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A study of the extraction behavior of thallium with tribenzylamine as the extractant

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Abstract

A simple solvent extraction study for thallium has been conducted based on the extraction of thallium as a chlorocomplex (tetrachlorothallate (III) anion) with tribenzylamine. Radiolabelled Tl (III) was used to study the extraction behavior of thallium. The beta activity of the extracted ion-association complex has been monitored using liquid scintillation counting and Geiger Muller counter. The effect of various diluents such as toluene, chloroform and isobutylmethylketone (MIBK) were studied. The extraction efficiency was 95% when chloroform and MIBK were used as diluents for tribenzylamine at an overall concentration of 0.25 mol dm^{-3} NaCl and 0.5 mol dm^{-3} H_2SO_4. The phenomenon of severe chemical quenching was observed with chloroform as the diluent. The recovery of thallium was found to be 95% at varying concentrations ranging from 5 to 20 $\mu g\,ml^{-1}$ Tl (III) with a relative standard deviation of 2.5%.

Keywords: Thallium; Solvent extraction; Chlorocomplex; Tribenzylamine; Liquid scintillation counting

1. Introduction

Thallium is a trace element that occurs mostly in sulfur containing ores [1]. The common oxidation states of thallium are +1 and +3, respectively. Thallium is a highly toxic element and Tl (I) is known to replace potassium ions in the activation of enzymes [2]. The contamination of the environment with thallium results mainly from nonferrous mines, coal combustion and cement plants [3]. Solvent extraction is used in chemical industries to purify chemical elements, in environmental waste management and in the nuclear industry for the reprocessing of spent nuclear fuels [4]. High molecular weight amines such as trioctylamine [5], *N*-benzyl aniline [6] and *n*-octyl aniline [7] have been used for the extraction of thallium. In equilibrium with acidic solutions the amine is first protonated and in this form it acts as an anion exchanger.

$$2R_3N : + H_2SO_4 \rightleftharpoons (R_3N^+H)_2SO_4^{2-}$$

The protonated amine can be extracted as an ion-association complex with the metal ion into an immiscible solvent. The solvent extraction of Tl (III) has been studied using hexa-acetylcalix (6) arene using toluene as the diluent [8]. The extracted thallium could be stripped using HCl or HNO_3. Shilimkar et.al. [9] have studied the extraction of Tl (III) using *n*-octylaniline from salicylate medium. An equilibration time of 20 min was required for quantitative extraction. The extractive separation of Tl (I) and Tl (III) has been carried out using thioxine and PAN in chloroform [10]. The extraction of thallium (III) as its tetrachlorocomplex into 2-propanol has been studied [11]. Tl (III) could be separated from a mixture of In (III), Bi (III) and Sb (III) using this method.

The sequential separation of Ga (III), In (III) and Tl (III) using cyanex-923 has been reported using toluene as the diluent [12]. A survey of the literature revealed that tribenzylamine has not been explored to study the extraction behavior of thallium. Tribenzylamine has been used for the sequential separation of zinc, cadmium and mercury [13]. The extraction of Sn (II) complex with ferroin using tribenzylamine as extractant has been reported [14]. The use of tribenzylamine and other long chain amines for the extraction of various metal ions has been reviewed in detail [4]. Since, literature reports on the extraction study of thallium using tribenzylamine are scarce, it was felt worthwhile to explore

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the capability of this reagent to study the extraction behavior of thallium in presence of various diluents such as MIBK, toluene and chloroform.

2. Experimental

2.1. Instrumentation

A Packard TriCarb 1500 Liquid Scintillation Analyzer and a Geiger Muller Counter was used for activity measurements.

2.2. Reagents and solutions

All reagents were of Analar Grade. Triple distilled and deionized water was used for the preparation of solutions. The Tl-204 tracer of specific activity 6.66×10^{10} Bq/g was procured from the Isotope Division, Bhabha Atomic Research Centre (BARC), Mumbai, India. A standard 1000 μg ml^{-1} Tl (I) solution was prepared by dissolving 1.303 g of thallium (I) nitrate in concentrated nitric acid and diluting it to 1 l with distilled water.

A 10 ml volume of 1000 μg ml^{-1} Tl (I) solution was mixed with approximately 6 MBq of Tl-204 tracer and oxidized with bromine water, the excess of which was destroyed by careful boiling. The solution was diluted to 100 ml with distilled water to give 100 μg ml^{-1} radiolabelled Tl (III) solution.

A stock solution of 0.1 mol dm^{-3} tribenzylamine was prepared by dissolving 2.874 g of tribenzylamine in 100 ml toluene. Stock solutions of tribenzylamine were also prepared using MIBK and chloroform as diluents.

A Packard Scint-A XF Scintillator solution was used. The scintillator solution consists of a solvent (toluene or pseudocumene), an emulsifier (a detergent type molecule to ensure proper mixing of aqueous samples) and a fluorescent solute.

An 83 ml volume of concentrated HCl was diluted to 1 l to give 1 mol dm^{-3} HCl solution. 5.85 g of NaCl was dissolved in 100 ml water to give 1 mol dm^{-3} NaCl.

2.3. Extraction procedure

A 1 ml volume of 100 μg ml^{-1} radiolabelled thallium (III) solution was placed in a separating funnel, 5 ml of 0.5 mol dm^{-3} HCl was added and the aqueous phase volume was maintained at 10 ml. The resulting chlorocomplex ($TlCl_4^-$) was equilibrated for 5 min with 10 ml of 0.1 mol dm^{-3} tribenzylamine in toluene. The beta activity of 2 ml each of the organic and aqueous phase was measured by mixing with 5 ml of the scintillation cocktail. The percentage extraction (E) was calculated as

$$D = \frac{E}{100 - E} \times \frac{\text{volume of aqueous phase}}{\text{volume of organic phase}}$$

where D, the distribution ratio, is the ratio of the activity of the extracted thallium in the organic phase to that in the aqueous phase.

Similarly, the extraction studies were also carried out using MIBK and chloroform as the diluents for tribenzylamine. In case of MIBK, the activity of the organic and aqueous phase was measured by liquid scintillation counting, and in the case of chloroform the activity of the phases was measured with a Geiger counter.

Table 1
Effect of concentration of HCl

Concentration of HCl (mol dm^{-3})	Distribution ratio (D)	Percentage extraction (E)
0.05	2.26	69.32
0.1	2.42	70.76
0.15	2.51	71.51
0.2	3.63	78.40
0.25	3.89	79.55
0.3	4.23	80.88
0.35	4.97	83.24
0.4	3.21	76.24

3. Results and discussions

3.1. Effect of the concentration of HCl

The concentration of HCl was varied in the range (0.05–0.4 mol dm^{-3}) maintaining an overall aqueous phase volume of 10 ml. The Tl (III) chloro complex was extracted with 10 ml of 0.1 mol dm^{-3} tribenzylamine in toluene. The distribution ratios and the percentage extraction are given in Table 1. The results reported in the table are the average of five determinations with an error of 0.5% in the percentage extraction. As can be seen from the table the percentage extraction decreases after 0.35 mol dm^{-3} of HCl probably due the formation of thallium as $TlCl_5^{2-}$ which could hinder the extractability of the tetrachloro-complex of thallium as an ion-pair with tribenzylamine.

3.2. Effect of NaCl and H_2SO_4

In order to improve the efficiency of extraction, NaCl and H_2SO_4 combination were studied, in place of HCl using toluene itself as the diluent for tribenzylamine. The concentration of NaCl was varied from 0.05 to 0.35 mol dm^{-3} and the concentration of sulfuric acid was maintained at 0.5 mol dm^{-3} maintaining an overall aqueous phase volume of 10 ml. The D values and percentage extraction are shown in Table 2. The percentage extraction increases from 72 to 82% in the above mentioned concentration range. The values reported in the table are the average of five determinations with an error of 0.35% in the percentage extraction. As can be seen from the table, it is evident that the extraction of thallium increases above 0.2 mol dm^{-3} NaCl and reaches saturation at 0.35 mol dm^{-3}. Hence, increasing the

Table 2
Effect of concentration of NaCl

Concentration of NaCl (mol dm^{-3})	Distribution ratio (D)	Percentage extraction (E)
0.05	2.61	72.29
0.1	2.82	73.82
0.2	3.63	78.40
0.25	4.38	81.41
0.35	4.58	82.07

Table 3
Summary of various diluents used for tribenzylamine

Diluent	Percentage extraction (*E*)
Toluene	82.63
Chloroform	95.11
MIBK	95.23

concentration of NaCl beyond 0.25 mol dm^{-3} did not have any significant enhancement in the extraction efficiency of thallium.

3.3. Effect of various diluents for tribenzylamine

The extraction tests for thallium were studied using a more polar solvent such as chloroform as the diluent for tribenzylamine. The concentration of HCl was varied in the range 0.1–0.35 mol dm^{-3} and the beta activity of the extracted species was measured using a Geiger Muller counter (since halogenated hydrocarbons would cause quenching in liquid scintillation counting). The efficiency of extraction improved considerably when a more polar solvent is used for extraction. Similar tests were carried out using isobutylmethylketone (MIBK) as the diluent for tribenzylamine. The concentration of NaCl was varied in the range 0.05–0.25 mol dm^{-3} maintaining an overall concentration of 0.5 mol dm^{-3}sulfuric acid and an aqueous phase volume of 10 ml. The activity of thallium in the organic phase was measured by mixing 2 ml of the extract with 5 ml of the scintillation cocktail. The efficiency of extraction was still better with MIBK, however at higher concentrations of NaCl, emulsion formation was observed in the organic layer leading to turbidity and difficult phase separation. The overall effect of the diluents is summarized in Table 3. The percentage extraction was found to be 82% using toluene as the diluent, whereas an extraction efficiency of 95% could be obtained using chloroform and MIBK as diluents. Hence, it is evident that among the three diluents, chloroform and MIBK prove to be more efficient in extracting thallium from the aqueous phase.

3.4. Effect of tribenzylamine concentration

Since, the extraction was more efficient with polar solvents such as chloroform and MIBK, the effect of concentration of tribenzylamine was examined. The concentration of tribenzylamine was varied from 0.05 to 0.5 mol dm^{-3} using chloroform as the diluent. The results are presented in Table 4. An extraction efficiency of 95% could be obtained in the above mentioned concentration range of tribenzylamine. The fact that the percentage extraction was almost constant in the above concentration range shows that varying the tribenzylamine concentration does not have any significant effect in the extraction efficiency.

Table 4
Effect of concentration of Tribenzylamine in chloroform

Concentration of tribenzylamine in chloroform (mol dm^{-3})	Distribution ratio (*D*)	Percentage extraction (*E*)
0.05	19.8	95.19
0.1	22.1	95.67
0.2	22.6	95.76
0.5	21.9	95.63

3.5. Quenching studies

Since, the extracted ion-association complex was colorless, the phenomenon of color quenching was not observed. Chemical quenching was not observed with toluene and MIBK as the diluents. This was confirmed from the fact that there was no significant decrease in the activity of the organic layer as a function of time. In case of chloroform as the diluent, severe quenching was observed. This was evident from the drastic decrease in the activity of the organic layer as a function of time when liquid scintillation counting was used and hence, the activity of the extracted thallium was monitored using a Geiger Muller counter.

3.6. Re-extraction of thallium from the organic phase

The re-extraction of thallium from the organic phase was examined using a variety of stripping agents such as water, sodium hydroxide and sodium sulfite, respectively. Experiments were carried out using 100 μg labelled Tl (III) and the resulting chlorocomplex was equilibrated for 5 min with tribenzylamine. The amount of thallium stripped from the organic phase was ascertained by measuring the aqueous phase activity. It was found that 0.1 mol dm^{-3} sodium sulfite was effective in the re-extraction of thallium from the organic phase.

3.7. Recovery studies in varying concentrations of radiolabelled Tl (III)

The extraction tests were performed using varying concentrations of radiolabelled Tl (III) ranging from 5 to 20 μg ml^{-1} using MIBK and chloroform as the diluents for tribenzylamine. An extraction efficiency of 95% could be obtained in the above mentioned concentration range.

3.8. Precision studies

The recovery of thallium was found to be 95% at varying concentrations ranging from 5 to 20 μg ml^{-1} Tl (III) with a relative standard deviation of 2.5%.

4. Conclusion

The studies carried out showed that Tl (III) could be extracted almost quantitatively using tribenzylamine as the extractant with the use of proper diluents. Among the various diluents studied, MIBK and chloroform could extract thallium with an efficiency of 95%. The phenomenon of color quenching was not observed, but chemical quenching was severe with chloroform when liquid scintillation counting was used. The recovery of thallium was found to be 95% in the range 5–20 μg ml^{-1} Tl (III) when MIBK and chloroform were used as diluents for tribenzylamine. The

coefficient of variation was found to be 2.5%. Even though, the extraction of Tl (III) is more efficient with high molecular weight amines such as trioctylamine [5], the studies carried out with tribenzylamine show that by proper manipulation of the various experimental parameters and solvents, there could be greater enhancement in the efficiency of extraction.

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