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# Study of the Kinetics of Copper Extraction with (*anti*)-2-Hydroxy-5-nonylbenzophenone Oxime Using a Rotating Diffusion Cell

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## Abstract

A rotating diffusion cell was used to study the chemical reaction in which copper is transferred from an aqueous sulfate phase to an organic phase containing a copper-complexing agent (purified *anti*-2-hydroxy-5-nonylbenzophenone oxime) dissolved in *n*-decane. A mathematical model was developed to describe the contributions of the kinetic and diffusive resistances to the overall resistance to mass transfer. Application of this model to the experimental data enabled an overall rate equation for the reversible copper extraction reaction to be written. The active oxime species in the extraction reaction was found to be the monomer with first-order kinetics. The extraction reaction rate was also found to be dependent on aqueous phase hydrogen ion concentration with negative first-order kinetics. The extraction rate constant was determined as $1.3 \times 10^{-5}$ cm/s. Assumption that the reverse rate is dependent on hydrogen ion concentration

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with first-order kinetics enabled the reverse rate constant to be calculated as $6.8 \times 10^{-3}$ $cm^4/mol \cdot s$.

## INTRODUCTION

Copper extraction with organic chelating reagents has been studied during the past 15 years. One of the chelating reagents used industrially is *anti*-2-hydroxy-5-nonylbenzophenone oxime (*anti*-HNBPO), the active ingredient of LIX65N sold commercially by Henkel Corp. During the course of extraction, water of hydration is removed from the copper cation and replaced by chelating groups. The resulting coordination compound is soluble in the organic phase. An overall equation for this reaction is

$$Cu^{2+}(H_2O)_{x(aq)} + 2RH_{(org)} \rightleftharpoons CuR_{2(org)} + 2H^+_{(aq)} + xH_2O_{(aq)} \quad (1)$$

where HR is the *anti*-HNBPO and $CuR_2$ is the copper/oxime coordination compound. The structures of these two compounds are presented in Fig. 1.

Other investigations of copper extraction kinetics using *anti*-HNBPO are summarized in Table 1. Most experimenters reported first-order kinetics with respect to copper ion concentration, but there is little agreement among the observed reaction orders with respect to oxime and hydrogen ion concentrations. These inconsistencies are the result of the following:

1. The oxime used in their experiments was seldom purified; hence, impurities have altered the kinetic behavior.
2. Some experimenters failed to account for the dimerization of the oxime, using analytic oxime concentration rather than monomeric oxime concentration for the active oxime species.
3. The experimental apparatuses and concentrations were different.
4. The mathematical models applied to each of their apparatuses did not quantify the diffusional contribution to the overall resistance to mass transfer due to indescribable hydrodynamics.
5. The experimental techniques employed do not provide an accurate measurement of the interfacial area.
6. The aqueous phase media were different (sulfate, nitrate, chloride).
7. Different organic diluents were used.

In this study the oxime was purified and dimerization was accounted

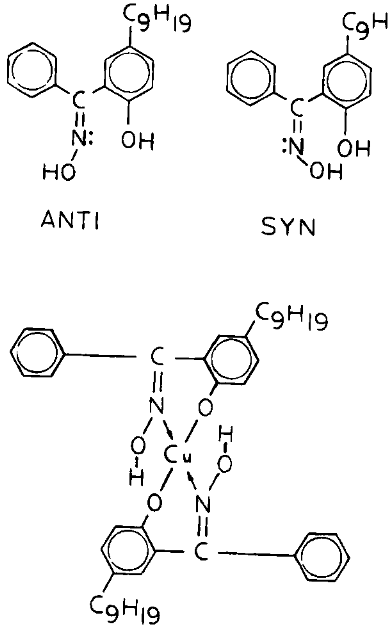

FIG. 1. Structures of the *anti* and *syn* isomers of 2-hydroxy-5-nonylbenzophenone oxime (MW = 339.0) and the extracted copper complex of the *anti* isomer (MW = 739.54).

for by using a dimerization constant equal to 120 $dm^3/mol$ (*21*). The rotating diffusion cell (*22*) was chosen since the hydrodynamics are well defined (*23, 24*) and the interfacial area is easily measured accurately. The rotating diffusion cell is shown in Fig. 2.

This paper reports data for copper extraction under the following conditions:

1. Aqueous total copper concentration is 1000 ppm in a sulfate medium.
2. The pH range is from 2.0 to 3.0.
3. The analytic oxime concentration ranges from 0.05 to 0.125 $mol/dm^3$.
4. The concentration of the aqueous stripping phase is 0.5 $mol/dm^3$ sulfuric acid.

TABLE 1
Extraction Kinetics of Copper Using 2-Hydroxy-5-nonylbenzophenone Oxime[a]

| Ref. | Apparatus | Active oxime concentration | Was oxime purified? | Observed reaction orders | | | pH | Experimental concentration (mmol/dm$^3$) | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | $[Cu^{2+}]$ | $[H^+]$ | [RH] | | $[Cu^{++}]$ | $[RH]_{analytic}$ |
| *1* | Stirred-cell | | | 1 | −0.5 to −0.75 | | | | |
| *2* | AKUFVE | Analytic | No | 1 | −1 | 1 | 3.02 to 4.45 | | 3.3[h] |
| *3* | AKUFVE | Analytic | No | 1 | −0.85 to −1.22 | 1.01 to 1.27 | 2 to 4.5 | 0.13 to 0.91 | 3 to 20[h] |
| *4* | Single-drop | Analytic | No | 1 | 0 | 0.5 | 3.0 | 16 | 33 to 153[h] |
| *5* | AKUFVE | Analytic | No | 1 | 1[b] | 1.0 to 1.3 | 3.02 to 4.45 | 0.15 | 3 to 20[h] |
| *6* | Single-drop | Analytic | No | 1 | N.D. | 0.5[c] | 1.77 | 45 | 100 to 1000[h] |
| *7* | Lewis cell | Analytic | Yes | 1 | 0[d] and −1[e] | 1.26 | 3.7 to 4.0 | 50 | 0.10 to 10 |
| *8* | Single-drop | Monomeric | Yes | 1 | −1 | 2 | 1.6 | 41.5 | 100 |
| *9* | Lewis cell | Analytic | Yes | 1 | −0.6 | 1.10 | 4.0 | 75 | 3 to 13 |
| *10* | Single-drop | Monomeric | N.A. | 1 | −1 | 2 | | | |
| *11* | Lewis cell | Analytic | Yes | 0 to 1 | 0 to −2 | 1 to 2[f] | 3.6 to 4.2 | 25 | 2 to 13 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| *12* | Stopped-flow spectrophotometer | Analytic | No | 1 | 0 | 1 | 2.1 to 4.9 | 0.027 to 0.054 | 2.4 to 7.1 |
| *13* | Stirred-cell | Analytic | Yes | 1 | −1 | 2 | 3 to 4 | 0.01 | 0.75 to 3.75 |
| *14* | Single-drop | Monomeric | Yes and no | 1 | −1 | 1 | 1.07 to 4.4 | 10 to 200 | 8 to 40[g] |
| *15* | Stirred-transfer cell | Monomeric | Yes and no | 1 | −1 | 1 | 1.0 to 2.5 | 10 to 200 | 17 to 170[g] |
| *16* | Stirred-cell | Monomeric | No | 0.5 | −0.5 | 1 | 0.8 to 5.0 | 0.01 to 50 | 50 to 100[h] |
| *17* | Liquid jet recycle reactor | Analytic | Yes | 1 | Empirical | Empirical | 1.3 to 3.9 | 30 to 200 | 24 to 770[i] |
| *18* | Stirred-transfer cell | Monomeric | Yes | 1 | −1 | 1 and 2 | | | 0.2 to 300[g] |
| *19* | Rotating diffusion cell | Monomeric | Yes | 1 | −1 | 1 | 3.3 to 4.5 | 15.7 to 157 | 50 to 125[g] |

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[a] N.A. = not applicable. N.D. = not determined.

[b] With regard to back reaction.

[c] Averaged from published data.

[d] At high pH.

[e] At low pH.

[f] Depends upon pH.

[g] Monomeric concentration.

[h] Calculated using Ref. *20* analysis.

[i] Based on 73% active isomer and MW = 339.5.

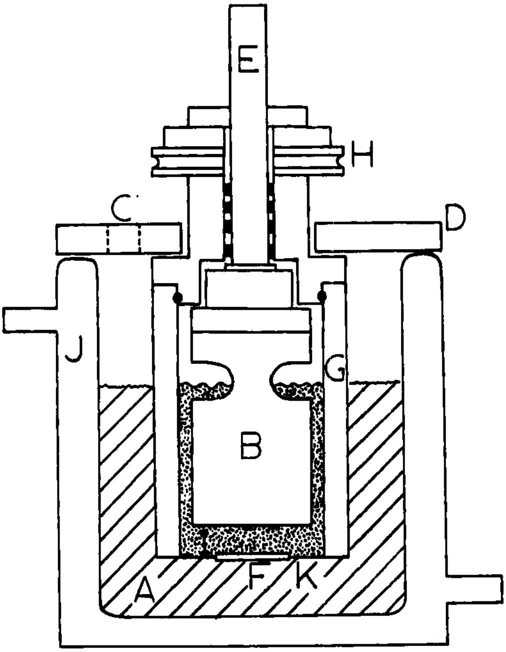

FIG. 2. Schematic diagram of the rotating diffusion cell. A: Outer phase. B: Stationary Teflon baffle. C: Outer phase sample port. D: Plexiglas cover plate. E: Hollow shaft supporting baffle and entire inner cell. F: Active area of Millipore filter. G: Plexiglas cell housing. H: Pulley ring. I: Inner phase. J: Jacketed glass vessel. K: Collapsed (inactive) area of filter.

## REAGENTS

All chemicals used in this study were AR grade.

1. Anhydrous copper sulfate.
2. *Anti*-HNBPO was purified from commercially available LIX65N (heavy solids) as described in Ref. *25*.
3. The diluent for the oxime was *n*-decane.
4. The extracted aqueous phase was prepared by dissolving anhydrous copper sulfate in a sodium citrate buffer for oxime kinetics experiments and in deionized water for hydrogen ion kinetics experiments. Concentrated sulfuric acid was used to adjust the pH. This solution was presaturated with *n*-decane by contacting it with a small volume of *n*-decane in a separatory funnel for 24 h.

5. The stripping aqueous phase was prepared by dissolving concentrated sulfuric acid in deionized water. This solution was also presaturated with *n*-decane in the manner described above.
6. The organic phase was prepared by weighing the copper/oxime salt into a separatory funnel containing 50.0 dm$^3$ *n*-decane. The copper was removed using sulfuric acid washes: ten 50.0 dm$^3$ washings were added to, mixed in, and removed from this separatory funnel, and one final washing was permitted to remain in the separatory funnel overnight to guarantee complete copper removal.

## EXPERIMENTS

***Equilibrium Experiments.*** Equal volumes of aqueous and organic phases (10 cm$^3$) were placed in a 50-cm$^3$ flask which was shaken periodically and immersed in the constant temperature bath. A couple of experiments were conducted in a constant temperature shaker bath.

***Membrane Preparation*** (*26*). The membranes used were 0.22 μm Millipore Type GS (48 cm diameter). Millipore membrane cement was used to mount the membranes onto the Plexiglas cell housing. This was allowed to dry for at least 1 h. Extra cement was then applied around the edges to insure a complete seal. Another 1 h drying period followed. The inner cell was inverted and placed in the clamp. The Plexiglas cell housing was attached and secured by an O-ring. The inner cell was then rotated at speeds of 150–250 rpm. While the membrane was rotating, a collapsing solution (33% dioxane, 33% dichloroethane, 33% hexane, and 1% water) was applied with a paint brush to the membrane surface. It was applied from 0.5 cm away from the center of the membrane outward to the edge of the membrane. This reduces the active membrane diameter to about 1 cm and renders the remainder of the membrane impermeable. After the membrane has dried overnight, it is water washed two or three times in order to remove a water-soluble surfactant contained within the pores. The membrane is dried overnight in a desiccator prior to use.

***Starting a Kinetics Experiment.*** The circulating temperature bath is turned on and set to 25.0°C. The outer aqueous phase is added from a 250 cm$^3$ buret; a total of 230 cm$^3$ is added to the jacketed glass vessel. A 40.0-cm$^3$ aliquot of the inner phase solution is pipetted into a volumetric flask which is then inserted into the constant temperature bath. A period of 30 min or so is required to bring both phases up to temperature. The membrane is removed from the desiccator and rendered hydrophobic by placing several drops of a 2% solution of dimethyldichlorosilane in carbon tetrachloride on both surfaces. Once this solution has evaporated, the membrane is impregnated with the oxime/*n*-decane organic phase. When it appears that the entire membrane is saturated with the organic phase, the inner aqueous phase is added to the Plexiglas cell housing. The housing is immediately secured in place and the outer phase solution is aligned and raised until the liquid level is the same for both aqueous phases. The rpm controller is turned on and the stopwatch is started. Samples are withdrawn every half hour or so using pipettes. The samples are diluted with deionized water and analyzed for copper using absorption spectrophotometry.

The aqueous phases can be oriented in two ways: the extracted aqueous phase (copper rich) can either be the inner phase or the outer phase. Experiments in which the extracted phase is the inner phase and the stripping phase is the outer phase are termed "normal phase" experiments, while those in which the extracted phase is the outer phase are termed "reverse phase" experiments.

***Oxime Kinetics Experiments.*** The extracted phase pH is maintained constant using a sodium citrate/sodium hydroxide buffer. Membranes were used for only one experiment each. All oxime kinetics experiments were "normal phase" experiments. Two cubic centimeter samples were withdrawn using an adjustable pipette inserted through the sample port in the Plexiglas cover plate.

***Hydrogen Ion Kinetics Experiments.*** The extracted phase was unbuffered for these runs. Membranes were washed with hexane and reused two or three times each. Some of these experiments were "reverse phase" and some were "normal phase." One cubic centimeter samples were withdrawn by using a pipette inserted through the hollow shaft for the reverse phase experiments.

## MATHEMATICAL MODEL (*19*, *27*)

The basis of the resistance model is that the extraction rate is first-order with respect to copper concentration and the reaction occurs at the aqueous/organic interface. The overall reversible reaction can be expressed as

$$\mathrm{Cu}^{2+}_{(\mathrm{aq})} \underset{k_{r,\mathrm{ext}}}{\overset{k_{f,\mathrm{ext}}}{\rightleftharpoons}} \mathrm{CuR}_{2(\mathrm{org})} \tag{2}$$

where $k_{f,\mathrm{ext}}$ and $k_{r,\mathrm{ext}}$ are pseudo-first-order rate constants since they are functions of oxime and hydrogen ion concentrations:

$$k_{f,\mathrm{ext}} = k_f^* \frac{[\mathrm{HR}]^p_{\mathrm{active}}}{[\mathrm{H}^+]^q} \tag{3}$$

$$k_{r,\mathrm{ext}} = k_r^*[\mathrm{H}^+] \qquad \text{(assumed)} \tag{4}$$

The overall distribution coefficient, $K_{D,\mathrm{ext}}$, can be defined as

$$K_{D,\mathrm{ext}} \equiv \frac{k_{r,\mathrm{ext}}}{k_{f,\mathrm{ext}}} = \frac{[\mathrm{Cu}^{2+}]_{(\mathrm{aq})}}{[\mathrm{CuR}_2]_{(\mathrm{org})}} \tag{5}$$

Note that the overall distribution coefficient is not defined in the usual way of (organic/aqueous) partition. The equilibrium constant, $K_{\mathrm{eq}}$, can be expressed as

$$K_{\mathrm{eq}} = \frac{1}{K_{D,\mathrm{ext}}} \left\{ \frac{[\mathrm{H}^+]}{[\mathrm{HR}]_{\mathrm{active}}} \right\}^2 \tag{6}$$

The copper concentration profile within the rotating diffusion cell is illustrated in Fig. 3. The following set of flux equations can be written with regard to Fig. 3:

$$J = \frac{D_{\mathrm{ext}}}{\delta_{\mathrm{ext}}} A(C_1 - C_2) \tag{7}$$

$$J = aA(k_{f,\mathrm{ext}}C_2 - k_{r,\mathrm{ext}}C_3) \tag{8}$$

$$J = \frac{aD_{\mathrm{org}}}{t}(C_3 - C_4) \tag{9}$$

$$J = aA(k_{r,\mathrm{strip}}C_4 - k_{f,\mathrm{strip}}C_5) \tag{10}$$

$$J = \frac{D_{\mathrm{strip}}}{\delta_{\mathrm{strip}}} A(C_5 - C_6) \tag{11}$$

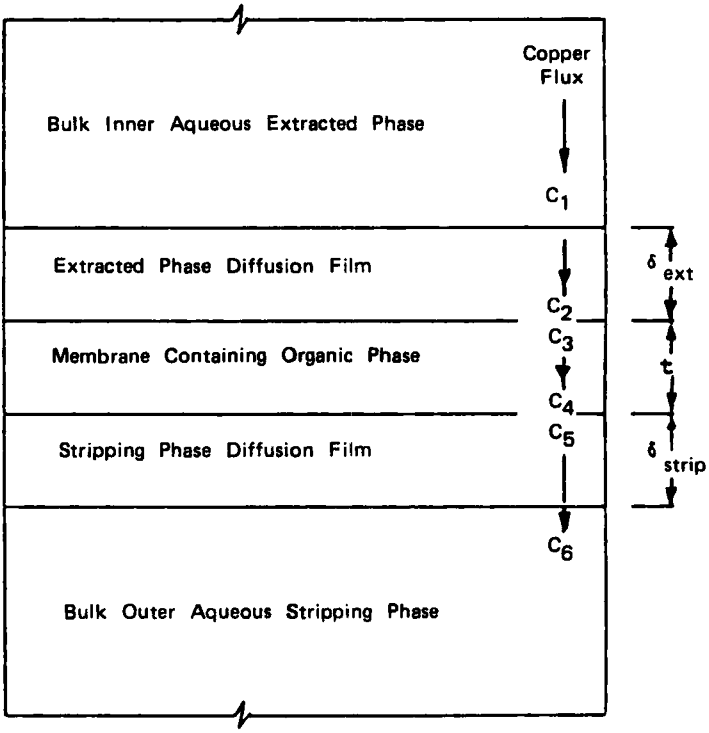

FIG. 3. Copper concentration profile within the rotating diffusion cell.

In the above flux equations, the variables are as follows:

$A$ = surface area of membrane
$a$ = porosity of the membrane
$C$ = concentration
$D$ = diffusivity
$J$ = flux
$t$ = membrane thickness
$\delta$ = diffusive film thickness

This set of equations can be manipulated in order to eliminate all of the concentrations except for $C_1$ and $C_6$. An overall mass transfer coefficient $k_0$ is defined, and the resulting equation is simplified based upon our experimental conditions. Incorporation of the Levich equation

$$\delta = 1.61D^{1/3}\nu^{1/6}\omega^{-1/2} \tag{12}$$

where $D$ = diffusivity, $cm^2/s$
$\nu$ = kinematic viscosity, $cm^2/s$
$\omega$ = angular velocity, rad/s

yields the final resistance model:

$$J = k_0AC_1 \tag{13}$$

where

$$\frac{1}{k_0} = 1.61D_{ext}^{-2/3}\nu^{1/6}\omega^{-1/2} + \frac{1}{ak_{f,ext}} \tag{14}$$

The concentration $C_6$ vanishes because it is multiplied by a small quantity which is the ratio of the extracted phase distribution coefficient to the stripping phase distribution coefficient.

The steady-state copper flux, $J$, is calculated by

$$J = \frac{(\Delta ppm)(V_{strip})}{(10^6)(MW)(\tau)} \tag{15}$$

where $J$ = steady-state flux of copper, mol/s
$\Delta$ppm = change in stripping phase copper concentration, ppm
$V_{strip}$ = average outer phase volume for run, $cm^3$
$\tau$ = run time, s
MW = molecular weight of copper, 63.54 g/mol

In general, the copper flux is dependent on angular velocity. Several experiments using identical concentrations must be run at different angular velocities in order to obtain flux per unit area data as a function of angular velocity. A straight-line plot of the reciprocal of the flux per unit area versus $\omega^{-1/2}$ will yield an intercept equal to the $(A/J)$ contribution to the kinetic resistance:

$$\left(\frac{A}{J}\right)_{\omega^{-1/2}\to 0} = \frac{1}{aC_1k_{f,ext}} \tag{16}$$

Most of the experimental concentrations dictate that the diffusive resistance in Eq. (14) is negligible relative to the kinetic resistance. In this case, the flux is no longer dependent on angular velocity; the $(A/J)$ value obtained at one angular velocity represents the kinetic contribution.

***Oxime Kinetics Experiments.*** Equation (3) can be substituted into Eq. (16) which, upon rearrangement, yields the following:

$$\left(\frac{A}{J}\right)_{\omega^{-1/2}\to 0} = \left(\frac{[\mathrm{H}^+]^q}{aC_1k_f^*}\right)[\mathrm{RH}]_{\mathrm{active}}^{-p} \tag{17}$$

Taking the logarithm of the above equation yields:

$$\log\left(\frac{A}{J}\right)_{\omega^{-1/2}\to 0} = -p\log[\mathrm{HR}]_{\mathrm{active}} + \log\left(\frac{[\mathrm{H}^+]^q}{aC_1k_f^*}\right) \tag{18}$$

Plotting log $(A/J)$ at infinite rotation $(\omega^{-1/2}\to 0)$ versus the log of each of the three possible active oxime concentrations (analytic, monomeric, and dimeric) should yield a straight line for the correct active oxime concentration having a slope equal to $(-p)$.

***Hydrogen Ion Kinetics Experiments.*** Equation (17) can be rearranged to give

$$\left(\frac{A}{J}\right)_{\omega^{-1/2}\to 0} = \left\{\frac{1}{aC_1k_f^*[\mathrm{RH}]_{\mathrm{active}}^p}\right\}[\mathrm{H}^+]^q \tag{19}$$

Taking the logarithm of the above equation and utilizing the definition of pH yields

$$\log\left(\frac{A}{J}\right)_{\omega^{-1/2}\to 0} = -q\,\mathrm{pH} + \log\left(\frac{1}{aC_1k_f^*[\mathrm{RH}]_{\mathrm{active}}^p}\right) \tag{20}$$

Plotting the log $(A/J)$ versus pH should yield a straight line having a slope equal to $-q$ and an intercept from which the forward rate constant $k_f^*$ can be elicited for the unbuffered case.

## RESULTS AND DISCUSSION

***Equilibrium Experiments.*** The results of the equilibrium experiments are presented in Tables 2 and 3. It is seen from Table 2 that monomeric

TABLE 2
Calculation of Distribution Coefficients ($K_D$) and Equilibrium Constants ($K_{eq}$) for Buffered Equilibrium Experiments

| Run | Initial analytic [RH] (mol/dm$^3$) | Final pH | $K_D$ | Equilibrium constants | | |
|---|---|---|---|---|---|---|
| | | | | Monomer | Dimer | Analytic |
| 4A | 0.05 | 2.5 | 0.108 | 1.53 | 1.76 | 0.186 |
| 4B | 0.05 | 2.5 | 0.108 | 1.53 | 1.76 | 0.186 |
| 4C | 0.10 | 2.5 | 0.0284 | 1.54 | 0.470 | 0.0722 |
| 4D | 0.10 | 2.5 | 0.0280 | 1.57 | 0.478 | 0.0733 |
| 4E | 0.125 | 2.5 | 0.0205 | 1.54 | 0.339 | 0.0556 |
| 4F | 0.15 | 2.5 | 0.0169 | 1.45 | 0.245 | 0.0421 |
| 4G | 0.15 | 2.5 | 0.0166 | 1.47 | 0.249 | 0.0427 |
| 4H | 0.05 | 2.9 | 0.325 | 0.0623 | 0.0553 | 0.00639 |
| 4I | 0.075 | 2.9 | 0.158 | 0.0661 | 0.0303 | 0.00422 |
| 4J | 0.10 | 2.9 | 0.0995 | 0.0661 | 0.0191 | 0.00296 |
| 4K | 0.10 | 2.9 | 0.100 | 0.0655 | 0.0186 | 0.00293 |

TABLE 3
Calculation of Distribution Coefficients ($K_D$) and Equilibrium Constants ($K_{eq}$) for Unbuffered Equilibrium Experiments

| Run | Initial analytic [RH] (mol/dm$^3$) | Final pH | $K_D$ | Equilibrium constants | | |
|---|---|---|---|---|---|---|
| | | | | Monomer | Dimer | Analytic |
| 4L | 0.05 | 0.4 | 311 | — | — | — |
| 4M | 0.10 | 0.4 | 299 | — | — | — |
| 4N | 0.10 | 1.67 | 0.0168 | 124 | 39.0 | 5.95 |
| 4O[a] | 0.10 | 1.78 | 0.0137 | 89.5 | 27.6 | 4.23 |
| 4P[a] | 0.10 | 1.77 | 0.0137 | 93.4 | 28.8 | 4.41 |

[a] Conducted in a temperature-controlled shaker bath.

oxime appears to be the active specie since the equilibrium constants calculated by using the monomeric concentration are the most constant at both pH values. The average equilibrium constant for the unbuffered case (Table 3) for pH of approximately 1.7 using monomeric oxime as the active specie is 102.

***Oxime Kinetics.*** The results of the oxime kinetics experiments are plotted in Figs. 4 and 5, and the straight-line fits using linear regression are summarized in Tables 4 and 5. Based on both the equilibrium

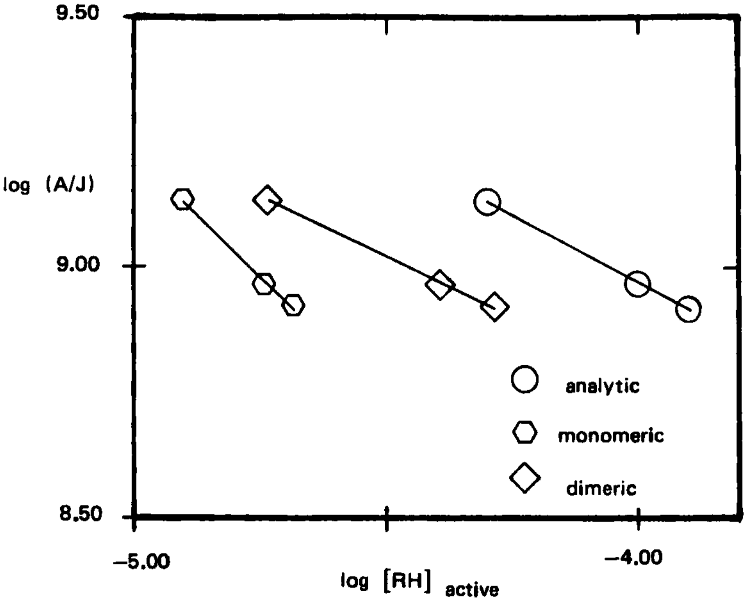

FIG. 4. Plot of log ($A/J$) vs log active oxime concentration for oxime experiments at pH = 2.5 (buffered).

TABLE 4
Linear Regression Results of Log ($A/J$) at Infinite Rotation vs Log of Oxime Concentrations for pH = 2.5

| | Active oxime concentration | | |
|---|---|---|---|
| | Analytic | Monomeric | Dimeric |
| Slope (= $p$) | −0.527 | −0.964 | −0.468 |
| Intercept | 6.86 | 4.41 | 6.92 |
| Correlation coefficient | 0.9998 | 0.9986 | 1.000 |

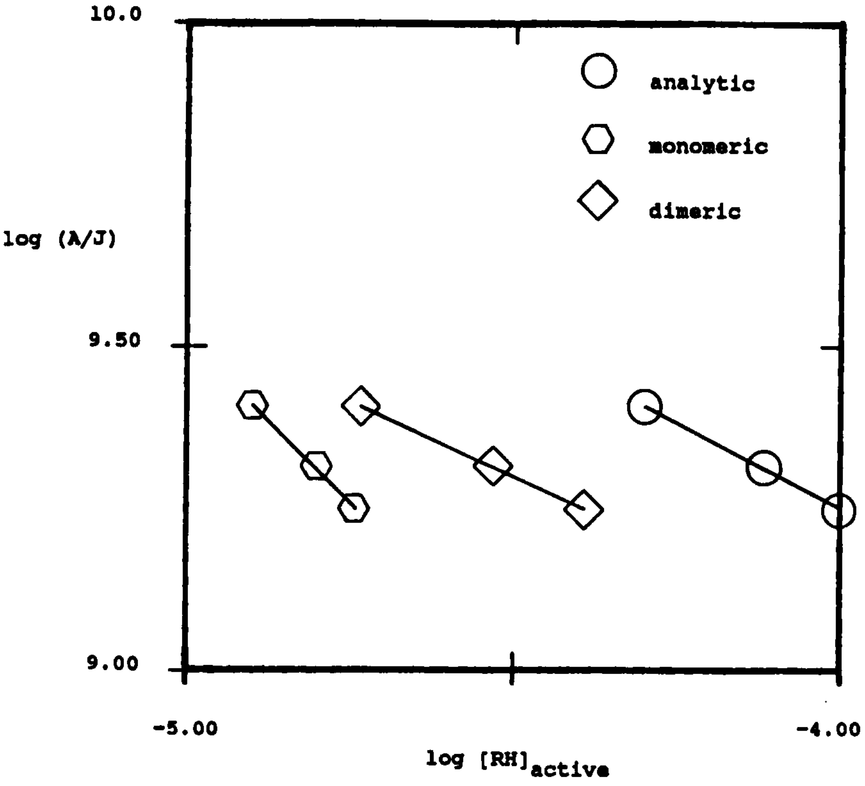

FIG. 5. Plot of log $(A/J)$ vs log active oxime concentration for oxime experiments at pH = 2.9 (buffered).

TABLE 5

Linear Regression Results of Log $(A/J)$ at Infinite Rotation vs Log of Oxime Concentrations for pH = 2.9

| | Active oxime concentration | | |
|---|---|---|---|
| | Analytic | Monomeric | Dimeric |
| Slope (= $p$) | −0.531 | −0.990 | −0.469 |
| Intercept | 7.13 | 4.56 | 7.19 |
| Correlation coefficient | 0.9982 | 0.9949 | 0.9991 |

experiments and the kinetics experiments, monomeric oxime appears to be the active oxime specie with first-order kinetics.

***Hydrogen Ion Kinetics.*** The results of the hydrogen ion kinetics experiments are shown in Table 6. These data are plotted in Fig. 6. The reference line having a slope of −1.0 fits the data within the error bars; hence, we conclude that negative first-order kinetics with respect to hydrogen ion concentration adequately describes the experimental data.

***Rate Constants.*** The intercept in Fig. 6 is used to determine the forward extraction rate constant $k_f^*$. The free (dissociated) copper concentration, $C_1$, is calculated as 80% of the total analytical copper concentration of 1000 ppm (*28*). The membrane porosity was specified by the manufacturer to be 0.75. Using these numbers with Eq. (20) enables the forward rate constant to be calculated as $1.3 \times 10^{-5}$ cm/s. The following equation is derived from the definition of $K_{D,\text{ext}}$ using Eqs. (3), (4), and (6):

$$k_r^* = \frac{k_f^*}{K_{\text{eq}}[\text{RH}]_m} \tag{21}$$

Substitution of the appropriate values of $K_{\text{eq}}$ and $[\text{RH}]_m$ into the above equation yields a reverse rate constant equal to $6.8 \times 10^{-3}$ cm$^4$/mol · s.

Reference *19* observed the same active species and reaction orders, and

TABLE 6
Hydrogen Ion Kinetic Experimental Results

| Run | Average pH | Log $(A/J)^a$ |
|---|---|---|
| 3A | 3.0 | 8.70 |
| 3B | 3.0 | 8.70 |
| 3C | 3.0 | 8.76 |
| 3D | 2.6 | 9.03 |
| 3E | 2.6 | 9.15 |
| 3F | 2.6 | 9.01 |
| 3G | 2.1 | 9.39 |
| 3H | 2.1 | 9.49 |
| 3I | 2.1 | 9.45 |
| 3J | 2.1 | 9.57 |

$^a(A/J)$ is calculated as cm · s/mol.

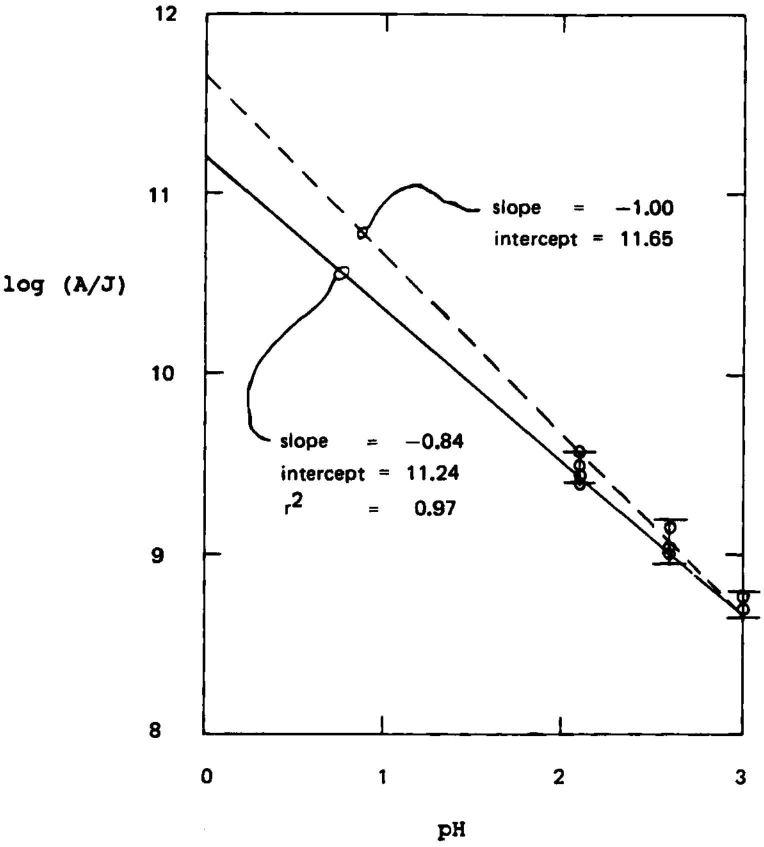

FIG. 6. Plot of log (*A*/*J*) vs pH for hydrogen ion kinetics experiments (unbuffered). The units for (*A*/*J*) are $cm^2 \cdot s/mol$.

reported a forward rate constant of $4.0 \times 10^{-6}$ cm/s using a rotating diffusion cell at a higher experimental pH range. Their value is 3 times smaller than the one reported here. Rather than measure copper flux directly as was done in this study, the copper flux was calculated from the rate of NaOH solution added to maintain a constant pH in the extracted copper phase. They assumed that all of the hydrogen ions liberated by the extraction reaction were neutralized by the NaOH.

It was observed in this study that the copper flux inferred from pH change is considerably less than that obtained from direct measurement of total copper. These findings are summarized in Table 7. The average ratio of measured copper flux to inferred copper flux is 1.54.

TABLE 7
Inferred Copper Flux vs Measured Copper Flux (normal phase experiments)

| Run | Initial pH | Final pH | $\Delta[H^+]$ (mol/dm$^3$) | Inferred $\Delta$ ppm $Cu^{2+}$ | Measured $\Delta$ ppm $Cu^{2+}$ | Ratio of (measured/inferred) |
|---|---|---|---|---|---|---|
| 9a | 2.532 | 2.434 | $7.44 \times 10^{-4}$ | 4.11 | 6.36 | 1.55 |
| 9b | 2.255 | 2.207 | $6.50 \times 10^{-4}$ | 3.59 | 5.31 | 1.48 |
| 9c | 2.104 | 2.058 | $8.79 \times 10^{-4}$ | 4.86 | 5.82 | 1.20 |
| 9d | 2.611 | 2.450 | $1.10 \times 10^{-3}$ | 6.07 | 10.26 | 1.69 |
| 9e | 2.605 | 2.465 | $9.45 \times 10^{-4}$ | 5.21 | 8.88 | 1.70 |
| 9f | 2.78 | 2.58 | $9.71 \times 10^{-4}$ | 5.36 | 9.32 | 1.74 |
| 9g | 2.81 | 2.56 | $1.21 \times 10^{-3}$ | 6.66 | 9.64 | 1.45 |
|  |  |  |  |  | Average | 1.54 |

## CONCLUSIONS

The rotating diffusion cell provided a good kinetic model for copper extraction using *anti*-HNBPO. Data for the hydrogen ion kinetics experiments showed good agreement between "reverse phase" and "normal phase" configurations under identical conditions. The resulting kinetic model for our experimental conditions is as follows:

$$\frac{\text{Rate}}{\text{Area}} = (1.3 \times 10^{-5}\ \text{cm/s})\,\frac{[\text{RH}]_m}{[\text{H}^+]}\,[\text{Cu}^{2+}]_{\text{aq}} - \left(6.8 \times 10^{-3}\,\frac{\text{cm}^4}{\text{mol} \cdot \text{s}}\right)[\text{H}^+][\text{CuR}_2]_{\text{org}}$$

Our measured copper fluxes were significantly larger than the copper fluxes calculated from the change in hydrogen ion concentration.

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