

Hydrometallurgical Studies for the Extraction and Recovery of Cobalt (II) with Tertiary Amines

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Summary: The Investigations describe a comparative study with various high molecular weight tertiary Amines to develop a hydrometallurgical method for the extraction and recovery of Co (II) from aqueous acidic media. Limits such as, the effect of acid, extractant, and stripping agents concentration, time of contact, and diverse ions were optimized. Maximum percentage extraction and recovery of Cobalt (II) ions were achieved with 5 % solution of trioctylamine in benzene.

Introduction

New and versatile techniques of liquid-liquid extraction have been referred to as "Liquid ion exchanger". The use of high molecular weight amines and amine salts has been made for the removal of mineral acids, organic acids, complex metal acids from aqueous solutions, and organo-phosphorous acids for removal might be said to date from 1948, when Smith and Page [1] published their paper entitled "The acid bonding properties of long chain aliphatic amines". However, interest for their application in industrial processes for the recovery of metals is relatively recent. This procedure has also been used commercially for the extraction of metals from ores and metallic minerals. A number of research papers have been published in the field of inorganic- analytical chemistry of cobalt metal. Most of these studies have been confined to the characterization, thermodynamics, mechanism and co-ordination of the cobalt and cobalt group metals in the form of their chelates and metals complexes [2-37]. The present work deals with the application of hydrometallurgical method for the extraction and recovery of cobalt (II) from synthetic mixtures with 5% solution of trioctylamine in benzene.

Results and Discussion

Effect of acid concentration

The effect of acid (HCl) concentration in molar range (0.5 M- 9.50 M) was studied and 94 % extraction was noted at 9.0M concentration of HCl using 10 ml (5ml+ 5ml) solution of 5% trioctylamine in benzene and performing the extraction in portions / double extraction.

Effect of Shaking times

The effect of shaking time, in the range 0.5-5.00 minutes, was carried out after optimizing the effect of hydrochloric acid concentration. It was found that 2 minutes time is the optimum shaking time for maximum (99 %) extraction. The results are depicted in Fig. 1.

Effect of phase-volume ratios

The phase-volume ratio (V_{org} / V_{aq}) was varied by keeping the volume of organic phase as constant [10 ml + 5 ml portions), and varying the volume of the aqueous phase from 5 ml up to 30 ml. The ratio 1 : 1 was found to be the most suitable ratio for efficient extraction of Co (II). The data are depicted in Fig. 2.

Effect of various extractants.

The effect of a number of extractants i.e Tribenzylamine (TBA), Triethylamine (TEA), Tricaprylamine (TCA), tricaprylmethyl ammonium chloride (Aliquot-336) and Trioctylamine (TOA) in different solvents (Chloroform and benzene) were studied on the overall extraction of Co (II). Tricaprylamine in benzene was found to be the most suitable extractant.

Effect of extractant concentrations.

The effect of extractant (TOA in benzene) concentration in molar range (0.01M - 0.23M) was also carried out after optimizing the effect of acid

(HCl) concentration, shaking time and phase-volume ratio. These observations are presented in Fig. 3.

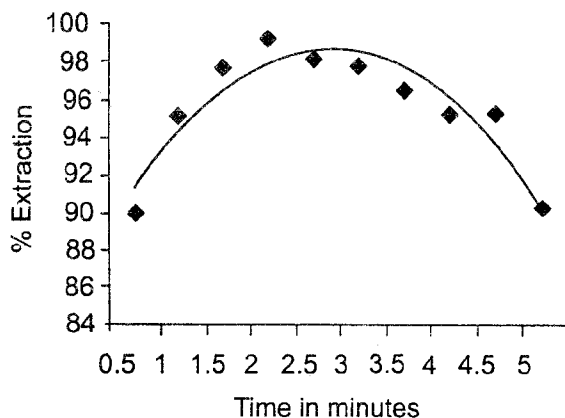


Fig. 1: Effect of shaking time on % extraction of Co (II) with TOA.

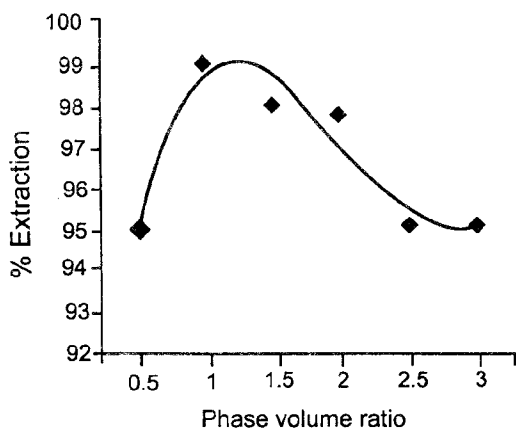


Fig. 2: Effect of phase volume ratio (Vorg:Vaq) on % extraction of Co (II).

Effect of cobalt concentration.

Further studies were also carried out to study the effect of cobalt concentration, 10 to 100 μg , on the overall extraction with TOA in benzene. Minor differences were found in the extraction efficiency above 50 μg . The effect is illustrated in Fig. 4.

Effect of organic solvent

Various organic solvents were used as diluent for trioctylamine. Benzene was found to be the most suitable diluent. The effect is summarized in Table-1.

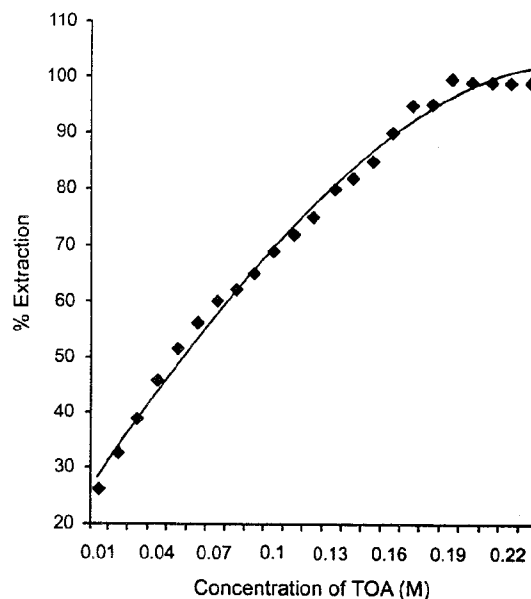


Fig. 3: Effect of TOA concentration on % extraction of Co(II).

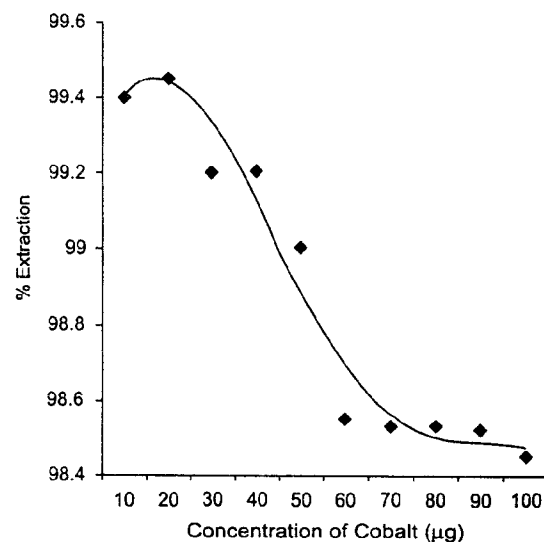


Fig. 4: Effect of Cobalt concentration on % extraction of Co (II).

Effect of diverse ions.

The Cobalt concentration (20 μg) was kept constant and the effect of various diverse ions in the range 100-1000 $\mu\text{g}/\text{ml}$ (05-50 fold excess), that may probably cause interference during the extraction and recovery of the metal (cobalt) with TOA in benzene

Table - 1: Effect of various organic solvents on % Extraction of Cobalt (II)

S. No.	Solvents / Diluents	Conc. of Cobalt (μg)			% Extraction
		Added	Found	Extracted	
1.	Toluene	20.00	4.41	15.59	78.40
2.	Carbon tetrachloride	20.00	5.60	14.40	72.00
3.	Butane-1-01	20.00	16.99	3.01	15.05
4.	Methyl Isobutyl Alcohol	20.00	13.9	6.05	30.25
5.	n-Pentane	20.00	3.25	16.75	83.75
6.	Propanol	20.00	9.80	10.20	51.00
7.	Butyl Alcohol	20.00	10.79	9.21	46.05
8.	Methyl Benzol	20.00	5.98	14.02	70.11
9.	2- Methyl-propanol (I)	20.00	15.65	4.35	21.75
10.	Chloroform	20.00	5.80	14.20	71.03
11.	Ethylene Dichloride	20.00	2.80	17.20	86.00
12.	Cyclohexane	20.00	4.35	15.65	78.25
13.	o-xylene	20.00	4.04	15.96	79.80
14.	p-xylene	20.00	3.95	16.05	80.25
15.	Methyl Isobutyl-Ketone	20.00	6.69	13.31	66.55
16.	Dioxane	20.00	11.45	8.55	42.75
17.	Trichloroacetic Acid	20.00	3.58	16.42	82.10
18.	Benzene	20.00	0.20	19.80	99.00

was studied. It was observed that Fe (II) and Fe (III) do not interfere even if present in the 50 fold excess. Reproducible results were also achieved with Au (III) when present in 5-20 fold excess. Mn (II), Mg (II), Sn (II), Au (II), Ti (IV), Pb (II) and Ni (II) also do not interfere if present in the 5 fold excess. However, this trend decreases by 10 to 15 % if the diverse ions concentration is increased from 25 to 50 fold excess. Moreover, the % age extraction of Cobalt decreases from 4-15% due to the presence of V (V), Cr (III), and Cd (II) but this diversity is not so pronounced in case of Ag (I), Si (IV), Zn (II) and thus show minor diverse effect. These observations are tabulated in Table-2

Analysis of synthetic mixtures.

As a final check on the method, various synthetic mixtures were prepared and analysed by the foregoing procedure. The data are given in Table- 4

Single extraction with 5ml of 5 % Tertiary amines from different Extractant.

The extraction studies of cobalt (II) from various acidic media were made with 5 ml of 5 % solutions of tribenzylamine and triethylamine in chloroform, alamine-336, aliquat-336, and trioctylamine in benzene. Maximum extraction was obtained with 5 % solution of trioctylamine in benzene from acidic chloride medium. The comparative studies are illustrated in Fig. 5

Extraction in Portions with 10 ml of 5 % trioctylamine in benzene from acidic media.

After ascertaining the best extractant of the above mentioned tertiary amines the studies were extended to investigate the effect of double extraction/extraction in portions (10 ml divided in 5

Table - 2: Effect of diverse ions on % extraction of Cobalt (II)

S. No.	Diverse ions	Conc. of diverse ions (μg)	Concentration of Cobalt (μg)			% Extraction
			Added	Found	Extracted	
1.	Zn(II)	100	20.00	0.50	19.50	97.50
		500	20.00	1.00	19.00	95.00
		1000	20.00	2.00	18.00	90.00
2.	Cr(III)	100	20.00	0.80	19.20	96.00
		500	20.00	1.00	19.00	95.00
		1000	20.00	1.25	18.75	93.75
3.	Mn(II)	100	20.00	0.40	19.60	98.00
		500	20.00	0.60	19.40	97.00
		1000	20.00	2.95	17.05	85.25
4.	Fe(III)	100	20.00	0.20	19.38	99.00
		500	20.00	0.20	19.80	99.00
		1000	20.00	0.20	19.80	99.00
5.	Ca(II)	100	20.00	0.45	19.55	97.75
		500	20.00	1.55	18.45	92.25
		1000	20.00	2.00	18.00	90.00
6.	Mg(II)	100	20.00	0.40	19.60	98.00
		500	20.00	0.45	19.55	97.75
		1000	20.00	1.83	18.17	90.85
7.	Cd(II)	100	20.00	1.60	18.40	92.00
		500	20.00	1.65	18.35	91.75
		1000	20.00	1.95	18.05	90.25
8.	Al(III)	100	20.00	0.20	19.80	99.00
		500	20.00	0.25	19.75	98.75
		1000	20.00	0.40	19.60	98.00
9.	Pb(II)	100	20.00	0.38	19.62	98.10
		500	20.00	1.97	18.03	90.15
		1000	20.00	2.40	17.60	88.00
10.	Si(IV)	100	20.00	0.55	19.45	97.25
		500	20.00	1.00	19.00	95.00
		1000	20.00	2.20	17.80	89.00
11.	Bi(III)	100	20.00	0.80	19.20	96.00
		500	20.00	1.00	19.00	95.00
		1000	20.00	1.08	18.92	94.60
12.	Sn(II)	100	20.00	1.00	19.00	95.00
		500	20.00	0.96	19.04	95.20
		1000	20.00	1.03	18.97	94.85
13.	Ti(IV)	100	20.00	0.25	19.75	98.75
		500	20.00	1.60	18.40	92.00
		1000	20.00	2.00	18.00	90.00
14.	W(VI)	100	20.00	1.96	18.04	90.20
		500	20.00	2.60	17.40	87.00
		1000	20.00	3.19	16.81	84.05
15.	V(V)	100	20.00	1.00	19.00	95.00
		500	20.00	2.00	18.00	90.00
		1000	20.00	2.77	17.23	86.15
16.	Ni(II)	100	20.00	0.43	19.57	97.85
		500	20.00	0.80	19.20	96.00
		1000	20.00	0.85	19.15	95.75
17.	Ag(I)	100	20.00	0.44	19.56	97.80
		500	20.00	1.00	19.00	95.00
		1000	20.00	2.00	18.00	90.00
18.	Au(I)	100	20.00	0.29	19.71	98.55
		500	20.00	0.80	19.20	96.00
		1000	20.00	0.85	19.15	95.75

ml portions) with 5 % solutions of trioctylamine in benzene from aqueous acidic media. The most important feature of the experiment is that extraction in portion enhances the percentage from 94 to 99 % in chloride system. The data obtained is depicted in Fig. 6.

Effect of stripping agent (HCl) on % recovery ← HCl of Co (II)

Recovery of cobalt (II) from organic phase back into aqueous phase was carried out using dilute solutions (0.01M - 0.10M) of HCl. Maximum

recovery was 99% with 0.01M solution of HCl. The data obtained from these investigations is depicted in Fig. 7

Table-3: Instrumental conditions for Cobalt

Conditions	Cobalt
Lamp current (mA)	10.00
Wavelength (nm)	240.70
Spectral slit (nm)	0.20
Oxidant pressure (kg/ cm ²)	1.60
Fuel pressure (kg/ cm ²)	0.35
Burner height (mm)	10.00

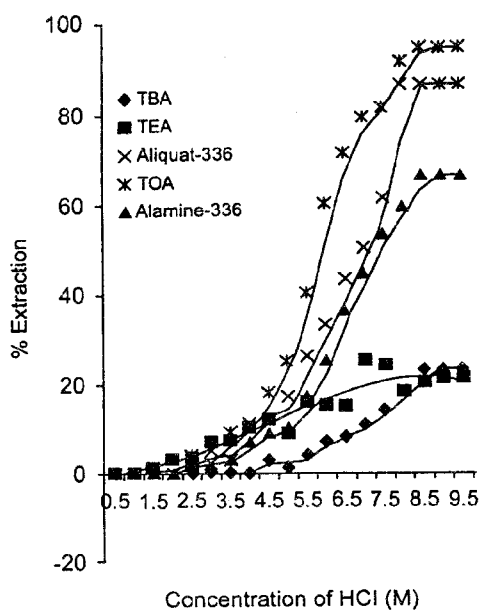


Fig. 5: Single extraction of Co (II) with 5 ml of 5 % tertiary amines.

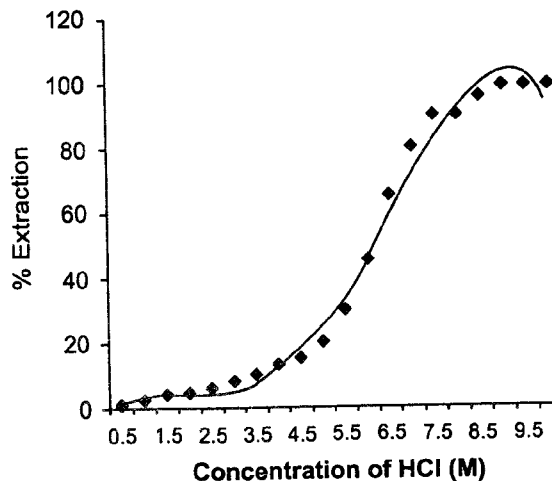


Fig. 6: Double extraction/ extraction in portions with 10 ml (5 ml+5 ml portions) of 5 % TOA/ benzene.

Experimental

Instrumentation

Hitachi Polarized Zeeman atomic absorption spectrophotometer (Model Z-8000) in the flame mode was used through out these studies. Instrumental conditions are summarized in Table-3.

Reagents

All the reagents and solvents used were of analytical grade. All aqueous solutions were prepared in distilled water. All working solutions were prepared by dilution as required.

Cobalt (II) solution was prepared by dissolving the requisite amount of cobalt metal in 1:1

Table-4 Analysis of synthetic mixtures for cobalt (II).

S. No	Concentration of Cobalt (μg)			Other Elements Present (100 μg) each.
	Present	Recovered	% Recovery	
1.	20.00	19.78	98.90	Ca, Mg, Si, Al, Fe, Na, K, Ni, Zn, Mn, Cu, Pb, Cr, Ag.
2.	20.00	19.80	99.00	Ca.
3.	20.00	19.80	99.00	Ca, Mg.
4.	20.00	19.92	99.60	Ca, Mg, Si.
5.	20.00	19.60	98.00	Ca, Mg, Si, Al.
6.	20.00	19.50	97.50	Ca, Mg, Si, Al, Fe.
7.	20.00	19.40	97.00	Ca, Mg, Si, Al, Fe, Na.
8.	20.00	19.60	98.00	Ca, Mg, Si, Al, Fe, Na, K.
9.	20.00	19.70	98.50	Ca, Mg, Si, Al, Fe, Na, K, Ni.
10.	20.00	19.65	98.25	Ca, Mg, Si, Al, Fe, Na, K, Ni.
11.	20.00	19.73	98.65	Ca, Mg, Si, Al, Fe, Na, K, Ni, Zn.
12.	20.00	19.63	98.15	Ca, Mg, Si, Al, Fe, Na, K, Ni, Zn, Mn.
13.	20.00	19.75	98.75	Ca, Mg, Si, Al, Fe, Na, K, Ni, Zn, Mn, Cu, Pb.
14.	20.00	19.77	98.85	Ca, Mg, Si, Al, Fe, Na, K, Ni, Zn, Mn, Cu, Pb, Cr.
15.	20.00	19.78	98.90	Ca, Mg, Si, Al, Fe, Na, K, Ni, Zn, Mn, Cu, Pb, Cr, Ag.

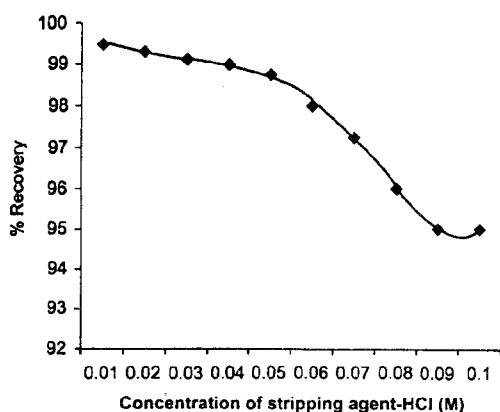


Fig. 7: Effect of stripping agent (HCl) on % recovery of Co (II).

HCl. The working standards and the blanks were acidified to the same extent as the samples. 5 % solution of Analar grade tertiary amines supplied by BDH were prepared by dissolving in thiophene free benzene and chloroform.

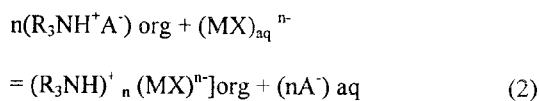
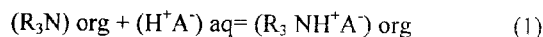
Procedure

17.5 ml of pure and concentrated hydrochloric acid (73 % δ p. gr. = 1.19) were added to the aqueous solution containing known amount (20 μ g) of Co (II) in a 100 ml separating funnel. The solution was diluted to 20 ml with distilled water, so that the final HCl concentration is 9.0 M. 5 ml of 5 % trioctylamine (TOA) in benzene solution were added to the resulting acidic aqueous solution. The two phases were shaken manually or on a mechanical shaker for 2 minutes and left over for an hour, so that the two phases may get complete separation and attain equilibrium. The loaded organic amine phase was separated from the acidic aqueous phase into a dried beaker after passing through a Schwarzband \emptyset 5.5 cm filter paper to remove the suspended water droplets. Fresh 5 ml of 5 % TOA in benzene were added to the aqueous phase left in the separating funnel and the extraction was made again as earlier. The two batches of the loaded organic amine phases were combined and stripped with 0.01 M HCl. The stripped aqueous solution as well as the aqueous phase left in the separating funnel were analysed for Co (II) using atomic absorption spectrophotometry. The percentage extraction of Co (II) was calculated from the difference of the known amount (20 μ g) of Co (II) added and left if any in the barren raffinate. Similarly the percentage recovery of Co (II) was

calculated from the known amount of Co (II) added and the amount recovered back into the aqueous phase.

Conclusions

It can be concluded from the preceding investigations that cobalt ion makes colourless chloro-complex with HCl at a specific molar concentration (9.0 M). The chloro-complex formed being anionic in nature is quantitatively extracted into the liquid ion exchanger (trioctylamine). It is obvious that 99 % cobalt is quantitatively extracted into the organic amine phase from the synthetic mixtures even in the presence of 25 fold excess of most of the interfering metal ions. The same percentage of cobalt content is also recovered with a dilute solution of HCl (0.01 M) as its chloride salt. The hydro-metallurgical method is being successfully applied for the extraction and recovery of cobalt from indigenous cobalt ore. The experimental details and the data obtained from these investigations is being presented in the form of a research publication. The technology developed is economically feasible by regeneration and recycling of the used solvent just after washing with distilled water. The overall reaction between cobalt (M) and tertiary amines (R_3N) may be represented by the following equations.



where R_3N = Tertiary amine

H^+A^- = An inorganic acid

$(MX)^{n-}$ = Anionic complex, where, M is a metal ion and X is a ligand.

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