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SynergisticExtractionofMn(II) UsingTPPOandTBuA

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Abstract

Synergistic extraction (SX) of Mn(II) containing a mixture of Triphenylphosphine oxide (TPPO)andTributylamine(TBuA)inxylenefromsulphuric,nitric,hydrochloricandperchloricacid solutions has been studied. The investigations were attempted to select optimal conditions were establishedbyvaryingtheparameterssuchas-pHoftheaqueousphase,concentrationofmetalion, diluent and synergistic mixture. Nature ofthe 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 ofmanganese from all possible sources needs attention. Industrialwastewatercontainingcobalt(Co)andmanganese(Mn)arefamiliarsourcesofheavymetal pollution and causes a significant threat to the environment [1].

Synergisticsystemsconsistofhydrophobicternaryadductismostlyresponsibleforenhancedtransfer of metal complex into organic phase [2]. Lanthanides and actinides are more prone to synergistic extractionowingtotheirhigherco-ordinationnumber.Severalworkers[3-12]haveperformed/carried outsynergistic extraction of Mn (II)using different extractingagents- Cyanex 272 and Cyanex 301; D2EHPA and Cyanex 272 ;D2EHPA and TBP with thenoyltrifluoroacetone 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.

Materialsandmethods

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 gradeand 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 usedfor the equilibration studies. Mn(II) content in the samples was determined by Atomic Absorption Spectrophotometer of AAS-SVL Spectronics Model 205.

GeneralExtractionProcedure

Ina250mlseparatingfunnel,10mlportionsofeach2.5x10^{-2}MofTPPO+TBuAmixtureinxylene (preequilibratedwith0.1Mmineralacid)wasaddedtoanequalvolumeofmanganese(II)(1.0x10^{-3} M) alongwithappropriatemineralacid.Itwas thenshakenthoroughlyforfiveminutesandthetwo layerswereseparated.ConcentrationofMn(II)intheaqueousphasebeforeandafterextractionwas estimatedusingAASwhilethatofmetalconcentrationintheorganicphasewasdeterminedbytaking thedifferenceintheinitialMn(II)concentrationandtheequilibriummanganese(II)concentrationin theaqueousphase.Itwasclearlynoticedthattheexperimentalconditionsweresoarrangedthat Mn (IV) could not be co- extracted. Equilibration studies carried to study the effect of temperature in a temperature controlled mechanical shaker beyond which distributionratio (D) was determined

Results and discussion

Effect of equilibration time

Extraction**of**Manganese(II)usingTPPOinxylenefordifferenttimeperiods(0,5,10,15and20 minutesrevealstheequilibrium isachieved within 15 minutes of shaking. Further continuation beyondthis time of equilibration does not affect the extraction equilibrium (Figure1).

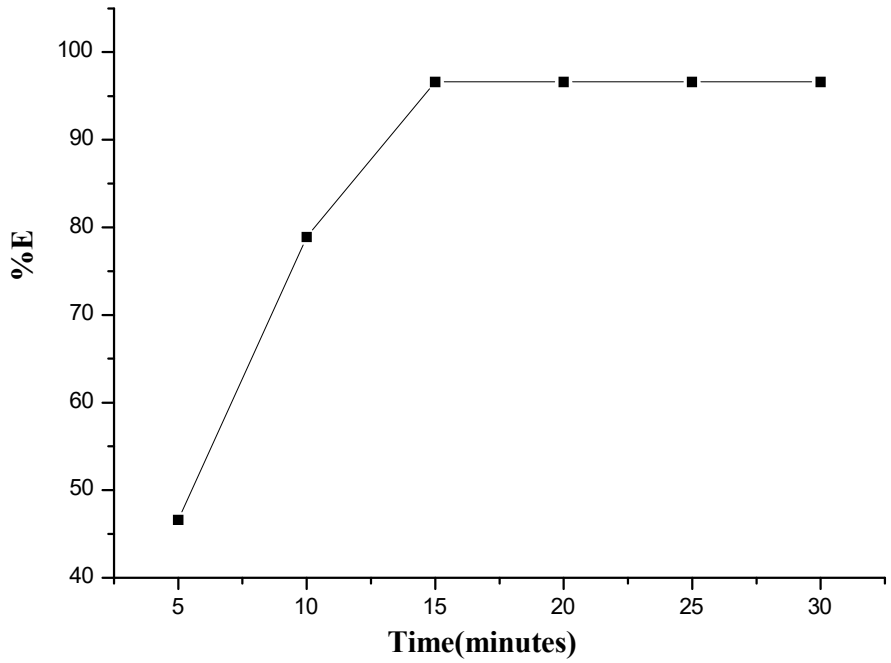

Figure1:TimeVariation

EffectofpH

VariationofpHontheextractionofMn(II)hasbeendonebykeepingtheextractantconcentrationat 0.025M.Itwasfoundthatthepercentageextractionincreasedwithincreasingp Hfrom1.0to5.0in

case of sulphuric as well ashydrochloric acid media andthere is a gradual decrease in pH(1.0 -5.0) incaseofnitricacid.Inthecaseofperchloricacidsolutionsthereisanincreaseinpfrom1.0–3.0 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).

Effectofstrippingagent

Mn(II)fromtheorganicphasewasextractedbackintotheaqueousphasebystrippingwith10ml reagentsofHCl,H2SO4,HNO3andNaOHsolutionshavingconcentrationsrangingfrom0.01-1.0M 1 more effective stripping agentfor 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%).Hencethissolutionwasconsideredassuitablereagentthroughoutthecourseofstudy. No improvement in stripping efficiency wasnoticed beyond 1.0 M HNO_3concentration.

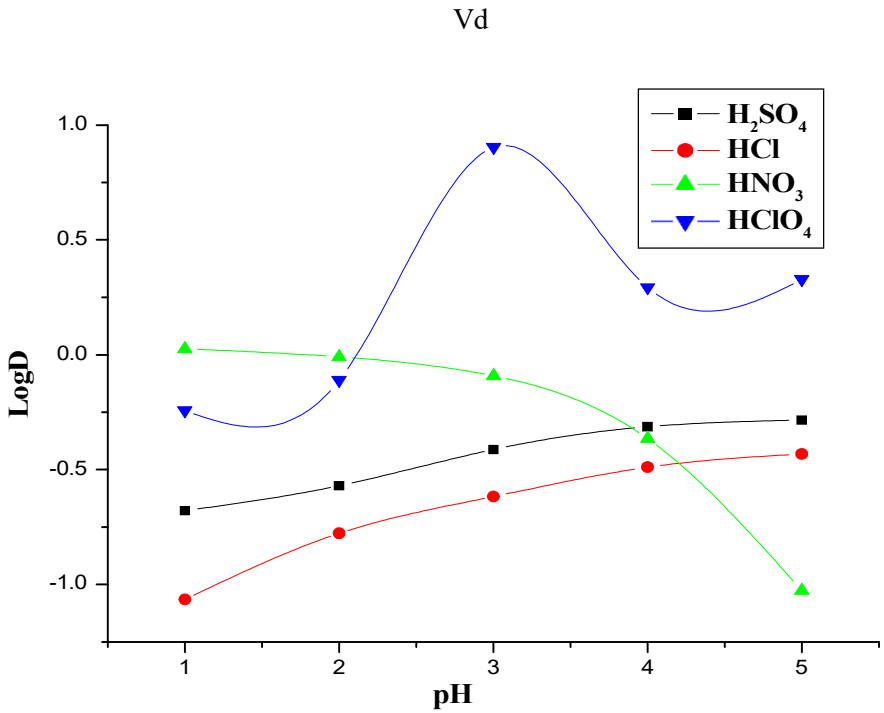

Figure2:pHvariation

Effectofdiluents

Extractionofmanganese(II)byTPPOinxylenehasbeencarriedoutusingvariousdiluentsas indicated in Table 1.

Table1:Distributionratioand%EatpH3.0,$HClO_4$mediumindifferentsolvents

Solvent	Distributionratio(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
Carbontetrachloride	0.497	33.2

VariationofextractionofMn(II)withTPPO

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 ofTPPO is involved in the extraction process.

$$[Mn^{+2}]aq+2X^{-}+[TPPO]_{org} \overset{k}{\leftrightarrow} MnX_2.TPPO_{org} \quad \text{.....(1)}$$

$$k = \frac{[MnX_2.TPPO]_{org}}{[Mn^{+2}]_{aq}[X]^{2-}[TPPO]} \quad \text{.....(2)}$$

$$\text{andDistributionratio,} D = \frac{[MnX_2.TPPO]_{org}}{[Mn^{+2}]_{aq}}$$

Takinglogarithmandputtingthevalueof Dineq.(1)wehave,

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

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

$$Mn^{+2}aq+2X^{-}+[TPPO]_{org} \overset{k}{\leftrightarrow} [MnX_2..TPPO]_{org} \quad \text{.....(4)}$$

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

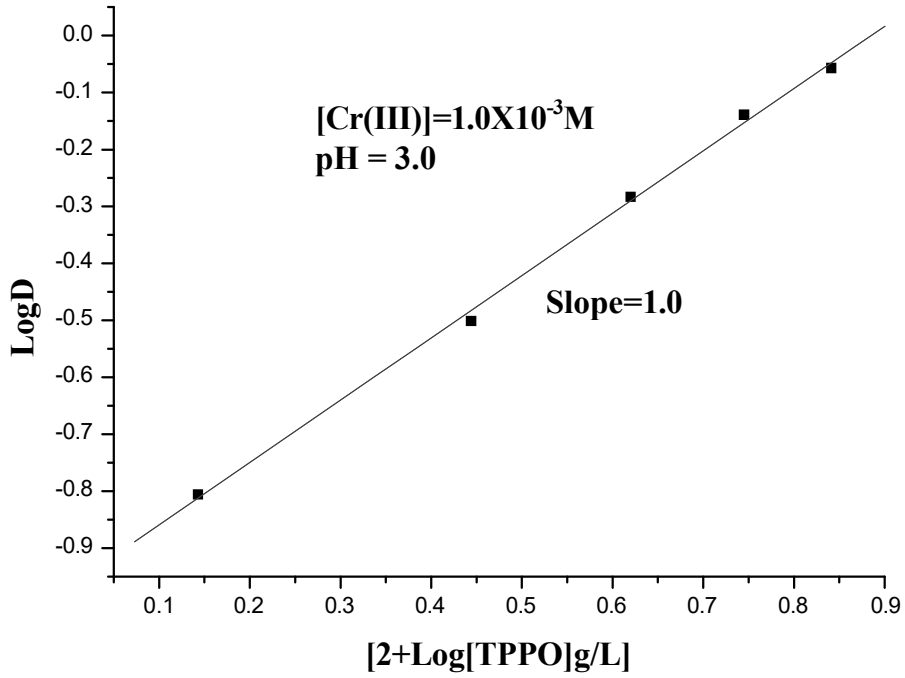

Figure3:ExtractantVariationof(Mn(II)withTPPO)

ExtractionofMn(II)withTBuA

Variation in the concentration of TBuA in xylene for the extraction of manganese (II) has been studied.representativeplotsoflogDvs.log[TBuA]gaveastraightlinewithaslopeof~1.0(Figure 4), indicating one molecule of TBuA is involved in the extraction process.

SynergisticextractionofMn(II)inpresenceofTPPOandTBuA

ItisclearlyevidencedfromtheindividualextractantsforMn(II)usingTPPOandTBuAresultedin low extraction efficiency. However, whenTPPOis mixed with TBuA, a marked enhancement in the extentofmanganese(II)extractionwasnoticed.AsD_{mix}isalwaysgreaterthanD_{TPPO}andD_{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).

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

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

Where,D_{mix}=distributioncoefficientinpresenceofbinarymixture.D_{TPPO}=distributioncoefficient in presence of TPPO only.D_{TIOA}= distribution coefficient inpresence of TBuAonly.

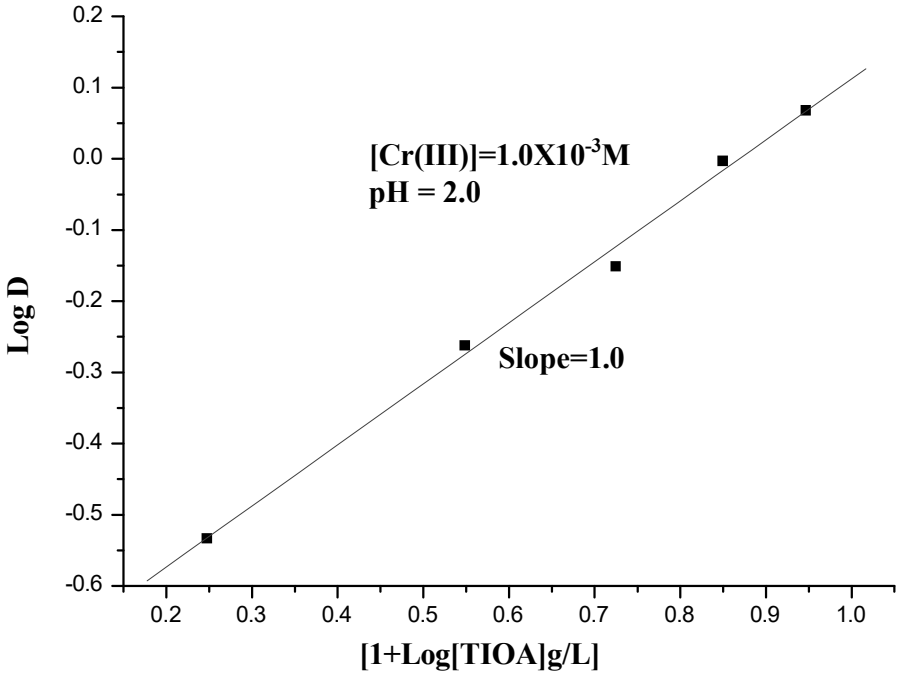

Figure4:ExtractantVariationofMn(II)withTBuA

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 ofeach TPPO andTBuAas per the following equations :

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

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

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

SubstitutingvaluesofDinD_{mix}expressionandtakinglogvaluesbothsides, Log

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

Table2:ResultsofsynergisticextractionofMn(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

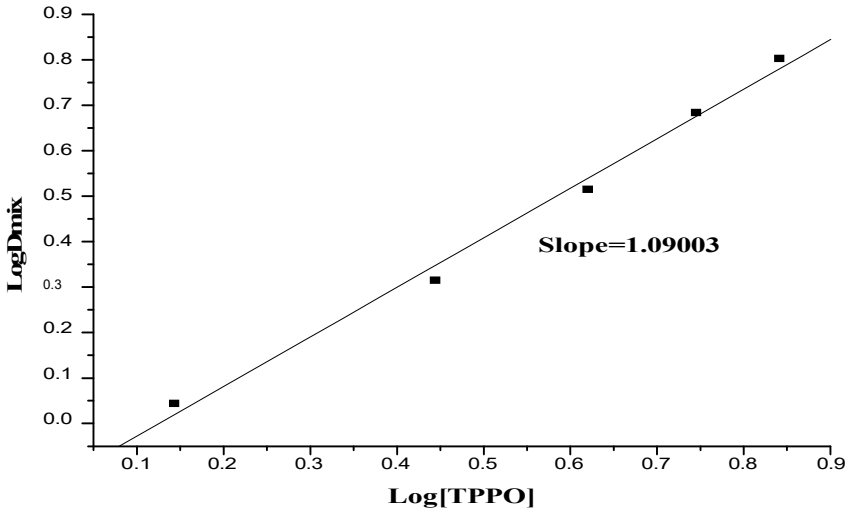

Figure5:PlotofLogDmixvs.Log[TPPO]insynergisticextractionofMn(II)

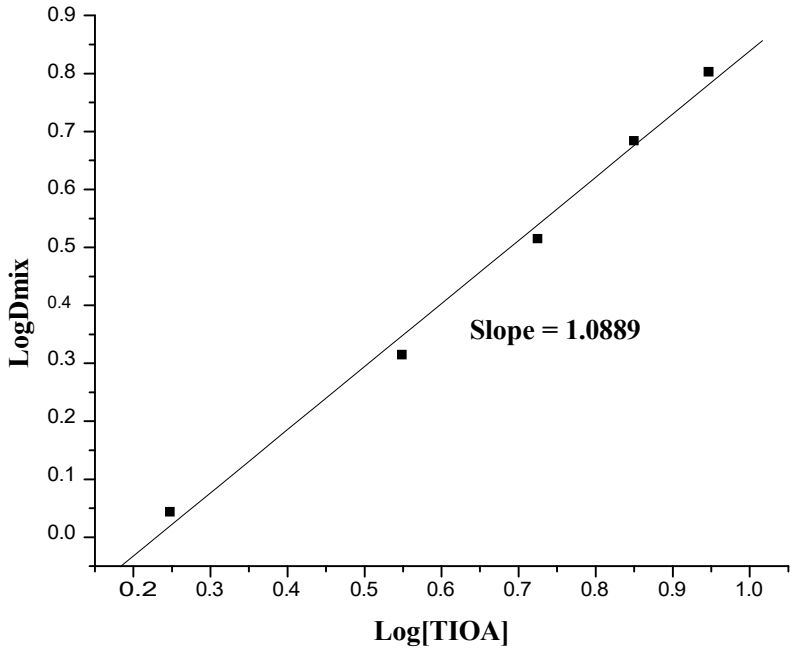

Figure6:PlotofLogDmixvs.Log[TBuA]insynergisticextractionofMn(II)

Possibleextractedspeciesintheorganicphasemaybegivenas,

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

Effectoftemperature

Inthecaseofbinaryandternaryextractionsystems,highertemperatureleadstoincreaseinthe

Mn (II) extraction atthis aqueousphase acidity. Equations (5) and (9) are used for the calculation of equilibrium extraction constant logK for the complexes studied.

Fromthevaluesofequilibriumextractionconstantoverthetemperaturerangewasinvestigated. Vant

Hoff equation was used to calculate the enthalpy change,

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

IntheplotoflogKagainst1/Tisastraightline(Figure7)slopegivestheenthalpyofreaction(ΔH°) andtheinterceptscorrespondtoentropy(ΔS°)value.ThevaluesofΔG°,ΔH°,ΔS°arepresentedin (Table 3).

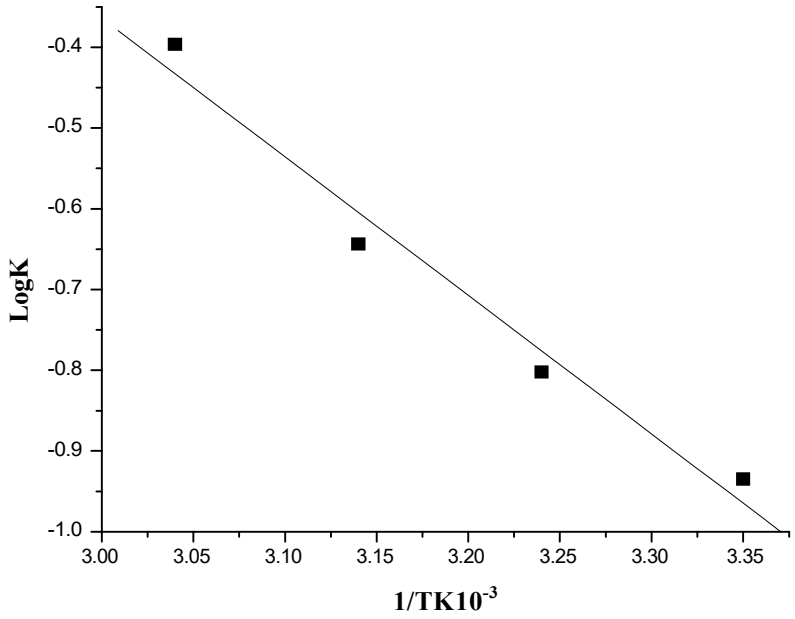

Figure7:TemperatureVariation

Table3:ThermodynamicParameters

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
	Carbontetrachloride	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

Datashowsthatextractionsareentropyfavouredbutenthalpydisfavoured.Duringextractionprocess bond breaking occurs as indicated by positive values of ΔH^0. Release of water molecules in mixed extractionareevidencedbypositivevaluesofentropy.Extensivedisruptionofmetalhydrationsphere results in the release of such water molecules during adduct formation

Effectofstrippingagent

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 andmetal concentrationsin aqueous phaseswere determined by AAS.
The results obtained on stripping of manganese (II) indicated that maximum stripping was obtained with1.0MHNO_3(Figure8).(>95%).Itwasnoticedthatfurtherincreaseinacidconcentrationhasno significant effect on of manganese (II) stripping.

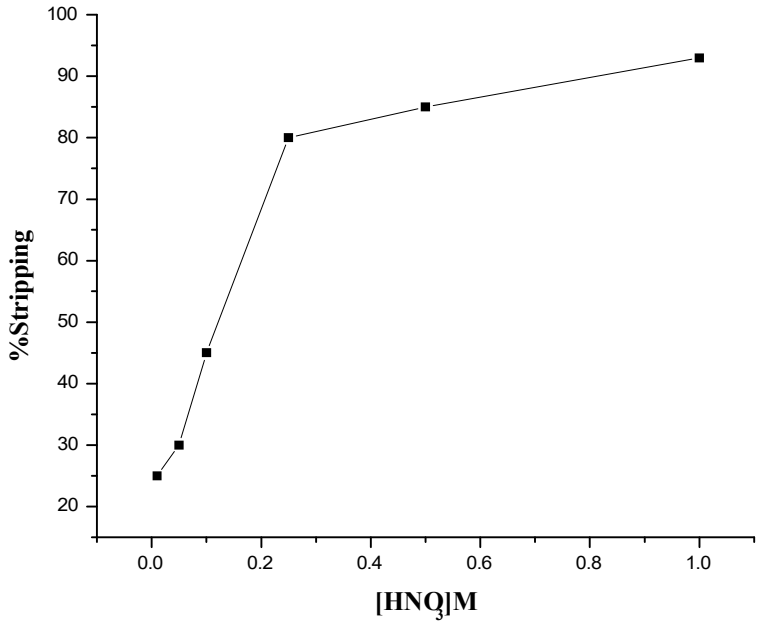

Figure8:StrippingofMn(II)

DeterminationofMninsyntheticsamplesandalloys

Basedontheresultsobtainedinthepresentmethodanattemptedhasbeencarriedouttoanalyzereal samples and alloys for content manganese (II). A known weight of manganese alloy (stainless steel sample)wasdissolvedin10mlofaquaregia.Itwasevaporatedtodrynessandextractedwith10mlof hydrochloric acid solution. The precipitate was filtered and quantitatively washed for complete recoveryofmetal.10mlofthissolutionwasextractedwithanequalvolumeof0.025MTPPO+TBuAin 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).

Table5:EstimationofmanganeseinSyntheticsamplesandalloys

Sample	manganese present	manganesefound after recoveryby extraction	Recovery
Syntheticsample	(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
Stainlesssteel alloytype	%		%
1	11.5	11.3	98.26
2	14.0	11.8	98.57

*(AverageofFourdeterminations)

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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