International Journal of Science and Research (IJSR)
ISSN: 2319-7064
Impact Factor 2025: 7.089

# Studies on Effect of $\beta$ −Picoline as Synergist in the Solvent Extraction of Co (II) with Anthranilic Acid Using Radiometric Technique

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**Abstract:** ***The effect of β-picoline as synergist in solvent extraction of Co (II) with anthranilic acid in Water-Benzene system has been studied using Radiometric technique. The extraction of metal ions from aqueous phase to organic phase is enhanced significantly if the metal carboxylates is extracted in the presence of nitrogen containing organic base which acts as Synergist. The quantitative estimation of Cobalt in the solvent extraction aliquots has been done by radiometric technique using Cobalt-58 radioactive isotope. The gamma activity of the aliquot has been measured using NaI (Tl) scintillation counter. The effect of various variables such as pH of the aqueous phase, metal ion concentration, anthranilic acid concentration, and base concentration has been reported. The most probable composition of the synergistic adduct has been postulated on the basis of slope analysis method.***

**Keywords:** Solvent Extraction, β-picoline, Cobalt (II), Anthranilic acid, Synergism, Radiometric technique, Distribution ratio, Slope analysis method

## 1. Introduction

Solvent extraction, rated as one of the most useful separation techniques, can be safely extended from microlevels to macro-concentrations. This technique is very simple and produces cleaner separation of materials with high decontamination factor. The extraction of a number of metal ions by solvent extraction process using carboxylic acids either singly or in conjunction with some synergist, has been widely studied and reported [1 – 11]. Gogia, Singh and Tandon [12] have studied the extraction of Co (II) with propionic, butyric or valeric acid in the presence of $\beta-picoline$, pyridine or quinoline into chloroform and has reported the extracted species as $CoA_2.2HA.2B$ where HA is acid and B is base, for all systems except the butyric acid-quinoline system for which they has reported the extracted species as $CoA_2.HA.2B.H_2O$. Anthranilic acid, one of the most useful complexing agent in analytical practice, gives chelate complexes with a variety of metal ions. However, metal anthranilates show poor extraction into non-polar solvents like chloroform and benzene. Not much work has been reported on the extraction of metal anthranilates into non-polar solvents in the presence of synergists. Jain, Singh, Goyal and Tandon [13] have studied the extraction of Zn (II) and Cd (II) with anthranilic acid in the presence of pyridine / β-picoline / quinoline and have reported that zinc and cadmium anthranilates do not extract into non-polar solvents alone in the pH range 4.5 – 6.5 but their extraction is synergistically enhanced in the presence of heterocyclic nitrogen containing bases due to displacement of coordinated water. They have reported extracting species as $[Zn(\text{anthra})_2.B.H_2O]$ and $[Cd(\text{anthra})_2.2B]$. In this research article, outcome of the work carried out on the extraction of Co (II) in aqueous phase into benzene with anthranilic acid in the presence of β-picoline, has been reported. The theoretical concept and mathematical formulation used in the present research work is as follows:

Liquid-liquid extraction or solvent extraction involves the partition or distribution of a solute between two immiscible liquids in contact with each other. According to Distribution law, the Distribution ratio, D is given by –

$$D = \frac{\text{Concentration of metal ion in the organic phase}}{\text{Concentration of metal ion in the aqueous phase}}$$

$$\text{Therefore, } D = \frac{[M]_{org}}{[M]_{aq}}$$

$$\text{Percent Extraction, } \%E = \frac{\text{Concentration of metal ion in the organic phase}}{\text{Total metal ion concentration}} \times 100$$

The reaction for mixed ligand formation may be given as:

$$M^{n+}(aq) + (p+q)\,HA\,(aq) + (n-p+y)\,H_2O + x\,B\,(aq) \rightleftharpoons \left[MA_p.qHA.(n-p)OH^-.yH_2O.xB\right](org) + n\,H^+\,(aq)$$

Where, $M^{n+}$ = metal ion, HA = anthranilic acid, A = anthranilate anion, B = base, n = valency of metal ion, p = number of anthranilate coordinated, x = number of base molecule coordinated, q = number of acid molecule coordinated, y = number of water molecule coordinated

Assuming anthranilate anion as bidentate ligand, Coordination number of the metal in the Extracted species may be given by:

$$C.N. = p + q + n + x + y$$

If, $[MA_p.qHA.(n-p)OH^-.yH_2O..xB]$ is represented by [Extracted species] then:

$$K_{ex} = \frac{[Extracted\ species]_{org} \cdot [H^+]^n_{aq}}{[M^{n+}]_{aq} \cdot [HA]^{p+q}_{aq} \cdot [B]^x_{aq}}$$

$where\ K_{ex} = Extraction\ Constant$

$$Putting, \quad \frac{[Extracted\ species]_{org}}{[M^{n+}]_{aq}} = Distribution\ ratio = D$$

$$we\ have, \quad K_{ex} = \frac{D \cdot [H^+]^n_{aq}}{[HA]^{p+q}_{aq} \cdot [B]^x_{aq}}$$

$$Thus, \log D = \log K_{ex} + (p+q)\log[HA]_{aq} + x\log[B]_{aq} + n\,pH$$

Assuming that the metals do not form any other complex with excess of ligand, the mass balance for base is given by:

$$[B]_{total} = [B]_{org} + [B]_{aq} + x[MA_p.qHA.(n-p)OH^-yH_2O.xB]_{org} + [BH^+]_{aq}$$

Hence, $B_{aq}$ is given by,

$$[B]_{aq} = \frac{[B]_{total} - x.[M]_{org}}{P_B + 1 + \frac{[H^+]}{K_{BH^+}}}$$

Where,

$P_B = \frac{[B]_{org}}{[B]_{aq}}$ = Partition Coefficient of base, B between organic and aqueous phases

$K_{BH^+} = \frac{[H^+]\,[B]_{aq}}{[BH^+]_{aq}}$ = Ionization constant of $BH^+$

The metal anthranilate complexation reaction may be given as:

$$M^{n+}(aq) + p\,HA\,(aq) \rightleftharpoons MA_p^{(n-p)+}(aq) + p.H^+\,(aq)$$

$$Equilibrium\ Constant, K_1 = \frac{[MA_p^{(n-p)+}]_{aq} \cdot [H^+]^p_{aq}}{[M^{n+}]_{aq} \cdot [HA]^p_{aq}}$$

$$Considering, \quad [MA_p^{(n-p)+}]_{aq} = [Extracted\ species]_{org}$$

$$we\ get, \quad \log D = \log K_1 + p\,.pH$$

In the present study, the solvent extraction of Co (II) in Water-Benzene system with Anthranilic acid in the presence of β-picoline, has been carried out. The quantitative estimation of Cobalt in the solvent extraction aliquots has been done by radiometric technique using Cobalt-58 radioactive isotope. The gamma activity of the aliquot has been measured using NaI(Tl) scintillation counter.

The Distribution ratio (D) and Percent extraction has been calculated as:

$$D = \frac{activity\ in\ the\ organic\ phase}{activity\ in\ the\ aqueous\ phase}$$

$$\%E = \frac{activity\ in\ the\ organic\ phase}{activity\ in\ the\ organic\ phase + activity\ in\ the\ aqueous\ phase} \times 100$$

The effect of various variables such as pH of the aqueous phase, metal ion concentration, anthranilic acid concentration, and base concentration has been reported. Extraction constant has been calculated and the most probable composition of the synergistic adduct has been postulated on the basis of slope analysis method.

## 2. Materials and Method

In this investigation, all the chemicals used were of AR/GR grade. The radioisotope used for distribution studies of Co (II) was $^{58}$Co which was procured from Bhabha Atomic Research Centre, Bombay (India) by Department of Chemistry, University of Roorkee, Roorkee (presently Indian Institute of Technology, Roorkee). A well-type NaI (Tl) Scintillation Counter coupled with a single channel analyzer (ECIL, India) was used for counting the gamma activity of $^{58}$Co. Co (II) solutions of various concentrations as per requirement, were obtained by dissolving Cobalt sulphate in doubly distilled water and standardization of solution was done using EDTA titration. Anthranilic acid was recrystallized and freshly prepared solutions of anthranilic acid were used throughout the investigation. Standardization of anthranilic acid solution was carried out using acid-base titration.

***Analytical procedure***

In each set, 10 ml of aqueous phase containing metal ion, anthranilic acid, β-picoline, $^{58}$Co radioactive isotope and 10 ml benzene were shaken in separating funnel at room temperature ($30 \pm 2^oC$) for 5 minutes to achieve complete equilibration. The ionic strength of the aqueous phase was maintained constant at 0.1M by adding Sodium perchlorate. The pH of the aqueous phase was adjusted with perchloric acid or sodium hydroxide. After equilibration, the two phases were separated. The pH measurements of aqueous phase before and after equilibration were made on an expanded scale pH-meter (ECIL, India). Gamma ray activity in 1.0 ml aliquots of each of aqueous and organic phase were counted using NaI (Tl) scintillation counter.

In order to study the effect of pH on the extraction of Co (II) into benzene, the extraction procedure was repeated in the pH range 4.8 – 7.0 at constant metal ion ($1.0 \times 10^{-4}M$), anthranilic acid (0.125M), and β-picoline (1.5M) concentrations. The investigations on the effect of equilibrium pH of the aqueous phase on the extraction reveal that the extent of extraction increases with the increase in pH and reaches a maximum at pH 7.0. Therefore, all further studies on Co (II) extraction have been carried out at pH 7.0.

In order to investigate effect of metal ion concentration, extraction procedure was carried out at various metal ion concentration in the range $5.0 \times 10^{-5} - 1.0 \times 10^{-3}M$ at constant anthranilic acid concentration (0.05M), constant β-picoline concentration (1.5M) and at pH = 7.

Effect of acid concentration on the extraction of Co (II) was investigated by varying the acid concentration from 0.01M to

0.05M keeping metal ion ($1.0 \times 10^{-4}M$), β-picoline (1.5M) concentrations constant and pH = 7.0.

The effect of base concentration on the extraction of Co (II) was investigated by carrying out the extraction process at constant metal ion ($1.0 \times 10^{-4}M$), constant acid (0.05M) concentrations and at pH = 7 with varying β-picoline concentration from 0.2M to 1.5M.

## 3. Results and Discussion

### 3.1 Effect of pH of the Aqueous Phase

The calculated value of Distribution ratio, D and Percent extraction, %E from experimental data has been placed in TABLE – 1. The data reveal that with increase in pH of the aqueous phase, extraction of Co (II) increases and reaches a maximum at pH = 7. The plot of log D versus pH of the aqueous phase gives straight line with slope value about one [Figure 1], suggesting the release of one proton by the utilization of one acid molecule per metal atom to neutralize the charge on the metal ion.

**Table 1:** Distribution ratio (D) for Co (II) between aqueous phase and benzene as a function of pH of the aqueous phase at constant anthranilic acid and β-picoline concentrations

| $[Co\ (II)]_T = 1.0 \times 10^{-4}M, [Acid]_T = 0.125M,$ $[\beta - picoline]_T = 1.5M$ | | | |
|---|---|---|---|
| pH | D | Log D | %E |
| 4.8 | 0.320 | -0.494 | 24.242 |
| 5.2 | 0.536 | -0.271 | 34.895 |
| 5.3 | 0.718 | -0.143 | 41.792 |
| 5.4 | 0.794 | -0.100 | 44.258 |
| 6.0 | 2.007 | 0.302 | 66.744 |
| 6.5 | 3.849 | 0.585 | 79.377 |
| 7.0 | 8.862 | 0.947 | 89.860 |

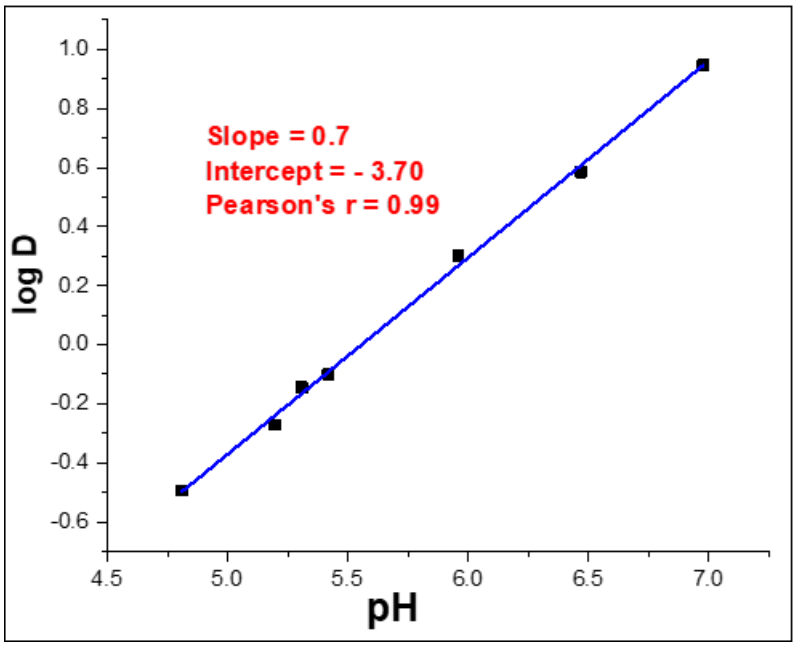


**Figure 1:** Effect of pH of the aqueous phase on the extraction of Co (II) at constant metal ion ($1.0 \times 10^{-4}M$), anthranilic acid (0.125M), and β-picoline (1.5M) concentrations

### 3.2 Effect of Metal Ion Concentration

The effect of metal ion concentration in the range $5.0 \times 10^{-5} - 1.0 \times 10^{-3}$M on the extraction of Co (II) is found to be practically insignificant (±3%). This rule out the possibility of extraction of any polymeric species in the above-mentioned concentration range. A concentration of $1.0 \times 10^{-4}M$ of Co (II) has been chosen to carry out the present investigation.

### 3.3 Effect of Acid Concentration

The experimental data of distribution ratio for Co (II) between aqueous phase and benzene as a function of anthranilic acid concentration at constant Co (II) concentration, constant pH and constant β-picoline concentration has been placed in TABLE – 2. From the observation of the experimental data it is found that with the increase in the concentration of acid the extraction increases. The plot of $\log D$ versus log of anthranilic acid concentration gives straight line with slope near two [Figure 2] suggesting the utilization of two acid molecules per metal atom during the formation of extracted species.

**Table 2:** Distribution ratio (D) for Co (II) between aqueous phase and benzene as a function of anthranilic acid concentration at constant Co (II) concentration, β-picoline concentration, and at pH = 7.

| $[Co\ (II)]_T = 1.0 \times 10^{-4}M,$ $[\beta - picoline]_T = 1.5M, pH = 7.0$ | | | |
|---|---|---|---|
| $[ANTHRA]_T$ | log $[ANTHRA]_T$ | D | log D |
| $1.002 \times 10^{-2}$M | -1.99888 | 2.212 | 0.34481 |
| $1.526 \times 10^{-2}$M | -1.81626 | 4.304 | 0.63389 |
| $2.018 \times 10^{-2}$M | -1.69488 | 6.971 | 0.84332 |
| $3.024 \times 10^{-2}$M | -1.51943 | 13.221 | 1.12126 |
| $3.999 \times 10^{-2}$M | -1.39805 | 21.607 | 1.33459 |
| $4.913 \times 10^{-2}$M | -1.30867 | 31.665 | 1.50058 |

### 3.4 Effect of Base Concentration

Distribution ratio, D for extraction of Co (II) as a function of base concentration is calculated and is placed in TABLE – 3. Data reveal that extraction of Co (II) in organic phase increases with increase in base concentration. The log-log plot of distribution ratio versus β-picoline concentration has been drawn which gives straight line with slope near two [Figure 3]. This suggests the ratio of metal to base in the extracted species as 1:2.

**Table 3:** Distribution ratio (D) for Co (II) between aqueous phase and benzene as a function of β-picoline concentration at constant Co (II) concentration, anthranilic acid concentration, and pH = 7.

| $[Co\ (II)]_T = 1.0 \times 10^{-4}M$, $[ANTHRA]_T = 0.05M, pH = 7.0$ | | | |
|---|---|---|---|
| $[\beta - picoline]_T$ | $\log[\beta - picoline]_T$ | D | log D |
| 0.2 M | -0.6989 | -0.625 | -0.625 |
| 0.4 M | -0.3979 | 0.069 | 0.069 |
| 0.6 M | -0.2218 | 0.378 | 0.378 |
| 0.8 M | -0.0969 | 0.570 | 0.570 |
| 1.0 M | 0.0000 | 0.778 | 0.778 |
| 1.3 M | 0.1139 | 1.076 | 1.076 |

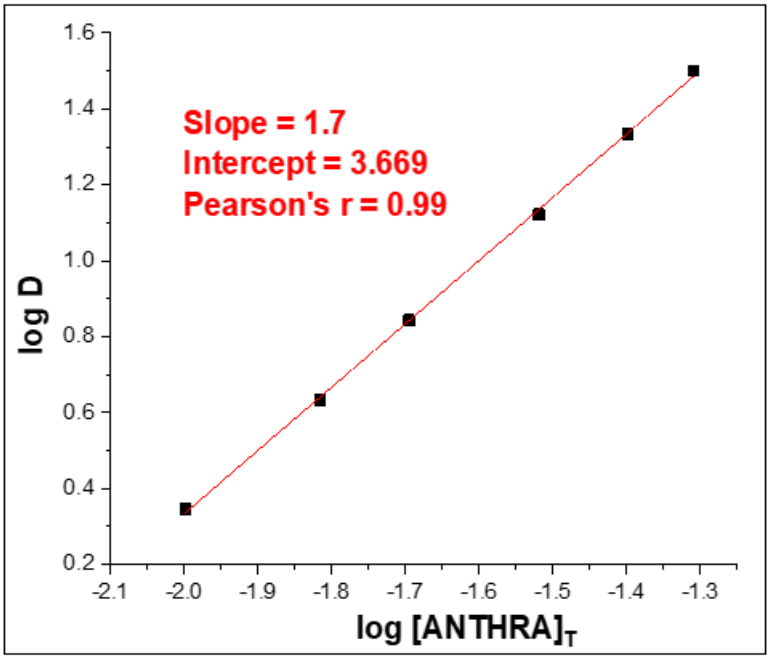


**Figure 2:** Variation of distribution ratio for Co (II) as a function of anthranilic acid concentration at constant metal ion $(1.0 \times 10^{-4}M), \beta - picoline$ $(1.5M)$ concentrations, and pH = 7.

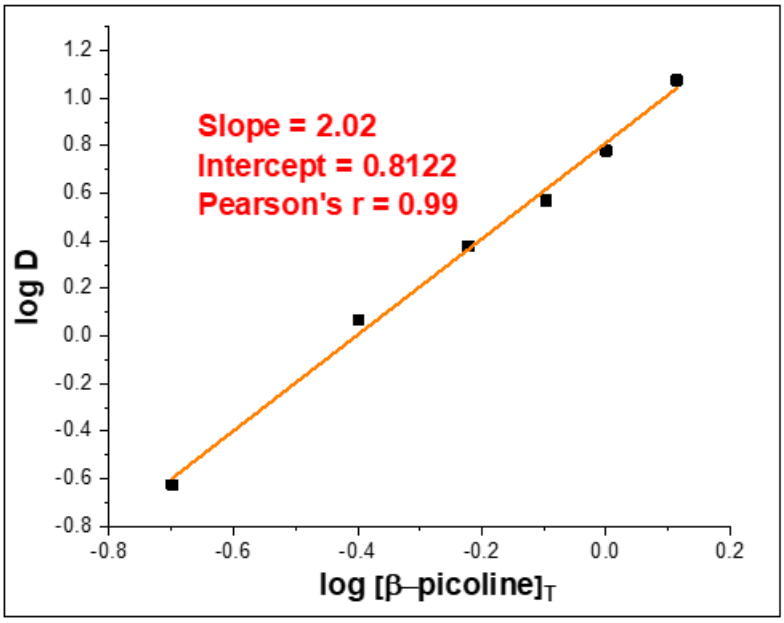


**Figure 3:** Variation of distribution ratio (D) for Co (II) as a function of β-picoline concentration at constant metal ion $(1.0 \times 10^{-4}M)$ concentration, constant anthranilic acid (0.05 M) concentration, and pH = 7.

### 3.5 Extracted Species

From the above-mentioned studies we get:

$$p = 1, p + q = 2, x = 2 \text{ and } n = 2$$
$$Thus, p = 1, q = 1, x = 2, n = 2 \text{ and } C.N. = p + q + n + x + y$$

Assuming coordination number of Co (II) in the extracted species to be six then $y = 0$

$$The\ hypothetical\ extracted\ species\ is\ [MA_p.qHA.(n - p)OH^-.yH_2O.xB].$$
$$\therefore Extracted\ species = [MA.HA.OH^-.2B]$$

Therefore, the possible composition of the extracted species may be represented as;

$$Co(OH)A.HA.2B$$

### 3.6 Calculation of Extraction Constant ($K_{ex}$)

$[B]_{aq}$ is calculated by using the equation:

$$[B]_{aq} = \frac{[B]_{total} - x.[M]_{org}}{P_B + 1 + \frac{[H^+]}{K_{BH^+}}}$$

The values of $P_B$ and $K_{BH^+}$ have been taken from literature [13, 14] and ionization constant of β-picoline, $K_b = 4.27 \times 10^{-9}$ ($pK_b = 8.37$).

The average value of partition coefficient, $P_B$ for β-picoline is 1.85 and ionization constant of $\beta - picolinium\ ion, K_{BH^+}$ is taken equal to $2.34 \times 10^{-6}$.

Putting the values of $logD$, $\log[HA]_{aq}$, $\log[B]_{aq}$, pH and n = 2, x = 2, p = 1, q = 1 in the following equation

$$logD = logK_{ex} + (p + q)\ log[HA]_{aq} + x\ log[B]_{aq} + n\ pH$$

Extraction constant, $K_{ex}$ is computed [TABLE – 4].

**Table 4:** Variation of $[\beta - picoline]_{aq}$ in Co (II) extraction at constant metal ion concentration ($1.0 \times 10^{-4}$ M), constant anthranilic acid concentration (0.05 M) and pH = 7.

| $[B]_{total}$ | log D | log $[B]_{aq}$ | log $K_{ex}$ | Mean of log $K_{ex}$ |
|---|---|---|---|---|
| 0.2 M | -0.625 | -1.161 | -4.00 | -3.97 |
| 0.4 M | 0.069 | -0.860 | -3.91 | |
| 0.6 M | 0.378 | -0.684 | -3.95 | |
| 0.8 M | 0.570 | -0.559 | -4.01 | |
| 1.0 M | 0.778 | -0.462 | -3.99 | |
| 1.3 M | 1.076 | -0.348 | -3.93 | |

Computed log $K_{ex}$ value for the extraction of Co (II) with anthranilic acid using $\beta - picoline$ as synergist is -3.97 and the corresponding Extraction constant, $K_{ex}$ is $1.072 \times 10^{-4}$. In case of extraction of Fe (III) with anthranilic acid in the presence of $\beta - picoline$ as synergist, extraction constant, $K_{ex}$ is reported $1.413 \times 10^7$ [15]. This suggests that iron forms more stable complex with anthranilic acid than cobalt.

The plot of logD versus $\log[B]_{aq}$ is drawn [Figure 4] using data from [TABLE 4].

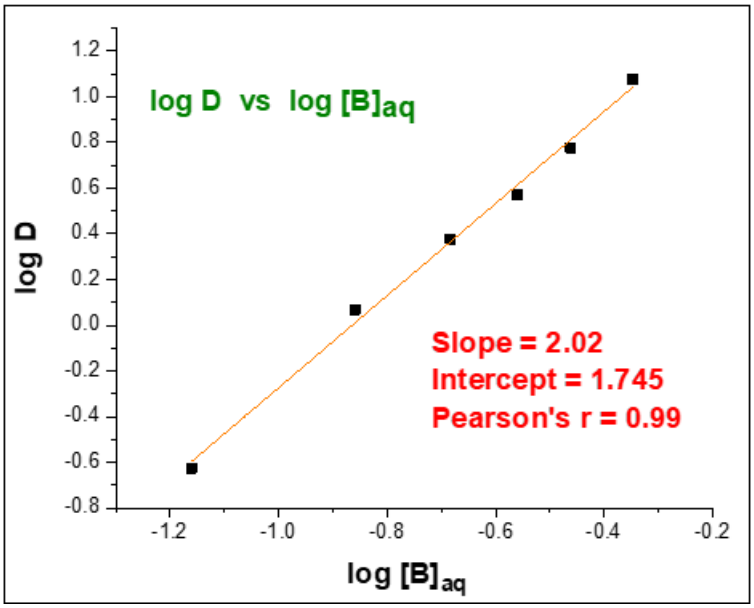


**Figure 4:** Plot of logD vs $\log[B]_{aq}$ for variation of β-picoline concentration at constant Co (II) concentration, pH, and anthranilic acid concentration.

The plot gives straight line with a slope nearly two which again suggests incorporation of two base molecules per metal atom during the formation of extracting species.

## 4. Conclusion

The present research studies conclude that the extraction of Co (II) from aqueous phase to benzene, with anthranilic acid in the presence of β-picoline is significant. Possible composition of the extracted species, a mixed ligand complex, is represented as:

$$[Co(OH)A.HA.2B]$$

The proposed extracting species contains hydroxyl group in the coordination sphere. It is expected considering the pH of the aqueous phase. The extraction constant, $K_{ex}$ is reported as $1.072 \times 10^{-4}$. The extraction constants of Co (II) and Fe (III) under similar conditions, are compared. This suggests that iron forms more stable complex with anthranilic acid than cobalt.

**Acknowledgement**
The present research work has been completed during my stay in University of Roorkee, Roorkee (presently, Indian Institute of Technology, Roorkee). I am too much grateful to teachers and staffs of the Chemistry Department for their valuable support in completing this work.

**Conflict of Interest**
The author declares that there is no conflict of interest.

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