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Extraction of uranium from sulfuric acid media using amino-diamide extractants

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Abstract

Two extractants, *N,N'*-((octylazanediy)bis(ethane-2,1-diyl))dioctanamide (**LI**) and *N,N'*-((octylazanediy)bis(ethane-2,1-diyl))di-2-methylheptanamide (**LII**), have been synthesised in two steps starting from diethylenetriamine and involving a peptide coupling step. The efficiency and selectivity of the extractants in dodecane/octanol (95/5 v/v) toward the extraction of uranium from sulfate media have been investigated showing that the uranium extraction from sulfuric acid is more efficient at a low H₂SO₄ concentrations. Slope analysis method revealed 2:1 extractant/metal ratio, which is in accordance with NMR titration as well as DFT calculations. The extractants are found to be selective toward uranium over competitive cations present in a simulated leach solution. Finally, a stripping step has been performed and given rise to a successful quantitative recovery of uranium.

Keywords

Uranium; Sulfuric acid; Solvent extraction; Amino-diamide extractants

1. Introduction

Uranium can be found in association with many other elements in the Earth crust at different concentrations from a few ppb in seawater to more than 100 ppm in its ores.(Anon., 2019) Due to a very high energy density (*i.e.* amount of heat/energy released by a combustion/fission of a specified amount of a fuel) uranium has been in use as a main component of the fuel in nuclear power plants. Therefore, the extraction and purification of uranium are of significant importance, and many processes have been proposed for the production and processing of uranium.

Uranium extraction from seawater is an alternative to land-mining operations with an estimated total content of uranium amounts over 1000 times more than terrestrial sources.(Abney et al., 2017; Ivanov et al., 2019) However, the low concentration of the uranyl ion in seawater and the presence of competitive ions complicate its recovery.(Kim et al., 2013) Uranium continue to be mined from geological deposit. After leaching by acid or alkaline solutions, the concentration and purification of uranium is mainly performed through hydrometallurgical processes and, with varying degrees of efficiency, by solvent extraction, ion exchange, or precipitation.(Edwards and Oliver, 2000; Lunt et al., 2007; Wang and Zhuang, 2019)

Liquid-liquid extraction is one of the most effective methods for the recovery of uranium and its' separation from the associated impurities present in orebodies as well as those present in spent nuclear fuels. Spent nuclear fuels are currently reprocessed by using the PUREX process (Plutonium Uranium Reduction Extraction) with TBP (tri-n-butyl phosphate) as extracting agent.(Lanham and Runion, 1949) For the extraction and separation of uranium whether for the upstream or downstream of the nuclear fuel cycle, many different extracting agents have been developed such as amides and diamides (Manchanda and Pathak, 2004; Pathak, 2014; Yan et al., 2016), trialkyl amines (Quinn et al., 2013), trialkyl phosphines,(Orabi, 2013) carbamoylalkyl-phosphonates derivatives (Turgis et al., 2014a; Turgis et al., 2014b) dialkyl phosphonic acids,(Balaguer et al., 2012) as well as macrocycles including calixazacrowns (Wehbie et al., 2018) or crown ethers such as dicyclohexano-18-crown-6 (DCH18C6)(Kumar et al., 2011; Shukla et al., 1993). Extraction efficiency and selectivity toward the target element can be piloted by choosing an appropriate extracting agent to a given application.

The organophosphorus extractants show high extraction and separation performances for uranium. The extraction of uranium from sulfuric leach liquor has been notably implemented by the 'DiAlkyl Phosphoric acid EXtraction' (DAPEX) process involving di-2-ethyl-hexyl-phosphoric acid (HDEHP), through a cationic exchange mechanism, in combination with various synergistic reagents.(Blake et al., 1956) The DAPEX process was superseded by the 'AMine EXtraction' (AMEX) process, which is based on the use of amines as extractants, because tertiary amines are more selective than HDEHP for uranium extraction from acidic sulfate solutions (Coleman et al., 1958), through an anionic exchange mechanism.(Sukhbaatar et al., 2019) One of the drawbacks of phosphorylated derivatives is that they nonincinerable nature lead to the formation of solid phosphate residues during their destruction. Also the formation

of degradation products by radiolysis makes the management of the solvent complex.(Berthon and Charbonnel, 2009) CHON extractant (composed exclusively of only Carbon, Hydrogen, Oxygen, and Nitrogen) which include amine derivatives provide innocuous degradation products after their complete combustion and the cleaning of spent solvents is easier than phosphorus-based compounds (Casparini and Grossi, 1980).(Berthon et al., 2001)(Ruikar et al., 1993) which allows also to minimise the secondary radioactive waste. However, some problems could be encountered with the use of amines, such as the degradation of tertiary amines by acidic hydrolysis and oxidation by nitrate(Munyungano, 2007) or radical reaction in the presence of vanadium(V).(Chagnes et al., 2011) In addition, because molybdenum(VI) extraction is stronger than U(VI) with tertiary amines, the presence of Mo(VI) will decrease the uranium extraction or the loading capacity of the amine. Furthermore, the solubility of the Mo(VI) complex with tertiary amines is low in aliphatic diluents, which results in the formation of a third phase.(McDonald et al., 1981)

Since their first description given by Stephan et al.,(Stephan et al., 1991b)(Stephan et al., 1991a) tridentate diamides extractants such as diglycolamides and imino diacetamides have gained special importance in the extraction and separation of metal cations. (Sasaki et al., 2009; Shimojo et al., 2008; Wehbie et al., 2017; Wehbie et al., 2016a; Wehbie et al., 2016b) The affinity of these tridentate extractants for trivalent cations is higher than that of bidentate counterparts due to the corresponding complex stabilities. Sasaki and Choppin (Sasaki and Choppin, 1996) (Sasaki and Choppin Gregory, 1998) showed that tridentate diglycolamides are more efficient for the extraction of lanthanides and transuranic actinides than bidentate malonamides. In general diglycolamides, with a hard donor central oxygen atom, are more selective toward the extraction of lanthanides over actinides.(Ansari et al., 2012; Huang et al., 2014; Iqbal et al., 2012; Sasaki et al., 2001) Recently, the extraction behaviour of multidentate extractant *N,N,N''',N'''*-tetraoctyl-*N'',N''*-ethidene diglycolamide (TOE-BisDGA) has been investigated showing that the extraction of uranium(VI) from nitric aqueous solution was presumed to proceed by neutral extraction or ion association extraction mechanism.(Xiao et al., 2019)

Researchers have shown that the replacement of the central oxygen atom in tetraoctyl diglycolamide (TODGA) by a soft N atom could enhance the selectivity of these extractants toward actinides.(Iqbal et al., 2010; Manna and Ghanty, 2012; Sasaki et al., 2013a; Sasaki et al., 2013b) The imino diamide compounds containing two hard oxygen donor atoms which stabilise the complexed metal cation, and a soft nitrogen atom that governs the selectivity toward target actinides. Imino diamides such as imino-diacetamide with one carbon atom separating the amine and the amides sites show lower efficiency toward the extraction of lanthanides and actinides with respect to their analogous oxo-diacetamide moieties (DGA)(Sasaki et al., 2009), and they show higher selectivity toward molybdenum, the main competitor ion for uranium extraction in sulfuric acid media.(Ruhela et al., 2014)

In our previous work, imino diamide extractant have been introduced on *t-butyl*-calix[4]arene at the distal-1,3-positions of the lower rim. Preliminary extraction studies and mechanistic

investigations highlighted the potential of such N-alkylcalix[4]azacrown for the selective extraction of uranium (VI) at low sulfuric acid concentration. (Wehbie et al., 2018)

On the basis of these observations, in the present work, we have synthesised two imino diamide type extractants, where the central nitrogen atom is linked to the terminal amides moieties by two ethylene linkers. We used these extractants for the extraction and separation of uranium from a synthetic sulfuric acid leach solution containing competitive metallic cations.

The effects of different parameters such as acidity of the aqueous phase, as well as the concentration of the extractant and the effect of temperature have been studied. The formation of 2:1 complexing species between uranium and the extractants is suggested by the slope method, NMR and DFT calculations.

2. Experimental

Chemicals and analysis

Chemicals (analytically pure) were purchased from Sigma-Aldrich or Alfa Aesar and were used without further purification. Anhydrous solvents were purchased from Acros (AcroSeal®). Reactions were monitored by thin-layer chromatography (Merck TLC Silica Gel 60 F254).

Flash chromatography was performed using a Combiflash Reveleris X2. NMR analyses were performed on a Bruker 400 Ultrashield VS spectrometer. Displacements are reported in parts-per-million using the solvent (CDCl_3 : 7.26 ppm for ^1H ; 77.16 ppm for ^{13}C) as an internal reference. Fourier transform infrared (FTIR) measurements were performed on a PerkinElmer Spectrum 100 instrument in ATR (Attenuated Total Reflection) mode. The wavenumber range was from 400 cm^{-1} to 4000 cm^{-1} . The beam resolution was 4 cm^{-1} . Background acquisition was done before measurement. ESI-MS was performed on a Flexar SQ 300 MS instrument.

Metal concentrations were determined using a Spectro ARCOS inductively coupled plasma-atomic absorption spectrometer (ICP-AES). The wavelengths for the measurements for the U (279.394, 367.057, 385.958 and 409.017 nm), Ce (413.380, 413.765, 418.650 and 448.691 nm), Fe (238.204, 239.562, 259.941, 261.187, 275.573 and 373.486 nm), La (333.749, 379.478, 408.672, 412.323 and 419.655 nm), Mo (202.095, 203.909, 204.664, 281.615 nm), Ti (307.864, 323.452, 334.187, 334.941 and 336.121 nm) and Zr (257.139, 272.262, 339.198 and 343.823 nm) were chosen to avoid any spectral interference between the elements.

Synthesis

General procedure for the peptide coupling (1a,b)

A carboxylic acid, octanoic acid or 1-methylheptanoic acid (2.79 g, 19.38 mmol), and hydroxyl benzotriazole (1.61 g, 10.66 mmol) were poured into 40 mL CHCl_3 in a round-bottomed flask at $0\text{ }^\circ\text{C}$. Then, *N,N'*-dicyclohexylcarbodiimide (DCC, 2.19 g, 10.66 mmol) was added, and the obtained mixture was stirred for 30 min at room temperature. Then, diethylenetriamine (1 g,

9.69 mmol) was added to the resulting suspension, which was left to stir for two days at room temperature. After filtration, the filtrate was washed with water (2 × 30 mL), 1 M HCl (2 × 30 mL), and a saturated solution of NaCl (2 × 30 mL). The organic collections were then dried over anhydrous Na₂SO₄ and evaporated under vacuum to afford compounds **1a** and **1b** as cream-coloured pastes.

Diethylenetriamine-1,7-dioctamide, 75%, 1a

¹H-NMR (400 MHz, CDCl₃) δ [ppm]: 0.86 (t, J = 6.4 Hz, 6 H, CH₂CH₃), 1.27 (m, 16 H, CH₂CH₃), 1.61 (t, J = 6.8 Hz, 4H, CH₂-CH₂-CO), 2.17 (t, J = 7.6 Hz, 4 H, -CH₂-CO), 2.74 (t, J = 5.6 Hz, 4 H, NH-CH₂), 3.32 (m, 4H, CO-NH-CH₂), 6.32 (m, 2H, CO-NH) (Figure SI-1).

¹³C-NMR (400 MHz, CDCl₃) δ [ppm]: 14.1, 22.6, 25.8, 29.1, 29.3, 31.7, 36.8, 39.1, 48.5, 173.7 (Figure SI-2).

Diethylenetriamine-1,7-dimethylhexamide, 78%, 1b

¹H-NMR (400 MHz, CDCl₃) δ [ppm]: 0.87 (t, J = 6.4 Hz, 6 H, CH₂CH₃), 1.12 (d, J = 6.8 Hz, 6H, CHCH₃), 1.27 (m, 12 H, CH₂CH₃), 1.62 (m, 4H, CH₂-CH₂-CO), 2.21 (m, 2 H, -CH), 2.76 (t, J = 6 Hz, 4H, NH-CH₂), 3.33 (q, J = 5.6 Hz, 4H, CO-NH-CH₂), 6.14 (bs, 2H, CO-NH) (Figure SI-3).

¹³C-NMR (400 MHz, CDCl₃) δ [ppm]: 14.0, 17.9, 22.6, 27.2, 31.8, 34.3, 39.0, 41.5 (CH), 48.6, 177.16 (Figure SI-4).

General procedure for the preparation of 4-octyldiethylenetriamine-1,7-diamide (2a,b)

A solution of the diamide (**1a** or **1b**) (0.5 g, 1.4 mmol) and K₂CO₃ (0.12 g, 0.84 mmol) in dry CH₃CN (20 mL) was stirred under nitrogen for 1 h. Then, the octyl iodide (0.33 g, 1.42 mmol) was added to the mixture. The resulting mixture was refluxed overnight, and, then, the solvent was evaporated under vacuum. Finally, 30 mL of CH₂Cl₂ was added to the crude product, and the formed precipitates were filtered off. The desired products were obtained after evaporation of the dichloromethane, affording the pure products.

4-Octyldiethylenetriamine-1,7-dioctamide, 85%, 2a

¹H-NMR (400 MHz, CDCl₃) δ [ppm]: 0.85 (m, 9 H, CH₂CH₃), 1.26 (m, 26 H, CH₂CH₃), 1.35 (m, 2H, CH₂), 1.59 (t, J = 6.8 Hz, 4H, CH₂), 2.18 (t, J = 7.6 Hz, 4 H, -CH₂-CO), 2.39 (t, J = 7.6 Hz, 2H, N-CH₂), 2.55 (t, J = 5.6 Hz, 4 H, NH-CH₂), 3.27 (q, J = 5.6 Hz, 4H, CO-NH-CH₂), 6.58 (bs, 2H, CO-NH) (Figure SI-5).

¹³C-NMR (400 MHz, CDCl₃) δ [ppm]: 14.1, 22.6, 22.7, 25.9, 27.1, 27.4, 29.1, 29.4, 29.6, 31.7, 31.8, 36.6, 37.2, 53.7, 54.1, 173.8 (Figure SI-6).

MS m/z: 468.46 [(M+H)⁺].

4-Octyldiethylenetriamine-1,7-dimethylhexamide, 83%, 2b

¹H-NMR (400 MHz, CDCl₃) δ [ppm]: 0.86 (m, 9 H, CH₂CH₃), 1.12 (d, J = 6.8 Hz, 6H, CHCH₃), 1.25 (m, 22 H, CH₂CH₃), 1.36 (m, 4H, CH₂), 1.61 (m, 2H, CH₂), 2.22 (m, 2 H, -CH), 2.39 (t, J = 6 Hz, 2 H,

NH-CH₂), 2.54 (t, 4H, CO-NH-CH₂), 3.33 (q, J = 5.6 Hz, 4H, CO-NH-CH₂), 6.23 (bs, 2H, CO-NH) (Figure SI-7).

¹³C-NMR (400 MHz, CDCl₃) δ [ppm]: 14.1, 17.9, 22.6, 22.7, 27.2, 27.3, 27.5, 29.4, 29.6, 31.8, 31.9, 34.3, 37.2, 41.4, 53.6, 177.03 (Figure SI-8).

MS *m/z*: 468.46 [(M+H)⁺].

4-Octyldiethylenetriamine-1,7-dioctamide-uranium complex

Solutions of uranyl sulfate (conversion from nitrate to sulfate) in methanol (0.5 mL) and **LI** in chloroform (0.5 mL) were mixed in an open 2-mL vial at [LI]/[UO₂²⁺] ratios from 1:0.25 to 1:1.5. The obtained solutions were heated for 1 h at 60 °C then left standing overnight at room temperature; after this, they were dried under vacuum to obtain the complex as a brown powder.

¹H-NMR (400 MHz, CDCl₃) δ [ppm]: 0.88 (m, 9 H, CH₂CH₃), 1.28 (m, 26 H, CH₂CH₃), 1.6 (m, 4H, CH₂), 1.71 (m, 2H, CH₂-CH₂-Hexyl), 2.25 (t, J = 7.2 Hz, 4H, N-CH₂), 3.18 (t, J = 6.8 Hz, 4 H, -CH₂-CO), 3.37 (t, J = 7.6 Hz, 2H, N-CH₂-CH₂-NH), 3.64 (t, J = 5.6 Hz, 4 H, N-CH₂-CH₂-NH), 7.72 (m, 4H, CO-NH).

¹³C-NMR (400 MHz, CDCl₃) δ [ppm]: 14.15, 22.62, 22.64, 25.52, 28.58, 29.08, 29.33, 31.65, 31.73, 34.93, 36.13, 54.37, 54.53, 175.64.

Extraction experiments

2.1.1. Liquid-liquid extraction procedure

The extraction and selectivity profiles of **LI** and **LII** were established for the extraction of uranium from three different solutions: i) the acidity effect on the extraction performance was studied over a range 0.02 to 5 M sulfuric acid, ii) the individual extraction of uranium at 250 ppm was studied in 0.02 M sulfuric acid solution, and iii) a 0.1 M sulfuric acid solution containing U(VI), Mo(VI), Zr(IV), Ti(IV), La(III), Ce(III), and Fe(III) (25 ppm for each cation) was used to study the selectivity and the recovery of uranium. The metal stock solutions were prepared at the desired acidity from 1000 or 10000 mg L⁻¹ ICP standards from SCP Science. The desired concentrations were prepared by dilution with ultrapure water (MilliQ, Millipore, > 18 MΩ cm⁻¹), and the acidity was adjusted with sulfuric acid.

Different solutions of extractants were prepared in dodecane/octanol (9.5/0.5, v/v). Octanol was used as a modifier to avoid the formation of a third phase and to enhance the solubility of the extractant. The extraction ability of the extractant decreased with increasing feed acidity from 0.02 to 5 M H₂SO₄. The effect of the extractant was studied for metal/extractant ratios of 1:10 up to 1:80. The stoichiometry of the complex was estimated using the slope method and ¹H-NMR and MS analysis. The recovery of the extracted metals from the organic phases was successfully performed by stripping with ammonium carbonate, ammonium oxalate, and sodium carbonate aqueous solutions.

Several organic solutions were prepared from **LI** or **LII** at different specific concentrations in a mixture of dodecane/octanol (95/5 v/v). Octanol was used as a phase modifier. Turbid solutions were obtained when solutions without the phase modifier were mixed with sulfuric acid.

The organic phases were pre-equilibrated with an aqueous phase at the same acidity as the extraction step without metal cations. The pre-equilibrated organic phases were then contacted with an equal volume of an aqueous acidic stock solution of the cations (typically 500 μ L) in a thermostated shaker (Infor-ht[®] Ecotron) at 25 °C for 1 h at 400 rpm. Phases were separated after centrifugation at 4000 rpm for 30 min (Sigma 3-16 PK).

The metal distribution ratios were measured under batch conditions. Equal volumes of aqueous and organic solutions were vigorously shaken at 25 °C to obtain a good emulsion by means of an automatic vortex shaker equipped with a thermostated cell for 30 min for equilibrium distribution measurements. After phase separation by centrifugation, the aqueous phase was analysed by ICP-AES (Spectro ARCOS) to measure the concentrations of cations.

From the results obtained by ICP-AES, the distribution ratios ($D_M = [M^{n+}]_{\text{org}} / [M^{n+}]_{\text{aq}}$) were determined at equilibrium. The experiments were carried out in duplicate measurements with a precision of $\pm 5\%$. In addition, the separation factor for a specific metal to another is defined by the ratio of the distribution coefficient such as: $SF_{M_1/M_2} = D_{M_1}/D_{M_2}$.

2.1.2. Back-extraction experiments

The loaded organic phase was stripped with solutions of ammonium carbonate, ammonium oxalate (typically 0.5 M), and sodium carbonate. Back-extraction was performed at room temperature (22–25 °C) by mixing equal volumes of organic and aqueous phases for 1 h (A/O ratio of 1). After separation by centrifugation (4000 rpm for 10 min), the metal concentrations were measured in the aqueous phase by ICP/AES.

2.1.3. Computational methods

The theoretical calculations were carried out by using the density functional theory (DFT) method implemented in the Gaussian 09 program [Complete list of authors of Gaussian 09 is provided in supporting information] and the three-parameter hybrid functional B3LYP was used.(Becke, 1993; Lee et al., 1988) Previously, this level of theory has been demonstrated to produce good structural and energetic results for actinide and lanthanide complexes.(Di Bernardo et al., 2012; Di Bernardo et al., 2009) The Stuttgart–Dresden small core potential (Cao and Dolg, 2004; Cao et al., 2003; Küchle et al., 1994) was employed for uranium and have been obtained from the EMSL basis set library.(Feller, 1996; Pritchard et al., 2019; Schuchardt et al., 2007) Other elements (H, C, N, O) were treated using the 6-31+G* Gaussian-type basis set. Solvent effect was taken into account by using the polarizable continuum model (PCM)(Tomasi et al., 2005) for which the cavity has been constructed using the UFF radii for the spheres centered on each atom of the solute.

3. Results and discussion

3.1. Synthesis

4-Octyldiethylenetriamine-1,7-diamide derivatives were synthesised via a synthetic route in two steps, as illustrated in Figure 1. The diethylenetriamine-1,7-diamides (**1a**, **b**) were prepared by coupling diethylenetriamine with octanoic acid for **1a** and 2-methylheptanoic acid for **1b** in the presence of *N,N'*-dicyclohexylcarbodiimide (DCC) / hydroxybenzotriazole (HOBT) as coupling reagent for amide formation. Then, the corresponding 4-octyldiethylenetriamine-1,7-dialkylamides (**2a**, **b**) were obtained by direct alkylation of the central amino group with *n*-octyl iodide in CH₃CN and in the presence of K₂CO₃ as a base. The success of the amide formation at the terminal amine groups was determined from the ¹H-NMR spectra, which contained a signal at 6.32 ppm for **LI** and at 6.14 ppm for **LII**, corresponding to the amide NH. In addition, the ¹³C-NMR spectra contained signals at 173.75 and 177.15 ppm, corresponding to the amide CO of **LI** and **LII**, respectively. Also this was confirmed by the IR spectra which showed vibrations at 1640 cm⁻¹ corresponding to amide-1 arising from ν(CO) and at 1550 cm⁻¹ for amide-2 modes predominantly coming from NH in-plane bending (δ(NH)).

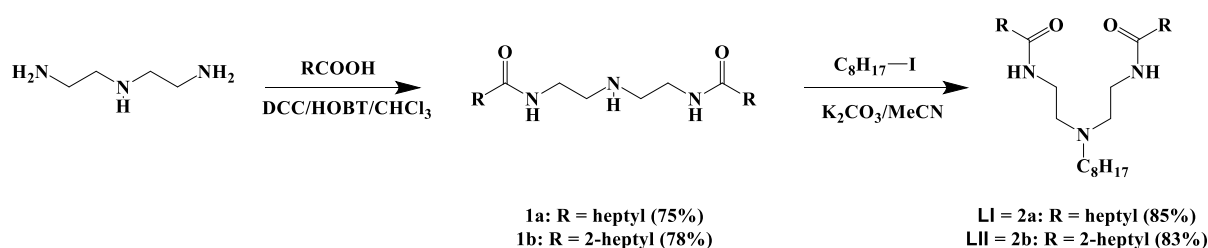


Figure 1: Synthesis scheme of iminodiamides **LI** and **LII**.

3.2. Recovery of uranium from the simulated sulfuric acid leach solution

3.2.1. Effect of sulfuric acid concentration

The effect of the feed solution acidity on the extraction of uranium was investigated by mixing uranium solutions at different sulfuric acid concentrations from 0.02 to 5 M with extracting solution containing 0.02 M of the aminodiamide extractants in dodecane/octanol (95/5 v/v) in a 1:1 volume ratio. Figure 2 exhibit a clear dependence of the extraction efficiency of the extractants on the sulfuric acid concentration. The distribution ratio (*D*) values have decreased sharply from 11.94 to 0.3 for **LI** and from 2.83 to 0.2 for **LII**, respectively, with increase in sulfuric acid concentration from 0.02 to 1 M, and the *D* values for both extractants approach zero at 5 M sulfuric acid concentration. This behaviour is in good agreement with the liquid-liquid extraction studies reported for the extraction of uranium with tertiary amine extractants. (Ahmed et al., 2013; Ramadevi et al., 2012; Yakubu and Dudeney, 1987) The reduced extraction capacity of the extractants with increasing sulfuric acid concentration is mainly due to the increasing competition from HSO₄⁻ and SO₄²⁻ anions, which compete with the

uranyl sulfate anions, preventing the interaction with the protonated amino group. In comparison to alamine 336, the most common tertiary amine used for the extraction of uranium from sulfuric acid media, it appears that the extractant **LI** exhibit interesting properties. Indeed, for a 0.02 M H_2SO_4 aqueous solution containing 1mM of U(VI) the alamine 336 at a 0.02 M concentration display a distribution ratio of 2.71 which is close to the value obtained for the extractant **LII** and four times lower than extractant **LI**.

From the comparison of two extractants extraction efficiency, it can be easily noticed that the **LI** containing linear alkyl chains on the amide N atoms results in a higher extraction efficiency than the **LII** containing branched 2-heptyl group. This behaviour has been observed by McCann *et al* for the extraction of hexavalent over tetravalent cations by monoamides with decrease in metal distribution when branching of the chain of the monoamide.(McCann *et al.*, 2018) Additional supramolecular studies on the formation of aggregates could explain this difference in behaviour.(Rey *et al.*, 2017; Rey *et al.*, 2016)

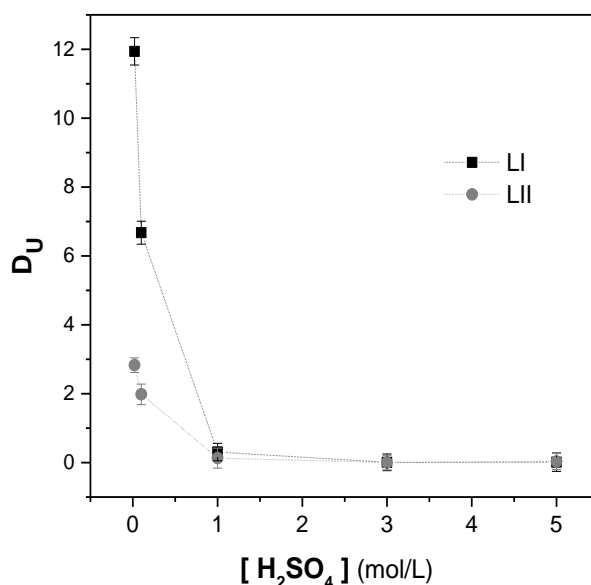


Figure 2: Effect of sulfuric acid concentration on the distribution ratio of uranium.

Extraction conditions: O/A = 1; $T^\circ = 25^\circ\text{C}$. Extraction time: 1 h. Org. phase: [LI]= 20 mM or [LII]= 20 mM in dodecane/*n*-octanol (95/5 v/v); aq. phase: [U]= 1 mM, [H₂SO₄]= 0.02–5 M.

3.2.2. Uranium concentration dependence

To estimate the impact of uranium loading on the extraction, a 30-mM solution of extractant **LI** or **LII** was mixed with a solution of sulfuric acid (0.02 M) containing various U(VI) concentrations from 0.85 to 17 mM (0.2 to 4 g/L) at a fixed A/O phase ratio of 1:1 at 25°C.

No third phase was observed, even at a high concentration of uranium in the organic phase. The results presented in Figure 3 indicate a loading capacity of 1.2 and 0.6 g/L of uranium for

LI and **LII**, respectively. As highlighted by the efficiency results, the loading capacity of the straight chain alkyl groups of the extractant **LI** is higher than the extractant **LII** with branched chain alkyl groups.

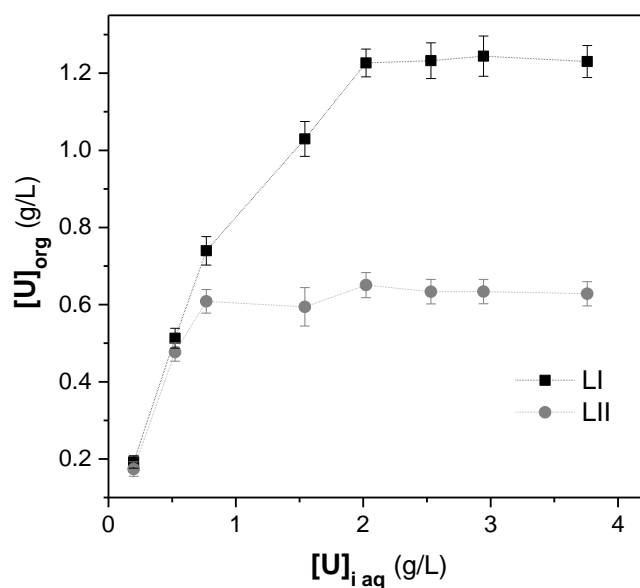


Figure 3: U(VI) organic concentration for different initial concentrations in the aqueous phase for **LI** and **LII**. Extraction conditions: O/A = 1; $T^\circ = 25^\circ\text{C}$. Extraction time: 1 h. Org. phase: [**LI**] = 30 mM or [**LII**] = 30 mM in dodecane/*n*-octanol (95/5 v/v); aq. phase: [U] = 0.85 – 17 mM, [H₂SO₄] = 0.02 M.

3.3. Extraction mechanism

3.3.1. Effect of the extractant concentration dependence

To study the influence of the extractant concentration on the uranium distribution ratio, experiments were performed at a constant acidity (0.02 M sulfuric acid) with several extractant concentrations from 10 to 50 mM for **LI** and from 10 to 80 mM for **LII** in dodecane/octanol with a 1:1 aqueous phase to organic phase ratio (A/O).

Increasing the concentration of the extractants resulted in progressive improvement in the distribution coefficient, as shown in Figure 4. For equivalent performance, an **LII** concentration almost twice as high as **LI** is required.

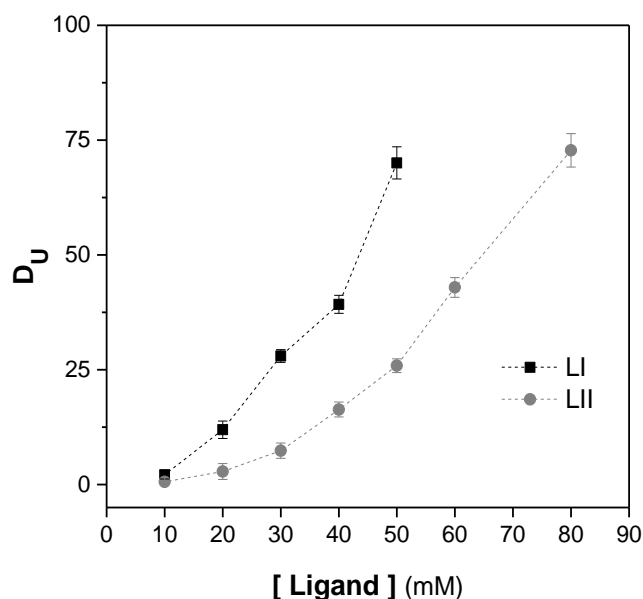


Figure 4: Variation of the distribution ratio as a function of the concentration of extractant.

Extraction condition: $O/A = 1$; $T^\circ = 25^\circ\text{C}$. Extraction time: 1 h. Org. phase: [LI]= 10–50 mM or [LII] = 10–80 mM in dodecane/*n*-octanol (95/5 v/v); aq. phase: [U]= 1 mM, [H₂SO₄] = 0.02 M.

The slope analysis method (Figure 5) has been used to estimate overall stoichiometric numbers within the extracted species/complex formed. The plot of $\log(D_U)$ versus $\log[\text{extractant}]$ indicates linear behaviour with a slope close to 2, and straight lines with slopes of 1.998 and 2.299 were found, respectively, for LI and LII, which suggests the formation of a 2:1 complex between the extractant and the uranyl cation.

Uranyl sulfate species can exist as UO_2SO_4 , $UO_2(SO_4)_2^{2-}$, and $UO_2(SO_4)_3^{4-}$, depending on the sulfuric acid and sulfate concentrations. Referring to the literature, (Geipel et al., 1996) (Bernhard et al., 1998) at pH 2, uranium is present in the aqueous solution as uranyl sulfate UO_2SO_4 in its predominant form and as a uranyl disulfate $UO_2(SO_4)_2^{2-}$ at a minor quantity (10%).

At high concentrations of H_2SO_4 , a majority of bisulfate and trisulfate anions can exist. Several different mechanisms have been proposed as a function of the concentration of sulfate: at high concentrations, an anionic exchange mechanism is suggested, whereas, at low sulfate concentrations, transfer by a neutral mechanism (adduct formation) has been highlighted for uranium extraction by amines. (McDowell and Coleman, 1967)

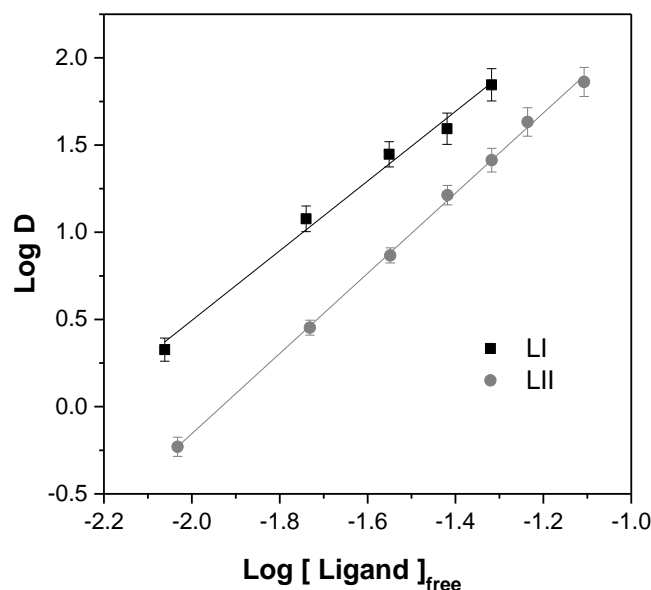


Figure 5: Logarithm of the distribution coefficient of uranium (VI) as a function of $[L]_{\text{free}}$

Extraction conditions: $O/A = 1$; $T^\circ = 25^\circ \text{C}$. Extraction time: 1 h. Org. phase: $[LI] = 10\text{--}50 \text{ mM}$ or $[LII] = 10\text{--}80 \text{ mM}$ in dodecane/*n*-octanol (95/5 v/v); aq. phase: $[U] = 1 \text{ mM}$, $[\text{H}_2\text{SO}_4] = 0.02 \text{ M}$.

$$\log(D_U) = f(\log[LI]_{\text{free}}): y = 1.998(\pm 0.111)x + 4.490(\pm 0.182); R^2 = 0.998.$$

$$\log(D_U) = f(\log[LII]_{\text{free}}): y = 2.299(\pm 0.034)x + 4.443(\pm 0.051); R^2 = 0.998$$

The extractant used in this study is a bi-functional compound containing a neutral complexing amide and an anionic exchanger (Figure 6). Therefore, there is a balance/competition between these two groups in the uranium extraction as function of the speciation in the aqueous solution. Due to this bi-functional feature and increasing portion of uranyl disulfate (and uranyl trisulfate in lesser extend), the anion exchange mechanism prevails over the solvating/adduct formation when sulfuric acid concentration increases. But at low concentration of sulfuric acid, uranyl sulfate is the predominant specie which is extracted by the adduct formation mechanism as proposed in the Figure 6a.

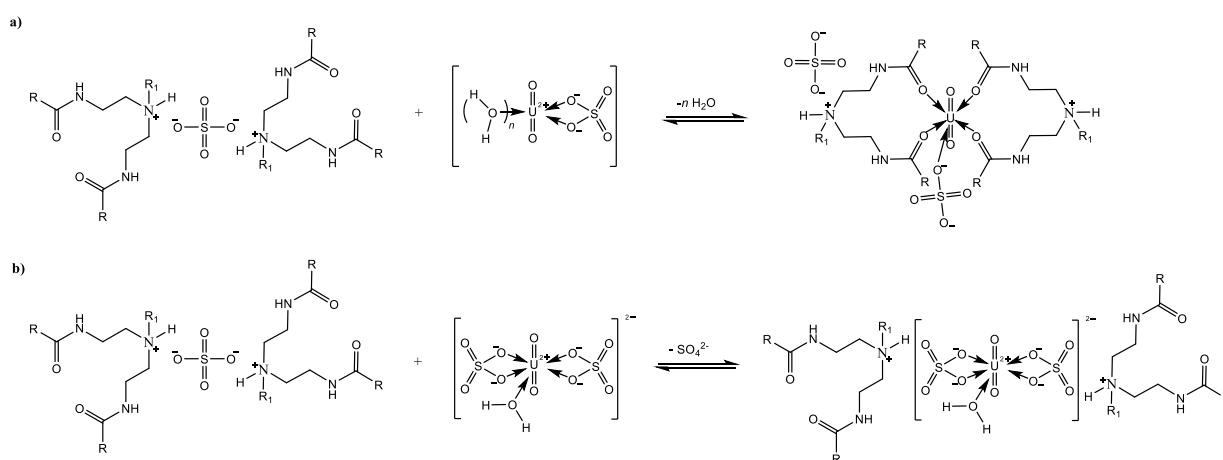
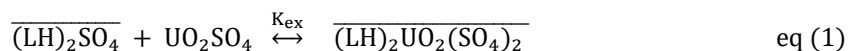


Figure 6: Illustration of potential mechanism involved as function of the uranium speciation: a) extraction by adduct formation via complexation / chelation; b) extraction by ion exchange

Therefore, at pH 2, considering that the extraction of uranyl is based on the solvating mechanism, it can be represented by the following equation:



where $\overline{(\text{LH})_2\text{SO}_4}$ represents the “dimer” form of the protonated extractant, and $\overline{(\text{LH})_2\text{UO}_2(\text{SO}_4)_2}$ represents the metal–extractant complex. The overbar refers to species in the organic phase, and the absence of the overbar denotes aqueous species. In these conditions, the coordination number of the metallic centre (CN_U) in the predominant uranyl sulfate specie, which has initially been completed by water molecules ($n=2$ to 3 depending on the sulfate denticity) in an aqueous medium, is completed by the unbound electron pairs of the extractants’ amide groups during the extraction.

The extraction constant, K_{ex} , can be represented as:

$$K_{\text{ex}} = \frac{[\overline{(\text{LH})_2\text{UO}_2(\text{SO}_4)_2}]}{[\text{L}]^2 \times [\text{H}^+]^2 \times [\text{SO}_4^{2-}] \times [\text{UO}_2\text{SO}_4]} \quad \text{eq (2)}$$

The distribution coefficient for the extraction of uranium is defined by the following relationship by supposing that uranium is extracted only as $\overline{(\text{LH})_2\text{UO}_2(\text{SO}_4)_2}$ so that $[\text{UO}_2^{2+}]_{\text{org,total}} = [\overline{(\text{LH})_2\text{UO}_2(\text{SO}_4)_2}]$:

$$D_U = \frac{[\text{UO}_2^{2+}]_{\text{org,total}}}{[\text{UO}_2^{2+}]_{\text{aq,total}}} = \frac{[\overline{(\text{LH})_2\text{UO}_2(\text{SO}_4)_2}]}{[\text{UO}_2\text{SO}_4]} \quad \text{eq (3)}$$

By substituting the D value from eq (3) into eq (2), the constant of extraction can be expressed as:

$$K_{\text{ex}} = \frac{D}{[\text{L}]^2 \times [\text{H}^+]^2 \times [\text{SO}_4^{2-}]} \quad \text{eq (4)}$$

By substituting the concentration of each species at equilibrium in eq (4), the extraction constant K_{ex} can be calculated at different concentrations of the extractants; therefore, the average constant for the extraction equilibrium was estimated to be 9.1 for **LI** and 8.6 for **LII**.

To confirm the expected stoichiometry of the complexes, analysis by spectroscopic methods, including NMR, Fourier transform (FT)-IR, and DFT calculations have been carried out.

3.3.2. NMR studies

The complexation of uranium by the extractant **LI** was investigated by NMR studies including ^1H -NMR, ^{13}C -NMR, correlation spectroscopy (COSY), and heteronuclear single quantum coherence (HSQC) experiments. The ^1H -NMR titration spectra of **LI** with variable amounts of uranyl cation show appreciable shifts in the resonance signals with increasing uranyl concentration (Figure 7).

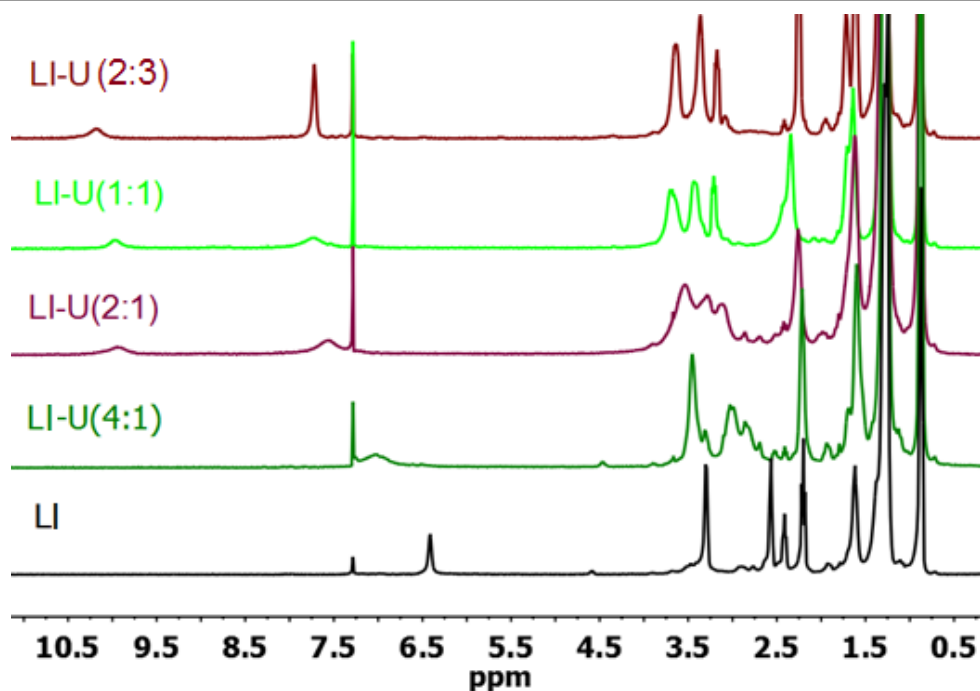


Figure 7: Titration spectra of the extractant LI with uranium at different ratios varied from ($[L]/[UO_2] = 1:0$ to $2:3$), $[L] = 30$ mM in $CDCl_3$, aq. phase: $[U] = 7.5\text{--}45$ mM, $[H_2SO_4] = 0.02$ M.

The extractant/metal ratio (2:1) estimated by the slope method was in good agreement with the results of 1H -NMR titration, in which the characteristic resonance signals of the chelating site corresponding to the free extractant shifted significantly when $[L]/[UO_2^{2+}] = 2:1$. However, slight changes were observed when $[L]:[UO_2^{2+}] > 2:1$.

The contribution of the amidic groups to the coordination of the metal centre is revealed from the downfield shift of the amide NH groups from 6.58 ppm in the 1H -NMR spectrum of the free extractant to 7.72 ppm in the 1H -NMR spectrum of the complex. Also this was highlighted by the upfield shift of the C=O signal from 175.6 to 173.8 ppm in the ^{13}C -NMR spectra on complexation (Figure SI-9, see Supporting Information). The appearance of a broad singlet at 10.17 ppm indicates that the amine group is protonated upon the complexation of uranium. The protonation of the amine group resulted in a downfield shift of the two triplets of the diethylenetriamine group initially located at 2.55 and 3.28 ppm to 3.37 and 3.64 ppm, respectively, as well as the downfield shift of the signal corresponding to the methylene proton of the octyl chain bounded to the amine from 2.39 to 3.18 ppm. The methylene groups of the diethylenetriamine (DETA) and the methylene group of the octyl chain of the free extractant were assigned using the COSY-NMR spectrum (Figure SI-10, see Supporting Information). The COSY-NMR shows correlations between neighbouring protons, such as the correlation between the $-CH_2$ peak located at 2.55 ppm with the amide $-NH$ proton at 6.58 ppm, the correlation between the two methylene groups of the DETA moiety located at 2.55 and 3.28 ppm, and the correlation between the two-methylene group of the octyl chain linked to the amine functionality located at 3.17 and 1.72 ppm. The assignment of the same groups in the complex

was carried out by comparing the HSQC-NMR spectra of the complex to its corresponding free extractant, in which they showed similar correlation patterns, although their ^1H -NMR spectra were dissimilar (Figure SI-11 and SI-12, see Supporting Information).

The structure of the complexing species was characterised by ^1H -NMR, ^{13}C -NMR, COSY, and HSQC-NMR, which suggest that the extractant binds the uranyl group through the two amidic oxygen atoms.

3.3.3. Infrared study

In addition to the NMR study, the complexes were studied by FT-IR spectroscopy. Figure 8 shows the IR spectra of UO_2^{2+} , the free extractant (LI), and the extractant/metal complex (LI-U) complex (2:1). The C=O stretching band of neat LI was observed at 1646 cm^{-1} , while the corresponding band after complexation was shifted to 1595 cm^{-1} . This redshift supports the results obtained in the ^1H and ^{13}C -NMR analyses that the amidic carbonyl oxygen atoms of LI molecules contribute to the coordination of LI to U(VI). Furthermore, there was a redshift in the asymmetric uranyl stretch, assigned as the stretching band (ν_3) of UO_2 ($\text{O}=\text{U}=\text{O}$), (Quilès and Burneau, 1998), (Gatehouse and Comyns, 1958), (Ohwada, 1976) from $960\text{--}935\text{ cm}^{-1}$ in free uranyl to $940\text{--}920\text{ cm}^{-1}$ in the complexes. The fact that the ν_3 band is observed at a slightly lower wavenumber indicates the dehydration of the uranyl group and its coordination with the amidic oxygens. (Johnson et al., 2015)

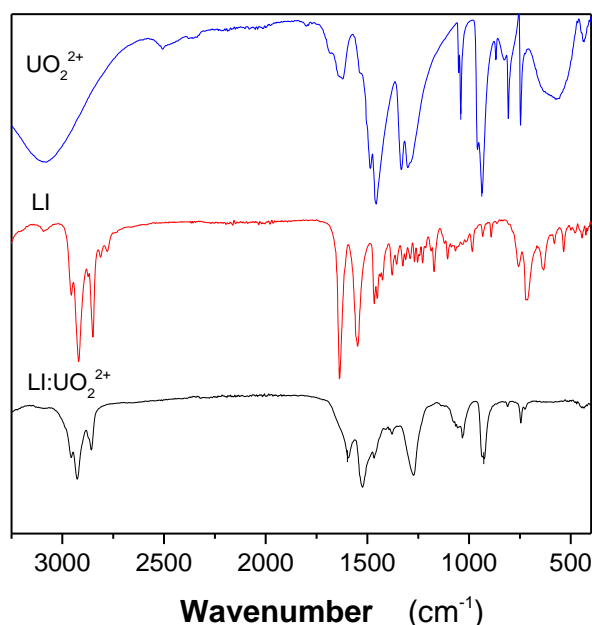


Figure 8: IR spectra of uranyl, LI, and the LI-U complex ($[\text{LI}]/[\text{UO}_2] = 2:1$, $[\text{L}] = 30\text{ mM}$ in CDCl_3 , aq. phase: $[\text{U}] = 15\text{ mM}$, $[\text{H}_2\text{SO}_4] = 0.02\text{ M}$).

3.3.4. DFT calculations

To obtain complementary data, DFT calculations were performed on simplified extractant (L) (Figure 9), protonated extractant (LH) and complex (LH:UO₂²⁺). The minimum energy structures of protonated extractant and complexes obtained from DFT calculations using are depicted in the supporting information (Figure SI-13).

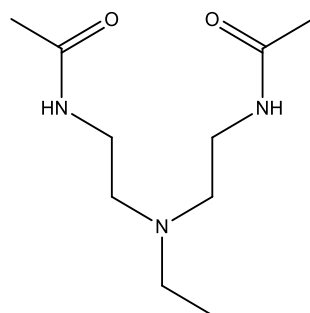


Figure 9. Simplified extractant (L) used for DFT Calculation

The ammonium form of the extractant is the predominant form involved in the formation of the complex. DFT calculations were made on two conformations in the gas phase where the tertiary amine or amide group is protonated. The computational results show that the protonated tertiary amine is more stable than the protonated amide group (ΔG (amide – amine) = 20 kcal/mol). The structures were optimized in gas phase, then re-optimized in PCM *n*-dodecane to take into account bulk solvation effects on the energy and structure of the reactants and products. To examine the binding ability of LH toward uranyl, the complexation reaction is introduced: $[LH^+] + [UO_2^{2+}] \rightarrow [UO_2^{2+}][LH^+]$.

The Gibbs free energy of the complexation is equal to -1.7 kcal/mol. Here following thermodynamic convention, the negative ΔG values show that the complexation reactions of uranyl by two extractant LH⁺ is favourable in thermodynamics. The proposed structure by DFT allow to confirm the 2:1 stoichiometric number for the LH⁺:UO₂²⁺ complex.

These results are in agreement with the behaviour observed and the mechanism proposed for tertiary amine analogue 'alamine 336' which is a classical extractant used in the AMEX process.

3.3.6. Temperature dependence of uranium extraction

The uranium distribution ratio has been determined at various temperatures from 25 to 50 °C in 0.02 M H₂SO₄ with 20 mM of LI in dodecane/octanol (95/5 v/v). The effect of the temperature on the distribution coefficient of uranium (VI) is illustrated by an Arrhenius plot in Figure 10. The results indicated that the distribution coefficient of U slightly increases with increasing temperature, indicating no clear influence of the temperature on the extraction performance of the extractant. The thermodynamic parameters can be calculated using the Van't Hoff relationship, where R is the gas constant:

$$\text{Log}K_{ex} = -\frac{\Delta H}{2.303R} \cdot \frac{1}{T} + \frac{\Delta S}{2.303R} \quad \text{eq (5)}$$

From the plot of $\log K_{\text{ex}}$ versus $1/T$, a straight line was obtained, as shown in Figure 8, and the enthalpy of the reaction was calculated to be about $\Delta H = 8.62$ kJ/mol for the **LI** system. The entropy was estimated in a first approximation to be $\Delta S = 237.04$ J/K.mol from the intercept values.

The free energy change, ΔG , for the extraction at 298 K was obtained from the Gibbs–Helmholtz equation.

$$\Delta G = \Delta H - T\Delta S = -2.303RT \text{ Log } K \quad \text{eq (6)}$$

The thermodynamic parameters, ΔH , ΔS , and ΔG , for the extraction of **LI** are summarised in Table 1. The overall enthalpy change depends on several contributing factors such as (i) the dehydration of metal ions (ΔH_1), (ii) formation of neutral extracted species (ΔH_2), and (iii) dissolution of the metal complex in the organic phase (ΔH_3).

The small positive value of ΔH suggests that the complexation between UO_2^{2+} species and the neutral extractant molecule is slightly endothermic (Table 1) and, thus, is governed by the entropic phenomena. The positive entropy change ($+\Delta S$) suggests the loss of a few water molecules in the primary coordination sphere of UO_2^{2+} . Interestingly, the negative value of ΔG at room temperature indicates that the extraction reactions are spontaneous.

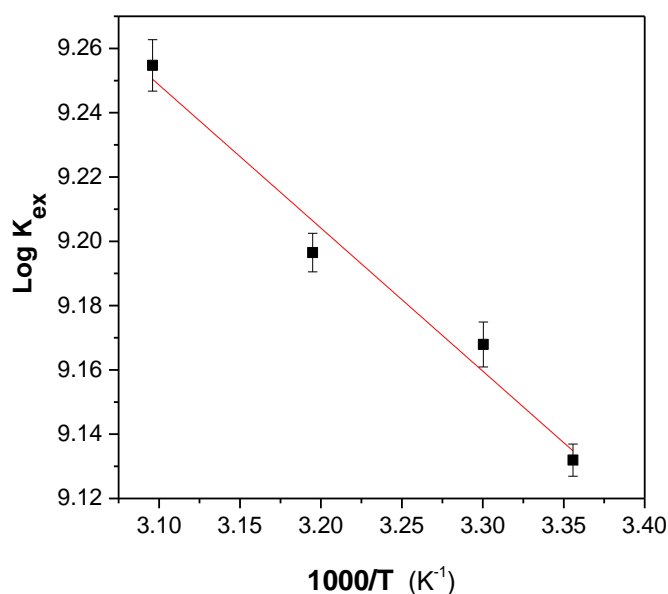


Figure 10: Effect of temperature on the apparent extraction equilibrium constants $\log K_{\text{ex}}$.

Extraction conditions: O/A = 1; $T^\circ = 25\text{--}50^\circ\text{C}$. Extraction time: 1 h. Org. phase: [LI] = 20 mM in dodecane/*n*-octanol (95/5 v/v); aq. phase: [U] = 1 mM, [H₂SO₄] = 0.02 M.

$$\text{Log}(K_{\text{ex}}) = f(1000/T): y = -0.4479(\pm 0.05)x + 12.377(\pm 0.17); R^2 = 0.964.$$

Table 1 : Thermodynamic parameters (ΔH , ΔS , and ΔG) for the extraction of uranium at 298 K.

System	Slope	Intercept	ΔH (kJ/mol)	ΔS (J/(K mol))	ΔG (kJ/mol)
(LI) ₂ U	-0.45 ± 0.05	12.38 ± 0.17	8.62 ± 0.96	237.04 ± 3.27	-62.02 ± 0.01

Org. phase: 20 mM LI in dodecane/*n*-octanol (95/5 v/v); aq. phase: [U]= 1 mM, [H₂SO₄]= 0.02 M.

3.4. Extractant selectivity study

3.4.1. Extraction experiments

Considering the performances and the potential of LI and LII for the extraction of U, the efficiency and the selectivity of these two systems were studied for the preferential extraction of U from a solution containing seven elements at 25 ppm each (U(VI), Mo(VI), Zr(IV), Ti(IV), La(III), Ce(III), and Fe(III)) in 0.1 M sulfuric acid. The selectivity toward uranium was studied for both extractants LI and LII at 30 mM in dodecane/*n*-octanol (95/5 v/v). The extraction data presented in Table 2 clearly shows that both extractants are more selective toward uranium than any other element.

Table 2 : Distribution coefficient values and selectivity factors of LI, LII and alamine 336 toward U, Ti, Mo, Zr, La, Fe, and Ce cations.

Extractant/Metal		U	Ti	Mo	Zr	La	Fe	Ce
LI	<i>D</i>	25.69 ± 1.26	0.01	5.18 ± 0.26	0.82 ± 0.06	0.001	0.002	0.001
	<i>S</i> _(U/M)		2569	5	31	>25690	12845	>25690
LII	<i>D</i>	12.29 ± 0.56	0.02	4.65 ± 0.19	0.39 ± 0.02	0.01	0.01	0.01
	<i>S</i> _(U/M)		614	2.7	31	1229	1229	1229
Alamine 336	<i>D</i>	1.15 ± 0.25	0.009	0.88 ± 0.06	0.2 ± 0.01	0.001	0.004	0.001
	<i>S</i> _(U/M)		128	1.3	5.8	>1150	288	>1150

Extraction conditions: O/A = 1; *T*° = 25°C. Extraction time: 1 h. Org. phase: [LI]= 30 mM [LII]= 30 mM or alamine 336 in dodecane/*n*-octanol (95/5 v/v); aq. phase: [U] = [Ti] = [Mo] = [Zr] = [La] = [Fe] = [Ce] = 25 ppm, [H₂SO₄] = 0.1 M.

Even though molybdenum is also extracted, interesting selectivity factors, *S*_(U/Mo), were obtained: 4.96 and 2.64 for LI and LII, respectively which are higher than that observed for Alamine 336. The selective extraction of U with respect to Mo is one of the main challenging aspects in the processes based on amine extractant such as the AMEX process.(McDonald et al., 1981)

The data in Table 2 confirm that LI is more efficient than LII, and the *D*_U for LI is about twice that of LII. The same trend was observed for the selectivity, in which the selectivity

factors of **LI** toward U over the six other metals are higher than the selectivity factors of **LII** toward the same target metals. This suggests that substituting the linear chain (octyl) by a branched chain (2-heptyl) on the amide nitrogen atoms had a negative influence on the efficiency and selectivity of these types of extractants toward the extraction of uranium. The decrease in the efficiency of **LII** could originate from the steric hindrance generated by the branched 2-heptyl group, which prevents the uranyl sulfate anions from reaching the amino/amides chelating sites easily.

3.4.2. Stripping and recovery of U

After the successful extraction of U from the leaching solution by **LI**, another set of experiments was carried out to recover the extracted target metal from the organic phase. The organic phase already loaded with the extracted metals was stripped with ammonium carbonate, ammonium oxalate, and sodium carbonate in an A/O ratio of 1. The recovered amounts after stripping the organic phase with the various aqueous bases are presented in Table 3.

The stripping solutions displayed promising results when the back-extraction was performed with an A/O ratio of 1. As shown in Table 3, U can be quantitatively recovered after stripping the organic phase with ammonium carbonate or sodium carbonate. The stripping of uranium was not effective with ammonium oxalate, but the molybdenum could be stripped. Therefore, after the extraction step, the loaded organic solution can be treated first with ammonium oxalate to remove the extracted molybdenum selectively, leaving uranium to be recovered with a carbonate solution.

Table 3: Recovery of uranium from an organic phase (30 mM extractant in dodecane/*n*-octanol (95/5)) by various aqueous bases.

Stripping solution	U recovery (%)	Mo recovery (%)	Zr recovery (%)
[(NH₄)₂C₂O₄] (sat)	6 ± 1.2	81 ± 0.8	2 ± 1.5
[(NH₄)₂CO₃] (1 mol/L)	99 ± 0.3	96 ± 0.8	96 ± 0.7
[Na₂CO₃] (1 mol/L)	97 ± 0.8	99 ± 0.4	79 ± 0.9

After the extraction step, the loaded organic solution contains about 22.3, 19.5, and 9.8 ppm of U, Mo, and Zr, respectively, initially present in the sulfuric acid solution.

Back-extraction condition: O/A = 1; T° = 25°C. Extraction time: 1 h. Org. phase: [LI] = 30 mM or [LII] = 30 mM in dodecane/*n*-octanol (95/5 v/v); aq. phase: [U] = [Ti] = [Mo] = [Zr] = [La] = [Fe] = [Ce] = 25 ppm, [H₂SO₄] = 0.1 M

4. Conclusions

The syntheses of two amino-diamide derived from DETA have been performed through a peptide coupling with a satisfactory yield of around 65%. The efficiency of the extractants has been investigated through the individual and mutual extraction of uranium. Individual extraction experiments have been performed to estimate the mechanism of extraction. The effects on the uranium extraction of various parameters, such as the feed solution and extractant concentration, have been studied. The slope analysis, $^1\text{H-NMR}$ titrations revealed a 2:1 stoichiometric number for the extractant: UO_2^{2+} complex. The calculated thermodynamic parameters showed that the extraction with this kind of extractants is spontaneous. Both extractants have a good selectivity for uranium over other metal ions present in the simulated solution. Furthermore, uranium has efficiently been stripped using 1 M ammonium carbonate or sodium carbonate.

Different behaviour has been observed between the “free” imino diamides and the imino diamides functionalized-calixarene concerning the stoichiometry of complexation, in which the free extractants showed 2:1 complexing species, while the cyclized calixarene showed only 1:1 complexation. In comparison to imino diamides introduced on calixarene, the “free” extractants appear more efficient and selective for the individual and mutual extraction of uranium.(Wehbie et al., 2018)

The ability of the imino diamide extractant to extract uranium at low pH from sulfuric media, and their reusability, make it a promising extractant for uranium extraction at the front end of the nuclear fuel cycle including the pre-concentration of uranium from lean streams, decontamination of wastestreams...

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Appendix A. Supplementary material

Supplementary data associated with this article are available.

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Supplementary information

Extraction of uranium from sulfuric acid media using amino-diamide extractants

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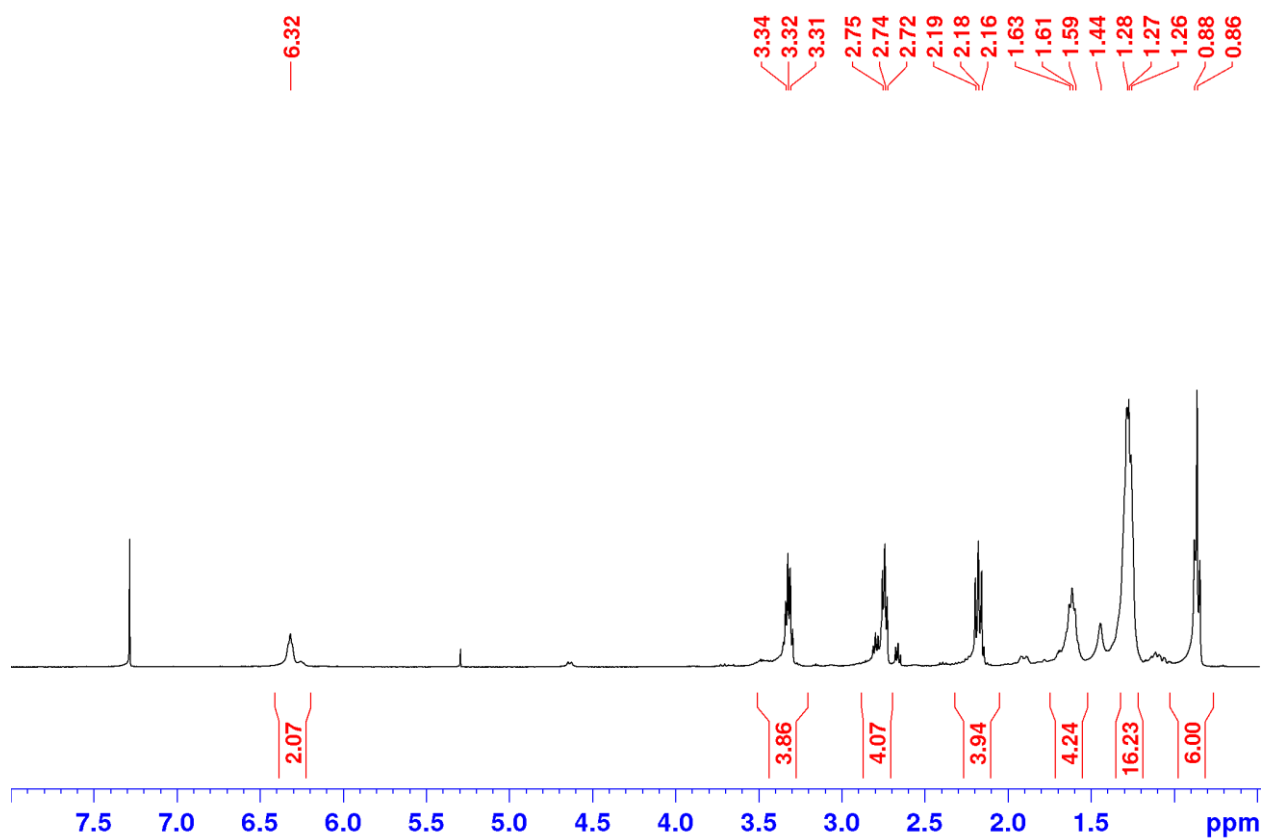


Figure SI- 1: ^1H NMR Spectrum of compound **1a**

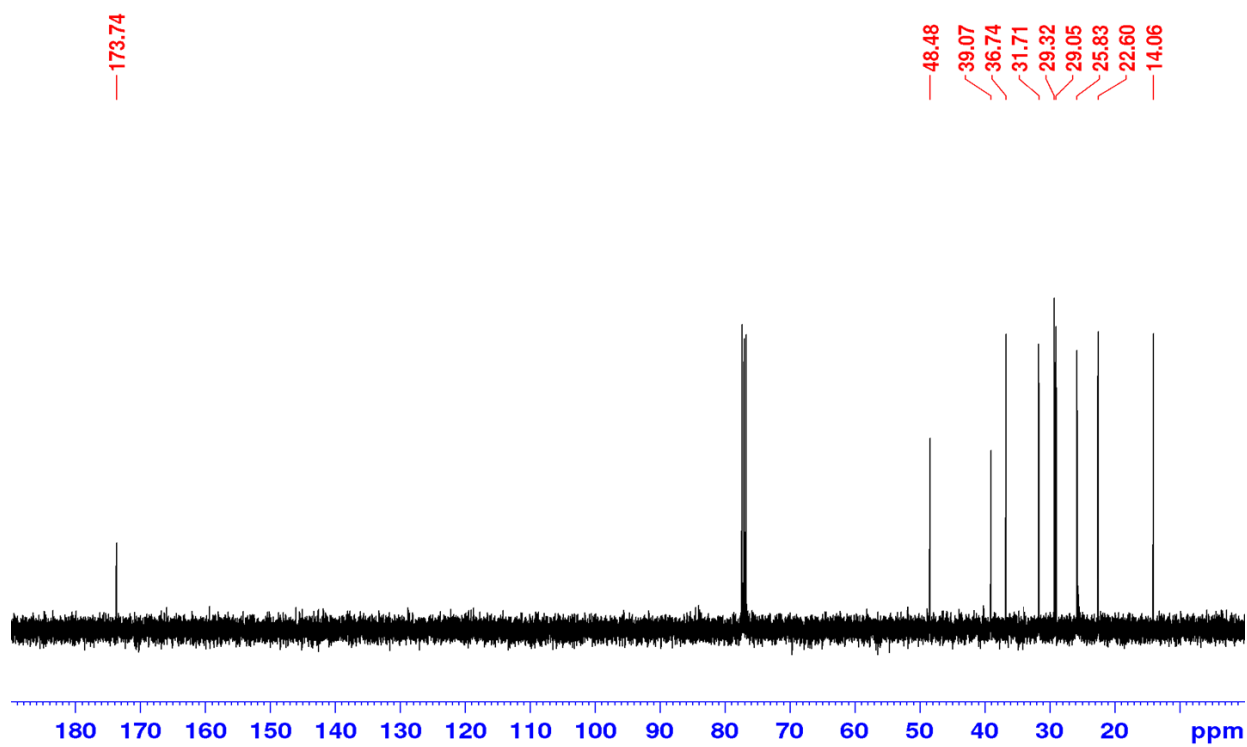


Figure SI- 2: ^{13}C NMR Spectrum of compound **1a**

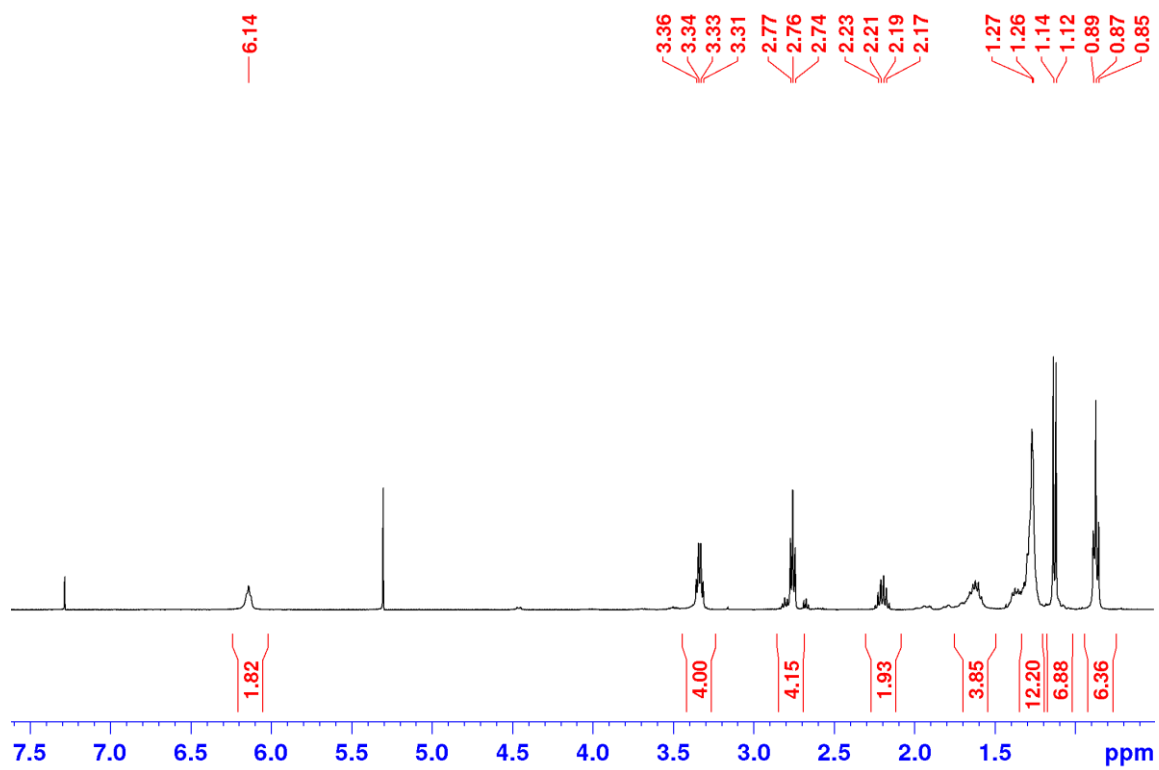


Figure SI- 3: ^1H NMR Spectrum of compound **1b**

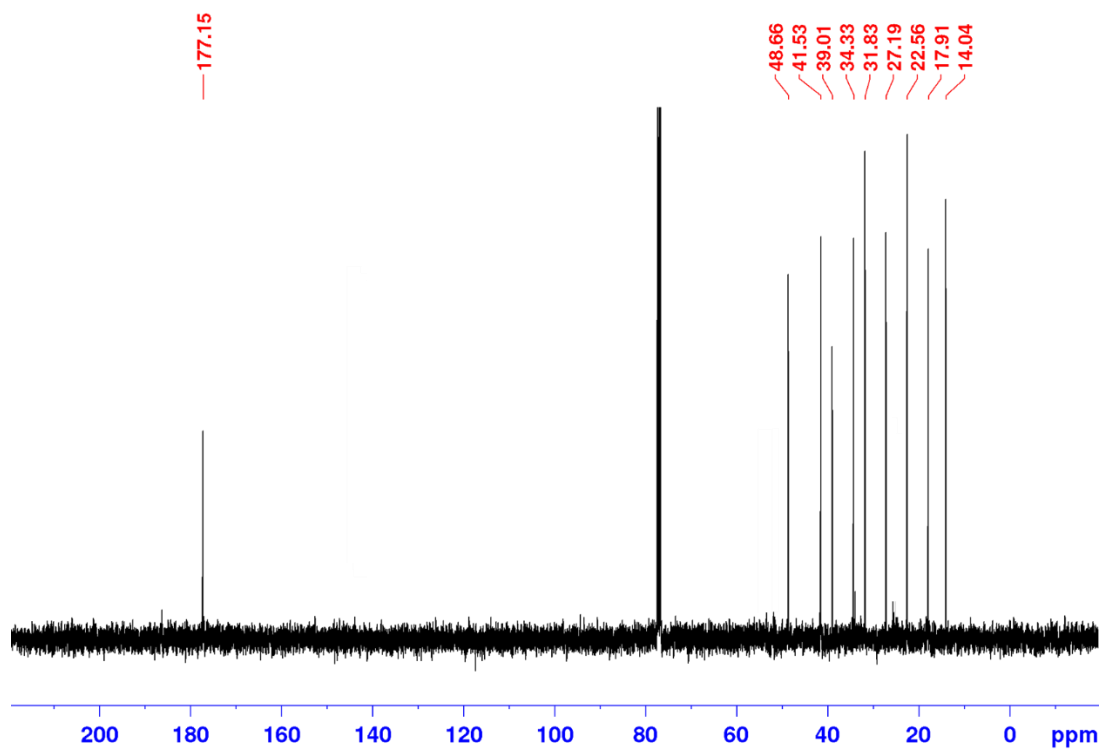


Figure SI- 4: ^{13}C NMR Spectrum of compound **1b**

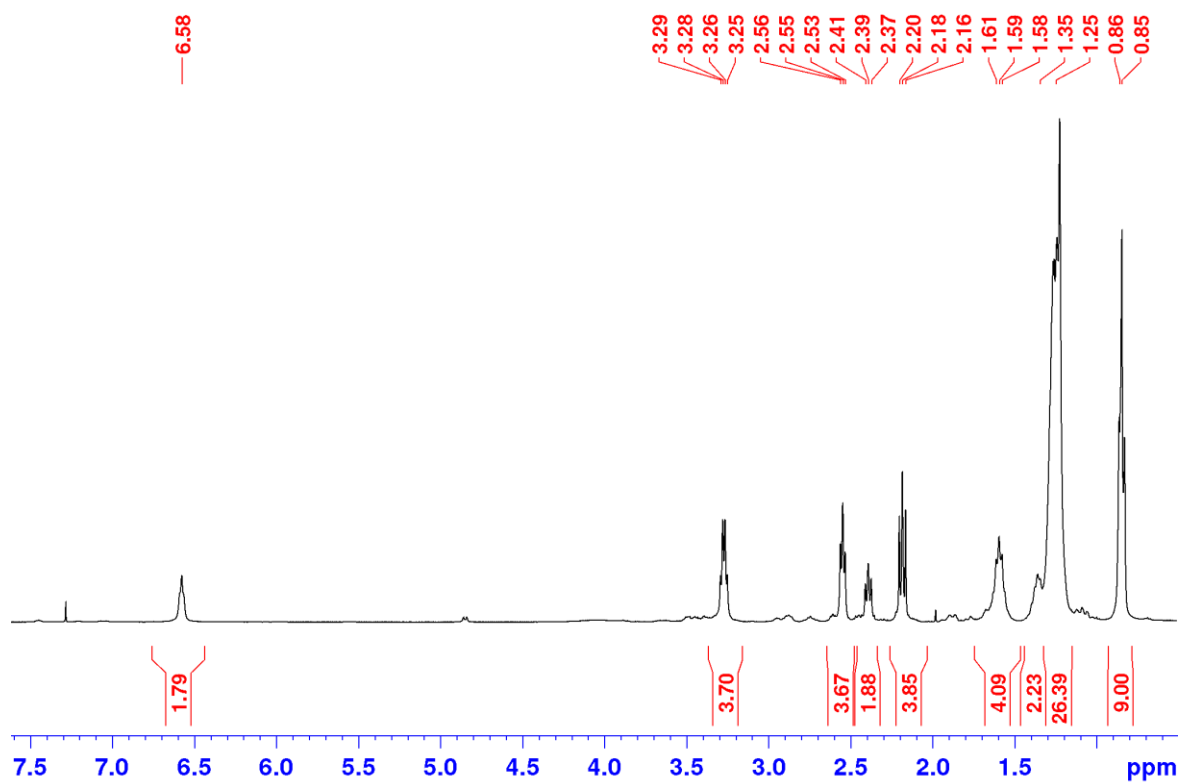


Figure SI- 5: ^1H NMR Spectrum of compound **2a**

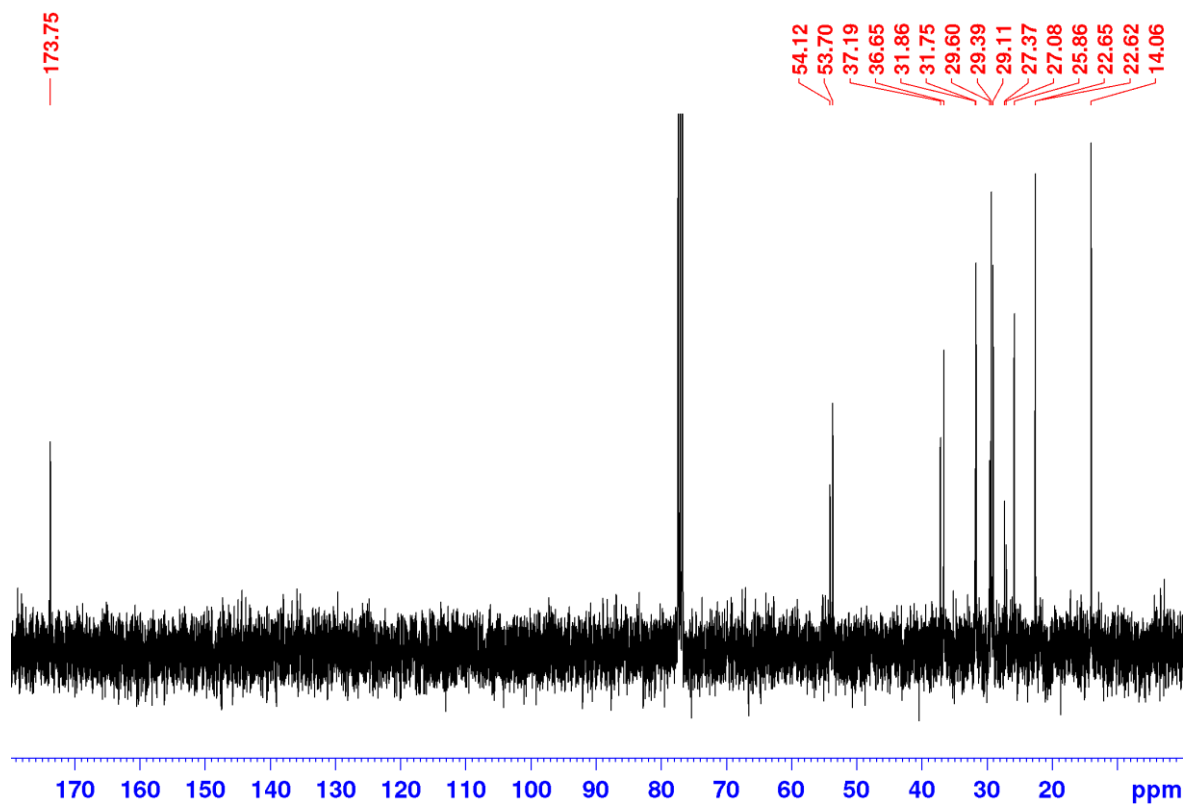


Figure SI- 6: ^{13}C NMR Spectrum of compound **2a**

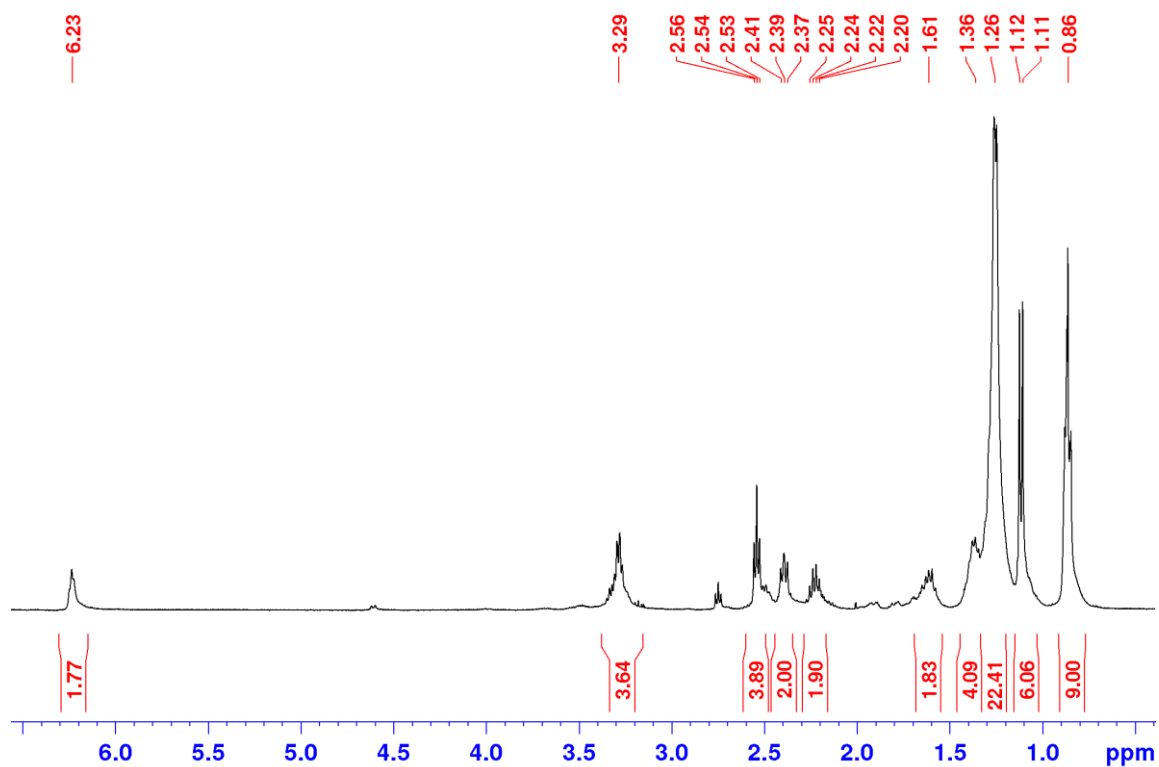


Figure SI- 7: ^1H NMR Spectrum of compound **2b**

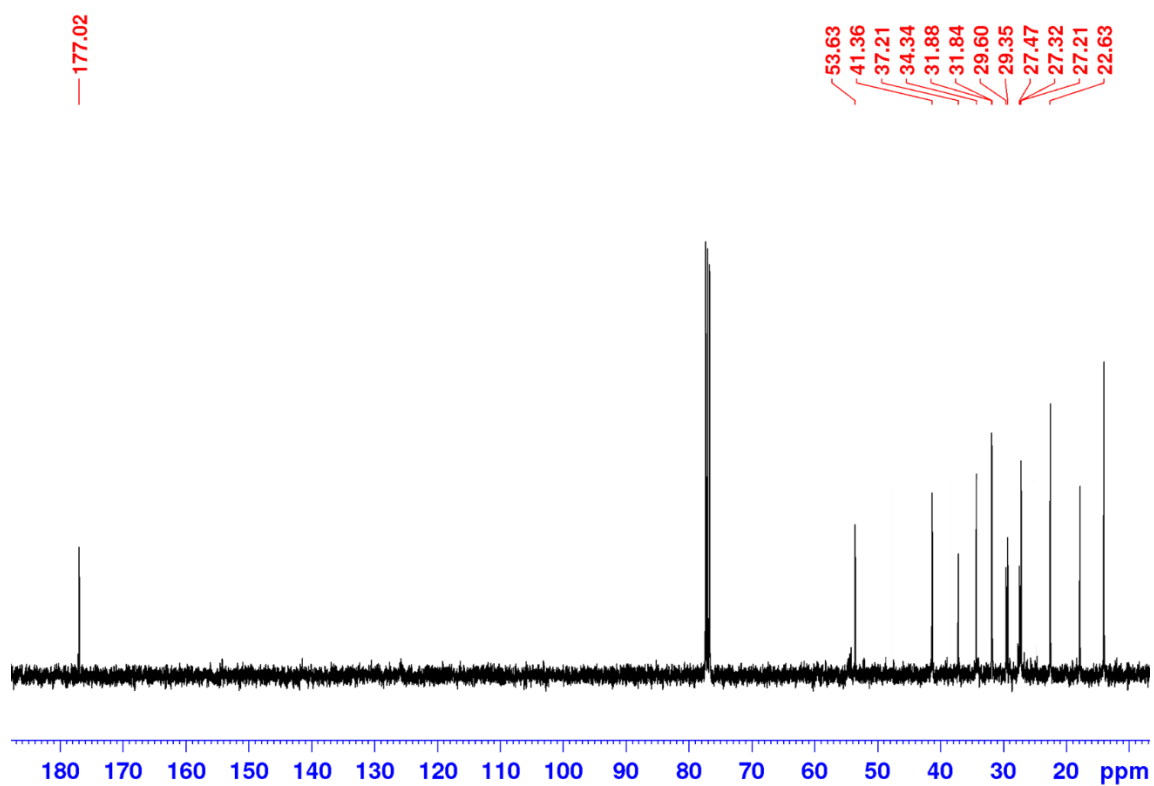


Figure SI- 8: ^{13}C NMR Spectrum of compound **2b**

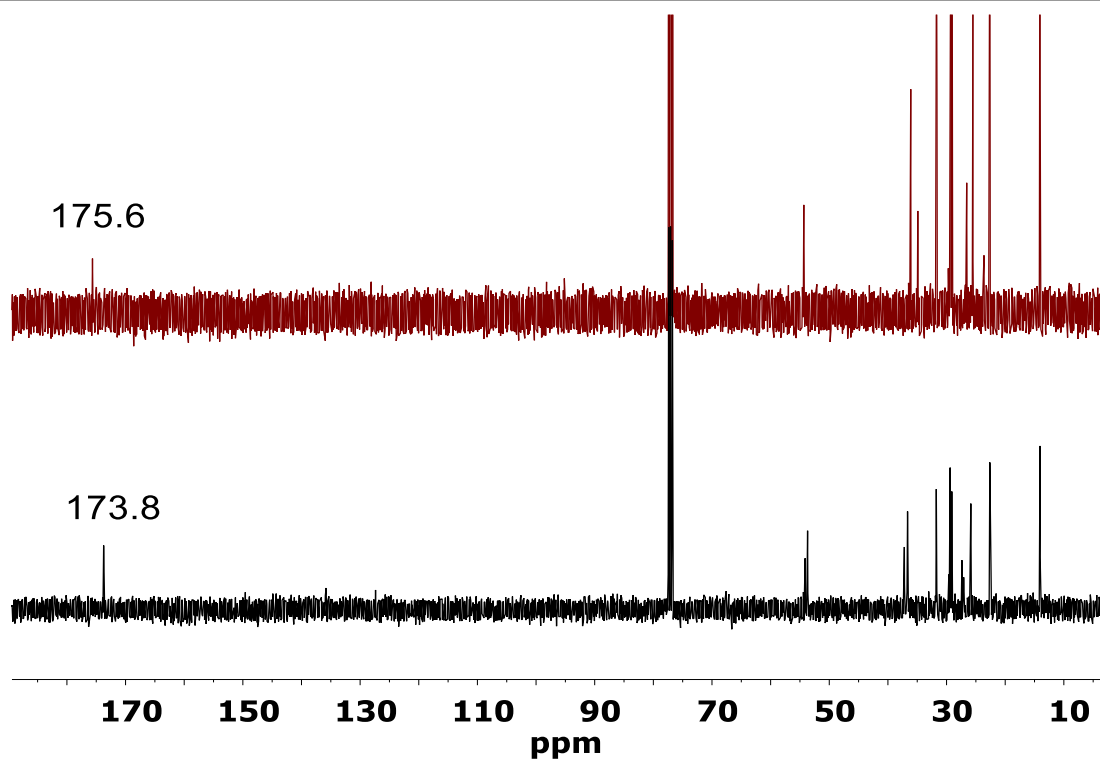


Figure SI- 9 : ^{13}C -NMR spectra of the free extractant LI (top) and the complex (bottom) at $[\text{LI}]/[\text{UO}_2] = 2:1$.
 $[\text{L}] = 30 \text{ mM}$ in CDCl_3 , aq. phase: $[\text{U}] = 15 \text{ mM}$, $[\text{H}_2\text{SO}_4] = 0.02 \text{ M}$.

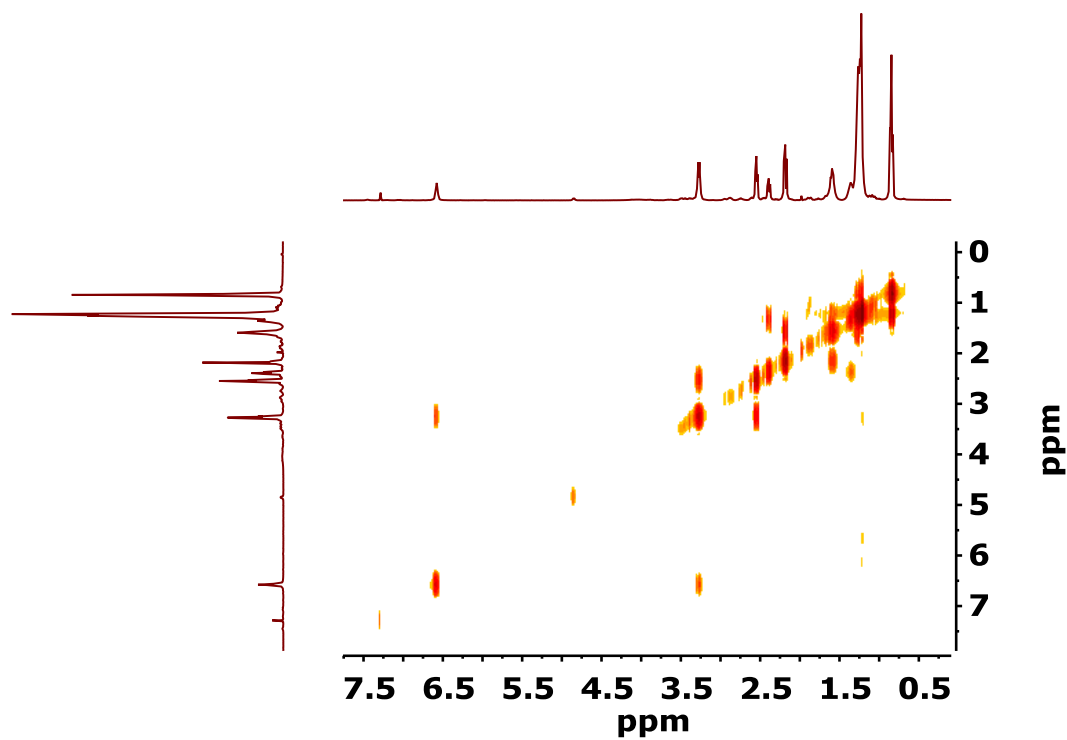


Figure SI- 10: COSY-NMR spectrum of extractant LI.

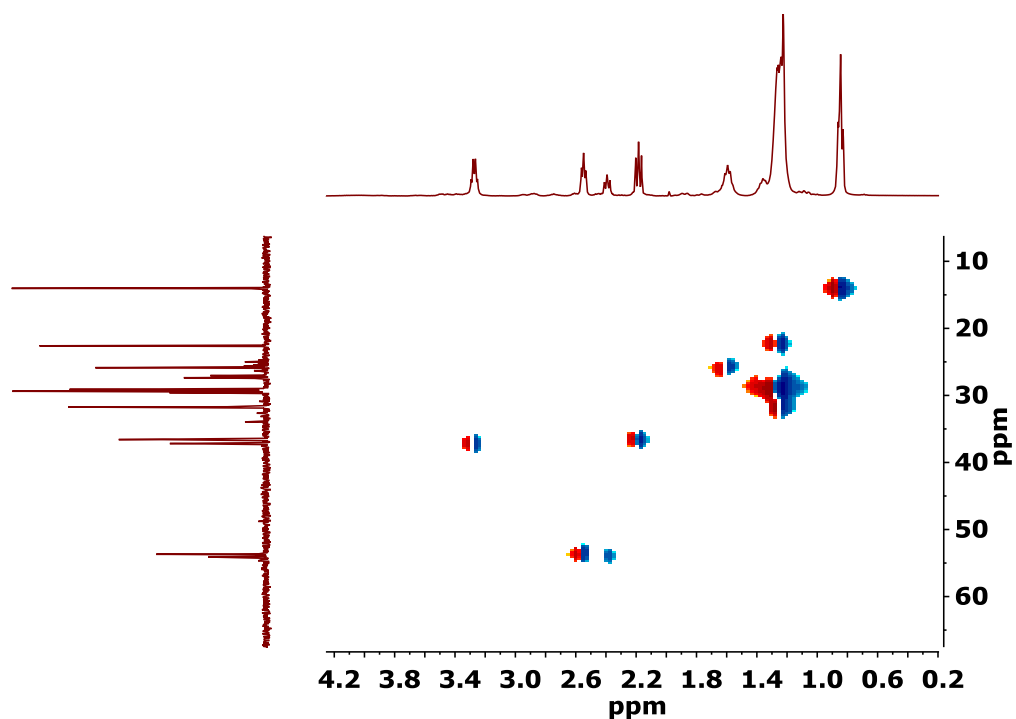


Figure SI- 11: HSQC-NMR spectrum of extractant LI

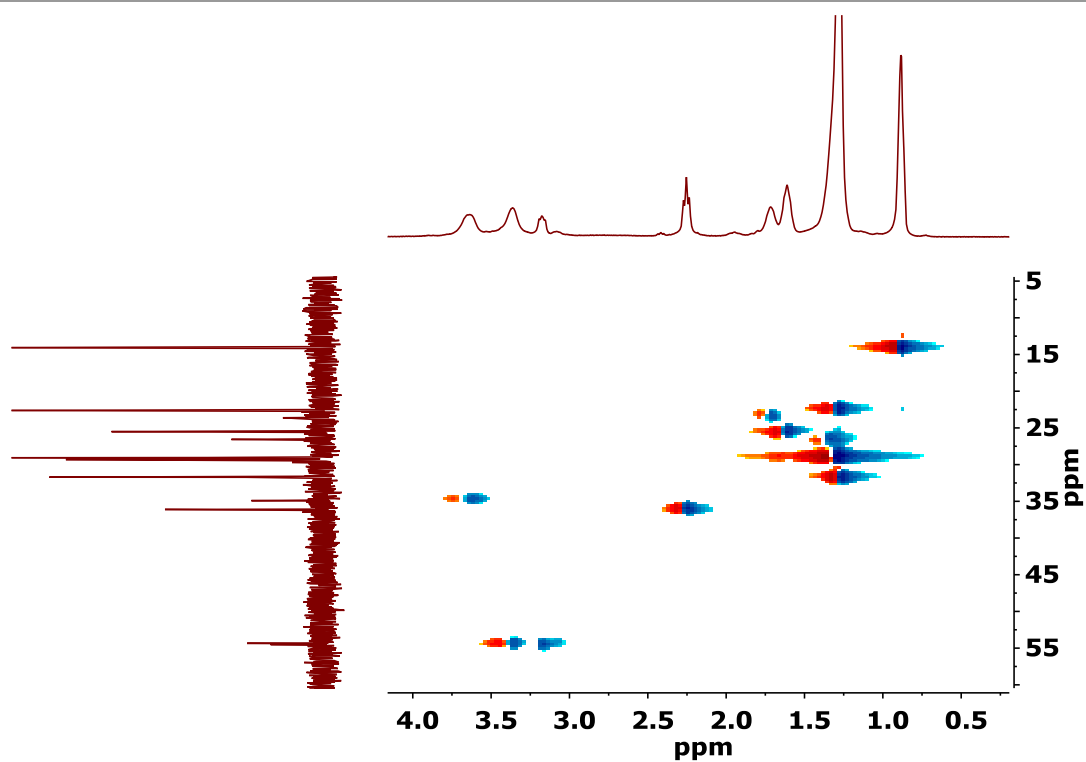
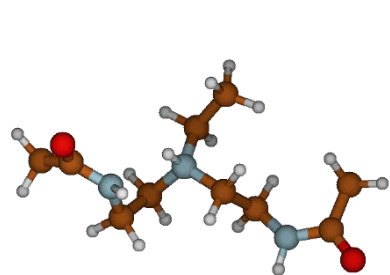
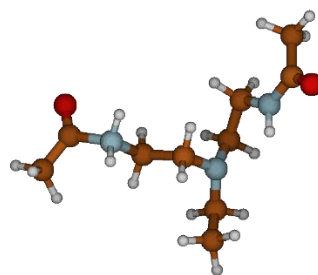


Figure SI- 12: HSQC-NMR spectrum of the LI-U complex, $[LI]/[UO_2] = 2:1$.

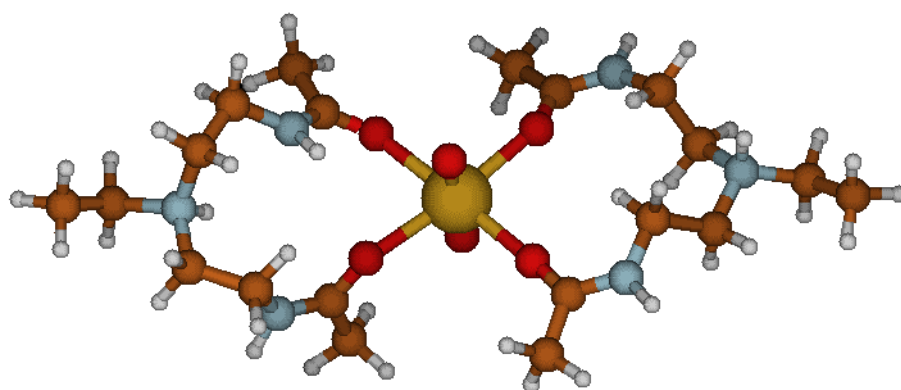
$[L] = 30 \text{ mM}$ in $CDCl_3$, aq. phase: $[U] = 15 \text{ mM}$, $[H_2SO_4] = 0.02 \text{ M}$.



LH (protonated tertiary amine)



LH (protonated amide)



[UO₂²⁺][LH⁺]₂ complex

Figure SI- 13: Structures of protonated extractant and complexes obtained from DFT calculations.
