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# Comparative Studies on The Extraction of Cobalt from Chloride Medium using Different Extractants

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**Abstract**

The extraction of cobalt from chloride medium using two organophorous extractants: bis (2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272) and di-(2-ethyl-hexyl) phosphoric acid (D2EHPA) was studied. The important parameters governing the extraction of cobalt have been studied. These parameters are the aqueous phase pH, the extractant concentration and the stripping phase type and concentration. A comparison between Cyanex 272 and D2EHPA has been established. The distribution of cobalt (II) 100 ppm between aqueous chloride medium and kerosene solutions of Cyanex 242 or D2EHPA has been studied. The extraction equilibrium is influenced by the extractant concentration and the equilibrium pH value of the aqueous medium. The distribution data have been graphically analysed. The results show that the species extracted into the organic phase have the composition of $CoA_2$.3HA for cyanex 272.$CoA_2$.HA was also observed. As for D2EHPA, $CoA_2$ was observed and the polymerized tetrahedral complex. The extraction constant with Cyanex 272 was higher than D2EHPA. The stripping was studied for both extractants using H2SO4 and HCl. Cobalt (II) of the extracted Co (II) was stripped from Cyanex 272 at lower acid concentration than D2EHPA.

**Keywords:** Cyanex 272/D2EHPA/Cobalt extraction/chloride medium

## 1. Introduction

Cobalt is an essential element in our life and is widely used in many industrial and nuclear applications. On the other hand, if it is present in large concentrations in the liquid wastes, it may cause a serious environmental pollution. Accordingly, its separation and recovery from waste materials (industrial and nuclear) is of important need before disposal to the landfill[1].

Solvent extraction technique is one of the various methods used for the extraction of cobalt from aqueous solutions[2-6]. Organophosphorous extractants are the most widely established reagents for the extraction of cobalt [2-4, 7-9].

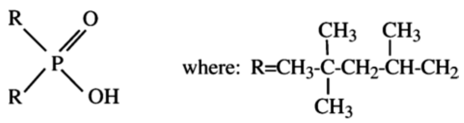
K. Sarangi et al. studied the extraction of cobalt (II) and nickel (II) from chloride medium using Na-Cyanex 272. The found that one mole of $H^+$ exchanged with 1 mole of the extracted metal species and two moles of the extractant were associated with the extracted metal species [10]. Wu Jinguang et al. studied the structure and aggregates formed from cobalt-D2EHPA complexes in solvent extraction from chloride medium using FT-IR, UV-Vis and photon correlation spectroscopic (PCS) techniques [11]. They found that tetrahedral $CoA_2$ is formed. A polynuclear tetrahedral complex may also be formed [11]. Fernandes et al. investigated the recovery and separation of Co and Ni from batteries waste dissolved in 8M HCl using Cyanex 923 as extractant. They found that >99% of the extracted metals are separated using a nitrate strip [12].

The aim of the present work is to study the efficiency of using two different acidic compounds of such organophosphorous extractants for separation of cobalt from an aqueous chloride medium. These two extractants are bis (2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272) and di-(2-ethyl-hexyl) phosphoric acid (D2EHPA). The different parameters affecting the extraction and stripping processes using both extractants will be investigated. A comparative study on the results obtained from both extractants will be established.

## 2. Experimental

### 2.1 Solutions and reagents

Stock solutions of 100 ppm cobalt (II) were prepared by dissolving analytical grade $CoCl_2{\cdot}6H_2O$ in distilled water. The aqueous solutions for the solvent extraction experiments were prepared in 1 M NaCl solution to maintain constant ionic strength of the aqueous phase. Stock solutions of 1.0 M $H_2SO_4$ and HCl were prepared for the stripping of cobalt from the loaded organic phase. The commercial extractant Cyanex 272 was kindly supplied by Cytec and was used without further purification. It has the structure:



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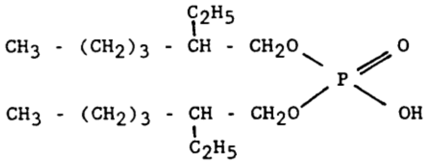
The commercial extractant D2EHPA was supplied by MERCK and has the following structure:



Commercial grade kerosene was supplied by Misr Company for Petroleum. The stock solutions of Cyanex 272 or D2EHPA were prepared by dilution in kerosene at a predetermined concentration.

**2.2 Solvent extraction procedures**

Equal volumes of the organic phase containing the extractant dissolved in kerosene and the aqueous phase containing 100 ppm of cobalt (II) in 1M NaCl medium of a constant ionic strength were shaken mechanically at constant speed and temperature. Different time intervals of shaking were used and checked till reaching equilibrium. Solutions were centrifuged to obtain complete phase separation. Known aliquots from the aqueous phase were withdrawn for analysis. Samples that formed third phase were excluded.

The distribution ratio (D) of Cobalt in each sample was calculated from eq. (1)[13]:

$$D = \frac{\sum[M]_{t,org}}{\sum[M]_{t,aq}} \qquad (1)$$

Where $[M]_{t,org}$ is the total metal ion concentration in the organic phase and $\sum[M]_{t,aq}$ is the total metal ion concentration in the aqueous phase

The percent extraction (%E) was calculated using eq. (2)[13]:

$$\%E = \frac{D}{1+D} X100 \qquad (2)$$

The stripping behavior was studied by shaking equal volumes of the stripping phase and the organic phase loaded with cobalt mechanically. Different time intervals of shaking were used and checked till reaching equilibrium. . Solutions were centrifuged to obtain complete phase separation. Known aliquots from the aqueous phase were withdrawn for analysis.

**2.3 Analytical methods**

The concentration of cobalt in the aqueous phases was measured by uv-vis spectrophotometer using the thiocyante method for concentrations above 7ppm and the nitrosonaphthol method for concentrations lower than 7 ppm[14].

**3. Results and discussion**

**3.1 Extraction equilibrium of cobalt**

The extraction of cobalt by organic acids such as Cyanex 272 and D2EHPA can be represented by the following general reaction:

$$M_{aq}^{+n} + (n+m)HA_{org} \rightarrow MA_n.mHA_{org} + nH^+ \qquad (1)$$

The extraction constant can be written as:

$$K_{ex} = \frac{[MA_m.mHA_{org}][H^+]^n}{[M^{+n}][HA_{org}]^{(n+m)}} \qquad (2)$$

The distribution ratio of the metal can be defined as:

$$D_M = \frac{[MA_n.mHA_{org}]}{[M^{+n}]} \qquad (3)$$

By the substitution from eq. (3) into eq. (2):

$$K_{ex} = D_M \frac{[H^+]^n}{[HA_{org}]^{(n+m)}} \qquad (4)$$

And rearrangement:

$$D_M = K_{ex} \frac{[HA_{org}]^{(n+m)}}{[H^+]^n} \qquad (5)$$

Taking the logarithm for both sides:

$$\log D_M = \log K_{ex} + (n+m)\log[HA_{org}] - n\log[H^+] \qquad (6)$$

$$\log D_M = \log K_{ex} + (n+m)\log[HA_{org}] + n\,pH \qquad (7)$$

**3.2 Effect of equilibrium pH**

The extraction of cobalt from a solution of cobalt (II) in 1M NaCl was studied using Cyanex 272 (0.1 M) in the equilibrium pH range from 3.2-5.8 and D2EHPA (0.1M) in the equilibrium pH range from 2-5.4.The pH was adjusted using diluted solutions of NaOH and HCl. The effect of the equilibrium pH on the extraction of cobalt from the chloride solution is shown in Fig. 1. The percentage extraction of cobalt was observed to increase remarkably from 11.55% to 98.8% with increasing the equilibrium pH up to 5.8 in the aqueous phase for Cyanex 272 and from 9.7% to 97.6 with increasing the equilibrium pH up to 5 in the aqueous phase for D2EHPA.Cyanex 272 showed $pH_{50}$ of 4.5 while D2EHPA showed a lower $pH_{50}$ at 3.75. The extraction of cobalt at pH values higher than 7.0 is not desirable since cobalt hydroxide may precipitate.

**3.3 Slope analysis**

The dependency of Log D on the equilibrium pH values for the extraction of cobalt using 0.02 M and 0.1 M for both extractants, D2EHPA or Cyanex 272 was illustrated in Figs. 2 and 3, respectively. For both extractants, straight line were obtained of slopes 0.66 and 0.88 in case of

D2EHPA which indicates that one mole of $[H^+]$ is released in the aqueous medium. In case of Cyanex 272, the slope was found to equal 1.78 and 1.54 which indicates that two moles of $[H^+]$ are released in the aqueous medium.

From eq. (7), $\text{Intercept} = \log K_{ex} + (n+m)\log[HA_{org}]$

Substituting the values of the intercept and the extractant concentration resulted in two linear equations for each extractant. By solving the two equations simultaneously, the conditional extraction constant ($K_{ex}$) and the total number of the extractant molecules involved were obtained. Cyanex 272 showed a higher extraction constant of 0.0162 than D2EHPA of 0.0053.

Form the free energy equation $\Delta G^{\circ}_{ex} = -RT \ln K_{ex}$ [12]

The free energy of extraction of cobalt using Cyanex 272 was 10.215 Kj/mol. For D2EHPA, it was 12.983 Kj/mol. The extraction of cobalt using Cyanex 272 is more thermodynamically feasible than using D2EHPA, because it showed relatively less positive free energy of extraction.

The total number of extractant molecules involved was 1 in case of D2EHPA and 5 in case of Cyanex 272. In case of D2EHPA, the total number of the involved extractant molecules was in confirmation with the slope analysis. The extracted species should take at least two extractant molecules in the coordination sphere. The lower obtained number may be due to polymerization and aggregation. In case of Cyanex 272, two molecules are in the coordination sphere obtained from slope and three are hydrogen bonded to the tetrahedral complex form the difference between the total number of involved molecules calculated from the intercept and the coordinated molecules calculated from slope.

### 3.4 Effect of extractant concentration

The effect of D2EHPA and Cyanex 272 concentrations on the distribution coefficient is shown in Fig.4 and Fig.5 respectively. The data indicate that increasing the extractant concentration caused an increase in the distribution ratio. Straight lines were obtained from the plots of log extractant concentration. versus log D.

For D2EHPA, two linear plots were obtained at two equilibrium pH 4 and 4.5 with slopes of 1.62 and 1.7, respectively. The slope is equal to the total number of involved extractant molecules in the extracted species. This means that two D2EHPA molecules contribute to the extracted species forming a tetrahedral complex with the loss of the ionizable hydrogens. This is different from the data obtained from the slope and intercept analysis of Fig.2. D2EHPA tends to polymerize in high concentration and low equilibrium pH values. The difference may originate from that.

As for Cyanex 272, two linear plots were obtained at two equilibrium pH 5 and 5.5 with slopes of 2.83 and 2.89 respectively. That means that three Cyanex 272 molecules contribute to the extracted species.Two of them are in the coordination sphere according to the slope analysis of Fig.3. forming a tetrahedral complex with the loss of the ionizable hydrogens . The remaining molecule is hydrogen bonded to the tetrahedral complex. This is different from the slope and intercept analysis of fig.3.

This may be attributed to the high tendency of phosphinic acid molecules in general and Cyanex 272 molecules to form hydrogen bonds with each other at various orientations [15]. High concentrations of Cyanex 272 and low equilibrium pH increase hydrogen bonding. So the hydrogen bonded cyanex 272 molecules to the tetrahedral complex decreases due to higher equilibrium pH.

### 3.5 Stripping

The cobalt-loaded solutions were stripped with equal volumes of varying concentrations of mineral acids and the stripping behaviors of cobalt with respect to the different mineral acids and concentrations are shown in fig. 4 and fig.5. The stripping of cobalt increased with increasing the mineral acid concentration for both Cyanex 272 and D2EHPA.

**Table 1.** gives the minimum concentrations of the mineral acids required for efficient stripping from both extractants obtained from fig.4 and fig.5.

| | Cyanex 272 | D2EHPA |
|---|---|---|
| **$H_2SO_4$** | 0.016 M | 0.032 M |
| **HCl** | 0.04 M | 0.05 M |

Table1. The minimum concentrations of the mineral acids required for efficient stripping from cobalt-loaded Cyanex 272 and D2EHPA.

It can be seen that the stripping from Cyanex 272 and D2EHPA is more efficient using $H_2SO_4$ as stripping agent than hydrochloric acid for both extractants.

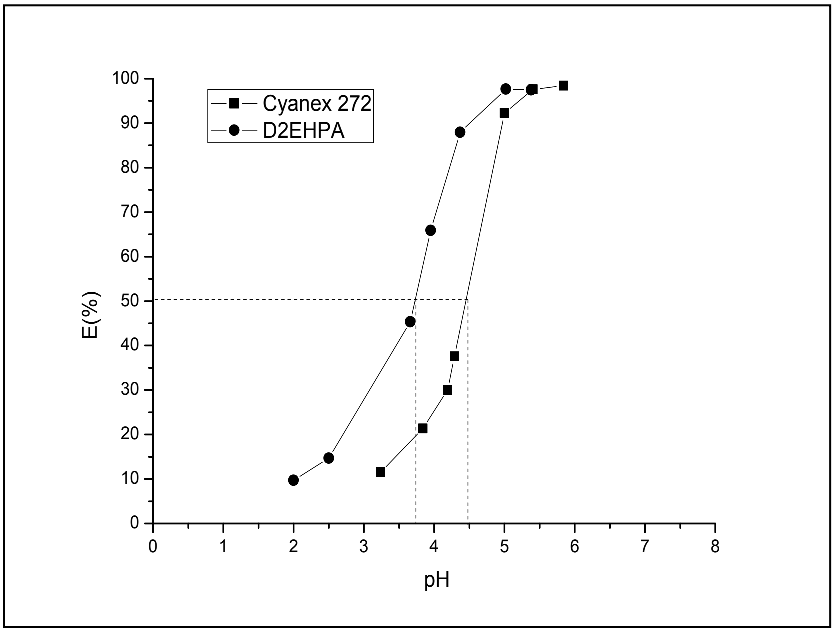



**Fig 1.** Effect of pH on the extraction of cobalt. Organic phase: 0.1M Cyanex 272 (■) or 0.1 M D2EHPA (●). Aqueous phase: 100 ppm cobalt (II) in 1 M NaCl

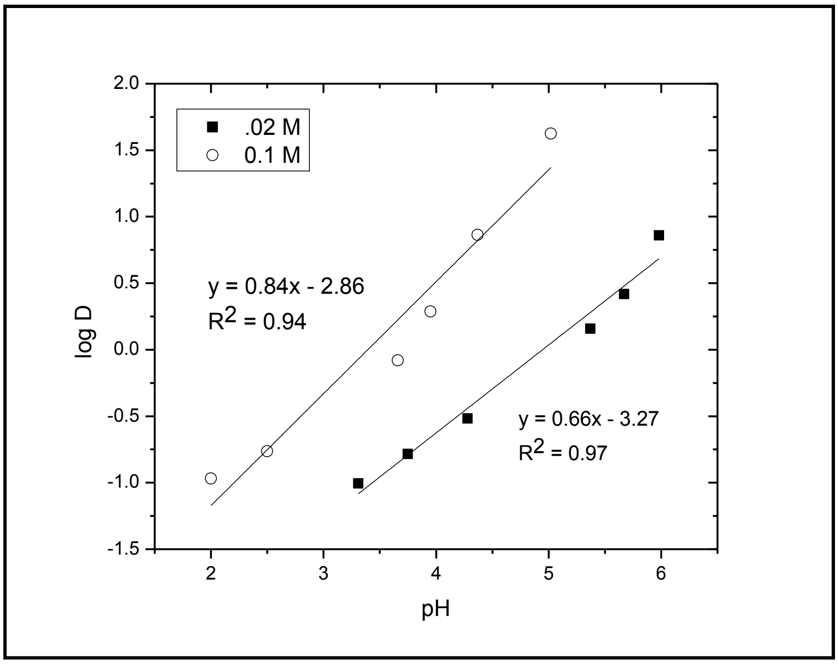



**Fig 2.** Effect of pH on log D.Organic phase: 0.02M D2EHPA (■) or 0.1 M D2EHPA (○). Aqueous phase: 100 ppm cobalt (II) in 1 M NaCl.

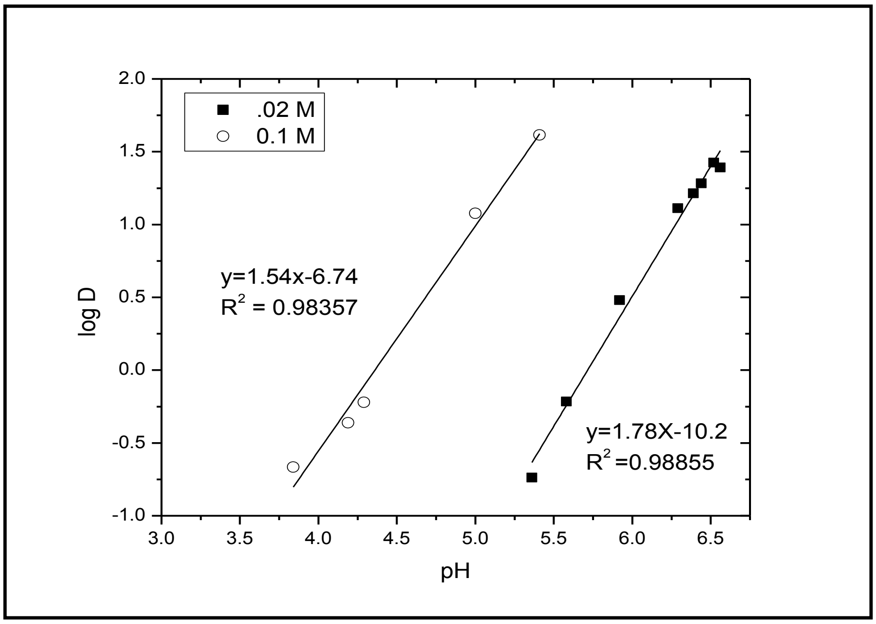



**Fig 3.** Effect of pH on log D. Organic phase: 0.02M Cyanex 272(■) or 0.1 M Cyanex 272 (○). Aqueous phase: 100 ppm cobalt (II) in 1 M NaCl.

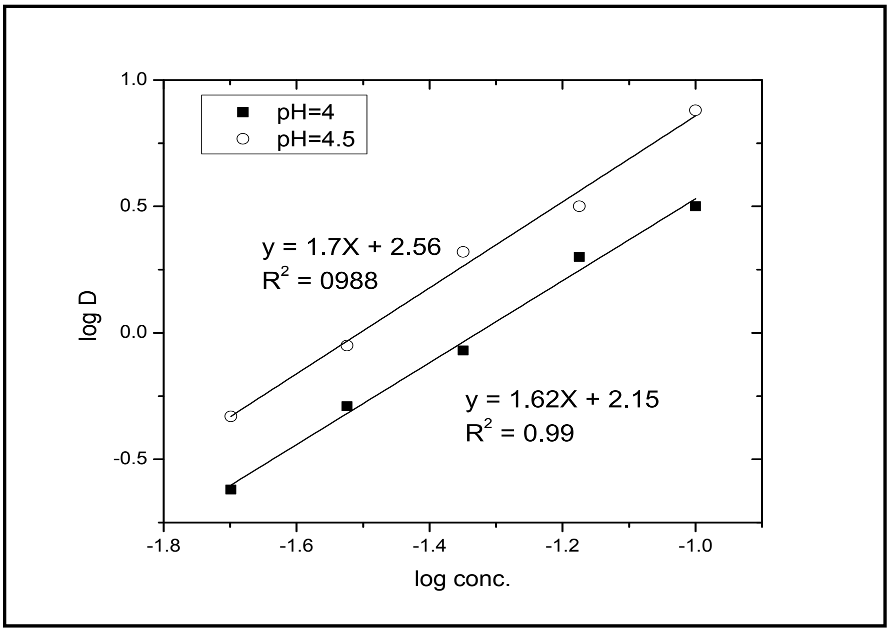



**Fig 4.** Effect of log of D2EHPA concentration on log D at two different equilibrium pH: pH = 4 (■) and pH = 4.5 (○). Organic phase: 0.1 M D2EHPA. Aqueous phase: 100 ppm cobalt (II) in 1 M NaCl.

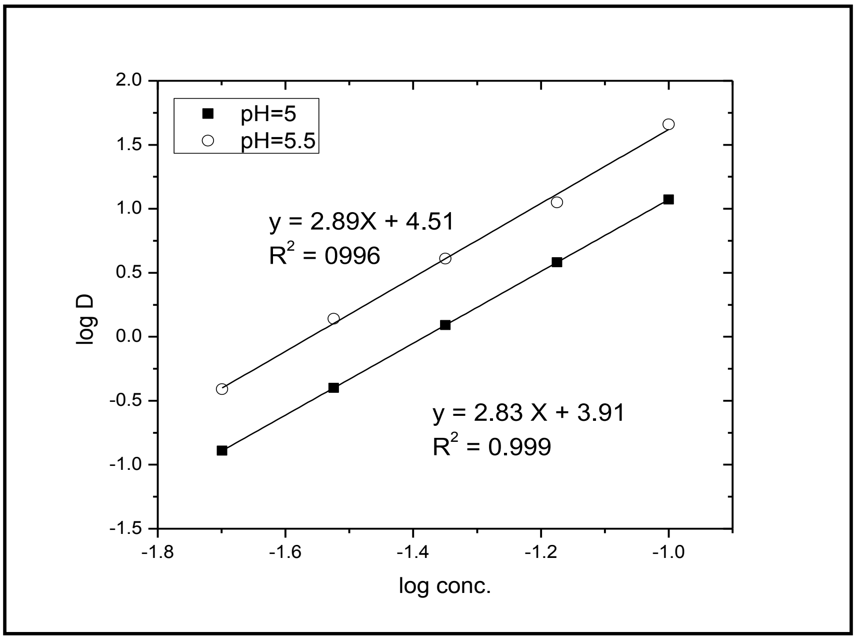



**Fig 5.** The Effect of mineral acids concentration on stripping of cobalt from loaded organic phase using different mineral acids. Organic phase: 0.1 M D2EHPA loaded with cobalt. Strip phase: sulphric acid (■) or hydrochloric acid (●).

**4. Conclusion**

Extraction of cobalt from a chloride solution has been studied using Cyanex 272 and D2EHPA. Cyanex 272 requires a little higher equilibrium pH than D2EHPA to achieve the desired extraction efficiency. Stripping studies of cobalt from the loaded organic phase with $H_2SO_4$ and HCl showed that $H_2SO_4$ is a better stripping agent and the stripping from loaded Cyanex 272 solution is easier than loaded D2EHPA solution.

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