Understanding of Uranium Extraction Mechanisms from Phosphoric and Sulfuric Media using DEHCNPB

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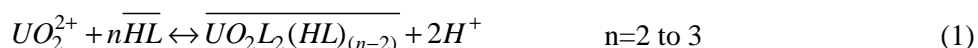
The extraction of uranium(VI) from phosphoric and sulfuric acid solutions using DEHCNPB (butyl-1-[*N,N*-bis(2-ethylhexyl)carbamoyl]nonyl phosphonic acid) was studied to understand the influence of the original acidic medium on uranium extraction (phosphoric acid 5 mol/L or sulfates 1.6 mol/L at pH=1). Uranium(VI) extraction isotherms highlight different extraction behaviors depending on the initial medium with a lower [DEHCNPB]/[U] ratio reached at saturation with the phosphoric medium. Slope analysis showed different average stoichiometries: 1.9 and 3.3 for the phosphate and sulfate experiments respectively. The co-extraction of water with uranyl was evidenced by Karl-Fischer titrations and ESI-MS measurements and ESI-MS analysis confirmed the presence of uranyl/DEHCNPB complexes with one molecule of water, probably in the first coordination sphere.

1. Introduction

Phosphoric acid is largely produced from phosphate ores, which contain a small concentration of uranium (from 30 to 300 ppm) but are abundant. Therefore, there is a substantial quantity of uranium potentially recoverable from phosphate rocks (around 4 Mt), which constitutes an important secondary source for uranium production [1]. Recovering uranium from wet-phosphoric acid would allow the decontamination of phosphoric acid from uranium and the valorization of uranium for the nuclear industry. The extraction of uranium from wet phosphoric acid was carried out at an industrial scale using various processes and extractants [2]. For instance, the synergistic mixture HDEHP/TOPO is a well know system used for this purpose since the 1950s [3]. Nevertheless, those systems present several drawbacks, like the distribution ratio of uranium(VI) which is not high enough to develop a compact process, and the selectivity towards iron which could be improved. Such processes should enable the recovery of uranium from concentrated phosphoric acid (high complexation effect of uranium in the aqueous phase) while showing high selectivity versus impurities. Indeed, high concentrations of iron and aluminum are present in phosphate rocks (about 2 to 6 g/L), so extraction systems with high U(VI)/Fe(III) selectivity are expected in order to reach specifications for uranium decontamination.

The extractant DEHCNPB (butyl-1-[*N,N*-bis(2-ethylhexyl)carbamoyl]nonyl phosphonic acid, structure Figure 1) was recently developed [4] and showed good performances for the extraction of

U(VI) from phosphate media with very high selectivity for U(VI) towards iron (about 30 times higher than with the mixture HDEHP/TOPO) [5, 6]. DEHCNPB is also considered as a suitable extractant for uranium recovery from conventional ores. The main difference in this latter perspective is that uranium should be extracted from a sulfuric medium (leaching solutions) [7]. In order to develop an efficient process to recover uranium from a sulfuric medium, there is a need for understanding and characterizing the different extraction mechanisms of uranium depending on the initial medium (phosphoric or sulfuric). Though the

Figure 1. Molecular structure of DEHCNPB extractant.

extraction of uranium from a phosphoric medium using DEHCNPB was extensively studied during the development of the process [8, 9], the extraction mechanisms of uranium are still misunderstood and there are few data published on the extraction of uranium from a sulfuric medium [10]. DEHCNPB is a cationic exchanger and the extraction mechanism should involve the exchange of two protons from the phosphonic acid function as depicted in the following equation:

$$UO_2^{2+} + n\overline{HL} \leftrightarrow \overline{UO_2L_2(HL)_{(n-2)}} + 2H^+ \qquad \text{n=2 to 3} \qquad (1)$$

Previous studies showed that this simple extraction mechanism is not sufficient to describe extraction of uranium from a phosphoric acid solution, especially at high uranium concentration range in the organic phase where polymetallic species should be taken into account [4]. Concerning the characterization of complexes formed in the organic phase, the participation of the amide function to the coordination in the first coordination sphere at high concentration of uranium was also considered [8]. In the present study, extraction data of uranium from both phosphoric and sulfuric media using DEHCNPB are reported and compared (slope analysis and extraction isotherms). Water extraction was also investigated and complexes formed in the organic phase were characterizes by ESI-MS to provide more understanding on the impact of the initial medium (phosphate or sulfate) on uranium extraction behavior.

2. Experimental

2.1. Materials and Sample preparation

Batch solvent extraction experiments were performed in order to study the influence of uranium and acid total concentrations on uranium distribution ratios. Organic phases were prepared by diluting DEHCNPB (synthesized by Pharmasynthese and purified by preparative chromatography, purity ~99 % determined by GC-FID) at 0.1 mol/L in hydrogenated tetrapropylene (TPH purchased from NOVASEP, France). The concentration of DEHCNPB in the organic phases was determined accurately by titration using sodium hydroxide 0.1 mol/L (AVS Titrinorm), in ethanol/water mixture (60/40%$_{v/v}$). Aqueous solutions of uranium phosphate were prepared from uranyl nitrate $UO_2(NO_3)_2$ (purchased from PROLABO) dissolved in water and precipitated into uranyl hydroxide by addition of sodium hydroxide. The isolated $UO_2(OH)_2$ precipitate was then washed three times with deionized
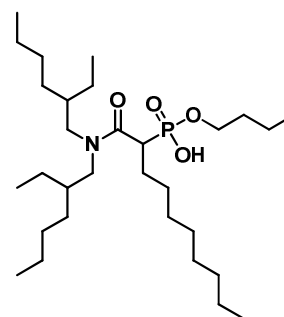
water and dissolved in 5 mol/L phosphoric acid (PROLABO). For sulfate solutions, uranium peroxide was dissolved in 0.6 mol/L sulfuric acid solution. Aqueous phases were then prepared by dilution of the concentrated uranium mother solution in sulfuric acid (PROLABO) and sodium sulfate (Sigma-Aldrich) solutions to adjust to pH=1 with a total concentration of sulfates equal to 1.6 mol/L (comparable with industrial leaching solutions).

2.2. Batch extraction experiments

For all extraction experiments, aqueous solutions were contacted until equilibrium was reached (20 min) at 25±1°C with equal volumes of organic phase (V_{aq} = V_{org}) by means of an automatic vortex shaker equipped with a thermostated cell. After phase separation by centrifugation, aqueous phases were diluted in 0.3 mol/L HNO_3 and organic phases in TPH. Uranium concentration was measured by ICP-AES (Perkin Elmer Optima 8300DV) in the initial and equilibrium aqueous phases. Selected wavelengths for uranium were 386, 367, 409, 393 and 424 nm. Scandium was introduced in all diluted samples as an internal standard at 5 mg/L. Aqueous phases containing low uranium concentrations (below 1 ppm) were analyzed by ICP-MS (Perkin Elmer Q-ICP-MS Elan DRCe). Organic phases at equilibrium were analyzed by the same ICP-AES instrument after dilution in TPH, using a parallel path micronebulizer (Burgener MiraMist) for sample introduction into the plasma torch. Total concentrations of phosphoric acid in aqueous phases were determined by potentiometric titration using NaOH, and pH was measured at equilibrium for all extraction tests from sulfate solutions. The H_2O content in organic phases was determined by Karl-Fischer titrations.

2.3. Characterization of complexes in the organic phase

Mass spectra of organic phases were acquired after dilution (100 fold) in methanol using Bruker micrOTOF-QII equipped with an electrospray ionization source and a time-of-flight analyzer.

3. Results and Discussion

3.1. Extraction experiments

3.1.1 Uranium extraction isotherms

Uranium extraction isotherm from a phosphoric medium was acquired during a previous study [4] by increasing the concentration of uranium (from 1 mmol/L up to 0.55 mol/L) in the initial solution of phosphoric acid 5 mol/L. These data are compared in Figure 2 with uranium extraction isotherm from a sulfuric medium ($C_{(SO4)2-}$= 1.6 mol/L, pH= 1) established in the present work. Uranium extraction isotherms show different behaviors depending on the aqueous medium. The saturation of the organic phase is obtained when 0.056 mol/L of uranium is extracted from a phosphoric medium ($C_{DEHCNPB}/Cu^{org}$ = 1.8). Whereas, the maximum uranium concentration loaded in the organic phase is 0.045 mol/L ($C_{DEHCNPB}/Cu^{org}$ = 2.2) when extracted from a sulfuric medium. In both cases, this lower ratio at saturation suggests that new complexes are formed with around two molecules of DEHCNPB for the extraction of one uranyl cation. As mentioned in our previous study [4], it is necessary to take into account the formation of bimetallic species $\overline{(UO_2)_2L_4}$ to better model extraction isotherm saturation from the phosphoric medium. The shape of the extraction isotherm suggests that the saturation of the organic phase is not reached in the sulfuric experiment, but it was difficult to prepare more concentrated solutions of uranium in sulfates. In addition, the

extraction isotherms do not show the same behavior between 0.03 mol/L and 0.05 mol/L of uranium in the organic phase. In fact, the isotherm acquired from a sulfuric medium takes shape of a Langmuir isotherm, while the one acquired from a phosphoric medium shows a more complex behavior. Since the complexation effect is more important in the phosphate medium compared with the sulfate, the saturation of the organic phase should be reached faster when increasing the concentration of uranium in the initial aqueous phase, which is not the case. Those results suggests that different extraction mechanisms should take place depending on the initial

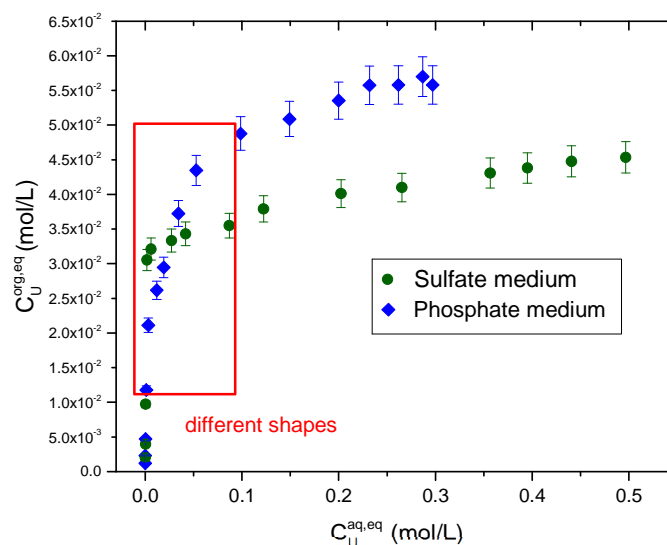Figure 2. Uranium extraction isotherms. DEHCNPB 0.1 mol/L in TPH. Phosphate medium: $[H_3PO_4]=$ 5 mol/L ; sulfate medium: $C_{(SO4)2-}$= 1.6 mol/L ; pH= 1; O/A= 1 ; T= 25 °C.

medium. Nevertheless, no phosphate or sulfate was observed to be co-extracted with uranyl cation. Extraction of phosphoric acid in the organic phase was investigated by means of ^{31}P-NMR measurements, showing that phosphoric acid is not involved in the extraction mechanism of uranium [10]. For sulfates, direct measurements of sulfur in loaded organic phases were investigated by ICP-AES and showed no significant signal for sulfur. Additional data are then required to better understand differences in extraction mechanisms.

3.1.2 Influence of DEHCNPB concentration on uranium(VI) extraction

The influence of DEHCNPB concentration on uranium(VI) extraction from a phosphoric medium was already reported in a previous study [10]. Those data are reported in Figure 3 and compared with the same experiment performed from a sulfuric medium. The determination of free extractant concentration in the organic phase using ^{31}P-NMR was performed as described before.[10] The average stoichiometry of the complexes formed in the organic phase was estimated using slope analysis. Activity coefficients and speciation in the aqueous phase were calculated using a dedicated Scilab program. Based on the general extraction mechanism (Equation 1), the extraction constant can be defined by equation (2):

$$K_{ex} = \frac{[\overline{UO_2L_2(HL)_{(n-2)}}].[H^+]^2}{[UO_2{}^{2+}].[\overline{HL}]^n} . \frac{\gamma(\overline{UO_2L_2(HL)_{(n-2)}}).\gamma(H^+)^2}{\gamma(UO_2^{2+}).\gamma(\overline{HL})^n} \qquad (2)$$

While the distribution ratio of uranium can be expressed as follows:

$$D_U = \frac{C_U^{org}}{C_U^{aq}} = \frac{[\overline{UO_2L_2(HL)_{(n-2)}}]}{[UO_2^{2+}](1+\sum_i [A^{z-}]^v.\beta_i)} \qquad (3)$$

In those equations, γ_I is the activity coefficient of species I, A is the anion participating in the formation

of aqueous complex i, z its charge, υ its stoichiometric coefficient, and β_i the formation constant of complex i. Activity coefficients in the organic phase are supposed to be equal to unity. By combining equations (2) and (3), the following relationship may be proposed:

$$K_{ex}^{app} = \frac{D_U . [H^+]^2 . (1 + \sum_i [A^{z-}]^\upsilon . \beta_i)}{[\overline{HL}]^n} \frac{\gamma(H^+)^2}{\gamma(UO_2^{2+})} \tag{4}$$

$$\log(D_U) \underbrace{- 2.pH + \log(1 + \sum_i [A^{z-}]^\upsilon . \beta_i) + 2.\log\gamma(H^+) - \log\gamma(UO_2^{2+})}_{X} = n.\log([\overline{HL}]_{free}) + \log(K_{ex}^{app}) \tag{5}$$

In equation (5), n is the average stoichiometric coefficient of DEHCNPB and can be measured as the slope obtained when plotting $\log(D_U)$ + X as a function of $\log[\overline{HL}]_{free}$ as shown in Figure 3. For the extraction of uranium from a phosphoric medium, the slope analysis shows a linear behavior with a slope of 1.9, which indicates the formation of a 1:2 complex between the ligand and the uranyl cation. Concerning the extraction of uranium from a sulfuric medium, a slope of 3.3 is obtained. This observation would suggest the extraction of uranium by three molecules of DEHCNPB in average (or three dimers). As this stoichiometric coefficient is not an

Figure 3. Slope analysis: $\log(D_U)$ + X as a function of free DEHCNPB concentration logarithm. Phosphate medium: C_U= 1.2 g/L; [H$_3$PO$_4$]= 5 mol/L; sulfate medium: C_U= 1.0 g/L; $C_{(SO4)2-}$= 1.6 mol/L; pH$_{initial}$ =1; O/A=1; T=25 °C.

integer, uranium may be extracted from a sulfuric medium according to a complex mechanism, involving the formation of multiple complexes in the organic phase. However, this average stoichiometry shows that more DEHCNPB molecules are required to extract uranium from a sulfuric medium compared to phosphoric acid, and thus different mechanisms could be involved depending on the initial medium. Slope analysis is also consistent with uranium extraction isotherms, showing that a higher [DEHCNPB]/[U] ratio is reached at saturation when uranium is extracted from a sulfate medium.

3.1.3 Extraction of water

The content of water extracted in the organic phase as a function of uranium concentration was determined starting from a solution of phosphoric acid 5 mol/L or a solution of sulfates (1.6 mol/L at pH=1) and results are reported in Figure 4. The quantity of water extracted increases when uranium
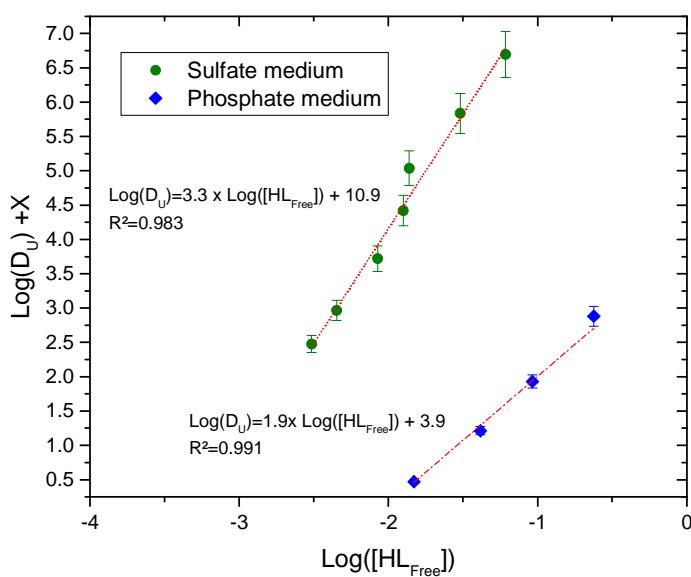
content loaded in the organic phase gets higher. This observation suggests that there is some water co-extracted in the organic phase with uranium. This tendency is observed for both media. The ratio of water over uranium content in the organic phase tend to 1, which means that around one molecule of water is co-extracted with one uranyl cation. Species like $\overline{UO_2(H_2O)L_2(HL)_{2n-2}}$ could be formed in both cases. But in the case of uranium extraction from phosphoric acid, a maximum is reached (53 mM of water for 40 mmol/L of uranium) before decreasing at higher concentration of uranium. This behavior would suggest that a non-hydrated complex appears

Figure 4. Evolution of water content in organic phases as a function of uranium concentration. Phosphate medium: $[H_3PO_4]$= 5 mol/L; sulfate medium: $C_{(SO4)2-}$= 1.6 mol/L; $pH_{initial}$ = 1; O/A=1; T=25 °C.

when the organic phase is saturated. This is also an additional indication showing that different extraction mechanisms are involved when uranium is extracted from a phosphoric medium, with different hydration of extracted complexes when the concentration of uranium reaches saturation.

3.2. Characterization of uranium complexes in the organic phase by ESI-MS

Electrospray ionization (ESI) is a soft ionization technique that allows the transfer of pre-existing ions from the solution into the gas phase so that speciation information in solution can be obtained. This technique has been used successfully to characterize metal-ligand complexes in solution involving liquid-liquid extraction systems containing uranyl cation [11, 12]. Loaded organic phases of DEHCNPB 0.1M in TPH were analyzed by ESI-MS after dilution in methanol to characterize species formed after extraction of uranium from both media ($[H_3PO_4]$= 5 mol/L and $C_{(SO4)2-}$= 1.6 mol/L at pH=1). In the phosphoric medium experiment, almost all the DEHCNPB ions detected contain uranium and only one ion of protonated DEHCNPB $[HL.H]^+$ remains (L corresponding to the deprotonated form of DEHCNPB). Whereas in the sulfuric medium experiment, the most abundant ions correspond to Na^+ adducts such as $[HL.Na]^+$, $[(HL)_2.Na]^+$ and $[(HL)_3.Na]^+$. The aqueous phase is prepared from sodium sulfate whereas the phosphoric solution is only made of phosphoric acid explaining why higher amounts of sodium could be present in the sulfate experiment. Monometallic species where observed in the phosphate medium extraction: $[(HL)_2.UO_2]^{2+}$ and $[HL.L.UO_2]^+$ and $[L.UO_2.H_2O.CH_3OH]^+$. The most intense species is $[L.UO_2.H_2O.CH_3OH]^+$ containing one molecule of water and one molecule of methanol. This observation confirms the potential participation of water to the complexes formed in the organic phase. Moreover, the fragmentation of this ions has been performed, and leads to $[L.UO_2.H_2O.]^+$ and $[L.UO_2.(H_2O)_2.]^+$ respectively with the loss of a methanol molecule and with the exchange of a methanol molecule with a water molecule remaining in the gas
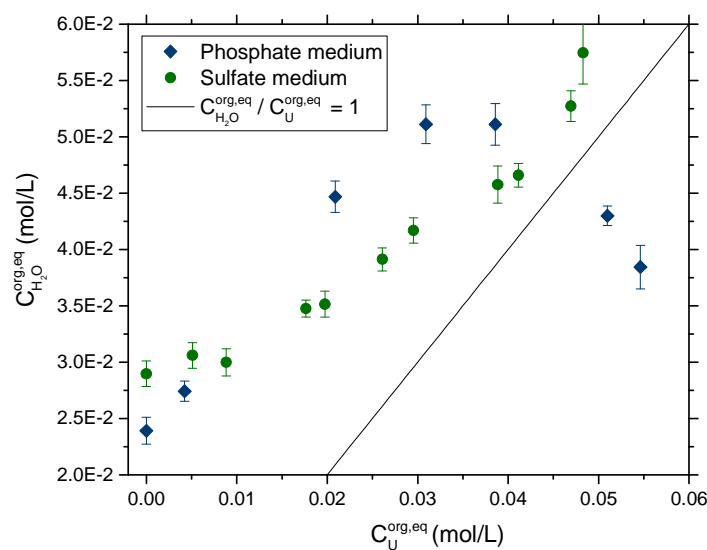
phase. Water was also found in the $[L_2.(UO_2)_2.(H_2O)_2.]^{2+}$ bimetallic species. The formation of $[L.UO_2.H_2O.CH_3OH]^+$ is also observed in the sulfuric medium experiment but with a lower intensity. Those results consolidate the hypothesis that some water is co-extracted with uranium and is strongly bound to uranyl (potentially in the first coordination sphere) since no loss of water molecule was observed during fragmentation experiments. Many polymetallic species could be observed in the phosphoric experiment ($[L_2.(UO_2)_2.(H_2O)_2.]^{2+}$, $[HL.L_2(UO_2)_2]^{2+}$, $[L_4.(UO_2)_3]^{2+}$, $[HL.L_4.(UO_2)_3]^{2+}$ and $[(HL)_2.L_4.(UO_2)_2]^{2+}$), which confirm the hypothesis proposed before to model the behavior of uranium extraction isotherm at saturation.[4] Two polymetallic species could also be observed in the sulfate experiment: $[(HL)_2.L_3.(UO_2)_2.Na]_2^+$ and $[(HL).L_5.(UO_2)_3.Na]^{2+}$. Other uranyl species were detected in the sulfate experiment with sodium like $[(HL)_2UO_2Na_2]^{2+}$, $[(HL)_2.L_2.UO_2.Na_2]^{2+}$ and $[HL.L_2UO_2Na]^+$ with only one uranyl center. Those ESI-MS experiments confirm the possible formation of hydrated uranyl complexes and bimetallic species at high concentration of uranium in the organic phase after extraction from a phosphoric and sulfuric media. Those species are less intense in the case of sulfuric medium but it might be due to a lower concentration of uranium in the organic sample (lower saturation of the extractant) and the presence of sodium, which might interfere in the response factor of species formed during ionization in the gas phase.
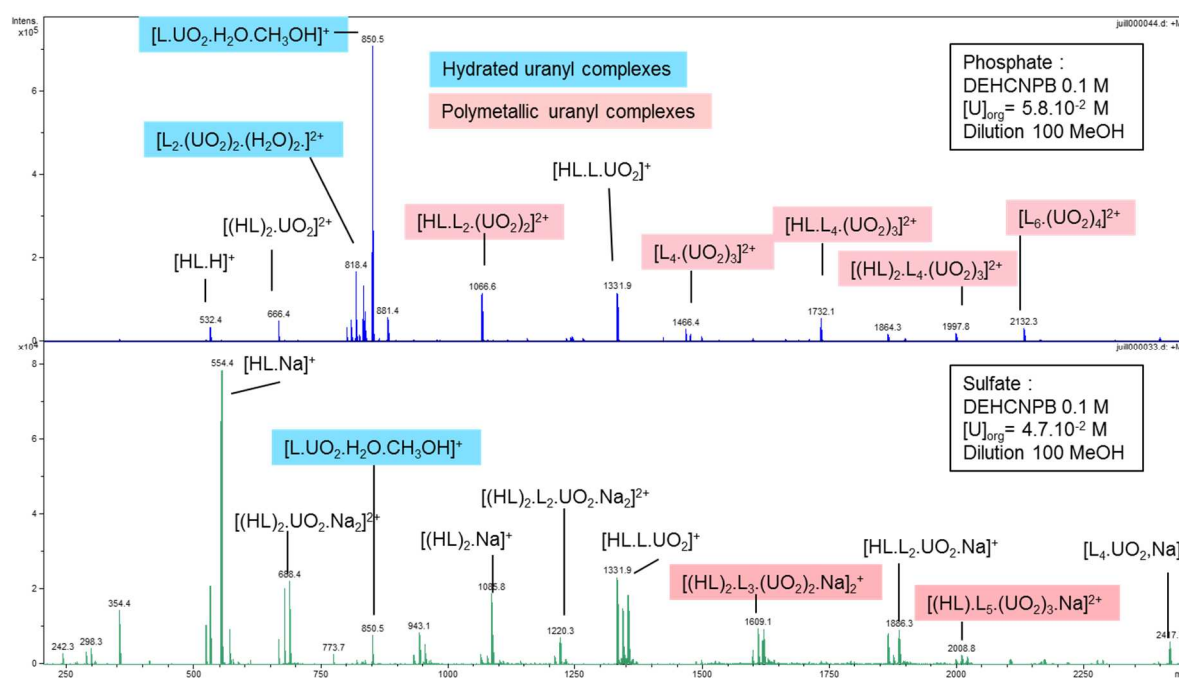

Figure 5. ESI-MS spectra of loaded organic phases (0.1 mol/L DEHCNPB in TPH, HL=DEHCNPB) with uranium after dilution 100 in methanol. Phosphoric medium: C_U^{ini} = 75 g/L ; $[H_3PO_4]$= 5 mol/L; sulfate medium : C_U^{ini} = 135 g/L; $C_{(SO4)2-}$= 1.6 mol/L; $pH_{initial}$ = 1; O/A= 1; T = 25 °C.

4. Conclusion

Uranium extraction isotherms acquired with the solvent DEHCNPB 0.1 mol in TPH from phosphoric acid 5 mol/L or sulfate medium (1.6 g/L of sulfates at pH=1) showed different behaviors. A higher saturation of the extractant DEHCNPB could be reached starting from the phosphoric acid

solution with a [DEHCNPB]/[U] ratio of 1.8 instead of 2.2 for the sulfuric experiment. Since the complexation effect is more important in the phosphate medium, this result highlights different extraction mechanisms depending on the initial medium. No evidence could be found for phosphate or sulfate counter anions co-extraction with uranyl (the extraction mechanism should then rely exclusively on a cation exchange mechanism). Slope analysis showed different average stoichiometries: 1.9 and 3.3 for the phosphate and sulfate experiments respectively, which is consistent with the lower [DEHCNPB]/[U] ratio reached in the uranium isotherm experiment from phosphoric acid. Karl-Fischer measurements showed that some water molecules are co-extracted with uranyl cation and that the uranyl/water ratio is close to one at saturation. But with phosphates, the behavior is different at saturation and the water content decreases when $C_U^{org} > 40$ mmol/L. Finally, ESI-MS measurements confirmed the presence of complexes with one molecule of water per uranyl cation in the loaded organic phases.

Acknowledgement

References

1) S. Gabriel, A. Baschwitz, G. Mathonnière, T. Eleouet, F. Fizaine, *Ann. Nucl. Energy,* **58**, 213-220 (2013).

2) D. Beltrami, G. Cote, H. Mokhtari, B. Courtaud, B.A. Moyer, A. Chagnes, *Chem. Rev.,* **114**, 12002-12023 (2014).

3) F.J. Hurst, D.J. Crouse, K.B. Brown, *Ind. Eng. Chem. Process Des. Dev.,* **11**, 122-128 (1972).

4) M. Miguirditchian, G. Bernier, V. Pacary, C. Balaguer, C. Sorel, R. Berlemont, B. Fries, M. Bertrand, B. Camès, A. Leydier, R. Turgis, G. Arrachart, S. Pellet-Rostaing, H. Mokhtari, *Solvent Ext. Ion Exch.,* **34**, 274-289 (2016).

5) M. Miguirditchian, G. Bernier, C. Balaguer, X. Hérès, V. Pacary, M. Bertrand, B. Camès, H. Mokhtari, *Proceedings ISEC 2014,* (2014).

6) G. Arrachart, N. Aychet, G. Bernier, F. Burdet, A. Leydier, M. Miguirditchian, S. Pellet-Rostaing, G. Planque, R. Turgis, E. Zekri, *Patent,* WO2013EP59352 20130506 (2013).

7) P. Baron, G. Bernier, D. Hartmann, C. Laluc, M. Marbet, *Patent,* WO2014139869 A2014139861 (2013).

8) O. Pecheur, D. Guillaumont, S. Dourdain, L. Berthon, R. Turgis, C. Fillaux, G. Arrachart, F. Testard, *Solvent Ext. Ion Exch.,* **34**, 260-273 (2016).

9) R. Turgis, A. Leydier, G. Arrachart, F. Burdet, S. Dourdain, G. Bernier, M. Miguirditchian, S. Pellet-Rostaing, *Solvent Ext. Ion Exch.,* **32**, 685-702 (2014).

10) B. Fries, C. Marie, V. Pacary, C. Berthon, M. Miguirditchian, H. Mokhtari, M.C. Charbonnel, *Procedia Chem.,* **21**, 93-100 (2016).

11) L.W. McDonald, J.A. Campbell, T. Vercouter, S.B. Clark, *Anal. Chem.,* **88**, 2614-2621 (2016).

12) F. Rodrigues, G. Ferru, L. Berthon, N. Boubals, P. Guilbaud, C. Sorel, O. Diat, P. Bauduin, J.P. Simonin, J.P. Morel, N. Morel-Desrosiers, M.C. Charbonnel, *Mol. Phys.,* **112**, 1362-1374 (2014).