# Extraction Behaviour of Dioctylamine and Tricaprylamine Toward Uranium and Some of the Metal Ins

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## Abstract

The extraction behaviour of a secondary amine (Dioctylamine) and a combination of secondary amine and tertiary amine (Tricapryl amine) toward some of the metal ions were investigated. Two types of diluents were applied, namely, mesitylene and treated Kerosene fraction.

The extractability of dioctylamine and different combinations of tertiary amine and secondary amine toward uranium were investigated.

The distribution coefficients and the separataion factors of uranium from the metal ions were calculated.

## Introduction

Is is well- knowu that, amines are derivatives of ammonia in which one, two or all three hydrogen atoms have been replaced by organic radicals R. the capacity of amines to act as extractants is related to their basicity, i.e., to the fact that their nitrogen atom has a mobile ione electron pair, capable of forming coordinate bonds with molecules of other compounds. This is why amines are capable of adding acids HA to form amine salts of the type $R_3N$: HA, which are often also basic and act as extractanats. These amine salts are in general essentially insoluble in water but readily soluble in organic solvents (1-3).

The extraction mechanism is most likely to be of the following type (1, 4):

- The organic solvent containing the amine can extract an aqueous acid to form an amine salt in the organic phase:

$$(R_3N)_{org.} + H^+_{aq.} + A^-_{aq} \rightarrow (R_3NH^+A^-)_{org.}$$

- An amine salt in the organic phase can undergo anion exchange with an ion in the aqueous phase:

$$(R_3NH^+A^-)_{org} + B^-_{aq} \rightarrow (R_3NH^+B^-)_{org.} + A^-_{aq.}$$

where

$A^-_{aq.}$ = anion of a simple acid.

$B^-_{aq.}$ = anion in the aqueous phase.

The first detailed publications, which are concerned with studies of radiation and chemical stability of amines, were done by Baroncelli et al (5). They found that the effect of the irradiation varied strongly with the experimental conditions. If the system amine diluent is irradiated in the absence of $HNO_3$, the composition and the extraction properties of the extractant remain practically unchanged following the irradiation. In the presence of $HNO_3$, the irradiation results in a marked decomposition of the tertiary amine, which is converted to a secondary amine. This decomposition of the extractant results in a decrease in the overall separation factor (6, 7).

The aims of the study were:

- To investigate the behaviour of some of the metal ions with secondary amines.
- Due to the radiolytical and chemical degradations of tertiary extractant, resulting in the formation of different quantities of secondary amines depending on the rediolytical and chemical conditions of the medium, therefore, a mixture of both secondary and tertiary amines were used as extractants. The extractability of the mixture toward some of the fission products were investigated.
- To study the extractability of uranium with different nitric acid molarities using dioctylamine and a mixture of dioctylamine and tricaprylamine as extractants.
- A comparison between two types of diluents, namely mesitylene and kerosene was carried out.

## Experimental

Tricaprylamine (TCA), a camrbian product and Dioctylamine (DOA), a merck product were used without further purification. Mesitylene and Nitric acid, analar grade supplied by BDH. Analar uranyl nitrate supplied by Riedel AG.

Kerosene was treated with conc. sulfuric acid, then washed several times with water and finally distilled. A fraction of the kerosene between 160- 220°C was collected.

Tracers used in this study were obtained from the Radiochemical centre, Amersham, England. The tracers were $Cr^{51}$, $Ru^{103}$, $Cs^{137}$, $Ce^{141}$, $Eu^{152}$ as $Na_2CrO_4$, $RuCl_3$, CsCl, $CeCl_3$ $EuCl_3$, respectively.

Amine nitrate were prepared by contacting the amine mesitylene solution with a tenfold volume of nitric acid of the desired concentration, the phase disengagement, usually very rapid, was improved by centrifugation. Freshly prepared solutions were empolyed each time to avoid ageing effect.

**Extraction procedure of metal ions:** Extractions were concluded with equal volumes of aqueous and organic phase. The organic phase containing the amine nitrate were contacted with the aqueous phase containing the tracer. The phases were agitated mechanically for 15 minutes to attain equilibrium. Phase separation was improved by centrifugation then suitable aliquots of both phases were counted using NaI(Tl) counting system. The extraction behaviour of the metal ions were compared using three sets of extraction diluent systems: Dioctylamine in mesitylene a combination of 3% Tricaprylamine and 3% Dioctylamine in mesitylene and finally a combination of 3% Tricaprylamine and 3% Dioctylamine in treated kerosene. The extraction experiments were repeated in the same manner as above, with the only exception being the addition of carriers to the system.

**Extraction and determination of uranium:** Uranium solutions previously prepared in nitric acid (1- 6M), were mixed with the same volume of the extractant, shaked mechanically for 15 minutes and the two phases were separated after centrifugation for 2 minutes. Aliquot of the aqueous phase was analysed spectrophotometrically applying dibenzoyl methane method. This method is based on the selective

extraction of uranium as teterapropylmmonium- uranyl trinitrate complex and colour developing with dibenzoylemthane. The absorbance was measured at 415 nm.

The extractability of the amines toward uranium were studied as a function of nitric acid molarities. Secondary amine (DOA) and different volume ratios of mixtures of tertiary amine (TCA) and secondary amine (DOA) were applied as extractants.

## Results

**Extraction of some of the metal ions with DOA in mesitylene:** The extraction is conducted with 6% DOA in mesitylene as diluent from nitric acid solution of molarities between 1- 6. The metal ions studied were Ce, CS, Ru and Eu. The distribution coefficient D, are listed in table (1). The effect of addition of carriers to the system was studied. A representative plot of percentage extraction against metal- Cs- concentrations is given in fig. (1).

**Extraction of some of the metal ions with 3% DOA and 3% TCA in mesitylene:** The same metal ions as above were extracted with a total of 6% of extractant (3% DOA + 3% TCA), in mesitylene. The distribution coefficients- D- and are given in table (2).

**Extraction of some of the metal ions with 3% DOA and 3% TCA in kerosene:** The above metal ions were extracted with a combination of 3% TCA and 3% DOA in kerosene. The results are in table (3).

**Extractions of Uranium with DOA:** Uranium is extracted with different volume ratios of DOA in mesitylene. The nitric acid molarities were between 1 and 6. Plots of the distribution coefficients of uranium against nitric acid molarities are given in fig. (2).

**Extraction of Uranium by varying volume ratios of TCA and DOA in Mesitylene:** Varying volume ratios of a combination of TCA and DOA in mesitylene were applied for the extraction of uranium from different nitric acid molarities. Plots of the distribution coefficients of uranium versus nitric acid molarities are shown in figure 3.

## Discussion

The results in table 1 for the extraction behaviour of Ce, Cs, Ru and Eu isotopes with dioctylamine in mesitylene show that these isotopes are being slightly extracted, distribution coefficient varies from less than 0.001 up to 0.006, thus, one might expect that DOA causes a major contamination in the extraction process. Tertiary amines and in particular tricaprylamine has a high separation factor (8) when used in a pure form with no degradation, but a previous work (6) on the stability of tertiary amines toward radiation, showed that tertiary amine undergo degradation to some extend depending on the radiation dose and presence of nitric acid. The major degradation product is the secondary amine. Many degradation mechanisms where given by many authors, in all cases secondary amine is being formed by the action of high radiation doses and nitrous acid, thus resulting in the rupture of nitrogen carbon bond.

A comparison between the extend of contamination caused by the metal ions in the extraction process using a combination of 3% TCA plus 3% DOA as extractant in two types of diluents, (1) Aromatic diluent (Mesitylene), (2) A treated kerosene fraction (160°-220°C) was investigated. It is obvious from table 2 and table 3 that the distribution coefficients of a particular metal ion is higher when kerosene is used as a diluent than when mesitylene is used as a diluent. Thus, kerosene as a diluent causes a greater contamination for the system.

The effect of metal concentration (loading) on the extraction ability of 6% DOA in mesitylene solution has been studied. It is found that the distribution coefficient and consequently the percentage extraction does not change upon the increase of a given metal concentration, in figure 1 a representative plot of Cs isotope is shown.

Plots of the distribution coefficients of uranium against nitric acid concentration- Fig. (2) and (3) show that the distribution coefficients gradually increase as nitric acid concentration increase up to a certain maximum (about 4M) then start to decrease. This is due to the presence of high concentrations of nitric acid which act as salting out agent. The decrease in the distribution coefficient beyond 5M nitric

acid could be explained on the basis of the changes that took place in the aqueous phase, i.e., to the uranium nitrate salt, in presence of different concentration of nitric acid. The following chemical equilibrium is formed:

$$UO_2^{+2} + NO_3^- \xrightarrow{K_1} UO_2NO_3^+$$

$$UO_2NO_3^+ + NO_3^- \xrightarrow{K_2} UO_2(NO_3)_2$$

$$UO_2(NO_3)_2 + NO_3^- \xrightarrow{K_3} UO_2(NO_3)_3^-$$

$$UO_2(NO_3)^-{}_3 + H^+ \xrightarrow{K_4} HUO_2(NO_3)_3$$

at higher nitric acid concentrations $HUO_2(NO_3)_3$ is formed which is inextractable by the amine, thus a decrease in the distribution coefficient (9, 10). Also in fig. (2) and (3), the percent extraction of uranium by a mixture containing mainly tertiary amine and slight quantities of secondary amine is much higher than that with pure secondary amines. In both cases, mesitylene is the diluent used. This increase in the extractability is obviously due to the change in the structure of the amine from dialkyl amine to the trialkyl amine. This imposes a change in the electronic and steric factors related to the amine molecule, but these effects are opposed to one another. One can conclude from the results in figures 2 and 3 that the electronic factor plays the important role over the steric factor.

In fig. (3) the distribution coefficients of uranium are plotted versus nitric acid molarities, three sets of amine combinations were used assuming in the first set that 5% of the extractant is degradated to the secondary amine and in the second combination 10% of the extractant is degradated, and in the last case 20% of the extractant is degradated. It is obvious from the plots that as the degradation increase, the distribution coefficient of uranium decreases which indicates that secondary amine (DOA) is a poorer extractant than tertiary amine (TCA).

Table (4) gives the separation factor of uranium/ metal ions in the system dioctylamine/ mesitylene. At nitric acid molarity equals to 5, where high extractability of uranium was observed, the separation of uranium from Ce, Cs, Ru and Eu were calculated. These values

indicate that these metal ions cause contamination during uranium extraction by dioctylamine/ mesitylene.

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**Table (1) Variation of the distribution coefficients of Ce, Cs, Ru and Eu with nitric acid concentrations in the system 6% dioctylamine/ mesitylene.**

| Nitric acid molarities | Distribution Coefficient of Ce | Distribution Coefficient of Cs | Distribution Coefficient of Ru | Distribution Coefficient of Eu |
|---|---|---|---|---|
| 1 | 0.0020 | 0.0014 | 0.0015 | 0.0010 |
| 2 | 0.0061 | 0.0015 | 0.0015 | 0.0008 |
| 3 | 0.0017 | 0.0014 | 0.0016 | 0.0010 |
| 4 | 0.0020 | 0.0015 | 0.0021 | 0.0011 |
| 5 | 0.0037 | 0.0024 | 0.0015 | 0.0013 |
| 6 | 0.0031 | 0.0015 | 0.0015 | 0.0014 |

**Table (2) Variation of the distribution coefficients of Ce, Cs, Ru and Eu with nitric acid concentrations in the system 3% dioctylamine and 3% tricaprylamine in mesitylene.**

| Nitric acid molarities | Distribution Coefficient of Ce | Distribution Coefficient of Cs | Distribution Coefficient of Ru | Distribution Coefficient of Eu |
|---|---|---|---|---|
| 1 | 0.0020 | 0.0002 | 0.0017 | 0.0027 |
| 2 | 0.0020 | 0.0009 | 0.0023 | 0.0026 |
| 3 | 0.0014 | 0.0009 | 0.0024 | 0.0023 |
| 4 | 0.0012 | 0.0012 | 0.0034 | 0.0023 |
| 5 | 0.0013 | 0.0061 | 0.0034 | 0.0017 |
| 6 | 0.0017 | 0.0010 | 0.0015 | 0.0015 |
| 7 | 0.0020 | 0.0056 | 0.0015 | 0.0014 |

**Table (3) Variation of the distribution coefficient of Ce, Cs, Ru and Eu with nitric acid concentrations in the system 3% dioctylamine and 3% tricaprylamine in kerosene.**

| Nitric acid molarities | Distribution Coefficient of Ce | Distribution Coefficient of Cs | Distribution Coefficient of Ru | Distribution Coefficient of Eu |
|---|---|---|---|---|
| 1 | 0.0022 | 0.0025 | 0.0033 | 0.0048 |
| 2 | 0.0023 | 0.0037 | 0.0039 | 0.0049 |
| 3 | 0.0021 | 0.0027 | 0.0035 | 0.0042 |
| 4 | 0.0027 | 0.0021 | 0.0058 | 0.0042 |
| 5 | 0.0021 | 0.0024 | 0.0031 | 0.0030 |
| 6 | 0.0025 | 0.0026 | 0.0021 | 0.0025 |
| 7 | 0.0030 | 0.0031 | 0.0018 | 0.0024 |

**Table (4) The separation factors of uranium from the metal ions in the system dioctylamine mesitylene at 5M nitric acid.**

| Metal ion | Distribution Coefficient at 5M nitric acid | Separation factor of U/Metal |
|---|---|---|
| U | 0.2500 | |
| Ce | 0.0037 | 67.2 |
| Cs | 0.0024 | 104.1 |
| Ru | 0.0015 | 166.6 |
| Eu | 0.0013 | 192.3 |

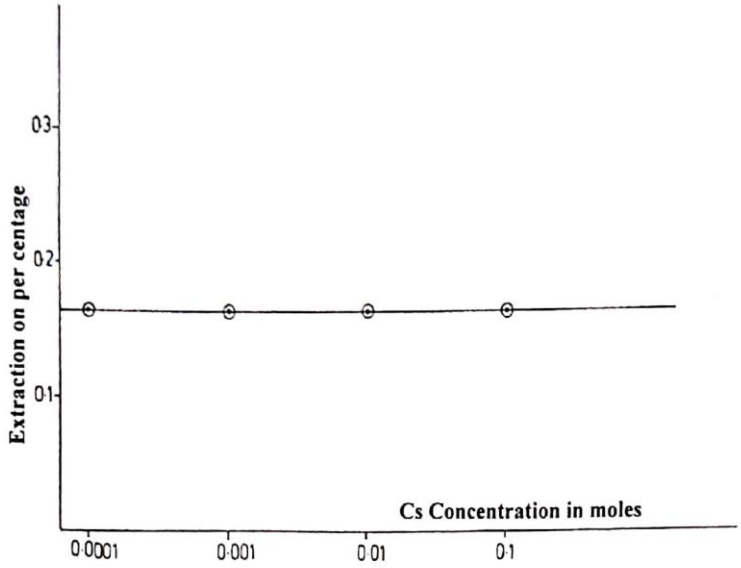


**Fig. (1) A plot of the percentage extraction of Cs against the Concentration in moles of Cs.**

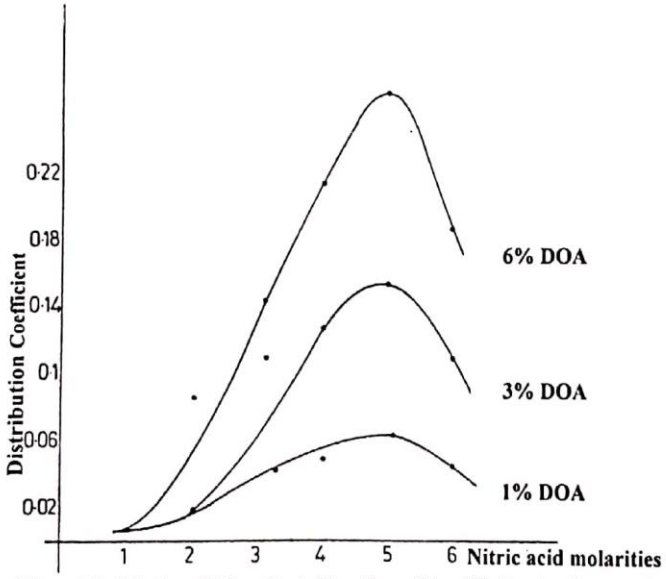


**Fig. (2) Plots of the distribution Coefficient of uranium as a function of nitric acid molarities**

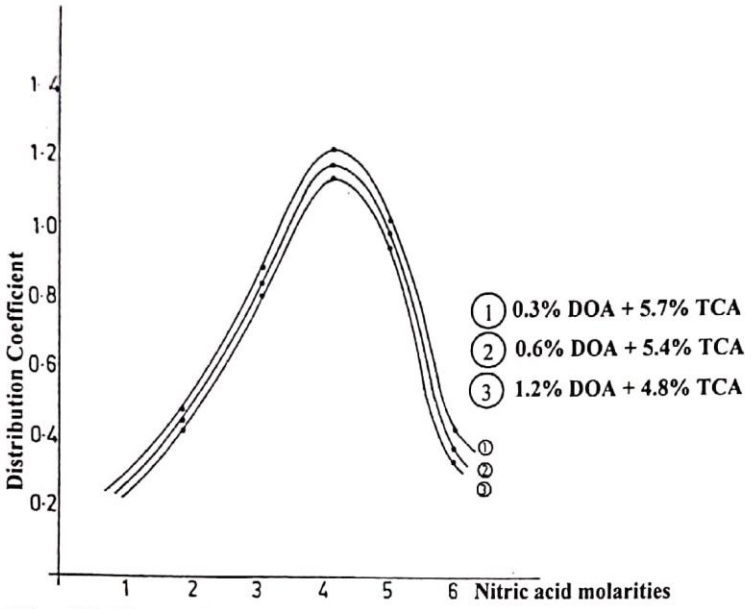


**Fig. (3) Plots of the distribution Coefficient of uranium as a function of nitric acid molarities**

مجلة ابن الهيثم للعلوم الصرفة والتطبيقية المجلد 18 (3) 2005

# التصرف الاستخلاصي لثان اوكتيل امين وخليط من ثان اوكتيل امين وثالث كابريال امين تجاه اليورانيوم وعدد من العناصر

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## الخلاصة

درس التصـــرف الاستخلاصـــي للامين الثنائي (ثان اوكتيل امين) وخليط من الامين الثنائـــي والامين الثلاثي (ثالث كابريال امين) تجاه عدد من العناصر. استعمل نوعان من المخففـــات احدهما مخفف اروماتي (المستلين) والاخر النفط المعامل، كما درست القابلية الاستخلاصـــية لـــثان اوكتيل أمين تجاه اليورانيوم. حسب معامل التوزيع ومعامل فصل اليورانيوم عن العناصر المدروسة.