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Extraction Behaviour of Fe^{3+} From Chloride Solution by Technical Grade D2 EHPA: A Comparison with the Results Obtained by Analytical Grade

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Abstract. The solvent extraction of Fe^{3+} from chloride solution by technical grade (t.g) di-(2-ethylhexyl) phosphoric acid, D2EHPA dissolved in kerosene has been investigated over a wide range of aqueous acidity as a function of phase contact time, concentrations of Fe^{3+}, HCl, H^+ and Cl^- in the aqueous phase, D2EHPA concentration in the organic phase and temperature and the results have been compared to that reported for analytical grade (a.g). Equilibrium time is 60 min, compared to 50 min for a.g. Natures of Fe^{3+} concentration dependences are not similar and the values of extraction ratio are usually hundred times greater for t.g. than for a.g. under similar conditions. The HCl dependence plots pass through a maximum and a minimum at 1.6 M and 1.1 M HCl, respectively, whereas, these are at 1.2 M and 0.3 M HCl, respectively, for a.g. At $[Cl^-]$ = 3 M, the shape of H^+ dependence plot for t.g. reagent differs widely from that for the a.g. The extraction is also found to be immenesely dependent on $[Cl^-]$ for both the grades of extractant, but the extent of dependence under similar condition depends on the grade of extractant used. The extractant dependences are lower for t.g. compared to those for a.g. Reactions are exothermic in higher temperature region, whereas, the extraction is almost independent of temperature in its lower regions. The apparent enthalpy change, ΔH value in the higher temperature region is decreased with decreasing H^+ concentration in the aqueous phase. But the opposite trend was observed with a.g. The loading capacity depends on the aqueous acidities and grades of D2EHPA. It is 13.05 and 6.83 g of Fe^{3+} per 100 g D2EHPA (t.g.) at [HCl] of 0.13 and 3 M, respectively, compared to 8.38 and 3.14 g of Fe^{3+} per 100 g D2EHPA (a.g.) at [HCl] of 0.05 and 1 M, respectively. Mechanism of extraction is complicated by the simultaneous extractions of Fe^{3+}, $FeCl^{2+}$, $FeCl_2^+$, $FeCl_3$, $HFeCl_4$, etc. in both cases. It is observed that 99.4 % of iron species extracted by D2EHPA (t.g.) in the organic phase can be stripped by 5 M HCl in three stages at organic to aqueous phase ratio of unity. Organic phase after one cycle can be recycled after adding 0.72 g dm^{-3} mono-(2-ethylhexyl) phosphoric acid, M2EHPA.

Keywords: extraction equilibrium, iron(III) extraction, technical grade D2EHPA, chloride medium, stripping

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Introduction

Iron and its alloy-steel are the most important technological materials in the world. Iron can be easily produced from the iron bearing ores by pyrometallurgical method. Iron-bearing compounds like iron oxide, iron sulfide, iron silicate, iron aluminate, metallic ferrites etc. are also present as gangue materials in ores of many common metals. For example, ilmenite contains ferric oxide and other metallic oxides as impurities. Therefore, it becomes necessary to separate iron from a leach solution of an ore for the production of a pure metal hydrometallur-gically and this can be carried out by the solvent extraction technique.

Previously, the separation of Fe^{3+} from the H_2SO_4 leach solution of ilmenite ($TiFeO_3$) involving D2EHPA, (a.g.) has been thoroughly investigated (Islam *et al*, 1979; 1978). Extractions of Fe^{3+} from perchlorate medium by D2EHPA have been investigated (Roddy *et al.,* 1971; Karpacheva and Ilozheva, 1969; Baes and Baker, 1960). Similarly, Sato *et al.* (1985a, 1985b) have reported the same, but extracted from sulfate, nitrate and chloride solutions. Arunkumar *et al.* (1998) have reported the extraction equilibria of Fe^{3+} from chloride solution by D2EHPA (a.g.). The extraction of Fe^{3+} from chloride solution by D2EHPA (a.g.) and the stripping of the extracted complex of the Fe^{3+} from Cl^- medium by D2EHPA (a.g.) using HCl solutions have been reported from the kinetic view points (Biswas and Begum, 2001; 1999). Unfortunately, literature is not available on the extraction of Fe^{3+} from any medium by D2EHPA (t.g.). The D2EHPA (t.g.) (produced by Fluka) contains 43% monoester, mono-(2-ethylhexyl) phosphoric acid, M2EHPA. The innovative use of pure M2EHPA as a selective extractant for the extraction from concentrated H_2SO_4 solution has been started by Demopoulos and Pouskouleli (1989). They used this reagent with a long chain alcohol as modifier to convert the extractant in the monomeric form. A comparative study on the extraction behaviours of Fe^{3+} from sulphate and chloride medium by D2EHPA, and M2EHPA, has been reported by Principe and Demopoulos (1998). It is reported in the that M2EHPA is a better extractant than D2EHPA for Fe^{3+}, but the solvent loss due to aqueous

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*Author for correspondence; E-mail: rkbiswas53@yahoo.com solubilities is greater for M2EHPA than for D2EHPA. Due to the presence of monoester in D2EHPA (t.g.), this reagent is expected to behave differently from D2EHPA (a.g.). The price of D2EHPA (t.g.) is about one third of the price of D2EHPA (a.g.). Thus, an attempt has been taken to use a cheaper extractant for the extraction of Fe^{3+}. The extraction characteristics of Fe^{3+} from chloride solution by D2EHPA (t.g.) dissolved in kerosene have been investigated and compared to that already published for D2EHPA (a.g.) (Arun Kumar, *et al.*, 1998). Stripping ability of the extracted complexes has also been investigated.

Materials and Methods

Reagents. Technical grade D2EHPA was bought from Fluka, Switzerland. It was found to contain 43% (mole) M2EHPA (monoester) and 57% (mole) D2EHPA by potentiometric titration; and used as such. Since the molecular weights of dimeric D2EHPA and M2EHPA are 644 and 420, the molecular weight in dimeric form of D2EHPA (t.g.) was taken as $644 \times 0.57 + 420 \times 0.43 = 548$. Consequently, 1 M D2EHPA (t.g.) would contain 0.43 M M2EHPA and 0.57 M D2EHPA. Kerosene was obtained from the local market and distilled to collect the fraction distilling over 200-260 °C. It was colorless and mostly aliphatic in nature. As a source of Fe^{3+}, ferric chloride (Loba Chemie, 99%) was used. All other chemicals were of reagent grade and used without further purifications.

Analytical. The concentration of Fe^{3+} in the aqueous phase was determined by the thiocyanate method (Bassett *et al.* 1979) at 480 nm using a WPA S104 spectrophotometer. The standard solution of Fe^{3+} was prepared by dissolving 0.846 g A.R. $FeNH_4(SO_4)_2$ in 1litre 0.1 M H_2SO_4 solution (1 ml = 0.1 mg Fe^{3+}). The acidity of the aqueous phase was adjusted by the addition of HCl, whereas the chloride ion concentration was adjusted by the addition of NaCl. The concentrations of M2EHPA and D2EHPA in the aqueous phase were determined by break down of the extractants by heating with concentrated H_2SO_4 acid followed by the estimation of the orthophosphate produced using the phosphomolybdate method at 830 nm (Bassett *et al.*, 1979).

Extraction procedure. A stock solution of $FeCl_3$ was prepared to contain 0.18 M Fe^{3+}, 1.0 M H^+ and 1.54 M Cl^-. This solution was used to prepare the aqueous phases containing different amounts of H^+, Cl^- and Fe^{3+} for extraction. The extraction procedures are given elsewhere (Arun Kumar, *et al.*, 1998; Islam and Biswas, 1981). Equal aliquots of organic and aqueous phases (25 ml each) were taken in a 125 ml reagent bottle and agitated for a predetermined time (1 h) at 303 ± 1 K in a thermostatic water bath. After mechanical shaking, the phases were settled and separated; and the aqueous Fe^{3+} concentration was estimated (Bassett *et al.*, 1979). The concentration of Fe^{3+} in the organic phase was calculated by difference. The value of the distribution ratio (D) was calculated as the ratio of the concentration of Fe^{3+} in the organic phase to that existing in the aqueous phase at equilibrium.

Preparation of the organic phase for stripping. Aliquots of 200 ml aqueous solutions containing 0.018 M Fe^{3+} and 2, 1.3 and 0.3 M H^+ ($[Cl^-] = [HCl]$) were mixed with equal volumes of 0.05 M D2EHPA (t.g.) and equilibrated for 1 h. The respective organic phases were found to contain 0.0174, 0.0168 and 0.0147 M Fe^{3+}. These solutions were used for stripping. In the last two aqueous acidities, ~2 and 15 % of formed complexes were isolated out, respectively, as solids.

Stripping procedure. Stripping of the extracted complexes obtained at the above three aqueous acidities were investigated by HCl and H_2SO_4 solutions of various concentrations. For stripping, 20 ml of Fe^{3+} loaded organic phase was equilibrated with either HCl or H_2SO_4 solution of particular concentration for 1 h at 303 ± 1 K. After equilibration, the phases were settled and disengaged. The aqueous phase was analysed for Fe^{3+} content. The Fe^{3+} concentration in the organic phase was calculated by differences. The stripping ratio (S) was calculated by dividing the concentration of Fe^{3+} in the aqueous phase by that in the organic phase at equilibrium.

Loading procedure. Loadings of 0.1 M D2EHPA (t.g.) were done by vigorous contact of this phase (25 ml) repeatedly with fresh aqueous solutions (containing either 0.13 or 3.0 M HCl and 0.02 M Fe^{3+}) of same volume until the organic phases were saturated with Fe^{3+}. On loading, same complex was isolated as solid in the case of loading at aqueous acidity of 0.13 M.

Results and Discussion

It is found that the concentration ratio ($[Fe^{3+}]_{(o)}/[Fe^{3+}]_{(a)}$) increases almost exponentially with increasing phase contact time up to 60 min for extracting of Fe^{3+} from Cl^- medium by D2EHPA (t.g.) indicating that the equilibration time for this system is 60 min., Previously, it has been reported that the equilibration time for the extraction of Fe^{3+} from sulphate solution by D2EHPA (a.g.) in benzene is 3 h (Islam and Biswas, 1981) and that from chloride medium by D2EHPA (a.g.) in kerosene is 50 min (Arunkumar *et al.*, 1998) whereas, that from the sulphate medium by M2EHPA is only 5 min (Demopoulos and Pouskouleli, 1989). So the equilibration times for extraction of Fe^{3+} from chloride medium by and (t.g.) D2EHPA (a.g.) are almost equal, which means that the pres-

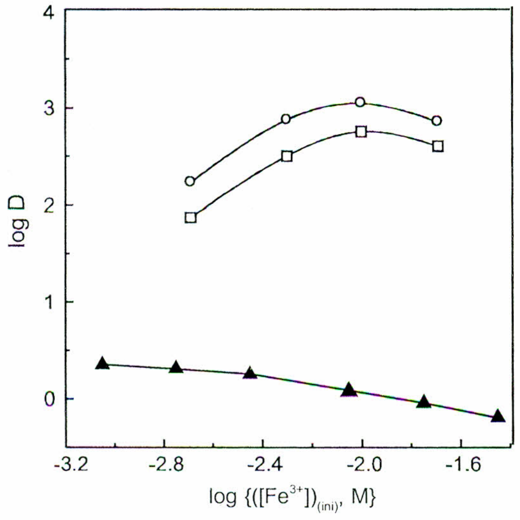

Fig. 1. Dependence of extraction ratio (D) on initial [Fe^{3+}] in the aqueous phase. [HCl] = 0.13 M; Temp = (303±1) K; Equilibration time = 1 h; (□) = 0.05 M D2EHPA (t.g.); (○), = 0.10 M D2EHPA (t.g.).

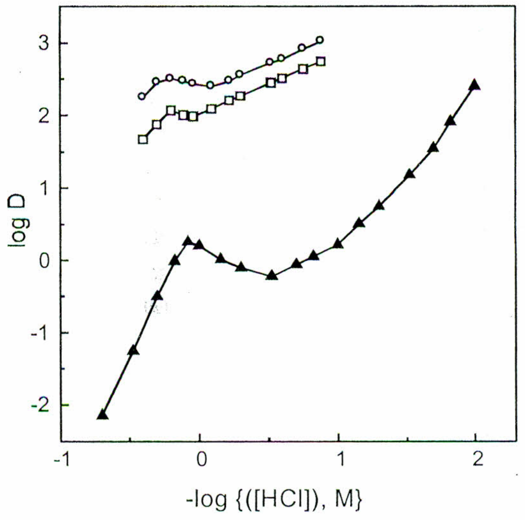

Fig. 2. Dependence of extraction ratio of Fe^{3+} on [HCl]. [Fe^{3+}]$_{(ini)}$ = 8.95 mM; shaking time = 1 h; Temp = (303±1) K; (□) = 0.05 M D2EHPA (t.g.); (○) = 0.20 M D2EHPA (t.g.); (▲), 0.05 M D2EHPA (a.g.).

ence of M2EHPA in D2EHPA (t.g.) does not affect the equilibration time.

Fig. 1 shows the variation of D with initial [Fe^{3+}] (2 mM-20 mM) at 0.13 M HCl in log-log scale, when extractions are made by 0.05 and 0.10 M D2EHPA (t.g.) solutions. The figure also reproduces the log D vs log {([Fe^{3+}]), M} plot at 0.13 M [HCl] for (a.g.) [D2EHPA] of 0.05 M (Arunkumar *et al.*, 1998) for comparison. Under similar experimental conditions, the plots obtained by D2EHPA (t.g.) differ in nature and positions from those obtained by a.g. extractant. In case of D2EHPA (t.g.), D value is increased 7-fold on increasing [Fe^{3+}] from 2 mM to 10 mM and then decreases considerably. On the other hand, for D2EHPA (a.g.), D value is decreased 4-fold on increasing [Fe^{3+}] from 0.9 mM to 35.9 mM. Under similar conditions, D is almost 100 times greater for t.g. than for D2EHPA (a.g.). These results indicate that the extent of Fe^{3+} extraction by D2EHPA is extensively enhanced by the presence of M2EHPA in t.g. reagent. This may also be due to the existence of various Fe^{3+}-Cl$^-$ complex species formed on the variation of [Fe^{3+}] in the aqueous phase and of synergism.

Variations of D on [HCl] (without keeping [Cl$^-$] at a constant value) are shown in Fig. 2 as log D vs - log {([HCl]), M} plots for both D2EHPA (t.g.) and (a.g.). For both 0.05 and 0.20 M t.g. D2EHPA, a similar behaviour is observed in the sense that plots pass through maxima at 1.6 M HCl and minima at 1.0 M [HCl]. Within 2.5 M to 1.6 M [HCl], the slopes of the plots are 2 for D2EHPA (t.g.) system. But for the a.g. reagent, the plot passes through a maximum at 1.25 M [HCl] and a minimum at 0.30 M [HCl]. Within 5 to 1.25 M [HCl], slope of the plot is 3.5. Within 1.6 M and 1.0 M [HCl], slopes of the curves for t.g. reagent are -0.5 but for a.g. reagent, slope within 1.25 to 0.3 M [HCl] is -1.0. At any [HCl] lower than the [HCl] at which a minimum is obtained, slopes of the curves are unity for D2EHPA (t.g.) system but for the D2EHPA (a.g.) system, slope of the curve varies from zero to about 3 on deceasing [HCl] It is therefore, concluded that the positions and natures of curves obtained by variation of HCl concentration using D2EHPA (t.g.) differ widely from those obtained using a.g. reagent.

Fig. 3 displays log D vs - log {([H$^+$]), M} plots: one for t.g. reagent and the other for a. g. reagent at 3 M [Cl$^-$]. In case of D2EHPA (a.g.), the slope of the plot varies from-1 in higher [H$^+$] region to + 2 in lower [H$^+$] region with a minimum appearing at about 0.2 M [H$^+$]. On the other hand, slopes of log D vs -log [H$^+$] plot for D2EHPA (t.g.) are ~1, 0.3 and 1 in higher, intermediate and lower [H$^+$] regions, respectively. It is therefore concluded that for t.g. reagent, extraction reactions involving net elimination of H$^+$ occur over the entire [H$^+$] region under investigation, but for D2EHPA (a.g.), the extraction reaction involving the addition of a H$^+$ occurs within 0.3-3 M [H$^+$]; whereas, that involving the elimination of two H$^+$ occurs within 0.01 - 0.1 M [H$^+$].

The log D vs - log {[Cl$^-$], M} plots are shown in Fig. 4. For D2EHPA (t.g.), plots at [H$^+$] of 2 and 0.3 M are straight lines with slopes + 1 and 0.3, respectively, indicating the elimination of Cl$^-$ in extraction reaction, but the plot at 1.2 M [H$^+$] is

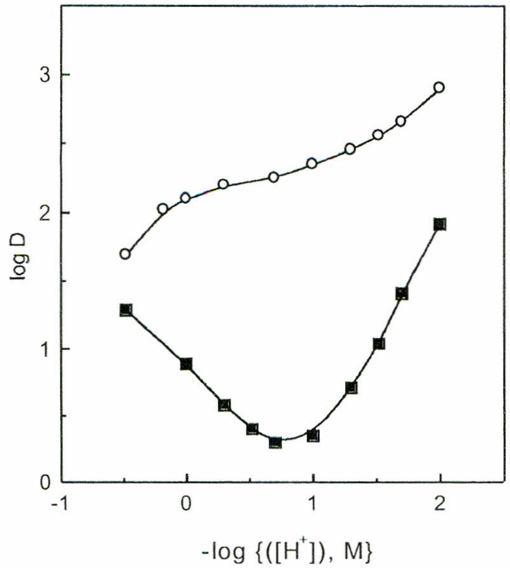

Fig. 3. Dependence of extraction ratio of Fe^{3+} on $[H^+]$. $[Fe^{3+}]_{(ini)}$ = 8.95 mM; temp = (303±1) K; $[H_2A_2]$ = 0.10 M; shaking time = 1 h; $[Cl^-]$ = 3 M; (○) = (t.g.) extractant; (●) = (a.g.) extractant.

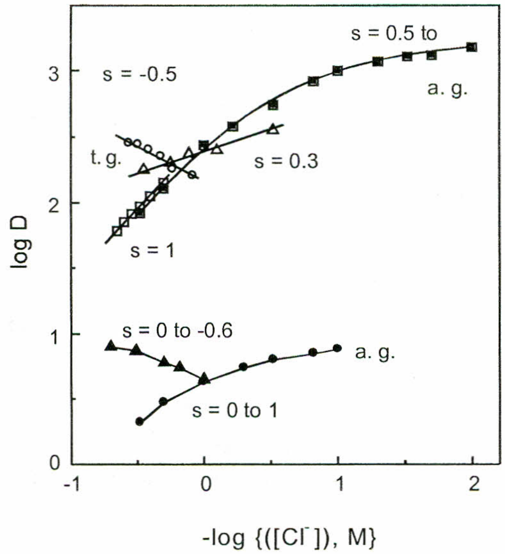

Fig. 4. Dependence of extraction ratio of Fe^{3+} on $[Cl^-]$. $[Fe^{3+}]_{(ini)}$ = 8.95 mM; temp = (303±1) K; shaking time = 1 h; $[H_2A_2]_{(o)}$ = 0.10 M; technical grade (□) $[H^+]$ = 2 M; (○) $[H^+]$ = 1.2 M; (Δ) $[H^+]$ = 0.30 M; analytical grade (▲) $[H^+]$ = 1 M; (●) $[H^+]$ = 0.1 M; (■) $[H^+]$ = 0.01 M.

a straight line with slope corresponding to 0.5 indicating the addition of 0.5, mole Cl^- per mole of Fe^{3+} species in the extraction reaction. On the other hand, for a.g. reagent, curves are obtained. For 1.0, 0.1 and 0.01 M $[H^+]$ systems, the slopes vary within 0 to - 0.6, 0 to 1.0, and 0.5 to 1.0, respectively.

temperature independent in the l.t.r. for D2EHPA (t.g.). On the other hand, for the a.g. reagent, the extraction reaction is endothermic in nature either in the h.t.r. or over the entire temperature region depending on $[H^+]$.

The measured ΔH value is shown to be dependent on $[H^+]$. The variations of ΔH value obtained in h.t.r. for D2EHPA (a.g.)

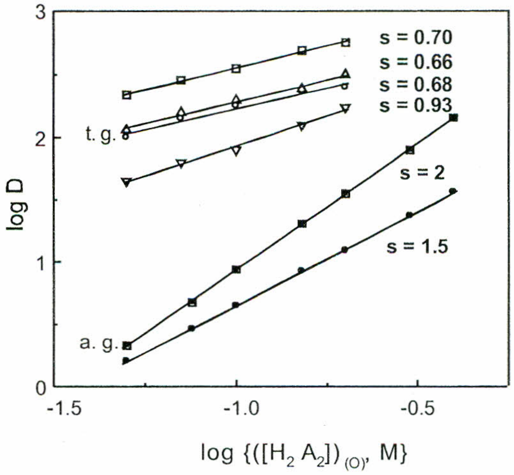

Fig. 5. Dependence of extraction ratio of Fe^{3+} ratio on [extractant]. $[Fe^{3+}]_{(ini)}$ = 8.95 mM; temp = (303±1) K; shaking time = 1 h; $[Cl^-]$ = [HCl] = $[H^+]$.(t.g): (□); [HCl] = 0.3 M; (Δ) [HCl] = 1.6 M; (○), [HCl] = 1.1 M; (∇), [HCl] = 2.5 M; a.g: (■) [HCl] = 0.1 M; (●) [HCl] = 1.0 M.S.

The dependences of extraction ratio on extractant concentration are given in Fig. 5. It is clear from the figure that the extractant dependence is less than unity for t. g. reagent, whereas, it is greater than 1.5 for a.g. reagent. The lower dependency of the t.g. extractant indicates its strong affinity towards Fe^{3+} species.

Fig. 6 shows the dependence of extraction ratio on temperature. The extraction with D2EHPA (t.g.), is little influenced by variation of temperature in lower temperature region (l.t.r.), whereas, in the higher temperature region (h.t.r.), the extraction ratio is decreased with increasing temperature. Figure also contains two plots for a.g. reagent. In this case, log D values are increased linearly on increasing temperature (lowering of 1/T value), when H^+ concentrations kept at and below 0.10 M; however, at higher $[H^+]$ regions, the log D vs 1/T K plots pass through maxima at ~35°C. From the slope of the lines in h.t.r., the apparent enthalpy change for the extraction reactions (ΔH) values have been evaluated for D2EHPA (t.g.) systems. On the other hand, for a.g. reagent, the ΔH values have been evaluated from the straight line or tangential line in the l.t.r. The estimated ΔH values indicate that the overall extraction reaction is exothermic in nature in the h.t.r. but is almost

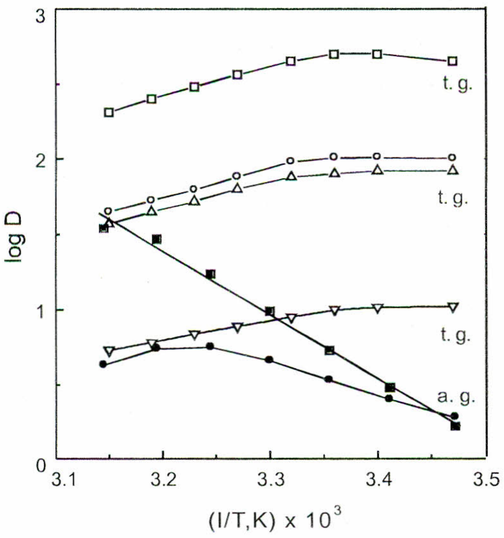

Fig. 6. Dependence of extraction ratio of Fe^{3+} on temperature. $[Fe^{3+}]_{(ini)}$ = 8.95 mM, shaking time = 1h; $[H_2A_2]_{(o)}$ = 0.05 M; $[Cl^-]$ = 3 M; (□) $[H^+]$ = 0.1 M; s_{htr} = 2000; (○) $[H^+]$ = 1.0 M; s_{htr} = 1950; (Δ) $[H^+]$ = 1.2 M; s_{htr} = 1666; (∇) $[H^+]$ = 3.0 M; s_{htr} = 1154; (■) $[H^+]$ = 0.1 M; s = -4540; (●) $[H^+]$ = 1M s_{ltr} = -2123.

system and those obtained in the l.t.r. for D2EHPA (t.g.) with the variation of log $[H^+]$ are shown in Fig. 7. The figure shows that ΔH value is too much dependent of $[H^+]$ for D2EHPA (a.g.) and the value of ΔH is increased with increasing $[H^+]$. In case of D2EHPA (t.g.), ΔH value is almost independent on $[H^+]$ below 1.2 M and above 1.2 M $[H^+]$, the value is slightly increased with increasing acid concentration.

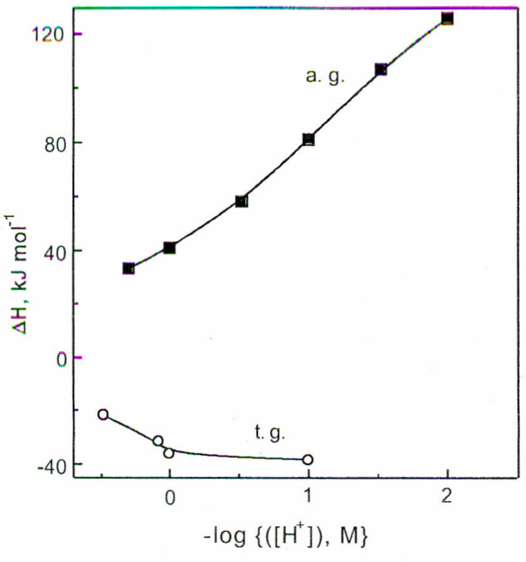

Fig. 7. Variation of ΔH value on $[H^+]$.

Fig. 8 represents the loading results for both grades of D2EHPA. With D2EHPA (a.g.), 0.5 M D2EHPA can load up to 0.485 M Fe^{3+} at [HCl] of 0.05 M and 0.1974 M Fe^{3+} at [HCl] of 1 M. In the first case, D2EHPA to Fe^{3+} mole ratio in saturated organic phase is 1, whereas, in the second case, the ratio is 2.5. The loading capacities are 8.38 g Fe^{3+} and 3.41 g Fe^{3+} per 100 g D2EHPA (a.g.). On the other hand, for t.g. D2EHPA, 0.1 M extractant can load up to 0.13 M Fe^{3+} at $[Cl^-]$ = 3 M and $[H^+]$ = 0.13 M, whereas, 0.061 M Fe^{3+} at $[Cl^-]$ = 3 M and $[H^+]$ = 3 M. In the first case extractant to Fe^{3+} mole ratio is ~0.7, whereas, it is ~1.5 in the second case and the loading capacities are 13.13 and 6.19 g Fe^{3+} per 100 g t.g. extractant, respectively.

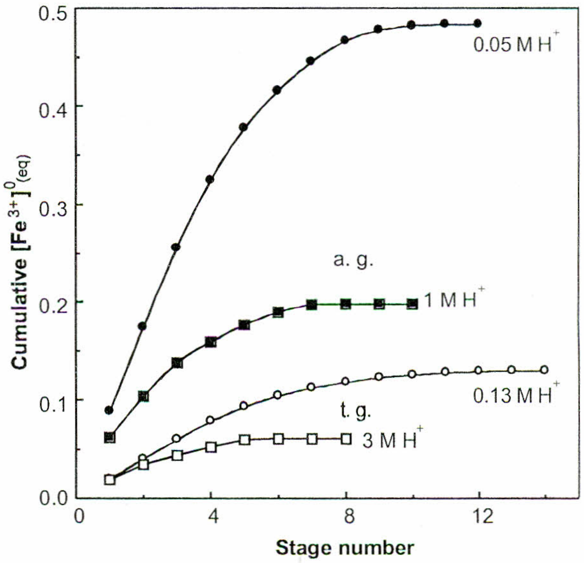

Fig. 8. Loading of organic phase by Fe^{3+}. For D2EHPA (t.g.): $[Fe^{3+}]_{(ini)}$ = 0.02 M; $[H_2A_2]_{(o)}$ = 0.1 M; $[Cl^-]$ = 3 M; shaking time = 1 h; (○) $[H^+]$ = 0.13 M; (□) $[H^+]$ = 3 M; For D2EHPA (a.g.): $[Fe^{3+}]_{(ini)}$ = 8.95 mM; shaking time = 1 h; $[H_2A_2]_{(o)}$ = 0.5 M; Temp = (303±1) K; (●), $[H^+]$ = 0.05 M; (■), $[H^+]$ = 1 M.

The aqueous chemistry of Fe^{3+} in the chloride medium is very complicated. According to Gamlen and Jordan (1953), Fe^{3+} forms various Fe^{3+}- Cl^- complex species with increasing $[Cl^-]$ in the aqueous phase. At assumed 0.005 M Cl^-, Fe^{3+} or $[Fe(H_2O)_6]^{3+}$ exists principally and as concentration of Cl^- increases, $FeCl^{2+}$, $FeCl_2^+$, $FeCl_3$, $HFeCl_4$, etc are formed gradually. At about 1 M Cl^- or HCl solution $FeCl^{2+}$, $FeCl_2^+$ and $FeCl_3$ are present. The species $HFeCl_4$ appears at $[Cl^-]$ of 3 M. The species H_xFeCl_{3+x} (where x>1) also appeared at higher $[Cl^-]$, Nechtrieb and Conway (1948).

In case of extraction with D2EHPA (a.g.), the involvements of Fe^{3+}, $FeCl^{2+}$, $FeCl_2^+$, $FeCl_3$, etc. during extraction have been suggested and the experimental data have been quantitatively analyzed (Arunkumar *et al.*, 1998). But the quantitative explanation of the extraction data with D2EHPA (t.g.) seems to be very difficult because of the involvement of at least eight extraction reactions {four types of Fe^{3+} species, combining with D2EHPA (H_2A_2) and M2EHPA (H_4A_2)}.

However, M2EHPA possesses three coordinating atoms. Therefore, if a M2EHPA molecule or ion (H_4A_2 or $H_3A_2^-$) combines to an iron species through two coordination positions then the remaining coordinating atom may combine with another iron species to form polymeric species (Islam and Biswas, 1981). This may account for very low extractant dependence of 0.66 to 0.93. The change of the extratant dependence will be illustrated in the following mechanism part.

The literature reports (Arunkumar *et al.*, 1998; Aprahamian and Demopoulos, 1995) indicate that in 3 M [Cl^-] or [HCl] medium 0% Fe^{3+}, 5.1% $FeCl^{2+}$, 22.7 % $FeCl_2^+$, 70.7% $FeCl_3$ and 1.5% $HFeCl_4$ exist. In 3 M Cl^- and high [H^+] region of investigation, the H^+ and Cl^- dependences of minus unity suggest the following reactions for extraction (H_4A_2 represents M2EHPA which may be replaced by H_2A_2 representing D2EHPA):

$$HFeCl_4 + H_4A_2 \leftrightarrows FeCl_3.H_4A_2 + H^+ + Cl^- \tag{1}$$

$$FeCl_3 + H_4A_2 \leftrightarrows FeCl_2.H_3A_2 + H^+ + Cl^- \tag{2}$$

Second reaction seems to be more probable as $FeCl_3$ exists in 3 M Cl^- medium upto 70.7 %. Extractant dependence of less than unity suggests the co-extractions of $FeCl_3.H_4A_2$ and $FeCl_2.H_3A_2$, with parallel formations of $FeCl_3.H_2A_2$ and $FeCl_2.HA_2$, respectively by D2EHPA.

At about 1 M [H^+], Fe^{3+} is extracted from 3 M Cl^- medium by following reactions (H^+ dependence is almost zero and Cl^- dependence is + 0.5):

$$FeCl_2^+ + Cl^- + H_4A_2 \leftrightarrows FeCl_3.H_4A_2 \tag{3}$$

$$FeCl_3 + H_4A_2 \leftrightarrows FeCl_3.H_4A_2 \tag{4}$$

together with the extracted species being $FeCl_3.H_2A_2$ in both cases with D2EHPA.

Around 0.1 M [H^+] and 3 M [Cl^-], H^+ dependence of about -1 and Cl^- dependence of about -0.3 suggest the extraction by following reactions:

$$FeCl_2^+ + H_4A_2 \leftrightarrows FeCl_2.H_3A_2 + H^+ \tag{5}$$

$$FeCl_3 + H_4A_2 \leftrightarrows FeCl_2.H_3A_2 + H^+ + Cl^- \tag{6}$$

If due to kinetic factor, most of the reaction product, $FeCl_2.H_3A_2$ (~70%) is formed via equation (5) and the rest via equation (6), then the H^+ and Cl^- dependences may be explained. If the kinetics of the reaction represented by equation (5) is fast, then the quick extraction of $FeCl_2^+$ from the aqueous solution results in the disturbance on equilibria between the Fe^{3+} and Cl^- species and consequently, $FeCl_2^+$ will be formed in the medium from $FeCl_3$ and $FeCl^{2+}$. The corresponding D2EHPA extracted species is $FeCl_2.HA_2$.

Above reactions for extraction are just proposed, not proved. $FeCl_3.H_4A_2$ and $FeCl_2.H_3A_2$ may extract more $FeCl_3$ by following type of reaction:

$$FeCl_3.H_4A_2 + FeCl_3 \leftrightarrows 2FeCl_3.H_2A \tag{7}$$

$$FeCl_2.H_3A_2 + FeCl_3 \leftrightarrows 2FeCl_2.HA + Cl^- + H^+ \tag{8}$$

The very low extractant dependence has been proved by the loading results. The extraction of 0.13 M Fe^{3+} by 0.1 M t.g. extractant suggests the presence of less than one dimeric molecule of extractant (H_2A_2 or H_4A_2) in the extracted species. Thus, the extraction by above two reactions is also feasible. In case of pure D2EHPA, the extractant dependences are greater than unity (Arunkumar *et al.*, 1998) and therefore, the existence of synergism cannot be ruled out. Although the synergistic extraction of Fe^{3+} from Cl^- medium by a mixture of D2EHPA and PC-88A / Cyanex 272 has been proved by Sandhibigraha *et al.* (2000 and1996), the same by a mixture of D2EHPA and M2EHPA is yet to be established on carrying out a separate thorough study.

The stripping of Fe^{3+} from the organic phase by both HCl and H_2SO_4 solutions has been investigated. Fig. 9 illustrates the stripping results, where the percentage of Fe^{3+} stripped has been plotted against [HCl] and [H_2SO_4]. For HCl, it is found that the stripping percentage of Fe^{3+} is increased considerably

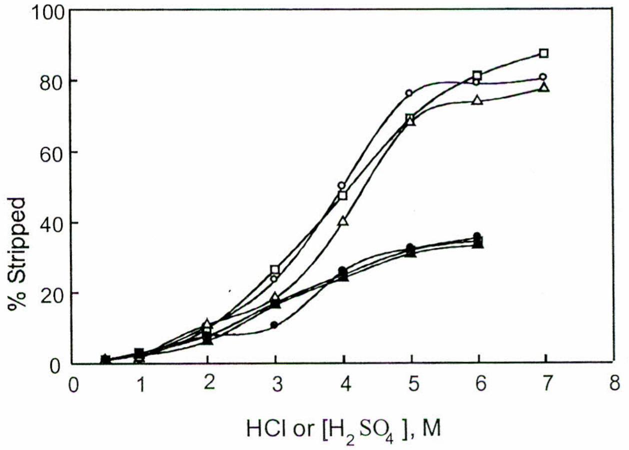

Fig. 9. Stripping of Fe^{3+} by HCl and H_2SO_4 solutions. Strippable organic phases were prepared at [HCl] of 2 M (○ ,●); 1.3 M (□ ,■) and 0.3 M (Δ, ▲). Open and closed symbols are for HCl and H_2SO_4, respectively. Temp = 303 K, time = 1h.

with increasing acid concentration particularly within 3 ~ 5 M. Below 3 M and above 5 M, the variation of stripping % of Fe^{3+} is low. Stripping percentage of Fe^{3+} is little varied on the variation of aqueous acidity used in the extraction for preparation of strippable organic phase. Sulphuric acid solution is found to be less effective for stripping. A 6 M H_2SO_4 solution can strip ~35 % Fe^{3+}; whereas, a 5 M HCl solution can strip ~70% Fe^{3+} within 1 h. It is therefore recommended to use 5 M HCl as stripping agent.

Fig. 10 represents the results of stagewise stripping. If 5 M HCl is used as stripping agent at organic to aqueous phase ratio of 1, then cumulative ~93 % Fe^{3+} is stripped in second stage and 99.4 % Fe^{3+} is stripped in the third stage. Therefore, it is suggested to perform stage stripping by 5 M HCl for quantitative stripping of Fe^{3+}. The regenerated organic phase can be reused in extraction after making up the solution with calculated amounts of M2EHPA (Hoechst Chemical Co. under trade name LPKN), with the consideration that M2EHPA washes out more than D2EHPA during extraction and stripping. However, the solubilities depend on the concentration regions of extractants used and of H^+ in the aqueous phase. In general, M2EHPA will be more soluble than D2EHPA because the former contains one C_8 chain, whereas, the latter contains two C_8 - chains. In the case of Co/Ni separation in weak sulphuric acid solutions, the solubility of D2EHPA has been reported in the order of 30 ppm (Ritcey *et al.*, 1975). In a McGill University / CANMET pilot plant study, M2EHPA levels in generated raffinates and HCl strip liquors are reported to be 80 and 500 ppm, respectively. This implies that M2EHPA solubility or degradation (hydrolysis of the ester to orthophosphoric acid and alcohol) is much higher in the strong HCl strip liquor than in the H_2SO_4 - based raffinates.

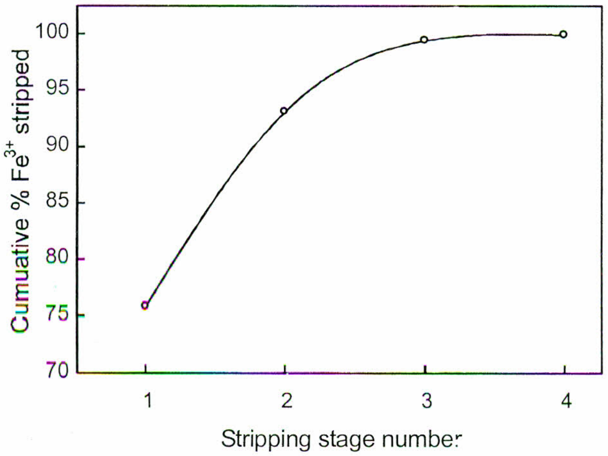

Fig. 10. Stage-wise stripping. Strippable organic phase was prepared at [HCl] = 2 M. Stripping agent = 5 M HCl; temp = 303 K; time = 1 h (each stage).

It can be demonstrated that 0.10 mol dm^{-3} D2EHPA (t.g.) and 0.057 M dm^{-3} D2EHPA (a.g.) on contact with 0.5 M dm^{-3} H_2SO_4 solution for 1 h (phase separation time = 24 h) at 25 °C produce aqueous solutions containing 3.25 mg dm^{-3} and 0.35 mg dm^{-3} phosphorous, respectively. Therefore, 3.215 mg dm^{-3} phosphorous comes from M2EHPA present in D2EHPA (t.g.). These results indicate that the solubilities of M2EHPA and D2EHPA from 0.1 M dm^{-3} D2EHPA (t.g.) are 21.78 mg dm^{-3} and 0.36 mg dm^{-3}, respectively. Similarly, 0.1 M dm^{-3} D2EHPA (t.g.) and 0.057 M dm^{-3} D2EHPA (a.g.) on contact with 5 M dm^{-3} HCl solution for 1 h (phase separation time = 24 h) at 25 °C produce aqueous solutions containing 34.45 mg dm^{-3} and 0.10 mg dm^{-3} phosphorous, respectively. Therefore, 34.35 mg dm^{-3} phosphorous comes from M2EHPA present in D2HPA (t.g.). These results indicate that the solubilities of M2EHPA and D2EHPA from 0.1 M dm^{-3} D2EHPA (t.g.) in 5 M dm^{-3} HCl are 232.7 mg dm^{-3} and 1.04 mg dm^{-3}, respectively. Consequently, the losses of M2EHPA and D2EHPA from 0.1 M dm^{-3} t.g. D2EHPA in single stage extraction followed by three stage stripping with 5 M dm^{-3} HCl are estimated to be 720 mg dm^{-3} and 3.15 mg dm^{-3}, respectively.

Conclusion

The following conclusions can be drawn

- D2EHPA (t.g.) containing 43% M2EHPA is a very effective extractant for extracting Fe^{3+} from acidic chloride solution.
- D2EHPA (t.g.) can extract more than 90 % Fe^{3+} from high acidic solution (say 5 M) compared to some 1 % extraction by D2EHPA (a.g.). At lower [H^+] (say 1 M-0.1 M) in the aqueous phase more than 99 % extraction occurs by D2EHPA (t.g.), whereas, some 50 % extraction occurs by D2EHPA (a.g.). Therefore, D2EHPA (t.g.) finds its application in Fe^{3+} removal particularly from the medium having very high concentration of HCl.
- Mechanism is difficult to provide due to the presence of many probable extraction reactions involved there.
- The extraction processes are exothermic for (t.g.), whereas, endothermic for (a.g.). The variation of ΔH value with [H^+] is not so pronounced in the case of t.g. compared to that in the case of D2EHPA (a.g.).
- Hydrochloric acid (5 M) is found to be effective for three stage-stripping (quantitative) of Fe^{3+}. Sulphuric acid is not so effective; 6 M H_2SO_4 strips only 35 % Fe^{3+} in single stage.
- Recycling of the organic phase needs to make up this phase with calculated amount of M2EHPA,

which depends on extractant concentration, nature of diluent, aqueous acidities in extraction and stripping together with the number of stripping stages.

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