Chemical Kinetics and Mechanisms in Solvent Extraction of Copper Chelates

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Received June 2, 1976

From being a curiosity in the late 19th century, solvent or liquid–liquid extraction has developed into a highly sophisticated process with wide applications in the laboratory and in industry. It is useful in analytical chemistry, in radiochemistry, in the oil and heavy organic chemical industries, in the pharmaceutical industry, in nuclear fuel reprocessing, and most recently in general hydrometallurgical processing.

From the partition of simple solutes between partially miscible or wholly immiscible liquids, the process has now broadened to encompass the use of a wide variety of reagents which by means of chemical reaction, ion association, or solvation facilitate the desired extraction. The introduction of such reagents, soluble in one phase only, which can interact either chemically or physically with the substance of interest and thus selectively extract it from one phase to another has had an enormous impact in analytical chemistry. For the last decade or so, it has also had an ever increasing impact in hydrometallurgical processing.

Hydrometallurgy is concerned with aqueous solutions, and thus metal ions are the species of interest. Extraction of metal ions directly into a water-immiscible oil phase is energetically unfavorable, and this process can only be accomplished by arranging that the metal ion be transferred to the organic phase as a neutral species. Such species can be produced by aqueous complexing or by association with anions whereby, by careful choice of ligand concentration, a neutral species extractable by an organic solvent can be produced. Such extractions can be assisted by addition of solvating agents to the organic phase.

Alternatively, anionic species can be extracted by amines in the salt form present in the organic phase, by an anion-exchange process. Also reaction of the metal ion with an organic acid can produce a neutral salt insoluble in the aqueous phase but soluble in the organic phase. All these types of extraction systems are in commercial use in hydrometallurgy. The subject has recently been surveyed.[1]

Of major importance in recent years has been the introduction of acidic chelating extractants specially designed for hydrometallurgical applications. While chelating reagents are common in analytical chemistry, their use in a commercial situation was attendant on several economic factors, namely, a cheap source of supply, low aqueous solubility, high organic phase solubility for both reagent and metal complex, ease of recovery of metal from the organic phase, and regeneration of the reagent for recycle. Finally the rate of extraction had to be high enough to achieve acceptable throughputs per unit volume of equipment to avoid high capital cost.

The majority of analytical chelating extractants did not fulfill all these criteria, and special reagents had to be developed. The most important of these to date have been developed specially for extraction of copper from dilute leach liquors. The application of solvent extraction in copper hydrometallurgy has been reviewed recently,[2] as has the current status of metal chelate solvent extraction by means of hydrometallurgical reagents.[3a]

While a considerable body of data exists on the equilibrium properties of the reagents, their metal chelates (especially with copper), and the likely stoichiometry of the extracted species, much less information is available on rates of metal extraction. This lack of data tends to inhibit optimal design and equipment selection. Furthermore, until recently all the kinetic and mechanistic studies on metal chelate systems related to those used in analytical chemistry. Because of their somewhat different physical properties, such mechanisms perhaps do not obtain with the commercial reagents. It is therefore important to elucidate the chemical kinetics and mechanism of metal extraction with these new reagents.

Classical Mechanisms and Their Limitations

The classical description of metal chelate extraction requires partition of the chelating agent from the organic phase into the aqueous phase, ionization of the chelating agent in the aqueous phase, sequential stepwise chelate formation, and finally partition of the neutral chelate back into the organic phase, i.e.

$$\overline{RH} \rightleftharpoons RH \qquad P_{RH} = \frac{(\overline{RH})}{(RH)} \tag{1}$$

$$RH \rightleftharpoons R^- + H^+ \qquad K_d = \frac{(R^-)(H^+)}{(RH)} \tag{2}$$

$$\frac{M^{n+} + R^- \rightleftharpoons MR^{(n-1)+}}{MR_{n-1}^{+} + R^- \rightleftharpoons MR_n} \qquad K_f = \frac{(MR_n)}{(M^{n+})(R^-)^n} \tag{3}$$

$$MR_n \rightleftharpoons \overline{MR}_n \qquad P_{MR_n} = \frac{(\overline{MR}_n)}{(MR_n)} \tag{4}$$

Equations 1–4 can be combined to give the overall extraction reaction

$$M^{n+} + n\overline{RH} \rightleftharpoons \overline{MR}_n + nH^+ \tag{5}$$

where M^{n+} is an n-valent metal ion, RH is the mo-

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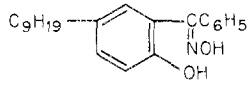
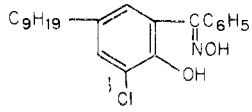
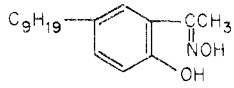
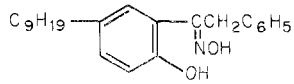
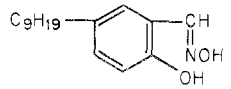
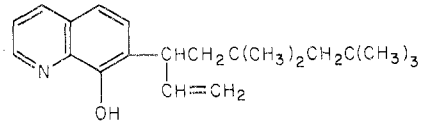
(1) D. S. Flett, *Ingenieursblad*, 41, 424 (1972).
(2) D. S. Flett, *Inst. Min. Metall. Trans., Sect. B*, 83, C30, (1974).
(3) (a) A. W. Ashbrook, *Coord. Chem. Rev.*, 6, 285, (1975); (b) A. W. Ashbrook, *Anal. Chim. Acta*, 58, 115, (1972).

Table I
Chelating Copper Extractants

Reagent	Name	Mol wt	Aqueous solubility, g $l.^{-1}$ [a]
$CH_3(CH_2)_3CH(C_2H_5)CH(OH)-C(=NOH)CH(C_2H_5)(CH_2)_3CH_3$	LIX 63[b]	282	0.006
	LIX 65N[b]	339	0.006
LIX 65N + LIX 63	LIX 64N[b]		0.006
	LIX 70[b]	373.5	
	SME 529[c]	277	
	P 17[d]	353	
	P 50[d]	263	
	Kelex 100[e]	311	<0.001

[a] Aqueous solubility data from Ashbrook.[3b] [b] General Mills Inc., U.S.A. [c] Shell Chemicals Ltd., U.K. [d] Acorga Ltd., U.K. [e] Ashland Chemical Co., U.S.A.

noacidic chelating agent, and bars denote the organic phase.

Defining an overall mass-action constant K as

$$K = \frac{(\overline{MR}_n)(H^+)^n}{(M^{n+})(\overline{RH})^n} \tag{6}$$

and a distribution coefficient D as $\bar{M}/M$, which in the present case equals $(\overline{MR}_n)/(M^{n+})$, the familiar expression for log D may be derived

$$\log D = \log K + n\text{pH} + n \log (\overline{RH}) \tag{7}$$

where

$$\log K = P_{MR_n} K_f (K_d)^n (P_{RH})^{n-} \tag{8}$$

Until fairly recently all chemical kinetic studies of metal chelate solvent extraction were interpreted with apparent success using essentially this model. Clearly the model does require a minimum degree of reagent solubility in the aqueous phase to be credible. For that reason problems arise when the kinetic behavior of proprietary reagents is considered, such as those used commercially for copper solvent extraction; for economic reasons, they have very low aqueous solubilities.

The most important compounds either proposed or already in commercial use for selective solvent extraction of copper are summarized in Table I. Examination of the table shows that these compounds all have very low aqueous solubilities, and thus difficulties are likely to arise with the application of the classical ionic homogeneous aqueous phase reaction model to these compounds. These difficulties can be quantified as follows.

In the classical reaction scheme the rate-controlling step is often the first stepwise addition reaction of the chelating agent (eq 3), i.e.

$$M^{n+} + R^- \rightarrow \text{products}$$

When the back extraction reaction is negligible, the rate of metal removed is

$$\frac{d(M^{n+})}{dt} = k_f (M^{n+})(R^-) \tag{9}$$

where k_f is the forward rate constant.

Integration of eq 9 between the limits $t = 0$ and $t = t$ seconds yields eq 10. At the half-life time of this first

$$\log (M^{n+})_t = \log (M^{n+})_{t=0} - \frac{k_f t (R^-)}{2.303} \tag{10}$$

order reaction eq 10 reduces to eq 11, where $t_{0.5}$ is the

$$k_f = \frac{0.693}{t_{0.5}(R^-)} \tag{11}$$

half-life.

From Table I, the aqueous solubility of LIX 65N is $<2 \times 10^{-5}$ M and of Kelex 100 is $<3 \times 10^{-6}$ M. Consider the case of Kelex 100. From dissociation constant data for 8-hydroxyquinoline,[4] Kelex 100 is estimated to have an acid dissociation constant of $\sim 10^{-10}$. Thus at pH 3.0 $(R^-) < 3 \times 10^{-13}$ M. Substituting this value into eq 11 yields eq 12. Equation 12 shows that even with a

(4) "Stability Constants", *Chem. Soc., Spec. Publ.*, No. 17, 597 (1964), Table 720.

$$k_f > \frac{0.231 \times 10^{13}}{t_{0.5}} \quad (12)$$

half-life of 1 min the value of k_f will be greater than the second-order rate of water exchange for copper, taking account of 2-fold coordination,[5] i.e., 7.2×10^6 l. mol^{-1} s^{-1}. Therefore any interpretation of the kinetics of copper extraction with Kelex 100 using this ionic homogeneous aqueous mechanism cannot be tenable. Similar arguments obtain for the LIX reagents.

Thus, although ionic species of the reagents in the aqueous phase are not involved in the extraction reaction, un-ionized species could possibly participate. Substitution of RH for R^- in eq 11 shows that homogeneous aqueous reaction between un-ionized extractant and copper is quite likely and should feature in extraction mechanism considerations.

Physical Chemical Considerations

All extractants are interfacially active. Adsorption at the interface lowers the interfacial tension and facilitates dispersion of the phases. In a well-dispersed system with appreciable adsorption of the extractant at the interface, the interfacial population will considerably exceed the aqueous concentration of the extractant. Thus reactions of kinetic importance could take place at the interface as well as in the bulk aqueous phase.

For a bulk aqueous phase rate-controlling chemical reaction, the extraction rate is proportional to the distribution coefficient of the extractant which is affected by the choice of diluent and the ionic strength of the aqueous phase but not directly by the molecular geometry of the extractant or the interfacial area. Unfortunately no distribution data exist to permit detailed analysis of this situation.

For chemical rate-controlling processes at the interface, the interfacial concentration of the extractant is of prime importance in determining the observed rate of extraction, as is the interfacial area. Observed extraction rates therefore depend on interfacial concentrations and interfacial areas. Interfacial concentrations depend on the interfacial activity of the extractant, its molecular geometry, its bulk phase concentration, and the diluent type. Increasing the bulk phase concentration increases the interfacial population up to the point of interfacial saturation.

The degree of solvency shown by the diluent toward the extractant will be reflected in the bulk phase concentration of extractant required to saturate the interface which will vary directly with the degree of solvency. Bulky, heavily substituted extractant molecules would be expected to occupy more interfacial area per molecule than unsubstituted ones. Thus the rate of extraction should increase with diminishing interfacial area per molecule, increasing bulk phase extractant concentration and decreasing solvency of the diluent. Of the proprietary reagents, most data are available on the performance of hydroxyoximes.

When a pure hydroxyoxime is dissolved in an organic diluent there is only a negligible decrease in the air/organic surface tension with increasing hydroxyoxime concentration.[6,7] However hydroxyoxime solutions exhibit marked interfacial tension lowering, with bulk phase concentration at an organic/aqueous phase boundary. Hydroxyoxime molecules preferentially adsorb at this interface presumably due to interaction with water molecules (hydrogen bonding) and thus would be expected to adsorb with a preferred orientation. In the bulk organic phase hydroxyoximes tend to be dimeric,[8,9] and the degree of dimerization varies with the diluent. For example, the dimerization constant for P50 in hexane is 117, while for toluene it is 11.5.[9]

Price and Tumilty[10] have deduced that a dimer would adsorb at the organic/aqueous interface with such an orientation that the lone-pair electrons on the phenolic oxygens are adjacent to the interface so that preferential hydrogen bonding between the phenolic oxygens and water can take place; i.e., the dimer would assume a boat configuration. However dimer adsorption at the interface is unlikely, for hydrogen bonding with water molecules will compete with the hydrogen bonding responsible for dimer formation. Thus Dalton et al.[9] have reported that the calculated interfacial area of P50 dimers is 125 Å^2, while the experimentally determined value is 60-70 Å^2 compared with 17 Å^2, the calculated interfacial area per molecule for the monomer, assuming a perpendicular orientation of the rest of the molecule to the interface.

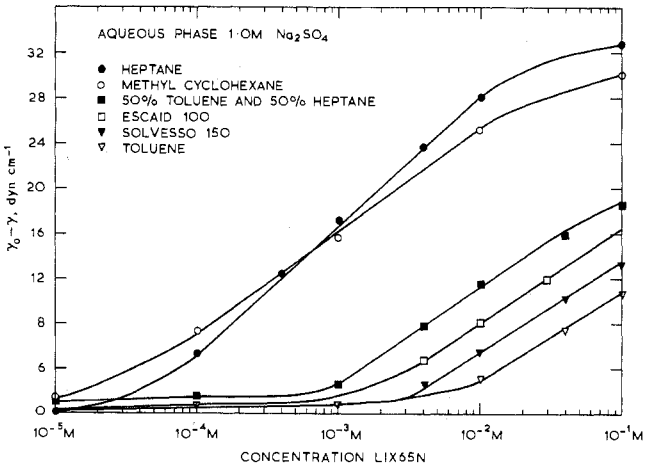


Figure 1. Variation of the interfacial tension of LIX 65N with concentration in various diluents.

Table II
Variation of Interfacial Area per Molecule with Diluent Compositions

Diluent	Composition: Aromatics, %	Aliphatics, %	Naphthenes, %	Area/molecule Å^2
Heptane	0	100	0	83.4
Methylcyclohexane	0	0	100	106.5
Heptane/toluene	50	50	0	102.0
Escaid 100	20	56.6	23.4	118.0
Escaid 350 (Solvesso 150)	97	3	0	123.0
Toluene	100	0	0	114.0

(5) E. F. Caldin, "Fast Reactions in Solution", Blackwell Scientific Publications, Oxford, 1964, pp 256–257.
(6) S. Dobson and A. J. Van der Zeeuw, *Chem. Ind. (London)*, 175 (1976).
(7) Warren Spring Laboratory, unpublished data, 1975.
(8) B. N. Laskorin, V. V. Yakshin, V. S. Ul'yanov, and A. M. Mirokhin, *Proc. ISEC 74, SCI London*, **2**, 1775 (1974).
(9) R. F. Dalton, F. Hauxwell, and J. A. Tumilty, *Chem. Ind. (London)*, 181 (1976).
(10) R. Price and J. A. Tumilty, "Hydrometallurgy", *Inst. Chem. Eng. Symp. Ser.*, **No. 42**, Paper No. 18 (1975).

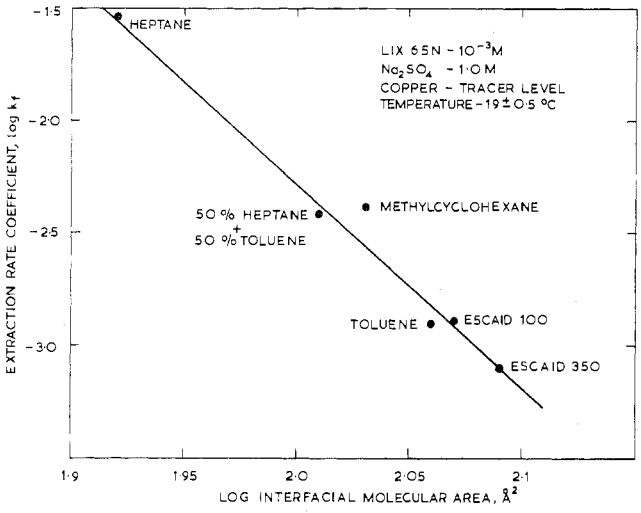


Figure 2. Effect of diluent variation on rate of copper extraction by LIX 65N: relationship between interfacial area per molecule and extraction rate coefficient.

The interfacial area per molecule varies with the diluent. Figure 1 shows the variation in interfacial pressure with concentration from Du Nuoy ring data for LIX 65N in a variety of diluents. Quantitatively the interfacial area per molecule for each diluent is given in Table II together with the relevant information on diluent composition.

These results show that the interfacial area per molecule varies not only with the aromaticity of the diluent but also with the percent of naphthenes contained therein.

The effect of alkyl substituents on the rate of copper extraction and copper stripping with hydroxyoximes has been determined by Price and Tumilty,[10] who show that the presence of bulky substituents in the 3-position on the β-hydroxyphenone oximes limits the ability of the phenolic oxygen to approach the interface, thus reducing extraction rates. This effect is particularly marked in the stripping rates.

The effect of the diluent type on the rate of copper extraction with both LIX 65N and Kelex 100 has been investigated. Price and Tumilty,[10] Dalton et al.,[9] and Dobson and Van der Zeeuw[6] have shown that faster extraction occurs when aliphatic diluents are used. The relationship between interfacial area per molecule of LIX 65N in a variety of diluents (data from Figure 1) and the rate coefficients for copper extraction (from AKUFVE data) has also been studied recently,[11] and the results are shown in Figure 2. The figure shows that the points all cluster around a straight line, which indicates that the variation in interfacial area per molecule caused by changing the diluent has a direct effect on the rate of copper extraction.

What are now lacking are similar data for hydroxyoximes of differing molecular geometry and distribution coefficients for the various hydroxyoximes between the aqueous phase and the various diluents.

The diluent effect for Kelex 100 is much less pronounced than for LIX65N, with the log k_f value only decreasing from −1.80 in heptane to −1.75 in toluene. It is not known why this effect is so small with this extractant. It is worth noting that addition of nonylphenol, the recommended modifier for this system, to heptane solutions of Kelex 100 also decreases the extraction rate and increases the interfacial tension. It was thought that this effect was due to H-bond formation between the nonylphenol and Kelex 100 similar to the interaction already found between a carboxylic acid and Kelex 100[12] which caused a similar increase in interfacial tension. As yet, however, no direct spectroscopic evidence of such an interaction between nonylphenol and Kelex 100 has been found.

(11) Kinetic data by private communication from D. R. Spink, University of Waterloo, Waterloo, Ontario, Canada.

Mechanistic Kinetic Studies

It is not possible from the available physical chemical evidence alone to establish with certainty the location of the rate-controlling chemical reaction. Thus fundamental kinetic studies are necessary. There have been several such studies recently on the extraction of copper by LIX reagents and Kelex 100.[13-17] These studies have employed a variety of techniques and equipment. An AKUFVE apparatus[18] has been employed for two of these studies.[13,14] This apparatus consists of a stirred vessel for mixing of the two phases and a centrifuge for rapid and complete phase separation. The phases so separated are returned to the mixer. Thus on-line continuous monitoring of the concentration of the partitioning species, in this case copper, can be made. The interfacial area between the phases cannot be determined in this equipment, and thus for a heterogeneous reaction, absolute rate constants cannot be measured.

In two other studies[15,16] a single drop technique was used. This technique requires that drops of known size and hence interfacial area be passed through the other phase contained in a vertical column and that the time of passage be varied by varying the column length. When the organic phase is less dense than the aqueous phase, aqueous drops pass down the column (organic continuous condition) or organic phase drops pass up it (aqueous continuous condition). This technique relies on internal circulation within the drops to aid mass transfer and diffusion.

This problem of boundary layer renewal is avoided in the third type of equipment known as the Lewis cell. This apparatus simply consists of a vessel containing the phases which are stirred simultaneously to achieve mixing within each phase without causing dispersion. The interfacial area is controlled by the vessel geometry, and the rate of mass transfer per unit interfacial area from one phase to another can therefore be measured.

In the AKUFVE work a relaxation technique was employed which permits not only the examination of kinetics at essentially zero mass transfer conditions but also the determination of both the forward and backward rate coefficients. For both LIX 65N and

(12) D. S. Flett, M. Cox, and J. D. Heels, *J. Inorg. Nucl. Chem.*, **37**, 2197, (1975).
(13) D. S. Flett, D. N. Okuhara, and D. R. Spink, *J. Inorg. Nucl. Chem.*, **35**, 2471 (1973).
(14) D. S. Flett, J. A. Hartlage, D. R. Spink, and D. N. Okuhara, *J. Inorg. Nucl. Chem.*, **37**, 1967, (1975).
(15) R. J. Whewell, M. A. Hughes, and C. Hanson, *J. Inorg. Nucl. Chem.*, **37**, 2303, (1975).
(16) R. L. Atwood, D. N. Thatcher, and J. D. Miller, *Metall. Trans., B*, **6**, 465, (1975).
(17) C. A. Fleming, "The Kinetics and Mechanism of Solvent Extraction of Copper by LIX 64N and Kelex 100", N.I.M. Report No. 1793, 1976, Johannesburg, S. Africa.
(18) J. Rydberg, H. Reinhardt and J. O. Liljenzin, *Ion Exch. Solvent Extract.*, **3**, 111 (1973).

Kelex 100[13,14] the extraction rate was found to be first order with respect to copper concentration, extractant concentration, and pH. The same result was obtained for LIX 65N from the Lewis cell work[17] under conditions far from equilibrium, but for Kelex 100 the rate was second order with respect to extractant concentration. In the AKUFVE studies no sensible variation of rate with ionic strength was found, while from the Lewis cell studies the extraction rate was found to be independent of ionic strength.

It is now well known that addition of LIX 63 to LIX 65N accelerates the rate of copper extraction. From Table I LIX 64N is a mixture of LIX 65N and LIX 63. The single-drop studies[15,16] have been concerned with LIX 65N/LIX 63 mixtures and LIX 64N. Whewell et al.[15] using aqueous continuous conditions found that the extraction rate of copper with LIX 64N was dependent on the pH and was directly proportional to the interfacial area. No chemical order was ascribable to LIX 64N concentration. Atwood et al.,[16] on the other hand, using organic continuous conditions found that the extraction rate for copper with LIX 64N was proportional to the interfacial area and was first order with respect to copper concentration and one-half order with respect to LIX 63 and LIX 65N but independent of the hydrogen ion concentration. This finding is considered to be invalid as these authors assumed that the reaction is pH independent before analyzing their data. When their data are reworked to take account of all possible kinetic parameters, a much improved straight line fit of the data points results together with a reduction in the apparent lag time of ~7 s to ~1 s, consistent with the lag times found by Whewell et al. The relationship reported between the forward and backward rates is also thermodynamically incorrect.

Further detailed work on the LIX 65N/LIX 63 system has been carried out both in AKUFVE[13] and Lewis cell[17] studies. Both studies agree that the rate of copper extraction is first order with respect to copper concentration, LIX 65N concentration, and pH and one-half order with respect to LIX 63 concentration.

From these studies, because the rate is found to be proportional to the interfacial area and independent of ionic strength, the rate-controlling reaction must take place with extractant molecules adsorbed at the interface. For LIX 65N and Kelex 100 the rate-controlling step is considered to be the formation of the neutral complex at the interface, while for the LIX 65N/LIX 63 system it is the formation of the mixed complex between copper, LIX 63, and LIX 65N at the interface.

That is, the rate-controlling reactions are

$$CuR^{65+} + (R^{65}H)_i \rightleftharpoons (CuR^{65}{}_2)_i + H^+$$

for LIX 65N alone and

$$CuR^{63+} + (R^{65}H)_i \rightleftharpoons (CuR^{65}R^{63})_i + H^+$$

for LIX 65N + LIX 63, where $R^{65}H$ and $R^{63}H$ represent LIX 65N and LIX 63 and the subscript i denotes interfacially adsorbed species. The CuR^+ species is formed by fast reaction between RH and Cu^{2+} in the aqueous phase.

Thus for LIX 65N and Kelex 100 the theoretical reaction orders should be first order with respect to copper and pH and second order with respect to extractant concentrations. For the LIX 65N + LIX 63 system the reaction orders should be first order with respect to copper, LIX 65N, and LIX 63 concentrations and pH. The rate-controlling reaction at equilibrium appears to be the same as that under conditions far removed from equilibrium.

For the copper Kelex 100 system the Lewis cell work agrees with the theoretical reaction orders, but the AKUFVE study finds a reaction order of unity for Kelex 100. No explanation of this discrepancy is possible at present. With regard to the copper/LIX 65N system, both Lewis cell and AKUFVE studies find a reaction order of unity for LIX 65N instead of the expected second-order dependency. Interfacial tension studies in connection with the Lewis cell work are reported to show the formation of a 1:2 complex at the interface between the copper LIX 65N complex and free LIX 65N. Thus the slow rate of extraction exhibited by LIX 65N is attributed to a decrease in effective interfacial concentrations of LIX 65N caused by this adduct formation, which is also shown to produce the apparent reaction order of unity with respect to LIX 65N. Similar interfacial tension studies at Warren Spring Laboratory have not shown this effect, and mixed solutions of the copper complex and free LIX 65N give interfacial tensions which reflect the LIX 65N content only, up to quite high conversion of LIX 65N to the copper complex. The apparent reaction order of unity for LIX 65N could alternatively be caused by dimerization of the extractant in the bulk organic phase, and there is ample evidence for such behavior.[8-10] It was thus surprising to find that molecular weight determinations in connection with the Lewis cell work found LIX 65N to be monomeric in cyclohexane. More work is required to resolve these discrepancies.

In these molecular weight determinations LIX 63 was found to be dimeric, and this dimerization accounts for the one-half order found for LIX 63 in the LIX 65N/LIX 63 mixed system. Fleming[17] claims that addition of LIX 63 to the system inhibits formation of the 1:2 adduct formed between the copper/LIX 65N complex and free LIX 65N, thus "enhancing" the extraction rate. Interfacial tension studies at Warren Spring Laboratory and in South Africa agree that in mixed solutions of LIX 65N and LIX 63 the interfacial tension reflects the concentration of LIX 65N alone and the values are not pH dependent. The reaction order of unity found for LIX 65N presents problems if LIX 65N is dimeric in the organic phase and further work here is required. It has been reported[17] that the reaction between copper and LIX 63 in aqueous solution is considerably faster than the analogous reaction with LIX 65N and that the aqueous solubility of this 1:1 complex is greater than that of the corresponding copper LIX 65N complex. This observation alone could account for the enhanced rate in this system. Formation of a mixed complex species at the interface requires a ligand exchange reaction finally to produce the copper LIX 65N complex. The very rapid nature of such a ligand exchange reaction in the bulk organic phase has been qualitatively confirmed recently at Warren Spring Laboratory.

Other accelerator compounds have been discovered recently. For example, Morin and Peterson[19] have patented the use of sulfonic acids and sulfosuccinates as accelerators for copper extraction by LIX 65N, while

(19) E. A. Morin and H. D. Peterson, U.S. Patent 3 878 286 (1975).

Hazen Research Inc.[20,21] has had two patents granted which cite alkylphosphoric acids and carboxylic acids as accelerators for the same reaction. Interfacial tension measurements at Warren Spring Laboratory have shown that addition of dinonylnaphthalenesulfonic acid (DNNSA) to LIX 65N causes total displacement of LIX 65N from the interface. Thus this accelerator mechanism obviously proceeds via interaction of the copper with ionized DNNSA (a strong acid) at the interface and formation of the copper LIX complex through a ligand-exchange reaction in the bulk organic phase. It would seem logical to conclude that the action of the alkylphosphoric and carboxylic acids would be similar but scaled in proportion to their acid strengths. This mechanism is identical with phase transfer catalysis.

(20) W. C. Hazen and E. L. Coltrinari, U.S. Patent 3 872 209 (1975).
(21) M. B. Goren and E. L. Coltrinari, U.S. Patent 3 927 169 (1975).

Conclusions

The extraction of copper by the proprietary chelating extractants LIX 65N and Kelex 100 cannot proceed by the classical mechanism involving sequential chelating reaction in the bulk aqueous phase between copper cations and the anions of the ionized extractant. The available physical chemical and kinetic data show that the site of the rate-controlling reaction is the aqueous organic interface. Solvent effects and physical organic interaction play an important role in determining the behavior of LIX and Kelex reagents in various diluents, and much remains to be done in this area. Unambiguous detailed mechanisms cannot as yet be produced from kinetic data. More work is required in this area, particularly with respect to the significance of pathways involving aqueous phase intermediates and the nature of the species adsorbed at the interface.

Additions and Corrections

Volume 9, 1976

Noal Cohen: Asymmetric Induction in 19-Norsteroid Total Synthesis.

Page 416. The following corrections should be made to Table I: Entry 35, the product should read **25f**. Entry 36, the amino acid should read (*R*)-Tryptophan. Entry 37, the solvent should read CH_3CN. Entry 38, the amino acid should read (*R*)-Valine.