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# Efficiency of tri-n-octylamine for the liquid-liquid extraction of Co (II) from acidic chloride medium

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**Abstract**

Cobalt criticality is increasing as a function of time and this concern has impelled researchers to ascertain efficient recovery schemes of cobalt. In this paper, an extraction strategy for cobalt utilizing tri-n-octylamine (TOA) in kerosene from acidic chloride media has been developed. The extraction percentage was found to be 76.7 using 1.5 M TOA. Influence of various salting out agents like $NH_4Cl$, KCl, and NaCl on the percentage extraction has been analysed and KCl emerged as beneficial for extraction. The positive value of enthalpy change indicates that high temperature favors the formation of extractable complex (Co (II)-TOA complex) and the positive value of entropy change indicates inner sphere complexation. Kerosene as diluent was proved to be efficient in comparison to other aromatic hydrocarbons for the extraction of Co under the present experimental conditions. In order to examine the interaction between cobalt and TOA, FTIR analysis has been carried out. The changes in absorption peak position of functional groups confirmed binding of TOA with Co (II).

## 1. Introduction

Cobalt, a critical element identified by European commission is now receiving a lot of buzz due to its limited availability and diverse range of applications in advanced technologies [1,2]. Growing concern for cobalt is due to its excellent properties i.e., malleability, ductility, high melting point and boiling point making it useful for industrial and military applications [3]. The rapidly growing demand of cobalt is fueled by its vast use in rechargeable batteries. Li-ion batteries contain substantial amount of cobalt (5-20%) whereas NiMH batteries contain 4.6% cobalt [4,5]. These spent batteries hold almost 43 tons of cobalt of worth 2.2 million euros [6]. Nevertheless, it is hard to recover cobalt from its primary deposits as it exists in aggregated form. It occurs in accumulation with other metal minerals like pyrite, chalcopyrite, pentlandite, and carrollite, etc. [7]. As a byproduct, Cobalt is produced during the mining of copper, iron and nickel. But the matter of vexation is, the toll of these raw materials has been reduced and subsequently, legion mines have started to knock off [8]. This lack of balance between supply and demand opens the doors for the development of potent methods to recover and recycle cobalt.

Various methods have been applied for separating and purifying the elements concentrated in primary ores or secondary resources. However, solvent extraction is a simple and novel technique for the separation and purification of metals from mixed metal solution [9,10]. It is a separation technique which is simple, less time consuming, cost effective and industrially applied to get high-purity metals and is accepted as the remediation for environmental issues [11]. Here, the separation technique involves the discriminatory distribution of elements in two unlike immiscible liquids i.e. one is aqueous phase feed with metal and another is organic phase comprising extractant, diluent and modifier (in some cases). This technology offers cleaner separation [12].

Park *et al.* investigated the extraction efficiency of Cyanex 272 for the separation of Co (II) and Ni (II) from aqueous medium containing sulfuric acid. Cyanex 272 of 0.2 M was observed to be efficient for the separation of Co (II) (80%) and Ni (II) (1.9%) at 1:1 O/A ratio [13]. A process to recover Co (II) from secondary resources like Co-Mo and Co-Mn catalysts using Cyanex 923 has been developed by Gupta *et al.* [14] About 95% Co (II) with 99% purity has been reclaimed from the waste catalysts. They also investigated the extraction efficiency of Co (II) with different organic solvents or diluents like n–hexane, kerosene, xylene, toluene, chloroform and cyclohexanone. Kerosene (74%) and n-hexane (75%) with less dielectric constant value shows maximum extraction efficiency. Nayl *et al.* employed different forms of Aliquat 336 to selectively extract Co (II) from the aqueous phase containing Ni (II) and sulfuric acid [15]. Aliquat 336 thiocyanate (0.36 M), 2 M $H_2SO_4$, pH 4.8, 20 min shaking time are the optimum operating conditions where highest separation factor ($S_{Co/Ni}$ = 606.7) was observed. Synergistic mixture of HDEHP and LIX 860 has been applied by Elizalde *et al.* for Co (II) extraction from the feed solution containing 1 M $KNO_3$ [16]. The selectivity of extractants (Aliquat 336, Alamine 336, Alamine 300, Alamine 308, and tri-n-octyl phosphine oxide (TOPO), tri-butyl phosphate (TBP)) for the separation of molybdenum and Co (II) from the chloride aqueous feed containing aluminium has been investigated [17]. The results revealed that amine based

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extractants show selectivity towards Co whereas extractants with O-donor atom (TOPO and TBP) show selectivity towards Mo. Furthermore, among the extractants based on amine, tertiary amines were noticed as the potential extractants for extracting metals. Slimani *et al.* investigated the extraction efficiency of Co (II) in sulphate medium exploiting capric acid as extractant and chloroform as diluent [18].

Literature survey shows that solvent extraction of cobalt has been studied with high hydrochloric acid concentration using TOA in xylene. The present study focused on the solvent extraction of Co (II) from hydrochloric acid medium in presence of chloride salt using tri-n-octylamine in kerosene. To avoid the environmental issue, salt was added to the extraction process which minimizes the utilization of acid in TOA system. The extraction equilibrium of Co (II) has been evaluated by varying different operating parameters like phase contact time, concentration of TOA, HCl, cobalt and salting out agent, temperature, O/A ratio. In order to investigate role of diluents, extraction has been performed with different diluents.

## 2. Experimental procedure

### 2.1 Materials and methods

Tri-n-octylamine (TOA) purchased from Merck was used as extractant. Commercially available kerosene was used as organic phase diluents. $CoCl_2$, KCl, HCl, $NH_4Cl$, NaCl, $NH_4SCN$ used in this present investigation, all are of AR grade and were purchased from Merck. Xylene, toluene and benzene were acquired from Merck.

$CoCl_2$ (0.1 M) was prepared with the help of appropriate amount of $CoCl_2$ in distilled water. A small amount (1 mL) of conc. HCl was added to prevent hydrolysis. TOA (1.5 M stock solution) was prepared by dissolving requisite amount of TOA in kerosene. The aqueous phase containing cobalt (0.01 M), KCl (1.5 M) and HCl (3 M) was shaken with the organic phase for a period of equilibration time. The mentioned concentration of Co (II), KCl and HCl varies for respective variation experiments. After equilibration, both the phases were allowed to separate and raffinate was collected for the analysis of cobalt by thiocyanate method using UV-Visible spectrophotometer at 625 nm [19]. All the experiments are done in triplicate to avoid any kind of error.The extraction scheme is displayed in Figure 1.

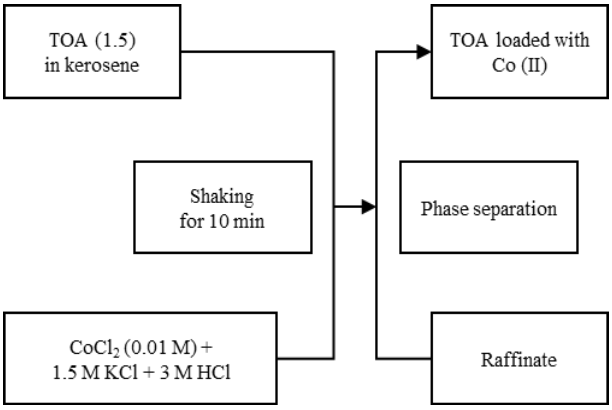

**Figure 1.** Extraction scheme of Co (II) from acidic chloride medium using TOA.

### 2.2 Instruments used

Citizen (CY320C) digital balance with accuracy ±0.001 g was used for weighing chemicals. Organic phase and aqueous phase were mixed properly with the help of magnetic stirrer (Spinot model MC- 02). In raffinate, Co (II) content was measured by Systronics UV-Visible spectrophotometer (model no. 2202). FTIR analysis was done by using Perkin Elmer FTIR Spectrometer.

### 2.3 Data analysis

Solvent extraction involves the measurement of equilibrium concentration of Co (II) in the aqueous phase and the organic phase, respectively. The extent of extraction has been estimated using various terms are discussed below:

Distribution ratio (D): It represents the ratio of concentration of Co (II) in the organic phase to that in the aqueous phase after extraction.

$$D = \frac{[Co]_{org}}{[Co]_{aq}} = \frac{[Co]_{bef} - [Co]_{aft}}{[Co]_{aft}} \quad (1)$$

Where $[Co]_{bef}$ and $[Co]_{aft}$ represents the concentrations of Co (II) in the aqueous phase before and after extraction, respectively.

Percentage of extraction (%E): The extent of Co (II) extracted to the organic phase with respect to the total amount of Co (II) present in aqueous phase before extraction is known as the percentage of extraction (%E).

$$\%E = \frac{100D}{D + \frac{V_{aq}}{V_{org}}} \quad (2)$$

Where $V_{aq}$ and $V_{org}$ represent the aqueous phase and organic phase volumes, respectively.

## 3. Results and discussion

### 3.1 Influence of aqueous and organic phase contact time

The extraction equilibrium is achieved in a definite time period which is specific for each extraction system. In order to know the minimum time required for attainment of equilibrium in case of Co (II) extraction with TOA, the contact time between the aqueous phase and organic phase has been varied in the range of 5 min to 30 min. The percentage extraction of Co (II) has been found to be 59.75% at 5 min contact time which rose to 61.06% when the contact time of both the phases became 10 min and remained unvaried (i.e. 61.04% and 61.02%) even if contact time was later increased to 20 min and 30 min (Table 1). So, for further investigations, the contact time was fixed at 10 min.

### 3.2 Effect of TOA molarity

As extractants are involved in the complex formation with the metal ion, their concentration boosts the extraction process. More the concentration of extractants more will be the availability of extractants for cobalt and hence, the complexation between cobalt and TOA becomes more. In this context, the influence of TOA concentration variation on the extraction of 0.01 M Co (II) has been explored. The molarity of TOA has been varied from 0.08 M to 0.5 M. The extraction of Co (II) was enhanced from 38.57% to 73.46% with the rise in TOA molarity from 0.08 M to 1.5 M (Figure 2 and Table 2). The logarithmic plot of distribution ratio and TOA molarity yields a slope of 0.512 indicating the participation of one mole of TOA in the extraction equilibrium.

### 3.3 Influence of HCl concentration

The acid concentration in the aqueous feed solution has a significant role in case of metal extraction with tertiary amine. The pKa value of HCl(=-7) is very less than that of TOA(=35) and therefore it gives proton easily to TOA and being a tertiary amine gets protonated first and then extract the cobalt complex into the organic phase. Besides, it has been reported that the extraction efficiency of amine based extractants towards Co (II) enhances by HCl molarity in aqueous phase [17]. Therefore, the influence of HCl concentration on the extraction of 0.01 M Co (II) using 0.1 M TOA diluted in kerosene has been examined. The molarity of HCl was varied in the range of 2.5 to 4 M. After extraction, it was found that %E increased from 29.58% to 65.18% with increase in HCl molarity from 2.5 to 4 M (Figure 3 and Table 3).

**Table 1**. Influence of contact time on Co (II) extraction. [aqueous phase: [Co (II)] = 0.01 M, [HCl] = 3 M, [KCl] = 1.5 M, T = 298 K, and organic phase: [TOA] =0.1 M, O/A ratio = 1:1, equilibration time = 5-30 min].

| Time (min) | D | %E |
|---|---|---|
| 5 | 1.48 | 59.75 |
| 10 | 1.57 | 61.06 |
| 20 | 1.57 | 61.04 |
| 30 | 1.57 | 61.02 |

**Table 2**. Influence of concentration of TOA on Co (II) extraction. [aqueous phase: [Co (II)] = 0.01 M, [HCl] = 3 M, [KCl] = 1.5 M, T = 298 K, and organic phase: [TOA] =0.08-0.5 M, O/A ratio = 1:1, equilibration time = 10minutes].

| [TOA] (M) | D | %E |
|---|---|---|
| 0.08 | 0.63 | 38.57 |
| 0.1 | 1.57 | 61.06 |
| 0.15 | 1.68 | 62.75 |
| 0.2 | 1.78 | 64.07 |
| 0.5 | 2.77 | 73.46 |

**Table 3**. Influence of concentration of HCl on Co (II) extraction. [aqueous phase: [Co (II)] = 0.01 M, [HCl] = 2.5-4 M, [KCl] = 1.5 M, T = 298K, and organic phase: [TOA] =0.1 M, O/A ratio = 1:1, equilibration time = 10 min].

| [HCl] (M) | D | %E |
|---|---|---|
| 2.5 | 0.42 | 29.58 |
| 3 | 1.57 | 61.06 |
| 3.5 | 1.75 | 63.80 |
| 4 | 1.87 | 65.18 |

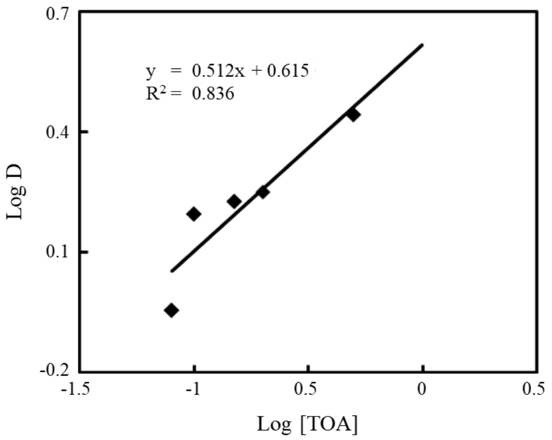

**Figure 2.** Logarithm plot of distribution ratio and TOA concentration for the extraction of Co (II). [aqueous phase: [Co (II)] = 0.01 M, [HCl] = 3 M, [KCl] = 1.5 M, T = 298 K and organic phase: [TOA] = 0.08-0.5M in kerosene, equilibration time = 10 min, O/A ratio=1:1].

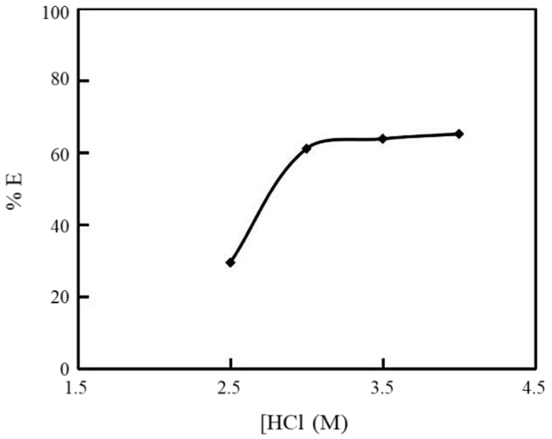

**Figure 3.** Plot of %E of Co (II) versus [HCl], M. [aqueous phase: [Co (II)] = 0.01 M, [KCl] = 1.5 M, [HCl] = 2.5-4 M, T = 298K and organic phase: [TOA] = 0.1 M in kerosene, equilibration time = 10 min, O/A ratio=1:1].

### 3.4 Effect of various salts

In the present investigation, Co (II) is extracted as chloride complex. Therefore, the presence of chloride salt in the aqueous feed enhance the extraction efficiency. To study the influence of chloride salt on the extraction efficiency, the extraction of 0.01 M Co (II) from the aqueous feed solutions containing different salts like NaCl, KCl and $NH_4Cl$ has been carried out using 0.1 M TOA in kerosene as organic solvent. The concentrations of different salts were varied in the range of 0.5 to 1.5 M. The presence of chloride salts in the aqueous feed increases the extraction of cobalt even with low concentration of acid due to salting out effect and common ion effect (as per the suggested extraction equilibrium) [20]. It was found that the extraction percentage of Co (II) increases in the order $NH_4Cl$<NaCl<KCl (Figure 4). This is attributed to the larger size of $K^+$, being larger in size it becomes less hydrated than $Na^+$ and hence, the ability to remove the hydration sphere of metal ion increases resulting maximum salting out effect.

For the case of $NH_4^+$, the minimum salting out effect may be attributed to the possibility of formation hydrogen bond with water molecules. Table 4 shows the variation of distribution ratio of Co (II) as a function of various salt concentrations.

## 3.5 Mechanism for extraction of Co (II) with TOA

In the chloride medium, $Co^{2+}$ ion exists in the form of several complexes. During extraction with amine, anionic species of cobalt gets exchanged with the counter ion of the protonated amine. It is decided by the oxidation state of cobalt and distribution of chloride ions [21]. Lee et al. [22] has developed a model based on the ionic equilibrium of cobalt (II) in chloride solution. They observed that the formation constant (log K) for $CoCl_2$ and $CoCl_3^-$ are -3.95 and -3.02, respectively. Basing on the slope analysis results obtained in this study and considering the log K values of cobalt complexes, it has been suggested that cobalt is extracted in the form of cobalt-chlorido complex. Here, TOA extracts Co (II) simply by addition reaction (Figure 5). The following equation expresses the proposed extraction mechanism for the extraction of Co (II) with TOA.

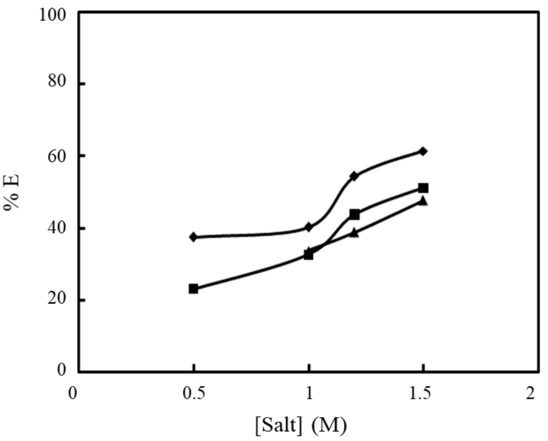

**Figure 4.** Plot of %E of Co (II) versus chloride salt concentration. [aqueous phase: [Co (II)] = 0.01 M, [HCl] = 3 M, [Salt] = 0.5 M, 1 M, 1.2 M and 1.5 M, ♦ KCl, ■NaCl, ▲$NH_4Cl$ , T = 298 K and organic phase: [TOA] = 0.1 M in kerosene, equilibration time = 10 min, O/A ratio = 1:1].

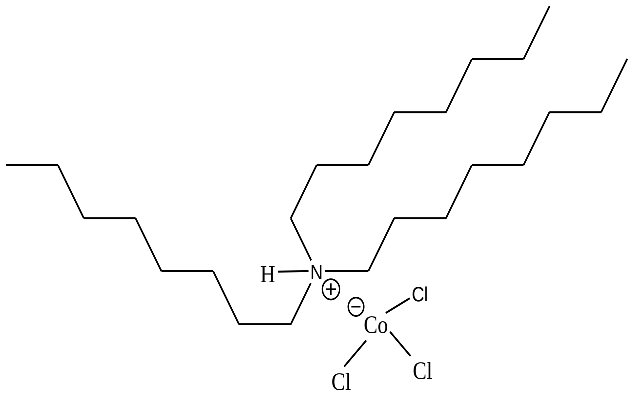

**Figure 5**. Structure of extractable complex formed between TOA and cobalt.

**Table 4**. Variation of distribution ratio of Co (II) as a function of various salt concentrations. [aqueous phase: [Co (II)] = 0.01 M, [HCl] = 3 M, [KCl], [NaCl], [$NH_4Cl$] = 0.5-1.5 M, T = 298 K, and organic phase: [TOA] = 0.1 M, O/A ratio = 1:1, equilibration time = 10 min].

| [Salt] (M) | D | | | %E | | |
|---|---|---|---|---|---|---|
| | KCl | NaCl | $NH_4Cl$ | KCl | NaCl | $NH_4Cl$ |
| 0.5 | 0.60 | 0.30 | 0.32 | 37.27 | 23.01 | 24.39 |
| 1 | 0.67 | 0.48 | 0.51 | 40.11 | 32.46 | 33.65 |
| 1.2 | 1.18 | 0.78 | 0.63 | 54.22 | 43.71 | 38.69 |
| 1.5 | 1.57 | 1.04 | 0.91 | 61.06 | 51.09 | 47.58 |

Protonation of amine

$$R_3N(org) + HCl(aq) \rightarrow R_3NHCl(org) \qquad (3)$$

Complexation of cobalt with protonated amine

$$CoCl_2(aq) + Cl^-(aq) + R_3NH^+(org) \leftrightarrow (R_3NH)CoCl_3\,(org) \qquad (4)$$

The equilibrium constant is given by

$$K_{eq} = \frac{[(R_3NH)CoCl_3\,(org)]}{[CoCl_2(aq)][Cl^-(aq)][R_3NH^+(org)]} \qquad (5)$$

$$K_{eq} = \frac{D}{[Cl^-(aq)][R_3NH^+(org)]} \qquad (6)$$

$$logD = logK_{eq} + log[Cl^-] + log\,[R_3NH^+] \qquad (7)$$

## 3.6 Effect of temperature

Thermodynamic study is of great importance in the process of solvent extraction. Lower the operating temperature of extraction process, less energy is consumed. The extraction of Co (II) with 0.1 M TOA in kerosene was carried out at 298 K, 308 K, 318 K and 328 K.respectively. It was found that the percent of extraction increased from 61.06% to 72.49% with the increase in temperature (Figure 6 and Table 5). The plot of log $K_{eq}$ against 1000/T gives the slope (-0.824) and intercept (3.767) from which $\Delta H^\circ$ and $\Delta S^\circ$ values were determined with the help of Van't Hoff equation (equation 8). From the plot (Figure 5) $\Delta H^\circ$ and $\Delta S^\circ$ values were evaluated as 15.77 $kJ\cdot mol^{-1}$ and 72.13 $J\cdot K^{-1}mol^{-1}$, respectively. The positive value of enthalpy shows that the binding of TOA with Co (II) proceeds with absorption of heat and increase in temperature favors the extraction of Co (II) with TOA. The positive value of entropy reveals the release of water molecules from the Co (II)-hydrated species resulting inner sphere complexation between Co (II) and TOA.

$$log\,K_{eq} = -\frac{\Delta H^0}{2.303\,RT} + \frac{\Delta S^0}{2.303R} \qquad (8)$$

## 3.7 Influence of molarity of Co (II) in aqueous feed on the extraction

To know the metal loading capacity of the extractant, the molarity of Co (II) was varied in the range of 0.005 M to 0.03 M along with

1.5 M KCl, 3 M HCl in aqueous phase and extraction has been performed with 0.1 M TOA in kerosene as organic phase. It has been noticed that the extraction percentage decreased from 66.7% to 31.0% when Co (II) concentration changed from 0.005 M to 0.03 M (Table 6). At higher Co (II) concentration, less amount of available extractant results in the observed decrease in the percentage of extraction.

### 3.8 Effect of diluents

Diluent plays an important role in determining solvent characteristics and transport properties. Its polarity also influences the complexation process. Hence, it is important to study the impact of diluents on extraction [23]. Influence of diluents on the extraction of Co (II) with TOA has been thoroughly investigated with various organic diluents like benzene, toluene, kerosene and xylene. Maximum extraction of Co (II) has been achieved using kerosene as diluent (Table 7). Kerosene is non polar and less toxic and cheaply available. It has been observed that increase in extraction of Co (II) occurs with the decrease in dielectric constants of the diluents.

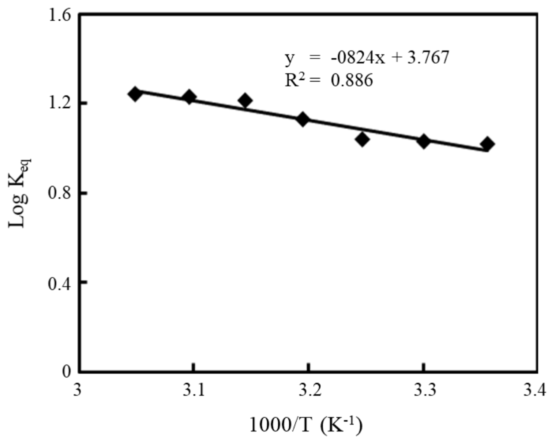

**Figure 6.** Plot of log $K_{eq}$ against 1000/T. [aqueous phase: [Co (II)] = 0.01 M, [HCl] = 3 M, [KCl] = 1.5 M, T = 298 K, 308 K, 318 K and 328 K and organic phase: [TOA] = 0.1 M in kerosene, O/A ratio = 1:1, equilibration time = 10 min].

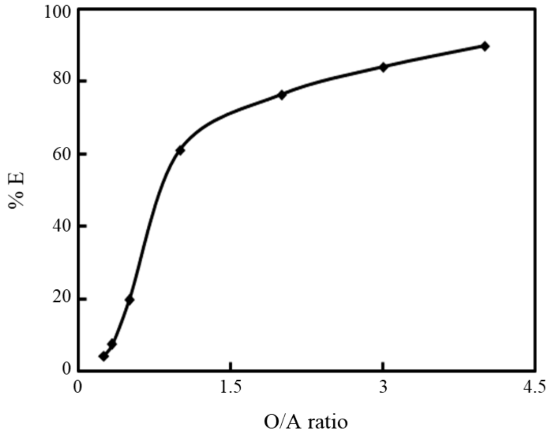

**Figure 7.** Plot of %E versus Co (II) concentration in the aqueous feed. [aqueous phase: [Co (II)] = 0.01 M, [HCl] = 3 M, [KCl] = 1.5 M, T = 298 K and organic phase: [TOA] = 0.1 M in kerosene, O/A ratio = 1:4-4:1, equilibration time = 10 min].

### 3.9 Influence of organic phase volume: aqueous phase volume ratio in extraction

Organic to aqueous phase volume ratio plays a significant role in the extraction process. The possibility of maximum extraction of Co (II) in single contact and the number of stages required for maximum extraction at the chosen O/A phase volume ratio could be predicted by varying the phase volume ratios. In this extraction process, the O/A phase volume ratio was raised from 1:4 to 4:1. It was found that the extraction of Co (II) was enhanced from 15% to 68.61% (Figure 7 and Table 8).

**Table 5.** Variation of distribution ratio of Co (II) as a function of T. [aqueous phase: [Co (II)] = 0.01 M, [HCl] = 3 M, [KCl] = 1.5 M, T = 298 K, 308 K, 318 K and 328 K and organic phase: [TOA] = 0.1 M in kerosene, O/A ratio = 1:1, equilibration time = 10 min].

| Temperature (K) | D | %E |
|---|---|---|
| 298 | 1.57 | 61.06 |
| 303 | 1.61 | 61.70 |
| 308 | 1.65 | 62.21 |
| 313 | 2.02 | 66.93 |
| 318 | 2.46 | 71.07 |
| 323 | 2.55 | 71.83 |
| 328 | 2.64 | 72.49 |

**Table 6.** Variation %E of Co (II) as a function of its initial concentration in the aqueous feed. [aqueous phase: [Co (II)] = 0.005-0.03 M, [HCl] = 3 M, [KCl] = 1.5 M, T = 298 K and organic phase: [TOA] = 0.1 M in kerosene, O/A ratio = 1:1, equilibration time = 10 min].

| [Co (II)] (M) | D | %E |
|---|---|---|
| 0.005 | 2.00 | 66.70 |
| 0.01 | 1.57 | 61.06 |
| 0.02 | 0.94 | 48.53 |
| 0.03 | 0.45 | 31.00 |

**Table 7**. Influence of diluents on Co (II) extraction. [aqueous phase: [Co (II)] = 0.01 M, [HCl] = 3 M, [KCl] = 1.5 M, T = 298 K, and organic phase: [TOA] =0.1 M, O/A ratio = 1:1, equilibration time = 10 min].

| Diluent | Dielectric constant | D | %E |
|---|---|---|---|
| Xylene | 2.46 | 0.353 | 26.09 |
| Toluene | 2.38 | 0.355 | 26.21 |
| Benzene | 2.28 | 0.422 | 29.70 |
| Kerosene | 1.82 | 1.568 | 61.07 |

**Table 8.** Variation %E of Co (II) as a function of O/A phase volume ratio. [aqueous phase: [Co (II)] = 0.01 M, [HCl] = 3 M, [KCl] = 1.5 M, T = 298 K and organic phase: [TOA] = 0.1 M in kerosene, O/A ratio = 1:4-4:1, equilibration time = 10 min].

| O/A ratio | D | %E |
|---|---|---|
| 0.25 | 0.04 | 4.07 |
| 0.33 | 0.08 | 7.40 |
| 0.50 | 0.24 | 19.52 |
| 1 | 1.57 | 61.06 |
| 2 | 3.22 | 76.30 |
| 3 | 5.21 | 83.90 |
| 4 | 8.72 | 89.71 |

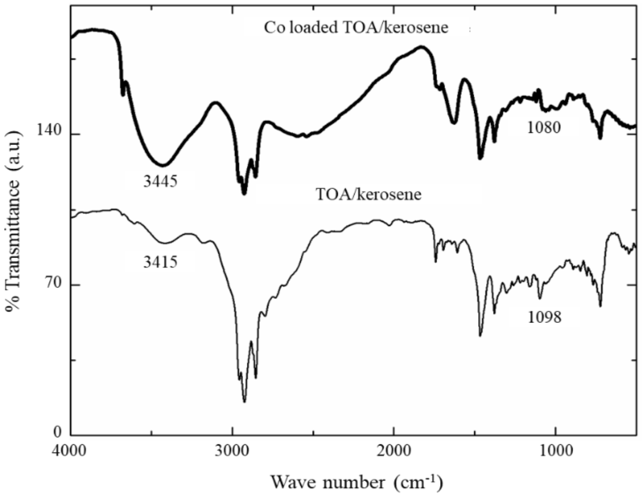

**Figure 8.** FTIR spectra of TOA in kerosene and organic extract with Co (II).

### 3.10 FTIR analysis

The FTIR spectra of organic extract containing 0.1 M TOA in kerosene and organic extract with Co (II) has been presented in Figure 8. The analysis shows that the peaks corresponding to -C-H stretching vibrations are same in both TOA/kerosene and Co loaded TOA in kerosene. Nonetheless, there is a shifting in the peak position from 3415 $cm^{-1}$ in TOA/kerosene to 3445 $cm^{-1}$ in Co loaded TOA in kerosene which is due to –O-H stretching vibration. The peak at 1098 $cm^{-1}$ in TOA in kerosene due to –C-N stretching vibration has been shifted to 1080 $cm^{-1}$ in case of Co (II) loaded TOA in kerosene which indicates that there is complexation between Co (II) and TOA [24].

## 4. Conclusions

The extraction results obtained from various investigations for the extraction of 0.01 M Co (II) from the aqueous feed containing 3 M HCl, 1.5 M KCl and 0.1 M TOA in kerosene shows that a maximum extraction of 89.71% occurs at 4:1 O/A ratio. TOA concentration, salt concentration and O/A ratio have positive influence on the percentage of extraction of Co (II). KCl shows maximum extraction efficiency due to higher salting out effect than $NH_4Cl$ and NaCl. Thermodynamic study confirms that the extraction equilibrium is endothermic and degree of disorderness increases due to release of water molecules of hydration during cobalt complexation. FTIR data confirms the binding of Co (II) with TOA. The extraction of Co (II) using TOA in non-toxic diluent kerosene from low acidic chloride medium may have significant contribution to the metallurgical research relevant for the recovery of cobalt from secondary resources.

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