# Comparative Study of Solvent Extraction of Uranium with Alamine 336 and Aliquat 336: Application to the Uranium-Bearing Solutions of Niger Republic

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## Abstract

This study focuses on the liquid-liquid extraction of uranium by anionic extractants of Alamine 336 and Aliquat 336. The objective of this study is to determine the parameters allowing the optimization of the extraction percentage of uranium, and other metals such as molybdenum, zirconium and vanadium. The extraction kinetics of uranium is achieved in 2 minutes. Sulfuric acid solutions are the media per excellence when using Alamine 336 as extractant. However,with Aliquat 336, it is orthophosphoric acid. Uranium is extracted at 99% in a single contact from the ratio: organic phase over aqueous phase (O/A) equals 1. The extraction of uranium with Alamine 336 depends on the initial pH of the aqueous phase as well as the Alamine 336 concentration. Alamine 336 tends to release the uranium and the extracted zirconium until the 3rd contact to the benefit of the molybdenum due to the natural occurrence of $Cl^{-}$,$NO_3^{-}$ and $F^{-}$ ions in the uranium-bearing solutions which have the tendency of breaking the anion complexes. Vanadium, which is not extracted by Alamine 336 and Aliquat 336, can, in the hydrodynamic conditions of this work, be extracted by increasing the redox potential to 800 mV and pH ≥ 1.

**Keywords:** Alamine 336, Aliquat 336, Liquid-liquid extraction, Molybdenum, Uranium

## Introduction

The hysteria some countries have over the use energy derived from uranium fission caused by industrial and nuclear accidents (Chernobyl (1986) and Fukushima (2011) and the desire to manage long-life radioactive waste drove some countries to question the use of this energy and to turn towards green power. However, the increasing demand for energy caused by a population growth on the rise, but also the arms race in which some military powers have thrown themselves into, make nuclear power to be the sole alternative (Evry & Essonne, 2012; Services, 2011; Yuan et al., 2014; Mohapatra et al., 2014; Kumar,J.R.,et al., 2010; Ali, M. M., et al,. 2014). This alternative pushes to the research and development of new uranium deposits.

Thus, in uranium-producing countries where the uranium content of the ore is very weak, the treatment is done wet. This is the case for uranium companies of Niger Republic where the thickness of the deposits may vary between 1 and 10 m and an ore having between 0.2 and 0.6% of uranium content. These factories condensate and purify the uranium ore by hydrometallurgy. This process is a succession of physico-chemical operations, characterized by the dissolution of the metal and its elaboration from the solution. In Niger Republic, this process uses liquid-liquid extraction also known as solvent extraction as a purification method (Agnès M., 1985).

For this purpose, this process uses various molecules able to selectively extract the metals. The tertiary amines such as Alamine 336 widely used in the extraction of uranium by AMEX process (Kumar, J.R.., Kim, J.S., Lee, J.Y., Yoon, H.S., 2011; El-Nadi, Y.A., 2017), the phosphated extractants such as the trioctylphosphine oxide (TOPO), the di-2-ethylhexylphosphoric acid (D2EHPA or HDEHP) in synergy with tributylphosphate (TBP) through DAPEX process (El-Nadi, Y.A., 2017; Khanramaki, F., Shirani, A.S., Safdari, J., Torkaman, R., 2017; Kim, J.S., Han, K.S., Kim, S.J., Kim, S.D., Lee, J.Y., Han. C., Kumar, R.J., 2016) are widely used for the extraction, the separation and the purification various metals.

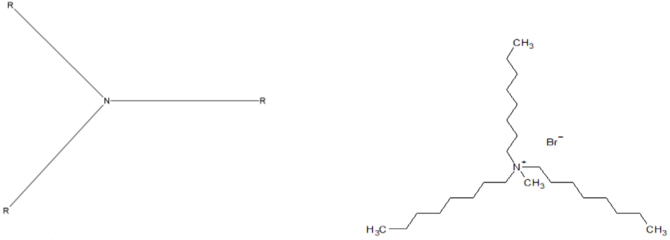
Generally confined to the uranium ore, zirconium, molybdenum and vanadium, due to the similarity in their chemicals properties, are found in varying proportions in the ores depending on the deposit in operation (Miguirditchian, M., Baron, P., Bisel I., Dinh, B., Sorel, C., 2011; Floreancig, A., Trescol, J., Siffert. B., 1981; Hawk. D.G., 1965; Lunt, D., Boshoff, P., Boylett,M., El-Ansary, Z., 2007); case depicted in Niger Republic. These metals represent impurities that penalize an industry wanting to preferentially valorize uranium.

It is in this regard that we focused on the liquid-liquid extraction of uranium by Alamine 336 and Aliquat 336 with the aim of studying their behavior on the uranium-bearing solutions resulting from the leaching of Niger Republic’s uranium ore.

## Material and Methods

### The reactants

This part of the work gives the extractants used as well as the diluents and added alcohol to avoid the formation of the 3rd phase. Alamine 336 Fig.1. (a) with a flashpoint of 179 °C is provided by Cognis Corporation, and the 1-Octanaminium, N-methyl-N,N-dioctyl-Bromide ($C_{25}H_{54}BrN$) or Aliquat 336 Fig.1. (b) provided by Molekula are prepared in various diluents, kerosene (TOTAL), toluene (Prolabo) and diisobutyl ketone (Prolabo) in the presence of isotridecanol (BASF) which has a flashpoint of 122.5 °C. The mixture of these reagents forms the organic phase.



(a)

(b)

**Fig.1.** Chemical structures: (a) Alamine 336 (R = $C_8$-$C_{10}$) and (b) 1-Octanaminium,N-methyl-N,N-dioctyl-,bromide($C_{25}H_{54}BrN$) or Aliquat 336.

The synthetic uranium solutions are prepared at (5 g/L) from the triuranium octoxide $U_3O_8$ (99.968% ± 0.018 U) provided by NBL and the yellow cake $Na_2U_2O_7$ (75% U, Na/U < 6%, Ca/U < 0.15%, Mo/U < 0.05%, Zr < 0.06%, V/U ≈ 0%) from companies of Niger Republic.

The metal salts $(NH_4)_6Mo_7.4H_2O$ at 99% (MERK), $NH_4VO_3$ 99% (MERK) are prepared at (5 g/L) in various minerals acids and the sodium chlorate ($NaClO_3$) used as an oxidant in vanadium extraction. All the solutions are prepared in demineralized water at pH = 1 and the experimental temperature is maintained at 30 °C. Metals are attacked by the following minerals acids: $H_2SO_4$ 95% (VWR), $HNO_3$ 65% (VWR), HCl 37% (VWR), $H_3PO_4$ 85% (VWR).

Table 1 provides the content of certain metals of the uranium-bearing solutions of Niger Republic's factories with free acidity ($H^+$) of 22 g/L.

**Table 1.** Composition of uranium-bearing solutions samples

| | **Sample 1** | **Sample 2** |
|---|---|---|
| **Uranium (mg/L)** | 3698 | 1602 |
| **Molybdenum(mg/L)** | 52 | 60 |
| **Vanadium (mg/L)** | 2423 | 137.286 |
| **Zirconium (mg/L)** | 20 | 54 |
| **Iron (mg/L)** | 465 | 180 |
| **pH** | 1 | 1 |
| **Redox Potential (mV)** | 496 | 448 |

### Extraction procedure

The extraction process is done in 100 mL separatory funnels perfectly shaken. The shaking speed was set to 70 oscillations/min on an AGITELEC-branded agitator. The pH is determined with a device branded Knick pH-Meter 766 Calimatic and the redox potential with a Mettler Toledo-branded device.

In a separatory funnel, 10 ml of the aqueous phase containing the metal salt and 10 ml of the organic phase containing the extractant are brought into contact and this for 2 minutes, time sufficient for the transfer of solute from one phase to the other until the determined equilibrium determined by a kinetic study is reached. At the end of the extraction, the two phases are separated by decantation. Vanadium and molybdenum are analyzed using a Varian AAFS240 atomic absorption spectrophotometer equipped with an acetylene-nitrous oxide burner at the respective wavelengths 318 and 313 nm. The determination of the metals of the aqueous phase was carried out directly after an adequate dilution. The uranium resulting from the nitric solution is extracted with trioctylphosphine oxide (TOPO) in a kerosene medium and is then assayed by colorimetry after the solvent has been added to the dibenzoylmethane reagent (DBM) and the zirconium is determined by the orange xylenol reagent in medium hydrochloric. Uranium and zirconium are analyzed by UV-Vis spectrophotometry with a Varian Cary 50 UV-Vis Spectrophotometer device at the respective wavelengths of 405 and 540 nm.

The distribution coefficient (1) and the extraction percentage (2) are respectively determined by the relations:

$$D = \frac{[\mathbf{M}]_{\mathbf{org}}}{[\mathbf{M}]_{\mathbf{aq}}} \qquad (1) \qquad\qquad E\,(\%) = \frac{\mathbf{D}}{\mathbf{D} + \frac{\mathbf{V_{aq}}}{\mathbf{V_{org}}}} \times 100 \qquad (2)$$

$[M]_{org}$ = Metal concentration in the organic phase (mg/L)
$[M]_{aq}$ = Metal concentration in the aqueous phase (mg/L)

## Results and discussion

### Extraction kinetics of uranium

With a view to obtaining the contact time necessary to reach extraction equilibrium, the kinetic study of the transfer of the metal ions between the organic phase and the aqueous phase was carried out in two contacts. The aqueous phase has a uranium concentration of 3698 mg/L from uranium-bearing solution and pH = 1. The Alamine 336 concentration in the organic phase is of 0.1 M. The extraction is done at 30 °C. The obtained results are displayed in Fig.2. According to these results, the extraction kinetics of uranium is fast. The peak obtained before two minutes reflects that the best time seen fit to reach equilibrium is 2 minutes. In literature, research done by (Zhu, Z., Pranolo, Y., Cheng, C. Y., 2016; Agrawal, A., Mishra, D., Sahu, K. K., 2016) also show that this time do not exceed 3 minutes.

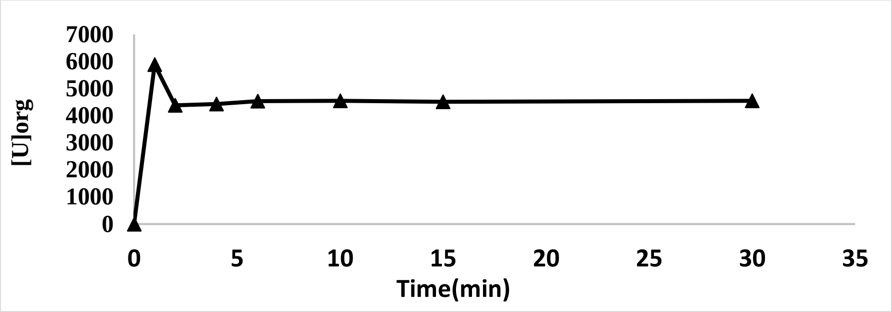


**Fig.2.** Extraction kinetics of uranium

## Effect of the etching solution

Different mineral acids ($H_2SO_4$, $HNO_3$, HCl, $H_3PO_4$) were used in order to determine the best solublization medium. The aqueous phase prepared form $Na_2U_2O_7$ has a uranium concentration of 3 g/L. The extractants used are Alamine 336 and Aliquat 336 at 0.2 M. The pH is set at 1 and the redox potential at 628 mV. Fig.3 shows the obtained results. For Alamine 336, the extractability sequence of uranium follows the order next off: $H_2SO_4 > H_3PO_4 > HCl > HNO_3$. For Aliquat 336, the sequence follows the order: $H_3PO_4 > HCl > HNO_3 > H_2SO_4$.

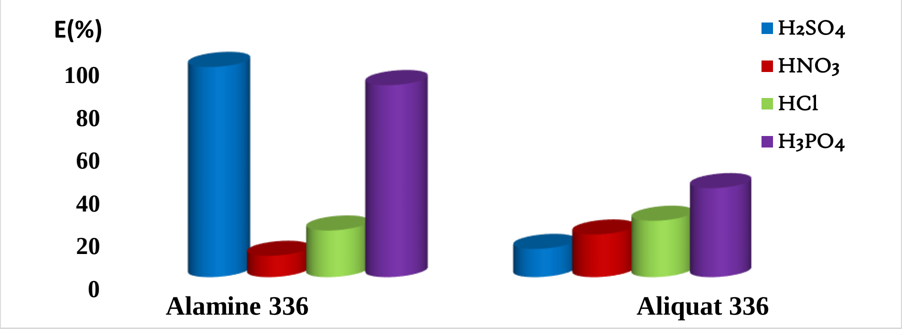


**Fig.3.** Effect of acid on the extraction of uranium by Alamine 336 and Aliquat 336

## Effect of solvent

Kerosene, toluene and diisobutyl ketone (DIBK) were used on the extraction of uranium. The aqueous phase prepared from $Na_2U_2O_7$ has a concentration of 3 g/L in uranium. The organic phase has an Alamine 336 concentration of 0.2 M. The pH is set at 1 the redox potential at 628 mV. Fig.4. shows the obtained results. The extraction percentage of uranium grows according to the order: Toluene > Kerosene ≈ DIBK.

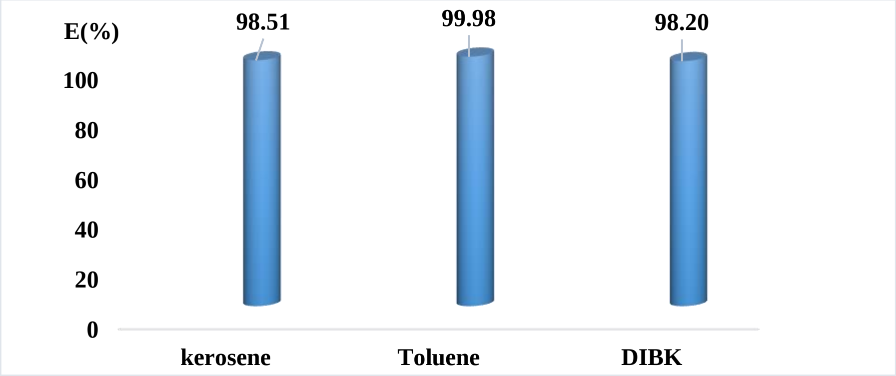


**Fig.4.** Effect of the solvent on the extraction of uranium by Alamine 336

### Effect of the ratio between the organic phase and the aqueous phase

The aqueous phase prepared from $U_3O_8$ has a uranium concentration of 3 g/L and pH = 1. The organic phase has an Alamine 336 concentration of 0.2 M. The experimental temperature is maintained at 30 °C. The effects of the variation of volume ratio of the two phases to the extraction efficiency were studied and illustrated on Fig.5. This work clearly shows that from a ratio O/A = 1, we can retrieve at 99% the uranium contained in the aqueous phase with a single contact.

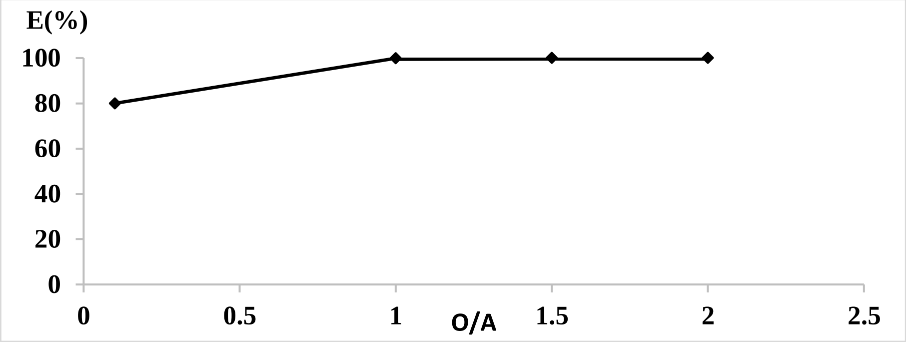


**Fig.5.** Extraction percentage of uranium as a function of the ratio of the organic phase and the aqueous phase

### Effect of the Alamine 336 concentration

The uranium-bearing solutions in Niger Republic have a free acidity ($H^+$) of 22 g/L. In order not to render the sulfate ion predominant in the medium and cause a drop in the extraction percentage, the Alamine 336 is contacted with a sulfuric acid solution according to the reaction (3):

$$2(R_3N)_{org} + (H_2SO_4)_{aq} \rightleftarrows [(R_3NH)_2SO_4]_{org} \qquad (3)$$

It is a sulfatation reaction

The aqueous phase prepared from $U_3O_8$ has a uranium concentration of 5 g/L and pH = 1. The Alamine 336 concentration in the organic phase varies from $10^{-3}$ M to 0.2 M. The experimental temperature is maintained at 30 °C.

During the extraction, the nature of the chemical species formed in the organic phase is characterized by the "slopes" method. This method is based on the determination of the values of the distribution coefficient (D) of metal ions by varying the initial pH of the aqueous phase and the concentration by extractant. Fig.6. shows the log D as a function of the log [Alamine 336]. The correlation between the distribution coefficients logarithms and the Alamine 336 concentration shows a linearity which is expressed by the relation:

$D = (K[R_3NH]^p)$ with a slope (p) close to 2. This correlation also shows that 2 molecules of Alamine 336 complex one mole of uranyl sulfate. Likewise, rising the concentration of Alamine 336 (from $10^{-3}$ M to 0.2 M) increases the extraction percentage from 1% to 99%.

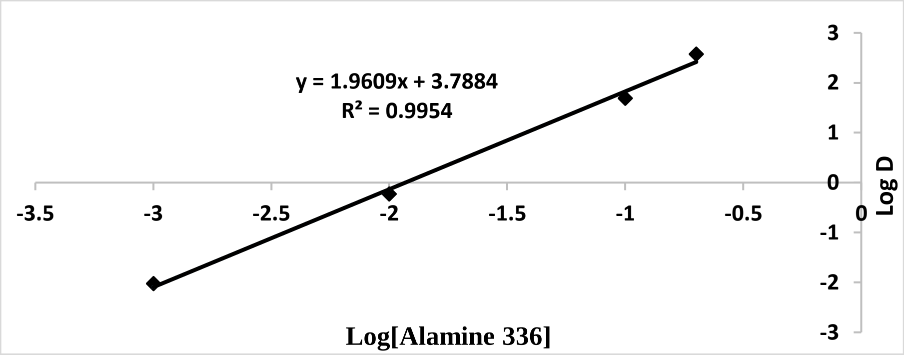


**Fig.6.** Graph logarithm of the distribution coefficient as a function of the logarithm of the Alamine 336

## Effect of the initial pH of the aqueous phase

During the uranium extraction by the Alamine 336, we extract the uranium under its valence 6 corresponding to the cation of the uranyl $UO_2^{2+}$ (Baron, P., Bernier, G., Hartmann, D., Laluc,C., Marbet, M., 2014) with the release of $SO_4^{2-}$ ions reflected by the equation (4):

$$2[(R_3NH)_2SO_4]_{org} + [UO_2(SO_4)_2^{2-}]_{\mathbf{aq}} \rightleftarrows [(R_3NH)_4UO_2(SO_4)_3]_{org} + [SO_4^{2-}]_{aq} \quad (4)$$

It is an anion exchange reaction.

To see the influence of the acid on this balance, various pH of the aqueous phase have been studied during the uranium extraction by Alamine 336. The aqueous phase prepared from $U_3O_8$ has a uranium concentration of 3 g/L and pH = 1. The concentration of Alamine 336 in the organic phase is of 0.2 M. The experimental temperature is maintained at 30 °C. Fig.7. gives the obtained results. The increase in the pH toward 5 decreases the distribution coefficient, because from pH = 2 uranium tends to precipitate into its form $UO_2(OH)_2$, this result is in agreements with that works (Bhargava, S.K., Rahul, R., Pownceby, M., Grocott, S., Ring, B., Tardio, J., Jones, L., 2015). The study of the logarithm of the distribution coefficient as a function of the pH variation between 1 to 5 shows a linearity with a slope of around -2. This result states that 2 moles of $H^+$ ions are released for the uranyl sulfate to form and the decrease of the percentage of uranium extraction due to pH rise still justifies that extraction follows the mechanism of anion exchange extraction.

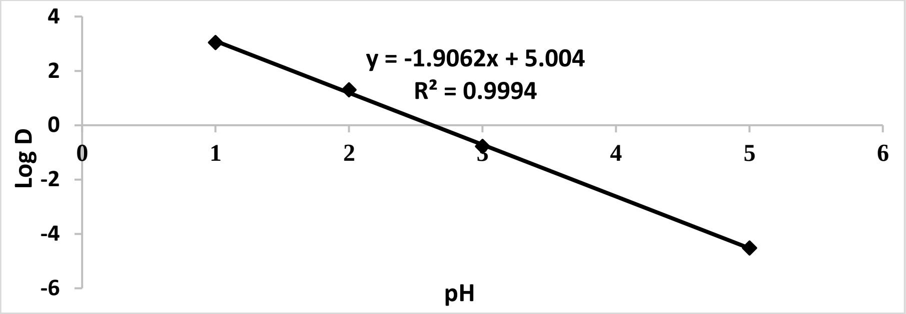


**Fig.7.** Graph logarithm of the distribution coefficient against the initial pH of the aqueous phase

It is clear from the earlier results Fig.6. and Fig.7., that the reaction of the uranium extraction by Alamine 336 in sulfuric medium is reflected by the relation (5), similar result with the literature (Avelar, E.C., Alvarenga, C. L. G., Resende, G. P. S., Morais, C. A., Mansur, M. B., 2017; Kumar, J. R., Kim, J. S., Lee, J. Y., & Yoon, H. S., 2010; Schrötterová,D., Nekovář, P., Mrnka, M., 1992) confirm these results:

$$[UO_2(SO_4)_2^{2-}]_{aq} + [x(R_3NH)_2SO_4)]_{org} \rightarrow [x(R_3N)_2UO_2(SO_4)_2^{2-}]_{org} + [xH^+, SO_4^{2-}]_{aq} \qquad (5)$$

$$K_{eq} = \frac{[x(R_3N)_2UO_2(SO_4)_2^{2-}]_{org}[\,x\,H^+]_{aq}}{[UO_2(SO_4)_2^{2-}]_{aq}[x(R_3NH)_2SO_4)]_{org}}$$

Where Keq: equilibrium constant

$$K_{eq} = \frac{D[\,xH^+]}{[\,x(R_3NH)_2SO_4)]}$$

D : distribution coefficient

$$D = \frac{[\,x(R_3N)_2UO_2(SO_4)_2^{2-}]_{org}}{[\,Uo_2(So_4)_2^{2-}]_{aq}}$$

$$\mathbf{Log\ D = \log K_{eq} + \log [x(R_3NH)_2SO_4)] - \log [xH^+]} \qquad \mathbf{(6)}$$

According to the relation (6) the uranium extraction depends on the pH of the solution as well as the concentration of Alamine 336.

## Effect of the Alamine 336 /Aliquat 336 synergism in function of the number of contact

Fig.8. shows the results obtained on the effect of the synergism coupled to the number of contact. The number of contact consists in maintaining a

constant volume of the organic phase and varying the volume of the aqueous phase after every 2 minutes of agitation. The aqueous phase prepared from $Na_2U_2O_7$ has uranium concentration of 3 g/L. The organic phase has 0.2 M of Alamine 336 concentration and 0.1 M of Aliquat 336 concentration. The pH is fixed to 1 and the redox potential to 628 mV. Until the 2nd contact the Alamine 336 charges to 99% in uranium and after the percentage drops. The addition of the Aliquat 336 at 0.1 M has no effect on the extraction percentage. Nevertheless, we notice a linear drop in the extraction percentage due to a competition between the two anionic extractants.

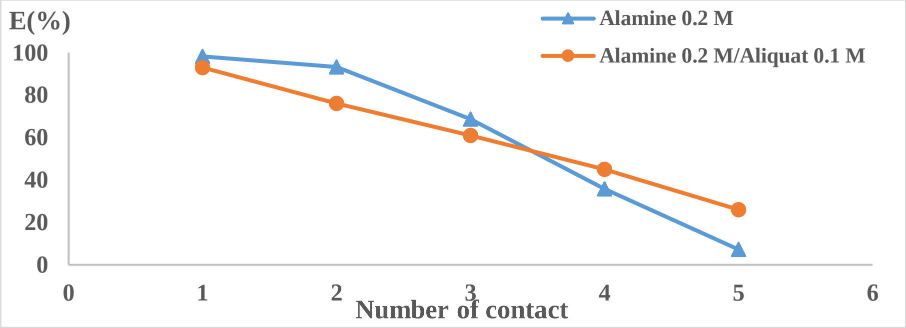


**Fig.8.** Extraction percentage of uranium as a function of the effect of the Alamine 336/Aliquat 336 synergism and the number of contact

## Effect of the number of contact

The extraction was performed on uranium-bearing solutions of Niger Republic containing the following metals: uranium = 1602 mg/L, molybdenum = 60 mg/L, vanadium = 137.286 mg/L, zirconium = 54 mg/L, iron = 180 mg/L, pH = 1, the redox potential is to 448 mV and the organic phase has an Alamine 336 concentration of 0.15 M. The experimental temperature is maintained at 30 °C. Fig.9. shows that for low levels of molybdenum, the Alamine 336 continues to charge to more than 85% in uranium until the 4th contact with a molybdenum content of 27%. After the 4nd contact, the Alamine 336 tends not to load in uranium and molybdenum anymore.

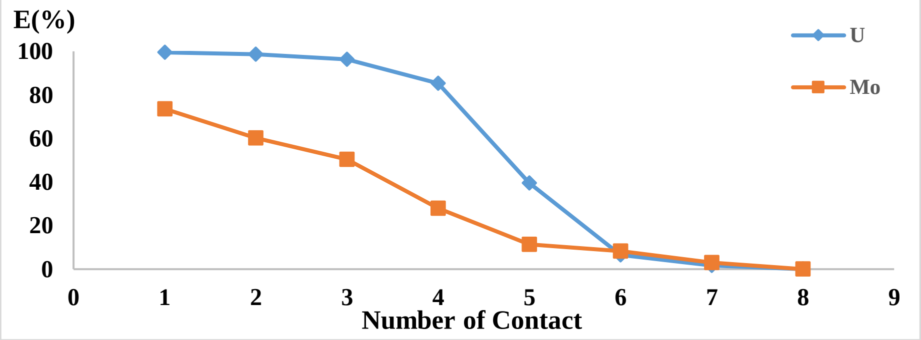


**Fig.9.** Extraction percentage of uranium and molybdenum as a function the number of contact

## Effect of the molybdenum and vanadium concentration on the uranium of extraction by Alamine 336

The molybdenum and vanadium contents in the uranium-bearing solution were raised respectively by the addition of $(NH_4)_6Mo_7.4H_2O$ and $NH_4VO_3$. The new aqueous phase has the following contents: U = 1602 mg/L, Mo = 1 g/L, V = 1107 mg/L and Zr = 54 mg/L, pH = 1, the redox potential is at 448 mV and the organic phase has an Alamine 336 concentration of 0.15 M. The experimental temperature is maintained at 30 °C. Fig.10. shows the obtained results. The increase in the concentration of molybdenum also causes its extraction percentage to grow hence making the valorization of the uranium difficult. The Alamine 336 tends to release the uranium and the zirconium extracted until the 3rd contact to the benefit of the molybdenum. This release seems to be caused by the natural presence of ions $Cl^-$,$NO_3^-$, $F^-$ which tend to break the anionic complexes. The extraction of vanadium is non-existent in these hydrodynamic conditions.

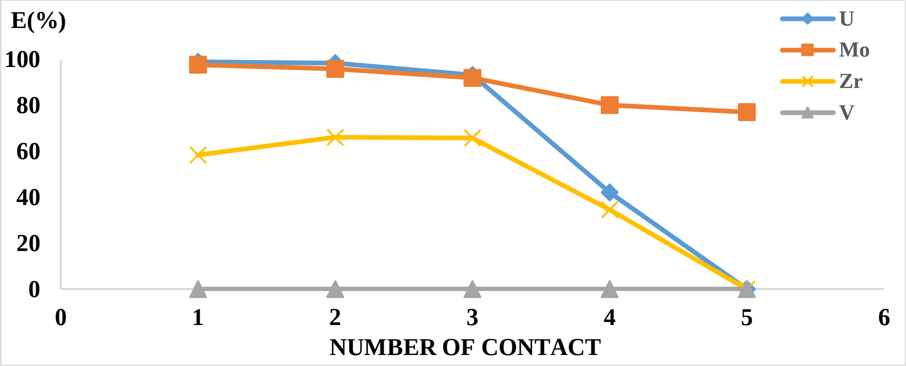


**Fig.10.** Extraction percentage of uranium, molybdenum, zirconium and vanadium by Alamine 336 as a function of the number of contact

## Effect of the formation of the 3rd phase on the decantation

Decantation is one among the important parameters in liquid-liquid extraction. Fig.11. shows: (A) synthetic solution containing only uranium at a concentration of 1 g/L from $U_3O_8$ and (B) uranium-bearing solutions. The pH = 1, the redox potential is at 448 mV for the aqueous phases and the organic phase has an Alamine 336 concentration of 0.2 M. The experimental temperature is maintained at 30 °C. On Fig.11. (A) until the 5th contact we get a perfect separation of the two phases while in (B) the solution loaded with several metals leads to the formation of a 3rd phase making the decantation difficult. The formation of the 3rd phase appears to be due to the presence of several metals in the solutions.

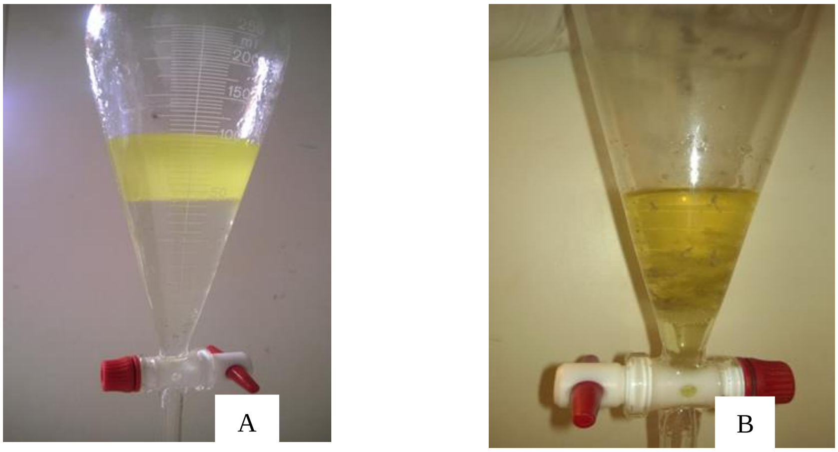


**Fig.11.** Formation of the 3rd phase during the uranium extraction by Alamine 336

## Effect of the molybdenum and vanadium concentration on the uranium extraction by Aliquat 336

The uranyl sulfate extraction by Aliquat 336 in a sulfuric medium (El Sayed, M. S., 2003) is described according to equation (7):

$$4[R_3N^+CH_3Br^-]_{org} + [UO_2(SO_4)_3^{4-}]_{aq} \rightleftarrows [(R_3NCH_3)_4UO_2(SO_4)_3]_{org} + 4\,[Br^-]_{aq} \qquad (7)$$

In this study the contents of molybdenum and vanadium in the uranium-bearing solutions were raised respectively by the addition of $(NH_4)_6Mo_7.4H_2O$ and $NH_4VO_3$. The new aqueous phase contains the following levels: U = 1602 mg/L, Mo = 1 g/L, V = 1107 mg/L and Zr = 54 mg/L, pH = 1, the redox potential is to 448 mV and the organic phase has an Aliquat 336 concentration of 0.15 M. The experimental temperature is maintained at 30 °C. Fig.12. shows the obtained results. Aliquat 336 extracts the molybdenum to 99% up to the 5th contact, the zirconium concentration goes from 65% between the 1st and 2nd contact to 35% at the 5th contact, as for the uranium the percentage goes from 20% at the 1st contact to 5% at the 5th contact, vanadium is not extracted either in these hydrodynamic conditions.

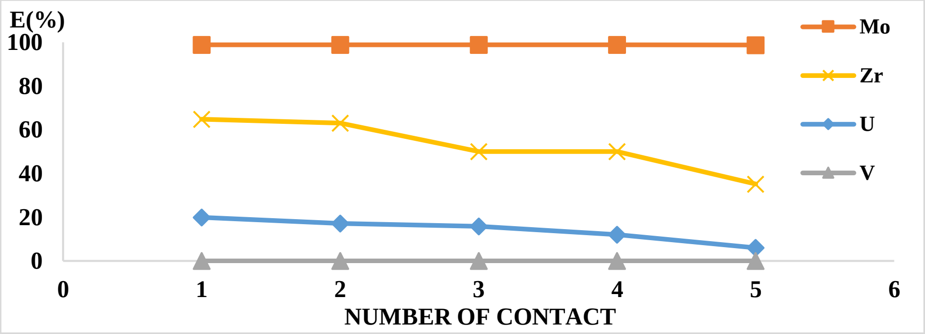


**Fig.12.** Extraction percentage of uranium, molybdenum, zirconium and vanadium by Aliquat 336 as a function of the number of contact

### Effect of the pH on the uranium extraction by Aliquat 336

In order to study the low rate of uranium extraction by Aliquat 336, the initial pH of the aqueous phase was varied. The aqueous phase prepared from $Na_2U_2O_7$ has a uranium concentration of 3 g/L. The organic phase has an Alamine 336 concentration of 0.2 M. The redox potential is at 628 mV and the experimental temperature is maintained at 30 °C. Fig.13. shows the obtained results. Aliquat 336 extracts very weakly the Uranium with low pH and the more we tend toward high pH, the more we achieve efficiencies reaching 99%. However, at these pH uranium tends to precipitate in the form of $UO_2(OH)_2$ with redox potential of 628 mV.

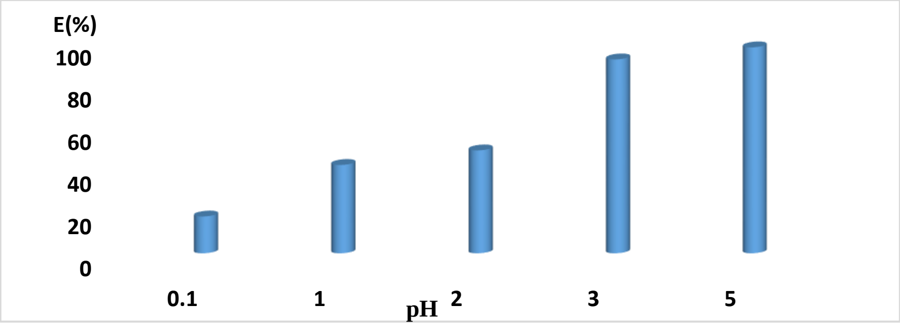


**Fig.13.** Extraction percentage of uranium by Aliquat 336 as a function of the pH

### Effect of the redox potential on the vanadium extraction

Vanadium in an aqueous solution shows different speciations which make the study of its complexes difficult. However at pH < 2 values, vanadium comes out mainly in its cationic form $VO_2^+$ (Olazabal, M. A., Orive, M. M., Fernandez, L. A., Madariaga, J. M., 1992; Sahu, K. K., Agrawal, A., Mishra, D., 2013; Nayl, A. A., Aly, H. F.. 2015; Hossein, M., Beiranvand, B., Ghorbanian, S. A., Mallah, M. H., 2014).In a sulfuric medium, according to the work (Yang, X., Zhang, Y., Bao, S., 2016; Chagnes, A., Rager, M., Courtaud, B., Thiry, J., Cote, G,. 2010) vanadium is in its $VO_2SO_4^-$ form whose extraction mechanisms by Alamine 336 and Aliquat 336 translate respectively by equations (8) and (9):

$$[2VO_2SO_4^-]_{aq} + [2(R_3NH^+)(SO_4)^{2-}]_{org} \leftrightarrows 2[(R_3NH)^+(VO_2SO_4)^-]_{org} + [SO_4^{2-}]_{aq} \qquad (8)$$

$$[VO_2^+]_{aq} + [H_2SO_4]_{aq} + [(R_3NCH_3{}^+Br^-)]_{org} \leftrightarrows [(VO_2SO_4)R_3NCH_3]_{org} + 2[H^+]_{aq} + [Br^-]_{aq} \qquad (9)$$

In order to study the non-extractability of vanadium by Alamine 336 and Aliquat 336, the variation of the redox potential was tested on a synthetic solution titrating at 5 g/L from $NH_4VO_3$. The organic phase has 0.2 M of concentration in Alamine 336 and in Aliquat 336 respectively. The initial redox potential fixed at 826 mV, the pH is fixed at 1. The experimental temperature is maintained at 30 °C. Fig.14. gives the obtained results. The increase in the redox potential causes to the extraction percentage of uranium to increase to 30% for the Alamine 336 and 16% for the Aliquat 336.

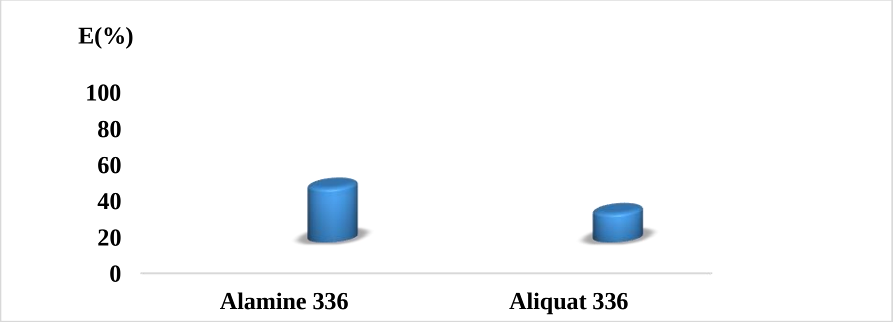


**Fig.14.** Extraction percentage of vanadium by Alamine 336 and Aliquat 336

## Extraction of vanadium obtained from the uranium-bearing solutions with high redox potentials

The redox potential of the uranium-bearing solutions of Niger Republic was raised by the addition of the $NaClO_3$, the aqueous medium is initially at potentials between 448-500 mV, the aqueous phase has concentrations of 3698 mg/L in uranium and 2423 mg/L in vanadium. The organic phase has an Alamine 336 concentration of 0.1 M. Fig.15. shows the obtained results. The extraction percentage of vanadium is 0% between (448-500 mV), at this potential a large part of the vanadium is in the + 4 oxidation state. However, this form of vanadium is non-extractable by tertiary amines (Floh (Miss), B., Abrao, A., Calmon Costa, E., 1971). That is why the reoxidation according to equation (10) of iron (II) naturally present in the environment (from the gangue) by the $NaClO_3$ made it possible to oxidize the vanadium. The oxidation of V(IV) to V(V) has allowed to increase the extraction percentage of vanadium from 0% to 15%. Likewise, his increase simultaneously leads to the drop in the extraction percentage of uranium.

$6FeSO_4 + NaClO_3 + 3H_2SO_4 \rightarrow 3Fe_2(SO_4)_3 + NaCl + 3H_2O$ (10)

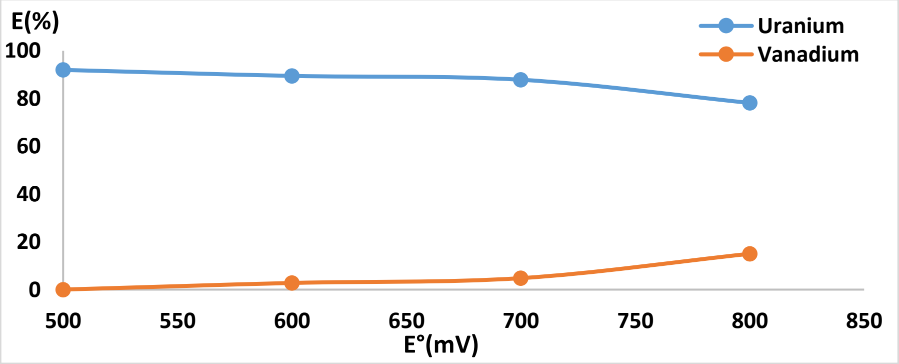


**Fig.15.** Extraction percentage of uranium and vanadium by Alamine 336

## Conclusion

Alamine 336 and Aliquat 336 were used on the uranium extraction of synthetic solutions as well as uranium-bearing solutions coming from two major mining companies Niger Republic. From this work, it appears that the kinetics of extraction is reached in 2 minutes with an extraction percentage reaching the 99% level from a ratio O/A = 1. The best etching medium for Alamine 336 obeys the following extractability sequence of uranium: $H_2SO_4 > H_3PO_4 > HCl > HNO_3$. Aliquat 336, the sequence follows the order $H_3PO_4 > HCl > HNO_3 > H_2SO_4$.

Toluene, kerosene and diisobutyl ketone (DIBK) show the same behavior towards the uranium extraction.

The extraction by Alamine 336 follows the extraction mechanism by anionic exchange. The distribution coefficient rises with the increase in the Alamine 336 concentration and drops at higher pH levels. Due to the natural presence of ions such as $Cl^-, NO_3^-, F^-$ in the uranium-bearing solutions, the Alamine 336 tends to release uranium and zirconium loaded at the 3rd contact to reach 0% at the 5th contact to the benefit of the molybdenum.

By varying the redox potential and the pH, vanadium can be extracted from the uranium-bearing solutions at 30% and 15% respectively for Alamine 336 and Aliquat 336 based on the number of contact.

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