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“SYMPHOS 2015”, 3rd International Symposium on Innovation and Technology in the Phosphate Industry

Carbamoylalkylphosphonates type ligand for uranium extraction from phosphates ores

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Abstract

Carbamoylphosphonic acid and carbamoylphosphonate ligands have been synthesized and studied for uranium extraction from phosphates ores. From a structure-selectivity approach, the molecular design of such ligands was optimized leading to a specific one called DEHCNPB which exhibits outstanding results for the selective extraction, and quantitative recovery of uranium in phosphoric acid compared to the URPHOS reference system.

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Keywords: Bifunctional extractants; Uranium extraction; Phosphoric acid; DEHCNPB

1. Introduction

Natural phosphates rocks, commonly used for the production of phosphoric acid or fertilizers, contain uranium (from 20 to 200 ppm depending on deposits) as well as other common impurities such as rare earths, chromium, vanadium, titanium (hundreds ppm) and mainly aluminium and iron (ranging from 2000 to 5000 ppm).

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Considering the amount of phosphate rock processed annually for the production of phosphoric acid, it represents one of the most attractive unconventional resources of uranium to supply the global uranium demand [1,2].

For this purpose, several solvent extraction processes such as the URPHOS [3], OPAP [4] and OPPA [5] processes have been implemented for recovering uranium from WPA.

While the OPAP and OPPA processes are very attractive in regards to the uranium extraction efficiency from WPA, the use of iron powder in order to reduce the uranium(VI) in uranium(IV) is a major drawback which results in a poor uranium(IV) selectivity toward iron(III) [4]. The degradation of OPPA by hydrolysis into monoalkylorthophosphoric acids is also an important issue [5].

The URPHOS process, which consists in a synergistic combination of di-2-ethyl-hexyl-phosphoric acid (HDEHP) as a cationic exchanger and trioctyl-phosphine oxide (TOPO) as a neutral donor is recognized as the best system since it extracts hexavalent uranium U(VI), avoiding the reduction step of uranium, and is a more stable and selective solvent (especially against iron) than OPAP and OPPA. However a multiple cycle scheme is needed to offset the low extraction strength and the iron contamination as a consequence of an insufficient selectivity of HDEHP-TOPO system.

For these reasons, the development of new efficient, selective, and robust extractants, for the recovery of uranium in high concentrated phosphoric acid media, used in synergistic mixtures or singly have been proposed [6].

Various works reported the substitution of the HDEHP or the TOPO in HDEHP-TOPO mixtures leading to other synergistic reagents [6-8] or the improvement using new cation exchangers and solvating agents involved in synergistic mixtures such as the URPHOS-bis process [9] which combine two different ligands: bis(di-n-butoxy-1,3-propyl-2-)phosphoric acid (HBiDiBOPP) and di-n-hexylmethoxyoctylphosphine oxide (DinHMOPO). With respect to the efficiency of the different systems studied the selectivity toward iron remains low.

The second approach consisting in the use of a single molecule or “aut synergistic” molecule which combine both cationic exchanger and neutral donor functions in a same molecular architecture is less described in the literature. O-methyldihexylphosphine oxide O'-hexyl- 2-ethyl phosphoric acid such as bifunctional extractants containing both phosphine oxide and phosphate groups have been developed for this purpose [10]. Whatever the extraction conditions, this bifunctional extractant results in higher extraction abilities than URPHOS system but a lower selectivity towards iron(III). However, some limits are inherent to the use of such phosphate ester function such as its hydrolysable ability in acidic conditions and the formation of a third phase during extraction which is not applicable for industrial process.

Considering the potential of this approach, we synthesized bifunctional extractants based on an amide group and a phosphonic acid [11] or a phosphonate group [12]. This system is a combination of a cationic exchanger (the phosphonic acid or phosphonate part) and a solvating exchanger (the amido part) (Fig. 1). The influence of the molecular design including the nature of alkyl chains on the amide part, the spacer length between the two functions, and the degree of steric hindrance on the spacer of such carbamoylphosphonic acid or carbamoylphosphonate ligands are discussed here and highlight the impact of the molecular structure on the efficiency to extract selectively the uranium(VI) from phosphoric acid solutions.

2. Results and discussion

The influence of the molecular design on the properties of the amido-phosphonic acids and amido-phosphonate ligands to selectively extract uranium(VI) over Fe(III) from phosphoric acid solutions have been studied including (Fig. 1):

- length and ramifications of alkyl chains on amide group (**R1** and **R2**)
- spacer length and degree of steric hindrance on the spacer (**n**, **R4** and **R5**)
- length of alkyl chain of phosphonate (**R3**)

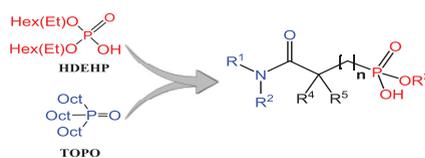


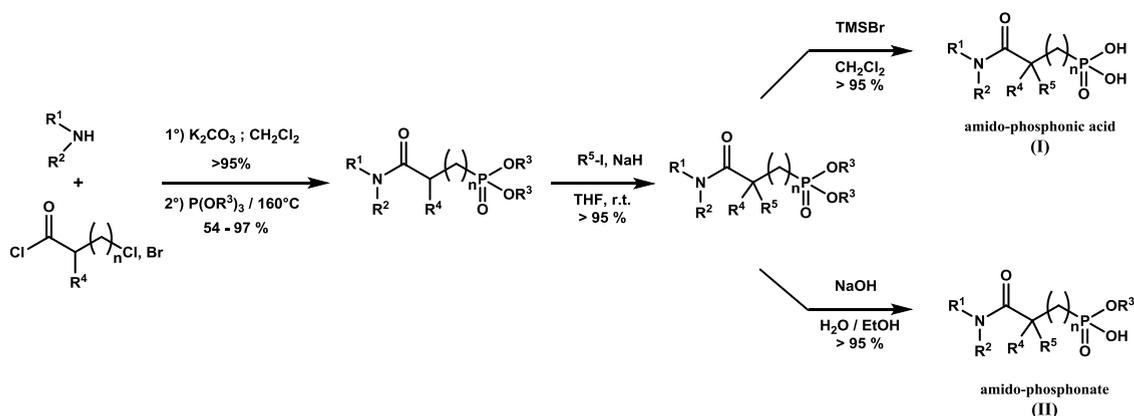
Fig. 1. Structural modifications considered for the amido-phosphonic acid and amido-phosphonate ligands

2.1. Extractant synthesis

The amido-phosphonic acid (I) and amido-phosphonate (II) ligands were synthesized *via* a general synthetic approach in four steps according to Scheme 1. Amidation of *N,N*-dialkylamine with halogeno-acylchloride in the presence of K_2CO_3 in dichloromethane afforded intermediary amide which is then engaged in an Arbuzov reaction with triethylphoshite or tributylphoshite to give the *N,N*-dialkylcarbamoylalkylphosphonate. The products were then alkylated by reaction of a halogenoalkyl reactivities and sodium hydride in order to introduce various alkyl functions on the methylene bridge.

The corresponding amido-phosphonic acid (I) or amido-phosphonate (II) ligands were obtained respectively by hydrolysis with bromotrimethylsilane or by mono-saponification with aqueous sodium hydroxide.

The products were obtained at multigram scale in good to excellent yields [11,12]. The simple and general approach allowed us to design more than fifty different ligands which were then engaged in solvent extraction experiments.



Scheme 1. General synthesis of amido-phosphonic acid (I) and amido-phosphonate(II) ligands

2.2. Extraction and back-extraction experiments

The extraction experiments were performed starting from an aqueous phase containing a mixture of 250 mg/L of U(VI) and 2500 mg/L of Fe(III) in 5M H_3PO_4 solution and an organic phase prepared by dissolving ligands in dodecane (at 0.25M unless otherwise cited). Extractions were performed at room temperature ($22-24^\circ C$) by vortexing equal volumes of organic and aqueous phase during 1 hour. After separation by centrifugation (4000 rpm for 10 min), the extraction of uranium and iron by the ligand in the organic phase was followed by X-ray Fluorescence and confirmed by ICP/AES (aqueous phase). Distribution coefficients ($D_M = [M]_{org}/[M]_{aq}$) and separation factors ($SF = D_{M1}/D_{M2}$) were determined in order to evaluate the efficiency of the molecule to extract selectively uranium(VI) towards Fe(III).

The loaded organic phase was stripped with a solution of ammonium carbonate (typically 0.5M) by contacting equal volumes of organic and aqueous phase during 1 hour. After separation by centrifugation (4000 rpm for 10 min), uranium and iron concentrations were measured in each phase by X-ray Fluorescence and confirmed by ICP/AES (aqueous phase).

2.3. Structure - selectivity relationship study

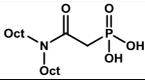
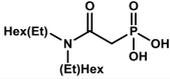
2.3.1. Length and ramifications of alkyl chains on amide group (R1 and R2)

The influence of the alkyl group on the amide has been studied in regards to the length and ramifications of alkyl chains with $R_1 = R_2 =$ hexyl, octyl, ethylhexyl and decyl chain.

The optimum alkyl chain length toward precipitation and third phase formation appears to be a C8 chain: octyl, ethylhexyl [11].

Interestingly, while keeping a constant alkyl chain mass (C8 chains) the steric hindrance effect using an ethylhexyl group instead of octyl group results in a significant improvement of the extraction with distribution coefficient 10 times higher compared to the linear chain and the selectivity is greater than one indicating the affinity in favour of U(VI) (Table 1). Moreover, octanol was needed to dissolve the amido-phosphonic acid with R1 = R2 = octyl which was not necessary for the branched ethylhexyl group. Considering the extractions results obtained with the presence of the 2-ethylhexyl chains, this group has been kept for the next studies.

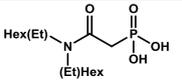
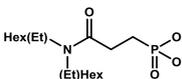
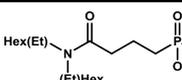
Table 1. Influence of amide group (R1 and R2): Extraction results for amido-phosphonic acid compound

Compounds	D _U	SF _{U/Fe}
	0.2	0.1
	2.0	1.5

2.3.2. Length and degree of steric hindrance of the spacer (n, R4 and R5)

Firstly we focused our attention on the linker length between the cationic exchanger and the neutral donor function. Increasing the distance between the phosphorus and the amide yields a significant decrease in the distribution coefficients (Table 2). The spacer length impacts strongly the extraction properties and a methylene bridge which offers a 6 atoms chelate is ideal over the others spacer length.

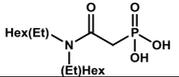
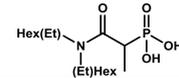
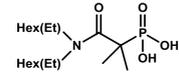
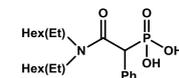
Table 2. Influence of spacer length (n): Extraction results for amido-phosphonic acid compound

Compounds	D _U	SF _{U/Fe}
	2.0	1.5
	0.09	0.3
	0.09	2

In order to investigate the steric hindrance effect, methyl, dimethyl or phenyl groups have been introduced on the methylene bridge. The extraction results in Table 3 show that the introduction of a methyl substituent lead to a distribution ratio 5 times greater than the dimethylated compound which is close to the performances of the non-alkylated molecule but with very similar selectivity towards iron. A significant rise was observed by increasing the steric hindrance through the addition of a phenyl group (D value up to 8) but a small amount of octanol was used in order to complete the solubilization. In this case the significant increase is also observed for the selectivity which is increased by a factor of 50. Introduction of alkyl group provides an increase of the extraction properties which is probably linked to the steric hindrance and/or a better organization of the system in regards to the uranyl cation.

From these statements it appears that the length and steric hindrance of the methylene bridge are very important parameters with regard to the efficiency of extraction of U(VI) from phosphoric acid.

Table 3. Influence of spacer steric hindrance (R4 and R5): Extraction results for amido-phosphonic acid

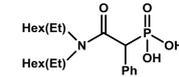
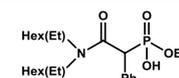
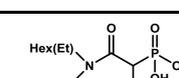
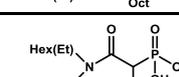
Compounds	D _U	SF _{U/Fe}
	2.0	1.5
	5.4	1
	1.2	1.8
	8	80

2.3.3. Length of alkyl chain of phosphonate (R3)

The feedback on amido-phosphonic acids ligands helped to highlight that: the amide group has to be alkylated by branched aliphatic chains (2-ethylhexyl chain); amide and phosphonic group have to be separated by a methylene bridge; and the methylene bridge has to be alkylated (typically by a phenyl or an alkyl group).

Starting from these findings and in order to improve selectivity and solubility, extraction efficiency as well as the behavior of the molecule during extraction process, we studied the influence of the alkyl chain of phosphonate (R3≠H). Monosaponified phosphonate ligands exhibit better efficiency than the phosphonic derivative in terms of extraction and selectivity properties (Table 4).

Table 4. Influence of alkyl chain of phosphonate (R3): Extraction results for amido-phosphonic acid and amido-phosphonate compound

Compounds	D _U	SF _{U/Fe}
	8	80
	65	1800
	120	1900
	117	2800

The D value are 8 times higher and selectivity 22 times higher for the monoester phosphonate in comparison to the phosphonic acid. This result highlights the importance of the presence of monosaponified phosphonate in the bifunctional ligands. The length and steric hindrance of the monoester phosphonate was investigated by studying the alkyl chain R3= ethyl, butyl, ethylhexyl. No significant change was observed in regards to the extraction efficiency or selectivity which exhibit very high value. Efficiency of the extraction is not influenced by the alkoxy group on the

phosphonate moieties. In order to get better ligand lipophilicity it appears more interesting on the phosphonate group to have a butyl chain than an ethyl one. Furthermore, this lipophilicity can be improve with the introduction of an octyl group on the methylene bridge which overcomes problems observed during uranium stripping such as jellification or third phase appearance.

From a structure-efficiency study, we highlighted the DEHCNPB compound (Butyl-N,N-bis(ethylhexyl)-carbamoylnonyl phosphonate) as optimized ligand for the selective extraction of uranium from phosphoric acid (Fig. 2).

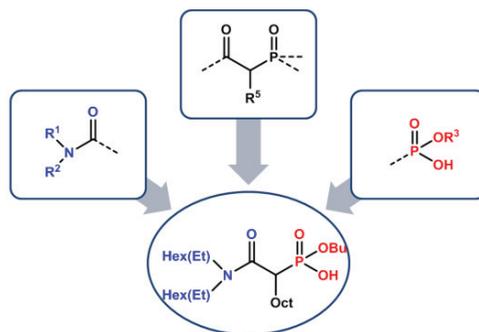


Fig. 2 DEHCNPB ligand as best candidate for uranium extraction from phosphoric acid media

The DEHCNPB ligand exhibits outstanding properties for both extraction and back-extraction processes and appears to be much more efficient than the reference URPHOS system (Table 5). The performances obtained for DEHCNPB are respectively 30 times and 15 times higher for D_U and $SF_{U/Fe}$. Moreover, D_U and $SF_{U/Fe}$ are much higher even with lower concentration of extractant respectively 20 times and 45 times higher for DEHCNPB at 0.1M in dodecane than HDEHP-TOPO system at 0.25M.

Table 5. Comparison of extraction efficiency of HDEHP-TOPO system and DEHCNPB ligands

Compounds	[ligand] (mol/L)	D_U	$SF_{U/Fe}$
HDEHP/TOPO (4/1)	0.25	4	200
	0.25	117	2800
DEHCNPB	0.1	82	8700
	0.05	20	30 000

2.4. Extraction mechanism with DEHCNPB

Additional investigations have been carried out such as the influence of the DEHCNPB and acid concentration on uranium extraction or the influence of uranium loading in order to emphasize the stoichiometry of the complex involved in the extraction.

2.4.1. DEHCNPB and H_3PO_4 concentration dependencies

To study the influence of the ligand concentration on the uranium distribution ratio, experiments were performed at a constant acidity (5 M H_3PO_4) with several DEHCNPB concentrations from 0.05 to 0.25 M in dodecane. The plot of $\log D_U$ versus $\log [DEHCNPB]_{free}$ results in a linear relationship with a slope of ~ 1.9 which reflects that the uranium is extracted by two molecules of DEHCNPB. The extraction by two molecules corresponds to the release of two protons in the aqueous phase, this was confirmed with a slope about 2 for the plot of $\log D_U$ versus $\log [H^+]_{free}$ by measuring the distribution coefficient of uranium for different phosphoric acid concentrations (from 1.8 to 9 M) (Fig. 3) [12].

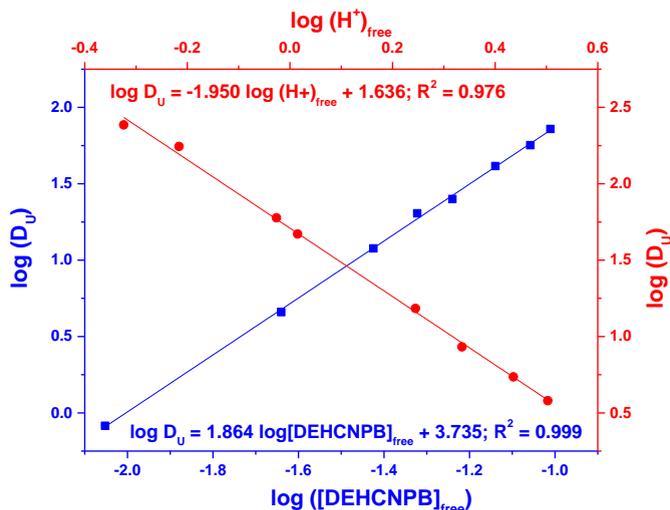


Fig. 3. Influence of DEHCNPB and H₃PO₄ concentration
 $\log(D U) = f(\log[\text{DEHCNPB}]_{\text{free}})$: initial concentration [U] = 250 mg/L; [H₃PO₄] = 5 M; O/A = 1;
 $\log(D U) = f(\log[\text{H}^+]_{\text{free}})$: initial concentration [U] = 2500 mg/L; [Fe] = 2500 mg/L; [DEHCNPB] = 0.1 M; O/A = 1

2.4.2. Uranium concentration dependency

The loading capacity of uranium in organic phase with 0.1 M of DEHCNPB seems to be close to 5 g/L of uranium without forming third phase or precipitates [12]. This statement clearly shows the possibility to concentrate uranium in organic phase with this solvent. Also when considering the molar DEHCNPB / U ratio at saturation it seems to suggest that 4 molecules of DEHCNPB are needed to extract uranium. According to the 1:2 stoichiometry highlighted by the slope method, DEHCNPB molecules could be organized as 2 dimers as proposed in Fig. 4. This hypothesis was recently supported by SAXS, SANS and FT-IR measurements [13].

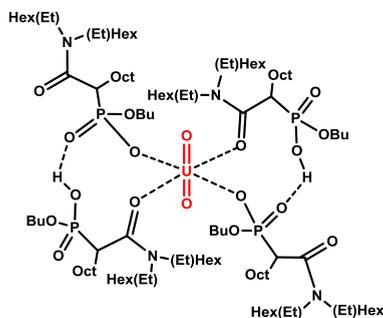
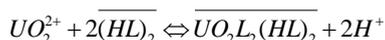


Fig. 4. Proposed coordination of uranium(VI) with DEHCNPB.

From the different experimental results and considering the extractant as a cationic exchanger (HL) the form of the equilibrium can be described as follows:



The proposed mechanisms for the extraction of uranium and iron and the associated constants of the extraction equilibria have been recently determined [14].

2.4.3. Temperature dependency on uranium extraction

The effect of temperature on the distribution coefficient of uranium (VI) was studied from 25 to 55°C at 5 M H₃PO₄ with 0.1 M DEHCNPB (Table 6). The distribution coefficient decreases from as the temperature is increased, which exhibits the exothermic nature of the extraction process.

Table 6. Distribution coefficients for the extraction of U(VI) with DEHCNPB at various temperature

T (°C)	25	35	45	55
D _U	70	30.9	17.8	9.3

The recommended temperature range for the primary extraction of uranium is reported to be around 40–50°C [15]. At 45 °C the D value remains high (D around 18), therefore it would be possible to operate at high temperatures, as is the case with the reference system. The effect of temperature on the distribution coefficient has been quantified using the Vant Hoff equation, which relays the chemical equilibrium constant with temperature. The Arrhenius plot yields a straight line and from this plot the enthalpy of reaction was estimated at -51.5 kJ/mol [12]. The value obtained is within the same order of magnitude as the one calculated for the URPHOS system reported in the literature [16].

2.5. Extraction from a genuine industrial phosphoric acid

The possibility of transposing the DEHCNPB ligand on an industrial scale was evaluated with a genuine industrial phosphoric acid solution. The results are close to those obtained with synthetic solution containing only uranium and iron. The results reported in Table 7 indicate that the ligand is selective to U(VI) with respect to all other cations, with separation factors higher than 1000. Among the impurities only Mo was slightly extracted but it is only present as traces in WPA and the selectivity SF_{U/Mo} is high (> 650). Furthermore, 99% of uranium was recovered in a single stage by contacting the loaded solvent with 0.5 M ammonium carbonate avoiding the formation of cruds or third phase. Iron and molybdenum traces can be easily stripped from the organic phase with ammonium oxalate.

Taking into account the performances of the DEHCNPB ligand in order to recover the uranium from high phosphoric acid solution a flowsheet has been proposed for an industrial application [14].

Table 7. Initial composition for the genuine industrial phosphoric acid solution and distribution ratio of DEHCNPB (0.1 M in dodecane); * not measurable.

Elements	U	Fe	As	Mo	Cr	Zn	Cd	W	Al	V	Ti	Zr
Concentration mg/L	155	2470	16	6	276	393	19	14	1880	264	55	44
D _M	>100	0.01	*	0.15	*	*	*	*	*	*	*	*

3. Conclusions

We have reported an efficient way to synthesize in high yield a new family of bifunctional ligands bearing a cationic exchanger based on a phosphonic acid or phosphonate group and neutral donor based on an amide group. In order to exhibit high efficiency extraction, we showed the importance of the presence of monosaponified phosphonate moiety and amide group alkylated by branched aliphatic chains (2-ethylhexyl chain). Both functionalities amide and phosphonate group have to be separated by a methylene bridge; and the presence of a pendant alkyl chain on this methylene bridge allow a significant increase of the selectivity towards iron.

Combining these parameters, the butyl-N,N-bis(EthylHexyl)carbamoylnonyl phosphonate (DEHCNPB) offers the best results with extraction efficiency up to 30 times higher and selectivity 15 times higher than the synergistic

HDEHP/TOPO reference system, without third phase formation during the extraction and back-extraction processes. Moreover the DEHCNPB is very selective for uranium extraction from phosphoric acid, even in the presence of many impurities such as in genuine industrial phosphoric acid solution, which opens the scope for industrial application and as an alternative to the URPHOS process.

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