Extraction of tris (oxalato) chromate (III) by Tri -iso-octyl amine

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Abstract

Extraction of trisoxalate chromate (III) has been studied by Tri-iso-octyl amine (TiOA) dissolved in chloroform. Effect of several variables like– pH, effect of standing time on extraction, concentration of metal ion, extractant etc on the extraction process has been followed in order to identify the nature of the extracted species.

Key words - *Extraction, Chromium (III), Oxalate,Tri-iso-octyl Amine (TiOA),chloroform.*

I. INTRODUCTION

Chromium is considered important among other heavy metals [1, 2]. Out of the two most stable forms, Cr (III) is less toxic than Cr (VI) [3]. Cr (III) is found to be essential to human beings s well as animals as it plays vital role in insulin metabolism as the glucose tolerance factor (GTF). Due to its inert nature, limited work has been reported on the liquid – liquid extraction of chromium (III).

Extraction of chromium (III) from different acid media using various extracting systems [4-7] has been carried out. Extraction of tris (oxalato) chromate (III) by high molecular weight amines has been studied by Singh and
Co-workers [8]. But no reports are available in literature on the extraction of chromium (III) with tri–iso-octyl amine. The present investigation accounts for the extraction behavior of chromium (III) from oxalate solutions at different pH conditions has been studied using a tertiary amine, Tri–iso-octyl amine (TiOA) dissolved in chloroform.

II. EXPERIMENTAL

A 0.25M chromium nitrate (EMerck) stock solution was prepared and standardized titrametrically, with a standard solution of ferrous ammonium sulphate after oxidation of Cr(III) to Cr (VI) (using ceric ammonium nitrate as oxidant) with n-phenyl anthranilic acid (NPA) as indicator . Solutions of different concentrations were prepared by diluting the stock solution appropriately. 0.45 M Tri iso-octyl amine (TiOA) [sigma Aldrich] was prepared by weighing an appropriate amount in chloroform. All other chemicals used in the study were of AnalaR grade or samples purified   according to standard methods. Double distilled water was used throughout the studies.

Procedure

An aliquot (10 ml) containing chromium (III) of morality in the range $(1.15X10^{-4}$ and $1.0 \ X10^{-5}M)$, oxalic acid (or sodium oxalate) and required quantity of hydrochloric acid were thermo stated for 20 min at different temperatures. It was then shaken with an equal volume (10 ml) solution of (0.05 M) TiOA in chloroform for about fifteen minutes. Chromium (III) concentration both in the aqueous phase before and after extraction was estimated using AAS Atomic absorption spectrophotometer type – SVL Spectronics model - 205.

III. RESULTS AND DISCUSSION

The effect of variables like pH, standing time, oxalate ion and concentration of TBA on the extraction of chromium (III) by TBA were presented in **Tables 1 and 2**.

Table-1: Effect of pH on the extraction of chromium (III)
$[Cr (III)]=1.25X10^{-4} M$ $[TiOA] =2.50X10^{-2} M$
$[Oxalic \ acid] =2.5X10^{-1}M$ Standing time = 18 hrs

S.no.	pH	% Extraction
1	1.0	22.70
2	2.0	29.50
3	3.0	51.35
4	4.0	65.20
5	4.5	84.70
6	5.0	98.80
7	5.5	99.50
8	6.0	97.65
9	7.0	93.20

Table-2: Time variation for extraction
$[Cr (III)]=1.25X10^{-4} M$;   pH = 5.5;
Standing time = 18 hrs
$[TiOA] =2.50X10^{-2} M$, $[Oxalic\ acid] =2.5X10^{-1}M$

S. no.	Standing time (hrs.)	% Extn(Temp30.5^0 C)	%Extn.(Temp4 1.5^{0}C)
1	0	33.2	38.6
2	5	57.4	67.2
3	10	78.8	81.8
4	12	83.3	84.7
5	15	91.9	92.4
6	16	93.8	94.2
7	18	98.5	99.3
8	20	98.5	99.3

% Extraction of chromium (III) was found to increase gradually with increasing pH from 1.0 to 5.5 followed by decrease in efficiency (Table-1). As the extraction in the present study are carried out under acid deficient conditions (pH 5.5) the reaction,

$R_3N_{(org)} + H_2O \rightleftharpoons R_3NH^+ + OH^-$
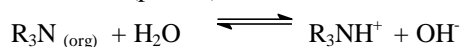
Maximum extraction efficiency obtained in the pH range 5.0 - 7.0 may be due to the successful competition of the anionic oxalate or chloride ions (pH < 5.0) with the extraction of the metal oxalate complex, which occurs according to the following equation

$R_3N_{(org)} + H^+ HOX^- \rightleftharpoons R_3NH^+HOX^-_{(org)}$
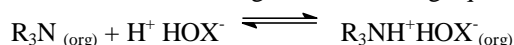
Results obtained on the variation of the % extraction of chromium (III) with the standing time of chromium (III) oxalate solutions   show a clear indication that the complexation between chromium (III) and oxalate goes to a near completion even at room temperature and maximum extraction is achieved after 18 hours only beyond which it remained the same. This has been confirmed by an absorbance Vs time obtained by recording the absorption spectrum at a wavelength (λ) of 570 nm for the aqueous solutions of $1.25X10^{-4}M$ chromium (III) dissolved in $2.5X10^{-1}M$ oxalic acid dissolved at room temperature (pH =5.5 at 30.5^0C) for different time periods(**Table.2**). The effect of variation of the concentration of oxalate ion on chromium (III) extraction reveal that the extraction efficiency of 99.3% with TiOA is achieved at pH 5.5 (maximum efficiency) followed by decrease in extraction probably due to hydrolysis of chromium species.

Composition of the extracted species:

Extraction isotherm method [9] and distribution ratio method [10] were used to study the formation of most probable extracted species. In the extraction isotherm method, plot of [Metal complex] $_{org}$ Vs [Metal complex] $_{aq}$. with maximum loading of $2.5X10^{-2}M$ TBA yields a limiting value of [Cr(III)] / [TBA] as 0.335 .In the distribution ratio method log -log plot of K_d vs.[TBA]

gave straight line with a slope of 3.0 which indicates that the mole ratio [TiOA] / [Metal complex] in the extracted species is 3.0(**Fig.1**).This shows the presence of tri negative chromium (III) containing ion, in the extracted metal complex salt most probably be $[Cr(OX)_3]^{3-}$which   has been further confirmed by spectral studies.

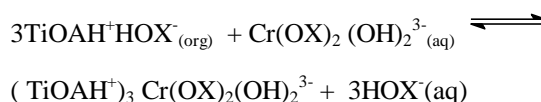Fig.1 Extractant Variation
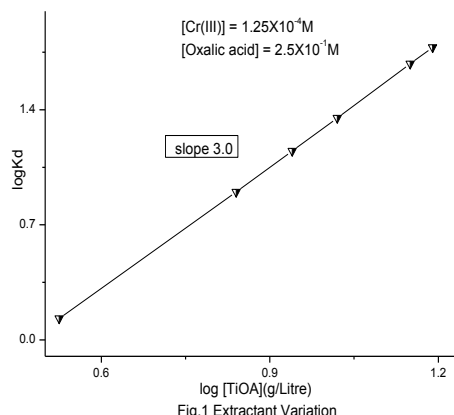
Absorption spectrum

The visible absorption spectrum of the metal complex from   0.05 M hydrochloric acid indicates two absorption maxima at 420nm (Є=95.0) and 570nm (Є=74.0).These maxima can be attributed to the existence of $[Cr(OX)_3]^{3-}$. The conclusion of the extraction of the species $[Cr (OX)_3]^{3-}$ is in accordance with the data published on the TLA-tris (oxalate) chromate(III) system[8]. On the other hand the spectra of the organic extract from the aqueous phase containing < $1.0X10^{-4}M$ chromium (III) exhibit absorption maxima at 415nm and 570 nm .The spectral data support the presence of both oxalate and hydroxy ligands in the extracted   tri negative chromium (III) containing complex .Further , the spectra of the organic extracts obtained by carrying out extraction of chromium ($<10^{-4}M$) at various pH conditions (ranging 5.0 – 7.0) show the formation and extraction of chromium (III) as...
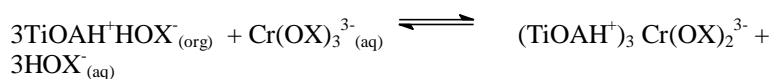$[Cr (OX)_2(OH)_2]^{3-}$ which is supported by similar type of species reported by Rao and Sastri[11].
Based on this, the mechanism of extraction with TiOA may be described as follows:
With Cr (III) solutions ($<10^{-4}M$):

$3TiOAH^+HOX^-_{(org)} + Cr(OX)_2 (OH)_2^{3-}_{(aq)} \rightleftharpoons$

$(TiOAH^+)_3 Cr(OX)_2(OH)_2^{3-} + 3HOX^-(aq)$

With Cr (III) solutions ($\geq 10^{-4}M$):

$3TiOAH^+HOX^-_{(org)} + Cr(OX)_3^{3-}_{(aq)} \rightleftharpoons (TiOAH^+)_3 Cr(OX)_2^{3-} + 3HOX^-_{(aq)}$

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