

# RECOVERY OF ACIDS FROM SPENT PICKLE LIQUOR OF ELECTROPLATING INDUSTRY BY SOLVENT EXTRACTION

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## Abstract

Spent pickle liquor (SPL) of electroplating industry is a major source of hazardous industrial wastes. Various methods have been investigated for the recovery of acid(s), Hydrochloric acid and Sulfuric acid from SPL. Each has got its own merits and demerits.

Solvent extraction is one of the method used for recovery of inorganic acids from wastewater. Extraction of hydrochloric acid and sulfuric acid by solvents was studied from spent pickle liquor containing 92 g/l hydrochloric acid and 491g/l sulfuric acid. Recovery of all two acids increased with the increasing concentration of the solvents. For all the solvents studied, the species extracted into the organic phase appears to be associated with nearly one mole of solvent.

The acids extracted by Aliquat 336 and Tributyl phosphate (TBP) were easily stripped with water. But sulfuric acid extracted with Alamine 336 was not stripped with water. The stripping efficiency was ~11% with dilute sulfuric acid and increased with 0.1 N NaOH for acid loaded onto Alamine 336.

*IndexTerms* - Alamine 336, Aliquat 336, TBP, solvent, spent pickle liquor

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## 1.0 Introduction

For efficient electroplating of zinc, pretreatment of steel surface is necessary; metal oxide and scales should be removed from the metal surface before electroplating. In order to clean the surface, the metal sheet, strip, wire etc. are pickled in hydrochloric acid or sulfuric acid or phosphoric acid bath. Carbon steels, with an alloy content less than or equal to 6%, are usually pickled in hydrochloric or sulfuric acid. Steels with an alloy content greater than 6% are pickled in two steps and other acids are used, such as phosphoric, nitric and hydrofluoric acid. For picking of rust and acid-resistant chromium-nickel steels a bath of hydrochloric and nitric acid is used. Most copper alloys are pickled in dilute sulfuric acid, but brass is pickled in concentrated sulfuric and nitric acid mixed with sodium chloride and soot [1].

Steels are usually pickled in 20% HCl at 60–70°C. When the concentration of HCl becomes around 10% and the metallic impurities concentration such as Fe, Zn, Cr, etc. increases up to a certain level due to repetition of pickling in the same liquid, the pickle liquid becomes unusable and discharged as spent pickle liquor. Because of hazardous nature it cannot be disposed into land or water bodies without treatment. Conventional method of the pickle liquor disposal is acid neutralization with alkali, precipitation of metals and the sludge generated is disposed as landfill, or by evaporation and pyrohydrolysis of the pickle liquor. Due to this method there is acid loss as well as loss of metal values. Hence, it is necessary to develop a method to recover acid and iron values from these wastes. One of the good recovery method is solvent extraction process.

Scientists have reported the use of Tri-butyl phosphate (TBP) for the extraction of acid [2-3]. The solvent extraction of inorganic acids by Cyanex 923 [4] and tri-n-octylphosphine oxide was studied and reported. Although appreciable research has been reported for the extraction/recovery of different acids using solvents

such as TBP, Alamine 993 (tri-n-octyl phosphine oxide and tris 2-(ethyl hexyl) amine, Alamine 336, Aliquat 336 etc., studies for the recovery of acids using different extractants and their comparison are not sufficient.

For the extraction of sulphuric acid using Alamine 336 was studied by Agrawal et al. [5] and found that the extraction of sulphuric acid increased with the increase in the Alamine 336 concentration. Although, Alamine 336 showed higher extraction ability for sulphuric acid than Cyanex 923, the acid extracted was not stripped completely using hot water.

Experiments were carried out to recover HCl and H<sub>2</sub>SO<sub>4</sub> using different solvents and the results obtained are reported in this paper.

## 2.0 Materials And Methods

### 2.1 Materials:

The spent pickle liquor (SPL) used in this study were containing Hydrochloric acid and Sulfuric acid. The SPL containing Hydrochloric acid and Sulfuric acid was procured from nearby electroplating industries. All the chemicals and reagents used in this study were of analytical grade and were of S D Fine Chemicals Ltd., Mumbai and Qualigens Chemicals, Mumbai.

The extractants (solvents) used were TBP, Aliquat 336 and Alamine 336 for Hydrochloric acid and Sulfuric acid containing SPL.

### 2.2 Methods

#### 2.2.1 Analysis of Spent Pickle liquor (SPL)

##### 2.2.1.1 Determination of iron content and free acid in spent pickle liquor

The iron content and free acid in sulfuric acid spent pickle liquor was estimated using the method given by Fred and Neil [6]. The method used by Fred and Neil [8] was used for iron content and free acid from hydrochloric acid spent pickle liquor. Free Phosphoric acid in Phosphoric acid spent pickle liquor was determined by the method reported by M. Lynch [7].

##### 2.2.1.2 Determination of heavy metals in spent pickle liquor

The concentration of heavy metals like Fe, Zn, Pb, Cd, Ni and Cu present in spent pickle liquors were determined by the standard methods reported in APHA (American Public Health Association)[9].

##### 2.2.1.3 Determination of TSS, TDS & Chlorides in spent pickle liquor

The values of TSS, TDS & Chlorides present in spent pickle liquors were determined by the standard methods reported in APHA (American Public Health Association)[9].

**2.2.1.4 Determination of pH in spent pickle liquor:** pH of all two spent pickle liquors were determined by usual standard methods.

**2.2.1.5 Determination of boiling point and specific gravity in spent pickle liquor:** Boiling point and specific gravity in spent pickle liquor were determined by usual standard methods.

### 2.3 Recovery of acid(s)

#### 2.3.1 Liquid-liquid extraction

Desired volume of SPL sample and solvent were shaken well manually in separating funnel for 5-10 minutes. After phase disengagement, the aqueous phase was separated and acid concentration was estimated volumetrically. The concentration of acid in organic phase was calculated from the difference between

concentration in the aqueous phase before and after extraction. Also organic phase was filtered, stripped by water and analyzed for free acid.

Stripping of loaded organics: Stripping of loaded organics was carried out at an equal volume ratio of loaded organic and distilled water in separating funnels. After contacting for 5 minutes the phases were allowed to disengage. The two phases, aqueous phase and organic phases were separated and analyzed.

Then distribution coefficient (D) was calculated. The graph was plotted between log D and log of concentration of solvent. Thus mathematical equation was developed relating concentration of solvent and distribution coefficient.

For recovery of HCl from SPL solvents like Alamine 336, Aliquat 336 and TBP were used during extraction. Effect of change in concentration of these solvents as well as change in time of extraction on recovery of hydrochloric acid was studied.

The same solvents were also used for the recovery of sulfuric acid from SPL containing sulfuric acid. Effect of change in concentration of these solvents on recovery of sulfuric acid and rate of extraction of sulfuric acid has been investigated.

### 2.3.2 Analysis of Recovered acids by HPLC

The samples of recovered acids HCl/H<sub>2</sub>SO<sub>4</sub> were analyzed by HPLC for the confirmation of the acids. The results were also confirmed by routine chemical analysis.

## 3.0 Results and Discussion

### 3.1 SPL containing Hydrochloric Acid

#### 3.1.1 Analysis of Spent Pickle Liquor (SPL) containing Hydrochloric Acid

The analysis of SPLs containing hydrochloric acid is depicted in Table 3.1. It was found that the SPL contains Fe in large quantity followed by Zn and Cu. The other metals include Pb, Cd, and Ni. The pH value recorded was 0.80 while free acid concentration was 9.2 % in the two sample of SPL containing hydrochloric acid. It was also observed that concentration of Fe in samples was maximum than other metals followed by Zn, Cu, Pb, Ni, Cd respectively in decreasing order. Total dissolved solids (TDS), Total suspended solids (TSS) and chlorides values were 249 g/l, 0.1 mg/l, 248.1 g/l respectively and Boiling point recorded was 1090C. The specific gravity was 1.05.

**Table 3.1: Analysis of SPL (Hydrochloric acid) from local electroplating industry**

Component	Zn (mg/l)	Pb (mg/l)	Cd (mg/l)	Ni (mg/l)	pH	Fe (g/l)	Cu (mg/l)	Free acid (%)	TDS (g/l)	TSS (mg/l)	Chlorides (g/l)	Boiling Point °C
Concentration	157.54	13.56	0.82	6.49	0.80	44.36	46.25	9.20	146.1	0.1	145.72	105



### 3.1.2 Liquid- liquid Extraction method

Experiments were carried out to study the recovery of hydrochloric acid from the SPL using solvent extraction method. For this purpose, the extractants (solvents) used were TBP, Aliquat 336 and Alamine 336 for Hydrochloric acid containing SPL [10].

#### 3.1.2.1 Recovery of Hydrochloric acid by extraction with Alamine 336

Alamine 336 concentration was varied from 10 to 100 vol.% and the extraction of hydrochloric acid was studied.

It can be observed that the extraction of the acid increased from 5.1% to 31.5% with increasing Alamine 336 concentration from 10 to 100 vol.%. However, the time taken for phase separation increased from 1 to 25 min with the increase in Alamine 336 concentration. At higher concentration of Alamine 336 difficulty in phase separation was observed. Stripping of loaded acid was not possible by water and it was low for 0.1 N HCl and was 99 % for 1 N NaOH.

The graph of log D vs. log [Alamine 336] was a straight line with a slope of 1. This indicated the Alamine 336 molecule with the extracted species was 1 (fig. 3.1). From this plot,  $K_{LLE}$  was calculated to be 0.251 [10].

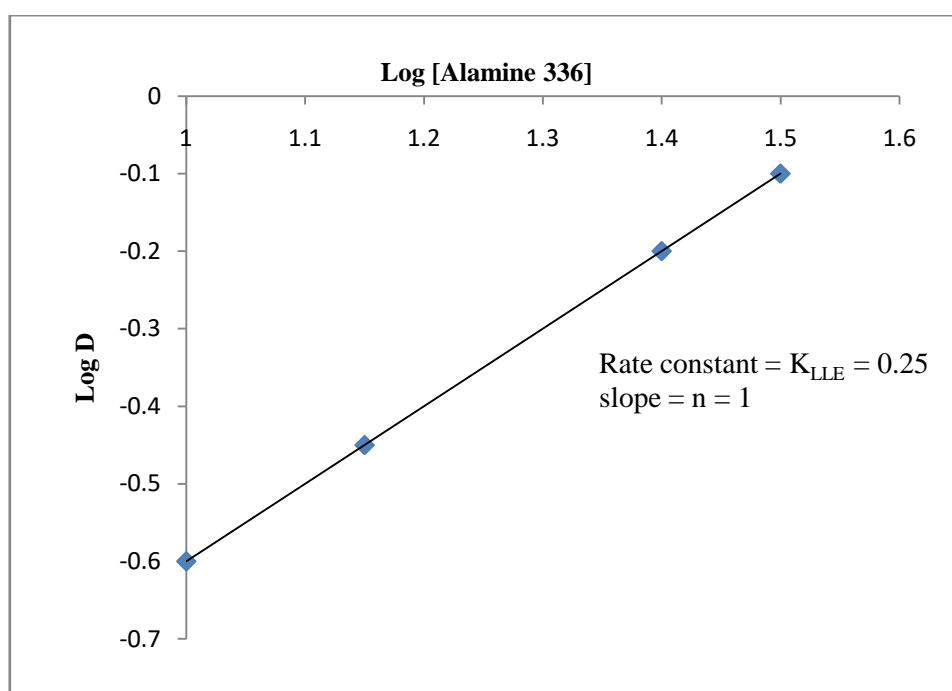


Fig. 3.1: Effect of Alamine 336 concentration on distribution coefficient for hydrochloric acid SPL

#### 3.1.2.2 Recovery of HCl using Aliquat 336

The extraction of HCl by Aliquat 336 can be represented in the same format as described above.

The extraction of acid at different concentrations of Aliquat 336 indicates that the percentage of acid extraction increased from 2.1 to 12.1 when the Aliquat 336 concentration was increased from 10 to 80 vol.%. The time for phase separation decreased from 3.0 to 1.5 min with the increase of Aliquat 336 concentration from 10 to 50% and then increased to 2.5 min. with the further increase of Aliquat 336 concentration to 80%. The slope of log D vs. log [Aliquat 336] plot for extraction of acid with Aliquat 336 was 0.67. This indicated the involvement of one Aliquat 336 molecule with the extracted species. From this graph  $K_{LLE}$  was also calculated to be 0.239 (Fig. 2.2). Due to high viscosity of Aliquat 336 the result with 100% Aliquat 336 was not possible.

Recovery of HCl using Aliquat 336 increased from 27.50 % to 40.83 % in single stage extraction at different phase ratio(A:O) for 1;1 efficiency was 27.50 %, for 1:2 ratio efficiency was 31.56 and for 1:3 efficiency was 40.83.

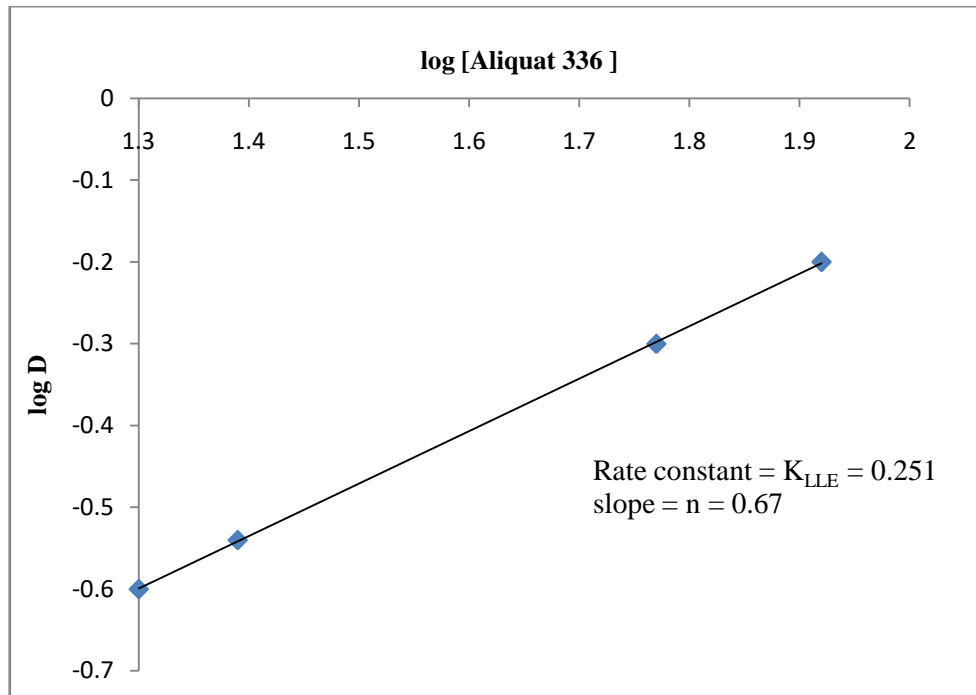


Fig. 3.2 :Effect of Aliquat 336 concentration on Distribution coefficient for hydrochloric acid SPL

### 3.1.2.3 Recovery of HCl using Tri-butyl phosphate (TBP)

The log [TBP] vs. log D plot was a straight line with a slope of 0.71 and confirms the association of one TBP molecule with the extracted species. The  $K_{LLE}$  value was calculated from the graph and found to be 0.309 (Figure 3.3). Single-stage extraction tests were carried out with 100% TBP at the A:O phase ratios of 1:1, 1: 2, 1:3. The extraction efficiencies obtained were 18.75, 26.25 and 32% respectively at the above phase ratios [11]. For the systems tested, the acid extraction increased with the increase in the solvent concentration.

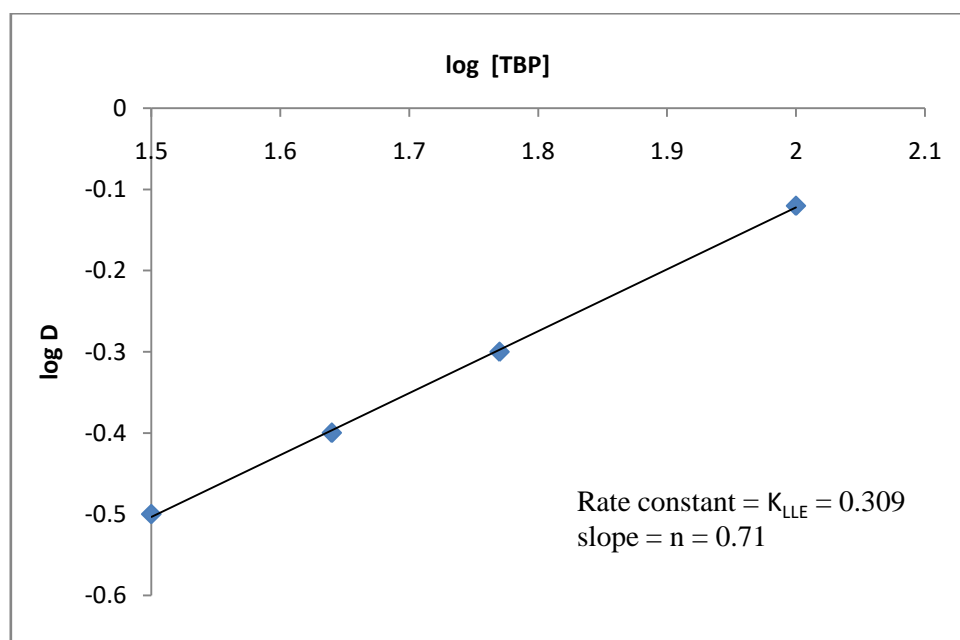


Fig. 2.3: Effect of TBP concentration on Distribution coefficient for Hydrochloric Acid SPL

## 3.2 SPL containing Sulfuric acid

### 3.2.1 Analysis of Spent Pickle Liquor containing Sulfuric Acid (SPL)

The analysis of SPL containing sulfuric acid is reported in Table 3.2. It was found that the SPL contains Fe in large quantity followed by Zn and Cu. The other metals include Pb, Cd, and Ni in all three SPL(s). It was also observed that concentration of Fe in sample is maximum than other metals followed by Zn, Cu, Pb, Ni, Cd respectively in decreasing order. The pH values recorded for the SPL containing sulfuric acid was 1.21, while free acid concentration was 49.1 %. Total dissolved solids (TDS) and Total suspended solids (TSS) values were 1203.8 g/l and 0.02 mg/l respectively. Boiling point recorded was 150°C and specific gravity

**Table 3.2: Analysis of SPL (Sulfuric acid) from local steel industry**

was 1.135.

Component	Zn (mg/l)	Pb (mg/l)	Cd (mg/l)	Ni (mg/l)	pH	Fe (g/l)	Cu (mg/l)	Free acid (%)	TDS g/l	TSS mg/l	Boiling Point <sup>0</sup> C
Concentration	157.31	12.73	1.91	4.41	1.21	44.35	70.61	49.10	1203.80	0.02	150

### 3.2.1.1 Analysis of SPL (Sulfuric Acid) from local steel industry

#### 3.2.1.1.1 Alamine336

#### 3.2.1.1.2 Rate of extraction of sulfuric acid with Alamine 336

For study of kinetics of sulfuric acid extraction, both aqueous and organic phases were contacted for various time intervals up to 10 min. After 5 min. of contact time the percentage extraction remained same so shaking time was fixed as 5 min [12].

#### 3.2.1.1.3 Effect of Alamine336 concentration on acid extraction

Solvent concentration was varied from 10% to 35% (v/v) in kerosene using 10% isodecanol as phase modifier. There was increase in the acid extraction with an increase in the concentration of Alamine. Extraction of Sulfuric acid by 80% Alamine 336 increased from 78.5 % to 85.5 % in single stage extraction at different phase ratio (A:O) i.e. for 1:1 efficiency was 78.5%, for 1:2 efficiency was 80.83% and for 1:3 efficiency was 85.5%. When Alamine concentration was increased phase separation time also increased.

When solvent concentration was increased above 35% phase separation problem was observed, hence 35% Alamine336 concentration was finalized for optimization experiment. Plot of log D (Distribution coefficient) vs log Alamine 336 concentration (Fig. 2.4) resulted in slope of 0.9. This indicated that 1 mol of Alamine 336 was required for 1 mol of acid. These results are in nearly agreement with that reported in the literature [12].



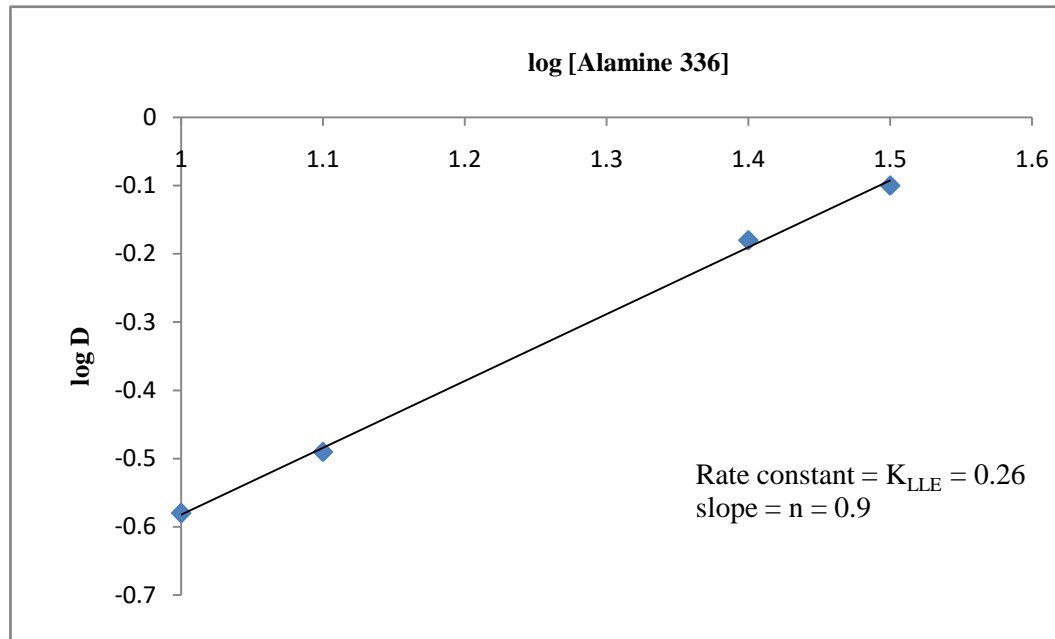


Fig. 3.4: Effect of Alamine 336 concentration on Distribution coefficient for Sulfuric Acid SPL

Only 11%  $H_2SO_4$  was stripped from the Alamine 336 system. Agrawal A. et al. (2007) also reported the difficulty in stripping the sulfuric acid from the Alamine 336 using deionised water [13]. Stripping the extracted acid with 1 N NaOH gave good results.

### 3.2.1.1.4 Aliquat 336

#### 3.2.1.1.4.1 Rate of extraction of sulfuric acid with Aliquat 336

For study of kinetics of sulfuric acid extraction, both aqueous and organic phases were contacted for various time intervals up to 10 min. After 5 min. of contact time the percentage extraction remained same so shaking time was fixed as 5 min [14].

#### 3.2.1.1.4.2 Effect of Aliquat 336 concentration on acid extraction

There was increase in the acid extraction with an increase in the concentration of Aliquat 336. Extraction of Sulfuric acid by Aliquat 336 increased from 8 % to 14.5 % in single stage extraction at different phase ratio (A:O) i.e. for 1:1 efficiency was 8%, for 1:2 efficiency was 12.54% and for 1:3 efficiency was 14.5%.

The values of distribution coefficient were low varying from 0.1 to 0.36. Plot of log D vs log Aliquat 336 concentration (Fig. 3.5) a slope of 0.9 was obtained. This indicated that 0.9 mol of Aliquat 336 was required for extraction of 1 mol of acid.

In general, it can be concluded that Aliquat 336 was a poor extractant for sulfuric acid.

Stripping of acid was possible by water in this case.



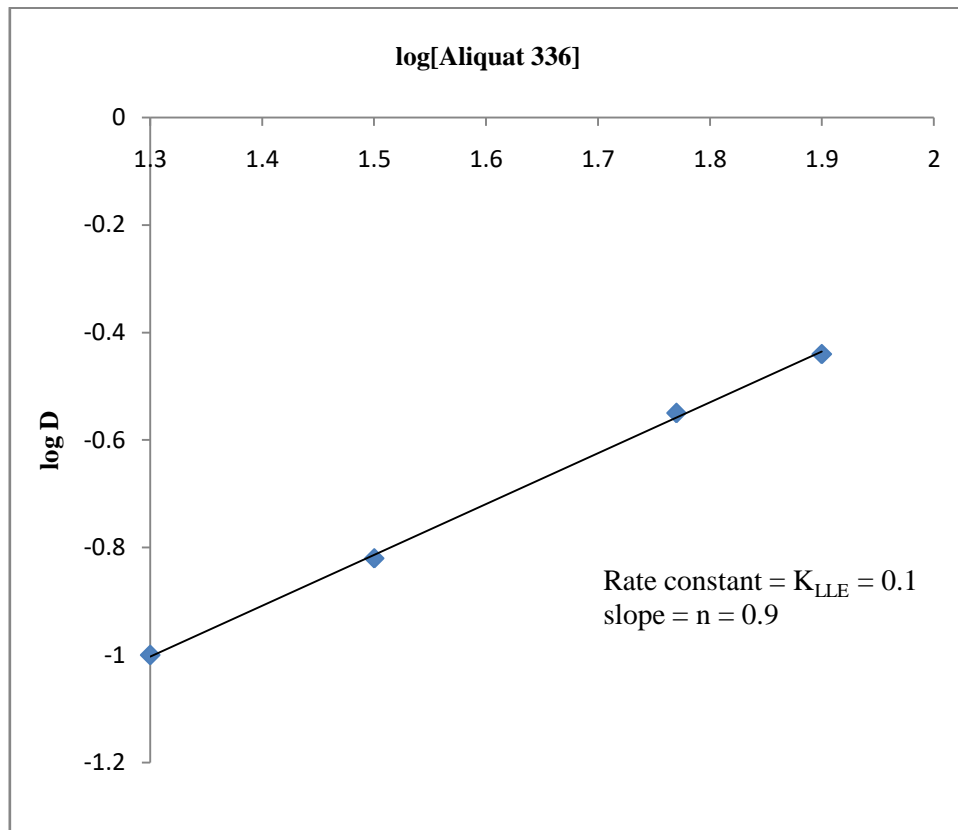


Fig.3.5 Effect of Aliquat 336 concentration on Distribution coefficient for Sulfuric Acid SPL

### 3.2.1.1.4.3 Tri-butyl- phosphate (TBP)

#### Rate of extraction of sulfuric acid with TBP

For study of kinetics of sulfuric acid extraction, both aqueous and organic phases were contacted for various time intervals up to 10 min. After 5 min. of contact time the percentage extraction remained same so shaking time was fixed as 5 min.

#### Effect of concentration of TBP on acid recovery

As concentration of TBP was increased % acid recovery increased.

The percentage extraction of acid increased from 10 to 45 with the increase of TBP concentration from 20 to 100%. The log [TBP] vs. log D plot was a straight line with a slope of 0.617 and confirmed the association of one TBP molecule with the extracted species. The  $K_{LLE}$  value was calculated from the graph and found to be 0.141. Single-stage extraction tests were carried out with 100% TBP at the A:O phase ratios of 1:1, 1:2, 1:3. The extraction efficiencies obtained were 18.75, 26.25 and 32% respectively at the above phase ratios.

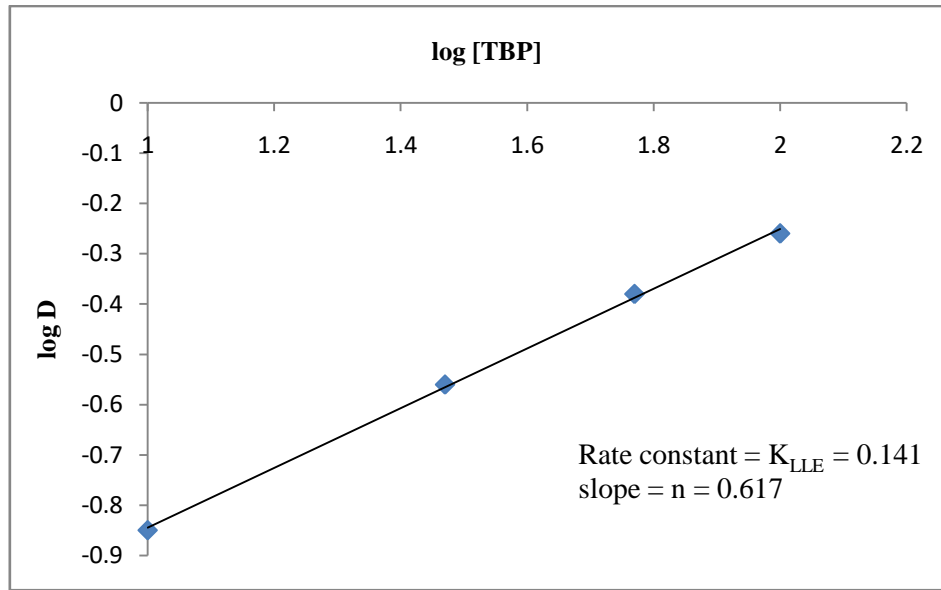


Fig.3.6: Effect of TBP concentration on Distribution coefficient for Sulfuric Acid SPL

## Conclusion

Solvent extraction studies of hydrochloric acid and sulfuric acid was carried out by extraction using TBP, Aliquat 336 and Alamine 336. In case of kinetic study of the liquid-liquid extraction the values for mass transfer coefficient  $K_{LLE}$  in most of the solvents (extractants) for hydrochloric acid and sulfuric acid were better than that reported in literature.

For hydrochloric acid and sulfuric acid for each extractant log distribution coefficient vs. log extractant concentration plot was straight line. The significance of this is that the upper limit for extractant concentration is fixed. As concentration of extractant was increased acid extracted % increased for the two acids. In case of liquid-liquid extraction for hydrochloric acid SPL, acid extraction efficiency was maximum for Alamine 336, followed by TBP and Aliquat 336.

### Sulfuric acid

The value of distribution coefficient was maximum for Alamine 336. Hence the solvent Alamine 336 was best out of three solvents Alamine 336, Aliquat 336 and Tributyl Phosphate used for liquid-liquid extraction of sulfuric acid.

### Hydrochloric acid

The solvent Alamine 336 was best out of three solvents Alamine 336, Aliquat 336 and Tributyl Phosphate used for liquid-liquid extraction of hydrochloric acid as the distribution coefficient and concentration of stripped acid was maximum for Alamine 336.

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## Nomenclature

Sr. No.	Symbol	Meaning
1	Zn	Zinc
2	Pb	Lead
3	Cd	Cadmium
4	Ni	Nickel
5	Fe	Iron
6	Cu	Copper
7	TDS	Total Dissolved Solids
8	TSS	Total Suspended Solids
9	D	Distribution Coefficient

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