

# Extractive Separation and Determination of Zinc, Cadmium, and Mercury Using Tributyl Phosphine Oxide as Extractant in Salicylate Medium

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**Abstract:** *The Present study describes extractive separation of Zinc, Cadmium and Mercury with Tri-n-butylphosphine oxide (TBPO) as an extractant. There are various methods for extraction of Zn(II), Cd(II) and Hg(II). However, they suffer from longer extraction period, incomplete extraction and use of salting out agents. The optimum extraction conditions for Zinc, Cadmium and Mercury are evaluated by changing concentration of extractant, sodium salicylate, pH, diluents and shaking period. The extraction takes place by solvation mechanism, where metal salicylate is solvated by TBPO rendering it hydrophobic and facilitating extraction into the organic phase. The method is simple, rapid and selective. It facilitates mutual separation and estimation of Zinc, Cadmium and Mercury in thirty minutes. It is also applied to separation and estimation of Zn (II), Cd(II) and Hg(II) from various industrial, Pharmaceutical and Environmental samples.*

**Keywords:** solvent extraction; Tributylphosphine oxide; salicylate complexation; spectrophotometry; trace metal analysis; mutual separation.

## 1. Introduction

Zinc, Cadmium and Mercury are industrially important metals. They also have large applications in pharmaceutical industry. Zinc is essential in galvanizing metals like iron and steel to prevent rusting. Zinc is crucial in die-casting processes, especially for electronic hardware. In the nuclear reactor, cadmium rods help control chain reactions by absorbing stray neutrons. Cadmium also plays a role in rechargeable nickel-cadmium batteries which keeps satellites running and backup systems alive. Mercury is a highly toxic metal but has major use in thermometers, fluorescent lamps and dental amalgams. Quick and easy separation and estimation of Zinc, Cadmium and Mercury from mixtures and commercial samples is of great importance. In this project, new solvent extraction methods were developed for extraction of Zinc, Cadmium and Mercury. These metal ions are extracted from salicylate media from real samples whereby they are separated and estimated. The separation and estimations are in microgram range which indicates sensitivity of the method Developed. The major success of the project is the ability of the method to mutually separate and estimate zinc, cadmium and mercury together in a single mixture.

The solvent extraction methods developed for Zinc, Cadmium and Mercury utilize Salicylate media which is novel media which is free from toxicity and harmful corrosive nature generally seen in mineral acids media. The individual method for each metal ion is developed first. The difference in pH values for quantitative extraction allowed mutual separation of three commonly associated metal ions which are in the same group. The methods develop are also sensitive and rapid.

The estimation is done in the organic phase with addition of Pyridyl Azo Naphthol (PAN) as a Spectrophotometer

Reagent. This greatly saved time of the analysis and estimation of individual Metal Ion Become easy as Back Extraction from Organic Phase and subsequent losses are avoided. The Methods are also applied for separation and Estimation of Zinc, Cadmium and Mercury from real samples like Pharmaceutical, Food and Environmental Samples. The Results obtained are in Excellent Agreement with standard values

## 2. Experimental

### Apparatus and Reagents

Absorbance and pH measurements were made on Spectronic® Genesys8™ Spectrophotometer and a LAB INDIA Controlled pH analyzer PHAN with combined Glass electrode.

### Reagents

The Stock solution of Zn, Cd, and Hg were prepared by dissolving 1.13 gm of zinc sulphate, 2.85 gm of cadmium sulphate and 1.67 gm of mercury (II) chloride, in 250 ml of distilled water containing a minimum amount of appropriate acid to prevent hydrolysis. The solutions were standardized by standard methods<sup>21,22,23</sup> and the test solutions of the required concentration were prepared by suitable dilution. A 0.1% (m/v) methanolic solution of 1-(2- PyridylAzo)-2-Naphthol (PAN) <sup>19,20</sup> was used for the spectrometric determination of zinc, cadmium and mercury. Tributylphosphine Oxide (TBPO) (Aldrich) dissolved in toluene was used for extraction studies without further purification. All chemicals were of analytical reagent grade.

### General extraction procedure

Microgram amounts of zinc, cadmium and mercury were extracted from 25 ml aliquot solution adjusted pH and sodium salicylate concentration. The pH was adjusted with sodium hydroxide and hydrochloric acid solutions. Then the

aqueous phase is introduced into separating funnel and equilibrated with Tributylphosphine oxide dissolved in toluene for required time period. Zinc, cadmium and mercury are determined spectrophotometrically with 0.1% Pyridyl Azo Naphthol (PAN) solution in organic phase.

Optimum extraction conditions are evaluated by varying several parameters like pH, strength of extractant etc. They are reported in table 1.

**Table 1:** Optimum Extraction Conditions for zinc, cadmium and mercury

Metal ion	Aqueous phase		Organic phase (5 cm <sup>3</sup> in Toluene)	Extraction period	Stripping solution	Determination
	Salicylate, mol/dm <sup>3</sup>	pH				
Zn (10-50 µg)	1.5 X 10 <sup>-3</sup> - 2.0 X 10 <sup>-3</sup>	3.9 - 4.7	2.1X 10 <sup>-1</sup> - 2.5 x 10 <sup>-1</sup> mol/dm <sup>3</sup> TBPO	90 sec.	-	Determined in organic phase with PAN
Cd (5-20 µg)	1.7 X 10 <sup>-3</sup> - 2.0 X 10 <sup>-3</sup>	6.0 - 7.2	2.9X 10 <sup>-1</sup> - 3.2 x 10 <sup>-1</sup> mol/dm <sup>3</sup> TBPO	60 sec.	-	Determined in organic phase with PAN
Hg (1-5 mg) (5-25 µg)	2.4 X 10 <sup>-3</sup> - 5.0 X 10 <sup>-3</sup> 1.7 X 10 <sup>-3</sup> - 2.0 X 10 <sup>-3</sup>	5.5 - 6.6	5.2X 10 <sup>-1</sup> - 6.5 x 10 <sup>-1</sup> and 2.9X 10 <sup>-1</sup> - 3.2 x 10 <sup>-1</sup> mol/dm <sup>3</sup> TBPO mol/dm <sup>3</sup> TBPO	60 sec.	0.1-0.2 mol/dm <sup>3</sup> HCl-	Titrimetry with EDTA Determined in organic phase with PAN

### 3. Result and Discussion

#### Extraction conditions

Standard solutions of Zinc, Cadmium and Mercury were prepared and standardized from known methods<sup>23</sup>. The optimum extraction conditions for zinc, cadmium and mercury were established by varying several experimental parameters, such as the pH, sodium salicylate concentration, Tributylphosphine oxide (TBPO) concentration and several organic solvents such as xylene, benzene, hexane, carbon tetrachloride, chloroform and toluene were examined for the extraction of zinc, cadmium and mercury. Toluene was used as a diluent for further studies as it gives clear phase separation.

The general extraction procedure involves addition of required amount of sodium salicylate to microgram amount of metal ion in a total volume of 25 ml to give final required concentration. The pH was adjusted with sodium hydroxide and hydrochloric acid solutions. Then the aqueous phase is introduced into separating funnel and equilibrated with Tributylphosphine oxide dissolved in toluene for required time period. It was found that zinc was quantitatively extracted at pH 3.9-4.7 from 1.5x10<sup>-3</sup>-2.0x10<sup>-3</sup> sodium salicylate with 2.1x10<sup>-3</sup>-2.5x10<sup>-3</sup> mol dm<sup>-3</sup> TBPO dissolved in toluene. For cadmium extraction was quantitative at pH 6.0-7.2 from 1.7x10<sup>-3</sup> - 2.0 x10<sup>-3</sup> mol dm<sup>-3</sup> sodium salicylate with 2.9x10<sup>-3</sup>-3.2x10<sup>-3</sup> TBPO dissolved in toluene. And for mercury extraction method workout to microgram and milligram concentration so sodium salicylate TBPO concentration changes for Hg(1-5mg) determined spectrophotometrically with 0.1% Pyridyl Azo Naphthol (PAN) solution in organic phase. Optimum extraction conditions were reported in table 1.

Variation in the shaking period from 5 sec to 120 sec indicates that the shaking period for zinc, cadmium and mercury was 90 sec, 60 sec and 60 sec respectively. However, it was observed that prolonged shaking had no adverse effect on the extraction.

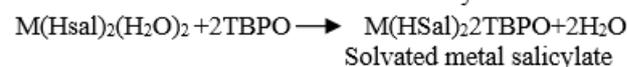
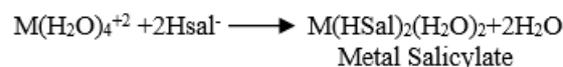
Various diluents like toluene, xylene, benzene and carbon tetrachloride are tried for their suitability as diluents. It is observed that the quantitative extraction was feasible only in

toluene and xylene. Toluene was used as a diluent for further studies as it gives clear phase separation.

Several stripping agents like nitric acid, hydrochloric acid, sulphuric acid, ammonium hydroxide and sodium hydroxide were used for the back extraction Zinc, Cadmium and Mercury. It was observed that 0.1-0.2 mol/dm<sup>3</sup> HCL strip mercury. Zinc and cadmium were stripped by distilled water.

#### Nature of extracted species:

The composition of the extracted species is ascertained using log-log plots. The plot of log of distribution ratio versus log of sodium salicylate concentration (at fixed pH, and TBPO concentrations) gives slope of **2.2, 2.3 and 2.2 (fig2)** for Zn, Cd and Hg respectively. This indicates a molar ratio of 1:2 of the Zinc, Cadmium and Mercury with respect to salicylate. Similarly, the plot of log of distribution ratio versus log of extractant concentration (at fixed pH and salicylate concentration) gives straight lines with slopes **1.9, 1.9 and 2.0 (fig.3)** for Zn, Cd and Hg respectively. The slopes predict the number of extractant molecules coordinated with the metal ion. Thus, the probable extracted species for all three metals were metal salicylates solvated by TBPO as shown below by following reactions,



where Hsal<sup>-</sup> stands for the salicylate ion. The metal salicylate is solvated by the extractants and transferred into the organic phase. The extraction takes place by solvation mechanism.

#### Effect of diverse ions:

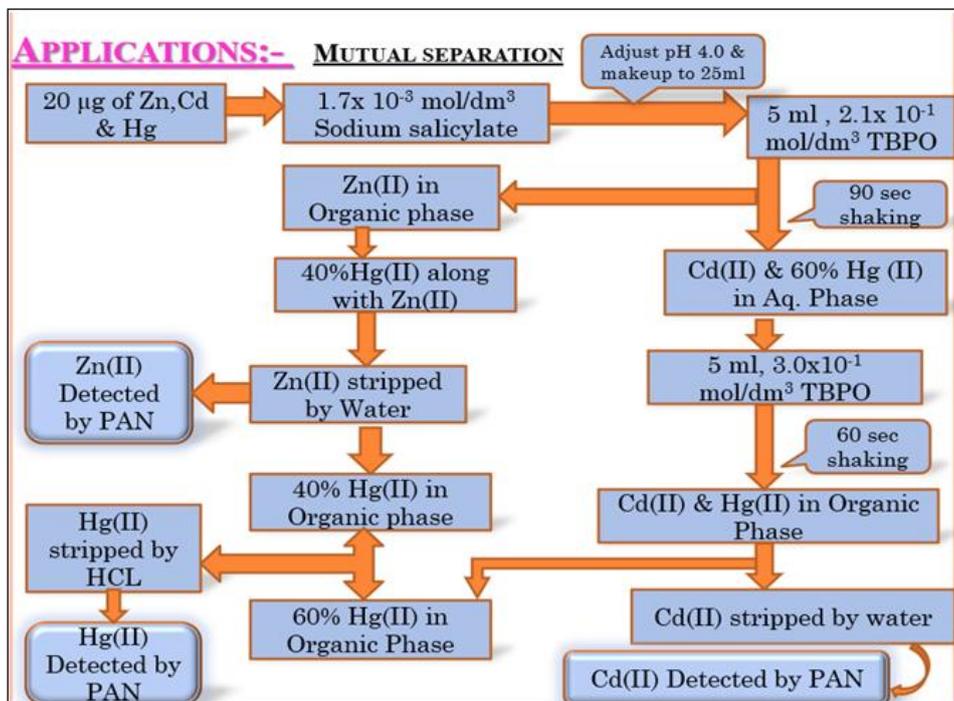
Varying amounts of foreign ions are added to the fixed amount of Zn, Cd and Hg to study their interference in general extraction and subsequent determination of Zn, Cd and Hg. The tolerance limit is set at the amount of the foreign ion causing ±2% error in the recovery of the Zn, Cd and Hg. The results are reported in Table 2.

4. Applications

The scheme for mutual separation of Zn, Cd and Hg is given as follows in Fig. 4.

Mutual separation of Zn, Cd and Hg:

Zinc, Cadmium and Mercury are mutually separated from each other by proposed method. The recovery of all the metals is quantitative. The results are reported in table 3.



Estimation of Zinc from Pharmaceutical samples: -

The applicability of the proposed method was checked by separation and estimation of Zinc, in different pharmaceutical real samples. The results are reported in table 4.

Analysis of water samples: -

Proposed method was applied to separation and determination of Zinc and Mercury from Industrial wastewater and well water from thane region. The results were compared with those of the atomic absorption spectroscopic method the recoveries were excellent and are reported in table.5.

5. Conclusions

The developed solvent extraction method employing tributylphosphine oxide in salicylate medium enables rapid and selective separation of zinc, cadmium, and mercury with high reproducibility. Quantitative recoveries obtained within short extraction times demonstrate the suitability of the approach for trace analysis in pharmaceutical and environmental matrices. The spectrophotometric determination in the organic phase eliminates back extraction losses and enhances analytical efficiency. Overall, the method offers a practical alternative for multicomponent metal ion analysis with potential applicability in routine laboratory and environmental monitoring contexts.

Acknowledgement

The authors thank all the colleagues from Dept. of Chemistry, K. J. Somaiya college of science and commerce,

Vidyavihar (E), Mumbai for their support and to the University of Mumbai, India for financing the project.

Table 2: Diverse ion effect

For Zinc (II)		For Cadmium (II)		For Mercury (II)	
Foreign ions	Tolerance limit, µg	Foreign ions	Tolerance limit, µg	Foreign ions	Tolerance limit, µg
Cu(II)	100	Cu(II)	250	Cu(II)	100
Pb(II)	200	Pb(II)	200	Pb(II)	200
Mn(II)	2000	Mn(II)	500	Mn(II)	300
Ba(II)	400	Ba(II)	200	Ba(II)	200
Cd(II)	100	Zn(II)	10	Zn(II)	100
Mg(II)	200	Mg(II)	50	Mg(II)	100
Sb(III)	500	Sb(III)	50	Sb(III)	20
Al(III)	500	Al(III)	300	Al(III)	100
La(III)	2000	La(III)	2000	La(III)	2000
Fe(III)	none	Fe(III)	50	Fe(III)	50
Th(IV)	200	Th(IV)	500	Th(IV)	1000
Zr(IV)	1200	Zr(IV)	1500	Zr(IV)	1500
Hf(IV)	400	Hf(IV)	100	Hf(IV)	500
Ti(IV)	500	Ti(IV)	800	Ti(IV)	500
Ce(IV)	200	Ce(IV)	600	Ce(IV)	1000
Te(IV)	200	Te(IV)	200	Te(IV)	200
V(V)	2000	V(V)	2000	V(V)	500
U(VI)	1000	U(VI)	800	U(VI)	500
Cr(VI)	250	Cr(VI)	250	Cr(VI)	100
Mo(VI)	150	Mo(VI)	150	Mo(VI)	100
SO4 <sup>2-</sup>	none	SO4 <sup>2-</sup>	300	SO4 <sup>2-</sup>	100
Cl <sup>-</sup>	1000	Cl <sup>-</sup>	100	Cl <sup>-</sup>	500
NO3 <sup>-</sup>	2000	NO3 <sup>-</sup>	250	NO3 <sup>-</sup>	1400
SCN <sup>-</sup>	250	SCN <sup>-</sup>	500	SCN <sup>-</sup>	250

**Table 3:** Mutual separation of Zn (II), Cd (II) and Hg (II)

Sample No.	Amount taken, $\mu\text{g}$			Amount found, $\mu\text{g}$			Recovery*, %		
	Zn	Cd	Hg	Zn	Cd	Hg	Zn	Cd	Hg
1	20	20	20	19.5	20.1	19.7	97.5	100.5	98.5
2	25	20	15	24.9	19.9	14.9	99.6	99.5	99.3
3	15	25	20	15.1	24.9	19.9	100.6	99.6	99.5

- Average of triplicate analysis

**Table 4:** Estimation of Zinc from pharmaceutical samples

a -mg per tablet.

Sample	Composition	Zn(II) Certified value, mg	*Recovery of Zn(II),mg	R.S.D. (%)
Supradyn (Roche)	Copper sulphate IP, 3.39 mg; zinc sulphate IP, 2.20 mg; sodium borate IP, 0.88 mg	0.5a	0.47	1.56
Zevit (SKF)	Zinc sulphate, 61.8 mg; thiamine monohydrate IP, 10 mg; nicotinamide IP, 75 mg; pyridoxine hydrochloride IP, 2 mg; cyanocobalamin IP, 7.5 $\mu\text{g}$ ; calcium pantothenate, 25 mg; tocopheryl acetate IP, 20 mg; ascorbic acid IP, 150 mg	22.5a	22.49	1.12
Nycil (Glindia)	Chlorphenesin BP, 1%; boric acid IP, 5%; Zinc oxide IP, 16%; Starch IP, 51%; talc purified IP to 100%	12.8b	12.75	1.08

b -mg per 100 mg of powder.

- \* Average of triplicate analysis

**Table 5:** Analysis of waste water samples

Sample	Zinc content found by AAS	Zn found by proposed method	Standard deviation	*Relative standard deviation (%)
Industrial waste water	1.6 ppm	1.56 ppm <sup>a</sup>	0.006	0.85
Well water from Thane	0.32 ppm	0.33 ppm	0.004	0.58
Industrial waste water	0.62 ppm	0.69 ppm <sup>a</sup>	0.081	0.138
Well water from Thane	0.14 ppm	0.15 ppm	0.052	0.102

a- ppm : parts per million

- \*-: Average of six determinations

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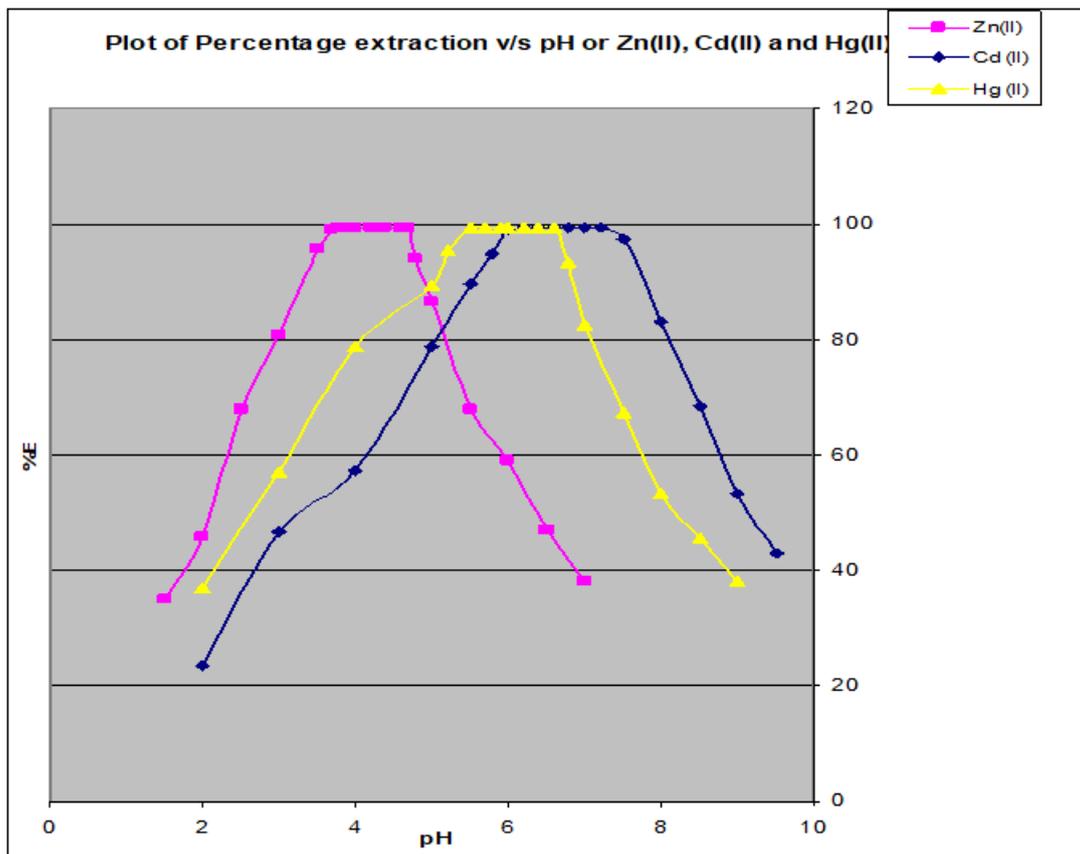


Figure 1: Percentage extraction (%E) as a function of pH

- = Zn(II)
- = Cd(II)
- ▲— = Hg(II)

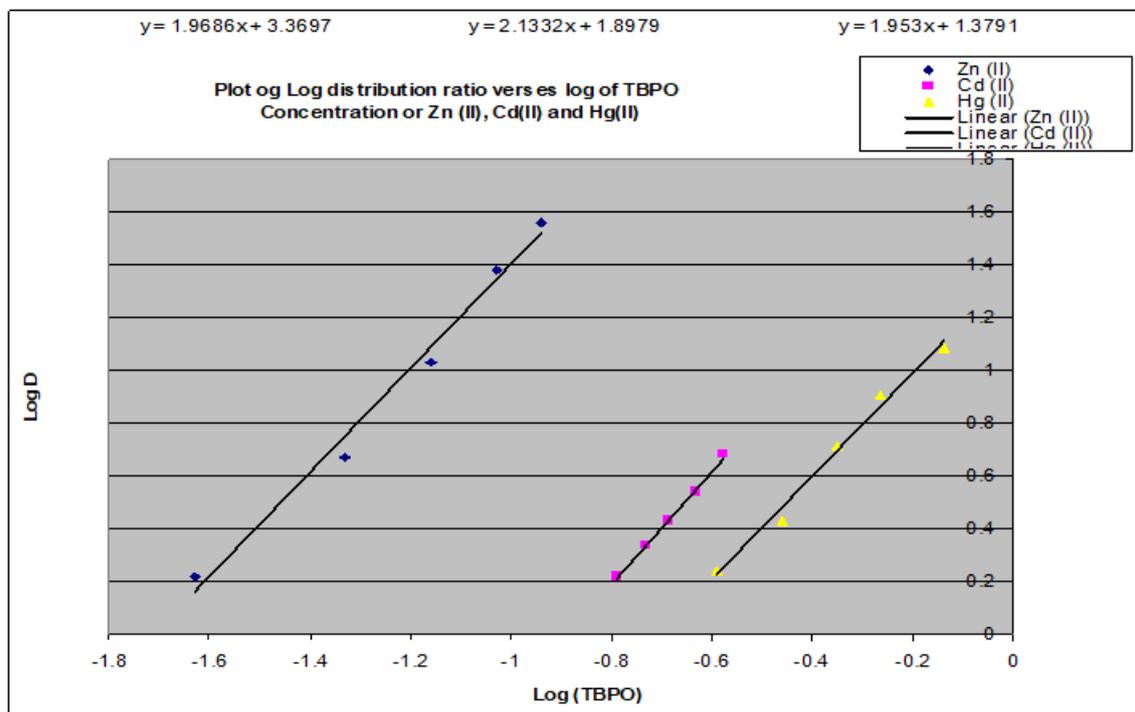


Figure 2: Variation of the distribution ratio as a function of the sodium salicylate concentration

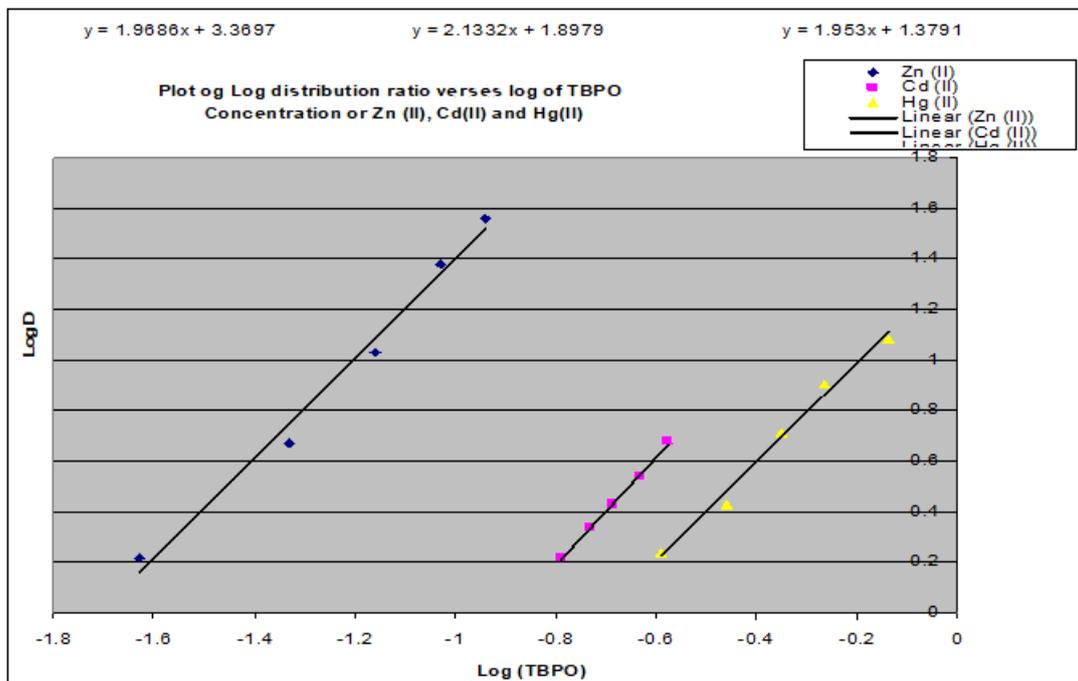


Figure 3: Variation of the distribution ratio as a function of the TBPO concentration