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Solvent Extraction Of Chromium (VI) From Aqueous Acid Solutions By Tricaprylamine Oxide

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ABSTRACT: The extraction of chromium (VI) from hydrochloric, hydrobromic, and acetic acid solutions with Tri caprylamine oxide (TCAO) in benzene has been studied. The extractions from hydrochloric and hydrobromic, acid solutions are nearly quantitative and are partial from acetic acid solutions. The optimum conditions for extraction were established from the study of the effect of several variables like– concentration of amine-oxide, metal ion, acidity, foreign ions etc. The extracted species are identified.
Key words: Chromium (VI) - Tri caprylamine oxide (TCAO)- Solvent extraction - Toxic metal – benzene.

INTRODUCTION:

The use of phosphorus bonded oxygen donor extractants for metals has been attempted by several workers[1-4] . Very few workers have reported[5-8] the extraction of chromium (VI) by amine oxides as extractants. In the present communication the results obtained on the extraction of Chromium (VI) by Tricapryl amine oxide (TCAO) from hydrochloric, hydrobromic and acetic acid solutions has been discussed.

EXPERIMENTAL

TCAO was synthesized[9] by N-oxygenation of Tricapryl amine using hydrogen peroxide as oxidizing agent. Its purity was checked by identifying the characteristic IR absorption band[10] for N—>O at 930 cm^{-1} and by following conversion of TCA to TCAO by thin layer chromatographic technique[11]. A 0.2 M of TCAO (stock solution) in benzene was prepared and diluted appropriately to get the required concentration. Chromic acid (E.Merck) was used for preparing Chromium (VI) stock solution (0.5M) used as such without any further purification. All other chemicals used were of Anala R grade or samples purified according to the standard methods. The radioisotopes used in this study were obtained from Board of Radiation and Isotope Technology, Department of Atomic Energy, Government of India, Mumbai.

CHROMIUM (VI) EXTRACTION:

Chromium (VI) distribution studies were made using appropriate concentrations of chromic acid and mineral acid by equilibrating with an equal volume of TCAO in benzene (0.025M) pre-equilibrated with 0.1M mineral acid. The chromium (VI) concentrations in the aqueous phase before and after extraction was estimated spectrophotometrically[12] by measuring the absorption of Cr (VI) – DPC complex at 540nm, using Shimadzu UV-Visible Spectrophotometer type UV-260. The equilibrium chromium (VI) concentration in the organic phase was determined by taking the difference in the initial CHROMIUM (VI) CONCENTRATION AND THE EQUILIBRIUM CHROMIUM (VI) CONCENTRATION IN THE AQUEOUS PHASE.

RESULTS AND DISCUSSION

The results obtained on the extraction of chromium (VI) as a function of aqueous phase concentration of mineral acid (HCl, HBr and CH_3COOH) are presented in Table-1. In the case of hydrochloric and hydrobromic acid solutions the extraction of chromium (VI) by TCAO in benzene as a function of acidity, the distribution ratio (K_d) increased abruptly with increasing the concentration of the acid up to 1.0 M acidity and there is no change in K_d between 1.0 – 2.15 M acidity followed by a gradual fall up to 3.0M,

beyond which chromium (VI) under goes reduction to chromium(III). The extractions are nearly quantitative from both the acid solutions (Table 1). On the other hand the extractions are partial from acetic acid solutions with a maximum extraction at 0.82 M followed by a gradual fall in K_d with increasing acidity . Addition of NaCl, NaBr and CH_3COONa to aqueous phases in the respective acid media resulted in a significant decrease in extraction, the decrease being in the order, CH_3COOH >HCl > HBr.

An attempt is made to characterize the nature of the extracted Chromium (VI) species in hydrochloric acid media using ^{36}Cl as a function of aqueous chromium (VI) concentration reveal whether or not the involvement of the anion in the nature of the extracted species (Fig-1). These studies reveal that under saturation condition the molar ratio, Cr: TCAO: Cl^- varied from 1.0:1.0:0.43 to 1.0:1.0:0.28. This indicates the involvement of anion of the acid in the extracted chromium (VI) species in hydrochloric acid system(Table-2).

COMPOSITION OF THE EXTRACTED SPECIES:

The composition of the extracted species was determined by the extraction isotherm method[13] and the distribution ratio method[14]. The maximum loading of $1.0 x\ 10^{-3}$ M TCAO with chromium (VI) at aqueous acidity (0.1M&1.0M HCl), yielded a mole ratio of the [extractant] to [chromium (VI)] $_{org}$ unity (Fig-2).

The log-log plots of K_d Vs. TCAO from invariable concentrations of the acid solutions (0.1, 1.0 and 1.5 M) gave straight lines (Fig-3). With acetic acid solutions the log-log plot gave straight line of unit slope irrespective of the acid concentrations used. On the other hand, the slope analysis of the distribution data in hydrochloric acid solutions indicates that the solvation number depends on concentration of the acid. At low acid concentrations (< 1.0 M) the slope of the log K_d Vs. log [TCAO] plots show that the solvation number is close to unity (1.07 at 0.1 M HCl) and 1.59 at 1.0M & 1.77 at 1.5 M HCl). As the concentration of the acid in the aqueous phase is increased, the stoichiometric ratio of the components of the organic phase increases gradually indicating that different extraction mechanisms are operating probably due to the formation of a mixture of chromium (VI) species in both HCl and HBr solutions..

ABSORPTION SPECTRA:

The absorption spectra of chromium (VI) in the organic phase obtained by extraction from hydrochloric acid media exhibit absorption bands at 245, 285 and 355 nm indicating the presence of chlorochromate ($HCrO_3Cl$) in the extracted species. In these acid systems molar extinctions at 285 nm lie in the range 1885-1380 and at 355nm lie at 1015 - 1030

range. The ratio varied in the range (1.85-1.34) with the change in the concentration of acid solutions indicating the presence of a mixture of chromium (VI) species, predominantly $CrO3A(A=Cl^-$ or Br^- and $Cr_2O_7^{2-}$ and/or $HCr_2O_7\ Cr_2O_7^{2-}$ (Table-3).

CHOICE OF STRIPPING AGENT:

After the extraction of chromium (VI) by 0.025 M TCAO, it was stripped with 10 ml reagents of various concentrations (0.01 – 0.1 M) of HCl, HNO_3, NaCl, $NaNO_3$ and NaOH solutions. It was observed that HCl, NaCl, and $NaNO_3$, are extremely poor stripping agents for chromium (VI). On the other hand, 0.1 M HNO_3 alone is a good stripping agent. However in no case HNO_3 strips out all the chromium (VI) in a single extraction. It was observed that 99.9% chromium (VI) could be recovered from organic phase by making contact three times with equal volumes of 0.1 M HNO_3.

EFFECT OF DIVERSE IONS:

The effect of several diverse ions on the extraction of chromium (VI) was studied using the general extraction procedure. The tolerance limit was set at the amount of diverse ion required to cause $\pm$ 2% error in the recovery of chromium (VI) (13.5 μg/ 20 ml). The results show that the ions such as Al (III), Ba (II),Cu (II), Ce (IV), Mn (II), Co (II), Th (IV), Zn (II), Acetate ,Ascorbate, Chlorate , Oxalate Selenite, Tellurite, Phosphate and Tartarate, , are tolerated in the ratio 1:200 and the ions such as Bi (II), Ca (II),Pb (II), Pd (II), Ru (III), U (VI), Sr (II), VO_3^{-} WO_4^{2-}, and malonate^{2-} do not interfere even if present in the ratio 1:100. The ions showing small tolerance limit in the ratio 1:50 are Fe (III) and F^- .It is thus possible, to extract chromium (VI) in the presence of large number of cations and anions. The average recovery of chromium (VI) was 99.7 $\pm$ 0.3 %. The relative standard deviation and relative error calculated from ten repeated determinations with 13.5 μg of Cr (VI) were found to be $\pm$ 1.02 % and $\pm$ 0.8 % respectively.
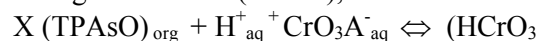
The observed chromium: Extractant molar ratio of unity from acetic solutions (by distribution ratio method) could be explained as arising from the extraction of chromium (VI) by the following solvation mechanism.
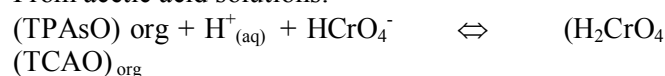
From acetic acid solutions:
(TPAsO) org + $H^+_{(aq)}$ + $HCrO_4^-$ $\Leftrightarrow$ (H_2CrO_4 (TCAO) $_{org}$
From Hydrochloric and hydrobromic acid solutions:
At higher acidities (>0.1M),
X (TPAsO) $_{org}$ + H^+_{aq} $^+CrO_3A^-_{aq}$ $\Leftrightarrow$ ($HCrO_3$ A. x (TCAO) $_{org.}$
At lower acidities (≤ 0 .1M),

$$X \ (TPAsO)_{org} + H^+_{aq} + HCrO_4^- \Leftrightarrow (HCrO_3 \ A. \ x \ (TCAO)_{org.}$$

$(A = Cl^-, Br^-) \ (X = 1-2)$
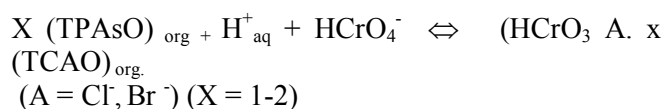
On the basis of the proposed mechanism for the extraction of chromium (VI), the dependence of the distribution ratio on the concentration of the mineral acid. The decrease in the distribution ratio at higher acidities (>3.0M) can be explained as due to the greater extractability of the mineral acid over the chromium (VI) species.

The precision and accuracy of the method of extraction for recovery of chromium has been tested by analyzing real samples and chrome alloys. It is done by extracting chromium from synthetic samples (composition Cr = 10.0&15.0 %).

About 0.5 gm of a chrome alloy (Type 410 & 416) was dissolved in 10ml aquaresia .The solution was evaporated and extracted with 20ml of dil. hydrochloric acid solution .to dryness. The resulting solution was made up to 100ml.An aliquot (10ml) of the filtered solution was taken.. The interference due to Ni(II)& Mn(II) were removed by precipitating them as complex .Then precipitate was filtered and quantitatively washed for complete recovery of chromium. It was made up to 100ml.10.0 ml of the solution was extracted with an equal volume of 0.025M TCAO in benzene followed by stripping with 0.1M HNO3 and estimated the chromium content as Cr(VI) –DPC complex as per the procedure described earlier. The results are presented in Table -4.

TABLE – 1:Percentage Extraction of chromium (VI) by TCAO from various acid solutions

[Cr(VI)] = 1.03 x 10⁻³ M				[TCAO] = 1.0 x 10⁻² M	

Acid		**HCl**			
Molarity	1.00	1.25	1.50	1.75	2.00
% Extraction	99.21	99.21	99.21	99.17	99.06

		HBr			
Molarity	1.00	1.25	1.50	1.75	2.00
% Extraction	99.51	99.51	99.06	98.15	97.75

		CH3COOH			
Molarity	0.1	0.5	0.8	1.0	1.5
% Extraction	85.62	89.91	90.43	86.32	83.20

TABLE – 2:Composition of the Organic Phase under Saturation condition with Chromium (VI) – HC1³⁶ Medium
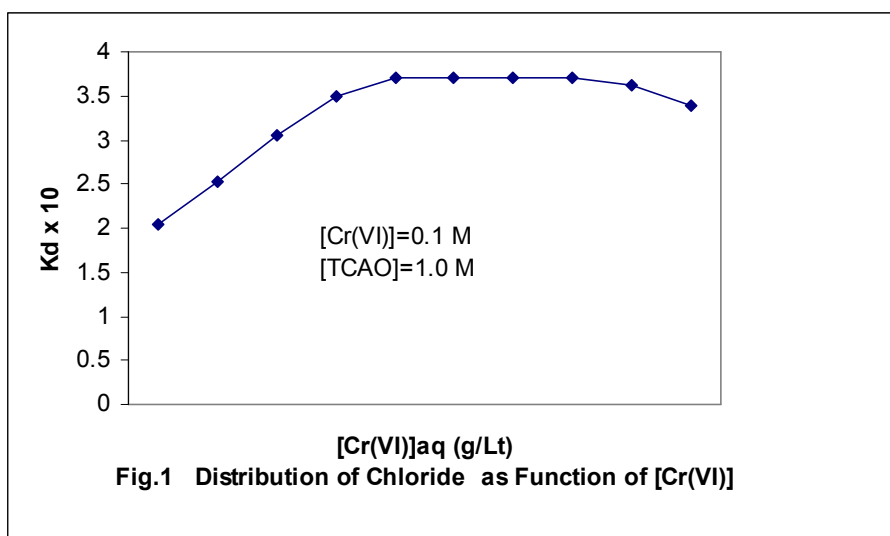
[TCAO] = 0.1 M: [HC1] = 1.0 M

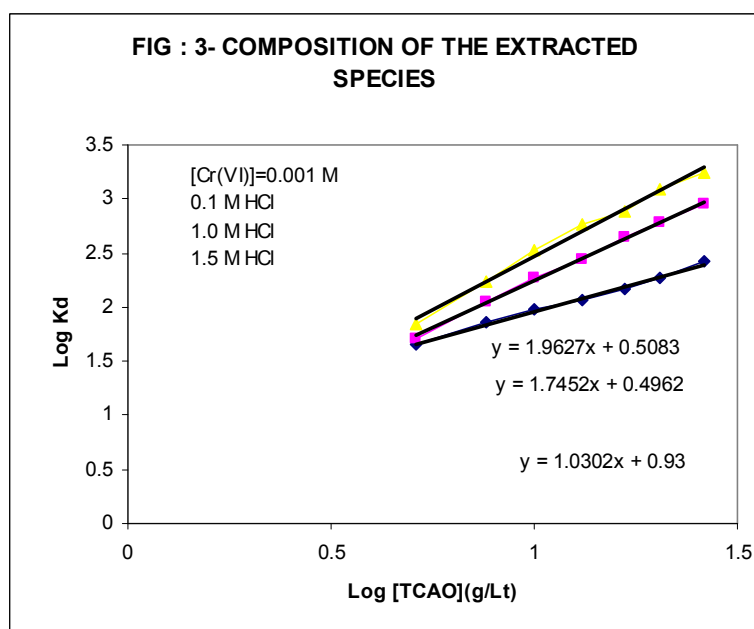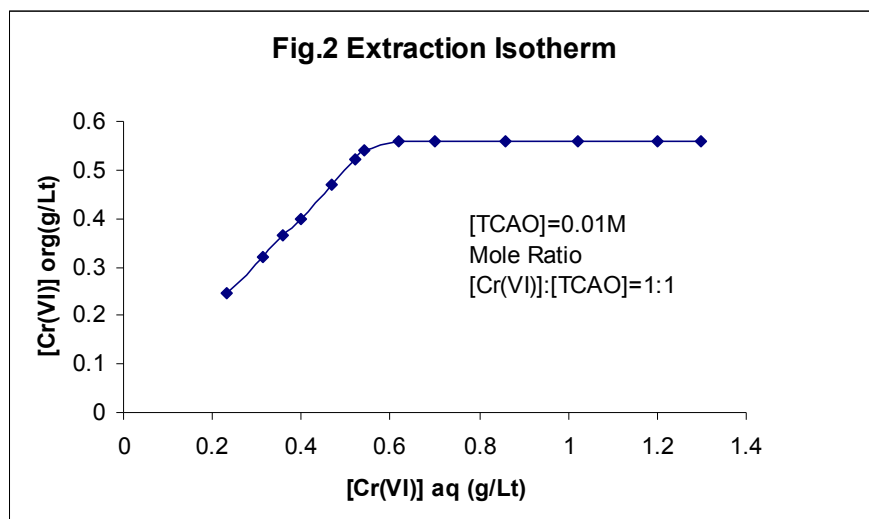| Initial aq. Phase [Cr (VI)]	Concentration of organic phase (M)		Molar ratio		
(M)	Cr (VI)	Cl-	Cr	TACO	Cl⁻
0.05	0.05	0.025	0.5	1.0	0.25
0.10	0.08	0.030	0.8	1.0	0.30
0.125	0.09	0.032	0.9	1.0	0.32
0.15	0.10	0.041	1.0	1.0	0.41
0.175	0.10	0.043	1.0	1.0	0.43
0.20	0.10	0.043	1.0	1.0	0.43
0.25	0.10	0.043	1.0	1.0	0.43
0.30	0.10	0.040	1.0	1.0	0.40
0.40	0.10	0.038	1.0	1.0	0.38
0.50	0.10	0.034	1.0	1.0	0.34
0.60	0.10	0.028	1.0	1.0	0.28

TABLE – 3: Percentage Extraction of chromium (VI) by TCAO from various acid solutions
[Cr(VI)] = 0.0005M   [TCAO] = 0.035 M

Acid (M)		Molar Extinction (E) at		$(\varepsilon_{285}/\varepsilon_{355})$
		285nm	**355nm**	
HCl	0.1	1855	1030	1.80
	0.5	1385	1025	1.35
	1.0	1630	1020	1.60
HBr	0.1	1880	1020	1.84
	0.5	1390	1015	1.37
	1.0	1450	1020	1.42
CH3COOH	0.1	1870	1025	1.82
	0.5	1870	1020	1.83
	1.0	1865	1015	1.83

Estimation of chromium in Synthetic samples and chrome alloys

Sample	Chromium(VI) present (%)	Chromium found after recovery by extraction (%)	Recovery (%)
Synthetic sample			
1	10	9.78	97.8
2	15	14.86	99.0
3	18	17.75	98.6
Stainless steel alloy type			
1	11.5	11.22	98.3
2	14.0	13.85	98.9

Fig.1   Distribution of Chloride as Function of [Cr(VI)]

Fig.2 Extraction Isotherm

FIG : 3- COMPOSITION OF THE EXTRACTED SPECIES

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