

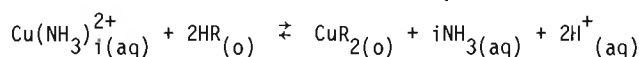
EQUILIBRIUM AND KINETICS OF COPPER EXTRACTION FROM AMMONIACAL SOLUTIONS BY HYDROXOXIMES WITH PARTICULAR EMPHASIS ON TRANSPORT PHENOMENA

J.D. Miller, H.H. Haung and E.F. Pereira

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The chemistry of copper extraction from ammoniacal solutions by hydroxyoxime extractants was studied. Equilibrium measurements were made by shakeout experiments with subsequent analysis of the aqueous and/or organic phases. The kinetic experiments were carried out in a single drop reaction cell in order to establish the details of the intrinsic reaction kinetics for this system.

Equilibrium measurements indicated that the extraction involves complete displacement of ammonia ligands from the coordination sphere of the cupric ion by the extractant molecules. The extraction reaction has the following stoichiometry:



and as might be expected the extraction coefficient was found to be sensitive to the ammonia concentration and the pH of the system. These results were interpreted in terms of the mass action expression and explained by taking into consideration the stability of the various cupric ammonia complexes,

$$\log E = \log K - \log \left(1 + \sum_{i=1}^6 \beta_i [\text{NH}_3]^i \right) + 2 \log [\text{HR}]_{(o)} + 2\text{pH}$$

From single drop experiments, it appears that the kinetics of extraction are controlled by reactant transfer in the dispersed phase, a conclusion which is supported by a low apparent activation energy of 5.3 kcal/mole. Based on first principles, the reaction rate was explained to be due to molecular diffusion for small drop sizes which behaved as stagnant spheres, while convective transport contributed significantly to the reaction rate for larger drop sizes and other circumstances which result in internal circulation. Rate control by reactant transport in dispersed phase is valid under normal conditions regardless of which phase is the dispersed phase. It was predicted and demonstrated that only when the ratio of the reactant concentration in the continuous phase to the reactant concentration in the dispersed phase is less than approximately 0.05 will resistance due to reactant transport in the continuous phase become significant. The rate of copper extraction from ammoniacal solutions is at least one order of magnitude faster than the rate of extraction from acidic solutions. This was to be expected in as much as extraction from acidic solution has been reported to be controlled by a complex surface reaction having an apparent activation energy from 7 to 15 kcal/mole.

FUNDAMENTAL ASPECTS OF SOLVENT EXTRACTION PHENOMENA

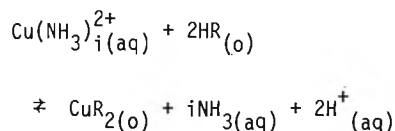
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INTRODUCTION

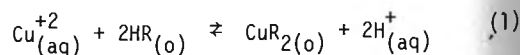
A significant research effort has been devoted to develop ammonia oxidative leaching processes for copper sulfide concentrates (1,2,3) and low grade native copper ore (4). This has led to process development studies and finally to construction of plants to treat copper sulfide concentrates and copper scrap (5,6). When compared with conventional sulfuric acid leaching processes, the major advantage of the ammoniacal system is its ability to reject iron and many acid consuming gangue minerals.

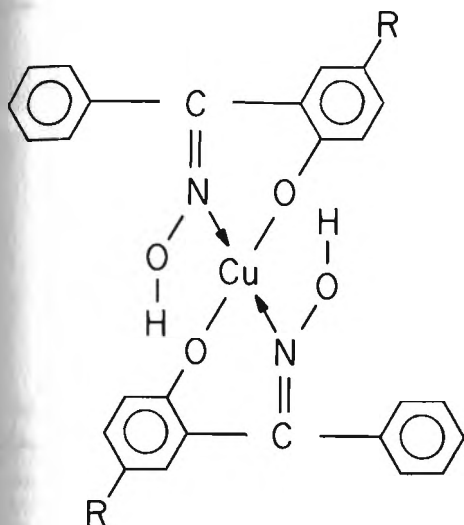
An important unit operation in any hydrometallurgical process is the concentration and purification of the leach liquor for metal recovery, which frequently is accomplished by solvent extraction. A major class of extractants for the recovery of copper from leach liquors has been hydroxyoximes; chelating extractants such as LIX reagents developed by General Mills. Currently other companies such as Shell Chemical Ltd. and Acorga Ltd. produce similar extractants. The most widely used extractant, however, is LIX 64N a mixture of hydroxyoximes consisting of two components, the aliphatic hydroxyoxime (LIX 63) and the aromatic β hydroxyoxime (LIX 65N). The β hydroxyoxime is capable of existing as either the syn- or anti-isomer. Detailed discussion on the chemistry and the structure of LIX 64N has been reported in other literature (7).

A considerable amount of research has been done on the extraction of copper from acidic solutions both with regard to equilibrium and kinetic behavior (7-10). Very little is known about important factors which govern the equilibrium and kinetic behavior of copper extraction from ammoniacal solutions. A research program involving equilibrium and kinetic measurements of copper extraction from ammoniacal solution by LIX reagents has been completed. In the equilibrium study, the results have been analyzed from solution thermodynamic considerations. In the kinetic study, the results have been analyzed in terms of heterogeneous reaction kinetics especially taking into consideration transport processes in both the dispersed and continuous phases.

Equilibrium in Copper Extraction

The chemistry of copper extraction from acidic solution by hydroxyoxime reagents has been extensively investigated by several researchers (7,11). Spectrophotometric evidence (7) indicates that a copper β hydroxyoxime chelation complex is the extracted product and that the stoichiometry is given by the following reaction:



EXTRACTED COMPLEX, $R_2^{65}Cu$

The extraction coefficient (copper concentration in the organic phase divided by copper concentration in aqueous phase) can be calculated from the equilibrium constant, K:

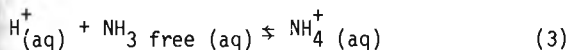
$$\log E = \log K + 2 \log [HR]_{(o)} + 2pH \quad (2)$$

where,

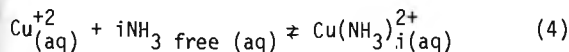
- E = extraction coefficient
 $= [CuR_2]_{(o)} / [Cu^{2+}]_{total(aq)}$,
 K = equilibrium constant for reaction presented in Equation 1 including activity coefficients,

$[HR]_{(o)}$ = concentration of extractant in organic phase

In the ammoniacal system this analysis must be altered due to the presence of free ammonia. To begin with, acid neutralization must be considered,

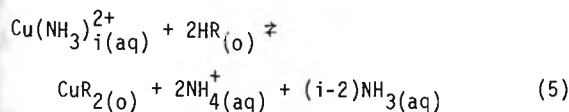


which has a positive effect on the extraction; and secondly the stability of the cupric-ammine complexes must be considered,



which has a negative effect on the extraction.

Copper extraction from these solutions can be represented in the following way;



Thermodynamically, however, the copper extraction reaction written for acidic solutions, Equation 1, can still be applied to the ammonia system, but the

activity of the cupric ion will be much lower than the total copper concentration. In ammoniacal solutions, the cupric ion concentration can be calculated from the stability constants for the formation of cupric-ammine complexes according to reactions as given in Equation 4,

$$[Cu^{2+}]_{aq} = \frac{[Cu(NH_3)_i^{2+}]_{(aq)}}{\beta_i [NH_3]^i \text{ free}(aq)} \quad (6)$$

where

$[Cu(NH_3)_i^{2+}]_{(aq)}$ = concentration of the *i*th cupric-ammine complex in the aqueous solution,

$[Cu^{2+}]_{(aq)}$ = concentration of simple hydrated cupric ion in the aqueous solution,

$[NH_3]_{\text{free}(aq)}$ = concentration of free ammonia in the aqueous solution

β_i = overall stability constant of the *i*th cupric-ammine complex

The values of β_i for the cupric-ammine complexes are listed below(12),

$$\log \beta_1 = 4.15 \quad \log \beta_2 = 7.67 \quad \log \beta_3 = 10.54$$

$$\log \beta_4 = 12.67 \quad \log \beta_5 = 12.17 \quad \log \beta_6 = 9.67 \quad (7)$$

If metal hydrolysis can be ignored, then the fraction of cupric ion to total cupric concentration in the aqueous phase can be expressed as,

$$\frac{[Cu^{2+}]_{(aq)}}{[Cu]_{total(aq)}} = \frac{1}{1 + \sum_{i=1}^6 \beta_i [NH_3]^i \text{ free}(aq)} \quad (8)$$

Consequently, an additional term will contribute to the expression for the copper extraction coefficient,

$$\log E = \log K + \log \left(1 + \sum_{i=1}^6 \beta_i [NH_3]^i \text{ free } (aq) \right) + 2 \log [HR]_o + 2pH \quad (9)$$

From examination of the stability constants for the cupric-ammine complexes, it is seen that the tetra-ammine cupric ion and the penta-ammine cupric ion have the highest β values. This suggests that for normal ammoniacal leaching systems, in which the concentration of free ammonia is about 16 gpl the average number of ammine ligands coordinated to a cupric ion will be between 4 and 5.

Kinetics of Copper Extraction

Several fundamental kinetic studies have been reported on the extraction of copper by LIX reagents in acidic systems (10,11,13). These studies have employed a variety of experimental techniques. The results indicate that the copper extraction reaction by LIX

65N/LIX 63 reagents is heterogeneous and that the rate is controlled by a surface chemical reaction at the aqueous/organic interface. Results also show that the addition of LIX 63 to LIX 65N enhances the reaction kinetics without disturbing the final equilibrium, LIX 63 being characterized as a catalyst in the system. Flett (11) indicated that the activation energy for LIX 65N is about twice as large as that for a mixture of LIX 65N and LIX 63, a result which supports this catalytic role played by LIX 63 in acidic extraction systems.

The proposed surface reaction mechanisms by several investigators differ significantly. Results from experiments with AKUFVE system by Flett (11) and the Lewis cell by Fleming (13) indicate that the rate limiting step is the addition of an extractant molecule, the second ligand for the cupric ion, at the interface. However, the results from single drop experiments (10) indicate that the rate of extraction is independent of hydrogen ion concentration at relatively high pH values (2.21 - 4.98) and the rate controlling step was suggested to be the addition of the first extractant molecule.

Hydrodynamics of Liquid Spheres Moving Through an Immiscible Liquid Field

Among the three techniques that have been used for the study of extraction kinetics; the AKUFVE system, the Lewis cell and Single Drop Reaction Cell, the single drop technique seems to have two unique features; a well defined interfacial area and fairly well established hydrodynamic behavior for liquid spheres.

Liquid spheres differ from solid spheres in that the dispersed liquid can be set in motion by the viscous drag from the continuous liquid through which the drop moves. Additionally, drops can be subjected to deformation because of the differences in pressure acting on various parts of the surface. As a result of these considerations, the terminal velocity of a liquid drop may differ significantly from the corresponding velocity for a solid sphere. Figure 1 shows the terminal velocity of a liquid drop as a function of the drop diameter. Three distinct regions can be identified (14-16). For small drops in region A, the liquid boundary layer inside the drop remains rigid and the liquid drop will be spherical in shape and behave like a solid sphere. The terminal velocity will generally be that of a solid sphere of equal size and density moving in the same continuous phase. In region B, the boundary layer inside the drop will no longer remain rigid, and the momentum from the continuous phase will be transferred to the drop which develops internal circulation. Under these circumstances the terminal velocity will be greater than that of the non-circulating drop, the solid sphere. As the drop size is increased, region C, the larger drop will travel at about the same speed, independent of size. Oscillation of the drop can be observed in this region and the internal flow pattern is a combination of eddy flow and circulation.

Viscosity, interfacial surface tension and density difference will also influence circulation of the liquid sphere. For example, fully developed circulation in a drop of specified size can be damped out if the viscosity of the dispersed phase is increased (17).

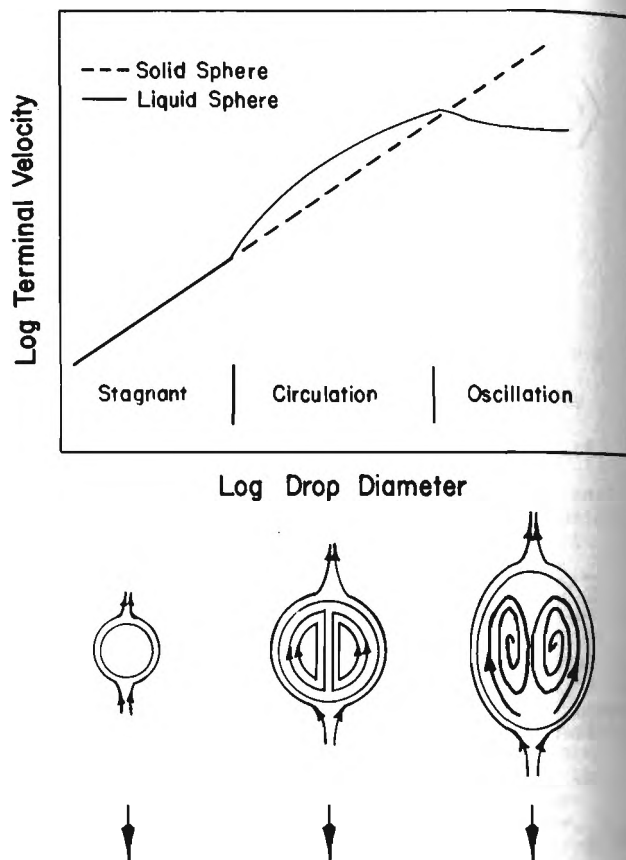


Figure 1. Terminal velocity and internal flow pattern for a liquid sphere as a function of drop diameter.

The surface tension reduces the circulation in such a way that the higher surface tension the more energy it takes to create the new surface at the front of the drop and hence a higher surface tension reduces the extent of circulation (18).

Mass Transfer in Single Drop Reaction Cells

Mass Transfer in the Dispersed Phase

Due to the change in the internal flow pattern of the moving drop, mass transfer in the dispersed phase must also be evaluated in three different regions; the stagnant region, the circulation region and the oscillation region.

The mass transfer equation for a stagnant drop can be derived from the continuity equation based on Fick's 2nd law for which the transport depends only on molecular diffusion. The integrated expression for mass transfer in the stagnant drop is found to be (19),

$$\frac{C_o - \bar{C}_t}{C_o - C_s} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left[- Dn^2 \pi^2 t / a^2 \right] \quad (10)$$

where

D = diffusion coefficient

a = drop radius

t = reaction time

C_0 = Initial concentration in dispersed phase (uniform distribution of concentration is assumed)

\bar{C}_t = average concentration in dispersed phase at time t

C_s = surface concentration at time t

If internal mass transfer is the rate controlling step, surface concentration, C_s , will be equal to the equilibrium concentration at the interface. As will be shown from the equilibrium study, for the typical experimental conditions that were used in the kinetic study ($[\text{NH}_3]_{\text{total}} = 0.5M$, $\text{pH} = 10$, Extractant 1 to 10 vol.%) the extent of extraction will be close to 100% as long as the copper concentration is greater than 0.05 gpl. This means that in most kinetic experiments the surface concentration of reactant would be close to zero. However for higher free ammonia concentrations this may not be true and the equilibrium concentration at the interface would have to be considered.

For short reaction times, the integrated rate equation can be approximately by the following parabolic relationship; (19)

$$\frac{C_0 - \bar{C}_t}{C_0} = \frac{\Delta \bar{C}_t}{C_0} = 3.38 \left(\frac{Dt}{a^2}\right)^{1/2} \quad (11)$$

and the rate of mass flow can be written as

$$I = \frac{4}{3}\pi a^3 \frac{d\bar{C}_t}{dt} = -7.09 C_0 a^2 \left(\frac{D}{t}\right)^{1/2} \quad (12)$$

The mass transfer equation for a circulating drop is more complicated in that both molecular diffusion and convective transport must be considered. Kronig and Brink(20) have derived a mass transfer equation using streamline functions together with an expression for molecular diffusion from one streamline to another. The integrated mass transfer equation is, (21,22)

$$\frac{C_0 - \bar{C}_t}{C_0} = 1 - \frac{3}{8} \sum_{n=1}^{\infty} B_n^2 \exp \left[-\lambda_n \frac{16 Dt}{a^2}\right] \quad (13)$$

where

λ_n = eigenvalues

B_n = function of eigenfunction

For short reaction times ($t_{\text{max}} < 25$ sec) and considering the values for λ_n and B_n (23), the equation can be simplified as,

$$\frac{C_0 - \bar{C}_t}{C_0} = 4.65 \left(\frac{Dt}{a^2}\right)^{1/2} \quad (14)$$

and the rate of mass flow can be derived as,

$$I = -9.73 C_0 a^2 \left(\frac{D}{t}\right)^{1/2} \quad (15)$$

A comparison of Equation 15 with Equation 12 indicates that for short reaction times, the rate of transport in a circulating drop is increased by almost 40 percent due to the convective contribution to the transport process.

Because of the complexity of the internal flow pattern of the oscillating drop, there is no satisfactory model for internal mass transfer derived from first principles but some empirical equations exist (24). Drop oscillation occurs when the diameter of the drop is greater than 5 mm, a size which generally is not of interest in solvent extraction systems. As a result, internal mass transfer for the oscillating drop will not be considered.

Mass Transfer in the Continuous Phase

When the reaction rate is controlled by mass transfer in the continuous phase, the reactant species has to pass through the mass transfer boundary layer adjacent to the drop surface. Levich (25) has derived a theoretical expression for mass transfer in the continuous phase. The rate of mass flow can be determined by the following equation,

$$I = 5.79 \left(\frac{\mu_c}{\mu_c + \mu_d}\right)^{1/2} \left(\frac{DU}{a}\right)^{1/2} a^2 \Delta C_c \quad (16)$$

where,

μ_c, μ_d = viscosities of the continuous phase and dispersed phase, respectively

U = terminal velocity

ΔC_c = concentration difference between the bulk and the surface concentrations in the continuous phase

Other investigators have used dimensional analysis to obtain empirical correlations; Skelland and Cornish (26) for stagnant drops and Garner and Tayeban (27) for circulating and oscillating drops.

Relative Significance of Mass Transfer in the Dispersed and Continuous Phases

In order to assess the relative significance of mass transfer in the dispersed and continuous phases, a comparison was made, as shown in Figure 2, where the modified rate of mass flow (mass flow rate divided by the initial concentration of the reactant in the dispersed phase) is plotted as a function of the drop travel time. Figure 2 was constructed by using the stagnant model for mass transfer in the dispersed phase (Equation 12) and the Levich equation for mass transfer in the continuous phase (Equation 16). A family of curves for several initial concentration ratios, $C_{c,0}/C_{d,0}$, is shown where $C_{c,0}$ is the initial concentration of the continuous phase reactant and $C_{d,0}$ is the initial concentration of

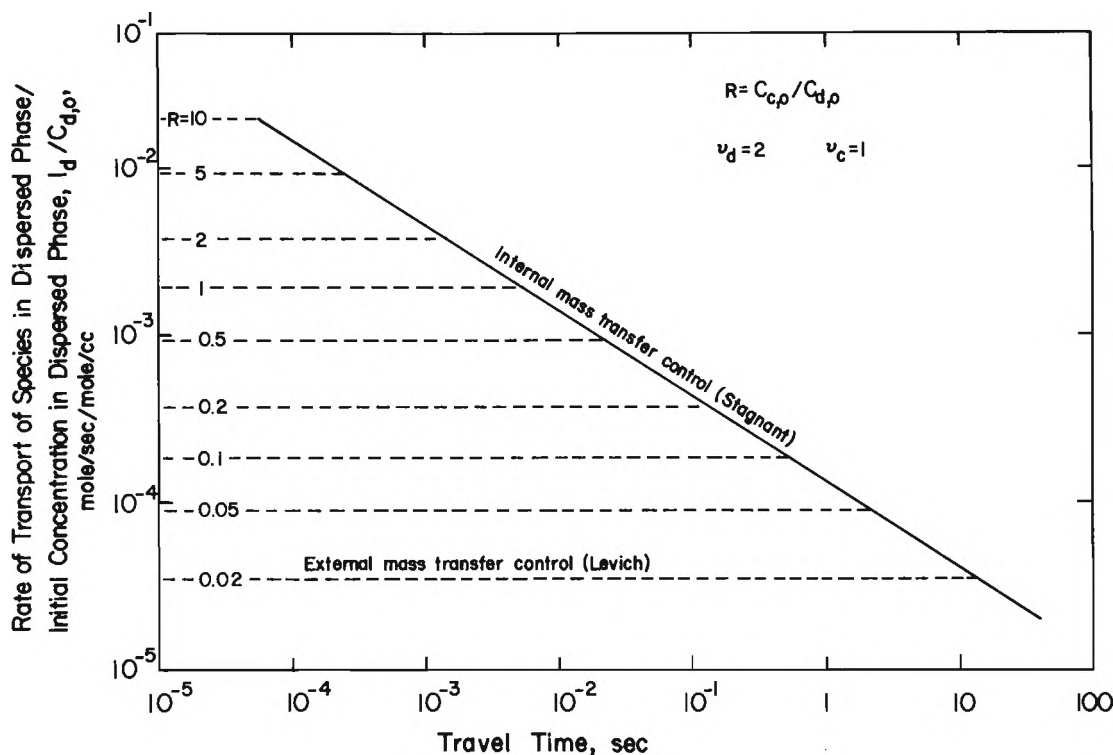


Figure 2. Representation of the relative importance of transport processes in the continuous and in the dispersed phase for various reactant concentration ratios. Intersection of horizontal dashed line with diagonal line indicates the critical time (t_c) during which the rate is limited by mass transfer in the continuous phase.

$$\text{Conditions: } D_c = 7.5 \times 10^{-6} \text{ cm}^2/\text{sec}, \quad D_d = 4 \times 10^{-6} \text{ cm}^2/\text{sec},$$

$$a = 0.1 \text{ cm}; \quad \mu_c = 1 \text{ cp}, \quad \mu_d = 1.68 \text{ cp},$$

$$U = 10 \text{ cm/sec}; \quad \nu_d = 2, \quad \nu_c = 1 \quad (\nu = \text{stoichiometry coefficients})$$

dispersed phase reactant. The mathematical analysis indicates that the rate is controlled initially by mass transfer in the continuous phase and after some critical time resistance due to mass transfer in the dispersed phase becomes predominant. This critical time, t_c , depends on the ratio of the reactants' initial concentrations. Normally, the time interval during which the reaction rate would be limited by mass transfer in the continuous phase is too small to be significant unless the initial concentration ratio $C_{c,0}/C_{d,0}$, is smaller than 0.05. This suggests that in most solvent extraction systems mass transfer in the continuous phase will be faster than mass transfer in the dispersed phase so that generally for a fast chemical reaction mass transfer in the dispersed phase will be rate limiting.

End Effects in Single Drop Reaction Cells

In the single drop experiments mass transfer can occur not only during the travel time but also during the drop formation and coalescence period. As a result, the extent of reaction may be greater than the values predicted by a particular model. A much used technique to correct for these effects has been to plot the overall extent of reaction as a function of

the drop travel time, and then extrapolate to the ordinate at zero time to determine the extent of reaction contributed by the end effects (23,28-29). Atwood (10) also tried to correct for end effects by extrapolating the rate curve to the abscissa value for no reaction to determine a lag time which represents the time that the drop is not traveling but during which reaction occurs.

Two different mechanisms for internal mass transfer to a growing drop have been proposed. The surface stretch model (30) assumes that all elements at the surface remain and stretch as the drop grows. The penetration model (31) assumes that the growth of a drop is preceded by the addition of fresh elements which penetrate to the surface. Popovich (31) showed that the above models could be reduced to a general form,

$$N = 4\pi G \Delta C \left(\frac{3qt}{4\pi}\right)^{2/3} \left(\frac{Dt}{\pi}\right)^{1/2} \quad (17)$$

where

$$N = \text{total amount of mass (moles) transferred in time } t \text{ (sec).}$$

q = volume rate of flow into the drop, cc/sec.

ΔC = difference between bulk concentration and surface concentration, moles/cc.

G = constant, 1.31 for surface stretch model, 1.52 for penetration model.

According to Equation 17, the fraction extracted by transport processes in the dispersed phase during drop formation for the typical conditions specified in this kinetic study will be less than 1% of the total extraction, taking $G = 1.31$.

Most of the studies on mass transfer during the drop coalescence period have been with respect to the diffusion from the newly settled drop phase to the coalescence interface (23,32). In this kinetic study on copper extraction however, the mass transfer from the continuous phase to the coalescence interface can also play a significant role. For both cases important parameters to determine the rate of reaction during the drop coalescence will be the coalescence interface, diffusion coefficients, frequency of drop coalescence and the volume of the drop. Experimental results indicate that for a small coalescence area, reaction during drop coalescence is negligible.

EXPERIMENTAL

The research effort on copper extraction from ammoniacal solution has been divided into two major sections. The equilibrium study and the kinetic study. The experimental approach was to identify the important variables in each section in order to provide fundamental information for further application.

Chemicals

The primary extractant for this study was LIX 64N (Lot no. 3K19304 and GH19245C). In a few experiments other extractants, LIX 65N (lot no. 6A19205) and LIX 54, a β -diketone extractant (33) (Lot no. 7A15808) were used. All extractants were provided by General Mills and used without further purifications. The organic diluent was commercial Escaid 200 which has less than 1% aromatic content.

Extraction Equilibrium

The chemistry of copper extraction from ammoniacal solution was investigated by using a shake-out test procedure with separatory funnels. The organic solution, LIX 64N in Escaid 200, was shaken in a separatory funnel with an aqueous solution containing copper and ammonia from which the extraction was to be made. After about 30 minutes of vigorous shaking on the wrist shaker the phases were allowed to separate. Each phase was analyzed for copper by atomic absorption; for the aqueous phase the amount of free ammonia had to be neutralized by sulfuric acid, and for the organic phase the copper was stripped out with an aqueous sulfuric acid solution. The results were used to calculate the distribution coefficient and the amount of copper loaded in the organic phase.

Extraction Kinetics

The kinetic study was carried out in a single drop reaction cell. The apparatus consisted of a reaction cell, orifice for drop formation, provision for drop removal and temperature controller. The schematic diagram of the apparatus for a short cell length is shown in Figure 3. A similar type of construction was

A: Dispersed phase reservoir
B: Temperature controller
C: Head Tank
D: Reaction Cell
E: Syringe needle
F: Continuous phase
G: Volumetric
H: Oil bath
I: Pump

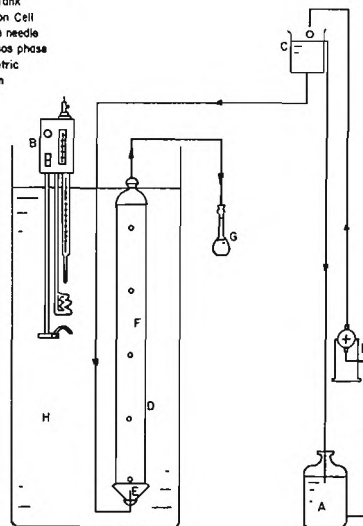


Figure 3. Schematic diagram of Single Drop Reaction Cell.

used for longer cell lengths as well. Depending upon the density difference of the dispersed phase and continuous phase, the data can be collected either for a falling drop or a rising drop. After the dispersed phase was selected, the solution was introduced from the head tank to the reaction cell by hydrostatic pressure for the short cell lengths and by pressure from a nitrogen gas cylinder for the long cell lengths. For organic dispersed experiments, the organic drops were formed at the bottom of the cell from the syringe needle. After rising through the cell, the drop coalesced at the top of the aqueous/organic interface, and discharged through a tube, being collected outside the cell. For aqueous dispersed experiments, the system was reversed, and the aqueous drops were allowed to fall through the cell. The size of the drop was varied by using stainless steel needles with different size openings which ranged from gauge numbers 24 to 33.

By controlling the head pressure, a constant frequency of droplet generation could be obtained which was usually on the order of 100 drops per minute. Under this drop frequency the end effect was found to be insignificant. The average drop size was calculated from the number of drops required to collect a specific volume and the contact time during the steady state travel was measured by timing the travel of a drop from the tip of the needle to the coalescence interface. The travel time was varied by changing the length of the cell which ranged from 13 to 160 cm for the short cell and from 47 to 390 cm for the long cell. The amount of copper extracted or amount of LIX reagent consumed for each experiment was determined by measuring the copper concentration with an atomic absorption spectrophotometer (the same method used in the equilibrium study).

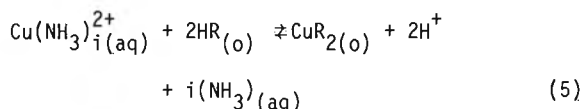
Experiments were designed so that the kinetics of extraction could be investigated for both rising drops (organic dispersed) and falling drops (aqueous dispersed). The rate data were analyzed in terms of the theoretical considerations associated with mass transfer phenomena to determine the effect of copper concentration in the aqueous solution, LIX 64N concentration in organic phase, drop size and temperature.

RESULTS AND DISCUSSION

Extraction Equilibrium

It has been reported that the copper extraction by LIX 64N in acidic media involves complete displacement of coordinated water molecules of the cupric ion by the LIX 64N extractant. In this study an infrared spectrophotometric analysis was used to compare the copper complex extracted from ammoniacal solution with that from the acidic solution. The results indicate that the extracted complex is identical for both systems and suggest that copper extraction from ammonia solution also involves complete displacement of coordinated ammine ligands. The absence of a primary absorption band near 3300 cm^{-1} for any ammonia molecules retained by the chelate structure confirms this conclusion. In addition, Kjeldahl analysis for ammonia showed that the organic phase contained a negligible amount of ammonia.

From the above findings the chemical reaction can be written as,



and the extraction coefficient can be presented as,

$$\log E = \log K - \log \left(1 + \sum_{i=1}^6 \beta_i [\text{NH}_3]^i \right) + 2 \log [\text{HR}]_0 + 2\text{pH} \quad (9)$$

Effect of Free Ammonia

Figure 4 shows the effect of free ammonia concentration on copper extraction at a constant pH value (10.2 to 10.5), maintained by keeping the ratio of $[\text{NH}_3]_{\text{free}}/[\text{NH}_4^+]$ constant at 2:1. The system had an excess amount of extractant so that the concentration of the extractant can be considered to be constant, and the amount of coordinated ammonia can be neglected. As expected from the extraction coefficient equation, Equation 9, the results (Figure 4) show that the copper extraction decreases as the ammonia concentration increases for both LIX 64N and LIX 54. The results indicate that the LIX 64N extractant forms a more stable copper complex than LIX 54 in ammoniacal solution.

According to Equation 8, a plot of $\log E$ and $\log [\text{NH}_3]_{\text{free}}$ should be indicative of the number of coordinated ammonia molecules, Figure 5 is such a plot and the average slopes for both extractants is seen to be 4.5. This suggests that the cupric ion in this ammoniacal solution is coordinated by an average of 4 to 5 ammonia molecules which is in good agreement with the value that would be predicted from the stability constants for copper-ammine complexes.

Effect of pH

The effect of pH on copper extraction was determined by keeping the total amount of ammonia, $[\text{NH}_3]_{\text{free}} + [\text{NH}_4^+]$, constant at 0.5 M. In this case, the extraction of copper is more complicated due to the fact that the pH value has a positive effect on extraction while free ammonia concentration has a negative effect, shown by Equation 9. As a result Figure 6

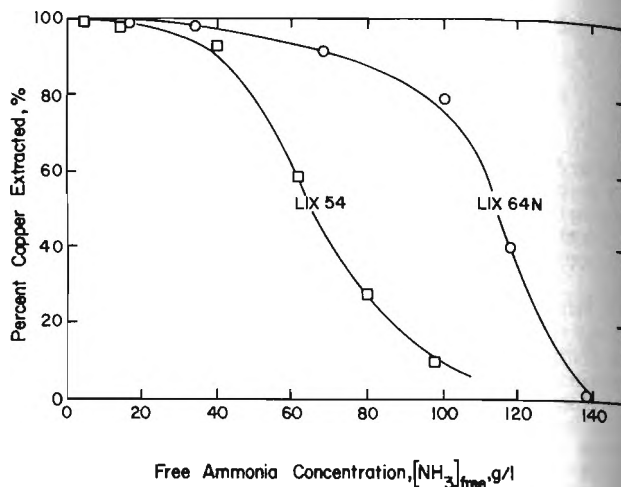


Figure 4. Effect of ammonia concentration on copper extraction at constant pH (10.2-10.5).

LIX 64N: 0.004M Copper; 40% LIX 64N in Escaid 200; A/O 1:1; $\text{NH}_3/\text{NH}_4^+$ 2:1
LIX 54: 0.004M Copper; 38% LIX 54 in Cyclosoil 63, A/O 1:1; $\text{NH}_3/\text{NH}_4^+$ 2:1
Free Ammonia, mole/l

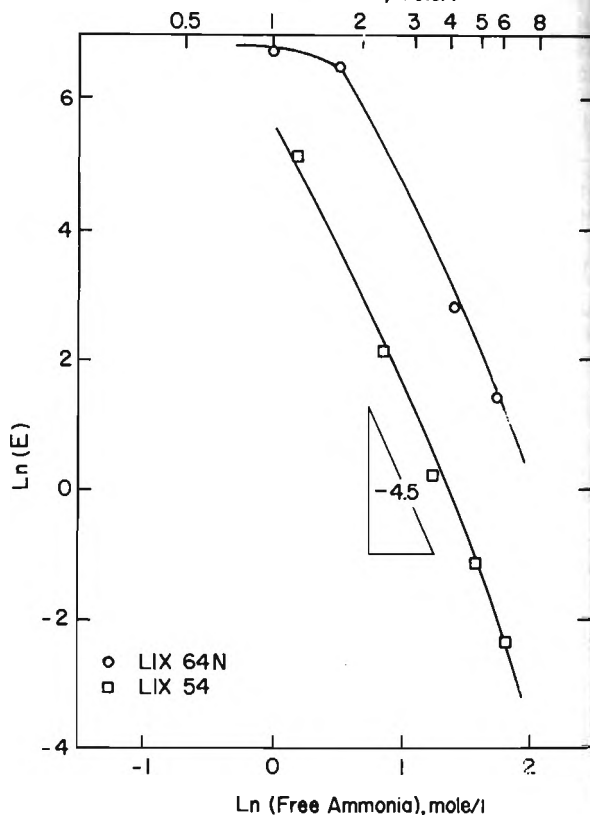


Figure 5. Slope analysis plot indicative of the number of ammonia molecules coordinated by the cupric ion under the conditions specified in Figure 4.

$$\log E = \log K + \log \left(1 + \sum_{i=1}^6 \beta_i [\text{NH}_3]^i \right) + 2\text{pH} + 2 \log [\text{HR}]_0$$

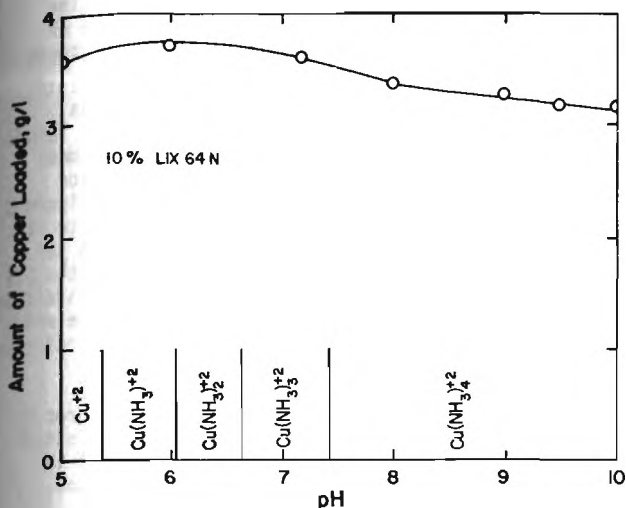


Figure 6. Effect of pH on copper extraction at a constant total ammonia concentration of 0.5 M.

shows a parabolic-type of curve for a plot of copper extraction as a function of pH. For low pH values, copper extraction increases as the pH increases, which may be due to the pH effect only, because the concentration of free ammonia is negligibly small at these low pH values. However, at high pH values the concentration of the ammonia and the number of ammonia ligands will be increased significantly. In this region the ammonia effect will overcome the pH effect and the copper extraction will decline. Predominate copper species are indicated in Figure 6 for various pH regions. Similar effects have been found in the extraction of nickel from ammoniacal solution (34).

Comparison between Acidic and Ammoniacal Systems

According to the equilibrium expression, Equation 9, the thermodynamics for copper extraction seems to be more favorable in the ammoniacal system than in the acid system. The reason is due to high pH values in the ammoniacal solution overwhelming the negative effect of the free ammonia if the concentration of free ammonia is not extremely high. This analysis is supported by the experimental results of the equilibrium extraction isotherms for both acidic and ammoniacal systems (shown in Figure 7). It can be seen that the isotherm for the ammoniacal system is steeper than that for the acid system suggesting that the amount of copper loaded into the organic phase will be higher for the same concentration of copper in the aqueous phase. The pH values listed in Figure 7 were initial values; no attempt was made to buffer the pH.

Other information also can be found from the extraction isotherms. First, due to the steeper isotherm the number of stages required in the extraction from the ammoniacal solution is normally less than that required for extraction from acidic solution. (35)

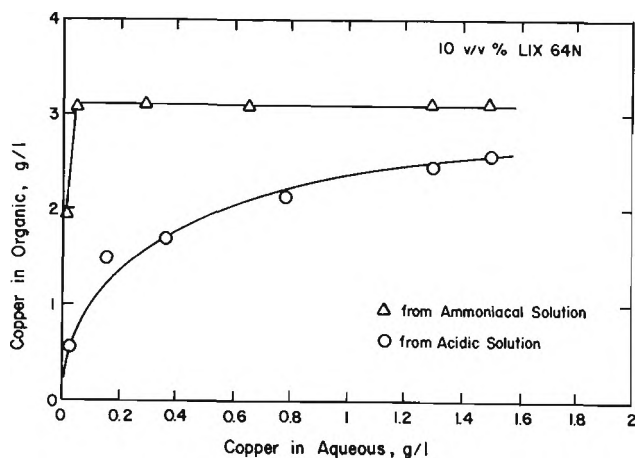


Figure 7. Equilibrium extraction isotherms of copper extraction by 10 V/V % LIX 64N from ammoniacal solution (0.5 M NH_3 , 0.5 M NH_4^+ , pH = 9.70) and from acidic solution (pH = 1.79).

Second, at relative low cupric concentrations in ammoniacal solutions, the isotherm has already reached maximum loading which indicates that the equilibrium concentration of the extractant required is quite small. This observation simplifies subsequent analysis of the rate data as explained in the introduction during the derivation of transport equations.

Extraction Kinetics

The kinetics were studied in both rising drop and falling drop experiments. The results were used to analyze the effect of drop size, temperature and reagent concentrations both in the dispersed phase and in the continuous phase. By considering all these effects, the rate controlling step was identified and a comparison between experimental results and theoretical predictions was made. Normally, the organic phase consisted of the diluent, Escaid 200, which contained from 1 to 50 volume percent of extractant (LIX 64N). The copper concentration in the aqueous phase ranged from 0.5 to 4.3 gpl copper, as cupric sulfate, with 1 M total ammonia (0.5 M free ammonia) at a pH of 9.75. The drop size varied from 0.84 to 1.52 mm in radius.

Rising Drop Experiments

In this series of experiments the continuous phase was always the ammoniacal solution of copper sulfate, and the dispersed phase was the organic solution (LIX 64N in Escaid 200). Normally the initial copper concentration in the organic was zero. The amount of copper extracted into the organic solution is related to the change in the LIX concentration by the stoichiometry of the reaction,

$$-\Delta[\text{HR}]_{d,t} = 2\Delta[\text{CuR}_2]_{d,t} \quad (18)$$

where

$\Delta[\text{HR}]_{d,t}$, $\Delta[\text{CuR}_2]_{d,t}$ = change in concentration of extractant and copper, respectively, in dispersed organic phase at time, t

All data from rising drop experiments are represented in the figures by open symbols.

Significance of end effects and back reaction kinetics. End effects in this kinetic study were determined by the extrapolation method (23). Under normal experimental conditions the end effects were found to be insignificant due to the high frequency of drop formation and small coalescence area of 0.64 cm^2 (see Figures 9 and 16). As mentioned previously it is expected from theoretical considerations that less than 1% of the total extraction occurs during drop formation. Also shown in Figure 16, for one special set of experiments, is data for which the coalescence interfacial area was increased to 1.54 cm^2 and under these circumstances end effects were found to be important.

The significance of the back reaction in the range of variables evaluated in this study was assessed by initially loading the organic phase with copper at the 10% and 30% level. No decrease in the extraction rate could be observed when the results were compared to the rate of extraction when the initial copper concentration in the dispersed organic phase was zero. From these results the back reaction kinetics were not considered to contribute significantly to the overall reaction rate.

Effect of LIX 64N and copper concentration. Experimental results for two drop sizes with several concentrations of LIX 64N in the dispersed organic phase and several concentrations of copper in the continuous aqueous phase are presented in Figure 8.

Because the reaction is directly proportional to the interfacial area, Figure 8 was plotted in terms of extent of copper reacted per unit area versus the travel time of the drop. Consideration of the experimental conditions, where $[\text{HR}]_{d,0}/[\text{Cu}]_{c,0}$ ranges from 10 to 0.22, in terms of the analysis presented in Figure 2, suggests that rate control by mass transfer in the continuous phase should not be important under these conditions and that internal mass transfer would limit the rate for a fast surface reaction. The experimental results shown in Figure 8, seem to support this hypothesis in that the rate is largely independent of copper concentration in the continuous phase, but distinctly dependent on the LIX 64N concentration in the dispersed phase. In addition the rate curves appear to be parabolic in shape which would be expected for rate control by mass transfer in the dispersed phase (Equations 11 and 14).

More experimental data are provided in Figures 9 and 10 in which the extent of extraction is plotted against a parabolic scale corrected for change in area as would be suggested by the equation below,

$$[\text{CuR}_2]_{d,t} = k' [\text{HR}]_{d,0}^{1/2} (t/a^2)^{1/2} \quad (19)$$

where the value of k' depends on whether the drop is circulating or stagnant. A linear relationship can be found for all concentrations of LIX 64N. Figures 9 and 10 also indicate, as mentioned earlier, that the correction for end effects during drop formation and drop coalescence is unnecessary.

The reaction order calculation based on experimental results indicates that the rate has a first order dependence on the extractant concentration and zero order dependence on the copper concentration. These results suggest that the rate of extraction is limited by mass transfer in the dispersed phase.

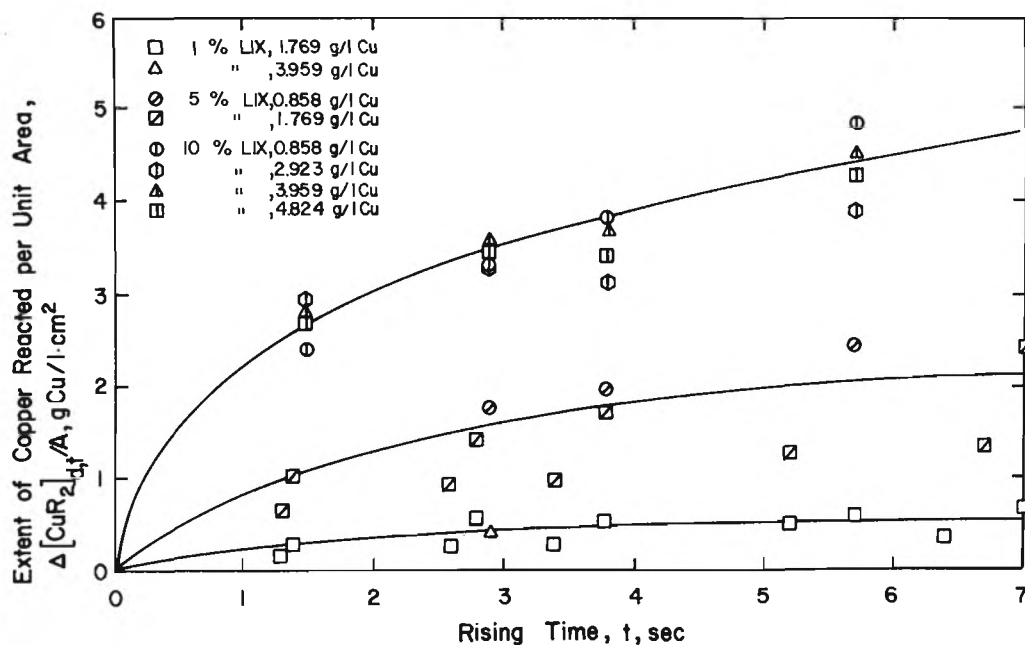


Figure 8. Copper extraction into rising drop for various dispersed (organic) and continuous (aqueous) phase reactant concentrations

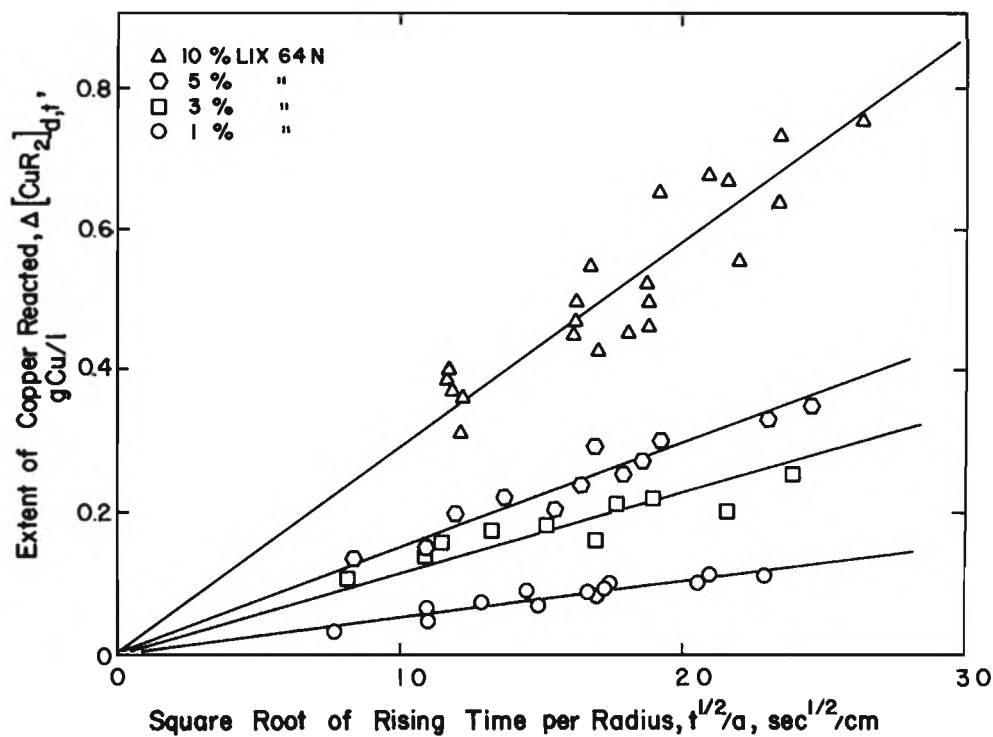


Figure 9. Parabolic plot of rate data illustrating that the kinetics conform to the linear relationship required for rate control by mass transfer in the dispersed phase. Various copper concentrations.

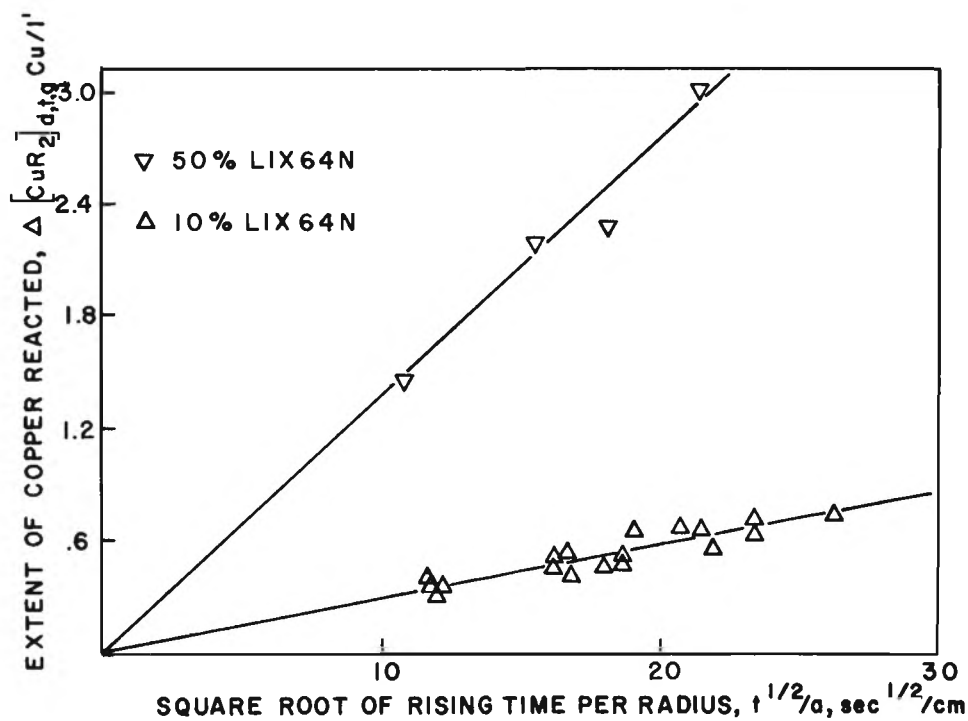


Figure 10. Parabolic plot of rate data illustrating that the kinetics conform to the linear relationship required for rate control by mass transfer in the dispersed phase. Various copper concentrations.

Effect of temperature. The hypothesis of rate control by mass transfer in the dispersed phase also is supported by the low temperature coefficient ob-

served from the data presented in Figure 11. This figure shows that the rate of copper extraction increases as the temperature increases. It also shows

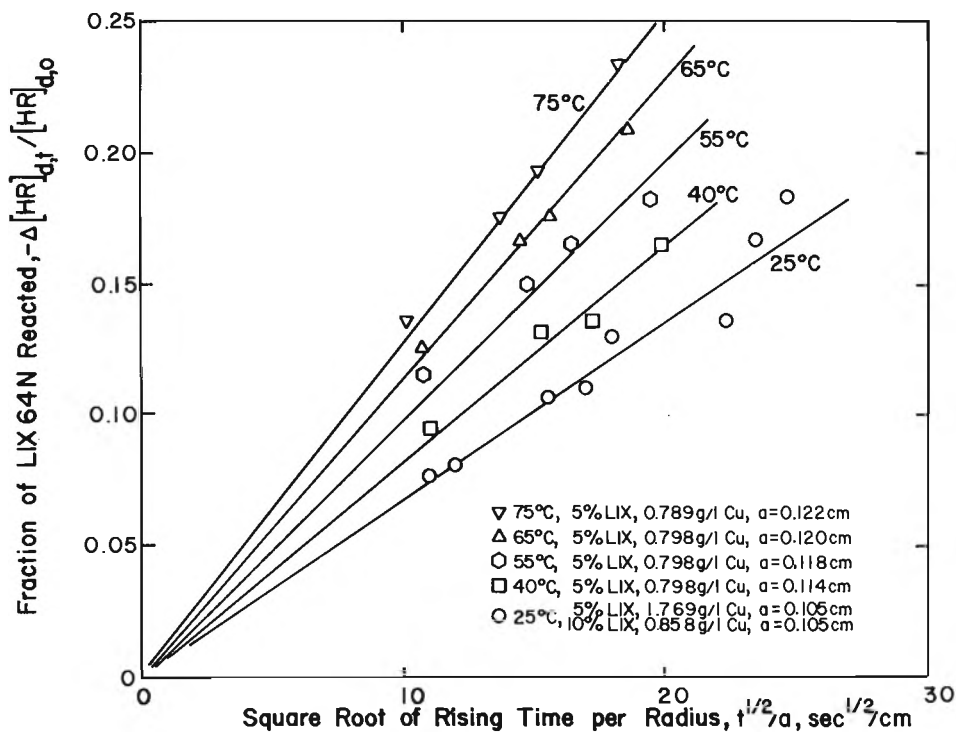


Figure 11. Parabolic plot of rate data for extraction into rising drops at various temperatures.

that the rate curves for all temperatures are parabolic which indicates that the rate controlling step does not change in the temperature range of this study. For this parabolic plot, the dependent variable has been normalized with respect to the initial concentration of the extractant in the dispersed phase. The corresponding Arrhenius calculation reveals a low apparent activation energy of 5.0 kcal/mole.

Comparison of theory with experimental results. In order to theoretically predict the rate of reactant transport in the dispersed phase for both the stagnant model and the circulation model, the diffusion coefficient of LIX 64N in Escaid 200 has to be known and, in this regard, was estimated by the method of Wilke and Chang (36) to be 4.34×10^{-6} cm²/sec. In subsequent Figures in this section theoretical predictions are given by solid and dashed lines. A close agreement between experimental data and the theoretical predictions is shown in Figure 12 for several concentrations of LIX 64N for both small and large drop sizes. The results indicate that the rate follows the stagnant model (molecular diffusion, Equation 11) for LIX 64N concentrations greater than 5%, and that the rate follows the circulation model (convective transport plus molecular diffusion, Equation 14) for LIX 64N concentrations less than 5%. This observation which indicates a change from the circulation model to the stagnant model for an increase in LIX concentration has not been satisfactorily explained on the basis of the change in the physical properties of the system.

The effect of the drop size on the kinetics of the extraction is shown in Figure 13. For small drops ($a = 0.108$ cm), the experimental data seems to be in

the stagnant region; and for large drops ($a = 0.135$ cm) the experimental data seems to be close to the circulation region. These results are consistent with the expected hydrodynamic behavior of larger drops which would have a greater tendency to circulate.

Kinetics of extraction with different LIX reagents. The kinetics of copper extraction by LIX 65N from acidic solution is slow and consequently LIX 63 is added to catalyze the reaction, the mixture of the extractants is called LIX 64N and this combination enhances the rate significantly (7-10). In the ammoniacal system however, the rate appears to be limited by the transport of the reactant in the dispersed phase and under these circumstances should not be expected to be dependent on the composition and the chemical properties of the extractant. Such is the case for the rate of copper extraction by LIX 64N, LIX 65N and LIX 54 (a β -diketone extractant) as shown in Figure 14. The results indicate that the rate of extraction is limited by mass transfer in the dispersed phase for all extractants and the rates are insensitive to the chemical nature of the extractant. These results provide one more piece of evidence which supports rate control by transport in the dispersed phase. Note that no catalytic effect from LIX 63 is observed in the ammoniacal system and it is clear why LIX 65N rather than LIX 64N would be suitable in ammoniacal systems such as the Arbiter process.

Change in rate control from mass transfer in the dispersed phase to mass transfer in the continuous phase. As mentioned previously, mass transfer in the dispersed phase is normally slower than mass transfer in the continuous phase. However, the latter step can become rate limiting if the initial concentration ratio $[Cu]_{c,0}/[HR]_{d,0}$ is less than 0.05 (see Figure 2).

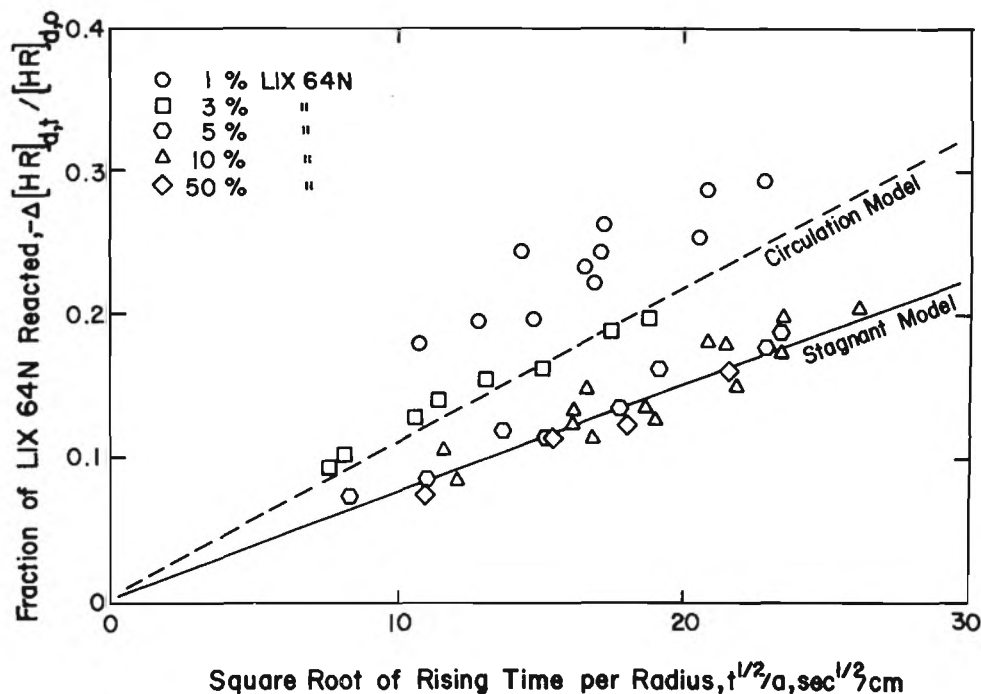


Figure 12. Comparison of experimental results with theoretical predictions for rate control by mass transfer in the dispersed phase (See equations 11 and 14) showing the concentration effect. Various copper concentrations.

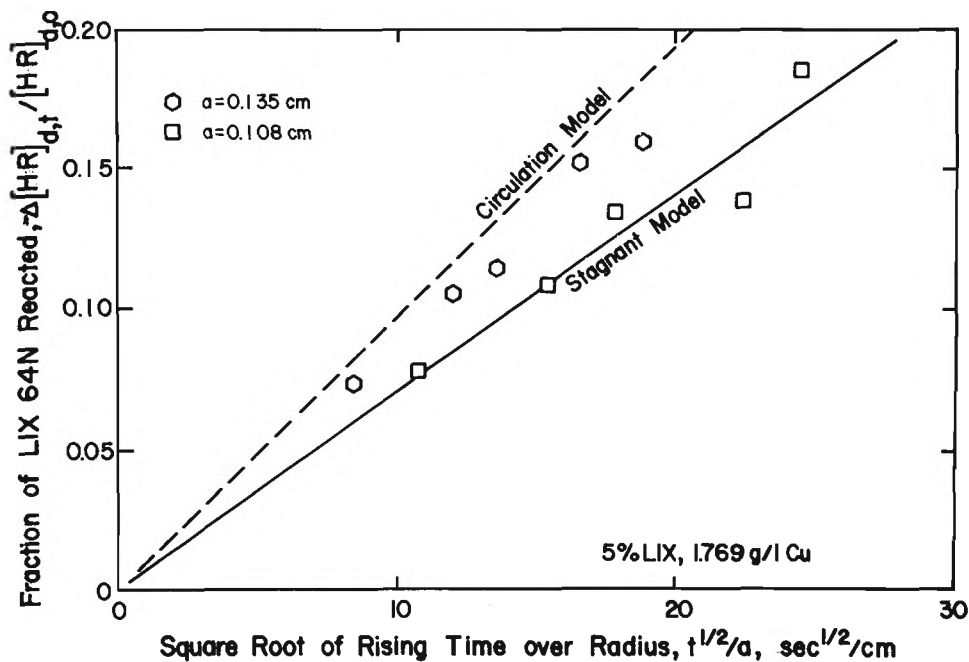


Figure 13. Comparison of experimental results with theoretical mass transfer showing the drop size effect.

Experiments were run to test this hypothesis by selecting concentration ratios of 0.14 and 0.027. When the concentration ratio was 0.14, the experimental results, as expected, followed the stagnant model of internal mass transfer with results similar to those presented previously. However when the concentration

ratio was lowered to 0.027, the rate data did not fit the dispersed phase transport model, but was found to fit the Levich model for external mass transfer as shown in Figure 15.

Long cell experimental results. In order to con-

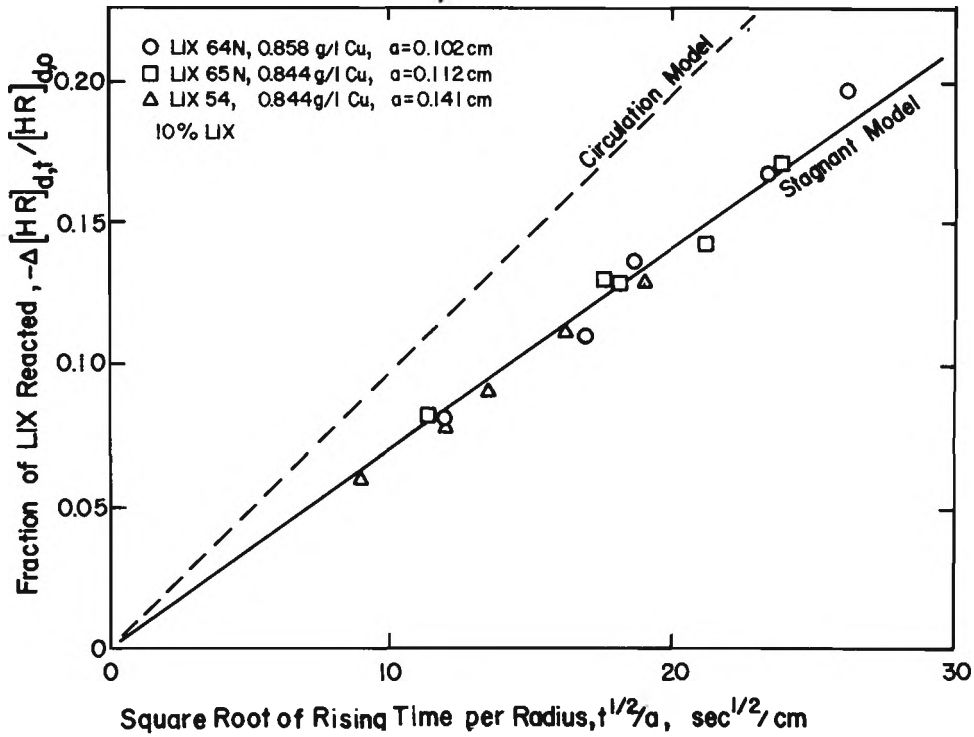


Figure 14. Parabolic plot of rate data for different chelating extractants. Note that the kinetics are essentially independent of the extractant and that 'no' catalytic effect from LIX 63 is observed.

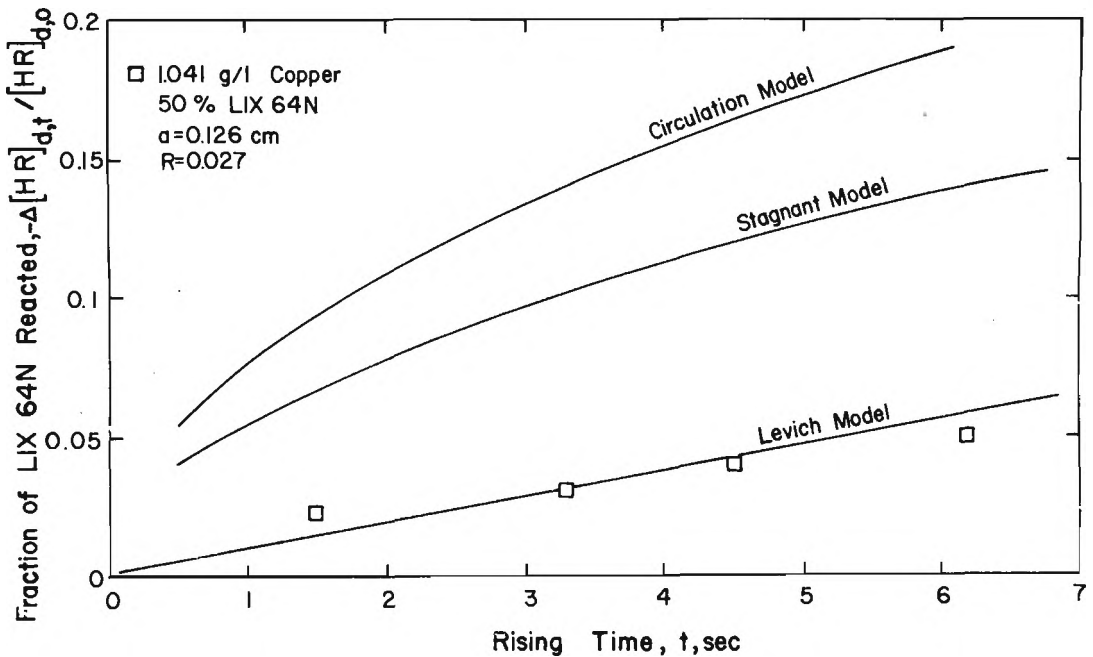


Figure 15. Demonstration of change in rate control from dispersed phase mass transfer limiting to continuous phase mass transfer limiting for small values of the parameter R defined as $[Cu]_{c,0} / [HR]_{d,0}$. For $R < 0.05$ reaction rates should be limited by reactant transport in the continuous phase. See Figure 2.

firm the results obtained with short cells, experiments were performed in which the main objective was to achieve a greater extent of reaction by longer

contact time. Figure 16 shows the results obtained compared with those results from shorter cell experiments under similar conditions. These results show

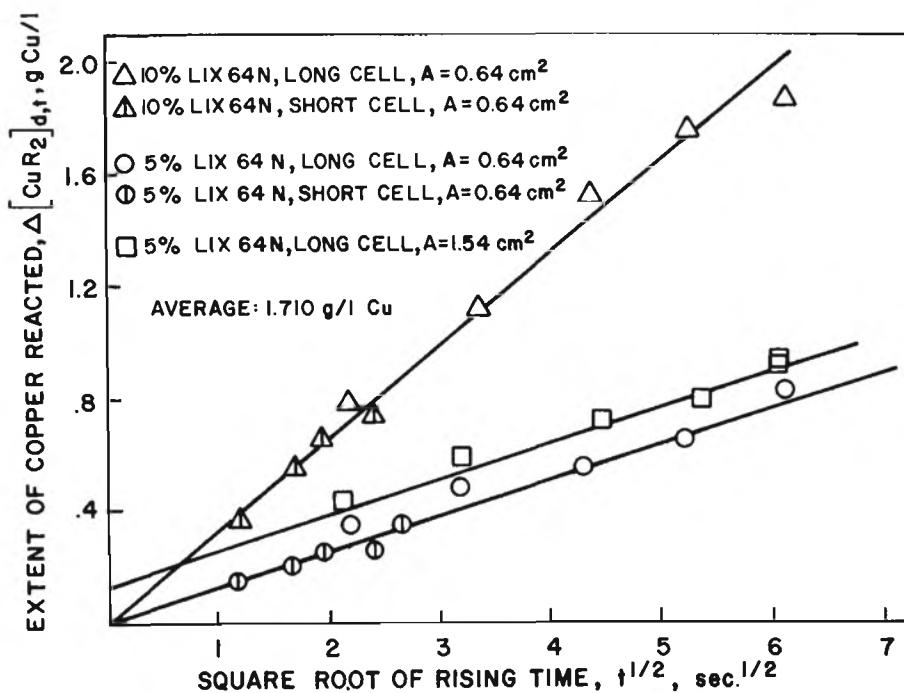


Figure 16. Comparison of experimental results obtained from long and short cells for similar experimental conditions. The effect of the aqueous/organic interfacial area is shown. Note that extrapolation of the curve with larger interfacial area to the ordinate at time zero determines the extent of reaction which can be attributed to the end effects.

that the rate curves are parabolic, consistent with the results of the shorter cell experiment, indicating that the rate controlling step does not change even for longer contact times. In another set of experiments the coalescence interfacial area was increased from 0.64 cm^2 to 1.54 cm^2 and under these circumstances a significant end effect can be detected.

Falling Drop Experiments

In this series of experiments the aqueous phase and the organic phase were reversed. The aqueous phase became the dispersed drops and the organic solution became the continuous phase. Under these circumstances, of course, the aqueous drops fell through the continuous organic phase. All data from falling drop experiments are represented by closed symbols.

Effect of copper and LIX 64N concentration. If the reaction were still controlled by mass transfer in the dispersed phase as predicted from arguments associated with the construction of Figure 2, the rate should be dependent on the dispersed aqueous phase copper concentration and independent of the continuous organic phase LIX 64N concentration. The falling drop results, shown in Figures 17 and 18 indicate the rate increases as the copper concentration increases (Figure 17) and that the rate does not change as the LIX 64N concentration increases (Figure 18). Again, as for the rising drop experiments, the rate follows parabolic kinetics for both the small drop ($\bar{a} = 0.087 \text{ cm}$) experiments, results of which are shown in Figure 19, and the large drop ($\bar{a} = 0.128 \text{ cm}$) experiments, the results of which are shown in Figure 20. Analysis of the rate constants shows that the kinetics are first order with respect to the copper concentration for both drop sizes and suggests that the rate is

still limited by reactant transport in the dispersed phase even when the phases are inverted.

Comparison of theory with experimental results. The mass transfer equations for the stagnant model and circulation model can still be applied for the falling drop. However, the diffusing species is no longer the hydroxyoxime molecule but the copper-ammonia complex. The diffusion coefficient for the hydrated cupric ion has been reported in the literature to be $7.5 \times 10^{-6} \text{ cm}^2/\text{sec}$ (37). If the diffusion coefficient of copper ammonia complex is assumed to be the same as the hydrated cupric ion, the reaction rate can be predicted from first principles. Using Equations 11 and 14 the comparison of experimental data with theoretical predictions can be made and is shown in Figures 21 and 22 where close agreement between theory and experiment is observed. Figure 21 shows that as the copper concentration decreases the drops tend to circulate more. A similar effect was seen for rising drops when the hydroxyoxime concentration was reduced. However, for the same experimental conditions, the falling aqueous drops tend to circulate more than the rising drops. Compare Figure 21 with Figure 12. This may be due to a viscosity effect, more circulation for lower viscosity drops. The viscosity of the aqueous drop for these conditions is about 1.0 cp while the viscosity of the organic drop is about 1.7 cp.

The effect of the drop size on the kinetics of extraction in the falling drop experiments is shown in Figure 23. Again the results appear to follow the anticipated hydrodynamic behavior in which the larger the drop the greater the circulation.

The combined effect of both concentration and drop

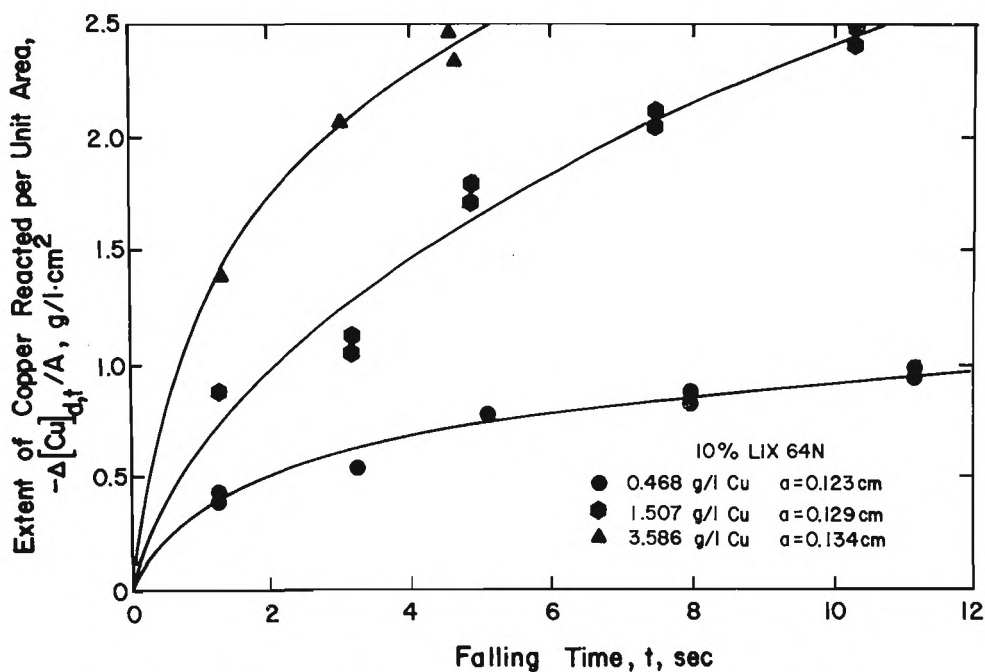


Figure 17. Copper extraction from large falling drops for various initial copper concentrations.

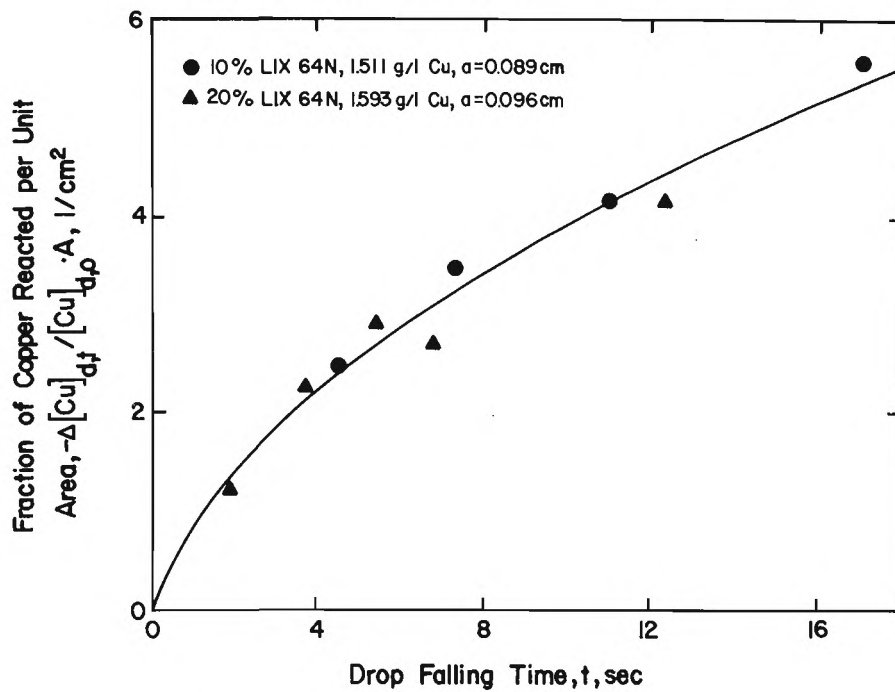


Figure 18. Copper extraction from falling drops for various initial LIX 64N concentrations.

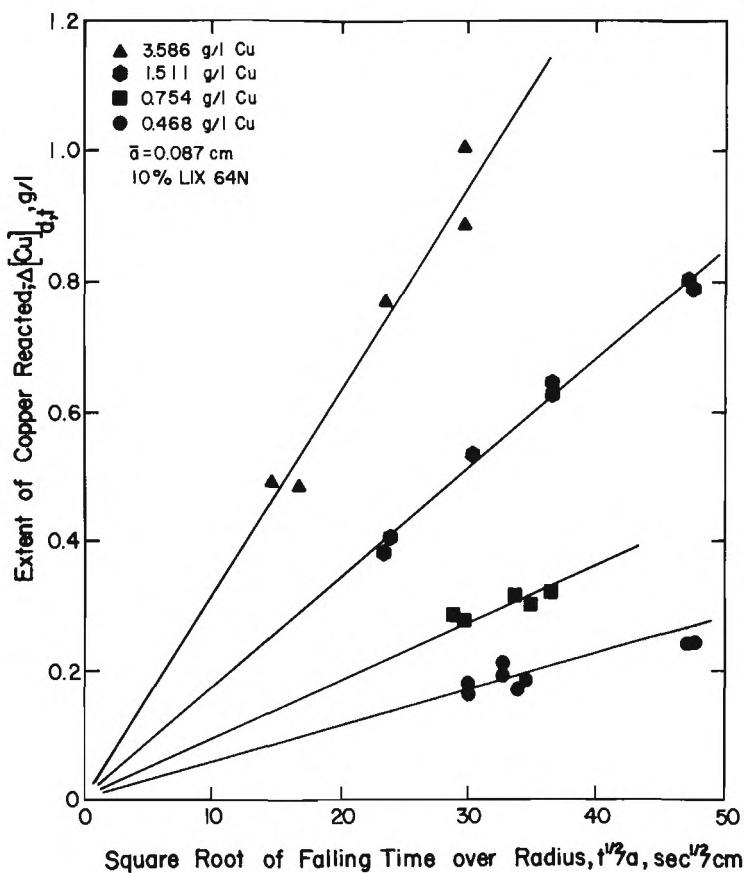


Figure 19. Parabolic plot of rate data for small falling drops illustrating that the kinetics conform to the linear relationship required for rate control by mass transfer in the dispersed phase.

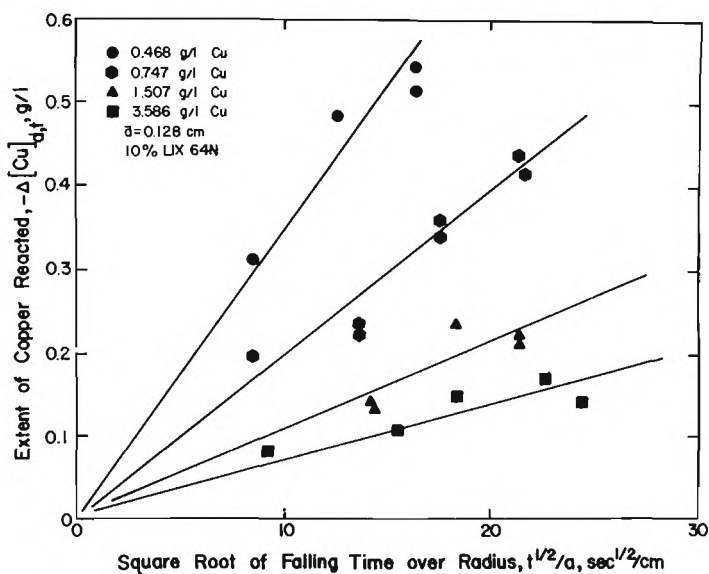


Figure 20. Parabolic plot of rate data for large falling drops illustrating that the kinetics conform to the linear relationship required for rate control by mass transfer in the dispersed phase.

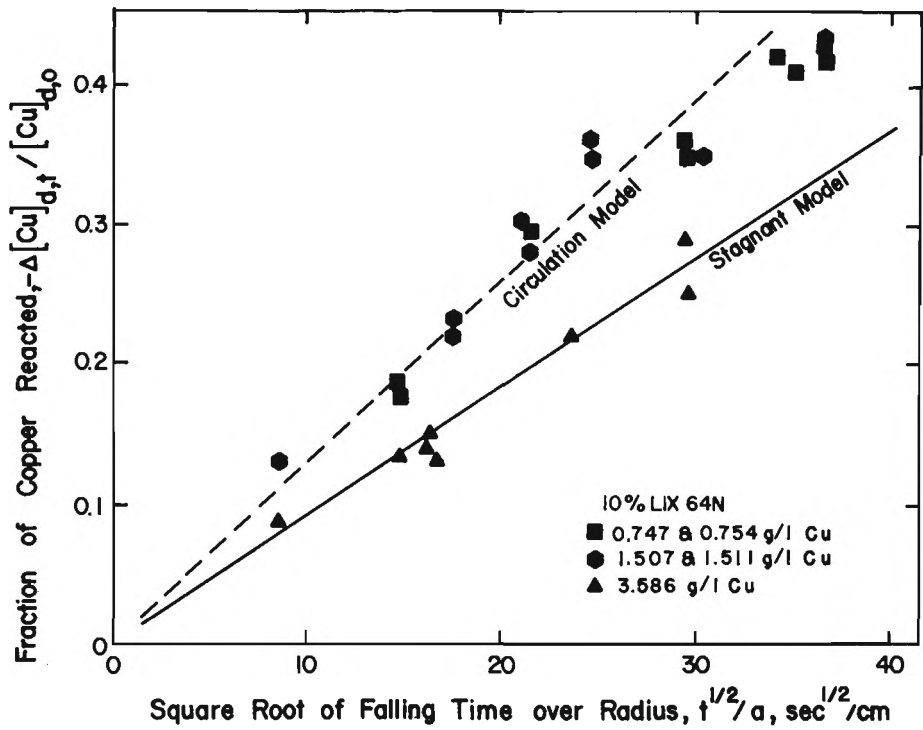


Figure 21. Comparison of experimental results with theoretical predictions for rate control by mass transfer in the dispersed phase for various copper concentrations (Equations 11 and 14).

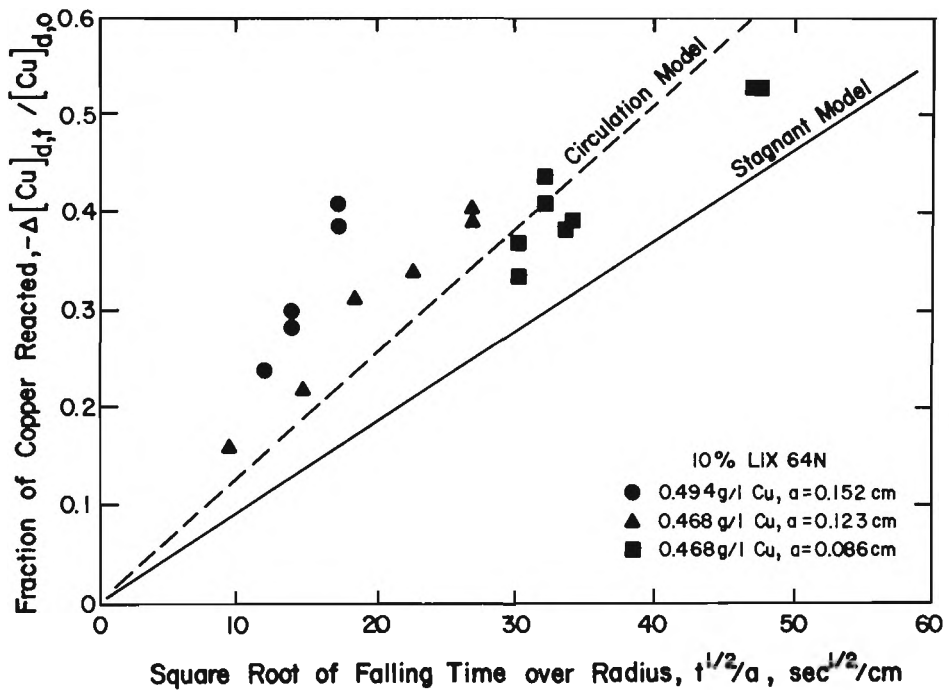


Figure 22. Comparison of experimental results with theoretical predictions for rate control by mass transfer in the dispersed phase for various drop sizes.

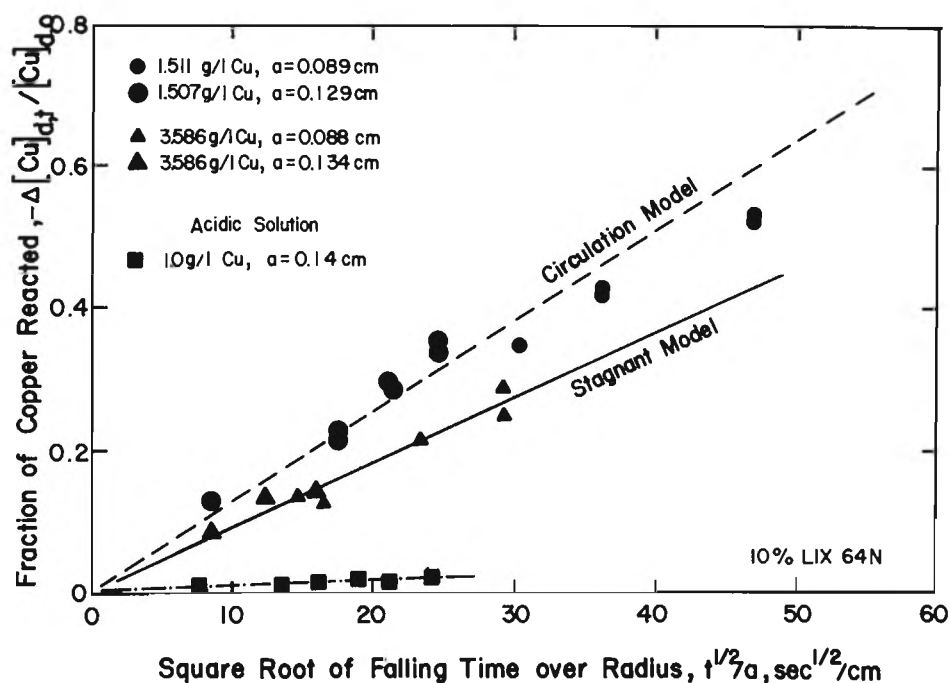


Figure 23. Combination effect of drop size and concentration on extraction kinetics compared with theoretical prediction for dispersed phase reactant mass transfer control. The kinetics of extraction in acidic solution is also shown which illustrate the rate is slower and not controlled by mass transfer processes.

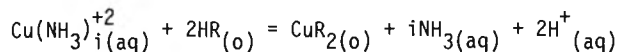
size on the kinetics of extraction is shown in Figure 23. As the concentration decreases or drop size increases the amount of circulation increases.

All the experimental results provide strong evidence that extraction of copper by LIX 64N from ammoniacal solution normally will be controlled by transport of the reactant in the dispersed phase. This result is quite different from the kinetics of copper extraction from acidic solution, a reaction which has been shown to be limited by a surface chemical reaction (9,10). The difference in the reaction rate between extraction from ammoniacal solution and from acidic solution for similar experimental conditions is also shown in Figure 23 and the rate of copper extraction from ammoniacal solution is about one order of magnitude greater than extraction from acidic solution. Because the extraction rate in acid systems is much slower than the slowest type of mass transport, as predicted from the stagnant model, as well as other strong evidence, such as reaction orders, etc., it is clear that the extraction rate in acid systems is limited by a surface chemical reaction. The reason for the slow surface chemical reaction in acidic media is undoubtedly due to the contribution from the back reaction kinetics which is not a factor in ammoniacal systems. In addition, the high polarity of coordinated water molecules in the hydration sheath of the cupric ion may inhibit the extraction rate, in acid systems via a hydrogen bond linkage with the aqueous phase. On the other hand, displacement of the much less polar, coordinated ammonia molecules may represent a significantly lower resistance which facilitates the rate of reaction to such an extent that the rate becomes limited by reactant transport.

SUMMARY AND CONCLUSIONS

The equilibrium state and the kinetics involved in copper extraction from ammoniacal solutions by hydroxyoxime extractants have been studied. The equilibrium study involved shake-out tests, infrared analysis, as well as chemical analysis. The kinetic experiments were accomplished in a single drop reaction cell of variable length. The experimental results and data analysis suggest the following conclusions:

1. Copper extraction from ammoniacal solution by hydroxyoxime extractants involves a complete displacement of ammonia ligands from the coordination sphere of the cupric ion. The chemical reaction can be written as,



2. The extraction coefficient is sensitive to the ammonia concentration and the pH of the system, which various cupric ammine complexes,

$$\log E = \log K - \log\left(1 + \sum_{i=1}^6 [\text{NH}_3]_i^i(\text{aq})\right) + 2 \log [\text{HR}]_{(o)} + 2\text{pH}$$

3. Theoretical analysis and the experimental results from single drop experiments indicate that the kinetics of extraction appear to be controlled by reactant mass transfer in the dispersed phase (irrespective of which phase is dispersed), a conclusion which is supported by a low apparent activation energy of 5.3 kcal/mole.

4. The mass transfer process is explained to be

due to molecular diffusion for small drop sizes, while convective transport contributes to the reaction rate for larger drop sizes provided the viscosity of the dispersed phase is not too high.

5. As a result, rate of copper extraction from ammoniacal solutions is significantly faster than from acidic solutions in which the rate is known to be controlled by a chemical reaction at the liquid/liquid interface. The reason for the low extraction kinetics in the acidic system is the significant contribution of back reaction kinetics to the overall rate of reaction which is not significant in ammoniacal systems.

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