

Estimation of Interaction Parameter of FeCl^+ from Hydrochloric Acid Solution by Solvent Extraction with Amine

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Distribution diagram of FeCl_2 in HCl solution indicated that FeCl^+ was a predominant species in strong HCl solution up to 10 M. Solvent extraction of FeCl_2 has been performed in the HCl concentration range from 5 to 9 M by using Alamine336 as an extractant. Interaction parameter of FeCl^+ for Bromley equation was estimated from our solvent extraction data. This parameter thus obtained in our study can be employed in calculating the activity coefficient of FeCl^+ in high concentration of HCl.

Key Words : Ferrous chloride, Interaction parameter, Solvent extraction, Amine

Introduction

Process for the recovery of metal is divided into pyrometallurgy and hydrometallurgy. In pyrometallurgy, the target metal is reduced from the ores by using reducing agent in a furnace. In hydrometallurgy, metals are dissolved from the ores in acidic or alkaline solution. Most ores contain iron oxide or sulphide as their constituent and removal of iron from the leaching solution of these ores has been an important task in hydrometallurgy.¹ In the hydrometallurgical processes for the recovery of precious metals, iron in the ores dissolved as ferric owing to the oxidizing nature of the acid solution. Leaching of mineral ores after reduction treatment results in a solution where iron is present as ferrous. Oxidation of Fe(II) to Fe(III) is practiced to remove iron by precipitation.¹

In order to predict ionic equilibria and to calculate the activity of a species in strong acid solution, consideration of activity coefficient of solutes is needed. Several equations have been reported to calculate the activity coefficients of solutes in aqueous solution.² Bromley equation is one of these equations and its merits are simple to use and accurate up to ionic strength up to 6 M.^{2,3} In using Bromley equation, interaction parameter of a chemical species is necessary. Many studies have been reported on the ionic equilibria of FeCl_3 in HCl solution owing to its importance in many fields.⁴⁻⁸

In the removal of iron by precipitation, ferrous ion is oxidized to Fe(III) and the kinetics of this oxidation reaction depends on the activity of ferrous ion. However, few data are available regarding the complex formation of ferrous containing species and the interaction parameter of these species.⁹ In this study, Bromley's interaction parameter of FeCl^+ in HCl solution was estimated from the solvent extraction data. For this purpose, solvent extraction experiments of FeCl_2 by Alamine336 (Tertiary amine, R_3N , $\text{R}=\text{CH}_3(\text{CH}_2)_7$) were performed in the HCl concentration range from 5 to 9 M.

Experimental

Stock solution of iron(II) was prepared by dissolving $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ in doubly distilled water. The concentration of HCl was adjusted by adding the necessary amount of HCl (35%) to the FeCl_2 solution. All chemicals were of reagent grade. Alamine336 (Cognis Co.) 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 mL separatory funnel and shaken at ambient temperature with Wrist Action Shaker for 30 mins. 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.

In solvent extraction, distribution coefficient (D) of a metal is defined as the ratio of metal concentration in the organic to that in the aqueous after extraction.

Results and Discussion

Distribution Diagram of FeCl_2 in HCl Solution. In strong HCl solution, the concentration of hydroxide ion is negligible. Therefore, only the complex formation of ferrous with chloride ion was considered in this study. Table 1 represents the standard Gibbs free energy change for the formation of FeCl^+ and $\text{FeCl}_{2\text{aq}}$.¹⁰ Equilibrium constants for the complex formation of each reaction were obtained by using $\Delta G^\circ = -RT \ln K$ as follows



Distribution diagram of ferrous species with HCl concentration was obtained by utilizing mass balance, charge balance and chemical equilibria. The followings represent mass and charge balance in FeCl_2 -HCl- H_2O system of strong acidity.

Table 1. Thermodynamic data for the species at 25 °C

Species	ΔG° (kJ/mol)	Reference
Cl^-	-131.0563	11
Fe^{2+}	-78.87	12
$\text{FeCl}_{2\text{aq}}$	-341.37	11

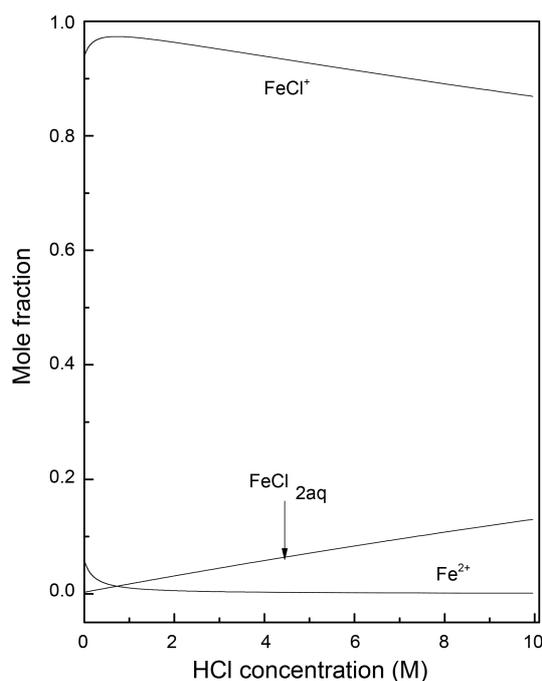
$$[\text{FeCl}_2]_{\text{total}} = [\text{Fe}^{2+}] + [\text{FeCl}^+] + [\text{FeCl}_2^0] \quad (3)$$

$$[\text{Cl}]_{\text{total}} = 2[\text{FeCl}_2]_{\text{total}} + [\text{HCl}]_{\text{total}} = [\text{Cl}^-] + [\text{FeCl}^+] + 2[\text{FeCl}_2]_{\text{aq}} \quad (4)$$

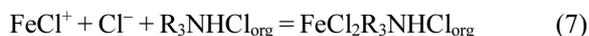
$$[\text{H}^+] = [\text{HCl}]_{\text{total}} \quad (5)$$

At given total concentration of FeCl_2 and HCl , the concentration of Fe^{2+} , FeCl^+ , aqueous FeCl_2 , and Cl^- was calculated by solving the above equations together with chemical equilibria. Figure 1 shows the calculated results when the total concentration of FeCl_2 was 0.1 M. It is seen in Figure 1 that the predominant species of iron(II) in strong HCl solution is FeCl^+ . The mole fraction of FeCl^+ steadily decreased with the increase of HCl concentration and was 0.85 at 10 M HCl solution. Mole fraction of aqueous FeCl_2 increased with the increase of HCl concentration. The mole fraction of Fe^{2+} was negligible in strong HCl solution.

Solvent Extraction of FeCl_2 from HCl Solution by Alamine336. Many studies have reported that amine extractants react with inorganic acid to form salt and that these salts take part in the solvent extraction reaction of metal ions.¹¹⁻¹⁴ The following equation represents the formation of Alamine336 salt (R_3NHCl) in HCl solution.

**Figure 1.** Distribution diagram for 0.1 M FeCl_2 in HCl solution—showing mole fraction of species (Activity coefficients of species were assumed to be unity).

Solvent extraction reaction of metal ion by amine may be viewed as either anion exchange or adduction formation reaction.¹¹ Distribution diagram of FeCl_2 in HCl solution indicated that most of iron(II) existed as FeCl^+ even in strong HCl solution. In this case, adduct formation reaction may be responsible for the extraction of iron(II) by amine, which can be represented as



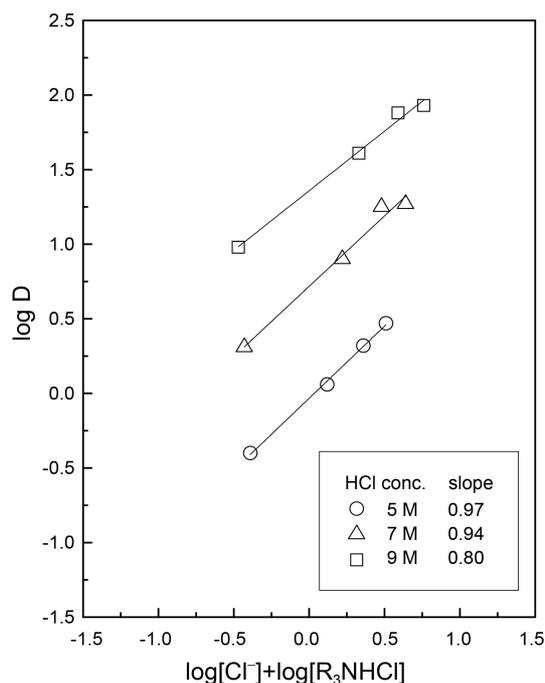
Slope analysis method was employed to verify the above solvent extraction reaction in our experimental range. Inserting the definition of distribution coefficient into equilibrium constant for Eq. (7) and then taking logarithm on both sides of the resulting equation leads to

$$\log D \cong \log K_{\text{ex}} + \log[\text{Cl}^-] + \log[\text{R}_3\text{NHCl}] \quad (8)$$

where K_{ex} represents the equilibrium constant of Eq. (7).

Equation (8) indicates that a plot of $\log[\text{Cl}^-] + \log[\text{R}_3\text{NHCl}]$ against $\log D$ would give a straight line with a slope of unity. Figures 2 and 3 show these plots for the solvent extraction data obtained at the initial iron concentration of 0.07 and 0.14 M, respectively. The distribution coefficient of Fe(II) increased linearly with Alamine336 concentration when HCl concentration was constant. At the constant concentration of Alamine336, the distribution coefficient of Fe(II) increased with the increase of HCl concentration. The slope of the plots in Figure 2 and 3 was between 0.75 and 0.97 and Eq. (7) is responsible for the solvent extraction of FeCl_2 in the tested range.

Estimation of the Interaction Parameter of FeCl^+ . The equilibrium constant for the solvent extraction of iron(II) from HCl solution by Alamine336 can be represented as

**Figure 2.** Identification of solvent extraction of FeCl_2 by Alamine336 from HCl solution ($[\text{FeCl}_2]_{\text{initial}} = 0.07 \text{ M}$).

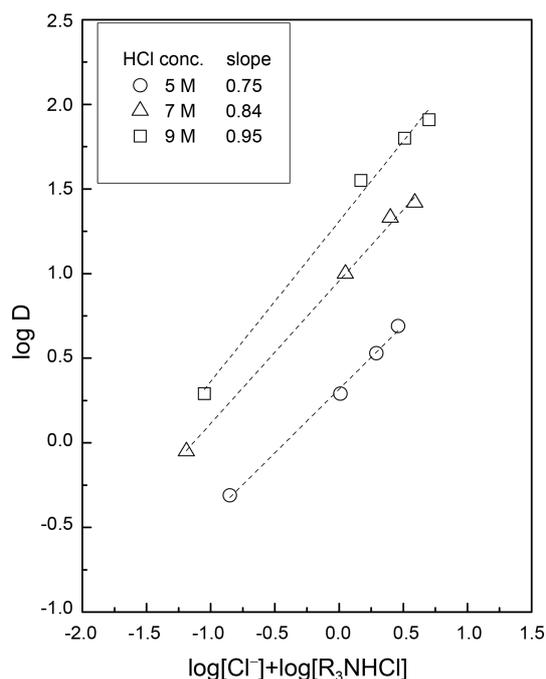


Figure 3. Identification of solvent extraction of FeCl_2 by Alamine336 from HCl solution ($[\text{FeCl}_2]_{\text{initial}} = 0.14 \text{ M}$).

$$K_{\text{ex}} = \frac{[\text{FeCl}_2\text{R}_3\text{NHCl}]}{[\text{FeCl}^+][\text{Cl}^-][\text{R}_3\text{NHCl}]} \times \frac{\gamma_{\text{FeCl}_2\text{R}_3\text{NHCl}}}{\gamma_{\text{FeCl}^+}\gamma_{\text{Cl}^-}\gamma_{\text{R}_3\text{NHCl}}}$$

$$= K_{\text{ex,eff}} \times \frac{\gamma_{\text{FeCl}_2\text{R}_3\text{NHCl}}}{\gamma_{\text{FeCl}^+}\gamma_{\text{Cl}^-}\gamma_{\text{R}_3\text{NHCl}}} \quad (9)$$

In the above equation, $K_{\text{ex,eff}}$ represents the effective equilibrium constant. Effective equilibrium constant is a function of concentration, while equilibrium constant is a function of activity.

In aqueous solution, the activity coefficient of solutes can be calculated by using several equations, such as Bromley, Pitzer and Meissner.^{2,3} However, unlike aqueous solution, general equations have not been developed to calculate the activity coefficient of solutes in organic solution. Therefore, the activity coefficient of solutes in organic solution was regarded as unity.¹⁵

Considering that most of iron(II) exists as FeCl^+ in high concentration of HCl, Bromley equation for the activity coefficients of FeCl^+ and Cl^- at 25 °C is represented as follows^{2,4}

$$\log \gamma_{\text{FeCl}^+} = -\frac{0.51081I^{0.5}}{1+I^{0.5}} + \left[\frac{0.06+0.6B_{\text{FeCl}^+-\text{Cl}^-}}{(1+1.5I)^2} + B_{\text{FeCl}^+-\text{Cl}^-} \right] [\text{Cl}^-] \quad (10)$$

$$\log \gamma_{\text{Cl}^-} = -\frac{0.51081I^{0.5}}{1+I^{0.5}} + \left[\frac{0.06+0.6B_{\text{FeCl}^+-\text{Cl}^-}}{(1+1.5I)^2} + B_{\text{FeCl}^+-\text{Cl}^-} \right] [\text{FeCl}^+] \quad (11)$$

In the above equations, I and B represent the ionic strength of solution and interaction parameter between cation and anion.

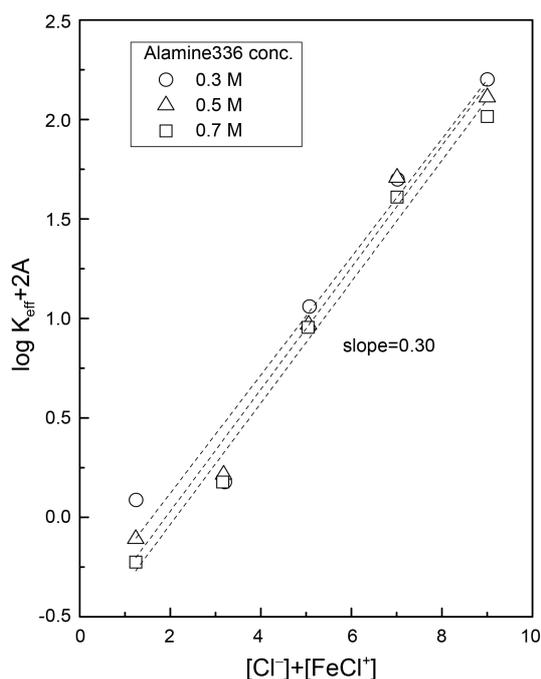


Figure 4. Evaluation of Bromley interaction parameter from the extraction data at 0.14 M FeCl_2 by using Eq. (10).

Taking logarithm of Eq. (9) and inserting Eqs. (10) and (11) to the resulting equation gives the following equation

$$\log K_{\text{ex}} + \left[\frac{0.06+0.6B_{\text{FeCl}^+-\text{Cl}^-}}{(1+1.5I)^2} + B_{\text{FeCl}^+-\text{Cl}^-} \right] ([\text{Cl}^-] + [\text{FeCl}^+])$$

$$= \log K_{\text{eff}} + 2 \times \frac{0.51081I^{0.5}}{1+I^{0.5}} \quad (12)$$

The above equation indicates that the slope in the plot of $[\text{Cl}^-] + [\text{FeCl}^+]$ against the right hand side of Eq. (12) is related to the interaction parameter between FeCl^+ and Cl^- . Effective equilibrium constant in the above equation is a function of equilibrium concentration of species which takes part in the solvent extraction data. In general, solvent extraction data are the overall concentration of the metals in aqueous and organic phases after extraction. Equilibrium concentration of chemical species appearing in Eq. (9) was calculated from our solvent extraction data by using complex formation reaction together with mass balance for Fe(II) and chloride.

Figure 4 represents the plot thus obtained when the initial concentration of Fe(II) was 0.14 M. The slope in Figure 4 was found to be 0.30 irrespective of the concentration of Alamine336 from 0.3 to 0.7 M. The value of interaction parameter between FeCl^+ and Cl^- was determined as follows

$$B_{\text{FeCl}^+-\text{Cl}^-} = 0.29$$

Conclusions

Distribution diagram of FeCl_2 in HCl solution was obtained by considering mass and charge balance together with

complex formation reaction. This diagram indicated that most of iron(II) was present as FeCl^+ in strong HCl solution up to 10 M. Solvent extraction data of FeCl_2 from strong HCl solution by Alamine336 was used to estimate Bromley interaction parameter of FeCl^+ in chloride solution. This interaction parameter thus obtained in this study can be used in predicting the effect of ionic strength on the activity of FeCl^+ and in analyzing the oxidation of Fe(II) to Fe(III) in strong HCl solution.

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