Synergistic Extraction of Mn (II) Using TPPO and TBuA

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Abstract

Synergistic extraction (SX) of Mn(II) containing a mixture of Triphenylphosphine oxide (TPPO) and Tributyl amine (TBuA) in xylene from sulphuric, nitric, hydrochloric and perchloric acid solutions has been studied. The investigations were attempted to select optimal conditions were established by varying the parameters such as - pH of the aqueous phase, concentration of metal ion, diluent and synergistic mixture. Nature of the extracted species in both individual and mixed extraction was proposed by slope ratio analysis method. Extraction mechanism has been explained using the thermodynamic parameters controlling the nature of metal extraction at different temperatures.

Keywords: Mn (II) - Triphenylphosphine oxide (TPPO) and Tributylamine (TBuA) Synergistic extraction – Xylene

Introduction

Manganese, among non-ferrous elements, plays an essential role in dry battery technology, the chemical industry etc. Hence, the extraction of manganese from all possible sources needs attention. Industrial wastewater containing cobalt (Co) and manganese (Mn) are familiar sources of heavy metal pollution and causes a significant threat to the environment [1].

Synergistic systems consist of hydrophobic ternary adduct is mostly responsible for enhanced transfer of metal complex into organic phase [2]. Lanthanides and actinides are more prone to synergistic extraction owing to their higher co-ordination number .Several workers[3-12] have performed/ carried out synergistic extraction of Mn (II) using different extracting agents - Cyanex 272 and Cyanex 301; D2EHPA and Cyanex 272 ; D2EHPA and TBP with thenoyl trifluoroacetone and neutral unidentate and bidentate ligands .The present paper describes the results obtained on the synergistic extraction of Mn (II) using TPPO and TBuA which were optimised by the study of effect of several variables such as temperature dependence and nature of the extractant etc.

Materials and methods

Stock solution for Mn (II) was prepared and standardized using standard EDTA solution complexometrically[12]. Triphenylphosphine oxide (TPPO) and Tributylamine (TBuA) stock solutions were prepared i.e., 0.25M in xylene and eventually diluted to acquire the desired concentration. All chemicals used were of AR grade and purified appropriately to reach the standard methods.

pH measurements were carried by digital pH meter equipped with a single electrode. Mechanical shaker with temperature controlled (KEMI) was used for the equilibration studies. Mn(II) content in the samples was determined by Atomic Absorption Spectrophotometer of AAS-SVL Spectronics Model 205.

General Extraction Procedure

In a 250 ml separating funnel, 10 ml portions of each $2.5x10^{-2}$ M of TPPO +TBuA mixture in xylene (pre equilibrated with 0.1 M mineral acid) was added to an equal volume of manganese (II) ($1.0x10^{-3}$ M) along with appropriate mineral acid. It was then shaken thoroughly for five minutes and the two layers were separated. Concentration of Mn (II) in the aqueous phase before and after extraction was estimated using AAS while that of metal concentration in the organic phase was determined by taking the difference in the initial Mn (II) concentration and the equilibrium manganese (II) concentration in the aqueous phase. It was clearly noticed that the experimental conditions were so arranged that Mn (IV) could not be co- extracted. Equilibration studies carried to study the effect of temperature in a temperature controlled mechanical shaker beyond which distribution ratio (D) was determined

Results and discussion

Effect of equilibration time

Extraction **of** Manganese (II) using TPPO in xylene for different time periods (0, 5, 10, 15 and 20 minutes reveals the equilibrium is achieved within 15 minutes of shaking. Further continuation beyond this time of equilibration does not affect the extraction equilibrium (Figure1).

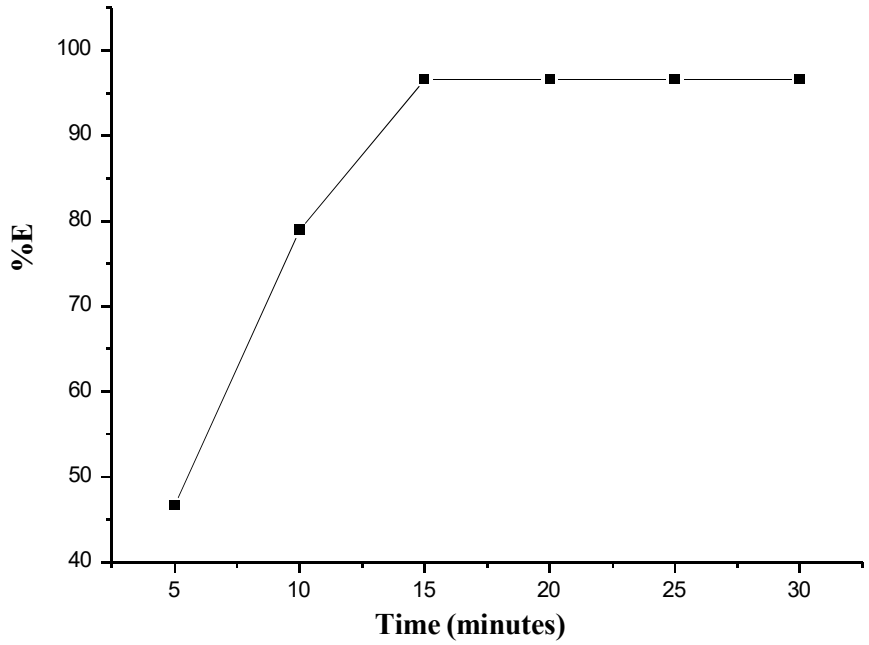

Figure 1: Time Variation

Effect of pH

Variation of pH on the extraction of Mn (II) has been done by keeping the extractant concentration at 0.025M. It was found that the percentage extraction increased with increasing pH from 1.0 to 5.0 in

case of sulphuric as well as hydrochloric acid media and there is a gradual decrease in pH (1.0 -5.0) in case of nitric acid . In the case of perchloric acid solutions there is an increase in pH from 1.0 – 3.0 and above pH 3.0 extraction efficiency decreases perhaps due to hydrolysis. Maximum extraction efficiency (88.88%) was observed at pH 3.0 from perchloric acid solutions (Figure 2).

Effect of stripping agent

Mn (II) from the organic phase was extracted back into the aqueous phase by stripping with 10ml reagents of HCl, H2SO4, HNO3 and NaOH solutions having concentrations ranging from 0.01-1.0M 1 more effective stripping agent for Mn (II) in three attempts. The results obtained on stripping of manganese (II) reveal that maximum stripping is obtained with 1.0 M HNO3 solution) in three attempts(95%). Hence this solution was considered as suitable reagent throughout the course of study. No improvement in stripping efficiency was noticed beyond 1.0 M HNO_3 concentration.

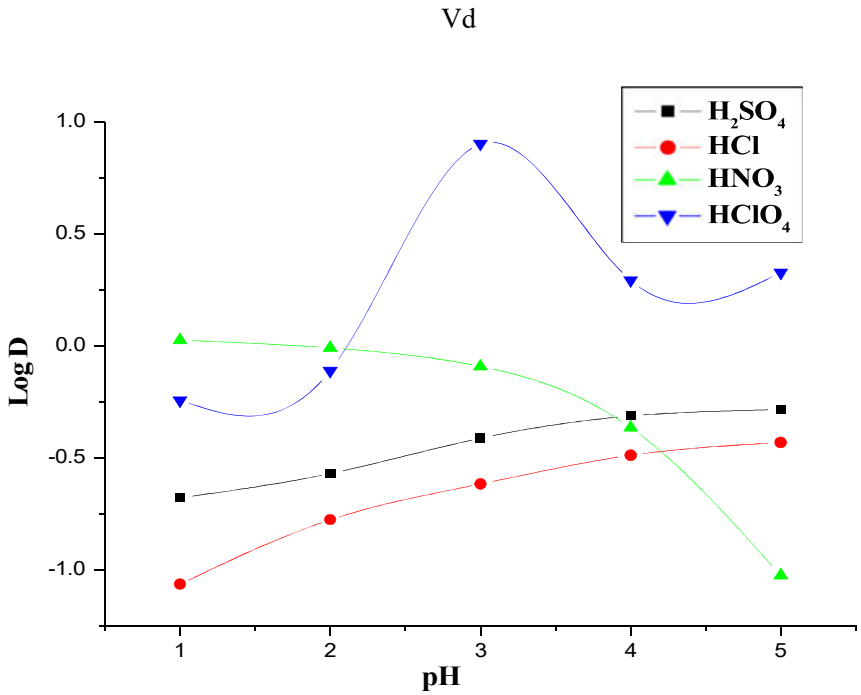

Figure 2: pH variation

Effect of diluents

Extraction of manganese (II) by TPPO in xylene has been carried out using various diluents as indicated in Table 1.

Table 1: Distribution ratio and %E at pH 3.0, $HClO_4$ medium in different solvents

Solvent	Distribution ratio (D)	%E
Xylene	0.893	47.2
Toluene	0.633	38.8

Benzene	0.672	40.2
Cyclohexane	0.575	36.5
Nitrobenzene	0.512	33.9
Carbon tetrachloride	0.497	33.2

Variation of extraction of Mn (II) with TPPO

Extraction of manganese (II) by TPPO in xylene in the concentration range (0.025 to 0.005 M) indicates that the distribution ratios were very poor (46.6%). The composition of extractable species was obtained from the plot of log D vs. log[TBuA] and the data are fitted to a straight line equation with an average slope of ~ 1 (Figure 3) , indicating one molecule of TPPO is involved in the extraction process.

$$[Mn^{+2}]aq + 2X^{-} + [TPPO]_{org} \overset{k}{\leftrightarrow} Mn\,X_2.TPPO_{org} \quad \text{.....(1)}$$

$$k = \frac{[Mn\,X_2.TPPO]_{org}}{[Mn^{+2}]_{aq}\,[X]^{2-}\,[TPPO]} \quad \text{.....(2)}$$

$$\text{and Distribution ratio, } D = \frac{[Mn\,X_2.TPPO]_{org}}{[Mn^{+2}]_{aq}}$$

Taking logarithm and putting the value of D in eq. (1) we have,

$$\log D = \log k + \log [TPPO]_{org} \quad \text{.....(3)}$$

Stoichiometric co-efficient for the extraction reaction can be determined from the plot of log D against log $[TPPO]_{org}$. , Slope of unity is observed from all the acids employed in the study (Figure 3) and hence individual extraction reaction of $Mn^{+2}$by TPPO is described as,

$$Mn^{+2}aq + 2X^{-} + [TPPO]_{org} \overset{k}{\leftrightarrow} [Mn\,X_2.\,.TPPO]_{org} \quad \text{.....(4)}$$

$$\log k = \log D - \log [TPPO]_{org} \quad \text{.....(5)}$$

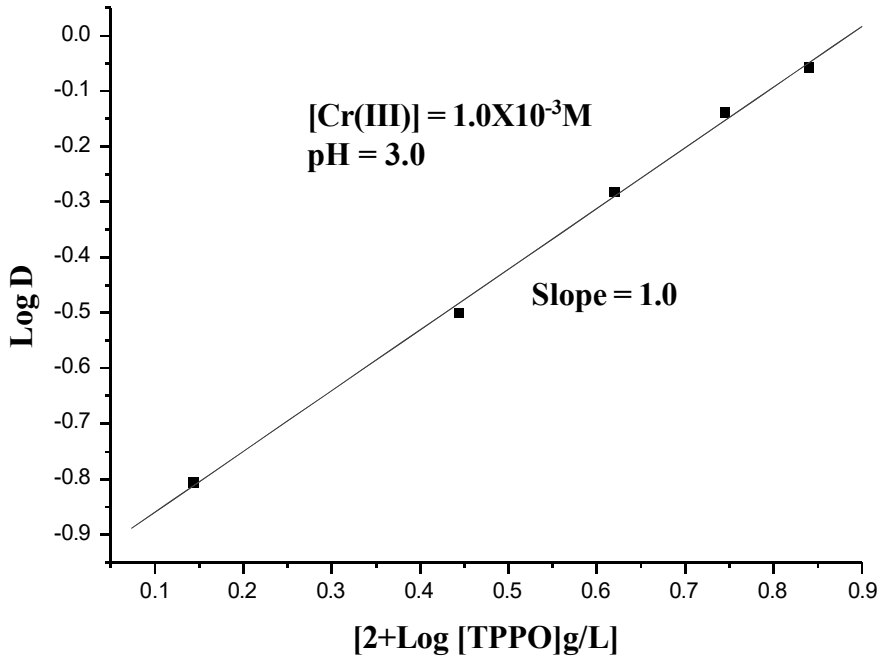

Figure 3: Extractant Variation of (Mn (II) with TPPO)

Extraction of Mn(II) with TBuA

Variation in the concentration of TBuA in xylene for the extraction of manganese (II) has been studied .representative plots of log D vs. log [TBuA] gave a straight line with a slope of ~ 1.0 (Figure 4), indicating one molecule of TBuA is involved in the extraction process.

Synergistic extraction of Mn (II) in presence of TPPO and TBuA

It is clearly evidenced from the individual extractants for Mn (II) using TPPO and TBuA resulted in low extraction efficiency. However, when TPPO is mixed with TBuA, a marked enhancement in the extent of manganese (II) extraction was noticed. As D_{mix} is always greater than D_{TPPO} and D_{TBuA}, this process of extraction definitely leads to synergism with positive values of S.C & ΔD. Synergistic effect has been evaluated as per the following equation mentioned below (Table 2).

$$\text{Synergistic Coefficient} \quad S.C = \log \frac{D_{mix}}{(D_{TPPO} + D_{TBuA})}$$

$$\Delta D = D_{mix} - (D_{TPPO} + D_{TBuA})$$

Where, D_{mix} = distribution coefficient in presence of binary mixture. D_{TPPO} = distribution coefficient in presence of TPPO only. D_{TIOA} = distribution coefficient in presence of TBuA only.

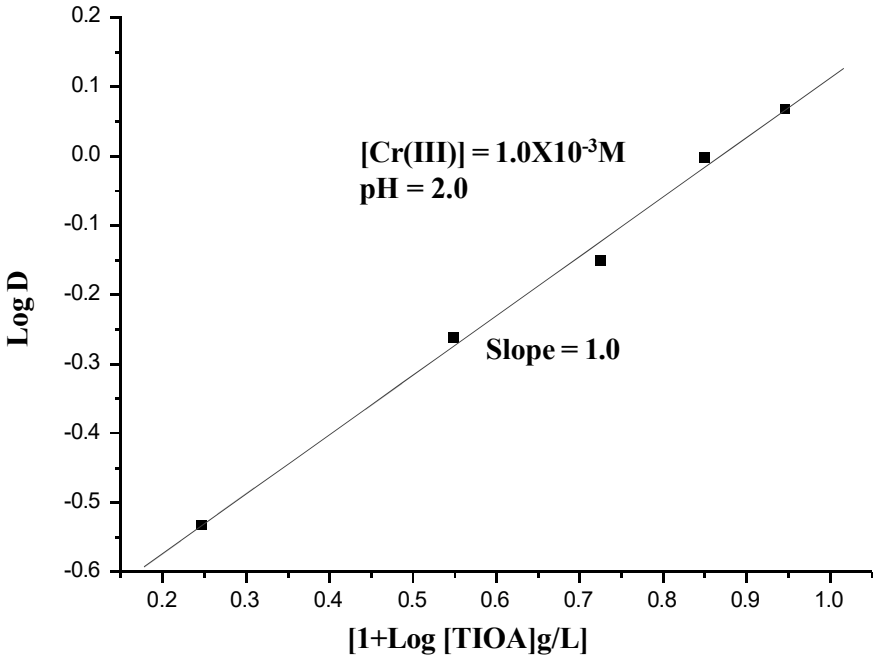

Figure 4: Extractant Variation of Mn(II)with TBuA

The plot of log (D_{mix}) against both log [TPPO] and log [TBuA] yielded straight lines of unit slope (Figure 5) and (Figure 6) confirming that the ternary extracted species consists of one mole of each TPPO and TBuA as per the following equations :

$$[Mn^{+2}]_{aq} + [TPPO]_{org} + [TBuA]_{org} \overset{K}{\leftrightarrow} [Mn^{+2}(TPPO).(TBuA)]_{org} \quad (6)$$

$$K = \frac{[Mn^{+2}.\ (TPPO).\ (TBuA)]_{org}}{[Mn^{+2}]_{aq} \times [TPPO]_{org} \times [TBuA]_{org}} \quad (7)$$

$$D_{mix} = \frac{[Mn\ (TPPO).\ (TBuA)]_{org}}{[Mn^{+2}]_{aq}} \quad (8)$$

Substituting values of D in D_{mix} expression and taking log values both sides,

$$\text{Log } K = \log [D_{mix} - D]_{org} - \log [TPPO]_{org} - \log [TBuA]_{org} \quad (9)$$

Table 2: Results of synergistic extraction of Mn (II)

Solvent	[TBuA] (M)	D_{TPPO}	D_{mix}	%E	SC	ΔD

Xylene	0.025 0.02 0.015 0.01 0.005	0.893	8.564 7.769 1.926 1.543 1.259 1.109	89.54 88.88 85.22 60.67 55.73 52.58	0.32 0.59 0.05 0.10 0.16 0.39	3.54 5.95 0.20 0.31 0.39 0.66
Cyclohexane	0.025 0.02 0.015 0.01 0.005	0.633	1.916 1.962 1.759 1.406 0.093	65.71 66.23 63.75 58.43 8.50	0.32 0.42 0.46 0.47 -0.44	1.18 1.21 1.15 0.93 -0.16
Chloroform	0.025 0.02 0.015 0.01 0.005	0.542	1.095 1.016 0.092 0.080 0.055	52.26 50.39 8.42 7.40 5.05	0.22 0.31 -0.49 -0.37 -0.36	0.44 0.52 -0.19 -0.11 -0.10
Benzene	0.025 0.02 0.015 0.01 0.005	0.672	1.309 1.168 0.099 0.086 0.078	56.69 53.87 9.00 7.91 8.86	0.17 0.16 -0.74 -0.67 -0.27	0.42 0.36 -0.44 -0.32 -0.07
Carbon tetrachloride	0.025 0.02 0.015 0.01 0.005	0.447	1.994 1.763 1.549 1.321 1.014	66.59 63.80 60.76 56.91 50.34	0.20 0.27 0.40 0.57 0.72	0.75 0.82 0.93 0.96 0.82
Toluene	0.025 0.02 0.015 0.01 0.005	0.694	3.451 2.969 2.437 1.665 1.008	77.53 74.80 70.90 62.47 50.20	0.40 0.46 0.51 0.51 0.48	2.09 1.94 1.68 1.16 0.64

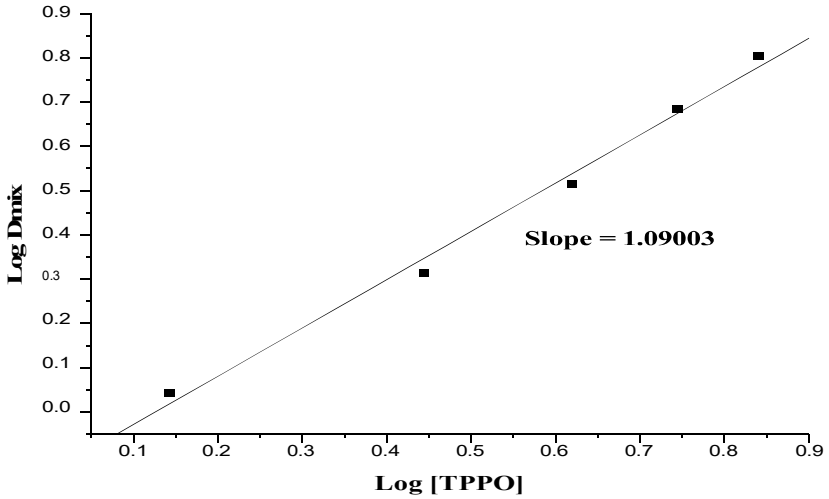

Figure 5: Plot of Log Dmix vs. Log [TPPO] in synergistic extraction of Mn(II)

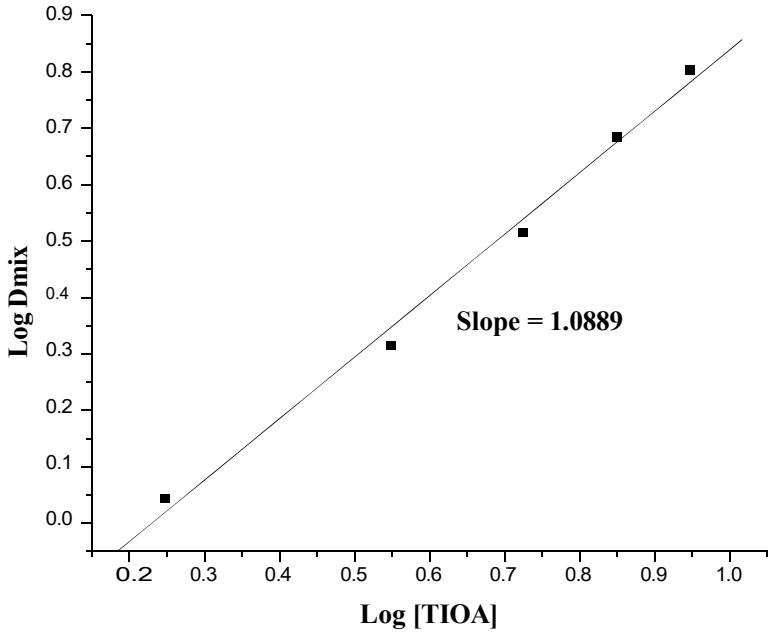

Figure 6: Plot of Log D mix vs. Log [TBuA] in synergistic extraction of Mn (II)

Possible extracted species in the organic phase may be given as,

$$[MnX_2\ (TPPO)\ (H_2O)\ _2] + TiOAH^+ \longrightarrow [MnX_2\ (TPPO)\ (H_2O)\ TBuAH^+]\ _{org} + H_2O$$

Effect of temperature

In the case of binary and ternary extraction systems, higher temperature leads to increase in the

Mn (II) extraction at this aqueous phase acidity. Equations (5) and (9) are used for the calculation of equilibrium extraction constant logK for the complexes studied.

From the values of equilibrium extraction constant over the temperature range was investigated.

Vant Hoff equation was used to calculate the enthalpy change,

$$\log K = -\Delta H/2.303RT + \Delta S/2.303R \quad \text{..... (10)}$$

In the plot of log K against 1/T is a straight line (Figure 7) slope gives the enthalpy of reaction (ΔH°) and the intercepts correspond to entropy (Δ S°) value. The values of Δ G°, ΔH°, Δ S° are presented in (Table 3).

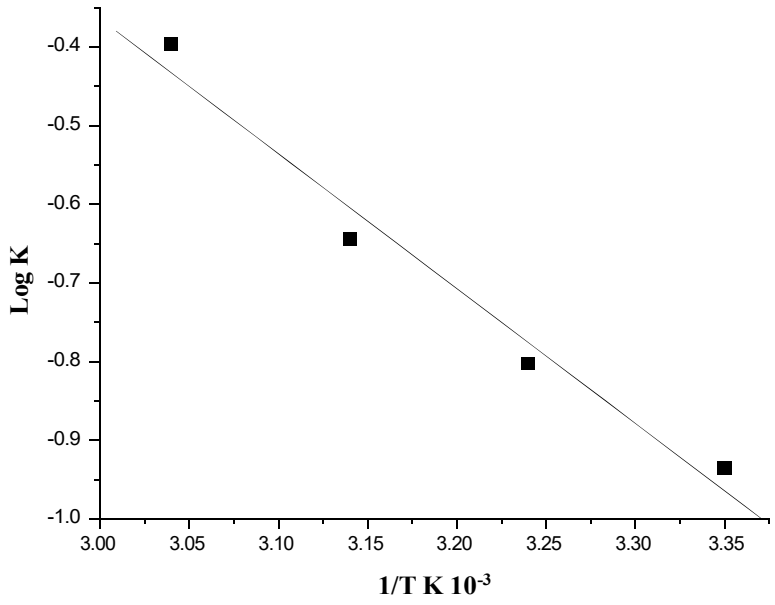

Figure 7: Temperature Variation

Table 3: Thermodynamic Parameters

System	Solvent	ΔH° (kJK^{-1}. mol^{-1})	ΔS° (JK^{-1}. mol^{-1})	ΔG° (kJK^{-1}. mol^{-1})
Mn(II)- TPPO-TBuA	Cyclohexane	18.56	48.36	-14.43
	Carbon tetrachloride	17.23	44.28	-13.21
	Benzene	20.43	58.90	-21.76
	Nitrobenzene	22.68	72.59	-17.79
	Toluene	15.80	34.90	-10.42
	Xylene	19.26	39.76	-11.86

Data shows that extractions are entropy favoured but enthalpy disfavoured. During extraction process bond breaking occurs as indicated by positive values of ΔH^0. Release of water molecules in mixed extraction are evidenced by positive values of entropy. Extensive disruption of metal hydration sphere results in the release of such water molecules during adduct formation

Effect of stripping agent

Manganese (II) from the organic phase has been brought back using different reagents of varying concentrations. A 10 ml portion of the reagents HCl, H_2SO_4, HNO_3 and NaOH solutions with concentrations in the range (0.01 – 1.0 M) were adopted for the study. It was observed that HCl, H_2SO_4 and NaOH are extremely poor stripping agents whereas 1.0 M HNO_3 was found to be more efficient for Mn(II) and can strip back in three attempts. After shaking, organic and aqueous phases were separated and metal concentrations in aqueous phases were determined by AAS.
The results obtained on stripping of manganese (II) indicated that maximum stripping was obtained with 1.0 M HNO_3 (Figure 8). (>95%). It was noticed that further increase in acid concentration has no significant effect on of manganese (II) stripping.

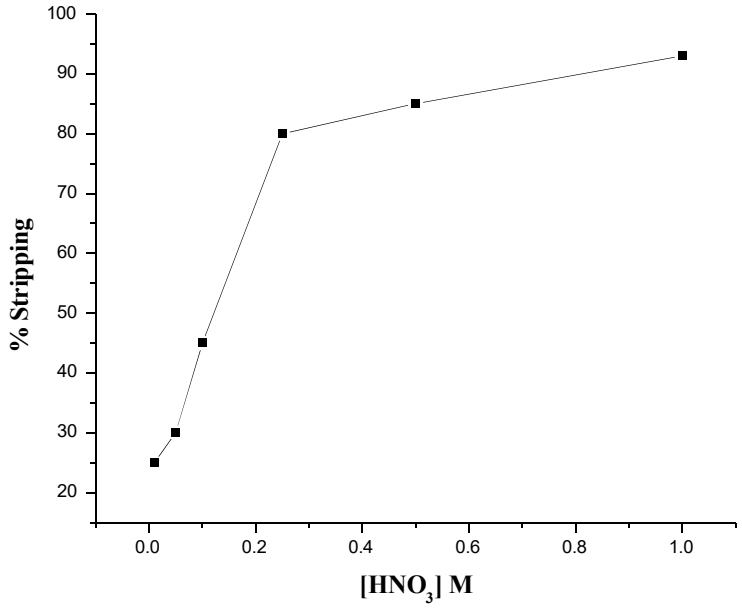

Figure 8: Stripping of Mn(II)

Determination of Mn in synthetic samples and alloys

Based on the results obtained in the present method an attempted has been carried out to analyze real samples and alloys for content manganese (II). A known weight of manganese alloy (stainless steel sample) was dissolved in 10 ml of aquaregia. It was evaporated to dryness and extracted with 10 ml of hydrochloric acid solution. The precipitate was filtered and quantitatively washed for complete recovery of metal. 10ml of this solution was extracted with an equal volume of 0.025 M TPPO+TBuA in xylene followed by stripping with 1.0M HNO_3 and estimated the content as per the procedure described earlier. The results are presented in (Table 5).

Table 5: Estimation of manganese in Synthetic samples and alloys

Sample	manganese present	manganese found after recovery by extraction	Recovery
Synthetic sample	(g/lit)	(g/lit)*	%
1	0.20	0.198	98.50
2	0.30	0.295	98.33
3	0.40	0.391	97.75
Stainless steel alloy type	%		%
1	11.5	11.3	98.26
2	14.0	11.8	98.57

*(Average of Four determinations)

Conclusions

The distribution ratio values used for calculating Thermodynamic parameters in the synergistic extraction of Mn(II) indicated that it is entropy favoured (endothermic in nature) resulted in the release of water molecules.

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