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Cyanex 302: An extractant for Fe^{3+} from Chloride Medium

M. R. Ali[a], R. K. Biswas[a]*, S. M. A. Salam[a], A. Akhter[b], A. K. Karmakar[a] and M. H. Ullah[a]

[a]*Department of Applied Chemistry and Chemical Engineering, Rajshahi University, Rajshahi-6205, Bangladesh and* [b]*Bangladesh Council of Scientific and Industrial Research Laboratories, Binodpur Bazar, Rajshahi-6206, Bangladesh*

Abstract

The solvent extraction of Fe^{3+} from aqueous chloride solution by bis-(2,4,4-trimethylpentyl) monothiophosphinic acid (Cyanex 302, H_2A_2) dissolved in kerosene has been investigated over a wide range of aqueous acidity as a function of phase contact time, concentrations of Fe^{3+}, H^+ and Cl^- in the aqueous phase, Cyanex 302 concentration in the organic phase and temperature. The equilibration time is 50 min. The distribution ratio is found to be independent on $[Fe^{3+}]$ in the aqueous phase at a constant aqueous acidity and extractant concentration. The H^+, extractant and Cl^- dependences are -1, 0.5 in low concentration region of extractant and -0.5, respectively; which suggest that extraction occurs via the following two parallel reactions: (i) $FeCl_3 + 0.5\ H_2A_{2(o)}$ ⇌ $FeCl_2.A_{(o)} + H^+ + Cl^-$; and (ii) $FeCl_2^+ + 0.5\ H_2A_{2(o)}$ -----$FeCl_2A_{(o)} + H^+$. Temperature dependence data give ΔH value of 9.95 kJ/ mol. The loading capacity of Cyanex 302 towards Fe^{3+} is 29.41 g Fe^{3+}/100 g Cyanex 302. The extraction equilibrium constant (K_{ex}) is $10^{-0.632}$. Extraction ratio is found to be dependent on diluent used. Stripping of the extracted complex is found to be a difficult task, but may be made effective by a solution containing 6 M H_2SO_4 and 1 M $Na_2C_2O_4$.

Keywords: Extraction equilibrium, Fe^{3+} extraction, Cyanex 302, Chloride medium.

Introduction

Iron-bearing compounds like oxide, sulfide, silicate, aluminates and metallic ferrites etc. are present as gangue materials in sulfide and non-sulfide ores of many common valuable metals. Therefore, it becomes necessary to separate iron from an acidic leach solution of an ore for the production of a pure metal hydrometallurgically and this can be carried out by the solvent extraction technique.

The solvent extraction of Fe^{3+} by various organophosphorous compounds has been investigated widely. The works with tributylphosphate (TBP), dibutylphosphate (DBP), dodecylphosphoric acid etc. have been referenced by Sekine and Hasegawa (1977). Di-2-ethylhexylphosphoric acid (D2EHPA) has been widely used for the extraction of Fe^{3+} (Islam and Biswas, 1981; Roddy *et al.,* 1971; Karpacheva and Ilozheva, 1969; Baes and Baker, 1960; Sato *et al.* 1985a, 1985b; Biswas and Islam, 1982, 1985; Biswas and Begum, 1998, 1999, 2001). Demopoulos and Pouskouleli (1989) and Principe and Demopoulos (1998) have used mono-2-ethylhexylphosphoric acid (M2EHPA) for the same. The phosphinic acid derivative, bis-(2,4,4-trimethylpentyl) phosphinic acid (BTMPPA, commercially known as Cyanex 272) has also been used for the extraction of Fe^{3+} (Miralles *et al.,* 1992; Demopoulos *et al.*, 1993; Biswas and Singha, 2006; Biswas *et al.*, 2007).

About 15 years back, American Cyanamide introduced two thiophosphinic acid extractants, Cyanex 301 (bis-(2,4,4-trimethylpentyl) dithiophosphinic acid, $C_{16}H_{35}PS_2$) and Cyanex 302 (bis-(2,4,4-trimethylpentyl) monothiophosphinic acid, $C_{16}H_{35}POS$). The yellow colored Cyanex 302 contains 83 - 87% of bis-(2,4,4-trimethylpentyl) monothiophosphinic acid and there is still no way to purify it more. Some physical constants of the supplied Cyanex 302 are pK_a in water = 5.63, density = 930 kg m^{-3}, viscosity = 19.5 kg m^{-1} s^{-1}, molar mass = 306 g mol^{-1}, aqueous solubility = 15.1 mg dm^{-3}, flash point = 145°C, auto ignition temperature = 415°C and decomposition temperature = 337° C. Sulphur substitution increases the acidity of phosphinic acid and this makes the extractant particularly suitable for the extractions of soft Lewis acid (Class B type) metal ions, such as Ag(I), Ni(II), Zn(II), Cu(I), Au(I) and Pt(II) in accordance with the HSAB principles.

*Corresponding author. E-mail: rkbiswas53@yahoo.com

Using Cyanex 302 as an extractant, the extractions of Zn(II) by Benito *et al.* (1996); Ho(III), Y(III) and Er(III) by Wu *et al.* (2007); U(VI) by Karve and Gaur (2007); rare earth ions by Wu *et al*. (2006); Zr(IV) by Reddy *et al*. (2004); U(IV) by Abdel Rahman *et al.* (2003); Pb(II) by Argekar and Shetty (1998); Cu(II) by El-Hefny and Daoud (2007); extractive separation of Sb(III) and Bi(III) by Sarkar and Dhadke (1999) etc. have been reported. There appears no thorough study on the extraction equilibrium of Fe(III) from any medium by Cyanex 302 in the literature; though a report on the extractive separation of Fe(III) and Al(III) using this extractant by Ajgaonkar and Dhadke (1997) has been published. Therefore, it appears worthy to make a thorough investigation on the mechanistic extraction equilibrium of the Fe(III)-Cyanex 302 system. This paper discusses the possibility of the extraction of Fe^{3+} from chloride medium by Cyanex 302 dissolved in kerosene with an aim to apply these equilibrium data in cases of hydrochloric acid leached as well as pickled solutions of any metallic source.

Materials and Methods

Reagents

Cyanex 302 was gifted by Cytec Canada Inc. 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 grades and used without further purifications.

Analytical

The concentration of Fe^{3+} in the aqueous phase was determined by the thiocyanate method (Bassette *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 1 litre 0.1 M H_2SO_4 solution (1 mL = 0.1 mg Fe^{3+}). The acidity of the aqueous phase was adjusted by addition of HCl; whilst the chloride ion concentration was adjusted by addition of NaCl.

Extraction procedure

 A stock solution of $FeCl_3$ was prepared to contain 10.01 g Fe^{3+} (0.179 M Fe^{3+}), 0.12 M H^+ and 0.657 M Cl^-. This solution was used to prepare the aqueous phases containing different amounts of H^+, Cl^- and Fe^{3+} for the study of the extraction behavior of Fe^{3+}. The extraction procedures are

given elsewhere (Biswas and Begum, 1998; Biswas *et al.*, 2007). Equal aliquots of organic and aqueous phases (20 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 allowed to settle, separated and the Fe^{3+} concentration in the separated aqueous phase was estimated as stated. The concentration of Fe^{3+} in the organic phase was calculated by mass balance. The value of the extraction or 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.

Loading procedure

Loading of Fe^{3+} in 0.1 M Cyanex 302 solution was carried out by vigorous contact of this phase (50 mL) repeatedly with fresh aqueous solutions (containing 0.083 M Fe^{3+}, 0.02 M H^+ and 1 M Cl^-) of same volume until the organic phase was saturated with Fe^{3+}. After each contact, the phases were disengaged and aqueous phases were analyzed for Fe^{3+} contents. The amount of Fe^{3+} transferred into the organic phase during each contact was then calculated by difference and cumulative concentrations of Fe^{3+} in the organic phase (cumulative $C^o_{Fe^{3+}}$, g/L) achieved after each stage of contact were determined.

Stripping Procedure

Equal aliquots (25 mL) of the organic phase containing 1 g/L Fe^{3+} with practically no free extractant in kerosene were contacted with various stripping agents such as 1 and 6 M HCl, HNO_3, H_2SO_4, $HClO_4$ and a solution containing 6 M H_2SO_4 and 1 M $Na_2C_2O_4$ for 1 h at 303 K. After shaking, the phases were disengaged and the aqueous phases were analysed for Fe^{3+} contents.

Results and Discussion

The preliminary experiments show that the concentration ratio ($[Fe^{3+}]_{(o)}/[Fe^{3+}]_{(aq)}$) increases almost exponentially on increasing phase contact time up to 50 min for the investigated system, which indicates that the equilibration time for the system is 50 min. In all subsequent experiments, the phase contact time of 1 h has been allowed to ensure equilibration under different experimental conditions. Previously, it has been reported that the equilibration times for the extraction of Fe^{3+} from chloride medium by D2EHPA in kerosene (Biswas and Begum, 1998) and by Cyanex 272 in kerosene (Biswas and Singha, 2006) are 50 min. So the equilibration

time for the extraction of Fe^{3+} from chloride medium by Cyanex 302 in kerosene is similar to that by D2EHPA as well as Cyanex 272 in kerosene.

Figure 1 shows the variation of D with initial $[Fe^{3+}]$ (3.67 mM - 85.9 mM) at 1.0 M HCl in log-log scale. It is found that the distribution ratio (D) is independent on the initial Fe^{3+} concentration in the aqueous phase. In chloride medium, Fe^{3+} is believed to exist as Fe^{3+}, $FeCl^{2+}$, $FeCl_2^+$, $FeCl_3$ and $HFeCl_4$ etc. in the aqueous phase (Gamlen and Jordan, 1953). Their proportions may vary with the concentration of Cl^- and Fe^{3+} in the aqueous phase. However, the independence of distribution ratio on initial Fe^{3+} concentration in the aqueous phase suggests that the extraction of a particular Fe^{3+}- Cl^- species causes simultaneous rapid equilibrium shifts among the various Fe^{3+}- Cl^- species existing in the aqueous phase.
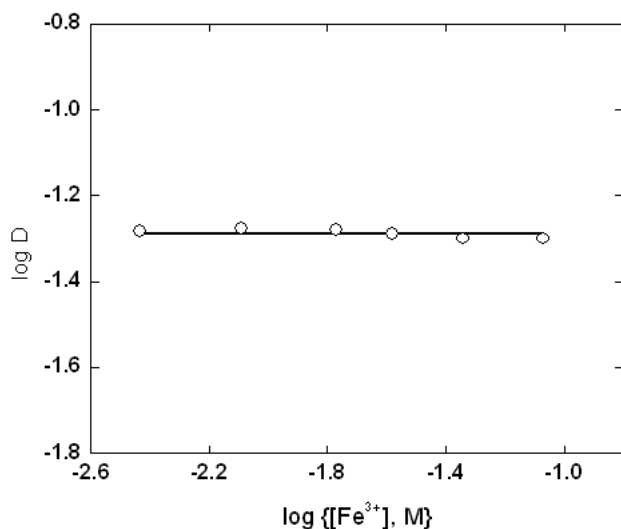
Fig. 1: Dependence of distribution ratio (D) on initial $[Fe^{3+}]$ in the aqueous phase. $[H^+]$ = 1.0 M; $[Cl^-]$ = 1.0 M; [Cyanex 302] = 0.2 M; Temp. = (303 ± 1) K; Equilibrium time = 1 h.

Variations of D with H^+ concentration (keeping Cl^- concentration at 1.0 M) are shown in Fig. 2 as log D vs - $\log\{(H^+)$, M} plots at constant Cyanex 302 concentrations of 0.01 and 0.10 M. The experimental points for a particular Cyanex 302 concentration system fall on a straight line of unity slope. The Least Squares Slope (s) and Intercept (*I*) of the lines are: *s* = 1.02, *I* = -1.552 for 0.01 M Cyanex 302 system and *s* = 1.05, *I* = -1.292 for 0.1 M Cyanex 302 system. The H^+ dependence of -1 indicates the liberation of 1 g ion of H^+ during extraction of 1 g ion of Fe^{3+} by Cyanex 302. Low $[H^+]$- functionality shows that ~10% extraction at $[H^+]$ = 0.3 g

ion is increased to only ~90% extraction at at $[H^+]$ = 0.005 g ion by 0.10 M extractant.
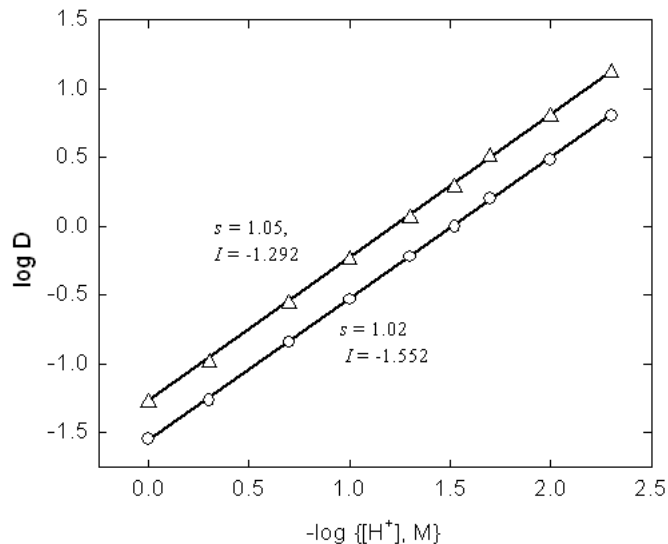
Fig. 2: **Dependence of distribution ratio of Fe^{3+} on $[H^+]$. $[Fe^{3+}]_{(ini)}$ = 3.58 mM; shaking time = 1 h; Temp. = (303 ± 1) K; $[Cl^-]$ = 1.0 M; (ο) = 0.01 M Cyanex 302; (Δ) = 0.1 M Cyanex 302.**

Figure 3 represents the log D vs log {[Cyanex 302], M}$_{(ini)}$ plots for 0.01 and 0.02 M H^+ concentrations (at constant $[Cl^-]$ of 1.0 M). The plots are straight lines with a low positive slope of ~0.50 up to 0.01 M extractant concentration, and above this concentration, the increasing rate of log D with
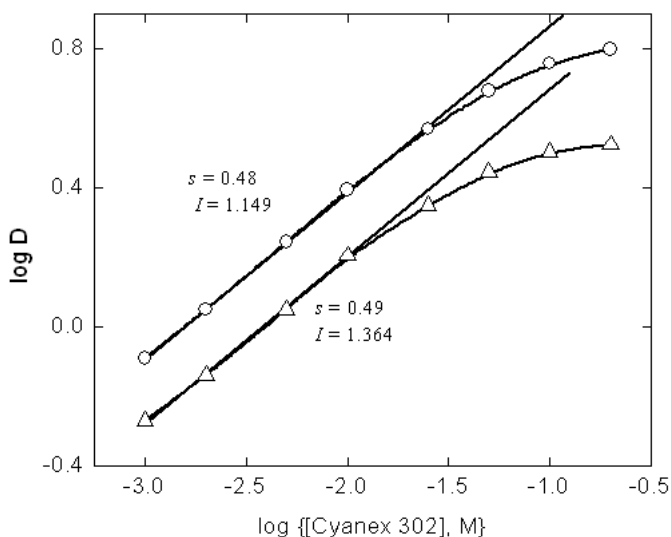
Fig. 3: **Dependence of distribution ratio of Fe^{3+} on [Cyanex 302]. $[Fe^{3+}]_{(ini)}$ = 3.58 mM shaking time = 1 h; Temp. = (303 ± 1) K; $[Cl^-]$ = 1.0 M; (Δ) = 0.01 M H^+; (ο) = 0.02 M H^+.**

increasing log [Cyanex 302] is decreased to level off approximately. It is therefore concluded that the extraction ratio is directly proportional to the square root of extractant concentration up to its concentration of 0.01 M and is almost independent of extractant concentration in its concentration region above 0.3 M. It is also clear that Cyanex 302 possesses very low functionality towards the extraction of Fe^{3+}. The intercept of the extraploted inclined straight lines are 1.364 and 1.149 for 0.01 and 0.02 M H^+ systems, respectively.

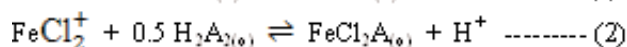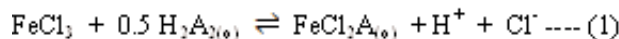Figure 4 shows the dependence of distribution ratio on chloride ion concentration as log D vs -log{[Cl⁻], M} plots at 0.01 and 0.02 M H^+ - concentration systems for 0.05 M Cyanex 302. The distribution ratio is found to increase with the increase of chloride ion concentration in the aqueous phase. The experimental points for a particular H^+ - concentration system fall on a straight line. The Least Squares Slope and Intercept of the lines are: $s = 0.44$, $I = 0.681$ and $s = 0.44$, $I = 0.453$ for 0.01 and 0.02 M H^+ systems, respectively.
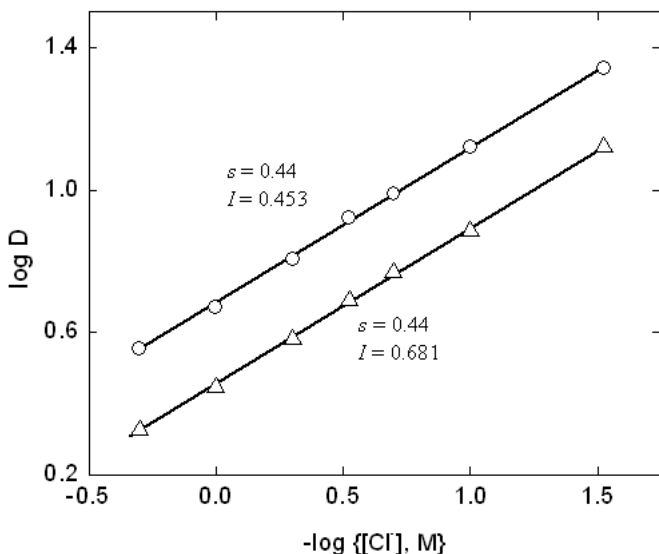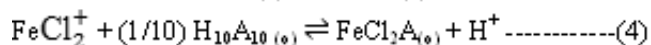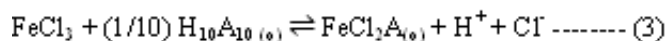

Fig. 4: **Dependence of distribution ratio of Fe^{3+} on [Cl⁻]. $[Fe^{3+}]_{(ini)} = 3.58$ mM; shaking time = 1 h; Temp. = (303 ± 1) K; [Cyanex 302] = 0.05 M; (O) = 0.01 M H^+; (Δ) = 0.02 M H^+.**

The literature reports (Biswas and Begum, 1998) indicate that in 1 M [Cl⁻] medium 20% Fe^{3+}, 15.8 % $FeCl^{2+}$, 39.2% $FeCl_2^+$ and 43% $FeCl_3$ exist. The acidic species such as $HFeCl_4$ (or, H_xFeCl_{3+x}) start to appear at [Cl⁻] > 2 M. It is therefore expected that the predominant aqueous Fe^{3+} species taking part in the extraction process are $FeCl_3$ and Fe . However, the equilibrium shifts among the mentioned Fe^{3+}

species cannot be ruled out during the progress of extraction. In 1 M [Cl⁻] and lower concentration region of Cyanex 302; the H^+, Cyanex 302 (H_2A_2) and Cl⁻ dependences are -1, 0.5 and -0.5, respectively, suggesting that the extraction occurs via the combination of the following two parallel reactions with almost equal contributions:

$$FeCl_3 + 0.5\ H_2A_{2(o)} \rightleftharpoons FeCl_2A_{(o)} + H^+ + Cl^- \ ---- (1)$$
$$FeCl_2^+ + 0.5\ H_2A_{2(o)} \rightleftharpoons FeCl_2A_{(o)} + H^+ \ -------- (2)$$

With the progress of extraction, the depletion of $[FeCl_2^-]$ is compensated by its rapid formation from $FeCl^{2+}$ and Fe^{3+}. The system is therefore a very complicated one due to extraction of various species with different kinetics resulting in the equilibrium shifts of various aqueous Fe^{3+}-Cl⁻ species. Furthermore, the experimental data of higher concentration region of extractant can be explained by its vigorous polymerization. Below its concentration of 0.01 M, Cyanex 302 is dimerized but with its increasing concentration polymerized species exists probably. If decameric species, for example, is supposed to exist in about 0.3 M Cyanex 302 solution, then the extractant dependence should be 0.10, according to the following reactions:
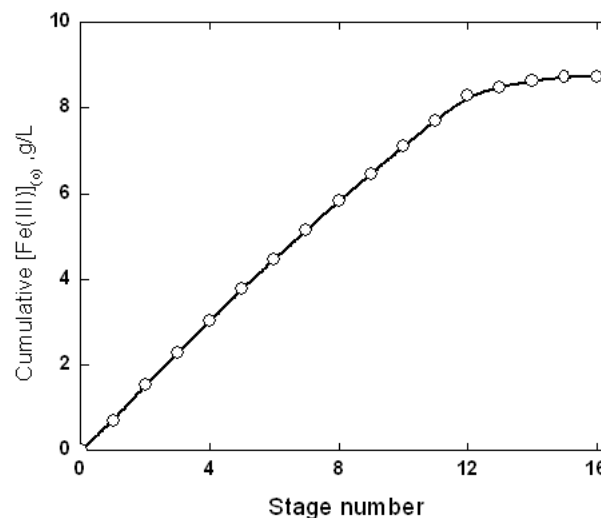
$$FeCl_3 + (1/10)\ H_{10}A_{10\ (o)} \rightleftharpoons FeCl_2A_{(o)} + H^+ + Cl^- \ -------- (3)$$
$$FeCl_2^+ + (1/10)\ H_{10}A_{10\ (o)} \rightleftharpoons FeCl_2A_{(o)} + H^+ \ ----------- (4)$$

The effect of temperature on the extraction of Fe^{3+} with 0.1 M Cyanex 302 has been studied in the temperature range of 20 to 45° C. Figure 5 shows the log D vs $(1/T\ K) \times 10^3$ plots for 0.03 M H^+ and 1.0 M Cl⁻ concentrations. It is found that the distribution ratio is increased with increasing temperature. The log D vs $(1/T\ K) \times 10^3$ plot is a straight line with slope equaling to -0.52×10^3 giving ΔH value of 9.95 kJ/ mol. The positive ΔH value indicates that the extraction process under investigation is over-all endothermic in nature and its low magnitude suggests that one of the extractable species formation reactions [by either Eq. (1) or Eq. (2)] might be exothermic.

The loading capacity defined as the amount of metal ion (g) extracted per 100 g of pure extractant, is a very important factor for commercially applicability an extractant. High loading capacity is desired for a particular extractant - metal ion system. Moreover, the species extracted at high loading may be easily converted to pure (usually solid) complexes for its structure determination by chemical and instrumental analysis. The cumulative $C^o_{Fe^{3+}}$ vs contact number plot is
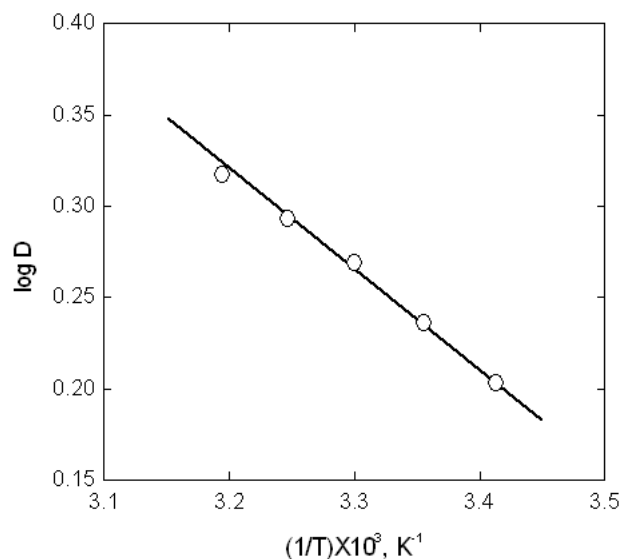
Fig. 5: Dependence of distribution ratio of Fe^{3+} on temperature. $[Fe^{3+}]_{(ini)} = 3.58$ mM; shaking time = 1 h; $[Cl^-] = 1.0$ M; $[H^+] = 0.03$ M; [Cyanex 302] = 0.1 M.

Fig. 6: Loading of organic phase (Cyanex 302) by Fe^{3+}. $[Fe^{3+}]_{(ini)} = 3.58$ mM; shaking time = 1 h; Temp. (303 ± 1) K; [Cyanex 302] = 0.1 M; $[H^+] = 0.02$ M; $[Cl^-] = 1.0$ M

given in Fig. 6. It is indicated that most of the Fe^{3+} existing in the aqueous phase is almost quantitatively extracted into the organic phase up to the 12th contact. Then the uptake of Fe^{3+} by Cyanex 302 is gradually decreased to zero at the 15th contact. This indicates the very high affinity of Cyanex 302 for Fe^{3+}. It is found from Fig. 6 that 1 L 0.1 M Cyanex 302 solution may extract as high as 8.72 g Fe^{3+}; indicatingthat the loading capacity of Cyanex 302 toward Fe^{3+} is 29.41 g Fe^{3+}/100 g Cyanex 302 in comparison to 8.38 g Fe^{3+}/100 g analytical grade D2EHPA (Biswas *et al*., 1998) and 13.13 g Fe^{3+}/ 100 g technical grade D2EHPA (Biswas *et al*., 2007).

The loading capacity indicates the association of 1 g ion of monomeric Cyanex 302 with 1 g ion of Fe^{3+}; ie. the extracted species is $FeCl_2A$. Thus the composition of extractable species at high loading is not changed from that at low loading (vide, Eqs. (1)-(4)).

From the intercepts of the lines in Figs 2, 3 and 4, the value of apparent extraction equilibrium constant [K_{ex}; average of K_{ex} for reactions represented by Eqs. (1) and (2)] for the extraction of Fe^{3+} by dilute Cyanex 302 solution (<0.01 M) has been evaluated and tabulated (Table I). The average

Table I: Elucidation of the value of apparent extraction equilibrium constant (K_{ex}) for the extraction of Fe^{3+} from 1 M Cl^- medium by Cyanex 302 dissolved in kerosene at 303 K.

Fig. No.	H^+], M	[Cyanex 302], M	$[Cl^-]$, M	Intercept, I	$\log K_{ex} = I - 0.5 \log$ [Cyanex 302] $+ 0.5 \log [Cl^-]$	$\log K_{ex} = I + \log [H^+] + 0.5 \log [Cl^-]$	$\log K_{ex} = I + \log [H^+] - 0.5 \log$ [Cyanex 302]	Average $\log K_{ex}$	Standard deviation
2		0.01	1.0	-1.552	-0.552	-	-		
		0.10	1.0	-1.292	-0.792	-	-		
3	0.01		1.0	1.364	-	-0.636	-	-0.632	0.09
	0.02		1.0	1.149	-	-0.550	-		
4	0.01	0.05		0.681	-	-	-0.668		
	0.02	0.05		0.453	-	-	-0.595		

value of log K_{ex} is -0.632 with a standard deviation of 0.09. The value of log K_{ex} for the Fe^{3+}-Cl^--Cyanex 272 system (Biswas *et al.*, 2006) is -2.3. This indicates that Cyanex 302 as a dilute solution is a better extractant for the extraction of Fe^{3+} from 1.0 M Cl^- medium than Cyanex 272.

The effect of diluents on the extraction of Fe^{3+} from (0.025 M H^+-1.0 M Cl^-) medium by 0.01 M Cyanex 302 has been investigated. Under similar extraction condition, the extraction ratio is found to vary in the following order: n-hexane (D = 2.45) > kerosene (D = 1.08) > toluene (D = 0.82) > cyclohexane (D = 0.53) > hexanol-1 (D = 0.12). It appears therefore that kerosene is a good diluent for the system considered but n-hexane is the best.

The stripping of the extracted species by 1 M and 6 M HCl, H_2SO_4, HNO_3 and $HClO_4$ as well as by (6 M H_2SO_4 + 1 M $Na_2C_2O_4$) mixture have been examined and the results are tabulated (Table II). It is seen that the mineral acid solutions (diluted or concentrated) are not at all effective for stripping of Fe^{3+} from $[FeCl_2A]_{(o)}$. However, the stripping may be made effective by a mixture of 6 M H_2SO_4 and 1 M $Na_2C_2O_4$. A three-stage stripping by this mixture may bring back ~95% Fe^{3+} into the aqueous phase. The stripping data indicates that the extracted complex is rather inert like Cr(III) complexes (Islam and Biswas, 1979).

from 1 M chloride medium. The equilibration time is 1 h, which is similar to that in the Fe^{3+}-Cl^--D2EHPA-kerosene system. The distribution ratio is independent of the initial Fe^{3+} concentration in the aqueous phase. The H^+, Cyanex 302 and Cl^- dependences of -1, 0.5 and -0.5, respectively, suggest that the extraction occurs via the combination of the following two parallel reactions:

$$FeCl_3 + 0.5\ H_2A_{2(o)} \rightleftharpoons FeCl_2A_{(o)} + H^+ + Cl^-$$
$$FeCl_2^+ + 0.5\ H_2A_{2(o)} \rightleftharpoons FeCl_2A_{(o)} + H^+$$

A very high loading capacity (29.41 g Fe^{3+}/ 100 g Cyanex 302) is obtained showing that the composition of extractable species at high loading is not changed from that at low loading. The value of the apparent extraction equilibrium constant (average of equilibrium constants for two parallel reactions) is estimated to be $10^{-0.632}$. The extraction process is over-all endothermic with ΔH value 9.95 kJ/ mol. Kerosene next to n-hexane is shown to be the best diluent for the system.

Acknowledgement

Table II: **Stripping of Fe^{3+} extracted $FeCl_2A$ complex.**
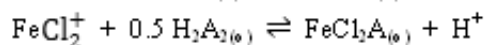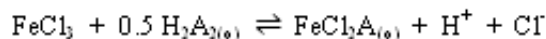   **$[Fe^{3+}]_{(o)}$ = 1 g/L, [Cyanex 302]$_{(ini)}$ = nil (practically), phase ratio = 1 (aqueous phase = 25 mL), temp. = 303 K, equilibration time = 1 h**

Stripping agent	Concentration of stripping agent, M	Stage No.	% stripped
HCl	1	1	~ 5
	6	1	~ 9
HNO_3	1	1	~ 6
	6	1	~ 11
HCl_4	1	1	~ 6
	6	1	~ 10
H_2SO_4	1	1	~ 6
	6	1	~ 11
(H_2SO_4 + $Na_2C_2O_4$)	(6 + 1)	1	~ 65
		2	~ 86 (cumulative)
		3	~ 95 (cumulative)

Conclusion

It is concluded that the dilute solution of Cyanex 302 in kerosene is a very effective extractant for extracting Fe^{3+}

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