Mass Transfer Based on Chemical Potential Theory: $ZnSO_4/H_2SO_4$/D2EHPA

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A fundamental model based on chemical reaction kinetics and diffusional mass transfer for the extraction of zinc sulfate with di(2-ethylhexyl) phosphoric acid (D2EHPA) in n-heptane at 25°C was developed. Gradients of the chemical potential were used as the driving force for diffusion. Activity coefficients and their derivatives were calculated from the Pitzer equation in the aqueous phase, while the organic nonideality was considered by the Hildebrand-Scott treatment. The Nerst-Planck equation was chosen for describing the diffusion of aqueous ions, paying special care to the formation of hydrogen sulfate. It was assumed that this fast ionic reaction can be described in terms of the mass action law in the bulk and film. For the multicomponent mass transfer of the organic species, the Maxwell-Stefan theory was adopted. A kinetic equation for the extraction of zinc with D2EHPA, which considers the adsorption of the D2EHPA molecules at the interface based on the Langmuir law, was suitable for our experimental data. Organic zinc concentration vs. time was obtained in a type of Lewis cell with vibrational mixing. Molar fluxes were calculated by fitting it with rational functions, which were analytically differentiated. Initial conditions of the experiments cover a wide range of the zinc (0.1 mM to 0.05 M), D2EHPA, and sulfuric acid concentration. Experimental fluxes could be well described by this model when chemical kinetics and mass transfer were considered. In particular, the resistance to mass transfer in the organic film is important.

Introduction

The zinc sulfate/D2EHPA system is used commercially for the recovery of zinc from waste streams and secondary materials. The system has also become of interest as a test system for the characterization of extraction equipment (Sainz-Díaz et al., 1996; Slater, 1987; Hancil et al., 1990). Despite the advantages of extraction columns, mixer settler units are used in almost all commercial applications of metal extraction. The main reason is the lack of models for the rate of extraction, taking into account the complex coupling of a reversible chemical kinetics with the multicomponent mass transfer of the reactants and products, which are the central point for the layout and simulation of columns.

The kinetics of zinc extraction with D2EHPA in different solvents—*n*-dodecan (Cianetti and Danesi, 1983), *n*-heptane (Ajawin et al., 1980; Murthy and Perez de Ortiz, 1986), isopar-H (Aparicio and Muhammed, 1989), kerosene (Huang and Juang, 1986), cumene (Svendsen et al., 1990)—has been addressed several times in the literature. Mainly, constant interface cells of the Lewis type were chosen to investigate the time dependence of the extraction. The stirring speed was

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adjusted to the highest possible extent without disturbing the interface, and the zinc concentration was generally kept very low to reach a kinetically controlled regime (Danesi and Chiarizia, 1980) where the diffusional transfer of the reactants and products is much faster than the chemical reaction. Thus, the modeling could be performed by simply using a kinetic law. Nevertheless, the independence of the extraction rate on the stirring speed is not always clear evidence of kinetic limitation. Often the agitators lose efficiency at higher speed and the diffusional mass transfer becomes unaffected by the increased rotation (Danesi and Chiarizia, 1980). In this case the diffusional contribution to the overall extraction rate may still be significant or even dominating. Danesi et al. (1980b) found that their interface two-step consecutive reaction mechanism (ITSCR) can in principle be simulated by a diffusion-controlled process.

Apart from the work of Cianetti and Danesi (1983) and Murthy and Perez de Ortiz (1986), who used an empirical equation for the activity coefficient of D2EHPA, the effect of nonideality in both phases has been neglected. Also the equilibrium of the second dissociation step of hydrogen sulfate has not been taken into consideration when aqueous sulfate media were used (Ajawin et al., 1980; Murthy and Perez de Ortiz, 1986; Huang and Juang, 1986; Svendsen et al., 1990), despite the fact that in the pH range of interest, a significant amount of the hydrogen ions was bound as hydrogen sulfate.

Because of the high interfacial activity of D2EHPA, it is assumed that the reaction between metal cations and D2EHPA takes place at the interface (Vandegrift and Horwitz, 1977; Danesi et al., 1980a). Ajawin et al. (1980) demonstrated that the rate of extraction is proportional to the area of the interface, while it is inversely proportional to the phase volume. This finding can be regarded as additional proof of an interfacial mechanism.

In our previous studies (Sainz-Díaz et al., 1996; Klocker et al., 1996) on the zinc extraction with D2EHPA in *n*-heptane, we could show that the equilibrium can be well described by the formation of the single organic zinc complex $ZnR_2(RH)$, when activity coefficients are used and the hydrogen sulfate equilibrium in the aqueous phase is included. Activity coefficients of the aqueous ions were calculated from the equation of Pitzer (Pitzer, 1973), while the organic ones were obtained by the regular solution theory of Hildebrand and Scott (1950).

The purpose of this work was to study the extraction rate of zinc on the basis of this equilibrium model. In contrast to the main portion of earlier works, where only the initial rate was used for modeling the kinetics, we study the whole path from the start of the extraction experiment to the equilibrium condition. The wide range of the initial zinc and D2EHPA concentrations investigated makes it necessary to allow for the mass transfer of all species, because in a constant interface cell, a kinetically controlled regime can only be reached when both concentrations are sufficiently low. From the point of view of irreversible thermodynamics, the driving force for diffusion has to be expressed in terms of the chemical potential (Taylor and Krishna, 1993; Krishna and Standart, 1979). The derivatives of the activity coefficients with respect to the composition of the two phases were obtained from the Pitzer and the Hildebrand–Scott model, making use of the same interaction parameters as in our equilibrium studies (Klocker, et al., 1996). The transport of ions in the aqueous phase is described by the Nernst–Planck equation, which should hold also for moderately dilute systems, when the composition gradients are corrected with activity coefficients (Newman, 1991). For the diffusion of the zinc complex and of D2EHPA in the heptane phase, the Maxwell–Stefan equations were applied. The Maxwell–Stefan diffusion coefficients are only slightly dependent on the system composition. Thus, it should be reasonable to assume their constancy over the range of conditions that are common in solvent extraction processes with D2EHPA.

Model Equations

In this section, the complete set of model equations describing the rate of the zinc extraction is developed. The solution of the algebraic and differential equations yields the molar flux of zinc over the interface water-*n*-heptane, N_{Zn}, as a function of the bulk compositions of both phases. The model includes a kinetic law, equations for the nonelectrolyte diffusion in the organic phase, and the diffusion equations for the aqueous ions in combination with a differential form of the mass-action law of the hydrogen sulfate equilibrium. The small number of parameters in the model equations that are not directly accessible, for example, kinetic constants, should be determined on the basis of experiments performed in a type of Lewis cell. As to that, the increase of the zinc concentration in the organic phase with time was measured in several experiments with different initial concentrations. The resulting curves have to be differentiated to get the experimental zinc flux N_{Zn}. The missing parameters in our model are obtained from a comparison between experimental and calculated fluxes on the basis of a least-squares criterion.

Equilibrium

It was found in prior studies (Sainz-Díaz et al., 1996; Klocker et al., 1996) that zinc is extracted by D2EHPA in *n*-heptane according to the following reaction:

$$Zn^{2+} + 1.5\overline{R_2H_2} \leftrightarrow \overline{ZnR_2(RH)} + 2H^+ \qquad K_{1,3} \qquad (1)$$

In the aqueous phase, the hydrogen sulfate equilibrium has to be considered

$$H^+ + SO_4^{2-} \leftrightarrow HSO_4^- \qquad K_{HS}, \qquad (2)$$

with the equilibrium constant $K_{HS} = 1/0.0105$ given by Pitzer et al. (1977). Figure 1 shows the Lewis mixing cell. The Masson equation is used for converting molarities to molalities used in the Pitzer equation. Single-ion Masson parameters, together with the Pitzer parameters for the binary and ternary interactions of the ions Zn^{2+}, H^+, $SO_4{}^{2-}$, and $HSO_4{}^-$, are given in Klocker et al. (1996). The solubility parameter δ of the Hildebrand and Scott theory for the dimeric D2EHPA was set equal to that of *n*-heptane (7.45 $cal^{1/2}cm^{-3/2}$). When the following values are assigned to the parameters $K_{1,3}$ and δ of the zinc complex $ZnR_2(RH)$:

$$\log_{10} K_{1,3} = -0.9439 \qquad \delta_{\overline{Zn}} = 9.085,$$

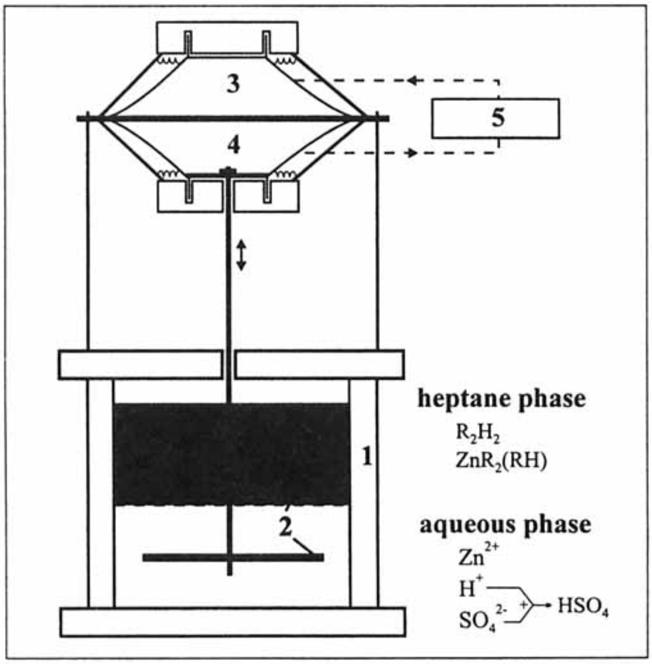

Figure 1. Modified Lewis cell with vibrational mixing.

1: Cylindrical jacketed vessel containing both phases; 2: titanium plates with radial slits; 3: driving loudspeaker; 4: measuring loudspeaker; 5: frequency generator with amplitude regulation.

a good representation of the extraction equilibrium was obtained (Klocker et al., 1996). Additivity of the molar volumes of the organic species was assumed for the conversion of concentration units to mole fractions.

Kinetics

A kinetic model was developed based on the preceding equilibrium reactions. The mechanism includes two consecutive reaction steps.

$$\begin{aligned} &Zn^{2+} + 2(RH)_{ad} \Leftrightarrow (ZnR_2)_{ad} + 2H^+ && k_{f1}, k_{b1} \\ &(ZnR_2)_{ad} + 1.5\overline{R_2H_2} \Leftrightarrow \overline{ZnR_2(RH)} + 2(RH)_{ad} && k_{f2}, k_{b2}. \end{aligned} \tag{3}$$

Applying the steady-state approximation for the interfacially adsorbed zinc complex $(ZnR_2)_{ad}$ leads to the overall kinetic law:

$$N_{Zn} = \frac{R_{Zn}}{\mathfrak{a}} = a_{RHa}^2 \cdot \frac{\dot{\kappa}_f \cdot a_{R2H2}^{1.5} \cdot a_{Zn} - \dot{\kappa}_b \cdot a_H^2 \cdot a_{\overline{Zn}}}{a_{R2H2}^{1.5} + C_1 \cdot a_H^2} \tag{4}$$

with

$$K_{1,3} = \frac{\dot{\kappa}_f}{\dot{\kappa}_b} \qquad \dot{\kappa}_f = \frac{k_{f1}}{\mathfrak{a}} \qquad \dot{\kappa}_b = \frac{k_{b1} \cdot k_{b2}}{\mathfrak{a} \cdot k_{f2}} \qquad C_1 = \frac{k_{b1}}{k_{f2}}.$$

The activity of the adsorbed monomeric D2EHPA, a_{RHa}, can be approximated by a Langmuir-type relation:

$$a_{RHa} = \frac{\alpha \cdot \dfrac{a_{RH}}{\gamma}}{1 + \dfrac{a_{RH}}{\gamma}}. \tag{5}$$

It is further assumed that the monomeric extractant is in equilibrium with its dimeric form:

$$\frac{1}{2}\overline{R_2H_2} \leftrightarrow \overline{RH} \qquad K_{0,1} = \frac{a_{RH}}{\sqrt{a_{R2H2}}}. \tag{6}$$

By combining the Eqs. 5 and 6 with Eq. 4, a kinetic law with three unknown parameters κ_f, C_1, and C_2, can be achieved:

$$N_{Zn} = \frac{\kappa_f \cdot a_{R2H2}^{1.5} \cdot a_{Zn} - \kappa_b \cdot a_H^2 \cdot a_{\overline{Zn}}}{a_{R2H2}^{1.5} + C_1 \cdot a_H^2} \cdot \left(\frac{\sqrt{a_{R2H2}}}{C_2 + \sqrt{a_{R2H2}}} \right)^2$$

$$K_{1,3} = \frac{\kappa_f}{\kappa_b} \quad \kappa_f = \frac{\alpha^2 \cdot k_{f1}}{\mathfrak{a}} \quad \kappa_b = \frac{\alpha^2}{\mathfrak{a}} \cdot \frac{k_{b1} \cdot k_{b2}}{k_{f2}} \quad C_2 = \frac{\gamma}{K_{0,1}}. \tag{7}$$

The reverse rate constant, κ_b, can be expressed in terms of the equilibrium constant, $K_{1,3}$, and the overall forward kinetic constant, κ_f.

Ajawin et al. (1980) proposed a model for the zinc extraction with D2EHPA in the same diluent (*n*-heptane) as in our studies. These authors used extra amounts of sodium sulfate to maintain constant ionic strength, and consequently the aqueous activity coefficients. To compare their model with ours, activity coefficients have to be introduced, resulting in the following kinetic law:

$$N_{Zn} = \kappa_f \cdot \frac{a_{Zn} \cdot a_{R2H2}}{a_H} - \kappa_b \cdot \frac{a_H \cdot c_{\overline{Zn}}}{\sqrt{c_{R2H2}}}. \tag{8}$$

The ITSCR mechanism of Cianetti and Danesi (1983) can be converted to the stoichiometry of our equilibrium reaction Eq. 1. Written in terms of activities, the flux equation becomes:

$$N_{Zn} = \kappa_f \cdot \frac{a_{R2H2}^{1.5} \cdot a_{Zn}}{a_{R2H2}^{1.5} + C_1 \cdot a_H^2} - \kappa_b \cdot \frac{a_H^2 \cdot a_{\overline{Zn}}}{a_{R2H2}^{1.5} + C_1 \cdot a_H^2}. \tag{9}$$

The kinetic constant for the backward reaction in Eqs. 8 and 9 is related to the equilibrium constant via $K_{1,3} = \kappa_f / \kappa_b$.

Mass transfer in the aqueous phase

According to the Nernst–Planck equation for diffusion processes in electrolyte solutions the molar flux of a species *i* is made up of four terms (Taylor and Krishna, 1993; Newman, 1991):

$$N_i = -D_i \cdot \nabla c_i - D_i \cdot c_i \cdot \nabla \ln \gamma_i - c_i \cdot z_i \cdot D_i \cdot \frac{\mathfrak{F}}{RT} \cdot \nabla \phi + c_i \cdot u_n. \tag{10}$$

The first two terms can be combined to give the diffusional contribution. The concentration gradient is corrected by the influence of nonideality through the gradient of the activity coefficient. The other two terms correspond to migration and convection. Since water is not extracted into the organic phase (Sainz-Díaz et al., 1996), its velocity, u_n, is zero, and convection need not be considered.

The gradient of the electrical potential, $\nabla\phi$, in the migration term is the same for all ions in the mixture. If no current is flowing through the mixture, as is encountered in an extraction process, $\nabla\phi$ can be eliminated to give

$$N_i = -D_i\cdot\nabla c_i - D_i\cdot c_i\cdot\nabla\ln\gamma_i + \frac{t_i}{z_i}\cdot\sum_{j=1}^{n_I} z_j\cdot D_j\cdot\nabla c_j + \frac{t_i}{z_i}\cdot\sum_{j=1}^{n_I} z_j\cdot c_j\cdot D_j\cdot\nabla\ln\gamma_j, \tag{11}$$

where the transference number of an ion is defined by

$$t_i = \frac{c_i\cdot z_i^2\cdot D_i}{\sum_{j=1}^{n_I} c_j\cdot z_j^2\cdot D_j}. \tag{12}$$

For one-dimensional transport, one can write

$$N_i = -D_i\cdot\frac{dc_i}{dz} - D_i\cdot c_i\cdot\frac{d\ln\gamma_i}{dz} + \frac{t_i}{z_i}\cdot\sum_{j=1}^{n_I} z_j\cdot D_j\cdot\frac{dc_j}{dz} + \frac{t_i}{z_i}\cdot\sum_{j=1}^{n_I} z_j\cdot c_j\cdot D_j\cdot\frac{d\ln\gamma_j}{dz}. \tag{13}$$

The gradients of the activity coefficients cannot be determined directly. Making use of the total differential:

$$\frac{d\ln\gamma_i}{dz} = \sum_{j=1}^{4}\left\{\left(\frac{\partial\ln\gamma_i}{\partial c_j}\right)_{c_n\neq c_j}\cdot\frac{dc_j}{dz}\right\}, \tag{14}$$

these gradients can be obtained from the partial derivative of the activity coefficient with respect to the composition. These derivatives can be calculated numerically from the Pitzer equation.

The formation of hydrogen sulfate according to Eq. 2 is a fast ionic reaction. It is therefore assumed that the mass action law

$$K_{\mathrm{HS}} = \frac{a_{\mathrm{HS}}}{a_{\mathrm{H}}\cdot a_{\mathrm{S}}} = \frac{c_{\mathrm{HS}}\cdot\gamma_{\mathrm{HS}}}{c_{\mathrm{H}}\cdot\gamma_{\mathrm{H}}\cdot c_S\cdot\gamma_S} \tag{15}$$

is valid everywhere in the aqueous phase. This equation can be differentiated to give a relation between the gradients of H^+, SO_4^{2-} and HSO_4^-:

$$\frac{d\ln\gamma_{\mathrm{H}}}{dz} + \frac{1}{c_{\mathrm{H}}}\cdot\frac{dc_{\mathrm{H}}}{dz} + \frac{d\ln\gamma_{\mathrm{S}}}{dz} + \frac{1}{c_{\mathrm{S}}}\cdot\frac{dc_{\mathrm{S}}}{dz} = \frac{d\ln\gamma_{\mathrm{HS}}}{dz} + \frac{1}{c_{\mathrm{HS}}}\cdot\frac{dc_{\mathrm{HS}}}{dz}. \tag{16}$$

Since the aqueous phase needs to be electrically neutral, the equation

$$2\cdot\frac{dc_{\mathrm{Zn}}}{dz} + \frac{dc_{\mathrm{H}}}{dz} - \frac{dc_{\mathrm{HS}}}{dz} - 2\cdot\frac{dc_{\mathrm{S}}}{dz} = 0 \tag{17}$$

must hold.

Equations 13, 14, 16 and 17 are linear in the concentration gradients. It is possible to obtain explicit analytical expressions for the gradients of the form:

$$\frac{dc_i}{dz} = f(c_{\mathrm{Zn}}, c_{\mathrm{H}}, c_{\mathrm{HS}}, c_{\mathrm{S}}, N_i). \tag{18}$$

The numerical integration of this system of ordinary first-order differential equations can be performed if the fluxes are assumed to be constant over the integration path, which corresponds to the film model. This fact can be applied directly to the flux of the zinc ions:

$$\frac{dN_{\mathrm{Zn}}}{dz} = 0 \Rightarrow N_{\mathrm{Zn}} = \mathrm{const.} \tag{19}$$

Because of the reaction of hydrogen ions to hydrogen sulfate, only the sum of the fluxes N_{H} and N_{HS} can be considered constant. This follows from the continuity equation by eliminating the reaction rate R:

$$\frac{dN_{\mathrm{H}}}{dz} = -\mathrm{R} \quad\text{and}\quad \frac{dN_{\mathrm{HS}}}{dz} = \mathrm{R} \Rightarrow N_{\mathrm{H}} + N_{\mathrm{HS}} = \mathrm{const.} \tag{20}$$

The stoichiometry of Eqs. 1 and 2 leads to the following relation between the flux of Zn^{2+} and the sum of N_{H} and N_{HS}:

$$N_{\mathrm{Zn}} = -\frac{1}{2}(N_{\mathrm{H}} + N_{\mathrm{HS}}). \tag{21}$$

Mass transfer in the organic phase

The transport of the zinc complex and the dimeric D2EHPA was described by the Maxwell–Stefan equations for molecular diffusion. In the $(n-1)$ matrix form, these equations can be written as

$$(J) = -c_t\cdot[B]^{-1}\cdot[\Gamma]\cdot(\nabla x). \tag{22}$$

The matrix $[B]$ is a function of the system composition and the Maxwell–Stefan diffusion coefficients (Taylor and Krishna, 1993; Krishna and Standart, 1979):

$$B_{ii} = \frac{x_i}{\text{Đ}_{in}} + \sum_{\substack{k=1\\k\neq i}}^{n}\frac{x_k}{\text{Đ}_{ik}} \tag{23}$$

$$B_{ij} = -x_i\cdot\left(\frac{1}{\text{Đ}_{ij}} - \frac{1}{\text{Đ}_{in}}\right). \tag{24}$$

The system discussed here is a ternary mixture of the components D2EHPA, the zinc complex, and the diluent heptane. Therefore, the matrices $[B]$ and $[\Gamma]$ in Eq. 22 have the dimension 2×2. Only two composition gradients are independent. The matrix of thermodynamic factors relating the composition gradients to the gradients of the chemical potential is defined by

$$\Gamma_{ij} = \delta_{ij} + x_i \cdot \left(\frac{\partial \ln \gamma_i}{\partial x_j} \right)_{P,T,\Sigma} \tag{25}$$

The constrained derivatives of the Hildebrand–Scott model were obtained analytically. When it is assumed that this matrix is constant over the integration path, an analytical solution of the Maxwell–Stefan equations for the film model can be found:

$$\begin{aligned} J_{\mathrm{R2H2},B} &= -k_{11} \cdot (c_{\mathrm{R2H2},B} - c_{\mathrm{R2H2},I}) - k_{12} \cdot (c_{\overline{\mathrm{Zn}},B} - c_{\overline{\mathrm{Zn}},I}) \\ J_{\overline{\mathrm{Zn}},B} &= -k_{21} \cdot (c_{\mathrm{R2H2},B} - c_{\mathrm{R2H2},I}) - k_{22} \cdot (c_{\overline{\mathrm{Zn}},B} - c_{\overline{\mathrm{Zn}},I}). \end{aligned} \tag{26}$$

The matrix of mass-transfer coefficients $[k]$ is defined by

$$[k] = \frac{[B_B]^{-1} \cdot [\Gamma_{\mathrm{av}}]}{l_o} \cdot [\Xi_B]. \tag{27}$$

The matrix $[B]$ must be determined at the composition of the organic bulk, while the thermodynamic factors have to be calculated at the average mole fractions between bulk and interface. The correction matrix for high fluxes, $[\Xi_B]$, is close to the identity matrix for the magnitude of fluxes involved in extraction processes. Nevertheless, we included this correction for the sake of completeness. The definition of this matrix can be found elsewhere (Taylor and Krishna, 1993; Krishna and Standart, 1979). As the molar fluxes and the interface composition have to be known in advance for calculating $[\Xi_B]$ and $[\Gamma_{\mathrm{av}}]$, an iterative procedure (Taylor and Krishna, 1993) is necessary for obtaining the mass-transfer coefficient matrix $[k]$ from Eq. 27. The closure relations ("the bootstrap problem," Krishna and Stardart, 1979; Taylor and Krishna, 1993) for converting the diffusion fluxes, J, in the bulk to the molar fluxes, N, are as follows

$$\begin{aligned} N_{\overline{\mathrm{Zn}}} &= J_{\overline{\mathrm{Zn}},B} + x_{\overline{\mathrm{Zn}},B} \cdot N_t \\ N_{\mathrm{R2H2}} &= J_{\mathrm{R2H2},B} + x_{\mathrm{R2H2},B} \cdot N_t, \end{aligned} \tag{28}$$

where the total flux N_t is

$$N_t = N_{\overline{\mathrm{Zn}}} + N_{\mathrm{R2H2}} = -\frac{1}{2} \cdot N_{\overline{\mathrm{Zn}}} = \frac{1}{3} \cdot N_{\mathrm{R2H2}}. \tag{29}$$

Concentrations were converted to the mole fractions by assuming additivity of the molar volumes. Molar volumes of the species involved can be found in (Klocker et al., 1996).

Solving the Model Equations

If the kinetic parameters κ_f, C_1, C_2 and the film thicknesses of the aqueous, l_a, and the organic, l_o, phases are given, the set of model equations can be solved. As the molar flux of zinc has to be known to integrate over the aqueous film, an iterative calculation is required. First, the bulk concentrations of all species in the organic and aqueous phases are calculated from the initial concentrations of the kinetic experiment and the organic sample concentration at time t on the basis of 100% dissociated sulfuric acid:

$$\begin{aligned} c_{\mathrm{H,tot},B}(t) &= c_{\mathrm{H,tot},B}(t=0) + 2 \cdot c_{\overline{\mathrm{Zn}},B}(t) \cdot \frac{V_{\mathrm{org}}}{V_{\mathrm{aq}}} \\ c_{\mathrm{R2H2},B}(t) &= c_{\mathrm{R2H2},B}(t=0) - \frac{3}{2} \cdot c_{\overline{\mathrm{Zn}},B}(t). \end{aligned} \tag{30}$$

In the aqueous phase, the hydrogen sulfate equilibrium has to be considered. Solving the balance equations of H^+, $SO_4{}^{2-}$ and $HSO_4{}^-$ together with the mass-action law equation (Eq. 15) leads to the bulk concentrations of these species. Because the aqueous activity coefficients calculated from the model of Pitzer are not known in advance, an iterative procedure starting with $\gamma_i = 1$ for all species is necessary. Subsequently, a small value for the flux of zinc in the aqueous phase is assumed. Then, the integration over the aqueous film starting at the composition of the aqueous bulk with $z = 0$ can be performed. We used the third-order Runge–Kutta method. The interface concentrations of all aqueous ions are obtained, when the end of the integration interval is reached ($z = l_a$). Now, the set of nonlinear equations consisting of the transport equations (Eqs. 26), the conversion to the molar fluxes (Eqs. 28), the kinetic law (Eq. 7, 8 or 9), and the Hildebrand–Scott equation for the activity coefficients at the composition of the interface can be solved for the fluxes of the zinc complex and of the dimeric D2EHPA using Newton's method. Further iterations are required if the correction matrix for high fluxes and the thermodynamic factors were included. The resulting flux of the zinc complex should be equal to the flux of the aqueous zinc ions. Based on the calculated organic zinc flux, a new estimation is assumed for the aqueous one, and the calculus is repeated until convergence in the zinc flux is reached.

For carrying out a parameter estimation study, the preceding algorithm was implemented in the least-squares routine ORGLS (Bushing and Levy, 1962). The ability of a model to fit a set of data according to the least-squares criterion is given by the agreement factor σ (Moyer et al., 1993; Baes et al., 1987), which is defined by

$$\sigma = \left[\frac{\sum_{i=1}^{N_E} w_i \cdot \{(N_{\mathrm{Zn}})_{i,\mathrm{exp}} - (N_{\mathrm{Zn}})_{i,\mathrm{calc}}\}^2}{N_E - N_P} \right]^{1/2}, \tag{31}$$

where N_P is the number of simultaneous estimated parameters, while N_E represents the number of experimental data points (zinc fluxes). The weighting factor, w_i, is the reciprocal of the square of the uncertainty, σ_i, in the flux, N_{Zn}. The relative experimental error of the zinc fluxes, $\sigma_i / N_{\mathrm{Zn}}$, was assumed to be 0.15. For a perfectly fitting model, σ would be unity if the uncertainty in the data is correctly estimated. Examples for the discrimination between different models for solvent extraction equilibria on the basis of σ can be found elsewhere (Moyer et al., 1993; Baes et al., 1987, 1990).

The program was written in FORTRAN 90 and was run on a Siemens Nixdorf SC900 supercomputer. Numerical FORTRAN routines—Newton equation solver, Runge–Kutta integrator—were taken from Engeln-Mülliges and Reutter (1988).

Experimental Studies

D2EHPA (98%; Merck) was purified as described in (Sainz-Díaz et al., 1996). The analysis of the product by the titration method of Sainz-Díaz et al. (1996) showed a purity of 99.3%. Stock solutions of $ZnSO_4 \cdot 7H_2O$ (pro analysis; Merck) were prepared in freshly distilled, deionized water. These mixtures were diluted to the required experimental conditions after adding certain amounts of a 0.1-M aqueous solution of H_2SO_4 (Titrisol; Merck). Heptan (pro analysis; Merck) was used as received. A radioactive tracer method was chosen for analyzing the organic zinc concentration. A $Zn^{65}Cl_2$ solution with an activity of 950 kBq/g was supplied by the Physikalisch Technischen Bundesanstalt, Braunschweig, Germany. The $ZnSO_4$ form of the tracer was obtained by repeated evaporation to dryness with dilute sulfuric acid under reduced pressure. The residuum was dissolved in 9 mL of 0.1-M H_2SO_4.

The kinetic experiments were performed in a type of Lewis cell. The cell was shown earlier in Figure 1. Instead of the usual rotators, two vibrating plates fixed on a common rod, which is driven by a loudspeaker, provide the mixing of both phases (Hancil et al., 1978). A digital frequency generator, which can produce sinus waves with a frequency of 0 to 100 Hz, is used as the power supply for the loudspeaker. The plates with radial slits achieve a circular flow pattern around the rod in both phases. Regulation for the amplitude was constructed to raise the reproducibility and to compensate for the viscosity changes of both phases. A second loudspeaker mounted airtight under the first gives a voltage signal proportional to the amplitude. This signal is integrated and sent back to the regulator. The amplitude of the plates can be adjusted from 0 to 1.00 mm with a precision of ± 0.01 mm. The cell consists of a cylindrical jacketed vessel and the thermostat was set at 25 ± 0.1°C.

Both phases were put into the cell by means of shaking funnels equipped with flexible tubes. First, 150 mL of the aqueous phase was brought into the thermostated cell. An amount of 0.1 to 0.3 mL of the $Zn^{65}SO_4$ tracer solution was added. Pure heptane was carefully poured on the aqueous phase. The frequency generator was turned on for at least 30 min to ensure that both phases reached the required temperature of 25°C.

In the meantime, a concentrated solution of D2EHPA in *n*-heptane was preheated to 25°C. Then the frequency generator was stopped, a sample of the aqueous phase (1.5 mL) was taken, and a certain amount of the D2EHPA concentrate was added to the organic phase by means of a pipette. The total volume of the organic phase was always equal to the aqueous one (150 mL). Afterward, the drive was started, and time zero was set. With a transfer pipette, six samples of the organic phase (0.5 mL) were taken at different times. These small-sample amounts guarantee a volume error of less than 2%. The experiments lasted 3 h in the case of low and middle zinc concentrations (0.1 mM and 0.005 M), and 2 h for higher concentrations of zinc (0.05 M). Within this time span more than 90% of the equilibrium zinc concentration in the organic phase was reached.

For all experiments, a frequency of 50 Hz was used. The amplitude was adjusted to the highest possible value (0.47 mm), where the plane interface is still undisturbed. When low zinc concentrations are used, the initial rate of the zinc extraction becomes nearly independent of the amplitude in the range of 0.37 to 48 mm. Nevertheless, it is difficult to exclude any influence of mass transfer for reasons explained previously.

The concentration vs. time curves were fitted with rational functions (Kamenski and Dimitrov, 1993). The reaction rates of zinc were then obtained by analytically differentiating these functions with respect to time and calculating the value of the derivative at the point of time of the experimental data points. By dividing these rates with the specific interfacial area of the cell, a (31.17 m^2/m^3), the fluxes, N_{Zn}, are obtained. In verifying our model, 265 experimental fluxes from 41 kinetic runs were used.

The viscosity of the purified D2EHPA was measured by means of a Couette flow viscosimeter (Rotavisko; Haake).

Results and Discussion

The diffusion coefficients of the aqueous ions were taken from Newman (1991). The infinite dilution diffusion coefficients of $ZnR_2(RH)$ in D2EHPA and in heptane and of D2EHPA in heptane were calculated with the Wilke–Chang correlation (Wilke and Chang, 1955). Because of the limited concentration range of D2EHPA and the zinc complex involved in solvent extraction practice, it was assumed that these diffusion coefficients can be set equal to the binary Maxwell–Stefan diffusion coefficients, $Đ_{ij}$ (Table 1).

First, the 121 experimental fluxes under the condition of low zinc concentration (0.05 to 0.4 mM) were used to test our model. The film thickness of both phases was assigned a value of zero, which corresponds to infinite mass-transfer resistance. The concentration of the hydrogen ions was corrected by the hydrogen sulfate equilibrium. Using our model for the kinetics, an agreement factor σ of 1.72 was obtained, which corresponds to a good description of the experimental zinc fluxes. The values for the three parameters, κ_f, C_1 and C_2, are given in Table 2.

The representation of the experimental data with the rate equation (Eq. 8) was clearly worse. The adjustment of the single parameter κ_f led to a value of 2.86 for σ. The agreement factor for the model (Eq. 9) with two parameters κ_f and C_1 was 1.92. This is slightly but notably higher than in the case of our model.

The influence of mass transfer was checked by varying the film thickness together with the three kinetic constants of our

Table 1. Maxwell–Stefan Diffusion Coefficients for Organic Species

Diffusive Interaction	$Đ$ [m^2/s]
$ZnR_2(RH)$–heptane	8.17×10^{-10}
$ZnR_2(RH)$–D2EHPA	2.01×10^{-11}
D2EHPA–heptane	1.03×10^{-9}

Table 2. Parameters for the Kinetic Eq. 7 and the Thickness of the Aqueous and Organic Film at 25°C

Data Set	Data Points	κ_f^* [$m \cdot s^{-1}$]	C_1 [$mol^{-1/2} \cdot m^{3/2}$]	C_2 [$mol^{1/2} \cdot m^{-3/2}$]	l_a [m]	l_o [m]
Low zinc concentration	121	1.047×10^{-5}	1.126	0.5910	0	0
All data	265	1.740×10^{-5}	1.057	1.251	0	1.250×10^{-4}

*κ_b calculated with $\kappa_b = \kappa_f / K_{1,3}$, where $K_{1,3} = 10^{-0.9439}$ $mol^{1/2} \cdot L^{-1/2} = 3.598$ $mol^{1/2} \cdot m^{-3/2}$.

model. No improvement was obtained when l_o was fitted together with the kinetic parameters. Optimizing the aqueous film thickness leads to a minimum in σ at l_a at 7.4×10^{-5} m with an agreement factor of 1.71. This slight improvement in σ can hardly be seen as a proof for a significant aqueous resistance to mass transfer. In addition, the error in the four parameters was much higher than usual. It can be concluded that the experimental conditions were sufficient to provide a pure kinetically controlled extraction mechanism.

Modeling the whole set of our 265 experimental data from 0.1-mM to 0.05-M zinc on the basis of our kinetic law gave satisfying results only when mass-transfer resistance was included. Optimizing the parameters κ_f, C_1, and C_2 led to an agreement factor of 2.50. Varying the aqueous film thickness did not lower the value of σ. However, including the parameter l_o gave a distinct improvement of the model. A value of 1.87 for σ demonstrates the important role of the organic mass-transfer resistance. The organic film thickness was estimated to be 1.25×10^{-4} m. The kinetic parameters are summarized in Table 2. Concentration vs. time curves can be obtained, when the flux, N_{Zn}, is calculated at different amounts of zinc extracted in the organic phase. The integration according to:

$$t_n = t_{n-1} + \frac{(c_{\overline{Zn}})_n - (c_{\overline{Zn}})_{n-1}}{a \cdot N_{Zn}} \tag{32}$$

yields the corresponding times. The integration error can be kept low when 100 steps between zero zinc concentration in the organic phase and the equilibrium condition are calculated.

In Figures 2 to 4 the organic zinc concentration is shown as a function of time for 15 of our 41 experimental runs in the vibrational cell. The agreement between the proposed model and the experimental data is generally very good. Small deviations occurred at high D2EHPA concentrations.

The rate equations (Eqs. 8 and 9) were not able to describe our 265 experimental data with sufficient accuracy. Including organic mass-transfer resistance, these equations gave agreement factors of 3.03 and 2.41, respectively.

Analyzing the mass-transfer model of the organic phase, we evaluated three starting points for simplifications. The relatively low fluxes involved in metal extraction processes make it possible to approximate the enhancement factor matrix, $[\Xi]$, with the identity matrix. Also the matrix of thermodynamic factors $[\Gamma]$ was generally close to the identity matrix. The agreement factor was not affected significantly when these two simplifications were introduced. The third point would involve the neglect of the off-diagonal elements in the mass-transfer-coefficients matrix $[k]$, which would lead to a "pseudo"-binary treatment of the diffusion problem. We found that the contribution from these elements to the fluxes was normally higher than 10%. Peak values of more than 25% were calculated for some data points. Therefore, a multicomponent treatment of the mass transfer in the organic phase seems to be unavoidable.

Conclusions

A kinetic model for the extraction of zinc with D2EHPA in *n*-heptane was developed. The mass transfer of the species in

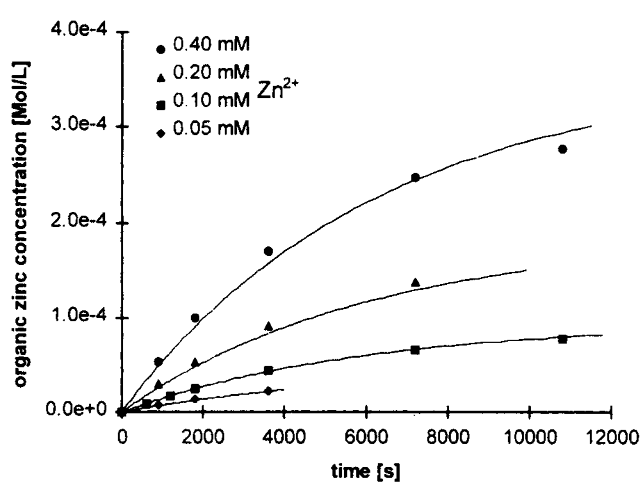

Figure 2. Organic zinc bulk concentration vs. time at different aqueous zinc concentrations.

$[H^+] = 1.1$ mM; $[D2EHPA]_{tot} = 0.01$ M; lines calculated with the model proposed.

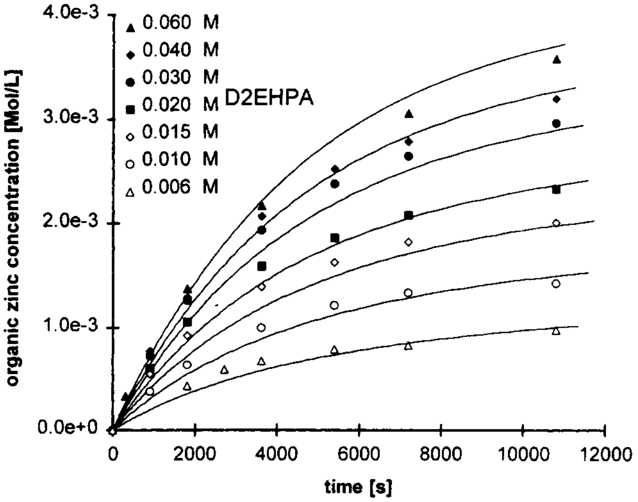

Figure 3. Organic zinc bulk concentration vs. time at different D2EHPA concentrations.

$[Zn^{2+}]_{ini} = 0.005$ M; $[H^+] = 1.1$ mM; lines calculated with the model proposed.

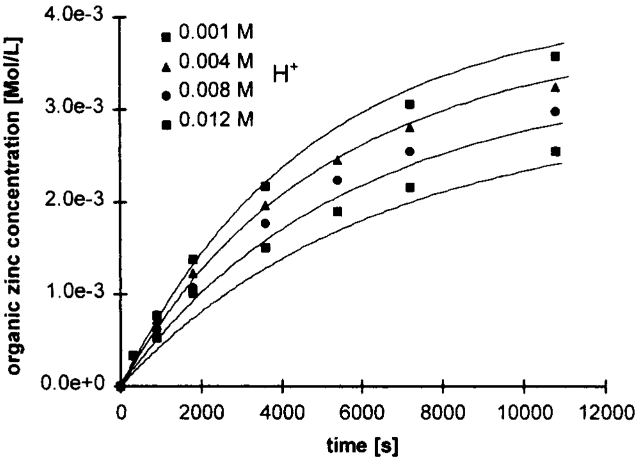

Figure 4. Organic zinc bulk concentration vs. time at different H^+-concentrations.

$[Zn^{2+}]_{ini} = 0.05$ M; $[D2EHPA]_{tot} = 0.1$ M; lines calculated with the model proposed.

the organic phase was included with the Maxwell-Stefan equations. The Nernst-Planck equation was used to describe the diffusion of the aqueous ions. According to the theory of irreversible thermodynamics, the gradient of the chemical potential was used as the driving force for diffusion in both phases. Activity coefficients in the aqueous phase were calculated with the Pitzer equation, while organic concentrations were converted to activities with the Hildebrand-Scott treatment. The fast ionic reaction of the hydrogen and sulfate ions to hydrogen sulfate was assumed to be in equilibrium everywhere in the aqueous phase. The model equations were solved on the basis of the film model. Experiments in a type of Lewis cell with vibrational mixing with the thermostat set at 25°C were used to verify our model. The experimental zinc fluxes at low initial zinc concentrations could be modeled on the basis of the proposed kinetic law without taking into consideration the mass transfer in either phase. Other rate laws from the literature were not able to provide a satisfying representation of our data. For reaching a good description of the whole set of our experiments, with initial zinc concentrations ranging from 0.1 mM to 0.05 M, it was necessary to allow for the mass transfer in the organic phase. The 2×2 matrix of mass-transfer coefficients was dominated by the elements on the main diagonal. Nevertheless the influence of the cross coefficients was usually higher than 10%, which emphasizes the necessity of using multicomponent mass-transfer relations instead of a "pseudo"-binary approach. No aqueous resistance to mass transfer could be found. The calculated concentration vs. time curves agree well with the experimental data points.

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Notation

a_i = activity of a species
α = constant in Langmuir's law
C = constants in the kinetic law
c = concentration, mol/m^3
δ_{ij} = Kronecker delta
$[\Gamma_{av}]$ = matrix of thermodynamic factors calculated at the average composition between bulk and interface
γ = constant in Langmuir's law
$\mathfrak{F}$ = Faraday constant, C/mol
$K_{0,1}$ = equilibrium constant for the formation of monomeric D2EHPA
n = number of components in the organic phase
n_I = number of ions in the aqueous phase
t_i = transference number of ion i
V_{aq} = volume of aqueous phase
V_{org} = volume of organic phase
x_i = mole fraction of species i
z_i = charge of an ion i

Subscripts

B = concerning the bulk
I = concerning the interface
RH = monomeric D2EHPA
RHa = monomeric D2EHPA adsorbed at the interface
R2H2 = dimeric D2EHPA
tot = total concentration based on 100% dissociated H_2SO_4
$\overline{\text{Zn}}$ = zinc/D2EHPA complex in the organic phase

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