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MODELLING OF IONIC EQUILIBRIA IN ZINC SULPHATE – SULPHURIC ACID SOLUTIONS

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A mathematical model is developed for the ionic equilibrium of zinc sulphate – sulphuric acid aqueous solution, taking into account the effect of ionic strength. The model is reduced to a quadratic equation in the bisulphate ion and zinc ion. Results of this analysis indicate that ion interactions can significantly change the ionic concentration of the solutions which could lead to errors with evaluation of data on zinc extraction kinetics or equilibrium. The operating line between hydrogen ion and zinc ion concentration is necessary in the analysis of equilibrium and kinetic data in the liquid-liquid two phase extraction system. It is shown that results simulated with the developed model are in good agreement with experimental data.

Key words: Ionic equilibria, Zinc, Hydrogen ions, Ionic strength.

Introduction

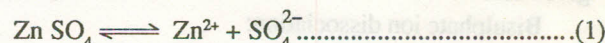
The successful application of the liquid-liquid extraction at industrial scale for the recovery/separation of metals has encouraged fundamental research on the equilibrium and kinetics of extraction phenomena. Equilibrium and kinetic studies of zinc extraction by organic chelating agents have been widely investigated [1-11] because of the practical importance of these reactions in the hydrometallurgical field. It is assumed that the reactant in the chelation reaction is the free zinc ion. Earlier workers [2-4,9] in the hydrometallurgical field approximated the zinc ion concentration by assuming no ion-pair association for the zinc sulphate in the aqueous phase. In order to develop the equilibrium and/or kinetic model for the two phase extraction system, it is necessary to have an accurate measure of the reactive dissociated zinc and hydrogen ions in the aqueous phase. In their work, Tavlarides *et al.* [12,13] developed models for estimating the equilibrated ionic species concentration in the copper sulphate – sulphuric acid and ferric sulphate – sulphuric acid systems. The analysis included the effects of ionic strength and temperature and results were successfully applied to model the chemical equilibrium of both extraction systems.

The purpose of this work is to present a comprehensive model for the zinc sulphate – sulphuric acid aqueous phase ionic equilibria to predict the concentration of ionic species. Simulated results are compared with experimental values of pH obtained for the extraction of zinc from acidic aqueous sulphate solution by di (2-ethylhexyl) phosphoric acid in *n*-heptane.

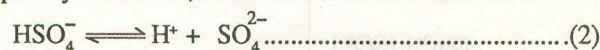
Aqueous phase ionic equilibria. Models for the zinc sulphate ion-pair dissociation and bisulphate dissociation which account for the effects of ionic strength and temperature of the

solution can be developed from information available in the literature. The aqueous phase under consideration is a solution of zinc sulphate, sodium sulphate and sulphuric acid. It can be assumed that sodium sulphate completely dissociates.

Studies on the composition of zinc sulphate solutions reveal that zinc sulphate exists at least as a mixture of free zinc ions, free sulphate ions and zinc sulphate ion pairs represented by the equilibrium:



Sulphuric acid is a diprotic acid in which the first dissociation can be considered complete for the solutions of interest in hydrometallurgical applications. The bisulphate ion does not completely dissociate, however the reaction must be



considered. This equilibrium has received considerable attention [14-16]. Young *et al.* [14] used Raman spectroscopy to measure sulphate and bisulphate concentrations at various ionic strengths.

Concentrations of zinc ion, hydrogen ion and other ionic species in the aqueous solution of zinc sulphate, sodium sulphate and sulphuric acid are estimated by modelling the aqueous phase mathematically. The species considered to be present are the zinc ion, the sulphate ion, the hydrogen ion, sodium ion, the bisulphate ion and the zinc sulphate ion-pair. Higher order associations are ignored.

The ionic strength, *I*, is defined by the following equation:

$$I = 1/2 \sum_{i=1}^n C_i z_i^2 \dots \dots \dots (3)$$

where C_i and z_i are the molar concentration and ionic charge of the species *i*, respectively. Thus for the system under consideration,

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$$2I = 4[Zn^{2+}] + [H^+] + [Na^+] + [HSO_4^-] + 4[SO_4^{2-}] \dots\dots\dots(4)$$

where the square brackets denote the actual concentration of the specified ion in the solution.

Writing $M_{H_2SO_4}$, $M_{SO_4^{2-}}$ and C_{Zn} for the formal concentration of the sulphuric acid, the formal total sulphate concentration and formal concentration of zinc sulphate respectively, it can be shown that

$$[H^+] = 2 M_{H_2SO_4} [HSO_4^-] \dots\dots\dots(5)$$

$$[SO_4^{2-}] = M_{SO_4^{2-}} - [HSO_4^-] - [Zn SO_4] \dots\dots\dots(6)$$

$$[Zn^{2+}] = C_{Zn} - [Zn SO_4] \dots\dots\dots(7)$$

and

$$[Na^+] = 2 (M_{SO_4^{2-}} - M_{H_2SO_4} C_{Zn}) \dots\dots\dots(8)$$

Substitution of equations (5), (6), (7) and (8) into equation (4) gives

$$I = 3M_{SO_4^{2-}} + [Zn^{2+}] - 2[HSO_4^-] - 3[ZnSO_4] \dots\dots\dots(9)$$

$M_{SO_4^{2-}}$, formal total sulphate concentration, is a known quantity. In order to calculate the ionic strength, the values of $[HSO_4^-]$ and $[Zn^{2+}]$ must be estimated from the dissociation equilibrium of bisulphate ion and zinc sulphate, which are given below:

Bisulphate ion dissociation:

$$K_b = \frac{[H^+] [SO_4^{2-}]}{[HSO_4^-]} \dots\dots\dots(10)$$

Zinc sulphate dissociation:

$$K_z = \frac{[Zn^{2+}] [SO_4^{2-}]}{[Zn SO_4]} \dots\dots\dots(11)$$

It is also assumed that the presence of zinc sulphate does not affect the dissociation equilibrium relation for bisulphate ion. Substitution of equations (5) and (6) into equation (10) yields a quadratic equation in $[HSO_4^-]$:

$$[HSO_4^-]^2 - (M_{SO_4^{2-}} + 2M_{H_2SO_4} + K_b) [HSO_4^-] + 2M_{SO_4^{2-}} M_{H_2SO_4} = 0 \dots\dots(12)$$

The roots of this equation are given by

$$[HSO_4^-] = \frac{1}{2} (M_{SO_4^{2-}} + 2M_{H_2SO_4} + K_b) \pm \frac{1}{2} \left((M_{SO_4^{2-}} + 2M_{H_2SO_4} + K_b)^2 - 8 M_{H_2SO_4} M_{SO_4^{2-}} \right)^{1/2} \dots\dots(13)$$

Similarly substitution of equations (6) and (7) into equation (11) also yields a quadratic equation in $[Zn^{2+}]$:

$$[Zn^{2+}]^2 + (M_{SO_4^{2-}} - [HSO_4^-] - C_{Zn} + K_z) [Zn^{2+}] - K_z C_{Zn} = 0. (14)$$

The roots are given by

$$[Zn^{2+}] = \frac{-1/2 (M_{SO_4^{2-}} - [HSO_4^-] - C_{Zn} + K_z) \pm 1/2 \left((M_{SO_4^{2-}} - [HSO_4^-] - C_{Zn} + K_z)^2 + 4K_z C_{Zn} \right)^{1/2}}{\dots\dots\dots} (15)$$

The equations (13) and (15) can be solved for the calculation of bisulphate and zinc ion concentrations respectively. The values of equilibrium constants which are dependent on ionic strength should be used. The roots of the equations (13) and (15) must be positive and the resulting values for concentrations must be physically meaningful.

Zinc interfacial flux. Murthy [4] studied the extraction equilibrium for the zinc/di (2-ethylhexyl) phosphoric acid (DEHPA) system and reported that two complexes of zinc-DEHPA are formed in n-heptane. He also reported that the rate controlling reaction is interfacial.

The following kinetic model was proposed based on extraction and stripping studies conducted in a cell with constant interfacial area [2-4] in the chemical control regime.

$$R_z = k_{Ia} \frac{C_{za} \alpha_o}{C_H} - k'_{Ia} \frac{C_{zo} C_H}{\alpha_o + 0.75 \alpha_o} \dots\dots\dots(16)$$

where K_{Ia} = extraction reaction rate constant, k'_{Ia} = stripping reaction rate constant, α_o = activity of extractant and C_{za} , C_H and C_{zo} are the concentrations of zinc ions, hydrogen ions and organic zinc complex.

Since the location of the chemical reaction is reported to be the interface, the concentrations in equation (16) are interfacial concentrations. Under the conditions of chemical control, the interfacial concentrations are almost equal to bulk concentrations. In the mixed regime (chemical and mass transfer control), the interfacial flux depends on the rate of both mass transfer and chemical reaction. As the interfacial concentrations are not measurable quantities, the reaction rate equation must be combined with the flux equations to obtain the interfacial concentrations of the species involved according to the reaction stoichiometry.

For any increment of height, δh , in the column where the continuous phase remains stagnant and in the absence of variation in concentration with height, the mass balance on zinc gives

$$\frac{dC_{za}}{dt} = -R_z \alpha_c \dots\dots\dots(17)$$

where R_z is the interfacial flux of zinc and α_c is the interfacial area per unit volume of continuous phase.

Since chemical reactions are involved, the extraction flux, R_z , is 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 hold-up and mean drop diameter.

Experimental

Experiments were performed in a glass spray column of 0.05m diameter and adjustable height. Effective heights of 1.25, 1.55 and 2.4m were used. Sampling points were placed at 20cm intervals along its height. The dispersed phase was introduced through four nozzles situated at the base of the column. The drops were formed on four sharp edged glass capillary nozzles. The nozzle tips were immersed in the stationary continuous aqueous phase, contained in the column. Samples of the aqueous phase were taken at different time intervals for the measurement of pH. The flow rate through the nozzles was measured and controlled individually. Two flat windows, one at the top and the other at the bottom, allow for the dispersion to be photographed. The column was operated in a semi-batch mode, i.e. the continuous aqueous phase was kept stagnant, and the dispersed phase was not recirculated. Full details of the setup and procedure are given elsewhere [17].

The $ZnSO_4 \cdot 7H_2O$, Na_2SO_4 and H_2SO_4 were of Analar grade and used as supplied by the manufacturer without further purification. The *n*-heptane supplied by shell was of knock-testing grade and was used without further purification. The di(2-ethylhexyl) phosphoric acid (DEHPA) was of technical grade obtained from BDH Ltd. and purified by the method of Partridge and Jensen [18].

The ionic strength of the aqueous phase was kept constant for each run with the addition of calculated amount of sodium sulphate so that activity co-efficients of species should not change during the reactions.

Results and Discussion

For the calculation of the values of $M_{H_2SO_4}$ and $M_{SO_4^{2-}}$ which would give the required pH and ionic strength, the iteration method was employed by using guessed values of $M_{H_2SO_4}$ and $M_{SO_4^{2-}}$. Baes [19] 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 show 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 [19] values were used for the calculation of K_b . In order to calculate the composition of aqueous phase, i.e. Zn^{2+} , H^+ and ionic strength from the known values of zinc sulphate, sodium sulphate and sulphuric acid, a set of mass balance and dissociation equilibrium equations were solved [20].

A numerical calculation routine (CO_2 AEF) written by Numerical Algorithm Group (NAG) and filed in the library of

routines of Department of Chemical Engineering and Chemical Technology, Computer Centre, Imperial College, London was used for polynomial equation to calculate interfacial flux. A computer programme was written to perform the numerical integration of differential equation (17) to predict the hydrogen ion concentration - time profile during the zinc extraction, process. The operating relation $C_H - C_{Za}$ was used by taking the stoichiometric 2:1 ratio of hydrogen flux to zinc flux, i.e. $R_H = 2R_Z$ and the actual concentration of hydrogen and zinc ions in the aqueous phase were calculated by allowing for the incomplete dissociation of bisulphate ion and zinc sulphate. The differential equation (17) was solved by using Runge-Kutta method. Predicted pH versus time curves were calculated for all extraction runs. Figure 1 shows some typical simulated results for pH-time profiles.

In order to study the variation of pH with time, several samples of aqueous phase were taken during the course of each extraction run. The pH value of each sample was measured with a Philips PW 9409 digital pH meter. Some of simulated results are compared with experimental data in Fig. 1. The continuous lines in this figure represent the simulated results. Agreement between simulated and experimental data is good.

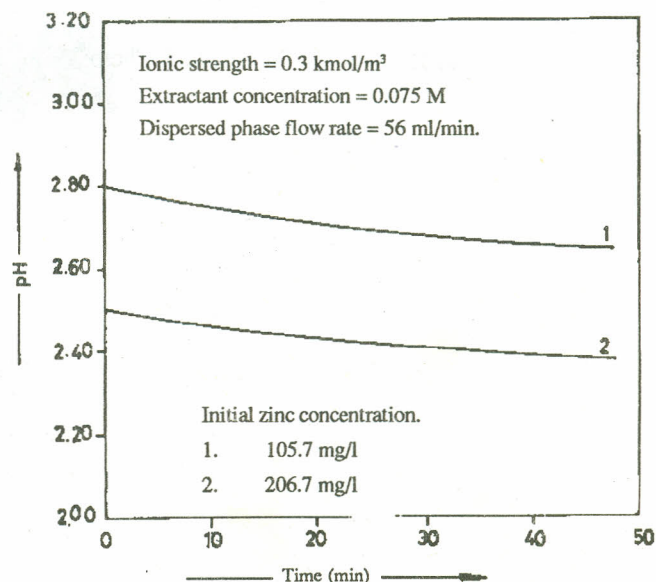


Fig. 1. Comparison of experimental and predicted pH values.

Conclusions

A chemical equilibrium model is developed to predict hydrogen ion, zinc ion concentration and ionic strength in the zinc sulphate - sulphuric acid system. The ionic equilibria in this system has been shown to be significant in solutions of interest in hydro-metallurgical operations. The operating line between hydrogen ion and zinc ion concentration is necessary

in the analysis of equilibrium and kinetic data in the liquid-liquid two phase extraction system. pH - time profiles simulated with the developed model are in agreement with the experimental data.

The temperature dependence of the ionic equilibria can be included if temperature dependence of the equilibrium constants can be obtained. This dependence can be estimated by the Van't Hoff equation if the enthalpy change for each reaction is available.

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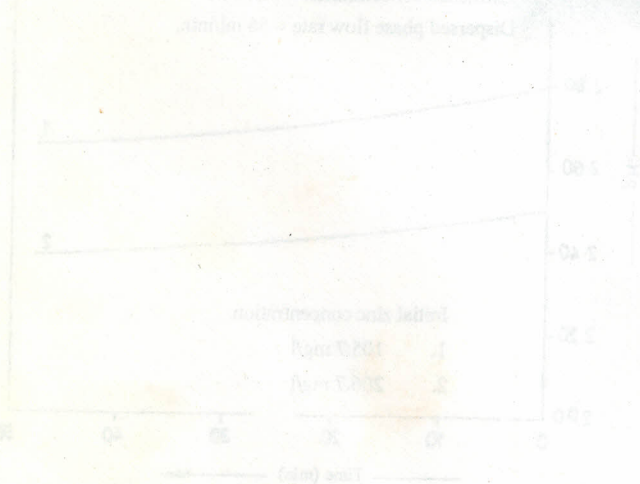


Fig. 1. Comparison of calculated and experimental pH values.

Conclusions

A chemical equilibrium model is developed to predict the distribution of zinc, copper, lead and iron species in the liquid-liquid extraction system. The ionic equilibria in this system have been shown to be significant in solution of zinc, copper, lead and iron species. The operating line between distribution and zinc concentration is necessary

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Results and Discussion

For the calculation of the values of M_{Zn} and M_{Cu} which would give the required pH and ionic strength, the iteration method was employed by using guessed values of M_{Zn} and M_{Cu} . The values of M_{Zn} and M_{Cu} were iteratively adjusted until the values of M_{Zn} and M_{Cu} for the system sodium sulphate and zinc sulphate were constant. The values of M_{Zn} and M_{Cu} were constant as the composition K_1 is nearly constant as the composition K_2 changed, even though the accompanying change in ionic strength is considerable. The values of M_{Zn} and M_{Cu} were used for the calculation of K_1 in order to calculate the composition of species, i.e. Zn^{2+} and ionic strength from the known values of zinc sulphate, sodium sulphate and sulphuric acid. A set of mass balance and dissociation equilibrium equations were solved [20].

A numerical calculation routine (COAL) written by Numerical Algorithms Group (NAG) and included in the library of