

Solvent Extraction Equilibria of FeCl₃ from Hydrochloric Acid Solution with Alamine336

Man-Seung Lee^{1,*}, Kyoung-Ju Lee¹ and Young-Joo Oh²

¹Dept. of Advanced Materials Science and Engineering, Mokpo National Univ., Chonnam 534-729, Korea

²Metal Processing Research Center, Korea Institute of Science and Technology, P.O. Box 131, Seoul, 136-791, Korea

We have conducted solvent extraction experiments of FeCl₃ in HCl solution with Alamine336 as an extractant. Solvent extraction reaction depended on the ratio of initial concentration of Alamine336 to FeCl₃. When the concentration of Alamine336 was in excess to that of FeCl₃, the extractant reacted as a dimer. When the initial concentration ratio of Alamine336 to FeCl₃ was below three, ferric chloride was extracted by monomeric extractant. The equilibrium constants of solvent extraction were determined by applying ionic equilibria to the experimental data. These ionic equilibria consisted of chemical equilibria, mass and charge balance equations. The activity coefficients of solutes in aqueous phase were calculated by using Bromley equation. The predicted distribution coefficients of iron agreed well with those measured.

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1. Introduction

Ferric chloride solution is used as a leaching agent for sulfide minerals and an etching agent for nickel lead frames owing to its strong oxidizing property. Several studies have been performed on the ionic equilibria of FeCl₃ in chloride solution.¹⁻⁴⁾ As ferric ions tend to form complexes with chloride ion such as FeCl₃ and FeCl₄⁻, FeCl₃ can be regenerated from spent FeCl₃ solution by employing a solvent extraction method with a neutral or anion exchange extractants. TBP(tri-butyl-phosphate) is widely used in solvent extraction of ferric chloride because of its low solubility in water.⁵⁻⁷⁾ Alamine336 (Tertiary amine, R₃N, R=CH₃(CH₂)₇), a sort of anion exchange type extractants, is also used extensively in extracting various metal ions.⁸⁻¹⁰⁾ Solvent extraction of FeCl₃ with amine extractants have, however, been conducted only in the low concentration range of FeCl₃.¹¹⁻¹³⁾ Since iron concentration is high in the spent FeCl₃ solution, an investigation of the solvent extraction with Alamine336 in a high concentration range of FeCl₃ is needed.

In this study, equilibrium constants for the solvent extraction of FeCl₃ with Alamine336 were obtained in the FeCl₃ concentration range from 0.1 to 1.0 mol/dm³. Complex formation reactions for ferric complexes with chloride and hydroxide ion were considered. The activity coefficients of chemical species present in the aqueous phase were calculated with Bromley equation.¹⁴⁾ The equilibrium constants obtained in this study was verified by comparing distribution coefficients of iron measured with those calculated in this study.

2. Experimental

Stock solution was prepared by dissolving FeCl₃·6H₂O and HCl in distilled water. All chemicals were of reagent grade. Alamine336 was first treated with HCl solution before extraction and then diluted with toluene.

Equal volume of aqueous and organic phase was placed in

a 100 cm³ separatory funnel and shaken for 30 min with a wrist action shaker. The aqueous phase was separated after settling the mixture for 1 h. The concentration of iron in the aqueous phase was measured with ICP-AES (Spectroflame EOP). The iron concentration in the organic phase was obtained by using mass balance.

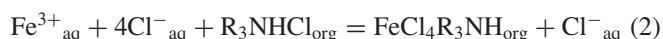
Distribution coefficient of iron was defined as,

$$D = \frac{\text{iron concentration in organic phase}}{\text{iron concentration in aqueous phase}} \quad (1)$$

3. Results and Discussion

3.1 Solvent extraction of FeCl₃ with Alamine336 salt

Iron extraction from chloride solution with amine extractant could be described as,¹⁵⁾



where subscript aq and org represent aqueous and organic phase, respectively.

The effect of HCl concentration on the solvent extraction of Fe³⁺ with 1.5 mol/dm³ Alamine336 salt(R₃NHCl) was investigated by varying HCl concentration from 0.5 to 3.0 mol/dm³. The distribution coefficients of iron are shown in Fig. 1 as a function of HCl concentration. The distribution coefficients of iron increased linearly with HCl concentration when FeCl₃ concentrations were 0.1 and 0.5 mol/dm³. However, the HCl concentration had negligible effect on the distribution coefficient of iron when FeCl₃ concentration was 1.0 mol/dm³. From this result, it is known that the dependence of distribution coefficient of iron on HCl concentration was influenced by the concentration ratio of Alamine336 to FeCl₃.

Figure 2 shows the effect of Alamine336 concentrations on the distribution coefficient of iron when the HCl concentration was 1.0 mol/dm³. It is seen that the distribution coefficient of iron increased with Alamine336 salt concentration and the distribution coefficient of iron decreased with an increase in FeCl₃ concentrations at the same concentration of extractant.

*Corresponding author, E-mail: mslee@mokpo.ac.kr

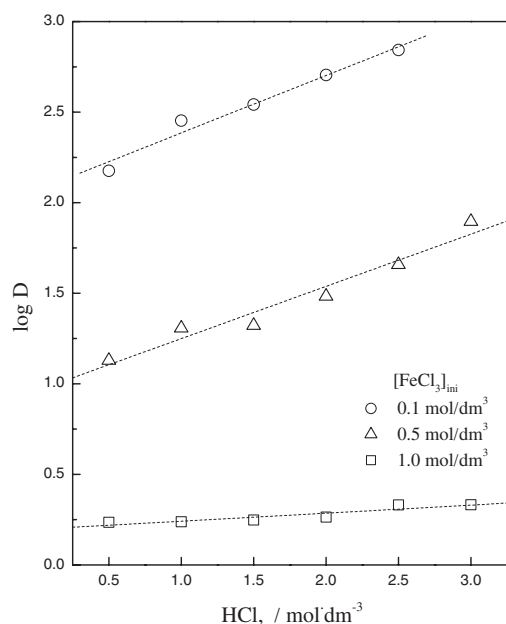


Fig. 1 Effect of HCl concentration on the extraction of FeCl₃. ([R₃NHCl]_t = 1.5 mol/dm³)

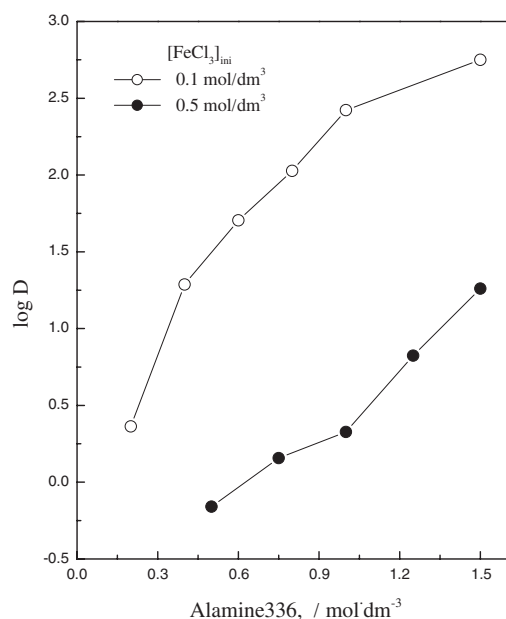


Fig. 2 Effect of the initial concentration of Alamine336 salt on the extraction of FeCl₃.

Figure 3 shows the equilibrium loading of 0.5 mol/dm³ Alamine336 when HCl concentration was 1.0 mol/dm³. It is seen in Fig. 3 that 0.5 mol/dm³ Alamine336 was saturated with about 0.3 mol/dm³ iron in the organic phase. The concentration ratio of Alamine336 to iron in the organic phase was about 1.7. The value of this concentration ratio implied that monomeric and dimeric form of Alamine336 coexisted in the extracted iron species. Solvent extraction reaction of FeCl₃ with dimeric form of Alamine 336 could be represented by,

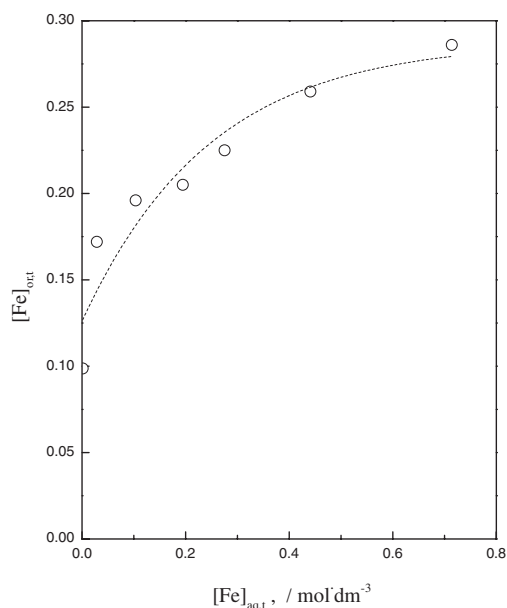
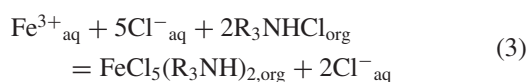


Fig. 3 Equilibrium loading curve for FeCl₃ extraction by 0.5 mol/dm³ Alamine336 at 1.0 mol/dm³ HCl concentration.

In order to decide the condition where eq. (3) dominates in solvent extraction of FeCl₃ with Alamine336, a slope analysis method was adopted. The equilibrium constant for eq. (3) might be written as,

$$K_{\text{ex}} = \frac{[\text{FeCl}_5(\text{R}_3\text{NH})_2]}{[\text{Fe}^{3+}][\text{Cl}^{-}]^3[\text{R}_3\text{NHCl}]^2} \times \frac{\gamma_{\text{FeCl}_5(\text{R}_3\text{NH})_2}}{\gamma_{\text{Fe}^{3+}}(\gamma_{\text{Cl}^{-}})^3(\gamma_{\text{R}_3\text{NHCl}})^2} \quad (4)$$

After the definition of distribution coefficient was substituted into eq. (4), the following equation was obtained by taking logarithm on both sides of this equation.

$$\log D = \log(\alpha_0 K_{\text{ex}}) + 3 \log[\text{Cl}^{-}] + 2 \log[\text{R}_3\text{NHCl}] + \log \left(\frac{\gamma_{\text{Fe}^{3+}}(\gamma_{\text{Cl}^{-}})^3(\gamma_{\text{R}_3\text{NHCl}})^2}{\gamma_{\text{FeCl}_5(\text{R}_3\text{NH})_2}} \right) \quad (5)$$

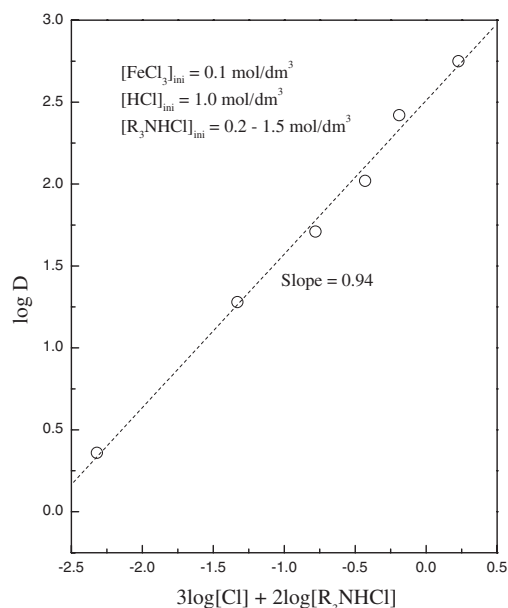
where α_0 represents the concentration ratio of ferric ion to the total iron in aqueous phase.

It is known from eq. (5) that a plot of $3 \log[\text{Cl}^{-}] + 2 \log[\text{R}_3\text{NHCl}]$ against $\log D$ should give straight line with a slope of unity. Figure 4 shows the plot of eq. (5) in the Alamine336 concentration range of 0.2 to 1.5 mol/dm³ when FeCl₃ concentration was 0.1 mol/dm³ and HCl concentration was 1.0 mol/dm³. The slope of this figure was close to 1 and this fact indicated that Alamine336 participated in solvent extraction as a dimer rather than as a monomer when the concentration of Alamine336 was at least twice as much as that of iron.

3.2 Determination of the equilibrium constant

In order to calculate equilibrium constant for solvent extraction, the equilibrium concentration and the activity coefficient of chemical species present in both phases are required. Ionic equilibria were analyzed for FeCl₃–HCl–H₂O–Alamine336 salt–toluene system. Chemical equations considered in this study and equilibrium constants for each reaction at 298 K are listed in Table 1.⁴⁾

From the chemical equilibria together with solvent

Fig. 4 Equilibrium plot of FeCl₃-Alamine336 extraction system.

extraction reaction, mass and charge balance equations were obtained as follows when the volume ratio of aqueous to organic phases was unity,

$$[\text{Fe}]_t = [\text{Fe}^{3+}] + [\text{FeCl}_2^{2+}] + [\text{FeCl}_2^+] + [\text{FeCl}_3] + [\text{FeCl}_4^-] + [\text{FeOH}^{2+}] + [\text{Fe}(\text{OH})_2^+] + 2[\text{Fe}_2(\text{OH})_2^{4+}] + [\text{FeCl}_{3+a}(\text{R}_3\text{NH})_a] \quad (6)$$

$$[\text{Cl}]_t = [\text{Cl}^-] + [\text{FeCl}_2^{2+}] + 2[\text{FeCl}_2^+] + 3[\text{FeCl}_3] + 4[\text{FeCl}_4^-] + 3[\text{FeCl}_{3+a}(\text{R}_3\text{NH})_a] \quad (7)$$

$$[\text{R}_3\text{NHCl}]_t = [\text{R}_3\text{NHCl}] + a[\text{FeCl}_{3+a}(\text{R}_3\text{NH})_a] \quad (8)$$

$$[\text{H}^+] + 3[\text{Fe}^{3+}] + 2[\text{FeCl}_2^{2+}] + [\text{FeCl}_2^+] + 2[\text{FeOH}^{2+}] + [\text{Fe}(\text{OH})_2^+] + 4[\text{Fe}_2(\text{OH})_2^{4+}] = [\text{Cl}^-] + [\text{FeCl}_4^-] + [\text{OH}^-] \quad (9)$$

where subscript t represents the initial total concentration.

The activity coefficient of solutes present in the aqueous phase was calculated with Bromley equation.¹⁴ Equation (10) represents the Bromley equation for cation M at 298 K;

$$\log \gamma_M = -\frac{0.5108(z_M)^2 I^{0.5}}{1 + I^{0.5}} + F_M \quad (10)$$

$$F_M = \sum_X \left[\frac{(0.06 + 0.6B_{MX}) \times |z_M z_X|}{\left(1 + \frac{1.5}{|z_M z_X|} I\right)^2} + B_{MX} \right] \times \frac{(|z_M| + |z_X|)^2}{4} [X] \quad (11)$$

where z is the ionic charge and I is ionic strength of solution and B_{MX} is the interaction parameter between cation M and anion X. It was reported that the Bromley equation gave good results for strong electrolytes up to ionic strength of 6 mol/kg.¹⁴ In order to calculate activity coefficients with the Bromley equation, a value of interaction parameter B_{MX} between cation M and anion X is needed. We previously proposed a method to calculate the interaction parameters³⁾

Table 1 Complex formation reactions and equilibrium constants at 298 K.

Reaction	Log K	Ionic strength
$\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$	14.00	0
$\text{Fe}^{3+} + \text{Cl}^- = \text{FeCl}_2^{2+}$	1.31	0
$\text{Fe}^{3+} + 2\text{Cl}^- = \text{FeCl}_2^+$	1.98	0
$\text{Fe}^{3+} + 3\text{Cl}^- = \text{FeCl}_3^\circ$	1.19	0
$\text{Fe}^{3+} + 4\text{Cl}^- = \text{FeCl}_4^-$	-1.31	0
$\text{Fe}^{3+} + \text{OH}^- = \text{FeOH}^{2+}$	11.82	0
$\text{Fe}^{3+} + 2\text{OH}^- = \text{Fe}(\text{OH})_2^+$	22.95	0
$2\text{Fe}^{3+} + 2\text{OH}^- = \text{Fe}_2(\text{OH})_2^{4+}$	25.12	0

Table 2 Estimated values for the interaction parameter of ions at 298 K.

Species	B , $\text{dm}^3 \cdot \text{mol}^{-1}$	δ
Cl^-	0.0643*	-0.067*
ClO_4^-	-0.002*	0.79*
Fe^{3+}	-0.02208	0.154
FeCl_2^{2+}	-0.1488	0.304
FeCl_2^+	-0.4945	0.736
FeOH^{2+}	0.04776	0.0935
$\text{Fe}(\text{OH})_2^+$	0.2525	-0.154
$\text{Fe}_2(\text{OH})_2^{4+}$	0.01841	0.0627

*: reported by Bromley (unit: $\text{kg} \cdot \text{mol}^{-1}$)

and these values are listed in Table 2.

The number of chemical species present in both phases after extraction is 15 (Cl^- , Fe^{3+} , FeCl_2^{2+} , FeCl_2^+ , FeCl_3 , FeCl_4^- , FeOH^{2+} , $\text{Fe}(\text{OH})_2^+$, $\text{Fe}_2(\text{OH})_2^{4+}$, H^+ , OH^- , H_2O , $\text{FeCl}_3(\text{R}_3\text{NHCl})_a$ Alamine336 salt, toluene). In order to calculate the concentrations and activity coefficients of 13 species excluding H_2O and toluene, 26 independent equations are required. In addition to these equations, two equations are needed to calculate the activity of water and toluene. We obtained these 28 equations from 8 chemical equilibria shown in Table 1, solvent extraction reaction, three mass balance equations (eqs. (6), (7), (8)), charge balance (eq. (9)), 13 activity coefficient equations of solutes and two activity equations. The solution of these 28 nonlinear equations was obtained by using the Newton-Raphson method.

We assumed that the activity coefficients of Alamine336 salt and extracted iron species in the organic phase were unity due to a lack of equations in the organic phase. Also the activity coefficient of diluent was assumed to be unity. With this assumption, the equilibrium constant of solvent extraction reaction becomes

$$K_{\text{ex,m}} = \frac{[\text{FeCl}_4\text{R}_3\text{NH}]}{[\text{Fe}^{3+}][\text{Cl}^-]^3[\text{R}_3\text{NHCl}]} \times \frac{1}{\gamma_{\text{Fe}^{3+}}(\gamma_{\text{Cl}^-})^3} \quad (12)$$

$$K_{\text{ex,d}} = \frac{[\text{FeCl}_5(\text{R}_3\text{NH})_2]}{[\text{Fe}^{3+}][\text{Cl}^-]^3[\text{R}_3\text{NHCl}]^2} \times \frac{1}{\gamma_{\text{Fe}^{3+}}(\gamma_{\text{Cl}^-})^3} \quad (13)$$

where subscript m and d represent the monomeric and dimeric form of Alamine336, respectively.

Table 3 shows the experimental conditions together with the results of extraction experiment. The equilibrium constants were obtained from the experimental data by applying ionic equilibria and were represented as follows,

Table 3 Equilibrium conditions and calculated results.

N	[FeCl ₃] _{ini}	[HCl] _{ini}	[R ₃ NHCl] _{ini}	SR	log <i>D</i> _{expt}	dimer	Monomer
1	0.1	0.5	0.5	5	1.139	1.377	—
2	0.1	1.0	0.5	5	1.463	1.653	—
3	0.1	1.5	0.5	5	1.603	1.733	—
4	0.1	2.0	0.5	5	1.827	1.730	—
5	0.1	2.5	0.5	5	1.872	1.681	—
6	0.1	3.0	0.5	5	2.569	1.602	—
7	0.1	1.0	0.2	2	0.363	—	0.329
8	0.1	1.0	0.4	4	1.287	1.325	—
9	0.1	1.0	0.6	6	1.705	1.896	—
10	0.1	1.0	0.8	8	2.027	2.243	—
11	0.1	1.0	1.0	10	2.423	2.491	—
12	0.1	0.5	1.5	15	2.176	2.624	—
13	0.1	1.0	1.5	15	2.453	2.908	—
14	0.1	1.5	1.5	15	2.542	2.990	—
15	0.1	2.0	1.5	15	2.704	2.985	—
16	0.1	2.5	1.5	15	2.844	2.937	—
17	0.3	1.0	1.5	5	2.319	2.568	—
18	0.7	1.0	1.5	2.1	0.616	—	1.047
19	0.5	0.5	1.5	3	1.129	1.841	0.950
20	0.5	1.0	1.5	3	1.308	2.048	1.170
21	0.5	1.5	1.5	3	1.322	2.115	1.239
22	0.5	2.0	1.5	3	1.482	2.111	1.234
23	0.5	2.5	1.5	3	1.658	2.064	1.185
24	0.5	3.0	1.5	3	1.896	1.988	1.105
25	0.5	1.0	0.5	1	−0.159	—	0.298
26	0.5	1.0	0.75	1.5	0.157	—	0.652
27	0.5	1.0	1.0	2	0.327	—	0.886
28	0.5	1.0	1.25	2.5	0.824	—	1.049
29	1.0	1.0	1.5	1.5	0.238	—	0.808
30	1.0	1.5	1.5	1.5	0.248	—	0.875
31	1.0	2.0	1.5	1.5	0.265	—	0.867
32	1.0	2.5	1.5	1.5	0.331	—	0.818
33	1.0	3.0	1.5	1.5	0.332	—	0.741
34	0.2	1.0	0.5	2.5	0.779	—	0.717
35	0.3	1.0	0.5	1.7	0.276	—	0.583
36	0.4	1.0	0.5	1.3	0.023	—	0.440
37	0.5	1.0	0.5	1	−0.089	—	0.298
38	0.7	1.0	0.5	0.7	−0.232	—	0.055
Sd						0.19	0.17

log *D*_{expt}: measured distribution coefficients of iron

dimer: logarithm of the calculated distribution coefficients of iron according to the reaction,



monomer: logarithm of the calculated distribution coefficients of iron according to the reaction,

SR: initial concentration ratio of Alamine336 to FeCl₃

$$K_{\text{ex,m}} = 2.22 \times 10^4$$

$$K_{\text{ex,d}} = 6.41 \times 10^5$$

The distribution coefficients of iron predicted by these equilibrium constants are also shown in Table 3. Figure 5 shows the distribution coefficients of iron obtained experimentally and the calculated values. It was known that the form of Alamine336 reacting with iron during solvent extraction reaction varied from a monomer to a dimer when the initial concentration ratio of Alamine336 to FeCl₃ increased.

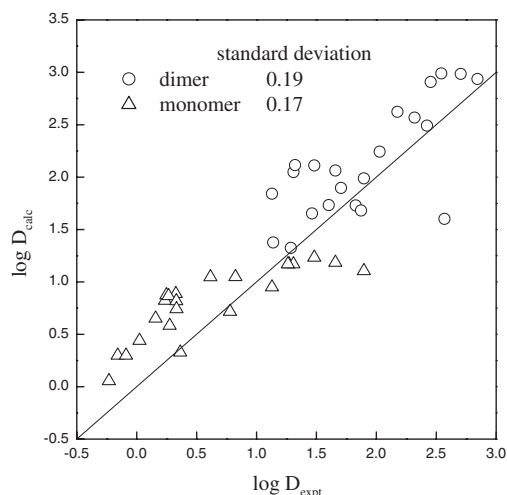


Fig. 5 Comparison of the distribution coefficients of iron between experimentally measured and calculated in this study.

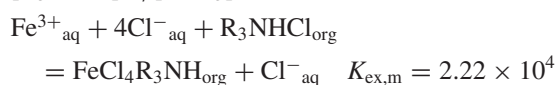
This ratio was evaluated to be 3 by minimizing of the sum of the squares of the difference between predicted and measured distribution coefficients of iron. From Table 3 and Fig. 5, it is known that the distribution coefficients of iron obtained experimentally agreed well with those predicted in this study.

It is seen in Table 3 that the distribution coefficients of iron experimentally measured increased with an increase in HCl concentration when FeCl₃ and Alamine336 concentration were kept constant. However, the distribution coefficient of iron calculated in this study increased to a maximum with HCl concentration and then decreased with further increasing HCl concentration. The discrepancy between experimentally measured and calculated distribution coefficient with HCl concentration might be explained with the distribution of ferric chloride complexes with HCl concentration. Figure 6 shows the distribution of ferric chloride complexes as a function of HCl concentration when FeCl₃ concentration was constant. It is known from Fig. 6 that there exists HCl concentration where mole fraction of FeCl₃ is maximized. Further comprehensive study on the equilibria of FeCl₃ is needed to explain well the behavior of iron species in strong HCl solution.

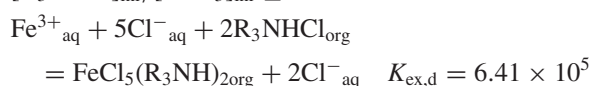
4. Conclusions

Equilibrium constants for the solvent extraction reaction of FeCl₃ with Alamine336 salt were determined from the extraction data by analyzing ionic equilibria in the following experimental conditions *i.e.*, FeCl₃ concentration ≤ 1.0 mol/dm³, HCl concentration ≤ 3.0 mol/dm³, Alamine336 concentration ≤ 1.5 mol/dm³.

$$[\text{R}_3\text{NHCl}]_{\text{ini}}/[\text{FeCl}_3]_{\text{ini}} < 3 :$$



$$[\text{R}_3\text{NHCl}]_{\text{ini}}/[\text{FeCl}_3]_{\text{ini}} \geq 3 :$$



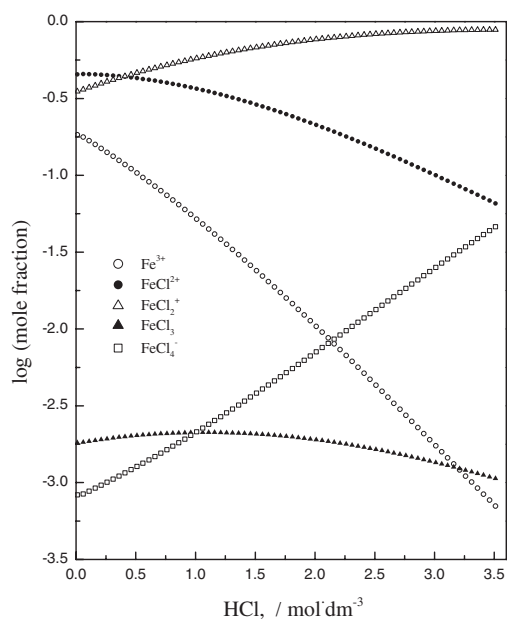


Fig. 6 Distribution of iron chloride complexes with the HCl concentration. ($[\text{FeCl}_3]_t = 1.0 \text{ mol/dm}^3$)

The equilibrium concentrations of iron species were calculated by considering chemical equilibria, mass and charge balance equation. The activity coefficients of species

in the aqueous phase were calculated by using Bromley equation. The experimentally obtained distribution coefficients of iron agreed well with those predicted in this study.

REFERENCES

- 1) H. Majima and Y. Awakura: *Metall. Trans. B* **16B** (1985) 433–439.
- 2) H. Majima and Y. Awakura: *Metall. Trans. B* **17B** (1986) 621–627.
- 3) M. S. Lee, J. G. Ahn and Y. J. Oh: *Materials Trans.* **44** (2003) 957–961.
- 4) Y. Belaustegi, M. A. Olazabal and J. M. Madariaga: *Fluid Phase Equilibria* **155** (1999) 21–31.
- 5) M. S. Lee and G. S. Lee: *J. Kor. Inst. Met. & Mater.* **41** (2003) 518–524.
- 6) B. R. Reddy and P. V. R. Bhaskara Sarma: *Hydrometallurgy* **43** (1996) 299–306.
- 7) J. Saji and M. L. P. Reddy: *Hydrometallurgy* **61** (2001) 81–87.
- 8) H. Watanabe and K. Akatsuka: *Analytica Chimica Acta* **38** (1976) 547–552.
- 9) N. Y. Yakubu and A. W. L. Dudeney: *Hydrometallurgy* **18** (1987) 93–104.
- 10) H. F. Gai, J. L. Shen and M. A. Hughes: *Hydrometallurgy* **25** (1990) 293–304.
- 11) P. Mühl, K. Gloe and C. Fischer: *Hydrometallurgy* **5** (1980) 161–178.
- 12) M. Harada, M. Araki, A. H. Bokhari, W. Eguchi and Y. Yamada: *The Chemical Engineering Journal* **26** (1983) 135–142.
- 13) C. C. Chang, T. M. Chiu, Y. C. Hoh and W. K. Wang: *Hydrometallurgy* **17** (1986) 1–13.
- 14) L. A. Bromley: *AIChE Journal* **19** (1973) 313–320.
- 15) P. Mahi and N. T. Bailey: *Hydrometallurgy* **13** (1985) 293–304.