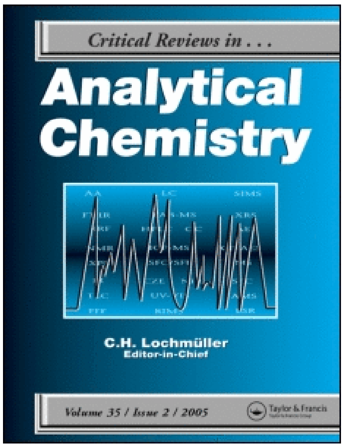

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Chemistry and Analytical Characterization of the Effect of Hydroxyoxime Structure upon Metal-Complexing and Extraction Properties

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Chemistry and Analytical Characterization of the Effect of Hydroxyoxime Structure upon Metal-Complexing and Extraction Properties

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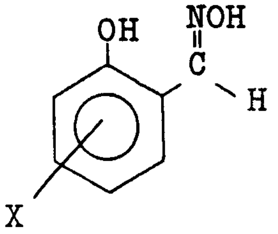
KEY WORDS: hydroxyoximes, metals, complexes, extraction.

I. INTRODUCTION

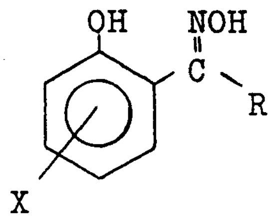
Hydroxyoximes are well established copper extractants that are used in several high-scale industrial installations for producing cathodic copper from oxide ores. The most economically produced copper is obtained by means of hydrometallurgical processes in which hydroxyoximes are used to separate the copper from iron and to concentrate its aqueous solution. The industrial application of hydroxyoxime extractants and their properties have been discussed in several previous papers.[1-13] Some comprehensive reviews of the chemistry of transition metal complexes with oximes have been presented.[14,15] The kinetics and mechanism of metal extraction with hydroxyoximes were also reviewed.[1,11,13,16] The aim of this work is to review the chemistry of metal extraction with hydrophobic hydroxyoxime extractants, with emphasis upon: (1) the characterization of the composition and stability of hydroxyoxime complexes with metals; (2) hydroxyl group acidity; and (3) $pH_{0.5}$ values, including the effect of hydroxyoxime structure. Appropriate tabular data are presented.

II. STRUCTURE OF METAL-HYDROXYOXIME COMPLEXES

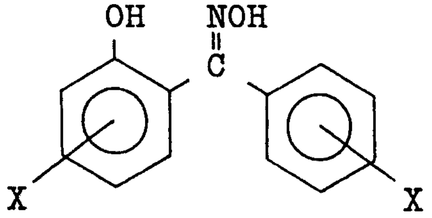
Compounds which have a group with an easy dissociated proton near an atom with a free electron pair are metal chelating systems. There are four principal types of structures to which such compounds belong: 2-hydroxybenzaldehyde oxime derivatives (I), aliphatic-aromatic hydroxyoximes (II), 2-hydroxybenzophenone oxime derivatives (III) and α-acyloin oximes (aliphatic hydroxyketone oximes) (IV).



I



II



III

$R = CH_3 - C_{12}H_{25}$
$X = R$, halogen, NO_2

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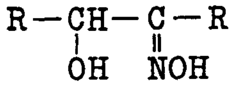


$R-CH(OH)-C(=NOH)-R$

IV

Hydroxyoximes of Structures I to IV have two chemically active groups: a phenolic group (oximes I to III) or an aliphatic hydroxyl group (oximes IV), and an oximino group with a free pair on the nitrogen atom in all oximes considered above.[1,2,10-15] The acidity of the phenolic group is higher than that of the aliphatic hydroxyl and of the oximino group. As a result, in normal extraction systems only the dissociation of the phenolic group in hydroxyoximes I to III can be considered, and hydroxyoximes of this type can be abbreviated as HR.

In strongly alkaline media the dissociation of the phenolic group is so strong that the sodium salt can be formed and hydroxyoximes I to III can be precipitated. The dissociation of the oximino group is also observed; however, such systems have no practical importance.

A more complex situation is observed in the case of α-acyloin oximes(IV) for which, depending upon extraction conditions, in addition to the chelation nitrogen present in the oximino group, the dissociation of the hydroxyl group or of both the hydroxyl and oximino groups must be taken under consideration. As a result, these oximes can form a broader variety of metal complexes which will be abbreviated as H_2L.

A variety of spectrophotometric methods (e.g.: the Vosburgh-Cooper method,[17] the Job method of continuous variations,[18,19] the slope ratio method of Harvey and Manning,[20] the molar ratio method, and the logarithmic method of Bent and French[21]) potentiometric, conductometric, amperometric and oscillometric titration, gravimetric, and other methods have been used to determine stoichiometric composition of hydroxyoxime complexes with metals.

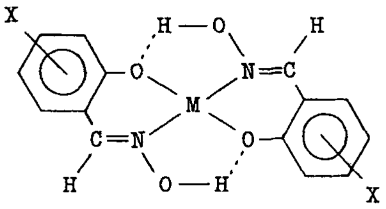
The results of these analyses indicate that hydroxyoximes I, II, and III form complexes with copper(II), nickel(II), cobalt(II), palladium(II), manganese(II), etc., having a molar ratio of ligand-to-metal of 2:1.[22-54] Only iron(III), depending upon the acidity of aqueous phase, may form complexes having a molar ratio of ligand-to-metal of 1:1 and 3:1.[31,46] Also, in the case of cobalt(II) extraction with 2-hydroxy-5-nonylbenzophenone oxime, two different complexes were observed,[30] probably as the result of Co(II) oxidation in the complex to Co(III).

Hydroxyoximes of types I-III extract only cobalt(II) at pH above 3 to 6; cobalt(III) is not extracted. However, in the organic phase, cobalt(II) is not extracted. However, in the organic phase, cobalt(II) is oxidized in the chelate to cobalt(III). This reaction is of second order with respect to hydroxyoxime and Co(II).[55] As a result, a very stable complex is formed which is very difficult to strip.[56-60]

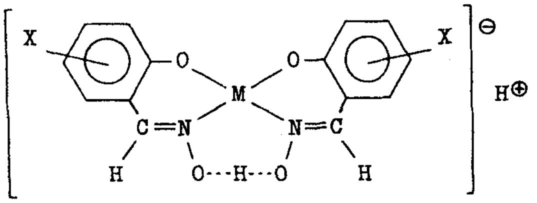
Spectrophotometric and other methods (UV-VIS, IR, NMR, EPR, MS, X-ray crystal structural analysis, Mössbauer spectroscopy, and magnetic moment measurements) provided fundamental information about the type and strength of the bonds formed in metal-hydroxyoxime complexes. Keeney et al.[15] have presented a review of works concerning the application of these methods to the study of metal-hydroxyoxime complexes. Important information about the structure of complexes of α-acyloin oximes and salicylaldehyde oxime with metals is given by Chakravorty.[14]

Burger et al.[22,23] and Ramaswamy et al.[61] have shown that 2-hydroxybenzaldehyde oxime derivatives (Structure I) form chelates which have the structure V or VI, upon the complexing metal, where the strength of the intramolecular hydrogen bonds depends on the metal and the type of substituent on the aromatic ring.

V

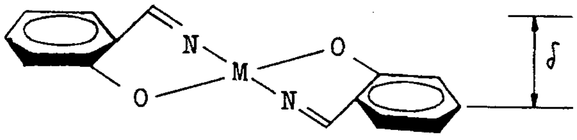


VI



X = alkyl, halogen, NO_2

X-ray diffraction studies of the crystal structures have been carried out only for copper, nickel, and palladium complexes with 2-hydroxybenzaldehyde oxime and 5-chloro-2-hydroxybenzaldehyde oxime.[62-66] The trans 2-hydroxybenzaldehyde oxime ligands in the complex are joined by hydrogen bonds between the phenolic oxygen of one ligand and the oxime hydroxyl group of the other (Structure V). The length of the phenolic oxygen-oxime oxygen bond increases in the order Ni < Cu < Pd.[62-65] The complex molecule shows significant deviation from complete planarity, and it has a "chair" type structure. This is caused by additional interactions between the atom of metal with oxygen atoms of oximino groups. The distance δ between two parallel planes of aromatic rings is in the range 0.013 to 0.024 nm (Structure VII).



VII

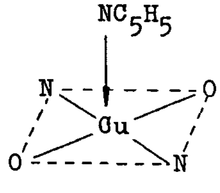
A similar structure was stated for the copper(II) complex with 5-chloro-2-hydroxybenzaldehyde oxime,[66] where the distance δ increased to 0.076 nm.

The hydrogen bond is not symmetrical, but the position of hydrogen is not univocally explained.[23,67] Based on ultraviolet and ultrared absorption spectra, Burger et al.[23] found that in copper(II) and nickel(II) complexes with salicylaldehyde oxime, the hydrogen atom is bonded stronger with the oxygen atom of the oximino group than with the oxygen atom of the hydroxyl group (Structure V). However, a study by Khariton et al.[37] which took into account mass spectrometry results, proposed the opposite situation, i.e., that the hydrogen atom is more strongly bonded with the oxygen atom of the hydroxyl group than with the oxygen atom of the oximino group.

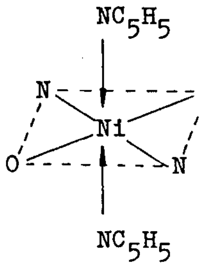
Based on the ultraviolet absorption spectra of Mn(II), Fe(II), Co(II), and Zn(II) complexes with 2-hydroxybenzaldehyde oxime derivatives carried out in alkaline media, Burger et al.[23] attributed Structure VI to these chelates, where the hydrogen bond between the oxygen atoms of the two oxime groups is symmetric. The observation that the complexes, when prepared as solids in alkaline media, showed the composition M(R)(HR)Na (H_2R-hydroxyoxime) is, in our opinion, only weak evidence confirming the Structure VI. Moreover, it was not possible to carry out X-ray crystal structural analysis to confirm this structure because appropriate crystals of these complexes were not obtained, with the exception of nickel, for which crystalline complex was obtained.[68]

Using infrared spectroscopy, Burger et al.[22,23] demonstrated the existence of two various types of bonds in the chelate: the chelating ligand-metal bond and π donor metal-ligand bond. A change of the electron density of the nitrogen atom of the ligand changes the relative strength of both these bonds. We can suppose that oximes of II and III type form complexes of identical structure, which is confirmed by spectroscopic spectra.

O'Brien and Thornback,[69,70] based on studies of the copper complex with the commercial reagent SME 529 by electron spin resonance, proved that, if pyridine is added to the organic solution or copper is extracted from ammoniacal solution, a five-coordinated square pyramidal species is formed (Structure VIII).



VIII



IX

Basolo and Matoush[71] isolated pseudo-octahedral adducts bis-(2-hydroxybenzaldehyde oxime) nickel(II), with two pyridine molecules occupying trans-axial positions (Structure IX).

The formation of ammonia adducts with hydroxyoxime metal complexes should increase the amount of ammonia transferred into the organic phase during copper and nickel extraction from ammonia media with commercial hydroxyoxime extractants. This transfer is actually observed,[72-75] but the amount of ammonia transferred in the organic phase decreases as the complex concentration in this phase increases, according to Murayama[72] and Flett and Melling,[73] and increases, according to Brown et al.[74] This transfer depends mainly upon the ammonia and hydroxyoxime concentrations in the aqueous and organic phase, respectively, and the following empirical relationship was proposed by Brown et al.[74] for the system, Cu-Ni-NH_3-CO_2-LIX 64N (Equation 1):

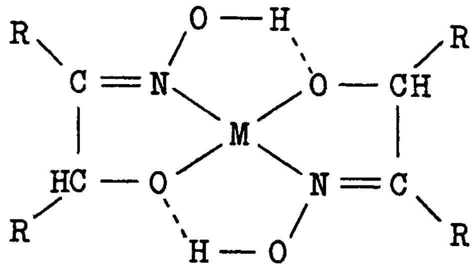
$$[NH_3]_o = z_1 + z_2[HR]_o[NH_3]_w + z_3\frac{[Ni]_o[NH_3]^2L_w}{1 + [NH_3]_w^2} \qquad (1)$$

where z_1, z_2, and z_3 are constants, HR denotes LIX 64N, and subscripts o and w stand for the organic phase and the aqueous phase, respectively.

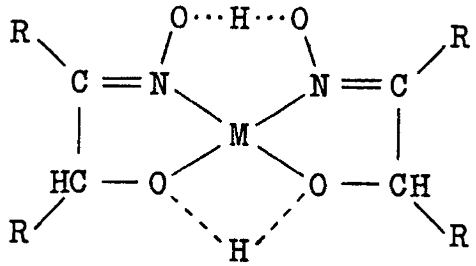
Metal complexes of aliphatic α-hydroxyketone oximes, i.e., oximes of type IV, are not so well described as those of oximes I to III. The first works in this area dealt with α-benzoin oxime and its derivatives,[76-88] while the most recent works have concentrated on metal complexes of 5,8-diethyl-7-hydroxy-6-dodecanone oxime,[69,89-99] which is the active component of LIX 63 (and is also present in small amounts as the accelerator in LIX 64N).

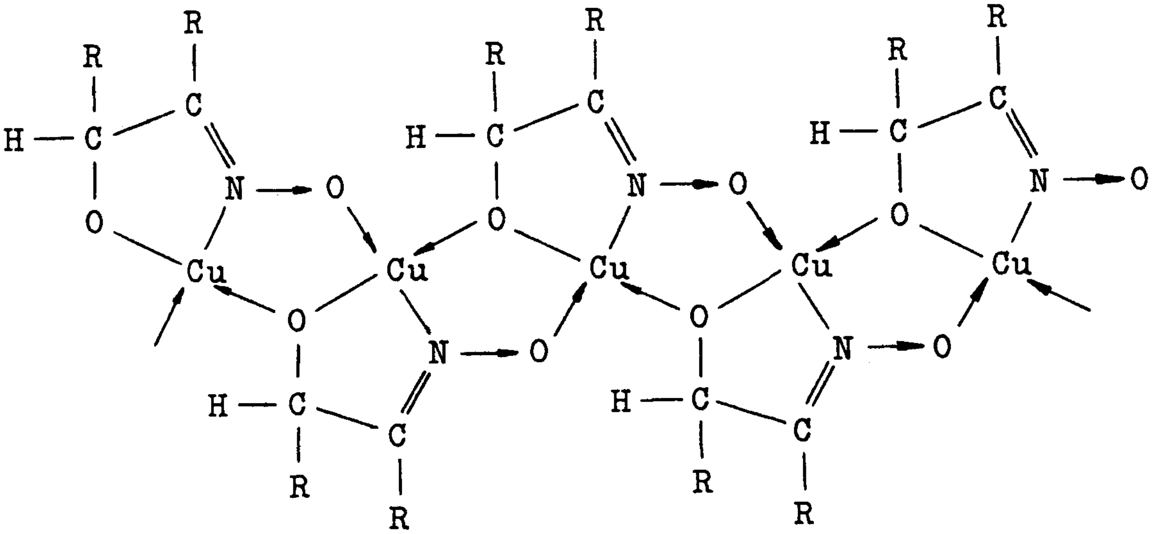
The more recent studies[69,89-92] showed that, according to the extraction conditions (i.e., the molar ratio of metal-to-oxime and the pH), hydroxyoximes of type IV can form complexes having a molar ratio of ligand to metal of 2:1 (Structures X and XI) or polymeric complexes (Structure XII).

X



XI





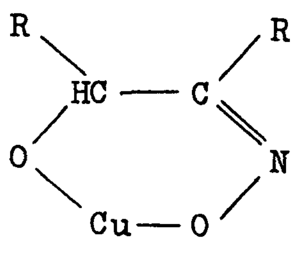
XII

A low acidity of the aqueous phase favors the formation of 2:1 complexes. These 2:1 complexes are formed as the molar ratio of hydroxyoxime to metal, copper (II) or nickel (II), present in the organic phase and the aqueous one, respectively, is above 2.[69,89-92] The polymeric 1:1 complexes are formed in systems containing an excess of metal.

The formation of 2:1 complexes was also reported for molybdenum (VI) and tungsten (VI).[84,86,95] However, 2:4 complexes were demonstrated for titanium (IV) α-benzoin oxime.[87] The formation of complexes of molar ratio 2:1 have been confirmed by spectroscopic and extraction studies,[69,89-92] but only the nickel complex with 5,8-diethyl-7-hydroxy-6-dodecanone oxime was isolated.[92] Spectral analysis suggest that this complex is cis-square-planar with bifurcated hydrogen bridges (Structure XI).

There is some information concerning the formation of copper and nickel polymeric complexes with α-acyloin oximes at lower ligand concentrations (Structure XII). These complexes are flat systems, consisting of five-membered chelate rings, which leads to strong metal-metal coupling.[69,88,90-92,96] Oligomeric complexes of 5,8-diethyl-7-hydroxy-6-dodecanone oxime with Cu(II) and Ni(II) have been synthesized.[92,96] These chelates, $[M(L)]_n$ are oligomeric complexes with pseudo-octahedral geometry and low magnetic moments characteristic of oligomeric complexes. Association numbers in toluene for $[Cu(L)]_n$ and $[Ni(L)]_n$ are 7-11 and 5, respectively.[90,92,98]

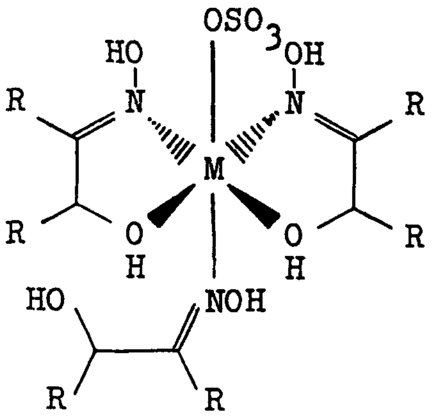
There is no convincing evidence about the formation of monomeric complexes of molar ratio 1:1 in which copper is a component of a six membered ring (Structure XIII).[89]



XIII

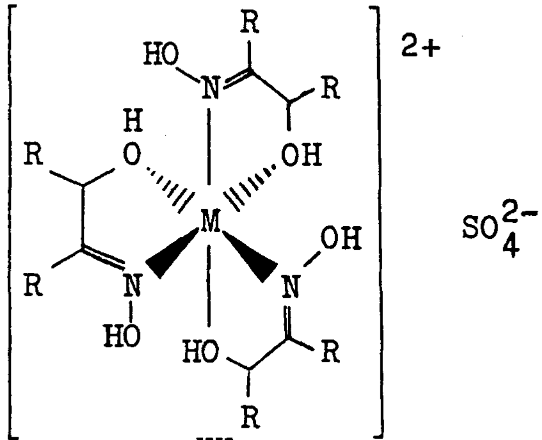
The formation of a 1:1 complex of vanadium (V) with α-benzoin oxime at pH 1.5 was proposed by Hoens and Stone.[84] α-Acyloin oximes can also form mixed complexes in acidic solutions, in which metal, hydroxyoxime molecules, and sulfate, nitrate, and chloride ions are present.

Keeney and Osseo-Asare[92,96] separated mixed complexes of octahedral structure from sulfate solutions which contained neutral hydroxyoxime molecules and sulfate ions (viz., $Ni(H_2L)_3SO_4$ and $Cu(H_2L)_3SO_4$). The following Structure XIV was proposed:



XIV

Chelate XIV, if precipitated, does not dissolve in organic solvents, and undergoes a transition into salt XV, which exhibits an IR band at 950 cm^{-1} characteristic for noncoordinated SO_4^{2-} ion.



XV

Hummelstedt[97] also demonstrated the formation of various complexes of LIX 63 with copper(II), depending upon the pH of the aqueous phase. At high pH, the formation of oligomeric 1:1 complexes, $(CuL)_n$, was proposed. Monomeric 2:1 complexes, $Cu(HL)_2$, are formed at low pH, but at $pH < 0.5$ some other complexes are formed which transfer sulfate ions into the organic phase.

As a result of this, the extraction of copper(II) with α-acyloin oximes decreases significantly as the acidity of the aqueous phase increases, and stops at pH 3. However, a further increase of the sulfuric acid concentration up to about 200 g dm^{-3} causes an important increase of copper extraction, which occurs probably according to the following reaction:[100-102]

$$[Cu(HSO_4)_2]_w + [H_2SO_4]_w + [3H_2L]_o$$

$$= [CuHSO_4(HL)]_o + [2(H_3L)HSO_4]_o \quad (2)$$

where w and o denotes the water and organic phase, respectively. Simultaneously with copper extraction, the protonation of hydroxyoxime is observed, and some amounts of sulfuric acid are trasferred into the organic phase. Copper can be stripped from the organic phase only by its washing with water.

In chloride systems, depending upon the acidity of the aqueous phase and chloride concentration, LIX 63 forms typical 2:1 complexes, $Cu(HL)_2$, or neutral solvates, probably $CuCl_2{\cdot}2(H_2L)$[104] in which copper is solvated with oxygen atoms present in both the hydroxyl and oximino groups. The extraction of chlorocomplexes $CuCl_2{\cdot}HCl$ or $CuCl_2{\cdot}2HCl$ with 1 or 2 hydroxyoxime molecules was also proposed.[103] Typical 2:1 complexes, $Cu(HL)_2$, are formed at higher pH, above 2, and low chloride concentrations.

Iron(III) is extracted from chloride media probably as $FeCl(HL)_2$.[103]

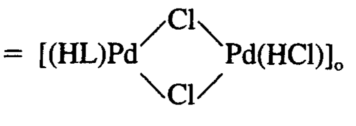
α-Acyloin oximes are effective extractants of palladium(II),[105,106] which is extracted in the form of mixed complexes according to Reactions 3 and 4:

$$[PdCl_4^{2-}]_w + [H_2L]_o = [PdCL(HCl)]_o$$

$$+ [H^+]_w + [3Cl^-]_w \quad (3)$$

or

$$[2PdCl_4^{2-}]_w + [2H_2L]_o$$



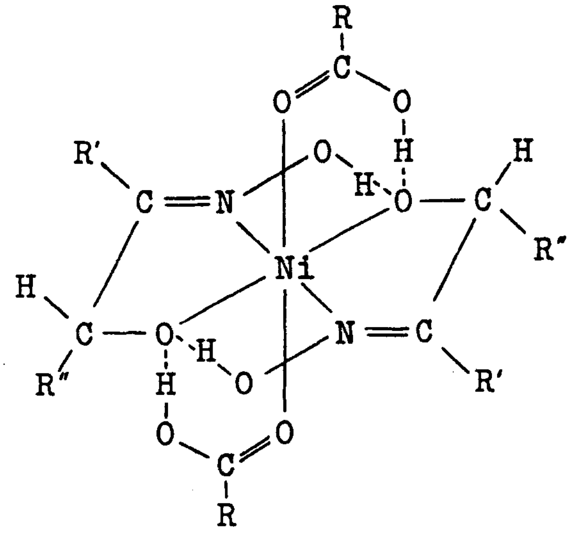
$$= [(HL)Pd\overset{Cl}{\underset{Cl}{\diamond}}Pd(HCl)]_o$$

$$+ [2H^+]_w + [6Cl^-]_w \quad (4)$$

Zapatero et al.[98] demonstrated the formation of the following complexes in copper(II) extraction from nitrate solutions with 5,8-diethyl-7-hydroxy-6-dodecanone oxime: $Cu(NO_3)HL(H_2L)_2$, $Cu(HL)_2(H_2L)_z$ and $(CuL)_n$. The first and the second complex are dominant at low and high pH of the aqueous phase. The complex solvation with hydroxyoxime molecules ($z = 1$) is only observed at higher hydroxyoxime concentrations. The polymeric complex having the average degree of oligomerization of 11 is formed in systems containing an excess of copper.

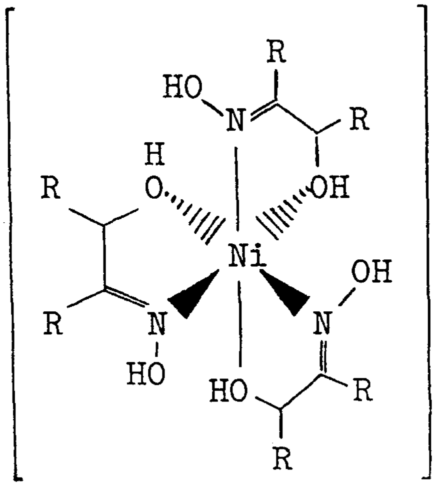
Similar types of complexes are formed with nickel(II).[99]

Mixed complexes are also formed in systems containing, in addition to an α-acyloin oxime, a carboxylic acid or an organic sulfonic or phosphoric acid. In systems containing carboxylic acids, the molar ratio of α-acyloin oxime:carboxylic acid:metal was determined in the formed complexes as 2:2:1,[89,107-109] and Structure XVI was proposed.

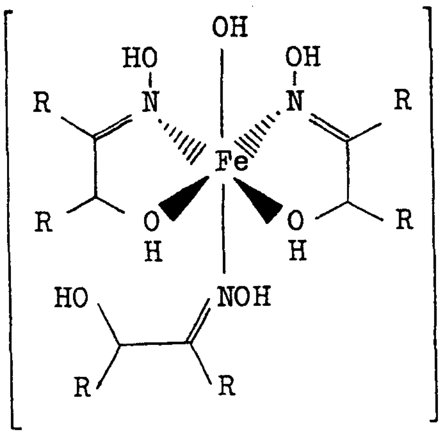


XVI

Quite different structures were proposed by Osseo-Asare et al.[110-112] for nickel(II) and iron(III) complexes extracted in systems containing α-acyloin oxime (LIX 63) and dinonyl-naphthalenesulfonic acid (HD): $Ni(H_2L)_3D_2$ (Structure XVII) and $Fe(OH)(H_2L)_3D_2$ (Structure XVIII).



XVII



XVIII

The nickel complex is more stable than the iron one, probably due its symmetrical structure. The iron(III) complex is formed the most easily at pH 2 to 3.5 when $Fe(OH)^{2+}$ species are dominant in $Fe(III)\text{-}NO_3^-\text{-}H_2O$ phase. The complex $Fe(H_3L)_3D_3$ is not formed, probably due to the steric effect.[110]

The formation of mixed complexes was also proposed by Aguilar et al.[113] for nickel(II) extraction from acidic nitrate solutions with 5,8-diethyl-7-hydroxy-6-dodecanone oxime, (H_2L) and di(2-ethylhexyl)phosphoric acid, (HR), or dioctylphosphinic acid, (HR'). The formation of the following complexes was proposed: $Ni(HL)_2HR$ or $Ni(HL)NO_3HR$, and $Ni(HL)_2HR'$ or $Ni_2(HL)_2(NO_3)_2HR'$, respectively.

As discussed above, studies of the metal extraction mechanism and the structure of extracted α-acyloin oxime complexes are difficult in view of the formation of different kinds of complexes.

III. DISSOCIATION OF HYDROXYOXIMES AND STABILITY OF THEIR COMPLEXES WITH METALS

A. Dissociation of Hydroxyoximes

The proton-hydroxyoxime ligand and metal-hydroxyoxime ligand stability constants in most cases have been determined using the Bjerrum-Calvin[114-116] potentiometric titration technique adopted by Irving and Rossotti.[117,118] Comparison of the stability constants of different hydroxyoximes is often very difficult. The determination of constants was carried out in mixed solvents of various polarity and at various temperatures due to the weak solubility of hydroxyoximes and their complexes in water. Proton-ligand stability constants regarding water solutions found in literature for hydrophobic oximes are, in most cases, extrapolated data.

Hydroxyoximes of types I to III contain the phenolic and oximino groups. If protons of these two groups could dissociate, then two proton stability constants (K_1^H and K_2^H for the phenolic and oximino group, respectively) should be obtained. In reality, in most cases (Tables 1 to 4) only one value of proton-ligand stability constant was obtained. The overall constant, $\beta_2^H = K_1^H \cdot K_2^H$, achieves usually negative values, as the dissociation of both the phenolic and oximino group is considered.[119]

K_2^H values were reported only in few cases for salicyl-aldehyde oxime.[120,124,125] In these cases, values of 8.35 and 12.05,[124] 8.85 and 11.07,[125] and 9.30 and 12.10[125] were reported for K_1^H and

TABLE 1
Proton-Ligand Stability Constants for Commercial Hydroxyoxime Extractants

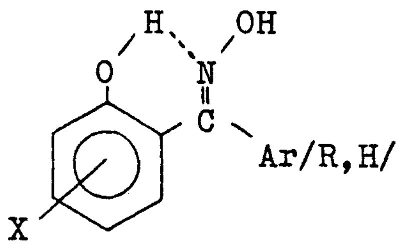
Extractant	10% Acetone, 90% water	70% Dioxane, 30% water	70% Dioxane, 30% water	Water	Ethanol	Ref.
P 50	14.48	—	—	—	—	123
P 17	14.58	—	—	—	—	10
SME 529	14.79	—	—	—	—	121
Z-LIX 64	—	12.19	10.72	8.72	—	10
E-LIX 64	—	13.83	12.34	9.75	—	126[S.M.]
Z-LIX 65N	12.25	11.95	10.56	8.60	—	
E-LIX 65N	14.82	13.82	12.33	9.65 8.75[130]	13.2	
Z-LIX 70	—	11.02	9.58	7.60	—	
E-LIX 70	—	12.98	11.46	8.80	—	
LIX 63	17.0	—	—	12.30[130]		

Note: Values determined by potentiometric titration and extrapolated for aqueous solutions, S.M.: spectrophotometric method, E-LIX 65N in water: 8.70,[127] 8.74,[128] and 8.52[129] from partition in extraction system, P 50 in water at pH 11: 9.50,[123] SME 529 in 20% ethanol: 9.50,[123] and LIX 63 in 70% ethanol: 13.3[121].

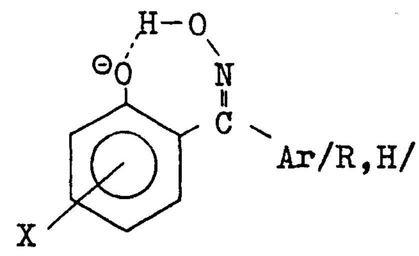
K_2^H, respectively. The acidity of the oximino group is much weaker in comparison to the phenolic group, and in aqueous solutions K_2^H values are approximately three orders higher than K_1^H. These differences disappear in water-dioxane systems, and values of 11.72 and 12.08 were reported for K_1^H and K_2^H, respectively. Thus, in aqueous solutions only the dissociation of the phenolic group can be considered. The degree of dissociation is very small in acidic aqueous solutions and substantially increases only in alkaline media.

On the basis of proton-ligand stability constants (K_1^H) for three types of hydroxyoximes having the same substituents in the aromatic ring, we can assume that hydroxyoxime acidity decreases in the following order: 2-hydroxybenzaldehyde oxime derivatives (I) > aliphatic-aromatic hydroxyoximes (II) > 2-hydroxybenzophenone oxime derivatives (III). Also, literature data concerning commercial extractants show that dissociation of the phenolic group decreases in the order: Z-LIX 65N ≫ P 50 > SME 529 > E-LIX 65N (Table 1). It is clearly seen that the location of oximino group (Z- and E-isomer) has a much stronger effect on the acidity of the phenolic group than the type and structure of substituents bonded with the aromatic skeleton.

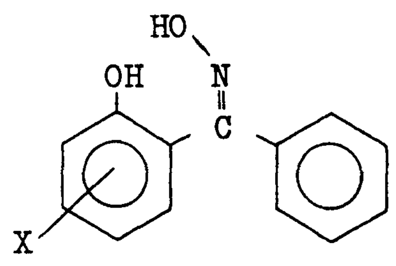
This is consistent with the stability of intramolecular hydrogen bond, which exists in the undissociated (E) hydroxyoxime molecule between the phenolic oxygen and the nitrogen of oxime group (Structure XIX):



XIX



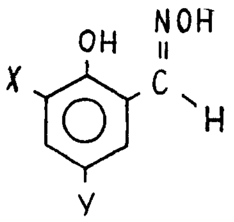
XX



XXI

Such a hydrogen bridge may exist only in isomer E molecules, not in neutral isomer Z molecules. In the case of Z isomer, only the phenolate ion can be stabilized by an intramolecular hydrogen bond between oxygen atoms of oximino and phenolic groups (Structure XX). As a result, Z isomers of 2-hydroxybenzophenone oxime derivatives (Structure XXI), (considering hydroxyoximes of types I-III, only compounds of type III exist in the form of the two isomers, E and Z) are much stronger acids than E isomers.

TABLE 2
Proton-Ligand and Metal-Ligand Stability Constants for 2-Hydroxybenzaldehyde Oxime Derivatives



Oxime structure		System	Proton-Ligand		Metal-Ligand			
X	Y	—	Log K_1^H	Ref.	Metal	Log β_2	Log K_1	Ref.
H	H	Water	8.97	122, 131	Cu (II)	15.2[a]	—	133
			8.85	132	Ti (IV)	31.15	16.3	125
			8.9[a]	133	Ti (IV)[b]	35.7[a]	18.5	125
			8.95	124	Zr (IV)	—	12.4	125
			8.85	125	Zr (IV)[b]	—	17.9[a]	125
			9.3[b]	125	Hf (IV)	—	11.05	125
			9.02[e]	131	Hf (IV)[b]	—	16.7[a]	125
					UO_2 (II)	22.9	13.9	124
		Water: Dioxane = 1:3 (v/v)	11.72	120	Cu (II)	21.5	—	22, 23
			11.0	122, 131	Cu (II)	23.8	12.64	134
			10.7	22	Cu (II)	21.35	—	133
					Cu (II)	21.4	—	122
					Ni (II)	14.3	6.9	22, 23
					Co (II)	13.5	6.4	22, 23
					Fe (III)	—	11.16[c]	133
					Fe (II)	16.73	9.38	22, 23
					Mn (II)	11.9	5.8	22, 23
					Zn (II)	13.5	6.3	22, 23
		Water: Dioxane = 9:1 (v/v)			Mn (II)	—	5.0	33
		Water: ethanol = 1:1 (v/v)	10.23[d]	135	Zn (II)	—	< 5.2	135
					Cd (II)	—	< 4.4	135

TABLE 2 (continued)
Proton-Ligand and Metal-Ligand Stability Constants for 2-Hydroxybenzaldehyde Oxime Derivatives

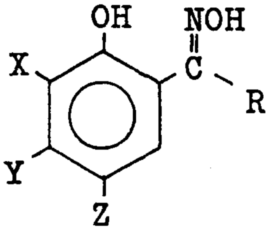
Oxime structure		System	Proton-Ligand		Metal-Ligand			
X	Y	—	Log K_1^H	Ref.	Metal	Log β_2	Log K_1	Ref.
H	CH_3	Water:	11.27	122	Cu (II)	22.2	—	22, 23
		dioxane	11.06	22	Cu (II)	22.6	—	122
		= 1:3			Ni (II)	14.7	7.2	22, 23
					Co (II)	14.34	6.82	22, 23
					Fe (II)	17.4	9.7	22, 23
					Mn (II)	12.28	6.14	22, 23
					Zn (II)	14.3	7.0	22, 23
H	C_4H_9	As above	11.55	122, 131	Cu (II)	23.7	—	122
H	C_6H_{13}	As above	11.66	122, 131	Cu (II)	24.2	—	122
H	C_8H_{17}	As above	11.73	122, 131				
H	$C_{12}H_{25}$	As above	11.82	122, 131				
H	t-C_4H_9	As above	11.56	122, 131				
H	t-C_8H_{17}	As above	11.54	136	Cu (II)	22.32	11.70	136
			11.76	122				
H	Cl	As above	10.25	22	Cu (II)	21.0	—	22, 23
					Ni (II)	13.7	6.6	22, 23
					Co (II)	13.3	6.3	22, 23
					Fe (III)	14.6	8.2	22, 23
					Mn (II)	10.5	4.8	22, 23
					Zn (II)	11.6	5.8	22, 23
H	NO_2	As above	8.72	22	Ni (II)	13.8	6.5	22, 23
					Co (II)	12.9	6.3	22, 23
					Fe (II)	12.5	6.9	22, 23
					Mn (II)	8.32	4.42	22, 23
					Zn (II)	10.9	5.3	22, 23
NO_2	t-C_8H_{17}	As above	8.45	122, 131				
Cl	t-C_8H_{17}	As above	10.17	122				
H	C_4H_9	e	9.59	131				
H	C_6H_{13}	e	9.71	131				
H	$C_{12}H_{25}$	e	9.90	131				
H	t-C_4H_9	e	9.61	131				
NO_2	t-C_8H_{17}	e	6.52	131				
NO_2	t-C_8H_{17}	Water	6.41	131				

Note: Ionic Strength = 0.1 M; 25—30°C.

[a] Extrapolated value.
[b] Ionic strength = 0.
[c] Ionic strength = 0.3 M
[d] Ionic strength = $45 \cdot 10^{-3}$ M.
[e] In an aqueous solution from partition data.

Substituents located in the 3 or 5 position of the aromatic ring influence the magnitude of hydroxyoxime proton-ligand stability constants. If a nucleophilic substituent exists in an aromatic ring (for example, an alkyl group) which increases the electron density of the phenolic oxygen, then the acidity of the hydroxyoximes decreases. This phenolic group acidity decrease is the result of an induction effect and the hyperconjugation of the alkyl groups. On the other hand, the introduction of an electrophilic substituent into the aromatic ring (for example, a hal-

TABLE 3
Proton-Ligand and Metal-Ligand Stability Constants for Aliphatic-Aromatic Hydroxyoximes



Oxime structure					Stability constants						
					Proton-Ligand		Metal-ligand				
R	X	Y	Z	System	log K_1^H	Ref.	Metal	log β_2	log K_1	Ref.
CH_3	H	H	H	Water:	11.86	137—140	Cu(II)	21.41	10.99	140
				dioxane	11.95	119, 141	Ni(II)	—	7.80	140
				= 1:3			Co(II)	20.86	11.43	140
				(v/v)	—		Mn(II)	18.18	10.26	140
					—		Zn(II)	—	9.19	140
						—	VO(II)	24.36	12.47	137
					—		UO_2(II)	21.11	10.66	138
					—		Dy(III)	18.27	9.40	139
					—		Nd(III)	17.73	9.16	139
					—		Pr(III)	17.89	9.27	139
					—		Ce(III)	17.86	9.21	139
				water:	—		MoO_2(II)	8.97^a		34
				ethanol						
				= 1:1						
				(v/v)						
CH_3	H	H	CH_3	water:	12.11	137—140	Cu(II)	22.04	11.33	140
				dioxane	11.99	119	Ni(II)	—	8.41	140
				= 1:3			Co(II)	17.31	9.20	140
				(v/v)			Mn(II)	—	7.86	140
							Zn(II)	—	8.85	140
							VO(II)	21.91	11.72	137
							UO_2(II)	20.42	10.56	138
							Dy(III)	18.95	9.73	139
							Nd(III)	18.20	9.31	139
							Pr(III)	18.34	9.55	139
							Ce(III)	18.45	9.59	139
				water:	—		MoO_2(II)	8.69^a		37
				ethanol	—					
				= 1:1						
				(v/v)						
CH_3	H	CH_3	H	water:	11.71	139				
				dioxane						
				= 1:3						
				(v/v)						
CH_3	CH_3	H	H	As above	12.05	137—140	Cu(II)	22.40	11.47	140
					11.86	141	Ni(II)	—	7.97	140
							Co(II)	—	8.89	140
							Mn(II)	—	8.67	140
							Zn(II)	—	9.03	140
							VO(II)	21.95	11.80	137
							UO_2(II)	20.24	10.64	138
							Dy(III)	19.34	10.04	139

TABLE 3 (continued)
Proton-Ligand and Metal-Ligand Stability Constants for Aliphatic-Aromatic Hydroxyoximes

Oxime structure					Stability constants					
					Proton-Ligand		Metal-ligand			
R	X	Y	Z	System	log K_1^H	Ref.	Metal	log β_2	log K_1	Ref.
							Nd(III)	17.68	9.24	139
							Pr(III)	17.51	9.13	139
							Ce(III)	19.03	10.11	139
CH_3	H	H	1,1,3,3-tetramethylbutyl	As above	11.81	136	Cu(II)	22.75	11.64	136
CH_3	H	H	Cl	As above	11.28	137—140	Cu(II)	21.11	10.77	140
					11.22	119	Ni(II)	—	7.59	140
							Co(II)	18.74	11.17	140
							Mn(II)	15.60	9.06	140
							Zn(II)	—	8.42	140
							VO(II)	20.99	11.22	137
							UO_2(II)	19.28	10.18	138
							Dy(III)	17.42	9.02	139
							Nd(III)	16.90	8.68	139
							Pr(III)	16.84	8.61	139
							Ce(III)	16.72	8.67	139
CH_3	H	H	Br	as above	11.27	137—140	Cu(II)	20.95	10.78	140
							Ni(II)	—	7.57	140
							Co(II)	19.56	11.22	140
							Mn(II)	16.95	9.30	140
							Zn(II)	—	8.26	140
							VO(II)	20.88	11.23	137
							UO_2(II)	19.13	9.91	138
							Dy(III)	17.24	8.96	139
							Nd(III)	16.20	8.34	139
							Pr(III)	16.29	8.49	139
							Ce(III)	16.87	8.92	139
CH_3	H	H	J	As above	11.16	137—140	Cu(II)	20.65	10.68	140
							Ni(II)	—	7.44	140
							Co(II)	18.45	11.04	140
							Mn(II)	—	8.31	140
							Zn(II)	—	8.09	140
							VO(II)	19.63	11.01	137
							UO_2(II)	17.95	9.33	138
							Dy(III)	16.66	8.45	139
							Nd(III)	15.85	8.18	139
							Pr(III)	16.12	8.29	139
							Ce(III)	16.96	8.97	139
CH_3	Cl	H	H	As above	10.77	137—140	Cu(II)	20.00	10.99	140
							Ni(II)	—	7.97	140
							Co(II)	17.55	10.35	140
							Mn(II)	—	7.78	140
							Zn(II)	—	7.76	140
							VO(II)	19.32	10.46	137
							UO_2(II)	17.42	9.14	138
							Dy(III)	16.44	8.52	139
							Nd(III)	15.36	8.04	139
							Pr(III)	15.72	8.20	139
							Ce(III)	15.88	8.32	139

TABLE 3 (continued)
Proton-Ligand and Metal-Ligand Stability Constants for Aliphatic-Aromatic Hydroxyoximes

Oxime structure					Stability constants					
					Proton-Ligand		Metal-ligand			
R	X	Y	Z	System	log K_1^H	Ref.	Metal	log β_2	log K_1	Ref.
CH_3	Br	H	H	As above	11.04	137—140	Cu(II)	21.31	11.19	140
							Ni(II)	—	8.02	140
							Co(II)	18.06	10.37	140
							Mn(II)	—	9.66	140
							Zn(II)	—	8.24	140
							VO(II)	19.27	10.62	137
							UO_2(II)	18.14	9.54	138
							Dy(III)	16.76	8.75	139
							Nd(III)	16.21	8.60	139
							Pr(III)	15.58	8.09	139
							Ce(III)	15.91	8.33	139
CH_3	H	H	NO_2	As above	8.97	137—140	Ni(II)	—	6.36	140
							Co(II)	15.65	9.26	140
							Mn(II)	—	6.17	140
							Zn(II)	—	5.53	140
							VO(II)	15.16	8.67	137
							UO_2(II)	14.30	7.64	138
							Dy(III)	12.34	6.61	139
							Nd(III)	11.45	6.14	139
							Pr(III)	11.92	6.32	139
							Ce(III)	12.27	6.63	139
CH_3	H	OH	H	As above	11.14	137—140	Cu(II)	21.77	11.10	140
							Ni(II)	—	8.23	140
							Co(II)	17.94	10.65	140
							Mn(II)	15.28	9.24	140
							Zn(II)	—	8.46	140
							VO(II)	20.55	10.86	137
							UO_2(II)	18.84	10.04	138
							Dy(III)	18.44	10.11	139
							Nd(III)	16.87	9.04	139
							Pr(III)	16.03	8.22	139
							Ce(III)	15.91	8.16	139
CH_3	H	H	OH	Water: ethanol = 1:1 (v/v)	—		MoO_2(II)	10.14[a]		36
CH_3	H	CH_3O	H	Water: dioxane = 1:3 (v/v)	—		Cu(II)	19.34	9.92	142
							Ni(II)	15.94	8.85	142
							Co(II)	12.87	6.78	142
							Mn(II)	10.75	5.67	142
							Zn(II)	12.65	6.68	142
							UO_2(II)	19.02	9.85	142
CH_3	Cl	H	Cl	As above	10.88	143	Ni(II)	15.65	8.25	143
					11.45[b]	143		16.30[b]		143
							Co(II)	14.12	7.52	143
								15.00[b]		143
							Mn(II)	12.12	6.30	143
								12.81[b]		143
							Zn(II)	15.97	8.40	143
								16.65[b]		143
							VO(II)	19.15	10.05	143

TABLE 3 (continued)
Proton-Ligand and Metal-Ligand Stability Constants for Aliphatic-Aromatic Hydroxyoximes

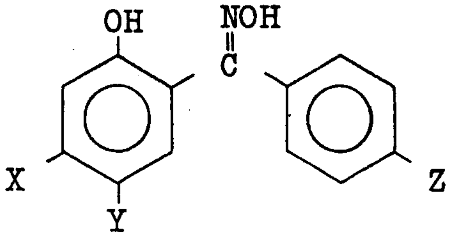
Oxime structure					Stability constants					
					Proton-Ligand		Metal-ligand			
R	X	Y	Z	System	log K_1^H	Ref.	Metal	log β_2	log K_1	Ref.
								20.02^b		143
							UO_2(II)	18.35	9.65	143
								19.24^b		143
							Be(II)	16.49	9.17	143
								17.32^b		143
							Cd(II)	10.22	5.47	143
								10.92^b		143
C_2H_5	H	H	Cl	As above	11.27	119				
C_2H_5	H	H	NO_2	As above	8.86^d	144	Ni(II)	11.74^d	5.64^d	144
					9.21^e	144		11.74^e	6.17^e	144
							Co(II)	14.03^d	8.71^d	144
								13.95^e	8.66^e	144
							Mn(II)	8.99^d	5.38^d	144
								8.98^e	5.31^e	144
							Zn(II)	8.89^d	4.17^d	144
								8.87^e	4.72^e	144
C_3H_7	H	H	H	As above	11.81	145, 146	Cu(II)	22.28	11.00	145 146
							Ni(II)	16.16	7.95	145 146
							Zn(II)	15.95	7.87	145, 146
C_3H_7	H	H	CH_3	As above	11.90	145, 146	Cu(II)	22.64	11.45	145 146
							Ni(II)	16.18	7.61	145 146
							Zn(II)	15.74	7.35	145 146
C_3H_7	CH_3	H	H	As above	12.16	145, 146	Cu(II)	23.31	11.52	145 146
							Ni(II)	17.04	8.07	145 146
							Zn(II)	16.58	8.17	145 146
C_3H_7	H	H	Cl	As above	11.03^d	147	Cu(II)	21.35^d	11.11^d	147
					11.09^e	147		21.37^e	10.92^e	147
							Ni(II)	14.54^d	6.18^d	147
								14.49^e	7.47^e	147
							Co(II)	15.39^d	8.80^d	147
							Mn(II)	—	8.92^f	147
							Zn(II)	14.28^d	6.43^d	147
								14.31^e	7.45^e	147
C_2H_5	H	OH	H	Water-ethanol	—		Fe(III)	—	3.15^c	148
C_3H_7	H	OH	H	Water-ethanol	—		Fe(III)	—	3.08^c	48
C_4H_9	H	OH	H	Water-	—		Cu(II)	8.58^c	—	49, 50
				ethanol	—		Ni(II)	7.45^c	—	49, 50

TABLE 3 (continued)
Proton-Ligand and Metal-Ligand Stability Constants for Aliphatic-Aromatic Hydroxyoximes

Oxime structure					Stability constants					
					Proton-Ligand		Metal-ligand			
R	X	Y	Z	System	log K_1^H	Ref.	Metal	log β_2	log K_1	Ref.
							Fe(III)	—	3.03^c	49, 50

Note: Values determined by potentiometric titration; 25 to 40°C; ionic strength = 0.1 M; a: Anderson method; b: ionic strength = 0; c: the molar ratio method; d: method of least square; e: half-integral method; f: point-wise calculation.

TABLE 4
Proton-Ligand and Copper(II)-Ligand Stability Constants for 2-Hydroxybenzophenone Oxime Derivatives



Oxime structure			Isomer	System	Stability constants				
					Proton-ligand		Metal-ligand		
X	Y	Z			Log K_1^H	Ref.	Log β_2	Log K_1	Ref.
H	H	H	E	Water	9.66^a	10			
			Z		8.48^a		10		
			E	Water:	13.72	10			
				dioxane	12.25	121			
			Z	= 3:7	11.77	10			
				(v/v)	10.30	121			
$C_{12}H_{25}O$	H	H	Z	Water	7.91^a	10			
			E	Water:	13.33	10			
				dioxane	11.89	121			
			Z	= 3:7	11.58	10			
				(v/v)	10.08	121			
H	1,1,3,3-tetramethylbutyl	H	E	Water:	12.42	136	22.98	11.80	136
			Z	dioxane	10.91	136	—		
				= 1:3					
				(v/v)					
H	C_9H_{19}	H	E	As above	12.61	27	23.44	11.93	27
			Z		10.82	27	—		
	LIX 65N		E	Ethanol	13.2$^{S.M.}$	126	26.5$^{S.M.}$	—	126
	LIX 65N			Water	8.75	130	3.11	4.42	130
H	H	C_9H_{19}	E	Water: dioxane = 1:3 (v/v)	12.38	27	23.72	12.19	27
H	Cl	H		As above	11.37	119	—		

Note: Values determined by potentiometric titration; 25 to 30°C; ionic strength = 0.1 *M*; a: extrapolated value; S.M.: spectrophotometric method.

ogen or nitro group) positively increases the phenolic group acidity. The type of halogen has no basic influence on hydroxyoxime acidity.

Biniakiewicz[122] investigated copper complexes with 2-hydroxybenzaldehyde oxime alkyl derivatives and found that the proton-ligand stability constant increases with an increase in the length of the alkyl group.Goszczynski et al.[27] studied the influence of the alkyl chain (5 or 4′) position in aromatic rings of 2-hydroxybenzophenone oxime and found that oximes which have an alkyl substituent in the 4′ position are slightly stronger acids.

Several reports state that the active component of LIX 63, 5,8-diethyl-7-hydroxy-6-dodecanone oxime, is a much weaker acid than other hydroxyoximes (Structures I, II, and III) due to the presence in its molecule of an alcoholic group, which is less dissociable than a phenolic group. Its proton-ligand stability constant is about 2.5 orders higher than that of hydroxyoximes of types I, II, and III.[123]

The data reported by Ashbrook[121] (Table 1) cannot be compared because they were determined for different systems (i.e., LIX 63 was dissolved in 70% ethanol, and LIX 64, LIX 64N, and LIX 70 were dissolved in 70% dioxane). Moreover, the errors of determination are very high, and are up to 1.5 units on the logarithmic scale.

B. Stability of Metal Complexes

The data shown in Tables 2 to 4 demonstrates that hydroxyoximes form highly stable complexes with metals. It is nearly impossible to isolate the intermediate complex MHL^+, since the differences between values of K_1^M and K_2^M are rather small (due to stabilizing intramolecular hydrogen bonds which are formed in the complexes' molecules; see Structures V and VI).

Hydroxyoximes form the most stable complexes with palladium(II) and copper(II). There are no data in the literature referring to the stability constants of palladium complexes, probably due to difficulties in determining such high values of $\lg \beta_2$. Extraction studies with LIX 65N show that extraction constants for palladium are 16 to 23 orders higher than extraction constants for copper and nickel,[149] from which it is evident that palladium complexes are more stable than other metal complexes.

The order of complex stability constants of type I hydroxyoximes is in accordance with the Irving-Williams order of Zn(II) < Cu(II) > Ni(II) > Co(II) > Mn(II).[150,151] Only the location of Fe(II) is different. However, this is not true for complexes of type II hydroxyoximes, and various orders of complex stability constants can be proposed. Specifically, it appears that the location of the considered metals in the order of complex stability is rather random, probably due to small differences in the stability constants (with the exception of copper complexes) and the presence of some impurities in type II hydroxyoximes.

Several works[137-139] have dealt with the determination of stability constants for 2-hydroxyacetophenone oxime derivative complexes with vanadium(IV), uranium(VI) and lanthanoids. The order of complex stability constants (β_2) for these elements is as follows: VO(II) > UO_2(II) ≫ Dy(III) > Nd(III) ≈ Pr(III) ≈ Ce(III). The stability of vanadyl complexes is similar to the stability of copper(II) complexes for appropriate hydroxyoximes.

Salicylaldehyde oxime forms a 2:1 complex with Ti(IV) and 1:1 complexes with Zr(IV) and Hf(IV). Their stability changes in the following order: Ti(IV) > Zr(IV) > Hf(IV) (Table 2).[125]

For hydroxyoximes of type III, only stability constants of complexes with copper(II) have been reported (Table 4).

Copper-ligand stability constants for hydroxyoxime structural types I to III change in the following order: oximes I > oximes II > oximes III; they are, however, of similar order. Nonetheless, these relatively small differences in the stability constants are sufficiently significant to observe different extraction strengths for the hydroxyoximes in actual extraction systems.

Substituents located in the 3 or 5 positions of the aromatic ring effect the metal-ligand stability constants. Nucleophilic substituents usually cause an increase of the complex stability. However, in some cases the opposite effects are observed (Table 3). This can probably be explained by the effect of the substituent upon the strength of the metal-ligand Π donor bond.[22,23]

Electrophilic substituents (e.g., a halogen or nitro group) cause a decrease in the stability of the complex.

As a result, the stability of metal-ligand complexes increases in the order: $NO_2 <$ halogen $<$ H $<$ alkyl. In this last case (i.e., hydroxyoximes having an alkyl group located at the 5 position of the aromatic ring which are used in copper extraction processes in industrial installations), the copper-ligand stability constants increase with an increase in the length of the alkyl group.[122,131]

The location of the alkyl group at the 5 or 4′ position in aromatic rings of 2-hydroxybenzophenone oxime only slightly affects the stability of the oxime-copper complexes (Table 4).[27] In addition, the copper extraction properties of these two types of oxime derivatives are almost identical, indicating that the position of the alkyl group in aromatic rings has no significant influence on such extractions.

The data presented show that the complex stability usually increases as the acidity of hydroxyoximes decreases (although in some cases the opposite effect was reported).

A similar change is observed when the solvent effect is considered (Table 2).[143] The acidity of hydroxyoximes increases and the stability of their metal complexes falls as the solvent dielectric constant increases.

There are no data in the literature about the stability of type IV hydroxyoxime complexes with metals.

IV. EQUILIBRIUM STUDIES OF METAL EXTRACTION FROM DILUTED SOLUTIONS

A. Stoichiometry of Extracted Complexes

Metal extraction from diluted acidic aqueous solutions with hydroxyoximes I-III (HR) dissolved in hydrocarbon solvents can be described by the simplified Equation 5:

$$[M^{n+}]_w + n[HR]_o = [MR_n]_o + n[H^+]_w \qquad (5)$$

where subscripts o and w denote the organic and water phases, respectively, and n stands for the molar ratio of ligand to metal in the complex.

As the hydroxyoxime association in the organic phase, and the complex polymerization and its solvation with hydroxyoxime molecules are taken under consideration, the extraction can be described by Equation 6:

$$\begin{aligned} k[M^{n+}]_w + \left(\frac{nk + l}{z}\right) [(HR)_z]_o \\ = [(MR_n)_k \cdot lHR]_o + n[H^+]_w \qquad (6) \end{aligned}$$

where z, l, and k denote the degree of hydroxyoxime association (z), complex solvation with hydroxyoxime molecules (l), and complex polymerization (k), respectively.

In this last case, the extraction constant is given by Equation 7:

$$K_{ex} = \frac{[(MR_n)_k \cdot 1HR]_o[H^+]_w^2}{[M^{n+}]_w^k[(HR)_z]_o^{(nk + 1)/z}} \cdot K_\gamma \qquad (7)$$

where K_γ is the activity coefficient constant. Assuming that the oxime association in the organic phase can be considered using the association (dimerization) constant determined for this system (or even neglected for very diluted systems) and that all extraction experiments are conducted under the same constant ionic strength (then K_γ is constant), and that polymerization of the complex is not observed ($k = 1$), the following Equation 8 for the metal distribution coefficient is obtained:

$$\begin{aligned} \log D = \log \times K'_{ex} + (n + 1)/z \log \\ [(HR)_z]_o + npH \qquad (8) \end{aligned}$$

where: $K'_{ex} = K_{ex} \cdot K_\gamma$ and $D = \Sigma[M^{n+}]_o/\Sigma[M^{n+}]_w$. This last assumption is true for hydroxyoximes of types I-III for which the complex polymerization was not observed (but it is not justified for α-acyloin oximes, as it was discussed previously in Section II.

Available literature data usually concern the extraction of copper(II) (and in some cases of nickel(II)) from acidic sulfate solutions, although the extraction of copper(II) and palladium(II) from chloride solutions was also described.

Regression coefficients for the relationship of log D vs. equilibrium pH are summarized in

Table 5 and illustrated in Figure 1. Linear relationships were observed for systems containing different diluents, such as aliphatic and aromatic hydrocarbons, with their slopes in most cases near the theoretical value of 2, although in several cases important deviations were observed. Thus, the experimental results support the proposed model of copper and nickel extraction with the formation of 2:1 complexes and the liberation of two hydrogen ions.[152-167]

In the work of Chengye et al.,[168] the slopes of the considered relationship for copper extraction from acidic sulfate solutions with oximes of type II and III dissolved in toluene were reported to be between 0.45 to 1.6.

For iron(III) extraction from acidic sulfate solutions with commercial extractant LIX 64N, Lakshmanan et al.[153] found that the slope of log D vs. pH depends upon extractant concentration, and changes from about 3 to 1.8 as the concen-

TABLE 5
Slope Analysis for Extraction of Metals with Various Hydroxyoxime Extractants

				lgD = f (pH) lgD = f (lg c_{ox})				
Metal	**Hydroxyoxime**	**Diluent**	**μ or concentration of anions [*M*]**	**Slope**	c_{oxime}	**Slope**	**pH**	**Ref.**
Cu^{2+} ($CuSO_4$)	LIX 65N	Heptane	$\mu = 3$ (1 M Na_2SO_4)	2	(6.5—6.7)	2^a	1.5	129
		Toluene		2		2^a	2.1	
		Benzene		2	$10^{-3}M$	2^a	1.5	
Cu^{2+} ($CuSO_4$)	LIX 65N	Dispersol	1/15 M Na_2SO_4	2				128
Cu^{2+} ($2{\cdot}10^{-5}M$ or $10^{-4}M$)	LIX 65N	Hexane Heptane CCl_4 $CHCl_a$ CH_2Cl_2 C_6H_5Cl Toluene	$\mu = 0.1$ ($NaCLO_4$ and perchloric acid)	2		2		127
Ni^{2+} ($2{\cdot}10^{-5}M$ or $10^{-4}M$)	LIX 65N	Hecane Heptane CCl_4 $CHCl_3$ CH_2Cl_2 C_6H_5Cl Toluene	$\mu = 0.1$ ($NaClO_4$ and acetate buffers)	2		2		
Cu^{2+} ($CuSO_4$)	LIX 65N	Methyl-cyclohexane perchlorethylene toluene	1 M Na_2SO_4	2	6.26—31.2 31.2 g dm^{-3}	2	1.5—2.0	152
Cu^{2+} ($5{\cdot}10^{-4}$—$2.5{\cdot}10^{-2}M$ $CuSO_4$)	LIX 64N	Kerosene Toluene Xylene	0.1 M (Na_2SO_4 and H_2SO_4)	1.95	0.2—25%			153
Fe^{3+}	LIX 64N	Kerosene	0.1 M	2.9	5—25%			
[$Fe_2(SO_4)_3$]			(Na_2SO_4 and H_2SO_4)	1.84	1%			
Cu^{2+} ($2{\cdot}10^{-4}M$ $CuSO_4$	LIX 65N	Toluene	1 M Na_2SO_4	2	3.2—31.2 g dm^{-3}	2	2—3	154
Cu^{2+} $7.81{\cdot}10^{-4}M$	2-hydroxy-5-	nonylbenzo-xylene	$5{\cdot}10^{-2}$ M Na_2SO_4	2.04	2.95—11.8	2.21 – $\cdot10^{-3}M$	2—3	27

TABLE 5 (continued)
Slope Analysis for Extraction of Metals with Various Hydroxyoxime Extractants

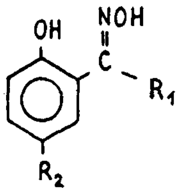
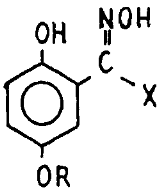
Metal	Hydroxyoxime	Diluent	μ or concentration of anions [*M*]	lgD = f (pH)	lgD = f (lg c_{ox})			Ref.
				Slope	c_{oxime}	Slope	pH	
			H_2SO_4					
$CuSO_4$	phenone oxime					*M*		
	2-hydroxy-4′-nonylbenzophenone oxime			2.16		2.11		
Cu^{2+} $CuSO_4$)		xylene H_2SO_4)	$5\cdot10^{-2}M$					156
	R_1 R_2							
	CH_3 C_9H_{19}			1.75	(3.6—	1.58	2—3	
	CH_3 $C_{12}H_{25}$			1.44	14.4)	2.02		
	C_9H_{19} CH_3			1.55	$\cdot10^{-3}$ *M*	2.25		
	$C_{11}H_{23}$ CH_3			1.46		2.12		
Cu^{2+}	2-hydroxy-	Toluene	μ = 0.1	2	$2\cdot10^{-3}$—	2	~2	157
(10—20 ppm)	benzaldehyde	Benzene	(acetate	2	$10^{-2}M$	2		
($CuSO_4$)	oxime	C_6H_5Cl	buffer)	2		2		
		CH_2Cl_2		2		2		
		$CHCl_3$	—	2		2		
		CCl_4		2		2		
		Hexane		3		3		
		Cyclohexane		3		3		
Co^{2+} (10—20 ppm) $(CH_3COO)_2Co$		The same solvents		2	$2\cdot10^{-3}$—$10^{+2}M$	2	5.6—6.6	
Zn^{2+}		Toluene		2	$5\cdot10^{-2}M$	2	6.4—	
(10—20 ppm)		CH_2Cl_2		2	$10^{-1}M$	2	7.6	
($ZnSO_4$)		$CHCl_3$		2	$10^{-1}M$	2		
		C_6H_6		2	$5\cdot10^{-2}M$	1		
		C_6H_5Cl		2	$5\cdot10^{-2}M$	1		
		CCl_4		2	$5\cdot10^{-2}M$	1		
Cu^{2+}		Toluene	c^{2-}_{SO} =	2	—	—	—	158
($CuSO_4$)		Kerosene	0.5^4M	2	—	~ 2	2	
		Diiso-	(Na_2SO_4 and	2	—	~ 2	1.7	
	R = C_2H_5 – – $C_{7-9}H_{15-19}$ X = $C_{17}H_{35}$ $C_8H_{17}C_6H_5$	propylbenzene	H_2SO_4)					
Cu^{2+} ($CuCl_2$)	LIX 64N	Kerosene	c_{Cl^-} = 1 *M*	2.0 ± 0.07	2—25%	1 ± 0.1	—	159
Fe^{3+}				2.95	2%	~ 1.5	—	

TABLE 5 (continued)
Slope Analysis for Extraction of Metals with Various Hydroxyoxime Extractants

			μ or concentration of anions [*M*]	lgD = f (pH) lgD = f (lg c_{ox})				
Metal	**Hydroxyoxime**	**Diluent**		**Slope**	**c_{oxime}**	**Slope**	**pH**	**Ref.**
(FeCl$_3$)				3.1[b]	10%	~ 1.5	—	
				2.45	25%	~ 1.5	—	
Cu^{2+} (2.5·10^{-4}— 2.5·10^{-2}*M* CuCl$_2$	LIX 70	Kerosene	c_{cl^-} = 4 *M*	1.92 ± 0.06	0.5— 10%			160
			c_{cl^-} =5·10^{-3} 4 *M*	1.985 ± 0.048	0.5—5%			
Cu^{2+} (5·10^{-4} *M* CuCl$_2$)	LIX 70	Kerosene	c_{cl^-} = 4 *M*	~ 2	1—10%			161
			$c_{cl^- + NO_3^-}$ = 4 *M*	~ 2	0.5%			
Cu^{2+}	LIX 64N	Xylene	1*M* NaCl pl 0—3 *M* NaNO$_3$	1.865— 1.89	5%			162
			0.5—2 *M* NaCl	1.191— 1.95	5%			
			3 *M* NaCl	2.06	5%			
			4 *M* NaCl	2.38	5%			
			1 *M* Na$_2$SO$_4$	1.805	5%			
Fe^{3+}	2-hydroxy-5-nonylbenzophenone oxime	Hexane	1 *M* buffer CH$_3$COONH$_4$					31
c_{Fe} = 5·10^{-3}*M*				1	5·10^{-2}*M*			
C_{Fe} = 5·10^{-4}*M*				1.4— 1.7	10^{-3}— 5·10^{-2}*M*			
c_{Fe}=5·10^{-5}*M*				2.5	5·10^{-4}*M*			
Pd^{2+} (100 mg dm^{-3}) (PdCl$_2$)	2-hydroxy-5-nonylacetophenone oxime (SME 529)	MSB 210	c_{NH_4cl} 0.8—3 M c_{Hcl}= 2—4 M c_{cl^-} = 3 M	2	21.7· 10^{-3}*M*	2[a]	c_{H^+} = 1 *M*	163
Pd^{2+} (PdCl$_2$)	LIX 65N	CHCl$_3$	1 *M* (HCl and HClO$_4$) or (HCl and NaCl)	2.02 ± 0.14	10^{-2} *M* c_{pd}= 10^{-4}*M* c_{cl^-}= 1 *M*	2.05 + 0.07	c_{HCl}= −1 *M* c_{Pd} = 5· 10^{-5}M	149
Cu^{2+} [Cu(NO$_3$)$_2$]	2-hydroxy-5-nonylbenzophenone oxime	Heptane Toluene Xylene	0.5 *M* (HNO$_3$ and NaNO$_3$)	2[a]			lgD[H$^+$]^2 = = f(lg c_{ox}) — 0.74—2.4	165
Ni^{2+}	2-hydroxy-5-nonylacetophenone oxime (SME 529)	MSB 210	(NH$_4$NO$_3$ and NH$_3$ or HNO$_3$	lg[NiR$_2$]$_o$ = = f {lg([Ni^{2+}] [H$^+$]} 1 *M*			1.15—7.1 ·10^{-1}*M*	164
Cu^{2+} (CuSO$_4$)	Hydroxy-oximes	Toluene	0.5 *M* (Na$_2$SO$_4$ and H$_2$SO$_4$)	0.45—1.6[b]				168

[a] Dimerization constant was taken into consideration during calculation of RH concentration.

[b] Values taken from diagram.

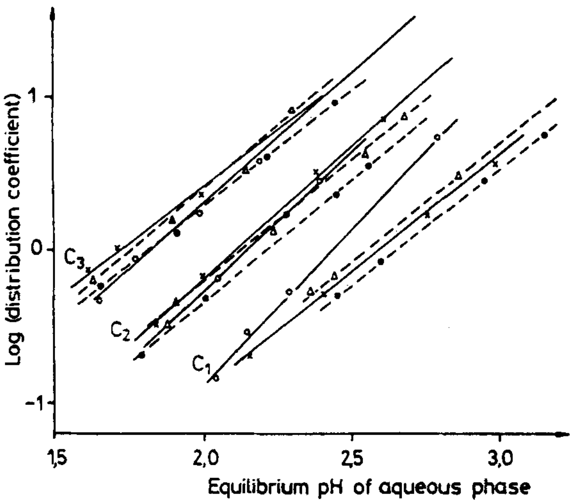


FIGURE 1. Relationship log D vs. equilibrium pH for copper(II) extraction from acidic sulfate solutions with -○-○-○ — 1-(2-hydroxy-5-nonylphenyl)-1-ethanone oxime, -×-×-× — 1-(2-hydroxy-5-dodecylphenyl)-1-ethanone oxime, -●-●-● — 1-(2-hydroxy-5-methylphenyl)-1-dodecanone oxime, -△-△-△ — 1-(2-hydroxy-5-methylphenyl)-1-decanone oxime (oxime concentration: $c_1 = 3.6 \cdot 10^{-3} M$; $c_2 = 7.2 \cdot 10^{-3} M$; $c_3 = 14.4 \cdot 10^{-3}$ M).[156]

tration decreases from 25 to 1%. The slope of 3 is observed in the concentration region of 5 to 25%.

In the case of iron(III) extraction from acidic chloride solutions, the slope changes with a change in extractant concentration; it equals about 3 for the concentration region of 2 to 10%, but decreases to 2.45 for a concentration of 25%. This is not the result of a reduction of Fe(III) to Fe(II) because iron(II) was not found in the system.[159]

A change in slope was also observed by Kasprzak et al.[31] for iron(III) extraction from an aqueous solution containing ammonium acetate buffer, using 2-hydroxy-5-nonylbenzophenone oxime.

The observed slope changes can be caused by a change in the formula of the complex extracted into the organic phase, but to date this is not well understood.

Linear relationships were also obtained as the logarithm of the distribution coefficient was correlated with hydroxyoxime concentration. Exemplary data are given in Figure 2 and summarized in Table 5.

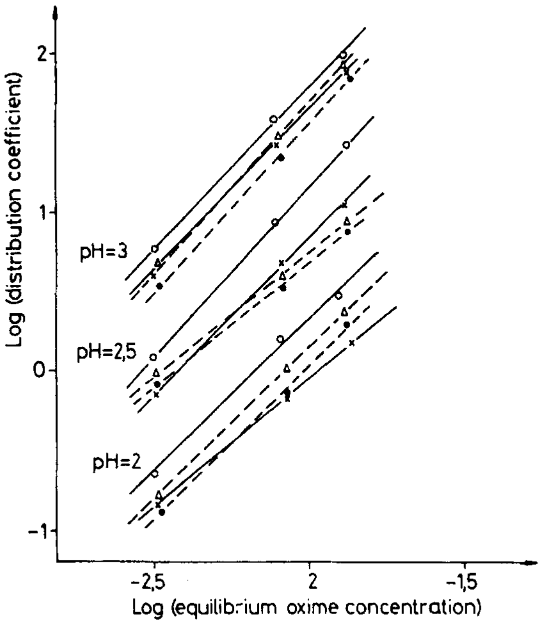


FIGURE 2. Relationship log D vs. log [RH] for copper(II) extraction from acidic sulfate solutions with -○-○-○ — 1-(2-hydroxy-5-nonylphenyl)-1-ethanone oxime, -×-×-× — 1-(2-hydroxy-5-dodecylphenyl)-1-ethanone oxime, -●-●-● — 1-(2-hydroxy-5-methylphenyl)-1-dodecanone oxime, -△-△-△ — 1-(2-hydroxy-5-methylphenyl)-1-decanone oxime.[156]

In most cases, a slope of 2 was obtained for Cu(II), Ni(II), Pb(II), and Co(II) extractions from diluted acidic sulfate or chloride solutions with diluted hydroxyoxime solutions in various aromatic hydrocarbons. This agreement with the theoretical value also means that hydroxyoxime association can be neglected in systems containing solvating diluents. In these systems the dimerization constants are low,[1,13] below 10 $dm^3 mol^{-1}$, and hydroxyoxime dimerization can be practically neglected for concentrations up to 0.1 mol dm^{-3}.

Much higher dimerization constant values are observed in systems containing nonsolvating diluents (i.e., aliphatic and cyclic hydrocarbons). The dimerization constants are in the range of a few tens to one hundred $dm^3 mol^{-1}$, and hydroxyoxime dimerization can only be neglected in a region of relatively low concentrations (i.e. below $5 \cdot 10^{-2}$ M).

This was demonstrated by Komasawa et al.[129,165] who studied the extraction of copper with 2-hydroxy-5-nonylbenzophenone oxime dissolved in heptane and toluene. In the system containing heptane, the correlation of log D vs. log [HR] significantly deviates from linearity. However, this deviation disappears as dimerization constant is considered, and slopes equal to the theoretical value of 2 are then obtained.

Similar results were obtained for the extraction of copper(II) and iron(III) from acidic chloride solutions with commercial LIX 64N dissolved in kerosene.[159] The slopes of 1 and 1.5 were reported for Cu(II) and Fe(III), respectively.

Thus, it seems that the extraction of divalent metals, including copper(II) with various hydroxyoxime extractants, can be described by Equation 9, which takes into account the hydroxyoxime dimerization:

$$[M^{2+}]_w + \frac{2}{z}[(HR)_z]_o = [MR_2]_o + 2[H^+]_w \qquad (9)$$

where z = 1 and 2.

Narayanan et al.[157] supported this model for the extraction of Cu(II), Co(II), and Zn(II) from acetate buffer with salicylaldehyde oxime dissolved in various solvents. However, in two cases other models were proposed. For copper(II) extraction in systems containing aliphatic hydrocarbons, slopes of 3 were obtained for the relationships of log D vs. pH and of log D vs. log [HR]. This was explained by the following extraction model:

$$\begin{aligned} &[Cu^{2+}]_w + 3[H_2Sal]_o \\ &\quad = 3[H^+]_w + Cu(HSal)_3^- \\ &\quad = Cu(HSal)_3^-[H^+]_o + 2[H^+]_w \qquad (10) \end{aligned}$$

where HSal denotes the salicylaldehyde oxime.

In observing slopes of 2 and 1, respectively, for the relationships of log D vs. pH and of log D vs. log (H_2Sal) for zinc(II) extraction with salicylaldehyde oxime dissolved in benzene, chlorobenzene, and carbon tetrachloride, Narayanan et al.[157] proposed the following extraction scheme:

$$[Zn^{2+}]_w + [H_2Sal]_o = [Zn(Sal)]_o + 2[H^+]_w \qquad (11)$$

Szymanowski et al.[136,167] took into account that the slopes of the considered relationships of log D vs. pH and of log D vs. log [HR] may also depend upon the solvation number l, as given in the general form of Equation 6. The slope of the relation log D vs. pH increases as the solvation number increases (Figure 3)[136] both for systems containing solvating and nonsolvating diluents. As a result, the theoretical value of 2 can be obtained as the solvation of the complex molecule by 0 to 2 hydroxyoxime molecules is considered. The optimum value of the solvation number depends upon the molar ratio of hydroxyoxime to copper ions and the type of diluent, and increases as the hydroxyoxime concentration increases. Higher values of the solvation number were predicted for extraction systems containing ethylene dichloride and xylene, in comparison to those containing aliphatic hydrocarbons.

The drawback of such predictions is the lack of confirmation by means of an experimental method. Moreover, for systems containing a large excess of hydroxyoxime, theoretical slopes of 2 can be obtained for various solvation numbers.

We believe that the stability of the extraction constant can be an appropriate criterion of the model validity. The data presented in Figure 4[136] demonstrate good stability of the extraction constant only for models in which the complex is not solvated with hydroxyoxime molecules. When the solvation number increases, then the extraction constant also increases as the results obtained for various equilibrium pH are taken under consideration. Moreover, the extraction constant increases more rapidly as higher solvation numbers are considered. Thus, these results suggest that solvation of the copper complex by hydroxyoxime molecules has little probability.

For palladium(II) extraction from acidic chloride solutions with 2-hydroxy-5-nonylacetophenone oxime dissolved in commercial Shell MSB 210, the linear relationship of log D vs. $[(HR)_2]$ was observed with a slope of 2. Again in this case, as the commercial solvent containing only 2% of aromatic hydrocarbons was used, hydroxyoxime dimerization had to be considered.[163]

Inoue and Maruuchi[163] determined the linear relationship of log D vs. log $[Cl^-]$ for palladium(II) extraction with commercial SME 529; a slope of -4 was obtained.

In most of the reported works concerning the extraction of palladium(II) and other divalent metals,[149,159-161,163] the slopes of relationships of log D vs. pH and of log D vs. log [HR] do not

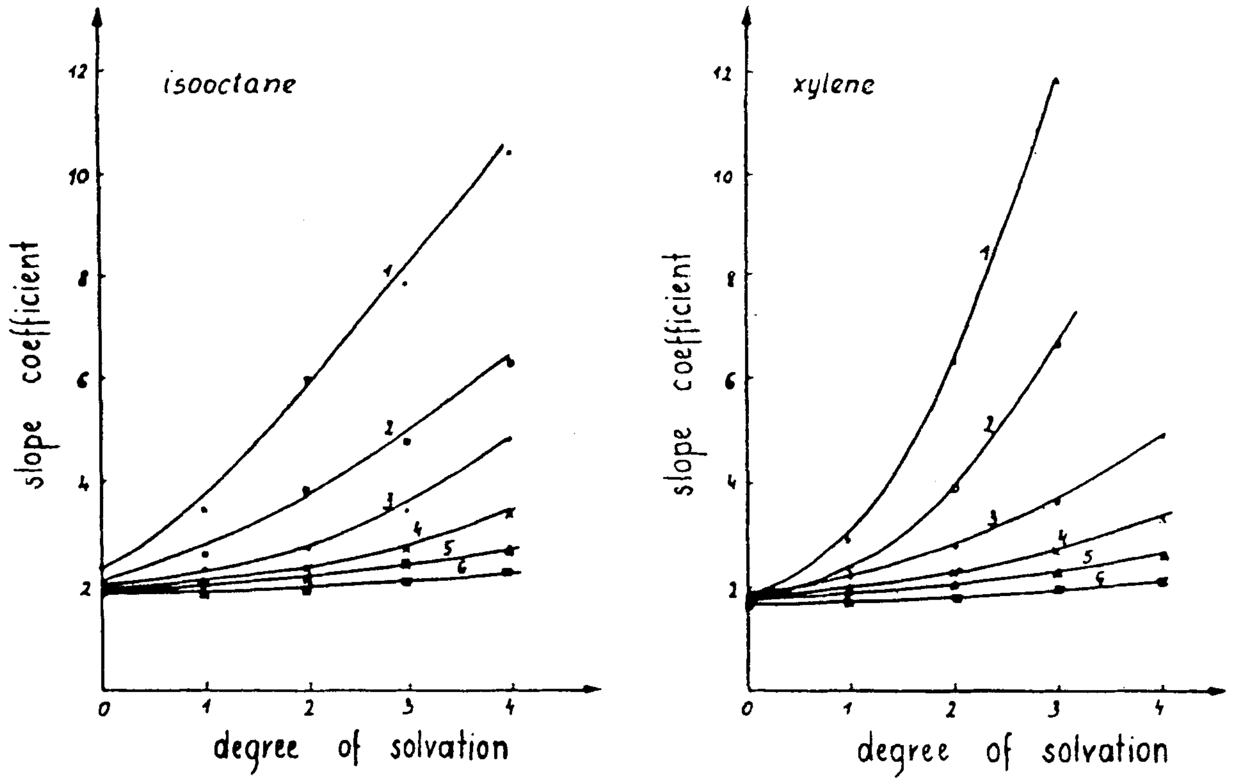


FIGURE 3. Effect of solvation degree upon slopes of relations log D vs. pH for copper(II) extraction with 2-hydroxy-5-(1,1,3,3-tetramethylbutyl) benzophenone oxime (1, c = $2.73 \cdot 10^{-3}$ *M* and z = 1; 2, c = $2.73 \cdot 10^{-3}$ *M* and z = 2; 3, c = $5.47 \cdot 10^{-3}$ *M* and z = 1; 4, c = $5.47 \cdot 10^{-3}$ *M* and z = 2; 5, c = $10.93 \cdot 10^{-3}$ *M* and z = 1; 6, c = $10.93 \cdot 10^{-3}$ *M* and z = 2; c and z denote oxime concentration and degree of oxime association, respectively).[136]

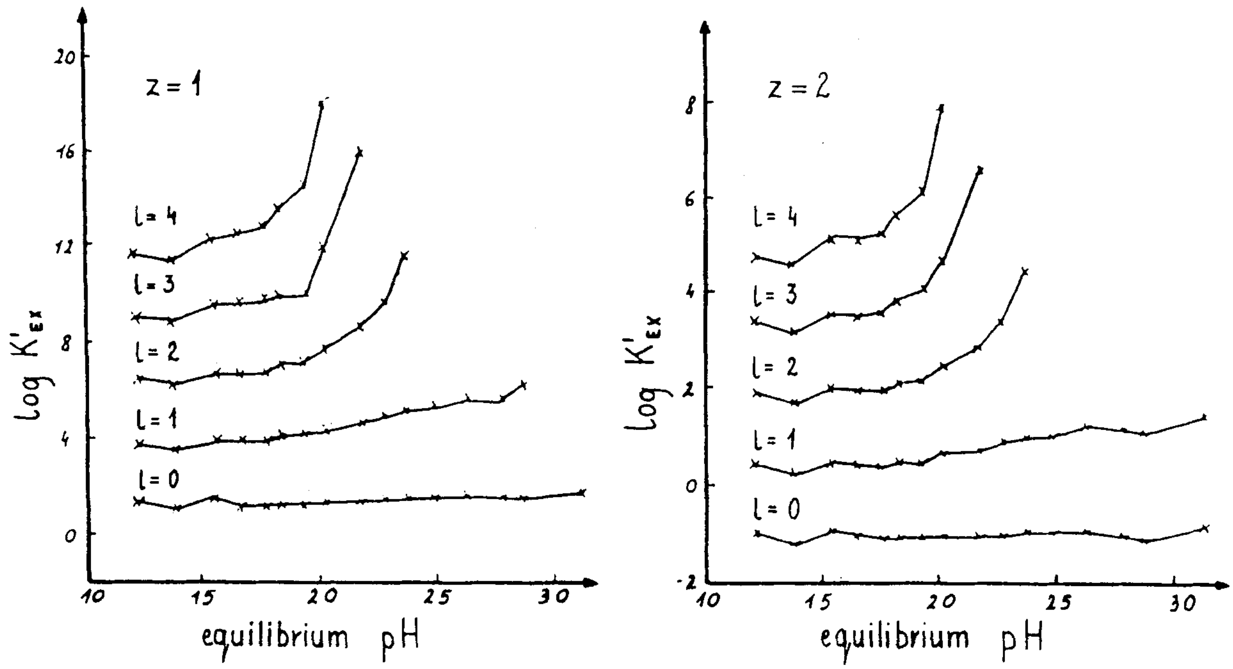


FIGURE 4. Effect of aqueous phase equilibrium pH upon copper(II) extraction constant with 2-hydroxy-5-(1,1,3,3-tetramethylbutyl)benzophenone oxime (isooctane; oxime concentration, $2.73 \cdot 10^{-3}$ *M*; z and l denote degrees of association and solvation, respectively).[136]

depend upon the chloride ion concentration. Only Cognet et al.[162] found that the slope of the relation of log D vs. pH for copper(II) extraction with LIX 64N increases above 2 as NaCl concentration increases above 2 M.

It seems that palladium(II) extraction with hydroxyoximes can be described according to Equation 12:

$$[PdCl_4^{2-}]_w + \frac{2}{z}[(HR)_z]_o = [PdR_2]_o + 2[H^+]_w + 4[Cl^-]_w \qquad (12)$$

where z = 1 and 2.

Extraction of copper(II) and other metals with α-acyloin oximes does not give such univocal results as in the case of metal extraction with hydroxyoximes I to III.

Different relationships of log D vs. pH were observed for Cu(II) extraction with LIX 63 from sulfate and chloride media.[103,104] In sulfate and nitrate media, linear relations were observed, with slopes of 1.6 and 1.5, respectively. In chloride media, concave curves of log D vs. pH were obtained, with a broad minima at pH about 1 (Figure 5). The slopes of the linear portions of these curves obtained at pH above 2 are approximately 1.4 to 1.5. The location of minimum depends upon the extraction conditions, including oxime and chloride concentrations. A slight increase of copper extraction at pH below 0.5 is associated with the formation of hydroxyoxime solvates with copper chlorocomplexes (see Section II).[103,104]

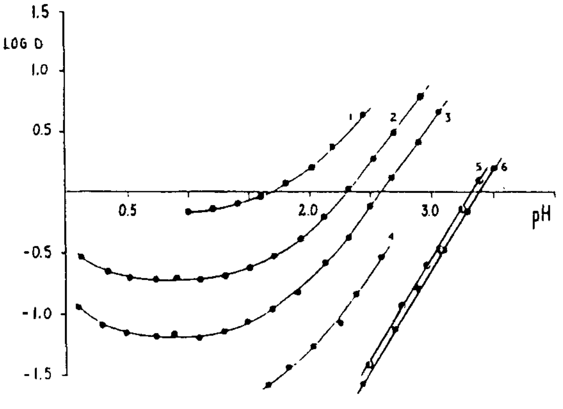


FIGURE 5. Copper(II) extraction from chloride and sulfate solutions with LIX 63 dissolved in kerosene (25°C; 5·10^{-3} *M* Cu(II); 1, 25% LIX 63; 2, 10% LIX 63; 3, 5% LIX 63; 4, 2% LIX 63; 5 and 6, 5% LIX 63; 1.0 *M* chloride solutions for 1 to 4; 0.33 *M* and 0.67 *M* sulfate solutions for 5 and 6, respectively).[103]

Linear relationships of log D vs. pH with slopes of 1.9 to 2.1 were obtained for iron(III) extraction with LIX 63, both for sulfate and chloride systems (Figure 6).[103] The amount of chloride transferred to the organic phase is proportional to the iron content in this phase. These results suggest that iron is extracted as $FeCl(HL)_2$.[103]

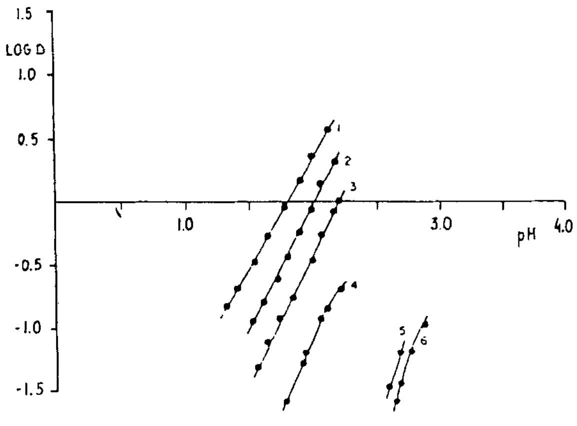


FIGURE 6. Iron(III) extraction from chloride and sulfate solutions with LIX 63 dissolved in kerosene (25°C; 5·10^{-3} *M* Fe(III); for key, see Figure 5).[103]

Important deviations from linearity in the relationship of log D vs. pH were also observed for copper(II) and nickel(II) extraction from nitrate solutions with 5,8-diethyl-7-hydroxy-6-dodecanone oxime (Figures 7 and 8).[98,99] For copper(II) extraction, the slope of this relation increases from 1 to 2 at higher pH values.[98] For nickel(II) a slope of 1 was obtained for oxime concentration above 0.1 M. However, for oxime concentrations below 0.1 M, the slope can change between 0 and 2.[99] In this case, log D increases up to pH 5, from which the experimental function reaches a kind of plateau, where log D seems to be independent of the acidity (slope near 0). Finally, from pH 6, the function follows a straight line of a slope close to 2.

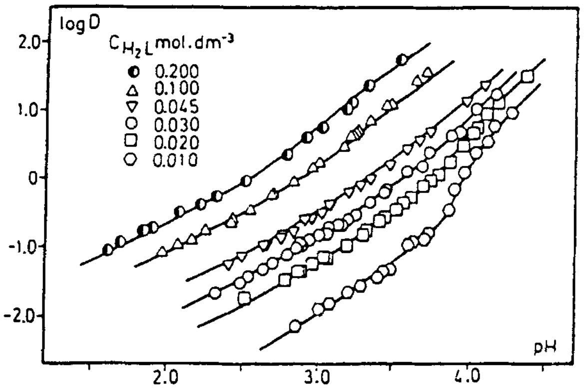


FIGURE 7. Relationship log D vs. equilibrium pH for copper(II) extraction from nitrate solutions with 5,8-diethyl-7-hydroxy-6-dodecanone oxime (initial copper and nitrate concentrations, 0.5 m*M* and 1.0 *M*, respectively).[98]

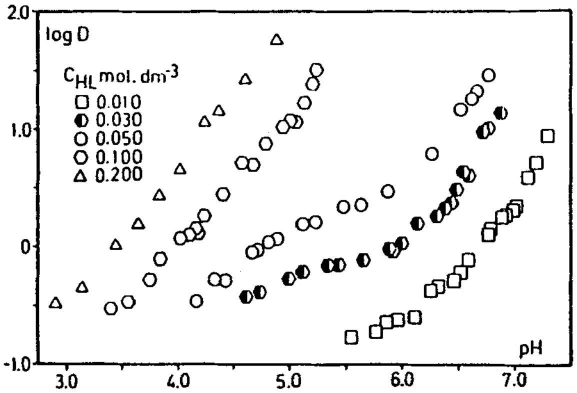


FIGURE 8. Relationship log D vs. equilibrium pH for nickel(II) extraction from nitrate solutions with 5,8-diethyl-7-hydroxy-6-dodecanone oxime (initial nitrate concentration, 1.0 *M*).[99]

This all confirms the formation of various complexes presented in section II. According to Zapatero et al.[98] the content of various complexes, including those solvated with hydroxyoxime molecules, depends both upon the acidity of the aqueous phase and the molar ratio of metal to hydroxyoxime (Figure 9).

Both the composition and the content of the proposed complexes were estimated from mathematical models using graphical and numerical treatment of the extraction data. As a result, there is no direct experimental confirmation of these predictions, as in the case of copper complexes with hydroxyoximes I to III.[136,167]

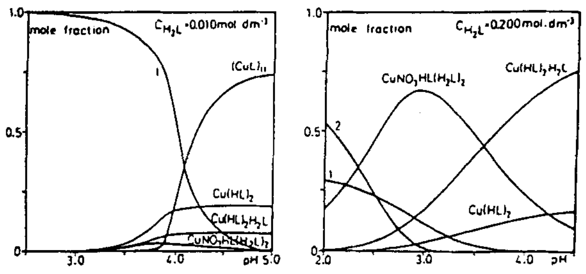


FIGURE 9. Distribution of proposed copper(II) - 5,8-diethyl-7-hydroxy-6-dodecanone oxime complexes (initial copper and nitrate concentrations, 0.5 m*M* and 1.0 *M*, respectively; curves 1 and 2 represent Cu·$\alpha_{Cu(NO_3)}$ and Cu(NO$_3$)$_2$(H$_2$L)$_4$ in the aqueous phase, respectively).[98]

Renninger and Osseo-Asare[94] found that the slope of the function log D vs. pH for nickel extraction from nitrate solutions with the active component of LIX 63 decreases from 1.9 to 1.3 as the phase contact time increases from 8 to 30 h. They attributed these results to a change in the complex structure from $Ni(HL)_2$ into $Ni(HL)(H_2L)_2^+$ and accepted an anion coordination. This is in agreement with the work of Tammi[169] in which he demonstrates that pH lowering favors the formation of solvates according to the following order: $Ni(HL)_2 < Ni(HL)_2(H_2L) < Ni(HL)(H_2L)_2^+ < Ni(H_2L)_3^{2+}$.

Slopes of 1.6 and 1.8 to 2.0 were obtained by Flett et al.[93] and Preston[90] for the extraction of nickel from nitrate solutions.

In all these works, the tendency of α-acyloin oximes towards hydrolysis and isomerization was neglected. We believe that these two phenomena may play an important role, affecting the experimental extraction data and their interpretation, especially in acidic systems and for long phase contact times.

The slope of the function log D vs. pH for cobalt(II) extraction from nitrate solutions decreases from 2.0 to 1.3 as the phase contact time increases from 4 to 30 h.[94] The extraction equilibrium in which $Co(HL)_2$ is extracted is achieved in 30 minutes. Then Co(II) is oxidized in the complex to Co(III), and the formation of $Co(HL)_2H_2L^+$ is proposed. As a result, coextraction of anions also takes place.

Due to the lack of extraction selectivity of copper with respect to iron and inappropriate range of extraction pH, LIX 63 is not used alone for metal extraction. It is used only as an additive to 2-hydroxy-5-alkylbenzophenone oxime to enhance the rate of copper extraction with commercial extractant LIX 64N. In several works, LIX 63 was also used with various organic acids and other reagents.

Flett et al.[93,107,108,170] used mixtures of LIX 63 with α-bromododecanoic acid and with naphthenic acids to extract copper(II) and nickel(II). In this case:[107]

$$[M^{2+}]_w + n[H_2L]_o + m[(HD)_2]_o = (ML_nD_{2m}H_{2m+2n-2})_o + 2[H^+]_w \quad (13)$$

where $(HD)_2$ denotes the dimer of the carboxylic acid, and the distribution coefficient is given by Equation 14:

$$\log D = \log K + 2pH + n \log[H_2L]_o + m \log[(HD)_2]_o \quad (14)$$

A slope near 2 was obtained for the relation log D vs. pH. Slopes near the expected value of 2 were also obtained for the relation log D vs. log $[H_2L]$. They were 2 and 1.7 for systems containing α-bromododecanoic acid and naphthenic acids, respectively. However, unexpected results were reported for the relation log D vs. log $(HD)_2$. A slope of 2 was reported for copper extraction with a mixture of LIX 63 and α-bromododecanoic acid.[107] The data suggest an unrealistic complex structure in which the molar ratio of metal to oxime and to acid is equal to 1:2:4 with the liberation of 2 protons.

For copper extraction with an α-acyloin oxime-carboxylic acid mixture, Flett et al.[93] and Castresana et al.[109] demonstrated a molar ratio of metal to hydroxyoxime to carboxylic acid as 1:2:2. Osseo-Asare et al.[110,111] proposed the following equation for iron(III) extraction from acidic nitrate solutions with an LIX 63-dinonylnaphthalene sulfonic acid mixture:

$$Fe(OH)^{2+} + (HD)_m \cdot 3H_2L = Fe(OH)(H_2L)_3D_2 + (m-2)/m(HD)_m + 2H^+ \quad (15)$$

A slope of 2 was obtained for the relation log D vs. pH, and due to this, the extraction of the dominant cation $Fe(OH)^{2+}$ was proposed.

The discussed literature data demonstrate only qualitative agreements between results reported by various authors. Several reasons for this can be pointed out. The precision of the extraction technique to determine the complex composition is not high, due to the possible analytical errors in the determination of the pH and the metal concentration in both considered phases. Usually, the metal content is determined only in one phase, the aqueous one, and the distribution coefficient is calculated from concentrations in this phase before and after extractions. The partition coefficients of hydroxyoximes and their association constants are usually neglected, as well as the formation of sulfate-complexes and of chlorocomplexes in the aqueous phase.

The experiments are often carried out in an inappropriate region of pH, and too small (below 10%) or too high values (above 90%) of the extraction percent are obtained. Simultaneously, various complexes can be formed which are not recognized by the discussed technique. As a result, an average statistical structure of extracted complexes is predicted.

In most of the discussed works, commercial extractants were applied. They cannot be well identified, considering that oximes I to III are obtained from commercial nonyl- and dodecylphenols, which are very complicated mixtures containing various groups of the products[171] and various alkyl chain isomers. Moreover, oximes of type III contain two types of isomer: the chemically active E isomer and nonactive Z isomer. Isomerization can occur during extraction and storage. This phenomenon was neglected in the works discussed herein. The same is true for oximes of types IV. In this last case, knowledge of hydroxyoxime isomerization is not sufficient, even among specialists in organic chemistry. Hydrolysis of these oximes is usually neglected. Moreover, hydroxyoximes of this type can be contaminated by dioximes whose presence in α-acyloin oximes used for metal extraction has not been revealed.

B. Effect of the Structure of Hydroxyoximes on Their Extraction Properties

The effect of extractant structure upon its extraction properties can be discussed using the extraction equilibrium constant (K_{ex}) or $pH_{0.5}$ which determines the equilibrium pH of the aqueous phase at which 50% of metal is transferred to the organic phase (i.e., D = 1). Location of the extraction isotherms can also be considered.

In real extraction systems in which concentrations instead of activities are considered, both K_{ex} and $pH_{0.5}$ depend upon the extraction conditions (i.e., the composition of both phases). The extraction constant is very sensitive to pH, and significantly different values are obtained at different pH. Moreover, the extraction constant is sensitive to extractant association, and complex solvation and polymerization. Depending upon the assumptions considered, significantly different values of the extraction equilibrium constant can be obtained. As a result, a comparison of the extraction equilibrium constant obtained in independent scientific centers is difficult and may lead to false conclusions.

We believe that the use of $pH_{0.5}$ is more convenient. This parameter also depends upon extraction conditions (i.e., ionic strength, the ratio of extractant-to-metal concentration, the type of diluent, etc.), but these effects are smaller in comparison to the change of extraction equilibrium constant. The $pH_{0.5}$ values obtained in independent research centers can be easily compared and used to predict appropriate conditions for the extraction of a metal and its separation from another metal.

The $pH_{0.5}$ values significantly decrease for the same composition of the aqueous phase (at the same metal concentration and constant ionic strength) as the hydroxyoxime concentration in the organic phase increases (Figures 10 and 11, Tables 6 to 9). Due to this, extractions can be carried out from more acidic solutions (both sulfate and chloride) as the hydroxyoxime concentration increases in concentration characteristic for the system considered (see asymptotes in Figure 10). A further increase in hydroxyoxime concentration only slightly effects the $pH_{0.5}$ values.

A similar effect is observed in the relationship between $pH_{0.5}$ vs. molar ratio of hydroxyoxime concentration in the organic phase to metal concentration in the aqueous phase are considered (Figure 12).[26,173]

A decrease of $pH_{0.5}$ with the increase of hydroxyoximes concentration and/or the molar ratio of hydroxyoxime-to-metal (copper or nickel) concentration, as well as the lowest $pH_{0.5}$ values (asymptotic ones), depend upon the type of diluent. These lowest $pH_{0.5}$ values for copper(II) and nickel(II) extraction with alkyl derivatives of 2-hydroxybenzaldehyde oxime dissolved in various diluents change very significantly according to the following order of diluents: 1,2-dichloroethane > xylene > octane.[26]

The $pH_{0.5}$ values also depend upon the metal concentration in the aqueous phase, and increase as the metal concentration increases. However, this effect is significantly weaker than the effect of hydroxyoxime concentration (Figure 13).[160]

The effect of various anions upon $pH_{0.5}$ is also relatively weak for copper(II) extraction from acidic sulfate and chloride solutions. It was found that $pH_{0.5}$ increases by 0.25 for copper extraction with LIX 64N as the sulfate ion concentration increases from $8 \cdot 10^{-3}$ to $8 \cdot 10^{-2} M$.[153] An increase of $pH_{0.5}$ of 0.25 to 0.35 was also observed for copper extraction with LIX 64N or LIX 70 dissolved in kerosene, as the chloride concentration increases from 0.2 to 4 *M*.[159,160] This effect disappears at lower chloride concentrations (i.e., below 0.2 *M*).

The $pH_{0.5}$ values given in Table 6 demonstrate that the extraction ability of various hydroxyoximes decreases in the following order: alkyl derivatives of 2-hydroxybenzaldehyde oxime (oximes of type I) > aliphatic-aromatic hydroxyketone oximes (oximes of type II) > alkyl derivatives of 2-hydroxybenzophenone oxime

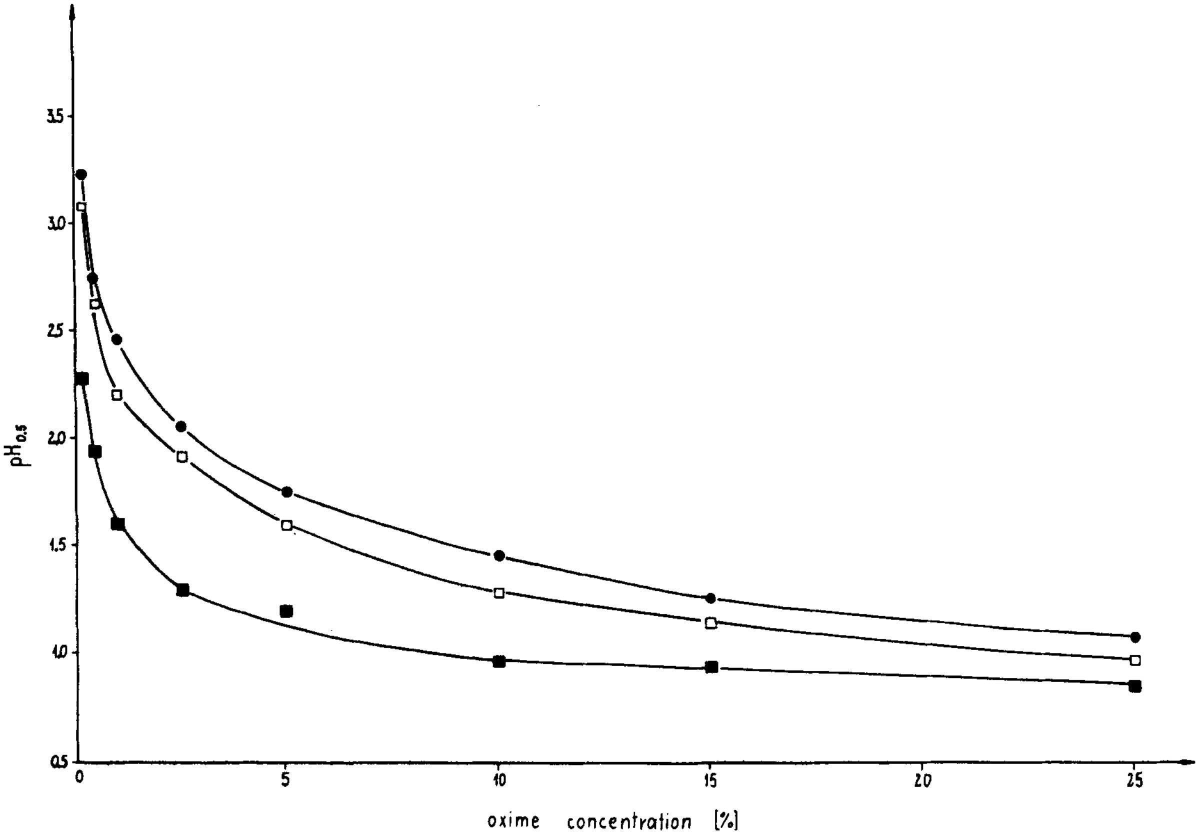


FIGURE 10. Effect of LIX 64N concentration upon pH$_{0.5}$ for copper(II) extraction from acidic sulfate solutions (initial copper concentration, $5 \cdot 10^{-4}$ *M*; ionic strength, 0.1 *M*; 1, ■, kerosene; 2, □, xylene; 3, ●, toluene).[153]

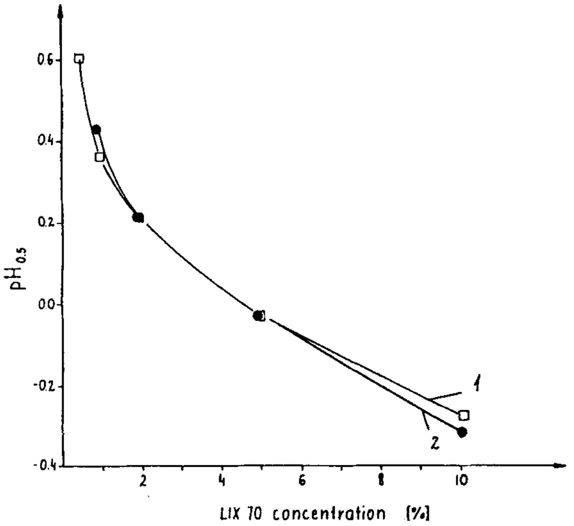
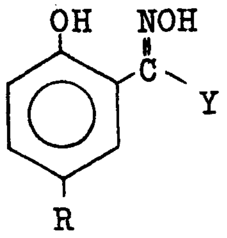


FIGURE 11. Effect of LIX 70 concentration upon pH$_{0.5}$ for copper(II) extraction from chloride solutions with LIX 70 (copper initial concentration: 1, □, $5 \cdot 10^{-4}$ *M* and 2, ●, $2.5 \cdot 10^{-3}$ *M*).[160]

(oximes of type III). The pH$_{0.5}$ values decrease in the opposite direction, i.e., the lowest values are obtained for alkyl derivatives of 2-hydroxybenzaldehyde oxime.

This order of extraction ability of various hydroxyoximes is in agreement with the acidity of the phenolic group, which decreases in the order: oximes I > oximes II > oximes III. It is confirmed by Parish's results[174] (Table 10), who extracted copper from acidic sulfate solutions with hydroxyoximes having various substituents. The presence of an electron-acceptor group near the phenolic group (e.g., a nitro group or chlorine atom in position 3), decreases the electron density on the oxygen atom of the phenolic group. Dissociation constants of these hydroxyoximes are several orders higher than those lacking an electron-acceptor group. They also demonstrate higher extraction strength, and can extract metals from more acidic solutions, as in the case of com-

TABLE 6
$pH_{0.5}$ Values for Copper Extraction from Acidic Sulfate Solutions with Various Hydroxyoximes



No.	Y	R	Oxime concentration [mmol dm^{-3}]	Ionic strength [mol dm^{-3}]	$pH_{0.5}$	Ref.
1	H	C_2H_5	7.81	0.27	1.64	167
2	H	t-C_4H_9	7.81	0.27	1.68	167
3	H	C_8H_{17}	7.81	0.27	1.62	167
4	H	$(CH_3)_3CCH_2(CH_3)_2C-$	2.73	0.27	2.41	172
			5.47	0.27	1.92	172
			7.81	0.27	1.62	167
			10.93	0.27	1.48	172
5	CH_3	$(CH_3)_3CCH_2(CH_3)_2C-$	2.73	0.27	2.58	172
			5.47	0.27	2.31	172
			10.93	0.27	1.94	172
6	C_6H_5	$(CH_3)_3CCH_2(CH_3)_2C-$	2.73	0.27	2.88	172
			5.47	0.27	2.41	172
			10.93	0.27	2.12	172
7	CH_3	C_9H_{19}	3.60	0.05	2.46	156
			7.20	0.05	2.13	156
			14.4	0.05	1.84	156
8	CH_3	$C_{12}H_{25}$	3.60	0.05	2.60	156
			7.20	0.05	2.19	156
			14.4	0.05	1.77	156
9	C_9H_{19}	CH_3	3.60	0.05	2.57	156
			7.20	0.05	2.14	156
			14.4	0.05	1.80	156
10	$C_{11}H_{23}$	CH_3	3.60	0.05	2.64	156
			7.20	0.05	2.21	156
			14.4	0.05	1.79	156
11	C_6H_5	C_9H_{19}	2.95	0.05	2.84	27
			5.90	0.05	2.51	27
			11.80	0.05	2.20	27
12	4′ $-C_9H_{19}-C_6H_4$	H	2.95	0.05	2.71	27
			5.90	0.05	2.47	27
			11.80	0.05	2.16	27

Note: Copper concentration - $7.81 \cdot 10^{-4}$M; xylene as diluent.

mercial extractants of the LIX series (Table 11). The extraction strength of commercial extractants of this series increases in the order of LIX 63 < LIX 64N < LIX 70, which is in agreement with the order of hydroxyl group acidity.

Chengye et al.[168] demonstrated a high extraction strength of hydroxyoximes having an alkoxyl group at the 4 position. These oximes (compound 3 and 8 in Table 12) exhibit a high acidity for the phenolic group, and can extract

TABLE 7
Effect of LIX 65N Concentration Upon Copper Extraction from Acidic Sulfate Solutions[152]

c_{oxime} [g dm^{-3}]	6.26	13.53	31.20
$pH_{0.5}$	2.7	2.35	1.95

Note: Ionic strength: 1 mol dm^{-3}, 25°C

TABLE 8
Effect of LIX 64N Concentration upon Copper(II) and Iron(III) Extraction from Acidic Solutions

LIX 64N concentration (%)	$pH_{0.5}$		
	Sulfate solutions[152]	Chloride Solutions[159]	
	Cu(II)	Cu(II)	Fe(III)
2	—	1.4	2.15[a]
2.5	1.36	—	—
5	1.14	1.1	1.95
10	1.02	0.9	1.8
15	0.87	—	—
25	0.83	0.75	1.65

Note: Kerosene as diluent; initial metal concentration: 5·10^{-3} mol dm^{-3}; ionic strength of aqueous sulfate phase: 0.1 mol dm^{-3}; chloride concentration in aqueous phase: 1 mol dm^{-3}; 25°C.

[a] Extrapolated value.

TABLE 9
Effect of Diluent upon $pH_{0.5}$ for Copper(II) and Nickel(II) Extraction with 1,1,3,3-Tetramethylbutylbenzaldehyde oxime[16]

Diluent	Molar ratio of oxime to metal	$pH_{0.5}$ Cu(II)	$pH_{0.5}$ Ni(II)
Octane	2:1	2.03	5.33
	6:1	—	3.99
	10:1	1.16	—
	20:1	1.08	3.83
Xylene	2:1	2.94	7.01
	6:1	—	6.42
	10:1	1.68	—
	20:1	1.32	5.95
1,2-Dichloroethane	2:1	3.20	7.65
	6:1	—	6.95
	10:1	1.88	—
	20:1	1.52	6.40

Note: Initial Cu(II) and Ni(II) concentration: 7.8·10^{-4} mol dm^{-3} and 8.5·10^{-4} mol dm^{-3}, respectively; ionic strength: 0.2 mol dm^{-3} Na_2SO_4).

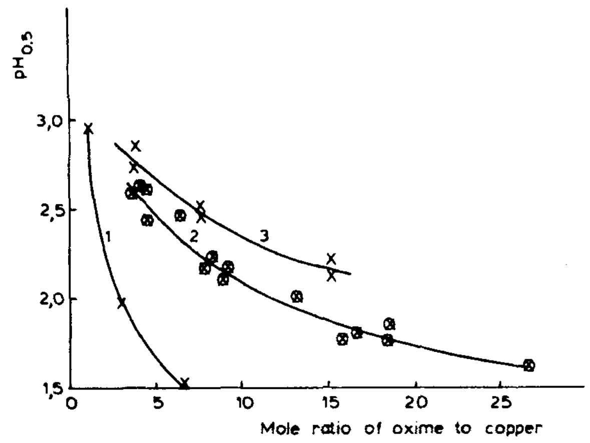


FIGURE 12. Effect of oxime to copper(II) molar ratio upon $pH_{0.5}$ values (1, 2-hydroxy-5-alkylbenzaldehyde oximes; 2, 1-(2-hydroxy-5-alkylphenyl)-1-alkanone oxime; 3, 2-hydroxy-5(4′)-alkylbenzophenone oxime).[173]

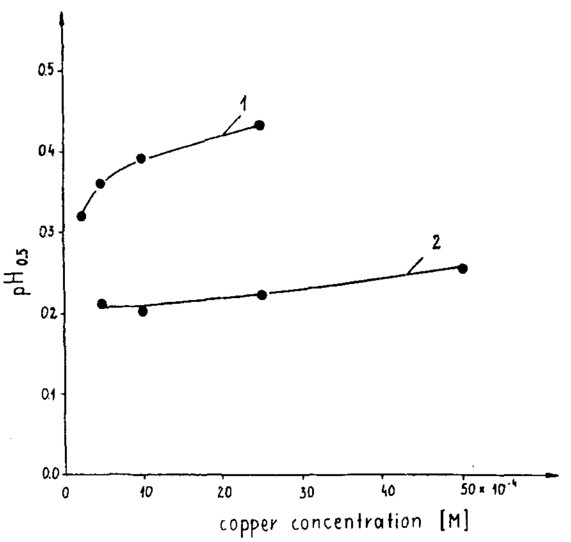
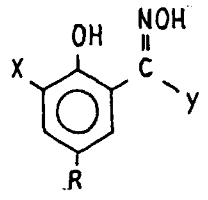


FIGURE 13. Effect of copper(II) concentration upon $pH_{0.5}$ for copper extraction from chloride solutions with LIX 70 (LIX 70 concentration, 1, 1% and 2, 2%; NaCl concentration, 4 *M*).[160]

copper at a lower pH than their homologs having an alkoxyl group at the 5 or an alkyl group at the 4′ position (compounds 2, 5, and 10 in Table 12). However, they also demonstrate similar $pH_{0.5}$ values for 2-hydroxy-5-octylbenzophenone oxime and 2-hydroxy-3-nitro-5-octylbenzophenone oxime (i.e. compounds 1 and 4), although their dissociation constants and extraction constants are significantly different and higher for compound 4. Due to this, these results should be treated cautiously.

TABLE 10
Effect of Hydroxyoxime Structure upon Copper Extraction from Acidic Sulfate Solutions[174]



Y	R	X	$pH_{0.5}$
C_6H_5	$C_{12}H_{25}$	H	1.4
CH_3	C_8H_{17}	H	1.2
H	C_8H_{17}	H	0.8
C_6H_5	C_8H_{17}	NO_2	0.3
C_6H_5	$C_{12}H_{25}$	NO_2	0.2

Note: Initial oxime and copper(II) concentration: 10^{-2} mol dm^{-3} and 6%, respectively; kerosene as diluent.

TABLE 11
$pH_{0.5}$ Values for Copper(II) Extraction with Commercial Extractants[54]

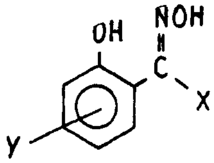
Extractant	$pH_{0.5}$
LIX 63	4.6
LIX 64	3.3
LIX 64N	2.9
LIX 70	2.6

Note: Oxime concentration: equivalent to maximum loading of 100 ppm; xylene as diluent.

Biniakiewicz and Szymanowski[167] studied copper(II) extraction with model individual 2-hydroxy-5-alkylbenzaldehyde oximes having from 2 to 8 carbon atoms in their alkyl group. They found that the effect of the length and structure of the alkyl chain is relatively small and can be neglected (Table 13). A similar conclusion was drawn by Laskorin et al.[158] (Table 14) who investigated copper(II) extraction with various hydroxyoximes having an alkoxyl group at the 4 position. They also demonstrated that oximes of aliphatic-aromatic hydroxyketones (oximes II) are stronger extractants than oximes of aromatic hydroxyketones (oximes III).

Goszczynski et al.[27] demonstrated that the

TABLE 12
Effect of Hydroxyoxime Structure upon Their Extraction Properties[168]



No.	X	Y	pK_a (ethanol)	$pH_{0.5}$	K_{ex}
1	C_6H_5	5-C_8H_{17}	11.12	1.93	0.1333
2	C_6H_5	5-$C_8H_{17}O$	11.48	2.05	0.0701
3	C_6H_5	4-$C_8H_{17}O$	10.99	1.45	1.6450
4	C_6H_5	3-NO_2, 5-C_8H_{17}	7.70	1.93	59.4977
5	4′-$C_{12}H_{25}C_6H_4$	H	11.29	1.72	0.4324
6	2′-Cl-C_6H_4	5-C_8H_{17}	11.08	1.94	0.1858
7	4′-CH_3O-C_6H_4	5-C_8H_{17}	11.08	1.93	0.1080
8	CH_3	4-$C_8H_{17}O$	10.56	1.44	2.5328
9	C_7H_{15}	4-$C_8H_{17}O$	10.68	>3	0.9363
10	CH_3	5-$C_8H_{17}O$	10.83	1.92	0.2091

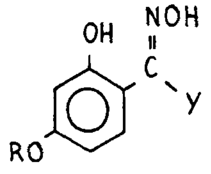
Note: Initial copper and oxime concentration: 10^{-2} mol dm^{-3} and $5 \cdot 10^{-2}$ mol dm^{-3}, respectively; ionic strength: 0.5 mol dm^{-3} (Na_2SO_4 and H_2SO_4); toluene as diluent.

TABLE 13
$pH_{0.5}$ Values for Copper Extraction with 2-Hydroxy-5-Alkylbenzaldehyde Oximes[167]

Diluent	Alkyl group	$pH_{0.5}$	Confidence interval α = 0.5
Isooctane	C_2H_5	—	1.13 ± 0.35
	t-C_4H_9	1.10	
	C_8H_{17}	—	
	$(CH_3)_3CCH_2(CH_3)_2C$-	1.15	
Decalin	C_2H_5	1.05	1.24 ± 0.22
	t-C_4H_9	1.35	
	C_8H_{17}	1.25	
	$(CH_3)_3CCH_2(CH_3)_2C$-	1.33	
Xylene	C_2H_5	1.64	1.64 ± 0.04
	t-C_4H_9	1.68	
	C_8H_{17}	1.62	
	$(CH_3)_3CCH_2(CH_3)_2C$-	1.62	
1,2-Dichloroethane	C_2H_5	2.07	1.91 ± 0.19
	t-C_4H_9	1.80	
	C_8H_{17}	1.88	
	$(CH_3)_3CCH_2(CH_3)_2C$-	1.90	

Note: Initial copper and oxime concentrations: $7.81 \cdot 10^{-4}$ mol dm^{-3} and $7.81 \cdot 10^{-3}$ mol dm^{-3}, respectively; ionic strength: 0.27 mol dm^{-3}.

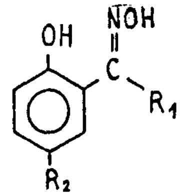
TABLE 14
Effect of Hydroxyoxime Structure upon $pH_{0.5}$ for Copper Extraction from Acidic Sulfate Solutions[158]



Y	R	$pH_{0.5}$
C_8H_{17}	C_2H_5	0.95
C_8H_{17}	C_8H_{17}	1.23
$C_{17}H_{35}$	C_2H_5	1.08
C_6H_5	$C_{7-9}H_{15-19}$	1.31
C_6H_5	$i\text{-}C_8H_{17}$	1.38

Note: Sulfate ion concentration: 0.5 mol dm^{-3}; toluene as diluent.

TABLE 15
$pH_{0.5}$ for Some Oximes of Aliphatic-Aromatic Hydroxyketones[175]



R_1	R_2	$pH_{0.5}$
CH_3	$t\text{-}C_8H_{17}$	1.46
CH_3	$n\text{-}C_8H_{17}$	1.48
$n\text{-}C_7H_{15}$	CH_3	1.56

Note: Initial copper(II) and oxime concentration: $2 \cdot 10^{-2}$ mol dm^{-3} and 0.1 mol dm^{-3}, respectively; Na_2SO_4 concentratioin: 0.5 mol dm^{-3}; toluene as diluent.

position of the alkyl group in 2-hydroxy-5(4′)-nonylbenzophenone oximes (compounds 11 and 12 in Table 6) only slightly affect their extraction properties, and, as a result, only slightly lower $pH_{0.5}$ values were obtained for oximes containing the alkyl group at the 4′ position. However, Chengye et al.[168] demonstrated a much higher extraction strength for 2-hydroxy-4′-dodecylbenzophenone oxime compared to 2-hydroxy-5-octylbenzophenone oxime (compounds 1 and 5 in Table 12).

The effect of the position of a long alkyl chain in oximes of aliphatic-aromatic hydroxyketones (oximes of type II) is also relatively small, and quite similar values of $pH_{0.5}$ were reported for various oximes of this type (compounds 7 to 10 in Tables 6 and 15). The effect of the alkyl length is also negligible. Only Chengye et al.[168] demonstrated the increase of $pH_{0.5}$ and the decrease of the extraction equilibrium constant for copper extraction with 1-(2-hydroxy-5-octylphenyl)-1-alkanone oximes (compounds 8 and 9 in Table 12) as the alkyl length increases. In this case, $pH_{0.5}$ values were even higher than those determined for alkyl derivatives of 2-hydroxybenzophenone oxime, which is in contradiction with all other works concerning both model and commercial extractants.

The $pH_{0.5}$ values depend significantly upon the type of organic diluent,[24-27,30-32,158,167,172,175-179] and this effect is often stronger than that associated with a change in hydroxyoxime structure. The extraction of copper(II) and nickel(II) increases and $pH_{0.5}$ decreases according to the following diluent order (Tables 9, 13, 16 to 19): chlorohydrocarbons ≤ aromatic hydrocarbons < cyclic hydrocarbons = aliphatic hydrocarbons.

The extraction of copper from acidic sulfate solutions with commercial P 17 and P 50 extractants dissolved in commercial diluents increases in the following order:[179] Aromasol H (ICI) ≪ Escaid 100 (ESSO) < Isopar L (ESSO) (i.e., as the content of aromatics decreases from 100% in Aromasol H to 20% in Escaid 100, to 0% in Isopar L). Thus, the best extraction effects are obtained as aliphatic and alicyclic hydrocarbons are used as diluents. However, commercial diluents contain some amounts of aromatic hydrocarbons (up to 20%) to improve the solubility of hydroxyoximes and their complexes in the organic phase.

The above orders of diluents can be attributed to the solvation of hydroxyoxime molecules with diluent molecules. The extraction significantly decreases as the solvation increases. As a result, an increase of $pH_{0.5}$ values and a decrease of extraction equilibrium constant (Tables 20 to 22)

TABLE 16
$pH_{0.5}$ Values for Copper Extraction with 2-Hydroxy-5-t-Butylbenzaldehyde Oxime[24]

Diluent	Oxime concentration $1.0 \cdot 10^{-3}M$	 $2.5 \cdot 10^{-3}M$	 $5.18 \cdot 10^{-3}M$
Octane	3.16	2.29	1.79
Isooctane	2.96	2.0	1.51
Xylene	2.6	1.47	—
1,2-Dichlorethane	2.6	1.47	—

Note: Copper concentration: $7.81 \cdot 10^{-4}$ mol dm^{-3}; ionic strength: $5 \cdot 10^{-2}$ mol dm^{-3}.

TABLE 17
$pH_{0.5}$ Values for Copper Extraction with 2-Hydroxy-5-Nonylacetophenone Oxime

Diluent	$pH_{0.5}$ Cu(II)[a]	 Cu(II)[b]	 Fe(III)[b]
Heptane	1.68	1.31	—
Isooctane	—	1.31	3.29
Methylcyclohexane	1.70	1.31	—
Shell Diluent MSB 210 (appr. 2% aromatics)	1.70	—	—
Escaid 100 (appr. 20% aromatics)	1.70	—	—
Toluene	2.14	1.58	3.95

Note: Na_2SO_4 concentration: 0.5 mol dm^{-3}; a: initial copper and oxime concentration — $2 \cdot 10^{-3}$ mol dm^{-3} and $2 \cdot 10^{-2}$ mol dm^{-3}, respectively.[176] b: initial metal and oxime concentration — $2 \cdot 10^{-2}$ mol dm^{-3} and 10^{-1} mol dm^{-3}, respectively.[175]

TABLE 18
$pH_{0.5}$ for Copper(II) Extraction with 2-Hydroxy-4-Alkoxy (C_7-C_9) Benzophenone Oxime[150]

Diluent	$pH_{0.5}$
Kerosene	<1
Butylbenzene	<1
Diisopropylbenzene	1.1
Toluene	1.26
Kerosene and 5% decanol	2.24

Note: SO_4^{2-} concentration: 0.5 mol dm^{-3}.

TABLE 19
$pH_{0.5}$ for Iron(III) Extraction with 2-Hydroxy-5-Nonyl-Benzophenone Oxime[31]

Diluent	Buffer [1 mol dm^{-3}]	$pH_{0.5}$
Hexane	Ammonium acetate	3.6
Hexane	Sodium acetate	4.3
Chloroform	Ammonium acetate	5.3[a]

[a] Value taken from diagram.

Note: Iron and oxime concentration: $5 \cdot 10^{-4}$ mol dm^{-3} and $5 \cdot 10^{-3}$ mol dm^{-3}, respectively.

TABLE 20
Equilibrium Extraction Constants for Cobalt(II) Extraction with 2-Hydroxy-5-Nonylbenzophenone Oxime[30]

Diluent	$pH_{0.5}$	lg K_{ex}	$K_{ex} \cdot 10^8$
Benzene	8.75	8.6	3.98
Chloroform	9.00	9.0	10
Hexane	7.65	6.9	0.079

Note: Initial cobalt and oxime concentration: 10^{-4} mol dm^{-3} and 10^{-3} mol dm^{-3}, respectively; ammonium acetate buffer.

is observed in solvating diluents such as chlorohydrocarbons and aromatic hydrocarbons.

Extraction equilibrium constants determined by Akiba and Freiser[127] for copper extraction with LIX 65N in systems containing aliphatic hydro-

TABLE 21
Equilibrium Extraction Constant for Copper(II) Extraction with 2-Hydroxy-5-Nonylbenzophenone Oxime Isolated from LIX 65N

Diluent	Aqueous solution	$K'_{ex}(K_{ex})$	Ref.
Heptane	Distilled water	56 (155)	129
	1 *M* Na_2SO_4(μ = 3 *M*)	4.9	129
	μ = 0.1 *M* ($NaClO_4$ and $HClO_4$)	22.4	127
	—	30.3 ± 6.1	166
	0.5 *M* (HNO_3, $NaNO_3$)	90	165 180
Hexane	μ = 0.1 *M* ($NaClO_4$ and $HClO_4$)	20.0	127
Dispersol	1/15 *M* Na_2SO_4	2.5	128
Xylene	0.5 *M* (HNO_3, $NaNO_3$)	1.5	165 180
Toluene	Distilled water	0.95 (3.6)	129
	1 *M* Na_2SO_4	$6.3 \cdot 10^{-2}$	129
	1 *M* Na_2SO_4	$7.2 \cdot 10^{-2}$	154
	μ = 0.1 *M* ($NaClO_4$ and $HClO_4$)	$6.3 \cdot 10^{-1}$	127
	0.5 *M* (HNO_3, $NaNO_3$)	1.5	165
Benzene	1 *M* Na_2SO_4	$4.4 \cdot 10^{-2}$	129
Chlorobenzene	μ = 0.1 *M* ($NaClO_4$ and $HClO_4$)	1.66	127
1,2-Dichloroethane	μ = 0.1 *M* ($NaClO_4$ and $HClO_4$	$5.5 \cdot 10^{-1}$	127
Chloroform	μ = 0.1 *M* ($NaClO_4$ and $HClO_4$)	$8.3 \cdot 10^{-1}$	127
Tetrachloromethane	μ = 0.1 *M* ($NaClO_4$ and $HClO_4$)	7.2	127
Nitrobenzene	0.5 *M* (HNO_3, $NaNO_3$)	$9.7 \cdot 10^{-2}$	180
n-Butyl ether	0.5 *M* (HNO_3, $NaNO_3$)	$3.0 \cdot 10^{-3}$	180
Methyl-n-heptyl ketone	0.5 *M* (HNO_3, $NaNO_3$)	$2.0 \cdot 10^{-3}$	180
2-Ethylhexanol	0.5 *M* (HNO_3, $NaNO_3$)	$1.3 \cdot 10^{-3}$	180

carbons are 20 to 40 times greater than those obtained for systems containing aromatic hydrocarbons and chlorohydrocarbons. A similar ratio of extraction constants determined for systems containing heptane and toluene was reported by Komasawa et al.[129] ($K_{ex\ heptane}/K_{ex\ toluene}$ was approximately 40 or 60 to 80, depending upon assumptions concerning the dissociation constants of $CuSO_4$ and H_2SO_4).

Some contradictory results were obtained for nickel(II) extractions, Akiba and Freiser[127] reported that the equilibrium constant for nickel extractions with LIX 65N does not depend upon the diluent type (hexane, heptane, tetrachloromethane, dichloromethane, chlorobenzene, toluene), and equals to about 10^{-6}. However, Komasawa and Otake[180] reported the relative extraction equilibrium constants as equal to 10^5: $1.7 \cdot 10^3$: 1 in systems containing heptane, xylene, and 2-ethylhexanol, respectively.

It was also stated, that diluents effect the selectivity of copper(II) extraction with respect to nickel(II). In this case, the selectivity of copper extraction decreases (the differences in $pH_{0.5}$ values decrease) in the following order of diluents: 1,2-dichloroethane > xylene > octane (Table 9).[26] However, copper-hydroxyoxime complexes are much more stable than nickel-hydroxyoxime complexes and copper equilibrium constants are 10^5 to 10^7 orders higher than those constants determined for nickel extraction (Tables 21 and 22). Taking this into account, copper can be quite selectively extracted in the presence of nickel with hydroxyoximes of types I to III, not only

TABLE 22
Equilibrium Extraction Constant for Nickel(II) Extraction with 2-Hydroxy-5-Nonylbenzophenone Oxime (HNBPO) and 2-Hydroxy-5-Nonylacetophenone Oxime (HNAO) Isolated from LIX 65N and SME 529

Oxime	Diluent	Aqueous phase	K'_{ex}	Ref.
HNBPO	Heptane	0.5 *M* (HNO_3, $NaNO_3$)	$1.2 \cdot 10^{-4}$	180
		μ = 0.1 *M* ($NaClO_4$) and acetate buffer	$1.0 \cdot 10^{-6}$	127
	Hexane	μ = 0.1 *M* ($NaClO_4$) and acetate buffer	$1.3 \cdot 10^{-6}$	127
	1,2-Dichloroethane	μ = 0.1 *M* ($NaClO_4$) and acetate buffer	$4.6 \cdot 10^{-7}$	127
	Chloroform	μ = 0.1 *M* ($NaClO_4$) and acetate buffer	$1.3 \cdot 10^{-6}$	127
	Tetrachloromethane	μ = 0.1 *M* ($NaClO_4$) and acetate buffer	$1.6 \cdot 10^{-6}$	127
	Chlorobenzene	μ = 0.1 *M* ($NaClO_4$) and acetate buffer	$1.6 \cdot 10^{-6}$	127
	Toluene	μ = 0.1 *M* ($NaClO_4$) and acetate buffer	$4.8 \cdot 10^{-7}$	127
	Xylene	0.5 *M* (HNO_3, $NaNO_3$) and acetate buffer	$2.0 \cdot 10^{-6}$	180
	2-Ethylhexanol	0.5 *M* (HNO_3, $NaNO_3$)	$1.2 \cdot 10^{-9}$	180
HNAO	MSB 210	1 *M* NH_4NO_3 and (NH_3 or HNO_3)	$3.2 \cdot 10^{-5}$	164 184

from acidic solutions, but, under appropriate conditions (i.e., high loading of the organic phase and appropriate pH), also from ammonia media. Nickel can also be selectively stripped with diluted sulfuric acid solution (3 g dm^{-3}).

In addition, hydroxyoximes of type IV extract copper(II) more effectively than nickel(II); the $pH_{0.5}$ values amount of 3 to 4 and 6 to 7, respectively.

Besides the extraction of copper(II) and nickel(II), hydroxyoximes of types I to III can also effectively extract palladium(II). Under some specific conditions they can also extract other metals (Tables 17, 23, and 24). At pH above 3 they can extract Ni(II), Co(II), and small amounts of Fe(III), Pb(II), Mg(II), and Cd(II). Zinc(II) is practically unextracted from acidic aqueous solutions; however, it can be extracted at pH 8 to 9 with the use of a large excess of hydroxyoxime extractant.[32,181]

The selectivity of copper extraction with hydroxyoximes of types I to III with respect to iron is high at low pH values (i.e., pH 1.5 to 2). Due to this, copper can be selectively extracted from aqueous solutions containing an excess of iron. This selectivity, so important in industrial processes, depends upon the type of extractant and diluent, and the composition of the aqueous phase. Higher selectivity is observed for copper extracting with alkyl derivatives of 2-hydroxybenzaldehyde oxime than with alkyl derivatives of 2-hydroxybenzophenone oxime, and for systems containing aromatic hydrocarbons in comparison to those containing aliphatic hydrocarbons.

A change of the extraction system from acidic sulfate to acidic chloride decreases the selectivity of copper extraction with respect to iron. As a result, smaller differences between $pH_{0.5}$ values determined for Cu(II) and Fe(III) are observed in systems containing chloride ions in the aqueous phase.

According to Eccles et al.,[182] sulfate ions significantly decrease the extraction of both copper(II) and iron(III) (Figure 14). However, the decrease of iron(III) extraction is stronger than that of copper(II), and, due to this, an increase in extraction selectivity is observed in systems containing higher concentrations of sulfate ions. The same concerns chloride systems (Figure 15), although the effect of chloride ion concentration

TABLE 23
$pH_{0.5}$ Values for Extraction of Metals with 2-Hydroxybenzaldehyde Oxime[181]

Metal	Cu	Ni	Pb	Co	Mg	Mn	Cd
$pH_{0.5}$	1.7	5.15	6.65	6.9	9.6	9.75	10.65

Note: Initial metal and oxime concentration: 10^{-4} mol dm^{-3} and 10^{-2} mol dm^{-3}, respectively; benzene as diluent.

TABLE 24
$pH_{0.5}$ Values for Copper(II) and Iron(III) Extraction with 2-Hydroxy-5-Octylbenzaldehyde Oxime(I) and 2-Hydroxy-5-Octylbenzophenone Oxime(II)[174]

	$pH_{0.5}$	
Oxime	Cu(II)	Fe(III)
I	0.75	1.96
II	1.43	3.11

Note: Initial metal and oxime concentration: 10^{-2} mol dm^{-3} and 6%, respectively; kerosene or xylene as diluent.

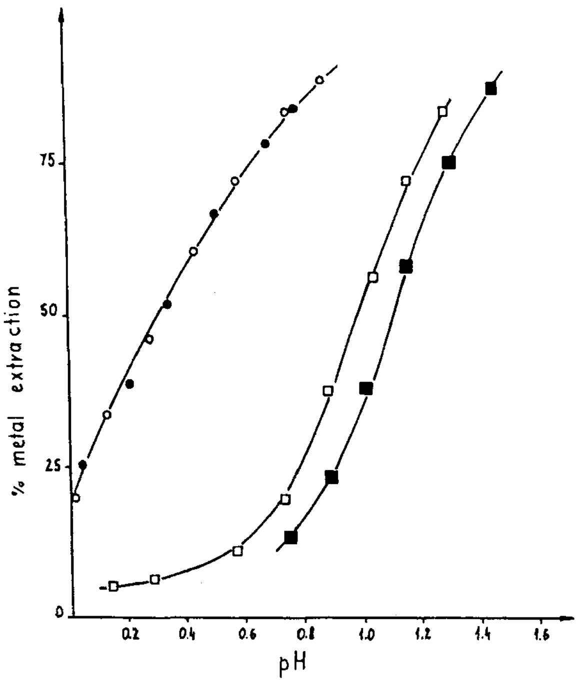


FIGURE 14. Effect of sulfate concentration upon extraction of Cu(II) and Fe(III) with LIX 64N (20°C; ○, 3.18 g dm^{-3} Cu(II) and 408 g dm^{-3} $NaNO_3$; ●, 3.18 g dm^{-3} Cu(II), 153 g dm^{-3} $NaNO_3$ and 96 g dm^{-3} Na_2SO_4; □, 1.4 g dm^{-3} Fe(III) and 410 g dm^{-3} $NaNO_3$; ■, 1.4 g dm^{-3} Fe(III), 155 g dm^{-3} $NaNO_3$ and 96 g dm^{-3} Na_2SO_4).[182]

is weaker in comparison to the effect of sulfate ions.

Hydroxyoximes of type IV do not selectively extract copper(II) with respect to iron(III). Moreover, they extract Fe(III) stronger than Cu(II), and $pH_{0.5}$ values amount to 2 to 2.5 and 3 to 4, respectively. As a result, they cannot be applied in industrial processes as individual extractants. A higher extraction efficiency of Cu(II) with LIX 63 is observed in chloride systems, in comparison to sulfate ones at comparable conditions of constant ionic strength. Extraction of iron(III) is also higher in chloride systems, and at pH below 3 significant amounts of Fe(III) are extracted with LIX 63 from chloride solutions but not from sulfate solutions.[103]

A temperature increase causes an increase in the copper distribution coefficient in agreement with the endothermic heat effect (ΔH = 21 kJ mol^{-1} and ΔH = 27 kJ mol^{-1} for chloride and sulfate systems).[153,159]. However, in chloride systems, the copper distribution coefficient decreases at temperatures above 30°C, probably due to the formation of chlorocomplexes, $CuCl^+$ and $CuCl_2$.[159]

The iron(III) distribution coefficient also increases with an increase in temperature, and this effect is stronger in comparison to that of copper(II).[182] As a result, the selectivity of copper extraction decreases as the temperature increases from 20 to 50°C.

Although hydrochloride extract palladium(II) well from hydroxyoxime solutions[105,106,183] there are very little physicochemical data upon this

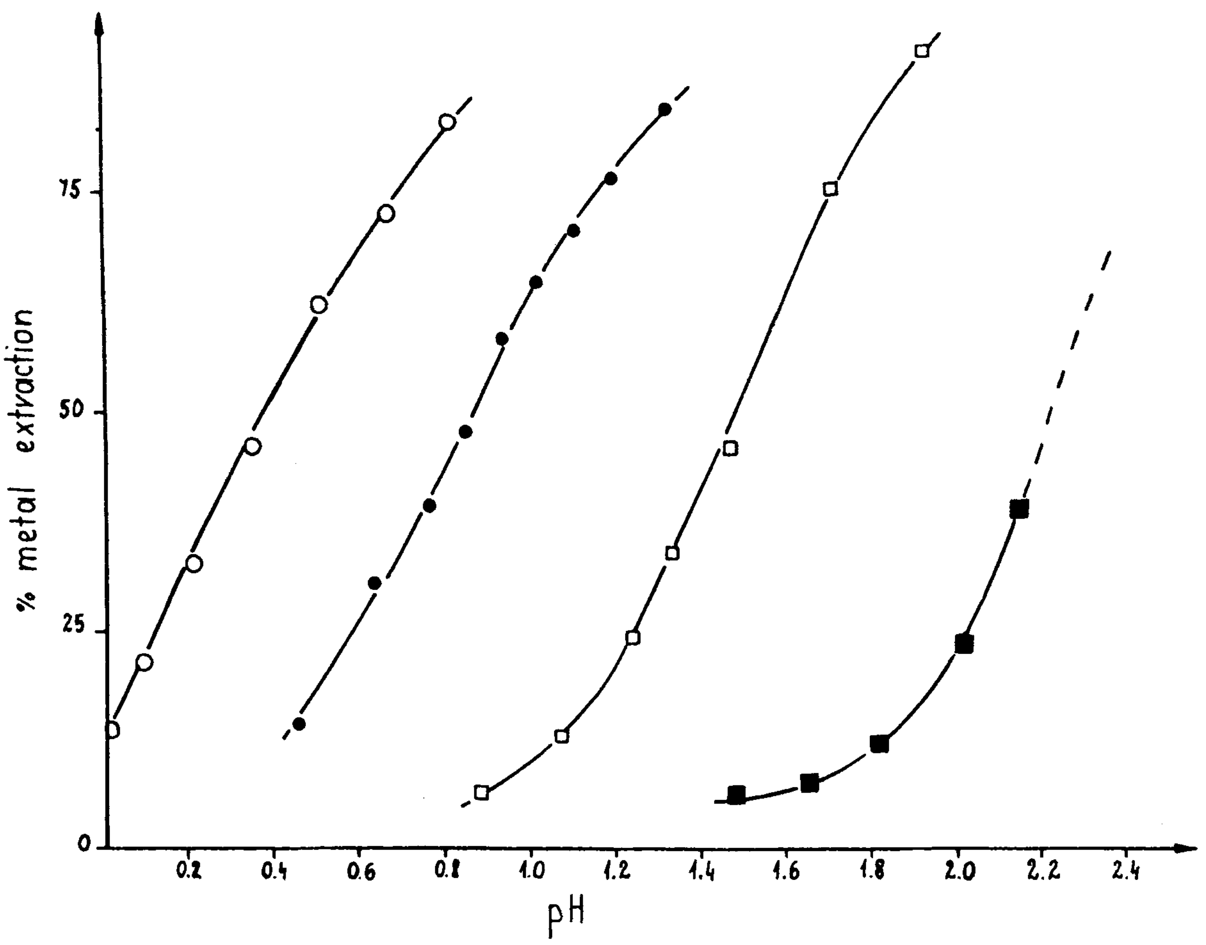


FIGURE 15. Effect of chloride concentration upon extraction of Cu(II) and Fe(III) with LIX 64N (20°C; ○, 3.18 g dm^{-3} Cu(II) and 412 g dm^{-3} $NaNO_3$; ●, 3.18 g dm^{-3} Cu(II), 327 g dm^{-3} $NaNO_3$ and 58 g dm^{-3} NaCl; □, 1.4 g dm^{-3} Fe(III) and 412 g dm^{-3} $NaNO_3$; ■, 1.4 g dm^{-3} Fe(III), 327 g dm^{-3} $NaNO_3$ and 58 g dm^{-3} NaCl).[182]

process. The extraction constants demonstrate only that hydroxyoxime complexes with palladium(II) are much more stable than those with copper (Tables 21 and 25).

As was already presented, hydroxyoximes of type IV are not convenient extractants for the extraction of copper(II) and nickel(II). Interesting results were obtained when they were used with various organic acids. Mixtures of α-acyloin oximes and carboxylic acids extract copper(II), nickel(II) and iron(III) from much more acidic solutions of pH below 2 (Figures 16 to 18). Cobalt(II) is extracted at pH below 3 (Figure 19); however, its extraction selectivity is worse.

The $pH_{0.5}$ values (Tables 26 and 27) and synergistic coefficients (defined as S = log D (combined extractants) − log [D (5,8-diethyl-7-hydroxy-6-dodecanone oxime) + D (carboxylic acid)]) demonstrate the great importance of carboxylic acid to the synergistic effect, which increases with an increase in acid dissociation (decrease of pK_a) (Figure 20).[109]

However, mixed complexes of Ni $(\text{hydroxyoxime})_2(\text{carboxylic acid})_2$ are formed only for acids having pK_a in the range of 1.5 to 4.7. Nickel carboxylates are formed as $pK_a < 1.5$, and nickel complexes with α-acyloin oxime are formed for acids having high pK_a values.[109]

The effect of carboxylic acids upon metal extraction with hydroxyoximes of types I to III is negligible, and the synergistic effect is not observed for the extraction of either copper(II) or iron(III).[153]

Synergistic effects are also observed as mixtures of 5,8-diethyl-7-hydroxy-6-dodecanone oxime and dinonylnaphthalenesulfonic acid (HD),

TABLE 25
Equilibrium Extraction Constants for Palladium(II) Extraction from Acidic Sulfate Solutions with 2-Hydroxy-5-Nonylbenzophenone Oxime (HNBPO) and 2-Hydroxy-5-Nonylacetophenone Oxime (HNAO) Isolated from LIX 65N and SME 529

Oxime	Diluent	K'_{ex}	K^a_{ex}	Ref.
HNAO	MSB 210 (approx. 2% aromatics)	$8.3 \cdot 10^5$	—	163
HNBPO	$CHCl_3$	$6.0 \cdot 10^4$	$1.995 \cdot 10^{16}$	149

[a] Stability constants for palladium(II) chlorocomplexes were taken under consideration.

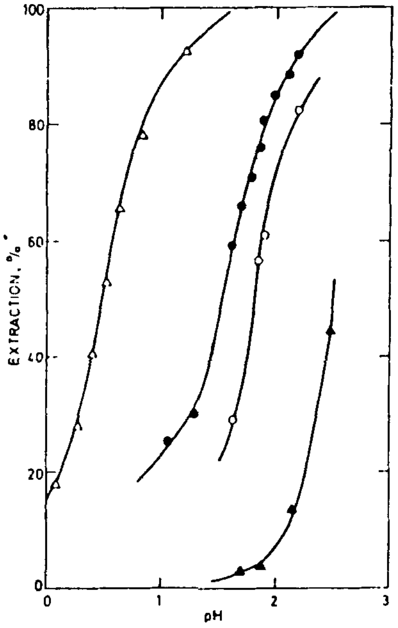


FIGURE 16. Extraction of copper(II) with LIX 63 and LIX 63/carboxylic acid mixtures (▲, 10 vol % LIX 63; ○, 10 vol% LIX 63/0.1 *M* naphthenic acid; ●, 10 vol% LIX 63/0.1 *M* versatic 9-11 acid; △, 10 vol% LIX 63/0.1 *M* α-bromolauric acid; kerosene as diluent; 5 m*M* Cu(II) in 1 *M* KNO_3 as aqueous phase).[108]

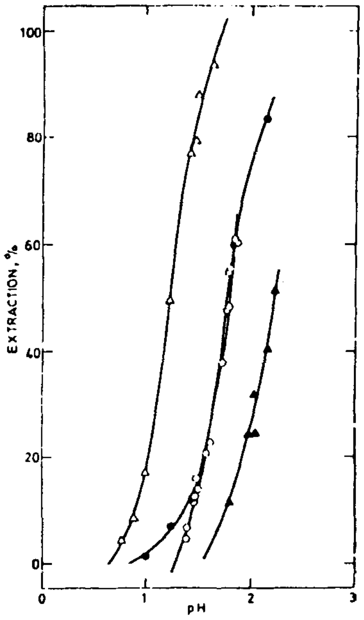


FIGURE 17. Extraction of ferric(III) with LIX 63 and LIX 63/carboxylic acid mixtures (▲, 10 vol% LIX 63; ○, 10 vol% LIX 63/0.1 *M* naphthenic acid; ●, 10 vol% LIX 63/0.1 *M* Versatic 9-11 acid; △, 10 vol% LIX 63/0.1 *M* α-bromolauric acid; kerosene as diluent; 5 m*M* Fe(III) in 1 *M* KNO_3 as aqueous phase).[108]

are used to extract nickel(II) and iron(III) from nitrate media.[110,111] These synergistic effects depend upon the molar ratio of the extractants considered and the pH of the aqueous phase, and are explained by the formation of mixed micelles $(HD)_m(H_2L)_n$ which are considered as active extractants (Equation 15).[110] The effect of pH is different for the extraction of nickel(II) and iron(III), probably due to the steric hindrance of iron(III) complex formation with 3 molecules of

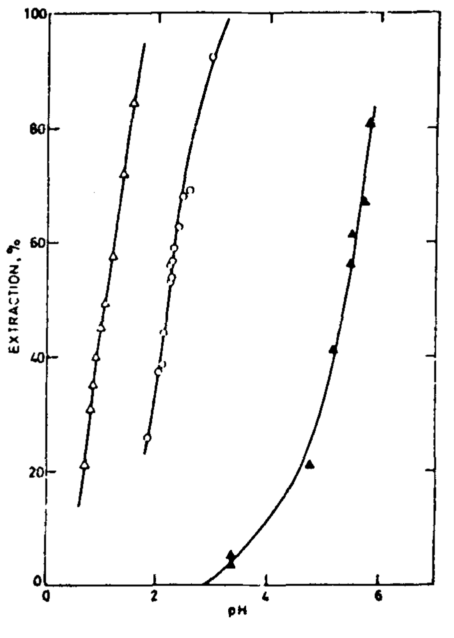


FIGURE 18. Extraction of nickel(II) with LIX 63 and LIX 63/carboxylic acid mixtures (▲, 10 vol% LIX 63; ○, 10 vol% LIX 63/0.1 *M* naphthenic acid; △, 10 vol% LIX 63/0.1 *M* α-bromolauric acid; kerosene as diluent; 5 m*M* Ni(II) in 1 *M* KNO_3 as aqueous phase).[108]

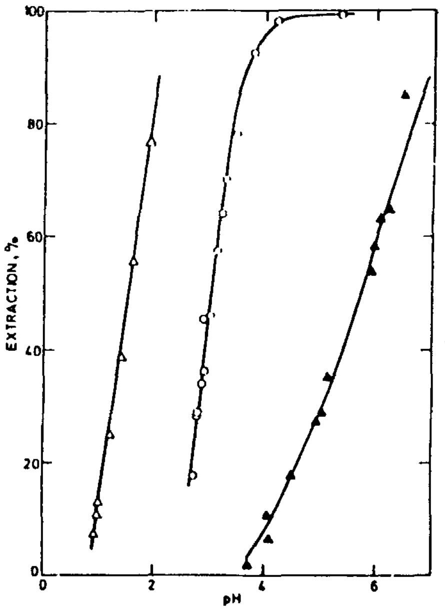


FIGURE 19. Extraction of cobalt(II) with LIX 63 and LIX 63/carboxylic acid mixtures (▲, 10 vol% LIX 63; ○, 10 vol% LIX 63/0.1 *M* naphthenic acid; △, 10 vol% LIX 63/0.1 *M* α-bromolauric acid; kerosene as diluent; 5m*M* Co(II) in 1 *M* KNO_3 as aqueous phase).[108]

sulfonic acid. As a result, a synergistic effect for Fe(III) extraction is observed at pH above 1.4, at which iron hydroxycomplexes are formed and iron is extracted, probably in the form of $Fe(OH)(H_2L)_3D_2$ (Equation 15).[110] At lower pH, iron(III) extraction is small and nickel(II) can be extracted quite selectively in the presence of iron(III).

Sulfate ions significantly decrease the extraction of iron(III), due to the formation of sulfate complexes.[110]

Synergistic effects are also observed for nickel(II) extraction from nitrate solutions with mixtures of 5,8-diethyl-7-hydroxy-6-dodecanone oxime (H_2L) with di(2-ethylhexyl)phosphoric acid (DEHPA) and dioctylphosphinic acid (DOPA).[113] Nickel(II) can then be extracted from very acidic solutions of pH 1 or even lower with a synergistic coefficient near 10 (Table 28).[113]

While interesting results were obtained when mixtures of α-acyloin oximes and various organic acids were used for extraction (especially of nickel(II), these systems have no practical importance. Extraction occurs very slowly and its equilibrium is achieved after several hours (15 to 20 h) of effective contact of both phases. Moreover, α-acyloin oximes are not stable reagents, are very sensitive to hydrolysis, and this process is accelerated by strong organic acids. In such a case, the hydrolysis of hydroxyoxime can occur in a homogeneous phase, and not only at the limited interface. Strong acids are effective catalysts of hydroxyoxime hydrolysis.

V. CONCLUSIONS

Although hydroxyoximes have become important industrial reagents and they are now used in several high-scale industrial installations for producing cathode copper from oxide ores, knowledge upon their complexing and extraction properties is incomplete. Studies were mainly orientated towards hydroxyoxime applications and the use of commercial extractants. These extractants are complex mixtures of incompletely identified composition. As a result, they are not suitable for basic physicochemical studies. We feel that many more studies are needed in the use of individual hydroxyoximes, including various

TABLE 26
$pH_{0.5}$ Values in the Extraction of Metal Ions with LIX 63/Carboxylic Acid Mixtures[108]

Extractant	$pH_{0.5}$					
	Cu^{2+}	Fe^{3+}	Ni^{2+}	Co^{2+}	Cd^{2+}	Zn^{2+}
LIX 63/α-bromolauric acid	0.46	1.30	1.02	1.48	ND	ND
LIX 63/Versatic 9—11	1.51	1.77	ND	ND	ND	ND
LIX 63/naphthenic acid	1.78	1.78	2.20	3.05	3.38	3.72
LIX 63	2.50	2.22	5.32	5.65	ND	Not extracted
α-Bromolauric acid	3.10	1.70	3.70	4.70	ND	ND
Naphthenic acid	4.54	2.75	6.80	6.99	ND	ND

Note: Acid concentration: 0.1 mol dm^{-3}; LIX 63 concentration: 10% vol.; kerosene as diluent; ND = not determined.

TABLE 27
Synergistic Coefficients (SC) and $pH_{0.5}$ Values for the Extraction of Nickel(II) from Nitrate Medium by LIX 63/Carboxylic Acid Mixtures (a) and Carboxylic Acid (b)[109]

Extractant system	S.C.	$pH_{0.5}$	
		a	b
LIX 63/hexanoic acid	3.02	3.27	—
LIX 63/lauric acid	3.18	3.19	7.17
LIX 63/α-bromolauric acid	6.64	1.46	5.88^{a}
LIX 63/2-thiododecylacetic acid	4.94	2.31	4.94^{a}
LIX 63/benzoic acid	4.54	2.51	4_{94a}
LIX 63/p-toluic acid	4.00	2.78	—
LIX 63/3-(2-hexadecyl)-5-methyl-salicylic acid	6.82	1.37	6.63
LIX 63	—	4.78	—

Note: Extractant concentration: $5 \cdot 10^{-2}$ mol dm^{-3} and a: 10^{-1} mol dm^{-3}; toluene as diluent).

homologs series, to define the effects of hydroxyoxime structure upon the complexing and extraction properties of hydroxyoximes.

Only limited data are available concerning the effect of various substituents in the aromatic ring on the acidity of the phenolic group, the stability of metal complexes, and $pH_{0.5}$.

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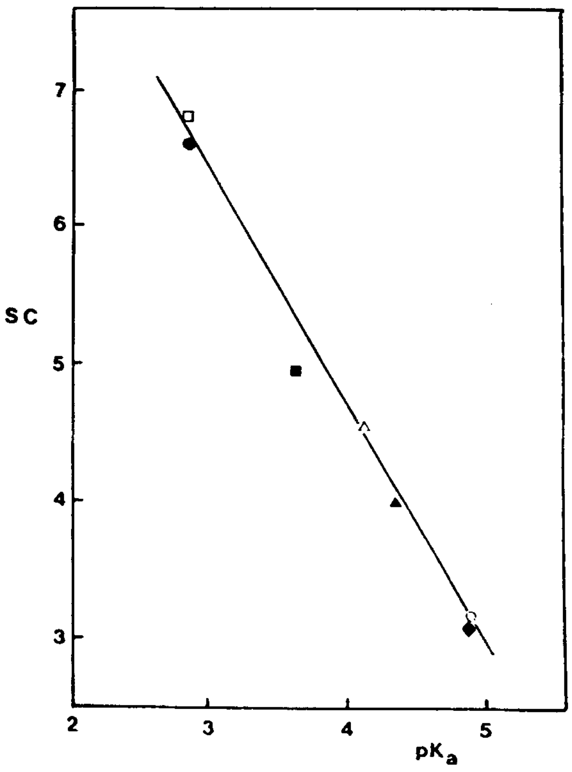

FIGURE 20. Effect of pK_a of carboxylic acid upon synergistic coefficient for nickel(II) extraction with 5,8-diethyl-7-hydroxy-6-dodecanone oxime/carboxylic acid mixtures (□, 3-(2-hexadecyl)-5-methylsalicylic acid; ●, α-bromolauric acid; ■, 2-thiododecylacetic acid; △, benzoic acid; ▲, p-toluic acid; ○, lauric acid; ◆, n-hexanoic acid).[109]

TABLE 28

Values of $pH_{0.5}$ and Synergistic Coefficients (SM) for the Extraction of Nickel(II) by 5,8-Diethyl-7-Hydroxy-6-Dodecanone Oxime (DEHO), Di(2-Ethylhexyl)-Phosphoric Acid (DEHPA), and Dioctylphosphinic Acid (DOPA)[113]

Extractant	$pH_{0.5}$	Extractant mixture	$pH_{0.5}$	S.C.
DEHO	4.78			
DOPA	6.08	DEHO + DOPA	1.13	7.30
DEHPA	5.11	DEHO + DEHPA	0.20	9.16

Note: Extractant concentration: $5 \cdot 10^{-2}$ mol dm^{-3}; toluene as diluent).

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