Modeling of Solvent Extraction of Zinc from Sulphate Solutions with D2EHPA

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A thermodynamic model based on chemical equilibria with mass and charge balance equations has been developed for the solvent extraction system consisting of $ZnSO_4$–H_2SO_4–H_2O-D2EHPA-kerosene. The activity coefficients of all solutes in the aqueous phase were calculated by Pitzer's equation. By applying this model, the equilibrium concentrations of solutes were calculated from the concentration of zinc and pH. The extracted metal species was $ZnHA_3$ and extraction equilibrium constant was found to have a value of 9.77×10^{-2} from the slope of the equilibrium extraction data. The predicted distribution coefficients of zinc were in good agreement with experimental results.

1. Introduction

Solvent extraction is widely used to separate and purify metals in hydrometallurgy. In developing a thermodynamic model on solvent extraction, nonideality of solutes must be considered. Many semi-empirically developed equations which could explain the nonideality of solutes at high ionic strength are proposed and widely used.[1-6]

Sulfuric acid solutions have been widely used as leaching agents in hydrometallurgical process. Due to the fact that the dissociation of bisulfate ion into hydrogen and sulfate ions is incomplete, the thermodynamic analysis of sulfuric acid solution is difficult.

A thermodynamic model on the solvent extraction of zinc from sulfuric acid solutions with D2EHPA (di-ethylhexyl phosphoric acid) was developed to predict the distribution co-efficients of zinc from initial extraction conditions. The extracted metal species and the equilibrium constant of extraction reaction were found by a graphical method. The activity coefficients of solutes in the aqueous phase were calculated by Pitzer equation. To check the validity of the model, experimental and calculated distribution coefficients of zinc were compared.

2. Theoretical Background

Assuming that D2EHPA exists as a dimmer in the diluent, the extraction reaction of zinc with D2EHPA can be written as

$$Zn_{aq}^{2+} + (1+x)H_2A_{2,or} = ZnH_{2x}A_{2+2x,or} + 2H_{aq}^+ \quad (1)$$
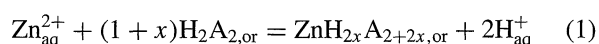
The distribution of metal is defined as

$$D = \frac{(Zn)_{or,t}}{(Zn)_{aq,t}} = \frac{\alpha_0(Zn)_{or,t}}{(Zn^{2+})} \quad (2)$$

In electrolyte solutions, various complexes between cation and anion are formed. Ionic strength has a great effect on the activity coefficients of solutes. To calculate the activity co-efficients of solutes, the complex formation reaction between opposite charge ions must be considered. Complex formation reactions considered in this study are shown in Table 1.[7,8] We assume that H_2SO_4 is not present as a molecule because of its complete dissociation into hydrogen and bisulfate ion. Mass balance and charge balance equations are also represented in Table 1.

The activity coefficients of solutes are calculated by Pitzer equation.

$$\ln \gamma_i = -A_\phi z_i^2 \left[\frac{\sqrt{I}}{1 + 1.2\sqrt{I}} + \frac{2}{1.2} \ln(1 + 1.2\sqrt{I}) \right]$$
$$+ 2 \sum_{j \neq H_2O} m_j B_{ij} + z_i^2 \sum_{j \neq H_2O} \sum_{k \neq H_2O} m_j m_k B'_{jk} \quad (3)$$

$$B_{ij} = \beta_{ij,0} + \frac{\beta_{ij,1}}{2I}[1 - (1 + 2\sqrt{I})\exp(-2\sqrt{I})] \quad (4)$$

$$B'_{jk} = \frac{\beta_{ij,1}}{4I^2}[-1 + (1 + 2\sqrt{I} + 2I)\exp(-2\sqrt{I})] \quad (5)$$

3. Experimental

Zinc sulfate solutions were prepared by dissolving $ZnSO_4 \cdot 7H_2O$ in distilled water. The pH of aqueous solution was controlled by adding H_2SO_4. The D2EHPA was purchased from Albright and Wilson Co., Ltd, and kerosene was used without further purification.

Equal volumes ($20\,cm^3$) of organic and zinc sulfate solutions were contained in a 100 ml separatory funnel and shaken mechanically for 30 minutes at 25°C. The aqueous phase was separated after settling the mixture for 24 hours. The concentrations of zinc in the aqueous phase were measured by I.C.P. (Thermo Jarrell ash, Model Polyscan 61E) and the concentrations of zinc in the organic phase were calculated by using mass balance for zinc. The pH was measured by a pH meter (Fisher Accumet pH model 620).

Table 1   Chemical reaction equilibria, mass and charge balance equations.

Reaction	Equilibrium constant	Ionic strength	Reference
$H_2O = H^+ + OH^-$	$K_1 = 1.0 \times 10^{-14}$	0	7
$H^+ + SO_4^{2-} = HSO_4^-$	$K_2 = 9.85 \times 10^1$	0	7
$Zn^{2+} + SO_4^{2-} = ZnSO_4$	$K_3 = 3.09 \times 10^2$	0	8
$Zn^{2+} + HSO_4^- = ZnHSO_4^+$	$K_4 = 2.29 \times 10^2$	0	8
$Zn^{2+} + OH^- = ZnOH^+$	$K_5 = 1.0 \times 10^5$	0	8
$Zn^{2+} + 2OH^- = Zn(OH)_2$	$K_6 = 1.26 \times 10^{11}$	0	8

Mass balance equations

$(Zn)^I = (Zn^{2+}) + (ZnSO_4) + (ZnHSO_4^+) + (ZnOH^+) + (Zn(OH)_2) + \frac{V_{or}}{V_{aq}} \times (ZnH_{2x}A_{2+2x})$

$(S)^I = (SO_4^{2-}) + (HSO_4^-) + (ZnSO_4) + (ZnHSO_4^+)$

$(A)^I = 2(H_2A_2) + 2(1+x)(ZnH_{2x}A_{2+2x})$

Charge balance equation

$(H^+) + (ZnHSO_4^+) + (ZnOH^+) + 2(Zn^{2+}) = (OH^-) + (HSO_4^-) + 2(SO_4^{2-})$

4.   Results and Discussion

4.1   Extracted metal species and equilibrium constant

The equilibrium constant of extraction reaction is represented as

$$K_{EX} = \frac{(ZnH_{2x}A_{2+2x})(H^+)^2}{(Zn^{2+})(H_2A_2)^{1+x}} \times \frac{\gamma_{ZnH_{2x}A_{2+2x}}\gamma_{H^+}^2}{\gamma_{Zn^{2+}}(\gamma_{H_2A_2})^{1+x}} \quad (6)$$

By inserting (2) into (6) and taking logarithm on both sides of (6), the following equation was obtained.

$$\log D - 2pH = (1+x)\log(H_2A_2) + \log K_{EX}$$
$$- \log \frac{\gamma_{ZnH_{2x}A_{2+2x}}}{\alpha_0 \gamma_{Zn^{2+}}(\gamma_{H_2A_2})^{1+x}} \quad (7)$$

In (7), (H_2A_2) is the concentration of D2EHPA after extraction and calculated by using mass balance for D2EHPA.

$$(H_2A_2) = (H_2A_2)^I - 2(1+x)(ZnH_{2x}A_{2+2x}) \quad (8)$$

Extracted metal species in the organic phase was identified from initial extraction conditions, equilibrium extraction data and (7) by the following graphical method. First, the concentration of free D2EHPA was calculated from (8) by varying the value of x from 0 to 1.5. The plot of $\log D$–$2pH$ against $\log(H_2A_2)$ should yield a straight line of slope $1 + x$. As is shown in Fig. 1, the plot yields a straight line with a slope of 1.68 only when x was assumed to be 0.5. By this graphical method, the extracted metal species was found to be $ZnHA_3$. The extraction reaction of zinc with D2EHPA can be represented as

$$Zn_{aq}^{2+} + 1.5H_2A_{2,or} = ZnHA_{3,or} + 2H_{aq}^+ \quad (9)$$
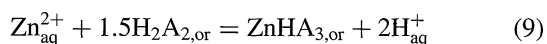
Sainz performed extraction experiments of zinc from phosphoric acid solutions with D2EHPA in heptane and identified the extracted metal species as $ZnHA_3$ by a graphical method and FT-IR.[9] Though acid and organic solvent used in Sainz's experiment are different from this work, the extracted metal species are same.

The equilibrium constant of extraction reaction is related with the intercept of Fig. 1. If the third terms on the right hand side of (7) is assumed to be zero, the equilibrium constant of reaction (9) was 9.77×10^{-2}.
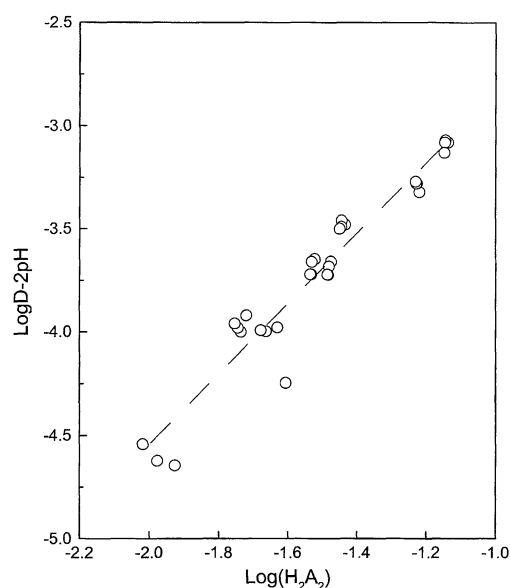

Fig. 1   Identification of extracted metal species by $\log(H_2A_2)$ vs. $\log D$-$2pH$ plot.

4.2   Estimation of interaction parameter

Bromley proposed that the interaction parameter of strong electrolyte was equal to the sum of interaction parameter of ions.[4]

$$\beta_{+-} = \beta_+ + \beta_- \quad (10)$$

Bromley obtained the interaction parameters of ions by setting those of sodium ion equal to zero. By the same method, the interaction parameters of ions were estimated from the β_0 and β_1 values of electrolytes which Pitzer reported and are shown in Table 2.[2]

Edwards applied Pitzer equation to the weak electrolyte solutions and obtained interaction parameters between ion and molecule by (11) and between molecule and molecule by (12).[10]

$$\beta_{\text{ion-molecule}} = \beta_{\text{ion}} + \beta_{\text{molecule}} \quad (11)$$

$$\beta_{ij} = 0.5(\beta_{ii} + \beta_{jj}) \quad (12)$$

4.3 Thermodynamic model

It is seen from Table 1 that the number of solutes in the aqueous phase before extraction is ten (Zn^{2+}, $ZnSO_4$, $ZnHSO_4^+$, $ZnOH^+$, $Zn(OH)_2$, H^+, OH^-, SO_4^{2-}, HSO_4^-, H_2O). Ten independent equations are necessary to solve for the ten unknowns.

If the total concentration of sulfate was not known, we must calculate the total concentration of sulfate before using the mass balance for it. First, the activity of water was calculated by the following Pitzer equation.[11]

$$\ln a_w = 18\left[\frac{2A_\phi I^{3/2}}{1 + 1.2\sqrt{I}} - \sum_{i \neq H_2O}\sum_{j \neq H_2O} m_i m_j \left\{\beta_0 + \beta_1 \exp(-2\sqrt{I})\right\}\right] - 18\sum_{i \neq H_2O} m_i \tag{13}$$

Second, the activity of hydrogen was obtained from the initial pH. The activity of remaining eight solutes was calculated by solving six chemical equilibria and one mass balance for zinc and charge balance equation simultaneously. After setting activity coefficients of all solutes equal to one, the eight equations were solved by Newton-Rahpson method. Ionic strength was obtained and the activity coefficients of solutes were calculated by Pitzer equation. All these steps were repeated until criteria was satisfied and the total concentration of sulfate was obtained.

Figure 2 shows the distribution of zinc containing solutes between pH 1 to 5 when total concentration of zinc was 0.00382 mol/dm³. The dominant species at low pH was $ZnHSO_4^+$ but the fraction of free zinc ion increased gradually with pH. The distribution of sulfate containing solutes between pH 1 to 5 is shown in Fig. 3 when total concentration of zinc was 0.00382 mol/dm³. It is shown from Fig. 3 that the fraction of free sulfate ion increased gradually with pH.

The number of chemical species after extraction is thirteen (Zn^{2+}, $ZnSO_4$, $ZnHSO_4^+$, $ZnOH^+$, $Zn(OH)_2$, H^+, OH^-, SO_4^{2-}, HSO_4^-, H_2O, H_2A_2, $ZnHA_3$, diluent). It is difficult to calculate the activity coefficients of chemical species in the organic phase because of the lack of information. Moyer calculated the activity coefficients of extracted metal species and extractant by applying regular solution model and found that the nonideality of solutes in the organic phase was small to
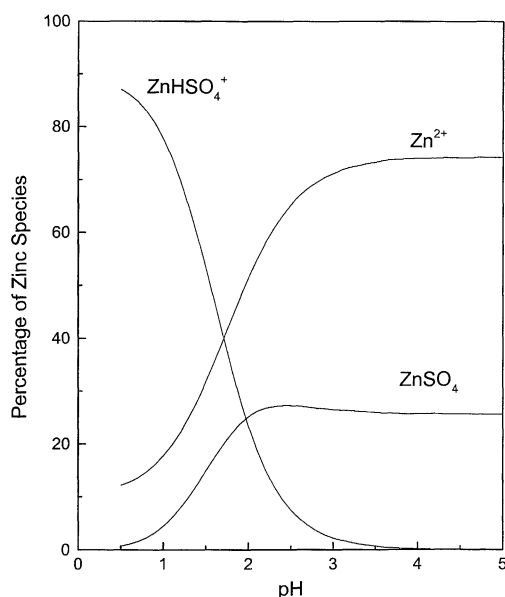
be negligible.[12] Therefore, the activity coefficients of species in the organic phase were assumed to be one. Twelve independent equations are required for calculating the activity of twelve chemical species and were obtained from seven chemical equilibria and three mass balance and charge balance and activity equation for water.

The mass balance for zinc is written by inserting chemical equilibria.

$$(Zn)^I = (Zn^{2+}) + (ZnSO_4) + (ZnHSO_4^+) + (ZnOH^+)$$
$$+ (Zn(OH)_2) + (ZnHA_3)$$
$$= (Zn^{2+})\left[1 + K_3 R_3(SO_4^{2-}) + K_4 R_4(HSO_4^{2-})\right.$$
$$+ K_5 R_5(OH^-) + K_6 R_6(OH^-)^2$$
$$\left. + K_{EX}\frac{(Zn^{2+})(H_2A_2)^{1.5}}{(H^+)^2} \times \frac{\gamma_{Zn^{2+}}}{\gamma_{H^+}^2}\right] \tag{14}$$
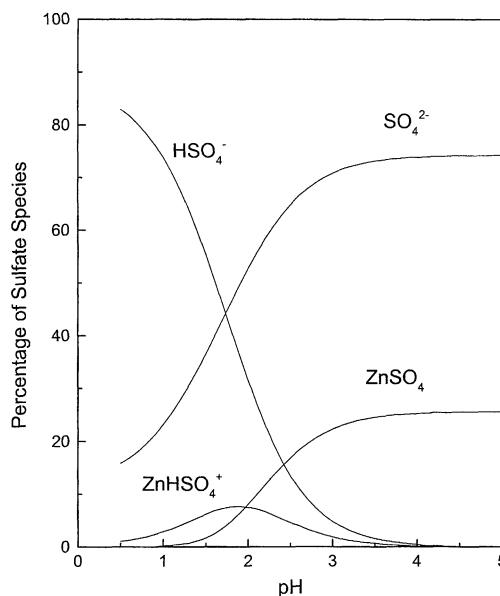
Fig. 3 Effect of pH on the distribution of sulfate. ($(Zn)^I = 0.00382$ mol/dm³).

Table 2 Estimated values for the interaction parameter of ions at 25°C.

Species	β_0	β_1
Cl^-	0.0765	0.2664
H^+	0.101	0.0281
OH^-	0.0864	0.253
SO_4^{2-}	0.01958	1.113
Zn^{2+}	0.1753	1.77

Fig. 2 Effect of pH on the distribution of zinc. ($(Zn)^I = 0.00382$ mol/dm³).

Table 3   Equilibrium and calculated data for the extraction of zinc.

No	$(Zn)^I$	$(Zn)_{aq,t}$	$(HA)^I$	$(pH)^I$	Log D_e	Log D_c	eq.pH$_e$	eq.pH$_c$
1	0.00382	0.00338	0.025	1.88	−0.8853	−0.7906	1.87	1.86
2	0.00382	0.00251	0.025	2.32	−0.2824	−0.1450	2.17	2.15
3	0.00382	0.00187	0.025	2.73	0.0182	0.1389	2.28	2.29
4	0.00382	0.00364	0.050	1.48	−1.3056	−1.3094	1.47	1.48
5	0.00382	0.00273	0.050	1.88	−0.3987	−0.3963	1.79	1.83
6	0.00382	0.00160	0.050	2.32	0.1422	0.2064	2.07	2.08
7	0.00382	0.00111	0.050	2.73	0.3876	0.4962	2.19	2.21
8	0.00382	0.00112	0.075	2.32	0.3821	0.4232	2.02	2.05
9	0.00382	0.00077	0.075	2.73	0.5977	0.7240	2.14	2.17
10	0.00382	0.00069	0.075	2.95	0.6566	0.8157	2.19	2.21
11	0.00382	0.00059	0.075	3.42	0.7382	0.9165	2.23	2.25
12	0.00765	0.00365	0.050	2.33	0.0398	−0.0527	1.98	2.02
13	0.00765	0.00321	0.050	2.77	0.1409	0.1426	2.07	2.11
14	0.00765	0.00296	0.050	3.02	0.1998	0.1957	2.09	2.14
15	0.00765	0.00271	0.050	3.49	0.2607	0.2426	2.11	2.16
16	0.00765	0.00266	0.075	2.33	0.2732	0.1334	1.96	1.97
17	0.00765	0.00225	0.075	2.77	0.3801	0.3297	2.02	2.06
18	0.00765	0.00218	0.075	3.02	0.3995	0.3842	2.06	2.08
19	0.00765	0.00204	0.075	3.49	0.4393	0.4327	2.08	2.10
20	0.0153	0.00643	0.100	2.41	0.1397	0.0044	1.81	1.88
21	0.0153	0.00592	0.100	2.84	0.1998	0.1176	1.83	1.94
22	0.0153	0.00584	0.100	3.07	0.2094	0.1468	1.85	1.95
23	0.0153	0.00559	0.100	3.52	0.2398	0.1746	1.87	1.96
24	0.0153	0.00543	0.150	2.41	0.2595	0.1708	1.79	1.82
25	0.0153	0.00479	0.150	2.84	0.3412	0.2842	1.81	1.87
26	0.0153	0.00464	0.150	3.07	0.3612	0.3139	1.82	1.88
27	0.0153	0.00443	0.150	3.52	0.3898	0.3423	1.83	1.89
28	0.0306	0.01251	0.200	2.50	0.1602	0.0067	1.62	1.73
29	0.0306	0.01167	0.200	2.94	0.2100	0.0787	1.64	1.76
30	0.0306	0.01151	0.200	3.17	0.2197	0.0966	1.65	1.77
31	0.0306	0.01134	0.200	3.64	0.2300	0.1140	1.68	1.78

subscript (e: experiment, c: calculated)

In the above equation, R is the ratio of activity coefficients and defined as follows

$$K_3 = \frac{(ZnSO_4)}{(Zn^{2+})(SO_4^{2-})} \times \frac{\gamma_{ZnSO_4}}{\gamma_{Zn^{2+}}\gamma_{SO_4^{2-}}} = \frac{(ZnSO_4)}{(Zn^{2+})(SO_4^{2-})} \times \frac{1}{R_3}$$

(15)

The experimental conditions and the extraction data are listed in Table 3. The distribution coefficients of zinc predicted by model are also represented in Table 3. To evaluate the validity of model, the distribution coefficients of zinc obtained experimentally and those calculated by model are plotted in Fig. 4. The standard deviation between these distribution coefficients is 0.09, indicating very good agreement between the two results.

5.   Conclusions

The following conclusions can be drawn from this study:

(1)   The extracted metal species was $ZnHA_3$ and the equilibrium constant of extraction reaction obtained by a graphical method was 9.77×10^{-2}.

(2)   The total concentration of sulfate was calculated from pH and the total concentration of zinc. Distribution of chem-
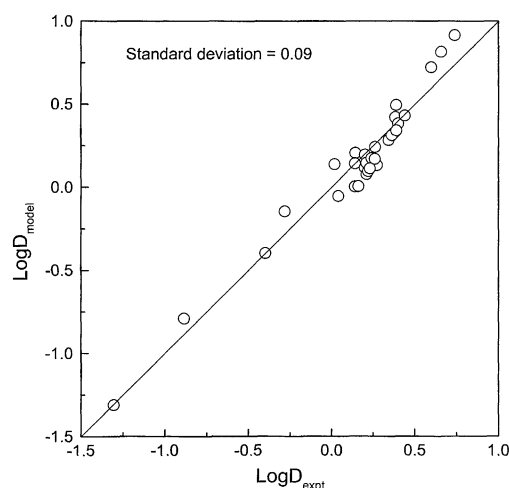

Fig. 4   Comparison between the distribution coefficients obtained experimentally and those calculated by model.

ical species between pH 1 to 5 was obtained and the fraction of free zinc ion increased with pH.

(3)   The calculated distribution coefficients of zinc were in good agreement with those obtained experimentally.

Nomenclature

a: activity
A: extractant anion
A_ϕ: Debye-Hückel constant
D: distribution coefficient
H_2A_2: extractant
I: ionic strength
K: equilibrium constant
m: molality
R: activity coefficient ratio
V: volume
Z: charge number
α_0: alpha function
β_1, β_2: interaction parameter
γ: activity coefficient
⟨Superscript⟩
I: initial total concentration
⟨Subscript⟩
aq: aqueous phase
aq,t: total concentration in the aqueous phase
EX: solvent extraction

or: organic phase
or,t: total concentration in the organic phase
x: degree of polymerization of extracted metal species

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