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Extraction of Iron(II) and Iron(III) with 4-Acyl-5-pyrazolones in Comparison with Long-Chain 1-Phenyl-1,3-(cyclo)alkanediones

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ABSTRACT

The extraction of iron(II) and iron(III) was studied with long-chain 4-acyl-5-pyrazolones and the corresponding 1-phenyl-1,3-(cyclo)alkanediones, and the extraction parameter $pH_{0.5}$ and log K_{ex} were determined. 4-Acyl-5-pyrazolones are able to extract iron(II) as well as iron(III) from stronger acid solutions than 1-phenyl-1,3-(cyclo)alkanediones. The composition of iron(II) complexes is ML_2, but the oxidation of iron(II) must be prevented by ascorbic acid. Iron(III) is extracted as ML_3 species. Iron can be separated from nickel, zinc, and cadmium by means of the studied compounds. The extraction isotherms of these metals with 1-phenyl-3-methyl-4-(2-ethylhexanoyl)-5-pyrazolone were determined.

Key Words. Liquid–liquid extraction; 4-Acyl-5-pyrazolones; Iron(II); Iron(III); Extraction isotherms of 1-phenyl-3-methyl-4-(2-ethylhexanoyl)-5-pyrazolone; pK_a values

INTRODUCTION

For the extraction of iron(II) as well as iron(III), derivatives of phosphoric acid such as DEHPA (1–3) and CYANEX (4, 5) are preferably used. A new extractant based on derivatives of aminomethylene phosphonic acids is not still available (6). Other suitable extractants are

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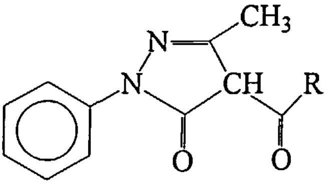
KELEX 100 and different LIX species (7–10). Beside these well-known reagents, pyrazolone derivatives are likewise able to extract iron selectively from aqueous solution (11–13). The use of pyrazolones for the extraction of copper, zinc, and cadmium (14–19) as well as for the extraction of lanthanides (20, 21) was reported recently. Generally, 4-acyl-5-pyrazolones extract metal ions at lower pH regions than do open-chain β-diketones.

In this work the extraction of iron(II) and iron(III) with different 4-acyl-5-pyrazolones was studied and compared with 1-phenyl-1,3-alkanediones having the same alkyl groups. As a technical extractant, LIX 54 (Henkel KGaA) was used. It is composed of a mixture of isomeric 1-phenyl-3-isoheptyl-1,3-propanediones (22). From the group of 4-acyl-5-pyrazolones, the compound 1-phenyl-3-methyl-4-(2-ethylhexanoyl)-5-pyrazolone was characterized by the extraction isotherms of iron(III) in comparison with nickel, zinc and cadmium. The isotherm of the extraction of copper from ammonia solution is given elsewhere (23).

EXPERIMENTAL

Extractants

The 4-acyl-5-pyrazolones examined are characterized by the formula



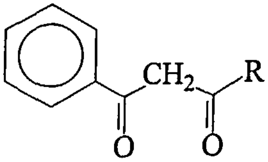
A survey of them is given in Table 1.

The syntheses were performed according the method of Jensen (24) by the reaction of 1-phenyl-3-methyl-5-pyrazolone with the corresponding acid chlorides.

TABLE 1
4-Acyl-5-pyrazolones

Symbol	4-Acyl group	R	pK_a
⊙	-Butanoyl	$-(CH_2)_2-CH_3$	5.97
●	-Octanoyl	$-(CH_2)_6-CH_3$	6.26
○	-Stearoyl	$-(CH_2)_{16}-CH_3$	6.99
□	-2-Ethylhexanoyl	$-CH(C_2H_5)-(CH_2)_3-CH_3$	6.89

The β-diketones studied have the general formula



They are collected in Table 2.

The syntheses were made by following a procedure of Hauser (25) by Claisen condensation of acetophenone and the corresponding phenyl or ethyl esters in the presence of sodium amide. Analytical data for the compounds summarized in Tables 1 and 2 were given recently (26).

Extraction Studies

The experimental conditions of the liquid–liquid extraction are collected in Table 3.

The pH adjustment was done by adding HNO_3 or NaOH. For the measurement of pH, a pH-meter MV 86 (Präcitronic, Dresden) with a glass electrode EGA 501 N (Forschungsinstitut, Meinsberg) was used. The metal concentrations were determined by atomic absorption spectrometry (AAS 1100 B, Perkin-Elmer). All chemicals used were of p.a. quality. The iron stock solutions were prepared by diluting a Merck standard solution (iron nitrates) with double-distilled water. The iron(II) solution was stabilized by addition of ascorbic acid.

The distribution coefficient $D = c_{M(o)}/c_{M(w)}$ was calculated from the metal concentration measured in the aqueous phase before and after extraction.

TABLE 2
β-Diketone

Symbol	Acyl group	R
*	*i*-Octanoyl (mixture)- (LIX 54)	*i*-C_7H_{13} (mixture)
▲	2-Ethylhexanoyl-	$—CH(C_2H_5)—(CH_2)_3—CH_3$
■	*n*-Octanoyl-	$—(CH_2)_6—CH_3$
◑	Cyclopentyl-propanoyl-	$—(CH_2)_2—C_5H_9$
	For Comparison, the Following Were Synthesized	
◪	1-(*p*-Hexylphenyl)-1,3-butanedione	
⊡	1-Phenyl-2-hexyl-1,3-butanedione	

TABLE 3
Experimental Conditions of Liquid–Liquid Extraction

$c_{Fe^{3+}}$	1.7905 × 10^{-5} mol·L^{-1} (I = 0.1 mol·L^{-1}; KNO_3)
$c_{Fe^{2+}}$	1.7905 × 10^{-5} mol·L^{-1} (I = 0.1 mol·L^{-1}; KNO_3 + 1.7905 × 10^{-4} mol·L^{-1} ascorbic acid)
c_{HL}	1.7905 × 10^{-3} mol·L^{-1} (solvent: kerosene)
Phase ratio	1 + 1 (20 mL separatory funnel)
Temperature	25°C
Extraction cycle	20–60 minutes (mechanical shaker)

For the extraction constant, the equation

$$-\log K_{ex}/n = pH_{0.5} + \log c_{HL}$$

is valid (n = number of liberated protons; $pH_{0.5}$ = pH for $\log D = 0$). The percentage of extraction was calculated by the equation $\%E = 100D/(1 + D)$.

RESULTS AND DISCUSSION

The extraction of iron(III) with 4-acyl-5-pyrazolones is shown in Fig. 1; the corresponding results for iron(II) are given in Fig. 2. The extraction

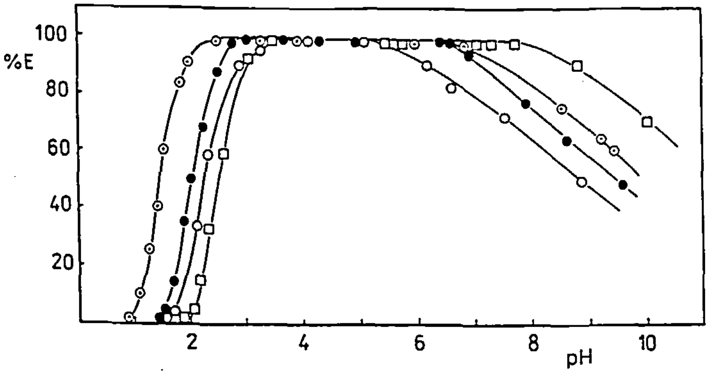


FIG. 1 Extraction of iron(III) with different 4-acyl-5-pyrazolones. $\%E = f(\text{pH})$. $c_{Fe^{3+}}$ = 1.7905 × 10^{-5} mol·L^{-1} (I = 0.1 mol·L^{-1} KNO_3). c_{HL} = 1.7905 × 10^{-3} mol·L^{-1} (solvent: kerosene). For symbols see Table 1.

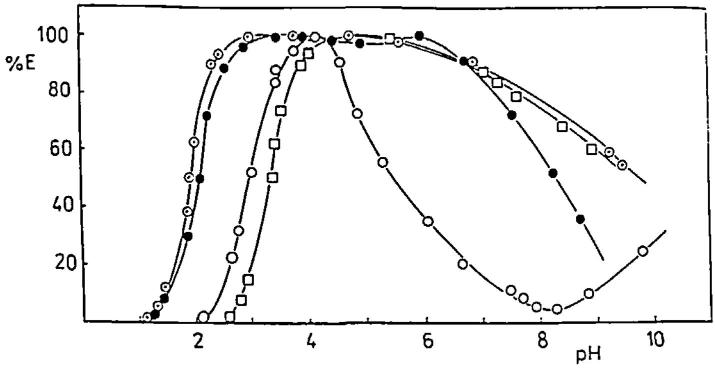


FIG. 2 Extraction of iron(II) with different 4-acyl-5-pyrazolones. %$E = f$(pH). $c_{Fe^{2+}} = 1.7905 \times 10^{-5}$ mol·L^{-1} ($I = 0.1$ mol·L^{-1} KNO_3) +, 1.7905×10^{-4} mol·L^{-1} ascorbic acid). $c_{HL} = 1.7905 \times 10^{-3}$ mol·L^{-1} (solvent: kerosene). For symbols see Table 1.

curves of iron(III) and iron(II) with 1-phenyl-1,3-alkanediones having comparable alkyl substituents are drawn in Figs. 3 and 4.

The composition of the extracted species was evaluated from the slope of the straight line resulting from the function log $D = f$(pH) (Figs. 5 and 6). Hence the extraction can be described by the equations

$$Fe^{3+}_{aq} + 3HR_{org} \rightleftharpoons FeR_{3org} + 3H^{+}_{aq}$$

$$Fe^{2+}_{aq} + 2HR_{org} \rightleftharpoons FeR_{2org} + 2H^{+}_{aq}$$

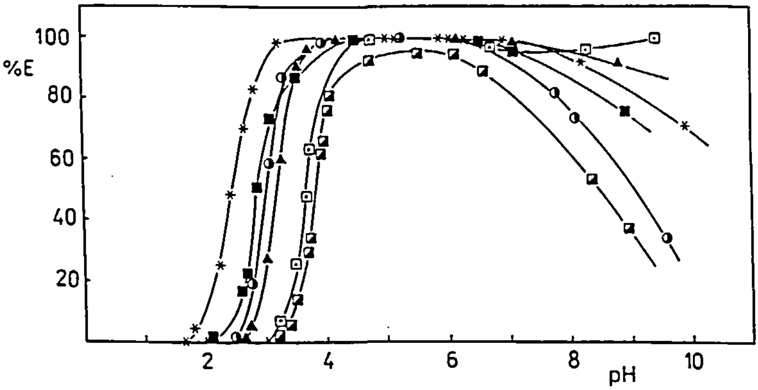


FIG. 3 Extraction of iron(III) with different β-diketones. %$E = f$(pH). Parameters as in Fig. 1. For symbols see Table 2.

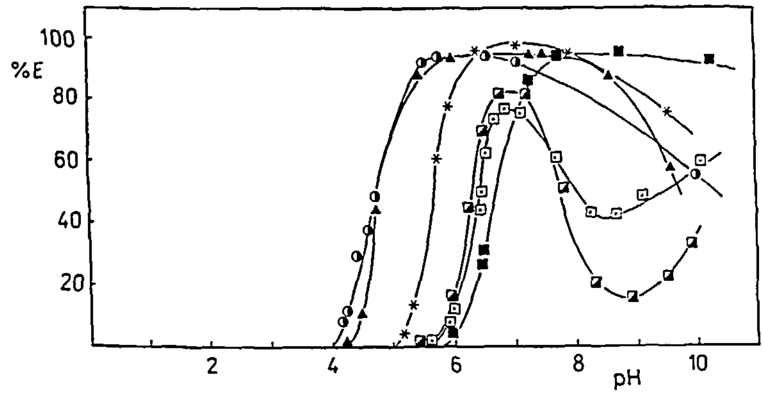


FIG. 4 Extraction of iron(II) with different β-diketones, %E = f(pH). Parameters as in Fig. 2. For symbols see Table 2.

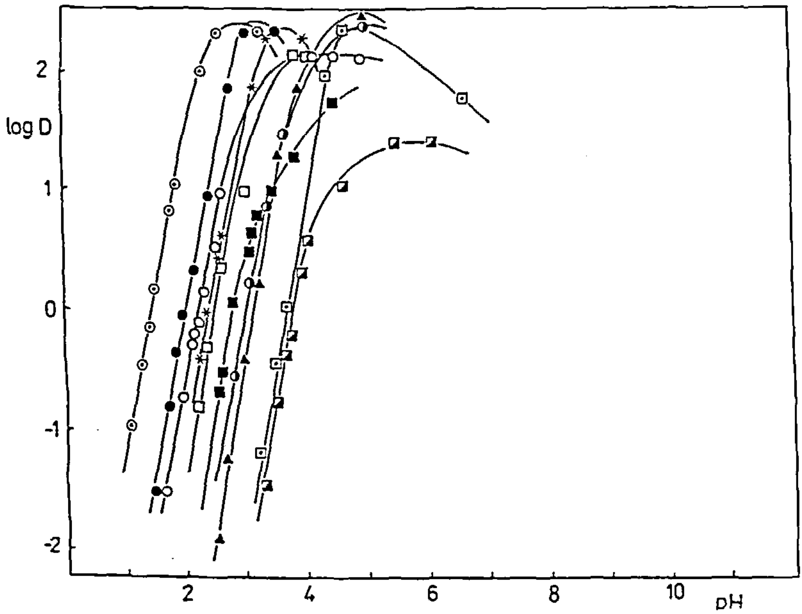


FIG. 5 Extraction of iron(III) with different 4-acyl-5-pyrazolones and different β-diketones. Log D = f(pH). Parameters as in Fig. 1. For symbols see Tables 1 and 2.

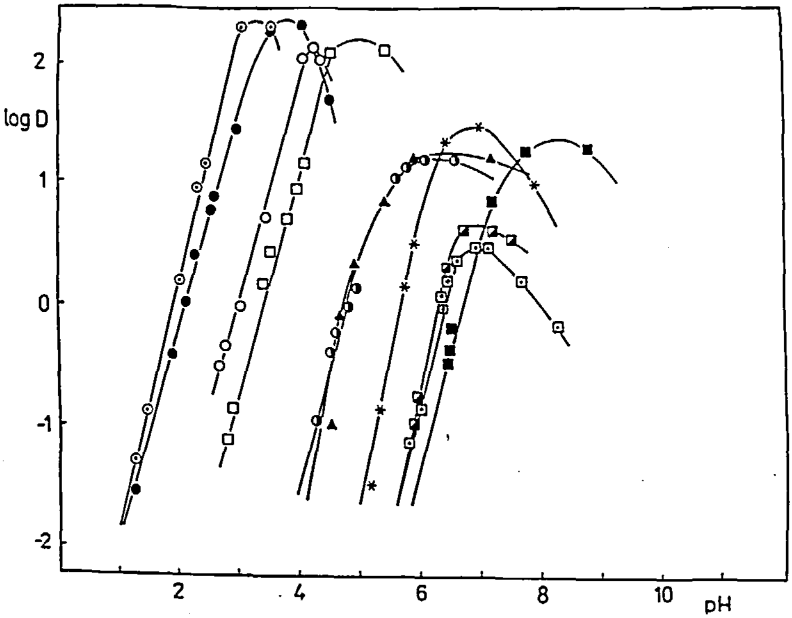


FIG. 6 Extraction of iron(II) with different 4-acyl-5-pyrazolones and different β-diketones. $\log D = f(\mathrm{pH})$. Parameters as in Fig. 2. For symbols see Tables 1 and 2.

In order to verify the validity of the extraction processes and the composition of the extracted species, the $\lg D = f(c_{\mathrm{HL}})$ function was investigated. Figure 7 representatively shows the results of the extraction of Fe(II) and Fe(III) with a commercial β-diketone (LIX 54) and with 1-phenyl-3-methyl-4-(2-ethylhexanoyl)-5-pyrazolone, respectively.

In the case of Fe(II), the slopes of the extraction curves for both the β-diketone and for the 4-acylpyrazolone were found to be 1.8 so that the pure 1:2 complex (FeL_2) was extracted. The formation of any self-adduct chelates could not be observed.

For Fe(III) the slopes of the curves are 2.8, so that the formation of an adduct could likewise be excluded in that case. A 1:3 complex (FeL_3) is extracted.

In the case of Fe^{2+}, possible oxidation to Fe^{3+} was hindered by ascorbic acid.

The extraction parameters are listed in Tables 4 and 5. The results show that iron(II) as well as iron(III) is extracted with 4-acyl-5-pyrazolones at

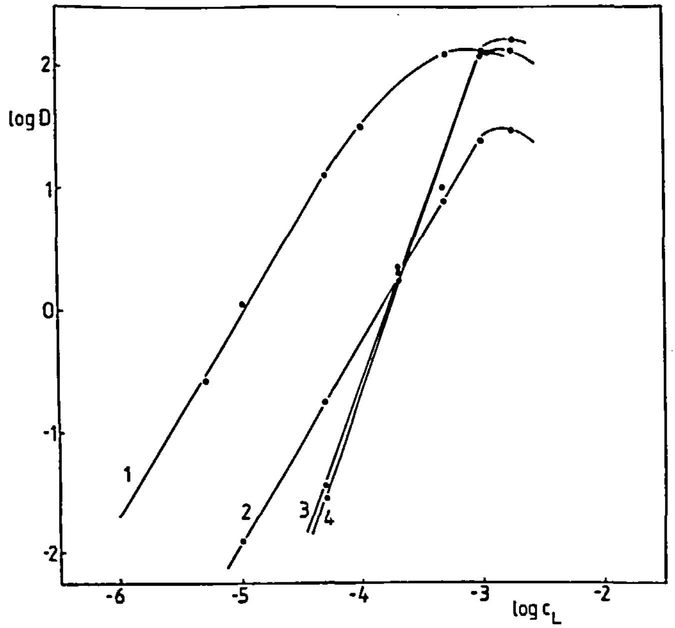


FIG. 7 Extraction of iron(II) (1, 2) and iron(III) (3, 4) with LIX 54 (2, 3) and 1-phenyl-3-methyl-4-(2-ethyl-hexanoyl-5-pyrazolon (1, 4). c_M = 1.7905 × 10^{-5} mol·L^{-1} (I = 0.1 mol·L^{-1} KNO$_3$). Log D = $f(c_{HL})$, pH 6.75, (2–4), pH 5.25 (1). In the case of Fe(III), 1.7905 × 10^{-4} mol·L^{-1} tartaric acid was added.

a lower pH than with comparable β-diketones (Figs. 1–4) because the pyrazolone derivatives are more strongly acidic than are the common β-diketones (Table 1). The extraction constants (Table 4) follow the same order as the pK_a values.

TABLE 4
Extraction Data of 4-Acyl-5-pyrazolones (for symbols, see Table 1)

	$pH_{0.5}$		lg K_{ex}	
Symbol	Iron(II)	Iron(III)	Iron(II)	Iron(III)
⊙	1.90	1.42	1.69	3.98
●	2.10	2.00	1.29	2.24
○	2.95	2.20	−0.40	1.64
□	3.38	2.50	−1.26	0.74

TABLE 5
Extraction Data of 1,3-Diketones (for symbols, see Table 2)

	$pH_{0.5}$		lg K_{ex}	
Symbol	Iron(II)	Iron(III)	Iron(II)	Iron(III)
*	5.65	2.40	−5.80	1.04
▲	4.75	3.18	−4.00	−1.29
■	6.70	2.80	−7.90	−0.16
◑	4.75	3.05	−4.00	−0.91
◪	6.35	3.80	−7.20	−3.15
⊡	6.40	3.70	−7.30	−2.86

Iron(III) in quantitatively extracted up to pH 6. A competitive reaction is hydrolysis of the metal ions.

A decrease of the extraction rate often occurs at low extraction times because hydrolysis runs quicker than extraction. This can be observed if

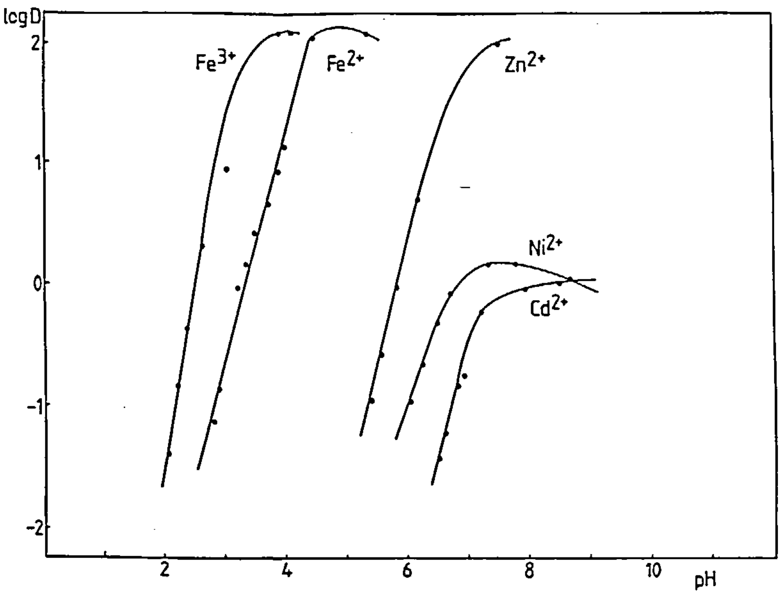


FIG. 8 Separation of iron(III), iron(II), zinc, cadmium, and nickel(II) with 1-phenyl-3-methyl-4-(2-ethylhexanoyl)-5-pyrazolone. Log $D = f(\text{pH})$. $c_M = 1.7905 \times 10^{-5}$ mol·L^{-1} ($I = 0.1$ mol·L^{-1} KNO_3). $c_{HL} = 1.7905 \times 10^{-3}$ mol·L^{-1} (solvent: kerosene).

the extractant has long-chain substituents. In the case of iron(II), the range of hydrolysis is pH 5.8–8.5. Indeed, extraction is hindered in this range (see Fig. 2).

The extraction of iron(III) and iron(II) with β-diketones requires very long extraction times. At least 60 minutes are necessary to attain extraction equilibrium.

In order to check the possibilities of metal separations, the extraction of iron was compared with that of nickel, zinc, and cadmium (see Fig. 8). 1-Phenyl-3-methyl-4-(2-ethylhexanoyl)-5-pyrazolone was chosen as the extractant. The extraction sequence is Fe(III) > Fe(II) > Zn > Ni > Cd. Figure 9 shows the sequence of extraction isotherms of these metals with 1-phenyl-3-methyl-4-(2-ethylhexanoyl)-5-pyrazolone. The loading capacity is limited to 4.7 $g \cdot L^{-1}$ in the case of nickel and to 7.7 $g \cdot L^{-1}$ in the case of zinc, whereas loading with iron and cadmium is possible up to 9.6 and 10.5 $g \cdot L^{-1}$, respectively. The loading of the organic phase is limited by the solubility of the metal chelates. Iron(III) can be quantitatively separated from nickel, zinc and cadmium in the pH range 3.8–4.5. Similarly, iron(II) can be separated from the other metal ions at pH 4.5. Zinc can be separated from cadmium at pH 7.5, but the separation of nickel from zinc and cadmium is not possible.

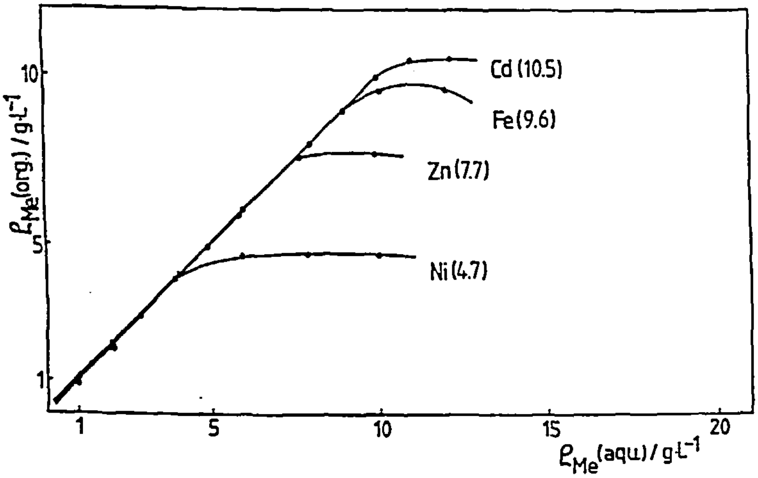


FIG. 9 Extraction isotherm of iron(III), zinc, cadmium, and nickel(II) with 1-phenyl-3-methyl-4-(2-ethylhexanoyl)-5-pyrazolone. $pH_{Fe(III)}$ 7.00, pH_{Zn} 7.10, pH_{Cd} 8.69, and pH_{Ni} 7.50. Mass concentration (HL) = 10%.

A separation coefficient ($\alpha = D_{M1}/D_{M2}$) at the pH 4 used for iron separation from zinc, nickel, and cadmium may be estimated as about $\alpha = 10^5$. Coefficient α for zinc-nickel/cadmium separation is about 10^2.

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