Structure and Composition of Commercial Copper Chelate Extractants

by R. L. Atwood and J. D. Miller

The structure, properties, and composition of commercial chelating-type copper extractants are examined. Characterization of these extractants was accomplished using organic separation techniques and analytical tools such as NMR and infrared spectroscopy. Results indicate that only the trans isomer of the diphenylhydroxy-oxime (LIX®64N) is capable of copper chelation. The effects of structural modification of the extractants on the extraction and stripping reactions are discussed.

The past decade has witnessed the introduction of six chelation-type reagents for the commercial extraction of copper from dilute leach liquors. The reagents are listed in the following table together with the year they were introduced to the copper industry:

Reagent	Company	Year
LIX®*63	General Mills	1963
LIX®64	General Mills	1965
KELEX®*100, 120	Ashland Chemicals	1968
LIX®64N	General Mills	1970
LIX®65N, 70, 71, 73	General Mills	1971

* LIX® is a registered trademark of General Mills Chemicals Inc.; KELEX® is a registered trademark of Ashland Chemicals.

The LIX® reagents are well covered in the world patent literature for both synthesis and use.[1-16]

Bagdad Copper Corp. was the first company to develop a pilot plant for the solvent extraction of copper using LIX®64.[17] Next, the Bluebird plant, a full-scale operation, was built and started production in March 1968, again using LIX®64.[18] Since then Bagdad has installed a solvent extraction plant capable of handling all their leach liquors.[19] At the present time these plants have a total copper production of 11,700 tpy using LIX®64N.[18,19]

Reagents similar to these commercial extractants have long been known by analytical chemists for their ability to extract metal ions by chelation.[20] These reagents, as well as the commercial extractants, are characterized by: 1) an exchangeable hydrogen atom, and 2) a nitrogen atom with a labile electron pair capable of coordination.

It has been well established that extraction reactions of this type have the following stoichiometry:[20]

$$Cu^{++} + 2RH \rightleftarrows CuR_2 + 2H^+.$$

Although a considerable amount of research has been done with regard to the stoichiometry of extraction and pH effects associated with it, little research has been done on the state of aggregation of these extractants in organic solutions. Also, little is known concerning reaction mechanisms associated with such extractions. The information and data presented in this paper were gathered in order to interpret the kinetics of the LIX®64N copper extraction reaction, presently being studied to determine the reaction mechanism.

Experimental Technique

All reagents used in this study were reagent grade with the exception of the commercial extractants. LIX®64N was from Lot No. OK 1556 and KELEX®100 was from Lot No. SR 12941.

The equilibrium studies were done in 125 ml separatory funnels. Maximum loading experiments were performed using 0.25 vol % commercial extractant in xylene. The aqueous phase consisted of a copper sulfate solution which had been equilibrated with copper hydroxide at pH 3.5. The phase ratio was 10:1, aqueous to organic, and the shake-out test was repeated until no change in pH was observed.

A separation technique was devised to isolate the components of LIX®64 and LIX®64N in order to explain the maximum loading data. The following procedure was used:

1) The commercial extractant was reacted with a 10 M solution of sodium hydroxide at 20°C.

2) The unreacted organic components were removed by centrifugation and separated from the solid sodium-extractant salt.

3) The sodium salt was washed with distilled water.

4) In some instances the sodium salt was converted back to the acid form with sulfuric acid solution.

5) Infrared spectra of the unreacted organic components was made using a Perkin-Elmer 521 infrared spectrophotometer.

The method of continuous variation was used to help identify the stoichiometry of the extracted copper complex. The equilibrium was studied in methanol at a constant copper concentration of 1×10^{-3} M and varying the extractant concentration from an extractant to copper mole ratio of 0.5 to 6.5.

Other equilibrium studies, including the pH_{50} curves and slope analysis, were performed by shake-out tests in 125 ml separatory funnels at a phase ratio of 1:1. The solutions were contacted for 1 hr on an automatic wrist shaker.

Chemical analysis of the aqueous phase was made by standard atomic absorption techniques on a Perkin-Elmer 303 atomic absorption spectrophotometer.

The organic phases were analysed either by difference, or by stripping with 50% hydrochloric acid at a phase ratio of 20:1 aqueous to organic. After stripping, the aqueous phase was analyzed by atomic absorption.

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Spectrophotometric analyses of the extractants and their components were made using infrared, ultraviolet, and NMR spectroscopy. The reported infrared analyses were done using a liquid cell with calcium fluoride windows at a 0.05-mm spacing on a Perkin-Elmer 521 spectrophotometer. The ultraviolet analyses were done using a Beckman DK-2 spectrophotometer with standard analytical techniques. The NMR work was done on a Varian spectrophotometer.

Experimental Results and Discussion

Experimental data consisted of equilibrium studies and spectrophotometric analysis.

Research was initiated with LIX®64N to confirm the reported structure of the copper extractant. General Mills reported that the LIX®64N has a structure similar to that shown in Table 1[21] and has a molecular weight of 339.[22] Consequently, assuming the complex to have a 2:1 mole ratio of extractant to copper, maximum loading for a 1.0 vol % LIX®64N-xylene solution would result in 0.84 gpl copper in the organic. However, as can be seen from Table 2, for LIX®64N, a concentration of only 0.412 gpl copper in the organic was obtained.

To account for this discrepancy either the reported molecular weight is too low, or the commercial extractant is not 100% active. NMR spectra of the purified acid form indicates that a molecular weight of 339 is a reasonable value.

The separation process on LIX®64N yielded a nonviscous organic phase, 53% by wt, which would not extract copper and whose infrared spectra indicated that its principle constituents were alkanes.

The aqueous suspension of the sodium salt of LIX®64N remaining from the separation was reacted with excess copper sulfate in the presence of carbon tetrachloride, CCl_4. The copper-LIX®64N complex thus formed was extracted into the CCl_4. After phase separation the CCl_4 was distilled away from the copper-LIX®64N salt at 40°C under vacuum for two days and then washed in methanol to remove organic impurities. The purified copper-LIX®64N salt was analyzed for copper and a mole ratio of 1.91:1, LIX®64N extractant to copper, was obtained using a molecular weight for the extractant of 339.

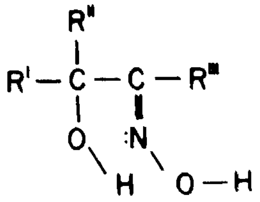
Also, the 2:1 ratio was confirmed using the method of continuous variation in a methanol solvent. As shown in Fig. 1, an abrupt change in slope occurs near two which indicates the complex formed has a mole ratio of 2:1, extractant to copper.

Further evidence for the stoichiometry of the complex was obtained by standard slope analysis techniques. From considerations of the extraction reaction equilibrium, it can be shown that by plotting the percent copper extracted vs. equilibrium pH, the slope at 50% extraction is $n \times 57.57$, where n is the number of hydrogen ions exchanged per copper ion extracted.[23] Fig. 2 shows such a plot for LIX®64N. The lines through the data points are drawn for a value of n equal 2. Alternately, the data may be represented in the traditional manner for slope analysis. As shown in Fig. 3, a slope of 1.94 ± 0.64 at 95% confidence, is obtained for a wide range of composition and is indicative of the stoichiometry of the complex, 2:1.

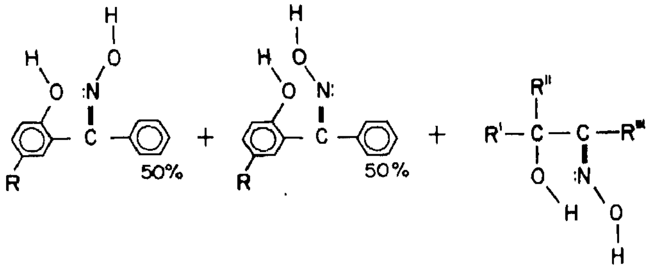
One assumption necessary for the preceding discussion and conclusion is that the extractant is present as a monomer. This assumption was shown to be valid by independent spectrophotometric analysis. Infrared spectra for various concentrations of LIX®64N in carbon tetrachloride are shown in Fig. 4. Dimerization of

Table 1—Commercial Copper Chelate Extractants

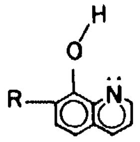
1. **LIX® 63**
Habashi[31] lists this as 5-8-Diethyl-7-Hydroxy-6-Dodecanone oxime and is in reasonable agreement with the patent held by General Mills.[3]



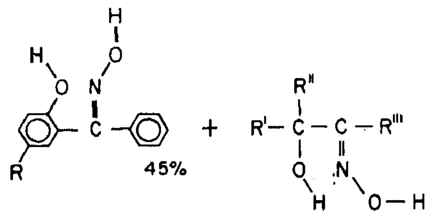
2. **LIX®64**
The parent structure is given by Cerrai[14] and by Habashi[10] states that the —R groups are —(CH$_2$)$_{11}$—CH$_3$. Two important things to note are LIX®64 is a Hydroxyoxime and there are two isomers.



3. **KELEX®100 + 120**
The R group in KELEX®100 is an alkane about 10 carbons long with at least one double bond in it.



4. **LIX®64N**
General Mills gives the M.W. of the active ingredient as 339[6]. This would require that R be —(CH$_2$)$_8$CH$_3$. General Mills[5] also states that the aliphatic extractant is only 1% of the active extractant. The important difference between LIX®64 and LIX®64N is that only the active isomer is present in LIX®64N.



LIX®65N

5. **LIX®70**
LIX®70 is a chlorinated LIX® 65N.

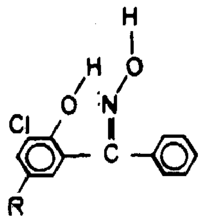


Table 2—Maximum Loading of Copper in Xylene Containing 1 Vol % Extractant

Extractant	Copper, Gpl (Organic)
LIX®63	0.864
LIX®64	0.428
LIX®64N	0.412
LIX®70	0.342
KELEX®100	0.832

organic molecules usually can be detected by the disappearance of one OH band and the appearance of another as the concentration of the organic molecule decreases.[24] Notice that as the concentration of LIX®64N decreases two bands, at 3350 and 1230 cm^{-1}, disappear but that no new bands appear.

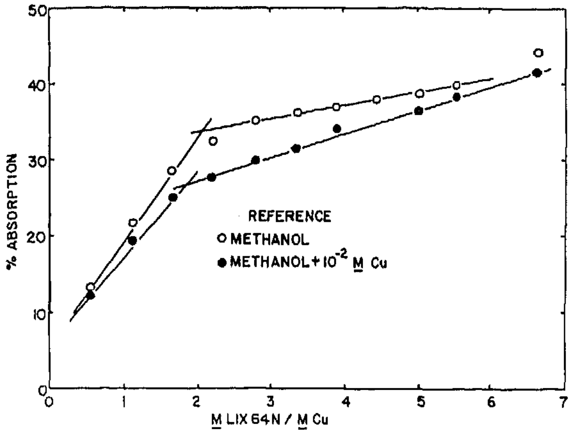


Fig. 1—The method of continuous variation for the LIX® 64N-copper system with a constant cupric ion concentration of 10^{-2} M.

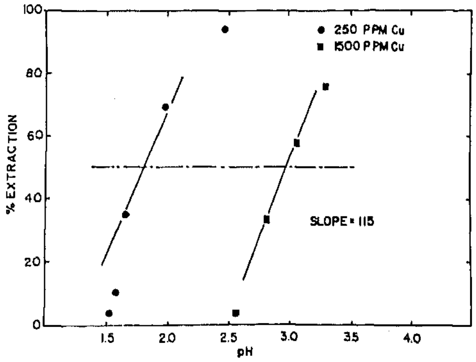


Fig. 2—Percent extraction as a function of equilibrium pH for the LIX®64N-copper system, in which the extractant concentration was varied and was always in excess of the cupric ion concentration.

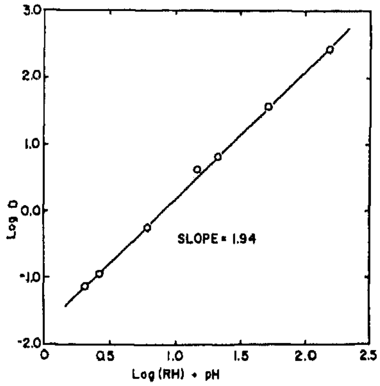


Fig. 3—Standard slope analysis plot showing log *D* vs. log (*RH*) + pH for the LIX®64N-copper system buffered near pH 2.40 with K_2SO_4 and H_2SO_4. The final extractant concentration varied from 0.909 to 0.0093 M and the initial copper concentration in the aqueous phase was 468 ppm.

The sharp band at 3570 cm^{-1} is characteristic of the free OH stretch while the broad band at 3350 cm^{-1} is assigned to polymeric hydrogen bonding. Because the intensity of the band at 3350 cm^{-1} is decreasing faster than the concentration, it follows that there is intermolecular bonding (bonding between molecules). Also, it will be noticed that the band at 3570 cm^{-1} becomes more pronounced as the concentration is decreased. This is because a greater proportion of OH bonds are free and can stretch in their normal mode. Alcohols and phenols display the same effect,[24,25] as has been shown for nonylphenol.[26] However, discrete dimers are not formed as is found with organic acids whose spectra do not exhibit a broad band at 3350 cm^{-1}.[27] Furthermore, it can be deduced that the phenol hydroxyl of LIX®64N does not form intramolecular bonds (bonding within the molecule) because the broad band at 3350 cm^{-1} in Fig. 4 disappears completely at low concentrations. If intramolecular bonds were formed the sharp band at 3570 cm^{-1} would not be enhanced as the concentration decreases and the broad band at 3350 cm^{-1} would not disappear.

Maximum loading results similar to those obtained with LIX®64N were also obtained with LIX64 as shown in Table 2. Consequently, LIX®64 was analysed by separation techniques similar to those used for LIX®64N. In this instance the organic liquid separated from the solid sodium salt was heavy, viscous, and very dark in color as opposed to the light nonviscous organic phase obtained from LIX®64N.

For each gram of LIX®64 reacted with sodium hydroxide, 0.6 g of the dark organic liquid was obtained. Infrared analysis of both phases revealed no noticeable structural differences between the liquid and the solid phases. Small differences in the spectra obtained indicated the liquid phase to have a higher percentage of aliphatics. Also, the liquid phase obtained with LIX®64 could be frozen and a yellow solid obtained; whereas, in the case of the liquid phase from LIX®64N, no solid could be precipitated by cooling to 0°C.

These results with LIX®64 can be explained by considering isomers of the extractant molecule. The syn- and anti-structures of LIX®64 are shown in Table 1. When the molecule is in the syn- form it will not extract because the nitrogen electron pair is not labile and will not coordinate with the copper atom. This phenomenon has been observed in other oxime systems.[28,29] It appears that for LIX®64 isomerization is inhibited severely, whereas for LIX®64N either rapid structural rearrangement is possible or the extractant is present entirely in the anti-form.

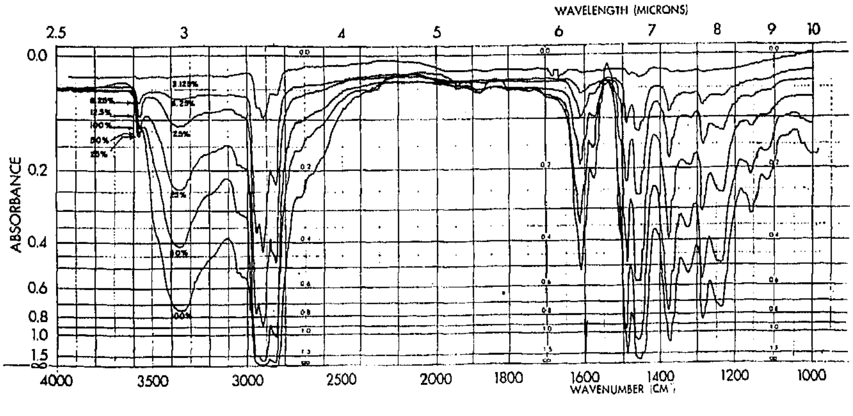


Fig. 4—Infrared spectra of LIX®64N diluted with CCl_4. Note that the 100% spectra is that of the commercial extractant.

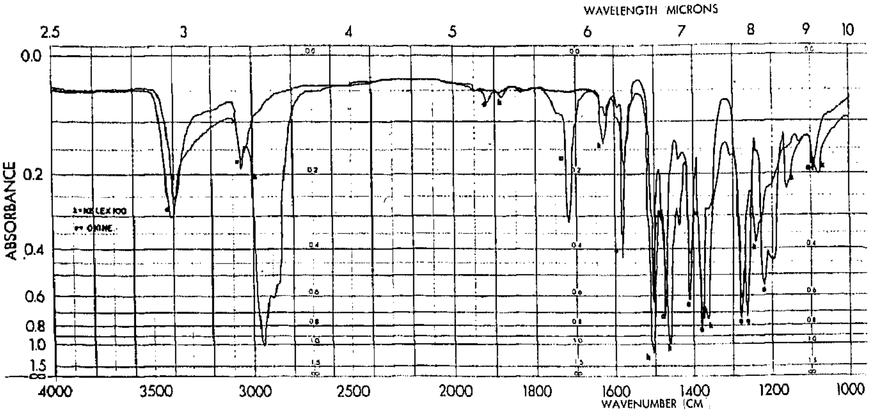


Fig. 5—Infrared spectra of oxine and KELEX® 100 in CCl_4 solvent.

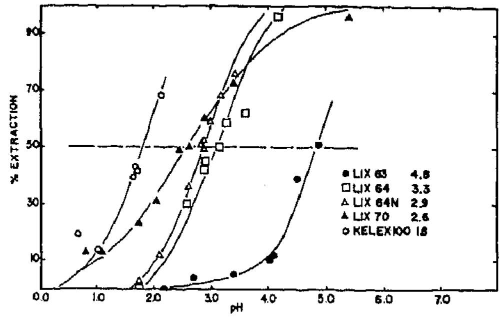


Fig. 6—pH_{50} plots for LIX®63, 64, 64N, 70, and KELEX®100, using an extractant-xylene solution that could be maximum loaded to 100 ppm Cu.

From these results it appears that LIX®64 is approximately 45 wt % active extractant.

Maximum loading experiments (see Table 2) and infrared analysis with LIX®70 yielded results similar to those obtained with LIX®64N. Chemical analysis by sodium fusion indicates that LIX®70 contains a halogen atom, probably chlorine. The infrared pattern of LIX®70 shows an ortho substitution of chlorine for hydrogen.[29] The observed change in the infrared spectra of LIX®70 compared to that of LIX®64N confirms this substitution and is consistent with the structure for LIX®70 as shown in Table 2. The assigned position of the halogen is that which would be expected from organic chemistry concepts for halogenation of compounds similar to the LIX®64 extractant.[11]

The maximum loading data for LIX®63, an alkyl α-hydroxyoxime, are presented in Table 2. Due to pH limitations, the use of LIX®63 has been restricted to laboratory and pilot plant applications. It is reported that LIX®63 or a similar reagent is added to the LIX®64 and LIX®64N, to aid the kinetics of the extraction reaction.[30]

KELEX®100 is an alkyl substituted oxine in which substitution is probably at the 5, 6, or 7 position. Note the similarity between the infrared spectra of KELEX®100 and oxine shown in Fig. 5. Infrared spectra suggests a double bond present in the alkyl chain as indicated by the absorption band present at 1580 cm^{-1}. Maximum loading for KELEX®100, is given in Table 2.

As is well known, the extraction reaction is controlled by the hydrogen ion concentration. Consequently, acidity of the reacting hydroxyl group is a very important parameter. Indeed, this very thing distinguishes one extractant from another.

The standard technique to demonstrate pH dependency is by pH_{50} plots. The plots are constructed such that the total exchange capacity is equal to the total amount of metal in the system while the pH is varied. Fig. 6 shows pH_{50} plots for each of the commercial extractants. Note that acidity increases in the series from LIX®63 to LIX®70. These results are to be expected from structural considerations in that the electrons associated with the hydroxyl group are delocalized when attached to an aromatic ring structure; further delocalization occurs by chlorination of the aromatic ring. Both effects have been seen with carboxylic acids in the extraction of copper, in which case the pH_{50} values go from 4.05 with an alkyl acid, to 3.76 with an aromatic acid, and finally 2.80 is obtained with α-bromolauric acid.[31]

Conclusions

Characterization of commercial copper chelate extractants has lead to the following conclusions:

1) The stoichiometry of the extraction reaction, taking into account the purity of the reagent, was found to be:

$$2RH_{(org)} + Cu^{++}_{(aq)} = CuR_{2(org)} + 2H^{+}_{(aq)}.$$

The commercial extractants, LIX®64, 64N, and 70 are about 45% active extractant.

2) Results indicate that the extractant, LIX®64N exists in the organic phases considered as a monomer with little intramolecular hydrogen bonding.

3) Finally, the acidity of the extractants, which controls the extraction reaction, can be understood from knowledge of their structure and increases in the order LIX®63, 64, 64N, 70, and KELEX®100.

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