complexation of Np with phenylphosphonic acid ( $\text{PhPO}_3\text{H}_2$ ) (PPA) as mimic for binding of aromatic phosphorus functionalities in humic substances by using electrochemical and UV–Visible absorption spectroscopy and density functional calculations. The cyclic voltammetric measurement indicates the complexation of both oxidation states (V & VI) of Np with  $[\text{PhPO}_3]^{2-}$ . The presence and stability region (via  $E_h$ -pH plot) of new species of Np- $\text{PhPO}_3$  in two different oxidation states (V & VI) in aqueous solution at varying physicochemical conditions are identified. The kinetics for reduction of Np complexes in different oxidation states are explored by evaluation of heterogeneous electron-transfer kinetic ( $D_0$ ,  $k^0$  and  $\alpha$ ) parameters by cyclic voltammetric results. The spectral parameters, namely  $\lambda_{\text{max}}$  and its molal extinction coefficient ( $\epsilon$ ) are obtained from UV–Visible spectrophotometric measurements and are found to be 988.2 nm and  $302 \pm 8 \text{ mol}^{-1} \text{ L cm}^{-1}$  respectively. The electrochemical as well as UV–Visible spectrophotometric measurements showed the formation of 1:1 complex only and the stability constant ( $\log\beta$ ) obtained for the same from both the methods found to be in agreement with each other. Density Functional Theory (DFT) calculations are carried out to optimize the geometries of Np- $\text{PhPO}_3$  complex for the Np in +5 and +6 oxidation states with  $[\text{PhPO}_3]^{2-}$  in mono and bidentate mode to identify the most probable coordination mode for complex formation.

## 1. Introduction

The aqueous chemistry of actinides (An) is of prime concern in nuclear engineering, especially for nuclear fuel reprocessing and risk assessments of radionuclide migration in the geosphere [1–3]. Metrical knowledge about actinides speciation in aqueous solution is essential in understanding the actinides solubility, stability, complexation, redox reaction, sorption and reactivity, for predicting the fate and transport of actinides under environmentally relevant conditions [4–8].

Neptunium (Np), is one of the artificial elements produced in significant quantities in nuclear reactors by  $\alpha$  decay of  $^{241}\text{Am}$  and (n, 2n) reaction of  $^{238}\text{U}$  followed by  $\beta$  decay of  $^{237}\text{U}$  [9]. Neptunium is key constituent in spent nuclear fuel, nuclear waste [9–11] and is

considered to be most problematic actinide [12]. It remains one of the least understood major transuranium elements though several decades have passed since the first experimental isolation of Np (1940) [13]. It is an  $\alpha$ -emitter with a long half-life [e.g.  $t_{1/2}$  ( $^{237}\text{Np}$ ) =  $2.14 \times 10^6$  years], having high solubility under environmentally relevant conditions. Thus, the long lived  $^{237}\text{Np}$  builds up in spent nuclear fuel and high level liquid waste (HLW) with time and is one of the important radionuclide of interest to consider for the transportation and migration in geosphere.

Np can exist in variety of possible oxidation states from III to VII in aqueous solution and the relative stabilities of the same are strongly affected by pH and the presence of complexing ligands [14,15]. Np in its higher valence states viz.  $\text{NpO}_2^+$  &  $\text{NpO}_2^{2+}$  are highly soluble

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among all its oxidation states, which in turn makes these two oxidation states of Np more mobile in geosphere. The reduction of these oxidation states to lower oxidation states leads to its precipitation and immobilization, thus the redox speciation of Np has phenomenal effect on its release, solubility and migration behaviour [16]. Neptunium speciation in aquatic media is mainly dominated by the pentavalent cation,  $\text{NpO}_2^+$ , under a wide range of environmental conditions [1].

Np redox chemistry is dominated by the dynamic equilibria as represented below by Eq. (1) [17–21]:



This redox mobility makes Np speciation highly dependent on the aqueous solution composition and the formation of coordination complexes that disturb the Np redox equilibrium. Further, for redox-sensitive radionuclides like Np, speciation is very complex due its propensity to exist in multiple oxidation states, susceptibility to hydrolysis, dependence on solution conditions and ability to coordinate with a wide range of ligands. Thus precise identification of speciation is tough, resulting in knowledge gap due to lack of comprehensive understanding of its behaviour [17]. Therefore the reliable spectroscopic signatures, complete understanding of Np redox reactions, and accurate determination of electrochemical potentials in presence of chelating agents, are of primary concern to generate input database for the accurate prediction of its transportation and migration in geochemical models. In addition, particular attention has been given on understanding the discrepancy in redox energetic, kinetics and spectral changes of Np species as a function of variation in the coordination environment (i.e. steric bulk and denticity) in presence of chelating agents. Therefore, there has been a renewed charm on understanding the redox speciation of Np species in presence of chelating agents [22]. In this context, it is quite interesting to ascertain the aqueous solution species of Np-phosphonate. Understanding of this system provides significant role in actinide solution chemistry to gain knowledge about transuranic ions regarding metrical information about a metal ion's speciation in aqueous solution.

Polycarboxylic and aminopolycarboxylic acid complexants are frequently used in actinide isolation and waste remediation, endure some significant limitations viz. ineffective complexation with actinides in acidic solutions, limitation of solubility and resistance for degradation [23]. The complexation tendency of Phosphonic acid towards the metal ions is stronger than the isostructural carboxylic acid [24–27]. One of the most important features of phosphonate ligand is its more probable deprotonation compared to carboxylic acid therefore metal ion can more effectively compete with  $\text{H}^+$  for truly anionic ligand binding sites in acidic solutions [26]. Therefore, recently simple phosphonic acid based chelating agents emerge as tenable option as sequestering agent for f-element. This ligand assimilating doubly ionizable phosphonate groups ( $-\text{PO}_3\text{H}_2$ ), possess many qualities which are unique chemically and assurance for more efficient separation processes related to waste remediation and environmental restoration [28,29]. Furthermore, these powerful f-element complexants can be easily destroyed at the end of their useful life by raising the temperature or adding mild oxidizing agents, which mitigates the possibility of ligand promoted actinide migration [26,30]. High fraction of phosphorus (P) exists in organic forms as derivatives of phosphonic acid in soils rich in organic matter [25]. The P content in humic substances (HS; Humic substances are naturally occurring polydisperse and heterogeneous mixtures of organic molecules that have a high affinity for metal ions) is 800–1500 mg/kg. Therefore, the phenylphosphonic acid (PPA) with  $\text{P}=\text{O}$  and  $\text{P}-\text{OH}$  functionalities can be acknowledge as primitive ligand for aromatic phosphorus functional groups in humic acid. Unique features of Phosphonic acids boost it as versatile ligands in the recent past with increasing attention due to their potential applications in nuclear waste remediation and actinide separation processes [26,31,32]. In Fig. 1 (a)–(g), the structures of the organic ligands that have been previously

used to study Np complexation have shown while (h) represents the structure of Phenylphosphonic acid which has been used as chelating ligand in the present work.

The complexation studies on Np have been reported with inorganic ligands ( $\text{CO}_3^{2-}$ ,  $\text{ClO}_4^-$ ,  $\text{NO}_3^{2-}$  and  $\text{SO}_4^{2-}$ ) [3,8,20] and some other organic chelating ligands including carboxylic acids, amides, and hydroxamic acids [33–41]. The crystal studies of Np with mono [42] and di phosphonate [43] are also available in literature. However, there is no report in the literature on aqueous solution chemistry of Np in presence of PPA as chelating agent. To the best of our knowledge, this is the first report on aqueous speciation and coordination behaviour of Np in different oxidation states (mainly V & VI) with PPA as complexing ligand. Direct determination of the coordination in solution is obligatory as the structure of a metal-ligand complex in the solid state may either differ from the structure in solution, or may only represent one possible coordination mode that exists in solution hence the results of the present work might be impressive over the previous crystal studies [20]. In the present work, the electrochemical and absorption spectroscopy methodology are employed to gain insight into the speciation and coordination chemistry of Np as a function of oxidation states and to benchmark the reduction potential and spectral characteristic of corresponding Np species. In addition, the electrochemical method is used to understand the reduction mechanism of Np-phenylphosphonate complexes. For further understanding of the possible coordination modes of Np with PPA in different oxidation states at the molecular level, quantum chemical calculations (density functional theory) are carried out. This electronic structure calculation affirms the possible structural details, which are found through experimental conditions.

## 2. Experimental

$^{237}\text{Np}$  is a radioactive isotope ( $t_{1/2} = 2.14 \times 10^6$  years) and an  $\alpha$ -emitter. It should be handled in dedicated facilities with appropriate equipment for radioactive materials to avoid health risks caused by radiation exposure. All the experiments dealing Np handling are carried out in the fume hood specially designed to carry out the radioactive experimentation and instrumentation.

### 2.1. Sample preparation

Sigma Aldrich make Sodium perchlorate (purity  $\geq 98\%$ ) and phenylphosphonic acid (PPA) (purity  $\geq 98\%$ ) are used in preparing respective stock solutions for the experiments. Neptunium was purified from laboratory stock solution by using an anion exchange resin in nitric acid medium [44]. The concentration of Np in the stock solution is determined by  $\alpha$  spectrometry using a surface barrier silicon detector coupled to a 4096 channel analyzer and UV-Visible spectrophotometry by measuring the absorbance at 981 nm. All the samples used for electrochemical and spectroscopic experiments are prepared from this stock solution. The hydrogen ion concentration (pH) in the samples is maintained by adding dilute  $\text{HClO}_4$  or  $\text{NH}_3$  and are measured using a pH meter (Lab India), based on a combination pH electrode (glass membrane electrode and a reference electrode). The calibration of pH meter was done by using standard buffer solutions (Merck) of pH 4, 7 and 9. The milliQ (resistivity 18  $\text{M}\Omega\cdot\text{cm}$ ) water was used to prepare all the stock and working solutions.

### 2.2. Instrumentation

#### 2.2.1. Electrochemical measurements

Cyclic and Differential pulse voltammetric measurements are carried out using electrochemical analyzer AUTOLAB with PGSTAT 100 with three electrode systems consisting of Glassy Carbon as working electrode,  $\text{Ag}-\text{AgCl}/\text{sat. KCl}$  as reference and Pt as auxiliary electrode. All the electrochemical measurements were carried out in inert nitrogen

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