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Extraction of Chromium (VI) From Mineral Acid Solutions by Tri-n-Octyl amine Oxide

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ABSTRACT

Chromium is an important non-ferrous metal with high corrosion resistance finding its application in electroplating, tannery, chloral kali industries etc. Out of the two most stable forms of Chromium hexavalent one considered as a serious health hazard and it has attracted attention as a pollutant in natural waters. In view of this the separation and determination of chromium has been receiving considerable attention. Solvent extraction of Chromium (VI) from hydrochloric, sulphuric, and nitric acid solutions with Tri-n-Octyl amine oxide (TOAO) in benzene has been studied. The optimum conditions for extraction were established from the study of the effect of several variables like concentration of extractant, metal ion, acidity etc. The extractions are nearly quantitative with hydrochloric and sulphuric acid & are partial from nitric acid solutions. The extracted species are also identified. The method has been applied for the recovery and determination of chromium in synthetic as well as stainless steel samples.

Keywords: Chromium (VI) -- Tri-n-Octyl amine oxide (TOAO) -- mineral acid

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INTRODUCTION

The sources of contamination of chromium in natural waters and in the environment are from electroplating, tanning industries and waste solution from oxidative dyeing and leaching from sanitary land – fills, Several workers[1-5] reported the extraction of Chromium(VI) using tertiary amines. Very few workers have reported[6-8] the extraction of chromium (VI) by amine oxides as extractants. There are no reports appeared in literature on the extraction of chromium (VI) by tri-n-octyl amine oxide. In this communication we report studies on the extraction of chromium (VI) by Tri-n-Octyl amine oxide (TOAO) from mineral acid solutions.

MATERIALS AND METHODS

A stock solution of 0.5M TOAO (3B Scientific company, USA Merck reagent grade, having molecular weight 369.67 was prepared in Benzene. Appropriate dilutions were made as per the requirement. Chromic Acid (E.Merck) was used for preparing chromium (VI) stock solution. All other chemicals used were AnalaR Grade or samples purified according to the standard methods.

Chromium (VI) Extraction:

An aqueous solution (10ml) of Chromium (VI) containing appropriate concentrations of chromic acid (1.05×10^{-4}M) and the acid has equilibrated with an equal volume of TOAO (0.01 M) in benzene pre equilibrated with 0.1 M mineral acid. The chromium (VI) concentration in the aqueous phase before and after extraction was estimated using Atomic absorption spectrophotometer. The equilibrium chromium (VI) concentration in the organic phase was determined by taking the difference in the initial chromium concentration in the aqueous phase.

RESULTS AND DISCUSSION:

Effect of Acidity:

The distribution ratio of chromium (VI) in the case of hydrochloric and sulphuric acid solution increases with increasing acidity up to 0.75 M & 1.0M respectively(Maximum extraction) followed by decreasing in efficiency. On the other hand Kd decreases gradually with increasing acidity in the case of nitric acid solutions under the same experimental conditions The results obtained on the extraction of chromium (VI) as a function of aqueous phase concentration of various acid solutions are presented in Table–1.

The Composition of the extracted species was determined by the maximum loading experiments and also by distribution ratio method[9,10]. To determine the loading capacity of TOAO for the extraction of Cr(VI) the metal ion solutions of different concentrations were subjected to extraction. The molar ratio of extractant to chromium (VI) of unity was noticed in the extraction

Table – 1: % Extraction of chromium (VI) by TOAO from various acid solutions

[Cr(VI)] = 1.05 x 10^{-4} M **[TOAO] = 1.0 x 10^{-2} M**

Acid			HCl		
Molarity	1.00	1.25	1.50	1.75	2.00
% Extraction	99.81	99.54	99.19	99.07	98.08
			H_2SO_4		
Molarity	1.00	1.25	1.50	1.75	2.00
% Extraction	99.22	99.31	98.14	98.05	97.55
			HNO_3		
Molarity	0.1	0.5	0.8	1.0	1.5
% Extraction	82.60	87.92	89.41	84.30	81.22

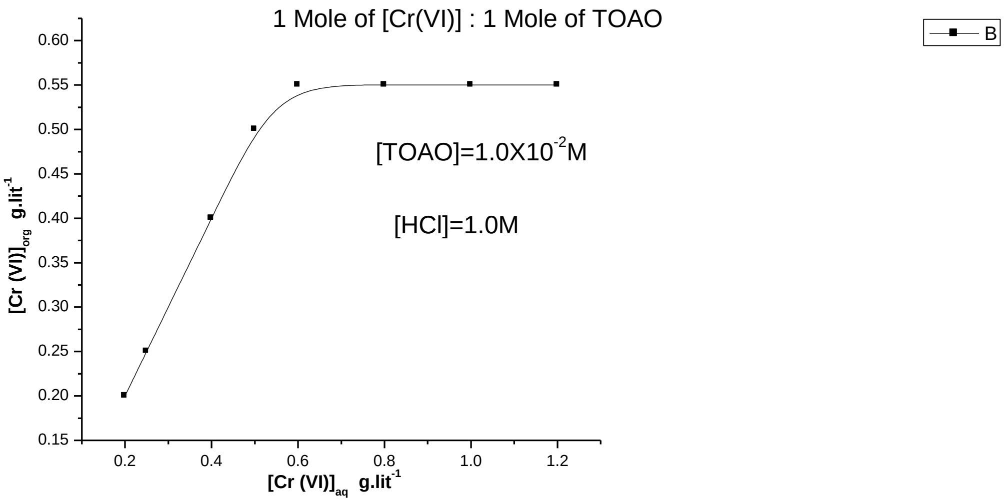

Figure.1 Extraction Isotherm (HCl medium)

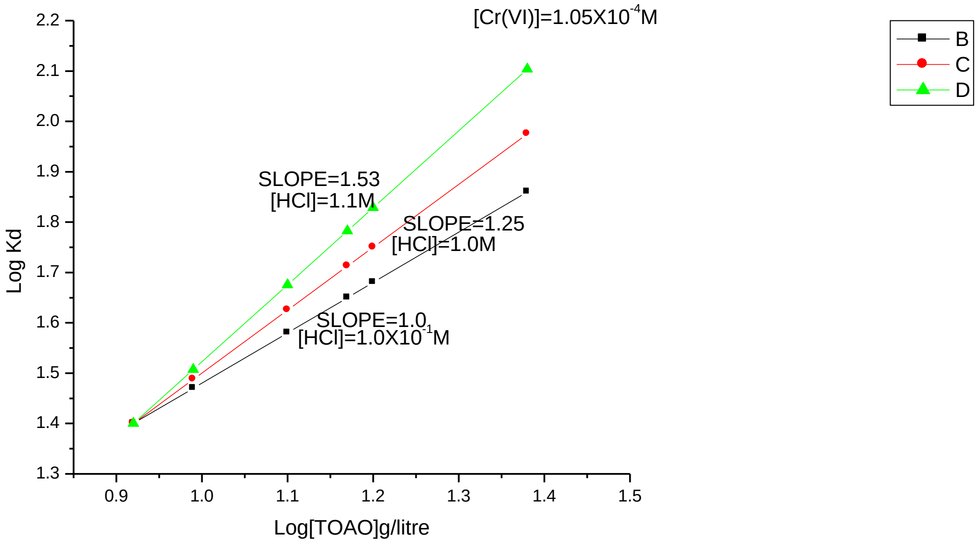

Figure 2 Extractant Variation

isotherm method with all the mineral acid systems. Representative data in hydrochloric acid has been presented in Fig.1. Further the log-log plots of equilibrium chromium (VI) concentration in the aqueous phase Vs. organic phase in the distribution studies with variation of aqueous chromium (VI) concentration at initial aqueous phase acidity of 1.0 M gave straight lines of unit slope indicating the extracted chromium (VI) species as monomeric in nature. The log-log plots of K_d Vs (TOAO) from different acid solutions gave straight lines. The plots from sulphuric acid gave a slope value of two and that of nitric acid media with unity irrespective of the acid concentration indicating the formation of monosolvates. On the other hand the slope analysis of the distribution data in hydrochloric acid solutions (at invariable acid concentration -0.1M, 1.0M, 1.5 M Figure 2 indicated that the solvation number is dependent on the concentration of acid.

Absorption Spectra:

The individual chromium (VI) species can be identified on the U.V. region [11-13]. The absorption spectra of chromium (VI) in the organic phase obtained by extraction from all the acid systems, exhibit absorption maxima at 285 and 355 nm. **(**Table-2). A comparison of the ratio of the molar extinctions (ε) at 285 nm and 355 nm as a function of acid molarity is taken as a criterion for identifying the species. The peak ratios are constant in other acid systems – confirming the presence of a single species. This is in conformity with the observation of Tuck and walters [14] using TBP as extractant. On the basis of these results, the extracted species appear to be predominantly HCrOCl from hydrochloric solutions. Further, it is concluded that from hydrochloric acid systems a mixture of species predominantly containing $HCrO_3A$ and/or H_2CrO_4 is extracted. The extracted species from mineral acid solutions is exclusively H_2CrO_4 extracted as H_2CrO_4.x (TOAO), (X = 1– 2).

Table – 2: Absorption spectra of chromium (VI) by TOAO from various acid solutions

[Cr(VI)] = 0.0005M **[TOAO] = 0.035 M**

Acid (M)		**Molar Extinction (E) at**		**(ε_{285} / ε_{355})**
		285nm	**355nm**	
HCl	0.1	1875	1030	1.82
	0.5	1425	1025	1.39
	1.0	1655	1020	1.60
H_2SO_4	0.1	1880	1020	1.84
H NO_3	0.1	1390	1015	1.37
	1.0	1455	1035	1.40

The observed chromium: TOAO molar ratio of unity from nitric acid solutions (by distribution ratio method) could be explained as arising from the extraction of chromium (VI) by the following solvation mechanism.

From sulphuric acid solutions

$$2\,(TOAO)_{org} + H^+ + HCrO_4^- \longrightarrow (H_2CrO_4.\ 2\,(TOAO)_{org}$$

From nitric acid solutions:

$$(TOAO)_{org} + H^+ + HCrO_4^- \longrightarrow (H_2CrO_4.\ (TOAO)_{org}$$

On the other hand the alteration of molar ratio from hydrochloric acid solutions suggests the extraction of a mixture of chromium (VI) species in the form of $HCrO_3A$. TOAO. and/or H_2CrO_4. (TOAO) at higher acidities (> 0.1 M) and as H_2CrO_4. (TOAO) at lower acidities ($\leq$ 0.1 M) by the following solvation mechanism.

$$X(TOAO)_{org} + H^+ + CrO_3Cl^- \longrightarrow (HCrO_3A.\ Cl(TOAO))_{org}$$

$$X(TOAO)_{org} + H^+ + HCrO_4^- \longrightarrow (H_2CrO_4.\ X(TOAO))_{org}\ (X= 1–2)$$

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 in aqueous phase may be explained as follows. Chromium (VI) is preferably extracted as a protonated species of the type $HCrO_3A$ and H_2CrO_4 in varying ratios from hydrochloric acid solutions and as H_2CrO_4 from other acid systems. The decrease in the distribution ratio at higher acidities can be explained as due to the great extractability of the mineral acid over the chromium (VI) species. 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.

Stripping of Chromium (VI):

Stripping of chromium (VI) was carried out using HCl, HNO_3, NaCl, $NaNO_3$ distilled water and NaOH as stripping agents. It can be seen that HCl, NaOH NaCl and $NaNO_3$ are extremely poor stripping agents for Chromium (VI). On the other hand 1.0M HNO_3 alone is a good stripping agent. However, in no case HNO_3 strips out all the Chromium (VI) in a single extraction. To determine whether this is due to a kinetic effect, since only three minutes contacts are used, stripping with a long time contacts are performed. But extending the contact time to 15 minutes or half an hour with mechanical shaker is no more effective. Thus stripping time between 3 to 5 minutes would be optimal to recover 99.9% of chromium (VI) by making contact three times with equal volumes of 1.0M nitric acid.

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 ± 2% error in the recovery of chromium (VI) (13.5 μg/20ml). The results show that the ions such as Al(III), Ce(IV), Cu(II), Sb(III), Sn(II), Mn(II), Co(II), Zn(II),Phosphate, Chlorate, Tartarate, Oxalate, Acetate Selenite, and Telluride are tolerated in the ration 1:200 and the ions such as Bi(II),), Ca(II), Pd(II), Ru(III), U(VI), Pb(II), Sr(II), VO_3^- and WO_4^{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 99.8 ± 0.2%. The relative standard deviation and relative error ± 1.04% and ± 0.8% respectively.

Determination of Chromium in Synthetic samples and chrome alloys

In order to test the applicability of the proposed method, it was applied to analyze real samples for chromium content in chrome alloys. About 0.5-1.0 gm of chrome alloy (stainless steel sample) was dissolved in 10 ml of aquaregia. The solution was evaporated to dryness and extracted with 10 ml of hydrochloric acid solution. The resulting solution was made up to 100 ml. The interference due to Ni (II) and ,Mn (II) were removed by precipitating them as complex. The precipitate was filtered and quantitatively washed for complete recovery of Chromium. It was then made up to 100 ml. 10ml of this solution was extracted with an equal volume of 0.01M TOAO in benzene followed by stripping with 1.0M HNO_3 and estimated the Chromium content as per the procedure described earlier. The results are presented in Table-3.

Table-3: Estimation of chromium in Synthetic samples and chrome alloys

Sample	**Chromium(VI) present (g/l)**	**Chromium found after recovery by extraction (g/l) ***	**Recovery (%)**
Synthetic sample			
1	0.25	0.248	99.2
2	0.30	0.296	98.67
3	0.35	0.342	97.71
Stainless steel alloy type	%	%	%
1	11.5	11.22	98.3
2	14.0	13.85	98.9

* (Average of Four determinations)

CONCLUSIONS:

The method was very selective and permits the separation and determination of chromium from different samples in minimum amount time with accuracy.

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