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Reactor Analysis of Metal Ion Extraction in Liquid Dispersions

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ABSTRACT

A comprehensive research program is undertaken to predict the effects of mixing on the extraction efficiency for $Co(NO_3)_2$-Di-2-ethylhexyl phosphoric acid in toluene system in mechanically agitated dispersed phase reactors. The experimental and theoretical studies on this complex hydrometallurgical extraction system have yielded the following results.

a) A two phase organic and aqueous equilibrium model, which accounts for the aqueous phase equilibria, is developed to predict the distribution of cobalt. The equilibrium model is based on cobalt ion complexation with the DEPHA dimer as suggested by Komasawa et al. [5]. The aqueous phase activities are represented by the Davies Model.

b) Physical mass transfer and chemical extraction experiments conducted in a stirred transfer reactor show that the reaction occurs in the aqueous film. A two film diffusion-reaction model is developed to accurately predict the observed fluxes over the experimental range.

The composition and temperature ranges for the equilibrium and kinetic experiments are, respectively: a) pH, 3-5; $[Co]_T$, 0.001 to 0.1 M; $[DEHPA]_2$, 0.1 to 1.0 M; T, 25-50°C, and b) pH, 3-5; $[Co]_T$, 0.001 to 0.1 M; $[DEHPA]_2$, 0.01 to 0.5 M; T = 25°C.

c) A previously developed Monte Carlo Simulation procedure is employed with the above equilibrium and kinetic models to predict the effect of droplet mixing on extraction efficiency for various process variables.

The above experimental and theoretical procedure can be applied to the study of other two phase dispersion systems and can be extended to multiple reactors.

INTRODUCTION

Cobalt has been widely used for catalysts in hydrocracking of crude oil, coal liquefaction and synthesis of fuel oil and plays a crucial role in America's defense. This metal is usually obtained as a by-product in the extraction of other metals such as copper, nickel, and gold. The separation of cobalt and nickel has aroused a lot of interest due to the co-occurrence of cobalt and nickel in many neutral ores [1]. A number of investigations have been published for the extraction of cobalt and nickel. These works were reviewed and discussed by Flett and Spink [2] and by Ritcey and Ashbrook [3].

Our research efforts are aimed at developing fundamental models for rational design and scale-up of liquid-liquid extraction reactions. These efforts resulted in the development of a basic, dispersed phase model structure which incorporates the details of thermodynamic chemical equilibria, chemical kinetics, mass transfer processes and the effects of droplet mixing.

Our present research efforts in reactor analysis for selective metal ion extraction in liquid dispersions are to - (i) implement stochastic models to determine and quantify the effect of droplet mixing on conversion and selectivity for the Co(II) and Ni(II)/NO_3^--Di(2-ethylhexyl) phosphoric acid (DEHPA) system and (ii) extend our models for a single extractor system to multiple stage extractors in various configurations. Fundamental understanding of the Co(II)/NO_3^--DEHPA system are obtained from experimental studies on chemical equilibria and kinetics. The equilibrium and kinetic models are then incorporated into simulation models to predict extractor behavior under various operating conditions. A specially designed capillary spectrophotometer system is being set up to obtain bivariate (concentration and size) drop distribution data and to validate our models.

EQUILIBRIA OF COBALT EXTRACTION BY DEHPA

The chemical equilibria in the extraction of Co(II)/NO_3^--DEHPA buffered with sodium hydroxide and acetic acid buffer solution were studied. The experimental techniques and the resulting equilibrium reaction model are presented below.

Chemicals

DEHPA, a commercially available extractant was used as supplied by the Mobil Chemical Company. The purity of DEHPA was determined to be 97% by titration with 0.1 N aqueous NaOH as described in the Mobil product Manual [4]. The dimerization of DEHPA in various diluents has been reported and has been considered in many divalent metal extraction systems by previous workers [5-10]. Our titration results showed that about 2% of the DEHPA was present in the monoethyl form. No purification of the DEHPA was attempted. Other chemicals used in the present studies - cobalt nitrate (Alfa chemical); nitric acid, toluene, sodium hydroxide and acetic acid (Fisher Chemical) are all of reagent grade.

Equilibrium Studies

Equilibrium studies were conducted at 25, 35 and 50°C; pH = 3 to 5, 0.001 to 0.1 M aqueous cobalt and 0.1 to 1.0 M dimeric DEPHA, $(DEHPA)_2$ in toluene solutions. The two phases are separated after equilibration and the aqueous phase total cobalt concentration was determined using the Perkin-Elmer 2380 Atomic Absorption (AA) Spectrophotometer by observing the absorbance at 240.7 nm. The cobalt complex concentration in the organic phase is determined by back extracting the cobalt into the aqueous phase and subsequent AA analysis.

The stoichiometry of the Co(II)/DEHPA extraction reaction as determined by Komosawa et al. [5],

$$Co^{2+} + 2\overline{(HR)_2} \rightleftharpoons \overline{CoR_2(HR)_2} + 2H^+ \tag{1}$$

was used to estimate the concentration of the unreacted $\overline{(HR)_2}$ in the organic phase at equilibrium. Here, $\overline{(HR)_2}$ represents organic dimeric DEHPA. The pH of the aqueous phase at equilibrium was also determined. It was observed that the pH of the aqueous phase changed substantially with increasing extraction of the cobalt.

Aqueous Phase Equilibria

In order to determine the concentration of Co^{2+} in the aqueous phase at equilibrium we have to consider the various equilibrium reactions occurring in the aqueous phase. These reactions are listed in Table 1. The stability constants S_1 through S_{12} at 25°C, obtained from Smith and Martell [11], Hogfeldt [12] and Sillen and Martell [13], are used in the following aqueous phase equilibrium model without any correction for temperature variation due to the lack of adequate thermodynamic data.

The aqueous phase equilibrium relations were used to write the individual species balances for cobalt, sodium, nitrate, acetate and the electroneutrality and ionic strength relationships. Including the dissociation of water this resulted in a set of seven nonlinear algebraic equations. For each of the equilibrium experiments the feed concentrations of total cobalt, sodium hydroxide and acetic acid along with the total cobalt at equilibrium were then used to determine the Co^{2+} and H^+ ion concentrations by solving this set of algebraic equations.

The above experimental scheme and aqueous equilibrium model thus resulted in the accurate determination of the concentrations of the ionic species Co^{2+}, H^+, the organic cobalt complex $\overline{CoR_2(HR)_2}$ and the DEHPA $\overline{(HR)_2}$ at equilibrium. It was observed that the fraction of the ionic species Co^{2+} varies significantly with both $[Co]_T$ and pH, from about 0.5 to 0.9. Hence, neglecting the aqueous phase equilibria in Co(II)-DEHPA extraction equilibria can lead to significant errors in the equilibrium constant.

TABLE 1
Aqueous Phase Equilibria for Cobalt Nitrate-Nitric Acid-NaOH-CH_3COOH System

$$\begin{array}{llcl}
Co^{2+} & + \; OH^- & \overset{S_1}{\rightleftharpoons} & CoOH^+ \\
Co^{2+} & + \; 2OH^- & \overset{S_2}{\rightleftharpoons} & Co(OH)_2 \\
2Co^{2+} & + \; OH^- & \overset{S_3}{\rightleftharpoons} & Co_2(OH)^{3+} \\
Co^{2+} & + \; NO_3^- & \overset{S_4}{\rightleftharpoons} & Co(NO_3)^+ \\
Co^{2+} & + \; 2NO_3^- & \overset{S_5}{\rightleftharpoons} & Co(NO_3)_2 \\
H^+ & + \; NO_3^- & \overset{S_6}{\rightleftharpoons} & HNO_3 \\
Na^+ & + \; NO_3^- & \overset{S_7}{\rightleftharpoons} & NaNO_3 \\
H^+ & + \; CH_3COO^- & \overset{S_8}{\rightleftharpoons} & CH_3COOH \\
Co_2^+ & + \; CH_3COO^- & \overset{S_9}{\rightleftharpoons} & CH_3COOCo^+ \\
Co^{2+} & + \; 2CH_3COO^- & \overset{S_{10}}{\rightleftharpoons} & (CH_3COO)_2Co \\
Na^+ & + \; CH_3COO^- & \overset{S_{11}}{\rightleftharpoons} & CH_3COONa \\
H^+ & + \; OH^- & \overset{S_{12}}{\rightleftharpoons} & H_2O
\end{array}$$

Equilibrium Model for $Co(II)/NO_3^-$-DEHPA Extraction

The thermodynamic equilibrium constant for the reaction (1) can be expressed as

$$K_{ex} = K_c \cdot K_\gamma \tag{2}$$

$$K_c = \frac{[\overline{CoR_2(HR)_2}][H^+]^2}{[Co^{2+}]\,[\overline{(HR)_2}]^2} \tag{3}$$

and

$$K_\gamma = \frac{\gamma^2_{H^+}}{\gamma_{Co^{2+}}} \tag{4}$$

where the square brackets represent the species concentrations and γ_i is the activity coefficient for species i. In the present model we assumed that the activity coefficient ratio in the organic phase is one, due to the lack of thermodynamic data to predict the organic phase activity coefficients. Further, the equilibrium constant K_c can be expressed as

$$\ln K_c = -\ln K_\gamma - \left(\frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}\right) - \frac{\Delta H^\circ}{R}\left(\frac{1}{T} - \frac{1}{\bar{T}}\right) \tag{5}$$

where ΔS° and ΔH° are the standard entropy and enthalpy changes and $\bar{T}$ is the reference temperature (chosen to be 25°C).

The aqueous phase activity coefficients, γ_{H^+} and $\gamma_{Co^{2+}}$ are obtained from one of the three following models:

(i) Davies Equation [14],

(ii) Debye-Huckle Theory [15], and,

(iii) Bauer and Chapman empirical correlation [16].

The experimental equilibrium data for the $Co(II)/NO_3^-$-DEHPA system and the aqueous equilibrium calculations are used to determine the unknown parameters for the above three models by linear regression. It was observed that all the three models represent the experimental equilibrium data adequately. Consequently the Davies model was chosen as it is the simplest of the three. The resulting equilibrium model is given by Eqs. (3)-(5) with the following relation and parametric values:

$$\log \gamma_i = 1.825 \times 10^5 (\varepsilon' T)^{-3/2} z_i^2 \left[\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I\right] \tag{6}$$

$$\frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R\bar{T}} = 13.6 \pm 0.17 \tag{7}$$

and $$\frac{\Delta H^\circ}{R} = -3077 \pm 1370\ ^\circ K \tag{8}$$

KINETICS OF COBALT(II) EXTRACTION BY DEHPA

The kinetics of cobalt extraction by DEHPA have been studied by Komosawa and Otake [6], Brisk and McManamey [8], and Hughes and Zhu [17]. The first two groups of investigators studied cobalt extraction in stirred transfer reactors and assumed an interfacial reaction mechanism. On the other hand, Hughes and Zhu [17] developed a kinetic model based on the following mechanism in which an aqueous film reaction was proposed.

$$2\overline{HR} \overset{K_2}{\rightleftharpoons} (\overline{HR})_2 \tag{9}$$

$$\overline{HR} \overset{P_{HR}}{\rightleftharpoons} HR \tag{10}$$

$$HR \overset{K_A}{\rightleftharpoons} H^+ + R^- \tag{11}$$

$$R^- + Co^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CoR^+ \tag{12}$$

$$CoR^+ + R^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CoR_2 \tag{13}$$

$$CoR_2 \overset{P_{CoR_2}}{\rightleftharpoons} \overline{CoR_2} \tag{14}$$

$$\overline{CoR_2} + (\overline{HR})_2 \overset{K_o}{\rightleftharpoons} \overline{CoR_2(HR)_2} \tag{15}$$

This mechanism is essentially the same as that postulated by Rod [18] except that the dissociation of dimeric DEHPA (Eq. (9)) and the association of CoR_2 with $(\overline{HR})_2$ (Eq. (15)) are also considered.

The above review of previous research efforts indicates that complete analysis of the intrinsic kinetics is not performed by considering both mass transfer resistances and aqueous phase ionic speciation. In addition, both interfacial reaction and aqueous film reaction mechanisms have been assumed for this cobalt(II)-DEHPA extraction system. The ambiguity of the reaction site encourages further studies of this system. Furthermore, the ranges of experimental variables covered by previous authors do not include the regions of interest for our dispersion studies. Therefore, it is necessary to develop a kinetic model in the experimental ranges of interest which can be directly applied for our studies on droplet mixing in liquid-liquid reactors.

Experimental Set-up and Operation

The kinetic experiments of cobalt(II) extraction by DEHPA are conducted in a stirred transfer reactor which was originally designed by Landau and Chin [19] and Demetropoulos [20]. The detailed construction of this contactor is given by Lee [21].

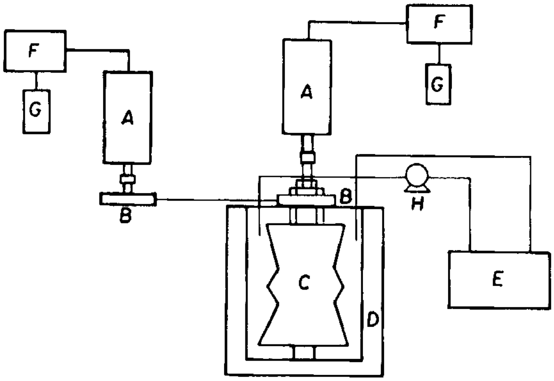

FIG. 1. Flow diagram of stirred transfer reactor. A - motor, B - pulley, C - stirred transfer reactor, D - thermostat, E - spectrophotometer, F - power supply, G - voltameter, H - pump.

The flow diagram of the modified stirred transfer reactor used in our kinetic experiments is shown in Figure 1. During the experiment, the contactor is half-filled with aqueous cobalt(II) nitrate solution, buffered by acetic acid-sodium hydroxide solution. The remaining portion is filled with organic DEHPA/toluene solution very gently, so as not to disturb the interface. The desired rotating speeds of the stirrers were set and the concentration of cobalt complex formed in the organic phase was continuously monitored using an on-line UV/VIS spectrophotometer (Perkin-Elmer 559). The experimental ranges of this kinetic study are $[Co]_T$ (0.001-0.1 M), $[\overline{(HR)_2}]$ (0.01-0.5 M), and pH (3.16-5.02) at a temperature of 298 K. It is noted that these experments are designed such that the maximum conversion of dimeric DEHPA is always less than 12% so as to minimize the polymerization of the cobalt complex. The rate of extraction of the cobalt complex into the organic phase is determined by curve fitting the concentration versus time data and calculating the time derivatives numerically.

Pure Mass Transfer and Extraction Rate Studies

In order to obtain the intrinsic kinetics of cobalt(II) extraction by DEHPA from extraction experiments, the effect of mass transfer on the observed fluxes has to be considered. The mass transfer characteristrics of the stirred transfer reactor used in this work are described by a semi-empirical correlation between the experimentally determined pure mass transfer coefficients ($k_{i,pm}$) in the aqueous phase film and the stirring speeds and other physicochemical parameters. The system of toluene-distilled water was chosen for this pure mass transfer experimental study and the Colburn-Welsch technique [22] was employed.

TABLE 2
Comparison of Observed Flux and the Pure Mass Transfer Flux

Run No.	$[Co^{2+}]$ x 10^2	$[H^+]$ x 10^3	$[(\overline{HR})_2]$ x 10	$\overline{[CoR_2(HR)_2]}$ x 10^3	Flux, obs x 10^8	Flux, pm x 10^8
7	0.553	0.115	4.94	3.007	0.713	0.753
16	0.059	0.103	4.99	0.191	0.145	0.071
30	0.193	0.012	0.348	7.576	1.046	0.176
33	0.218	0.012	0.860	6.978	1.147	0.279
17	8.071	0.226	0.986	0.689	0.690	0.717
22	8.753	0.773	0.998	0.092	0.063	0.188

Concentrations in M, fluxes in mol/cm^2-s, Flux,obs and Flux,pm are fluxes of observed cobalt(II) extraction and pure mass transfer respectively.

The experimentally determined extraction rates of cobalt(II) by DEHPA and pure mass transfer rates are compared in Table 2 for various concentration ranges. It is observed that the extraction rate is faster than the pure mass transfer rate for certain experimental conditions, especially in the ranges where the DEHPA concentration and pH are high. The higher extraction rate could be attributed to the enhancement by extraction reaction occurring in the aqueous film. If the reaction site is the interface, the maximum extraction rate could never be higher than the pure mass transfer rate because of the reversible nature of the reaction system. Therefore, only the aqueous film reaction is considered further in this kinetic modeling.

Theory

Based on the above experimental results, the reaction site is postulated to be the aqueous film. The mass transfer with aqueous film reaction in the stirred transfer reactor is modeled by assuming that the two-film theory applies. The resulting differential equations and the associated boundary conditions are given elsewhere [21,23].

The rate expression derived from the mechanism presented in Eqs. (9)-(15) with Eq. (12) assumed to be the rate determining step is given by

$$R_A = \frac{2k_1K_A}{C_{H^+}}\left[C_{Co^{2+}}C_{HR} - \frac{1}{K_{ex}}\frac{K_oP_{CoR_2}}{K_2P_{HR}^2}\frac{C_{CoR_2}C_{H^+}^2}{C_{HR}}\right] \qquad (16)$$

where, R_A is the rate of reaction of HR in the aqueous phase. In the present study, the limiting case of a pseudo first order reaction, as discussed by Rod [18] is used, i.e. $C_{Co^{2+}} = C_{Co_o^{2+}}$ and $C_{H^+} = C_{H_o^+}$ for $0 \leq x \leq \delta$. The resulting expression for the interfacial flux of HR [21] is

$$J_{HR_i} = -\theta_1^{1/2}\left[\frac{C_{Co^{2+}}}{C_{H^+}}\left(\frac{C_{\overline{HR}_i}^2}{P_{HR}^2} - C_{HR_o}^2\right)\right.$$

$$- \theta_2\left(\frac{2C_{H^+}C_{\overline{CoR}_{2,i}}}{P_{CoR_2}} + \frac{C_{H^+}C_{\overline{HR}_i}\mathcal{D}_{HR}}{P_{HR}\mathcal{D}_{CoR_2}}\right)\ln\frac{C_{\overline{HR}_i}}{C_{HR_o}P_{HR}}$$

$$\left. + \theta_2\frac{C_{H^+}\mathcal{D}_{HR}}{\mathcal{D}_{CoR_2}}\left(\frac{C_{\overline{HR}_i}}{P_{HR}} - C_{HR_o}\right)\right]^{1/2} \qquad (17)$$

Further, when the net mass transfer rate for HR into the aqueous bulk is zero, the net rate of reaction is zero in the aqueous bulk. Thus solving Eq. (16) for C_{HR_o} gives [21]

$$C_{HR_o} = \frac{1}{2}\left[\frac{-\theta_2 \mathcal{D}_{HR} C^2_{H^+}}{2\mathcal{D}_{CoR_2} C_{Co^{2+}}} + \sqrt{\left(\frac{\theta_2 \mathcal{D}_{HR} C^2_{H^+}}{2\mathcal{D}_{CoR_2} C_{Co^{2+}}}\right)^2 + \frac{2\theta_2 C^2_{H^+}}{C_{Co^{2+}}}\left(\frac{\mathcal{D}_{HR}}{\mathcal{D}_{CoR_2}} C_{HR_i} + 2C_{CoR_{2,i}}\right)}\,\right] \tag{18}$$

The organic side interfacial concentrations can be determined from the bulk organic concentrations, using an effective mass transfer coefficient

$$C_{\overline{HR}_i} = C_{\overline{HR}_o} - \frac{J_{HR_i}}{k_{\overline{HR},eff}} \tag{19}$$

$$C_{\overline{CoR}_{2,i}} = C_{\overline{CoR}_{2,o}} + \frac{J_{HR_i}}{2k_{\overline{CoR}_2,eff}} \tag{20}$$

It is assumed that $k_{\overline{HR},eff} = k_{\overline{CoR}_2,eff}$ (21)

We can further express $k_{\overline{HR},eff}$ as

$$k_{\overline{HR},eff} = E\, k_{\overline{HR},pm} \tag{22}$$

where E is the enhancement factor and $k_{\overline{HR},pm}$ is the pure physical mass transfer coefficient.

In Eqs. (17) and (18) the unknown parameters are

$$\theta_1 = 2\mathcal{D}_{HR} k_1 K_A \,;$$

$$\theta_2 = \frac{K_o P_{CoR_2}}{K_{ex} K_2 P^2_{HR}} \,;$$

the distribution coefficient,

$$P_{CoR_2} = \frac{C_{\overline{CoR_2},i}}{C_{CoR_2,i}} ;$$

the enhancement factor,

$$E = \frac{k_{\overline{HR},eff}}{k_{\overline{HR},pm}} \qquad (23)$$

and the diffusivity ratio,

$$R_D = \frac{\mathcal{D}_{HR}}{\mathcal{D}_{CoR_2}} .$$

From the experimental data on interfacial fluxes, the above unknown parameters can be determined by a nonlinear least square method and iteration on Eqs. (17)-(22).

Results and Discussion

The flux of aqueous DEHPA can be calculated from the experimentally observed rate of change of the cobalt complex concentration in the organic phase from

$$J_{HR,i} = -\frac{\bar{V}}{A}\frac{dC_{\overline{CoR_2(HR)_2}}}{dt}\left\{4 + \frac{1}{\sqrt{K_2 C_{\overline{(HR)_2}}}}\right\} \qquad (24)$$

where $\bar{V}$ is the organic phase volume and A is the interfacial area. The dissociation constant for the dimeric DEHPA K_2 is estimated by Komosawa et al. [5] to be $K_2 = 3.12 \times 10^4\ M^{-1}$.

In the weighted nonlinear least square analysis, the experimentally observed flux $J_{j,obs}$ and the predicted flux $J_{j,cal}$ from Eqs. (17)-(22) are compared to optimally determine the unknown parameters using a direct search procedure based on the optimization method developed by Powell [24]. The resulting parameter values are: $\theta_1 = 13.28\ cm^2/s^2$, $\theta_2 = 2.75$, $E = 3760$, $P_{CoR_2} = 26.23$ and $R_D = 23.46$. Details of the parameter evaluating procedure are given elsewhere [21,23].

SIMULATION OF COBALT EXTRACTION BY DEHPA IN LIQUID DISPERSIONS

The third phase of our research efforts to understand the extraction of cobalt by DEHPA is to quantify the effect of mixing on reaction rates and CFSTR performance for liquid-liquid reactors. Fundamental studies by our research group [25-29] resulted in the development of Monte Carlo Simulation models to predict the effect of mixing on pure physical mass transfer from the drop to continuous, continuous to drop and drop to drop phases. In these studies an event oriented simulation technique based on the Interval of Quiescence Method [30] is used. Details of the simulation techniques can be found in the above literature. Only a brief description of the Monte-Carlo Simulation method is given below.

Monte Carlo Simulation Technique

A representative fraction of the drop population is chosen and these drops are subjected to the same environment as the drop population in the reactor. For a CFSTR the drops in the sample are allowed to undergo the following four events:

(a) feed (monoparticle, exogenous), (b) exit (monoparticle, endogenous), (c) breakage (monoparticle, endogenous), and (d) coalescence (multiparticle, endogenous).

The feed event is considered deterministic while the occurrence of the other three events is highly random because of turbulent hydrodynamic conditions in the reactor. In the present study we assume that the turbulent characteristics in the reactor are position invariant and characterized by the viscous energy dissipation per unit mass, (ε) [31]. For an open agitated vessel with a 4 blade flat turbine impeller is given by Rushton et al. [32] as

$$\varepsilon = \frac{1.273\, P_N N_P^3 D_I^5}{d_t^2 h_1} \tag{25}$$

where the power number, P_N is taken to be 5 for tank Reynold's numbers greater than 100.

For a given set of physicochemical properties of the dispersion and the operating conditions of the CFSTR, unique long range event frequencies can be calculated (see Tavlarides and Stamatoudis [31]). The random intervent time for this Poisson arrival pattern is given by Gordon [33],

$$t_{IQ} = \frac{\ln \chi}{\Sigma f_i} \tag{26}$$

where χ is a uniform random number, f_i is the average frequency of the ith activity and t_{IQ} is the interval of quiescence.

During the interval of quiescence, no abrupt changes can occur due to drop birth or death, but interphase mass transfer and reaction do take place.

Application of Simulation Techniques to Cobalt-DEHPA Extraction Reaction

During the quiescence interval, the continuity equations for the individual drop and continuous phase concentrations can be written as,

$$\frac{dC^{(d)}_{i,j}}{dt} = \frac{6}{d_j} J_{i,j} \tag{27}$$

and

$$\frac{dC^{(c)}_{i}}{dt} = \frac{1}{\tau}\left(C^{(c)}_{if} - C^{(c)}_{i}\right) - \frac{1}{V_c}\sum_{j=1}^{N} \pi d_j^2 J_{i,j} \tag{28}$$

where i denotes species i, and j is the jth drop, d_j is the drop diameter, N is the total number of drops, τ is the CFSTR residence time, V_c is the continuous phase volume, $C^{(c)}_{if}$ and $C^{(c)}_{i}$ are the continuous phase feed and product concentration for species i, and $J_{i,j}$ is the interfacial flux of species i for the jth drop. $J_{i,j}$ is taken positive from the aqueous phase into the organic phase and is determined by the reaction rate in the aqueous film as given by Eqs. (16)-(22).

The above differential equations, Eqs. (27) and (28), are integrated using the Euler's Forward Difference scheme with the time step, $\Delta t = t_{IQ}$. The simulation algorithm shown schematically in Fig. 2 determines the quiescence interval t_{IQ} by calculating the four drop event frequencies based on the physicochemical data and reactor operating parameters such as the energy dissipation and residence time. The forward difference analogs of Eq. (27) and (28) are then solved and the individual drop, continuous phase concentrations are calculated. The aqueous equilibrium equations are solved to predict the new values of Co^{2+} and H^+ in the aqueous phase. The simulation time is then increased by t_{IQ} and the randomly determined event is executed. This procedure is repeated until the desired simulation time (steady state conditions in the CFSTR) are reached.

Results and Discussion

In Figs. 3 and 4, the feed concentrations for the aqueous phase are $[Co]_T = 0.01$ M, [NaOH] = 0.039 M, $[CH_3COOH] = 0.2$ M (this corresponds to a feed pH = 4) and for the organic phase $[(\overline{HR})_2] = 0.2$ M. The monomer $(\overline{HR})$ is assumed to be in equilibrium with the dimer as given by Eq. (9) and there are no cobalt complexes present in the organic phase feed. The interfacial tension is assumed to be constant at 9.22 dynes/cm throughout the simulation, and the dispersed phase volume fraction is assumed to be 0.1.

In Fig. 3, the extraction efficiency, η , and the sauter mean diameter, d_{32}, are plotted against the energy dissipation. The CFSTR

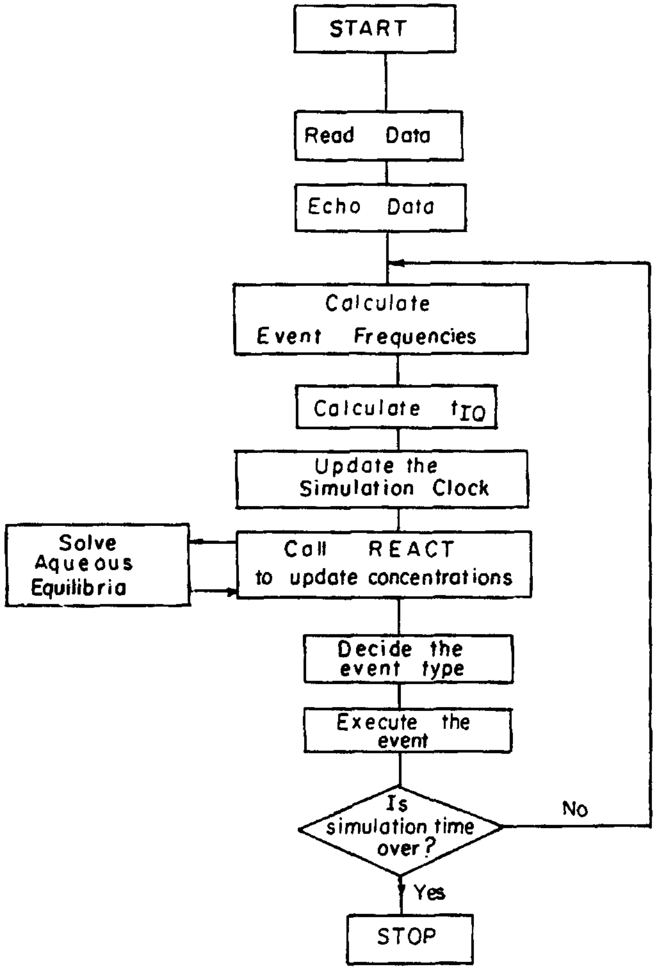

FIG. 2. Schematic of the Simulation Algorithm.

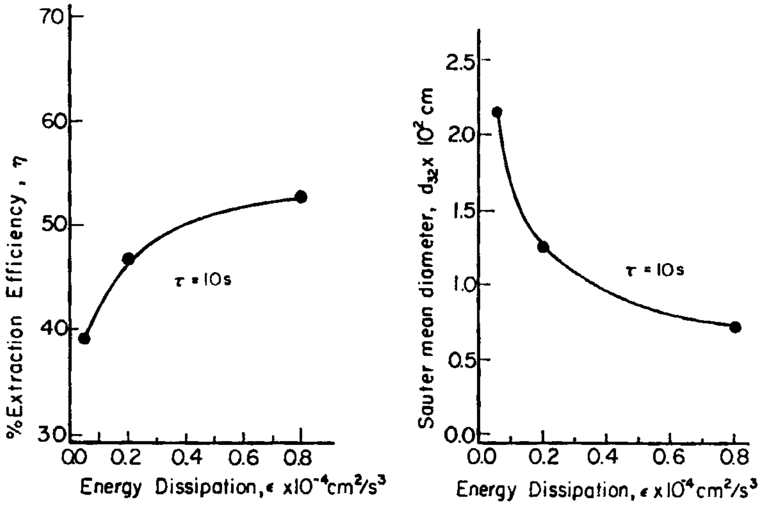

FIG. 3. Effect of Energy Dissipation on Sauter Mean Diameter and CFSTR Efficiency.

residence time is kept constant at 10 sec. The extraction efficiency is defined as

$$\eta = \frac{\overline{<CoR_2(HR)_2>}_{ss}}{\overline{CoR_2(HR)}_{2,eq}} \tag{29}$$

where the numerator on the right hand side is the mean dispersed phase concentration of the cobalt complex at steady state and the denominator is the expected equilibrium concentration for the given feed conditions. The equilibrium concentration thus corresponds to τ and ε both approaching infinite values. It is observed from Fig. 3, that as the agitation (ε) is increased the sauter mean diameter decreases uniformly and the extraction efficiency increases as would be expected.

In Fig. 4, η and d_{32} are plotted against η for a fixed value of $\varepsilon = 2000\ cm^2/s^3$. It is seen that the sauter mean diameter is approximately constant but the extraction efficiency increases uniformly due to increased residence time. The effect of mixing on the marginal volume density distribution of droplets is shown in Fig. 5. If the droplets of organic extractant are subjected to a reactor where no cobalt(II) is present in the aqueous phase, the volume density distribution will be a delta function with concentration of $\overline{CoR_2(HR)_2}$ zero. If both average residence time (τ) and rotational speed are very high in the reactor, the volume density distribution will also be a delta function with concentration of $\overline{CoR_2(HR)_2}$ which is equilibrated with the composition of

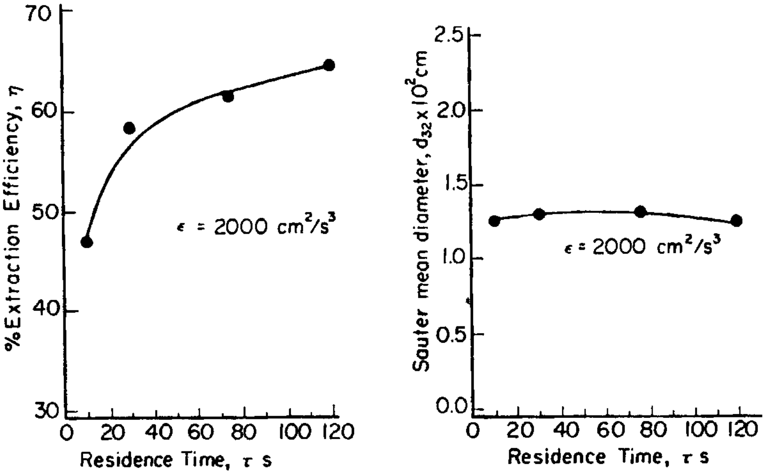

FIG. 4. Effect of Residence Time on Sauter Mean Diameter and CSFTR Efficiency.

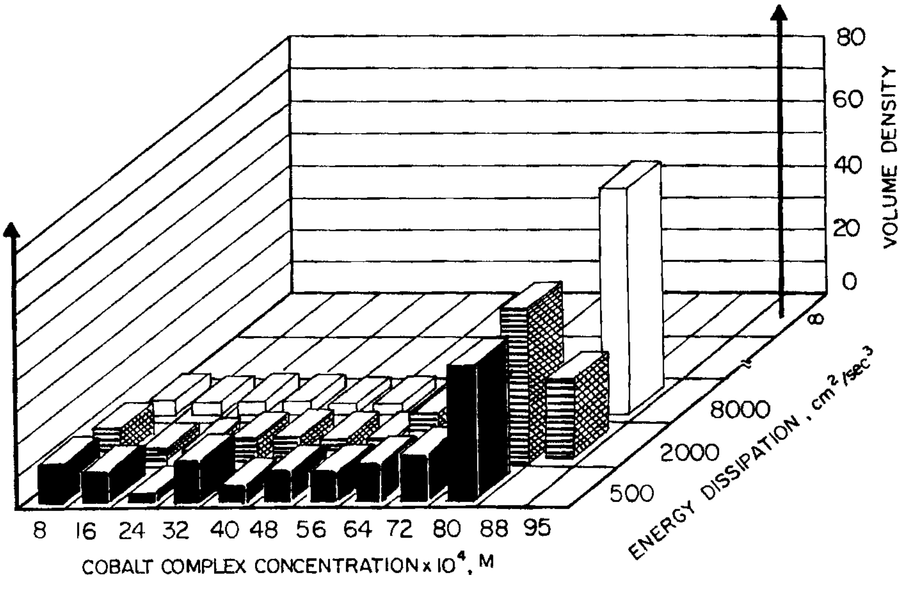

FIG. 5. Mixing Effect on the Volume Density Distribution Function at an Average Residence Time of 10 Second.

aqueous cobalt(II) present. Between these two extremes, one can see the variation of volume density distribution with the $CoR_2(HR)_2$ concentration. In Fig. 5, at the level of 500 cm^2/s^3 energy dissipation (ϵ) and τ = 10 second, most droplets have lower concentration of $CoR_2(HR)_2$. As ϵ increases to 2000 cm^2/s^3, the volume density distribution shifts to higher concentration of $CoR_2(HR)_2$. Further increases to 8000 cm^2/s^3 of ϵ, a volume density distribution of droplets with much higher $CoR_2(HR)_2$ concentration is obtained. The arrow designates the concentration all the drops would have if equilibrium exists between the dispersed phase and the continuous phase for an infinite rate of mixing ($\epsilon \rightarrow \infty$). This figure clearly shows the main thrust of this work and also shows the capability of our simulation technique to predict the effect of mixing on metals extraction in a CFSTR.

CONCLUSIONS

The above research program aimed at understanding and modeling the basic phenomena in the extraction of $Co(NO_3)_2$ by DEHPA has resulted in the development of reliable equilibrium and kinetic models. These models are incorporated into a simulation algorithm to predict the extraction efficiencies in a mechanically agitated stirred tank reactor.

The two phase equilibrium model, Eqs. (3)-(8) accounts for the effect of aqueous equilibria on cobalt-DEHPA complexation. Regression analysis of the equilibrium data resulted in the use of the Davies Model to calculate the aqueous phase activities.

The stirred transfer reactor is used to study the kinetics of cobalt extraction under conditions where the interfacial area is well defined. A comparison of the pure mass transfer flux against flux with reaction indicates that the extraction can be modeled as a reversible aqueous film reaction. The simplified reaction rate expression [18] is utilized to solve the film diffusion-reaction model. Nonlinear least square evaluation resulted in the determination of the appropriate kinetic parameters which could adequately predict the observed extraction fluxes.

The results of the above equilibrium and kinetic studies are utilized in the Monte Carlo simulation technique to observe the effects of micromixing on the extractor performance for various process variables.

The above experimental and theoretical program can be extended to predict the effects of droplet mixing for multiple CFSTRs and to understand other complex extraction systems from a fundamental viewpoint. Experiments are in progress to obtain bivariate drop distribution data to verify the above models and demonstrate the efficacy of these techniques to analyze mixing effects of the dispersed phase on conversion.

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NOMENCLATURE

A	interfacial area
C_i	concentration of species i
C_i^b	concentration of species i in the bulk
$C_i^{(c)}, C_{if}^{(c)}$	continuous phase product and feed concentration for species i
$C_{i,j}^{(d)}$	dispersed phase concentration of species i in the jth drop
d_{32}	Sauter mean diameter, cm
d_j	diameter of the jth drop
d_t	diameter of the impeller, cm
$\mathcal{D}_i$	diffusivity of species i
E	enhancement factor, Eq. (22)
f_i	frequency of the ith event
h_1	height of liquid filled in CFSTR
$HR, (HR)_2$	moneric and dimeric DEHPA respectively
ΔH	enthalpy change with reaction
I	ionic strength
$J_{i,j}$	interfacial flux of species i for the jth drop
k_1, k_{-1}	reaction rate constants, Eq. (12)
k_2, k_{-2}	reaction rate constants, Eq. (13)
$k_{i,pm}$	pure physical mass transfer coefficient for species i
$k_{i,eff}$	effective mass transfer coefficient for species i
K_o	equilibrium constant, Eq. (15)
K_2	equilibrium constant, Eq. (9)
K_A	equilibrium constant, Eq. (11)
K_c	equilibrium constant, Eq. (3)
K_{ex}	extraction equilibrium constant, Eq. (2)
K_γ	activity coefficient ratio, Eq. (4)

N_P	impeller speed, rps
P_{CoR_2}	distribution coefficient for CoR_2, Eq. (14)
P_{HR}	distribution coefficient for HR, Eq. (10)
P_N	power number
R	gas constant
R_A	reaction rate, Eq. (16)
S_i	stability constant for the ith reaction in Table 1
ΔS	entropy change with reaction
t_{IQ}	interval of quiescence
T	absolute temperature, K
$\bar{T}$	reference temperature, 298 K
V_c	volume of the continuous phase
$\bar{V}$	organic phase volume
Z_i	ionic charge

Superscripts

—	organic species

Subscripts

T	total concentration
o	bulk concentration
i	interfacial concentration

Greek Letters

γ_i	activity coefficient for species i
δ	film thickness
ε	viscous energy dissipation per unit mass, cm^2/s^3
ε'	dielelectric constant of solution
η	extraction efficiency, Eq. (29)

θ_1, θ_2	parameters, Eq. (17) and (18)
τ	CFSTR residence time, s
ϕ	dispersed phase volume fraction

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