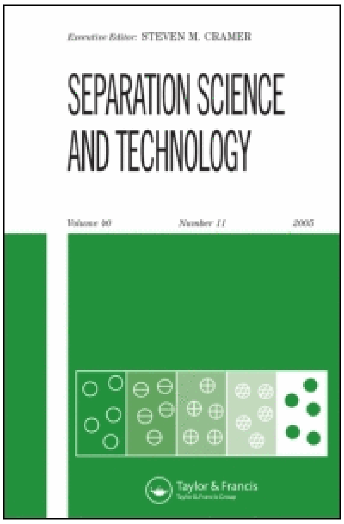

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Mechanistic Studies on the Extraction of Copper by 5,8-Diethyl-7-hydroxy-dodecane-6-one Oxime (LIX 63)

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Abstract

A detailed study of equilibrium and kinetic aspects of the extraction of Cu(II) from solutions containing nitriloacetic acid (NTA) or iminodiacetic acid (IDA) (H_nY) into chloroform solutions of LIX 63 (HL) (found to be monomeric) established the following equilibrium:

$$CuY^- + 2HL(o) \rightleftharpoons CuL_2(o) + HY^{2-} + H^+; \qquad K'_{ex}$$

with K'_{ex} values of $10^{-7.23}$ and $10^{-5.26}$ at 25°C and 0.1 *M* Na_2SO_4 when H_3Y or H_2Y represented NTA and IDA, respectively. From these data the extraction constant applicable in the absence of masking agents was calculated as $K_{ex} = 10^{-3.82\pm0.10}$. The experimental expression for the rate of extraction of Cu(II) by LIX 63 was found to be $-d[Cu]/dt = k'[Cu^{2+}][HL]/[HY^{2-}]^x$. The fractional order dependence on NTA ($x = 0.51$) or IDA ($x = 0.34$) is consistent with a mechanism in which concurrent reaction paths for $CuOH^+$ and CuY^- with neutral LIX 63 molecules in the aqueous phase to form CuL^+ represent the rate-limiting steps.

INTRODUCTION

An interesting symbiotic relationship exists between analytical and process scale solvent extraction. For example, the classical uranyl nitrate extraction by ethyl ether (*1*) was utilized in early process-scale uranium refinement in the Manhattan Project. Search for improved uranium extractants by Union Carbide led to the introduction of tributyl phosphate (TBP), trioctyl phosphine oxide (TOPO), and the alkylphosphoric acids which Fletcher

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Moore and others subsequently demonstrated had useful application in analytical extractions.

The situation in copper refining is analogous. In 1963, General Mills modified a traditional chelating agent, α-benzoinoxime, by introducing large alkyl groups for the purpose of decreasing water solubility and, therefore, reagent losses. The extractant, 5,8-diethyl-7-hydroxy-dodecane-6-one oxime (LIX 63), showed some promise for large-scale copper recovery. Shortly thereafter, the high molecular weight analog to salicylaldoxime, 2-hydroxy-5-nonylbenzophenone oxime (LIX 65), was introduced which was capable of extracting copper from more acidic solutions than could LIX 63 (*2*). Although LIX 65 is a better extractant than LIX 63 from a thermodynamic standpoint, inclusion of LIX 63 in the organic extractant solution will catalyze the Cu-LIX 65 extraction in a manner which is still not completely understood. These findings have important implications for future developments in analytical as well as process-scale solvent extraction.

This report follows our earlier study of the kinetic behavior of LIX 65 (*3*) and deals with the Cu(II)–LIX 63–chloroform system. Inasmuch as the chemistry of LIX 63 is complicated, e.g., under certain circumstances it forms a neutral 1:1 complex with Cu(II) which apparently is polymeric (*4*), we felt it necessary to include the study of the equilibrium aspects of the Cu(II)-LIX 63 extraction.

The study of the kinetics of inherently rapid reactions via solvent extraction techniques (*5*, *6*) is based on reducing the concentration of one of the reactants, i.e., the chelating ligand, by means of the unfavorable phase distribution. The technique can be extended to still faster reactions by reducing the concentration of the other reactant, i.e., the metal ion. This can be accomplished by the use of masking agents, such as the polyaminocarboxylic acids, provided that the complex(es) thus formed dissociate at rates much larger than that involved in the formation of the extractable complex. The extraction of Cu(II) by chloroform solutions of LIX 63 is too rapid to be followed by the technique described earlier, but is sufficiently slow in the presence of either nitrilotriacetic acid (NTA) or iminodiacetic acid (IDA) to permit a detailed kinetic study.

EXPERIMENTAL

Apparatus

The extraction kinetics apparatus has been described previously (*7*). Copper determinations were performed on a Varian AA-6 atomic absorption spectrophotometer equipped with a Westinghouse copper hollow cathode lamp at 324.7 mm with an air–acetylene flame and a spectral bandpass of 0.2

mm. All pH measurements were taken on an Orion 701 pH meter calibrated daily at pH 4.00 or 7.00 using buffer solutions obtained from Micro Essential Laboratory, Inc. A box-type Eberbach shaker with a shaking speed of 280 oscillations/min was used to equilibrate 20 mL volumes of mixed organic/aqueous phases in 60 mL glass vials fitted with polyethylene stoppers and plastic screw caps. Determinations of number-average molecular weight of LIX 63 in chloroform were carried out on a Hewelett-Packard 302B Vapor Pressure Osmometer at 37°C using benzil for calibration.

Reagents

5,8-Diethyl-7-hydroxy-dodecane-6-one oxime (LIX 63) was kindly supplied to us in its undiluted form by the Henkel Corp. All other chemicals were reagent grade. Chloroform was washed twice and distilled, stored in the dark, and kept no longer than 1 week. All aqueous metal solutions were prepared daily from a 1.047×10^{-2} *M* copper stock solution prepared by dissolving a weighed quantity of pure copper (>99.9%) in dilute nitric acid, evaporating to dryness, and diluting to volume with water. The buffers used were 0.1 *M* Na_2HPO_6/NaH_2PO_4 (5.5–7.5). All solutions were adjusted to an ionic strength of 0.1 with 1 *M* Na_2SO_4.

Extraction Procedure

The distribution of copper between equal volumes of chloroform and aqueous phases was examined as a function of concentrations of extractant, complexing-forming reagents, and hydrogen ion. A 10.0-mL portion of aqueous phase containing copper nitrilotriacetic acid (NTA) [or iminodiacetic acid (IDA)] buffer and Na_2SO_4 was added to a 50-mL glass vial along with 10.0 mL of a chloroform solution of LIX 63. The vials were capped and shaken for 3 h (IDA) and 12 h (NTA) to ensure tthat equilibrium was achieved. The equilibrium copper concentration in the aqueous phase was determined by atomic absorption. This value was subtracted from that of the original aqueous solution for copper to obtain the equilibrium organic phase concentration.

Extraction Kinetics Procedure (7)

Each phase was prepared separately in a 100-mL volumetric flask and immersed in a water thermostat at 25°C. After thermal equilibration (~30 min), the aqueous solution was transferred to the reaction flask. Next, the heavier chloroform solution was carefully poured into the flask through a long-stem glass funnel. The reaction was begun by starting the stirring motor and a laboratory timer simultaneously. A sample was removed at predetermined intervals by purging the vessel with nitrogen to force ~10 mL of the dispersion into a test tube without disturbing the course of the reaction in the flask. Samples were then centrifuged, and the aqueous phase was analyzed directly for copper by atomic absorption. Since, at the low copper concentrations used, the response of the spectrophotometer was linear with respect to copper concentration, absorbance readings, A, were used in all calculations. For reactions which proceeded essentially to completion, pseudo-first-order forward rate constants, k'_f, were determined from

$$\ln \frac{A_t}{A_0} = k'_f t \tag{1}$$

where t is the sampling time, A_t is the absorbance at time t, and A_0 is the initial absorbance ($t = 0$). When the reaction equilibrium constant was less than 10, rate constants were obtained from

$$\ln \frac{A_0 - A_e}{A_t - A_e} = (k'_f + k'_r)t \tag{2}$$

where A_e is the aqueous phase absorbance at equilibrium, and k'_r is the pseudo-first-order reverse rate constant. A_e was obtained by collecting ~20 mL of the reaction mixture in a glass vial at the end of the kinetic experiment, and allowing the reaction to reach equilibrium on a shaker. Determination of the extraction equilibrium constant provided a second independent equation which was used to separate k'_f from the sum $(k'_f + k'_r)$.

The nature of the dependencies of the observed rates on ligand and hydrogen ion concentrations were obtained from log-log plots of the pseudo-first-order rate constants against the appropriate parameter. Results are summarized in Table 4.

RESULTS AND DISCUSSION

Equilibrium Studies

In order to determine the stoichiometry of the equilibrium extraction-chelation reaction of copper with LIX 63 in the presence of NTA or IDA, the variation of log D with the log of the LIX 63, NTA, or IDA concentrations and with pH was examined. The data obtained are summarized in Tables 1 and 2. Table 1, from which it may be seen that D exhibits a second-order dependence of [LIX 63] and inverse first orders on

TABLE 1

Summary of Equilibrium Data for Extraction of Copper with LIX 63 in the Presence of NTA or IDA

Dependent variable	Range of variation	Slope of corresponding log D dependence	pK_{ex}
	Nitrilotriacetic Acid (NTA)[a]		
[LIX 63]	$(1\text{–}7.5) \times 10^{-2}\ M$	2.10 ± 0.15	7.42 ± 0.10
pH	4.95–6.60	0.94 ± 0.07	7.07 ± 0.12
[NTA]	$(0.03\text{–}2) \times 10^{-3}\ M$	-0.98 ± 0.04	7.23 ± 0.10
		From intercept	6.75 ± 0.20
		Mean $pK_{ex} = 7.24$	
	Iminodiacetic Acid (IDA)[b]		
[LIX 63]	$(1\text{–}7.5) \times 10^{-2}\ M$	2.08 ± 0.09	5.27 ± 0.23
pH	3.3–5.38	1.00 ± 0.05	5.26 ± 0.08
[IDA]	$(0.5\text{–}4) \times 10^{-3}\ M$	-1.05 ± 0.03	5.15 ± 0.10
		From intercept	5.26 ± 0.14
		Mean $pK_{ex} = 5.23$	

[a] $[Cu^{2+}] = 1 \times 10^{-5}\ M$; [LIX 62] $= 5 \times 10^{-2}\ M$; [NTA] $= 1 \times 10^{-6}\ M$, pH $= 6.95$.
[b] $[Cu^{2+}] = 2 \times 10^{-5}\ M$; [LIX 63] $= 5 \times 10^{-2}\ M$; [IDA] $= 1 \times 10^{-3}\ M$, pH $= 5.98$.

$[H^+]$ and [NTA] or [IDA]. Hence the extraction equilibrium can be quantitatively described by the expression

$$CuY^- + 2HL_{(o)} \overset{K'_{ex}}{\rightleftharpoons} CuL_2(o) + HY^{2-} + H^+ \qquad (3)$$

where HL represents LIX 63, H_3Y represents NTA or IDA, and K'_{ex} represents the extraction equilibrium constant corresponding to the reaction in Eq. (3).

TABLE 2

Estimation of Mean Aggregation Number of LIX 63 in Chloroform

Concentration of LIX 63, M	M_n	Mean aggregation number
1.48×10^{-2}	283.4	1.00
1.48×10^{-2}	289.6	1.03
3.03×10^{-2}	308.3	1.09
3.68×10^{-2}	307.2	1.09

Although the metal extraction equilibrium data strongly indicate that LIX 63 is monomeric in $CHCl_3$, earlier evidence for dimer formation (and higher aggregates) in other solvents suggested that it would be prudent to directly address this question, particularly prior to embarking on our kinetic studies. As may be seen from Table 2, summarizing the number-average molecular weight measurements, there is very little self-aggregation of LIX 63 in $CHCl_3$, probably reflecting the hydrogen bonding ability of chloroform.

It is of interest to note that the extractable complex has a 1:2 metal:ligand composition. Although 1:1 complexes of Cu acyloinoximes have been described in the literature, we found no indication of any but the 1:2 complex in our equilibrium studies. Of course, in all of the work the LIX 63 concentration was much higher than that of copper, which would tend to favor the 1:2 complex.

The value of the equilibrium constant for the extraction of Cu(II) by LIX 63 in the absence of masking agents, K_{ex}

$$Cu^{2+} + 2HL(o) \overset{K_{ex}}{\rightleftharpoons} CuL(o) + 2H^+ \tag{4}$$

can be obtained from the extraction data obtained in the presence of NTA or IDA by taking the extent of copper complex formation in the aqueous phase into account. It can be shown (*7*) that

$$D = \frac{K_{ex}[HL]^2}{[H^+]^2}\alpha_{Cu} \tag{5}$$

where

$$\alpha_{Cu} = [1 + \beta_{CuY}\alpha_Y C_Y]^{-1} \tag{6}$$

$$\alpha_Y \simeq K_3/[H^+] \tag{7}$$

β_{CuY} is the formation constant of the Cu complex of NTA or IDA, C_Y is the total concentration of NTA or IDA not bound to metal, and K_3 is the acid dissociation constant of HY^{2-}. Calculations made on this basis are summarized in Table 3. The excellent agreement within each system as well as in the cross-comparison of both NTA and IDA systems represents full confirmation of the validity of the extraction formulation as shown in Eq. (4).

The extraction constant is significantly lower than that for the Cu-LIX 65-$CHCl_3$ system [$10^{-0.64}$(*3*)]. Examination of the several component constants comprising K_{ex}

$$K_{ex} = \beta_2 K_a^2 K_{DC}/K_{DR}^2 \tag{8}$$

TABLE 3

The Extraction Constant for the Copper Complex with LIX 63

pH	$\log \alpha_y$	$\log \alpha_{Cu}$	$\log D_{Cu}$	$\log K_{ex}$
		Nitrilotriacetic Acid (NTA)		
5.55	−4.10	−4.84	−0.222	−3.88
5.71	−3.95	−4.99	−0.110	−3.94
5.90	−3.75	−5.19	0.165	−3.86
6.02	−3.65	−5.29	0.277	−3.87
6.20	−3.45	−5.49	0.442	−3.87
6.30	−3.35	−5.59	0.613	−3.80
6.60	−3.05	−5.89	0.830	−3.88
6.95	−2.70	−6.26	1.170	−3.89
			Mean	−3.85 ± 0.05
		Iminodiacetic Acid (IDA)		
4.94	−4.39	−3.18	0.428	−3.67
5.53	−3.79	−3.78	0.926	−3.76
5.98	−3.34	−4.23	1.252	−3.89
5.98	−3.36	−4.23	1.345	−3.79
			Mean	−3.78 ± 0.11

where β_2 is the overall formation constant of the Cu–LIX 63 chelate in the aqueous phase; K_a and K_{DR} are the aqueous acid dissociation constant and distribution constant of LIX 63, respectively; and K_{DC} the distribution constant of the chelate, should assist in understanding the lower K_{ex} value. The K_{DR} for LIX 63, $10^{5.1}$ (*7*), is somewhat larger than that of LIX 65 [$10^{4.6}$(*3*)]. Even this small change should be compensated for by a corresponding change in the K_{DC} values. Hence it is quite probable that the proton displacement constant, $\beta_2 K_a^2$, is about 10^3-fold smaller for the Cu chelate of LIX 63 than for that of LIX 65. Although insufficient formation equilibrium data exists in the literature for verification of this point, this finding is in keeping with our preconceived notion that solicylaldoxime analogs will have higher proton displacement constants for copper than will comparable acyloinoximes.

Kinetic Studies

In all of the kinetic experiments the extraction rates were found to be pseudo-first-order in metal ion, as might be expected from previous work. Variation of the slopes of the pseudo-first-order plots with the other concentration variables were used to obtain the kinetic orders for these variables, as shown in Table 4, and thus to the overall observed kinetic expression

$$-\frac{d[\mathrm{Cu}^{2+}]}{dt} = k' \frac{[\mathrm{Cu}^{2+}][\mathrm{HL}]_0}{[\mathrm{HY}^{2-}]^x[\mathrm{H}^+]^0} \tag{9}$$

where x is a fraction (0.51 for NTA and 0.34 for IDA).

It is noteworthy that, unlike that Cu–LIX 65 reaction (*3*), the rate exhibits a first-order dependency on the ligand, indicating that the formation of the 1:1 complex is rate determining. It was somewhat disconcerting, however, to find that the rate had a fractional order in the concentration of the masking agent (Table 5). It had been hoped that the CuY^- complex would dissociate rapidly relative to the formation of the Cu-LIX 63 complex, which would have resulted in an inverse first-order dependence in NTA or IDA, i.e.,

$$\mathrm{CuY}^- + \mathrm{H}^+ \overset{(K_{a}3\beta\mathrm{CuY})^{-1}}{\leftrightharpoons} \mathrm{Cu}^{2+} + \mathrm{HY}^{2-} \qquad \text{rapid preequilibrium} \tag{10}$$

$$\mathrm{Cu}^{2+} + \mathrm{HL} \overset{k_1}{\rightleftharpoons} \mathrm{CuL}^+ + \mathrm{H}^+ \text{ slow} \tag{11}$$

$$-\frac{d[\mathrm{Cu}^{2+}]}{dt} = k_1[\mathrm{Cu}^{2+}][\mathrm{HL}] = \frac{k}{K_{a3}\beta_{\mathrm{CuY}}K_{\mathrm{DR}}} \frac{[\mathrm{CuY}^-][\mathrm{HL}]_0[\mathrm{H}^+]}{[\mathrm{HY}^{2-}]} \tag{12}$$

From Eq. (12), both the $[\mathrm{HY}^{2-}]$ and $[\mathrm{H}^+]$ dependence can be seen to be

TABLE 4

Summary of Kinetic Parameters for LIX 63–Cu^{2+} Extraction in the Presence of NTA or IDA

Dependent variable	Number of determinations	Observed orders
	Nitrilotriacetic Acid (NTA)	
[LIX 63]	1	1.06 ± 0.13
$[\mathrm{H}^+]$	1	−0.08 ± 0.12
[NTA]	4	−0.51 ± 0.01
	Iminodiacetic Acid (IDA)	
[LIX 63]	1	0.90 ± 0.12
$[\mathrm{H}^+]$	1	0.13 ± 0.08
[IDA]	2	−0.34 ±0.05

TABLE 5

Effect of the Masking Agent Concentration on the Rate Constant: $[HL]_0 = 5 \times 10^{-2}\ M$

pH	$1/[HY^{2-}]$	k'_f
	Iminodiacetic Acid[a]	
5.53	50	1.13×10^{-2}
5.53	100	1.36×10^{-2}
5.53	201	1.52×10^{-2}
5.98	505	2.43×10^{-2}
5.98	1000	2.47×10^{-2}
4.94	1020	2.70×10^{-2}
5.98	1110	2.53×10^{-2}
5.98	2080	3.97×10^{-2}
	Nitrilotriacetic Acid[b]	
6.60	1×10^3	2.20×10^{-4}
6.95	2.04×10^3	3.10×10^{-4}
6.60	5.26×10^3	4.40×10^{-4}
5.75	8.33×10^3	4.70×10^{-4}
6.30	1.11×10^4	5.97×10^{-4}
6.60	1.11×10^4	5.94×10^{-4}
7.14	1.11×10^4	5.83×10^{-4}
6.60	1.43×10^4	7.28×10^{-4}
5.75	1.67×10^4	6.92×10^{-4}
7.14	2.50×10^4	9.93×10^{-4}
6.60	3.33×10^4	1.41×10^{-3}

[a] Least squares line: $k'_f = (1.30 \pm 0.12) \times 10^{-5}/[HY^{2-}] + 1.28 \pm 0.13 \times 10^{-2}$; correction coefficient = 0.97.

[b] Least squares line: $k'_f = (3.39 \pm 0.16) \times 10^{-8}/[HY^{2-}] + 2.10 \pm 0.26 \times 10^{5}$; correction coefficient = 0.99.

anomalous. A reasonable explanation of the fractional $[HY^{2-}]$ dependence is its direct combination with LIX 63 as one possible pathway, i.e.,

$$CuY^- + HL \xrightarrow{k_2} CuL^+ + HY^{2-} \qquad \text{slow} \qquad (13)$$

$$-\frac{d[Cu^{2+}]}{dt} = k_2[CuY^-][HL] = \frac{K_2}{K_{DR}}[CuY^-][HL]_0 \qquad ((14)$$

which is zero order in both $[H^+]$ and $[HY^{2-}]$. If Reactions (11) and (13) were both important in the determination of the rate of extraction, then fractional orders of both $[H^+]$ and $[HY^{2-}]$ of the same size would be observed.

Inasmuch as a virtual zero order in $[H^+]$ is observed, Reaction (11) is not likely, but rather, one of the following pathways is:

$$Cu^{2+} + OH^- \overset{\beta_{CuOH}}{\rightleftharpoons} CuOH^+ \qquad \text{rapid preequilibrium} \qquad (15)$$

$$CuOH^+ + HL \overset{k'_1}{\rightleftharpoons} CuL^+ \qquad \text{slow} \qquad (16)$$

$$-\frac{d[Cu^{2+}]}{dt} = k'_1[CuOH^+][HL] = \frac{k'_1\beta_{CuOH}K_w}{K_{a3}\beta_{CuY}K_{DR}}\,\frac{[CuY^-][HL]_0}{[HY^{2-}]} \qquad (17)$$

or

$$HL \overset{K_a}{\rightleftharpoons} H^+ + L^- \qquad \text{rapid} \qquad (18)$$

$$Cu^{2+} + L^- \overset{k''_1}{\rightleftharpoons} CuL^+ \qquad \text{slow} \qquad (19)$$

$$-\frac{d[Cu^{2+}]}{dt} = k''_1[Cu^{2+}][L^-] = \frac{k''_1K_aK_w}{K_{a3}\beta_{CuY}K_{DR}}[CuY^-][HL]_0 \qquad (20)$$

Inasmuch as the pH range of the kinetic study is not so far removed from Reaction (11) as it is from Reaction (15), the first of these two alternatives, i.e., Reactions (11) and (13), is much more attractive. (Indeed, in a calculation based on the scheme of Reactions 18 and 19, the value of K''_1 derived was unrealistically high, $\sim 10^{13}$.) From these considerations, the overall rate expression, i.e., combining Eqs. (13), (14) and (15), (16), would be

$$-\frac{d[Cu^{2+}]}{dt} = k'_1[CuOH^+][HL] + k_2[CuY^-][HL] \qquad (21)$$

$$= \left(\frac{k'_1\beta_{CuOH}K_w}{\beta_{CuY}K_{a3}K_{DR}}\,\frac{[HL]_0}{[HY^{2-}]} + \frac{k_2[HL]_0}{K_{DR}}\right)[CuY^-] \qquad (22)$$

which, after integration, becomes

$$\ln\frac{C_0}{C_t} = \left(\frac{K'_1\beta_{CuOH}K_w}{\beta_{CuY}K_{a2}K_{DR}}\,\frac{[HL]_0}{[HY^{2+}]} + \frac{k_2[HL]_0}{K_{DR}}\right) = k'_f t \qquad (23)$$

where C_0 and C_t represent the initial concentration of copper and that at time t.

As expected from Eq. (23), a plot of K'_f (see Eqs. 1 and 2) vs $1/[\mathrm{HY}^{2-}]$ should be linear with a slope proportional to k'_1 and an intercept involving k_2:

$$k'_1 = \frac{(\text{slope})K_{DR}\,\beta_1 K_{a3}}{\beta_{\mathrm{CuOH}} K_w [\mathrm{HL}]_0} \tag{24}$$

$$k_2 = (\text{intercept})\frac{K_{\mathrm{DR}}}{[\mathrm{HL}]_0} \tag{25}$$

Using a value of K_{DR} of $10^{5.2}$ (*8*); of $\beta_1 K_{a3}$ of $10^{3.29}$ and $10^{1.23}$ for NTA and IDA (*9*), respectively; of β_{CuoH} of $10^{6.3}$ (*9*); and K_w of 10^{-14}, values for k'_1 of 1.1×10^{10} and 1.1×10^{11} (geometric mean $= 3.3 \times 10^{10}$ $M^{-1}\mathrm{s}^{-1}$) were obtained. Considering the wide variation in the slopes of k'_f vs $1/[\mathrm{HY}^{2-}]$ (about 10^3), these values for the reaction rate constant of CuOH^+ with HL are in reasonable agreement. The values for K_2 of 6.31×10^2 $M^{-1}\mathrm{s}^{-1}$ are consistent with the expectations that (a) CuY would react much more slowly than CuOH^+ and that (b) the more stable NTA complex would react more slowly than that of IDA.

When LIX 63 is used to catalyze the extraction of Cu^{2+} by LIX 65, it is present in smaller concentration than that of LIX 65. The concentration differential in the aqueous phase is further heightened because the K_{DR} for LIX 65 is about four times smaller than that of LIX 63. The pH range of this catalyzed extraction is lower than that used in these experiments, resulting in a corresponding drop in the CuOH^+ concentration and, therefore, the rate of the Cu–LIX 63 reaction. These factors notwithstanding, the inherent 1000-fold advantage of the speed of LIX 63 over LIX 65 can be shown to result in the conclusion that in the catalyzed extraction systems the first step must be the rapid formation of a 1:1 Cu–LIX 63 complex. The reaction of this complex with neutral LIX 65 to form the neutral mixed ligand chelate would be the rate-determining step. Once in the organic phase, the mixed ligand chelate would be transformed to the thermodynamically favored 1:2 Cu–LIX 65 chelate. The catalytic role of LIX 63 in the Cu–LIX 65 system suggests a useful generalization: A chelating extractant can speed the rate of extraction of a metal by another extractant even though it is not thermodynamically favored over the second provided that it reacted more rapidly to form an intermediate complex. Inasmuch as the search for improved chelating extractants may well lead in the direction of still higher molecular weight and, therefore, probably slower extracting reagents, increasing understanding of the nature and mode of action of potential catalysts is a very important aspect of such research.

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