Solvent Extraction Separation of Cobalt(II) with 2-Ethylhexyl Phosphonic Acid Mono- -2-Ethylhexyl Ester (PC-88A)

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Liquid-liquid extraction of cobalt(II) from 0.25 mol l^{-1} ammonium acetate using 0.05 mol l^{-1} 2-ethylhexyl phosphonic acid mono 2-ethylhexyl ester (PC–88A) dissolved in toluene has been proposed. The stable blue coloured complex formed by PC–88A with cobalt(II) was used for direct spectrophotometric determination at 630 nm. It obeys Beer's law in the range 10–140 µg ml^{-1}. Effect of various parameters such as reagent concentration, equilibration period, effect of various diluents and foreign ions on percentage extraction of cobalt were studied. This method was extended for the determination of cobalt in real samples. The extraction reaction proceeds with cation exchange mechanism and the extracted species has the $Co_2Ac_2L_2 \cdot 2HL$ formula.

Przeprowadzono ekstrakcję kobaltu(II) z 0.25 mol l^{-1} roztworu octanu amonu za pomocą estru 2-etyloheksylowego kwasu 2-etyloheksylofosfonowego. Otrzymany niebiesko zabarwiony kompleks o maksimum absorpcji przy 630 nm wykorzystano do bezpośredniego spektrofotometrycznego oznaczania kobaltu. Prawo Beera jest zachowane w zakresie 10–140 µg ml^{-1}. Zbadano wpływ stężenia odczynnika, czasu wytrącania, różnych rozcieńczalników na procent ekstrakcji. Metodę zastosowano do oznaczania kobaltu w rzeczywistych próbkach. Proces ekstrakcji przebiega według mechanizmu wymiany jonowej, wyekstrahowany kompleks ma skład $Co_2Ac_2L_2 \cdot 2HL$.

Key words: cobalt(II), solvent extraction, 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester, spectrophotometry

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Studies on the kinetics of solvent extraction of cobalt(II) ion with different organophosphorus acid extractants have been reported [1–4]. Extensive work was carried out on the extraction of cobalt(II) with HDEHP (bis-(2-ethylhexyl) phosphoric acid), while PC–88A (2-ethylhexyl phosphonic acid mono 2-ethylhexyl ester) has been found to be a suitable extractant for the extraction of cobalt from aqueous solution [5,6].

The extraction capacity with 100% TBP (tri-*n*-butyl phosphate) for cobalt(II) from 10 mol l^{-1} LiCl as well as with 60 % TBP in toluene were studied by various workers [7]. De *et al.* [8] have reported the quantitative extraction of cobalt(II) from KSCN(6%) with TBP in the pH range 4.0–8.0. It was also extracted with methyl isobutyl ketone (MIBK) from 4 mol l^{-1} NH$_4$SCN [9].

Literature survey reveals that the use of solvent extraction technique for recovering cobalt from aqueous solution as well as its separation from nickel has received considerable attention over the past few years. The organophosphorus extractants have proved to be most selective and therefore they are extensively studied. However the major work was observed to be dealing with rate determination, equilibrium studies, extraction kinetics and mass transfer. The kinetics of cobalt(II) extraction with PC–88A in heptane from acetate system has been studied by Zhu *et al.* [10].

In the present paper a rapid method for quantitative extraction of cobalt(II) and its direct determination by spectrophotometry has been described. The method was found to be suitable for separation of cobalt from nickel, copper, iron and chromium. The applicability of the proposed method for determination of cobalt in various real samples is studied.

EXPERIMENTAL

The extractant, 2-ethylhexyl phosphonic acid mono 2-ethyl hexylester (PC–88A) was supplied by Dai-hachi Chemical Industries, Japan, and was used without further purification. Stock solution of cobalt(II) was prepared by dissolving 4.037 g of hydrated cobalt chloride, (CoCl$_2$ 6H$_2$O) in 5 ml of HCl and was further diluted to one litre with distilled water. Amount of cobalt in the stock solution was standardised by the gravimetric method [11]. The required concentration of cobalt was obtained by further dilution. All other chemicals used were of analytical grade.

All absorbance measurements were carried on GBC 911A UV–VIS spectrophotometer using 1cm path length quartz cell. Elico model LI–120 pH meter with combination electrode was used for H$^+$ ion concentration studies.
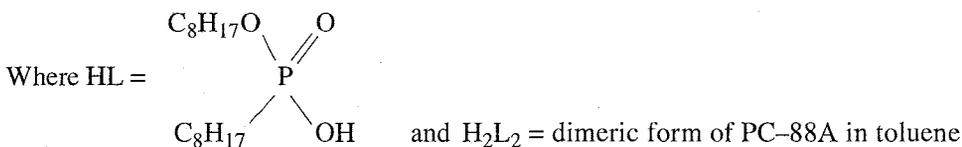
General procedure

An aliquot of cobalt(II) solution containing 40 µg ml^{-1} was taken and an appropriate amount of ammonium acetate solution was added to make its concentration of required molarity after final dilution up to 10 ml. Thereafter to the aqueous phase 10 ml of extractant (PC–88A) in toluene was added, equilibrated for 1 min and the both phases were allowed to separate. Once the equilibrium is attained, the two phases were allowed to separate and pH of the aqueous phase was measured. The amount of unextracted cobalt was determined by the nitroso-R-salt method[12]. The blue coloured complex formed in the organic phase was determined directly at 630 nm against reagent blank.

RESULTS AND DISCUSSION

Determination of complex composition

The equilibrium for extraction of Co(II) from acetate medium with PC–88A in toluene can be generalised as

$$pCo^{2+} + qAc^- + z\overline{H_2L_2} \underset{}{\overset{K_{ex}}{\rightleftharpoons}} \overline{Co_pAc_qL_zzHL} + zH^+ \tag{1}$$

Where HL =

$$\begin{array}{c} C_8H_{17}O \diagdown \diagup\!\!\!\diagup O \\ P \\ C_8H_{17} \diagup \diagdown OH \end{array}$$ and H_2L_2 = dimeric form of PC–88A in toluene

It is generally accepted that PC–88A is dimeric in solvents of low polarity [13].

$$K_{ex} = \frac{[\overline{Co_pAc_qL_zzHL}]\,[H^+]^z \times f(y)}{[Co^{2+}]^p\,[Ac^-]^q\,[\overline{H_2L_2}]^z} \tag{2}$$

where K_{ex} is the extraction equilibrium constant and f(y) refers to the equilibrium ratio of activity coefficient of species. Assuming f(y) is constant, the apparent equilibrium constant (K'_{ex}) is given as

$$K'_{ex} = \frac{[\overline{Co_pAc_qL_zzHL}]\,[H^+]^z}{[Co^{2+}]^p\,[Ac^-]^q\,[H_2L_2]^z} = \frac{K_{ex}}{f(y)} \tag{3}$$

If $[\overline{Co_pAc_qL_zzHL}]$ is the only extracted species, then, the distribution ratio (D) can be expressed as

$$D = \frac{[\overline{Co_pAc_qL_zHL}]}{[Co^{2+}]} \tag{4}$$

and the Eq.(3) can be written as

$$K'_{ex} = \frac{D\,[H^+]^z}{[Co^{2+}]^{p-1}\,[Ac^-]^q\,[\overline{H_2L_2}]^z} \tag{5}$$

Thus,

$$\log D = \log K'_{ex} + z\log[\overline{H_2L_2}] + z\,pH + (p-1)\log[Co^{2+}] + q\log[Ac^-] \tag{6}$$

The stoichiometry of the extracted species was determined by analysing the experimental data. The relationship between $\log D$ and equilibrium pH is linear with the slope equal 2.2 (Fig. 1), which confirms that two protons were released during the cation exchange reaction.

Dependence of distribution ratio on reagent concentration was found by ploting $\log D - 2pH$ *vs.* $\log[\overline{H_2L_2}]$ at constant 0.25 mol l^{-1} ammonium acetate. A linear graph
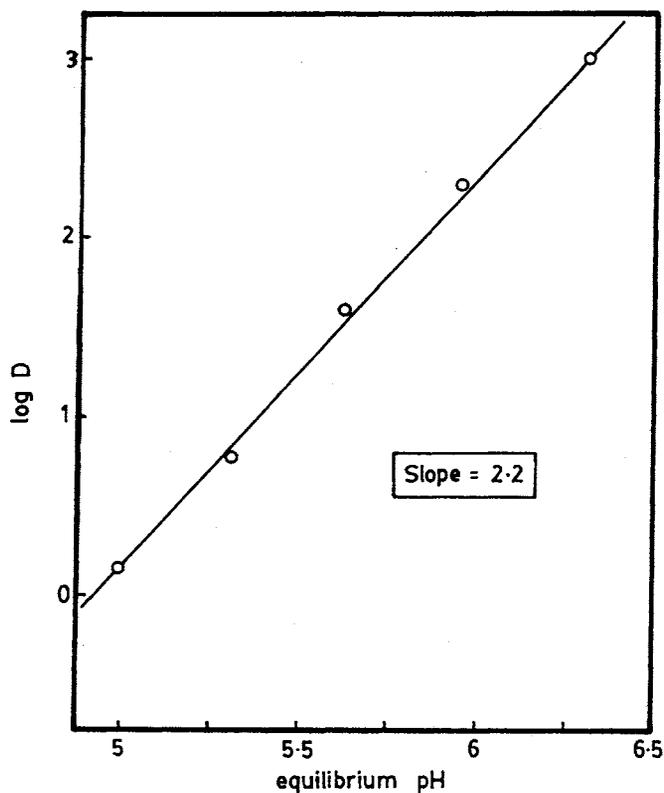
Figure 1. Dependence of log D on equilibrium pH for cobalt(II) extraction with 0.05 mol l^{-1} PC–88A in toluene
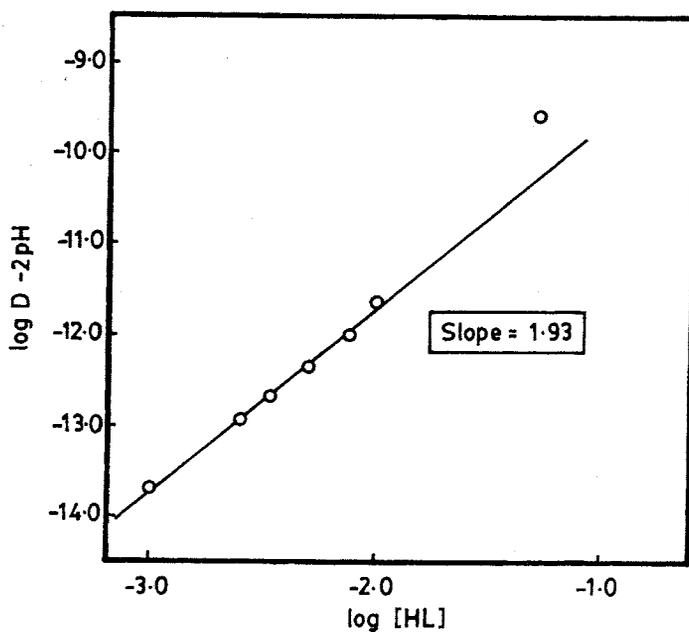

Figure 2. Dependence of log D for cobalt(II) extraction on logarithm of PC–88A concentration in toluene; ammonium acetate = 0.25 mol l^{-1}

with the slope 1.93 (Fig.2) indicates two ligand molecules involved in the extraction reaction. In order to find the dependence of the distribution coefficient, on the acetate ion concentration a graph of $\log D - 2\log[H_2L_2]$ against $\log[Ac^-]$ was plotted. It was observed that the linear graph has the slope 2.14 (Fig. 3) indicating two acetate ions consumed in the reaction.
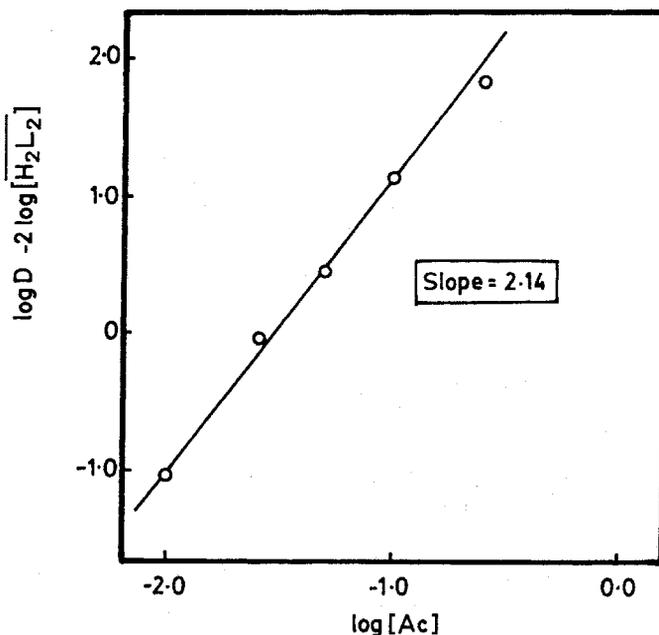

Figure 3. Dependence of log D − 2 log [H_2L_2] on the logarithm of acetate concentration; PC–88 A = 0.05 mol l^{-1}

The above experiments indicate the values q = 2, p = 2 and z = (2p − q) = 2 hence the extraction reaction is

$$2Co^{2+} + 2Ac^- + 2H_2L_2 == Co_2Ac_2L_22HL + 2H^+ \qquad (7)$$

RESULTS AND DISCUSSION

Effect of experimental parameters

The extraction of cobalt(II) with PC–88A dissolved in toluene was performed at varying concentrations (0.01–4.0 mol l^{-1}) of ammonium acetate (Table 1). It was observed that 0.1–0.5mol l^{-1} ammonium acetate is required for quantitative extraction of cobalt, hence all the extraction studies were carried out at 0.25 mol l^{-1} ammonium acetate. The increase in ammonium acetate concentration above 0.75 mol l^{-1} and the decrease in concentration below 0.05 mol l^{-1} gives lower distribution ratio (D) values, which is observed from the decrease of the absorbance of the blue coloured complex species formed.

Table 1. Effect of ammonium acetate concentration on the distribution ratio of cobalt(II). Co(II) = 40 μg ml^{-1}, PC–88A = 0.05 mol l^{-1}

Ammonium acetate (mol l^{-1})	% Extraction (E)	Distribution ratio (D)
0.01	58.3	1.40
0.025	87.4	6.94
0.05	97.6	40.67
0.1	99.5	199.0
0.25	99.9	999.0
0.5	99.9	999.0
0.75	98.3	57.82
1.0	97.2	34.71
1.5	94.1	15.95
2.0	90.3	9.31
3.0	81.1	4.29
4.0	71.3	2.48

A known aliquot of cobalt (40 μg ml^{-1}) in 0.25 mol l^{-1} ammonium acetate was extracted with different concentration (0.1–0.001 mol l^{-1}) of PC–88A dissolved in toluene. It was observed that minimum of 0.05 mol l^{-1} PC–88A was required to extract cobalt quantitatively.

The effect of various diluents on the percentage extraction of cobalt extraction with 0.05 mol l^{-1} PC–88A was studied. It was found that the extraction of cobalt was quantitative with toluene, xylene, chloroform, benzene, carbon tetrachloride, hexane and cyclohexane except MIBK (89.6%). Among the various solvent studied, toluene was preferred since it permits clear cut separation of the two phases.

Effect of equilibration time and metal concentration

When extraction of cobalt from 0.25 mol l^{-1} ammonium acetate using 0.05 mol l^{-1} PC–88A dissolved in toluene was carried out at different equilibration periods ranging from 1 min to 20 min equilibration is attained very rapidly, and shaking of the two immiscible phases beyond 1 min does not effect the extraction capacity of the reagent.

The extraction of cobalt at varying concentration ranging from 5 to 200 μg ml^{-1} was carried using 0.05 mol l^{-1} PC–88A in toluene with 1 min shaking. It was observed that the system confirms the Beer's law in the concentration range from 10 to 140 μg ml^{-1} of cobalt in the presence of 0.25 mol l^{-1} ammonium acetate. Sandell's sensitivity and molar absorptivity were found to be 0.045 μg ml^{-1} cm^{-2} and 5.3×10^3 l mol^{-1} cm^{-1}, respectively.

The extracted cobalt from the organic phase can also be back extracted quantitatively into the aqueous phase by stripping with 1.0 mol l^{-1} hydrochloric acid. Cobalt(II) after stripping was determined spectrophotometrically by nitroso-R-salt method [12].

The stability of blue coloured complex species formed by cobalt with PC–88A in toluene was determined by monitoring the absorbance value at 630 nm after definite time intervals. The complex was stable for almost 4 days.

Effect of foreign ions

The extraction of cobalt was carried out in the presence of large number of foreign ions. Their tolerence was decided to a limit causing not more than $\pm 1\%$ error in its determination (Table 2). It was observed that large number of ions were tolerated at varying ratios. Among these EDTA and Bi^{3+} showed strong interference.

Table 2. Effect of foreign ions

Tolerance limit						
<1 mg	<2 mg	<3 mg	<4 mg	<5 mg	<10 mg	<15 mg
Cr(VI),Ni(II) Al(III),Pb(II); Citrate,Fe(III)	Zn(II), Mg(II); Cd(II),Hg(II); In(III),Ba(II), Cu(II)	Mn(II); V(V); Ca(II)	Rb(I), Cs(I); Sr(II)	Br^- Tartrate Oxalate	Na(I); K(I); Cl^-	I^- SO_4^{2-} SO_3^{2-}

Separation of Cobalt(II) from binary mixtures

By exploiting the differences in various extraction conditions, cobalt can be separated from nickel(II), iron(III), chromium(VI) and copper(II) (Table 3). Whereas advantage of the differences in the extraction behaviour of PC–88A towards cobalt(II), copper(II) and iron(III) from acetate media in the presence of masking agent such as oxalate and fluoride can be taken for their separation. From a mixture of cobalt(II) and nickel(II), cobalt(II) was first extracted using 0.05 mol l^{-1} PC–88A in toluene at acetate concentration of 0.25 mol l^{-1} with an equilibration period of 1 min where nickel remains unextracted in the aqueous phase. During the separation of cobalt(II) from iron(III) and copper(II), 5% sodium fluoride and 2% oxalate solutions were used as masking agents. In the case of cobalt(II) and chromium(VI) mixture, cobalt(II) gets extracted first since chromium(VI) is masked with ammonium acetate.

Table 3. Separation of cobalt(II) from binary mixtures. The content of foreign ions was determined spectrophotometrically. Composition: ammonium acetate = 0.25 mol l^{-1}, PC–88A in toluene = 0.05 mol l^{-1}, equilibration time = 1 min

Mixtures µg, added			Found, µg		% Recovery	
Co	+	Ni(II)	Co	Ni	Co	Ni
800		70	786	68	98.3	97.1
800		400	790	385	98.8	96.3
800		700	785	671	98.1	95.9
Co	+	FeII	Co	Fe	Co	Fe
200		800	198	789	99.0	98.9

Table 3 (continuation)						
200		500	196	503	98.0	100.6
600		300	597	301	99.5	100.3
Co	+	Cr(VI)	Co	Cr	Co	Cr
200		100	200	99	100	99.0
300		50	295	49	98.3	98.0
100		200	101	203	101	101.5
Co	+	Cu(II)	Co	Cu	Co	Cu
600		200	603	193	100	96.5
200		300	200	301	100	100.3
200		400	196	390	98.0	97.5
600		100	589	101	98.1	101.0

[#] – Co was extracted by masking iron with 2 ml of 5% sodium fluoride.
[*] – Co was extracted by masking copper with 2 ml of 2% oxalate solution.

Analysis of real samples

Under the optimized conditions for cobalt extraction the method was applied in the analysis of real samples. The samples No. 1,2 and 3 were treated separately with 5 ml of aqua regia and evaporated to dryness and sample solutions were prepared and used for analysis. The results obtained were found to be in agreement with the label claimed (Table 4).

Table 4. Analysis of real samples

Samples	Co taken, μg	Co found, μg by AAS	Co found, μg* proposed method	% Recovery
1. Co–MgO Catalyst	200	200	201	100.5
	400	399	396	99.0
	600	599	598	99.7
2. Co–ZrO$_2$ Catayst	200	199	197	98.2
	250	251	250	100
	400	395	396	99.0
3. Vitamin B$_{12}$ injection (Glaxo Ltd.)	30 mg ml^{-1} (certified value)		29.8* mg ml^{-1}	99.3
Vitamin B$_{12}$ injection (Lupin Lab. Ltd.)	30 mg ml^{-1} (certified value)		29.9* mg ml^{-1}	99.6

* mean of three determinations.

CONCLUSION

The stoichiometry of the extracted spescies was determined by the conventional slope analysis method. The above results indicate that cobalt(II) is extracted by the cation exchange reaction. The nature of the extracted organic species is $Co_2Ac_2L_2$ 2HL.

The proposed method is simple, rapid and gives reproducible results. Cobalt can be determined directly in the organic phase and the coloured complex is stable for four days. The method can be used effectively for separation purpose. Determination of cobalt in various real samples is possible by the proposed method.

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