

to have the values: $\log K_1^H = 9.49$ and $\log K_2^H = 2.30$ at 25° and $0.1M$ $NaClO_4$. These values are in good agreement with those reported by Perrin³, who obtained the two pK values as $pK(\alpha-COOH) = 2.31$ and $pK(\alpha-NH_2) = 9.66$ at 20° and $1M$ KCl .

The pH titrations reveal that in $Hg(II)$ - α -amino-butyrate system the solution remains clear throughout but in the $Be(II)$ and $Cd(II)$ systems precipitation occurs at $pH \sim 7.0$ and ~ 9.5 , respectively. Calculations for \bar{n} values have been done only up to these pH values, before the precipitation starts.

The formation curves (Fig. 1) of the metal chelates show that in all the cases \bar{n} attains a maximum value of ≈ 2 and thus the formation of two chelates ML and ML_2 is indicated.

From an analysis of the formation curves, it is clear that for these systems K_1/K_2 ratio are ~ 10 , hence their stepwise stability constants have been computed by correction term and successive approximation methods. Results are presented in Table 1. ΔG values were calculated using the relation: $\Delta G = -RT \ln K$, and these are also given in Table 1.

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Solvent Extraction of $Cd(II)$ with N -Butylaniline in Chloroform from a Mixture of Potassium Iodide & Sulphuric Acid

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Cadmium is quantitatively extracted with N -butylaniline in chloroform from a mixture of $0.5M$ potassium iodide and $0.5M$ sulphuric acid. It is easily stripped from the organic phase with ammonia buffer ($pH = 10$) and determined complexometrically with EDTA using PAR as indicator. Cadmium is separated from many cations and anions. Log-log plot of the distribution coefficient versus concentration of amine indicates a 2 : 1 limiting mole ratio of amine to metal and the probable extracted species is $(R_2NH_2)_2CdI_4^{2-}$.

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IN the present investigation N -butylaniline¹ in chloroform is reported as a new analytical extraction reagent for $Cd(II)$ from a mixture of potassium iodide and sulphuric acid. Cadmium(II) is readily and quantitatively extracted from a mixture of $0.5M$ potassium iodide and $0.5M$ sulphuric acid.

General procedure—A $0.1M$ solution of $Cd(II)$ was prepared by dissolving the required amount of cadmium nitrate in redistilled water and standardized complexometrically with EDTA using PAR as indicator.

To an aliquot of solution containing up to 50 mg of $Cd(II)$ was added enough quantity of $6M$ freshly prepared solution of potassium iodide, $4M$ sulphuric acid and water so that the solution had $0.5M$ potassium iodide and $0.5M$ sulphuric acid in a volume of 15 ml. The solution was stirred for 1-2 min with a solution of N -butylaniline (0.7 g in 10 ml chloroform). The chloroform layer was separated and the aqueous layer reextracted with N -butylaniline solution (10 ml). The organic layers were combined and $Cd(II)$ stripped off from the organic phase by shaking for 2 min with ammonia buffer (25 ml, $pH = 10$). The aqueous phase separated, warmed and to this was added 4-(2-pyridylazo) resorcinol (PAR) indicator (0.1%, w/v in water) and titrated slowly with standard EDTA till the colour changed from red to yellow.

Cadmium(II) could be easily extracted and separated from many cations and most of the common anions did not interfere (Table 1). Antimony(III and V) was kept in solution in the presence of tartaric acid. Aluminium(III) was slightly extracted but in presence of citric acid it caused no interference. Common anions such as sulphate, chloride, citrate, phosphate, tartarate and fluoride did not interfere. Several binary synthetic samples were analysed and the relative error was found to be $\pm 2.5\%$.

The extraction is quantitative at aqueous to organic phase ratio of 1:1.5 and in the presence of

TABLE 1 — PERMISSIBLE AMOUNTS OF VARIOUS IONS IN THE EXTRACTION OF $Cd(II)$

[$Cd(II)$ added 11.24 mg; $0.50M$ KI and $0.50M$ H_2SO_4]

Foreign ion	Amount (mg)	Foreign ion	Amount (mg)
Co(II)	59	Nd(III)	14
Ni(II)	58	Gd(III)	15
Hg(II)	100	Rh(III)	5
Sb(III) ^a	120	La(III)	14
Fe(II)	110	Er(III)	16
Al(III) ^b	43	Sc(III)	25
Ca(II)	30	Y(III)	30
Sr(II)	30	W(VI) ^a	5
Mg(II)	30	Nb(V) ^a	7
Cr(III)	30	Ta(V) ^a	7
Zn(II)	32	Tartrate	1000
Ga(III)	50	Citrate	1000
Ce(III)	14	Phosphate	1000
Pr(III)	14	Fluoride	250

(a) In the presence of tartaric acid (1000 mg).

(b) In the presence of citric acid (500 mg).

Extraction of Pd(II)-Thiocyanate Complex with Ethyl Acetate from Aqueous Phase

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Pd(II)-thiocyanate complex has been extracted with ethyl acetate to the extent of $95 \pm 2\%$ from $2M$ HCl in the presence of NH_4Cl . The effects of acidity, ammonium thiocyanate concentration, salting-out agents (like $MgCl_2$, or NH_4Cl), period of extraction and presence of diverse ions on the extraction behaviour of Pd(II) have also been investigated.

NUMEROUS solvents have been used to extract Pd(II) from aqueous phase in its chloride, nitrate, thiocyanate and iodide forms¹⁻⁴. Previous work on the extraction of thiocyanate complex of Pd(II) from aqueous solution with tributyl phosphate was carried out by De and Sen⁵ and Berg⁶.

The present work shows that Pd(II) thiocyanate complex can be extracted with ethyl acetate from aq. phase. In its chloride, bromide or iodide forms, Pd(II) was not extracted at all with ethyl acetate. The effect of acidity, salting out agents, reagent concentration, period of extraction and interferences due to other cations and anions on the extraction behaviour is discussed.

The chemicals used were of CP or AR grade. Ethyl acetate (BDH) was distilled before use. A 2% aqueous solution of ammonium thiocyanate was used for complex formation.

A stock solution of palladium chloride was prepared by dissolving 1 g of $PdCl_2$ (Johnson Matthey) in 1 ml conc. hydrochloric acid and diluting to 250 ml with distilled water. The solution was standardized gravimetrically using dimethylglyoxime⁷ and was found to contain 2.53 mg of Pd(II) per ml.

Procedure — Calculated amount of hydrochloric acid of known strength was added to an aliquot containing 12.65 mg of Pd(II) to have the desired acid concentration ($2M$) followed by the addition of aqueous ammonium thiocyanate solution (2%, 2 ml) and volume made up to 20 ml with distilled water. The aqueous solution thus prepared was shaken with 10 ml of ethyl acetate for 10 min. The two layers were allowed to separate and the organic phase separated. Palladium was back-extracted from the ethyl acetate phase by shaking for 10 min with distilled water (3×15 ml). The aqueous extracts were combined and evaporated to dryness. The residue was then digested with perchloric acid to destroy ammonium thiocyanate and any other organic matter cooled, diluted with water and Pd(II) estimated gravimetrically by dimethyl glyoxime.

The extraction behaviour of Pd(II) with ethyl acetate was investigated with various concentrations of hydrochloric acid (from 0.06 to $5M$). Maximum extraction was 87% from $3M$ hydrochloric acid. Above $5M$ hydrochloric acid concentration the organic phase was found to be miscible with the aqueous phase.

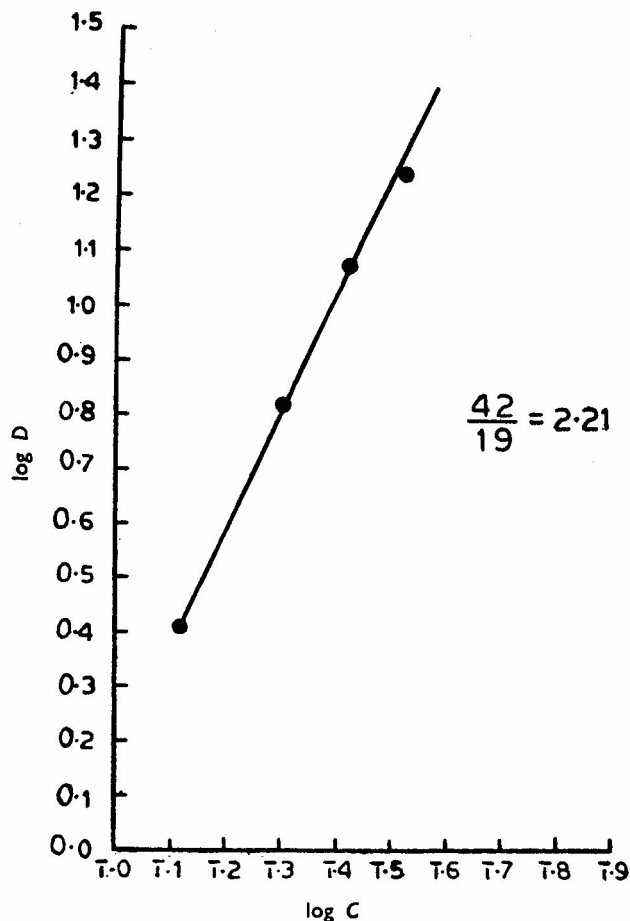


Fig. 1 — Plot of log D versus log C

0.5M KI and 0.5M H_2SO_4 . Two 10 ml portions of 7% extractant were sufficient to extract 50 mg of Cd(II) and larger amounts could be dealt with by further extraction. Quantitative extraction was achieved by equilibrating the aqueous and the organic phase for 2 min in the temperature range $15-40^\circ$.

Nature of extracted species — The nature of probable extracted species was investigated by single extraction of fixed amount of Cd(II) with varying concentrations of N-butylaniline, while keeping the other conditions constant as given under the general procedure. The ratio of the aqueous to organic phase was 1:1.5. The plot of log D (distribution coefficient) versus log C (concentration of N-butylaniline) gave a slope of 2.21 (Fig. 1) indicating that the probable extracted species is $H_2CdI_4 \cdot 2N$ -butylaniline.

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