International Journal of ChemTech Research
CODEN(USA): IJCRGG ISSN : 0974-4290
Vol. 3, No.2, pp 703-707, April-June 2011

Estimation of Iron in Pharmaceutical samples-A Solvent extraction study

A.V.L.N.S.H.Hariharan*, Ch. Sudhakar and D Muralikrishna

Department of Chemistry,
GIT, Gitam University. Visakhapatnam – 530 045,India.

Corres.author: ahharan@gmail.com

Abstract: The extraction of Iron (III) from hydrochloric, sulphuric and nitric acid solutions with Tribenzylamine (TBA) in chloroform has been studied. The extractions from hydrochloric and phosphoric acid solutions are nearly quantitative and are partial from nitric acid solutions. The optimum conditions for extraction were established from the study of the effect of several variables like– concentration of amine, metal ion, acidity, foreign ions etc. The extracted species are identified.. The method has been applied for the recovery and determination of iron in natural food as well as pharmaceutical samples.

Key words: Solvent extraction -iron (III) - Mineral acid- Tri benzylamine [TBA] -– pharmaceutical samples.

Introduction:

Several workers studied the extraction of iron (III) from aqueous hydrochloric[1,2] and sulphuric acid[3-8] solutions by various amines. Fewer studies appeared in literature on the extraction of iron (III) by amines especially in different acid media. .It is also observed from the above studies that the free amine cannot extract iron (III) from aqueous acid solutions. All these studies concern with extraction of iron with one acid system only. Keeping in view of this, it is proposed to take up systematic studies on the extraction of iron (III) by Tribenzyl amine (TBA) from hydrochloric sulphuric and nitric acid solutions.

Experimental:

A stock solution of 0.35 M TBA (Mol. wt. 287.398) in chloroform was prepared and diluted appropriately to get the required concentration. Ferric ammonium sulphate (E.Merck) was used for preparing iron(III) solution (0.5M) and was standardized using standard potassium dichromate solution volumetrically. All other chemicals used were of AnalaR grade . Double distilled water was used through out.

Iron(III) Extraction:

Iron (III) distribution studies were made using appropriate concentrations of the iron salt and mineral acid by equilibrating with an equal volume (20ml) of TBA in chloroform (0.05M) pre-equilibrated with 0.1M mineral acid. The solution was shaken for 5 minutes. The two phases were allowed to settle and separate .Iron(III)from the organic phase was stripped with 20ml of 0.1M H_2SO_4 and was estimated spectrophotometrically[7] by measuring the absorption of Fe(III) – thiocyanate complex at 480nm, using Shimadzu UV-Visible Spectrophotometer type UV-260. The equilibrium iron (III) concentration in the organic phase was determined by taking the difference in the initial iron (III) concentration and the equilibrium iron (III) concentration in the aqueous phase.

Results and Discussion:

The variation of distribution ratio as a function of aqueous phase concentration of mineral acid (HCl, H_2SO_4 and HNO_3) are presented in **Table-1.** In the case of hydrochloric and sulphuric acid solutions the extraction of iron (III) by TBA in chloroform as a function of acidity, the distribution ratio (K_d) increased with increasing the concentration of the acid up to 9.0 M acidity beyond which by a decrease in extraction there after. The extractions are nearly quantitative from both the acid solutions (Table 1). On the other hand the extractions are partial from nitric acid solutions with maximum extraction at 3.0 M(88.6%) followed by a gradual fall in K_d with increasing acidity.

Composition of the Extracted Species:

The extraction isotherm method[8] and distribution ratio method[9] were employed to determine the composition of the extracted species. In the extraction isotherm method the limiting ratio of the metal to TBA was found to be unity with all the acid systems (Fig-1).

The log-log plots of K_d Vs. TBA from various acid solutions gave straight lines. With hydrochloric and nitric acid acid solutions the log-log plot gave straight line of unit slope(Fig-2). On the other hand, the slope analysis of the distribution data in sulphuric acid solutions indicates that the solvation number is two (Fig-3).

Table – 1 : Percentage Extraction of iron (III) by TBA from mineral acid solutions

[Fe (III)] = 1.0 x 10^{-3} M [TBA] = 5.0 x 10^{-2} M

	HCl	H_2SO_4	HNO_3
Molarity(M)	%Extraction	%Extraction	%Extraction
0.5	84.6	83.9	83.5
1.0	86.3	86.6	83.9
1.5	86.8	88.6	84.6
2.0	87.5	90.0	85.7
2.5	89.3	91.7	86.8
3.0	89.9	93.2	88.6
4.5	90.3	93.7	85.2
4.8	90.7	94.0	82.5
5.5	93.5	94.3	78.3
7.5	94.3	95.2	75.9
8.0	95.7	96.6	72.6
9.0	98.2	98.5	70.3
10.0	97.1	97.3	65.8

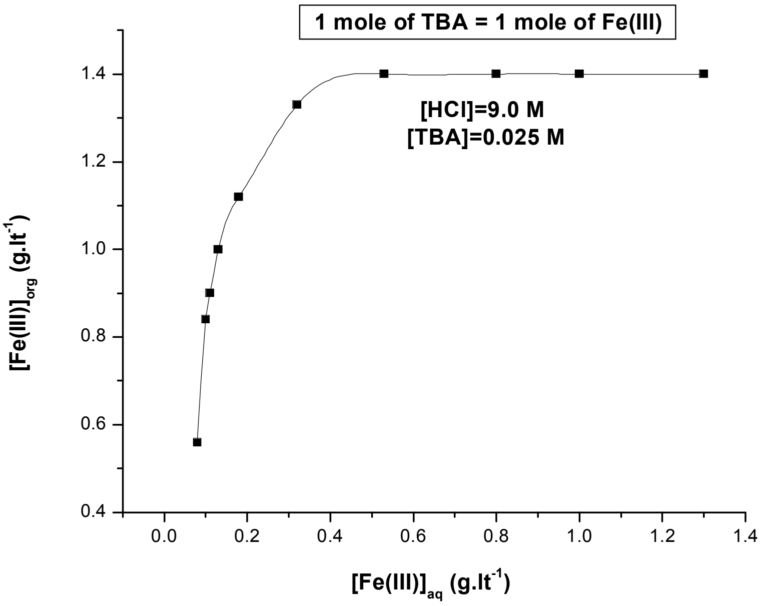

Fig.1. Extraction Isotherm method (HCl Medium)

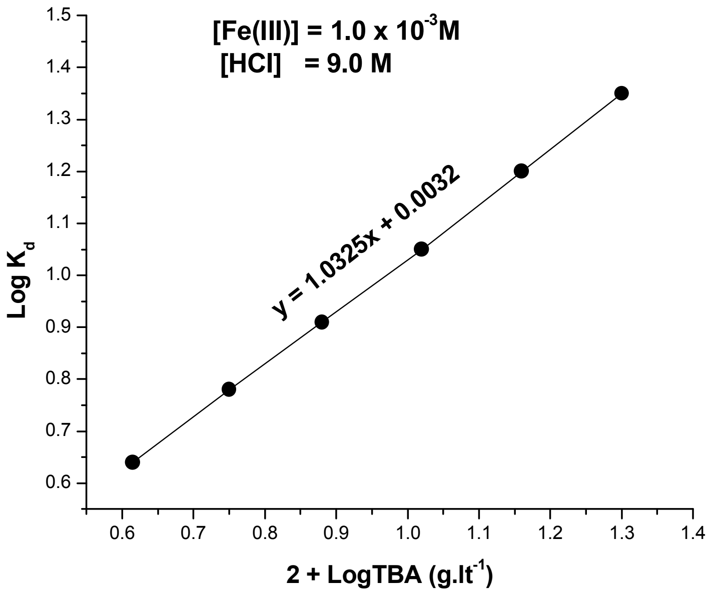

Fig. 2. Composition of the extracted species (HCl Medium)

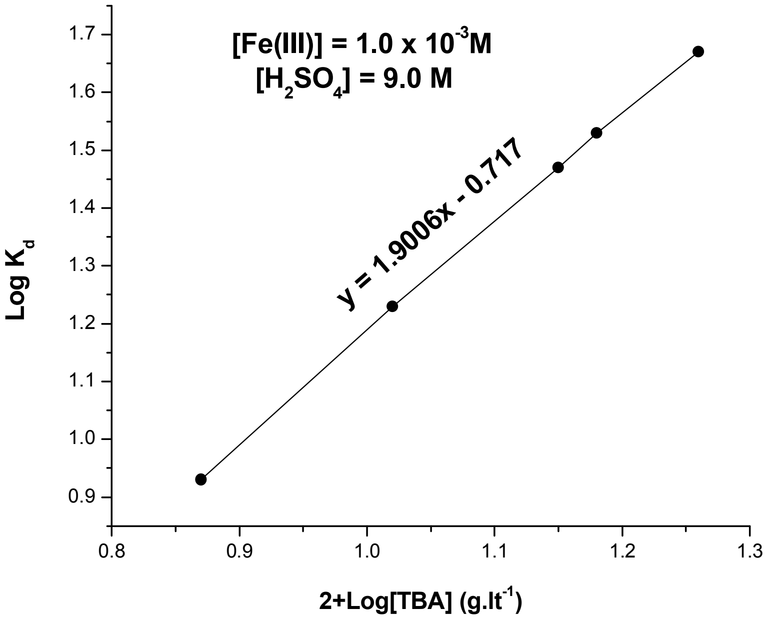

Fig. 3. Composition of the Extracted species (H_2SO_4 Medium)

Absorption Spectra:

The individual Iron (III) extracted species with TBA was studied in U.V. region[10-11]. The absorption spectra from sulphuric acid media exhibits absorption band at 295 and 355 nm . These two are the absorption characteristics of Fe(OH) and hydroxyl – group bridging species $Fe(OH)_2$ Fe respectively, and the appearance of new peak at 305 nm corresponds to the complexes $FeSO_4^+$ and $Fe(SO_4)^{-2}$.

The observed iron: Extractant molar ratio of unity from solutions (by distribution ratio method) could be explained as arising from the extraction of iron (III) by the following ion-exchange mechanism. According to Smulek , the extracted species in hydrochloric acid is $FeCl_4^-$ which associates with one amine cation to form an ion – pair.

From hydrochloric and nitric acid solutions:

$TBAHCl + Fe^{3+} + 4Cl^- \Leftrightarrow [TBAH^+ FeCl_4^-]_{org} + Cl^-$

$TBAHNO_3 + Fe^{3+} + 4\,NO_3^- \Leftrightarrow [TBAH^+ Fe\,NO_{3\,4}^-]_{org} + NO_3^-$

From sulphuric acid solutions:

$2(TBA)_2\,SO_4 + 2Fe^{3+} + 2SO_4^{2-} + 2\,H_2O_{(aq)} \Leftrightarrow [(TBAH)_2SO_4.FeOH(SO_4)_2]_{2\,org} + 2H^+$

On the basis of the proposed mechanism for the extraction of iron (III), the dependence of the distribution ratio on the nature of the mineral acid.

.

Table-2 : Effect of Diluents on Extraction

[Fe (III)] = 1.0 x 10^{-3} M [TBA] = 5.0 x 10^{-2} M

(From HCl medium)

Diluent	Dielectric constant	% extraction
Benzene	2.28	90.7
$CHCl_3$	4.81	98.2
CCl_4	2.23	96.5
Xylene	2.56	85.8
n-Hexane	1.89	80.5
Cyclo hexane	2.0	83.3
Dichloro methane	8.08	78.5
Toluene	2.43	82.7
n-heptane	1.92	79.7
Nitrobenzene	34.82	69.2

Table – 3: Estimation of iron in food and pharmaceutical samples

Sample	Iron present (%)	Iron found by extraction	% recovery
Ragi	3.00 ppm	2.92 ppm	97.3
Green gram	4.05 ppm	4.02 ppm	99.26
Dried ferrous sulphate(67mg)	20.07	19.92	99.25
Ferrous fumerate(300mg)	114.10	113.71	99.66
Ferrous dextrin(50mg)	100.22	99.65	99.43

Effect of Stripping Agents:

After extraction, iron(III) was stripped with 20ml reagents of various concentrations (0.1 – 2.0 M) of ACOH, H_2SO_4 and NaOH solutions.. It was observed that 1.0 M H_2SO_4 alone is a good stripping agent. However in no case the acid strips out all the iron (III) in a single extraction. 99.8% iron (III) could be recovered from organic phase by making contact three times with equal volumes of 1.0 M H_2SO_4.

Variation of Diluents

Besides chloroform various diluents used in the present study are benzene, xylene, toluene, carbon tetra chloride, n-hexane, n-heptane cyclohexane, 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-2). Hence the same diluent was used in all these studies. With, n-hexane, n-heptane, dichloromethane and nitrobenzene low % extraction was noticed (70 to 80%).

Analysis of iron in various samples

The precision and accuracy of the method of extraction for recovery of iron has been tested by analyzing food and pharmaceutical samples. Ten tablets were weighed accurately and finely powdered in a mortar. An amount of the powder equivalent to one tablet was transferred quantitatively to 100-ml volumetric flask and then 60 ml of 0.01 M HCl was added. The mixture was shaken well for about 15 min. 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 obtained was used as a stock sample solution and different aliquots of prepared solutions were diluted with 0.01 M HCl to produce different concentrations.

Conclusions

The developed method was applied to the extraction separation and determination of iron in food and pharmaceutical samples. The average % recovery of iron was found to be 98.5% and the determination can be achieved efficiently in minimum amount of time.

Acknowledgements:

Thanks are due to Dr. V. Muralidhara Rao, Retd. Professor, School of Chemistry, Andhra University, Visakhapatnam for his valuable suggestions. Thanks are also due to Principal, GIT and Management of GITAM University for providing necessary facilities to carry out these investigations.

References

1. Lee, MS Lee.K.J Sepn. of Iron by extraction, Hydrometallurgy, 2005, 80,163
2. Gupta,B. Deep,A. Singh,V. Tandon,SN. Hydro metallurgy 2003, 70,121
3. Seeley FG Mc Dowell, WJ. J. Inorg. Nucl. Chem 1981, 43 , 375
4. Alguacil, FJ and Amer,S Polyhedron 1986, 6 (11) ,1755
5. Baes, CF. USAEC. Report Ornl – 1955, 1930
6. Smulek W and Siekjerski,S J. Inorg. Nucl. Chem 1962, 24, 1651
7. Zhichun, WU Shuqin,YU CHEN Jiayoung Acta Mettallurgica Sinica Series B, 1990, 3(6) 391, .
8. Cattrall RW and West BO J. Inorg .Nucl .Chem 1966, 28, 3035
9. Vogel, A.I., “A Text book of quantitative Inorganic Analysis” 3rd Edition, 1962, Longman, London.
10. Coleman., CF., Brown., KB.,Moore. JG., and Allen. K. A., Proc.2nd Intl.
11. Conf., Peaceful uses of Atomic Energy, Geneva, 1958, C.10, Paper 510.
12. Hesford.E. and Mckay.H.A.C.,Trans Faraday Soc., 1958, 54, 573,.

*****