Study of Equilibrium & Mass Transfer of Co-Extraction of Different Mineral Acids with Iron(III) from Aqueous Solution by Tri-n-Butyl Phosphate Using Liquid Membrane

Diptendu Das, Vikas Kumar Rahi, V. A. Juvekar, and R. Bhattacharya

Abstract—Extraction of Fe(III) from aqueous solution using Tri-n-butyl Phosphate (TBP) as carrier needs a highly acidic medium (>6N) as it favours formation of chelating complex $FeCl_3.TBP$. Similarly, stripping of Iron(III) from loaded organic solvents requires neutral pH or alkaline medium to dissociate the same complex. It is observed that TBP co-extracts acids along with metal, which causes reversal of driving force of extraction and iron(III) is re-extracted back from the strip phase into the feed phase during Liquid Emulsion Membrane (LEM) pertraction. Therefore, rate of extraction of different mineral acids (HCl, HNO_3, H_2SO_4) using TBP with and without presence of metal Fe(III) was examined. It is revealed that in presence of metal acid extraction is enhanced. Determination of mass transfer coefficient of both acid and metal extraction was performed by using Bulk Liquid Membrane (BLM). The average mass transfer coefficient was obtained by fitting the derived model equation with experimentally obtained data. The mass transfer coefficient of the mineral acid extraction is in the order of $k_{HNO3} = 3.3 \times 10^{-6}$ m/s > $k_{HCl} = 6.05 \times 10^{-7}$ m/s > $k_{H2SO4} = 1.85 \times 10^{-7}$ m/s. The distribution equilibria of the above mentioned acids between aqueous feed solution and a solution of tri-n-butyl-phosphate (TBP) in organic solvents have been investigated. The stoichiometry of acid extraction reveals the formation of $TBP.2HCl$, $HNO_3.2TBP$, and $TBP.H_2SO_4$ complexes. Moreover, extraction of Iron(III) by TBP in HCl aqueous solution forms complex $FeCl_3.TBP.2HCl$ while in HNO_3 medium forms complex $3FeCl_3.TBP.2HNO_3$

Keywords—Bulk Liquid Membrane (BLM) Transport, Iron(III) extraction, Tri-n-butyl Phosphate, Mass Transfer coefficient.

I. INTRODUCTION

METAL extraction through solvent extraction is very well known process. But huge amount of solvent is required for the extraction and if stripping is not proper then solvent cannot be recycled back into the system. Also, always some amount of metal would be locked in the organic phase; hence efficiency of stripping becomes poor. Therefore, finding a suitable stripping media is a challenging job. Very high interfacial area of mass transfer for extraction in case of Liquid Emulsion Membrane (LEM) is advantageous as it reduces amount of solvent requirement. Similarly, rate of mass transfer study is essential for metal extraction process since it is useful to design extraction equipment. Unfortunately, it has been observed that TBP extracts both acids along with metal in LEM extraction, which causes inefficient stripping. In this paper difficulty in stripping due to co-extraction of acids with metal is investigated. Iron(III) is selected for establishing the theory. Normally Acidic Organo-phosphorous extractants such as di-(2ethylhexyl) phosphoric acid (DEHPA) and neutral solvating extractants such as Tributylphosphate (TBP) have been widely used for the extraction of Iron(III) from acidic chlorides solutions. However, difficulty arises in stripping of Iron(III) from loaded organic phase. DEHPA in organic phase can extract Iron(III) from lower acidity feed (pH) solution and strip at highly acidic solution (>6M HCl). On the other hand, TBP extracts Iron(III) from higher acidity solution and can strip at alkaline or very low acidity solution (0.1M HCl). But both TBP and DEHPA extraction stripping is always a problem. Several researchers carried out Iron(III) Extraction study to overcome the stripping problems. Sahu et al. (1997) studied the effects of hydrochloric acid concentration on Iron(III) stripping from loaded organic solvent systems consisting of TBP (100%), DEHPA (60%) and mixture of DEHPA(20%)-TBP(40%) solvent systems [3]. Using such high quantity of extractant, they observed maximum 65% stripping efficiency. Dessouky et al. (2008) studied several stripping agent for Fe(III) and found 0.1M HCl as best stripping media [5]. Majumder at al.(1960) investigated liquid-liquid extraction of Fe(III) with TBP and achieved very high distribution coefficient, D= $[Fe^{III}]_{org}/[Fe^{III}]_{aq}$ =70.4 at 6M HCl [4]. Saji et al. (2001) carried out liquid-liquid extraction separation iron(III) from titania waste using 70%TBP-30%MIBK systems and was able to extract Iron(III) chloride more effectively from lower acid concentration (2M HCl) and achieved D=1.18 [1], [2]. Lee et al. (2004) studied solvent extraction equilibrium of $FeCl_3$ with TBP and observed distribution of Iron(III) increases with concentration of chloride ion [14]. Singh et al. (2006) examined stripping of Iron(III) from D2EHPA-TBP mixture by oxalic acid and they observed around 80% stripping of Fe(III) at 10% Oxalic acid concentration [15]. Mishra et al. (2010) made a comparative study on extraction of Fe(III) from chloride leach liquor using TBP, cyanex 921, and cyanex 923, they also observed that

Diptendu Das, Vikas Kumar Rahi, and V. A. Juvekar are with the Department of Chemical Engineering, Indian Institute of Technology, Bombay. (e-mail: diptendudas@iitb.ac.in).
R. Bhattacharya is with the Atomic Energy Regulatory Board, Mumbai, India.

World Academy of Science, Engineering and Technology
International Journal of Materials and Metallurgical Engineering
Vol:7, No:6, 2013

extraction of Iron(III) increases with concentration of TBP and HCl [10]. Hirato et al. (1992) studied stripping characteristics of Fe(III) using DEHPA and TBP mixture and achieved maximum stripping efficiency 83% [6]. Lupi et al. (2000) observed that Fe(III) was easily extracted along with other elements such as Zinc or Cadmium but it was hard to strip from loaded organic phase, so a reduction from ferric to ferrous was carried out by zinc powder as reducing agent and around 70% stripping was achieved [11]. Therefore, it is observed that most of the investigators worked in the area of solvent extraction of Fe(III) and found suitable stripping reagent by optimising process parameters [4], [7]-[9], [12]. There is no literature available on study on co-extraction of metal and acids and explaining the difficulty on stripping in Liquid Emulsion Membrane (LEM) Extraction of Iron(III). Hence, there is a need to find insight of different acid extraction using TBP and to correlate inefficient stripping in LEM extraction. Based on the results of the acid extraction study, a suitable acid with lesser affinity with TBP should be used for LEM extraction of Fe (III) or any other metal. Bulk Liquid Membrane (BLM) is used for comparison of different acid extraction. BLM consists of a bulk aqueous feed phase, and strip (extract) phase separated by a bulk organic, water immiscible liquid phase. A mathematical model for acid extraction in presence and absence of Fe(III) is developed and discussed. Both mass transfer coefficient of individual acid and Fe(III) (k_{fo}, mass transfer coefficient Feed–Organic interface and k_{oe}, mass transfer coefficient Organic–Strip (extract) interface were derived using the developed model.

II. EXPERIMENTAL

A. Reagents and Solutions

The extractant n-TBP was used as supplied by the manufacturer M/s. Sigma Aldrich Co. Ltd, The average molecular weight of n-TBP is 266.42 and the density (20ºC) is 979kgm^{-3}. Light Paraffin oil diluent was also used as supplied by the manufacturer M/s. Mercks and viscosity 30cp, density 800kgm^{-3}; all other chemicals were of AR grade. n-Decanol (M/s. Merck) was added in organic phase to avoid any third phase formation.
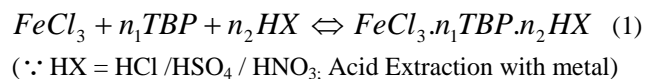
B. Apparatus and Procedure

Extraction was carried out by in-house designed Bulk Liquid Membrane (fig. 1) setup. The volume of each phase was equal to 100cm^3. The interfacial surface area was 17cm^2. The phases were mixed by individual stirrers. The mixing rate of all the phases were kept constant (100rpm). 0.5cm^3 samples of the organic phase (membrane phase) were taken in appropriate periods of time and stripped with 1cm^3 water. The concentration of Fe(III) in aqueous solution was then measured using UV Spectrophotometer (M/s Thermo Electronics, Model Helios alpha) at wavelength of 480nm by KSCN analysis method [13]. The concentration of organic phase was then calculated from the mass balance of Iron(III) with the assumption that Iron is neither lost nor consumed in any chemical reaction inside organic phase. The concentration

of acids in organic phase and strip phase were determined by titration with 0.01N NaOH and phenolphthalein as indicator.

Equilibrium extraction data were obtained by shaking 10ml organic with 10ml aqueous solution. Distribution coefficient of Fe(III) and acids were calculated by determining both equilibrium concentration in organic and aqueous phase.

Depending upon type of acids, Fe(III) forms chelating complex according to the following reactions

$$FeCl_3 + n_1 TBP + n_2 HX \Leftrightarrow FeCl_3.n_1 TBP.n_2 HX \quad (1)$$
($\because$ HX = HCl /HSO$_4$ / HNO$_3$; Acid Extraction with metal)

where n_1 and n_2 are number of moles of TBP and acid per mole of Fe(III) respectively which are attached with the metal complex.

Similarly free acid extraction by TBP can be represented as

$$TBP + n_3 HX \Leftrightarrow TBP.n_3 HX \quad (2)$$
(Free Acid Extraction)
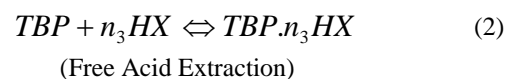
where n_3 is number of moles of acid is attached to per mole of TBP. The unknown n_1, n_2 and n_3 are determined by slope analysis from equilibrium study.
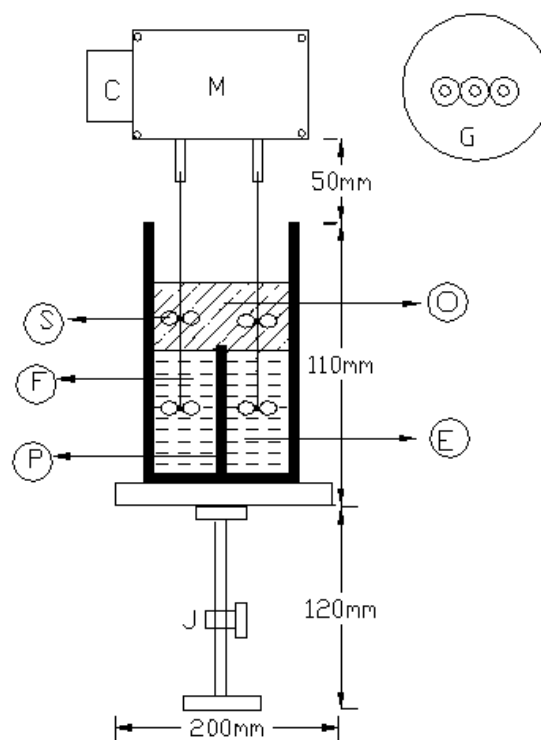

Fig. 1 Schematic of the Bulk Liquid Membrane M: Motor and Gear Assembly, C: Controller and Tachometer, G: Top view of Gear Assembly, F: Feed phase (aqueous), O: Organic Phase, E: Extract/Strip Phase (aqueous), P: Partition/Physical barrier, S: Stirrer, J: Rotating Jack/sliding assembly

World Academy of Science, Engineering and Technology
International Journal of Materials and Metallurgical Engineering
Vol:7, No:6, 2013

III. MATHEMATICAL MODEL

Transfer of Fe(III) and acid (HX= HCl/HSO$_4$/HNO$_3$) from feed to organic phase and organic phase to strip phase in the BLM can be described following set of differential equations with initial conditions:

The subscript "*f*", "*o*" and "*e*" denote feed, organic and extract (strip) phase, respectively. Presence of Fe (III) and HX shift the equilibrium towards the transfer of $FeCl_3.n_1TBP.n_2HX$.

Concentration of Fe (III) in aqueous feed phase

$$V_f \frac{dC_{Fe,f}(t)}{dt} = -k_{Fe,fo}A_{fo}\left(C_{Fe,f}(t) - \frac{C_{Fe,o}(t)}{D_{Fe,fo}(C_{Fe,f},C_{HX,f})}\right)$$

(3)

Concentration of Fe (III) in organic phase

$$V_o \frac{dC_{Fe,o}(t)}{dt} = k_{Fe,fo}A_{fo}\left(C_{Fe,f}(t) - \frac{C_{Fe,o}(t)}{D_{fo}(C_{Fe,f},C_{HX,f})}\right)$$
$$- k_{Fe,oe}A_{oe}\left(C_{Fe,o}(t) - D_{eo}(C_{Fe,f},C_{HX,f})C_{Fe,e}(t)\right)$$

(4)

Concentration of Fe (III) in strip phase

$$V_e \frac{dC_{Fe,e}(t)}{dt} = k_{Fe,oe}A_{oe}\left(C_{Fe,o} - D_{eo}(C_{Fe,f},C_{HX,f})C_{Fe,e}(t)\right)$$

(5)

Concentration of acid in aqueous feed phase

$$V_f \frac{dC_{HX,f}(t)}{dt} = -k_{HX,fo}A_{fo}\left(C_{HX,f}(t) - \frac{C_{HX,o}(t)}{D_{HX,fo}(C_{Fe,f},C_{HX,f})}\right)$$

(6)

Concentration of acid (HX) in organic phase

$$V_o \frac{dC_{HX,o}(t)}{dt} = k_{HX,fo}A_{fo}\left(C_{HX,f}(t) - \frac{C_{HX,o}(t)}{D_{fo}(C_{Fe,f},C_{HX,f})}\right)$$
$$- k_{HX,oe}A_{oe}\left(C_{HX,o}(t) - D_{eo}(C_{Fe,f},C_{HX,f})C_{HX,e}(t)\right)$$

(7)

Concentration of acid (HX) in strip phase

$$V_e \frac{dC_{HX,e}(t)}{dt} = k_{HX,oe}A_{oe}\left(C_{HX,o} - D_{eo}(C_{Fe,f},C_{HX,f})C_{HX,e}(t)\right)$$

(8)

Initial conditions

$$C_{Fe,f}(0) = C_{Fe,f}^0 \quad C_{Fe,o}(0) = 0 \quad C_{Fe,e}(0) = 0$$
$$C_{HX,f}(0) = C_{HX,f}^0 \quad C_{HX,o}(0) = 0 \quad C_{HX,e}(0) = 0$$

(9)

where C denotes the concentrations, D –the distribution coefficient, A is the interfacial mass transfer area, V is the phase volume and t the time. Subscript "*f*, "*o*", and "*e*" denote feed, organic and strip phases respectively. Superscript "0" denotes an initial value. The same relationship can be written for other compounds. The above equations are coupled with parts concerning mass transfer between phases and also with distribution coefficient depending on the concentrations of Fe(III) and acid. In general, they cannot be solved analytically and numerically methods are used to solve these equations. However, assuming pseudo steady state in the organic phase the system of coupled ODE can be analytically solved.

IV. RESULTS AND DISCUSSION

The overall mass transfer coefficients were calculated from experimental data for constant mixing rate. Kinetics of individual mineral acid extractions are described below. Good agreement was obtained between experimental and calculated concentration using the developed model. The only parameter to be fitted in the model was the average mass transfer coefficients for acids $k_{HX,fo}$, $k_{HX,oe}$ and for mass transfer coefficients for Iron(III) $k_{Fe,fo}$, $k_{Fe,oe}$. Its values were calculated using least square method, were collected in Table I.

TABLE I
MASS TRANSFER COEFFICIENTS OF ACIDS k_{fo}, k_{oe} IN 10% TBP; 40% N-DECANOL EXTRACTION

Stirring rate (rpm)	Initial Composition Feed phase	$D_{HX,fo}$	$k_{HX,fo}$ (m/s)	$k_{HX,oe}$ (m/s)
100	8(N) HCl without Fe(III)	0.05	1.15x10^{-7}	1.42x10^7
100	8(N) HCl 1000ppm Fe(III)	0.06	6.05x10^{-7}	5.9 x10^{-7}
100	8(N) HNO$_3$ without Fe(III)	0.08	2.04x10^{-6}	2.01 x10^{-6}
100	8(N) HNO$_3$ with 1000 ppm Fe(III)	0.12	3.3x10^{-6}	3.03x10^{-6}
100	8(M) H$_2$SO$_4$ with 1000 ppm Fe(III)	0.22*	1.85x10^{-7}	1.55x10^{-7}

"*" Third phase was formed. Third phase volume = 5.5ml, equilibrium concentration of H$_2$SO$_4$ in third phase =2.58N, dilute organic phase volume= 4.5ml and concentration of H$_2$SO$_4$= 0.006N.

World Academy of Science, Engineering and Technology
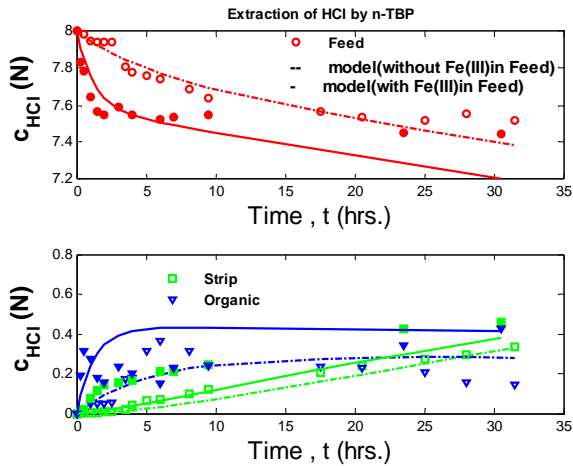International Journal of Materials and Metallurgical Engineering
Vol:7, No:6, 2013

Fig. 2 Experimental concentration profile of HCl and theoretical results from the fitting the model (10%TBP, stirrer rpm =100, 40% n-decanol, Initial Feed 8N HCl, $C_{Fe(III)}(0)$=1000ppm)

Fig. 2 represents extraction of HCl by TBP in a bulk liquid membrane set up, with and without presence of Fe(III) in the aqueous feed solution. It is observed when Iron(III) is present in the feed extraction of HCl is enhanced.
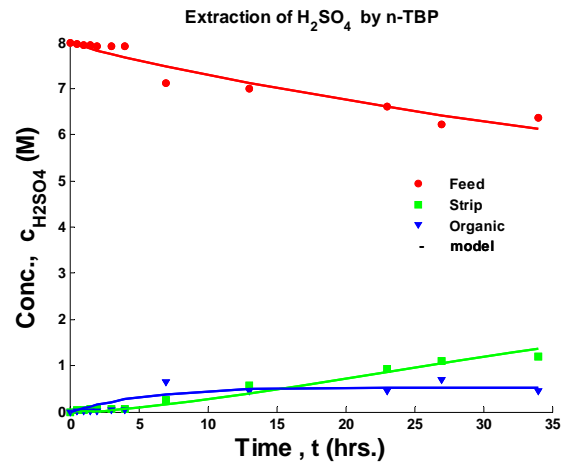

Fig. 3 Experimental concentration profile of Fe(III) and theoretical results from the fitting the model (10%TBP, stirrer rpm =100, 40% n-decanol in org phase, Feed 8N HCl, [Fe(III)] =1000ppm)

Fig. 3 represents extraction of HNO_3 by TBP. It is observed that extraction of HNO_3 by TBP increases in presence of Fe(III) in the feed.

Fig. 4 represents H_2SO_4 extraction by n-TBP in bulk liquid membrane (BLM).

Fig. 4 Experimental concentration profile of H_2SO_4 and theoretical results from the fitting the model (10%TBP, stirrer rpm =100, 40% n-decanol, Initial feed 8(M) H_2SO_4, $C_{Fe(III)}(0)$=1000ppm)

Fig. 4 described extraction of Fe(III) by n-TBP. Iron(III) concentration of in all three phases (feed, strip, and organic) is plotted with different time interval. It is observed that the developed model was able to predict concentration of acids in all the three phases (Feed, Strip & organic) successfully.
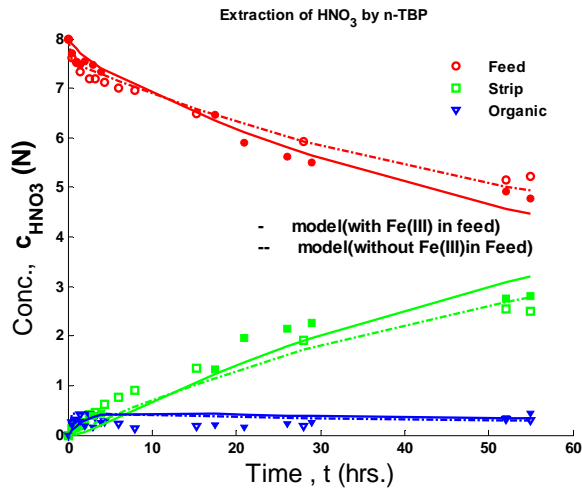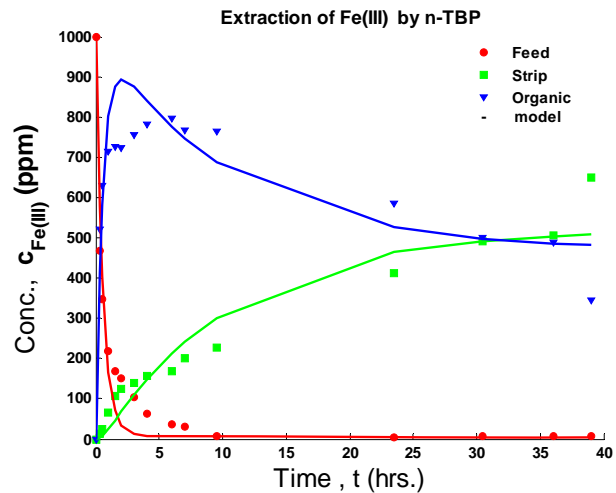

Fig. 5 Experimental concentration profile of Fe(III) and theoretical results from the fitting the model (10%TBP, stirrer rpm =100, 40% n-decanol in org phase, Initial Feed 8N HCl, $C_{Fe(III)}(0)$=1000ppm)

Fig. 5 shows the concentration profile of Fe(III) vs. time in 8N HCl feed. The concentration of acid kept 8M in feed phase in all of the experiments. Initial Fe(III) concentration was kept 1000ppm wherever Iron(III) was used in the feed. Mass transfer of Fe(III) between Feed and organic phase and Organic to Strip phase was also studied. Experimental concentration of Iron(III) data was fitted (fig. 5.) with the developed model and result of mass transfer coefficients are as obtained $k_{Fe,fo}$ =3.0x10^-5 m/s and $k_{Fe,fo}$ =2.9x10^-5 m/s.

World Academy of Science, Engineering and Technology
International Journal of Materials and Metallurgical Engineering
Vol:7, No:6, 2013

V. EXTRACTION EQUILIBRIUM

The reaction stoichiometry for both acid extraction with metal and free acid extraction by TBP were investigated using classical slope analysis technique by plotting experimentally determined distribution coefficient as a function of TBP concentration. The slope analysis results for free HCl extraction are shown in fig. 6. Using a least squares best fit methods , the slopes of line were determined to be 0.45 and 0.49(~0.5) with Fe(III) in the feed phase (n=0.5) fig. 6. Thus 1 mole of TBP is required per 2 moles of HCl extraction. The average value of equilibrium constant can be obtained by the intercept.

A. Stoichiometry of HCl Extraction:

The extraction of acid can be expressed by

$$HX + nTBP \Leftrightarrow TBP.nHCl \quad (10)$$

$$k_{eq,HCl} = \frac{D_{HCl}}{[TBP]^n} \quad (11)$$

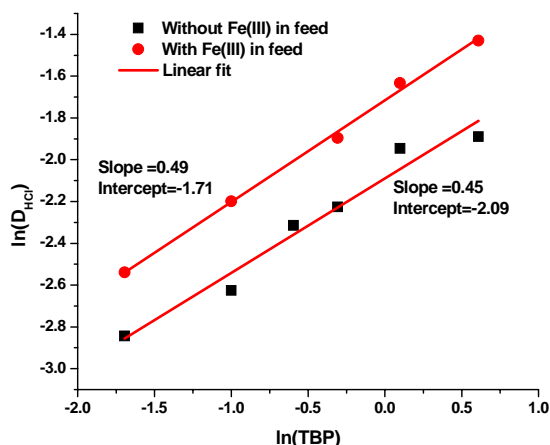$$\ln D_{HCl} = n \ln[TBP] + n \ln K_{eq} \quad (12)$$

Fig. 6 log-log relation between distribution coefficient of HCl extraction with and without Fe(III) in feed (TBP concentration varied from 5-50%, 40% n-decanol in org phase, Initial Feed 8N HCl, $C_{Fe(III)}(0)$=1000ppm)

Above Fig. 6 revealed higher distribution coefficient of acid extraction when Fe(III) was present in the feed solution containing HCl. Though, the molecularity of TBP.HCl complexation reaction does not change as indicated by equal slope. Hence, stoichiometry of free HCl extraction can be re presented as

$$TBP + 2HCl \Leftrightarrow TBP.2HCl \quad (13)$$

Equilibrium constant for HCl extraction:

$$k_{eq,HCl} = e^{-2.01} = 0.1225 \, \text{M}^{-0.5}$$

Thus, it is inferred that in presence of Fe(III) in the feed equilibrium concentration of HCl is enhanced due to simultaneous free acid extraction and HCl extraction with Fe(III). Hence, higher equilibrium distribution coefficient is achieved compared to the case without metal in the feed.

B. Stoichiometry of Fe(III) Extraction in HCl Medium in Feed

Fe(III) extraction can be represented as

$$FeCl_3 + TBP + 2HCl \Leftrightarrow FeCl_3.TBP.2HCl \quad (14)$$
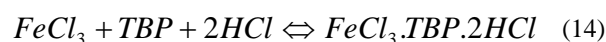
$$k_{eq,Fe} = \frac{D}{[TBP]^n} \quad (15)$$

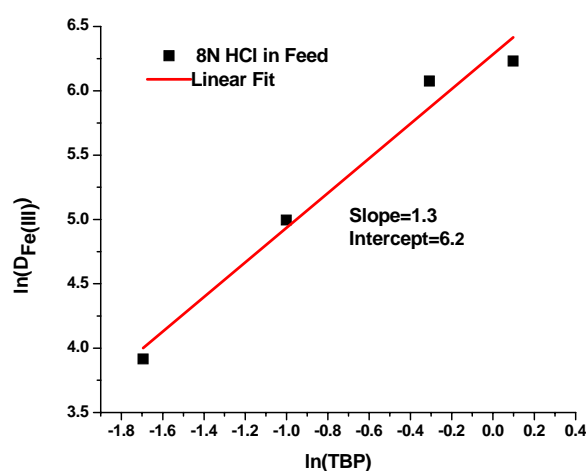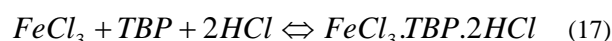$$\ln D_{Fe} = n \ln[TBP] + n \ln K_{eq,Fe} \quad (16)$$

Fig. 7 log-log relation between distribution coefficient of Fe(III) extraction (TBP concentration varied from 5-50%, 40% n-decanol in org phase in paraffin, Initial Feed 8N HCl, $C_{Fe(III)}(0)$=10000ppm)

The Fe(III) extraction reaction stoichiometry was determined with concentration ranging from 5% (0.183M) to 50 % (1.83M) TBP in paraffin with 40% n-decanol modifier in organic phase and keeping HCl concentrations constant 8N. N-Decanol was used in the paraffin to circumvent problem of limited solubility and third phase formation with TBP in paraffin. The slope analysis results are shown in fig. 7. Using a least square best fit method, the slope of line were determined as 1.3 for $FeCl_3.TBP.HCl$ system.

Hence stoichiometry of Fe(III) extraction in HCl medium in feed may be represented as

$$FeCl_3 + TBP + 2HCl \Leftrightarrow FeCl_3.TBP.2HCl \quad (17)$$

Equilibrium constant for Fe(III) extraction in HCl in feed

$$k_{eq,Fe} = e^{6.2} = 492.74 \, \text{M}^{-3}$$

World Academy of Science, Engineering and Technology
International Journal of Materials and Metallurgical Engineering
Vol:7, No:6, 2013

C. Stoichiometry of HNO₃ Extraction

Slope analysis techniques were also used to determine the TBP stoichiometric coefficients for the extraction of HNO_3. Equilibrium experiments were performed by varying TBP concentration 5-50% keeping HNO_3 concentrations constant 8(N). This allowed for an accurate measurement of the stoichiometric coefficients and equilibrium constants. Equilibrium constant for HNO_3 extraction $= k_{eq,HNO_3} = e^{-1.45} = 0.23\,M^{-0.5}$. A slope of 0.57 was obtained from fig. 8 which was generated from D_{HNO3} as a function of TBP concentration.
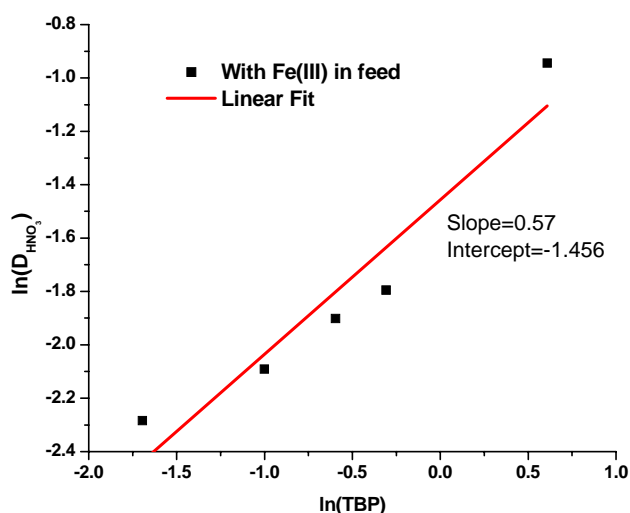

Fig. 8 log-log relation between distribution coefficient of HNO_3 extraction (TBP concentration varied from 5-50%, 40% n-decanol in org phase in paraffin, Initial Feed 8N HCl, $C_{Fe(III)}(0)$=1000ppm)

Hence stoichiometry of HNO_3 extraction feed can be represented as

$$TBP + 2HNO_3 \Leftrightarrow TBP.2HNO_3 \qquad (18)$$

D. Stoichiometry of Fe (III) Extraction in HNO₃ Medium in Feed

Based on the slope analysis of the obtained experimental equilibrium data the extracted iron species in HNO_3 medium is
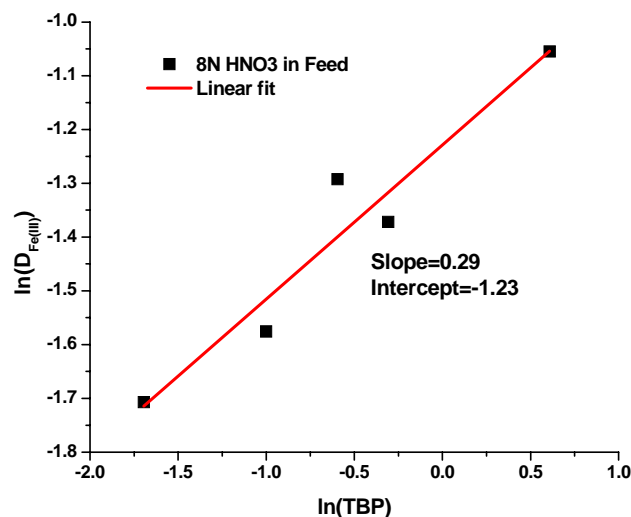
$$FeCl_3.nTBP.2HNO_3$$

Fig. 9 log-log relation between distribution coefficient of HNO_3 extraction (TBP concentration varied from 5-50%, 40% n-decanol in org phase in paraffin, Initial Feed 8N HCl, $C_{Fe(III)}(0)$=1000ppm)

Linear curve fit to the log $D_{Fe(III)}$ vs. log[TBP] was shown in Fig. 9 results in a slope 0.29 and intercept -1.23. Therefore, equilibrium constant for Fe(III) extraction in HNO_3 in feed $= k_{eq,Fe} = e^{-1.23} = 0.29\,M^{-5}$. Hence, stoichiometry of Fe(III) extraction in HNO_3 medium in feed may be represented as

$$3FeCl_3 + TBP + 2HNO_3 \Leftrightarrow 3FeCl_3.TBP.2HNO_3 \quad (19)$$
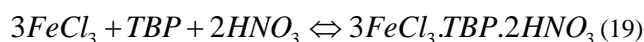
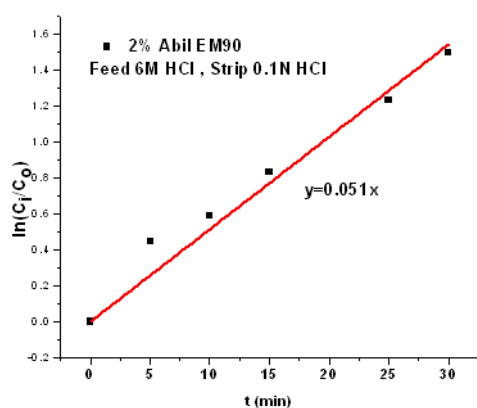## VI. Back Extraction in Liquid Emulsion Membrane (LEM)

With the established knowledge of co-extraction of acid and metal, further study was carried out using Liquid Emulsion Membrane (LEM) Extraction of Fe(III) from HCl solution in the feed. The emulsion composition used during the investigation of some important factors affecting the rate of permeation of iron through LEM is follows, unless otherwise stated : iron concentration in the external phase was 100ppm at 6M HCl, TBP concentration was (10%)(v/v), 2% polymeric surfactant Abil EM 90 in paraffin, ratio of organic phase to internal aqueous phase was taken to be 1(v/v), The (treat ratio) emulsion phase volume : external aqueous phase volume was 40:400, the temperature is 25°C, the internal aqueous phase strip phase is 0.1M HCl, pertraction stirring speed 400rpm, emulsification speed 8000rpm and emulsification time is 60 min.

Assuming LEM pertraction as batch mixed reactor and hence the volumetric mass transfer coefficient $k_L a$ of Iron(III) extraction can be estimated using following equation.
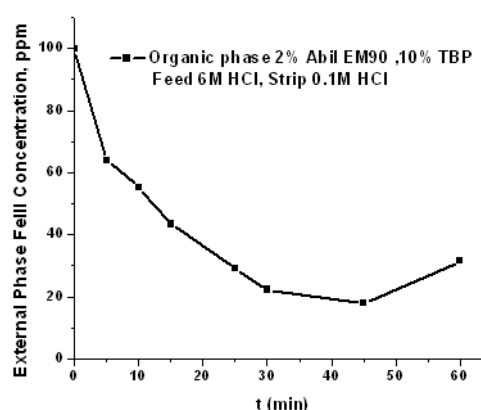
$$\ln\left(\frac{C_i}{C_o}\right) = k_L at \qquad (20)$$

World Academy of Science, Engineering and Technology
International Journal of Materials and Metallurgical Engineering
Vol:7, No:6, 2013

where C_i = initial concentration of Iron(III) in external phase and C_o = concentration of iron in the external phase after time, t of pertraction. The value of overall mass transfer coefficient, $k_L a$ is derived from the slope of the plot

$$\ln\left(\frac{C_i}{C_o}\right) \text{ vs. time, } t.$$

Fig. 10 shows the concentration profile of Fe(III) in raffinate/feed at different time intervals. It is observed that during LEM extraction the metal concentration initially falls rapidly and within 30 minutes reaches a minima and then concentration in the feed increases.

(a) Logarithmic Fe(III) conc. ratio with initial vs. time   (b) Change in conc. of Fe(III) vs. time (min)

Fig.10 Effect of Abil EM90 concentration on mass transfer rate of Iron(III)

This concentration minima was further investigated and it was noted that after 30min there is back extraction of Fe(III) from internal strip phase to outer aqueous feed, hence instead of decreasing feed metal concentration there is an increase in trend of metal extraction in feed after 30min. The internal strip phase was analysed after demulsification and within 15 seconds of pertraction the acidity of strip phase increased to 4N. Hence it is proven that due to acid extraction by TBP back extraction occurs and stripping becomes extremely difficult. The slope of 0.051 from Fig. 10 (a) indicated overall mass transfer coefficient; $k_L a = 0.051 \text{min}^{-1}$

VII. CONCLUSION

It is observed that due to co-extraction of acids and metal using TBP, reversal of driving force can occur and subsequently Iron(III) is re-extracted back from the strip phase into the feed phase after 5 minutes of LEM Extraction. Rate of HNO_3 extraction by TBP is found highest among the all other mineral acids whereas Iron(III) extraction is found highest in the HCl medium (equilibrium constant Fe(III) extraction in HCl in feed, $k_{eq,Fe} = 492.74 \text{ M}^{-3}$ is much higher than HNO_3 medium). The kinetics of acid extraction is studied using Bulk Liquid Membrane (BLM) and results obtained depict higher acid extraction for nitric acid compared to the other acids similar to the equilibrium study results. A mathematical model of extraction of acids and with and without Fe(III) in feed with n-tributyl phosphate (TBP) was designed and discussed. The back extraction behaviour of Fe(III) by n–TBP from HCl medium was investigated in LEM pertraction study using

TBP. It is concluded from the above study that either pertraction time should be minimised to avoid back extraction or alkaline medium in strip phase should be used to avoid inefficient stripping due to higher acidity in strip phase.

REFERENCES

[1] J. Saji, M.L.P. Reddy, Liquid–liquid extraction separation of iron(III)/from titania wastes using TBP–MIBK mixed solvent system, Hydrometallurgy 61:81–87(2001).
[2] J. Saji, M.L.P. Reddy, Liquid–liquid extraction separation of iron(III)/from titania wastes using TBP–MIBK mixed solvent system, Hydrometallurgy 61:81–87(2001).
[3] K.K. Sahu And R.P. Das, Synergistic Extraction of Iron(III) at Higher Concentrations in D2EHPA-TBP Mixed Solvent Systems, Metallurgical and Materials Transactions B , Vol 28B , 181-189 (1997).
[4] Santosh K. Majumdar, and Anl K. De, Liquid-Liquid Extraction of Iron(III) with Tributylphosphate, Pergamon Press Ltd Vol. 7, 1 – 6(1960).
[5] S.I. El Dessouky a, Y.A. El-Nadi a, I.M. Ahmeda, E.A. Saad b, J.A. Daouda, Solvent extraction separation of Zn(II), Fe(II), Fe(III) and Cd(II) using tributylphosphate and CYANEX 921 in kerosene from chloride medium , Chemical Engineering and Processing 47 177–183(2008).
[6] Tetsuji Hirato, Zhi-Chun Wu, Yoshiyasu Yamada and Hiroshi Majima, Improvement of the stripping characteristics of Fe (III) utilizing a mixture of di (2-ethylhexylphosphoric acid and tri-n-butyl phosphate, Hydrometalhtrgy, 28: 81-93(1992).
[7] Taichi Sato , Takato Nakamura And Masayoshi Ikeno, The Extraction Of Iron(III) From Aqueous Acid Solutions by Di(2-Ethylhexyl)Phosphoric Acid, Hydrometallurgy, 15 209--217(1985).

World Academy of Science, Engineering and Technology
International Journal of Materials and Metallurgical Engineering
Vol:7, No:6, 2013

[8] Archana Agrawal, S. Kumari, and K. K. Sahu, Iron and Copper Recovery/Removal from Industrial Wastes: A Review Ind. Eng. Chem. Res., 48, 6145–6161(2009).

[9] B.R. Reddy, P.V.R. Bhaskara Sarma, Extraction of iron(III) at macro-level concentrations using TBP, MIBK and their mixtures, Hydrometallurgy 43 299-306(1996).

[10] R.K. Mishra, P.C.Rout, K Sarangi, K.C. Nathsarma, Comparative study on extraction of Fe(III) from chloride leach liquor using TBP , Cyanex 921and Cyanex 923, Hydrometallurgy , 104:298-303(2010).

[11] C. Lupi , D. Pilone , Reductive stripping in vacuum of Fe(III) from D2EHPA, Hydrometallurgy 57 201-207 (2000).

[12] B.R. Reddy, P.V.R. Bhaskara Sarma, Extraction of iron(III) at macro-level concentrations using TBP, MIBK and their mixtures, Hydrometallurgy 43 (1996) 299-306.

[13] Vogel's Quantitative Chemical Analysis (5th Edition),1989.

[14] Man-Seung Lee, Gwang-Seop Lee and Keun Yong Sohn, Solvent Extraction Equilibria of FeCl3 with TBP, Materials Transactions 45, 6 (2004) 1859 -1863

[15] D.K. Singh, S.L. Mishra, H. Singh, Stripping of iron(III) from the D2EHPA + TBP extract produced during uranium recovery from phosphoric acid by oxalic acid, Hydrometallurgy 81 (2006) 214–218.