Studies on the Solvent Extraction of Iron (III) with Tri-iso-octylamine from Aqueous Mineral Acid Solutions

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ABSTRACT

Liquid-Liquid extraction of iron (III) was carried out with 5.0×10^{-2} M of Tri iso-octylamine in benzene from hydrochloric, sulphuric, nitric and perchloric acid. After extraction from the organic phase, iron was stripped with 1M H_2SO_4 and was determined spectrophotometrically at 480nm as thiocyanate complex. The extraction was quantitative only in the presence of hydrochloric acid solution and are partial form sulphuric, nitric and perchloric acid solutions. Based on the results obtained in this study, estimation of iron in food samples and alloys has been attempted.

INTRODUCTION

Iron is one of the most essential elements in the human body. People with insufficient iron will develop some illnesses such as iron deficiency anemia (IDA), stomatitis, chronic gastritis, etc.. Iron deficiency anemia is one of the world's most common nutritional deficiency diseases. Evidence has been presented that at low levels iron is an essential element in the diet, whereas at higher concentrations it is toxic [1]. Because of the different biological roles of iron in humans, animals, plants, and oceans, the need for analysis of iron in environmental and biomedical materials have been increased. The extraction of iron in its trivalent form from aqueous hydrochloric[2-6] and sulphuric acid[7-9] solutions by various amines has been studied. Earlier, we have reported extraction of iron(III) with TOA in chloroform from hydrochloric, sulphuric and nitric acid solutions[11].

However, there were no studies reported in literature on the extraction of iron (III) with Tri iso-octylamine (TIOA) or their suitable derivatives . Therefore this paper presents an account on systematic investigations of extraction of Iron (III) with Tri iso-octylamine (TIOA) in the presence of mineral acids. The applicability of the method was extended for separation of Iron (III) in food samples and iron alloys.

EXPERIMENTAL

Apparatus and Reagents

An ELICO SL 191 UV-Visible Double beam Spectrophotometer with matched 10 mm corex glass cuvetts were used to determine iron content.

A stock solution of Iron (III) was prepared by dissolving 482.25 g/mol of Ammonium iron(III) sulfate (E.Merck) in 500 ml of double distilled water. The solution was standardized volumetrically with potassium dichromate using diphenyl amine as the indicator. A diluted solution of iron (III) of appropriate concentration was prepared from the stock solution. A solution of 5.0×10^{-2} M TIOA in benzene is used for throughout the extraction.

General Procedure for Iron (iii) Extraction

An aliquot (10ml) of a solution containing iron (III) was taken and was added with appropriate concentration of mineral acid. The resulting solution was transferred to a separating funnel and 10 ml of 5×10^{-2} M of TIOA was added to it. The solution was vigorously shaken for five minutes. The two phases were allowed to settle and separate. Iron (III) from the organic phase was stripped with 10 ml of 1M H_2SO_4 and was determined spectrophotometrically[10] at 480 nm as its colored complex with thiocyanate. The concentration of Iron (III) was computed from the calibration curve.

RESULTS AND DISCUSSION

Extraction as a function of Acidity

Iron (III) was extracted from different mineral acids (HCl, H_2SO_4, HNO_3 and $HClO_4$) with 5.0×10^{-2} M TIOA in benzene and the results are presented in Table-1. The variation of distribution ratio as a function of aqueous phase concentration of the acid (HCl H_2SO_4, and $HClO_4$) solutions increased sharply with increasing concentration of the acid. From hydrochloric acid solutions, the distribution ratio (Kd) increased with increasing the concentration of the acid up to 8.0 M (Maximum extraction of 98.21%) and remained constant up to 10.0 M acidity. The extractions are nearly quantitative (Table 1). On the other hand the extraction of iron (III) from sulphuric, nitric and perchloric acid solutions by TIOA in benzene as a function of acidity, the distribution ratio (Kd) gradually increased with increasing the

concentration of the acid up to 10.0 M(maximum at 80.32%), 12.0 M (max. 79.12%) and 12.0 M (max. 68.16%) respectively.

Composition of the Extracted species

The extraction isotherm method[12] and 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 TIOA was found unity with all the acid systems. Representative data from hydrochloric acid solutions has been provided in Table-1.

Effect of Reagent Concentration

With all other factors being kept constant, iron (III) was extracted with 10 ml of TIOA with concentration, varying from 1.0×10^{-2} M to 4.5×10^{-2} M. The log-log plots of Kd Vs TIOA from various acid solutions gave straight lines of with unit slope expect sulphuric acid media (solvation number is two). Fig-1 corresponds to plot from hydrochloric acid media.

Effect of Diluents on Extraction

Several solvents with varying dielectric constants were tested as the diluents (Table -2). Quantitative extractions was achieved with benzene as diluent. More than 80% efficiency was obtained with hexane, carbon tetrachloride, xylene, toluene, cyclo hexane and benzene. Nitrobenzene and n-heptane were 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 stripped with 20ml reagents of various concentrations (0.1 – 1 .0 M) of HCl, HNO_3, ACOH, NaOH and H_2SO_4 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.

Absorption spectra

The individual Iron (III) extracted species with TIOA was studied in U.V. region[14-15]. The absorption spectra from sulphuric acid media exhibits absorption band at 295 and 355 nm . These

Table 1: Extraction as a function of varying Acidity

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

Molarity(M)	HCl %Extraction	H$_2$SO$_4$ %Extraction	HNO$_3$ %Extraction	HClO$_4$ %Extraction
1.0	55.99	37.39	30.05	25.65
2.0	82.82	50.98	39.95	29.95
3.0	91.77	58.50	44.45	37.39
4.0	94.71	63.51	51.50	44.54
5.0	95.71	65.44	57.51	53.46
6.0	96.42	68.16	60.44	58.50
7.0	97.42	72.24	63.16	61.00
8.0	98.21	76.02	68.24	64.05
9.0	98.21	79.12	72.42	65.44
10.0	-	80.32	76.64	66.15
11.0	-	80.32	76.95	67.16
12.0	-	-	79.12	68.16

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

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

Diluent	Dielectric constant	% extraction
Benzene	4.81	98.21
CHCl$_3$	2.28	92.24
CCl$_4$	2.23	90.86
Cyclo hexane	2.00	81.33
n-Hexane	1.89	83.57
n-heptane	1.92	74.72
Nitrobenzene	34.82	69.25
Toulene	2.43	84.39
Xylene	2.56	87.53

Table 3 : Analysis of Iron in Food Samples

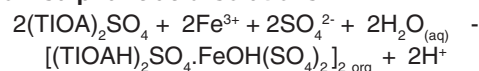| Sample	% of Fe (III) Present	% of Fe (III) Found	% Recovery
Ragi	3.00	2.84	94.66
Green gram	4.05	3.98	98.27
Soya beans	20.0	19.6	98.0
Dextrin	100.22	99.42	99.20

Table 4: Determination of Iron in Alloys

Material	Carbon	Manganese	Sulfur	Phosphorus	Silicon	Iron	Amount of Iron(III) taken (ppm)	Amount of Iron(III) found (ppm)	% Recovery
Cast Iron	3.430	0.880	0.041	———	2.120	91 - 91.2	91.1	90.9	99.78
Pig iron	3.5-4.5	0.5-2.5	0.018-0.1	0.03-0.1	0.25-3.5	91-94	92.0	91.6	99.56
Carbon steel	0.007-1.3	0.3-1.0	0.02-0.06	0.002-0.1	0.005-0.5	98.1-99.5	99.3	99.1	99.79
Wrought iron	0.05-0.25	0.01-0.1	0.02-0.1	0.05-0.2	0.02-0.2	99-99.8	99.5	99.1	99.59

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 $FeSO4^+$ and $Fe(SO4)^{-2}$.

The observed iron : TIOA molar ratio of two from sulphuric acid media and unity from other acid solutions (by distribution ratio method) could be explained as arising from the extraction of iron (III) by the following ion-exchange mechanism. From hydrochloric (Smulek[15]) nitric and perchloric acid solutions:

$$TIOAHCl + Fe^{3+} + 4Cl^- - [TIOAH^+ FeCl_4^-]_{org} + Cl^-$$

$$TIOAHNO_3 + Fe^{3+} + 4NO_3^- - [TIOAH + Fe(NO_3)^{4+}]_{org} + NO_3^-$$

$$TIOAHClO_4 + Fe^{3+} + 4ClO_4^- - [TIOAH + Fe(ClO_4)^{4+}]_{org} + ClO_4^-$$
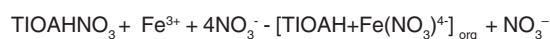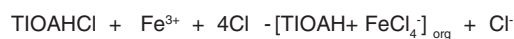
From sulphuric acid solutions

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

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 was well under stood.

Analysis of iron in various samples

The validity of the method of extraction for recovery of iron has been tested by analyzing food samples and iron alloys. The samples were weighed accurately (0.5 – 1.0 gm) and finely powdered in a mortar. A known weight of the powdered sample was dissolved in an aliquot of aquaregia. The solution was evaporated and extracted with dilute hydrochloric acid solution. 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 Whatmann filter paper No. 40. The first portion of filtrate was discarded. The clear solution obtained was made up to 100 ml and used as stock solution. 10 ml of this iron solution was shaken for five minutes with an equal volume of 5.0×10^{-2} M of TIOA. After separation of two phases, Iron (III) from the organic phase was stripped with 10 ml of 1.0M sulphuric acid and was determined spectrophotometrically as described earlier. Results are presented in Tables -3&4.
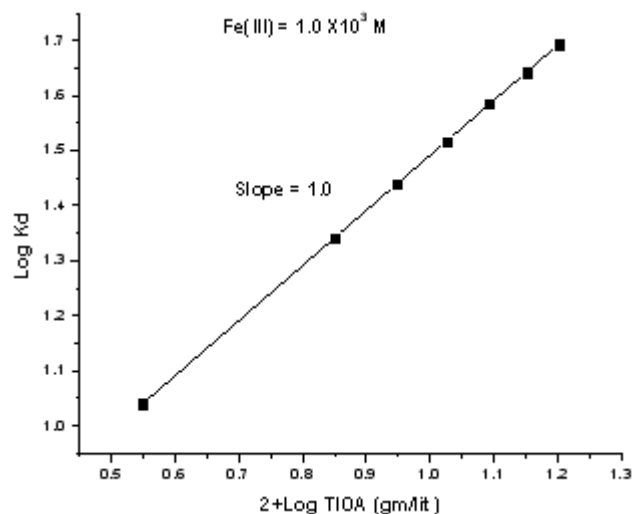
Fig. 1: Extractant variation at 8.0 M HCl

CONCLUSION

The proposed method is simple, rapid and selective. It does not take more than half an hour to extract and determine iron (III) content. The method has practical utility as iron(III) can be separated from manganese,   copper, cobalt, cadmium and zinc (under the experimental conditions) which are generally associated with it in alloys and minerals.

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