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SEPARATION AND LIQUID-LIQUID EXTRACTION OF THORIUM (IV) AS SULPHATE COMPLEX WITH SYNERGISTIC MIXTURE OF N-n-OCTYLANILINE AND TRIOCTYLAMINE AS AN EXTRACTANT

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ABSTRACT

Extraction of thorium from aqueous sulphuric acid medium with a synergistic mixture of N-n-octylaniline and trioctylamine (TOA) in xylene is reported in this paper. The effects of varying the concentration of sulphuric acid, N-n-octylaniline and trioctylamine on the distribution ratio of Thorium have been studied. Based on the results obtained, the possible extraction mechanism has been discussed. The determination of thorium and its separation from synthetic mixture has been suggested. The method has been extended to the analysis of thorium in monazite sand and gas mantle.

Keywords: N-n-octylaniline, Trioctylamine (TOA), Synergistic

INTRODUCTION

Most of the extraction of thorium by liquid anion exchangers has been carried out using nitric acid media with tri-n-octylamine (TOA)[1-2], Amberlite LA-1 or LA-2 in the presence of methanol[3] or ethanol[4]. The extraction of thorium is less effective from a hydrochloric acid solution[5,6]. Thorium was extracted from malonate, ascorbate and succinate solutions by Amberlite LA-1[7], Trioctylamine[8] and Aliquat 336S[9] respectively. It was also extracted from sulphuric acid by Amberlite LA-2[10] or tributylamine[11] or N-n-octylaniline[12].

Most of this metal extraction was carried out using commercial secondary amines, tertiary amines and quaternary ammonium salts. N-n-octylaniline alone has recently been used for the extraction of several metal ions[13-15]. The present work has therefore been undertaken to obtain some information on the synergistic extraction of thorium(IV) from sulphuric acid media by using synergistic mixture of .N-n-octylaniline and Trioctylamine in xylene. Commercial tri-n-octylamine is used while N-n-octylaniline is synthesized by known method and used. A novel method is proposed for the extractive separation and determination of thorium in the presence of a large number of elements.

EXPERIMENTAL

Reagents

N-n-octylaniline : The amine was synthesized and purified by distillation[16].Tri-n-octylamine (TOA) (Spectrochem) is used.

Synergistic mixture of N-n-octylaniline and Trioctylamine solution: The solution (% v/v) was prepared by taking equal volume of each in xylene having approximate isomeric composition, o-xylene – 10%, m-xylene and p-xylene 45% each.

Thorium solution: The stock solution of thorium was prepared by dissolving a suitable amount of thorium nitrate pentahydrate in 1% nitric acid and was standardized complexometrically. Thorium solution of 2 mg/ml was prepared by appropriate dilution.

EDTA solution: 0.01M solution was prepared by dissolving 3.722 g disodium salt of EDTA in demineralised water. 0.002M EDTA was prepared by appropriate dilution. All chemicals used were of analytical reagent grade.

Procedure

To an aliquot of solution containing 2 mg of thorium, required quantity of sulphuric acid was added to make a concentration of 0.1-5 M in a volume of 10 ml. The solution was shaken and swirled with 10 ml mixture of N-n-octylaniline and trioctylamine (0.5 - 1%) having volume ratio (1:1) in xylene for 3 minutes. The two layers were allowed to separate. The organic phase was stripped with 10 ml of 0.1 M nitric acid for 3 minutes. The pH of the stripped aqueous solution was adjusted to 2 with dilute solutions of nitric acid or sodium hydroxide. Then the thorium was determined by titrating the solution against 0.002M EDTA solution using xylenol orange indicator.

RESULTS AND DISCUSSION

Effects of the concentration of synergistic mixture and sulphuric acid on Th(IV) extraction:

Thorium was extracted using varying concentrations of synergistic mixture of N-n-octylaniline and Trioctylamine (0.5 – 1.0%) and sulphuric acid (0.1-5M) (*Refer Tables 1 and 2, Figure 2*). It was observed that the quantitative extraction of thorium could be attained at the concentrations 1% of the synergistic mixture and at 1.5 M sulphuric acid. Further increase in the concentration of amine had no adverse effect.

Effect of variation in the concentration of amines in the synergistic mixture on the Th(IV) extraction:

Variation in concentration of amines in the mixture was carried out (*Refer Table 7a & 7b and Figure 3a & 3b*). It was observed that the quantitative extraction of thorium could be attained at the 1% of synergistic mixture (mixture of 0.5% N-n-octylaniline and 0.5% Trioctylamine) in xylene. Change in concentration of either of the amine, results into less extraction.

Effects of various diluents on extraction of thorium (IV):

Various solvents such as xylene, toluene, benzene, chloroform, carbon tetrachloride and nitrobenzene were used as diluents for synergistic mixture of N-n-octylaniline and Trioctylamine. It was noted that non-polar diluents were more efficient. The clear phase separation was achieved by using xylene. Thus xylene was preferred as diluent throughout the work. (*Refer Table 3*).

Enrichment study:

The extraction was quantitative when the aqueous to organic volume ratio was up to 4 : 1 and extraction of thorium (IV) was decreased beyond it (*Refer Table 5*). Extraction equilibrium was reached within 3 minutes. There was no adverse effect on the extraction of thorium by increase in extraction and stripping period.

Effect of various stripping agents:

The extraction was followed by stripping the thorium (IV) with nitric acid and hydrochloric acid. It was observed that quantitative stripping was not possible with hydrochloric acid (0.1-1M). Thorium was quantitatively stripped with 0.1-0.4M nitric acid (*Refer Table 4*). At higher concentrations of nitric acid stripping was incomplete probably due to formation of an anionic nitrate complex of thorium.

Precision and accuracy:

The average of 10 determinations of thorium was 1.99 mg for the samples containing 2 mg of Th(IV), with standard deviation of 0.014 and variance of 0.0002. Variation from the mean at 95 % confidence limit was 1.99 ± 0.01.

Nature of extracted species:

The investigation of the ion association complex of thorium, sulphuric acid and synergistic mixture of N-n-octylaniline and trioctylamine was carried out from the plots of log D vs. log [N-n-octylaniline and trioctylamine] (*Figure 1*). The slopes obtained at 0.1M and 4.0M of sulphuric acid are 1.8 and 2.0 respectively indicating that metal to amine ratio in the extracted species is 1:2. Hence, the extracted species would be probably $[mRR'NH^{+}_{2}.Th(SO_4)_3^{2-}.nR''_3NH^{+}]$, as also reported in the literature.

The probable extraction mechanism is as follows:

$Th^{4+} + 3SO_4^{2-} \leftrightarrows [Th(SO_4)_3]^{2-}$

$mRR'\text{-}NH + nR''_3N + [Th(SO_4)_3]^{2-} \leftrightarrows mRR'NH^+_2 . Th(SO_4)_3^{2-} n R''_3NH^+$

Where $R = C_6H_5$ and $R' = R'' = C_8H_{17}$

Effect of foreign ions:

The solutions containing 2 mg of thorium(IV) (in final solution) and varying amounts of diverse ions were prepared and the content of thorium was determined after extraction. The following ions present/in mg/did not cause any interference: thiourea, acetate, ascorbate, citrate, tartarate, succinate/100/, Mg(II)/30/, Zn(II)/30/, Cd(II)/20/, Mn(II)/10/, Ni(II)/30/, Cu(II)/30/. Among the anions tested, phosphate, oxalate and thiocyanate interfered seriously with the extraction and determination. The cations Sn(II), Co(II), Zr(IV), Cr(III) and Fe(III) also interfered in the extraction and determination. However, the interference can be removed by masking. Sn(II) and Co(II) were masked with citrate/200/, Zr(IV) with tartarate/100/, Fe(III) with thiourea/100/ and Cr(III) with acetate/100/ . (*Refer Table 6*)

Applications:

The separation and estimation of thorium from monazite sand, gas mantles and synthetic mixtures was successfully carried out using the developed method. The results obtained indicate that the method is suitable for the extractive separation and estimation of thorium.

Thorium in synthetic mixtures:

Synthetic mixtures containing thorium along with various elements were prepared. The proposed method was applied to the extraction and separation of thorium from the mixtures. Thorium (IV) and uranium (VI) both from anionic sulphato complexes were extracted. Thorium was separated from uranium by selective stripping. Uranium was stripped with 0.5 M sodium hydroxide followed by stripping of thorium by 0.1M nitric acid.

Thorium was separated from the mixture of thorium, cerium and magnesium by selective extraction and stripping. Magnesium was not extracted. Thorium was stripped with 0.5M nitric acid. Thorium was also separated from the mixture of thorium, uranium and zirconium by selective stripping. Uranium was stripped with 1 M sodium hydroxide followed by stripping of thorium by 0.25 M nitric acid, while zirconium remained in the organic phase.

Similarly, from the mixture of thorium, titanium and mercury, thorium was separated by selective extraction and stripping. Mercury and titanium were not extracted whereas thorium was stripped with 0.5M nitric acid. From the mixtures of thorium, zirconium, bismuth and thorium, vanadium, thallium, thorium was selectively stripped with 0.25M and 0.5M nitric acid respectively.

Analysis of thorium in monazite sand:

2 g of monazite sand was digested for 2 hours with 50 ml of concentrated sulphuric acid. The solution was diluted to 250 ml with 0.1M hydrochloric acid, 2 g of ascorbic acid was added to the former solution. This aqueous phase was equilibrated with the organic phase following the general procedure. Cerium was incompletely extracted whereas iron(II) and calcium were not extracted. The interference of aluminum was removed by masking with 50 mg of acetate. Thorium was stripped with 0.1 M nitric acid, leaving cerium in the organic phase. Thorium was determined complexometrically. The amount of thorium obtained was 7.51% against the standard value of 7.56%.

Separation of thorium from gas mantles:

1 g of gas mantle of commercial grade was digested with 20 ml of concentrated sulphuric acid (A.R.) for about 4 hours. The mixture was extracted with 0.1 M hydrochloric acid and diluted to 100 ml. An aliquot of solution was extracted as usual with synergistic mixture of N-n-octylaniline and trioctylamine. Magnesium was not extracted. Cerium and beryllium, which were not stripped with 25 ml of 0.1M nitric acid and thorium was determined by general method. The content of thorium was 23.72% against a standard value of 24%.

CONCLUSION

The synergism is more quantitative at lower concentration of N-n-octylaniline and Trioctylamine in comparison with the extractions using single extractant. The synergistic extractant N-n-octylaniline and Trioctylamine can be used for extraction and estimation of thorium from sulphate media with acidic pH value. The mixture of these extractant produces a synergistic effect with respect to each extractant individually.

Table-1: Effect of different concentration of synergistic mixture of N-n-octylaniline and Trioctylamine on Th (IV) distribution ratio (at 1.5M H_2SO_4)

N-n-octylaniline and Trioctylamine (%)	Extraction %	Distribution Ratio (D)
0.5	60.87	1.5556
0.75	81.40	4.3763
1.0	99.80	499

Table-2: Effect of different concentration of sulphuric acid on Th (IV) distribution ratio (at 1.0 % synergistic mixture of N-n-octylaniline and Trioctylamine in xylene)

Sulphuric Acid (M)	Extraction %	Distribution Ratio (D)
0.1	19.57	0.2433
0.5	39.13	0.6428
1.0	82.61	4.7504
1.1	93.48	14.3374
1.3	99.80	499
1.5	99.80	499
1.7	99.80	499
2.0	97.83	45.0829
2.5	95.65	21.9885
3.0	91.30	10.4942
3.5	84.78	5.5703
4.0	63.04	1.7056
4.5	41.30	0.7035
5.0	23.91	0.3142

Table - 3: Effects of various diluents on extraction of thorium (IV)

Diluent's	Extraction %	Distribution Ratio (D)
Xylene	99.80	499
Chloroform	95.65	21.9885
Toluene	97.83	45.0829
Carbon tetrachloride	99.07	106.5269
Nitrobenzene	51.16	1.0475
Benzene	99.80	499

Table - 4: Effect of different stripping agent on stripping of Th (IV)

Stripping Agent	Stripping %									
	0.1M	0.2M	0.3M	0.4M	0.5M	0.6M	0.7M	0.8M	0.9M	1.0M
Hydrochloric acid	83.72	86.05	88.37	88.37	90.70	90.70	93.02	90.70	86.05	76.74
Nitric acid	99.80	99.80	99.80	99.80	97.67	95.35	90.70	81.39	--	--

Table - 5: Enrichment study

Aqueous to Organic phase	% Extraction
1:1	99.80
2:1	99.80
3:1	99.80
4:1	99.80
5:1	93.02
6:1	88.37
10:1	69.77

Table - 6: Effect of diverse ions

Diverse ions	Added as	Tolerance Limit, mg
Mn (II)	$MnSO_4.7H_2O$	10
Mg (II)	$MgSO_4.7H_2O$	30
Zn (II)	$ZnSO_4.7H_2O$	30
Ni (II)	$NiSO_4$	30
Cd (II)	$CdCl_2$	20
Cu (II)	$CuSO_4$	30
Bi (III)	$BiCl_3$	15
Sn (II)	$SnCl_2.2H_2O$	10
Co (II)	$Co(NO_3)_2.6H_2O$	10
Zr (IV)	$ZrO(NO_3)_2.H_2O$	10
Fe (III)	$FeCl_3.6H_2O$	10
Cr (III)	$CrCl_3.6H_2O$	10
Thiourea	Thiourea	100
Acetate	Sodium acetate	100
Ascorbate	Ascorbic acid	100
Citrate	Citric acid	100
Tartarate	Tartaric acid	100
Oxalate	Oxalic acid	None
Succinate	Sodium succinate	100
Thiocyanate	KSCN	None
Phosphate	Dissodium hydrogen Phosphate	None

Table – 7a: Effect of variation in the concentration of amines in the synergistic mixture on the Th(IV) extraction (Concentration of N-n-octylaniline – 0.5%)

TOA (%)	% Extraction
0.1	67.39
0.2	76.09
0.3	84.78
0.4	93.48
0.5	99.80
0.7	89.13
1.0	76.09

Table – 7b: Effect of variation in the concentration of amines in the synergistic mixture on the Th(IV) extraction (Concentration of Trioctylamine – 0.5%)

N-n-octylaniline (%)	% Extraction
0.1	63.04
0.2	73.91
0.3	86.96
0.4	95.65
0.5	99.80
0.7	93.48
1.0	84.78

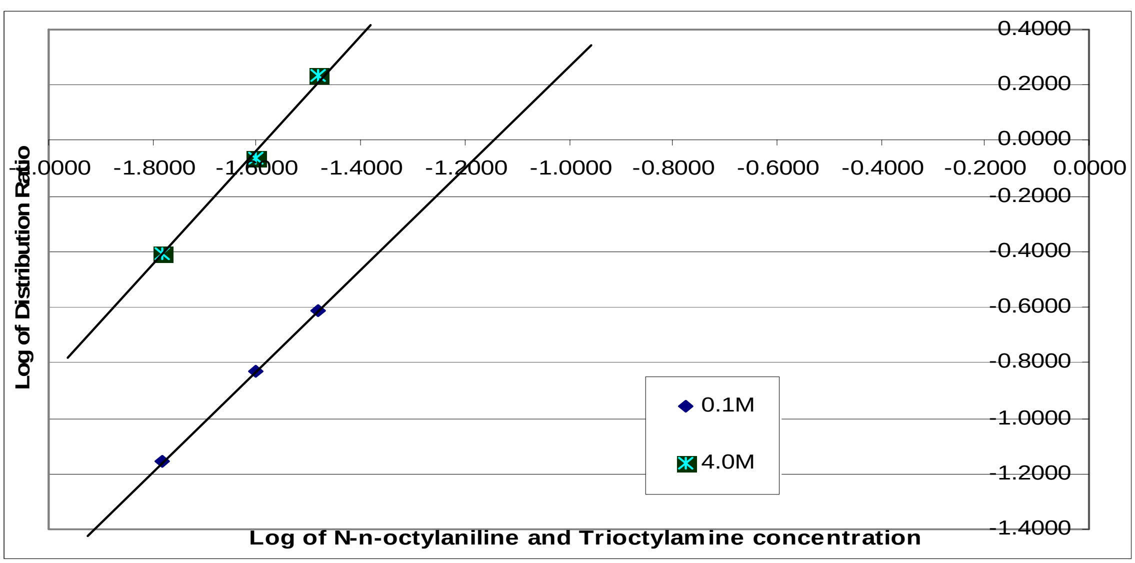

Fig.-1: Distribution Ratio of Thorium (IV) as function of synergistic mixture of N-n-octylaniline and Trioctylamine concentration at 0.1 and 4.0M sulphuric acid concentration.

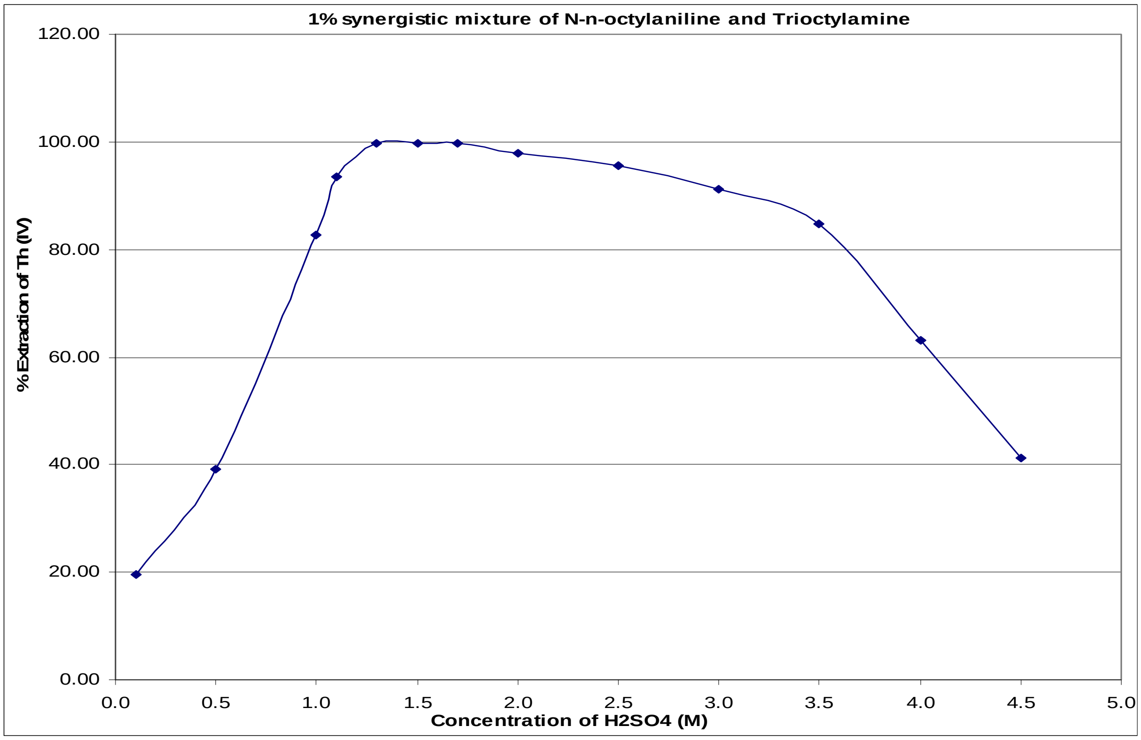

Fig.-2: Extraction behavior of Thorium (IV) as a function of concentration of sulphuric acid with 1% synergistic mixture of N-n-octylaniline and Trioctylamine.

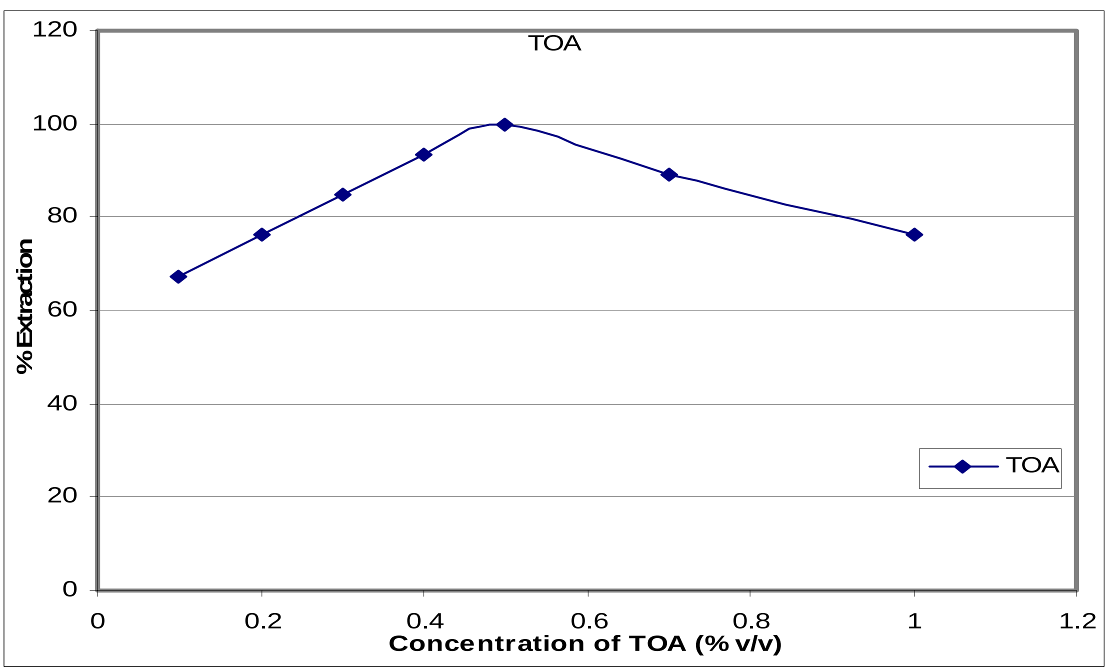

Fig.-3a: Extraction behavior of Thorium (IV) at fixed concentration of N-n-octylaniline (0.5%), by varying the concentration of Trioctylamine (TOA).

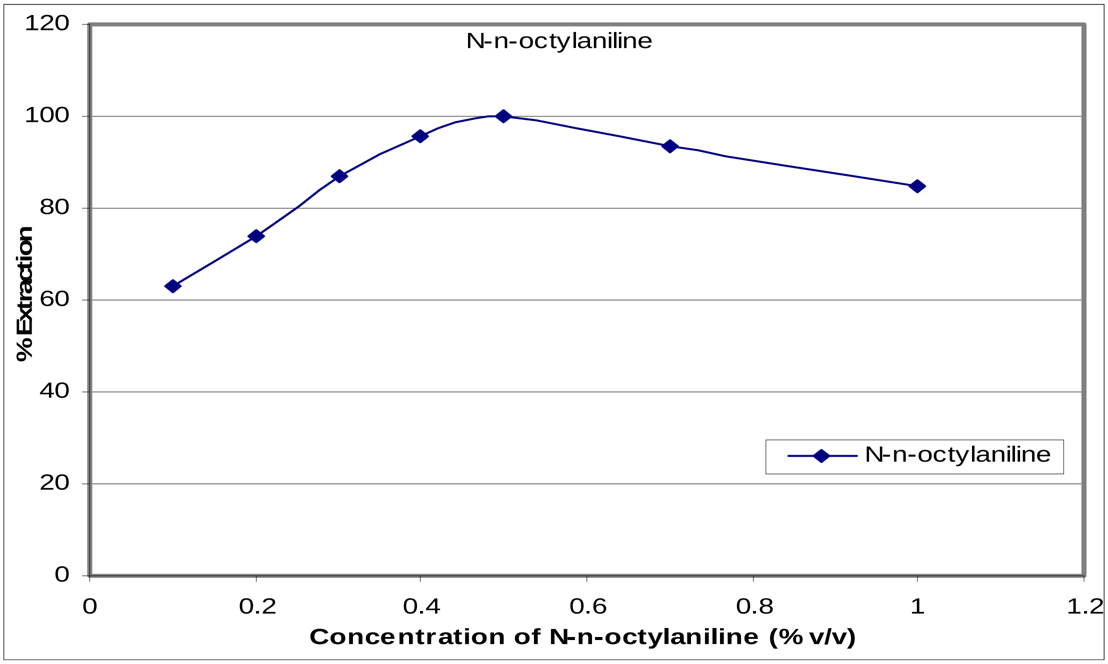

Fig.-3b: Extraction behavior of Thorium (IV) at fixed concentration of Trioctylamine (TOA) (0.5%), by varying the concentration of N-n-octylaniline.

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