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Mass Transfer Rates and Column Heights in Reactive Extraction Processes

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Abstract. A mathematical model, which is based on the simultaneous interfacial chemical reactions and diffusion processes, is developed for the extraction of zinc ions from sulphate solution by di(2-ethylhexyl) phosphoric acid in *n*-heptane diluent. Actual column heights were compared with the predicted ones, using the design algorithm based on chemical kinetics. The experimental values of mass transfer coefficients could be varied and were in the range of industrial interest. Using the physicochemical data, hydrodynamics, mass transfer coefficient parameters and reaction kinetics pertaining to the system, it was possible to predict the interfacial flux and column height from first principles with a reasonable degree of accuracy.

Keywords: interfacial flux, reactive extraction, chemical kinetics, zinc/DEHPA, spray column

Introduction

Continuous counter current contactors are usually designed assuming interfacial equilibrium. In the case of mass transfer with interfacial chemical reaction, this assumption is only valid if the chemical reaction is very fast with respect to the mass transfer rate (Chapman *et al.,* 1975). In hydrometallurgical processing, the use of liquid-liquid extraction systems are already very popular. The successful application of such related extraction processes has encouraged fundamental research on the extraction equilibria and kinetics leading to development of mathematical models for the solvent extraction of metals. The kinetics of these systems is generally controlled by a combination of diffusion and chemical rate factors and a properly developed model could become a design equation having practical significance. If all the parameters relating to the system, namely physicochemical, hydrodynamics, mass transfer, and the reaction kinetics are known, it would be possible to design extraction column from first principles.

In this paper a mathematical model is developed for interfacial flux, which is based on simultaneous interfacial chemical reactions and diffusion processes. An attempt has also been made to predict the column height from first principles. The system comprises the extraction of zinc ions from acidic aqueous phase by di(2-ethylhexyl) phosphoric acid (DEHPA) in *n*-heptane diluent. In order to check the validity of the model for design purposes, the predicted values are compared with actual heights.

Model formulation. In a column for continuous extraction in aqueous phase, with interfacial chemical reactions, the mass balance of zinc ions over a differential height δ h for unsteady state operation may be given as follows (Saeed and Jamil, 1998a):

$$\frac{\partial C_{za}}{\partial t}(1-\phi_D) = \frac{L_c}{S}\frac{\partial C_{za}}{\partial h} + E_{ax,c}(1-\phi_D)\frac{\partial^2 C_{za}}{\partial h^2} - R_z a_c (1-\phi_D) \qquad (1)$$

The first term on the right hand side of equation (1) accounts for convection, the second term for axial mixing and the third one represents the overall rate of interfacial transfer. The term on the left hand side represents the variation of zinc concentration with time.

A similar differential mass balance equation can be derived for metals in the dispersed organic phase (Saeed and Jamil, 1998a):

$$\frac{\partial C_{zo}}{\partial t}\phi_D = -\frac{L_d}{S}\frac{\partial C_{zo}}{\partial h} + E_{ax,d}\,\phi_D\frac{\partial^2 C_{zo}}{\partial h^2} + R_z a_d \phi_D \qquad (2)$$

Under steady state conditions, assuming constant flow rates and neglecting backmixing, equations (1) and (2) reduce to:

$$L_c \frac{dC_{za}}{dh} = R_z a_c S (1-\phi_D) \qquad (3)$$

and

$$L_d \frac{\partial C_{zo}}{\partial h} = R_z a_d S \phi_D \qquad (4)$$

which on integration give the contactor height:

$$H_c = \frac{L_c}{S}\int_1^2 \frac{dC_{za}}{R_z a_c (1-\phi_D)} \qquad (5)$$

and

$$H_c = \frac{L_d}{S}\int_1^2 \frac{dC_{zo}}{R_z a_d \phi_D} \qquad (6)$$

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In the extraction column the local volumetric extraction rate, r_z , is given by:

$$r_z = R_z a_c \tag{7}$$

Since chemical reactions are also involved, the interfacial flux, R_z, would be a function of chemical as well as mass transfer parameters, while the specific interfacial area depends on the operating conditions of the column, i.e., dispersed phase holdup and mean drop diameter.

In order to integrate equations (5) and (6) for calculating contactor height in a given extraction system, knowledge of R_z, a_c, a_d and ϕ_D is essential.

Interfacial area. Interfacial area between droplets and continuous phase is a function of drop size and dispersed phase holdup. The interfacial area per unit volume of the continuous phase is expressed as (Pilhofer and Schroter, 1986):

$$a_c = \frac{\partial\, \phi_D}{d_{32}\,(1-\phi_D)} \tag{8}$$

$$d_{32} = \frac{\Sigma n d^3}{\Sigma n d^2} \tag{9}$$

A correlation has been proposed that predicts the drop size in spray columns which claimed to be valid both for the absence or presence of mass transfer (Kumar and Hartland, 1984):

$$\frac{d_{32}}{d_n} = E\ddot{o}^{-0.38}\left[1.28\left[\frac{\Delta\rho}{\rho_d}\right]^{0.3} + \exp(-0.16\,Fr)\right] \tag{10}$$

for, $We_n < 8.64$

With a view to obtaining the holdup for the static continuous phase, ϕ, the following equation should be employed for calculating the countercurrent holdup, ϕ_D:

$$u_s = \frac{U_d}{\phi} = \frac{U_d}{\phi_D} + \frac{U_c}{(1-\phi_D)} \tag{11}$$

Mass transfer coefficients. In liquid-liquid extraction processes, the mass transfer coefficient would be dependent on whether the drops are rising, falling, internally circulating, or in oscillating state through continuous but immiscible liquid phase. However, it was observed both visually and from the analysis of photographic films taken with a cine camera for the dispersion in the column that the rising drops were oscillating (Saeed and Jamil, 1998a). Accordingly, the correlations for continuous phase and dispersed phase, mass transfer coefficients are dewelled upon only for oscillating drops.

The following correlation has been proposed for continuous phase mass transfer coefficient (Yamaguchi *et al.,* 1975):

$$K_c = 1.4\,\frac{D_c}{d_{32}}\left[\frac{\rho_c\,\omega\, d^2_{32}}{\mu_c}\right]^{0.5}\left[\frac{\mu_c}{\rho_c D_c}\right]^{0.5} \tag{12}$$

The correlation of Rose and Kintner (1966) for dispersed phase mass transfer coefficient is:

$$K_d = 0.95\, D_d^{0.5}\left[\frac{8\,\sigma\,(100\, d_{32})^{0.225}}{d^3_{32}\,(3\rho_d + 2\rho_c)}\right]^{0.25} \tag{13}$$

Diffusion coefficients. The diffusivity of strong electrolytes at infinite dilution on the assumption of complete dissociation can be calculated from the Nernst-Haskell equation (Reid *et al.,* 1977) as given below:

$$D^\circ_{12} = \frac{RT}{F^2}\,\frac{\dfrac{1}{n^+} + \dfrac{1}{n^-}}{\dfrac{1}{\lambda^\circ_+} + \dfrac{1}{\lambda^\circ_-}} \tag{14}$$

Harned and Hudson (1951) introduced a correction factor by taking into account the influence of ion-pair formation on the diffusion coefficient given as:

$$D_{12} = D^\circ_{12}\,[1 + 38.16 \times 10^{-2}\,(1-\alpha)] \tag{15}$$

The most general and widely used correlation for the prediction of diffusion coefficients of non-electrolytes in organic solvents at infinite dilution is that of Wilke and Chang (1955):

$$D^\circ_{AB} = 1.173 \times 10^{-16}\,\frac{(\Phi\, M_B)^{0.5}\, T}{\mu_B V_A^{0.6}} \tag{16}$$

A modified expression was proposed by Leffler and Cullinan (1970) for higher concentrations, taking viscosity into due account:

$$\frac{D_{AB}\,\mu_{AB}}{f^{\,th}} = (D^\circ_{AB}\,\mu_B)^{X_B}\,(D^\circ_{BA}\,\mu_A)^{X_A} \tag{17}$$

Extraction equilibria. The extraction chemistry of zinc with di(2-ethylhexyl) phosphoric acid (DEHPA) has been studied by numerous workers. Ajawin *et al.* (1983) reported the overall equilibrium as:

$$Zn^{2+} + 1.5\,\overline{(HL)}_2 \rightleftharpoons \overline{ZnL_2.HL} + 2H^+ \tag{18}$$

From the extraction equilibrium studies, Murthy (1987) reported that two complexes of zinc-DEHPA are formed in *n*-heptane according to the stoichiometry of the reactions:

$$Zn^{2+} + 1.5\,\overline{(HL)}_2 \rightleftharpoons \overline{ZnL_2.HL} + 2H^+ \tag{19}$$

$$Zn^{2+} + 2\,\overline{(HL)}_2 \rightleftharpoons \overline{ZnL_2\,(HL)}_2 + 2H^+ \tag{20}$$

where bars indicate the species in the organic phase and $(HL)_2$ in DEHPA in dimer form.

Extraction kinetics. From the kinetic studies (Murthy, 1987; Ajawin *et al.,* 1983; 1980) conducted in a cell with constant interfacial area in the chemical control regime, it has been reported that reactions (19) and (20) take place at the interface. The extraction rate of zinc ions is proportional to their concentration in the aqueous phase, dimeric DEHPA activity and inversely proportional to hydrogen ion concentration:

$$r_{ze} = 2\,k\,a_c\,\frac{C_{za}\,C_{oD}}{C_H} \quad \text{(Ajawin \textit{et al.}, 1983; 1980)} \tag{21a}$$

$$r_{ze} = k_I\,a_c\,\frac{C_{za}\,C_{oD}\,\gamma_o}{C_H} = k_I\,a_c\,\frac{C_{zo}\,a_o}{C_H} \tag{21b}$$

where:

$$k_I = 2\,k/\gamma_o$$

While stripping rate is first order with respect to zinc-DEHPA complex concentration, it is first order with respect to hydrogen ion concentration and is inversely proportional to the dimeric DEHPA activity factor ($a_o + 0.75\sqrt{a_o}$):

$$r_{zs} = k'_I\,a_c\,\frac{C_{zo}\,C_H}{a_o + 0.75\sqrt{a_o}} \tag{22}$$

From equations (21b) and (22), the overall extraction rate can be expressed as:

$$r_{zs} = k_I\,a_c\,\frac{C_{za}\,a_o}{C_H} - k'_I\,a_c\,\frac{C_{zo}\,C_H}{a_o + 0.75\sqrt{a_o}} \tag{23}$$

or

$$R_z = \frac{r_z}{a_c} = k_I\,\frac{C_{za}\,a_o}{C_H} - k'_I\,\frac{C_{zo}\,C_H}{a_o + 0.75\sqrt{a_o}} \tag{24}$$

The above equations indicate that reaction is independent of mass transfer control and, therefore, expected to yield the maximum interfacial flux for a given set of concentrations.

Baes and Baker (1960) have proposed the following relationship for the activity coefficients of the DEHPA dimer in aliphatic diluents:

$$\log\,\gamma_o = -\,0.586\,C_{oD}^{1/3} + 0.565\,C_{oD} \tag{25}$$

Activity coefficient correlation for zinc-DEHPA complex proposed by Koncar *et al.* (1988) is:

$$\frac{1}{\gamma_{Zo}} = 1 + 0.616\,\left[\frac{1.7\,C_{zo}}{a_o}\right]^{1.387} \tag{26}$$

The mechanism of transfer of the solute from one phase to the other may be very complexed. The trend of mass transfer is assumed to proceed according to the following three steps:

(i) zinc ions and DEHPA diffuse to the interface from the aqueous and the organic phases, respectively,
(ii) zinc ions and DEHPA react according to reactions (19) and (20), and
(iii) the liberated hydrogen ions and zinc-DEHPA complex diffuse from the interface into the aqueous and organic phases, respectively.

The three steps take place simultaneously and thus interfere mutually. A schematic diagram of the concentration profiles for all the species at the interface during zinc extraction is shown in Fig. 1. In the mixed control regime, the interfacial flux depends on the kinetics of both mass transfer and interfacial reaction. In the present case, the interfacial rate of extraction is still given by equation (24), but for the interfacial instead of bulk concentrations. Since the interfacial concentrations are normally not directly measureable quantities, these, it involve some mathematical manipulation as given below:

$$\begin{aligned} R_z &= K_{za}\,(C_{za} - C_{zai}) \\ R_z &= 1/1.7\,K_o\,(a_o - a_{oi}) \\ R_z &= -\,1/2\,K_H(C_H - C_{Hi}) \\ R_z &= -\,K_{zo}\,(C_{zo} - C_{zoi}) \end{aligned} \tag{27}$$

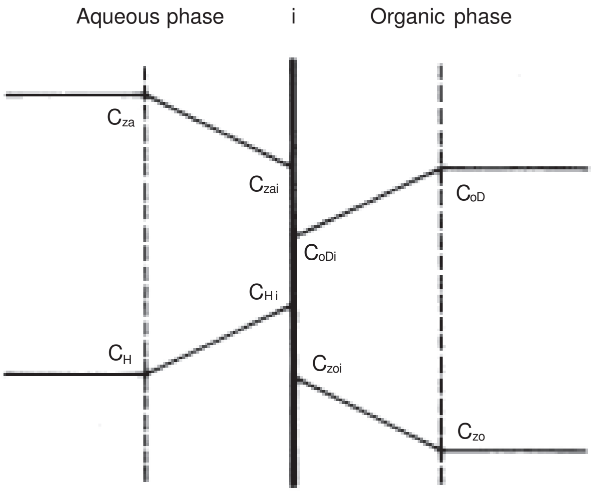

Fig. 1. Concentration profiles at the interface during metal extraction.

Eliminating the interfacial values from equations (24) and (27), the final kinetic expression for the interfacial flux comes out to be:

$$R_z = k_I\,\frac{\left[C_{za} - \frac{R_z}{K_{za}}\right]\left[a_o - 1.7\,\frac{R_z}{K_o}\right]}{\left[C_H + 2\,\frac{R_z}{K_H}\right]} - k'_I\,\frac{\left[a_{zo} + \frac{R_z}{K_{zo}}\right]\left[C_H + 2\,\frac{R_z}{K_H}\right]}{\left[a_o - 1.7\frac{R_z}{K_o}\right] + 0.75\sqrt{\left[a_o - 1.7\,\frac{R_z}{K_o}\right]}} \tag{28}$$

This gives R_z in terms of bulk concentrations of the species involved, individual mass transfer coefficients, and specific reaction rate constants for the extraction and stripping reactions.

Aqueous phase ionic equilibria. The aqueous phase under consideration is a solution of zinc sulphate, sulphuric acid and sodium sulphate. It may be assumed that sodium sulphate completely dissociates, whereas dissociation of zinc sulphate and bisulphate ions is incomplete, being according to the following equations:

$$ZnSO_4 \rightleftharpoons Zn^{2+} + SO_4^{2-} \tag{29}$$

$$HS\bar{O}_4 \rightleftharpoons H^+ + SO_4^{2-} \tag{30}$$

In the aqueous phase, the species namely zinc, sulphate, hydrogen, sodium, bisulphate and zinc sulphate ion-pair are being considered to be present in ionic form while higher order associations are ignored.

The ionic strength, I, of any solution is defined by the following equation:

$$I = \tfrac{1}{2} \sum_{i=1}^{n} C_i Z_i^2 \tag{31}$$

where:

C_i and Z_i are the molar concentration and ionic charge of the species i, respectively.

In the light of equations (29) and (30), equilibria constants and mass balances for various ionic species may be represented by the following relationships:

zinc sulphate ion-pair dissociation constant:

$$K_m = \frac{[Zn^{2+}][SO_4^{2-}]}{[Zn\,SO_4]} \tag{32}$$

bisulphate ion dissociation constant:

$$K_b = \frac{[H^+][SO_4^{2-}]}{[H\,SO_4^-]} \tag{33}$$

hydrogen ion balance:

$$[H^+] = 2M\,H_2SO_4 - [HSO_4^-] \tag{34}$$

sulphate ion balance:

$$[SO_4^{2-}] = MSO_4^{2-} - [HSO_4^-] - [ZnSO_4] \tag{35}$$

zinc ion balance:

$$[Zn^{2+}] = C_{zt} - [ZnSO_4] \tag{36}$$

sodium ion balance:

$$[Na^+] = 2\,(MSO_4^{2-} - MH_2SO_4 - C_{zt}) \tag{37}$$

where:

$M_{H_2SO_4}$, $M_{SO_4^{2-}}$ and C_{zt} are the formal concentration of sulphuric acid, the formal total sulphate concentration and formal total concentration of zinc sulphate, respectively.

Nomenclature used in the paper. a_c = interfacial area per unit volume of continuous phase, m^{-1}; a_d = interfacial area per unit volume of dispersed phase, m^{-1}; a_o = activity of DEHPA dimer, kmol/m^3; a_{zo} = activity of organic zinc, kmol/m^3; C = molar concentration, kmol/m^3; D = diffusion coefficient, m^2/s; d_{32} = Sauter mean drop diameter, m; d_n = inside nozzle diameter, m; Eö = nozzle Eotvos number, $\Delta\rho d_n^2\, g/\sigma$; E_{ax} = axial dispersion coefficient, m^2/s; F = Faraday constant, 9.65 x 10^7 C/kg equiv; Fr = Froude number, $u_n^2/g\, d_n$; f^{th} = thermodynamic factor; H_c = column height, m; K = mass transfer coefficient, m/s; k = concentration-based extraction rate constant, m/s; k_I = extraction rate constant, m/s; k'_I = stripping rate constant, m/s; L = volumetric flow rate, m^3/s; L' = volumetric flow rate m^3/s; M = molecular weight; n_+, n_- = valences of cation and anion respectively; R = gas constant, 8.314x 10^3 J/kmol K; R_z = zinc interfacial flux, kmol/m^2 s; r_z = volumetric extraction rate, kmol/m^3 s; S = cross-sectional area of column, m^2; T = absolute temperature, K; t = time, s; U = superficial velocity through the column, m/s; u_s = slip velocity of drops relative to continuous phase, m/s; V_A = molar volume of extractant at its normal boiling point, m^3/kmol; We_n = nozzle Weber number, $\rho_d d_n u_n^2/\sigma$; x = mole fraction.

Greek letters used in the paper. α = degree of dissociation of zinc sulphate; γ = activity coefficient; σ = interfacial tension, N/m; ρ = density, kg/m^3; $\Delta\rho$ = desnity difference, kg/m^3; μ = viscosity, kg/m s; ω = frequency of oscillation, $\sqrt{48\,\sigma/\pi^2 d_{32}^3 (3\rho_d + 2\rho_c)}$, s^{-1}; λ^0_+, λ^0_- = limiting (zero concentration) ionic conductances, S m^2/kg equiv; Φ = an association parameter for solvent; ϕ = dispersed phase holdup for $U_c = 0$; ϕ_D = dispersed phase holdup for countercurrent flow.

Subscripts used in the paper. 1 = outlet; 2 = inlet; A = extractant; B = organic solvent; AB = organic solution; c = continuous phase; d = dispersed phase; H = hydrogen ion; i = interface, interfacial values; o,oD = DEHPA dimer; za = aqueous phase zinc ions; zo = organic phase zinc; zt = total aqueous phase zinc.

Materials and Methods

The continuous aqueous phase contains zinc sulphate, sodium sulphate and sulphuric acid, whereas the dispersed phase consists of di(2-ethylhexyl) phosphoric acid (DEHPA) dissolved in *n*-heptane. The *n*-heptane used was of knock-testing grade without purifying anymore. The DEHPA was of technical grade obtained from BDH and was further purified by Partridge and Jensen (1969) method. The use of DEHPA to extract zinc was considered as a recommended system for liquid-liquid extraction studies (Hancil *et al.*,1990). These authors claimed that the use of glycol alone to remove monoester impurities from DEHPA adversely affected the subsequent zinc extraction kinetics. For impure DEHPA with monoester content ≤ 3 mol%, the kinetics of extraction were the same as for highly purified DEHPA produced using the copper precipitation method. The zinc sulphate, sodium sulphate and sulphuric acid were Analar grade. All the experiments were carried out at 25 °C and an ionic strength of 1 mol/dm^3.

Experiments were performed in a glass spray column of 0.05 m diameter with provision to adjust height. Effective heights of 1.25-2.4 m were used. The column was operated in a semi-batch mode, that is, the continuous aqueous phase was kept stagnant and the dispersed organic phase was not recirculated. The coalesced dispersed organic phase was drawn off from the top of the reservoir by a glass capillary siphon that resulted in a continuous flow of the coalesced phase. Full detail of the apparatus description, procedure and photographic set-up is given elsewhere (Saeed and Jamil, 1994a). The concentrations and operating conditions in the column are given below:

C_{zt}, initial aqueous phase zinc conc = 1.5x 10^{-3}-0.02 kmol/m^3; initial pH = 2.7-3.07; C_{oD}, DEHPA conc (dimer) = 0.025-0.075 kmol/m^3; diluent = *n*-heptane; L_d, dispersed phase flow rate = 3.67 x 10^{-7}-2 x 10^{-6} m^3/s; d_n, nozzle diameter = 0.8 x 10^{-3}-3.0 x 10^{-3} m; H_c, effective column height = 1.25-2.4 m.

Results and Discussion

Equations (32-36) are solved simultaneously for constant values of K_m and K_b to yield a cubic equation in zinc ion concentration. For the calculation of the values of $M_{H_2SO_4}$ and $M_{SO_4^{2-}}$, which would give the required composition of the aqueous phase, that is, [Zn^{2+}], [H$^+$] and ionic strength, the iteration method was employed by using guessed values of $M_{H_2SO_4}$ and $M_{SO_4^{2-}}$ for a given value of zinc sulphate. Baes (1957) reported the values of dissociation constant of bisulphate ion, K_b, for the system sodium sulphate-sulphuric acid, as a function of total sulphate concentration. His results showed that at constant total sulphate concentration, K_b is nearly constant as the composition is changed, even though the accompanying change in ionic strength is considerable. Baes values were employed for calculating K_b, while K_m value was taken from elsewhere (Smith and Martell, 1976).

Comparison of actual and predicted column heights. Analysis of photographic films gave drop size distribution, dispersed phase holdup and specific interfacial area. The values of hydrodynamic and mass transfer parameters for the system are given in Table 1. Considering R_z and a_c constant along the height and the column was operated while there was no net flow of continuous phase across the section, equation (1) becomes:

$$\frac{dC_{za}}{dt} = -R_z a_c \tag{38}$$

The physicochemical data for zinc/DEHPA system understudy is given below:

λ^o_+ (½ Zn^{2+}) = 5.3 S m^2/kg equiv; λ^o_- (½ SO$_4^{2-}$) = 8.0 S m^2/kg equiv; μ_B = 4 x 10^{-4} kg/m s; Φ = 1.0 (for *n*-heptane solvent); M_B = 100.2; V_A = 0.853 m^3/kmol (for DEHPA dimer); D_{za} = 1.08 x 10^{-9} m^2/s; D_o = 7.34 x 10^{-10} m^2/s; D_{zo} = 5.78 x 10^{-10} m^2/s; ρc = 1040 kg/m^3; ρd = 695 kg/m^3; μ_c = 1.023 x 10^{-3} kg/m s; μ_d = 4.733 x 10^{-4} kg/m s; σ = 20.5 x 10^{-3} N/m; k = 4.25 x 10^{-7} m/s (Ajawan *et al.*, 1983) and $k_I = 2k/\gamma_0$; k'_I* = 2.96 x 10^{-5} m/s (*modified value based on DEHPA and zinc-DEHPA complex activities).

Table 1. Measured and calculated hydrodynamic and mass transfer parameters in a spray column for Zn/DEHPA system; C_{oD} = 0.075 mol/dm^3

d_n x 10^3 m	L'_d x 10^8 m^3/s	d_e x 10^3 m	d_{32} x 10^3 m	ϕ x 10^3	a_c m^{-1}	K_{za} x 10^4 m/s	K_o x 10^4 m/s
0.8	9.2	3.99	3.99	1.55	2.32	2.43	1.1
	11.2	3.68	3.68	1.88	3.07	2.23	1.12
1.1	10.8	5.22	5.25	1.77	2.08	2.05	0.91
	12.5	5.0	5.04	2.09	2.58	2.12	0.92
	17.5	4.94	5.0	3.0	3.7	2.22	0.92
	23.3	2.81	2.86	4.0	8.5	2.65	1.24
	23.3	2.99*	3.03	4.12	8.27	2.55	1.39
3.0	24.2	6.28	6.31	4.15	4.1	1.98	0.69
	33.3	6.23	6.25	5.73	5.7	2.11	0.8
	50	6.07	6.09	8.54	8.73	1.95	0.79

*C_{oD}: 0.025 mol/dm^3

The values of various physical properties for the system needed in the calculation of Sauter mean drop diameter, diffusion and mass transfer coefficients were determined experimentally. The solution of DEHPA in *n*-heptane behaves like a non-ideal solution. The thermodynamic factor for the system was obtained from the slope of $\ln a_o$ versus $\ln x_A$ graph. The mass transfer coefficient of organic zinc complex was estimated using the penetration theory model which provides that the mass transfer coefficient is directly proportional to the square root of the molecular diffusivity. Although the intrinsic diffusivities of zinc and hydrogen ions are different, in order to maintain electric neutrality, K_{za} is taken equal to K_H. The calculated values of hydrodynamic and mass transfer parameters using different correlations agree well with the experimental values (Saeed and Jamil, 1998b; Saeed *et al.,* 1994; Saeed and Jamil, 1994a). The experimental interfacial flux data fits well in the design equation based on interfacial chemical kinetics (Table 1) (Saeed and Jamil, 1994b).

The values of chemical reaction rate constants at 25 °C and an ionic strength of 1 mol/dm^3 have been reported by Murthy (1987) and Ajawin *et al.* (1983; 1980). The authors have assumed complete dissociation of zinc sulphate in the aqueous phase for the purpose of calculations of reaction rate and equilibrium constants. The modified values of these constants, taking into account the incomplete dissociation of aqueous phase zinc sulphate, were used in the interfacial flux model. Equations (2) and (38) were solved numerically by the method of finite difference using the equation (28) for the interfacial flux. A numerical calculation routine (CO_2AEF), written by Numerical Algorithm Group (NAG), was used to solve the polynomial equation (28). In all cases, which were considered, there was only one real root for positive interfacial concentration.

Samples of the outlet dispersed organic phase were taken directly from the outflow of the siphon to estimate the zinc concentration. A known volume of the organic phase sample was stripped with 2 mol/dm^3 H_2SO_4 and the aqueous phase was analyzed using the atomic absorption spectrophotometer at λ 213.9 nm. In order to predict column heights for the corresponding outlet organic phase zinc concentrations, the required constants and other parameters such as Sauter mean drop diameter, mass transfer coefficients for continuous and dispersed phases, etc., were calculated using respective relationships as detailed in the preceeding paragraphs.

In the calculations, the following assumptions were made:

- DEHPA diffuses in the diluent as a dimer;
- mass transfer rate during drop formation and coalescence was the same as the one rate of rising drops;
- the rising velocity of the drops is the same throughout the column; and
- analysis of the samples of the continuous aqueous phase taken at different points along the column showed no variation of zinc concentration with height, therefore, the dispersive term in equation (2) was assumed to be negligible.

Comparison of actual and predicted heights using the design equation based on the interfacial chemical kinetics is shown in Fig. 2. The predicted values agree well with the actual ones showing that it is possible to design spray columns from first principles provided that the reliable physicochemical data, hydrodynamic and mass transfer parameters are available.

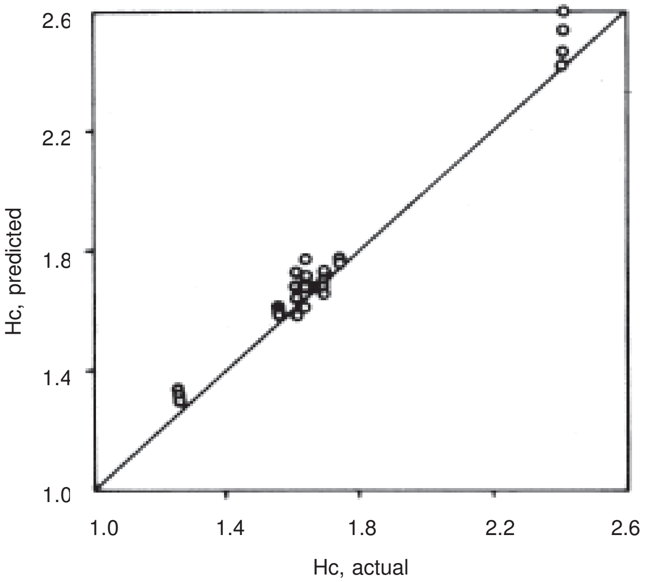

Fig. 2. Comparison of actual and predicted heights using design algorithm based on interfacial chemical kinetics.

Conclusion

The extraction of zinc from an acidic aqueous sulphate solution by di(2- ethylhexyl) phosphoric acid in *n*-heptane diluent has been carried out in a spray column of variable heights operated under semi-batch mode.

A comparison between actual heights and those predicted using the design algorithm based on the interfacial chemical kinetics indicates its applicability, being in good agreement. If all the parameters relating to the system, namely, physicochemical, hydrodynamics, mass transfer and the reaction kinetics are known, it is possible to design extraction column from first principles.

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