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CHELATING REAGENTS IN SOLVENT EXTRACTION PROCESSES: THE PRESENT POSITION

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A. INTRODUCTION

It is just over a decade since the introduction of the first chelating extractant for use in commercial solvent extraction processing [1,2], and it seems appropriate at this time to review the development of such reagents and their chemical properties.

Commercially-available chelating extractants are, at the present time, limited to two types; a series of substituted 2-hydroxybenzophenone oximes produced by General Mills Inc. under the same LIX reagents*, and a substituted 8-hydroxyquinoline produced by the Ashland Chemical Co. and marketed under the name Kelex**. Both these reagent types were developed for the specific extraction of copper from acidic leach liquors, and represent the first of what is predicted to be a series of metal-specific extractants for use in the separation of metals by solvent extraction processes.

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* LIX is a copyright trade mark of General Mills Inc.

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The first commercially produced chelating extractant, designed specifically for the selective extraction of copper from dilute dump leach liquors by solvent extraction, was designated LIX 63 and became available about 1963—4. This reagent had been reported to be 5,8-diethyl-7-hydroxy-6-dodecanone oxime [3], and this has recently been confirmed [22]. While this reagent constituted a major advance in attempts to develop copper-specific extractants it suffered from insufficient discrimination for copper over ferric iron, and from inadequate loading characteristics at the normal pH of dump leach liquors. Nevertheless, the properties of this extractant provided sufficient stimulus for further investigation of hydroxyoximes as copper-specific extractants. Thus in 1965 General Mills Co. introduced LIX 64 [4—6], a 2-hydroxybenzophenone oxime substituted in the 5-position by an alkyl group, which provided a significant advance over LIX 63 both in pH functionality and in selectivity for copper. However, it suffered from slow extraction kinetics.

In 1970 LIX 64N [7] was made available, again based on 2-hydroxybenzophenone oxime, which showed significantly improved extraction kinetics over LIX 64. The LIX 64N extractant has been the major workhorse of the LIX series, and has found use in at least five processes, and more are being constructed or planned [8].

More recently other LIX reagents, designed for use with liquors other than dump leach liquors, have been made available. Thus LIX 70 [9], a 3-chloro-5-alkyl substituted 2-hydroxybenzophenone oxime, was produced (1971) for use with highly acidic leach liquors. Further modifications for use with other types of liquors or at elevated temperatures, namely LIX 65N, 71 and 73 [10], have been made available.

The Kelex extractants were first marketed about 1968 [11], when quantities were available for experimental purposes. There are two Kelex extractants available, Kelex 100 and 120. The former is a technical grade 7-alkenyl-8-hydroxyquinoline, the latter a 20 vol per cent solution of Kelex 100 in *p*-nonyl phenol. This mixture was apparently formulated to provide better physical characteristics in solvent extraction operations than were provided by Kelex 100. However, Kelex 120 has not been much used or studied, and appears to have little application to solvent extraction processing. Application of the Kelex 100 extractant to commercial operations has not been as rapid as with the LIX extractants; most of the data reported so far concern bench scale or pilot plant studies [12—15].

While the application of these chelating extractants to commercial solvent extraction has been variously reported, little has been written on other aspects. Accordingly, this review is concerned mainly with the properties and chemistry of these extractants. Each of the two types of extractant is discussed separately. Their composition and physical properties are first described, followed by a review of their known metal extracting properties and the mechanisms involved. Finally, recent and future developments in metal-specific extractants are considered.

B. THE LIX EXTRACTANTS

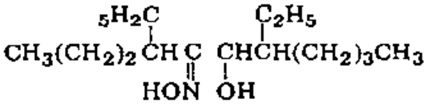
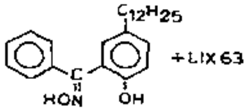
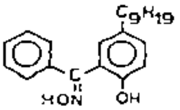
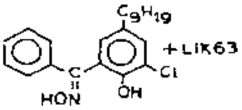
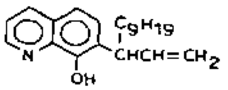
(i) *Composition*

Except for LIX 63, an aliphatic α-hydroxyoxime, the basic molecule from which the other LIX extractants are derived is 2-hydroxybenzophenone oxime, substituted in the 5-position by an alkyl group, and in LIX 70 also in the 3-position by a chlorine atom. It has been reported by Ashbrook [16] that four of these reagents are the parent compounds from which LIX 64N, 71 and 73 are obtained by mixing, as indicated in Table 1.

Those LIX extractants which contain LIX 63 are recommended by the

TABLE 1

Structure and composition of chelating extractants [16]

LIX 63	 $CH_3(CH_2)_2\overset{{}_5H_2C}{CH}\underset{HON}{C}\,\underset{OH}{\overset{C_2H_5}{CHCH}}(CH_2)_3CH_3$
LIX 64	 + LIX 63
LIX 64N	LIX 65N + LIX 63(~1 vol.%)
LIX 65N	
LIX 70	 + LIX 63
LIX 71	LIX 70 + LIX 65N
LIX 73	LIX 70 + LIX 65N + LIX 63
KELEX 100	
KELEX 120	20 vol.% KELEX 100 in *p*-NONYLPHENOL

All the aromatic LIX extractants contain about 40 vol.% of an inert diluent, probably Napoleum 470. Probably about 1 vol.% LIX 63 is added to those extractants which contain this reagent. Ratio of constituents in LIX 71 and 73 not known.

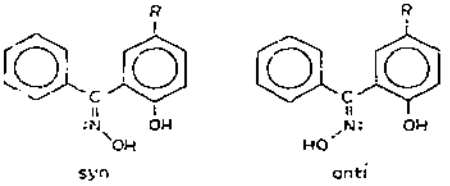
manufacturer for use below 40°C, whereas those not containing LIX 63 are recommended for use both above and below this temperature [10]. It would seem, therefore, that above 40°C LIX 63 is not stable, although no data appear to have been reported to confirm this. Above about 40°C it should be noted that the kinetic performance of those extractants not containing LIX 63 approaches the kinetic performance at room temperature of those which do contain LIX 63.

The aromatic LIX extractants dehydrate on heating to produce water and probably a benzisoxazole; thus these extractants dehydrate on vacuum distillation, and the distillation products show no hydroxyl absorption in the infrared [16]. There is no evidence that these extractants undergo a Beckman rearrangement on stripping with sulphuric acid.

(ii) Isomers

Unsymmetrical ketones, such as 2-hydroxybenzophenone can, theoretically, yield two isomeric oximes. Isolation of these isomers will depend on their stabilities; in some cases only one isomer, and in others both isomers, can be isolated.

Accordingly, 2-hydroxybenzophenones can give rise to two isomeric oximes, a syn form and an anti form:



In the anti isomer, the orientation of the oxime group is such that complexation with a metal ion is expected to be more rapid than with the sym isomer where isomerisation is necessary prior to complexation. Thus the rate at which the isomer complexes with a metal ion (Cu^{II}) can be used as a diagnostic test to differentiate between them [17,18].

Isolation of some of the isomers of LIX 64, LIX 65N and LIX 70 has been reported, and these have been distinguished by their rates of reaction with cupric ion [16]. The syn (inactive) isomers are all white, crystalline compounds; the anti (active) isomers of LIX 64 and LIX 65N are brown, viscous liquids; the anti isomer of LIX 70 is a white crystalline compound.

From elemental analysis of the isomers and from spectroscopic data it was concluded that the pure aromatic components of the LIX reagents have the structures indicated below [16]:

LIX 64: 2-hydroxy-5-dodecylbenzophenone oxime
LIX 65N: 2-hydroxy-5-nonylbenzophenone oxime
LIX 70: 2-hydroxy-3-chloro-5-nonylbenzophenone oxime.

TABLE 2

Isomer concentrations in as-received LIX extractants [16]

Extractant	As-received basis			[Anti]
	Anti wt, %	Syn wt, %	Ratio Anti/Syn	Molar
LIX 64	41.4	—	—	0.99
LIX 64N	40.1	7.2	5.6	1.04
LIX 65N	39.2	7.3	5.4	1.02
LIX 70	40.4	5.5	7.3	0.97

Analysis of the commercially available extractants for isomer concentration is shown in Table 2.

It has been stated that the LIX 64N extractant contains only the active (anti) isomer [19]. This is not the case; all LIX extractants contain both isomers, and experimental evidence has indicated that the ratio of isomers is the result of an anti—syn equilibrium condition [16]. After standing for several months the anti isomers were found to contain syn isomers. The position of the equilibrium changes somewhat for each extractant, as shown in Table 2. Of the total isomer content, about 85 per cent is the active or anti isomer.

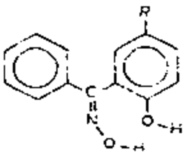
(iii) Spectra and hydrogen bonding

Infrared spectra of all the isomers showed two adsorption bands for OH in carbon tetrachloride medium [20]. A sharp band at 3600 cm^{-1} in all cases showed the presence of unassociated OH. A broad, intense, associated (hydrogen bonded) OH band, between 3200 and 3400 cm^{-1} indicated inter- or intra-molecular hydrogen bonding, again in all isomers. The syn isomers, in KBr discs, did not show the sharp adsorption at 3600 cm^{-1} but only the broad associated OH band. The free OH band was also absent in the syn isomers when the undiluted (neat) sample was used. It was concluded [20] that considerable association of the OH groups in these isomers occurs in the crystalline (syn) and liquid (anti) isomers, and that in carbon tetrachloride solution some (probably the oxime OH) hydroxy groups are free from hydrogen bonding.

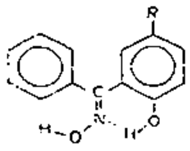
The usual test for intramolecular hydrogen bonding by dilution of the sample showed intramolecular hydrogen bonding to be present in the syn isomers; with the anti isomers, the evidence was not so apparent, although intramolecular bonding did appear to be involved. The major form of hydrogen bonding is of the intermolecular type in the anti isomers [20].

Further evidence for intermolecular bonding in the anti isomers is given by Neelameggham [21] who concludes, from slope analysis of studies on the extraction of copper(II) and iron(III) by LIX 64N, that this reagent exists as a dimer in kerosene solution.

NMR spectra of the LIX 64 and LIX 65N syn and anti isomers also indicated substantially more intramolecular hydrogen bonding in the syn isomers [20]. Thus in dilute solution ($CDCl_3$) the syn isomer hydroxyl protons both gave the same chemical shift (1—2τ) showing they experience much the same type of electronic environment, which can be attributed to intramolecular hydrogen bonding, for example:



OH ... H intramolecular hydrogen bonding



OH ... N intramolecular hydrogen bonding

Intramolecular hydrogen bonding in syn LIX 70 was not as pronounced as in the other syn isomers. In dilute solution the hydroxyl protons of the anti isomer showed only very weak signals, and this was interpreted in terms of intermolecular hydrogen bonding. These data are taken as evidence to support the view that intramolecular hydrogen bonding is prevalent in the syn isomers [20].

Infrared spectra [20] confirmed the conclusions of Atwood and Miller [19] that the LIX 70 molecule has a substituent ortho to the phenolic hydroxyl group. Elemental analysis showed this to be chloro-substitution. The conclusion that intramolecular hydrogen bonding does not occur in LIX 64N [19] has been shown not to be valid. However, since these spectra were done on mixed isomers, of which the anti isomer is the major component, it is not surprising that this conclusion was reached.

(iv) Proton—ligand stability constants

Thermodynamic proton—ligand constants, $^{T}pK_{OH}$, of the isomers of the LIX extractants, together with those of the isomers of the parent 2-hydroxybenzophenone oxime (HBPO) and also 2-hydroxy-4-dodecyloxybenzophenone oxime (HDBPO), are given in Table 3 [20]. Attempts to determine the proton-stability constant for oxime hydrogen gave negative values for K_{OH_1} and K_{OH_2}. It was concluded that either only the phenolic hydroxy group dissociates, or that the oxime hydroxy group dissociation is very weak, or perhaps overlaps the former.

The acid strength of the syn isomers is seen to be significantly greater than for the corresponding anti isomer by about two orders of magnitude, and this has been attributed to the intramoleculer hydrogen bonding which occurs in the syn isomers, providing for stabilisation of the anion of the oxime.

TABLE 3

Thermodynamic proton-ligand stability constants of oxime isomers [20]

Isomer	${}^{T}\mathrm{p}K_{\mathrm{OH}}$[a]					${}^{T}\mathrm{p}K_{\mathrm{OH}} =$
	n_2 0.083	n_2 0.123	n_2 0.174	n_2 0.240	n_2 0.330	$mn_2 + c$
Syn						
LIX 64	—	—	10.55	11.25	12.19	$10.51\ n_2 + 8.72$
LIX 65N	[b]	9.84	10.42	11.06	11.95	$10.19\ n_2 + 8.60$
LIX 70	—	—	9.40	10.08	11.02	$10.38\ n_2 + 7.60$
HBPO	9.32	9.71	10.20	10.86	11.77	$9.92\ n_2 + 8.48$
HDBPO			[b]	10.58	11.58	$11.11\ n_2 + 7.91$
Anti						
LIX 64		[b]	11.90	—	13.83	$12.37\ n_2 + 9.75$
LIX 65N		[b]	11.85	12.68	13.82	$12.63\ n_2 + 9.65$
LIX 70		[b]	11.00	11.83	12.98	$12.69\ n_2 + 8.80$
HBPO	[b]	11.18	11.79	12.60	13.72	$12.27\ n_2 + 9.66$
HDBPO				[b]	13.33	—

[a] At 25.0 ± 0.1°C; n_2 = mole fraction of dioxane.

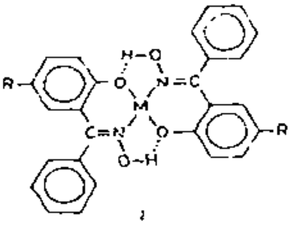
[b] Insufficient solubility at lower mole fractions of dioxane.

The increased acid strength of LIX 70 compared to the other extractants (considering only the anti or active isomers) is reflected in the ability of this extractant to extract copper at lower pH values than the others [9]. There is a slight increase in acid strength of the LIX 64 and LIX 65N reagents over the basic molecule *o*-hydroxybenzophenone oxime.

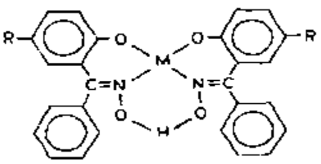
The ${}^{T}\mathrm{p}K_{\mathrm{OH}}$ values reported by Ashbrook [20] are considerably different from those reported by Atwood and Miller [19], namely 6.7 for LIX 63 and 3.3 for all the other LIX extractants. These latter data were calculated from the absorption frequencies of the free OH band of the extractants, and it is surprising that the $\mathrm{p}K_{\mathrm{OH}}$ values of the aromatic LIX extractants should be considered by these authors to be identical, since they state that the acidity of these compounds increases from LIX 63 to LIX 70, and indeed showed this in the order of $\mathrm{pH}_{\frac{1}{2}}$ values for the extraction of copper(II) (Table 5).

(v) Extraction of metals

That the $\mathrm{Cu^{II}}$—LIX complexes formed in the extraction of copper are of the type $\mathrm{CuL_2}$ (HL = LIX reagent) has been severally reported [19,21,46], and can also be inferred from solvent loading data [12]. In like manner other divalent metal ions are expected to form extractable species of either type (I) or (II):



I



II

The structure of the Cu^{II}, Ni^{II} and Pd^{II} complexes of salicylaldoxime (SALO) have been reported by Burger et al. [24] and Zolotov [23] to be of type (I), whereas those of Co^{II}, Zn^{II}, Fe^{II} and Mn^{II} have been reported [24] to be of type (II), and there appears to be no reason why type (II) structures should not be formed by the LIX reagents. Indeed, it is to be expected that SALO and LIX metal complexes will be similar in structure. Thus the high stability of the Cu^{II} complex of SALO allows for its quantitative formation at low pH values, and the same is evident with the Cu—LIX complexes. Thus in acidic ethanol solutions only the Cu^{II}—LIX 65N complex precipitated readily, the Ni^{II} complexing only very slowly. The Fe^{III}, Co^{II}, Zn^{II} and Mn^{II} complexes are all very soluble [25].

It appears most likely then that the Cu^{II} and Ni^{II}—LIX 65N complexes have structures of type (I). Whether the other metal complexes are of type (I) or (II) is not known. Some $\log \beta_2$ values for metal—SALO complexes are given in Table 4, and the order from Cu^{II} to Mn^{II} is expected to be essentially the same for extraction of these metals by the LIX extractants as a function of pH.

Cobalt appears to form CoL_2 and CoL_3 complexes with LIX 65N, depending on its oxidation state, and the same can be expected for iron. There is no evidence to indicate that adduct complexes, $ML_x{\cdot}yHL$, are formed by the LIX extractants, as in the case with Kelex (see below).

Surprisingly, little information is available on the extraction of metals other than copper by the LIX extractants; it can only be assumed that since

TABLE 4

Stability constants for some divalent metal-SALO complexes [26]

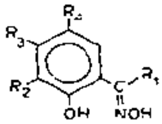
Metal	$\log\beta_2$ [a]
Cu	21.5
Fe	16.7
Ni	14.3
Co	13.5
Zn	13.5
Mn	11.9

[a] In 75 vol per cent dioxane at 25°C.

these reagents are known to be relatively specific for copper extraction from acid solutions, most investigators have been preoccupied with this metal. However, it appears reasonable to assume that the order of metal extraction by the LIX reagents, as a function of pH, will follow closely the Irving-Williams series, or the order of metal hydrolysis constants, unless complexation in the aqueous phase affects complexation with the extractant. Evidence for this assumption is provided by extraction data reported by Dahl [27] for several metals by SALO; thus the order of metal extraction is $\mathrm{Cu^{II}} < \mathrm{Ni^{II}} < \mathrm{Pb^{II}} < \mathrm{Co^{II}} < \mathrm{Mg^{II}} < \mathrm{Mn^{II}} < \mathrm{Cd^{II}}$ as a function of pH. The extraction of Zn was anomalously poor and varied with the concentration of extractant. This aspect of solvent extraction will not be discussed here; the effects of such variables and others, have been adequately dealt with elsewhere [23,28].

LIX 63 extracts metals in the order $\mathrm{Fe^{III}} < \mathrm{Cu^{II}} < \mathrm{Ni^{II}} \leqslant \mathrm{Co^{II}}$ as a function of pH [29]. It was noted that the extraction of $\mathrm{Ni^{II}}$ by a mixture of LIX 63 and naphthenic acid was slower than with LIX 63 alone, although this effect has not been reported for the aromatic LIX extractants.

Various derivatives of SALO, (III), have been prepared by Parrish [30] and examined for their metal-extractive properties. Similar selectivity for $\mathrm{Cu^{II}}$, $\mathrm{Ni^{II}}$ and $\mathrm{Fe^{III}}$ was shown by all the oximes.



III

For the case where R_1 = Ph, (III) becomes 2-hydroxybenzophenone oxime.

The effects of substitution of (III) in the R_1, R_2, R_3 and R_4 positions on the extraction of copper are shown in Table 5 as a function of $\mathrm{pH}_{\frac{1}{2}}$ values. Compound (VIII) is the pure component of LIX 64; Parrish notes that (VIII) and LIX 64 behaved in exactly the same manner with respect to copper extraction and $\mathrm{pH}_{\frac{1}{2}}$ values. Increasing size of substituent groups in the series (IX) to (XIII) is seen to increase the $\mathrm{pH}_{\frac{1}{2}}$ values for copper extraction, Laskorin et al. [73] suggest that this is mainly due to decreasing solubility of the copper—oxime complex in the solvent phase over this series of oximes. For example, they show that copper extraction decreases, as a fucntion of diluent, in the order: kerosene < butyl benzene < diisopropylbenzene < toluene kerosene + 5 percent decylic alcohol, using compound XII. Similar diluent effects have been reported with the LIX and Kelex extractants [12]. It should be noted that the sets of $\mathrm{pH}_{\frac{1}{2}}$ values given in Table 5 are not directly comparable because of the different conditions used [23,28]. Such values are useful in comparisons of the extraction characteristics of a series of extractants only where the conditions are maintained constant.

For a series of extractants, the decrease in $\mathrm{pH}_{\frac{1}{2}}$ values for the extraction of a particular metal indicates increasing acid strength of the extractant, and

TABLE 5

Extraction of copper by various oximes

Compound [30]	IV	V	VI	VII	VIII
$pH_{\frac{1}{2}}$	0.2	0.3	0.8	1.2	1.4
Compound [73]	IX	X	XI	XII	XIII
$pH_{\frac{1}{2}}$	0.99	1.07	1.23	1.32	1.39
Extractant [19]	LIX 70	LIX 64N		LIX 64	LIX 63
$pH_{\frac{1}{2}}$	2.6	2.9		3.3	4.8

IV : R_1 = Ph; R_2 = NO_2; R_3 = H; R_4 = $C_{12}H_{25}$.
V : R_1 = Ph; R_2 = NO_2; R_3 = H; R_4 = C_8H_{17}.
VI : R_1 = H; R_2 = H; R_3 = H; R_4 = C_8H_{17}.
VII : R_1 = CH_3; R_2 = H; R_3 = H; R_4 = C_8H_{17}.
VIII: R_1 = Ph; R_2 = H; R_3 = H; R_4 = $C_{12}H_{25}$.
IX : R_1 = C_8H_{17}; R_2 = H; R_3 = C_2H_5O; R_4 = H.
X : R_1 = $C_{17}H_{35}$; R_2 = H; R_3 = C_2H_5O; R_4 = H.
XI : R_1 = C_8H_{17}; R_2 = H; R_3 = $C_8H_{17}O$; R_4 = H.
XII : R_1 = Ph; R_2 = H; R_3 = $C_{7-9}H_{15-19}O$; R_4 = H.
XIII: R_1 = Ph; R_2 = H; R_3 = $i-C_8H_{17}O$; R_4 = H.

this is evident in Table 5. Thus metal extraction with the *o*-nitro-substituted oximes occurs at quite low pH values.

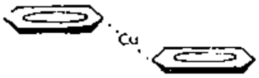
Decrease in electron density on the hydroxyl oxygen atom in such compounds is expected to result in a decrease in σ-bond stability of the O—metal bond, while increasing the π-acceptor properties of the ligand. Consequently, it might be expected that metal—ligand stability constants will decrease with increase in the —I and —R effects of substituents on the ligand. For example, substitution of SALO in the 5-position by Cl and NO_2 reduces the pK_{OH} value from 10.70 (SALO) to 10.25 (Cl) to 8.72 (NO_2), while $\log \beta_2$ values for some metal complexes decrease from SALO through the 5-chloro- and the 5-nitro derivatives [34]. However, the effects of pK_A and β_n values of ligands and metal complexes are not mutually exclusive; both constants may have rather involved relationships, consequently $pH_{\frac{1}{2}}$ values may not be directly a function of the metal—ligand stability constants, although this is generally assumed to be so.

It should be pointed out that the extraction of metals at increasingly higher hydrogen ion concentration in the aqueous phase requires increasingly higher acid concentration in the strip solution used to recover the metal from the solvent phase. A case in point is LIX 70, which extracts copper at a lower pH than does LIX 64N, but requires a much higher acid concentration for stripping the copper than does LIX 64N. This presents problems in the recovery of copper from the strip liquor by electrowinning. It must be remembered that unlike the analytical application of solvent extraction, the metal extracted in commercial operations must be economically recovered, in some way, from the solvent phase.

The unusual situation where log $K_2 > K_1$ for complexes of Co^{II}, Ni^{II}, Mn^{II} and Zn^{II} is shown by SALO and its 5-chloro and 5-nitro derivatives [24], and also by 2-hydroxyacetophenone oxime—copper(II) [31]. This has been plained in terms of stabilisation due to intramolecular hydrogen bonding. The phenomenon is not prevalent, and appears not to exist with other metal—hydroxyoxime complexes where intramolecular hydrogen bonding would be expected to occur, and situations in which log $K_2 >$ log K_1 would not appear to be simply the result of intramolecular hydrogen bonding. Whether such conditions exist for metal—LIX complexes remains to be determined, although models of such complexes indicate that intramolecular hydrogen bonding could easily be present.

The stability of Fe^{II}—SALO, 5-Cl—SALO and 5-NO_2—SALO complexes as reported by Burger and Egyed [24] would suggest similarly stable complexes with LIX extractants. No data have been reported on the extraction of ferrous ion by these reagents.

One interesting aspect of $Cu(SALO)_2$ complexes is the stepped arrangement between the planes of the benzene rings of the ligands [32]:



XIV

the stepped distance being greater in the 5-Cl—SALO than in the SALO—copper(II) complexes [33]. This same arrangement (XIV) is expected to be present in Cu—LIX complexes, as indicated by Fisher—Hirshfelter—Taylor models. The structural chemistry of 2-hydroxybenzophenone and similar oximes has recently been reviewed by Chakravorty [34].

Extraction of metals from alkaline solutions by the LIX extractants has been investigated. Thus both LIX 63 [35] and LIX 64N [36] have been proposed for the extraction of several metals from ammoniacal sulphate or carbonate solutions, and processes have or are being used for the separation of copper and nickel from other metals in such systems on a commercial scale [8,37].

The extraction of metals from ammoniacal solutions by any compound-forming extractant can be influenced by metal complexation in the aqueous phase. Thus if the stability of the metal ammine is greater than that of the metal—extractant complex, metal extraction will decrease as the pH of the system increases above about 7 provided, of course, that sufficient ammonia is available for ammine formation.

With LIX 63 and 64N, metal extraction from ammonium sulphate and carbonate solutions has been shown to decrease as the pH is raised to about 9 [35,36], and this same effect has been reported for the extraction of copper, nickel and cobalt by Versatic acids [38,39]. Thus extraction decreases in the order $Cu^{II} > Ni^{II} > Co^{II}$, which is just the order of decreasing log β_n values of these metal ammines [40].

Both Ni and Zn have been shown to be extracted by LIX 64N from ammoniacal solutions at pH 8.5 [37]. Stripping the solvent at pH 5.5 removes the Zn, but little of the Ni, which is what would be expected from the extraction data of Dahl [27] (see above).

The rate of copper extraction by the syn isomers of the LIX extractants is slow in acid systems. As the pH is increased, however, the rate of extraction increases, such that at pH 8—9 (ammoniacal system) the extraction of copper by this isomer is very fast. This has been attributed to the formation of a nitrone form of the oxime, allowing for a rapid change from the syn to the anti isomer, and subsequent rapid formation of the copper complex [20]. Consequently the total metal loading of a given concentration of an LIX extractant in the solvent phase should be greater from a basic system than from an acid system because of the utilisation of the syn isomer in the former.

It has been known for some time that cobalt, when extracted from an ammoniacal solution at pH 7—9 by the LIX and Kelex extractants, is very difficult to strip. Indeed, even concentrated acids have little effect on the extracted complex. This has generally been assumed to be the result of oxidation of Co^{II} to Co^{III} with the formation of a very stable Co^{III}—LIX or Co^{III}—Kelex complex in the solvent phase. Merigold and Suddereth [36] report that, depending on the conditions prevailing in the aqueous phase, Co^{III} may or may not be extracted. Thus using (presumably) hexaammine-cobalt(III) carbonate (in the presence of H_2O_2 to ensure complete oxidation of cobalt), with $[NH_4^+] > [CO_3^{2-}]$ (ammonium carbonate) some cobalt is extracted by LIX 64N. With $[NH_4^+] < [CO_3^{2-}]$ they report no cobalt extraction. This has been confirmed using aquopentaamminecobalt(II) sulphate [25].

However, the μ-peroxo-bis(pentammine cobalt(III))$^{4+}$ complex is rapidly extracted by LIX 64N at about pH 9 [25], and the extracted cobalt is again almost impossible to strip from the solvent. It can be removed by bubbling H_2S through the solvent, whereby CoS is precipitated [36]. The extraction of the μ-peroxo binuclear cobalt complex has not been investigated, but the complex formed with LIX 64N is very stable, and is reminescent of the stability of cobaloximes [41]. This area of metal extraction requires considerably more study.

(vi) Mechanisms of metal extraction

Mechanisms of metal extraction from aqueous solutions into an organic phase (heterogeneous system) by a number of extractants have been investigated intermittently over the last few years. Two extreme mechanisms can be defined: formation of the metal-extractant species in the aqueous phase (homogeneous reaction) followed by its transfer into the organic phase, or formation of the species at the aqueous—organic interface (heterogeneous system) followed by transfer into the solvent phase. Intuitively these two extreme cases (if they exist) should be differentiable by extraction rate studies, since the latter process will depend in large part on the interfacial area, and on other physical properties of the system. Such studies are complicated by the fact that both physical and chemical effects will influence the extraction rate, and the problem is then one of distinguishing between them. Attempts to determine the mechanism of extraction in several systems [42–48] have not been conclusive, and the problems are still not resolved.

One particularly interesting aspect of the extraction of copper from acid solution by the aromatic LIX extractants is the enhancement of the extraction rate of copper on the addition of a small amount of the aliphatic oxime LIX 63, which appears to act as a catalyst. This mechanism has been studied by Flett et al. [49] who, using the AKUFVE apparatus [50–52], reported an apparent rate equation:

$$-\frac{d[\mathrm{Cu}]}{dt} = k[\mathrm{Cu}]\,[\mathrm{LIX\ 65N}]\,[\mathrm{LIX\ 63}]^{1/2}[\mathrm{H}^+]^{-1} \tag{1}$$

for a system involving toluene as the diluent. The following reaction scheme was proposed:

$$\overline{\mathrm{RH}} \rightleftharpoons \mathrm{RH_s} \tag{2}$$

$$\mathrm{Cu^{2+}} + \mathrm{RH_s} \rightleftharpoons \mathrm{CuR^+} + \mathrm{H^+} \tag{3}$$

$$\mathrm{CuR^+} + \mathrm{BH_s} \rightleftharpoons \mathrm{CuRB_s} + \mathrm{H^+} \tag{4}$$

$$\mathrm{CuRB_s} \rightleftharpoons \overline{\mathrm{CuRB}} \tag{5}$$

$$\overline{\mathrm{CuRB}} + \overline{\mathrm{RH}} \rightleftharpoons \overline{\mathrm{CuR_2}} + \overline{\mathrm{BH}} \tag{6}$$

where RH = LIX 65N, BH = LIX 63, subscript s = the aqueous—organic interface, and the bar denotes the organic phase.

The rate controlling step is considered to be eqn. (4) because only this reaction is first order with respect to $\mathrm{Cu^{II}}$, pH and [LIX 65N]. Furthermore, the oximes are considered to react in the unionised form. Alternate reactions for (4), (5) and (6) were also proposed, namely:

$$\mathrm{CuR^+} + \mathrm{BH_s} \rightleftharpoons \mathrm{CuRBH_s^+} \tag{7}$$

$$\mathrm{CuRBH_s^+} \rightleftharpoons \overline{\mathrm{CuRBH^+}} \tag{8}$$

$$\overline{\mathrm{CuRBH^+}} + \overline{\mathrm{RH}} \rightleftharpoons \overline{\mathrm{CuR_2}} + \overline{\mathrm{BH}} + \mathrm{H^+} \tag{9}$$

by which the pH dependency of the formation of the interfacial species is eliminated. This mechanism then involves reactions in the aqueous phase, at the interface, and in the solvent phase.

In studies on the extraction of $\mathrm{Cu^{II}}$ and $\mathrm{Fe^{III}}$ by LIX 64N, Neelameggham [21] concluded that the extracted species is formed in the aqueous phase and then extracted into the organic phase, presumably because of the preferred solubility of the complex in this phase. The proposed mechanism involved:

$$\overline{R_2H_2} \rightleftharpoons \overline{2RH} \tag{10}$$

$$\overline{2RH} \rightleftharpoons 2RH \tag{11}$$

$$2RH \rightleftharpoons 2R^- + 2H^+ \tag{12}$$

$$Cu(OH_2)_6{}^{2+} + R^- \rightleftharpoons Cu(OH_2)_4R^+ + 2H_2O \tag{13}$$

$$Cu(OH_2)_4R^+ \rightarrow Cu(OH_2)_2R^+ + 2H_2O \tag{14}$$

$$Cu(OH_2)_2R^+ + R^- \rightleftharpoons CuR_2 + 2H_2O \tag{15}$$

$$CuR_2 \rightleftharpoons \overline{CuR_2} \tag{16}$$

in which the formation of the extracted species, CuR_2, occurs in the aqueous phase. The apparent rate proposed for this process was

$$-\frac{d[Cu]}{dt} = k[Cu]\,[RH]^{1/2}[H^+]^{-1} \tag{17}$$

There are objections which can be made to this mechanism. For example, the saturation solubility of both LIX 65N and LIX 63 in the aqueous phase would be less than $10^{-5}\,M$ [53], and the pK_{OH} values for LIX extractants [20] would provide a maximum concentration of ionised extractant of about $10^{-10}\,M$. It seems reasonable then to assume that the reaction involves mainly unionised ligand, which assumption was made by Flett [49]. Furthermore, Neelameggham appeared to be unaware that LIX 64N is a mixture of LIX 65N and LIX 63, thus the model proposed for the extraction of both Cu^{II} and Fe^{III} contributes little towards an understanding of the extraction mechanism.

The mechanism proposed by Flett et al. [49] involves the initial formation of a Cu—LIX 65N species, which then reacts with LIX 63. There appears to be no reason why the initial reaction should not involve a Cu—LIX 63 species, followed by reaction with LIX 65N. Thus a mechanism essentially the reverse of that proposed by Flett may be operative, in which the initial reaction is between the copper ion and LIX 63:

$$Cu^{2+} + BH_s \rightleftharpoons CuB_s^+ + H^+ \tag{18}$$

$$CuB_s^+ + RH_s \rightleftharpoons CuBR_s + H^+ \tag{19}$$

$$CuBR_s + RH_s \rightleftharpoons CuR_{2_s} + \overline{BH} \tag{20}$$

$$CuR_{2_s} \rightleftharpoons \overline{CuR_2} \tag{21}$$

Other, similar, equations can also be written.

There are essentially two reasons why this latter model appears more likely than that proposed by Flett, namely, the lability of the hydroxyl proton of LIX 63 [22], and the reported 1:1 complexes formed between Cu^{II} and α-acyloinoximes [54]. It would be useful, therefore, to use α-acyloinoximes other than LIX 63, which are known to form 1:1 copper complexes, in the extraction of copper by LIX 65N.

Perhaps the major objection which can be made to both Neelamegggham's and Flett's work is that both have used commercially produced reagents, without giving any consideration to the effects of isomers or impurities in such materials on the extraction mechanism. The role of LIX 63 in increasing the rate of metal extraction by LIX 65N is still not known.

(vii) Mixed solvent systems

Mixed solvent systems involving LIX extractants and di(2-ethylhexyl) phosphoric acid [55—57] (EHPA), or aliphatic carboxylic acids [29,58] have been shown to exhibit synergistic properties in the extraction of metals. Synergism has been shown to occur in many mixed solvent systems [59] but the actual mechanisms involved are still largely unresolved.

In the LIX 63—carboxylic acid systems, synergism is considered to result from the formation of a mixed ligand complex having a greater solubility in the solvent phase than either the metal—LIX or metal—carboxylate species. For example, the Cu—LIX 63-α-bromolauric acid complex extracted is thought to be $CuH_4L_2\text{-}R_4$ [58], where L refers to LIX 63 and R to the carboxylic acid. A comparative study of the extraction of copper by LIX 63—EHPA and LIX 63—carboxylic acid mixtures [60] showed that the selectivity for this metal was essentially kinetic in nature with the former mixed system, while an equilibrium selectivity occurred in the latter.

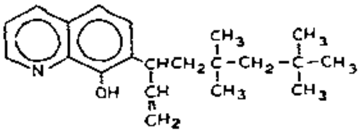
The application of such mixed-extractant systems to commercial operations has not yet been made. They suffer from problems such as poor stripping characteristics, or high solubility of carboxylic acids in the aqueous phase.

C. THE KELEX EXTRACTANTS

(i) Composition

There are presently two Kelex extractants available commercially, Kelex 100 and Kelex 120. The former is the as-produced material, while the latter is a 20 vol.% solution of Kelex 100 in *p*-nonyl phenol.

Kelex 100 is a β-alkenyl-8-hydroxyquinoline produced by the reaction of an alkenyl chloride with 8-hydroxyquinoline. As described in the patent covering this reagent [61] and from experimental evidence [16], the compound is 7-dodecenyl-8-hydroxyquinoline:



XV

The pure reagent, isolated from commercially available material by chromatography on silica gel [16] is a brown, viscous liquid. It can be distilled under vacuum, but decomposes when heated in air.

Prior to about the middle of 1973 commercially available Kelex 100 (designated here as Kelex I) contained a substantial amount of dark brown material which adhered strongly to silica gel, and fluoresced strongly under UV light [16]. Since this time, a purer product has been marketed (designated here as Kelex II) in which the amount of the fluorescent material is substantially reduced [16].

The fluorescent material would appear to be some decomposition product of Kelex, since the same material is produced on heating pure Kelex in air. However, since Kelex I is no longer available this is now more of academic interest. It does have some bearing, nevertheless, on published data concerned with the extraction of copper by Kelex I, and this will be discussed later.

Analysis of the Kelex I and II extractants for 8-hydroxyquinoline (oxine) showed a considerable increase in this material in Kelex II compared to Kelex I. Some analytical data on these two extractants are given in Table 6.

It is interesting to note the different Kelex concentrations in Kelex I and Kelex II as determined by titration in non-aqueous solution [62], the apparent Kelex concentrations being 3.26 and 2.83 *M*, respectively. Based on the data given in Table 6 the molarities of Kelex plus oxine, calculated as Kelex, are 2.30 and 2.55 *M*, respectively, using a molecular weight of 311. The fluorescent material in Kelex I extracts copper, and also titrates as a base. Thus the high apparent concentration of Kelex in this extractant is undoubtedly the result of titration of both Kelex and impurity.

TABLE 6

Some constituents of Kelex 100 [16]

Constituent	Kelex I wt.%	Kelex II wt.%
Kelex (free)	71.0 ± 0.1	77.7 ± 0.1 [a]
Oxine (free)	0.64 ± 0.03 [a] 0.66 [b]	3.70 ± 0.1 [a]
Iron	0.10	< 0.01

[a] By gas chromatography.
[b] By TLC and spectrophotometry.

(ii) Spectra and hydrogen bonding

The UV spectra of pure Kelex and oxine are almost identical, both having an absorption maximum at 242 nm in ethanol solution. Molar absorptivities were the same, $\log \epsilon = 4.55$ at this wavelength [20].

Infrared spectra [20] of pure Kelex (neat) showed OH absorption at 3400 cm^{-1} (strong, sharp) indicative of intramolecular hydrogen bonding. This was confirmed by spectra at different concentrations in carbon tetrachloride, and is similar to oxine where intramolecular hydrogen bonding is prevalent.

(iii) Proton—ligand stability constants

Practical proton-stability constants of pure Kelex have been determined [20] in aqueous dioxane media at 25.0°C and at $\mu = 0.10$ ($NaClO_4$). The solubility of Kelex limited these determinations to solutions of 50 vol.% dioxane and greater. In 75, 60 and 50 vol.% dioxane the values of ${}^{P}pK_{OH}$ were, respectively, 13.02, 12.54 and 12.21 ± 0.01. Extrapolation to zero dioxane ($\mu = 0.10$) gave 10.60. ${}^{P}pK_{NH}$ in 60 vol.% dioxane, 25.0°C and $\mu = 0.01$, was 2.79 ± 0.02.

The ${}^{P}pK_{OH}$ value in 50 vol.% dioxane is a little higher than that reported for oxine (11.54 at 25.0°C) which is to be expected due to the substituent in the 7-position in Kelex. The ${}^{P}pK_{NH}$ value is significantly lower than for oxine (3.97 at 25.0°C, 60 vol.% dioxane, $\mu = 0.10$ [20]). This has been attributed to the bulky dodecenyl group in the 7-position tending to push the OH towards the nitrogen atom and thus hindering the approach of protons.

(iv) Extraction of metals

While the Kelex extractants have not yet been used in commercial solvent extraction operations, studies have been reported on the general extraction of metals using both Kelex 100 and 120.

In acidic media (pH 0.5—6.0) the order of metal extraction by Kelex 100 (0.5 *M*) as a function of $pH_{1/2}$ values is [13]: $Mo^{VI} < Cu^{II} < Ni^{II} < Co^{II} \simeq Zn^{II} < Fe^{II}$. This agrees with the data of Stary [61] for 0.1 *M* oxine—$CHCl_3$ solutions, namely: $VO^{2+} < Fe^{III} < Cu^{II} < Bi^{III} < Ni^{II} < UO_2{}^{2+} < Al^{III} < Th^{IV} < Co^{II} < Zn^{II} < Cd^{II} < Pb^{II} < Mn^{II} < Ca^{II} < Sr^{II}$, and with the order of solubility products [31] and stability constants [31] of metal oxinates. Gentry and Sherrington [63] report an order of extraction by oxine, as a function of $pH_{\frac{1}{2}}$ values: $Sn^{IV} < Mo^{VI} < Fe^{III} \sim Cu^{II} < Ni^{II} \sim Al^{III} < Mn^{II}$.

Accordingly it seems most likely that the extraction of metals, other than those already reported, by Kelex will generally follow that for metal oxinates. The major difference between Kelex and oxine appears to be in the extraction of Fe^{III}, and is considered to be a kinetic effect. Evidence for this assumption is obtained from data reported by Ritcey [13], and from the fact that Kelex 100 contains a significant amount of oxine. The extraction of Fe^{III} by this particular sample of Kelex 100 was shown to be independent of pH over the range 0.5—2.5. The concentration of Fe^{III} in the solvent phase was just that which would be extracted by the oxine in this sample of Kelex (3.7 wt. % oxine [16]). Thus in the contact time used (5 min) Kelex did not extract any significant amount of Fe^{III}.

Flett [8], and Lakshmanan, Lawson and Nyholm [64], have shown that the slow extraction of Fe^{III} by Kelex is essentially a kinetic effect, and provided that contact times are kept short good discrimination of copper over ferric iron can be achieved. Ritcey and Lucas [13] have reported that in the presence of copper, Cu/Fe ratios in the solvent phase using both Kelex 100 and LIX 64N do not exceed about 100, even after 48 h contact time. While only the Cu/Fe ratios are reported, the extraction data (unreported) show that some Fe^{III} is rapidly extracted (< 1 min) by Kelex 100, but that no further extraction of Fe^{III} occurs for about 30 min, after which it increases with time. The Fe^{III} extracted initially can be quantitatively accounted for by the oxine in the Kelex (0.7 wt. % in this case).

The fact that Kelex 100 contained less oxine prior to about the middle of 1973 than it did after this date has not been generally known, and complicates the assessment of reported metal extraction data. For example, the studies reported by Spink and Okuhara [65] on the comparative kinetics of copper by LIX and Kelex extractants, in which the technical grade extractants were used, must be viewed with this fact in mind. Thus it cannot be known whether the copper (or part of it) was in fact extracted by the oxine, especially since tracer amounts of copper were used in some experiments.

Having a tertiary nitrogen atom, Kelex 100 forms acid salts which results in its ability to extract mineral acids from aqueous solutions. Flett has shown [8] that a 10 vol.% solution of Kelex 100 in an organic diluent has a limiting capacity for sulphuric acid of about 17 kg m^{-3}.

There appears to be some conflict regarding the extraction of chloride, or metal chlorides, by Kelex 100. Thus Itzkovitch et al. [66] indicated that this extractant contains chloride after the extraction of copper from a chloride system. This same result has been obtained by others [25]. However, Lakshmanan et al. [64] report that no chloride is transferred to the solvent phase on the extraction of copper from solutions containing up to 4 *M* chloride.

The extraction of metals by Kelex 100 from ammoniacal solutions has been reported, and here again the extraction of cobalt is similar in many ways to that encountered with the LIX extractants. However, Kelex 100 extracts cobalt from solutions containing $(NH_3)_5CoCl^{2+}$, which is not the case with LIX 64N [25]. That Kelex 100 forms stronger complexes with copper than do LIX 64N and 65N is indicated by the fact that copper extraction is not affected by increasing the pH of an ammonium sulphate or carbonate system to about 9, or by increasing ammonium ion concentration [15]. This is also reflected by the $pH_{\frac{1}{2}}$ value for the extraction of copper, which is lower than for any of the LIX extractants.

The order of extraction of some metals from both ammoniacal sulphate and carbonate solutions, over the pH range 7—9, is [15]: $Cu^{II} > Zn^{II} > Co^{II} > Ni^{II}$, and distribution coefficients are higher from the carbonate system. This may be the result of more stable ion-association complexes occurring in the sulphate system, or the lower dissociation of ammonium carbonate. The order of metal extraction appears anomalous in that it is not what might be expected from the formation constants of these metal ammines, nor is it the order of the stability constants of metal oxinates. Thus it would be expected that nickel would be extracted preferentially to zinc. This reversal in the order of metal extraction may be due to a kinetic effect, or to the formation of different species of nickel and zinc with Kelex 100 (see below). Cobalt is anomalous because of the oxidation which occurs during extraction in the presence of air. If cobalt is maintained in the Co^{II} state during extraction, stripping from the solvent phase is reported to be readily accomplished with acids [15].

Since Kelex 100 resembles oxine in its extractive properties towards metals, it seems reasonable to suppose that similarities exist in their other properties. For example, Stary [67] has shown that some metals are extracted by oxine as adduct complexes of the type $M(OX)_n \cdot m HOx$, where $m = 1,2$. Thus Co^{II}, Zn^{II} and Cd^{II} form $M(Ox)_2 \cdot 2HOx$ adducts; UO_2^{2+} and Ag^{I} form $M(Ox) \cdot HOx$ adducts; but Cu^{II}, Fe^{III}, Ni^{II}, Mn^{II} and Mg^{II} do not appear to form such complexes. This may then be the reason for the anomalous order of metal extraction (Zn, Ni) referred to above.

Preliminary studies have shown that Kelex 100 does indeed form an adduct, $ML_2 \cdot 2HL$, with Co^{II}, and that Ni^{II} forms only an ML_2 complex [25]. Lakshmanan and Lawson [68] have also concluded that the extracted cobalt(II)—Kelex species is of the type $CoL_2 \cdot 2HL$, and that cadmium(II) extracts as $CdL_2 \cdot HL$ [64]. The possibility then exists for varying the selectivity of Kelex for some metals by making use of the formation of adduct complexes. From Stary's data [67] it may also be predicted that Kelex 100 would be a good extractant for Mo^{VI}, and that good separation should be achieved from Cu^{II}, Fe^{III} and most other metals, with low pH systems. Furthermore, Pd^{II} should be more easily extracted than Mo^{VI} at low pH values; this may also apply to other noble metals. However, it may also be predicted that the stripping of Mo^{VI} and Pd^{II} from the solvent phase will be difficult with acids, and may require strongly alkaline solutions.

(v) Mixed solvent systems

Mixed solvent systems involving Kelex 100 have received little attention to date, only two investigations having been reported. Lakshmanan and Lawson [64,68] have studied the extraction of cobalt(II), cadmium(II) and zinc(II) by Kelex 100-Versatic 911 (an aliphatic tertiary carboxylic acid produced by the Shell Chemical Co.). They report that this mixed solvent system exhibits synergistic properties, and extracts cobalt(II) as a $Co(X_2R_2H_2)$ complex:

$$\mathrm{Co^{2+}} + \overline{\mathrm{2HX}} + \overline{\mathrm{2HR}} \rightleftharpoons \overline{\mathrm{Co(X_2R_2H_2)}} + \mathrm{2H^+} \tag{22}$$

where HX = Kelex 100, HR = Versatic 911. Similarly, cadmium forms an extractable complex $Cd(X_2R_2H_2)$.

The authors also note that Kelex 100 alone extracts cobalt(II), which is then very difficult to strip with acids, but that cobalt is readily stripped from the mixed solvent. This was rationalised by assuming that Co^{II} forms a very stable complex with Kelex 100, and in the presence of Versatic 911 forms a mixed complex (eqn. (22)) which is more easily dissociated by acids.

The formation of a stable Co^{II}—Kelex complex assumed by Lakshmanan and Lawson is in conflict with data reported by Ritcey [15] who reported that, provided the cobalt was maintained in the cobaltous state, it was readily extracted by, and stripped from, a Kelex-containing solvent. This conflict needs to be resolved.

D. RECENT AND FUTURE DEVELOPMENTS

The particular advances in the application of solvent extraction to the commercial separation and purification of metals in hydrometallurgical processing, afforded by the introduction of chelating extractants, will undoubtedly stimulate further applications of such reagents in this field.

Recent developments include the proposed use of an alkyl quinaldinic acid [69] which has been patented as an extractant for copper. This reagent is claimed to have good selectivity for copper in the presence of ferric ion in acidic solutions. However, the data given in the patent indicate that stripping of copper from the solvent phase may not be as readily achieved, with sufficiently low acid (H_2SO_4) concentrations, as would be required for copper recovery by electrowinning. Thus the reagent would appear to suffer, in this respect, from the same drawbacks as does LIX 70. The quinaldinic acid extractant has not, as yet, been made available for study.

The use of a substituted salicylaldoxime has been reported by Spitzer [70], again principally for the extraction of copper from acidic solutions. Produced by the Shell Chemical Company Ltd. [74], under the name Shell Metal Extractant 529, this reagent is essentially the same as LIX 65N except that the phenyl substituent on the oximino carbon atom of LIX is replaced by a methyl group. The main advantage of this alkyl derivative is reported to be better kinetics of extraction compared to LIX 64N, with comparable physical and chemical properties.

Other substituted salicylaldoximes have been produced by Acorga Ltd. as Acorga P1 and P17. Here the salicylaldoxime is probably substituted in the 5-position by a nonyl or *t*-amyl group. No other information on these extractants is available at this time.

Further modifications to the basic LIX 65N reagent have been given by Mattison and Swanson, who described a nitro derivative of 2-hydroxybenzophenone oxime [71]. Again, as with the alkyl quinaldinic acid and the salicylaldoxime reagents, this reagent is not yet available for study and little can be said about it. However, from what is known of nitrosalicylaldoximes, it would seem that the introduction of a nitro group would increase the acidity of the hydroxy group, but that metal complex stability would be lower, for example, than the chloro substituted LIX 70. Thus metal stability constants of salicylaldoxime, and its 5-chloro and 5-nitro derivatives have been shown by Burger and Egyed [26] to decrease in that order, while the pK_{OH} values indicate a substantial increase in acidity in going from the 5-chloro to the 5-nitro derivatives.

Undoubtedly, there is much work being carried on in the development of new, metal-specific, extractants. Much appears to be devoted to reagents involving N and O bonding to metal ions, and to modification of reagents known to be essentially specific for copper in acidic solutions.

While the concern for copper-selective extractants can be justified, it would be unfortunate if this were to be to the detriment of a search for specific extractants for other metals, such as nickel, cobalt, zinc and magnesium, especially for use in acidic solutions. The separation of nickel and cobalt, or zinc and magnesium, is of prime importance to the metallurgical industry. At present, the only solvent extraction process of importance in the separation of cobalt and nickel employs di(2-ethylhexyl) phosphoric acid as the extractant [72]. This is by no means a specific extractant, consequently metals such as iron, copper, zinc and calcium must be removed from the feed solution prior to the separation of cobalt and nickel by solvent extraction. The availability of a reagent specific for either cobalt or nickel, at low pH, would be of tremendous advantage.

It is evident that metal-specific extractants are modifications of reagents which have been used for analytical separations for many years, and which have been made applicable to commercial solvent extraction processing by the inclusion of a substituent that sufficiently decreases their solubility in an aqueous phase, and increases it in the solvent phase, to make it economic for use in commercial operations. Other approaches should include the application of stereo-chemical factors of ligands in the formation of metal chelates, spacial requirements of metals (O_h, T_d, etc.), kinetic factors, etc. The application of modern inorganic chemistry to this aspect of metal complexes would appear to offer the best approach to the development of metal-specific extractants, which could have far-reaching effects in the metallurgical industry.

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