Extraction of Cr(VI) from Orthophosphoric Acid Solutions by Trilauryl Amine

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The extraction of Cr(VI) from orthophosphoric acid solutions by trilauryl amine has been studied. The nature of the species extracted is established to be $Cr_2O_7^{2-}$.

QUANTITATIVE extraction of Cr(VI) as CrO_3Cl^- from hydrochloric acid media by tertiary amines and related systems has been reported[1-3]. Deptula[4] reported the Cr(VI) extraction from orthophosphoric acid media by tri-n-octyl amine. No phosphate was found in the organic phase and the extracted species was characterized as $Cr_2O_7^{2-}$. The results of our studies on the extraction of Cr(VI) by trilauryl amine (TLA) from orthophosphoric acid media are reported in this note.

Trilauryl amine (M/s General Mills, Kankakee, Illinois) was used as such. All other chemicals used were of analytical grade or samples purified according to the standard methods. Chromium-51 in the form of sodium chromate in isotonic saline solution (15 mCi/mg specific activity) and phosphorus-32 carrier-free in the form of orthophosphoric acid in hydrochloric acid were obtained from the Isotope Division, BARC, Bombay.

Extraction of orthophosphoric acid by TLA — Phosphoric acid extractions were carried out using 25 ml of the aqueous phase containing appropriate concentrations of orthophosphoric acid and added ^{32}P tracer by equilibrating with an equal volume of trilauryl amine in chloroform and the β-activity in both the phases was measured after separation with a liquid GM counting assembly.

Moore[5] observed that the extraction of orthophosphoric acid varied with aqueous volume. Our studies of the extraction of orthophosphoric acid into 0·025M TLA in chloroform are shown in Fig. 1.
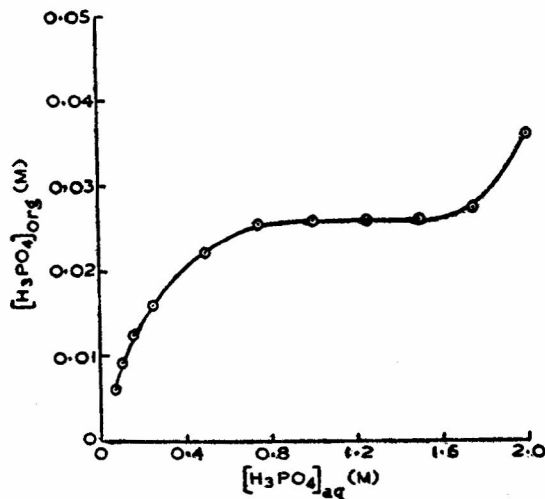
It is seen that 1:1 salt formation between TLA and H_3PO_4 occurs in the organic phase only from solutions containing phosphoric acid up to sixty times the concentration of amine. At higher concentrations of phosphoric acid there is an increase in the extraction indicating that the organic phase takes up more acid than that required for the formation of $(R_3NH^+H_2PO_4^-)$.

Chromium(VI) extraction — Chromium(VI) distribution studies were made using appropriate concentration of chromic acid, orthophosphoric acid and added tracer by equilibrating with an equal volume of trilauryl amine in chloroform, pre-equilibrated with 0·1M H_3PO_4. The γ-activities in the two separated phases were measured with a single channel analyser coupled with a 3″ well-type NaI(Tl) scintillation detector.

For finding out the effect of acidity, extractions were carried out using 0·05M trilauryl amine in chloroform pre-equilibrated with 0·1M H_3PO_4 and 0·025M chromic acid with added tracer at various concentrations of H_3PO_4. Up to 3M H_3PO_4 concentrations the extractions are quantitative and independent of acid concentration beyond which Cr(VI) undergoes reduction to Cr(III).

Composition of the extracted species — In order to determine the composition of the extracted species the extraction isotherm method[6] was employed. Extractions were carried out using different concentrations of Cr(VI) in 0·1M H_3PO_4 keeping [TLA] constant. A plot of $[Cr_{org.}]$ vs $[Cr_{aq.}]$ gave an extraction isotherm which rises steeply to a maximum value and remains practically constant thereafter. The ratio of concentrations of trilauryl amine to the maximum concentration of Cr(VI) extracted corresponds to a value of 1·05.

In view of the very high distribution coefficient values the distribution ratio method of Hesford and Mckay[7] could not be adopted for the evaluation of the composition of the extracted species.

Extractions of varying concentrations of Cr(VI) from H_3PO_4 solutions containing constant ^{32}P tracer were carried out using 0·05M TLA pre-equilibrated with 0·1M H_3PO_4. Fig. 2 shows the

Fig. 1 — Extraction of orthophosphoric acid into TLA (0·025M) in chloroform
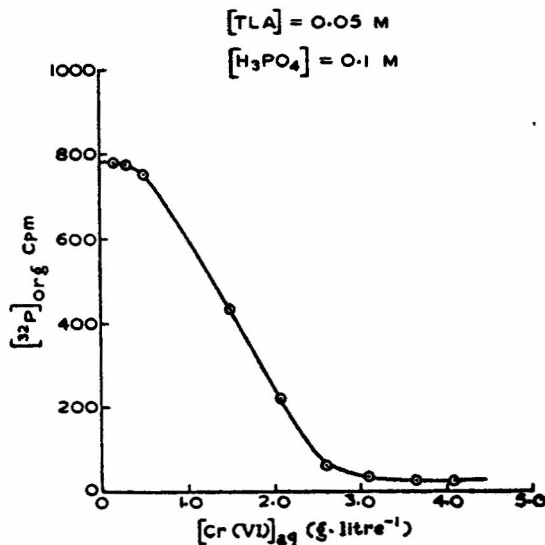

$[TLA] = 0.05$ M
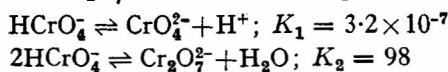$[H_3PO_4] = 0.1$ M

Fig. 2 — Distribution of ^{32}P activity as a function of [Cr(VI)]

distribution of activity of ^{32}P in the organic phase as a function of Cr(VI) concentration in the aqueous phase. It is seen that as long as the Cr(VI) concentration is significantly less than that required for 1:1 salt formation, the ^{32}P activity remains unaltered in the organic phase. However, as the Cr(VI) concentration in the aqueous phase approaches the amine concentration, the ^{32}P activity in the organic phase shows a decrease and finally as the Cr(VI) concentration becomes equal or greater than the amine concentration, all the ^{32}P activity is found in the aqueous phase. This experiment clearly confirms the absence of phosphate in the Cr(VI) species extracted into amine.

In aqueous systems Cr(VI) exhibits[8-10] various equilibria giving rise to different species. Under the experimental conditions the predominant species $HCrO_4^-$ and $Cr_2O_7^{2-}$ arise from the equilibria:

$$HCrO_4^- \rightleftharpoons CrO_4^{2-}+H^+; \quad K_1 = 3\cdot2\times10^{-7}$$
$$2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-}+H_2O; \quad K_2 = 98$$

These two species can be extracted as $(R_3NH^+HCrO_4^-)$ or $(R_3NH^+)_2Cr_2O_7^{2-}$ respectively by the extractant. In both the cases the extraction isotherm is expected to give a Cr(VI)-amine ratio of 1:1.

The UV spectrum of the extracted species shows maxima at 280 and 355 nm with a peak ratio of 1·8 (approximately two). These spectral characteristics are attributed to $Cr_2O_7^{2-}$ (ref. 2, 3).

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Extractive Titrimetric Determination of Hg(II), Cu(II) & Ag(I) Using Lead Diethyldithiocarbamate

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A procedure for the selective determinations of Hg, Ag, Hg-Cu and Ag-Cu is described. Lead diethyldithiocarbamate [Pb(DDC)₂] undergoes quantitative, stoichiometric and fast exchange reactions with Hg(II), Ag(I) and Cu(II), even near the equivalence point, making it a suitable reagent for their determinations. Cobalt does not interfere in the determination of these cations.

KREIMER *et al.*[1] used chloroform solution of Cu(DDC)₂ for extractive titration of Ag(I). Lead diethyldithiocarbamate has also been used by many workers[2-5] for the spectrophotometric determination of Cu(II). In this note Pb(DDC)₂ has been used as a potential extractive titrimetric reagent for the selective determination of Hg(II) and Ag(I) alone and in binary combinations with Cu(II).

A stock solution of Pb(DDC)₂ $(2\times10^{-4}M)$ was prepared by dissolving 101 mg/litre of Pb(DDC)₂ in chloroform and diluting with carbon tetrachloride (1:20, v/v) to make up to the mark. Similarly, its $1\times10^{-3}M$ solution was prepared. Dissolving Pb(DDC)₂ in carbon tetrachloride takes a long time and chloroform makes the preparation of titrant solution easy.

Metal ion solutions were prepared by dissolving analytical grade metal salts, standardizing by volumetric methods and then preparing more dilute solutions from these standardized solutions.

Acetate buffer was prepared by mixing 2M solutions of sodium acetate and acetic acid in the ratio 4:1 (v/v).

Erma photoelectric colorimeter AE-II was used for absorbance measurements. Titrations were performed using a specially constructed titration apparatus similar to that proposed by Galik[6].

Determination of Hg and Ag can be done by locating the end points visually, and also colorimetrically. The diethyldithiocarbamate of Hg and Ag formed during the titrations does not give any absorbance changes with the filter 420 nm used for measuring absorbance due to Cu(DDC)₂ formed during titrations.

Procedure for Hg(II) and Ag(I) — An appropriate amount of the metal ion to be analysed was taken, diluted to 20 ml with distilled water and the pH adjusted to 4·0-5·5 by adding 2 ml of acetate buffer. About 2 μg of Cu was added as indicator. Titrant $(2\times10^{-4}M)$ was added in 1 ml portions, shaking for half a minute each time and separating the extract after each addition. The titration was continued until the extract showed brownish colouration due to the formation of Cu(DCC)₂. The titration was repeated, adding in one lot the reagant solution (1 ml less than that is required in the first titration), retaining about 0·5 ml of the organic phase, then continuing with the addition of reagent in 0·1 ml portions until the extract showed brownish colouration.

For locating the end points colorimetrically, about 50 μg of copper was added to the aqueous phase taken in the titration apparatus containing 20 ml of CCl₄. Aqueous phase made nearly 20 ml and the pH adjusted to 4·0 to 5·5 as before. The titrant solution $(1\times10^{-3}M)$ was added in 0·1 ml portions with shaking of about 1 min each time. After setting the phases, absorbance of the organic phase was measured against CCl₄ blank. Absorbance of the organic phase does not change during the exchange of Hg or Ag with the titrant. After the end point, absorbance of the organic phase, started increasing owing to the formation of Cu(DCC)₂ giving a break in the titration curve.

Procedure for Hg-Cu and Ag-Cu — Simultaneous determinations of Hg-Cu and Ag-Cu were done by locating the end points colorimetrically and adopting the procedure as given for single cations. After