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COMMERCIAL CHELATING SOLVENT EXTRACTION REAGENTS

I. PURIFICATION AND ISOMER SEPARATION OF 2-HYDROXYOXIMES

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SUMMARY

The various proprietary substituted 2-hydroxybenzophenone oxime reagents, marketed by General Mills Inc. under the name LIX Reagents, as extractants for copper in solvent extraction processes, have been studied to determine their composition. Qualitative examination by thin-layer chromatography showed that the six aromatic extractants presently available: LIX 64, 64N, 65N, 70, 71 and 73, contain two isomers in about the same proportion and that four of these, LIX 64, 64N, 70 and 73, also contain LIX 63, an aliphatic α-hydroxyoxime.

Determination of the *syn* and *anti* isomer concentrations in the as-received extractants showed that the concentration of the *anti* (active) isomer is about 1 M in each case and that the ratio of *anti* to *syn* isomer varies between 5.4 and 7.3.

INTRODUCTION

Over the last decade, the commercial availability of copper-selective chelating reagents, as extractants in the solvent extraction processing of copper-containing leach liquors, has provided a particular stimulus to the use of solvent extraction as a hydrometallurgical unit process. At least five plants are in operation and more are planned, using chelating reagents as the extractant[1–7].

Commercially available chelating extractants are, at the present time, limited to two types: a series of substituted *o*-hydroxybenzophenone oximes, produced by General Mills Inc. (Tucson, Ariz., U.S.A.) under the name LIX® reagents, and a substituted 8-hydroxyquinoline, produced by Ashland Chemicals (Columbus, Ohio, U.S.A.) 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 metalspecific extractants for use in the separation of metals by solvent extraction processes.

There has been some conjecture as to the structure and composition of the LIX reagents and, to a lesser extent, to those of the Kelex reagents.

It is evident that all the LIX extractants are capable (at least theoretically) of existing in two isomeric forms: *syn* and *anti*.

anti   *syn*
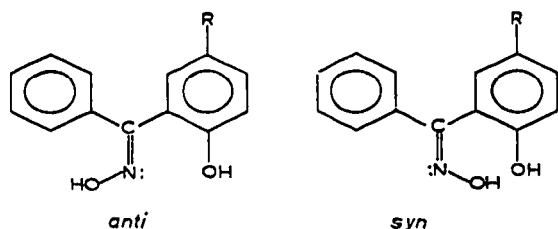
The reactive nature of the *anti* isomers of a-hydroxyoximes towards copper ion, and the relative unreactive nature of the *syn* isomers, have been used as a method of establishing the conformation of isomers of oximes[8-11]. This approach was taken here to differentiate between the *syn* and *anti* isomers of the various LIX extractants.

All the solvent extraction studies reported on the LIX and the Kelex extractants have involved either commercially available[1-4,12-19] or partially purified[20] materials. And while process studies must make use of the as-received extractants, it is dangerous to use these materials for more fundamental studies without a knowledge of their composition and properties. Since the manufacturers of the LIX and Kelex extractants have not made pure reagents available, nor indicated the actual composition of their extractants, it is important, in order to understand and predict the extraction of metals by these reagents, that their composition and the properties of their components be determined.

Studies were therefore undertaken to isolate pure reagents and, in the case of the LIX extractants, the isomers of the active components from the commercially available extractants. The physical and chemical properties of the pure components have been determined, together with the composition of the as-received extractants.

This paper describes the separation of the various isomers of the LIX extractants, their physical properties and the determination of the concentrations of the components in the as-received extractants. Subsequent papers will discuss other properties of the pure components of both the LIX and the Kelex extractants.

EXPERIMENTAL

Reagents and apparatus

All samples of the LIX extractants used in this work are presumed to be normal production materials. It should be noted that these extractants, as received, contain a substantial percentage (up to 40 vol. %) of an inert diluent (probably Napoleum 470*, added presumably to improve the handling characteristics since, as produced, they are very viscous liquids.

Thin-layer chromatography (TLC) plates used were Eastman (Rochester, N.Y., U.S.A.) No. 6061 silica gel. The silica gel used for column chromatography was Fisher Scientific (Pittsburgh, Pa., U.S.A.) No. 679, 100–200 mesh. This material contained a significant amount of iron, which was removed by hot hydrochloric acid leaching, followed by water washing; the silica gel was then dried at 130°.

The mobile phase used in all chromatographic work was a mixture of toluene

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* An essentially aliphatic diluent, produced by Kerr-McGee, Inc.

and ethyl acetate (96:4). TLC plates were developed with an ammoniacal cupric sulphate solution. All other reagents were of analytical quality.

A Cary 118C recording spectrophotometer was used for the spectrophotometric determination of isomer concentrations.

Procedures for purification and isomer separation
   Separation of active reagents
   The oxime reagents were separated from the diluent by precipitation with sodium hydroxide[20] as a gelatinous yellow-orange precipitate. Following separation of this precipitate from the liquid phases, hexane was added and the mixture thoroughly shaken. The phases were allowed to separate and the upper (hexane) phase was discarded. This procedure was repeated until the hexane phase was essentially colourless (about five extractions).

The aqueous phase was discarded and hexane was added to the remaining solid, followed by dilute sulphuric acid (25 vol.%), to produce the free oxime. After several contacts with fresh sulphuric acid, the organic phase containing the oxime was washed with water to remove free acid.

This procedure was adopted for all samples of LIX extractants to remove the diluent. It was also found convenient for the removal of most or all of the LIX 63 from those extractants containing this material, because LIX 63 does not precipitate with sodium hydroxide and is removed along with the diluent.

   LIX 64N and 65N
   Much of the preliminary work done on the separation of isomers in the LIX extractants was carried out on LIX 65N mainly for the reason that this does not contain LIX 63. The hexane solution of this oxime, obtained as described above, was evaporated slowly at ambient temperature, providing a white crystalline material. This was recrystallized from hexane, which afforded a crop of colourless, needle-shaped crystals. TLC of an acetone solution of the crystals showed only one spot (R_F 0.20). The spot was developed using an ammoniacal copper solution, which produced a brown colour with the oxime. A solution of the crystals in ethanol showed no initial reaction with an ethanolic solution of cupric chloride, but on standing the pale green colour of the solution slowly changed to brown, the colour change being visually evident after 30–60 min.

Rapid evaporation of the hexane solution of the oxime produced both crystals and a viscous yellow-brown liquid. Two spots were observed after TLC of an acetone solution of the crystals and liquid, having R_F values of 0.43 and 0.20. The viscous liquid reacted instantly in ethanol solution with cupric chloride to give a brown coloured solution. Dissolution of the viscous liquid in hexane, and slow evaporation, afforded only the crystalline product and no evidence of the starting material.

Heating the crystalline material to just above its melting point produced a pale yellow viscous liquid which, on cooling, did not solidify. TLC of this product showed two spots having R_F values of 0.43 and 0.19. The product obtained after prolonged heating of the molten crystals over several days or heating under vacuum until the liquid boiled, always showed two spots after TLC, in approximately the same ratio and having the same R_F values given above.

Addition of a sodium methoxide solution to a solution of the melted crystals

always produced a yellow colour, as it did with the viscous material produced by rapid evaporation of a hexane solution of the oxime. On the other hand, a solution of the unmelted crystals gave no reaction with base.

It was concluded that the crystalline and viscous liquid products were the two isomers of the LIX 65N oxime, the former being the *syn* (inactive) isomer, the latter the *anti* (active) isomer. Since the *syn* isomer could be readily prepared in a pure form from the as-received material and could be converted to a mixture of isomers on heating, isolation of the liquid *anti* isomer was achieved by column chromatography of a solution of the heated *syn* isomer. The same procedure was adopted for the separation of the isomers of LIX 64N.

LIX 64, 70, 71 and 73

Isomer separation for these four extractants, using the above described procedure, could not be satisfactorily achieved. Modified procedures, described below, were used for the isolation of the isomers, based on the use of their copper complexes.

Separation of syn isomers. After separation of the reagent and diluent, as described previously, the hexane solution of the mixed isomers was contacted with a solution of copper sulphate at just below the hydrolysis pH. Conversion of the *anti* isomer to the copper complex was checked by TLC in the usual way, the copper complex being well separated from uncomplexed isomer.

After discarding the aqueous phase, the organic phase was washed several times with 0.5 M sodium sulphate solution. The organic phase was then shaken with approximately 1 M sodium hydroxide solution ($A/O = 1$) until a sodium salt precipitated, which was transferred to another separatory funnel. Further contacts with sodium hydroxide solution were made until no further precipitation occurred.

The precipitate was washed with hexane until no green material (copper–*anti* isomer complex) was extracted by the hexane. After acidification of the precipitate (now enriched in *syn* isomer at about 80%) and extraction into hexane, the hexane solution was dried over sodium sulphate. It was then transferred to a silica gel column and the isomers separated by elution with toluene–ethyl acetate (96:4). The *syn* isomers of LIX 71 and 73 were obtained by evaporation as white, crystalline solids, and recrystallized from hexane. However, good separation of the *syn* isomers of LIX 64 and LIX 70 could not be achieved by this method and these isomers were obtained by TLC on silica gel of about 2000-μ thickness.

Separation of anti isomers. The mixture of isomers was separated from the diluent, and the copper complexes prepared as described previously. The copper complex of the *anti* isomer was obtained by extraction from the mixed copper complexes with hexane. This solution was concentrated by evaporation and applied to a silica gel column. Elution with the toluene–ethyl acetate solution gave the copper–*anti* isomer complex, which was decomposed by shaking with cold dilute sulphuric acid until free from copper. After washing with water and drying over sodium sulphate, the hexane was removed by evaporation. This afforded, in all cases, viscous pale brown liquid *anti* isomers, which were free from *syn* isomer as determined by TLC.

The *anti* isomer of LIX 70 crystallized after shaking for several days. This was the only solid *anti* isomer obtained from the LIX extractants.

Determination of isomer concentrations

   Separation by TLC. Concentrations of the *syn* and *anti* isomers in each of the as-received materials were determined spectrophotometrically, after separation by TLC and leaching the isomers from the TLC plate by ethanol. The absorbance of the solutions was determined at the appropriate wavelengths (spectra and molar absorptivities of the isomers had been previously determined[21]) and the isomer concentration was determined using the molar absorptivities.

   Anti isomer only. This procedure is based on the fact that the *anti* isomer only gives a yellow colour in alkaline solution. LIX 63 does not interfere. Thus, a weighed amount of as-received material was diluted with methanol, dilute sodium methoxide solution added and the solution further diluted to a given volume. After standing for 10 min, the absorbance of the solution was measured and the concentration of *anti* isomer calculated using the appropriate molar absorptivity[21]. Molecular weights used are given in Table I.

RESULTS AND DISCUSSION

   Analysis and melting points (where applicable) of the isolated isomers are given in Table I. Each isomer showed only one plot by TLC; no further attempts to determine the purity of the isomers were made. Also in Table I are given the substituents on the benzophenone oxime basic molecule, and the molecular weight of the various oximes which constitute the active ingredient of each of the LIX extractants examined. Structures are deduced from elemental analysis and spectra of the isomers, and from data given in the patent covering these reagents[22]. The molecular weights are those calculated from the compounds given.

   In Fig. 1 is shown a TLC plate obtained with all of the extractants studied in this work. The samples were all of as-received materials. Concentrations of the *syn* and *anti* isomers determined in as-received extractants are given in Table II.

   It is evident from Fig. 1 that four of the LIX extractants, LIX 64, 64N, 70 and 73, contain LIX 63, whereas LIX 65N and LIX 71 do not. Furthermore, from the
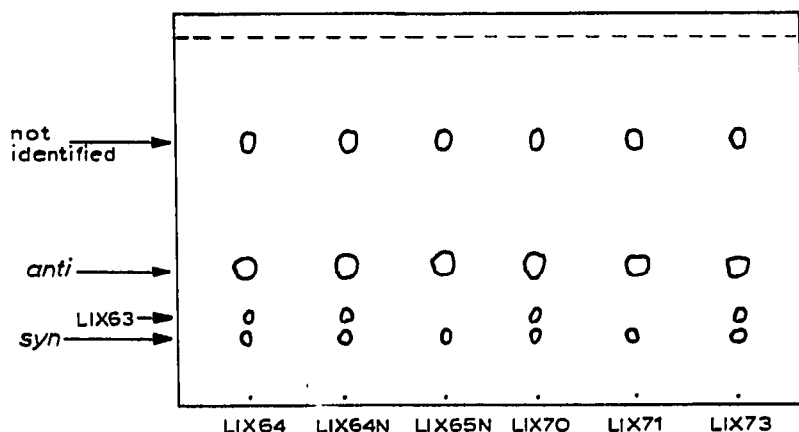

Fig. 1. TLC of as-received LIX extractants.

TABLE I

ANALYSIS AND MELTING POINTS OF ISOMERS OF LIX EXTRACTANTS

Extractant	Proposed substituted*	Anti isomer analysis					Theoretical					Syn isomer analysis				
		C (%)	H (%)	N (%)	Cl (%)	M.p. (°C)	C (%)	H (%)	N (%)	Cl (%)	Mol. wt.	C (%)	H (%)	N (%)	Cl (%)	M.p. (°C)
LIX 64	5-dodecyl	78.1	9.11	3.62	—	—	78.7	9.19	3.67	—	381	—	—	—	—	—
LIX 64N	5-nonyl	77.2	8.50	4.17	—	—	77.9	8.55	4.13	—	339	78.0	8.55	3.91	—	113–115
LIX 65N	5-nonyl	77.8	8.57	4.10	—	—	77.9	8.55	4.13	—	339	77.7	8.77	4.17	—	113–115
LIX 70	3-chloro-5-nonyl	70.9	7.64	3.83	9.70	79–81	70.7	7.50	3.75	9.50	373.5	—	—	—	—	—

* Substituent on 2-hydroxybenzophenone oxime.

TABLE II

CONCENTRATIONS OF ISOMERS IN AS-RECEIVED LIX EXTRACTANTS

Extractant	Sp. gr. at 25°*	As-received basis			Total isomer basis			Conc. of anti isomer (M)
		Anti** (wt.%)	Syn** (wt.%)	Ratio anti/syn	Anti** (wt.%)	Syn** (wt.%)	Ratio anti/syn	
LIX 64***	0.91	41.4	—	—	—	—	—	0.99
LIX 64N***	0.88	40.1	7.2	5.6	84.8	15.2	5.6	1.04
LIX 65N	0.88	39.2	7.3	5.4	84.3	15.7	5.4	1.02
LIX 70***	0.90	40.4	5.5	7.3	88.0	12.0	7.3	0.97
Melted LIX-65N syn isomer	—	—	—	—	79.5	20.5	3.9	—

   * Sp. gr. of LIX 71 and 73: 0.90 and 0.90, respectively.
  ** Average of three determinations; estimated error ±0.2%.
 *** These extractants contain LIX 63.

data published by General Mills[16] it is seen that those extractants which contain LIX 63 are recommended for use at temperatures less than 40°, while those not containing LIX 63 are recommended for use at temperatures greater than 40°.

All the aromatic LIX extractants dehydrate on heating, even under high vacuum. Thus, heating the as-received materials at temperatures near to their boiling points produces droplets of water in the organic phase. Presumably, dehydration results in the formation of phenyl benzisoxazoles. The products of vacuum distillation of LIX extractants showed no adsorption of hydroxyl groups in the infrared.

There are four parent extractants from which the others are apparently prepared by mixing. These, and the mixtures comprising the various extractants, are given in Table III. The ratio of LIX 70 to 65N in LIX 71 and LIX 73 was not determined.

Separation of the isomers of these latter extractants by TLC resulted in showing only two isomers, whereas four might be expected. The syn and anti isomers of LIX 65N and LIX 70 behave similarly on TLC under the conditions used in this work, as shown by chromatography using mixtures of the pure isomers. Other conditions, such as the use of different mobile phases, were not investigated.

TABLE III

LIX PARENT AND DAUGHTER PRODUCTS

Parent	Mixture	Product designation
LIX 63	—	—
LIX 64	LIX 64/63*	LIX 64
LIX 65N	—	—
	LIX 65N/63*	LIX 64N
LIX 70	—	—
	LIX 70/65N**	LIX 71
	LIX 70/65N**/63*	LIX 73

  * Probably about 1% LIX 63.
 ** Ratio of LIX 70 to 65N not known.

The same situation obtained using column chromatography either on the free oximes or on the copper–oxime complexes. However, separation of the *syn* and *anti* isomers of LIX 71 and 73, using the copper complex approach, afforded, after several recrystallizations, a white crystalline material from each extractant. Elemental analysis, spectroscopic investigation and melting point determination strongly suggested that this crystalline material was the same from both extractants, and was the same as the *syn* isomer of LIX 65N.

Isolation of the *anti* isomers from LIX 71 and 73 provided brown viscous liquids, which showed only one spot by TLC. Elemental analysis of these isomers gave results intermediate between those of the isomers of LIX 70 and LIX 65N. Data for both *syn* and *anti* isomers are given in Table IV.

TABLE IV

ANALYSES OF ISOMERS SEPARATED FROM LIX 71 AND LIX 73

Extractant	Isomer	Analysis				
		C (%)	H (%)	N (%)	Cl (%)	M.p. (°C)
LIX 71	Syn	77.3	8.61	4.05	0.00	113–115
	Anti	74.0	8.14	3.72	6.75	—
LIX 73	Syn	76.9	8.54	4.33	0.00	113–115
	Anti	73.9	8.43	3.99	5.04	—

On this basis and the fact that the spectra (IR, NMR and UV) of the *syn* isomers of LIX 65N and those obtained from LIX 71 and 73 are identical[21], it is concluded that the LIX 71 and 73 are mixtures of other LIX extractants.

Furthermore, Agers and DeMent[16] have illustrated that extraction of copper by the various LIX extractants (the so-called *K* curves) gives identical curves for both LI 71 and 73. This is taken as further evidence that these two extractants are composed of the same parent reagents, the only difference being that the LIX 73 contains LIX 63 added, presumably, to improve the kinetics of extraction.

Some comments are in order concerning the composition of LIX extractants, and some erroneous conclusions that have been drawn. Thus, Warshawsky[23] states explicitly that about 50% of the LIX extractant is *syn* isomer, implying that the *anti* isomer comprises the other 50%. He concludes this from the work of Atwood and Miller[20]. However, Atwood and Miller state only that LIX 64 contains approximately 45 wt.% active (*anti*) extractant, which is about right, although it can be implied from their paper that the remaining 55% is *syn* isomer. These investigators do report, however, that only the active isomer is present in LIX 64N[20]. This is not the case, as shown by reference to Fig. 1 and Table II. The ratio of *anti* to *syn* isomers is between about 5.5 and 7.5 in as-received materials, with total isomer concentrations between about 46 and 47 wt.%. Of the total isomer, the *anti* constitutes 84–88%, which, while somewhat higher than that obtained by heating the pure *syn* isomer of LIX 65N (Table II), is reasonably close. These data indicate that the *anti* to *syn* ratio is the result of an *anti–syn* equilibrium, thus the commercially available extractants can be expected to contain both isomers.

Concentrations of *anti* isomer in the LIX extractants obtained in the present studies are about 1.0 *M*. Thus, assuming a 2:1 extractant to metal ratio in the extracted species, a 1 vol.% solution of LIX 64N should have a maximum loading capacity for copper of about 0.32 kg m^{-3}, which includes the copper extracted by the LIX 63. Atwood and Miller[20] show 0.428 kg Cu m^{-3} extracted by LIX 64N. This difference could be the result of there being a higher concentration of *anti* isomer in the batch of LIX 64N used by these investigators, by extraction of copper by the *syn* isomer, or a combination of the two.

The rate of reaction of *syn* isomer with copper(II) is dependent on the pH of the system. Thus, as the pH is increased, the faster is the reaction; in ammoniacal solution, the reaction of the *syn* isomer with copper is very fast. It is to be expected, therefore, that the loading of copper by a given amount of LIX extractant in an ammoniacal system will be higher than for the same amount in an acid system (for the same contact time) by the ratio total isomer to *anti* isomer.

The conversion of the *anti* isomer to the *syn* isomer of all these oximes can be accomplished, to greater than 80%, by precipitation of the sodium salt with sodium hydroxide, allowing the precipitate to stand for several days. This observation presents interesting possibilities if LIX reagents are used in ammoniacal extraction systems.

The increasing rate of formation of a copper–*syn* isomer complex with increase in pH suggests that the double bond of the C=N–OH group is increasingly able to rotate freely, which, in turn, suggests that it must go through a transition state involving a single C–N bond. Such a state can be visualized by considering a nitrone from the oxime group[24] in which the C–N single bond is allowed free rotation (III). Assuming also that the phenolic hydroxyl group forms a phenolate anion in basic solution (formation of these species is indicated by the yellow colour given in basic solution), then, in the presence of a metal ion (Lewis acid), the formation of a metal complex is expected to be fast. Presumably the metal ion functions in the capacity of an electron sink, which is reminiscent of the suggested function of metal ions in biological systems[25].

I   II   III
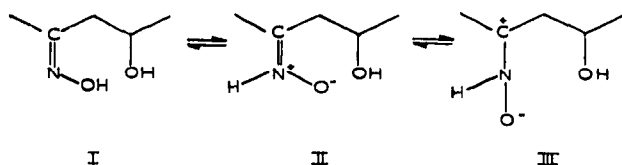
To summarize, the LIX extractants comprise four parent reagents, from which the others are apparently prepared by mixing. All extractants contain about 15% of total reagent in the form of an inactive isomer, and the as-received extractants are about 1 *M* in active reagent.

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