

STUDIES ON SOLVENT EXTRACTION OF CHROMIUM (III) BY TRIBENZYL AMINE FROM AQUEOUS OXALATE SOLUTIONS

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ABSTRACT

Extraction of chromium (III) from aqueous oxalate solutions by Tribenzyl amine (TBA) in chloroform has been studied. The optimum conditions for extraction were established from the study of the effect of several variables like- pH, effect of standing time on extraction, concentration of metal ion, extractant etc. The extracted species are identified.

Keywords: Extraction -Chromium (III) - Tribenzyl Amine (TBA) - Chloroform.

INTRODUCTION

Extraction of chromium (both the forms) has been reported by Rao and et. al, using different extracting systems¹⁻⁵. Singh and co-workers,⁶ also studied the extraction of tris (oxalate) chromate (III) by high molecular weight amines. The principal aim of this investigation is to study the extraction behavior of chromium (III) from oxalate solutions at different pH conditions of the aqueous phase by a tertiary amine tri benzyl amine (TBA) from aqueous oxalate solutions and to explain the mechanism of extraction.

EXPERIMENTAL

Chromium (III) stock solution

Stock solution of 0.5 M chromium chloride (E Merck) was prepared and standardized titrimetrically, 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.

A stock solution of 0.25 M Tribenzyl amine (TBA) [Merck] was prepared by weighing an appropriate amount and dissolving it 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

A mixture of 10 ml of an aqueous solution containing chromium (III) of appropriate molarity (10^{-4} – 10^{-3} M), oxalic acid (or sodium oxalate) and appropriate amount of hydrochloric acid or sodium hydroxide (to obtain required pH) was thermo stated for 20 min at required temperature. The aqueous solution was then shaken with 10 ml solution of (0.05 M) TBA in chloroform for about ten minutes. The organic and aqueous phases were then separated after allowing the mixture to settle for five minutes. The chromium (III) concentration in the aqueous phase before and after extraction was estimated using Atomic absorption spectrophotometer type AAS – SVL Spectronics model - 205.

RESULTS AND DISCUSSION

The results obtained on the effect of pH, standing time, oxalate ion and concentration of TBA on the extraction of chromium (III) by tri benzyl amine (TBA) from aqueous oxalate solutions has been presented in Tables 1-3. Extraction of chromium (III) was found to increase gradually with increasing pH up to 5.0 and thereafter remained constant in the pH range 5.0 - 8.0. On the other hand with the increase in acidity up to 0.1 M (with respect to HCl), the extraction of chromium (III) sharply diminishes (Table-1).

As the extraction in the present study are carried out under acid deficient conditions (pH >5.0) the reaction,



The occurrence of maximum extraction in the pH range 5.0 - 8.0 is perhaps 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



The data on the variation of the % extraction of chromium (III) with the standing time of chromium (III) oxalate solutions (Table.2) 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 reached after 16 hours only. This result has been confirmed by an absorbance Vs time curve obtained by recording the absorption spectrum at a wavelength (λ) of 570 nm for the aqueous solutions of $2.75 \times 10^{-4} M$ chromium (III) dissolved in $2.5 \times 10^{-1} M$ oxalic acid dissolved at room temperature (pH =5.0. at $30.5^\circ C$) for different time periods. The effect of variation of the concentration of oxalate ion on chromium (III) extraction reveal that the extraction efficiency of 97.2% with TBA is achieved at pH 5.0 (maximum efficiency) followed by decrease in extraction probably due to hydrolysis of chromium species.

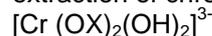
Composition of the Extracted Species

The composition of the extracted species was determined by the extraction isotherm method⁷ and distribution ratio method⁸. In the extraction isotherm method, the plot of [Metal complex]_{org} Vs [Metal complex]_{aq} with maximum loading of $2.5 \times 10^{-2} M$ TBA yields a limiting value of [Cr(III)] / [TBA] as 0.325. 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 [TBA] / [Metal complex] in the extracted species is 3.0. 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.

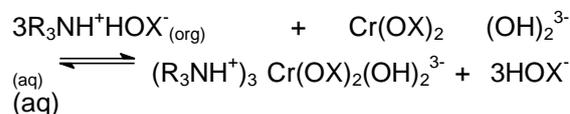
Absorption spectrum

The visible absorption spectrum of the metal complex from 0.05 M hydrochloric acid indicates two absorption maxima at 420nm ($\epsilon=95.0$) and 570nm ($\epsilon=74.0$). 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) system⁹. On the other hand the spectra of the organic extract from the aqueous phase containing $< 1.0 \times 10^{-4} M$ 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 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 – 8.0) show that the peak at longer wavelength exhibits a bathochromic shift and the peak at shorter wavelength is not much altered. This observation also supports the formation and extraction of chromium (III) as

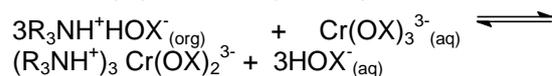


Based on this, the mechanism of extraction with TBA may be described as follows:

With Cr (III) solutions ($< 10^{-4} M$)



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



Where R_3N^+ is TBA

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Table 1: Effect of pH on the extraction of chromium (III)
[Cr (III)]= 2.75×10^{-4} M, [TBA] = 2.50×10^{-2} M
[Oxalic acid] = 2.5×10^{-1} M, Standing time = 16 hrs

pH	% Extraction
1.5	11.00
2.5	27.50
3.5	53.75
4.0	68.20
4.8	86.50
5.0	99.70
5.5	100.00
6.0	100.00
7.0	100.00

Table 2: Time variation for extraction
[Cr (III)]= 2.75×10^{-4} M pH = 5.0, [TBA] = 2.50×10^{-2} M
[Oxalic acid] = 2.5×10^{-1} M, Standing time = 16 hrs

S.no.	Standing time (hrs.)	% Extraction
1	0	37.8
2	5	52.3
3	10	75.5
4	12	85.9
5	15	92.9
6	16	97.2
7	18	97.2
8	20	97.2

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