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## The Solvent Extraction of Uranium (VI) using Hydroxyalkylenediphosphonic Acids

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**Abstract:** The solvent extraction of uranium (VI) from aqueous solutions has been investigated using hexadecylhydroxydiphosphonic acid (HHDDPA,  $H_4L^1$ ) and dodecylhydroxydiphosphonic acid (DHDPA,  $H_4L^2$ ), which were synthesized and characterized by elemental analysis and by FT-IR,  $^1H$  NMR,  $^{31}P$  NMR spectroscopy. In this study, we propose a tentative assignment for the shifts of those two ligands and their specific complexes with uranium (VI). A spectroscopic analysis has showed that coordination of uranium (VI) takes place via oxygen atoms. We carried out the extraction of uranium (VI) from aqueous solutions by HHDDPA and DHDPA in [carbon tetrachloride + 2-octanol (v/v: 90%/10%)] solutions at an aqueous to organic phase ratio (1/1) and at room temperature. The results showed that the extraction yields are more significant in the case of the HHDDPA (92%) which is equipped with a hydrocarbon chain, longer than that of the DHDPA (88%). Logarithmic plots of the uranium (VI) distribution ratio vs.  $pH_{eq}$  and the extractant concentration showed that the ratio of extractant to extracted uranium(VI) is 2:1. The metal complexes formed in organic phase are  $UO_2(H_3L^1)_2 \cdot 2H_2O$  and  $UO_2(H_3L^2)_2 \cdot 2H_2O$  for HHDDPA and DHDPA respectively. The equilibrium constants for the extraction of uranium(VI) were found to be 2 and 1.27 for HHDDPA and DHDPA, respectively.

**Key words:** Extraction, diphosphonic acids, HHDDPA, DHDPA, uranium

### INTRODUCTION

Uranium plays an important role in the generation of nuclear power. For this reason, the recovery, concentration and purification of uranium are of great importance. Therefore, many processes have been used for uranium purification from its ores at plant-scale. Leaching of uranium by acid or alkaline solutions, concentration and purification by solvent extraction or ion exchange and precipitation are the most commonly used methods; each has its merits and limitation in application (Edwards and Oliver, 2000; Lunt *et al.*, 2007).

Among these, the solvent extraction method has been applied extensively in the production and processing of uranium (Ritcey, 2006; Black *et al.*, 1958; Singh *et al.*, 2001; Girgin *et al.*, 2002). The solvent extraction process using acidic organophosphorus extractants is applied world-wide for the purification of crude uranium and also thorium (Kabachnik *et al.*, 1974; Didi *et al.*, 2002; Elias *et al.*, 1996; Didi *et al.*, 2004; Basuki, 1991; Largman and Sifniades, 1983; Hall *et al.*, 2005;

Chiarizia *et al.*, 2001; Urban *et al.*, 1998; Horwitz *et al.*, 1994; Curtui *et al.*, 2001).

In the present study we carried out the synthesis of new hydroxyalkylenediphosphonic acids which form stable complexes with metallic species is of great importance for improving existing hydrometallurgical processes for their recovery (Kabachnik *et al.*, 1974; Didi *et al.*, 2008; Blum *et al.*, 1981; Largman and Sifniades, 1983). The stability of the hydroxyalkylenediphosphonic acids with iron (III), thorium (IV) and uranium (VI) cations is particularly high (Kabachnik *et al.*, 1974; Didi *et al.*, 2002; Basuki, 1991; Tunick *et al.*, 1982; Burgada *et al.*, 2003; Reed *et al.*, 2007). The complex-forming properties of the hydroxyalkylenediphosphonic acids are due to their structures. The combination in one molecule of two highly acidic phosphono-groups and also hydroxy-group, which play the role of the basic centre in molecule, enable these ligands to form stable complexes (Kabachnik *et al.*, 1974). In fact, we have synthesized hexadecylhydroxydiphosphonic (HHDDPA,  $H_4L^1$ ) and dodecylhydroxydiphosphonic (DHDPA,  $H_4L^2$ ) for such a

purpose. The characterizations of these products were carried out by elemental analysis and by FT-IR, <sup>1</sup>H NMR, <sup>31</sup>P NMR spectroscopy. We have also tested the chelating properties of these extractants towards uranium (VI) from aqueous solutions.

### MATERIALS AND METHODS

This research project was conducted from March 2008 to March 2010 in the Nuclear Research Center of Draria, Algiers, Algeria.

**Reagents and solutions:** The reagents used in this work were palmitic acid (98%, Panreac), lauric acid (BDH), phosphorus trichloride (98%, BDH), anhydrous ethyl alcohol (Ficher), carbon tetrachloride (Labosi) and 2-Octanol (Prolabo). Uranyl nitrate hexahydrate was purchased from Merck (99%). The aqueous solutions of 4.2×10<sup>-2</sup> M uranium (VI) was prepared from uranyl nitrate hexahydrate and adjusted at pH 2 with nitric acid and NaOH. The aqueous solutions of uranium (VI) was fixed at pH 2, because hydrolysis of uranyl ion takes place as the pH varies from 1 to 3.0±0.1 (availability of free uranium ions). When pH increases beyond 3.0±0.1, uranium exists in hydrolyzed form and the following ionic species have been identified: UO<sub>2</sub><sup>2+</sup>, [(UO<sub>2</sub>)<sub>2</sub>(OH)<sub>2</sub>]<sup>2+</sup> dimer, [(UO<sub>2</sub>)<sub>3</sub>(OH)<sub>5</sub>]<sup>+</sup> trimer, precipitation starts due to the formation of complexes in aqueous solution (Kadous *et al.*, 2009). The organic solutions were prepared from of HHDPA and DHDPA (0.03 to 0.3 M) dissolved in the organic solvent [carbon tetrachloride + 2-octanol (v/v: 90%/10%)].

**Instrumentation:** <sup>31</sup>P(- <sup>1</sup>H) and <sup>1</sup>H NMR spectra were measured on a Bruker AC 250 working at 250 MHz in a carbon tetrachloride solution. Infrared spectra were measured on a Perkin Elmer 16 PC-FTIR equipped with a thermostat to maintain the temperature of the sample cell at 25±0.1°C. Elemental analyses were performed using a ThermoQuest NC2500 elemental analyser. Potentiometric measurements were taken on a Consort C 831. In a water-acetone mixture (3:17), a known mass of each sample titrated by a solution of NaOH (2×10<sup>-3</sup>M). The amount of uranium (VI) extracted was determined from the difference between the initial and final concentrations of uranium (VI) in aqueous solution using a GBC Cintera-40 UV-Visible spectrophotometer. The water was titrated in the organic phase by the use of a Mettler DL18 Karl Fisher Titrator.

**Synthesis of the extractants and characterisation:** HHDPA and DHDPA were synthesis following a method first described by Largman and Sifniades (1983) with an original modification developed in our laboratory (Didi *et al.*, 2002, 2008). The characteristics of these products are given in Table 1.

HHDPA and DHDPA were titrated by potentiometry. The pK<sub>a</sub> values indicated that in the water-acetone medium the first proton was strong and the other protons were weak.

The presence of a wide P = O band in the IR presence indicates intermolecular hydrogen bonds P = O...H-OP and C-OH...O = P. The equilibrium exists between the following two forms: C-O-H...O = P-C = O...H-O-P- which explains the presence of the 1700 cm<sup>-1</sup> band with H<sub>2</sub>O bending.

Table 1: HHDPA and DHDPA characteristics

Products	HHDPA				DHDPA			
Formula	C <sub>15</sub> H <sub>31</sub> C(OH)(PO <sub>3</sub> H <sub>2</sub> ) <sub>2</sub>				C <sub>11</sub> H <sub>23</sub> C(OH)(PO <sub>3</sub> H <sub>2</sub> ) <sub>2</sub>			
pKa	3.2, 6.36, 8.5, 11.1±0.05				3.66, 6.45, 8.66, 11.3±0.05			
Elemental analysis		%C	%H	%P		%C	%H	%P
	Exptl.	46.75	8.60	14.68	Exptl.	46.75	8.60	14.68
	Calcd	47.76	8.95	14.42	Calcd	41.76	8.95	14.42
FT-IR (cm <sup>-1</sup> )	3450-3000 (vs OH), 2925 (vas CH), 2854 (vs CH), 2700-2600 and 2350-2190(vs POH), 1465-1413 (d CH <sub>2</sub> ), 1204 (vs P = O), 1095 (vas P-OH), 937 (vs P-OH)				3445-3000 (vs OH), 2923 (vas CH), 2852 (vs CH), 2710-2620 and 2340-2200(vs POH), 1463-1415 (d CH <sub>2</sub> ), 1195 (vs P = O), 1090 (vas P-OH), 940 (vs P-OH)			
<sup>1</sup> H NMR	0.88 (t, 3H, (CH <sub>3</sub> )), 1.25(m, 26H,(CH <sub>2</sub> )), 2.40(s, 1H, (COH)), 8.07(m, 4H, (P(O)(OH) <sub>2</sub> ))				0.90 (t, 3H, (CH <sub>3</sub> )), 1.27(m, 26H,(CH <sub>2</sub> )), 2.41(s, 1H, (COH)), 8.10(m, 4H, (P(O)(OH) <sub>2</sub> ))			
δ (ppm)								
<sup>31</sup> P NMR	18 (s)				17.3(s)			
δ (ppm)								

Exptl. and calcd: Experimental and calculated percentages for the elemental analysis of the synthesized compounds, d (ppm): Chemical shift, s: Singlet, t: Triplet, m: Multiplet, vs: Symmetric stretching, vas: Antisymmetric stretching

**Extraction experiments:** The extraction experiments were performed using HHDPA and DHDPA as extractants. These substances were tested for uranium(VI) extraction from aqueous solutions at pH 2. Equal volumes of organic and aqueous phases (10 mL) were shaken together at 25°C for 15 min. Preliminary experiments showed that equilibration was complete in 15 min. The addition of 2-octanol in organic solution as modifier (10 vol %) was necessary to improve phase separation. This alcohol also prevents micelle formation and solvated metal-extractant complexes (Didi *et al.*, 2002; Kahlweit *et al.*, 1981; Strey and Jonstromer, 1992; Mellah and Benachour, 2006). It is very important to note that no third phase or any precipitation was observed during the extraction process. The phases were then allowed to separate. The amount of uranium (VI) extracted was determined by complexing the uranium (VI) in the aqueous phase before and after extraction with arsenazo III and by further visible spectrophotometric dosage of the complexes formed (Elias *et al.*, 1996; Marzenko, 1976). The water was titrated in the organic phase by the use of a Karl Fisher Titrator.

**RESULTS AND DISCUSSION**

**Extraction of uranium (VI) by HHDPA and DHDPA:** The extraction experiments results are discussed in term of extraction yield (Y) and distribution ratio (D) defined as follows:

$$Y(\%) = \frac{m_i - m_f}{m_i} \times 100 \tag{1}$$

$$D = \left( \frac{m_i - m_f}{m_f} \right) \times \frac{V_{aq}}{V_{org}} \tag{2}$$

Where:

- $m_i$  = Initial mass of uranium(VI) in aqueous phase
- $m_f$  = Mass of uranium(VI) after extraction
- $V_{aq}$  = The volume of the aqueous phase
- $V_{org}$  = The volume of the organic phase

The variable Q is the ratio of the number of moles of extractant in organic phase versus the number of moles of metal in aqueous phase before extraction:

$$Q = \frac{n_{extractant}}{n_{metal}} \tag{3}$$

The variation of the extraction yield test of the  $4.2 \times 10^{-2} M$  uranium (VI) from aqueous solutions as a function Q is shown in Fig. 1.

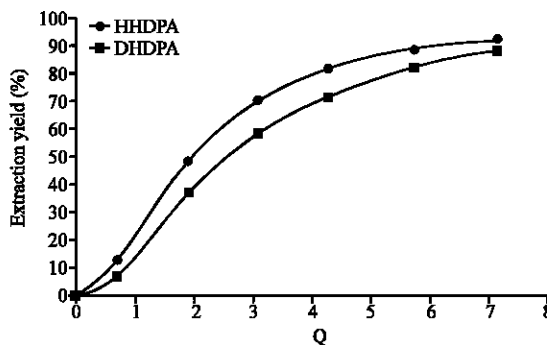
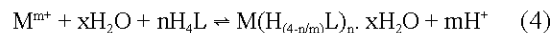


Fig. 1: Effect of molar ratio (Q) on the extraction yield of uranium (VI). pH = 2;  $[U(VI)] = 4.2 \times 10^{-2} M$ ;  $V_{aq}/V_{org} = 1$ ;  $t = 25^\circ C$

Figure 1 shows the yield of extraction of uranium(VI) increases with Q. Working with extractants concentrations range 0.03 to 0.3 M ( $Q = 0.7$  to 7), we reached a yield of 92% for HHDPA and 88% for DHDPA. The extractant with a longer alkyl group forms more hydrophobic complexes. HHDPA and DHDPA present a similar extraction power, but the hydrophobic character determines the amount of extraction. The hydrophobic character of ligand can be determined calculating log P which is defined as the partition coefficient between two phases of a substance, generally n-octanol and water. Modern molecular modeling software allows the log P values, calculated using ChemDraw Ultra (Cambridge Soft) are respectively 2.75 for DHDPA and 5.92 for HHDPA showing that HHDPA is strongly hydrophobic.

**Stoichiometry of extracted species:** In the work on stoichiometric relation for the extraction of uranium complex with HHDPA ( $H_4L^1$ ) and DHDPA ( $H_4L^2$ ), we have supposed that the solubilities of the extractant and the uranium-extractant complex in the aqueous phase are negligible; the overall reaction in the extraction of metal cations by cationic extractants, as the case of HHDPA and DHDPA, can be show as following:



where,  $H_4L$  is the molecule of extractant, M is the metal (U), m valence of metal (U(VI)), n molecules of extractant engaged in the reaction, n/m number of protons exchanged by each extractant and x number of molecules of water.

The equilibrium constant of the above reaction,  $K_{ex}$ , can be given as function of molar concentration:

$$K_{ex} = \frac{[M(H_{(4-n/m)}L)_n \cdot xH_2O] [H^+]^m}{[M^{m+}] [H_4L]^n} \tag{5}$$

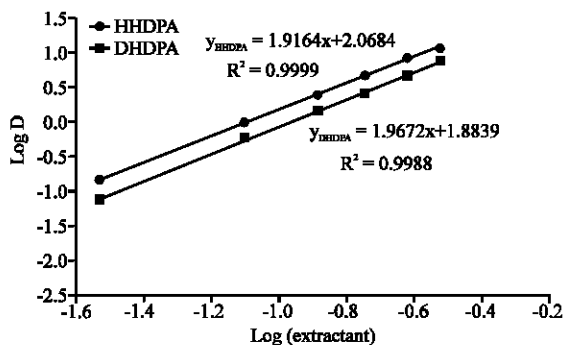


Fig. 2: Effect of the extractant concentration on the distribution ratio for uranium (VI). pH= 2; [U (VI)] =  $4.2 \times 10^{-2}$  M;  $V_{aq}/V_{org} = 1$ ;  $t = 25^\circ\text{C}$

Substitution of the distribution ratio, which is defined by the concentration of uranium (VI) in organic phase divided by that in aqueous phase, into Eq. 6 results in:

$$D = \frac{K_{ex} [H_4L]^n}{[H^+]^m} \quad (6)$$

Taking logarithms of Eq. 6, one obtains:

$$\log D = \log K_{ex} + n \log [H_4L] - m \log [H^+] \quad (7)$$

$$\log D = \log K_{ex} + n \log [H_4L] + m \text{pH} \quad (8)$$

The stoichiometry of the extracted species was determined by analysing the experimental data. The conventional slope analyses method was used. Figure 2 shows the plots of log D versus log [extractant] which gave two straight lines with good correlation coefficients 0.999 and 0.998 and slopes equal to 1.91, which is close to 2 and 1.96, which is close to 2 for HHDPA and DHDPA. This result suggests that two molecules of extractant react with one uranyl ion. Figure 2 also shows that the distribution ratio of uranium(VI) increases with the increase in extractant concentration. The distribution ratios are more significant in the case of the HHDPA which is equipped with a hydrocarbon chain, longer than that of the DHDPA. Figure 3 shows the plots of log D versus  $\text{pH}_{eq}$  which also gave two straight lines with good correlation coefficients 0.999 and 0.996 and slopes equal to 2.06, which is close to 2 and 2.11, which is close to 2 for HHDPA and DHDPA. This indicates that two protons are released during the cation exchange reaction. The plots log D versus log [extractant] and the plots log D versus  $\text{pH}_{eq}$  suggest that the ratio of extractant to extracted uranium(VI) is 2:1 (Basuki, 1991; Kabachnik *et al.*, 1974;

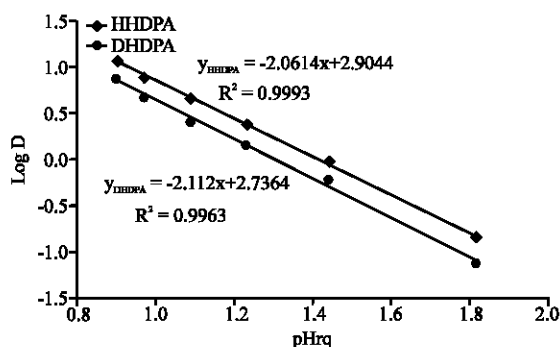


Fig. 3: Effect of equilibrium pH on the distribution ratio for uranium (VI). pH= 2; [U(VI)] =  $4.2 \times 10^{-2}$  M;  $V_{aq}/V_{org} = 1$ ;  $t = 25^\circ\text{C}$

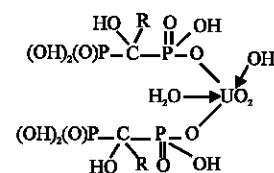


Fig. 4: Structures of the complex HHDPA- $\text{UO}_2 \cdot 2\text{H}_2\text{O}$  ( $R = \text{C}_{15}\text{H}_{31}$ ) and the complex DHDPA- $\text{UO}_2 \cdot 2\text{H}_2\text{O}$  ( $R = \text{C}_{11}\text{H}_{23}$ )

Reed *et al.*, 2007; Jacopin *et al.*, 2003; Burgada *et al.*, 2003; Hall *et al.*, 2005; Chiarizia *et al.*, 2001). The equations extraction equilibrium can thus be written as:



According to the above equations extraction equilibrium, the metal complexes formed in organic phase are  $\text{UO}_2(\text{H}_3\text{L}^1)_2 \cdot 2\text{H}_2\text{O}$  and  $\text{UO}_2(\text{H}_3\text{L}^2)_2 \cdot 2\text{H}_2\text{O}$  for HHDPA and DHDPA respectively. Proton, intervening in our extraction, corresponds to the  $\text{pK}_a$  of HHDPA and DHDPA, 3.2 and 3.66, respectively. HHDPA and DHDPA extract the uranyl ions in cationic exchange mode. The two last values of  $\text{pK}_a$  obtained by potentiometric measurement confirm that the extracting agent can exchange only one or two protons per molecule. We also note that the extraction of uranium (VI) by HHDPA and DHDPA is accompanied by two water molecules extraction. The equilibrium constants,  $K_{ex}$ , for the extraction of uranium(VI) were found to be 2 and 1.27 for HHDPA and DHDPA, respectively.

The structures of the complex HHDPA- $\text{UO}_2 \cdot 2\text{H}_2\text{O}$  and DHDPA- $\text{UO}_2 \cdot 2\text{H}_2\text{O}$  are indicated in Fig. 4.

Figure 4 shows that the uranium complexes,  $\text{UO}_2(\text{H}_3\text{L}^1)_2 \cdot 2\text{H}_2\text{O}$  and  $\text{UO}_2(\text{H}_3\text{L}^2)_2 \cdot 2\text{H}_2\text{O}$ , are formed by

coordinating of each uranyl ion to two phosphonate oxygen atoms from two molecules of extractant agent. Figure 4 shows also that these complexes contain two water molecules. The HHDPA and DHDPA form the high complexes with uranium(VI). This higher stability of the uranium complexes is mainly attributed to the high acidity of the diphosphonic acid group and the hydroxy-group (Kabachnik *et al.*, 1974; Van Hecke and Goethals, 2006; Sun *et al.*, 2003). The mechanism the two complex formations is based on the employment in the interaction with uranyl ions of the electron-donating functions of the oxygen atoms in the diphosphonic group and in the hydroxy-group at the carbon atom joined to diphosphonic group. These electron-donating functions of the oxygen atoms increases with increase the hydrocarbon chain of the extractant agent.

**HHDPA-UO<sub>2</sub> and DHDPA-UO<sub>2</sub> spectra:** The solid complex HHDPA-UO<sub>2</sub> was prepared by stirring the hydroxydiphosphonic acid in the organic solvent mixture (carbon tetrachloride + 2-octanol), with an aqueous solution of uranium (VI). After separation of the phases and evaporation of the organic solvents, the solid complex was washed with water and dried. We have observed a shift of P = O band from 1204 to 1115 cm<sup>-1</sup>. In the complex, a new IR band appears at 940 cm<sup>-1</sup> attributed to the distortion vibration PO-UO<sub>2</sub>. Similarly, comparison of the spectra of DHDPA and DHDPA-UO<sub>2</sub> show a shift the 1195 P = O band to 1096 cm<sup>-1</sup>. A new band in DHDPA-UO<sub>2</sub> appears at 933 cm<sup>-1</sup> attributed to the deformation vibration of PO-UO<sub>2</sub>. The two deformation vibrations PO-UO<sub>2</sub> showed that the bond between P-O and UO<sub>2</sub> for HHDPA is stronger than with DHDPA.

## CONCLUSIONS

HHDPA and DHDPA used as extractants in solvent extraction process for extract uranium (VI) from aqueous solutions. From the obtained results the following conclusions may be drawn:

The yields of extraction of uranium (VI) increases with the ratio Q. HHDPA and DHDPA can complex and extract respectively 92 and 88% of uranium (VI) by using a large excess extractant agent (Q = 7).

HHDPA ligand has a stronger extracting power for uranium (VI) than DHDPA. This fact is related to more hydrophobic character of HHDPA vs. DHDPA.

Logarithmic plots of the uranium (VI) distribution ratio versus pH<sub>eq</sub> and the extractant concentration showed that the ratio of extractant to extracted uranium (VI) is 2:1. The metal complexes formed in organic phase are UO<sub>2</sub>(H<sub>3</sub>L<sup>1</sup>)<sub>2</sub> · 2H<sub>2</sub>O and UO<sub>2</sub>(H<sub>3</sub>L<sup>2</sup>)<sub>2</sub> · 2H<sub>2</sub>O for HHDPA and

DHDPA, respectively. Proton, intervening in our extraction, corresponds to the pK<sub>a</sub> of HHDPA and DHDPA, 3.2 and 3.66, respectively. HHDPA and DHDPA extract the uranyl ions in cationic exchange mode. The two last values of pK<sub>a</sub> obtained by potentiometric measurement confirm that the extracting agent can exchange only one or two protons per molecule.

Extraction of uranium (VI) by HHDPA and DHDPA is accompanied by two water molecules extraction.

The equilibrium constants for the extraction of uranium (VI) were found to be 2 and 1.27 for HHDPA and DHDPA, respectively.

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