

SYNERGISTIC EXTRACTION OF CHROMIUM (VI) USING A COMBINATION OF TRI METHYL AMINE AND TRI ISO-OCTYL AMINE

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ABSTRACT

Solvent extraction of chromium (VI) from different acid solutions like hydrochloric, sulphuric, Perchloric, acetic, nitric and phosphoric acid using a mixture of TMA and TIOA in benzene as extractant has been studied. The extractions from phosphoric and sulphuric acid solutions are quantitative and are nearly quantitative from other acid media. The probable extracted species in each of the acid media has been identified.

KEYWORDS: Chromium (VI) – Tri Methyl Amine – Tri Iso-Octyl Amine-Benzene

Synergistic extraction of metals have been carried out by different extraction systems. Fischerman.et.al. (Fischman, Finston, and Goldberg ;1973) studied the extraction of Fe (III) with TOPO and TTA in Perchloric acid media. A mixture of TOPO or TBP in presence of BTFA was used to study the synergism by Sunderesan (Sunderesan and Sundaram ;1977). A mixture of naphthenic acid and other chelating reagents have been utilised for the synergistic extraction (Flett and Titmuss; 1969) of copper (II). Synergism in the extraction of some metal naphthanates such as Cd (II) in the presence of alkyl phenol has also been observed by Alekperov and Agaev (Alekperov and Azerb ;1980).

Hexavalent chromium is toxic in nature. Extraction of Cr (VI) by tertiary amines has been carried out by several workers (Venkateswaran and Palanivelu; 2004), (Yoshifumi Akama and Ahat Sali; 2002), (Goldoni et.al; 2005). In the present communication we describe our studies on the synergistic extraction of Cr (VI) using benzene solutions of TMA and TIOA.

MATERIALS AND METHODS

A 1M (stock) solution of Chromium (VI) oxide was prepared by weighing 5.2 gm in 100ml and 0.25M (stock solution) of each Tri methyl amine (TMA) and Tri iso octyl amine (TIOA) in benzene was prepared and diluted appropriately to get the required concentration. Chromium (VI) oxide was used for preparing Chromium (VI) stock solution (1M) used as such without any further purification. All other chemicals used were of Anala R grade or samples purified according to the standard methods.

CHROMIUM (VI) EXTRACTION

An aliquot of chromium (VI) [1.0×10^{-3} M] with corresponding mineral acid in a 250ml separating funnel was added to 10ml portions of each 2.5×10^{-2} M of TMA+TIOA mixture in benzene pre-equilibrated with 0.1M mineral acid.

The solution was shaken thoroughly for five minutes and was allowed to settle for few min. The chromium (VI) concentrations in the aqueous phase before and after extraction was estimated spectrophotometrically (Vogel; 1962) by measuring the absorption of Cr (VI) – DPC complex at 540nm, using Elico SL 177 Scanning mini spectrophotometer. 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, H₂SO₄, HClO₄, HNO₃, H₃PO₄ and CH₃COOH) is presented in Table 1 & Fig.1. In case of HCl, distribution ratio increases from 0.25 to 1.0M followed by a slight decrease in value up to 2 M acidity beyond which it decreases gradually. In the case of sulphuric acid solution the extraction of chromium (VI) by TMA+TIOA in benzene as a function of acidity, the percentage extraction (% E) increased with increasing the concentration of the acid up to 3.0 M acidity. In the case of phosphoric acid solutions the extraction of chromium (VI) by the percentage extraction (% E) remains unchanged under the experimental conditions 99.99%. The extractions are quantitative for both the acid solutions. From perchloric acid media, the %E was found to increase with increase in acid concentration up to 2.25M followed by decrease in extraction. On the other hand the extraction efficiency was found to decrease with increase in acid concentration in nitric and acetic acid media. Addition of sodium salts of corresponding acid media to aqueous phases resulted in a significant decrease in extraction. The decrease being in the order, H₃PO₄> H₂SO₄ > HCl > CH₃COOH > HClO₄ > HNO₃. The results obtained using various acids with different concentrations are given in Table 1.

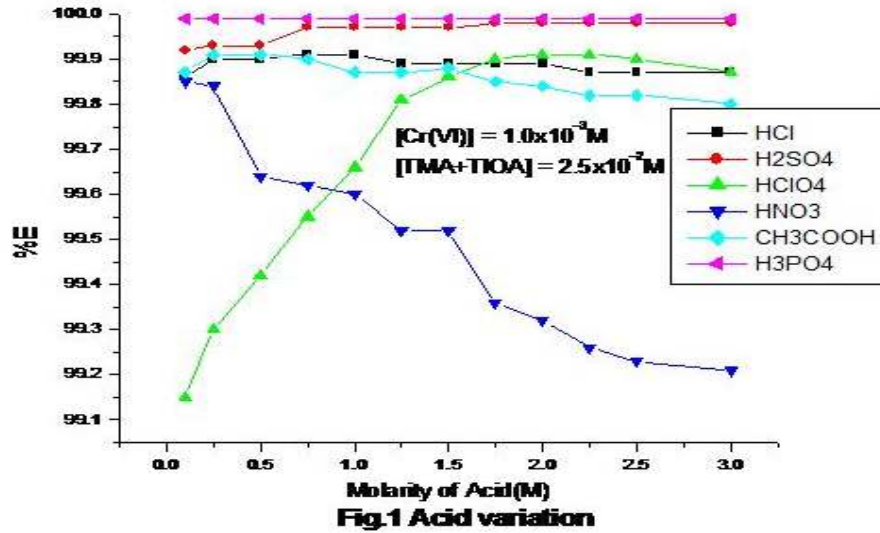


Table 1: % Extraction of chromium (VI)

[Cr (VI)] = 1.0×10^{-3} M [TMA+TIOA] = 2.5×10^{-2} M

Molarity (M)	HCl %E	H ₂ SO ₄ %E	H ₃ PO ₄ %E	HClO ₄ %E	HNO ₃ %E	CH ₃ COOH %E
0.1	99.86	99.92	99.99	99.15	99.85	99.87
0.25	99.90	99.93	99.99	99.30	99.84	99.91
0.5	99.90	99.93	99.99	99.42	99.64	99.91
0.75	99.91	99.97	99.99	99.55	99.62	99.90
1.0	99.91	99.97	99.99	99.66	99.60	99.87
1.25	99.89	99.97	99.99	99.81	99.52	99.87
1.5	99.89	99.97	99.99	99.86	99.52	99.88
1.75	99.89	99.98	99.99	99.90	99.36	99.85
2.0	99.89	99.98	99.99	99.91	99.32	99.84
2.25	99.87	99.98	99.99	99.91	99.26	99.82
2.5	99.87	99.98	99.99	99.90	99.23	99.82
3.0	99.87	99.98	99.99	99.87	99.21	99.80

COMPOSITION OF THE EXTRACTED SPECIES

The composition of the extracted species was determined by the extraction isotherm method (Davis and Prue;1955) and the distribution ratio

method (Neuss and, Rieman ;1934). The maximum loading of 1.0×10^{-3} M TMA+TIOA with chromium (VI) at aqueous acidity (0.75M H₂SO₄), yielded a mole ratio of the [extractant] to [chromium (VI)]_{org} unity (Fig. 2)

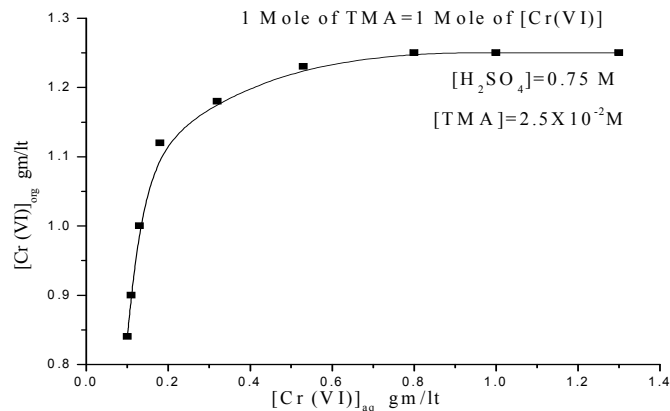


Fig.2 Extraction Isotherm (H_2SO_4 Medium)

The log-log plots of Log Kd Vs Log TMA and /or TIOA from invariable concentrations of the acid (HCl, $HClO_4$, HNO_3 , H_3PO_4 and CH_3COOH)

solutions (1.0 M) gave straight lines with slope one irrespective of the acid concentrations used. With sulphuric acid solutions the log-log plot gave straight line of slope two. Representative plots have been provided in Fig. 3 & Fig. 4.

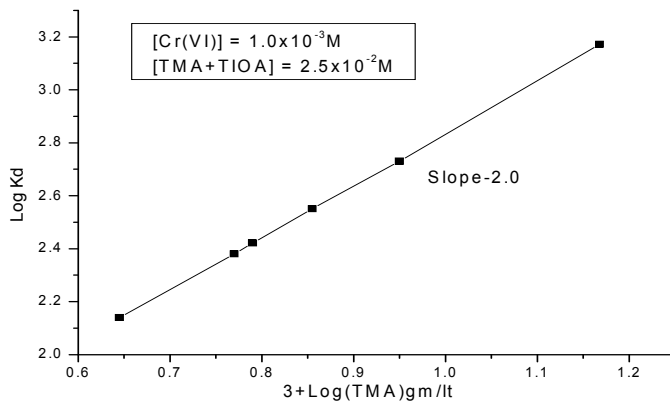


Fig.3 Extractant Variation

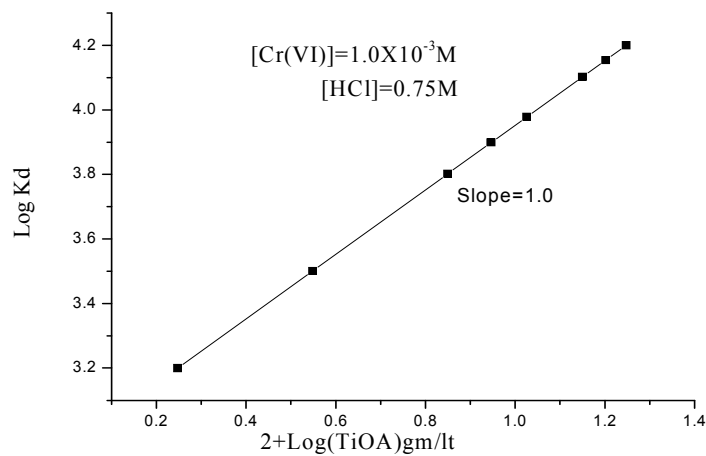


Fig. 4 Extractant variation

DILUENT VARIATION

Several solvents with varying dielectric constants were tested as diluents (T-2). It was observed that with benzene as diluent maximum extraction efficiency (99.99%) and minimum with cyclohexane (78.2 %) were obtained. Hence, benzene was preferred as diluent throughout the study.

Table 2: Effect of various diluents on extraction (H₂SO₄ medium)

[Cr (VI)]=1.0x10⁻³ M & [TMA+TIOA]=2.5x10⁻² M

Diluent	Dielectric constant	% extraction
Benzene	2.27	99.9
CHCl ₃	4.81	99.7
Nitrobenzene	34.82	96.5
Toluene	2.38	95.2
CCl ₄	2.23	90.8
Cyclo hexane	2.00	78.2
n-Hexane	1.89	80.5

CHOICE OF STRIPPING AGENT

After the extraction of chromium (VI) by 0.025 M TMA and / TIOA, it was stripped with 10 ml reagents of various concentrations (0.01 – 1.0 M) of HCl, HNO₃, NaCl, NaNO₃ and NaOH solutions. It was observed that HCl, NaCl, and NaNO₃ are extremely poor stripping agents for chromium (VI). On the other hand, 1.0 M HNO₃ alone is a good stripping agent. However in no case HNO₃ 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 1.0 M HNO₃.

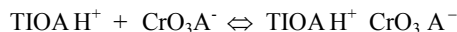
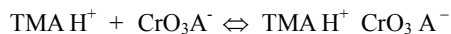
EFFECT OF DIVERSE IONS

On the extraction of chromium (VI) the effect of several diverse ions was studied using the general extraction procedure. In the recovery of chromium (VI) (27 µg/ 20 ml), the tolerance limit was set at the amount of diverse ion required to cause ± 2% error. The results show that the ions are tolerated in the ratio 1:200 are such as Cu (II), Ce (IV), Mn (II), Co (II), Zn (II) Chlorate, Oxalate, Selenite, Tellurite, Phosphate and Tartarate, and the ions do not interfere even if present in the ratio 1:100 are such as Ca (II), Pb (II), Pd (II), Mo(VI), Ru (III), U (VI), Sr (II), VO₃⁻ and WO₄²⁻. Fe (III) and F⁻ ions are showing small tolerance limit in the ratio 1:50. Chromium (VI) can be extracted in presence of large number of cations and anions with chromium recovery of 99.7 + 0.3 %. From ten repeated determinations with 27 µg of Cr (VI) the

relative standard deviation and relative error obtained were found to be ± 1.03 % and ± 0.7 % respectively.

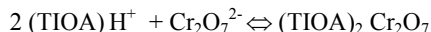
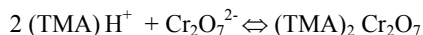
Based on the result obtained (as mentioned above), the following mechanism is suggested:

FROM OTHER ACID SOLUTIONS



Where A = Cl⁻, NO₃⁻, CHCOO⁻ and H₂PO₄⁻

FROM SULPHURIC ACID SOLUTIONS



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REFERENCES

- Fischman, A.J., Finston, H.L. and Goldberg, D.E.; 1973. J. Inorg. Nucl. Chem., 35: 2497.
- Sunderesan, M. and Sundaram, A.K.; 1977). Proc. Indian Acad. Sci. Sec. A., 85:75
- D.S. Flett, S. Titmuss, ; 1969.J. Inorg. Nucl. Chem., 31: 2612.
- R. A. Alekperov, Z.Z.Agaev, Azerb. Khim. Zh.; 1980. 3:113.
- P Venkateswaran and K.Palanivelu; 2004. Separation and Purification Technology, 40(3): 279 – 284.
- Yoshifumi Akama, and Ahat Sali; 2002. Talanta, 57(4): 681 – 686.
- M Goldoni ,A Caglieri ,D Poli. and M Vttoria ;2005.Anal.Chim Acta 5629(2): 229.
- Vogel, A.I.;1962.A Text Book of quantitative Inorganic Analysis. 3rd Edn 311, Longman, London.
- Davis W.G , and, Prue J.E;1955. Trans. Faraday Soc., 1: 45.
- Neuss J.D., and, Rieman W. J.;1934.Amer. Chem. Soc, 56:2238.