Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Kinetics and Mechanism of Copper Transfer by Hydroxy-Oximes in Three-Phase Liquid Systems

Z. Lazarova[a]; T. Sapundzhiev[a]; L. Boyadzhiev[a]
[a] BULGARIAN ACADEMY OF SCIENCES, INSTITUTE OF CHEMICAL ENGINEERING, SOFIA, BULGARIA

To cite this Article Lazarova, Z. , Sapundzhiev, T. and Boyadzhiev, L.(1992) 'Kinetics and Mechanism of Copper Transfer by Hydroxy-Oximes in Three-Phase Liquid Systems', Separation Science and Technology, 27: 4, 493 — 508

To link to this Article: DOI: 10.1080/01496399208018896

URL: http://dx.doi.org/10.1080/01496399208018896

SEPARATION SCIENCE AND TECHNOLOGY, 27(4), pp. 493–508, 1992

Kinetics and Mechanism of Copper Transfer by Hydroxy-Oximes in Three-Phase Liquid Systems

Z. LAZAROVA, T. SAPUNDZHIEV, and L. BOYADZHIEV
INSTITUTE OF CHEMICAL ENGINEERING
BULGARIAN ACADEMY OF SCIENCES
1113 SOFIA, BULGARIA

Abstract

A model of copper-facilitated transport in a three-liquid-phase pertraction system is proposed. The model takes into account the diffusional transport of copper species (ions and complexes) in all three liquids as well as the kinetics of chemical reactions. The latter, according to the model suggested, occurs in narrow reaction zones: aqueous layers adjacent to the donor membrane and acceptor–membrane interfaces. Experiments were carried out in a two-compartment agitated diffusion cell with a bulk liquid membrane: a 5% (vol) solution of the commercial copper extractant LIX 860 in C_{11}–C_{13} normal paraffins. The donor solution used contained 1 g/L copper and the acceptor liquid was a 4.5 *N* aqueous solution of sulfuric acid. On the basis of experimentally obtained pertraction curves and the model suggested, it was found that the overall rate of the process is controlled by the diffusion of copper ions in the donor phase as well as by copper–complex decomposition. By applying an optimization procedure, the mass transfer coefficients and the rate constants were evaluated under the experimental conditions of this study.

INTRODUCTION

Recent years have witnessed a growing interest toward the recovery of metal ions from their dilute aqueous solutions or wastewaters as a result of efficient methods developed to apply conventional liquid extraction, liquid membrane, or liquid pertraction techniques. The practical realization of these techniques by using commercial chelating agents from the LIX series (LIX 860, LIX 84, LIX 622), as well as Acorga, KELEX, etc., introduced for the treatment of copper-containing solutions, primarily requires comprehensive knowledge of the transport mechanism. Numerous studies involving copper(II) recovery in three-phase liquid systems have led to some contradictory results and interpretations with regard to this mechanism. Different opinions about the rate-determining step of the overall transport process have also been expressed.

According to Yagodin et al. (*1*), all cases of copper extraction using di-2-ethyl-hexyl phosphoric acid (D2EHPA) as the copper carrier are diffusion-controlled. This conclusion is based on the observation that complex formation and decomposition run faster than mass transfer. However, when oxime LIX 64N was used, the copper ion flux reduced abruptly due to the relatively slow chemical reaction. In addition, the flux across the interface is affected strongly by the presence of catalysts, which proves that chemical reaction kinetics prevail.

O'Hara et al. (*2*), following their study on copper transfer from alkaline solutions by the carrier LIX 54, established that by intensive mixing and a high initial copper concentration, diffusion in the membrane liquid is the rate-limiting step. Yoshizuka et al. (*3*), using the same carrier, found that at pH > 5 the rate-controlling step was copper diffusion in the donor phase or diffusion of the copper complex in the membrane liquid, while at low pH values the chemical reaction was the rate-determining step. Chiarizia et al. (*4*) considered that the overall process is controlled by diffusion in the membrane or in adjacent aqueous layers. According to the studies of Bart et al. (*5*), chemical kinetics governs the overall rate at low copper concentration and a high concentration of sulfuric acid. Danesi and coworkers (*6*) suggested that the overall transfer is controlled simultaneously by diffusion and the chemical reaction.

Unlike previous authors, Komasawa et al. (*7*) and Tallarico et al. (*8*) maintained that the overall process is dominated by the chemical reaction of copper–oxime complex formation which occurs at the interface between the treated aqueous solution and the organic membrane. It is noteworthy that most of the authors working on the subject, like the authors already mentioned, assume a chemical reaction localized at the interfaces. In general, this assumption has been motivated by the low solubility of aromatic hydroxy-oximes in aqueous solutions. This problem has been subject to extensive discussion in the literature on metal extraction by chelating solvents. Until recently, the so-called "interfacial mechanism" supported by Flett et al. (*9*) and others was considered predominant. This concept, based merely on proportionality between contact surface and the extraction rate observed, has also been supported by Komasawa et al. (*10*).

However, Valdes et al. (*11*) claimed that copper–oxime complexes are formed in the organic phases, while Whewell et al. (*12*) and Kojima and Miyauchi (*13*) supported the idea that the rate-controlling chemical reactions occur in the aqueous phase.

Attention is due to the studies of Freiser (*14*) which discussed the kinetics of metal ion recovery from aqueous solutions by using chelating agents. In contrast to the widespread concept of the "interfacial" nature of chemical reactions which consider that the rate of extraction is controlled by the interfacial chemical reaction, this author showed that the slowest rate-determining step is the reaction between the metal ion and the ligand dissolved in the aqueous phase. His "aqueous phase" mechanism was supported by ample experiments with the extractant Cu-LIX 65 (*15*, *16*). The authors presumed that if the extraction rate is dominated by chemical reaction in the aqueous phase, it would also be influenced by ligand solubility in water. They showed that even in the case of slightly soluble in water solvents like dithizone, with a distribution coefficient of $m_{HR} = 10^{5.9}$, copper recovery would be slow due to the low reaction rate in the aqueous phase. The values of the apparent rate constants obtained were close to those that would be valid for some copper-substitution reactions in aqueous media and rather smaller than the values which would be obtained if the chemical reaction had occurred at the interface, i.e., if the amount of solvent was much higher. According to these studies, the copper–oxime complex is formed in two steps:

$$Cu^{2+} + HR \underset{k_{r1}}{\overset{k_{f1}}{\rightleftharpoons}} CuR^{+} + H^{+} \tag{1}$$

$$CuR^{+} + HR \underset{k_{r2}}{\overset{k_{f2}}{\rightleftharpoons}} CuR_2 + H^{+} \tag{2}$$

Eq. (2) being slower than Eq. (1). All other steps, including reaction step (1), ligand dissolution, and complex transportation throughout the organic liquid, proceed relatively faster.

The present work is aimed at developing a mathematical model of copper ion transport in a three-phase liquid (pertraction) system by using a chelating agent as the carrier. The model accounts for diffusion in all the liquid phases as well as the two-step homogeneous reaction of copper complex formation and decomposition in the treated and receiving aqueous solutions.

THEORETICAL

The model is based on the following assumptions:

(1) The chemical reaction between the copper ions and the oxime molecules occurs in the aqueous layers adjacent to both sides of the intermediate membrane phase.

(2) The reaction follows the two-step path described by Eqs. (1) and (2), respectively.

(3) Hydrogen ion diffusion in both aqueous phases is much faster than copper ion diffusion from the reaction zones into the aqueous layers. The

same holds for ligand diffusion in the membrane phase with respect to copper–complex diffusion in the same phase.

The following steps represent the overall mechanism of copper transfer in a three-phase liquid system:

(a) Diffusion of copper ions from the bulk of the donor aqueous phase F to the reaction zone FS (cf. Fig. 1). The flux in this step is

$$j_F = k_F([Cu^{2+}]_F - [Cu^{2+}]_{FS}) \tag{3}$$

(b) Dissolution of the carrier HR from the membrane phase S into the aqueous reaction zone FS. Since the thickness of this zone is negligible, it is assumed that the equilibrium defined by the distribution coefficient m_{HRF},

$$m_{HRF} = \frac{[HR]_{SF}}{[HR]_{FS}} \tag{4}$$

is reached.

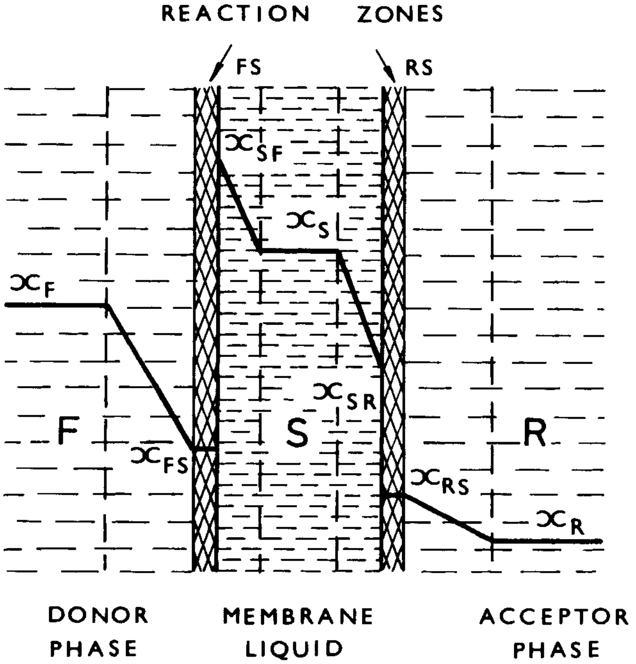

FIG. 1. Hypothetical concentration profiles of copper species in the three-phase liquid system.

(c) A reversible two-step chemical reaction between copper ions and hydroxy-oxime molecules HR within the reaction zone FS. Since the first step of the reaction (Eq. 1) is fast, equilibrium is attained, and the rates of the forward and the reverse reactions become equal, so that

$$k_{f1}[\mathrm{Cu}^{2+}]_{\mathrm{FS}}[\mathrm{HR}]_{\mathrm{FS}} = k_{r1}[\mathrm{CuR}^{+}]_{\mathrm{FS}}[\mathrm{H}^{+}] \tag{5}$$

Therefore the concentration of the primary complex CuR^{+} becomes

$$[\mathrm{CuR}^{+}]_{\mathrm{FS}} = \frac{k_{f1}[\mathrm{Cu}^{2+}]_{\mathrm{FS}}[\mathrm{HR}]_{\mathrm{FS}}}{k_{r1}[\mathrm{H}^{+}]_{\mathrm{FS}}} \tag{6}$$

Since the second step is rate controlling, i.e., Eq. (2) holds, the rate of the chemical reaction in zone FS is described by

$$r_{\mathrm{FS}} = k_{f2}[\mathrm{CuR}^{+}]_{\mathrm{FS}}[\mathrm{HR}]_{\mathrm{FS}} - k_{r2}[\mathrm{CuR}_2]_{\mathrm{FS}}[\mathrm{H}^{+}]_{\mathrm{FS}} \tag{7}$$

Substituting Eq. (6) in Eq. (7) yields

$$r_{\mathrm{FS}} = \frac{k_{f1}k_{f2}[\mathrm{Cu}^{2+}]_{\mathrm{FS}}[\mathrm{HR}]^2_{\mathrm{FS}}}{k_{r1}[\mathrm{H}^{+}]_{\mathrm{FS}}} - k_{r2}[\mathrm{CuR}_2]_{\mathrm{FS}}[\mathrm{H}^{+}]_{\mathrm{FS}} \tag{8}$$

which is the rate equation for a two-step homogeneous reaction when the second step is rate controlling.

(d) For the same reason as in Step (b), the concentration of copper complex CuR_2 in the membrane in the vicinity of the interface F/S is related to the copper species in the aqueous solution F by the apparent distribution coefficient, m_{F}, as

$$m_{\mathrm{F}} = \frac{[\mathrm{CuR}_2]_{\mathrm{S/F}}}{[\mathrm{Cu}^{2+}_{\mathrm{FS}}] + [\mathrm{CuR}^{+}]_{\mathrm{FS}} + [\mathrm{CuR}_2]_{\mathrm{FS}}} \tag{9}$$

(e) Diffusion of the complex CuR_2 across the membrane boundary layers:

$$j_{\mathrm{SF}} = k_{\mathrm{SF}}([\mathrm{CuR}_2]_{\mathrm{S/F}} - [\mathrm{CuR}_2]_{\mathrm{S}}) \tag{10}$$

$$j_{\mathrm{SR}} = k_{\mathrm{SR}}([\mathrm{CuR}_2]_{\mathrm{S}} - [\mathrm{CuR}_2]_{\mathrm{S/R}}) \tag{11}$$

(f) Dissolution of the complex CuR_2 into the reaction zone RS. The equilibrium is always attained and therefore the following expression is valid:

$$m_R = \frac{[\mathrm{CuR_2}]_{S/R}}{[\mathrm{Cu}^{2+}]_{RS} + [\mathrm{CuR}^+]_{RS} + [\mathrm{CuR_2}]_{RS}} \tag{12}$$

(g) Chemical reaction between the complex $\mathrm{CuR_2}$ and the acid in the acidic acceptor reaction zone RS is expressed by

$$r_{RS} = k_{r2}[\mathrm{CuR_2}]_{RS}[\mathrm{H}^+]_{RS} - k_{f2}[\mathrm{CuR}^+]_{RS}[\mathrm{HR}]_{RS} \tag{13}$$

The regenerated chelating agent dissolves in membrane S and then is transferred back to the donor liquid F, driven by its concentration gradient.

By accounting for the other reaction step in reaction zone RS which is reversible, one obtains the rate of copper complex decomposition:

$$r_{RS} = k_{r2}[\mathrm{CuR_2}]_{RS}[\mathrm{H}^+]_{RS} - \frac{k_{f1}k_{f2}[\mathrm{Cu}^{2+}]_{RS}[\mathrm{HR}]_{RS}}{k_{r1}[\mathrm{H}^+]_{RS}} \tag{14}$$

(h) Diffusion of Cu^{2+} ions from the reaction zone RS into the bulk of the receiving solution R is

$$j_R = k_R([\mathrm{Cu}^{2+}]_{RS} - [\mathrm{Cu}^{2+}]_R) \tag{15}$$

By assuming equal diffusion and reaction fluxes for each reaction zone, it follows that

$$j_F = r_{FS} = j_{SF} \tag{16}$$

and

$$j_{SF} = r_{RS} = j_R \tag{17}$$

Fluxes j_F and j_R are defined by

$$j_F = -\frac{d[\mathrm{Cu}^{2+}]_F}{(a_F/V_F)dt} \tag{18}$$

$$j_R = \frac{d[\mathrm{Cu}^{2+}]_R}{(a_R/V_R)dt} \tag{19}$$

From these equations, the relationships describing the copper ion concentration variation in both aqueous phases F and R can be derived as follows.

By combining Eqs. (3), (4), (8), (9), (10), and (16), the copper concentration in the donor solution F is obtained:

$$\frac{d[\mathrm{Cu}^{2+}]_\mathrm{F}}{dt} = -\frac{a_\mathrm{F}}{V_\mathrm{F}}\,\frac{\mathrm{A}_\mathrm{F}[\mathrm{Cu}^{2+}]_\mathrm{F} - \mathrm{B}_\mathrm{F}[\mathrm{CuR}_2]_\mathrm{S}/m_\mathrm{F}}{1 + \mathrm{A}_\mathrm{F}/k_\mathrm{F} + \mathrm{B}_\mathrm{F}/(m_\mathrm{F}k_\mathrm{SF})} \tag{20}$$

The acceptor solution R is obtained from Eqs. (11), (12), (14), (15), and (17):

$$\frac{d[\mathrm{Cu}^{2+}]_\mathrm{R}}{dt} = \frac{a_\mathrm{R}}{V_\mathrm{R}}\,\frac{\mathrm{B}_\mathrm{R}[\mathrm{CuR}_2]_\mathrm{S}/m_\mathrm{R} - \mathrm{A}_\mathrm{R}[\mathrm{Cu}^{2+}]_\mathrm{R}}{1 + \mathrm{A}_\mathrm{R}/k_\mathrm{R} + \mathrm{B}_\mathrm{R}/(m_\mathrm{R}k_\mathrm{SR})} \tag{21}$$

where B_F and B_R are defined as

$$\mathrm{B}_{\mathrm{F(R)}} = k_{r2}[\mathrm{H}^+]_{\mathrm{F(R)}} \tag{22}$$

while A_F and A_R are represented by the expression

$$\mathrm{A}_{\mathrm{F(R)}} = \frac{k_{f1}k_{f2}[\mathrm{HR}]_\mathrm{S}^2}{k_{r1}m_{\mathrm{HRF(R)}}^2[\mathrm{H}^+]_{\mathrm{F(R)}}} + k_{r2}[\mathrm{H}^+]_{\mathrm{F(R)}} + \frac{k_{f1}k_{r2}[\mathrm{HR}]_\mathrm{S}}{k_{r1}m_{\mathrm{HRF(R)}}} \tag{23}$$

In order to derive the final process description, the following mass balance equations must be added to Eqs. (20–23):

$$[\mathrm{CuR}_2]_\mathrm{S} = (V_\mathrm{F}/V_\mathrm{S})([\mathrm{Cu}^{2+}]_\mathrm{F}^0 - [\mathrm{Cu}^{2+}]_\mathrm{F}) - (V_\mathrm{R}/V_\mathrm{S})([\mathrm{Cu}^{2+}]_\mathrm{R} - [\mathrm{Cu}^{2+}]_\mathrm{R}^0) \tag{24}$$

$$[\mathrm{HR}]_\mathrm{S} = [\mathrm{HR}]_\mathrm{S}^0 - 2[\mathrm{CuR}_2]_\mathrm{S} \tag{25}$$

$$[\mathrm{H}^+]_\mathrm{F} = [\mathrm{H}^+]_\mathrm{F}^0 + 2([\mathrm{Cu}^{2+}]_\mathrm{F}^0 - [\mathrm{Cu}^{2+}]_\mathrm{F}) \tag{26}$$

and

$$[\mathrm{H}^+]_\mathrm{R} = [\mathrm{H}^+]_\mathrm{R}^0 - 2[\mathrm{Cu}^{2+}]_\mathrm{R} \tag{27}$$

The initial conditions (at $t = 0$) are:

$$[\mathrm{Cu}^{2+}]_\mathrm{F} = [\mathrm{Cu}^{2+}]_\mathrm{F}^0 \tag{28}$$

$$[\mathrm{CuR}_2]_\mathrm{S} = 0 \tag{29}$$

$$[Cu^{2+}]_R = 0 \tag{30}$$

$$[HR]_S = [HR]_S^0 \tag{31}$$

$$[H^+]_F = [H^+]_F^0 \tag{32}$$

$$[H^+]_R = [H^+]_R^0 \tag{33}$$

Equations (20) and (21), together with Eqs. (24)–(27) and initial conditions (28)–(33), describe the facilitated copper ion transfer in a three-phase liquid system.

EXPERIMENTAL

Model System and Reagents Used

The experiments were carried out by using the following solutions:

Phase F (the donor solution): A nonbuffered aqueous solution of $CuSO_4$ (p.a. grade reagent, a domestic product), containing ca. 1 g/L Cu^{2+}.

Phase S (the membrane solution): A solution of LIX 860, a commercial chelating agent containing 5-dodecyl salycil aldoxime, not purified additionally (Henkel Co.) [17], in normal paraffins, medium-boiling point fraction (Neftokhim Co., Burgas). The composition of the paraffinic solvent used is: C_{10}, 3.4 vol%; C_{11}, 17.3 vol%; C_{12}, 33.1 vol%; C_{13}, 45.7 vol%; C_{14}, 0.5 vol%; others, 0.1 vol%.

Phase R (the acceptor solution): A 4.5 *N* aqueous solution of sulfuric acid (Merck).

Analytical Methods Used

Copper ion concentration in the aqueous solutions was measured by complexometric titration with EDTA (*18*). In all cases the titrated solutions were buffered by sodium acetate (p.a. grade, a domestic product) or acetic acid (p.a. grade, Merck), depending on the pH value of the aqueous media.

Hydrogen ion concentration was controlled by a digital pH-meter, Type LP-17 (Analytic Co.). A neutralization volumetric analysis with sodium hydroxide solution was applied for samples with a pH value less than 1.

Experimental Procedures and Equipment

Extraction Equilibrium

The effect of pH on copper distribution was studied within the pH range −0.3 to 1.6. In all experiments, the LIX 860 concentration in the organic phase was 5 vol%.

Equal volumes of both liquids, i.e., the aqueous copper solution of ca. 1 g/L copper(II) and the oxime solution in paraffin oil, were mixed thoroughly in separation funnels at 22°C for 1 h by using a machine shaker equipped with a water bath. After complete phase separation, hydrogen and copper concentrations were measured in the aqueous phase by titration.

Carrier Distribution

Runs were performed to determine the partition of the LIX 860 active component between the aqueous and organic solutions in the absence of copper. In these runs the distribution coefficients, m_{HR}, were obtained using the procedure recommended by Ritcey and Ashbrook (*19*).

Description of the Pertraction Cell Used

Figure 2 presents the schematic setup of the laboratory equipment used to study the kinetics of copper pertraction by LIX 860 oxime. As seen from the figure, the equipment comprises a two-compartment glass cell. Apart from its simple design, the main advantage of this type of equipment compared with other equipment types for liquid–liquid transfer kinetic analysis, e.g., single drops and rotational diffusion cells, is its well-defined contact surface which remains constant during extraction.

The cell used consisted of two coaxial glass cylinders equipped with a jacket thermostat, blade agitators, and sampling outlets. Both compartments, separated by the inner cylinder wall, were used for the donor and the acceptor aqueous solutions, the volume of each being 120 cm^3. The donor copper-containing solution was placed in the outer compartment, while the inside compartment contained the acceptor solution. In order to verify the values of the mass transfer coefficients obtained by following the identification procedure described below, the locations of the aqueous solutions were changed in some experimental runs. The organic phase, i.e., the liquid membrane which contained the oxime, formed a layer of 150 cm^3 over the aqueous solutions, as shown in Fig. 2. The size of the compartments was designed to ensure an equal contact area of 36.5 cm^2 between equal volumes of the aqueous phases, F and R, and the membrane phase, S.

RESULTS AND DISCUSSION

Copper Distribution

The relationship between the distribution coefficient of copper m and the aqueous phase pH value is plotted in logarithmic coordinates in Fig. 3. As expected by the low concentrations of copper used, the data conform

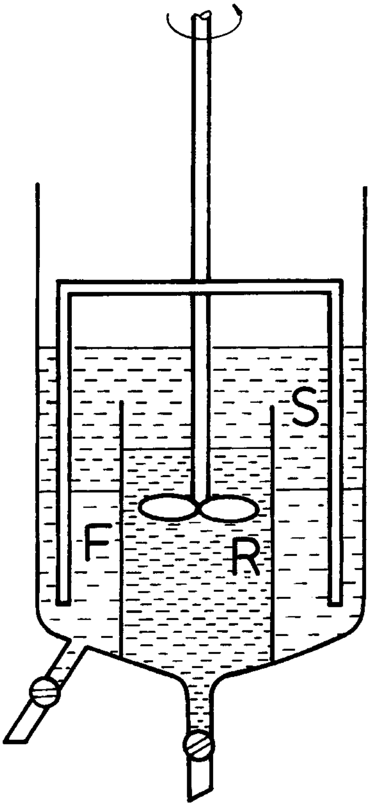

FIG. 2. Schematic diagram of the agitated transfer cell.

to a straight line with a slope close to 2. More accurately, this relationship can be expressed by the empirical equation

$$\lg m = -0.052 + 2.01 \text{ pH} \tag{34}$$

which was used for the evaluation of the distribution coefficients, m_F and m_R, participating in the above-mentioned pertraction model.

Oxime Distribution

Within the range of pH values and temperature used in this study, the concentration of the pure oxime in the aqueous phase was found to be 0.4 ppm by weight. However, to calculate the relevant distribution coefficient defined by the ratio of oxime concentration in the organic phase to the one in the aqueous phase, more information was needed concerning the active reagent content in the commercial product. Therefore, by using the method of Fleming and coworkers (*20*), we extracted the active oxime component from the commercial LIX 860 product and found that its concentration was 23 wt%. Therefore, we obtained a value of 23,750 for the relevant carrier distribution coefficient m_{HR} under the conditions studied.

Studies on the Transfer Kinetics of Copper Ions

In order to establish the effect of hydrodynamics on the copper ion transfer, experiments were carried out at three stirring speeds: 30, 50, and

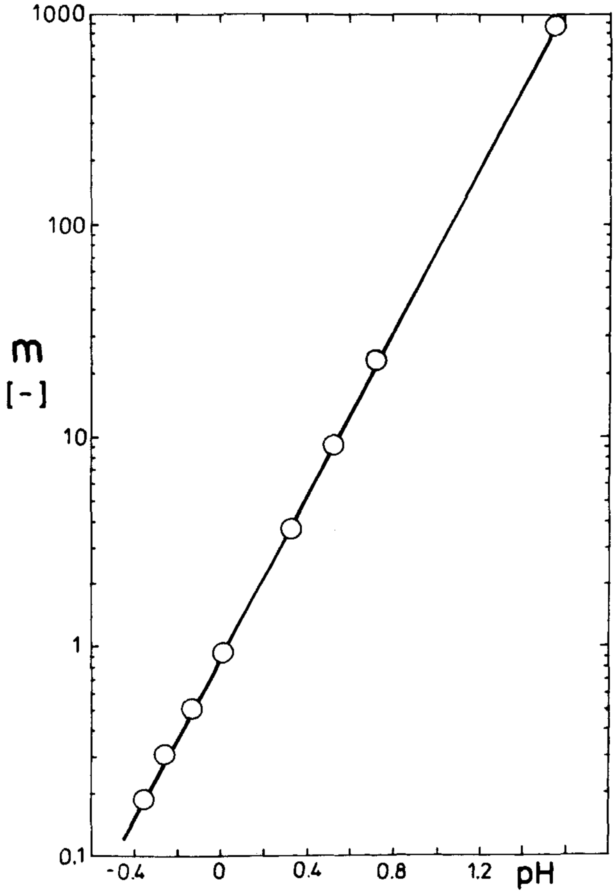

FIG. 3. Distribution coefficient of copper vs pH.

65 rpm. Figure 4 illustrates the copper ion concentration changes vs time in both aqueous phases F and R.

According to studies carried out in a similar cell by Ivakhno and coworkers (*21*), cases distinguished by relative fluxes ($j/[\mathrm{Cu}_F^{2+}]^0$) less than 1×10^{-5} m/s are characterized by relatively slow chemical reactions. In addition, when the chemical reaction is assumed to be localized at the interface, these fluxes should be not affected by the stirring intensity.

As seen from Fig. 4, the effect of stirring on the rate of transfer suggests a pronounced diffusional resistance. Furthermore, stirring intensity enhances only copper ion transport in the donor phase F. The stripping process, i.e., copper transfer from the membrane S to the acceptor solution R, was affected only slightly. Therefore, copper ion concentration in solution R remained almost constant regardless of the significant concentration change in the donor phase F.

On the other hand, the experimental values obtained for the relative

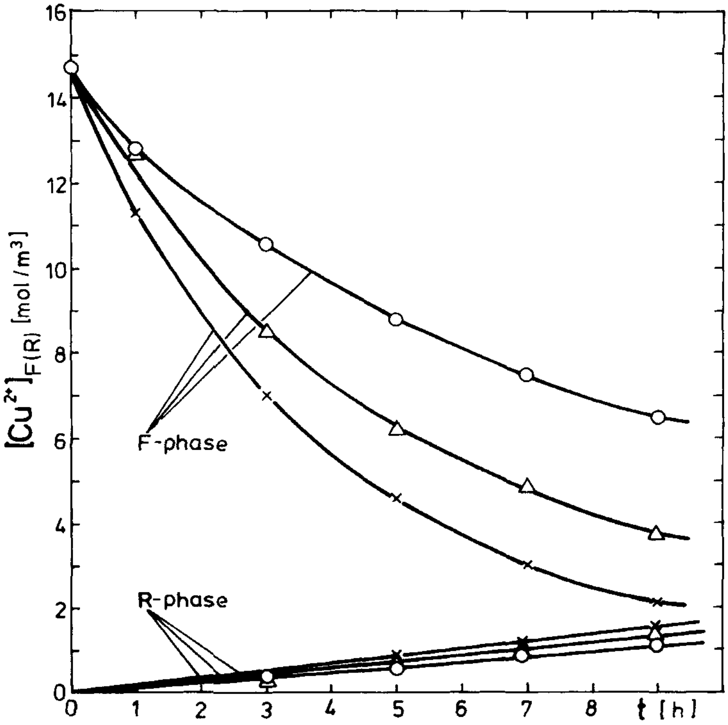

FIG. 4. Agitation speed vs pertraction rate of copper.

copper fluxes at various stirring speeds, n, i.e.,

$$n_1 = 30\ \text{rpm}, \qquad j_1/[\text{Cu}^{2+}]^0_\text{F} = 6.5 \times 10^{-7}\ \text{m/s}$$

$$n_2 = 50\ \text{rpm}, \qquad j_2/[\text{Cu}^{2+}]^0_\text{F} = 8.66 \times 10^{-7}\ \text{m/s}$$

$$n_3 = 65\ \text{rpm}, \qquad j_3/[\text{Cu}^{2+}]^0_\text{F} = 9.88 \times 10^{-7}\ \text{m/s}$$

are considerably lower than those reported by Ivakhno and coworkers, thus suggesting that the chemical reactions involved are far too fast. In principle, our results confirm that the assumption of a relatively slow decomposition of copper–oxime complex (CuR_2) in the acceptor-phase acidic medium is reasonable.

These conclusions were confirmed by numerical identification of the parameters of the proposed model. For these experiments, the dynamic simulator TUTSIM (*22*), incorporating an optimization procedure based on the Nelder–Meed simplex method (*23*), was used. The following objective function was formulated:

$$\Phi = \sum^{N} \{([\text{Cu}^{2+}]^i_{\text{F calc}} - [\text{Cu}^{2+}]^i_{\text{F exp}})^2 + ([\text{Cu}^{2+}]^i_{\text{R calc}} - [\text{Cu}^{2+}]_{\text{R exp}})\}^2 \qquad (35)$$

The identification result was used to evaluate the model parameters k_F, k_{r2}, and $k_e = k_{f1}k_{f2}/k_{r1}$.

Numerical analysis showed that the computed concentration profiles are practically independent of the mass transfer coefficients in the membrane phase, k_SF and k_SR, and of the one in the acceptor phase, k_R. This fact proves indirectly that the diffusion resistances in these liquids are negligible. In contrast, the influence of the mass transfer coefficient of the donor phase, k'_F, and the rate constant k_{r2} is significant. The effect of the complex $k_e = k_{f1}k_{f2}/k_{r1}$ was less pronounced. As a result, the values presented in Table 1 were obtained for these parameters.

TABLE 1

n (rpm)	k_F (m/s)	k_e (m³/mol·s)	k_{r2} (m³/mol·s)
30	2.71×10^{-6}	13.05	1.083×10^{-8}
50	3.46×10^{-6}	13.05	1.083×10^{-8}
65	4.46×10^{-6}	13.05	1.083×10^{-8}

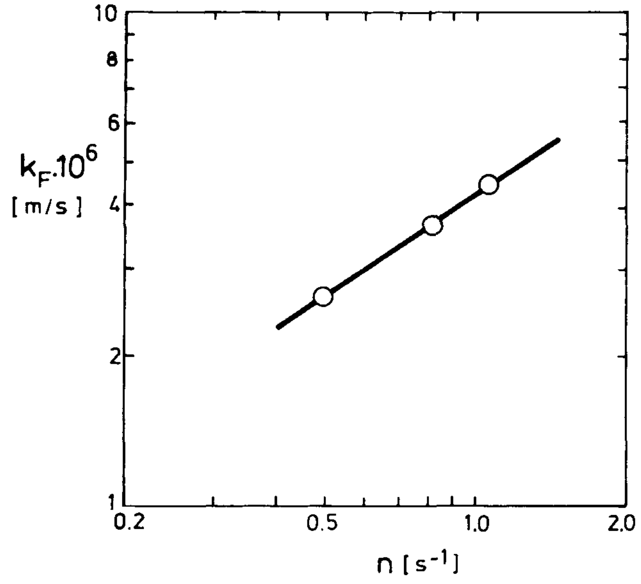

FIG. 5. Agitation speed vs donor phase mass-transfer coefficient.

The relationship of the donor side mass transfer coefficient k_F vs the stirring speed n obtained in our experiments is illustrated in Fig. 5. A good fit to these data was obtained by the correlation $k_F \approx n^{0.66}$, which we found to be in agreement with the data reported by Kataoka et al. (*24*).

CONCLUSIONS

On the basis of the hypothesis suggested for copper–chelate formation and decomposition in aqueous layers adjacent to both oil–water interfaces in a three-phase liquid system, a mathematical model is developed which describes copper ion transfer in a bulk-type liquid membrane process. The suggested mechanism accounts for diffusion in the three phases combined with homogeneous chemical reactions of copper complex formation and decomposition. The mass transfer coefficient k_F and the reaction rate constants are numerically evaluated for the particular case of copper(II) transfer in a two-compartment stirred diffusional cell using as a liquid membrane a 5 vol% solution of LIX 860 in C_{11}–C_{13} normal paraffins. It is established that the overall mass transfer rate in the diffusional cell used depends on: 1) the rate of mass transfer of copper ions from the donor solution bulk to the reaction zone FS adjacent to the interface, and 2) the rate of chemical reaction of copper complex decomposition in the acidic acceptor phase reaction zone.

SYMBOLS

a	interfacial area (m^2)
V	volume (m^3)
t	time (s)
j	flux ($mol/m^2 \cdot s$)
r	reaction rate ($mol/m^3 \cdot s$)
$m_{F,R}$	distribution coefficient of copper (—)
m_{HRF}, m_{HRR}	distribution coefficient of oxime (—)
k	mass transfer coefficient (m/s)
k_{f1}, k_{r1}	forward and reverse rate constants for the first reaction step ($m^3/mol \cdot s$)
k_{f2}, k_{r2}	forward and reverse rate constants for the second reaction step ($m^3/mol \cdot s$)
X, [ ]	species concentration (mol/m^3)
n	stirring speed (rpm)
F	donor aqueous phase
R	acceptor aqueous phase
S	organic liquid membrane
HR	oxime
CuR^+, CuR_2	organic–copper complexes
A	function defined by Eq. (23)
B	function defined by Eq. (22)
Φ	objective function defined by Eq. (35)

Subscripts

F	refers to the donor phase
S	refers to the membrane phase
R	refers to the acceptor phase
S/F	refers to the interface between S and F phases
S/R	refers to the interface between S and R phases
FS	refers to the reaction zone in the F phase
RS	refers to the reaction zone in the R phase
SF, SR	boundary layers in the S phase
HR	refers to the oxime

Superscripts

0	denotes initial value

REFERENCES

1. G. Yagodin, Y. Lopukhin, E. Yurtov, T. Gusseva, and V. Sergienko, *Proc. ISEC '83.*
2. P. O'Hara and M. Bohrer, *J. Membr. Sci., 44,* 273 (1989).
3. K. Yoshizuka, K. Kondo, and F. Nakashio, *J. Chem. Eng. Jpn., 19,* 312 (1986).

4. R. Chiarizia, A. Castagnola, P. Danesi, and E. Horwitz, *J. Membr. Sci.*, *14*, 1 (1983).
5. H. Bart, A. Baker, D. Lorbach, and R. Marr, *Chem. Eng. Sci.*, *60*, 169 (1988).
6. P. Danesi, E. Horwitz, G. Vandegrift, and R. Chiarizia, *Sep. Sci. Technol.*, *16*, 201 (1981).
7. I. Komasawa, T. Otake, and T. Yamashita, *Ind. Eng. Chem., Fundam.*, *22*, 127 (1983).
8. J. P. Tallarico, R. D. Noble, and G. J. Hanna, *Sep. Sci. Technol.*, *24*(3&4), 199–217 (1989).
9. D. S. Flett, D. N. Okuhara, and D. R. Spink, *J. Inorg. Nucl. Chem.*, *35*, 2471–2487 (1973).
10. I. Komasawa, T. Otake, and T. Muraoka, *J. Chem. Eng., Jpn.*, pp. 204–208 (1980).
11. C. J. Valdes, W. C. Cooper, and D. W. Bacon, *Proc. ISEC '80*, Paper 80-38.
12. R. J. Whewell, M. A. Hughes, and C. Hanson, *Proc. ISEC '77*, pp. 185–192.
13. T. Kojima and T. Miyauchi, *Ind. Eng. Chem., Fundam.*, *20*, 14–20 (1981).
14. H. Freiser, in *Developments in Solvent Extraction* (S. Alegret, ed.), Ellis Horwood, Chichester, 1988, pp. 31–35.
15. S. P. Carter and H. Freiser, *Anal. Chem.*, *52*(3), 511–514 (1980).
16. K. Akiba and H. Freiser, *Anal. Chim. Acta*, *136*, 329 (1982).
17. G. A. Kordosky, *The Chemistry of Metals Recovery Using LIX Reagents*, Minerals Industry Division Red Book, Henkel Corp., 1987–1988.
18. G. Schwarzenbach and H. Flashke, *Die komplexometrische Titration*, Stuttgard, 1965, p. 203.
19. G. M. Ritcey and A. W. Ashbrook, *Process Metallurgy, Part I, Solvent Extraction, Principles and Applications to Process Metallurgy*, Elsevier, Amsterdam, 1984, p. 321.
20. C. A. Fleming, M. J. Nicol, R. D. Hancock, and Finkelstein, "The Kinetics of the Extraction of Copper by LIX65N and LIX63: Discussion of the Rate Law," in *Proc. Int. Solv. Extr. Conf. ISEC '77*, p. 193.
21. S. Y. Ivakhno, A. W. Afanasiev, and G. A. Yagodin, *Itogi Nauki Teck., Neorg. Khim.*, *13*, 74 (1985).
22. *TUTSIM on IBM PC Computer*, User's Manual, Meerman Automation, The Netherlands, 1988.
23. J. A. Nelder and R. Meed, *Comput. J.*, *7*, 308–331 (January 1965).
24. T. Kataoka, T. Nishiki, and K. Ueyama, *Bull. Chem. Soc. Jpn.*, *55*(4), 1306–1309 (1982).

Received by editor March 18, 1991