Extraction Equilibria of Cobalt (II) with 3-Hexylaminopyridine in Kerosene from Aqueous Solution in Chloride Media

Maroti V. Kanetkar[1]*, Jivan M. Kondare[1], Gopal K. Kakade[2]

[1]*Department of Chemistry, Yogeshwari Mahavidyalaya Ambajogai, Maharashtra, India*, [2]*Department of Chemistry, Arts Commerce and Science College, Kille Dharur, Maharashtra, India*

ABSTRACT

Extraction equilibria of cobalt (II) from aqueous chloride solutions with 3-hexylaminopyridine (3-HAP) dissolved in kerosene was investigated. Results showed that KCl salt can greatly improve the cobalt (II) extraction efficiency. The distribution coefficients were significantly dependent on the concentration of chloride ions and the pH value in the aqueous phase because of mechanism of extraction and complex formation in the organic phase. With initial pH value of pH 1–2 and chloride ion concentration 1.0 mol L^{-1}, the maximum extraction (>90%) was observed. In addition, 2.0 mol L^{-1}–2.5 mol L^{-1} concentrations of hydrochloric acid in aqueous phase increase the extraction efficiency. Extraction equilibrium by 3-HAP with cobalt (II) was established within 10 min.

Key words: 3-Hexylaminopyridine, Extraction equilibria, Cobalt (II), Kerosene

1. INTRODUCTION

Solvent extraction, a hydrometallurgical separation and purification technique, is a selective, cost efficient, and simpler chemical process. In metal recovery and refining activities, this technique is proving to be a powerful tool, providing new opportunities to exploit low value metal ores and metal recycling [1]. Even though solvent extraction has been employed in the refining of nickel and cobalt since the early 1980, its commercial applications have been largely restricted to process relatively small flows of concentrated cobalt solutions. In the present scenario, treatment of low-value ores and recycling returns of these metals are not attractive enough to spend more money on the development of new extractant with high selectivity and efficiency. Hence, the development in the solvent extraction of metals is basically resorted on the utilization of existing commonly available commercial extractant. Step-wise approach or the use of more than 1 extractant type as an integrated solvent extraction circuit is often adopted [2]. Many authors have reported synergistic extraction of these metals using mixed extractant [3-5]. Recent review of the research reveals that cobalt recovery and separation are a major hydrometallurgical problem due to some practical difficulties. The main problem is associated with the change of pH of the aqueous phase after equilibration with organic phase when cationic types of extractant [6-8]. 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].

Here, the separation technique involves the discriminatory distribution of elements in two unlike immiscible liquids, that is, one is aqueous phase feed with metal and another is organic phase comprising extractant, diluent, and modifier. Coll *et al.* investigated the extraction efficiency of JMT-Cyanex272 for Co (II) from neutral chloride media [11]. A process to recover Co (II) from secondary resources such as Co-Mo and Co-Mn catalysts using Cyanex 923 has been developed by Gupta *et al.* [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]. Nayl *et al.* employed different forms of Aliquat 336 to selectively extract Co (II) from the aqueous phase containing Ni (II) and sulfuric acid [14]. 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$_3$ [15]. Recently, Mishra *et al.* investigated that the endothermic extraction of Co (II) from 3 M HCL solution using tri-octylamine extractant [16]. Furthermore, among the extractant based on amine, tertiary amines were noticed as the potential extractant for extracting metals. Slimani *et al.* investigated the extraction efficiency of Co (II) in sulfate medium exploiting capric acid as extractant and chloroform as diluent [17].

The literature survey showed that solvent extraction of cobalt has been studied with high hydrochloric acid concentration using tertiary amines in xylene. The present study focused on the solvent extraction of Co (II) from hydrochloric acid medium in the presence of chloride salt using 3-hexylaminopyridine (3-HAP) in kerosene. To avoid the environmental issue, salt was added to the extraction process which reduces the consumption of acids in extraction of Co (II). The extraction equilibrium of Co (II) has been assessed by varying different parameters such as phase contact time, concentration

*Corresponding author:
Maroti V. Kanetkar
E-mail: ubschemyma@gmail.com

of 3-HAP, HCl, pH range, and salting out agent. To investigate efficiency of diluents, extraction experiments have been performed with different diluents.

2. EXPERIMENTAL

2.1. Chemical Reagents and Apparatus

A Shimadzu UV–Visible spectrophotometer (UV 1800) with 1 cm² quartz cell was used and pH optimization carried out by Systronics digital pH meter Model L1-120 (±0.01). All chemicals used were AnalR grade and purchased from commercial suppliers Alfa Aesar (Thermo Fisher Scientific, Hyderabad, India) and Spectrochem (Spectrochem Pvt. Ltd., Mumbai, India). Chemicals were used as without purification. A stock solution of CoCl₂ was prepared by dissolving appropriate weight in 250 mL of distilled water and standardized gravimetrically and other solutions were prepared by dissolving desired amount in distilled water. Organic phase was prepared by dissolving 3-HAP in diluents.

2.2. Extraction Procedure

The equal volumes of aqueous phase containing Co (II), salts of chlorides, and HCl were shaken with the organic phase of 3-HAP for a period of extraction equilibration. The concentrations of Co (II), KCl, and HCl were made different for respective experiments. After equilibration, both the phases were allowed to separate and raffinate was collected. Analysis of Co (II) was performed by ninhydrin method using UV–Visible spectrophotometer at 395 nm [18].

The extractability, % E of cobalt ion was calculated using the equation:

$$\% \text{ E} = \frac{[M]_{org}}{[M]_{aq.init}} \times 100 \qquad [1]$$

$$[M]_{org} = [M]_{aq.init} - [M]_{aq} \qquad [2]$$

Where, $[M]_{org}$ is the concentration cobalt ions in the organic phase and $[M]_{aq.init}$ and $[M]_{aq}$ are the initial and final concentrations of cobalt ions, respectively, in the aqueous solution.

2.3. Extraction Mechanism

In the extraction experiments, extractant 3-HAP shows very good extractability for Co (II), plausible extraction mechanism discussed here for understanding the nature of ion pair complex of Co (II) in hydrochloric acid media with 3-HAP. The mechanism of ion pair complex was initiated through protonation of 3-HAP to form cationic species, while anionic species was formed by combining chloride ions with Co (II) and both of these formed the ion pair complex as given [9],

$$[3\text{-HAPH}]^+_{org} + [CoCl_3]^-_{aq} \rightarrow [3HAPH^+ : CoCl_3^-]_{org}$$
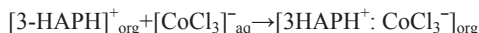
The subscripts org and aq denote the species in organic and aqueous phases, respectively.

3. RESULTS AND DISCUSSION

3.1. Effect of 3-HAP Molarity

The effect of the concentration of 3-HAP in the organic phase containing 0.01 mol/L–0.1 mol/L was investigated when kerosene, xylene, toluene, and benzene were as diluting reagent of the extractant on the extraction of 0.01 M Co (II). As shown in Figure 1, it can be seen clearly that kerosene exhibited the most excellent diluting performance for 3-HAP than other diluents. It is also shown that the extraction of Co (II) has fast increase by increasing 3-HAP from 0.01 mol L⁻¹ to 0.1 mol L⁻¹. The corresponding results of log D versus log [3-HAP]

are plotted in Figure 2, the linear plot of log D versus log [3-HAP] shows straight line (R² = 0.9980) with slope of 1.01. This observation supports the confirming the association of one mole of extractant with each of cobalt ion in the extracted species. Maximum extraction of Co (II) has been achieved using kerosene as diluent. 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.

3.2. Effect of Equilibrium pH on Copper (II) Extraction

The extraction of Co (II) ions from the aqueous solution is highly dependent on the solution pH. Therefore, the extraction efficiency of 0.1 M Co (II) by extracting reagent 3-HAP was determined at different pH level in the range of 0.25–5 with 10 min equilibrium time. The quantitative extraction values were observed between pH 1.0–2.0, significantly lower values were observed in low pH media. The possible reason for this may be excess of H⁺ ions which are reduced the formation of anionic complex species of extractant with metals in aqueous phase. The linear plot between log D versus equilibrium pH is presented in Figure 3. It shows straight line (R² = 0.9955) with slope of 2.0046 indicating the exchange of two mole of H⁺ ion per mole of Co (II) extraction. The resulted slope value was obtained to positive which is due to the increasing extraction tendency with increasing equilibrium pH of the solution up to certain limit.
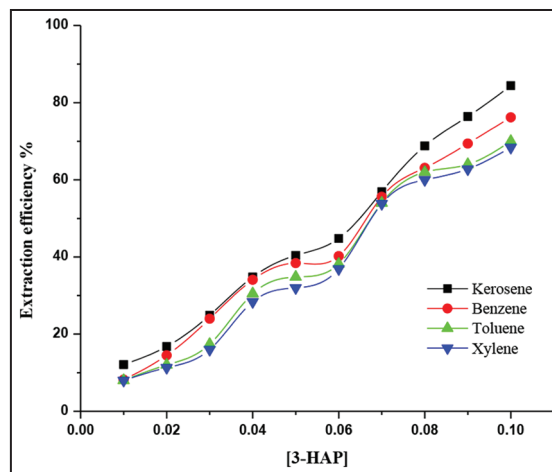

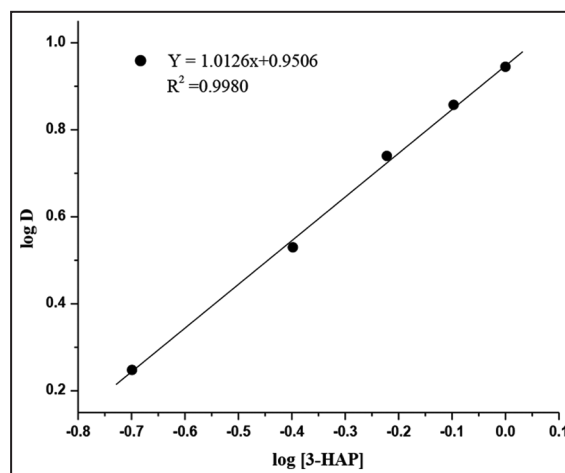**Figure 1:** Effect of 3-HAP concentration and diluents on the extraction of Co (II).

Figure 2: Plot of log D versus log [3-HAP].

3.3. Influence of HCl Concentration

The acid concentration in the aqueous feed solution has a significant role in case of metal extraction with secondary amine. The pKa value of HCl is very less than that of 3-HAP, and therefore, it gives proton easily to 3-HAP and then extract the cobalt complex into the kerosene. Besides, it has been reported that the extraction efficiency of amine-based extractant toward Co (II) improves 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 mol L^{-1} 3-HAP diluted in kerosene has been examined. The molarity of HCl was varied in the range of 0.02–5.00 M. After extraction, it was found that extraction efficiency increased from 32.84% to >90 with increase in HCl molarity, Figure 4.

3.4. Effect of Various Salts

In the present analysis, Co (II) is extracted as chloride complex. Therefore, the presence of salts of chloride in the aqueous phase enhances 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 such as NaCl, KCl, and NH$_4$Cl has been carried out using 0.1 M 3-HAP in kerosene as organic phase. The concentrations of different salts were varied in the range of 0.1–1.0 M. The presence of chloride salts in the aqueous feed increases the extraction of cobalt (II) even with low concentration of acid due to salting out effect and common ion effect [19]. It was found that the extraction percentage of Co (II) increases in the order NH$_4$Cl < NaCl < KCl, Figure 5. 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.

3.5. 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. To know the minimum time required for attainment of equilibrium in case of Co (II) extraction with 3-HAP, the contact time between the aqueous phase and organic phase has been varied in the range of 2–20 min. The percentage extraction of Co (II) has been found to be 64.80% at 4 min contact time which rise to 90.20% when the contact time of both the phases became 10 min and remained unvaried even if contact time was later increased to 15 min and 20 min. Hence, for further investigations, the contact time was fixed at 10 min. Results are shown in Figure 6.

3.6. Selective Separation of Co (II) from Base Metals

To check the selectivity of proposed method toward Co (II) extraction, experiments were carried out from binary mixtures of Co (II) with iron (III), nickel (II), copper (II), and zinc (II). Results are presented in Table 1, which clearly indicate that Co (II) was efficiently extracted from added base metals by 3-HAP at proposed conditions. Iron (III), cobalt (II), nickel (II), and copper (II) remain quantitatively in aqueous phase and determined spectrophotometrically with thiocyanate [20], 1-nitroso-2-napthol [20], DMG [20], and pyrimidine-2-thiol [20], respectively.
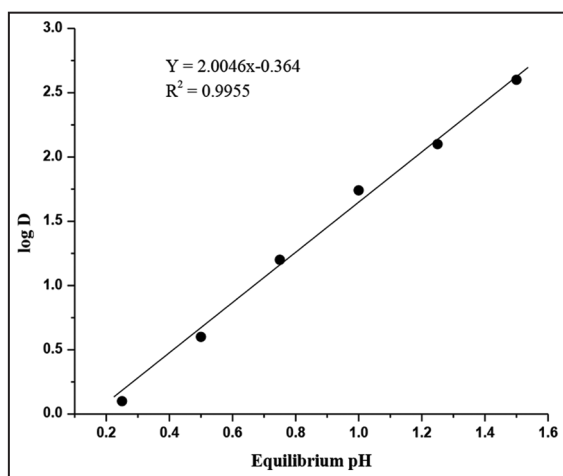

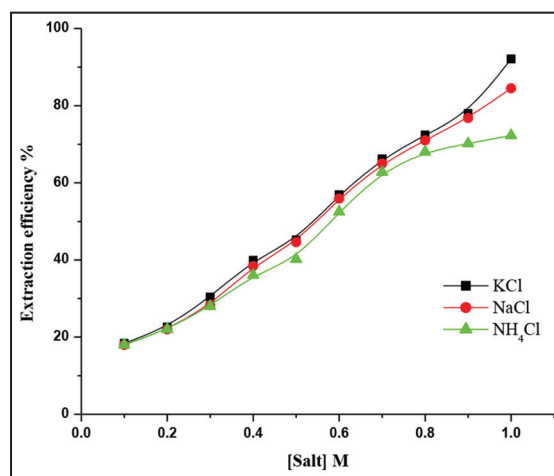**Figure 3:** Plot of log D versus equilibrium pH of aqueous phase.

Figure 5: Effect different salts on extraction of cobalt (II).
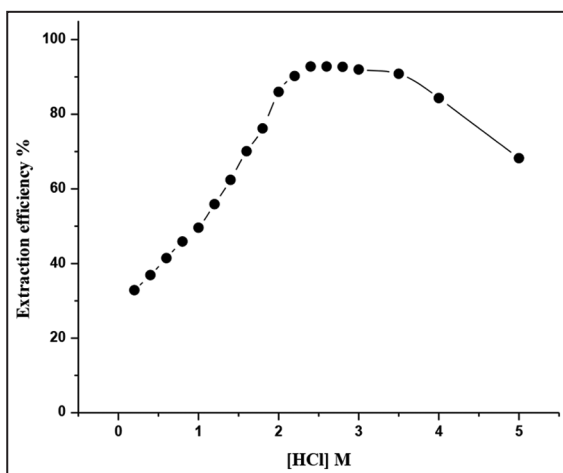

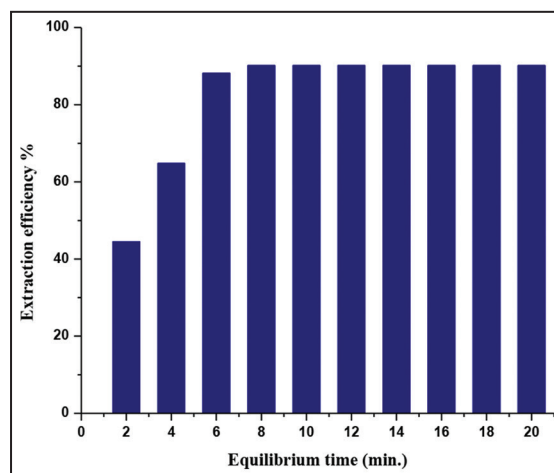**Figure 4:** Effect of HCl concentration on extraction of cobalt (II).

Figure 6: Effect of equilibrium time on the extraction of cobalt (II).

Table 1: Selective extraction of cobalt (II) from base metals.

Composition of metal ions (μg)	Recovery % of Co (II)	R. S. D.	*Recovery of added metals[a] %	R.S.D.*
Co (II), 100; Fe (III), 500	99.35	0.09	99.70	0.08
Co (II) 100; Ni (II), 500	99.30	0.15	99.50	0.18
Co (II) 100; Cu (II), 500	99.30	0.12	99.10	0.20
Co (II) 100; Zn (II), 500	99.40	0.05	99.40	0.20

*R.S.D.: Relative standard deviation

4. CONCLUSION

In this work, the extraction equilibria of cobalt (II) with 3-HAP dissolved in kerosene was studied. Extraction data were presented. Results showed that the chloride ions can greatly improve the extraction efficiency of Co (II). The extraction efficiency is high in the pH range 1–2 and then decreases. The distribution coefficient increases with increasing HCl concentration up to certain value and 3-HAP concentrations. The single-stage extraction efficiency by the proposed method is >90%.

5. ACKNOWLEDGMENTS

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***Bibliographical Sketch**

Dr. Gopal K. Kakade, biomimetic and biophysical chemist of national fame, is Professor & Head Department of Chemistry, M. S. P. Mandal's Arts, Commerce and Science College, Kille-Dharur. He has 23 years teaching experience to graduate and post graduate students. He published 42 research papers in national and international journals of repute and guided 4 students for Ph. D degree and 7 seven students are doing research. He also completed two research project funded by University Grants Commission, New Delhi.