

Solvent Extraction of Chlorocomplexes by Triisooctylamine/ Carbon Tetrachloride from Hydrochloric Acid Medium

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The extraction of different metal ions from aqueous solutions containing varying amounts of hydrochloric acid into carbon tetrachloride containing triisooctylamine has been investigated.

Solvent extraction using long chain alkyl amines such as triisooctylamine (Tioa) has been used for a long time by radio chemists. Thus, plutonium, thorium, americium, neptunium, and uranium have been separated from various elements by Tioa extractions.¹⁻¹⁰ The separation of tantalum from niobium¹¹ and trace amounts of zinc from nickel¹² as well as silver from cadmium and rhodium¹³ have been carried out by Tioa extraction using acetic, hydrochloric, nitric or sulfuric acid solutions.

Bruin *et al.*¹⁴ have studied the extraction of anionic beryllium complexes by Tioa, and extraction of chlorocomplexes of indium and gallium has been reported by Good and Holland Jr.¹⁵

The number of carbon atoms in the amines used in solvent extraction may vary. Long chained or branched primary, secondary, or tertiary amines are applicable. Carbon tetrachloride, xylene, benzene, kerosene *etc.* may be used as solvents. Obviously, such differences give raise to varying effects.¹⁶

The present study was undertaken to investigate the influence of the hydrochloric acid concentration of the extractability of chlorocomplexes into Tioa dissolved in carbon tetrachloride.

EXPERIMENTAL

Apparatus. A Zeiss spectrophotometer modell PMQ II and a Tastpolarograph, Selector D, were used to measure optical densities and diffusion currents, respectively. The extractions were undertaken by use of ordinary 100 ml separating funnels.

Materials. The triisooctylamine was obtained from Union Carbide Inc. A 20 %, v/v, solution in carbon tetrachloride, prepared fresh every day, was used. Stock solutions of the metal chlorides, about 0.1 M, were prepared by dissolving appropriate amounts of the oxides or the chloride salts in hydrochloric acid or water. All of them were standardized by ordinary analytical methods. (The stock solution of silver, lead, and thallium were

10^{-2} to 10^{-3} M.) The contents of hydrochloric acid were also determined. In order to prevent oxidation of Sn(II), Fe(II), Ti(III), and Cu(I), nitrogen was bubbled through the solutions.

Analytical methods. Whenever possible, EDTA-titrations (in some cases spectrophotometric or polarographic methods) were used to determine the concentrations of the metal ions. The hydrochloric acid content was determined argentometrically or by sodium hydroxide titration.

Procedure. To aliquots of the metal chlorides, different amounts of hydrochloric acid were added, and the solutions were then diluted to 50 ml with distilled water. The temperature was adjusted to 20°C before 10 ml of the Tioa solution was added to the aqueous phases. After 2 min of shaking the layers were separated. The amount of metal chloride remaining in the aqueous phase after extraction was determined. The difference between the amount added to the aqueous phase and the amount remaining in the aqueous phase after the organic layer is separated is assumed to have entered the organic phase. The percentage of the metal extracted, E , was calculated.

RESULTS

The extraction curves of various metals are given in Figs. 1, 2, and 3. The values of E from 1, 2, and 6 N hydrochloric acid solutions are given in Table 1.

Table 1. Metal extracted (%) at varying hydrochloric acid concentrations.

	1 N	2 N	6 N
Al	0	0	0
Ag	—	100	67
As(III)	7	10	81
As(V)	0	1	5
Bi(III)	100	100	76
Cd	99	99	100
Co	0.5	2	72
Cr(III)	0	0	0
Cr(VI)	100	100	—
Cu(I)	98	98	100
Cu(II)	8	23	87
Fe(II)	0	2	36
Fe(III)	87	100	100
Ga	10	57	100
Hg(II)	100	100	100
In(III)	60	77	100
Mn(II)	10	10	30
Mn(VII)	90	—	—
Mo(VI)	—	—	76
Ni	0	0	0
Pb(II)	72	68	15
Sn(II)	99	100	100
Sn(IV)	95	99	99
Ti(III)	0	0	0
Ti(IV)	0	0	0
Tl(I)	2	5	15
Tl(III)	100	100	100
V(V)	24	42	93
W(VI)	90	—	—
Zn	100	100	100

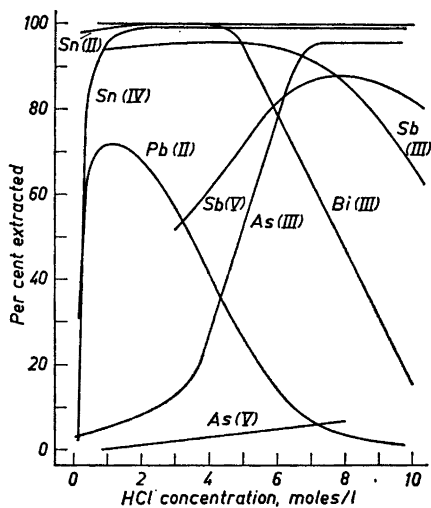


Fig. 1. Effect of hydrochloric acid concentration on the extractability of As-, Bi-, Pb-, Sb-, and Sn-chlorides by Tioa/CCl₄.

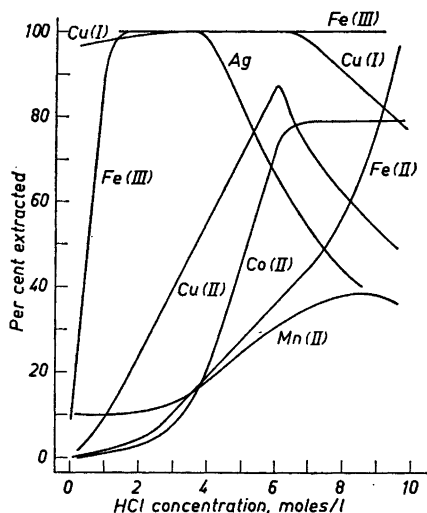


Fig. 2. Effect of hydrochloric acid concentration on the extractability of Cd-, Ga-, Hg-, In-, Mo-, Tl-, V-, and Zn-chlorides by Tioa/CCl₄.

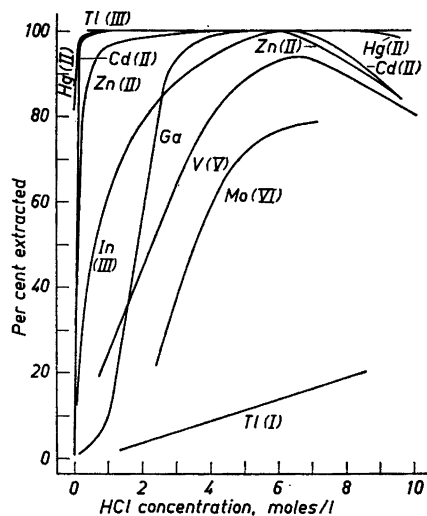


Fig. 3. Effect of hydrochloric acid concentration on the extractability of Ag-, Co-, Cu-, Fe-, and Mn-chlorides by Tioa/CCl₄.

Aluminium, titanium, chromium, nickel, arsenic(V), alkaline earth and alkali metals were not extracted even at higher hydrochloric acid concentrations (10 M). Other metals as As(III), V(V), Mn(II), Cu, Co, Fe(II), Ga, and In were extracted if the hydrochloric acid concentration was above 5 to 6 M. Bi, Sb, Sn, Tl, Hg, Cd, Zn, Cu(I), Ag, Fe(III), and Cr(VI) were conveniently

extracted from solutions of low acidity. Some metals as antimony, bismuth, copper, lead, and silver gave decreasing extractability at increasing acidity.

In the case of tin and bismuth very viscous organic layers were obtained.

Some elements, *e.g.* hexavalent tungsten, gave precipitates which partly entered the organic layer. Hexavalent molybdenum was extracted nearly 100 % from low acidic solutions. By increasing the acidity the extractability initially decreased (20 % from 2.5 M HCl) and then increased again.

Permanganate was extracted very easily at low hydrochloric acid concentration. However, at increasing acid concentration oxidation of the chloride ion occurred.

DISCUSSION

The transfer of the metal into the organic phase seems to involve an association of anionic chlorocomplexes with the amine. Increasing extractability on addition of more hydrochloric acid may be explained by the increasing concentration of anionic chlorocomplexes and also the formation of quaternary ammonium ions. In some cases (copper, silver, bismuth, antimony, and lead) the extractability will pass a maximum value if the hydrochloric acid concentration is increased. The regress after a maximum has been reached is caused not by the chloride ion, but by the hydrogen ion¹⁷ which competes more favorably than the quaternary ammonium ion for the anionic metal complexes to form hydrogen associated complex anions.

The different extractabilities give possibilities to separate several ions by Tioa/CCl₄-extractions by changing the hydrochloric acid concentration. Elements which form extractable chlorocomplexes in hydrochloric acid are easily separated from those not forming anionic complexes. Thus separation of iron from aluminium, chromium, titanium, and nickel is possible if the hydrochloric acid concentration in the solution is above 2 N. Separations of cobalt and nickel, copper and nickel as well as of zinc and nickel are easily undertaken from 6–7 N hydrochloric acid. Gallium, indium, and thallium are separated from aluminium at hydrochloric acid concentrations higher than 3 N.

Elements which form anionic chlorocomplexes at low hydrochloric acid concentrations may be separated from those forming anionic chlorocomplexes only at higher acid concentration. Thus iron may be separated from copper by performing the extraction in 1–2 N hydrochloric acid. Zinc and copper are separated nearly quantitatively if the extraction is done in 1 N hydrochloric acid. In 1 N hydrochloric acid bismuth and antimony may be separated from arsenic.

Separation of elements in higher and lower states of oxidation may be done in some cases. Thus, it is possible to separate iron(III) and iron(II) in 1–2 N, copper(II) and copper(I) in 1 N, arsenic(V) and arsenic(III) above 6 N and thallium(III) and thallium(I) in 1 N hydrochloric acid.

If the extractability decreases at increasing hydrochloric acid concentrations due to the formation of hydrogen associated complexes some separations are possible. The separation of lead and zinc at hydrochloric acid concentration above 6 N is an example.

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