Use of the Bromley Equation for the Analysis of Ionic Equilibria in Mixed Ferric and Ferrous Chloride Solutions at 25 °C

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The ionic equilibria in the mixed ferric and ferrous chloride solution were analyzed by considering the complex formation reactions as well as the mass and charge balance equations. The activity coefficients of the ions were calculated using the Bromley equation. The equilibrium constants for the formation of ferrous complexes were determined from the reported thermodynamic data. The interaction parameters of the ferric species were estimated from the reported values of $FeCl_3$ in an HCl solution. By applying the ionic equilibria, the speciation of the ferric and ferrous species with the composition was obtained. The predicted pH values of the $FeCl_3$-$FeCl_2$-HCl-H_2O system agreed well with the measured values at 25 °C in the ionic strength range of up to 9.34 m.
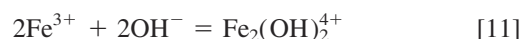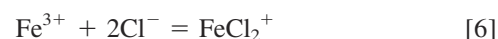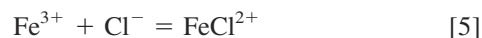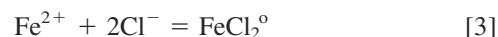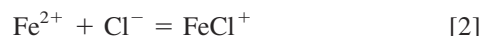
I. INTRODUCTION

FERRIC chloride solutions are used in the leaching of sulfide ore[1] and in the etching of nickel-lead frames owing to their strong oxidizing property. Ferrous chloride and other valuable metal ions coexist in a spent $FeCl_3$ solution. Ferric ion forms various complexes with chloride ion. Hence, ferric chloride in a spent $FeCl_3$ solution can be separated through solvent extraction with the use of neutral or anionic extractants.[2–7] Few data, however, are available regarding the complex formation of ferrous and chloride ions.[8] It was reported that the oxidation kinetics of ferrous ion in an HCl solution with molecular oxygen depended on the activity of HCl.[9] The knowledge of the distribution of the iron species with the composition of a spent $FeCl_3$ solution enables us to choose an extractant suitable for the solvent extraction of iron. Both complex formation reactions and activity coefficients of chemical species must be considered in analyzing the distribution of the iron species.

In this study, the ionic equilibria in the mixed ferric and ferrous chloride solution were analyzed by considering complex formation reactions as well as the mass and charge balance equations. The activity coefficient of the ions was calculated using the Bromley equation.[10] The equilibrium constants for the complex formation reaction of ferrous ion were determined from the reported thermodynamic data.[8,11,12] Bromley's interaction parameter of ferric ion in an HCl solution was estimated from the data reported in the literature.[13] The validity of the ionic equilibria for the $FeCl_3$-$FeCl_2$-HCl-H_2O system at 25 °C was verified by comparing the measured values of solution pH with those calculated in this study.

II. THEORETICAL BACKGROUND

In chloride solutions, ferric and ferrous ions form chemical complexes with chloride and hydroxide ions. The calculation results in this study suggest that the concentration of $Fe(OH)_2^o$,

$Fe_2(OH)_2^{2+}$, and $Fe(OH)_3^o$ are negligible ($<10^{-10}$ M) in the concentration ranges studied in this work. As such, the formation reaction of the preceding three complexes was not considered. The following equations represent the complex formation reactions in a concentrated HCl solution:[8,11–13]

$$H^+ + OH^- = H_2O \qquad [1]$$

$$Fe^{2+} + Cl^- = FeCl^+ \qquad [2]$$

$$Fe^{2+} + 2Cl^- = FeCl_2^o \qquad [3]$$

$$Fe^{2+} + OH^- = FeOH^+ \qquad [4]$$

$$Fe^{3+} + Cl^- = FeCl^{2+} \qquad [5]$$

$$Fe^{3+} + 2Cl^- = FeCl_2^+ \qquad [6]$$

$$Fe^{3+} + 3Cl^- = FeCl_3^o \qquad [7]$$

$$Fe^{3+} + 4Cl^- = FeCl_4^- \qquad [8]$$

$$Fe^{3+} + OH^- = FeOH^{2+} \qquad [9]$$

$$Fe^{3+} + 2OH^- = Fe(OH)_2^+ \qquad [10]$$

$$2Fe^{3+} + 2OH^- = Fe_2(OH)_2^{4+} \qquad [11]$$

Mass balance equations for chloride, Fe(II), and Fe(III) were obtained from the preceding complex formation reactions, as follows:

$$
\begin{aligned}
[Cl]_t &= 2[FeCl_2]_t + 3[FeCl_3]_t + [HCl]_t \\
&= [Cl^-] + [FeCl^+] + 2[FeCl_2^o] + [FeCl^{2+}] \\
&\quad + 2[FeCl_2^+] + 3[FeCl_3^o] + 4[FeCl_4^-] \qquad [12]
\end{aligned}
$$

$$
\begin{aligned}
[Fe(II)]_t &= [FeCl_2]_t = [Fe^{2+}] + [FeCl^+] \\
&\quad + [FeCl_2^o] + [FeOH^+] \qquad [13]
\end{aligned}
$$

$$
\begin{aligned}
[Fe(III)]_t &= [FeCl_3]_t = [Fe^{3+}] + [FeCl^{2+}] + [FeCl_2^+] \\
&\quad + [FeCl_3^o] + [FeCl_4^-] + [FeOH^{2+}] \\
&\quad + [Fe(OH)_2^+] + 2[Fe_2(OH)_2^{4+}] \qquad [14]
\end{aligned}
$$

where the subscript t represents total concentration.

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The following charge balance equation was obtained from the electroneutrality condition:

$$[H^+] + 2[Fe^{2+}] + [FeCl^+] + [FeOH^+] + 3[Fe^{3+}]$$
$$+ 2[FeCl^{2+}] + [FeCl_2^+] + 2[FeOH^{2+}]$$
$$+ [Fe(OH)_2^+] + 4[Fe_2(OH)_2^{4+}]$$
$$= [Cl^-] + [FeCl_4^-] + [OH^-] \quad [15]$$
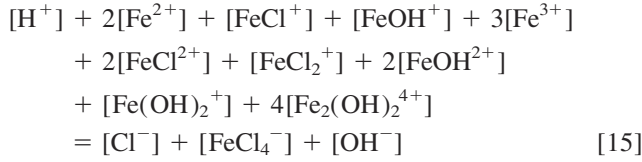
The activity coefficient of the ions was calculated using the Bromley equation. The Bromley equation for the activity coefficient of an individual ion at 25 °C is represented by the following equations:[10]

$$\text{Log } \gamma_M = -\frac{0.5108 \, (z_M)^2 \, I^{0.5}}{1 + I^{0.5}} + F_M \quad [16]$$

$$F_M = \sum_X \left[\frac{(0.06 + 0.6 B_{MX}) \times |z_M z_X|}{\left(1 + \frac{1.5}{|z_M z_X|} I\right)^2} + B_{MX} \right]$$

$$\times \frac{\left(|z_M| + |z_X|\right)^2}{4} [X] \quad [17]$$

In the preceding equations, z denotes the ionic charge, I denotes the ionic strength of the solution, and B_{MX} refers to the interaction parameter between cation M and anion X. The term $[X]$ represents the free concentration of anion X.

The water activity for a single electrolyte ij, $a_{w,ij}^o$, was calculated using the following Bromley equation for the osmotic coefficient, ϕ_{ij}:[14]

$$\phi_{ij} = 1 - 2.303 \left[\frac{0.5108 |z_i z_j|}{I} \left\{ 1 + \sqrt{I} - \frac{1}{1 + \sqrt{I}} \right. \right.$$

$$- 2\ln\left(1 + \sqrt{I}\right) \right\} - \frac{(0.06 + 0.6 B_{ij}) \times |z_i z_j|}{\frac{1.5}{|z_i z_j|}}$$

$$\times \left\{ \frac{1 + 2\frac{1.5}{|z_i z_j|} I}{\left(1 + \frac{1.5}{|z_i z_j|} I\right)^2} - \frac{\ln\left(1 + \frac{1.5}{|z_i z_j|} I\right)}{\frac{1.5}{|z_i z_j|} I} \right\} - 0.5 B_{ij} I \right] \quad [18]$$

$$\ln a_{w,ij}^o = -\frac{18.02 \, vm}{1000} \phi_{ij} \quad [19]$$

where v represents the number of moles of ions and m, the molality of the electrolyte.

Using Eq. [20], as suggested by Meissner, the water activity of the mixed electrolyte solutions was calculated from the water activity of a single electrolyte.[14]

$$\ln a_{w,mix} = \sum \sum \frac{I_i I_j}{I^2} \left[\frac{\left(|z_i| + |z_j|\right)^2}{|z_i z_j|} \right] \times \ln a_{w,ij}^o \quad [20]$$

where I_i represents the ionic strength of the individual ions, which equals $0.5 m_i (z_i)^2$.

III. EXPERIMENTAL

Chloride solutions with various compositions were prepared by dissolving $FeCl_2 \cdot 5H_2O$, $FeCl_3 \cdot 6H_2O$, and HCl in distilled water. All chemicals were of reagent grade. Known amounts of $FeCl_2$, $FeCl_3$, and HCl were added to 100 g of water. The mixture was then stirred for 30 minutes using a magnetic stirrer. After the chemicals were dissolved, the temperature of the solutions was controlled at 25 °C by immersing the beaker into a water bath.

Once the temperature of the solution was stable, solution pH was measured using a pH meter (Orion, 535A). The pH meter, which had a combination electrode, was calibrated before each set of measurements with the use of a buffer.

IV. RESULTS AND DISCUSSION

A. *Estimation of the Equilibrium Constant and Interaction Parameter*

Once metal salts are dissolved in an aqueous solution, complex formation reactions between cation and anion occur. The metals dissolved in an aqueous solution exist as free ions, charged complexes, and neutral molecules. Complex formation has a profound effect on the properties of a solution, and can be treated by considering the equilibrium constant for the formation reaction and the activity coefficients of the chemical species involved. To take into account the effect of ionic strength on the ionic equilibria, the equilibrium constant for the formation of complexes at zero ionic strength is required. Some data regarding the equilibrium constant for the formation of ferric complexes at zero ionic strength have been published.[13,15–17] Few data, however, have been reported regarding the equilibrium constant for the formation of ferrous complexes at zero ionic strength. Table I shows the reported equilibrium constant for the formation of $FeCl^+$ other than at zero ionic strength.[8] The equilibrium constant for the formation of $FeCl^+$ at zero ionic strength was determined from these reported values by using the following Vasil'ev equation:[18]

$$\text{Log } K = \text{Log } K^o + \frac{A_\phi \left(\sum_{i=1}^n v_i z_i^2\right)\sqrt{I}}{1 + 1.6\sqrt{I}} + BI \quad [21]$$

Table I. Reported Equilibrium Constant for the Formation of FeCl+ at 25 °C[8]

Medium	Ionic Strength	Log K
$HClO_4$	0.2	1.3
$NaClO_4$	1.0	0.78

In Eq. [21], K° and K represent the equilibrium constant at zero ionic strength and at ionic strength I, respectively; A_ϕ represents the Debye–Hückel constant, and v_i represents the stoichiometric coefficient. The symbol B is a constant characteristic of the reaction. The equilibrium constants shown in Table I, and the necessary parameters, were first substituted into Eq. [21]. Then, the equilibrium constant at zero ionic strength was determined by solving the resulting two equations.

The equilibrium constants for the formation of $FeCl_2^\circ$ and $FeOH^+$ were obtained from the thermodynamic data using Eq. [22]. Table II shows the thermodynamic data of ferrous species that were reported in the literature:[11,12]

$$\Delta G^\circ = -RT \ln K \qquad [22]$$

Table III lists the equilibrium constants of ferrous complexes determined in this study, and the equilibrium constant of ferric complexes at zero ionic strength obtained from the literature.[13]

Bromley proposed that the interaction parameter of a strong electrolyte MX could be approximated by the following equation:[10]

$$B_{MX} = B_M + B_X + \delta_M \delta_X \qquad [23]$$

where B and δ are the interaction parameter and correction value of an individual ion, respectively.

In Bromley's work, the interaction parameter of $FeCl_2$ was given, while that of $FeCl_3$ was not reported. Madariaga and his co-workers developed a chemical model to estimate the effect of ionic media on solution equilibria, and to calculate the interaction parameter by using the modified Bromley's methodology.[13,19–23] In their extensive work, Belaustegi et al. reported thermodynamic equilibrium constants and interaction parameters between Fe(III) and chloride ligands at 25 °C, which are listed in Table IV.[13] The use of these thermodynamic data promises a more reliable analysis of ionic equilibria in a ferric chloride solution at high ionic strength. The

interaction parameter of Fe^{3+} with Cl^- and with ClO_4^- can be represented by the following equations:

$$B[Fe^{3+}, Cl^-] = B_{Fe^{3+}} + B_{Cl^-} + \delta_{Fe^{3+}} \delta_{Cl^-} \qquad [24]$$

$$B[Fe^{3+}, ClO_4^-] = B_{Fe^{3+}} + B_{ClO_4^-} + \delta_{Fe^{3+}} \delta_{ClO_4^-} \qquad [25]$$

The interaction parameter and correction value of Cl^- and ClO_4^- that were reported by Bromley were first substituted into Eqs. [24] and [25]. These two equations were then solved to give the interaction parameter and correction value of Fe^{3+}.[24] Table V shows the interaction parameters and correction values of ferric species that were calculated using this method, together with the values reported by Bromley.

The activity coefficient of $FeCl_3^\circ$ was calculated using Eq. [26], in which $S_{FeCl_3,HCl}$ represents the salting coefficient $FeCl_3$ in an HCl solution.[13]

$$\text{Log } \gamma_{FeCl_3} = S_{FeCl_3,HCl} [HCl] \qquad [26]$$

The activity coefficient of $FeCl_2^\circ$ can also be calculated using Eq. [26]. In contrast to $FeCl_3^\circ$, there are no thermodynamic data on $FeCl_2^\circ$ that can be used to obtain $S_{FeCl_2,HCl}$. Neutral molecules have an activity coefficient essentially equal to unity in dilute solutions.[25] At high ionic strength, the activity coefficient of most neutral molecules was more than unity.[25] As long as the concentration of $FeCl_2^\circ$ is low, the inability to calculate the activity coefficient of $FeCl_2^\circ$ would be expected to have little effect on the calculated speciation. Hence, the activity coefficient of $FeCl_2^\circ$ was assumed to be unity.

B. Ionic Equilibria Analysis

When the complex formation reactions in Eqs. [1] through [11] for the mixed ferric and ferrous chloride solution were

Table II. Thermodynamic Data for the Species at 25 °C

Species	ΔG° (kJ/mol)	Reference
Cl^-	−131.0563	11
Fe^{2+}	−78.87	12
$FeCl_2^\circ$	−341.37	11
$FeOH^+$	−277.4	11
OH^-	−157.293	11

Table III. Equilibrium Constants of Chemical Reaction at 25 °C

Reaction	Log K	Reference
$H^+ + OH^- = H_2O$	14.00	8
$Fe^{2+} + Cl^- = FeCl^+$	1.90	—
$Fe^{2+} + 2Cl^- = FeCl_2^\circ$	6.79×10^{-2}	—
$Fe^{2+} + OH^- = FeOH^+$	7.23	—
$Fe^{3+} + Cl^- = FeCl^{2+}$	1.31	13
$Fe^{3+} + 2Cl^- = FeCl_2^+$	1.98	13
$Fe^{3+} + 3Cl^- = FeCl_3^\circ$	1.19	13
$Fe^{3+} + 4Cl^- = FeCl_4^-$	−1.31	13
$Fe^{3+} + OH^- = FeOH^{2+}$	11.82	13
$Fe^{3+} + 2OH^- = Fe(OH)_2^+$	22.95	13
$2Fe^{3+} + 2OH^- = Fe_2(OH)_2^{4+}$	25.12	13

Table IV. Bromley Interaction Parameters of Ferric Complexes at 25 °C[13]

Species	Values	Species	Values
$B[Fe^{3+}, Cl^-]$	−0.0016	$B[Fe^{3+}, ClO_4^-]$	0.0681
$B[FeCl^{2+}, Cl^-]$	−0.1469	$B[FeCl^{2+}, ClO_4^-]$	0.0381
$B[FeCl_2^+, Cl^-]$	−0.5248	$B[FeCl_2^+, ClO_4^-]$	0.0221
$B[FeOH^{2+}, Cl^-]$	0.0302	$B[FeOH^{2+}, ClO_4^-]$	0.0667
$B[Fe(OH)_2^+, Cl^-]$	0.1178	$B[Fe(OH)_2^+, ClO_4^-]$	0.0306
$B[Fe_2(OH)_2^{4+}, Cl^-]$	0.0460	$B[Fe_2(OH)_2^{4+}, ClO_4^-]$	0.1713

Table V. Estimated Values for the Interaction Parameter of Ions at 25 °C

Species	B	δ
Cl^-	0.0643*	−0.067*
Fe^{2+}	0.046*	0.21*
Fe^{3+}	−0.0556	0.154
$FeCl^{2+}$	−0.192	0.289
$FeCl_2^+$	−0.542	0.71
$FeOH^{2+}$	−0.0264	0.115
$Fe(OH)_2^+$	0.0516	−0.029
$Fe_2(OH)_2^{4+}$	−0.00369	0.218
$FeCl_4^-$	−0.6985	0.0
H^+	0.0875*	0.103*
OH^-	0.076*	−1.0*

*Reported by Bromley.

considered, there were 15 chemical species in the equilibrium state: $[Cl^-]$, $[Fe^{2+}]$, $[FeCl^+]$, $[FeCl_2^o]$, $[FeOH^+]$, $[Fe^{3+}]$, $[FeCl^{2+}]$, $[FeCl_2^+]$, $[FeCl_3^o]$, $[FeCl_4^-]$, $[FeOH^{2+}]$, $[Fe(OH)_2^+]$, $[Fe_2(OH)_2^{4+}]$, $[H^+]$, and $[OH^-]$. To calculate the equilibrium concentrations and the activity coefficients of these 15 chemical species and the water activity, 31 independent equations were needed. These equations were obtained from 11 complex formation reactions (Eqs. [1] through [11]), three mass balance equations (Eqs. [12] through [14]), a charge balance equation (Eq. [15]), 15 activity coefficient equations of chemical species, and the activity equation of water.

By inserting the complex formation reactions into the mass and charge balance equations, these independent equations were simplified into four nonlinear equations containing four ions, namely, Cl^-, Fe^{2+}, Fe^{3+}, and H^+. In solving these four equations using the Newton–Raphson method, the initial values of the concentration of these four ions are important to ensure convergence. The concentrations of Cl^-, Fe^{2+}, and Fe^{3+} were guessed by assuming that the electrolyte dissociated completely. The initial concentration of the hydrogen ion was obtained from the HCl concentration. After the concentrations of Cl^-, Fe^{2+}, Fe^{3+}, and H^+ were obtained by solving the four equations, the concentrations of various complexes were calculated from the complex formation reactions. When the concentrations of all chemical species were obtained, the value of the ionic strength was calculated. The activity coefficients of the ions were then calculated using the Bromley equation. The calculation was repeated until the relative error of the ionic strength was within an acceptable level. Figure 1 shows the algorithm used to calculate the concentrations of the chemical species from the composition of the electrolytes.

Figures 2 and 3 show the distribution of the ferric chloride and ferric hydroxide complexes with $FeCl_3$ concentration in 1.0 m HCl, at 25 °C, in the absence of $FeCl_2$. The mole fraction was defined as the ratio of the concentration of the ferric species to the total concentration of $FeCl_3$. As shown in Figure 2, most ferric species existed as $FeCl_2^+$ and $FeCl^{2+}$ in the $FeCl_3$ concentration ranges considered in this study. The mole fraction of $FeCl_4^-$ increased with increasing $FeCl_3$ concentration, while the mole fractions of $FeCl_3^o$ decreased with $FeCl_3$ concentration.

Figure 3 shows that most of the ferric hydroxide existed as $FeOH^{2+}$, and that the mole fraction of $Fe_2(OH)_2^{4+}$ was higher than that of $Fe(OH)_2^+$ in the concentration range of up to 2.5 m $FeCl_3$. The mole fraction of $FeOH^{2+}$ and $Fe(OH)_2^+$ decreased with $FeCl_3$ concentration, while that of $Fe_2(OH)_2^{4+}$ at first increased with $FeCl_3$ concentration and then decreased.

Figure 4 shows the distribution of the ferric chloride complexes with HCl concentration in the absence of $FeCl_2$ when $FeCl_3$ concentration was 1.0 m. This figure shows that the mole fractions of $FeCl_2^+$ and $FeCl_4^-$ increased with increasing HCl concentration, while those of $FeCl^{2+}$ and Fe^{3+} decreased with HCl concentration. The mole fraction of $FeCl_3^o$ was constant up to 3.0 m HCl concentration.

Figure 5 illustrates the distribution of the ferrous complexes with $FeCl_2$ concentration at 25 °C in the absence of $FeCl_3$ and HCl. This figure shows that most ferrous species exist as $FeCl^+$ in the concentration range of up to 4 m $FeCl_2$. As $FeCl_2$ concentration increased, the mole fraction of $FeCl_2^o$ also increased while that of Fe^{2+} decreased. The mole fraction of $FeOH^+$ decreased with increasing $FeCl_2$ concentration. The variation of the mole fraction of $FeOH^+$ with $FeCl_2$
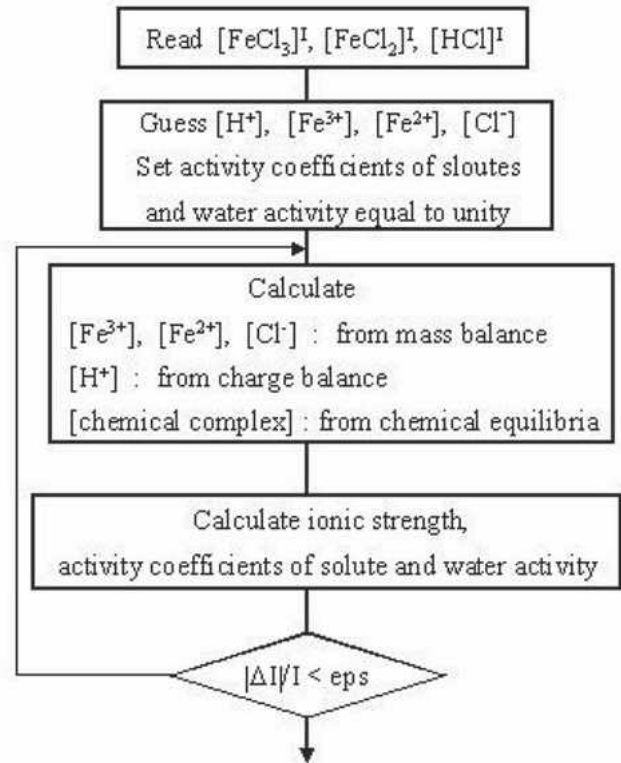

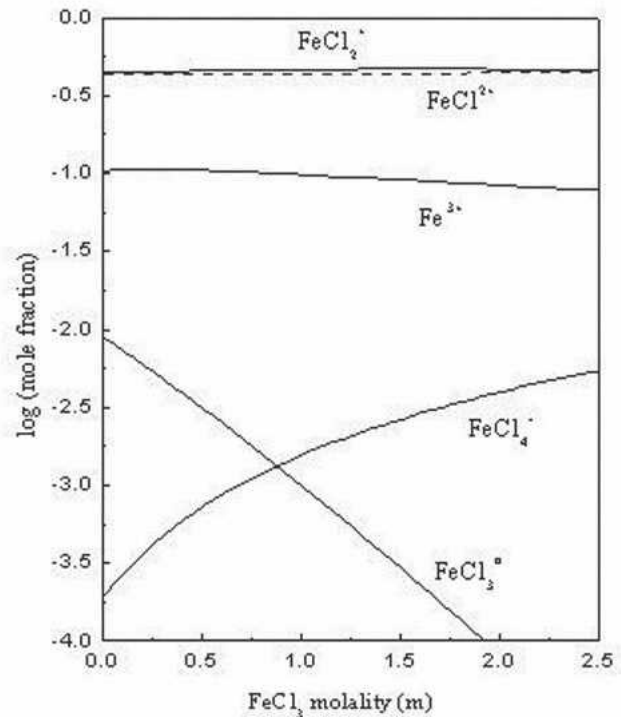Fig. 1—Flow chart for the calculation of the concentration of chemical species.

Fig. 2—Distribution of ferric chloride complexes with $FeCl_3$ concentration in the absence of $FeCl_2$ ($[HCl]_t = 1.0$ m).

concentration was ascribed to the following hydrolysis reaction of ferrous ion with water.

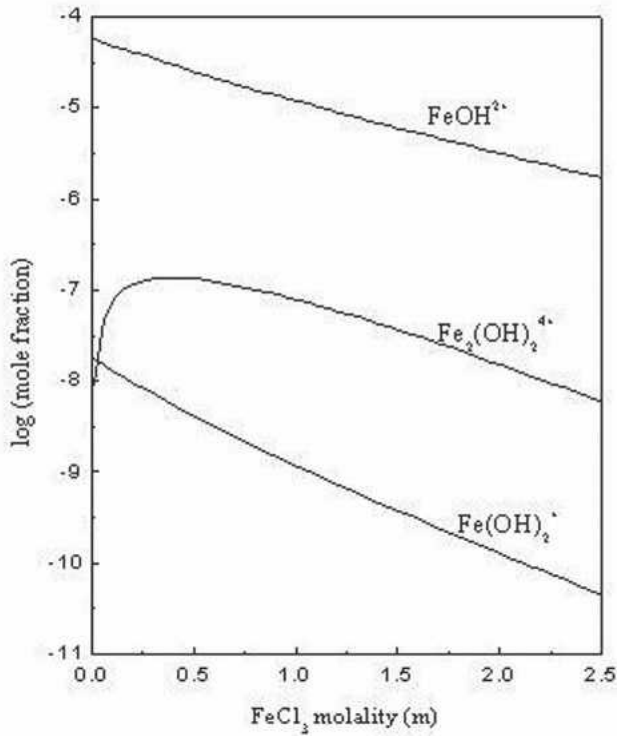$$Fe^{2+} + H_2O = FeOH^+ + H^+ \qquad [27]$$

Fig. 3—Distribution of ferric hydroxide complexes with FeCl$_3$ concentration in the absence of FeCl$_2$ ([HCl]$_t$ = 1.0 m).
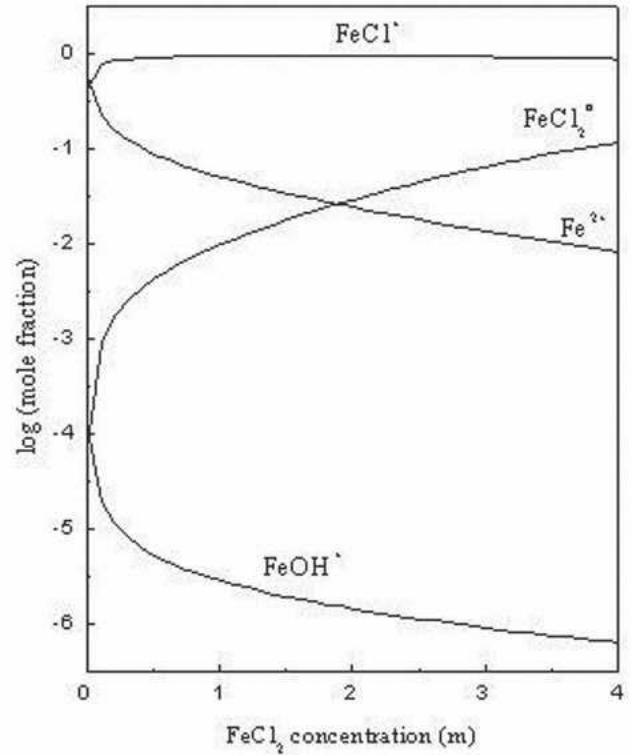

Fig. 5—Effect of FeCl$_2$ concentration on the distribution of ferrous species in the absence of HCl and FeCl$_3$.
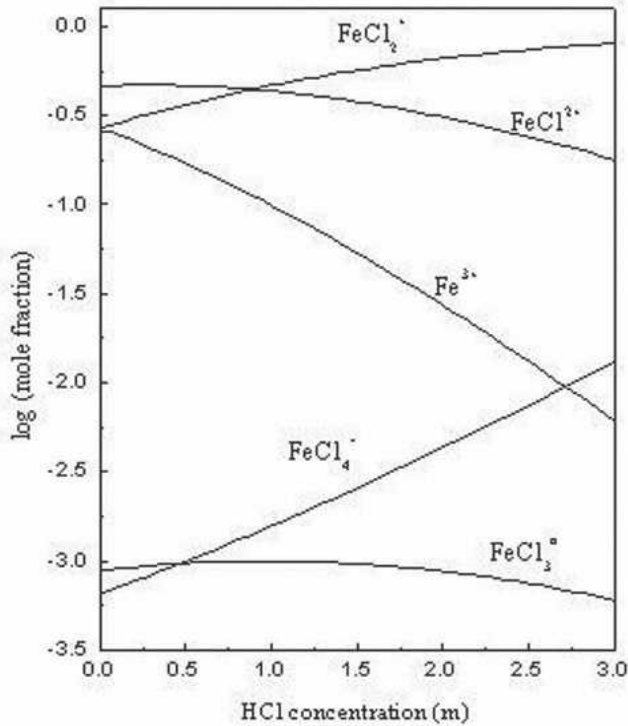

Fig. 4—Distribution of ferric chloride complexes with HCl concentration in the absence of FeCl$_2$ ([FeCl$_3$]$_t$ = 1.0 m).

Fig. 6—Effect of HCl concentration on the distribution of ferrous chloride complexes in the absence of HCl and FeCl$_3$ ([FeCl$_2$]$_t$ = 1.0 m).

As the hydrolysis reaction proceeds, hydrogen ion is produced and solution pH decreases. Hence, the mole fraction of hydroxide ion and consequently that of FeOH$^+$ decreased with FeCl$_2$ concentration.
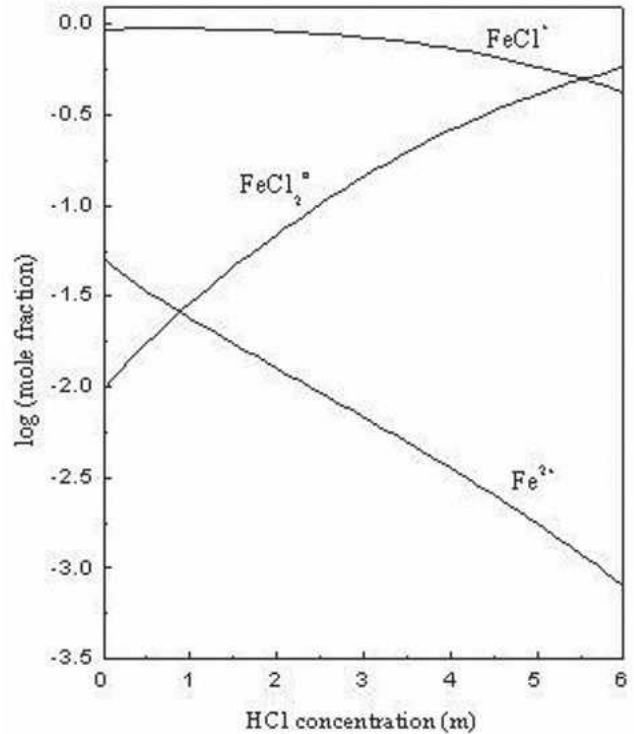
Figure 6 shows the distribution of the ferrous chloride species with HCl concentration in the absence of FeCl$_3$, when FeCl$_2$ concentration was 1.0 m. According to this figure,

Table VI. Experimental Conditions and Calculated Values of pH and Ionic Strength

N	$[FeCl_3]_t$	$[FeCl_2]_t$	$[HCl]_t$	PH	pH_C	I_C
1	0.101	0	0.202	0.75	0.84	0.61
2	0.311	0	0.415	0.38	0.49	1.42
3	0.533	0	0.640	0.14	0.25	2.12
4	0.768	0	0.878	0.09	0.05	2.78
5	1.017	0	1.130	−0.25	−0.13	3.43
6	1.151	0	1.151	−0.22	−0.16	3.73
7	1.138	0	1.480	−0.35	−0.30	3.80
8	1.130	0	1.696	−0.42	−0.38	3.86
9	1.111	0	2.222	0.56	0.55	4.07
10	1.280	0	1.397	0.43	0.29	4.07
11	1.074	0	3.221	0.86	0.80	4.64
12	1.561	0	1.681	0.53	0.45	4.74
13	1.859	0	1.983	0.66	0.60	5.42
14	2.178	0	2.303	0.73	0.75	6.14
15	2.710	0	2.710	0.87	0.95	7.28
16	0	0.101	0.201	0.83	0.82	0.33
17	0	0.308	0.410	0.49	0.49	0.76
18	0	0.523	0.628	0.22	0.28	1.20
19	0	0.748	0.854	0.01	0.10	1.65
20	0	0.981	1.090	0.15	0.06	2.12
21	0	1.225	1.336	0.35	0.20	2.60
22	0	1.479	1.593	0.47	0.34	3.11
23	0	1.744	1.861	0.60	0.47	3.64
24	0	2.022	2.141	0.78	0.60	4.19
25	0	2.472	2.472	−0.97	−0.77	4.96
26	2.990	0.449	1.495	−0.92	−0.70	7.87
27	1.279	0.384	2.558	−0.80	−0.71	4.80
28	3.228	0.484	3.228	−1.12	−1.18	8.62
29	3.171	0.951	1.585	−0.98	−0.80	8.40
30	1.344	0.807	2.689	−0.94	−0.79	5.28
31	3.439	1.032	3.439	−1.17	−1.28	9.34

N = number, pH = measured values of pH, pH_C = values of pH calculated in this study, and I_C = values of ionic strength calculated in this study.
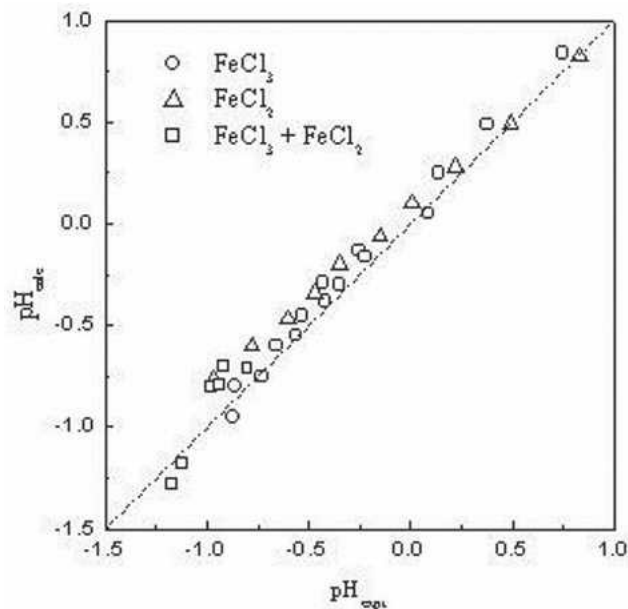

Fig. 7—Comparison of pH values between experimentally measured and calculated in this study.

tion behavior of ferrous ion in a chloride solution will improve the accuracy of the ionic equilibria in a ferrous chloride and the mixed ferric and ferrous chloride solution. Figure 7 shows the pH values obtained experimentally and the calculated values. From this figure and from Table VI, it can be seen that the experimental pH values agree well with the calculated values in the experimental ranges of the ionic strength of the solutions up to 9.34 m. The result of this work can be used in evaluating thermodynamic equilibrium constants for the solvent extraction of $FeCl_3$ or $FeCl_2$.

V. CONCLUSIONS

By considering the complex formation reactions as well as the mass and charge balance equations, the ionic equilibria in the mixed ferric and ferrous chloride solution were analyzed. The activity coefficients of the ions were calculated using the Bromley equation. By using the Vasil'ev correlation, the equilibrium constant for the formation of $FeCl^+$ was obtained from the reported equilibrium constant other than at zero ionic strength. The equilibrium constants for the formation of $FeCl_2^o$ and $FeOH^+$ were calculated from the thermodynamic data reported in the literature. By applying Bromley's approximation method, the interaction parameters of the ferric species were determined from the reported interaction parameters for $FeCl_3$ in an HCl solution. The distribution of ferrous and ferric complexes with HCl, $FeCl_2$, and $FeCl_3$ concentration was obtained by applying ionic equilibria. The predicted pH values agreed well with those experimentally measured at 25 °C up to 9.34 m ionic strength of the solution.

the mole fraction of Fe^{2+} decreased rapidly with increasing HCl concentration, while that of $FeCl_2^o$ increased greatly with increasing HCl concentration. The mole fraction of $FeCl^+$ was constant up to 2 m HCl, and then decreased gradually with the further increase of HCl concentration.

In highly acidic solutions, the measured pH value is a relative indicator of acidity, and differs significantly from the analytical concentration of hydrogen ion.[26] A pH meter, however, remains the most convenient way of studying the ionic equilibria of an aqueous electrolyte solution. Moreover, the activity of the hydrogen ion is a key parameter in aqueous reactions. For this reason, pH measurements were conducted to evaluate the validity of the ionic equilibria performed in this study.

Table VI shows the experimental compositions of the $FeCl_3$-$FeCl_2$-HCl-H_2O system, together with the pH values measured at 25 °C. The pH values and ionic strength calculated in this study are also listed in Table VI and the unit of concentration in this table was molality. The error between measured and calculated pH values was 0.08 for the $FeCl_3$ solution, 0.12 for the $FeCl_2$ solution, and 0.14 for the mixed ferric and ferrous chloride solution. The large discrepancy between the measured and predicted pH values of the ferrous chloride solution might be caused by the uncertainty in the values of the equilibrium constant for the formation of ferrous complexes. Further study on the complex forma-

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