J. Chem. Eng. Data **1999,** *44,* 1037−1040

Extraction of Iron(III) with Bis(2-ethylhexyl)phosphinic Acid and Bis(2-ethylhexyl)phosphoric Acid: Experimental Equilibrium Study

Mandar T. Naik and Purshottam M. Dhadke*

Department of Chemical Technology, University of Mumbai, Matunga, Mumbai 400 019, India

The distribution equilibrium of iron(III) between bis(2-ethylhexyl)phosphinic acid dissolved in hexane and acidic aqueous nitrate media has been investigated as a function of the concentration of extractant in the organic phase and the concentration of hydrogen ion and iron(III) the in aqueous phase. The extraction characteristics of bis(2-ethylhexyl)phosphoric acid toward iron(III) are also evaluated and compared with those of bis(2-ethylhexyl)phosphinic acid. The stoichiometry of the extracted species is determined on the basis of slope analysis. Iron is extracted by a cation-exchange mechanism as $FeR_3 \cdot 3HR$ by both extractants. The temperature dependence of the extraction equilibrium is examined by the temperature variation method to estimate the apparent thermodynamic functions (ΔH, ΔS, and ΔG). Both extraction processes are exothermic in nature, and an increase in temperature is not favorable.

Introduction

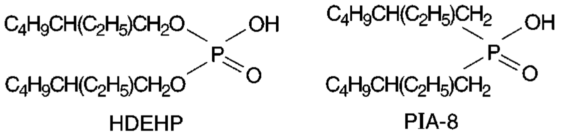
Iron is usually present as an impurity in leaching solutions, and its separation is of practical significance. The solid−liquid separations using precipitation of iron as iron compounds (such as jarosite, goethite, or ferric hydroxide) is expensive and tedious. It also results in adsorption of valuable metals on precipitates and pollution arising from long-term storage of the solid residue.

The removal of iron by solvent extraction especially by organophosphorus and carboxylic acid extactants is widely studied to prevent the formation and handling of solid precipitates. The common feature of these extractants is high selectivity for iron and difficult stripping of the iron-loaded organic phase (van der Zeeuw, 1977; Yu and Chen, 1989a). Some complicated techniques such as reductive stripping and hydrolytic stripping were suggested to solve this problem (Demopoulos, 1984; Majima et al., 1985; Monhemius and Thorsen, 1980; Muhl et al., 1980; Yu and Chen, 1989a).

Among the organophosphorus extractants, bis(2-ethylhexyl)phosphoric acid (HDEHP) is extensively studied for extraction of iron(III) (Baes and Baker, 1960; Sato and Nakamura, 1971). The kinetic aspects of this process suggest slow exchange rates in the presence of sulfuric acid (Coleman and Roddy, 1971; Sato and Nakamura, 1985). A number of new dialkyl phosphonic and phosphinic acid extactants have been commercialized in the last two decades. Yu and Chen (1989b) studied some of these extractants for iron in a synergistic study with amine extractants. Miralles et al. (1992) have given a computer analysis of the equilibrium data for extraction of iron(III) with bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex-272).

In the case of cobalt−nickel separation it has been revealed that the phosphinic acid extractants have better separation efficiency than the corresponding phosphoric or phosphonic acid derivatives (Pretson, 1982). The extractant bis(2-ethylhexyl)phosphinic acid (PIA-8) is found to be advantageous over Cyanex-272 for the refining of nickel sulfate solutions (Binghua et al., 1996) and in recovery of vanadium/molybdenum from a hydrodesulfurization catalyst (Pingwei, 1995). Bis(2-ethylhexyl)phosphinic acid is also used for extraction and separation of rare earths (Hino et al., 1996). Thus PIA-8 is a potentially promising extractant whose physiochemical properties are described elsewhere (Binghua et al., 1996).

In this paper we have compared the extractions of iron(III) from nitrate media with PIA-8 and HDEHP. The molecular structures of the two extractants are



Experimental Section

Chemicals.The extractants PIA-8 [bis(2-ethylhexyl)-phosphinic acid] and DP-8R [bis(2-ethylhexyl)phosphoric acid or HDEHP] were procured from Daihachi Chemical Industries, Japan. The reagents were found to be of high purity (98.3% and 97.9%, respectively) by two-phase potentiometric titration with 0.1 mol dm^{-3} NaOH in 80% ethanol−water medium and hence were used as received without any further purification. Hexane used as diluent was an analytical grade petroleum fraction.

Iron(III) stock solution was prepared by dissolving 7.234 g of iron(III) nitrate nonahydrate, $[Fe(NO_3)_3 \cdot 9H_2O]$, in doubly distilled water containing 10.0 mL of concentrated HNO_3 and diluting up to 1000 mL. The iron(III) concentration was found to be 1.796×10^{-2} mol dm^{-3} on titration with $K_2Cr_2O_7$ (Vogel, 1982). Working solutions of iron(III) were prepared by appropriate dilution of the standardized stock solution.

Apparatus. An Elico digital pH meter model LI-120 with a combined glass electrode was used for pH measurements (±0.01 pH). The meter was standardized against 4.01, 6.85, and 9.14 standard buffer solutions. A GBC model 911A UV−visible spectrophotometer with matched quartz cuvettes was used for the spectrophotometric determination

---

* Corresponding author. Fax: 91-22-4145614.

10.1021/je980280m CCC: $18.00

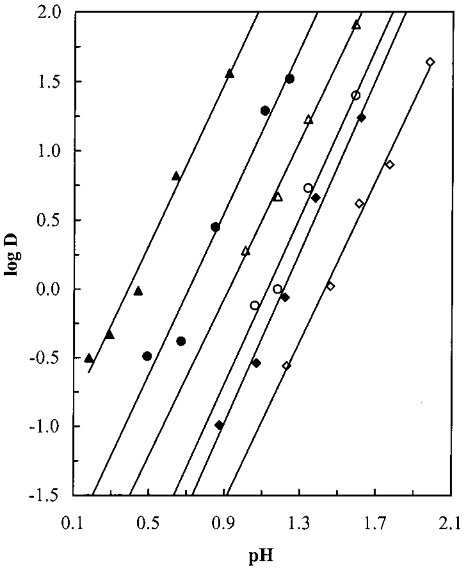


Figure 1. Effect of pH on extraction of Fe(III) with PIA-8 and HDEHP in hexane at the ionic strength I = 1.0 mol dm^{-3} ($NaNO_3$): (◇) 0.005 mol dm^{-3} PIA-8 {slope = 2.92, $R^2 = 0.991$}; (○) 0.009 mol dm^{-3} PIA-8 {slope = 3.06, $R^2 = 0.973$}; (△) 0.02 mol dm^{-3} PIA-8 {slope = 2.87, $R^2 = 0.995$}; (◆) 0.001 mol dm^{-3} HDEHP {slope = 3.12, $R^2 = 0.987$}; (●) 0.005 mol dm^{-3} HDEHP {slope = 2.95, $R^2 = 0.968$}; (▲) 0.01 mol dm^{-3} HDEHP {slope = 2.92, $R^2 = 0.984$}.

of iron. Each absorbance measurement (±0.001 absorbance units) was automatically integrated as a mean of triplicate readings.

General Extraction Procedure. All distribution equilibria studies were carried out at (303 ± 1) K (except for determining the effect of temperature) with an aqueous to organic phase volume ratio of 1:1. The ionic strength of the aqueous phase, [(Na^+, H^+, Fe^{3+}) NO_3^-], was kept constant at 1.0 mol dm^{-3} using sodium nitrate. The initial concentration of iron(III) in the aqueous phase was 8.95×10^{-5} mol dm^{-3} unless otherwise specified. An aliquot of 10 mL of extractant in hexane was equilibrated for 10 min with the same volume of aqueous iron(III) solution in a 125 mL separating funnel. After the phase separation, the pH of the aqueous phase was measured with a pH meter. The iron(III) concentration in the aqueous phase ($\pm 3 \times 10^{-7}$ mol dm^{-3}) was measured spectrophotometically at 480 nm using the thiocyanate method (Vogel, 1982). The iron(III) concentration in the organic phase was obtained by mass balance. The distribution coefficient D was obtained as the ratio of the equilibrium concentration of iron in the organic phase to that in the aqueous phase.

For determining the effect of temperature, the two phases were equilibrated in a glass reactor (inner diameter of 5 cm) with baffles, immersed in a thermostated oil bath with an accuracy of ±0.1 K using a four-blade glass stirrer. The mechanical stirring was carried out from outside using an automatically controlled electric motor at 100 ± 5 rpm after the two phases attained the requisite temperature. The iron content of the aqueous phase was estimated as explained earlier for a 5.0 mL sample of aqueous phase taken with a pipet.

Table 1. Extraction of Fe(III) as a Function of pH at Different PIA-8 Concentrations at the Ionic Strength I = 1.0 Mol dm^{-3} ($NaNO_3$)

$[H_2R_2]$/mol dm^{-3}	pH	[iron(III)]$_{aq}$/mol dm^{-3}	[iron(III)]$_{org}$/mol dm^{-3}	D
0.0025	1.23	7.02×10^{-5}	1.93×10^{-5}	0.275
0.0025	1.46	4.37×10^{-5}	4.58×10^{-5}	1.048
0.0025	1.61	1.73×10^{-5}	7.22×10^{-5}	4.17
0.0025	1.77	1.00×10^{-5}	7.95×10^{-5}	7.95
0.0025	1.98	0.20×10^{-5}	8.75×10^{-5}	44
0.0045	1.06	5.09×10^{-5}	3.86×10^{-5}	0.758
0.0045	1.18	4.48×10^{-5}	4.48×10^{-5}	0.998
0.0045	1.34	1.40×10^{-5}	7.55×10^{-5}	5.39
0.0045	1.59	0.34×10^{-5}	8.61×10^{-5}	25.3
0.010	1.01	3.08×10^{-5}	5.87×10^{-5}	1.91
0.010	1.18	1.58×10^{-5}	7.37×10^{-5}	4.66
0.010	1.34	0.50×10^{-5}	8.45×10^{-5}	16.9
0.010	1.59	0.11×10^{-5}	8.84×10^{-5}	80

Table 2. Extraction of Fe(III) As a Function of pH at Different HDEHP Concentrations at the Ionic Strength I = 1.0 mol dm^{-3} ($NaNO_3$)

$[H_2R_2]$/mol dm^{-3}	pH	[iron(III)]$_{aq}$/mol dm^{-3}	[iron(III)]$_{org}$/mol dm^{-3}	D
0.0005	0.87	8.12×10^{-5}	0.83×10^{-5}	0.102
0.0005	1.07	6.95×10^{-5}	2.00×10^{-5}	0.288
0.0005	1.22	4.78×10^{-5}	4.17×10^{-5}	0.872
0.0005	1.38	1.61×10^{-5}	7.34×10^{-5}	4.56
0.0005	1.62	0.49×10^{-5}	8.46×10^{-5}	17.3
0.0025	0.49	6.76×10^{-5}	2.19×10^{-5}	0.324
0.0025	0.67	6.32×10^{-5}	2.63×10^{-5}	0.416
0.0025	0.85	2.34×10^{-5}	6.61×10^{-5}	2.82
0.0025	1.11	0.44×10^{-5}	8.51×10^{-5}	19.3
0.0025	1.24	0.26×10^{-5}	8.69×10^{-5}	33
0.0050	0.18	6.80×10^{-5}	2.15×10^{-5}	0.316
0.0050	0.29	6.10×10^{-5}	2.85×10^{-5}	0.467
0.0050	0.44	4.53×10^{-5}	4.42×10^{-5}	0.976
0.0050	0.64	1.18×10^{-5}	7.77×10^{-5}	6.58
0.0050	0.92	0.24×10^{-5}	8.71×10^{-5}	36

Table 3. Effect of PIA-8 Concentration on Extraction of Fe(III) at the Ionic Strength I = 1.0 mol dm^{-3} ($NaNO_3$)

$[H_2R_2]$/mol dm^{-3}	pH	[iron(III)]$_{aq}$/mol dm^{-3}	[iron(III)]$_{org}$/mol dm^{-3}	D
0.0035	1.95	0.27×10^{-5}	8.68×10^{-5}	32
0.0030	1.90	0.41×10^{-5}	8.54×10^{-5}	20.8
0.0025	1.92	0.81×10^{-5}	8.14×10^{-5}	10.0
0.0020	1.92	1.02×10^{-5}	7.93×10^{-5}	7.77
0.0010	1.96	4.66×10^{-5}	4.29×10^{-5}	0.921

Table 4. Effect of HDEHP Concentration on Extraction of Fe(III) at the Ionic Strength I = 1.0 Mol dm^{-3} ($NaNO_3$)

$[H_2R_2]$/mol dm^{-3}	pH	[iron(III)]$_{aq}$/mol dm^{-3}	[iron(III)]$_{org}$/mol dm^{-3}	D
0.0010	1.50	0.54×10^{-5}	8.41×10^{-5}	15.6
0.0005	1.52	3.42×10^{-5}	5.53×10^{-5}	1.617
0.0003	1.54	5.58×10^{-5}	3.37×10^{-5}	0.604
0.0002	1.50	7.80×10^{-5}	1.15×10^{-5}	0.147

Results and Discussion

Stoichiometry of Extracted Species. The results for extraction of iron(III) for various concentrations of PIA-8 and HDEHP are shown in Figure 1 and Tables 1 and 2, respectively. The plots are straight lines with slopes = 3. This suggests full neutralization of the iron valency, leading to release of three protons. The distribution coefficient of iron at constant pH with both extractants was found to be independent of initial iron(III) concentration in range 1.75×10^{-5} to 3.58×10^{-4} mol dm^{-3}, indicating a mononuclear species under the experimental conditions. The extractants are known to exist as dimers in solvents of low polarity, and therefore the reaction can be given by eq 1.

$$Fe^{3+} + sH_2R_{2\,org} = FeR_3{\cdot}(2s - 3)HR_{org} + 3H^+ \quad (1)$$

If $FeR_3{\cdot}(2s - 3)HR$ is assumed to be the only species formed in the organic phase, the distribution coefficient D

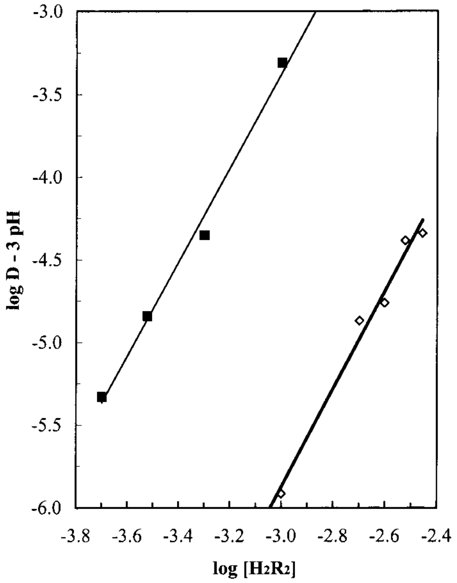


Figure 2. Effect of reagent concentration on extraction of Fe(III) at the ionic strength $I = 1.0$ mol dm^{-3} ($NaNO_3$): (◇) PIA-8 {slope = 2.96, $R^2 = 0.980$}; (■) HDEHP {slope = 2.85, $R^2 = 0.991$}.

and the apparent extraction equilibrium constant K'_{ex} are given as

$$D = \frac{[FeR_3{\cdot}(2s - 3)HR]_{org}}{[Fe^{3+}]} \qquad (2)$$

$$K'_{ex} = \frac{[FeR_s{\cdot}(2s - 3)HR]_{org}[H^+]^3}{[Fe^{3+}][H_2R_2]^s_{org}} = \frac{K_{ex}}{f(\gamma)} \qquad (3)$$

where K_{ex} is the extraction equilibrium constant and $f(\gamma)$ is the ratio of the activity coefficients of the species. Assuming $f(\gamma)$ is constant,

$$K'_{ex} = D \times \frac{[H^+]^3}{[H_2R_2]^s_{org}} \qquad (4)$$

$$\log K'_{ex} = \log D + 3 \log [H^+] - s \log [H_2R_2] \qquad (5)$$

$$\log D = \log K'_{ex} + 3pH + s \log [H_2R_2] \qquad (6)$$

Under the present experimental conditions the concentration of metal in the organic phase is negligible compared to the concentration of extractant (C_{HR}); therefore, the concentration of dimer was calculated as

$$[H_2R_2] = \frac{C_{HR}}{2} \qquad (7)$$

The plots of log D − 3pH against log $[H_2R_2]$ as shown in Figure 2 are straight lines with slopes of approximately 3, suggesting $s = 3$. The experimental data are given in Tables 3 and 4. The extracted species is thus concluded to be $FeR_3{\cdot}3HR$.

Effect of Temperature. An extraction study of iron(III) with both reagents was carried out in the range 303 K to 328 K. The extraction of iron decreases as the temperature increases, as shown in Tables 5 and 6. According to the Van't Hoff equation, the change in the equilibrium constant K'_{ex} with temperature is given as

$$\frac{\delta(\log K'_{ex})}{\delta(1/T)} = \frac{-\Delta H}{2.303R} \qquad (8)$$

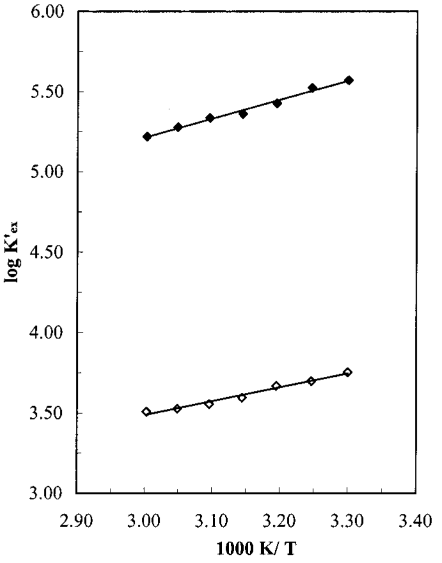


Figure 3. Effect of temperature on the extraction of Fe(III) at the ionic strength $I = 1.0$ mol dm^{-3} ($NaNO_3$): (◇) 0.009 mol dm^{-3} PIA-8 in hexane {slope = 0.86, $R^2 = 0.980$}; (◆) 0.01 mol dm^{-3} HDEHP in hexane {slope = 1.18, $R^2 = 0.986$}.

Table 5. Effect of Temperature on the Extraction of Fe(III) Using 0.0090 mol dm^{-3} PIA-8 in Hexane at the Ionic Strength $I = 1.0$ Mol dm^{-3} ($NaNO_3$)

T/K	pH	$[iron(III)]_{aq}$/mol dm^{-3}	$[iron(III)]_{org}$/mol dm^{-3}	D
303.0	1.06	5.03×10^{-5}	3.92×10^{-5}	0.779
308.0	1.04	5.60×10^{-5}	3.35×10^{-5}	0.598
313.0	1.03	5.89×10^{-5}	3.06×10^{-5}	0.520
318.0	1.02	6.34×10^{-5}	2.61×10^{-5}	0.412
323.0	1.05	6.12×10^{-5}	2.83×10^{-5}	0.462
328.0	1.04	6.38×10^{-5}	2.57×10^{-5}	0.403
333.0	1.05	6.33×10^{-5}	2.62×10^{-5}	0.414

Table 6. Effect of Temperature on the Extraction of Fe(III) Using 0.010 mol dm^{-3} HDEHP in Hexane at the Ionic Strength $I = 1.0$ mol dm^{-3} ($NaNO_3$)

T/K	pH	$[iron(III)]_{aq}$/mol dm^{-3}	$[iron(III)]_{org}$/mol dm^{-3}	D
303.0	0.44	4.54×10^{-5}	4.41×10^{-5}	0.971
308.0	0.44	4.78×10^{-5}	4.17×10^{-5}	0.872
313.0	0.45	5.13×10^{-5}	3.82×10^{-5}	0.745
318.0	0.43	5.74×10^{-5}	3.21×10^{-5}	0.559
323.0	0.44	5.72×10^{-5}	3.23×10^{-5}	0.565
328.0	0.46	5.71×10^{-5}	3.24×10^{-5}	0.567
333.0	0.45	6.12×10^{-5}	2.83×10^{-5}	0.462

The plots given in Figure 3 for log K'_{ex} versus $1/T$ were straight lines with positive slopes, indicating the exothermic nature of both processes. The enthalpy change was evaluated as $\Delta H = -16.47$ (± 0.05) kJ·mol^{-1} for PIA-8, and for HDEHP it is $\Delta H = -22.59$ (± 0.06) kJ·mol^{-1}.

The free energy change ΔG and entropy change ΔS are calculated from standard thermodynamic relationships, as shown in Tables 7 and 8. The negative free energy change suggests the spontaneous nature of both processes. The negative enthalpy change suggests that an increase in temperature will be unfavorable for both extraction processes.

Table 7. Thermodynamic Functions of Extraction of Iron(III) with PIA-8 in Hexane at the Ionic Strength $I = 1.0$ mol dm^{-3} ($NaNO_3$)

T/K	log D	log K'_{ex}	ΔG/ kJ·mol^{-1}	ΔS/ J·K^{-1}·mol^{-1}	ΔH/ kJ·mol^{-1}
303.0	−0.11	3.75	−21.77	17.49	−16.47 (± 0.05)
308.0	−0.22	3.70	−21.81	17.33	
313.0	−0.28	3.67	−21.98	17.60	
318.0	−0.39	3.60	−21.89	17.05	
323.0	−0.34	3.56	−21.99	17.09	
328.0	−0.39	3.53	−22.15	17.32	
333.0	−0.38	3.51	−22.37	17.72	

Table 8. Thermodynamic Functions of Extraction of Iron(III) with HDEHP in Hexane at an Ionic Strength, $I = 1.0$ Mol dm $^{-3}$ ($NaNO_3$)

T/K	log D	log K'_{ex}	ΔG/ kJ·mol^{-1}	ΔS/ J·K^{-1}·mol^{-1}	ΔH/ kJ.mol^{-1}
303.0	−0.01	5.57	−32.32	32.09	−22.59 (± 0.06)
308.0	−0.06	5.52	−32.57	32.39	
313.0	−0.13	5.43	−32.52	31.71	
318.0	−0.25	5.36	−32.64	31.58	
323.0	−0.25	5.34	−32.99	32.20	
328.0	−0.25	5.28	−33.14	32.16	
333.0	−0.33	5.22	−33.28	32.08	

Conclusion

Both PIA-8 and HDEHP extract iron(III) by a cation-exchange mechanism, and the species in the organic phase is $FeR_3{\cdot}3HR$. The thermodynamic parameters suggest that the complex ion is comparatively stronger for HDEHP, explaining the higher selectivity and difficult stripping shown by the extractant.

PIA-8 is known to have better separation efficiency and was found to more easily strip iron from the organic phase. Thus, it can be employed to separate impurity elements such as iron from other valuable elements.

Acknowledgment

The authors are thankful to Prof. S. M. Khopkar, Professor Emeritus, Indian Institute of Technology, Powai, Mumbai, for his encouragement in the research work and Daihachi Chemical Industries, Japan, for the gift samples of PIA-8 and DP-8R.

Literature Cited

Baes, C. F.; Baker, H. T. The Extraction of Iron(III) from Acid Perchlorate Solution by Di-(2-ethylhexyl) Phosphoric Acid in *n*-Octane. *J. Phys. Chem.* **1960**, *64*, 89−94.

Binghua, Y.; Nagaosa, Y.; Satake, M.; Nomura A.; Horita, K. Solvent Extraction of Metal Ions and Separation of Nickel(II) from Other Metal Ions by Organophosphorous Acids. *Solvent Extr. Ion Exch.* **1996**, *14*, 849−870.

Demopoulos, G. P. Iron(III) Removal from Base Metal Electrolyte Solution by Solvent Extraction. *Hydrometallurgy* **1984**, *12*, 299−315.

Hino, A.; Hirai, T.; Komasawa, I. Acidic Phosphinates with Different Alkyl Groups as Extractants for Rare Earths *J. Chem. Eng. Jpn.* **1996**, *29*, 1041−1044.

Majima, H.; Izaki, T.; Sanuki, S. Reductive Stripping of Fe(III)-Loaded D2EHPA with the Aqueous Solutions Containing Sulfur Dioxide. *Metall. Trans. B* **1985**, *16B*, 187−194.

Miralles, N.; Sastre, A. M.; Figuerola E.; Martinez, M. Solvent Extraction of Iron(III) by Bis(2,4,4-trimethylpentyl) Phosphinic Acid: Experimental Equilibrium Study. *Hydrometallurgy* **1992**, *31*, 1−12.

Monhemius, A. J.; Thorsen, G. The Application of Hydrolytic Stripping to the Iron Problem in Hydrometallurgy. *International Solvent Extraction Conference*, Liege, Sept. 6−12, 1980; University of Leige: Liege, 1980; Vol. 3, pp 80−91.

Muehl, P.; Gloe, K.; Fischer, C.; Ziegenbalg, S.; Hoffman, H. The Application of Liquid−liquid Extraction for the Separation of Iron during the Production of Alumina. *Hydometallurgy* **1980**, *5*, 161−178.

Pingwei, Z.; Katsutoshi, I. Recovery of Metal Values from Spent Hydrodesulfurisation Catalyst by Liquid−liquid Extraction. *Energy Fuels* **1995**, *9*, 213−219.

Preston, J. S. Solvent Extraction of Cobalt and Nickel by Organophosphorous Acids I. Comparison of Phosphoric, Phosphonic and Phosphinic Acid Systems. *Hydrometallurgy* **1982**, *9*, 115−133.

Roddy, J. W.; Coleman, C. F.; Arai, S. Mechanism of Slow Extraction of Iron(III) from Acid Perchlorate Solution by Di-(2-ethylhexyl) Phosphoric Acid. *J. Inorg. Nucl. Chem.* **1971**, *33*, 1099.

Sato, T.; Nakamura, T. Extraction of Iron(III) from Sulphuric and Hydrochloric Acid Solutions by Di-(2-ethylhexyl) Phosphoric Acid. *Solvent Extraction, Proceedings of the International Solvent Extraction Conference*, The Hague, April 19−23, 1971; Society of Chemical Industry: London, 1971; Vol. 1, pp 238−248.

Sato, T.; Nakamura, T. The Extraction of Iron(III) from Aqueous Acid Solutions by Di-(2-ethylhexyl) Phosphoric Acid. *Hydrometallurgy* **1985**, *15*, 209−217.

van der Zeeuw, A. J. Purification of Zinc Calcine Leach Solution by Exchange Extraction with the Zinc Salt of “Versatic” Acid. *Hydrometallurgy* **1977**, *2*, 275−284.

Vogel, A. I. (revised by Bassett, J.; Denney, R. C.; Jeffery, G. H.; Mendham, J.). *VOGEL's Textbook of quantitative inorganic analysis including elementary instrumental analysis*, 4th ed.; *The English Language Book;* Society & Longman Group Limited: London, 1982.

Yu, S.; Chen, J. Stripping of Fe(III) Extracted by Di-2-Ethylhexyl Phosphoric Acid from Sulfate Solutions with Sulfuric Acid. *Hydrometallurgy* **1989a**, *22*, 267−272.

Yu, S.; Chen, J. Synergistic Extraction of Ferric Ion in Sulphate Solution by Ternary Amine and 2-Ethylhexyl 2-Ethylhexyl Phosphonic acid or Diakyl Phosphonic Acid *Hydrometallurgy* **1989b**, *22*, 183−192.

Received for review November 12, 1998. Accepted June 15, 1999.

JE980280M