

Comparative study of solvent extraction of molybdenum by various extractants

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Abstract: Solvent extraction of molybdenum from various acid media by Alamine 336, Aliquat 336, TOPO, and DEHPA in kerosene was studied. The extraction efficiency of molybdenum by diisobutyl ketone (DIBK), the effects of various parameters like diluents, mineral acids, extractant concentration, and applications of these extractants on molybdenum extraction contained in the uranium-bearing ore solutions were investigated. DIBK used as solvent can indeed extract the molybdenum without adding any extractants in the range of 20–50 mg/L. Molybdenum was extracted by Aliquat 336 in all mineral acids at more than 90%. On the basis of slope analysis, the compositions of the extracted species were expressed by $R_3NH^+ \cdot HMoO_4^-$, $MoO_2(NO_3)_2(DEHPA)_2$, and $H_2MoO_4 \cdot TOPO$. Extraction from synthetic solutions showed that molybdenum was extracted by TOPO, Aliquat 336, and Alamine 336 at 99% until $[Mo] = 5$ g/L. For DEHPA the percentage of extraction was decreased from $[Mo] = 2$ g/L. The application of these extractants for the extraction efficiency of molybdenum contained in uranium-bearing solutions showed that TOPO, Aliquat 336, and Alamine 336 extracted the molybdenum beyond 60% until the fifth contact. As for DEHPA, it was extracted effectively only at the first contact by 66%.

Key words: Molybdenum, uranium-bearing solutions, extractant, contact number, acid medium

1. Introduction

The Republic of Niger exploits uranium deposits in a wet way through two mining companies. This hydrometallurgical process allows to purify and concentrate the uranium from deposits ranging in thickness from 1 to 10 m and from 0.2% to 0.6% in uranium content. The final product obtained is either sodium diuranate ($Na_2U_2O_7$) or magnesium diuranate (MgU_2O_7).

Generally, confined in uranium ore, vanadium, zirconium, and molybdenum are troublesome elements for the Republic of Niger, which prefers to valorize uranium. However, the recovery of these impurities can also be profitable if the content of the metal is significant. The case of molybdenum was illustrated in Akouta using the MoCa process, a process developed between the Alternative Energies and Atomic Energy Commission and Orano.^{1,2} This process is based on liquid-liquid extraction, also called solvent extraction, the extraction mechanisms of which differ according to the nature of the extractant and the interactions created during the transfer of the metal from the aqueous phase to the organic phase. Thus, three types of extraction are conventionally distinguished: cation exchange extraction, anion exchange extraction, and solvation extraction.^{3–5}

Tertiary amines such as Alamine 336 are widely used in the extraction of uranium by the AMEX

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process.^{6,7} The phosphated extractants such as trioctylphosphine oxide (TOPO) or di-2-ethylhexylphosphoric acid (DEHPA or HDEHP) in synergy with tributylphosphate (TBP) through the DAPEX process⁷⁻⁹ are widely used for the extraction, separation, and purification of various metals. Lee et al.¹⁰ studied the extraction and separation of hexavalent molybdenum from acidic sulfate solutions using Alamine 336 as an extractant and reported that the percentage extraction of molybdenum with Alamine 336 decreased with increasing acid concentration. They also reported that the effect of Alamine 336 concentration on the extraction of molybdenum and sulfuric acid increased with increasing Alamine 336 concentration. The mechanism of the extraction of molybdenum(VI) from diluted HCl and HNO₃ solutions with di-2-ethylhexylphosphoric acid was studied by James et al.¹¹ They reported that with DEHPA for both acids in the pH range of 1.0–6.0 the major extractable species was MoO₂²⁺ in n-hexane. Moría et al.¹² studied the extraction of molybdenum and tungsten by Alamine 336 and DEHPA and reported that the optimal selectivity for the extraction of molybdenum in the presence of tungsten is achieved at pH 3 and organic phase/aqueous phase volume ratio of 1/2. Coşar and Ziyadanogullari¹³ reported that molybdenum treated with H₂SO₄ could be separated from other metals in the third stage of the five-stage extraction of aqueous solutions with Alamine 336. Liquid-liquid extraction of molybdenum(VI) from aqueous acid solutions by TBP and TOPO was studied by Sato et al.¹⁴ The results showed that H₂MoO₄.TOPO was formed in the extractions from aqueous hydrochloric, nitric, and sulfuric solutions at low acidities.

In this regard, we focused on the liquid-liquid extraction of molybdenum by Alamine 336, Aliquat 336, DEHPA, and TOPO. To our best knowledge there are no reports on the detailed study of N-methyl-N,N-dioctyl-1-octanaminium bromide (C₂₅H₅₄BrN) or Aliquat 336 for industrial molybdenum extraction. The extraction efficiency of molybdenum by diisobutyl ketone (DIBK); the effects of various parameters like diluents, mineral acids, and extractant concentration; and applications of these extractants on molybdenum extraction contained in uranium-bearing solutions resulting from the leaching of the Republic of Niger's uranium ore were investigated. On the basis of slope analysis, the nature of the extracted species was established by evaluating the logarithm of distribution while varying the extractant concentration and pH.

2. Results and discussion

2.1. Effect of diluents

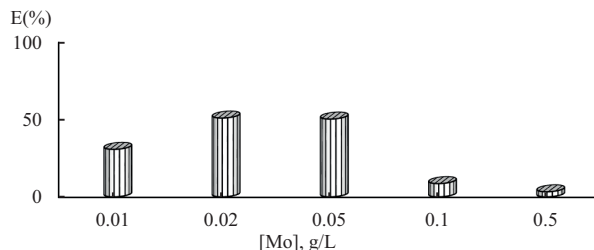
The choice of diluent during liquid-liquid extraction is essential. This choice depends on physicochemical properties such as flash point, viscosity, density, boiling temperature, evaporation rate, solubility, influence on the distribution ratio, selectivity, reaction with the extractant agent, and hydrodynamic conditions such as the formation of the third phase. The diluent chosen to dissolve the extractant(s) may be aromatic such as toluene, aliphatic such as kerosene, polar, or semipolar such as DIBK. The nature of the diluent has a significant effect on the kinetics of the process, including extraction and phase separation.¹⁵ Kerosene (dielectric constant $\epsilon = 1.8$), toluene ($\epsilon = 2.38$), and DIBK ($\epsilon = 9.9$) were used for the extraction of molybdenum. The aqueous phase prepared from (NH₄)₆Mo₇.4H₂O had a concentration of 5 g/L in molybdenum. The organic phase had an Alamine 336 concentration of 0.2 M. The pH was set at 1 and the experimental temperature was maintained at 30 °C. It was clear that all solvents had the same behavior with respect to the extraction efficiency of molybdenum with a percentage exceeding 99%. Also, toluene and DIBK supplied better separation phases, the same result having been reported by Talla et al.¹⁶ Nevertheless, the DIBK extracted molybdenum with a slight difference. This may be due to its semipolarity and higher dielectric constant than the other diluents (Table 1). Kerosene was used in the following of works for its availability.

Table 1. Effect of diluents on the extraction of 5 g/L molybdenum in sulfuric acid medium using 0.2 M Alamine 336.

Diluents	Density	Dielectric constant	% Extraction
Kerosene	0.788	1.8	99.82
Toluene	0.869	2.38	99.93
DIBK	0.8	9.9	99.98

2.2. Extraction of molybdenum by DIBK

In this part the extraction efficiency of molybdenum was determined in DIBK without addition of extractant. The molybdenum concentration ranged from 10 mg/L to 500 mg/L and the organic phase was formed only of DIBK. DIBK extracted 50% of molybdenum for concentrations between 20 mg/L and 50 mg/L, which follows the same trend as reported by Miyazaki et al.¹⁷ This extractability of DIBK may be due to a chelating effect of DIBK (Figure 1).

**Figure 1.** Extraction of molybdenum in sulfuric acid medium using only DIBK.

2.3. Effect of extraction of mineral acids

Various mineral acids (H_2SO_4 , HNO_3 , HCl , H_3PO_4) were used in order to determine the best solubilization medium. The aqueous phase prepared from $(\text{NH}_4)_6\text{Mo}_7\cdot 4\text{H}_2\text{O}$ had a molybdenum concentration of 1 g/L. The extractants used were Alamine 336, Aliquat 336, TOPO, and DEHPA at 10^{-2} M. It was found that Aliquat 336 can extract molybdenum with a percentage of extraction greater than 90%. The extraction by Alamine 336 was more marked in phosphoric acid medium and followed the following sequence: $\text{H}_3\text{PO}_4 > \text{H}_2\text{SO}_4 > \text{HNO}_3 > \text{HCl} > \text{HF}$, in accordance with Nguyen and Man's works.¹⁸ TOPO preferentially extracted in hydrofluoric acid medium at 86% and at 61% in a nitric acid medium. In our experimental conditions, the extraction efficiency of molybdenum by DEHPA at 10^{-2} M in all the mineral acids did not exceed 50%; this low extractability may be due to the acidity of the medium.^{19,20} The extraction efficiency of molybdenum in mineral acids was highest at pH values between 2 and 3 (Table 2).

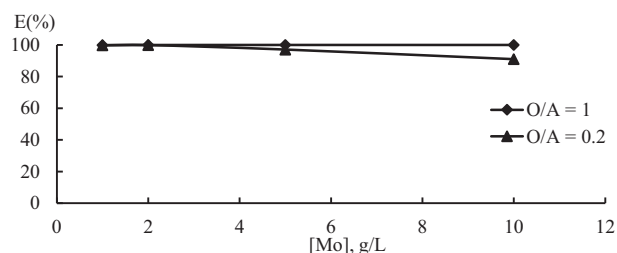
2.4. Effect of the ratio between the organic phase and the aqueous phase volume

The aqueous phase prepared from $(\text{NH}_4)_6\text{Mo}_7\cdot 4\text{H}_2\text{O}$ had a molybdenum concentration that varied from 1 g/L to 10 g/L and pH 1. The organic phase had an Alamine 336 concentration of 0.2 M in kerosene. The effects of the variation of volume ratio of the two phases on the extraction efficiency were studied. The volumetric concentrations of organic phase and aqueous phase were $O/A = 0.2$ (20% vol. of organic phase + 80% vol. of aqueous phase) and $O/A = 1$ (20% vol. of organic phase + 20% vol. of aqueous phase). It was observed that

Table 2. Effect of acid medium on the extraction of 1 g/L molybdenum using 0.01 M Alamine 336, 0.01 M Aliquat 336, 0.01 M TOPO, and 0.01 M DEHPA in kerosene.

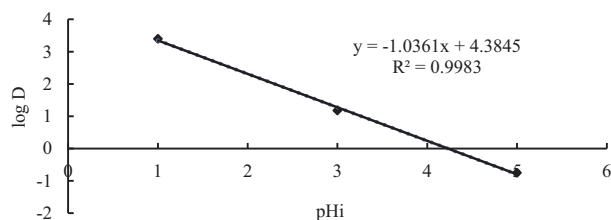
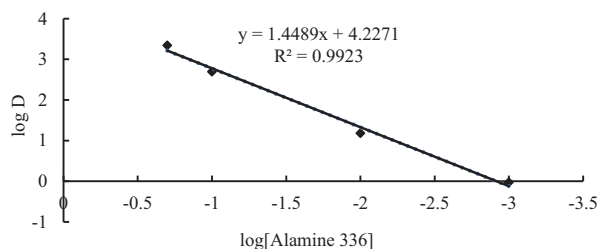
Acid medium,	Extractants			
pH 1	Alamine 336 % Extraction	Aliquat 336 % Extraction	TOPO % Extraction	DEHPA % Extraction
H ₂ SO ₄	92.32	95.38	21.87	0
HNO ₃	82.31	91.75	60.62	50
HCl	60.89	89.05	31.44	33.19
H ₃ PO ₄	98.20	91.72	5.05	0
HF	42.62	97	86.03	18.61

from a ratio of $O/A = 1$, we can retrieve 99% of the molybdenum contained in the aqueous phase with a single contact up to 10 g/L, while for a volume ratio of 0.2 the percentage decreases to 90% due to the saturation of the organic phase (Figure 2).¹²

**Figure 2.** Effect of the ratio between organic phase and aqueous phase volume on the extraction of molybdenum in sulfuric acid medium using 0.2 M Alamine 336 in kerosene.

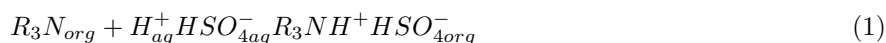
2.5. Effect of Alamine 336

The aqueous phase prepared from $(\text{NH}_4)_6\text{Mo}_7 \cdot 4\text{H}_2\text{O}$ had a molybdenum concentration of 5 g/L and pH 1. The Alamine 336 concentration in the organic phase was varied from 10^{-3} M to 0.2 M. During the extraction, the nature of the chemical species formed in the organic phase was characterized by the ‘slopes’ method. This method was based on the determination of the values of the logarithm of the distribution coefficient (D) of metal ions by varying the initial pH of the aqueous phase or the logarithm of Alamine 336 concentration (Figures 3 and 4).

**Figure 3.** Plot of log D versus initial pH for the extraction of 5 g/L molybdenum in sulfuric acid medium using 0.2 M Alamine 336.**Figure 4.** Plot of log D versus log [Alamine 336] for the extraction of 5 g/L molybdenum in sulfuric acid medium.

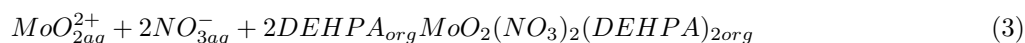
Thus, the extraction was carried out in a strong sulfuric acid medium with pH 1. In these conditions Alamine 336 extracted the molybdenum in its anionic form ($HM_oO_4^-$).^{12,18,21}

Eq. (1) gives the Alamine 336 sulfidation mechanism and the plot of log D as a function of pH variation between 1 and 5 showed linearity with a slope of around -1, which reflected the release of ion molecule HSo_4^- . Likewise, the correlation of log D and log [Alamine 336] showed linearity with a slope of 1.44, which illustrated the complexation of 1 mole of $HM_oO_4^-$ by one mole of Alamine 336 according to Eq. (2). Also, the increase of pH between 1 and 5 resulted in a decrease of the percentage of extraction efficiency and this result illustrated an extraction by anion exchange.^{10,18,22}



2.6. Effect of DEHPA

In order to study the mechanism of molybdenum extraction by DEHPA in nitric acid medium, the concentration of DEHPA was varied. The aqueous phase prepared from $(NH_4)_6Mo_7.4H_2O$ had a molybdenum concentration of 1 g/L and the concentration of DEHPA in the organic phase was varied from 10^{-3} M to 0.2 M. The temperature of the reaction medium was maintained at 30 °C with pH <2. Log D as a function of log [DEHPA] gave a slope curve of $p = 1.8754$, near 2 (Figure 5). This result indicated that the extraction mechanism involved two molecules of DEHPA per molybdenum atom extracted. For acid solutions with pH 1, the extracted species was in the form of MoO_2^{2+} . As a result, the mechanism was described according to Eq. (3).^{12,20,23,24}



2.7. Effect of TOPO

In order to study the mechanism of molybdenum extraction by TOPO in nitric acid medium, the concentration of TOPO was varied. The aqueous phase prepared from $(NH_4)_6Mo_7.4H_2O$ had a molybdenum concentration of 1 g/L and the concentration of TOPO in the organic phase was varied from 10^{-3} M to 0.2 M. The curve of variation of log D as a function of log [TOPO] yielded a slope of 1 (Figure 6). This result suggested that the species extracted by TOPO for pH <2 was H_2MoO_4 .^{19,20,25,26}

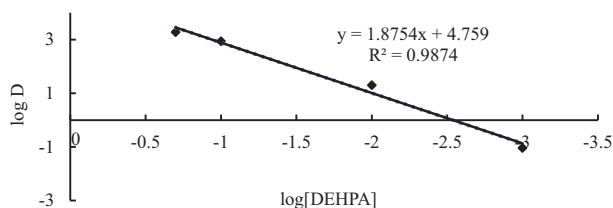


Figure 5. Plot of log D versus log [DEHPA] for the extraction of 1 g/L molybdenum in nitric acid medium.

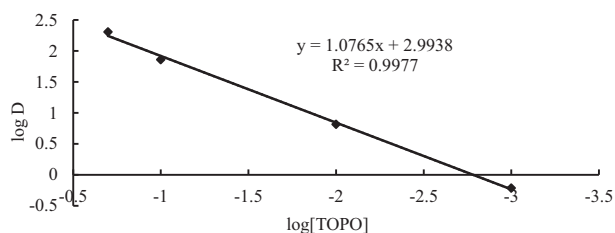


Figure 6. Plot of log D versus log [TOPO] for the extraction of 1 g/L molybdenum in nitric acid medium.

The extraction mechanism was described by Eq. (4)–(6):





2.8. Effect of molybdenum concentration

The aqueous phase was prepared from $(NH_4)_6Mo_7 \cdot 4H_2O$ and the organic phase had an extractant concentration of 0.2 M in kerosene. The extraction efficiency of molybdenum by Alamine 336 and Aliquat 336 was carried out in a sulfuric acid medium with pH 1 and in a nitric acid medium for TOPO and DEHPA. It was observed that for synthetic solutions of $(NH_4)_6Mo_7 \cdot 4H_2O$, the organic phases continued to charge at 99% up to 5 g/L of molybdenum for Alamine 336, Aliquat 336, and TOPO, while for the DEHPA the percentage of extraction decreased from 96% to 78% (Figure 7). This may be due to the fact that DEHPA is extracted in its dimeric form in nonpolar solvents and high pH.¹¹

2.9. Effect of contact number on molybdenum extraction from uranium-bearing solutions

2.9.1. Uranium-bearing solutions without fortification by molybdenum

The contact number consists of maintaining a constant volume of the organic phase and varying the volume of the aqueous phase after every 2 min of agitation. The extraction was performed on uranium-bearing solutions from the Republic of Niger containing the following metals: uranium = 1602 mg/L, molybdenum = 60 mg/L, vanadium = 137 mg/L, zirconium = 54 mg/L, iron = 180 mg/L; pH 1. The redox potential was 448 mV and the organic phase had Alamine 336 and DEHPA concentrations of 0.15 M. It was observed that for low molybdenum concentrations the extractants loaded efficiently from the first contact. Thus, the extraction efficiency percentage for Alamine 336 decreased from 73.58% to 11.43% at the fifth contact. As for DEHPA, the percentage decreased from 86.7% to 30% (Figure 8). For these two extractants, the drop in the percentage of extraction efficiency may be due to the fact that they extracted, in addition to molybdenum, other metals such as uranium, vanadium, and zirconium.¹³ For Alamine 336 the drop to 11.43% may be due to the breakdown of the anionic complexes by ions Cl^- , F^- , and NO_3^- naturally present in uranium-bearing solutions.

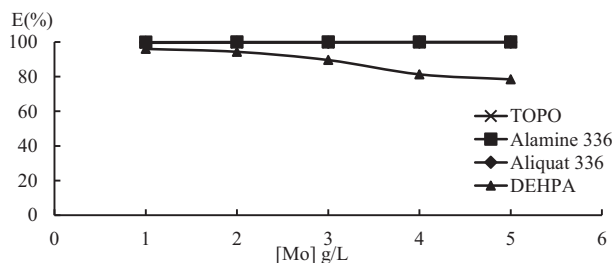


Figure 7. Effect of molybdenum concentration using 0.2 M Alamine 336, 0.2 M Aliquat 336, 0.2 M TOPO, and 0.2 M DEHPA in kerosene.

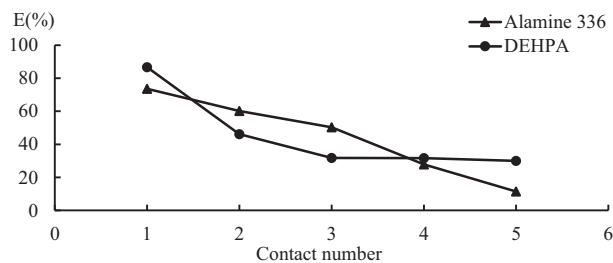


Figure 8. Effect of contact number on molybdenum extraction from uranium-bearing solutions using 0.15 M Alamine 336 and 0.15 M DEHPA in kerosene.

2.9.2. Uranium-bearing solutions fortified with molybdenum and vanadium

The molybdenum and vanadium contents in the uranium-bearing solutions were enhanced by the addition of $(NH_4)_6Mo_7 \cdot 4H_2O$ and $(NH_4)VO_3$. The new aqueous phase contained the following contents: uranium =

1602 mg/L, molybdenum = 1000 mg/L, vanadium = 1107 mg/L, zirconium = 54 mg/L, iron = 180 mg/L; pH 1. The redox potential was 448 mV and the organic phase had an extractant concentration of 0.15 M. It appeared that Aliquat 336 extracted molybdenum at 99% up to the fifth contact. Increasing the concentration of molybdenum to 1 g/L decreased the molybdenum extraction efficiency percentage from 98% to 77% for Alamine 336. TOPO extracted from 85% to the first contact to 66% at the fifth contact. DEHPA's extraction was only effective at first contact with 66%; afterwards, the percentage dropped to 1.53% at the fifth contact due first to saturation of the solvent and also to the fact that the extraction was carried out in a sulfuric acid medium²⁷ (Figure 9).

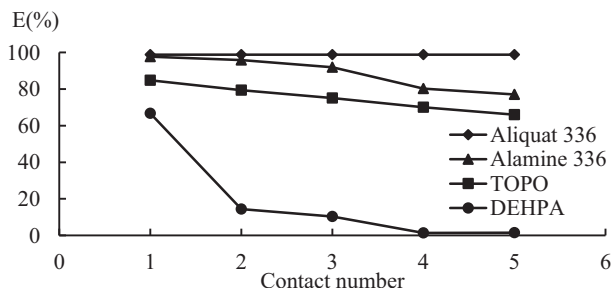


Figure 9. Effect of contact number on molybdenum extraction from uranium-bearing solutions fortified with 1000 mg/L molybdenum and 1107 mg/L vanadium using 0.15 M Alamine 336, 0.15 M Aliquat 336, 0.15 M TOPO, and 0.15 M DEHPA in kerosene.

2.10. Conclusions

Molybdenum extraction was studied using DEHPA, TOPO, Alamine 336, and Aliquat 336 in various diluents. In this work, Alamine 336 effectively extracted molybdenum in kerosene, toluene, and DIBK at 99%. The phosphoric acid medium was an excellent medium for Alamine 336, while nitric acid medium for DEHPA and hydrofluoric acid medium were excellent for Aliquat 336 and TOPO, respectively. The plot of $\log D$ versus $\log [\text{extractant}]$ showed that the extraction efficiency of molybdenum depended on the extractant concentration and the stoichiometry of metal species in the organic phase was suggested to be $R_3NH^+ \cdot HMoO_4^-$, $MoO_2(NO_3)_2(DEHPA)_2$, and $H_2MoO_4 \cdot TOPO$. The extraction efficiency of molybdenum also depended on the volume ratio O/A. With ratio O/A = 1, the extraction was 99%, whereas with ratio O/A = 0.2 it was 90%. The application of these extractants to uranium-bearing solutions showed that the extraction depended on the concentration of molybdenum, but also on the presence of other metals and ions, which generally tended to decrease the percentage of molybdenum extraction during the extraction cycle.

3. Experimental

3.1. 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 third phase. Alamine 336 (Figure 10a) was an anionic extractant with a flashpoint of 179 °C supplied by Cognis Corporation; the 1-octanaminium,N-methyl-N,N-dioctyl-bromide ($C_{25}H_{54}BrN$) or Aliquat 336 (Figure 10b) was an anionic extractant with a molecular weight of 448.61 g mol⁻¹ supplied by Molekula; tri-octylphosphine oxide (TOPO) (Figure 10c) was a solvating or neutral extractant with a molecular weight of 385.64 g mol⁻¹, with purity greater than 99%, and was supplied by Merck; and di-2-ethylhexylphosphoric acid (DEHPA) (Figure 10d) was an acidic extractant with a molecular weight of 322.43 g mol⁻¹, with purity greater than

95%, and was supplied by Alpha Aesar. They were prepared in various diluents, kerosene (TOTAL), toluene (Prolabo), and DIBK (Prolabo), in the presence of isotridecanol (BASF), which had a flashpoint of 122.5 °C. The mixture of these reagents formed the organic phase.

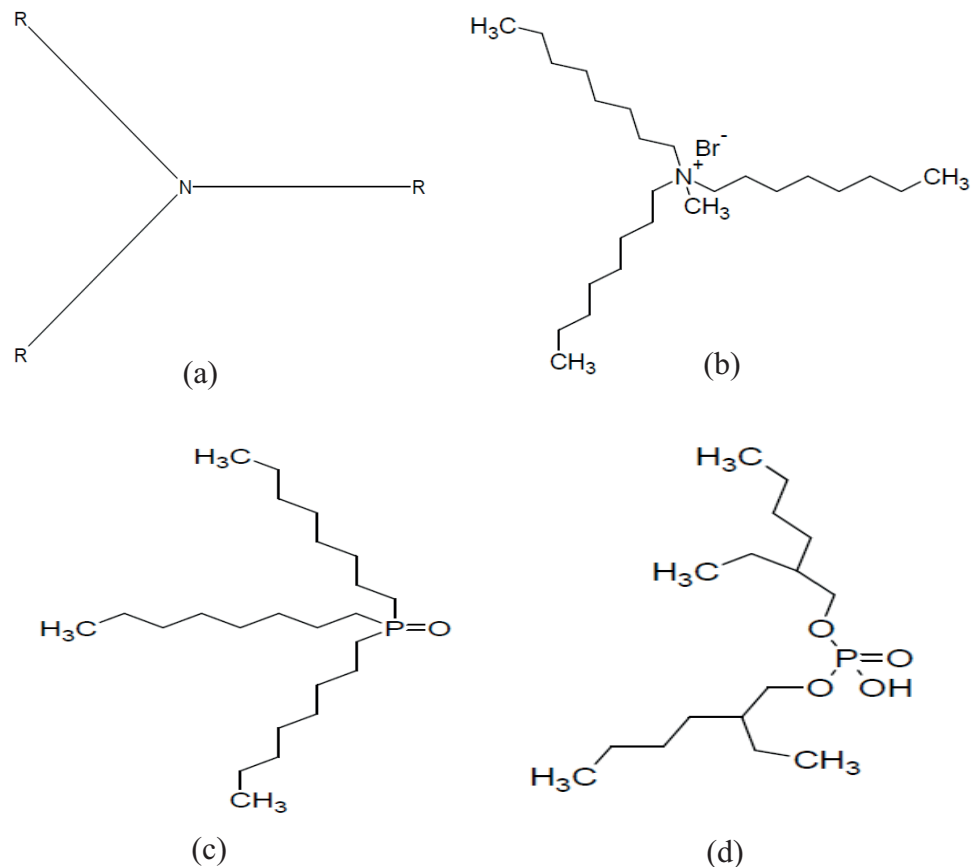


Figure 10. Chemical structures: (a) Alamine 336 ($R = C_8-C_{10}$), (b) N-methyl-N,N-dioctyl-1-octanaminium bromide ($C_{25}H_{54}BrN$) or Aliquat 336, (c) TOPO ($(C_8H_{17})_3OP$), and (d) DEHPA ($C_{16}H_{35}O_4P$).

The synthetic molybdenum solutions were prepared from $(NH_4)_6Mo_7 \cdot 4H_2O$ at 99% purity, supplied by Merck, in various mineral acids. All the solutions were prepared in demineralized water at pH 1 and the experimental temperature was maintained at 30 °C. Metals were attacked by the following mineral acids: H_2SO_4 95% (VWR), HNO_3 65% (VWR), HCl 37% (VWR), H_3PO_4 85% (VWR), HF 40% (VWR).

The compositions of uranium-bearing solutions, which had a free acidity (H^+) of 22 g/L, from the leaching of uranium ores of the Republic of Niger, are given in Table 3.

3.2. Extraction procedure

The extraction process was done in 100 mL separatory funnels, which were perfectly shaken. The shaking speed was set to 70 oscillations/min on an AGITELEC-branded agitator. The pH was determined with a Knick pH-Meter 766 Calimatic device and the redox potential with a Mettler Toledo 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 were brought into contact for 10 min, time sufficient for the transfer of solute

Table 3. Composition of uranium-bearing solution samples.

Sample	
Uranium (mg/L)	1602
Molybdenum (mg/L)	60
Vanadium (mg/L)	137
Zirconium (mg/L)	54
Iron (mg/L)	180
pH	1
Redox potential (mV)	448

from one phase to the other, until equilibrium as determined by a kinetic study was reached. At the end of the extraction, the two phases were separated by decantation. The determination of molybdenum in the aqueous phase was carried out directly after an adequate dilution with 5 mL of $\text{Al}(\text{NO}_3)_3$, 5 mL of KCl, and 5 mL of HNO_3 . Molybdenum was analyzed using a Varian AAFS240 atomic absorption spectrophotometer equipped with an acetylene-nitrous oxide burner at 313 nm.

The distribution coefficient relation of Eq. (7) and the extraction efficiency percentage relation of Eq. (8) were respectively determined by the following formulas:

$$D = \frac{[M]_{org}}{[M]_{aq}} \quad (7)$$

$$E(\%) = \frac{D}{D + \frac{V_{aq}}{V_{org}}} \times 100 \quad (8)$$

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

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

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