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Kinetic Studies of Zinc Extraction from Sulfate Solutions with *bis*(2-Ethylhexyl)thiophosphoric Acid

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ABSTRACT

This paper reports a study of the kinetics of zinc extraction from sulfate media with *bis*(2-ethylhexyl)thiophosphoric acid (D2EHTPA). A cell with a constant interfacial area and with vibrational mixing was used to measure the initial extraction and initial stripping rates under several operating conditions. The results obtained suggest that the extraction process can be described by the reaction mechanism scheme proposed by Ajawin et al. [Ajawin, L.A.; Pérez de Ortiz, E.S.; Sawistowski, H. Extraction of zinc by di(2-ethylhexyl)phosporic acid. Chem. Eng. Res. Des. **1983**, *61*, 62–66.] The reaction rate constants were evaluated by taking into account the nonideality of the aqueous phase. The activity coefficients of the ions in the $ZnSO_4-H_2SO_4-Na_2SO_4$ aqueous system

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were calculated by applying the Pitzer model. The thermodynamic kinetic constants for the forward and backward reactions were found to be $3.1 \times 10^{-5}\,\mathrm{m\,sec^{-1}}$ and $1.0 \times 10^{-6}\,\mathrm{kmol^{-0.5}\,m^{2.5}\,sec^{-1}}$, respectively, at 293 K. The ratio between these rate constants agrees satisfactorily with the thermodynamic equilibrium constant obtained in a previous study.

Key Words: Zinc extraction; Kinetics; *bis*(2-Ethylhexyl)thiophosphoric acid; Ion activity.

INTRODUCTION

The extraction of zinc from sulfuric media has experienced a renewed interest because of the use of this process on a commercial scale for treating waste streams and secondary materials.[1] Much work concerning the system $ZnSO_4$/*bis*(2-ethylhexyl)phosphoric acid (D2EHPA) has been published to characterize the extraction stoichiometry and to evaluate the kinetics.[1–11] Another important extractant is the equivalent form of D2EHPA with a sulfur atom, D2EHTPA. This liquid ion exchanger is able to extract zinc at lower pH values[12] but exhibits slower stripping kinetics.[13] Thus, its use seems to be very interesting in processes that afford large interfacial areas for contacting, such as emulsion liquid membranes and nondispersive solvent extractions by using hollow fibers. Most of the studies concerning the extraction of zinc with D2EHTPA are related to the application of the emulsion liquid membranes separation technique.[12–15] Reis and Carvalho reported a fundamental study of the extraction equilibrium of zinc from sulfate media with D2EHTPA.[16] Besides the equilibrium, reaction kinetics has to be known to describe the system. Regardless of the equipment used in traditional liquid–liquid extraction, emulsion liquid membranes, or in non-dispersive extraction, the knowledge of the equilibrium and kinetic parameters is obviously essential to the design of efficient contactors.

The present study is of the kinetics of zinc extraction from sulfate solutions with D2EHTPA. In this work, sodium sulfate was selected to maintain the ionic strength of the aqueous solution at a constant value. As in the previous studies,[16] the nonideal behavior of the $ZnSO_4–H_2SO_4–Na_2SO_4$ aqueous system was taken into account. The activity coefficients were calculated by applying the Pitzer ion-interaction model.[17] The kinetic experiments were carried out in a cell with a constant interfacial area, and the initial extraction and initial stripping rates were measured independently. The resulting rate constants were evaluated in terms of the activities of the aqueous phase. The results were compared with the thermodynamic equilibrium constant obtained in the previous work.[16]

THEORY

Previous studies[16] showed that the extraction of zinc with D2EHTPA, at low concentrations, can be described by the following overall equilibrium

$$\mathrm{Zn}^{2+} + 1.5(\mathrm{HR})_2 \leftrightarrows \mathrm{ZnR}_2 \cdot \mathrm{HR} + 2\mathrm{H}^+ \tag{1}$$

The thermodynamic equilibrium constant, given in terms of the aqueous phase, as

$$K_{\mathrm{ex}}^{0,\mathrm{aq}} = \frac{c_{\mathrm{ZnR}_2\cdot\mathrm{HR}} \cdot a_{\mathrm{H}^+}^2}{a_{\mathrm{Zn}^{2+}} \cdot c_{(\mathrm{HR})_2}^{1.5}} \tag{2}$$

was found to be 32 $\mathrm{kmol}^{0.5}\,\mathrm{m}^{-1.5}$ at 293 K.[16]

Because of the strong interfacial activity of D2EHTPA and its very low solubility in water, it is assumed that the reaction between zinc ions and D2EHTPA takes place at the interface. According to the literature,[2,4,5,7] the interface is regarded as the site of the chemical reaction between metal cations and D2EHPA, and several reaction mechanisms are based on this assumption.[18] Ajawin et al.[2] proposed that the reaction mechanism be represented by the following elementary steps:

$$(\mathrm{HR})_2 \leftrightarrows (\mathrm{R}_2\mathrm{H}^-)_{\mathrm{ad}} + \mathrm{H}^+, \quad K_3, k_3, k_{-3} \tag{3}$$

$$\mathrm{Zn}^{2+} + (\mathrm{R}_2\mathrm{H}^-)_{\mathrm{ad}} \leftrightarrows (\mathrm{Zn}R_2)_{\mathrm{ad}} + \mathrm{H}^+, \quad K_4, k_4, k_{-4} \tag{4}$$

$$(\mathrm{Zn}R_2)_{\mathrm{ad}} + (n\text{-}1)(\mathrm{HR})_2 \leftrightarrows \mathrm{Zn}R_2 \cdot (\mathrm{HR})_{2n-2} + 2\mathrm{H}^+, \quad K_5, k_5, k_{-5} \tag{5}$$

where k_i and k_{-i} are forward and backward rate constants of the ith reaction steps and K_i are equilibrium constants. The overall reaction results in the equilibrium of Eq. (1), with $n = 1.5$, in the present work, as obtained by other authors.[1–4] Considering that Eq. (4) is the rate-determining step (2), the extraction rate of zinc per unit interfacial area is obtained as follows:

$$N = k_{\mathrm{F}} \frac{c_{\mathrm{Zn}^{2+}} \cdot c_{(\mathrm{HR})_2}}{c_{\mathrm{H}^+}} - k_{\mathrm{R}} \frac{c_{\mathrm{H}^+} \cdot c_{\mathrm{ZnR}_2\cdot\mathrm{HR}}}{c_{(\mathrm{HR})_2}^{0.5}} \tag{6}$$

with $k_{\mathrm{F}} = K_3\, k_4$ and $k_{\mathrm{R}} = k_{-4}/K_5$. This reaction mechanism also was adopted by Svendsen et al.[5] and Mansur et al.[11]

If the activity coefficients are introduced in Eq. (6) to take into account the nonideality of the aqueous phase, the kinetic law will become

$$N = k_{\mathrm{F}}^{0,\mathrm{aq}} \frac{a_{\mathrm{Zn}^{2+}} \cdot c_{(\mathrm{HR})_2}}{a_{\mathrm{H}^+}} - k_{\mathrm{R}}^{0,\mathrm{aq}} \frac{a_{\mathrm{H}^+} \cdot c_{\mathrm{ZnR}_2} \cdot \mathrm{HR}}{c_{(\mathrm{HR})_2}^{0.5}} \tag{7}$$

with

$$\frac{k_{\mathrm{F}}^{0,\mathrm{aq}}}{k_{\mathrm{R}}^{0,\mathrm{aq}}} = K_{\mathrm{ex}}^{0,\mathrm{aq}}$$

The kinetic parameter $k_{\mathrm{F}}^{0,\mathrm{aq}}$, for instance, is related to the concentration-based rate constant, k_{F}, via

$$k_{\mathrm{F}}^{0,\mathrm{aq}} = k_{\mathrm{F}} \frac{\gamma_{\mathrm{H}^+}}{\alpha \gamma_{\mathrm{Zn}^{2+}}} \tag{8}$$

where γ_i is the activity coefficient of species i on the molarity scale (converted from the molality scale value obtained with the Pitzer method) and α is the fraction of free zinc ions. It is emphasized that Eq. (6) is written by considering that all zinc present in the aqueous solution exists as cationic species, Zn^{2+}. However, zinc sulfate solutions are known to undergo ion pairing, and the presence of the neutral complex $ZnSO_4$ must be taken into account in the aqueous solution. Besides this equilibrium, the incomplete dissociation of bisulfate ion must be considered, whereas, the dissociation of sodium sulfate can be assumed to be complete.[16] The species present in the $ZnSO_4{-}H_2SO_4{-}Na_2SO_4$ aqueous system to apply the Pitzer model are then the ions H^+, HSO_4^-, SO_4^{2-}, Zn^{2+}, Na^+, and the ion pair $ZnSO_4$. Hydroxide ion and zinc hydroxides are assumed to have negligible concentrations, as the pHs of the actual solutions are lower than 4.

EXPERIMENTAL

Reagents

Chemicals in the aqueous phase ($ZnSO_4$, H_2SO_4, and Na_2SO_4) were of high-purity analytical grade (Merck). The extractant D2EHTPA was kindly supplied by Höchst AG (Portugal) and used without purification. Its purity was determined via potentiometric titration in 2-propanol with 0.1 $\mathrm{kmol\,m^{-3}}$ tetrabutylammonium hydroxide (Merck) and was found to be 79%. The extractant was dissolved in Shellsol T (Shell Chemical Ltd.), a commercial aliphatic diluent similar to kerosene. After dilution, the organic phases were washed with deionized water to remove the soluble impurities.

Procedure

The concentration of zinc in the aqueous phase, as well as in the organic phase, was measured via atomic absorption spectroscopy (Perkin–Elmer 3100 and Perkin–Elmer 373 spectrometers, respectively). The deviations of the measured concentrations in the organic phase from the corresponding values obtained by mass balance were less than 5%. The level of acid in the aqueous phase was analyzed on a Metrohm 682 titroprocessor with 0.1 kmol m^{-3} sodium hydroxide (Titrisol, Merck) or 0.01 kmol m^{-3} sodium hydroxide (Fixanal, Riedel-de-Haën). The pH values of the aqueous solutions were varied by adjusting the amount of H_2SO_4 added and were measured on a Metrohm 682 titroprocessor at 298 K with a combined electrode. The densities of the aqueous solutions were measured to convert from the molarity scale to the molality scale. However, for most cases, the concentrations on these different scales do not differ more than 2%. The viscosity of the solutions was obtained with an Ubbelohde viscometer.

The extraction and stripping reactions were carried out in a modified Lewis cell with vibrational mixing according to Hancil and coauthors[19] (see Fig. 1). In this cell, each phase was mixed by a vibrating perforated plate. The plates were fixed to a common rod driven by the moving coil of a loudspeaker (Pioneer TS-G1030, 50 W, 4 Ω). This coil was fed by a frequency generator (GoldStar FG-2002C) with amplitude regulation (Sony TA-F420). A second loudspeaker with its coil mounted on the driving rod was connected to an oscilloscope (Kiotto G-5060 60 MHz) and used for indirect amplitude measurements.

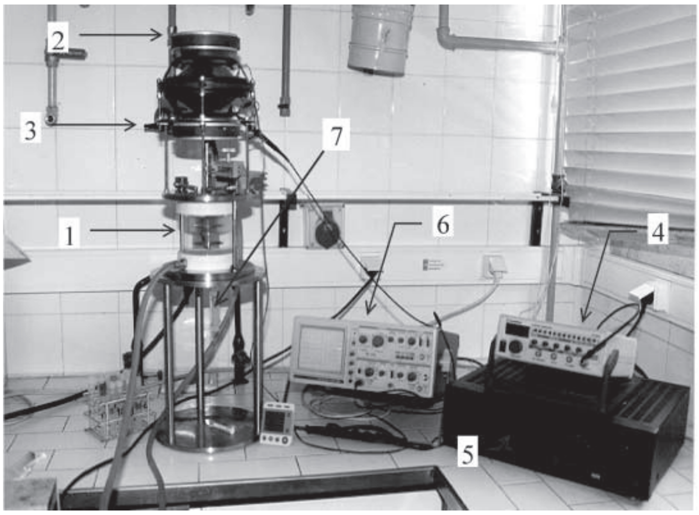

Figure 1. Kinetic studies apparatus. (1) Cylindrical jacketed cell; (2) driving loudspeaker; (3) measuring loudspeaker; (4) frequency generator; (5) amplifier; (6) oscilloscope; (7) sampling of aqueous phase.

The initial extraction and stripping rates were separately measured by the following procedure. An aqueous solution with a volume of 150 mL was first placed in the cell, and then an equal volume of the organic solution was carefully introduced into the cell. Attention was paid to the interface, where the disturbance must be minimized. The timing was started up on half-addition of the organic phase. The vibrational mixing was started simultaneously. The temperature was maintained at 293 ± 0.1 K, except when the effect of this variable on the kinetics was tested. About five or six samples (0.3-0.7 mL) were withdrawn from each phase with a hypodermic needle and a syringe at defined time intervals to be analyzed.

Initial extraction and stripping rates were calculated from the slopes of the straight lines (zinc concentration vs. time) according to

$$N = \frac{V_{\mathrm{org}}}{S}\frac{dc_{\mathrm{Zn(org)}}}{dt} \tag{9}$$

$$N' = \frac{V_{\mathrm{aq}}}{S}\frac{dc_{\mathrm{Zn(aq)}}}{dt} \tag{10}$$

where the interfacial area between the two phases, S, was 43.8 cm^2. The data were taken over a small fraction of the approach of the equilibrium, usually less than 10%.

RESULTS AND DISCUSSION

Forward Extraction Rate of Zinc

The forward extraction rate was measured under several vibrational mixing conditions. A plateau region was reached between 50 and 90 Hz, with an amplitude of 0.3 mm for two pH values of the aqueous phase, pH 1.5 and pH 3.5. Higher levels of agitation were tested, but the interface was no longer stable and the interface area was no longer constant. Thus, within the kinetic plateau at 70 Hz, the effect of some variables, such as the temperature, the pH of the aqueous phase, the concentration of sodium sulfate in the aqueous phase, and the concentration of extractant in the organic phase, on the extraction rate was studied.

Effect of Temperature on the Extraction Rate

The effect of temperature, in the range of 293–313 K, on the extraction rate was studied under different extraction conditions. The extraction rate was found to increase slightly with temperature at pH 3. However, the extraction rate was more dependent on temperature at pH < 3. The apparent activation energy was calculated from the slope of $\log N$ vs. $1/T$, shown in Fig. 2. The corresponding values at different pHs are as follows:

$$\mathrm{pH} = 1.5, \quad E_a = 45 \pm 10\,\mathrm{kJ\,mol^{-1}}$$

$$\mathrm{pH} = 2.5, \quad E_a = 43 \pm 5\,\mathrm{kJ\,mol^{-1}}$$

$$\mathrm{pH} = 3.0, \quad E_a = 17 \pm 1\,\mathrm{kJ\,mol^{-1}}$$

Even with the independence of the extraction rate on the agitation level within the plateau of kinetics, the results obtained suggest that the resistance of diffusion cannot be ignored. Moreover, the resistance of the chemical reaction is negligible in comparison with that of diffusion at pH 3. This fact was supported by measuring the viscosity of the aqueous phase in the same range of temperature. An apparent activation energy for the viscosity was found to be $16 \pm 2\,\mathrm{kJ\,mol^{-1}}$. The extraction kinetics of zinc with D2EHTPA, therefore, is controlled by the diffusion of zinc ion in the aqueous phase at pH higher than 2.5–3, and a mixed diffusion–chemical reaction mechanism can be assumed at lower pH. Mansur and coauthors[11] used a similar cell to

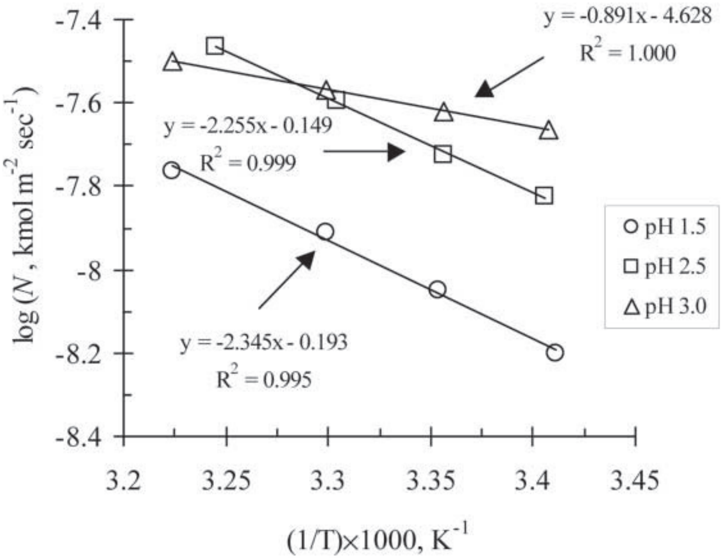

Figure 2. Dependence of the initial extraction rate on temperature. $\mathrm{HR_{total}} = 0.09$ $\mathrm{kmol\,m^{-3}}$. Aqueous phase: $\mathrm{Zn_{total}} = 4.59 \times 10^{-3}\,\mathrm{kmol\,m^{-3}}$, $\mathrm{Na_2SO_4} = 0.268\,\mathrm{kmol\,m^{-3}}$, pH = 1.5, 2.5, 3.0.

study the kinetics of zinc extraction with D2EHPA, and they also found that the rate of the extraction process generally is mixed controlled.

Evaluation of the Forward Rate Constant

If a mixed regime is assumed with the contribution of the chemical reaction and diffusion, the kinetic resistance can be evaluated from the measurement of the overall resistance of extraction. The overall coefficient of mass transfer, K_o, is obtained from the initial extraction rate, which can be expressed as follows:

$$N = -\frac{V_{aq}}{S}\frac{dc_{Zn(aq)}}{dt} = K_o c_{Zn(aq)} \tag{11}$$

and after integration gives

$$\ln\frac{c_{Zn(aq)}}{c_{Zn(aq),0}} = -\frac{S}{V_{aq}}K_o t \tag{12}$$

To derive the expression that relates the overall resistance of mass transfer to the kinetic resistance, the mass transfer rate of zinc in the aqueous phase was assumed as

$$N = k_{aq}(c_{Zn(aq)} - c_{Zn(aq),int}) \tag{13}$$

according to the two-film theory. From Eqs. (6), (11), and (13), and assuming that the resistance of mass transport in the organic phase is negligible (the distribution ratio is very high), as well as the resistance of mass transport of protons in the aqueous phase because of their high diffusivity, the following equation is obtained:

$$\frac{1}{K_o} = \frac{1}{k_{aq}} + \frac{c_{H^+}}{k_F c_{(HR)_2}} \tag{14}$$

where the contribution of the reverse reaction in Eq. (6) was neglected, as the data were taken far from the equilibrium.

The experimental data obtained in the range of pH from 1 to 3.5 allowed the calculation of K_o values. The plot of $1/K_o$ against c_H^+ is shown in Fig. 3. A straight line was obtained that confirms that the reaction is in inverse first order with respect to hydrogen ion concentration. Results with identical slopes of trendlines were obtained by varying the initial concentration of zinc in the range of $1.53 - 4.59 \times 10^{-3}\,\text{kmol}\,\text{m}^{-3}$. This fact corroborates that the reaction is first order with respect to zinc concentration and agrees with the kinetic model used to describe the interfacial reaction of extraction. The concentration-based kinetic constant evaluated from the slope of the straight line of Fig. 3 is found to be $(3.1 \pm 0.2) \times 10^{-6}\,\text{m}\,\text{sec}^{-1}$. This value

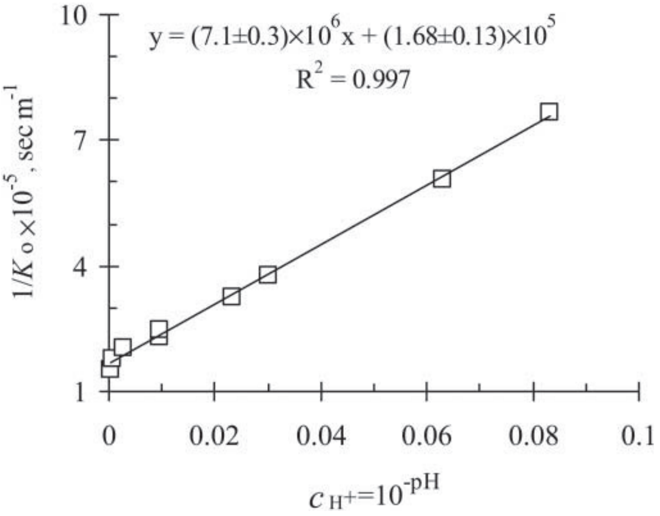

Figure 3. Overall resistance of mass transfer vs. $c_H^+ \cdot \mathrm{HR}_{\mathrm{total}} = 0.09\,\mathrm{kmol\,m^{-3}}$. Aqueous phase: $\mathrm{Zn}_{\mathrm{total}} = 4.59 \times 10^{-3}\,\mathrm{kmol\,m^{-3}}$, $\mathrm{Na_2SO_4} = 0.268\,\mathrm{kmol\,m^{-3}}$, pH = 1.0–3.5.

was calculated by considering $c_{\mathrm{dimer}} = c_{\mathrm{HR\ total}}/2$. The film mass transfer coefficient of zinc in the aqueous phase was evaluated as $k_{\mathrm{aq}} = 6.0 \times 10^{-6}\,\mathrm{m\,sec^{-1}}$. Miyake and coauthors[20] reported a value slightly higher, $k_{\mathrm{aq}} = 1.1 \times 10^{-5}\,\mathrm{m\,sec^{-1}}$, for a similar aqueous phase in a cell with a constant interfacial area. The diffusion coefficient of zinc in the aqueous solution was estimated as $7.5 \times 10^{-10}\,\mathrm{m^2\,sec^{-1}}$ at 293 K by using the Nernst equation.[21] The thickness of the aqueous film, therefore, is found to be $\approx 10^{-4}$ m, which is in agreement with the usual values exhibited in Lewis-type cells.[22]

Figure 4 illustrates the dependence of the extraction rate on the dimeric D2EHTPA concentration. The reaction rate seems to be first order with respect to the extractant concentration, which agrees with the kinetic law stated before.

Effect of Sodium Sulfate on the Extraction Rate

It is evident that the value of k_F changes with the aqueous composition or ionic strength, and with the organic diluent. For instance, the excess of sodium sulfate added to the solution to maintain the ionic strength at a constant value affects the activity of zinc ions. Consequently, the kinetics is influenced by the presence of salt and depends on its concentration. To calculate the activity of zinc ions, the speciation of the aqueous solution was done and the Pitzer

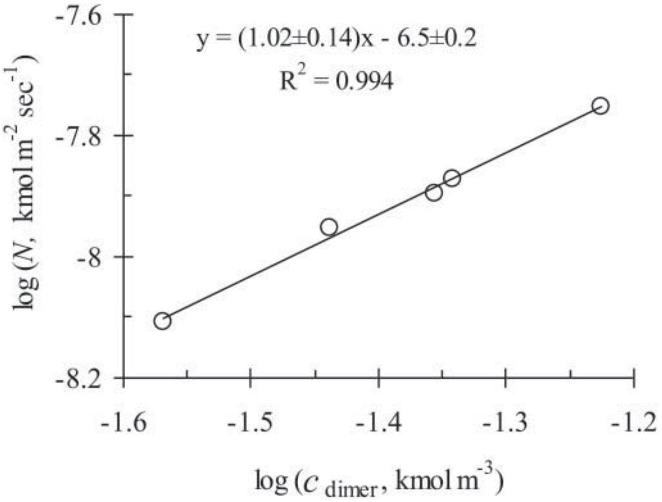

Figure 4. Initial extraction rate (log) vs. total concentration of extractant as dimer (log). Aqueous phase: $\text{Zn}_{\text{total}} = 4.59 \times 10^{-3}\,\text{kmol m}^{-3}$, $\text{Na}_2\text{SO}_4 = 0.268\,\text{kmol m}^{-3}$, pH = 1.5.

ion-interaction model[17] was applied, as stated before. The values of the Pitzer parameters were obtained from the literature.[6,23] At 298 K, the equilibrium constants corresponding to the dissociation of the bisulfate ion and to the formation of zinc sulfate ion pair were taken as 0.0105[23] and 239.9,[24] respectively. The activity coefficient of the zinc sulfate ion pair was set at unity.[25]

The influence of sodium sulfate on the initial extraction rate is shown in Fig. 5. When the salt concentration in the aqueous phase increases, the extraction rate decreases. This is caused by the variation of the activity of the extractable species in the range of salt concentrations tested, which also is shown in Fig. 5. The extraction decrease with the increase in the ionic strength for the zinc/D2EHPA system also is reported in the literature.[2,4]

The overall coefficient of mass transfer also was evaluated in terms of activity of zinc ions, $K_o/(\alpha\gamma_{\text{Zn}}^{2+})$, and the corresponding resistance of mass transfer was plotted against the activity of hydrogen ions. This representation can be observed in Fig. 6 for the test with $0.268\,\text{kmol m}^{-3}$ of sodium sulfate in the aqueous phase. The kinetic constant $k_F^{0,\text{aq}}$, therefore, is estimated from the slope of the straight line (Fig. 6) and is found to be $(3.0 \pm 0.2) \times 10^{-5}\,\text{m sec}^{-1}$. Table 1 lists all the values of the kinetic constants, k_F and $k_F^{0,\text{aq}}$, obtained in the range of ionic strengths tested. The results confirm that $k_F^{0,\text{aq}}$ is not practically influenced by the content of salt in the aqueous solution.

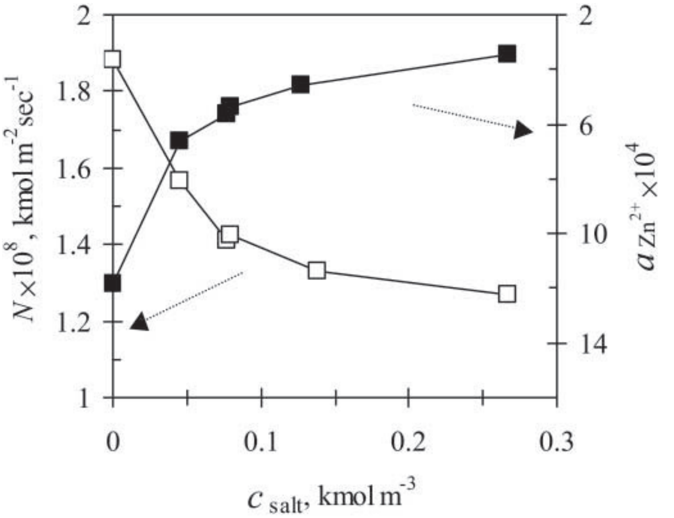

Figure 5. Effect of Na_2SO_4 concentration on the initial extraction rate and $a_{Zn^{2+}}$. $HR_{total} = 0.09\,kmol\,m^{-3}$. Aqueous phase: $Zn_{total} = 4.59 \times 10^{-3}\,kmol\,m^{-3}$, pH = 1.5.

As expected, the nonideal behavior of the aqueous phase explains the k_F decrease with the increase in sodium sulfate concentration and the discrepancy between the constants k_F and $k_F^{0,aq}$.

Stripping Rate of Zinc

The initial stripping rate was measured under several vibrational mixing conditions, as in the earlier experiments of these kinetic studies. The results obtained indicated that the metal fluxes are absolutely independent on the agitation power between 70 and 105 Hz, with an amplitude of 0.25 mm. The frequency of 100 Hz, therefore, was selected to carry out that set of experiments. The effect of hydrogen ions activity, zinc–D2EHTPA complex concentration, and free extractant in the organic phase on the initial stripping rate was investigated. It should be noted that the kinetics of stripping is rather slower than the kinetics of extraction. The fluxes are at least one order smaller. For practical reasons, most experiments were conducted with a loading ratio of D2EHTPA, defined as the ratio of the number of moles of Zn^{2+} extracted to the total number of moles of dimeric extractant molecules, equal to 0.19.

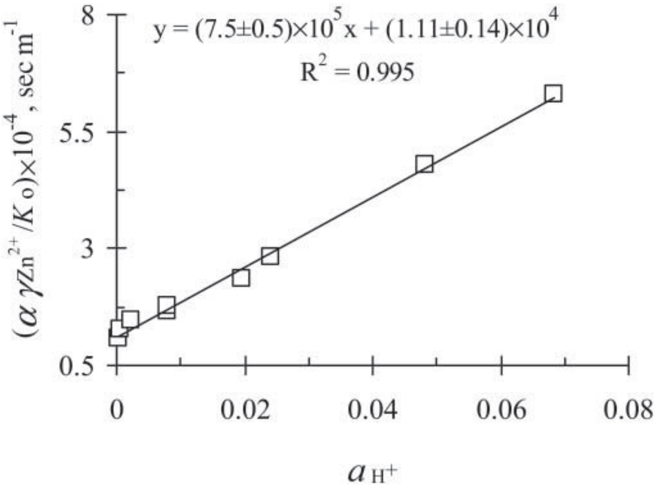

Figure 6. Overall resistance of mass transfer (in terms of activities: $\alpha\ \gamma^{2+}_{\mathrm{Zn}}/K_{\mathrm{o}}$) vs. $a_{\mathrm{H^+}}$ according to Pitzer model. (Experimental conditions: see Fig. 3.)

Effect of Hydrogen Ions Activity on Stripping Rate

Figure 7 shows the influence of the activity of hydrogen ions in the aqueous phase on the stripping rate. As expected, the stripping rate increases with the activity of hydrogen ions, and a straight line was obtained. This is in agreement with the reaction mechanism proposed and the corresponding kinetic law of Eq. (7). From the slope of the straight line represented in Fig. 7 and the initial concentrations of the zinc complex and free extractant, a first estimation of $k_{\mathrm{R}}^{0,\mathrm{aq}}$ was obtained as $k_{\mathrm{R}}^{0,\mathrm{aq}} = (1.1 \pm 0.2) \times 10^{-6}$ $\mathrm{kmol}^{-0.5}\,\mathrm{m}^{2.5}\,\mathrm{sec}^{-1}$. This value was calculated by assuming that the stripping rate of zinc is chemically controlled.

Table 1. Kinetic parameters obtained for zinc extraction at different concentrations of sodium sulfate (experimental conditions: see Fig. 3).

Na_2SO_4 ($\mathrm{kg}\,m^{-3}$)	Ionic strength (m)	k_{F} ($m\,\mathrm{sec}^{-1}$)	$k_{\mathrm{F}}^{0,\mathrm{aq}}$ ($m\,\mathrm{sec}^{-1}$)	Confidence interval (95%)
10.0–11.0	0.26	7.3×10^{-6}	3.1×10^{-5}	$(2.7–3.5) \times 10^{-5}$
18.0–20.0	0.44	5.0×10^{-6}	3.2×10^{-5}	$(2.8–3.7) \times 10^{-5}$
~38	0.83	3.1×10^{-6}	3.0×10^{-5}	$(2.8–3.2) \times 10^{-5}$

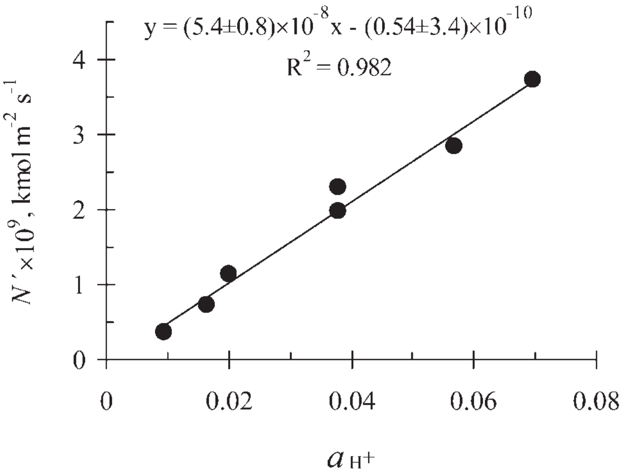

Figure 7. Influence of the activity of H^+ (Pitzer model) on the initial stripping rate. Aqueous phase: $H_2SO_4 = 0.021–0.126\,\mathrm{kmol\,m^{-3}}$, $Na_2SO_4 = 0.141\,\mathrm{kmol\,m^{-3}}$; organic phase: 0.54 g Zn $\mathrm{dm^{-3}}$, $HR_{\mathrm{total}} = 0.09\,\mathrm{kmol\,m^{-3}}$.

Contribution of Diffusional Resistance

To evaluate the contribution of diffusional resistance to the overall resistance of stripping, the procedure of Komasawa et al.[26–28] and Huang and Juang[4] was followed. The contribution of diffusional resistance to the overall stripping rate was estimated by comparing these rates with the maximum possible values of the simple physical transfer rate of the extractant. In the present work, the maximum value is given by $N' = 2/3\,k_{(\mathrm{HR})2} \cdot c_{(\mathrm{HR})2}$, where $k_{(\mathrm{HR})2}$ is the mass transfer coefficient of the extractant. To estimate this value, the diffusivity of the dimer was evaluated from the Wilke–Chang equation[29] and the value obtained was $3.4 \times 10^{-10}\,\mathrm{m^2\,sec^{-1}}$. The molar volume of the dimer at its normal boiling point was determined to be $887.6\,\mathrm{cm^3\,mol^{-1}}$ by the Le Bas method.[21] By assuming that the thickness of the organic film is about $10^{-4}\,\mathrm{m}$, $k_{(\mathrm{HR})2}$ was estimated to be $3.4 \times 10^{-6}\,\mathrm{m\,sec^{-1}}$. Huang and Juang[4] reported a film mass transfer coefficient for D2EHPA by using a correlation from Asai and coauthors,[30] and the value is of the same order of magnitude. The calculated maximum rate is $7.0 \times 10^{-8}\,\mathrm{kmol\,m^{-2}\,sec^{-1}}$ on the basis of $c_{(\mathrm{HR})2} = 0.03\,\mathrm{kmol\,m^{-3}}$ (average value) and is then found to be nearly 50 times greater than the observed stripping rate. Even though the diffusivity of the zinc complex in the organic phase is about 22% lower than the diffusivity of free extractant, the diffusional resistance is considered negligible under the present experimental conditions.

Evaluation of the Stripping Rate Constant

From the previous discussion and after several experiments with data that indicated the linear relationship between the initial stripping rate and the amount of zinc in the organic phase, it, therefore, is assumed that the initial stripping rate is given by the second term of Eq. (7). To estimate the parameter $k_R^{0,aq}$, all the experimental kinetic data of stripping were used and the least-squares method was adopted. The sum of the squared error, U, defined as

$$U = \sum (N'_{\mathrm{calc}} - N'_{\mathrm{exp}})^2 \tag{15}$$

was used in the minimization process, where N'_{calc} and N'_{exp} are the calculated and the measured stripping rates, respectively. The concentrations of free dimeric D2EHTPA were calculated by mass balances, considering the extraction stoichiometry of Eq. (1) and the equilibrium between monomeric and dimeric species. This equilibrium was considered due to the range of concentrations tested, being the fraction of monomers significant when the extractant concentration is very low. The dimerization constant of D2EHTPA was assumed to be 200, according to prior studies.[16]

The standard deviation, between experimental and calculated values, σ, was taken as

$$\sigma = \sqrt{\frac{\sum (N'_{\mathrm{calc}} - N'_{\mathrm{exp}})^2}{n-1}} \tag{16}$$

where n is the number of experimental points. The activity coefficients of the hydrogen ions were calculated by means of the Pitzer model, as was also previously stated. Figure 8 shows the results of the optimization, being the optimal value $k_R^{0,aq} = (1.04 \pm 0.03) \times 10^{-6}\,\mathrm{kmol}^{-0.5}\,\mathrm{m}^{2.5}\,\mathrm{sec}^{-1}$. The relative standard deviation between calculated and experimental values is 30%.

The results obtained in this work are in agreement with the ones reported in previous studies on equilibrium.[16] The ratio between the rate constants, $k_F^{0,aq}$ and $k_R^{0,aq}$, ought to correspond with the thermodynamic equilibrium constant, $K_{ex}^{0,aq}$. This constant was found to be $32\,\mathrm{kmol}^{0.5}\,\mathrm{m}^{-1.5}$,[16] as $k_F^{0,aq} = (3.1 \pm 0.3) \times 10^{-5}\,\mathrm{m\,sec}^{-1}$ (from Table 1) and $k_R^{0,aq} = (1.04 \pm 0.03) \times 10^{-6}\,\mathrm{kmol}^{-0.5}\,\mathrm{m}^{2.5}\,\mathrm{sec}^{-1}$, the corresponding ratio is $30 \pm 4\,\mathrm{kmol}^{0.5}\,\mathrm{m}^{-1.5}$, which is very satisfactory.

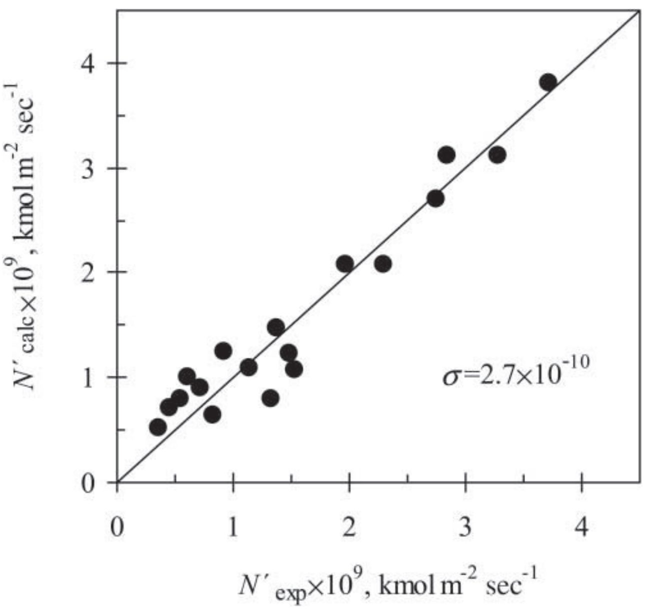

Figure 8. Calculated vs. experimental values of stripping rate for the optimal $k_R^{0,aq} = 1.04 \times 10^{-6}$ kmol$^{-0.5}$ m$^{2.5}$ sec^{-1}. Aqueous phase: $H_2SO_4 = 0.021$–0.126 kmol m^{-3}, $Na_2SO_4 = 0.141$ kmol m^{-3}; organic phase: 0.29–1.0 g Zn dm^{-3}, $HR_{total} = 0.06$–0.14 kmol m^{-3}.

CONCLUSIONS

The kinetics of zinc extraction with D2EHTPA from sulfate media has been investigated by measuring initial extraction and initial stripping rates in a modified Lewis cell. The forward extraction rate generally is mixed controlled, whereas, the stripping rate is chemically controlled under the experimental conditions studied. The results obtained suggest that the extraction process can be described by the reaction mechanism scheme proposed by Ajawin et al.[2] The reaction rate of zinc is given by Eq. (7), where the nonideality of the aqueous phase was taken into account by applying the Pitzer model. The thermodynamic kinetic constants for the forward and backward reactions, at 293 K, were found to be $k_F^{0,aq} = 3.1 \times 10^{-5}$ m sec^{-1} and $k_R^{0,aq} = 1.0 \times 10^{-6}$ kmol$^{-0.5}$ m$^{2.5}$ sec^{-1}, respectively. The ratio between $k_F^{0,aq}$ and $k_R^{0,aq}$ is in good agreement with the thermodynamic equilibrium constant found in previous studies.[16]

NOTATION

a	Activity
c	Concentration on the molarity scale, kmol m^{-3}
HR	General designation of extractant
$(HR)_2$	Extractant in dimer form
k	Concentration-based rate constant
k_{aq}	Mass transfer coefficient of zinc in the aqueous phase, m sec^{-1}
$k_F^{0,aq}$	Thermodynamic kinetic constant in terms of the aqueous phase, m sec^{-1}
$k_R^{0,aq}$	Thermodynamic kinetic constant in terms of the aqueous phase, kmol$^{-0.5}$ m$^{2.5}$ sec^{-1}
K_o	Overall mass transfer coefficient, m sec^{-1}
$K_{ex}^{0,aq}$	Thermodynamic extraction constant defined in Eq. (2), kmol$^{0.5}$ m$^{-1.5}$
m	Molality, mol kg^{-1} of solvent
N	Initial extraction rate per unit of interfacial area, kmol m^{-2} sec^{-1}
N'	Initial stripping rate per unit of interfacial area, kmol m^{-2} sec^{-1}
n	Number of experimental points used in the optimization
t	Time

Greek Letters

α	Molar fraction of total zinc in the form of Zn^{2+}
γ_i	Activity coefficient of species i (molarity scale)

Subscripts and Superscripts

0	Initial value
0,aq	Thermodynamic in terms of the aqueous phase
ad	Adsorbed extractant
calc	Calculated value
exp	Measured value
F	Forward reaction of extraction
aq	Aqueous phase
int	Interface
org	Organic phase

R	Backward reaction of extraction
total	Total, formal concentration
Zn	Total zinc

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