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Kinetics and Mechanism of Copper Extraction with Dialkylphosphoric Acids and Hydroxyoximes Studied by a Rotating Diffusion Cell

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A rotating diffusion cell with a porous membrane was used to study the kinetics of liquid/liquid extraction of copper ions using commercially important acidic extractants, i.e. dialkylphosphoric acids and hydroxyoximes. The reaction zone is assumed to be situated in a thin zone of varying thickness within the aqueous diffusion layer but adjacent to the aqueous/organic interface. The kinetic results were modeled by assuming a mixed control regime involving both chemical reaction and diffusion of reactants and products to and from the reaction zone as controlling steps. The "solubility" of the extractant in the aqueous phase, expressed in terms of the extractant distribution coefficient between the organic and aqueous phases, was shown to exert a considerable influence on the kinetic performance of the extractants. By the distribution coefficient being incorporated into the kinetic model, it is now possible to fully explain the behavior of the extraction rate curve with changing hydrogen ion concentration in the aqueous phase. The thickness of the reaction zone for hydroxyoximes is estimated to be of the order of $1.3 \times 10^{-3} \mu\text{m}$ while for dialkylphosphoric acids it is of the order of $0.7 \mu\text{m}$.

Introduction

Much controversy still exists as to the site of the chemical reaction involving divalent metal ions and acidic extractants in liquid/liquid extractions. The models which have been put forward to describe the kinetics of these reactions have adopted different approaches.

In one case it is considered possible that reactions involving ionic species are more likely to occur in a very thin zone on the aqueous side of the interface but within the diffusion layers (Hughes and Rod (1984), Dreisinger and Cooper (1989), Lazarova (1995), Harada and Miyake (1986), Chen and Zhu (1994), Tallarico et al. (1989)). In the limit, the reaction zone either can be of molecular dimensions when the reaction occurs at the molecular interface or can extend outward into the aqueous diffusion film or even further into the bulk of the aqueous phase. In any case, since ionic species are involved in the reaction, it is very unlikely for the reaction site to be situated in the organic phase due to its low dielectric constant.

Other researchers point to an interfacial reaction occurring at an interface of molecular dimensions (Albery et al. (1984), Flett et al. (1973), Nitsch (1984), Preston and Lukliska (1980)). These researchers have used the Langmuir and other adsorption isotherms to describe the extraction kinetics. In these studies a nonsaturated interface is assumed, but it is known that the interface is saturated at the range of extractant concentrations which are employed commercially. Kinetics have then been correlated by the interfacial population density of extractant molecules and the interfacial area. However, it should be noted that a dependence of rate on interfacial area cannot be held to prove a truly interfacial mechanism for the reaction, because the volume of a finite homogeneous interphase zone will be similarly dependent on the interfacial area. This last approach does not account for a variety of acid type extractants which exhibit different distribution

coefficients for partitioning between the water and organic phase.

The general model of Hughes and Rod (1984) presents the thin reaction zone theory. The metal extraction flux was formulated by considering the reaction processes occurring in the aqueous interfacial zone of reaction together with the diffusion equations. Rod (1986) has pointed out the importance of this approach to the liquid/liquid kinetic model for chemical engineering practice. In the model the hydrodynamic parameters such as the mass transfer coefficients are separated from the chemical and diffusion terms, so that the model can be applied to contactors with different geometry but using the same chemical systems. The model also incorporates appropriate equilibrium equations so that its application at positions near to equilibrium (industrial contactors) and far away from equilibrium (initial rate studies) is possible.

The "solubility" of dialkylphosphoric acid and hydroxyoxime extractants in water is governed by the distribution of the extractant between the organic and aqueous phases, which in turn depends on (i) the type of diluent used, (ii) the aqueous phase pH, and (iii) the structure of the organic extractant molecule. For any organic acid extractant it is expected that the aqueous phase would be favored by increased pH, increased polarity of the extractant molecule (at a given pH), and decreased molecular weight. In addition to the above, the degree of branching in any hydrophobic side-chain group could affect the distribution coefficient of the extractant molecules between the two phases. This aspect of the liquid/liquid extraction of metals by organic acids has not been highlighted by previous workers.

The purpose of this work is to explore further the model of mass transfer with chemical reaction (MTWCR) which was proposed by Hughes and Rod (1984) and to illustrate the dependence of the extraction kinetics on the changing solubility of the extractant in the aqueous phase.

We have explored a series of extractants from the hydroxyoxime and dialkylphosphoric acid types. Results for the rates of extraction with these extractants

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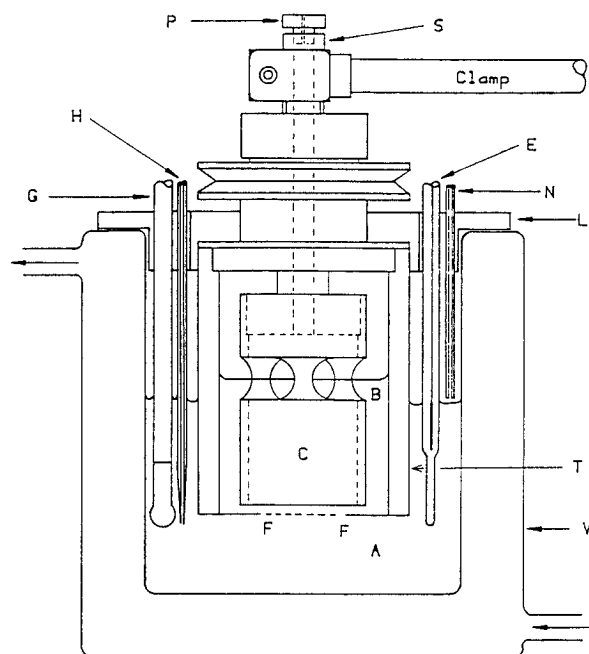


Figure 1. Diagram of the rotating diffusion cell (RDC). Key: A = aqueous phase, B = organic phase, C = P.T.F.E. baffle, E = calomel electrode, F = membrane, G = glass electrode, H = titrant delivery tube, L = perspex lid, N = nitrogen purge tube, P = P.T.F.E. plug, S = stainless steel hollow shaft, T = rotating chamber, V = stationary chamber (thermostatted glass vessel).

and the fit of the adjusted model to kinetic data are reported here.

Experimental Procedure

1. Reagents. The copper sulfate and the diluents were of analar grade. The dialkylphosphoric acids and hydroxyoximes were used in their purified forms (Kuipa (1995)). In all cases the purity of the extractants was above 98%. Water for interfacial tension measurements was double distilled.

2. Kinetic Experiments. The rotating diffusion cell (RDC) was used to study the kinetics in this work. The RDC was originally applied to metal extraction by Albery and Fisk (1981) and is shown in Figure 1. An important part of the RDC is a thin porous membrane which is attached to the bottom of a cylinder rotating round its axis. The porous membrane, in this case a 0.22 μm pore size Millipore type GS membrane with a porosity of 68%, provides a constant interfacial area that is undisturbed by flow patterns. The rotating cylinder which contains the lighter organic phase is placed in a stationary vessel filled with the heavier aqueous phase. The surface tension locates the interface between the aqueous and organic phases at the membrane surface. The rotation of the cylinder creates laminar flows both above and below the membrane disk. These laminar flows have been mathematically described, and an approximate solution regarding the thickness of the boundary layers, Z_D (m), as a function of the rotation speed, ω (Hz), kinematic viscosity, ν (Pa s), and diffusivity, D (m^2/s), is given by (Levich (1962), Albery (1975)):

$$Z_D = 0.643\omega^{-1/2}\nu^{1/6}D^{1/3} \quad (1)$$

Equation 1 is known as the Levich equation. The ability to calculate the diffusion barrier, Z_D , permits the

calculation of concentration gradients in the cell and consequently the concentration of reactants at the interface.

The inner cylinder has a inside baffle which counteracts wall effects on flow and produces rotating disk hydrodynamics on the inside of the membrane. The baffle prevents the lighter solution from rotating together with the motion of the cylinder. The release of protons from the organic phase into the aqueous phase during the extraction was followed by the pH-stat technique, in which the pH of the aqueous solution is controlled to a preset value by the addition of small amounts of a standardized base to neutralize the protons being released by the extraction reaction. A radiometer pH-stat apparatus consisting of (i) a PHM 82 standard pH meter, which was comprised of a G2040C glass electrode and a K4040 calomel reference electrode, (ii) an ABU 80 autoburette, (iii) a TTT 80 titrator, and (iv) a REC 80 servograph was used.

In all the kinetic experiments, 50 mL of the organic phase containing the extractant was contacted with 190 mL of the aqueous phase at a certain pH. The concentration of the extractant and copper(II) ions was 0.05 and 0.01 M, respectively. When the effect of varying the aqueous phase pH on the flux of metal transfer was studied, the pH was varied between 3 and 5.5. These boundaries were dictated by the lack of sensitivity of the pH-stat technique at pH values lower than 3 and the formation of metal-hydroxy flocs where possible at pH values greater than 5.5. All other experiments were carried out at pH 4.5.

The kinetic results were analyzed using the linear plots of the inverse flux against the inverse square root of the rotation speed (the Levich plot). The slope of the Levich plot is made up of bulk physical properties and refers to the diffusion of the components to the membrane surface and away from it. The intercept, on the other hand, is made up of an interfacial transfer term and a term representing transfer across the membrane.

The kinetic performance of extractants within a homologous series was compared by analyzing the extraction fluxes obtained at the same rotational speed of the RDC (3 Hz) and other operating variables, e.g. concentration, pH etc., being constant.

3. Extractant "Solubility" in the Aqueous Phase. The solubility of dialkylphosphoric acids in water was determined by contacting 0.05 M solutions of the extractants in either heptane or toluene, with water at the appropriate pH, followed by the total oxidation of the aqueous phase samples by potassium persulfate. The liberated phosphate ion was then determined spectrophotometrically as the molybdivanadophosphoric acid complex at 460 nm with a 4 cm path length cell (Menzel and Corwin (1965)). The calibration graph was plotted on results that were obtained by converting known amounts of potassium dihydrogen orthophosphate into the molybdivanadophosphoric acid complex.

In the case of hydroxyoximes, aqueous washing of the organic phase was first carried out in order to minimize the presence of any low molecular weight oximes. The Pye-Unicam ultraviolet spectrophotometer (SP8-100) was used to scan the wavelengths of the aqueous solutions from the shake-outs of 0.05 M solutions of the oxime in either heptane or toluene at the appropriate pH. A calibration was carried out on the areas under the peaks between 400 and 258 nm.

The interfacial tension between the organic and aqueous phases was determined by the drop volume

method at 25 ± 1 °C and pH 4.5 after pre-equilibration of the two phases.

Modeling of the Mass Transfer Process

Two classes of acid extractants, i.e. dialkylphosphoric acids and hydroxyoximes, are now treated by the MTWCR model.

Dialkylphosphoric acids exist as dimeric molecules in nonpolar organic diluents. They react with copper ions in the aqueous phase according to the following reaction:



This reaction is characterized by an overall extraction constant, K_{ex} , which is defined by the following equation:

$$K_{\text{ex}} = \frac{\bar{C}_{\text{CuR}_2(\text{HR})_2} C_{\text{H}^+}^2}{C_{\text{Cu}^{2+}} \bar{C}_{(\text{HR})_2}^2} \quad (3)$$

On the other hand, hydroxyoximes mainly exist as monomers in the organic phase and will react with copper ions in the aqueous phase according to the reaction:



The overall extraction constant for this reaction is defined as

$$K_{\text{ex}} = \frac{\bar{C}_{\text{CuR}_2} C_{\text{H}^+}^2}{C_{\text{Cu}^{2+}} \bar{C}_{\text{HR}}^2} \quad (5)$$

The overall reactions described by eqs 2 and 4 consist of a number of consecutive steps:

Step 1: (a) distribution of the active component of the extractant between the organic phase and the aqueous phase reaction zone; (b) diffusion of the metal ion from the bulk of the aqueous phase to the reaction zone which is situated within the aqueous diffusion layer but adjacent to the aqueous/organic interface.

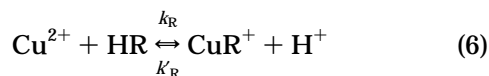
Step 2: chemical reaction in the aqueous phase reaction zone and formation of the metal-organic complex.

Step 3: partition of the reaction product into the organic phase. Step 2 consists of two consecutive steps involving the formation of the 1:1 complex and the 1:2 complex in the aqueous phase reaction zone.

The undissociated form of the monomer molecule of the hydroxyoxime extractant, HR, was identified as the active species in the reaction zone because these extractants have a high $\text{p}K_{\text{a}}$ value in water. In contrast, the dissociated form of the dimer molecule for dialkylphosphoric acids in water, HR_2^- , was assumed to be the active species; since in the pH range studied HR_2^- would be the most surface active species.

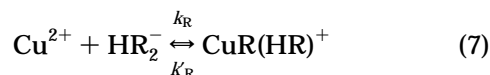
The following reactions are assumed to be rate controlling.

(i) for hydroxyoximes



where k_{R} and k'_{R} are the forward and reverse second-order rate constants, respectively.

(ii) for dialkylphosphoric acids



The Model for Hydroxyoximes. Now, using eqs 6 and 7 as rate controlling steps and applying the two-film theory (Whitman and Lewis (1924)) together with Astarita's equation (1967) the flux, J_{HR_i} , of the extractant at the interface is described as follows (Kuipa (1995)):

$$J_{\text{HR}_i} = \left[\frac{\theta_1}{D_{\text{c}}} C_{\text{M}^{2+}}^2 \left\{ 1 - \frac{\bar{C}_{\text{MR}_{2i}} C_{\text{H}^+}^2}{K_{\text{ex}} \bar{C}_{\text{HR}_i}^2 C_{\text{M}^{2+}}^2} \right\} (\bar{C}_{\text{HR}_i}^2 - \bar{C}_{\text{HR}}^2) \right]^{1/2} \quad (8)$$

where θ_1 is a grouped kinetic parameter, which is defined by the following equation:

$$\theta_1 = k_{\text{R}} D_{\text{HR}} \quad (9)$$

and D_{c} is the extractant distribution coefficient. When the model is used for cases in which the pH of the aqueous phase is varied, D_{c} is given as a function of pH. For the hydroxyoximes the dependence of D_{c} on pH can be estimated by the following expression,

$$D_{\text{c}} = \frac{P_{\text{HR}}}{1 + \frac{10^{-\text{p}K_{\text{a}}}}{10^{-\text{pH}}}} \quad (10)$$

The interfacial concentrations in eq 8 are defined by the following equations:

(i) for the organic phase

$$\bar{C}_{\text{HR}_i} = \bar{C}_{\text{HR}} - \frac{J_{\text{HR}_i}}{\bar{k}_{\text{HR}}} \quad (11)$$

$$\bar{C}_{\text{MR}_{2i}} = \bar{C}_{\text{MR}_2} - \frac{J_{\text{HR}_i}}{2\bar{k}_{\text{MR}_2}} \quad (12)$$

(ii) for the aqueous phase

$$C_{\text{M}^{2+}} = C_{\text{M}^{2+}} - \frac{0.5 J_{\text{HR}_i}}{2k_{\text{M}^{2+}}} + \left[\frac{0.5 D_{\text{HR}}}{D_{\text{H}^+} P_{\text{HR}}} \right] \{ \bar{C}_{\text{HR}_i} - C_{\text{HR}} P_{\text{HR}} \} \quad (13)$$

where θ_2 is a grouped physical property parameter

$$C_{\text{H}^+} = C_{\text{H}^+} + \frac{J_{\text{HR}_i}}{k_{\text{H}^+}} - \left[\frac{0.5 D_{\text{HR}}}{D_{\text{H}^+} P_{\text{HR}}} \right] \{ \bar{C}_{\text{HR}_i} - C_{\text{HR}} P_{\text{HR}} \} \quad (14)$$

$$C_{\text{HR}} = \frac{1}{P_{\text{HR}}} \left[\frac{-\theta_2 C_{\text{H}^+}^2}{4K_{\text{ex}} C_{\text{M}^{2+}}} + \sqrt{\left\{ \frac{\theta_2 C_{\text{H}^+}^2}{4K_{\text{ex}} C_{\text{M}^{2+}}} \right\}^2 + \frac{C_{\text{H}^+}^2}{K_{\text{ex}} C_{\text{M}^{2+}}} \left\{ \bar{C}_{\text{MR}_{2i}} + \frac{\theta_2 \bar{C}_{\text{HR}_i}}{2} \right\}} \right] \quad (15)$$

which is defined by the following expression.

$$\theta_2 = \frac{P_{\text{MR}_2} D_{\text{HR}}}{P_{\text{HR}} D_{\text{MR}_2}} \quad (16)$$

$$C_{MR_2} = K_{ex} \left(\frac{C_{HR}^2 C_{M^{2+}}}{C_{H^+}^2} \right) \frac{P_{HR}^2}{P_{MR_2}} \quad (17)$$

The set of eqs 8–17 is the overall model for the extraction of copper by hydroxyoximes.

The model for dialkylphosphoric acids is shown below as

$$J_{(HR)_{2i}} = \left[\left(\frac{\theta_1}{D_c^2} \frac{C_{MI}^{2+}}{C_{HI}^+} \right) \left\{ 1 - \frac{\bar{C}_{MR_2(HR)_{2i}} C_{H^+}^2}{K_{ex} \bar{C}_{(HR)_{2i}} C_{M^{2+}}^2} \right\} (\bar{C}_{(HR)_{2i}}^2 - \bar{C}_{(HR)_2}^2) \right]^{1/2} \quad (18)$$

where θ_1 is a grouped kinetic parameter, which is defined by the following equation:

$$\theta_1 = k_R D_{HR} K_a \quad (19)$$

and D_c is the extractant distribution coefficient. When the model is used for cases in which the pH of the aqueous phase is varied, D_c is given as a function of pH. For dialkylphosphoric acids, the dependence of D_c with pH can be estimated by the following expression,

$$D_c = \frac{A}{1 + \frac{10^{-B}}{10^{-pH}}} \quad (20)$$

where A and B are empirical coefficients found from experiments on the variation of solubility with pH.

The interfacial concentrations in eq 18 are defined by the following equations:

(i) for the organic phase

$$\bar{C}_{(HR)_{2i}} = \bar{C}_{(HR)_2} - \frac{J_{(HR)_{2i}}}{\bar{k}_{(HR)_2}} \quad (21)$$

$$\bar{C}_{MR_2(HR)_{2i}} = \bar{C}_{MR_2(HR)_2} - \frac{J_{(HR)_{2i}}}{2\bar{k}_{MR_2(HR)_2}} \quad (22)$$

(ii) for the aqueous phase

$$C_{MI}^{2+} = C_{M^{2+}} - \frac{0.5 J_{(HR)_{2i}}}{2k_{M^{2+}}} + \left[\frac{0.5 D_{(HR)_2}}{D_{H^+} P_{(HR)_2}} \right] \{ \bar{C}_{(HR)_{2i}} - C_{(HR)_2} P_{(HR)_2} \} \quad (23)$$

$$C_{HI}^+ = C_{H^+} + \frac{J_{(HR)_{2i}}}{k_{H^+}} - \left[\frac{0.5 D_{(HR)_2}}{D_{H^+} P_{(HR)_2}} \right] \{ \bar{C}_{(HR)_{2i}} - C_{(HR)_2} P_{(HR)_2} \} \quad (24)$$

$$C_{(HR)_2} = \frac{1}{P_{(HR)_2}} \left[\frac{-\theta_2 C_{H^+}^2}{4K_{ex} C_{M^{2+}}} + \sqrt{\left\{ \frac{\theta_2 C_{H^+}^2}{4K_{ex} C_{M^{2+}}} \right\}^2 + \frac{C_{H^+}^2}{K_{ex} C_{M^{2+}}} \left\{ \bar{C}_{MR_2(HR)_{2i}} + \frac{\theta_2 \bar{C}_{(HR)_{2i}}}{2} \right\}} \right] \quad (25)$$

where θ_2 is a grouped physical property parameter which is defined by the following expression,

$$\theta_2 = \frac{P_{MR_2(HR)_2} D_{(HR)_2}}{P_{(HR)_2} D_{MR_2(MR)_2}} \quad (26)$$

$$C_{MR_2(HR)_2} = K_{ex} \left(\frac{C_{(HR)_2}^2 C_{M^{2+}}}{C_{H^+}^2} \right) \frac{P_{(HR)_2}^2}{P_{MR_2(HR)_2}} \quad (27)$$

The set of eqs 18–27 is the overall model for the extraction of copper of dialkylphosphoric acids.

It should be noted here that the above equations improve the general model of Hughes and Rod (1984) especially when the effect of pH on flux is now accommodated. In the models the most important parameters are (i) the mass transfer coefficients, k_j (m/s), (ii) the overall extraction constants, K_{ex} , as defined by eqs 3 and 5, (iii) the grouped kinetic parameters, θ_1 , as defined by eqs 9 and 19, (iv) the grouped physical property parameters, θ_2 , as defined by eqs 16 and 26, and (v) the extractant distribution coefficients, D_c , as defined by eqs 10 and 20.

The sensitivity of the model to the four parameters above has already been explored in the original work of Hughes and Rod (1984) where the rate of changes in the flux of HR was investigated with respect to the parameters $k_{M^{2+}}$ or k_{HR} or θ_1 or θ_2 . Experiments to give data in the regions $C_{M^{2+}} \gg C_{HR}$ provide best estimates of k_{HR} while data from the region $C_{HR} \gg C_{M^{2+}}$ (which was the case in this work) give best estimates for $k_{M^{2+}}$. The grouped kinetic parameter, θ_1 , is best estimated when experimental conditions are such that $C_{HR}/2C_{M^{2+}} \approx k_{M^{2+}}/k_{HR}$. The sensitivity of the model to the grouped physical property parameter, θ_2 , is low.

A computer program which was written using the Runge–Kutta–Merson method for numerical integrations and the Marquardt optimization technique for parameter estimation (Press et al. (1992)) was modified accordingly and subsequently used in this work to fit the experimental data to the model. Subprograms for the calculation of the active species of extractant in the organic phase and the metal and hydrogen ions in the aqueous phase were incorporated into the model in order to account for extractant dimerization in the organic phase and the complex equilibria between the metal ion, the sulfate ion, and the protons in the aqueous phase.

Results and Discussion

The original form of the model (Hughes and Rod (1984)) has been used by other workers (Dreisinger and Cooper (1989), Patel (1988)) to fit kinetic data which vary with the concentration of either metal or extractant. The application of the modified model which is reported here to the pH data only is now given. The fit

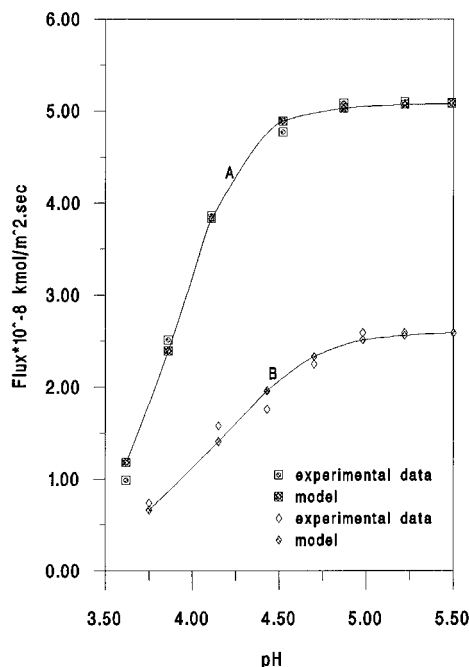


Figure 2. The fit of the model to kinetic data for the extraction of copper by D2EHPA in heptane (A) and toluene (B): $\bar{C}_{HR} = 0.05$ M, $C_{Cu^{2+}} = 0.01$ M, pH = 4.5, $\omega = 3$ Hz.

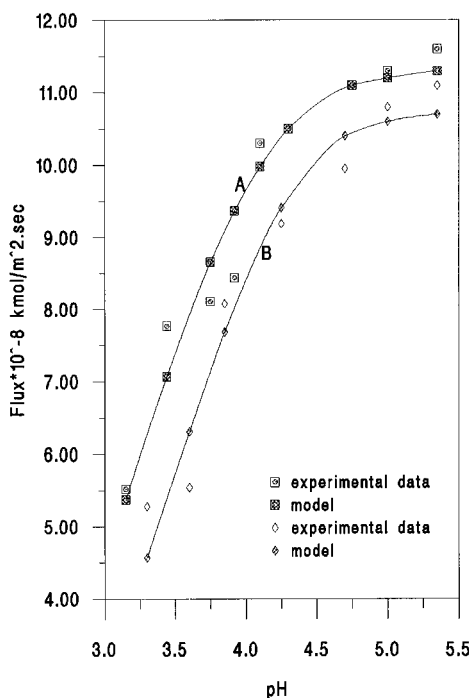


Figure 3. The fit of the model to kinetic data for the extraction of copper by P50 in heptane (A) and toluene (B): $\bar{C}_{HR} = 0.05$ M, $C_{Cu^{2+}} = 0.01$ M, pH = 4.5, $\omega = 3$ Hz.

of the models to the data (at 3 Hz) is shown in Figures 2 and 3 for copper extraction with hydroxyoximes and dialkylphosphoric acids, respectively. From these figures it can be seen that an increase in pH generally results in an increase in the extraction rate until a diffusion limit is reached. The increase in rates with pH is due to the fact that as the pH of the aqueous phase increases the dissociation of the extractant in the aqueous phase will also increase, thus "fixing" more extractant into the reaction zone. The distribution coefficient of the extractant molecule between the aqueous and organic phases will consequently decrease as the pH of the aqueous phase increases. Since the fit of

the kinetic data to the proposed models in Figures 2 and 3 is good, it is reasonable to conclude that the models are adequate for the description of the extraction rates involving hydroxyoximes and dialkylphosphoric acids as extractants of copper. The parameter estimates from the models together with the calculated mass transfer coefficients from theory are listed in Table 1.

The range of mass transfer coefficients, as predicted by the models above, is in the expected range for a RDC. The values of the θ_2 parameters for hydroxyoximes are relatively high because of the large difference between the partition coefficients of the metal complex and the extractant molecule; the metal complex has a much larger partition coefficient.

The calculated mass transfer coefficients in Table 1 come from the expression $k = D/z$, where D is the diffusion coefficient (m^2/s) and z is the equivalent boundary layer thickness (m). The diffusion coefficient is estimated from the Wilke and Chang correlation (1955).

It is seen from Table 1 that the calculated values of $k_{M^{2+}}$ are higher than those predicted by the model and the calculated values of k_{HR} are lower. It might seem reasonable to assume the calculated ones and apply them in the model to obtain estimates of θ_1 and θ_2 , but in calculating the organic phase mass transfer coefficients, the addition of the effective membrane thickness and the diffusion layer thickness to give the equivalent boundary thickness, z , may not be correct. It is not certain if the organic diffusion layer is within the membrane pores or situated just outside the membrane surface; for example, for the $Cu^{2+}-SO_4^{2-}/D2EHPA/heptane$ system the calculated diffusion layer thickness using eq 1 is 3.9×10^{-5} m while the effective thickness for the Millipore membrane which was used in this work is said to be 19.4×10^{-5} m (Fisk (1981)). In the work to follow, the estimated values of $k_{M^{2+}}$ and k_{HR} are used.

The second-order chemical rate constants for the extraction of copper by either hydroxyoximes or dialkylphosphoric acids can be predicted from the value of the optimized grouped kinetic parameter, θ_1 , if the diffusion coefficient of the extractant molecule in water and the aqueous phase dissociation constant are known. Thus, for the $Cu^{2+}-SO_4^{2-}/D2EHPA$ system, $k_R = 3.35 \times 10^5$ $m^3/(kmol \cdot s)$ and 2.22×10^5 $m^3/(kmol \cdot s)$ with heptane and toluene as diluents, respectively. For the $Cu^{2+}-SO_4^{2-}/P50$ system, $k_R = 9.37 \times 10^{10}$ $m^3/(kmol \cdot s)$ and 1.82×10^{10} $m^3/(kmol \cdot s)$ with heptane and toluene as diluents, respectively. The rate constants for the extraction of copper by hydroxyoximes as predicted by our models are similar to those for a fast chemical reaction involving water replacement on the Cu^{2+} ion by a ligand.

The mass transfer coefficients which were predicted by our models can be used to estimate the thickness of the reaction zone according to the treatment developed by Hughes and Rod (1984). The thickness of the reaction zone is estimated by the following expressions:

(i) for hydroxyoximes

$$\lambda_r = 3 \frac{D_{HR}}{P_{HR}} \left\{ \frac{\bar{C}_{HR}}{J_{HR_i}} - \frac{1}{\bar{k}_{HR}} \right\} \quad (28)$$

Table 1. Parameters Associated with the Model and Calculated Mass Transfer Coefficients

system	model parameters					
	predicted				calculated	
	θ_1	θ_2	$k_{M^{2+}}^a$	k_{HR}^a	$k_{M^{2+}}^a$	k_{HR}^a
Cu ²⁺ -SO ₄ ²⁻ /D2EHPA/heptane	3.1×10^{-6}	463	90.74	13.23	22.0	4.33
Cu ²⁺ -SO ₄ ²⁻ /D2EHPA/toluene	2.0×10^{-6}	1.0	62.75	38.88	22.0	3.03
Cu ²⁺ -SO ₄ ²⁻ /P50/heptane	47.60	5.07×10^6	43.10	20.90	22.0	7.14
Cu ²⁺ -SO ₄ ²⁻ /D2EHPA/toluene	9.263	22.49×10^6	16.41	9.97	22.0	5.00

^a m/s $\times 10^{-6}$

(ii) for dialkylphosphoric acids

$$\lambda_r = 3 \frac{D_{(HR)_2}}{P_{(HR)_2}} \left\{ \frac{\bar{C}_{(HR)_2}}{J_{(HR)_2i}} - \frac{1}{\bar{k}_{(HR)_2}} \right\} \quad (29)$$

For example, the reaction zone thickness for the Cu²⁺-SO₄²⁻/D2EHPA/heptane system was calculated to be 0.7 μm , while that for the Cu²⁺-SO₄²⁻/P50/heptane system was calculated to be $1.3 \times 10^{-3} \mu\text{m}$. This last value is at the lower end of the range of thicknesses which were reported by Neuman et al. (1993), i.e. 7×10^{-3} to $40 \times 10^{-3} \mu\text{m}$ (about 10–30 monolayers), for the extraction of nickel of D2EHPA in heptane. The value estimated for the extraction of copper by D2EHPA in this work seems to be much higher than Neuman's top value. Neuman et al. (1993) used an optical technique for the direct measurement of the thickness of a liquid/liquid interface.

The thickness of the diffusion layer was calculated from eq 1 and found to be 33 μm . The calculated reaction zone thicknesses for copper extraction with either P50 or D2EHPA are well within the diffusion layer. The reaction zone thickness for copper extraction with P50 is predicted to be of molecular dimensions: in agreement with a very low solubility of the P50 molecule in the aqueous phase.

The effect of the alkyl chain length of the extractant molecules on the extraction flux is summarized in Figures 4 and 5 for hydroxyoximes and dialkylphosphoric acids, respectively. The extraction flux increases as the alkyl chain length becomes shorter, i.e. as the solubility of the extractant in water increases and more extractant becomes available for reaction in the aqueous phase reaction zone.

The interfacial tensions for the liquid/liquid systems are compared to the extraction fluxes in Figures 6 and 7 for hydroxyoximes and dialkylphosphoric acids, respectively. The interfacial tension increases as the alkyl chain length decreases. Similar results were obtained by Miyake et al. (1986) and Al-Diwan et al. (1977) for the hydroxyoximes of the type that were studied in this work.

Thus, (i) extraction rates increase, (ii) solubility of the extractant in water increases, and (iii) interfacial tensions increase for shorter chain length molecules within a homologous series.

Conclusions

Two main points arise from this work. First, the behavior of extraction kinetics with varying pH is now accounted for in an analytical manner. Previously, Dreisinger and Cooper (1989) had used a semiempirical approach to account for the behavior of kinetics with changing pH. They corrected the pH of the bulk phase by an increment, ΔpH , such that the bulk phase proton

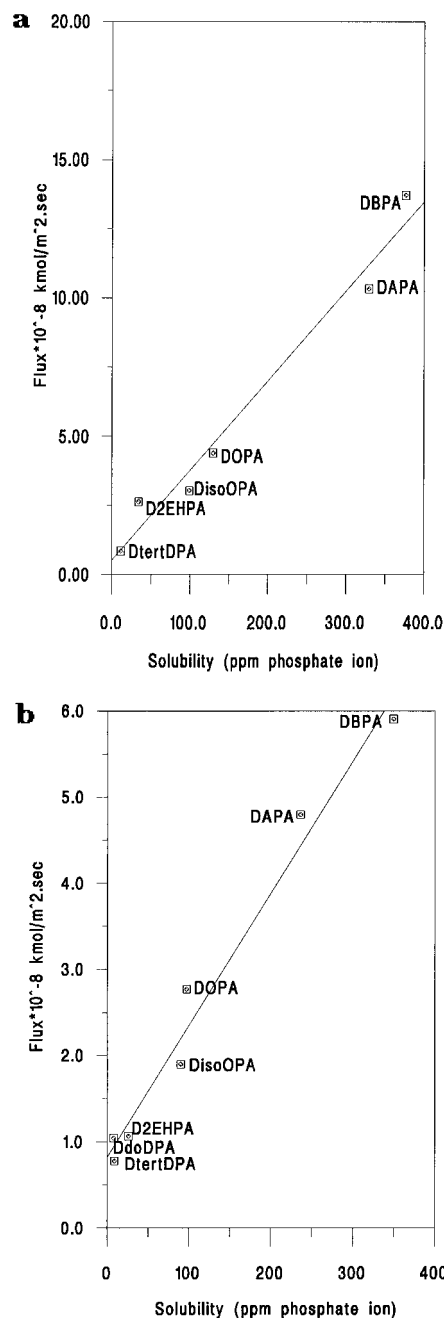


Figure 4. The effect of extractant solubility in water on the extraction flux for (a) the Cu²⁺-SO₄²⁻/dialkylphosphoric acid/heptane system ($\bar{C}_{HR} = 0.05$ M, $C_{Cu^{2+}} = 0.01$ M, pH = 4.5, $\omega = 3$ Hz) and (b) the Cu²⁺-SO₄²⁻/dialkylphosphoric acid/toluene system ($\bar{C}_{HR} = 0.05$ M, $C_{Cu^{2+}} = 0.01$ M, pH = 4.5, $\omega = 3$ Hz, $T = 25 \pm 1$ °C).

concentration in eqs 14 and 24 is defined by the following expression, $C_H = 10^{-(\text{pH} + \Delta\text{pH})}$. By including ΔpH as an extra parameter to be optimized by the computer program, its value could be evaluated. In the

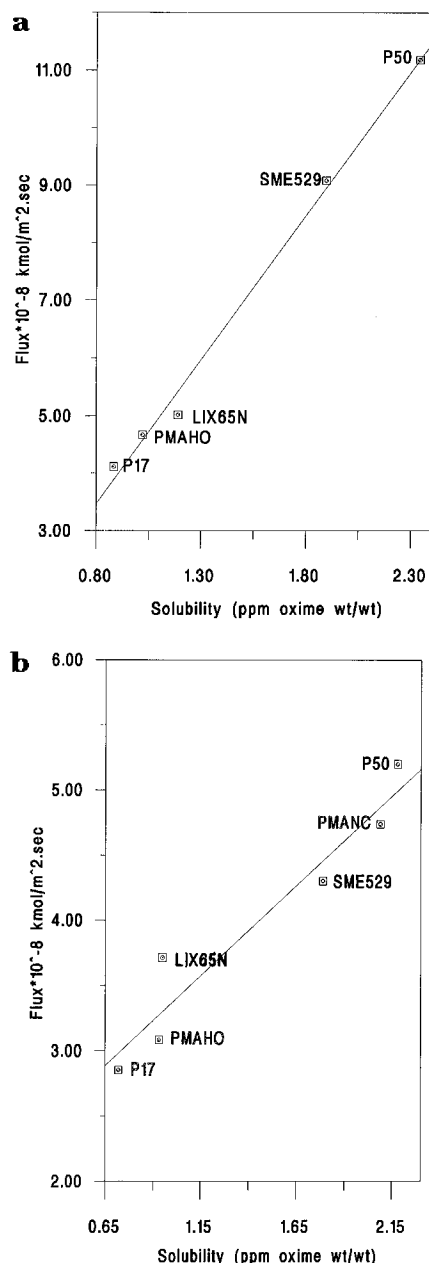


Figure 5. The effect of extractant solubility in water on the extraction flux for (a) the Cu^{2+} - SO_4^{2-} /hydroxyoxime/heptane system ($\bar{C}_{\text{HR}} = 0.05$ M, $C_{\text{Cu}^{2+}} = 0.01$ M, pH = 4.5, $\omega = 3$ Hz) and (b) the Cu^{2+} - SO_4^{2-} /hydroxyoxime/toluene system ($\bar{C}_{\text{HR}} = 0.05$ M, $C_{\text{Cu}^{2+}} = 0.01$ M, pH = 4.5, $\omega = 3$ Hz, $T = 25 \pm 1$ °C).

new model which is reported here, the change in extractant solubility with changing pH is taken into consideration. The partition coefficients previously employed in the original flux equations (Hughes and Rod (1984)) have been altered and substituted by expressions describing the relationships between the extractant distribution coefficient and pH.

Second, at a given constant pH the kinetics are shown to increase with decreasing chain length of an extractant and hence increasing solubility in the aqueous phase (see Figures 4 and 5).

We have been able to correlate the kinetics with both the extractant solubility in water and the system interfacial tension. The extent of the solubility is the most important factor for those extractants which can partition into the aqueous phase. Only in the case of totally aqueous insoluble extractants will the interfacial tension become significant.

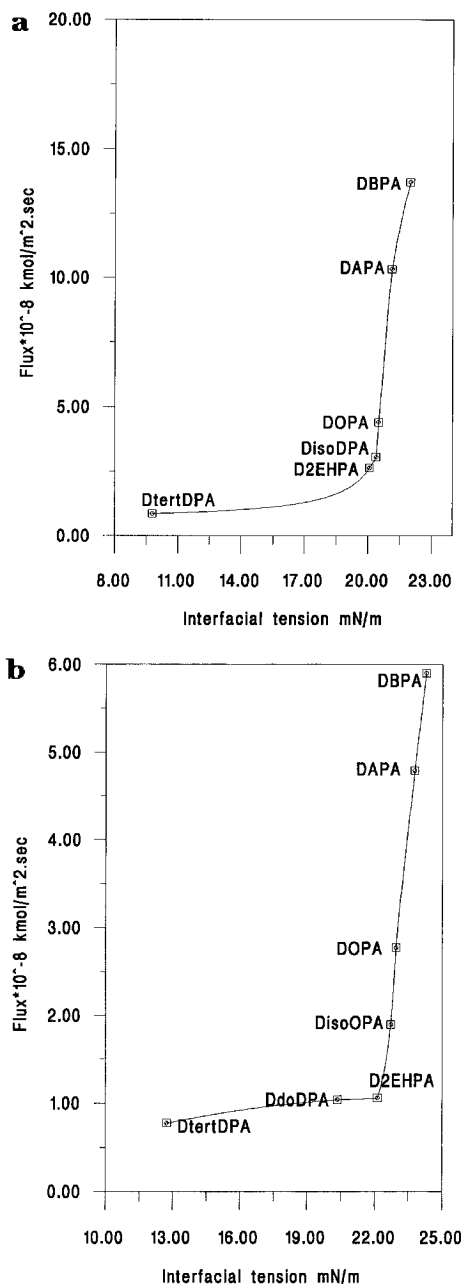


Figure 6. The effect of the interfacial tension of the liquid/liquid system on the extraction flux for (a) the Cu^{2+} - SO_4^{2-} /dialkylphosphoric acid/heptane system ($\bar{C}_{\text{HR}} = 0.05$ M, $C_{\text{Cu}^{2+}} = 0.01$ M, pH = 4.5, $\omega = 3$ Hz, $T = 25 \pm 1$ °C) and (b) the Cu^{2+} - SO_4^{2-} /dialkylphosphoric acid/toluene system ($\bar{C}_{\text{HR}} = 0.05$ M, $C_{\text{Cu}^{2+}} = 0.01$ M, pH = 4.5, $\omega = 3$ Hz, $T = 25 \pm 1$ °C).

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Chemical Abbreviations

(a) Dialkylphosphoric Acids

DBPA = dibutylphosphoric acid
 DAPA = di-*n*-amylphosphoric acid
 DOPA = di-*n*-octylphosphoric acid
 DisoOPA = diisooctylphosphoric acid
 D2EHFA = bis(2-ethylhexyl)phosphoric acid
 DdoDPA = didodecylphosphoric acid
 DtertDPA = ditetradecylphosphoric acid

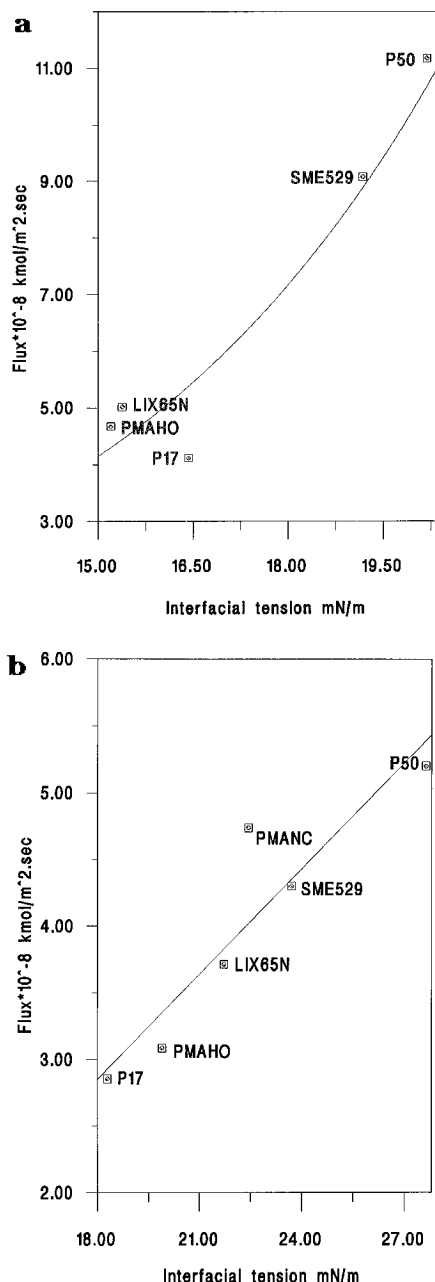


Figure 7. The effect of the interfacial tension of the liquid/liquid system on the extraction flux for (a) the Cu²⁺-SO₄²⁻/hydroxyoxime/heptane system ($\bar{C}_{\text{HR}} = 0.05$ M, $C_{\text{Cu}^{2+}} = 0.01$ M, pH = 4.5, $\omega = 3$ Hz, $T = 25 \pm 1$ °C) and (b) the Cu²⁺-SO₄²⁻/hydroxyoxime/toluene system ($\bar{C}_{\text{HR}} = 0.05$ M, $C_{\text{Cu}^{2+}} = 0.01$ M, pH = 4.5, $\omega = 3$ Hz, $T = 25 \pm 1$ °C).

(b) Hydroxyoximes

LIX65N = 2-hydroxy-5-nonylbenzophenone oxime

P50 = 5-nonylsalicylaldoxime

SME529 = 2-hydroxy-5-nonylphenyl-1-ethanone oxime

PMANC = 2-hydroxy-5-*tert*-octylbenzophenone oxime

PMAHO = 2-hydroxy-5-*tert*-dodecylbenzophenone oxime

List of Symbols

C_j = concentration of the j species (kmol/m³) (j = HR, (HR)₂, R⁻, HR₂⁻, Cu²⁺, H⁺, CuR₂, CuR₂(HR)₂, CuR⁺, CuR(HR)⁺)

J = extraction flux (kmol/(m² s))

k_j = mass transfer coefficient of j species (m/s)

K_a = acid dissociation constant (kmol/m³)

D_c = distribution coefficient of extractant molecules between the organic and aqueous phases (-)

P_j = partition constant of j species between the organic and aqueous phases (-)

Z_D = thickness of the diffusion layer (m)

Z = equivalent boundary layer (m)

ω = rotation speed of the RDC (Hz)

ν = kinematic viscosity (Pa s)

D_j = diffusivity of j species (m²/s)

γ = interfacial tension of the liquid/liquid system (mN/m)

K_{ex} = extraction constant (-)

k_R = reverse second-order reaction rate constant {m³/(kmol s)}

k_R = forward second-order reaction rate constant {m³/(kmol s)}

θ_1 = grouped kinetic parameter (m/s)² for D2EHPA and (m/s)² (m³/kmol) for P50

θ_2 = grouped physical property parameter (-)

Subscripts

i = value at the interface

HR = acidic extractant (also used in the models to denote the monomer species of extractant molecules)

(HR)₂ = dimeric species of extractant molecules

R⁻ = dissociated form of the monomeric extractant molecules in water

HR₂⁻ = dissociated form of the dimeric extractant molecules in water

Cu²⁺ = copper ions in the aqueous phase

H⁺ = hydrogen ions in the aqueous phase

CuR⁺ = 1:1 complex that is formed as a result of the reaction between Cu²⁺ ions and R⁻ in the reaction zone

CuR(HR)⁺ = 1:1 complex that is formed as a result of the reaction between Cu²⁺ ions and HR₂⁻ in the reaction zone

CuR₂ = 1:2 complex for hydroxyoximes

CuR₂(HR)₂ = 1:2 complex for dialkylphosphoric acids

Superscripts

Barred symbols refer to the organic phase.

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