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ESTIMATION OF ZN (II) IN PHARMACEUTICAL SAMPLES –A SOLVENT EXTRACTION STUDY

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Abstract– The current work reports on the extraction of Zinc from hydrochloric and nitric acid media by Tri-iso-octyl amine (TiOA) in xylene as diluent. The optimum conditions for extraction were established from the study of the effect of several variables on extraction process like–acid concentration, standing time, concentration of metal ion, extractant, diluent etc. The extractions are nearly quantitative (98%) with the acid systems employed in the study. Stripping of metal from the organic phase was achieved effectively using ammonia solution. The extracted species was also identified - Zn X_2. 2(TiOA) where X= chloride or nitrate ion. Analysis of natural synthetic mixtures and pharmaceutical samples has been attempted.

INTRODUCTION

Zinc, an essential nutrient which is very much needed in trace amounts at about 8 mg for women and 11mg for men respectively (Ranjan *et al*., 2003). It causes slow growth in infants and children. It can prevent absorption of iron which can lead to iron deficiency. Different compounds of zinc such as zinc gluconate, zinc sulfate and zinc acetate serve as dietary supplements. It is present in squash, pumpkin, quinoa, rice wheat, oats, bananas, cheese, milk, egg, and meat etc. Zinc is used in the treatment of common cold, wounds, diarrhoea, regulates heart beat, thyroid functioning etc.

Extraction of various metals including zinc has been reported using amines, HDEHP, ethyl hexyl phosphoric acids, Cynex-272 etc. (Azizitorghabeh *et al*., 2016; Owusu, 1998; Sinha *et al*., 2014; Kumar *et al*., 2006; Kitobo *et al*., 2010; Ahmadipour *et al*., 2011; Patnaik *et al*., 2013; Ahn *et al*., 2002). Majority of these systems are concerned with extraction of zinc (II) from chloride acid media only. A review on recent development on zinc extraction has been provided (Akash Deep *et al*, 2008). There was no work reported on the extraction of zinc (II) by Tri-iso-octyl amine. Therefore in the present communication deals with a systematic study on the extraction of zinc (II) by Tri-iso-octyl amine (TiOA) dissolved in xylene from hydrochloric and nitric acid solutions.

METHODOLOGY

A stock solution of 1.0M Tri-iso-octyl amine (TiOA) dissolved in xylene (Molecular wt. 353.67, B.P 164-168^{o}C, purity 99%) was used as extractant. Stock solution of Zn (II) was prepared by dissolving 11 g of zinc sulphate hepta hydrate in 1lt double distilled water and was standardized complexometrically with standard EDTA. A pH 10 buffer solution was prepared by adding 284 ml concentrated ammonia solution to 35 g ammonium chloride and dilute it to 500 ml with distilled water. 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.

Procedure

10 ml of Zn (II) of known concentration containing the respective acid was equilibrated with an equal volume of 0.5M Tri-iso- octyl amine (TiOA) dissolved in xylene pre-equilibrated with 0.1M mineral acid. After separation of the two phases, Zn (II) from the organic phase was stripped two times with 10 mL portions of 0.5 M ammonia solution. The equilibrium Zn (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 is presented in Table 1. In the case of hydrochloric and nitric acid solutions the extraction of Zn (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 2.5 M and 3.75 M acidity respectively followed by a gradual fall beyond this acidity. Quantitative extraction efficiency has been observed from both the acid media (Fig. 1).

Table 1. Effect of Diluent on Extraction
[Zn (II)] = 1.08 x 10^{-4} M; [TiOA] = 5.0 x 10^{-1} M

S. No	Diluent	Dielectric constant	% extraction
1	Benzene	2.28	70.45
2	Chloroform	4.81	42.58
3	CCl_4	2.23	66.26
4	Xylene	2.56	99.58
6	Cyclo hexane	2.0	68.75
7	Toluene	2.43	83.54
8	n-heptane	1.92	65.70
9	Nitrobenzene	34.82	77.28

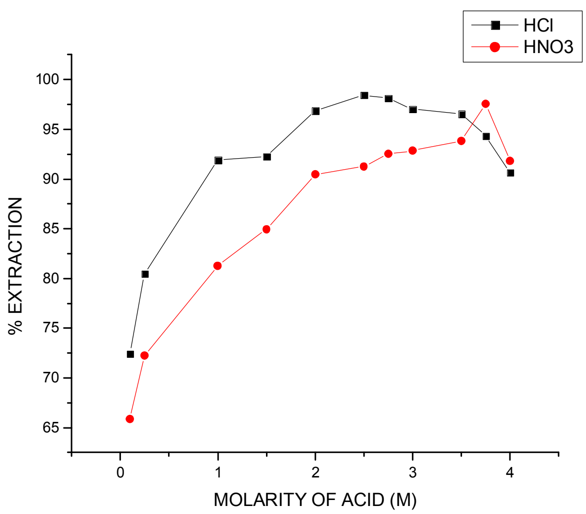

Fig. 1. Acid variation

Composition of extracted species

In the extraction isotherm method (Hesford, 1958) at particular constant concentration of TiOA the mole ratio [Zn (II)] vs. [Metal complex] in the extracted species is 1:1 indicates the formation of a single extracted species. Distribution ratio method (Oldham, 1965) was adopted to study the effect of TiOA on the extraction. Log-log plots of K_d vs. TiOA from both the acid solutions gave straight lines of slope two indicating involvement of 2 moles of TiOA. Results obtained on the extraction of Zn(II) in hydrochloric acid solutions has been given in Fig. 2.

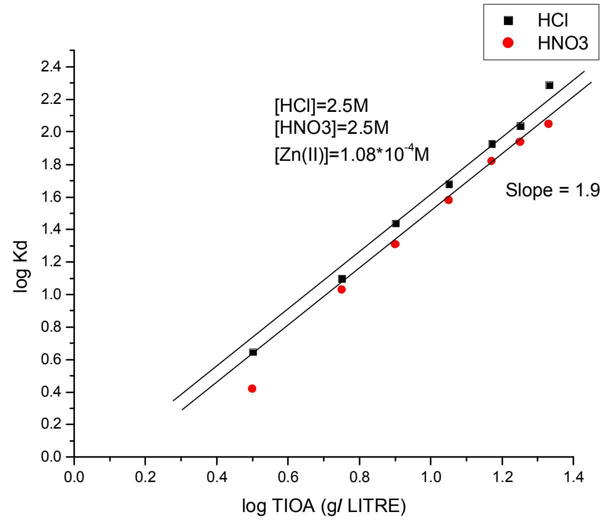

Fig. 2. Extractant variation

So, the extract ion equilibrium can be explained by the following solvation mechanism:

Zn^{2+} + 2TiOA + 2 X^- Û [Zn X_2. 2 (TiOA)] where X= Cl^- or NO_3^-

Stripping agent

The extraction of Zn (II) from the organic phase (TiOA) has been tried with 10 ml portions in the concentration range (0.1 – 0.5M) of HCl, H_2SO_4 and ammonia solutions. HCl and H_2SO_4 are found to be very poor stripping agents. But it was clearly noticed that more than 98.6 % Zn(II) could be recovered from organic phase by making contact two times with equal volumes of 0.5 M ammonia solution.

Variation of diluents

Effect of diluents on the extraction process has been tested with reagents such as benzene, chloroform carbon tetra chloride, cyclohexane, toluene, n-hexane, n-heptane, and nitrobenzene with wide verity in chemical nature and dielectric constant. Maximum extraction efficiency was achieved with xylene as diluent (Table 1).

Effect of diverse ions

The present method has been tested for the effect of different amounts of foreign ions on the extraction of zinc (II), with TiOA was studied under similar extraction conditions. The tolerance limit was set at the amount of foreign ion required to cause ± 2%

Table 2. Effect of diverse ions
[Zn (II) =30mg; [TiOA] =0.5 M; [HCl] = 2.5 M

Foreign ion	Tolerance limit	Foreign ion	Tolerance limit
Cd^{2+}	28	Ce^{4+}	57
Sn^{2+}	34	Sulphate	74
Ca^{2+}	47	Chloride	18
Bi^{2+}	58	VO_3^-	72
Pd^{2+}	64	$Acetate^-$	80
Ni^{2+}	19	ClO_3^-	84
Sr^{2+}	57	$Ascorbate^{2-}$	62
Cr^{3+}	17	$Oxalate^{2-}$	57
Mg^{2+}	28	Tartarate	48
Fe^{3+}	26	$S_2O_3^{2-}$	81
Mn^{2+}	22	PO_4^{3-}	46
Al^{3+}	25	Fluoride	97

error in the recovery of Zn (II) (30 mg/ 10 ml). The results show that the ions such as Al (III), Bi (II), Ca (II), Cu (II),Co(II), Cr (III),Cr (VI), Fe (III) Pb (II), Pd (II), Ru (III), Sr(II) and Mn (II) interfere above 10mg and the ions such as ascorbate, acetate, chloride, oxalate, phosphate and tartarate are tolerated up to 40 mg. The average recovery of zinc (II) was 99.7 ± 0.3 %. The relative standard deviation and relative error calculated from seven repeated determinations with 13.5 mg of Zn (II) were found to be ± 1.02 % and ± 0.8 % respectively. The separation of Zn (II) was possibly done in the presence of more than one foreign ion in the mixtures with an error of not more than 2% (Table 2).

Analysis of zinc in synthetic and pharmaceutical samples

The efficiency of the present method of extraction of zinc has been tested in synthetic and pharmaceutical samples.

The samples were finely powdered in a mortar followed by dissolving an accurately weighed (1.0g) sample in aquaregia. The solution was evaporated and added with 0.2 N permanganate solution and was heated for about 45 min. Excess permanganate was oxidized by using solid oxalic acid. It was then diluted up to 100 ml after filtration. 10 ml of this solution was extracted with an equal volume of Tri-iso- octyl amine (TiOA) in xylene as per the above procedure. The results obtained in these studies for pharmaceutical samples were compared by extracting zinc from synthetic samples under similar conditions with % composition Zn(II) = 3.0-25.0 ppm, Mn = 22ppm, Al=28 ppm and the corresponding results are presented in Table 3.

Table 3. Analysis of Zn (II) in various samples

S.No	Synthetic sample	Extraction by TiOA (ppm)	% Recovery
1	3.0	2.88	96.0
1	5.0	4.82	96.40
2	10.0	9.93	99.30
3	15.0	14.67	97.80
4	20.0	19.42	97.10
5	25.0	24.18	96.72
Pharmaceutical sample	**Present**	**Found**	
Zincovit	10.0	9.57	95.70
Zinc capsule	13.0	12.86	98.92
Zinc tablet	20.0	19.81	99.05

CONCLUSION

The results obtained on the extraction of zinc using TiOA indicate that the above stoichiometric equation holds good. Zinc was stripped from the organic phase quantitatively using 0.5 M ammonia solution. The developed method was applied successfully to the extraction separation and determination of zinc in synthetic as well as pharmaceutical samples.

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Table 2. Zn (II) recovery in presence of other ions

Sample	Result	Standard deviation	
1.	30.0 µg Zn + 10 mg Cu, Co, Ni + 1.0 M H_2 $S0_4$	29.6, 29.4, 29.3, 29.3, 29.2, 29.5,29.7	0.1665
2.	50 µg Zn + 10 mg Cu, Al + 1.0 M H_2 $S0_4$	49.5, 49.7,49.7,48.8 ,48.7, 49.5, 49.6	0.3922
3.	55 µg Zn + 20 mg Mn, Cu, Co + 1.0 M H_2 $S0_4$	54.8, 54.7,54.5,54.5,54.6, 54.8, 54.8	0.1278
4.	55 µg Zn + 10 mg Fe, Mg, Cu, Ni 1.0 M H_2 $S0_4$	54.8, 54.6, 54.8,54.9 ,54.6, 54.8, 54.5	0.1355

University for providing necessary facilities to carry out these investigations.

Conflict of interest

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

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