Extraction of Iron (III) by TBPO from nitric & perchloric acid solutions

A.V.L.N.S.H. Hariharan[*] D. Santhipriya[1] and A.Satheesh[1]

[*]*Department of Chemistry, GIT, GITAM University, Visakhapatnam – 530 045, India.*
[1]*Department of Chemistry, M.R.Degree College, Vizianagram, A.P India*

Abstract

Iron (III) has been extracted quantitatively from aqueous nitric and phosphoric acid solutions by benzene solutions of Tributyl phosphine oxide [TBPO] as extractant. Optimum conditions for extraction were established from the Study of the effect of several variables like– concentration of phosphine oxide, metal ion, acidity etc. The extracted species are identified. Stripping of iron (III) from the organic phase was also achieved with 1.0M NaOH. Extractions were nearly quantitative with both the acid solutions. Based on the results obtained, attempts were also made to estimate iron in industrial samples.

Key words - *Extraction, iron (III), Tributyl phosphine oxide [TBPO], Industrial samples.*

I. INTRODUCTION

Iron plays a vital role in biological systems. Iron deficiency in the human body leads to anaemia, nutritional deficiency diseases. Hence an analysis of iron in natural and industrial sources has been gaining considerable attention. Several workers have carried out extraction of iron (III) from mostly aqueous hydrochloric [1-5] and other acid solutions [6-10] using various extracting agents. There are very few reports available in the literature on the extraction of iron (III), especially from nitric acid and perchloric acid solutions. Therefore, the present communication comprises studies on the removal of iron (III) by benzene solutions of Tributyl phosphine oxide [TBPO] from nitric as well as perchloric acid media.

II. EXPERIMENTAL

Iron (III) stock solution of 0.5M was prepared by dissolving an appropriate amount of ammonium iron (III) sulfate (E.Merck) in 250 ml double distilled water and was standardized volumetrically with potassium dichromate using diphenylamine as the indicator [11]. Required concentrations of iron (III) solutions were prepared from the stock solution. A stock solution of $5.20X10^{-2}$ M TBPO in benzene was used throughout the course of investigations. Determination of iron content has been done AAS Spectrophotometer.

Procedure for Iron (III) Extraction:

An aliquot (10ml) of a solution containing iron (III) in corresponding acid media was equilibrated for 10 minutes with an equal volume of $5.20X\ 10^{-2}$ M of TBPO in a 125 ml reparatory funnel. After separation of the two phases; Iron (III) from the organic phase was stripped with 10 ml of 1M NaOH as removing agent. The concentration of Iron (III) was estimated using AAS SVL (Spectronics– model 205).

III. RESULTS AND DISCUSSION

Variation of Acidity

Iron (III) was extracted from different concentrations of the two acids with $5.20X10^{-2}$ M TBPO, and the results obtained are presented in Fig-1. Distribution ratio (Kd) in the nitric acid medium was found increased with increasing concentration of the acid up to 8.0 M (98.32%) and remained constant up to 9.0

M acidity beyond which a gradual fall in the efficiency of extraction was observed. In the case of perchloric acid media, maximum extraction efficiency was obtained at 9.0M (97.14%) acidity, followed by a continuous fall inefficiency (Fig.1). The extractions are nearly quantitative from both acid solutions.

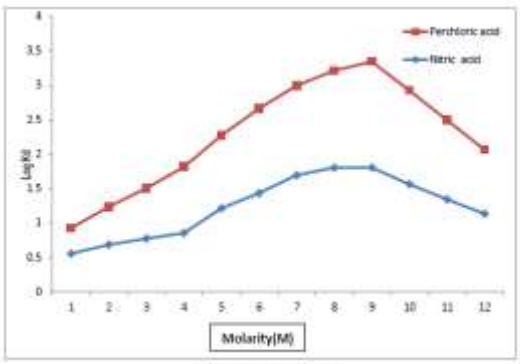

Fig 1. Variation of acidity

Composition of the Extracted species

The extraction isotherm method [12] and the distribution ratio method [13] were employed to determine the composition of the extracted species. In the extraction isotherm method, the limiting ratio of the metal to TBPO was found unity under the experimental conditions. Representative data from nitric acid solutions have been provided in **Fig.2**.

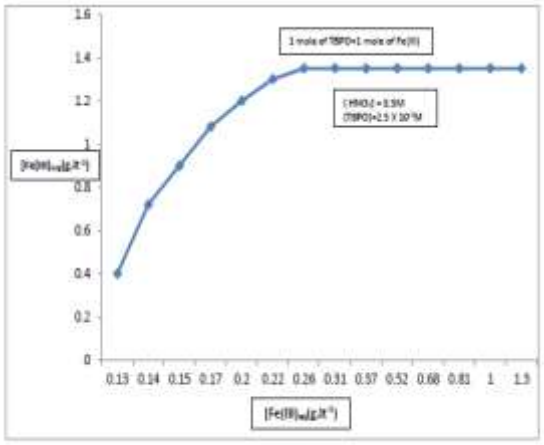

Fig.2 Extraction Isotherm

With all other factors being kept constant, iron (III) was extracted with 10 ml portions of varied concentrations of TBPO. The log-log plots of Kd Vs, TBPO from both the acid solutions, gave straight lines with the unit slope in both the acidic solutions (Fig.3).

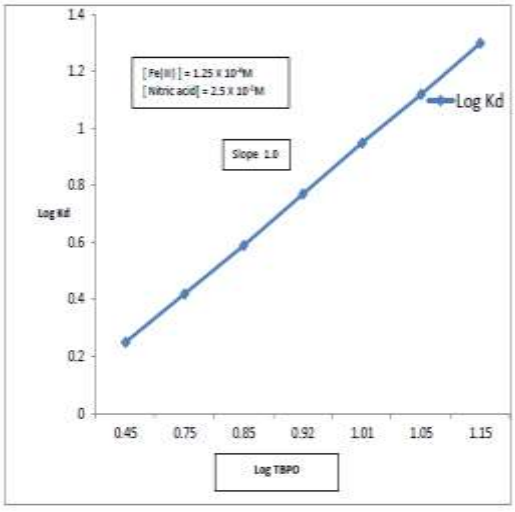

Fig. 3 Extractant Variation

Effect of diluents

Several solvents with varying dielectric constants were tested as the diluents (Table 1). Quantitative extractions were achieved with benzene as diluent. More than 80% efficiency was obtained with carbon tetrachloride, hexane, toluene, cyclohexane and xylene. Nitrobenzene was found to be poor in extraction. Hence benzene was preferred as diluent throughout the Study.

Effect of various stripping agents

After extraction, iron (III) was removed with 20ml reagents of different concentrations (0.1 – 1 .0 M) of HCl, H_2SO_4, HNO_3, ACOH, and NaOH solutions. It was observed that 1.0 M NaOH alone is a right stripping agent. However, in no case, the acid strips out all the iron (III) in a single extraction. 99.7% iron (III) could be recovered from the organic phase by making contact four times with equal volumes of 1.0 M NaOH.

The observed iron: TBPO molar ratio of one from both the acid media by distribution ratio method) could be explained as arising from the extraction of iron (III) by the following solvation mechanism:

From nitric acid solutions:

$$(TBPO)_{org} + H^+_{aq} + Fe^{3+} + 4NO_3^-{}_{aq} \rightleftharpoons [TBPO.H^+Fe(NO_3^-)_4]_{org.}$$

From perchloric acid solutions:

$$(TBPO)_{org} + H^+_{aq} + Fe^{3+} + 4ClO_4^-{}_{aq} \rightleftharpoons [TBPO.H^+Fe(ClO_4^-)_4]_{org.}$$

Analysis of iron in different samples

The present method of extraction for recovery of iron has been validated by estimating iron in Ferrochrome alloys. The slag sample in the current investigation is a composite obtained from Jindal Ferro Alloys Corporation [Kothavalasa, Visakhapatnam Dt.] with the following chemical composition: Cr_2O_3 10-17%, FeO 2-6%, SiO_2 25 – 28%, MgO 21-24%, $Al_2O_3$15-21%, rest CaO.

A known weight (1.0 gm) of the finely powdered slag sample was dissolved in aquaria. The solution was evaporated and extracted with the dilute hydrochloric acid solution. The mixture was shaken well for about 15 min. Taken care that chromium should not get extracted under the present experimental conditions. Then the mixture was diluted by 0.01 M HCl solution to the mark and then filtered by Whatman filter paper No. 40. The first portion of filtrate was discarded. The clear solution so obtained was made up to 250 ml and used as a stock solution. 10 ml of this iron solution was shaken for ten minutes with an equal volume of $5.20X\ 10^{-2}$ M of TBPO. After the separation of two phases, Iron (III) from the organic phase was stripped with 10 ml of 1.0M NaOH and was determined using AAS as described earlier. Results are presented in Table 2. The same procedure was adopted for a synthetic sample with the

following % composition- Fe =0 .10-0.30 g/Lt, Mg=0-2.0 g/Lt, Al=1.5-2.0 g/Lt, HNO_3 = 8.0 M.

The current method is fast and straightforward. It will take hardly half an hour to extract and can be applied successfully to estimate iron content in synthetic and also slag samples with accuracy.

.ACKNOWLEDGEMENTS

Thanks are due to and Management of GITAM University for providing necessary facilities.

REFERENCES

[1] J. Saji, R.T. Prasada C.S.P. Iyer and M.L. P. Reddy, (1998) *Extraction of iron (III) from acidic chloride solutions by Cyanex 923.* Hydrometallurgy*:* 49: 289-296.

[2] K.R. Staszak, R.Clerpiszewski and K.P.Ochaska, **(**2011), *Equilibrium and rate of Fe(III) extraction from chloride solutions"* Polish J. Chem. Tech. Supply. **:** 1: 1-5.

[3] B.Pospiech and W.Walkowiak,(2010), *Studies on iron (III) removal from chloride aqueous solutions by solvent extraction and transport through polymer inclusion membranes with D2EHPA*, J.Physico chem. Probl. Miner. Process: 44: 195-204.

[4] G.Chena,D.G.Weia,H.Zhaoa, anga, T.Qia, F.Menga and L.Menga,(2015), *Extraction of iron (III) from chloride leaching liquor with high acidity using TBP and synergistic extraction combined with MIBK*, J. Seprn. And Purfn. Tech.:150: 132–138.

[5] L.Man-Seung, L.Gwang-Seop andY.S. Keun ,(2004), *Solvent extraction equilibria of $FeCl_3$ with TBP*. Materials Transactions:45 (6): pp. 1859 -1863.

[6] F.J.Alguacil, and S.Amer,(1986), *Study of the amine prime 81R sulphate-$Fe_2(SO4)_3$ Extraction equilibrium system at low temperature*. Polyhedron: 6 (11): 1755.

[7] B. Gupta, A.Deep, V.Singh, and S.N.Tandon,(2003), *Appln of TBP for selective removal of Fe(III) by polymer inclusion membranes*, Hydrometallurgy: 70:121

[8] C.Lupi, and D. Pilone, (2000), *Reductive stripping in the vacuum of Fe(III) from D2EHPA*, J. Hydrometallurgy: 57(3): 201-207.

[9] AVLNSH, Hari Haran, Ch, Sudhakar and AS Naidu,(2011)Extraction of Fe (III) from acid Solutions by TOPO. Intl. J of Chem. Pharm. Res.:3(4): 945-950.

[10] J.Jayachandran, and P M Dhake , **(**1997*) Liquid-liquid extraction of iron(III) by 2-Ethylhexyl phosphonic acid mono 2 - ethylhexyl ester*. Talanta,: 44(7):1285- 1290.

[11] A. I Vogel.1962 (3rd Edn), A Textbook of quantitative Inorganic Analysis, Longman, London.

[12] C.F.Coleman, K.B. Brown, J.G. Moore, and K.A. Allen,(1958) Proc.2nd Intl. Conf., Peaceful Uses of Atomic Energy, Geneva: C.10:510.

[13] E Hesford, and H.A.C.Mckay, (1958), The extraction of nitrates by TBP, Part.3, Trans.Faraday Soc.:54: 573.

Table 1: Effect of diluent on extraction

[Fe(III)] = 1.2 x 10^{-3} M **;** [TBPO] = 5.0 x 10^{-2} M

(Nitric medium)

Diluent	Dielectric constant	% extraction
Benzene	4.81	95.22
$CHCl_3$	2.28	87.04
CCl_4	2.23	88.76
Cyclo hexane	2.00	82.20
n-Hexane	1.89	80.47
Nitrobenzene	34.82	67.54
Toulene	2.43	83.84
Xylene	2.56	85.15

Table 2: Analysis of Iron in slag and synthetic Samples

Sample	Iron (III) added (g/l)	Iron found after recovery extn. (g/l)*	% Recovery
Synthetic 1	0.10	0.0983	98.30
2	0.15	0.1456	97.06
3	0.20	0.1985	99.25
4	0.25	0.2448	99.31
5	0.30	0.2978	99.26
Slag sample (date)	Fe(III) present	Fe (III) found *	
1 (12/01/2020)	10.75	10.43	97.02
2 (26/01/2020)	12.58	12.35	80.97
3 (15/02/2020)	11.22	10.97	97.78

* **Average of 3 determinations**