Estimation of Chromium (VI) In Electroplating Effluents-A Solvent Extraction Study

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Abstract Extraction of chromium (VI) from hydrochloric, hydrobromic and sulphuric acid solutions by Tri benzylamine (TBA) dissolved in chloroform has been studied. The optimum conditions for extraction were established from the study of the effect of several variables like- concentration of amine, metal ion, acidity, diverse ions etc. The extractions from hydrochloric and sulphuric acid solutions are nearly quantitative with all the three acid systems. The extracted species are identified. The method has been applied for the recovery and determination of chromium in natural as well as electroplating effluents samples.

Keywords Solvent extraction -chromium (VI) - Tri benzylamine [TBA] – electroplating effluents

Introduction

Chromium enters in to the environment from electroplating, leather, textiles and metallurgical industries etc Chromium enters in to the environment from electroplating, leather, textiles and metallurgical industries etc. Chromium (VI) is more toxic than chromium (III).It is also responsible for chrome ulcer and kidney damage [1-2]. Several workers [3-7] reported the extraction of metals by high molecular weight as well as tertiary amines including chromium. Fewer studies appeared in literature on the extraction of Cr (VI) by amines especially in different acid media. In the present communication the results obtained on the extraction of Chromium (VI) by Tribenzyl amine (TBA) from hydrochloric hydrobromic and sulphuric acid solutions has been discussed.

Experimental work

Chromic acid (E. Merck) was used for preparing chromium (VI) stock solution (0.35M). A 0.25 M stock solution of TBA (Mol. wt. 287.4) in chloroform was prepared and diluted appropriately to get the required concentration. All other chemicals used were of A.R. grade or samples purified according to the standard methods. Double distilled water was used throughout the studies.

Chromium (VI) Extraction

An aliquot (10ml) of chromic acid and mineral acid was equilibrated with an equal volume of TBA in chloroform (0.025M) pre-equilibrated with 0.1M acid. The chromium (VI) concentration in the aqueous phase before and after extraction was estimated using Atomic absorption spectrophotometer type-AAS-SVL Spectronics–205 Model. 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 variation of distribution ratio as a function of aqueous phase concentration of the acid (HCl, HBr and H_2SO_4) is presented in Table 1. In the case of hydrochloric and sulphuric acid solutions the

extraction of chromium (VI) by TBA in chloroform as a function of acidity, the distribution ratio (K_d) increased with increasing the concentration of the acid up to 1.0 M and remained constant between 1.0- 1.5 M acidity respectively followed by a gradual fall up to 3.0 M, beyond which chromium (VI) under goes reduction to chromium (III). The extractions are nearly quantitative from all the acid solutions (Table 1). On the other hand from hydrobromic acid solutions, maximum extraction is noticed at 1.0 M followed by a gradual fall in K_d with increasing acidity.

Composition of the Extracted Species

The composition of the extracted species with all the acid systems was determined by the extraction isotherm method [8] and distribution ratio method [9]. In the extraction isotherm method the limiting ratio of the metal to TBA was found to be unity irrespective of the acid used in the study.

The log-log plots of K_d Vs TBA from various acid solutions gave straight lines. With hydrochloric and hydrobromic acid solutions the log-log plot gave straight line of unit slope (Figure 1). On the other hand, the slope analysis of the distribution data in sulphuric acid solutions indicates that the solvation number is two. The same is further confirmed with spectral studies. The individual chromium (VI) species can be identified on the UV region [10-12]. The absorption spectra of chromium (VI) in the organic phase obtained by extraction from different acid media exhibit absorption bands at 245, 285 and 355 nm. A comparison of the ratio of the molar extinctions (ε) at 285 nm and 355 nm a function of acid molarity is taken as a criterion for identifying the species as chloroform has cut off point at 245 nm. These ratios are independent of the concentration of all the acids used in the study. The peak ratios are constant ie, unity from hydrochloric, hydrobromic and two from sulphuric acid solutions confirming the presence of a single species (Table 2). This is in conformity with the observation of Tuck and walters [13] using TBP as extractant.
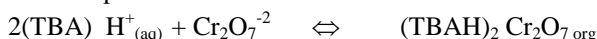
Based on the result obtained, the observed chromium: TBA molar ratio of two from all the acid solutions (by distribution ratio method) could be explained as arising from the extraction of chromium (VI) by the following solvation mechanism.

From Hydrochloric and hydro bromic acid solutions:

TBA H^+_{+} $CrO_3CX^-_{aq} \Leftrightarrow$ TBA $HCrO_3 X$
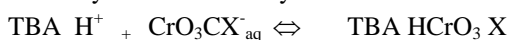
(Where X= Cl, Br)

From sulphuric acid solutions:

2(TBA) $H^+_{(aq)} + Cr_2O_7^{-2} \Leftrightarrow$ $(TBAH)_2 Cr_2O_{7\ org}$

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.

Variation of Diluents

Besides chloroform various diluents used in the present study are benzene, xylene, toluene, carbon tetra chloride, hexane, cyclo hexane, nitrobenzene, dichloro methane which are of wide verities in their chemical nature and dielectric constant. Maximum extraction efficiency was achieved with chloroform as diluent (Table 3). Hence the same diluent was used in all these studies. With dichloromethane lowest % extraction was noticed (72.15%).

Choice of stripping agent

The extraction of chromium (VI) from the organic phase (TBA) has been tried 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, 1.0 M NaOH alone is a good stripping agent. However in no case NaOH strips out all the chromium (VI) in a single extraction. It was observed that 99.85 % chromium (VI) could be recovered from organic phase by making contact three times with equal volumes of 1.0 M NaOH.

Effect of diverse ions

The effect of several foreign ions on the extraction of chromium (VI) with TBA was studied following 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) (27μg/ 10 ml). The results show that the ions such as Al (III), Ba (II), Co (II), Cu (II), Cd(II), Ce (IV), Mn (II), Zn (II), Acetate ,Ascorbate, Chlorate, Oxalate Selenite, Tellurite, Phosphate and Tartarate, are tolerated in the ratio 1:200 and the ions such as Ca (II), Pb (II), Pd (II), Ru (III), 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 99.7 ± 0.3 %. The relative standard deviation and relative error calculated from ten repeated determinations with 27 μg of Cr (VI) were found to be ± 1.03 % and ± 0.7 % respectively.

The separation of chromium (VI) is possible in the presence of more than one foreign ion in the mixtures with an error of not more than 2.05 %.

The accuracy of the method of extraction for   chromium has been tested by analyzing synthetic samples and electro plating effluents. It is done by extracting chromium from synthetic samples (composition Cr = 0.20 – 0.40 g/lt).

An aliquot (100 ml) of the filtered effluent sample is taken and boiled till its volume is reduced to about 1/5 of the initial volume (20 ml) Then chromium content present in it is oxidized to chromium (VI) using Ce(IV) as an oxidizing agent [14] (0.2 N solution of ammonium hexa nitrato cerate). After oxidation the solution is transferred to a 100 ml volumetric flask and made up to the mark. 20 ml of this solution is taken in 150ml separating funnel and is extracted with 10 ml of 0.025 M Tribenzyl amine (TBA) in chloroform. The aqueous phase is then neutralized with 1: 2 sulphuric acid and it was made up to 100ml.10.0 ml of the solution was extracted with an equal volume of 0.025M TBA in chloroform followed by stripping with 1.0 M NaOH and estimated the chromium content by AAS. The results are presented in Table 4.

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

[Cr(VI)] = 1.0 x 10^{-4} M   [TBA] = 2.50 x 10^{-2} M

Acid	**HCl**				
Molarity	1.00	1.25	1.50	1.75	2.00
% Extraction	99.91	99.91	99.91	99.17	98.06
	HBr				
Molarity	1.00	1.25	1.50	1.75	2.00
% Extraction	99.51	99.21	99.06	98.25	97.74
	H_2SO_4				
Molarity	1.00	1.25	1.50	1.75	2.00
% Extraction	99.87	99.87	97.43	96.62	93.25

Table-2 : Absorption spectra of chromium (VI) by TBA from various acid solutions

[Cr(VI)] = 4.5X 10^{-5} M   [TBA] = 2.5 X10^{-2} M

Acid (M)		Molar Extinction (E) at		(ε_{285}/ ε_{355})
		285nm	355nm	
HCl	0.1	1175	1070	1.09
	0.5	1110	1080	1.01
	1.0	1230	1170	1.05
H_2SO_4	0.1	1985	1005	1.98
	0.5	1960	995	1.97
HBr	0.1	1160	1025	1.13
	0.5	1075	965	1.11
	1.0	1005	995	1.01

Table 3: Effect of Diluents on Extraction

$[Cr(VI)] = 1.0 \times 10^{-4}$ M   (From HCl medium) $[TBA] = 5.0 \times 10^{-2}$ M

Diluent	Dielectric constant	% extraction
Benzene	2.28	90.82
Xylene	2.38	90.68
Toluene	2.3	80.46
CCl_4	2.24	90.54
$CHCl_3$	4.8	99.82
n-Hexane	1.90	85.77
Cyclo hexane	2.02	80.35
Nitrobenzene	36.10	80.73
Dichloro methane	8.08	72.15

Table 4: Analysis of electro plating effluents (Ebxtraction method)

Sample	Chromium (VI) added (g/lt)	Chromium found after recovery extraction (g/lt)	% recovery
Synthetic sample 1	0.20	0.198	99.00
2	0.30	0.297	99.00
3	0.25	0.245	98.00
4	0.40	0.394	98.50
Electroplating samples			
17-01-2016	---	---	32.6 (ppm)
03-02-2016	---	---	29.7
09-02-2016	---	---	28.3

Conclusions

The developed method was successfully applied to the separation and determination of chromium in synthetic samples as well as electroplating effluents. The average recovery % of chromium was found to be 98.7% each determination requires a minimum amount of 10 minutes time.

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