Research Article

# Liquid-Liquid Extraction and Separation of Bismuth (Iii) with Synergistic Mixture of N-N-Octylaniline and Trioctylamine as an Extractant From Thiocyanate Media

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**ABSTRACT**

The described procedure is for the liquid-liquid extraction of Bi (III) from thiocyanate and sulphuric acid medium using a synergistic mixture of N,n-octylaniline and trioctylamine in the xylene. The quantitative extraction of Bi (III) occurs from 0.3M to 0.5M thiocyanate and minimum 2.5M sulphuric acid using 1% of each N,n-octylaniline and trioctylamine in xylene. The extracted metal ion has been recovered by stripping with 25ml acetate buffer. The log-log plot of distribution ratio versus concentration of mixture of N,n-octylaniline and trioctylamine at 0.2M, 0.25M and 2.0M thiocyanate gave the slopes of 1.80, 2.08 and 2.34 respectively, indicating that the metal to amine ratio in extracted species is 1:2. Hence the probable extracted species is $[(RR^7NH_2^+)_2\ Bi(SCN)_5^{2-}]$ or $[(R_3NH^+)_2\ Bi(SCN)_5^{2-}]$.

In xylene and benzene, the ion pair complex has a high distribution ratio, while other polar solvents are poor. The extractants are stable towards prolonged acid and thiocyanate contacts and there is no loss in their extraction efficiencies. The extraction behavior of some commonly associated metal ions namely Th(IV), Ce(IV), Hg(II), Cr(III), Zr(IV), Fe(III), Co(II) has also been investigated. Based on partition data, conditions have been identified and used for the separation of Bi(III) from other metal ion. This method is extended for the extraction of Bi(III) from alloys, pharmaceutical sample and ceramic material.

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

## INTRODUCTION

Bismuth is mostly used in bismuth alloys, pharmaceuticals and chemicals. Bismuth metal is relatively inert, non toxic, soft and malleable. It has replaced toxic lead in many applications such as plumbing, bullets, metal alloys, soldering, etc. Bismuth is used in medicines for the treatment of stomach ulcers, soothing creams and cosmetics. Bismuth is also used as catalyst in the production of acrylic fibres. Most of the extraction of bismuth is carried out by using high molecular weight amines. N-n-octylaniline [1,2] and Aliquat-336-S [3,4] have been used for the extraction and separation of Bismuth (III) from acidic media. The organophosphorous extractants like triphenylphosphine oxide [5] tris(2- ethylhexyl) phosphate [6], bis(2,4,4-trimethylpentyl) phosphino –dithioc acid (Cyanex 301) [7], bis(2,4,4-trimethylpentyl) monothioc phosphinic acid (Cyanex 302) [8] are used for extraction of bismuth(III). Methyl isobutyl ketone (MIBK) is used as an extractant for bismuth iodide complex and then analysed by atomic absorption spectroscopy [9]. The extraction of bismuth (III) by N,N,N',N'-tetraacetyl-3-oxapentane diamide from nitric acid to n-dodecane has been reported [10]. Extraction of bismuth(III) was done using 2-bromo alkanoic acid. The precipitation of hydroxide is avoided by using highly acidic solution [11]. The present work has therefore been undertaken to obtain some information on the synergistic extraction of bismuth (III) from thiocyanate and sulphuric acid media using synergistic mixture of N-n-octylaniline and trioctylamine in xylene. Commercial trioctylamine 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 bismuth in the presence of a large number of elements.

## Materials and Methods

### Reagents

N-n-octylaniline : The amine was synthesized and purified by distillation [12]. Trioctylamine (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.

Bismuth solution: The stock solution of bismuth was prepared by dissolving a suitable amount of bismuth nitrate pentahydrate in 5ml of concentrated nitric acid and diluting it to 100ml with demineralised water. The solution was standardized complexometrically. It contained 5mg bismuth per ml. The bismuth solution of 2mg/ml was prepared by appropriate dilution.

Thorium solution: A 0.01 M solution was prepared by using thorium nitrate pentahydrate.

Acetate Buffer solution: A solution was prepared by dissolving 27.2gm of sodium acetate trihydrate in 400ml dimineralised water, adding 17ml of glacial acetic acid and diluting it to one litre.

EDTA solution: 0.01M solution was prepared by dissolving 3.722 g disodium salt of EDTA in 1000ml 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 bismuth, required quantity of sulphuric acid and potassium thiocyanate solution was added to make the concentration of 0.1M – 7.0M and 0.1M – 3.0M respectively in a volume of 10 ml. The solution was shaken and swirled in a 125ml separating funnel with 10 ml mixture of N-n-octylaniline and trioctylamine (0.5 - 2%) having volume ratio (1:1) in xylene for 3 minutes. The two layers were allowed to separate. The organic phase was stripped twice with 25 ml of acetate buffer for 3 minutes. The amount of bismuth in stripped solution was determined complexometrically [13], by adding excess of 0.002M EDTA and back titrating against 0.002M thorium nitrate using xylenol orange indicator. The endpoint is yellow to red.

## Results and discussion

### Effects of the concentration of synergistic mixture and sulphuric acid on Bi (III) extraction.

Bismuth was extracted using varying concentrations of synergistic mixture of N-n-octylaniline and Trioctylamine (0.5 – 2.0%), sulphuric acid (0.1-7M) and potassium thiocyanate (0.1 – 3.0M) (*Refer Tables 1, 2 and 3, Figure 2 and 3*). It was observed that the quantitative extraction of bismuth could be attained at the concentrations 2% of the synergistic mixture and at 2.5M sulphuric acid and 0.4M potassium thiocyanate. 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 Bi (III) extraction

Variation in concentration of amines in the mixture was carried out (*Refer Table 4 & 5 and Figure 4a & 4b*). It was observed that the quantitative extraction of bismuth could be attained at the 2% of synergistic mixture (mixture of 1.0% N-n-octylaniline and 1.0% Trioctylamine) in xylene. Increase in concentration of either of the amine, results into constant extraction.

### Effects of various diluents on extraction of bismuth (III)

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 6*).

**Enrichment study**

The extraction was quantitative when the aqueous to organic volume ratio was up to 4 : 1 and extraction of bismuth (III) was decreased beyond it (*Refer Table 7*). Extraction equilibrium was reached within 3 minutes. There was no adverse effect on the extraction of bismuth by increase in extraction and stripping period.

**Nature of extracted species**

The investigation of the ion association complex of bismuth, thiocyanate, 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 0.2M, 0.25M and 2.0M of potassium thiocyanate are 1.80, 2.08 and 2.34 respectively indicating that metal to amine ratio in the extracted species is 1:2. Hence, the extracted species would be probably $[(RR'NH_2^+)_2\ Bi(SCN)_5^{2-}]$ or $[(R_3NH_2)_2^+\ Bi(SCN)_5^{2-}]$

**The probable extraction mechanism is as follows:**

$$Bi(SCN)_3 + 2SCN^- \leftrightarrows Bi(SCN)_5^{2-} \quad \text{----------(1)}$$

$$[RR' NH]_{org} + HSCN \leftrightarrows [RR'NH_2^+ (SCN)^-]_{org} \quad \text{----------(2)}$$

$$[R3\ N]_{org} + HSCN \leftrightarrows [R_3NH^+ (SCN)^-]_{org} \quad \text{----------(3)}$$

$$2[RR'NH_2^+ (SCN)^-]_{org} + Bi(SCN)_5^{2-} \leftrightarrows [(RR'NH_2^+)_2\ Bi(SCN)_5^{2-}] + SCN^- \quad \text{----------(4)}$$

$$2[R_3NH^+ (SCN)^-]_{org} + Bi(SCN)_5^{2-} \leftrightarrows [(R_3NH_2)_2^+\ Bi(SCN)_5^{2-}] + SCN^- \quad \text{----------(5)}$$

**Effect of foreign ions**

The solutions containing 2 mg of bismuth (III) (in final solution) and varying amounts of diverse ions were prepared and the content of bismuth was determined after extraction. The following ions present/in mg/did not cause any interference: acetate, ascorbate, tartarate, succinate/200/, oxalate/150/, phosphate/50/, citrate, thiourea/25/, Mg(II)/40/, Mn(II)/30/, Cr(III)/30/, Hg(II)/25/, Ni(II)/10/, Ce(II)/10/, Th(IV)/10/, Zr(IV)/10/, Cd(II)/5/, Cu(II)/5/, Fe(III)/5/. Among the cations tested, Co(II) and Zn(II) interfere seriously with the extraction and determination. However, the interference can be removed by masking. Fe(III), Ni(II) and Ce(II) were masked with citrate/100, Cd(II) was masked with thiourea/100/, Cu(II) with ascorbate/200/, thorium(IV) with oxalate/100/. (*Refer Table 8*)

**Applications**

The separation and estimation of bismuth from pharmaceutical product, metal alloys 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 bismuth.

***Bismuth in synthetic mixtures***

Synthetic mixtures containing bismuth along with various elements were prepared. The proposed method was applied to the extraction and separation of bismuth from the mixtures. The results of analysis showed that Bi(III) could be separated and determined from synthetic multi-component mixtures.

***Analysis of bismuth in pharmaceutical product***

A tablet was dissolved in perchloric acid containing small amount of nitric acid. This is subjected to evaporation to dryness. The small amount of perchloric acid is added and evaporated to dryness. The residue obtained was leached with distilled water and diluted to 100ml with distilled water. An aliquat was taken for

extraction and estimation of bismuth was carried out by recommended procedure. The average of five results is reported.

***Separation of bismuth from metal alloys***

Bismuth is separated and determined from the alloys like wood's metal and white metal by the proposed method. 0.5 gm of alloy was dissolved in concentrated nitric acid. The solution obtained was filtered to remove metastanic acid from wood's metal and antimonic acids from white metal. The excess of acids from filtrate were evaporated to dryness. The solid obtained was leached with 0.2N hydrochloric acid and diluted to 100ml with distilled water. An aliquat of sample was extracted and estimated for bismuth using the proposed method. Elements such as copper, cadmium and nickel are interferred which was masked with ascorbate, thiourea and citrate respectively. Bismuth in organic phase was stripped with 0.1M nitric acid and determined as in the proposed method. The result of analysis was reported.

## 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 bismuth from thiocyanate media. The best synergism is observed when equal concentrations of both amines are used.

**Table 1: Effect of different concentration of synergistic mixture of N-n-octylaniline and Trioctylamine on Bi (III) distribution ratio (at 3.0M H2SO4 and 0.4M KSCN)**

| N-n-octylaniline and Trioctylamine (%) | Extraction % | Distribution Ratio (D |
|---|---|---|
| 1.07 | 9.55 | 3.89 |
| 1.58 | 7.50 | 7.00 |
| 2.09 | 9.80 | 499 |

**Table 2: Effect of different concentration of potassium thiocyanate on distribution of Bi (III) (at 2.0 % synergistic mixture of N-n-octylaniline and Trioctylamine in xylene) keeping 3M Sulphuric acid constant**

| KSCN (M) | Extraction % | Distribution Ratio (D) |
|---|---|---|
| 0.10 | 26.09 | 0.3530 |
| 0.15 | 69.57 | 2.2862 |
| 0.20 | 93.48 | 14.3374 |
| 0.25 | 97.83 | 45.0829 |
| 0.30 | 99.80 | 499 |
| 0.35 | 99.80 | 499 |
| 0.40 | 99.80 | 499 |
| 0.45 | 99.80 | 499 |
| 0.50 | 99.80 | 499 |
| 1.00 | 97.83 | 45.0829 |
| 1.50 | 71.74 | 2.5386 |
| 2.00 | 47.83 | 0.9168 |
| 2.50 | 32.61 | 0.4839 |
| 3.00 | 17.39 | 0.2105 |

**Table 3: Effect of different concentration of sulphuric acid on distribution of Bi (III) (at 2.0 % synergistic mixture of N-n-octylaniline and Trioctylamine in xylene) keeping 0.4M potassium thiocyanate constant**

| $H_2SO_4$ (M) | Extraction % | Distribution Ratio (D) |
|---|---|---|
| 0.10 | 89.13 | 8.1996 |
| 0.50 | 91.30 | 10.4943 |
| 1.00 | 93.48 | 14.3374 |
| 1.50 | 95.65 | 21.9885 |
| 2.00 | 97.83 | 45.0829 |
| 2.50 | 99.80 | 499 |
| 3.00 | 99.80 | 499 |
| 3.50 | 99.80 | 499 |
| 4.00 | 99.80 | 499 |
| 5.00 | 99.80 | 499 |
| 5.50 | 99.80 | 499 |
| 6.00 | 99.80 | 499 |
| 7.00 | 99.80 | 499 |

**Table 4: Effect of variation in the concentration of amines in the synergistic mixture on the Bi(III) extraction (Concentration of N-n-octylaniline kept constant = 1.0%)**

| Trioctylamine (%) | % Extraction |
|---|---|
| 0.1 | 83.33 |
| 0.2 | 85.42 |
| 0.3 | 87.50 |
| 0.4 | 89.58 |
| 0.5 | 91.67 |
| 0.6 | 93.75 |
| 0.7 | 95.83 |
| 0.8 | 97.92 |
| 0.9 | 99.80 |
| 1.0 | 99.80 |
| 1.1 | 99.80 |
| 1.2 | 99.80 |
| 1.3 | 99.80 |
| 1.4 | 99.80 |
| 1.5 | 99.80 |
| 1.6 | 99.80 |
| 1.7 | 99.80 |
| 1.8 | 99.80 |
| 1.9 | 99.80 |
| 2.0 | 99.80 |

**Table 5: Effect of variation in the concentration of amines in the synergistic mixture on the Bi(III) extraction (Concentration of Trioctylamine kept constant = 1.0%)**

| N-n-octylaniline (%) | % Extraction |
|---|---|
| 0.1 | 81.25 |
| 0.2 | 83.33 |
| 0.3 | 85.42 |
| 0.4 | 87.50 |
| 0.5 | 89.58 |
| 0.6 | 91.67 |
| 0.7 | 93.75 |
| 0.8 | 95.83 |
| 0.9 | 97.92 |
| 1.0 | 99.80 |
| 1.1 | 99.80 |
| 1.2 | 99.80 |
| 1.3 | 99.80 |
| 1.4 | 99.80 |
| 1.5 | 99.80 |
| 1.6 | 99.80 |
| 1.7 | 99.80 |
| 1.8 | 99.80 |
| 1.9 | 99.80 |
| 2.0 | 99.80 |

**Table 6: Effects of various diluents on extraction of bismuth (III)**

| Diluent's | Extraction % | Distribution Ratio (D) |
|---|---|---|
| Xylene | 99.80 | 499 |
| Toluene | 99.80 | 499 |
| Benzene | 99.80 | 499 |
| Carbon--tetra chloride | 99.15 | 116.6471 |
| Nitrobenzene | 98.72 | 77.125 |
| Chloroform | 71.06 | 2.4554 |

**Table 7: Enrichment study**

| Aqueous to Organic phase | % Extraction |
|---|---|
| 1:1 | 99.80 |
| 2:1 | 97.96 |
| 3:1 | 95.92 |
| 4:1 | 93.88 |
| 5:1 | 87.76 |
| 10:1 | 71.43 |

**Table 8: Effect of diverse ions**

| Diverse ions | Added as | Tolerance Limit, mg |
|---|---|---|
| Mn (II) | $MnSO_4.7H_2O$ | 30 |
| Mg (II) | $MgSO_4.7H_2O$ | 40 |
| Zn (II) | $ZnSO_4.7H_2O$ | Interference |
| Ni (II) | $NiSO_4$ | 10 |
| Cd (II) | $CdCl_2$ | 5 |
| Cu (II) | $CuSO_4$ | 5 |
| Co (II) | $Co(NO_3)_2.6H_2O$ | Interference |
| Zr (IV) | $ZrO(NO_3)_2.H_2O$ | 10 |
| Fe (III) | $FeCl_3.6H_2O$ | 5 |
| Cr (III) | $CrCl_3.6H_2O$ | 30 |
| Hg (II) | $HgCl_2$ | 25 |
| Ce (IV) | $2(NH_4)_2SO_4.Ce(SO_4)_2.2H_4O$ | 10 |
| Th (IV) | $Th(NO_3)_4.5H_2O$ | 10 |
| Acetate | Sodium acetate | 200 |
| Ascorbate | Ascorbic acid | 200 |
| Citrate | Citric acid | 25 |
| Oxalate | Oxalic acid | 150 |
| Phosphate | Dissodium hydrogen phosphate | 50 |
| Succinate | Sodium succinate | 200 |
| Tartarate | Tartaric acid | 200 |
| Thiourea | Thiourea | 25 |

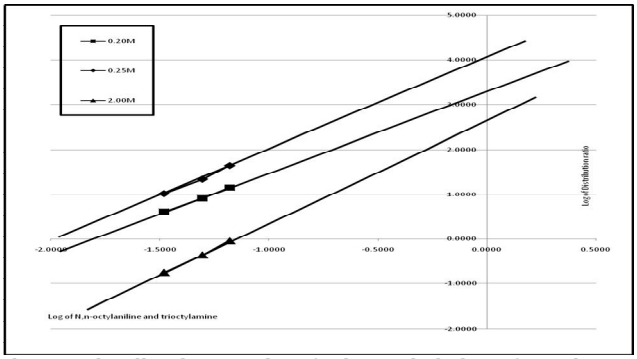


**Fig. 1: Distribution Ratio of Bismuth (III) as function of synergistic mixture of N-n-octylaniline and Trioctylamine concentration at 0.2M, 0.25 and 2.0M potassium thiocyanate concentration**

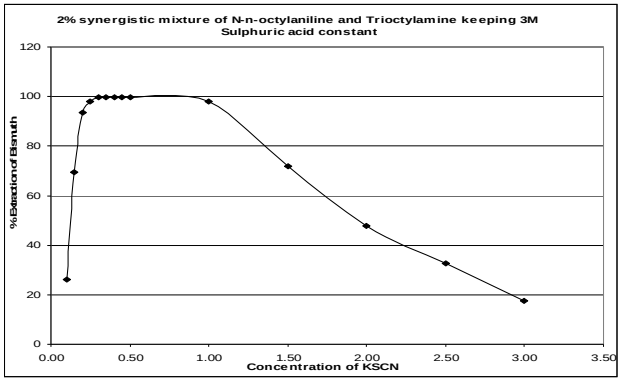


**Fig. 2: Extraction behavior of Bismuth (III) with 2% synergistic mixture of N-n-octylaniline and Trioctylamine concentration at 0.1 to 3.0M potassium thiocyanate and 3M sulphuric acid concentration.**

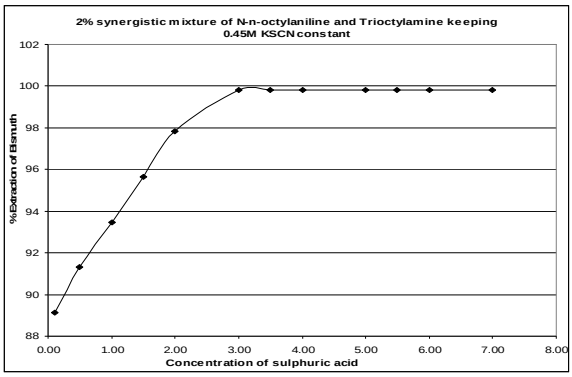


**Fig. 3: Extraction behavior of Bismuth (III) with synergistic mixture of N-n-octylaniline and Trioctylamine concentration at 0.1 to 7.0sulphuricacid and 0.4M potassium thiocyanate concentration.**

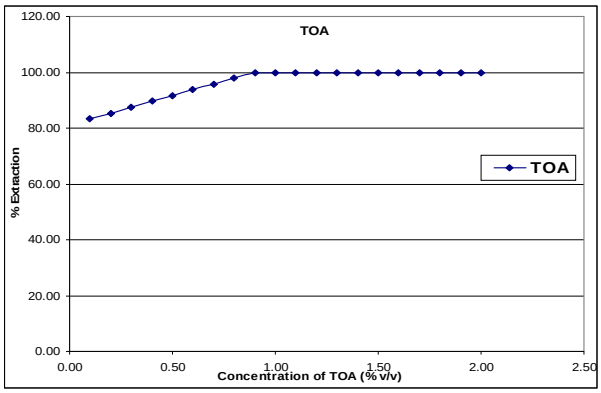


**Fig. 4a: Extraction behavior of Bismuth (III) at fixed concentration of N,n-octylaniline (1.0%), by varying the concentration of Trioctylamine (TOA).**

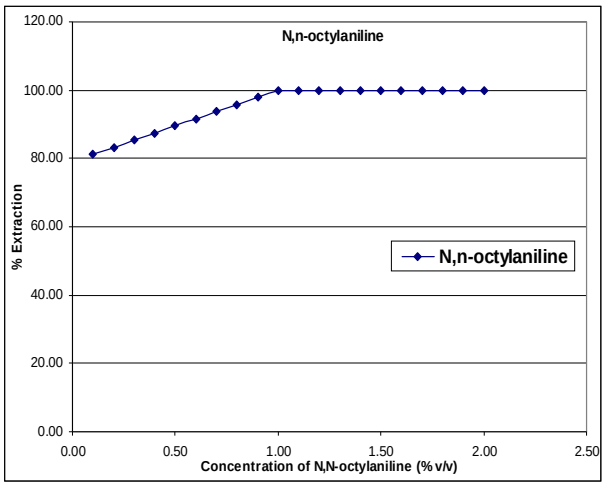


**Fig. 4b: Extraction behavior of Bismuth (III) at fixed concentration of Trioctylamine (TOA) (1.0%), by varying the concentration of N-n-octylaniline.**

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