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Extraction Of Mn (II) From Hydrochloric And Nitric Acid Media By TiOA.

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ABSTRACT

Solvent extraction of manganese from using hydrochloric and nitric acid solutions by Tri-iso-octyl amine (TiOA) in xylene has been studied. Stripping of manganese from the organic phase was done effectively using 1.0M HNO_3. The extractions are nearly quantitative with both the acid systems employed in the study. The probable extracted species was also identified - Mn X_2. 2(TiOA) where X= chloride or nitrate ion.
Keywords: Extraction -- Ferro Manganese Slag- Tri-iso- octyl amine (TiOA)-Xylene.

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INTRODUCTION

Manganese functions in the oxygen-evolving complex of photosynthetic plants, dry cell technology, chemical industry and manufacture of glass etc. Manganese enzymes are particularly essential in detoxification of superoxide [1, 2].

Extractions of metals have been reported using amines, phosphates and other reagents [3-10]. But there was no work concerned with the extraction of manganese (II) by Tri-iso-octyl amine. Therefore the present communication describes studies on the extraction of Manganese (II) by Tri-iso-octyl amine (TiOA) in xylene from hydrochloric and nitric acid solutions.

MATERIALS AND METHODS

A stock solution of 0.25M Tri-iso-octyl amine (TiOA) dissolved in xylene (Molecular wt. 353.67, B.P 164-168°C, purity 99%) was used as extractant. The Mn (II) stock solution was prepared by dissolving 1.52 g of manganese sulphate monohydrate in 1lt double distilled water and was standardized complexometrically with standard EDTA. The Ferro manganese slag was ground, clarified and analysed for particle diameter. Metal concentrations were analysed using Atomic absorption spectrophotometer type AAS – SVL Spectronics– model 205.

Extraction Procedure

An aliquot (20ml) of Mn (II) of appropriate concentration containing the respective acid was equilibrated with an equal volume of Tri-iso- octyl amine (TiOA) in xylene pre-equilibrated with 0.1M mineral acid. After separation of the two phases, Mn (II) from the organic phase was stripped with 10ml of 1.0M H_2SO_4. The equilibrium Mn (II) concentration in both the phases was determined by AAS.

RESULTS AND DISCUSSION

The results obtained on the variation of distribution ratio as a function of aqueous phase concentration of mineral acid (HCl and HNO_3) is presented in Fig-1. In the case of hydrochloric and sulphuric acid solutions the extraction of Mn (II) by TiOA in xylene as a function of acidity, the distribution ratio (K_d) increased with increasing the concentration of the acid up to 1.75 M & 1.25 M acidity respectively followed by a gradual fall up to 3.0 M, The extractions are nearly quantitative from both the acid media (Fig -1).

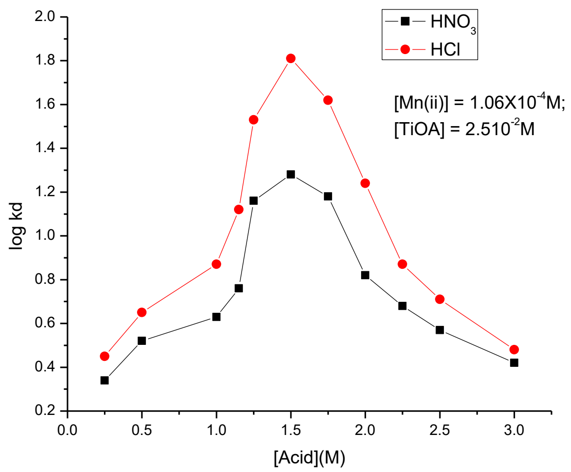

Fig.1: Acid variation

Composition of extracted species

In the extraction isotherm method [11] at particular constant concentration of TiOA the mole ratio [Mn(II)] vs. [Metal complex] in the extracted species is 1.0 indicates the formation of a single extracted species. From the distribution ratio method [12], the log-log plots of K_d vs. TiOA from both the acid solutions gave straight lines of unit slope. Representative results on the extraction of Mn(II) in hydrochloric acid solutions has been given in fig-2.

Hence manganese reacts with TiOA as per the following solvation mechanism

$$Mn^{2+} + 2TiOA + 2X^{-} \Leftrightarrow [Mn X_2 . 2 (TiOA)] \text{ where } X = Cl^{-} \text{ or } NO_3^{-}$$

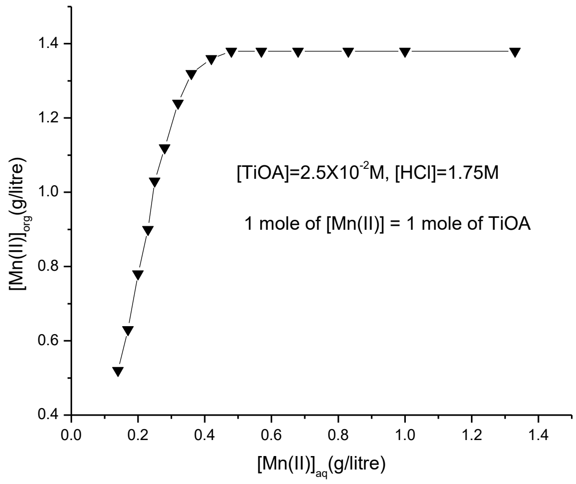

Fig.2: Metal variation

Stripping agent:

The extraction of manganese (II) from the organic phase (TiOA) has been tried with 10 ml portions in the concentration range (0.1 – 1.0 M) of HCl, H_2SO_4 and HNO_3 solutions. It was found that HCl and H_2SO_4 are poor stripping agents. On the other hand, 1.0 M HNO_3 alone is a good stripping agent. It was also noticed that 99.85% manganese (II) could be recovered from organic phase by making contact three times with equal volumes of 1.0 M HNO_3.

Variation of diluents

Various reagents were tested as diluents viz, chloroform carbon tetra chloride, toluene, n-hexane, n-heptane cyclohexane, and nitrobenzene with wide verity in chemical nature and dielectric constant. Maximum extraction efficiency was achieved with xylene as diluent (**Table-1**).

Table-1: Effect of Diluent on Extraction

[Mn (II)] = 1.06 x 10^{-4} M [TiOA] = 2.5 x 10^{-2} M

S. no	Diluent	Dielectric constant	% extraction
1	Benzene	2.28	70.65
2	Chloroform	4.81	82.52
3	CCl_4	2.23	76.36
4	Xylene	2.56	98.72
5	n-Hexane	1.89	72.47
6	Cyclo hexane	2.0	65.25
7	Toluene	2.43	63.56
8	n-heptane	1.92	55.72
9	Nitrobenzene	34.82	46.68

Effect of diverse ions:

Effect of various foreign ions on the extraction of Manganese (II), with TiOA was studied following the above extraction procedure. The tolerance limit was set at the amount of foreign ion required to cause ± 2% error in the recovery of Mn (II) (13.5 μg/ 20 ml). The results show that the ions such as Al (III), Bi (II),Cu (II),Co(II),Zn (II), ascorbate, selenite, tellurite, phosphate and tartarate are tolerated in the ratio 1:200 and the ions such as Ca (II), Pb (II), Pd (II), Ru (III) and Sr(II) do not interfere even if present in the ratio 1:100. The ions showing small tolerance limit in the ratio 1:50 are Cr (III),Cr (VI), Fe (III) acetate, chloride, oxalate and fluoride. So, it is possible to extract Mn (II) in presence of large number of cations and anions. The average recovery of manganese (II) was 99.6 ± 0.4 %. The relative standard deviation and relative error calculated from seven repeated determinations with 13.5 μg of Mn (II) were found to be ± 1.03 % and ± 0.7 % respectively. The separation of Mn (II) was possible done in the presence of more than one foreign ion in the mixtures with an error of not more than 2%(**Table-2**).

Table-2. Selective Recovery of Mn(II) in presence of other ions

Sample		Result	Standard deviation
1.	27.5 μg Mn + 10 mg Cu, Co, Ni + 1.0 M $H_2 SO_4$	27.6, 27.4, 27.3, 27.2, 27.2, 27.5,27.0	0.189
2.	55 μg Mn + 10 mg Cu, Al + 1.0 M $H_2 SO_4$	54.5, 54.7,54.7,54.8 ,54.7, 54.8, 54.6	0.099
3.	55 μg Mn + 30 mg Cu, Co, Ni + 1.0 M $H_2 SO_4$	54.8, 54.7,54.5,54.5,54.6, 54.8, 54.8	0.099
4.	55 μg Mn + 10 mg Fe + 1.0 M $H_2 SO_4$	54.7, 54.6, 54.8,54.9 ,54.8, 54.8, 54.5	0.128

Analysis of manganese in synthetic and slag samples

The efficiency of the present method of extraction of manganese has been tested in synthetic and slag samples. The slag generally contains manganese along with other metals such as calcium, magnesium, iron, silicon and aluminium.

Slag samples are obtained from Ferro Alloys Corporation (FACOR), Garividi, and Vizianagaram Dt. with chemical composition: MnO-17-29 %, FeO-13-19 %, SiO_2-21 – 26%, MgO-15-20 %, Al_2O_3 14-21% and CaO-12-17%.

The slag of required size was taken in a 250 ml and was leached with concentrated hydrochloric acid media. The samples were finely powdered in a mortar followed by dissolving an accurately weighed (1.0 gm) sample in aquaregia. The solution was evaporated and added with dilute hydrochloric acid solution and 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. 20 ml of this solution was extracted with an equal volume of Tri-iso- octyl amine (TiOA) in xylene as per the procedure described earlier. The results obtained in these studies for slag samples were compared by extracting manganese from synthetic samples under similar conditions with % composition Mn(II) = 5.0-11.0 ppm, Mg = 20ppm, Al=20ppm and the corresponding results are presented in **Table- 3**.

Table-3. Effect of diverse ions

[Mn(II)] =55 μg g; [TiOA] =0.025 M; [HCl] =1.25 M

Foreign ion	Tolerance limit	Foreign ion	Tolerance limit
Al^{3+}	243	Ni^{2+}	194
Bi^{2+}	277	Pd^{2+}	292

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Cu^{2+}	308	Sn^{2+}	445
Cr^{6+}	102	$Acetate^{-}$	980
Cr^{3+}	174	$Malonate^{2-}$	867
Cd^{2+}	468	Oxalate	704
Fe^{3+}	188	PO_4^{3-}	927
Pb^{2+}	873	Selenite	982
Ru^{3+}	739	$Fluoride^{-}$	725
Sr^{3+}	627	$S_2O_3^{2-}$	664
Zn^{2+}	402	tartarate	842

Table-3 . Analysis of Mn (II) in synthetic and slag samples

Sample	Mn (II) added (ppm)	Mn (II) found after recovery extraction (ppm)	% Recovery
Synthetic sample			
1	5.0	4.82	96.40
2	6.5	6.33	97.38
3	8.0	7.87	98.37
4	9.5	9.42	99.15
5	11.0	10.86	98.72
Slag sample	**Present**	**Found**	
1	7.50	7.24	96.53
2	9.25	9.02	97.51
3	10.45	10.21	97.70

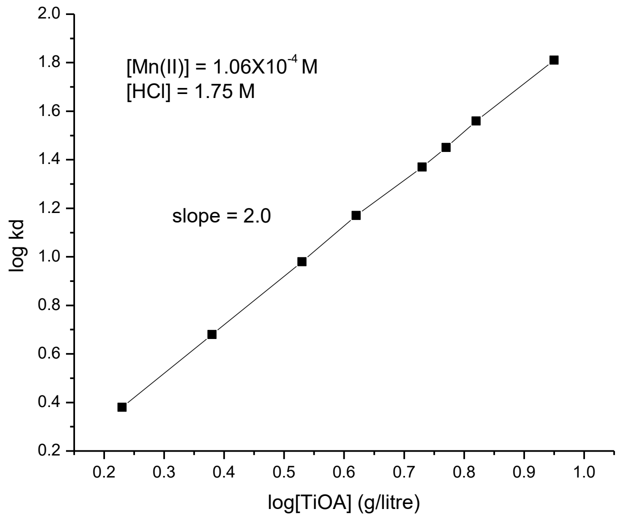

Fig.3 : Extraction variation

CONCLUSIONS

The results obtained on the extraction of manganese using TiOA dissolved in reagent indicate that the above stoichiometric equation holds good. Hence, it can be observed that TiOA selectively extracts manganese in presence and absence of impurities commonly associated with accuracy.

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Conflict of interest

The authors declare that there is no conflict of interest regarding the publication of this article.

REFERENCES

[1] De AK, 'Environmental Chemistry', New Age Intl. (p) Ltd.1996.
[2] Under EJ. Trace Elements in Human and Animal Nutrition', 4th edn. Academic press Inc. New York. 1977.
[3] Ola D, Kurobe Y, Matsumoto M, Solvent Extraction and Stripping of Fe and Mn from aqueous Solution Using Ionic Liquids. Engg.trans. 2017; 57.
[4] Man B, Lee S, Synergistic solvent extraction of Mn(II) with a mixture of Cyanex 272 and Cyanex 301 from chloride solutions, Hydrometallurgy 2013; 140; 89-94 (2**).**
[5] Patnaik P, Baba, AA. Nathsarma KC, Sarangi K, Subbaiah T. Separation of iron and zinc from manganese nodule leaches liquor using TBP as extractant, Mineral Processing and Extractive Metallurg*y* (Trans. Inst. Min. Metall. C) 2013; 122; 179-185.
[6] Bala Devi N ,Mishra S Solvent extraction equilibrium study of manganese(II) with Cyanex 302 in kerosene, Hydrometallurgy 2010; 103,(1–4) ; 118-123.
[7] Lee MS, Filiz M Solvent extraction of Mn(II) from hydrochloric acid solutions by Alamine336 .Mats. Trans*.,* 2008; 49(11); 2642-2647.
[8] Ahn, K, Park H, Sohn JS, Solvent extraction separation of Co, Mn and Zn from Ni rich leaching solution by Na-PC88A, Mat. Trans*.,* 2002; 43; 20169-20172.
[9] Mao X, Solvent extraction of iron (III) from chloride acid solutions by decanol, 3rd Intl.Conf. On Material, Mech. and Manufg. Engg. (IC3ME 2015); 2015.
[10] Cheng CY*,* Investigation of methods for removal and recovery of manganese in hydrometallurgical Processes, Hydrometallurgy*,* 101(1), 58-63. 2010.
[11] Hesford E, McKay HAC, Trans. Faraday Soc., 1958; 45537.
[12] Oldham KB, Solvent extraction of chromium: A review, Educ. Chem*.* 1965; 2; 7**.**