CHAPTER IV

ANALYSIS OF DATA

4.1 Determination of Dried Weight per Volume of Goethite Suspensions

The experimental data of dried weight and volume of goethite suspensions are shown in table 4.1.

Table 4.1 The experimental data of dried weight and volume of

goethite suspension

No.	Volume of goethite suspension (cm^3)	Dried weight goethite (g)	Average (g)
1	1.00± 0.01	0.024± 0.002	0.023 ± 0.002
2	1.00± 0.01	0.022± 0.002	
3	2.00± 0.02	0.037± 0.002	0.040 ± 0.002
4	2.00± 0.02	0.042± 0.002	
5	3.00± 0.03	0.060± 0.002	0.062 ± 0.002
6	3.00± 0.03	0.063± 0.002	
7	5.00± 0.01	0.100± 0.002	0.099 ± 0.002
8	5.00± 0.01	0.098± 0.002	

A plot between volume and dried weight of goethite gives a linear relationship as shown in figure 4.1.
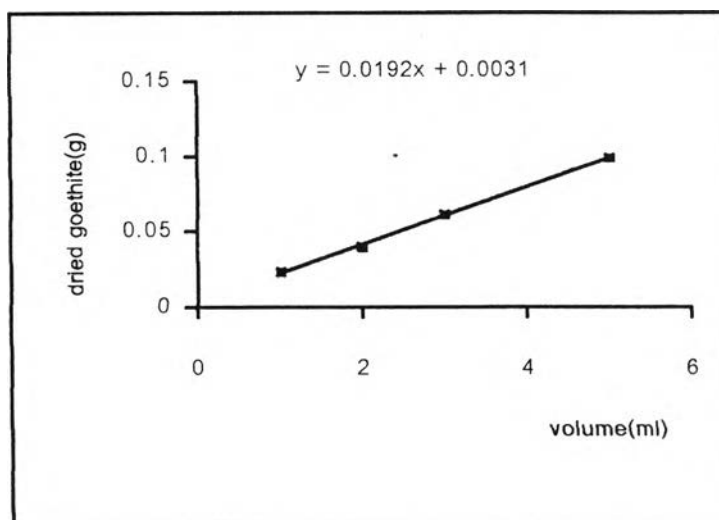

Figure 4.1 The relation between dried weight (g) and volume of goethite suspension (cm^3).

The weight of goethite in 1 L of goethite suspension can be calculated using linear relationship : $y = 0.0192x + 0.0031$. This gives dried weight per volume of goethite suspension to be 0.020 ± 0.002 g /cm^3 or 20 g /L.

4.2 Determination of the Standard Electrode Potential (E^0)

The electrode fitting program was used to evaluate the standard electrode potential (E^0) from the calibration data obtained in the experimental section 3.5.1(Appendix C). The non- linear Nernst's equation, equation (22), i.e.,

$E = E^0 + \left(\dfrac{RT}{F} \ln 10 \right) pH + a\dfrac{1}{H^+} + b[H^+]$ was used in the program. The values of the

standard electrode potential (E^0) and the correction factors a,b obtained from several calibrations were found to be in the following ranges:

Standard potential (E^0) = 380.0 to 401.3 mV

Correction factor a = -7695.1 to 37052

Correction factor b = -0.12 x 10^{-2} to -0.33 x 10^{-2}
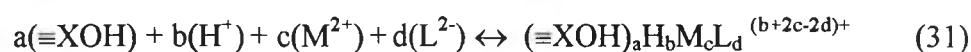
4.3 Determination of the Equilibrium Constants

The equilibrium constants were determined by a non- linear least square method using Superquad program. The computational procedure comprises: firstly, the assumption on the equilibrium model of the system which accounts for the experimental observations. This model is specified by a set of stoichiometry for each species formed. In this study, the active surface hydroxyl groups acts as a ligand that can take up and release hydrogen ions (H^+) and forms surface complexes with metal ions and anions. It's usually assumed that only a singly group ($\equiv XOH$) is involved in the surface complexation reactions.

The model of acid/base equilibria involving surface hydroxyl groups can be expressed in a general form as:

$$a \equiv XOH + b\, H^+ \leftrightarrow (\equiv XOH)_a\, H_b^{b+} \qquad (29)$$
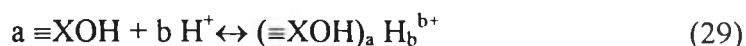
For complex equilibria, the model involves $\equiv XOH$, H^+, M^{2+} and L^{2-} expressed analogously as,

$$a \equiv XOH + bH^+ + cM^{2+} \leftrightarrow (\equiv XOH)_a H_b M_c^{(b+2c)+} \qquad (30)$$

$$a(\equiv XOH) + b(H^+) + c(M^{2+}) + d(L^{2-}) \leftrightarrow (\equiv XOH)_a H_b M_c L_d^{(b+2c-2d)+} \qquad (31)$$
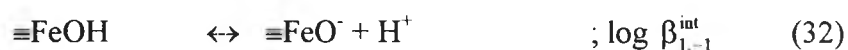
where a,b,c and d are the mole ratio of ligand,proton,metal and anion, respectively.

Secondly, the experimental data of the measured potentials, the total concentrations of metal, ligand(goethite),proton and titrant, together with the values of E^0 and K_w are used as the input for the program(Appendix D). This allows the concentrations of species including proton to be calculated from estimated values of stability constants (β) based on mass balance equations (24)-(28). Finally, the potential of solution at each titration point can be obtained from the values of E^0 and [H^+] according to equation (22). The standard deviation between this set of E values and the experimental set were evaluated. The "optimisation" procedure of the program minimizes this standard deviation to find the best fit values of the parameters (β, E^0, K_w and concentrations of metal, ligand, proton and titrant). The degree of confidence for the results is statistically determined in terms of chi-square value which should be less than 12.60. The results of the best fit are obtained from the output of the program (Appendix E).

4.3.1 Acid / Base Equilibrium Constants of Goethite

Following the above procedure, acid-base equilibrium of goethite was found to be

$$\equiv FeOH \quad \leftrightarrow \quad \equiv FeO^- + H^+ \qquad\qquad ; \log \beta^{int}_{1,-1} \qquad (32)$$

$$\equiv FeOH + H^+ \quad \leftrightarrow \quad \equiv FeOH_2^+ \qquad\qquad ; \log \beta^{int}_{1,1} \qquad (33)$$

The values of $\log\beta^{int}_{1,-1}$ and $\log \beta^{int}_{1,1}$, the intrinsic equilibrium constant, defined by equation (8) were obtained from the analysis, as shown in table4.2.

Table 4.2   Acid-base equilibrium constants of goethite surface with varying ionic strengths of $NaNO_3$ medium. Mole ratio of goethite : H^+ = 1:1, E^0 = 440.0 mV and K_w = -13.77.

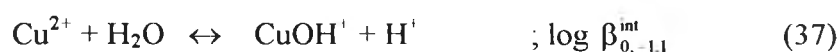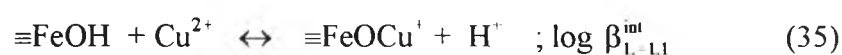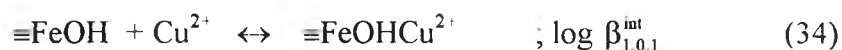| Ionic strength (M)	$\log \beta^{int}_{1,-1}$	$\log \beta^{int}_{1,1}$
0.001	-9.20 ± 0.07	5.83 ± 0.07
0.005	$-9.2_3 \pm 0.1^*$	$6.2_2 \pm 0.1^*$
0.010	$-9.1_7 \pm 0.1^*$	$6.0_2 \pm 0.1^*$
0.100	-9.85 ± 0.06	6.83 ± 0.05
0.500	-8.95 ± 0.03	6.30 ± 0.03

* The result includes the insignificant figure as a small number in the second decimal place to allow for detailed consideration
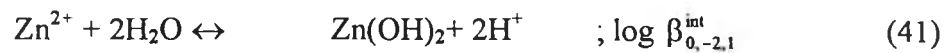
The results from table 4.2 show that $\log \beta_{1,-1}^{int}$ values vary within the range -9.85 to -8.95 while the values of $\log \beta_{1,1}^{int}$ vary within the range 5.83 to 6.83. The values of $\log \beta_{1,-1}^{int}$ and $\log \beta_{1,1}^{int}$ for 0.010, 0.005 and 0.001 M NaNO$_3$ were more or less the same within experimental error with the average values of -9.2±0.1 and 6.0±0.2, respectively.

4.3.2 Complex Stability Constants

4.3.2.1   The System of Goethite($\equiv$FeOH) - H$^+$- Cu^{2+}

The best fit of data was found with the complex model of the following equilibria:

$$\equiv FeOH + Cu^{2+} \leftrightarrow \equiv FeOHCu^{2+} \qquad ; \log \beta_{1,0,1}^{int} \qquad (34)$$

$$\equiv FeOH + Cu^{2+} \leftrightarrow \equiv FeOCu^{+} + H^{+} \quad ; \log \beta_{1,-1,1}^{int} \qquad (35)$$

$$\equiv FeOH + Cu^{2+} + H_2O \leftrightarrow \equiv FeOCuOH + 2H^{+} \quad ; \log \beta_{1,-2,1}^{int} \qquad (36)$$

$$Cu^{2+} + H_2O \leftrightarrow CuOH^{+} + H^{+} \qquad ; \log \beta_{0,-1,1}^{int} \qquad (37)$$

The values of $\log \beta_{1,0,1}^{int}$, $\log \beta_{1,-1,1}^{int}$ and $\log \beta_{1,-2,1}^{int}$ obtained from the analysis are shown in table4.3.

Table 4.3 Complex stability constants of Cu^{2+} on goethite surface with

varying ionic strengths of $NaNO_3$ medium. $E^0 = 440.0$ mV ,

$K_w = -13.77$ and log $\beta_{0,-1,1}^{int}$* $= -8.12[7,26]$.

Ionic strength (M)	log $\beta_{1,0,1}^{int}$	log $\beta_{1,-1,1}^{int}$	log $\beta_{1,-2,1}^{int}$
0.001	n.f.	1.27 ± 0.03	-7.96 ± 0.03
0.005	5.67 ± 0.05	0.55 ± 0.03	-7.75 ± 0.04
0.010	$5.9_8 \pm 0.1^*$	0.81 ± 0.04	-5.37 ± 0.08
0.100	$4.5_0 \pm 0.1^*$	$0.9 \pm 0.4^{**}$	$-7.2_3 \pm 0.1^*$
0.500	$4.8_7 \pm 0.1^*$	$0.9 \pm 0.4^{**}$	$-6.6 \pm 0.12^{**}$

* The result includes the insignificant figure as a small number in the
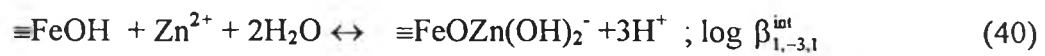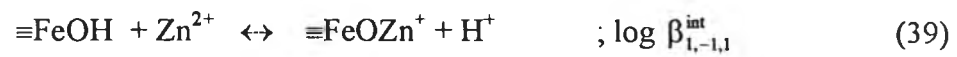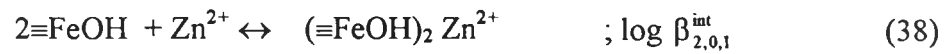second decimal place to allow for detailed consideration

** Fixed reference value in the calculations [7,26]

n.f. : not found

The results from table 4.3 show that the values of log $\beta_{1,0,1}^{int}$ vary

within the range 4.50 to 5.98, except for the unfound value in 0.001 M $NaNO_3$. The

values of log $\beta_{1,-1,1}^{int}$ vary within the range 0.81 to 1.27. This value increases with

increasing ionic strength from 0.005 to 0.500 M $NaNO_3$. The values of log $\beta_{1,-2,1}^{int}$

vary within the range -5.37 to -7.96. The lower value of log $\beta_{1,-1,1}^{int}$ in 0.005 M

$NaNO_3$ was expected for higher values of log $\beta_{1,0,1}^{int}$. Similar reason can account for

the higher value of log $\beta_{1,-1,1}^{int}$ in 0.001 M $NaNO_3$ when log $\beta_{1,0,1}^{int}$ was not found.

4.3.2.2 The System of Goethite($\equiv$FeOH) - H^+- Zn^{2+}

The following complex equilibria was found for the best fit of data.

$$2\equiv\text{FeOH} + \text{Zn}^{2+} \leftrightarrow (\equiv\text{FeOH})_2 \text{Zn}^{2+} \quad ; \log \beta_{2,0,1}^{int} \quad (38)$$

$$\equiv\text{FeOH} + \text{Zn}^{2+} \leftrightarrow \equiv\text{FeOZn}^+ + \text{H}^+ \quad ; \log \beta_{1,-1,1}^{int} \quad (39)$$

$$\equiv\text{FeOH} + \text{Zn}^{2+} + 2\text{H}_2\text{O} \leftrightarrow \equiv\text{FeOZn(OH)}_2^- + 3\text{H}^+ \quad ; \log \beta_{1,-3,1}^{int} \quad (40)$$

$$\text{Zn}^{2+} + 2\text{H}_2\text{O} \leftrightarrow \text{Zn(OH)}_2 + 2\text{H}^+ \quad ; \log \beta_{0,-2,1}^{int} \quad (41)$$

The values of $\log \beta_{2,0,1}^{int}$, $\log \beta_{1,-1,1}^{int}$ and $\log \beta_{1,-3,1}^{int}$ obtained from the analysis are shown in table 4.4.

Table 4.4 Complex stability constants of Zn^{2+} on goethite surface with

varying ionic strengths of $NaNO_3$ medium. $E^0 = 440.0$ mV ,

$K_w = -13.77$ and $\log \beta^{int}_{0,-2,1}{}^* = -17.10[7,26]$.

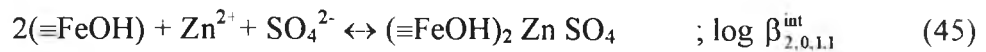| Ionic strength (M)	$\log \beta^{int}_{2,0,1}$	$\log \beta^{int}_{1,-1,1}$	$\log \beta^{int}_{1,-3,1}$
0.001	8.63 ± 0.07	-2.56 ± 0.04	-17.96 ± 0.04
0.005	$8.0_5 \pm 0.1^*$	-2.96 ± 0.05	-17.88 ± 0.06
0.010	9.21 ± 0.09	$-2.0 \pm 0.28^{**}$	$-18.20 \pm 0.14^{**}$
0.100	$8.8_0 \pm 0.1^*$	-2.19 ± 0.05	-17.53 ± 0.08
0.500	$8.7_1 \pm 0.1^*$	-1.87 ± 0.06	-16.35 ± 0.08

* The result includes the insignificant figure as a small number in the second
decimal place to allow for detailed consideration

** Fixed reference value in the calculations [7,26]

The results from table4.4 show that the values of $\log \beta^{int}_{2,0,1}$ vary

within the range 8.05 to 9.21. The values of $\log \beta^{int}_{1,-1,1}$ vary within the range

-1.87 to -2.96. The average value of $\log \beta^{int}_{1,-1,1}$ was found to be -2.05 ± 0.15 in 0.010

to 0.500 M $NaNO_3$. The values of $\log \beta^{int}_{1,-3,1}$ vary within the range -16.35 to -18.20.

The value of $\log \beta^{int}_{2,0,1}$ increases with decreasing ionic strength from 0.500 to 0.010

M $NaNO_3$ while the value of $\log \beta^{int}_{1,-3,1}$ decreases in this range.

4.3.2.3 The System of Goethite($\equiv$FeOH) - H^+- Cu^{2+}- SO_4^{2-}

The best fit of data was found for the complex model with addition of the following equilibria:

$$\equiv FeOH + Cu^{2+} + SO_4^{2-} \leftrightarrow \equiv FeOHCuSO_4 \quad ; \log \beta_{1,0,1,1}^{int} \tag{42}$$

$$\equiv FeOH + Cu^{2-} + SO_4^{2-} \leftrightarrow \equiv FeOCuSO_4^- + H^+ \quad ; \log \beta_{1,-1,1,1}^{int} \tag{43}$$

$$\equiv FeOH + Cu^{2-} + SO_4^{2-} + H_2O \leftrightarrow \equiv FeOCuOHSO_4^{2-} + 2H^+ \quad ; \log \beta_{1,-2,1,1}^{int} \tag{44}$$

The values of $\log \beta_{1,0,1,1}^{int}$, $\log \beta_{1,-1,1,1}^{int}$ and $\log \beta_{1,-2,1,1}^{int}$ obtained from the analysis are shown in table 4.5.

Table 4.5 Complex stability constants of Cu^{2+}-SO_4^{2-} on goethite surface with varying ionic strengths of $NaNO_3$ medium. $E^0 = 440.0$ mV, $K_w = -13.77$ and $\log \beta_{0,-1,1}^{int} {}^* = -8.12$[7,26].

Ionic strength (M)	$\log \beta_{1,0,1,1}^{int}$	$\log \beta_{1,-1,1,1}^{int}$	$\log \beta_{1,-2,1,1}^{int}$
0.005	13.00±0.06	8.5$_0$±0.1*	2.45±0.09
0.010	13.14±0.05	8.4$_2$±0.1*	1.75±0.04
0.100	13.72±0.04	8.95±0.09	1.68±0.06
0.500	11.0±0.1**	6.00±0.09	2.23±0.06

* The result includes the insignificant figure as a small number in the second decimal place to allow for detailed consideration

** Fixed reference value in the calculations [7,26]

The results from table 4.5 show that the values of log $\beta^{int}_{1,0,1,1}$ vary

within the range 11.0 to 13.72. This value increases with increasing ionic strength

from 0.005 M to 0.100 M $NaNO_3$. The values of log $\beta^{int}_{1,-1,1,1}$ vary within the range

6.0 to 8.95 while the values of log $\beta^{int}_{1,-2,1,1}$ vary within the range 1.68 to 2.45. The

lowest values of log $\beta^{int}_{1,0,1,1}$ and $\beta^{int}_{1,-1,1,1}$ were found in 0.500 M $NaNO_3$ while the

highest values were found in 0.100 M $NaNO_3$. The values of log $\beta^{int}_{1,0,1,1}$ and

log $\beta^{int}_{1,-1,1,1}$ for 0.010 and 0.005 M $NaNO_3$ were more or less the same within

experimental error.

4.3.2.4 The System of Goethite($\equiv$FeOH) - H^+- Zn^{2+}- SO_4^{2-}

The best fit of data was found for the complex model

with addition of the following equilibria:

$$2(\equiv FeOH) + Zn^{2+} + SO_4^{2-} \leftrightarrow (\equiv FeOH)_2\, Zn\, SO_4 \qquad ; \log \beta^{int}_{2,0,1,1} \qquad (45)$$

$$\equiv FeOH + Zn^{2+} + SO_4^{2-} \leftrightarrow \equiv FeOZn\, SO_4^- + H^+ \qquad ; \log \beta^{int}_{1,-1,1,1} \qquad (46)$$

$$\equiv FeOH + Zn^{2+} + SO_4^{2-} + 2H_2O \leftrightarrow \equiv FeOZn(OH)_2\, SO_4^{3-}+3H^+ \; ; \log \beta^{int}_{1,-3,1,1} \qquad (47)$$

The values of log $\beta^{int}_{2,0,1,1}$, log $\beta^{int}_{1,-1,1,1}$ and log $\beta^{int}_{1,-3,1,1}$ obtained from

the analysis are shown in table 4.6.

Table 4.6   Complex stability constants of Zn^{2+}-SO_4^{2-} on goethite surface with

varying ionic strengths of $NaNO_3$ medium. $E^0 = 440.0$ mV ,

$K_w = -13.77$ and log $\beta_{0,-2,1}^{int}$ * $= -17.10[7,26]$.

Ionic strength(M)	log $\beta_{2,0,1,1}^{int}$	log $\beta_{1,-1,1,1}^{int}$	log $\beta_{1,-3,1,1}^{int}$
0.005	18.00±0.07	12.9_0±0.1*	-2.50±0.06
0.010	20.25±0.08	13.0_8±0.1*	-2.53±0.06
0.100	19.50±0.09	12.6_4±0.1*	-2.54±0.08
0.500	18.20±0.07	11.7_2±0.1*	-2.50±0.06

*   The result includes the insignificant figure as a small number in the second
decimal place to allow for detailed consideration

The results from table 4.6 show that the values of log$\beta_{2,0,1,1}^{int}$ vary

within the range 18.00 to 20.25.This value increases with decreasing ionic strength

from 0.500 to 0.010 M $NaNO_3$. The values of log $\beta_{1,-1,1,1}^{int}$ vary within the range

11.72 to13.08. The average value of log $\beta_{1,-1,1,1}^{int}$ was found to be 12.85±0.25 in

0.005 to 0.100 M $NaNO_3$. The values of log $\beta_{1,-3,1,1}^{int}$ vary within the range –2.50 to

–2.54. The average value of log $\beta_{1,-3,1,1}^{int}$ was found to be -2.52±0.02 in 0.005 to

0.500 M $NaNO_3$. This value decreases with increasing ionic strength from 0.005 to

0.100 M $NaNO_3$.

4. 4 Adsorption Simulation

To simulate the surface complexation equilibria of Cu^{2+} and Zn^{2+} on goethite in an aqueous system, a chemical equilibrium modeling program, MINEQL was used. This program is capable of calculating aqueous speciation, solid phase saturation states, precipitation – dissolution, and adsorption. The procedure for solving chemical equilibrium problems involves 5 simple steps : (1) selection of the chemical components that will define the system ; (2) creation of chemical species from these components (this step may include scanning a database of thermodynamic constants or creating new species) ; (3) setting the total concentration of individual components. (4) running the calculation (this step may include setting ionic strength , temperature or surface complexation options) ; (5) viewing and extracting output data (this step may include creating graphics plots, specialized reports or saving data as files for use in other software).These procedures are summarized in Figure 4.2.
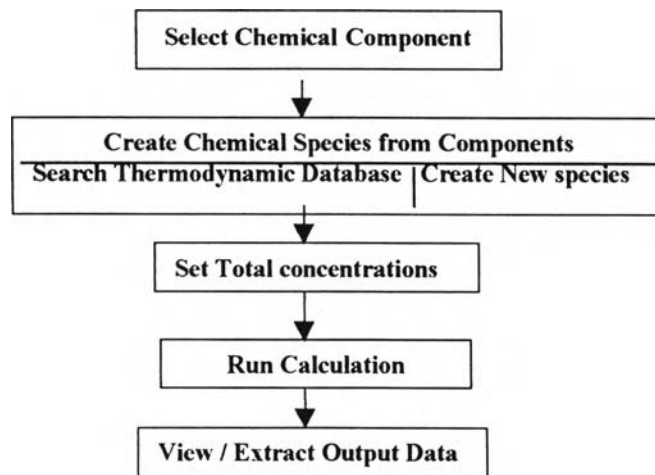
Figure 4.2 The flow chart of the procedure for chemical equilibrium modeling

There are three options of surface complexation model in MINEQL: Two-Layer Model (Diffuse Double Layer Model), Constant Capacitance Model, and Triple Layer Model. The details of these models are described in section 2.4.

In this work, the Constant Capacitance Model (CCM) was used to simulate the adsorption behavior of Cu^{2+} and Zn^{2+} on goethite surface. This model has the advantage because it assumes that the interaction of electrolyte with surface is negligible or constant. Therefore, there is only one potential (ψ_0) that is calculated from the net surface charge density (σ_0) and the capacitance of the surface layer (C) as in equation (13), i.e.,

$$\psi_0 = \frac{\sigma_0}{C}$$

Substituting ψ_0 into the Nernstian equation (16) gives,

$$PZC - pH = \log e \left(\frac{F}{RT} \cdot \frac{\sigma_0}{C} \right) \tag{48}$$

The surface charge density, σ_0, can be calculated from the measured pH and the volume of acid/base added at each data point (Appendix F) using equation (49), i.e.,

$$\text{Surface Charge Density } (\sigma_0) = (F/AS)(C_A - C_B - [H^+] - [OH^-]) \tag{49}$$

where F is the faraday constant, A is the specific surface area(m^2g^{-1}), S is the solid concentration (gdm^{-3}), and C_A is the molar concentration of added acid and C_B of added base. The molar concentrations of H^+ and OH^- are obtained from the pH

measurements. The surface charge density as a function of pH calculated from equation (49) are shown in figure 4.3. The resulting curves for five ionic strengths coincide at pH 7.0 ± 0.1, the PZC value.
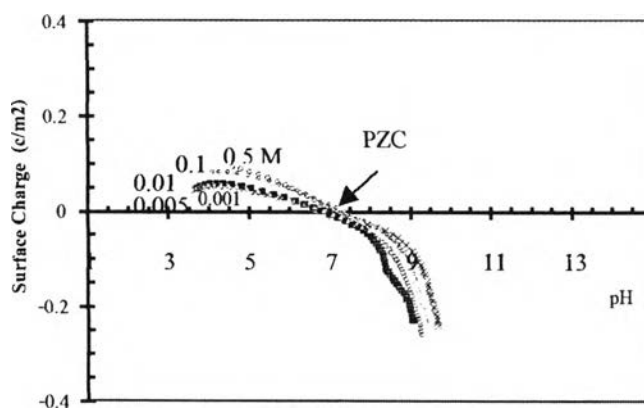
Figure 4.3   Surface charge density as a function of pH calculated from

equation (49) for various ionic strengths of $NaNO_3$.

The capacitance, C, can thus be obtained from the slope of the plot of

the PZC-pH values against surface charge density, σ_0, of goethite. These values for the

system in 0.001, 0.005, 0.010, 0.100 and 0.500 M $NaNO_3$ (Appendix G) are tabulated

in table 4.7.

Table 4.7 The values of capacitance for the system in 0.001, 0.005,0.010, 0.100

and 0.500 M $NaNO_3$

Ionic strength (M)	Capacitance (C/m^2)
0.001	0.50 ± 0.18
0.005	0.45 ± 0.12
0.010	0.54 ± 0.23
0.100	0.64 ± 0.11
0.500	0.80 ± 0.02

Other input parameters required in the program are the surface

complexation reactions, equilibrium constants(obtained from section 4.3.1and 4.3.2),

total concentrations of the components, surface area (m^2/g), solid concentrations (g/L),

the ionic strength of solutions(M) , the pH range and the number of titration points.

The outputs of MINEQL give the distribution diagrams of the surface

complex species on goethite as shown in figures 4.4-4.23. Using the input parameters

of Lovgren et al.[7,26] for the same system, the distribution diagrams of Cu^{2+} and Zn^{2+}

in 0.100 M $NaNO_3$ were prepared and shown in figures 4.9 and 4.15.

4.4.1 The System of Goethite($\equiv$FeOH) - H^+- Cu^{2+}

The species distribution diagrams from the simulation of Cu^{2+} surface

complex systems show that the formations of each complex species in five different

ionic strengths have the same pattern (figures 4.4-4.8). The adsorption of free Cu^{2+} on

goethite started below pH~4. In the acidic range, the major surface species was

$\equiv$FeOCu⁻ and the minor species were $\equiv$FeOHCu^{2+} and $\equiv$FeOCuOH. The concentration

of $\equiv$FeOCu⁺ was increasingly high up to about 60% at pH~6, except in 0.010M

NaNO₃, where the maximum concentration of $\equiv$FeOCu⁺ was found to be about 30% at

pH~5. The concentration of this species decreases slowly above pH~7. A small extent

of $\equiv$FeOHCu^{2+} (~4%) could be seen only in 0.010 and 0.005 M NaNO₃ (figures 4.6 and

4.7) probably due to slightly higher log β values obtained from the analysis (table 4.3).

Above pH~7, the concentration of $\equiv$FeOCuOH species becomes increasingly high

(>50%) and the adsorption of Cu^{2+} was complete at pH~7. The protonated-

deprotonated species of goethite apparently disappeared in this system. The results of

the simulation for the Cu^{2+} complex systems show that varying the values of the

capacitance has insignificant effect on the species distribution in different ionic

strengths. From Lovgren's work (figure 4.9), the nondeprotonated species, $\equiv$FeOHCu^{2+}

dominates with the maximum concentration of about 40% at pH~5 while our results

(figure 4.5) showed that this species was not found. The maximum concentration of

$\equiv$FeOCu species of the two diagrams appeared at the same pH(~ 6) but the percentage

of the formation obtained in this work was higher. The discrepancies could be due to

the higher literature value of log $\beta_{1,0,1}^{int}$ (8.8±0.20) than that obtained in this work

(4.5±0.1).
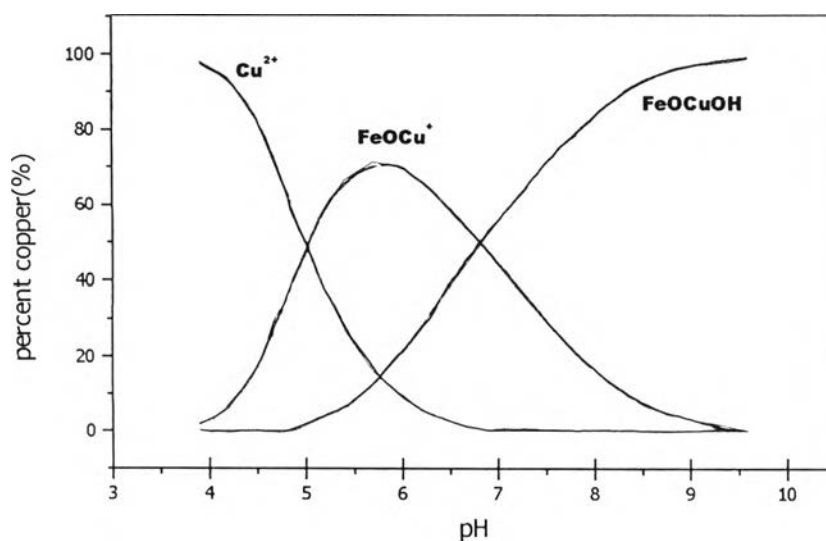
Figure 4.4 The distribution diagram of Cu^{2+} in 0.500 M $NaNO_3$
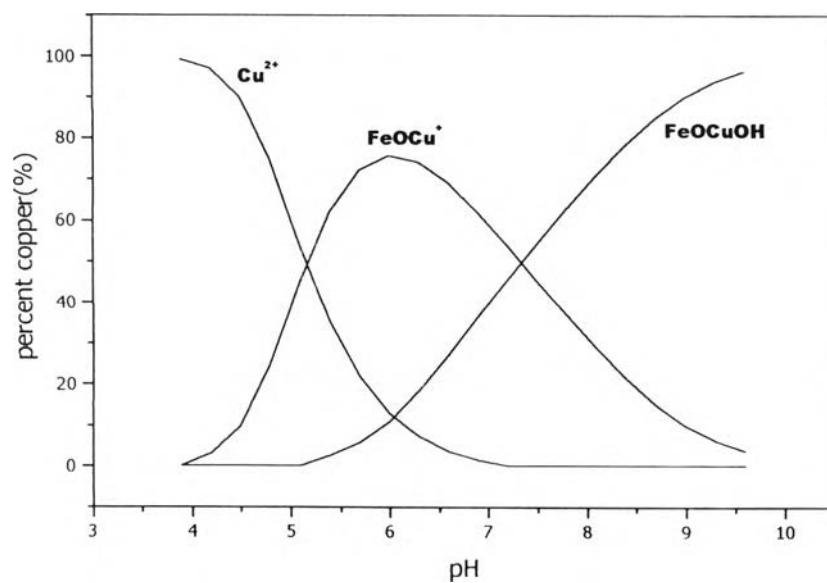
Figure 4.5 The distribution diagram of Cu^{2+} in 0.100 M $NaNO_3$
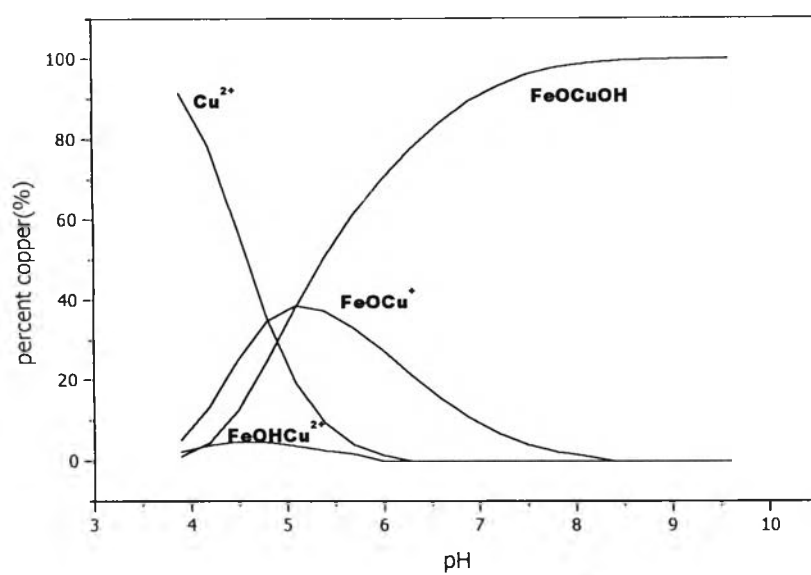
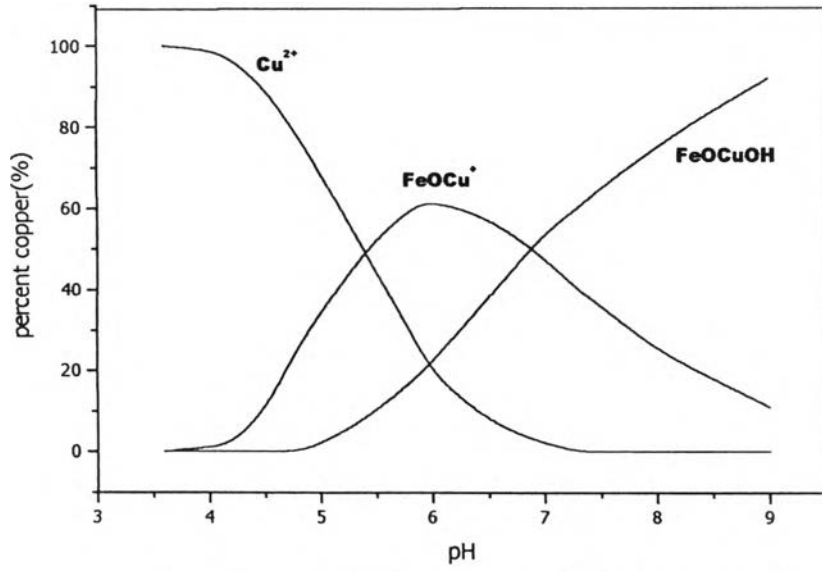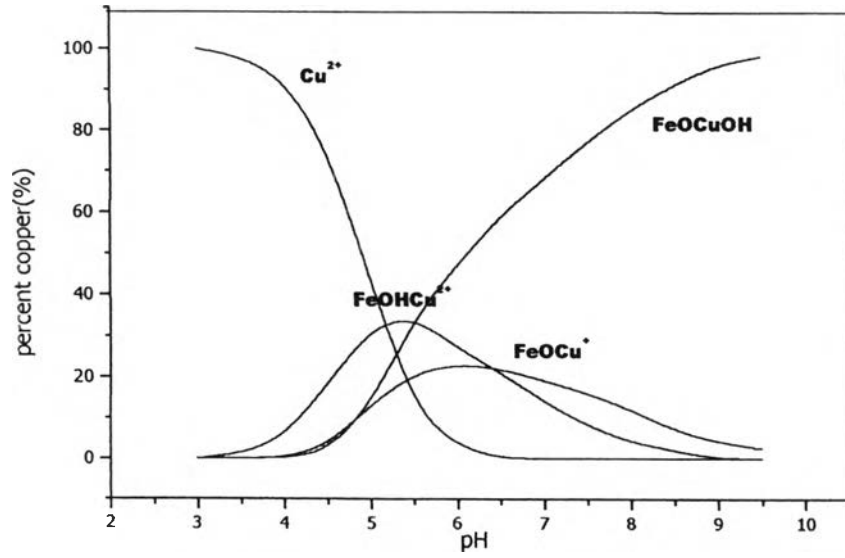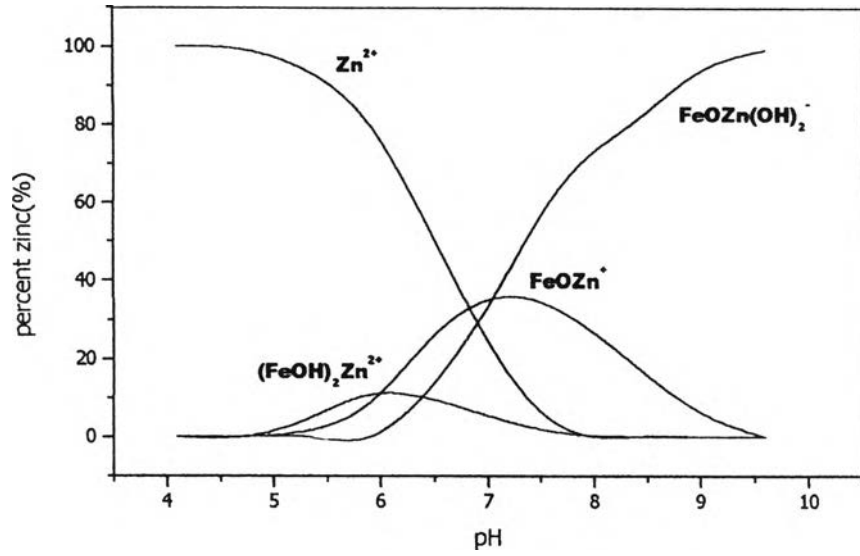Figure 4.6 The distribution diagram of Cu^{2+} in 0.010 M $NaNO_3$
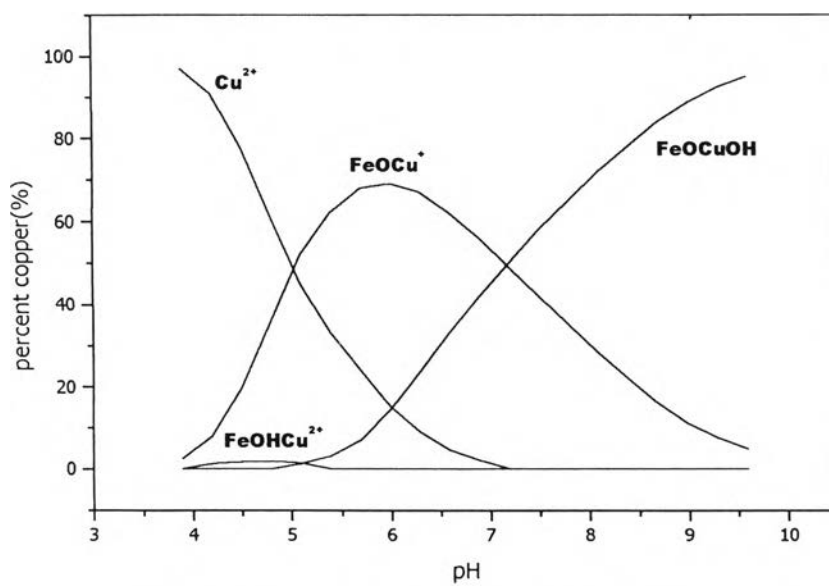
Figure 4.7 The distribution diagram of Cu^{2+} in 0.005 M $NaNO_3$

Figure 4.8 The distribution diagram of Cu^{2+} in 0.001 M $NaNO_3$

Figure 4.9 The distribution diagram of Cu^{2+} in 0.100 M $NaNO_3$[7]

4.4.2 The System of Goethite($\equiv$FeOH) - H$^+$ - Zn^{2+}

The species distribution diagrams of the Zn^{2+} surface complex systems in five ionic strengths showed similar pattern (figures 4.10-4.14). The adsorption of free Zn^{2+} on goethite started at pH~4 by the formation of the nondeprotonated species ($\equiv$FeOH)$_2$Zn^{2+} and the deprotonated species $\equiv$FeOZn$^+$. ($\equiv$FeOH)$_2$Zn^{2+} species are formed in the pH range 5-8 with the maximum concentration of about 10-20% at pH~6. Above pH~7, $\equiv$FeOZn$^+$ species becomes dominating (about 40-50%) in 0.500, 0.100, and 0.010 M NaNO$_3$ while in 0.005 and 0.001 M NaNO$_3$, the formation of $\equiv$FeOZn(OH)$_2^-$ is more favored. The hydrolyzed species $\equiv$FeOZn(OH)$_2^-$ appeared at pH~6 and became increasingly high (>50%) above pH~8. The adsorption of Zn^{2+} was complete at pH~8. As with Cu^{2+} complex systems, the protonated and deprotonated species were again not found in Zn^{2+} complex system and the variation of the capacitance has insignificant effect on the species distribution in different ionic strengths. From Lovgren's work (figure 4.15), the ($\equiv$FeOH)$_2$Zn^{2+} species were found to be predominantly formed with the maximum concentration of about 50% at pH~7.5 while it was only 10% at pH~6.5 from our results (figure 4.11). The maximum concentration of $\equiv$FeOZn$^+$ species of the two diagrams was found at the same pH(~7.8) but the percentage of the formation obtained in this work was higher. The discrepancies could be due to the slightly lower value of log $\beta_{2,0,1}^{int}$ obtained in this work (8.8±0.1)than the literature value(10.7±0.17).

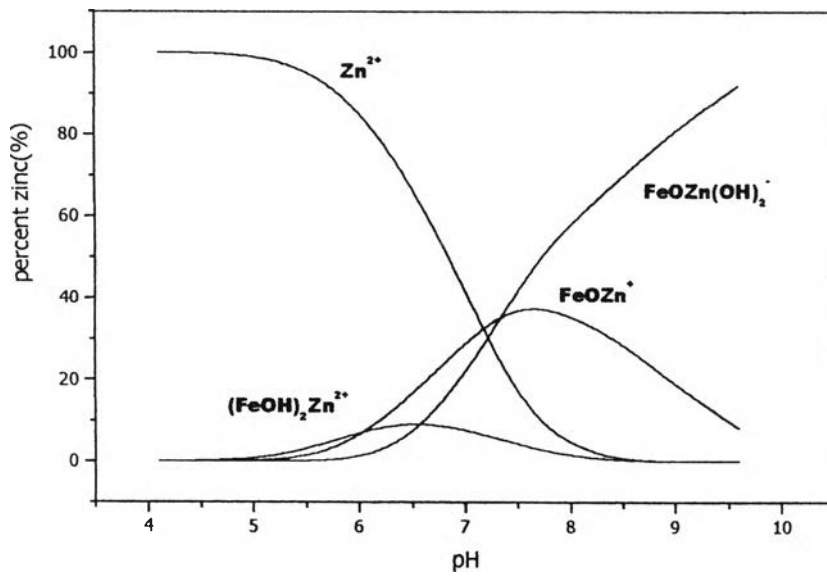Figure 4.10 The distribution diagram of Zn^{2+} in 0.500 M $NaNO_3$

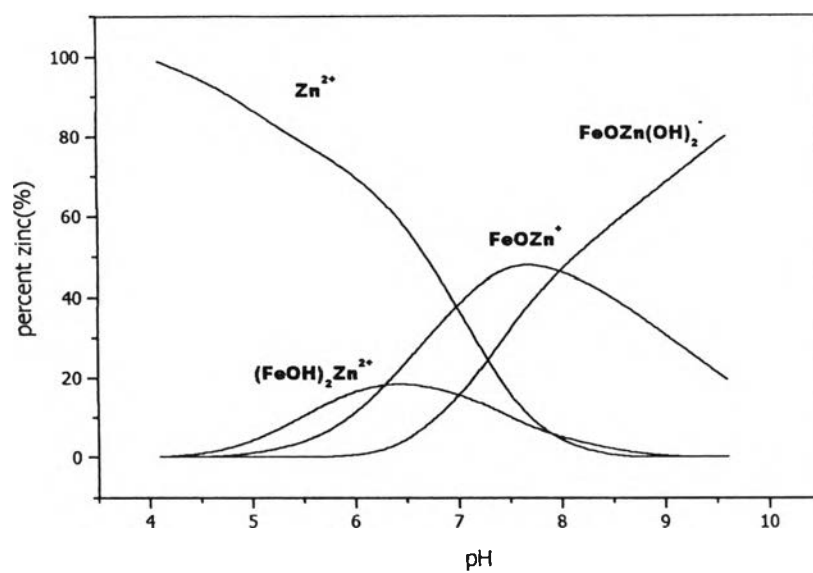Figure 4.11 The distribution diagram of Zn^{2+} in 0.100 M $NaNO_3$

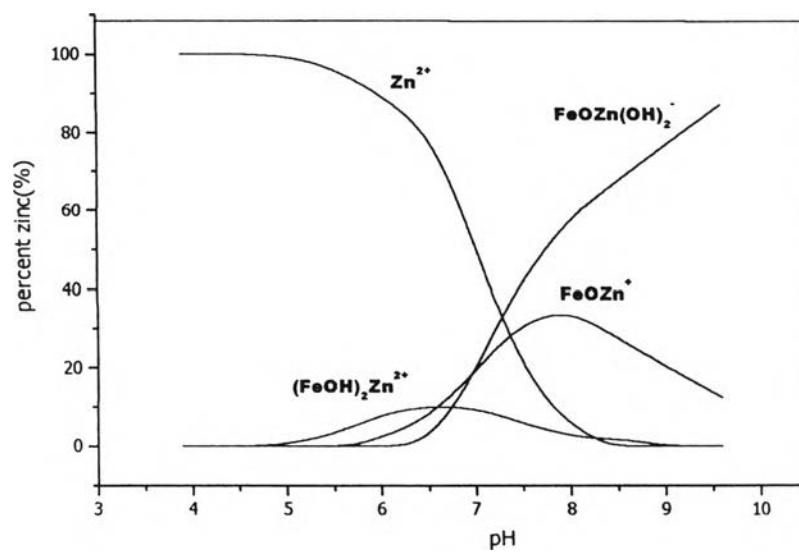Figure 4.12 The distribution diagram of Zn^{2+} in 0.010 M $NaNO_3$

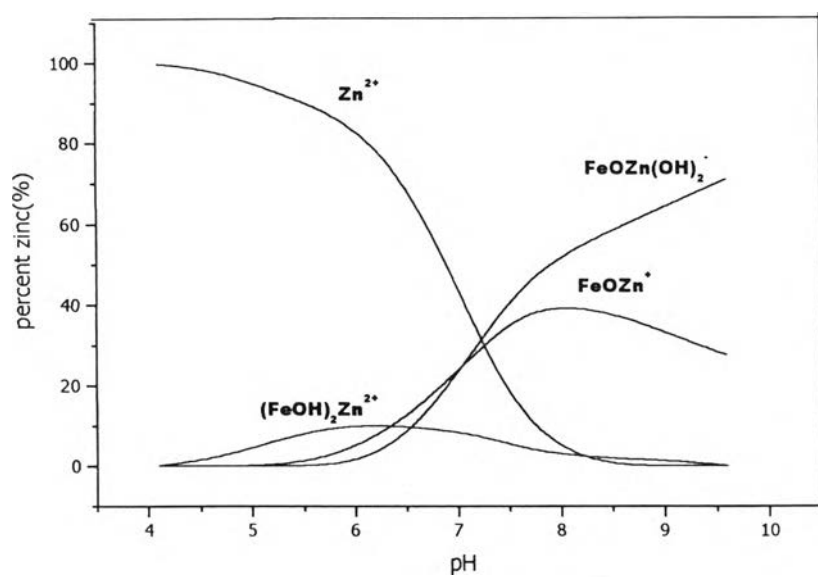Figure 4.13 The distribution diagram of Zn^{2+} in 0.005 M $NaNO_3$

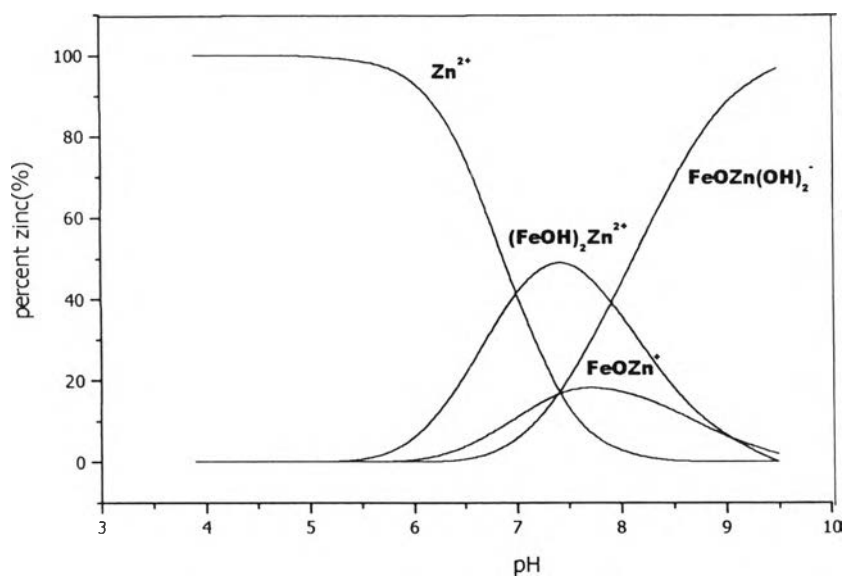Figure 4.14 The distribution diagram of Zn^{2+} in 0.001 M $NaNO_3$

Figure 4.15 The distribution diagram of Zn^{2+} in 0.100 M $NaNO_3$[26]

4.4.3 The System of Goethite($\equiv$FeOH) - H^+- Cu^{2+}- SO_4^{2-}

From the simulation diagrams of the Cu^{2+}- SO_4^{2-} complex systems (figures 4.16-4.19), the formation of surface complex species in 0.100, 0.010 and 0.005 M $NaNO_3$ showed the same characteristics. However, species distribution in 0.500 M $NaNO_3$ was markedly different. In the acidic range, the nondeprotonated species $\equiv$FeOHCuSO$_4$ are predominantly formed in 0.100,0.010,and 0.005 M $NaNO_3$ and the maximum concentration of about 80% was found at pH~3, except in 0.500 M $NaNO_3$ where the maximum concentration was only 30% at pH~4. The deprotonated complex species $\equiv$FeOCuSO$_4^-$ becomes more important above pH~5 and the maximum concentration of about 50% was found in 0.100,0.010,and 0.005 M $NaNO_3$. The lower concentration of $\equiv$FeOCuSO$_4^-$ (~ 10%) was observed in 0.500 M $NaNO_3$ due to the preferential formation of $\equiv$FeOHCuSO$_4$ at pH~4. The hydrolyzed species $\equiv$FeOCuOHSO$_4^{2-}$ are initially formed at pH~4 in 0.500 and 0.005 M $NaNO_3$ and at pH~5 in 0.100 and 0.010 M $NaNO_3$. The concentration of this species was increasingly high up to about 80% above pH~7. A small extent of $\equiv$FeOHCu^{2+} species (~2-4%) was found in 0.010and 0.005 M $NaNO_3$. In 0.500,0.100, and 0.010 M $NaNO_3$, a small quantity of the deprotonated complex species $\equiv$FeOCu$^+$ (~4-5%) was also observed. In comparison to the system of goethite ($\equiv$FeOH)-H^+-Cu^{2+} (section4.4.1), the introduction of SO_4^{2-} ion thus seems to promote adsorption of Cu^{2+} ion on goethite surface in 0.100 to 0.005 M $NaNO_3$ except in 0.500 M $NaNO_3$ where lesser effect was observed.
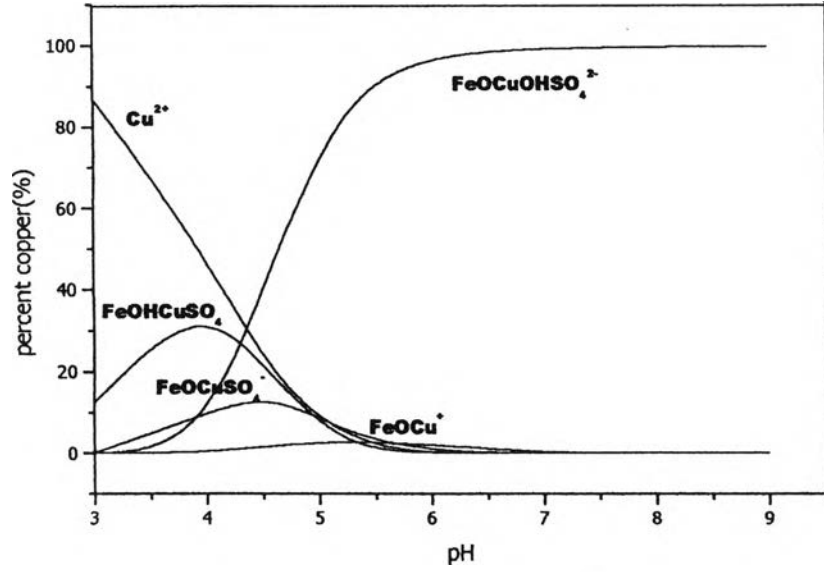
Figure 4.16 The distribution diagram of Cu^{2+}-SO_4^{2-} surface complexes system in 0.500 M $NaNO_3$
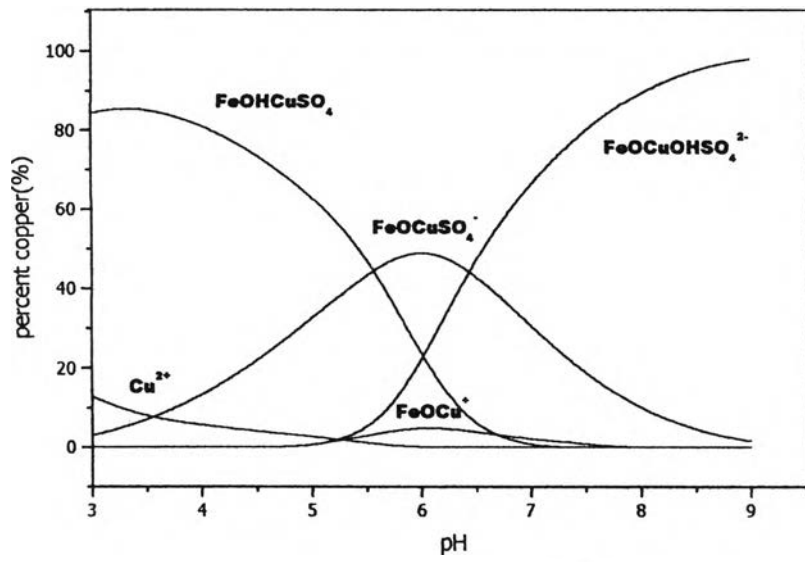

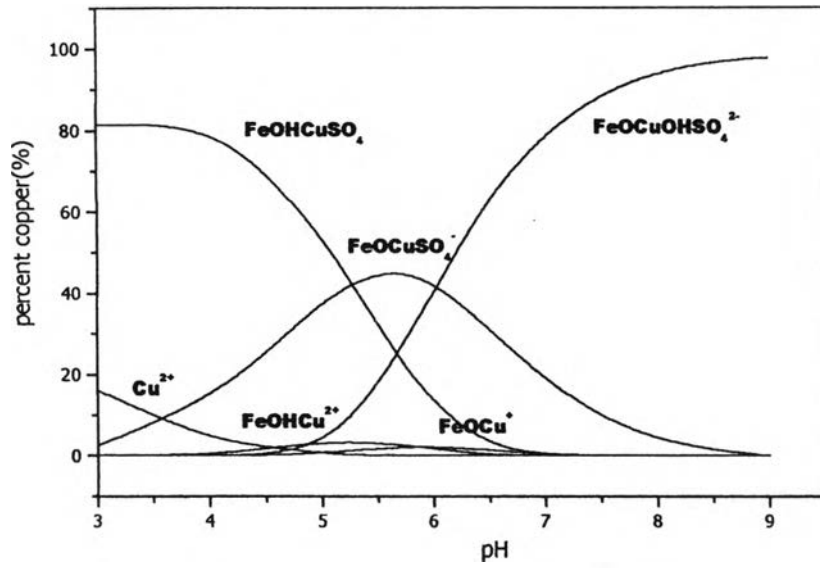Figure 4.17 The distribution diagram of Cu^{2+}-SO_4^{2-} surface complexes system in 0.100 M $NaNO_3$

Figure 4.18 The distribution diagram of Cu^{2+}-SO_4^{2-} surface complexes system in 0.010 M $NaNO_3$
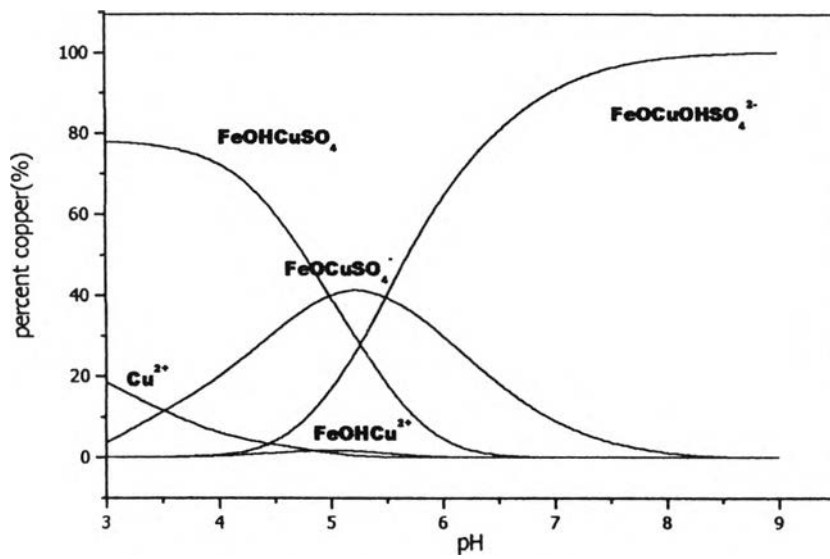

Figure 4.19 The distribution diagram of Cu^{2+}-SO_4^{2-} surface complexes system in 0.005 M $NaNO_3$

4.4.4 The System of Goethite($\equiv$FeOH) - H^+- Zn^{2+}- SO_4^{2-}

The species distribution diagrams of the Zn^{2+}- SO_4^{2-} complex systems in four ionic strengths showed the same pattern(figures 4.20-4.23). For pH$\geq$4, less than 20% of free Zn^{2+} ion was found in the system and a decrease of the initial concentration of free Zn^{2+} with ionic strength from 0.500 to 0.005 M $NaNO_3$ was also observed. Only two dominating surface complex species, i.e., $\equiv$FeOZnSO$_4^-$ and $\equiv$FeOZn(OH)$_2$SO$_4^{3-}$, were found in this system. In acidic range, $\equiv$FeOZnSO$_4^-$ species are predominantly formed and the maximum concentrations of about 90% in 0.500 M $NaNO_3$ and about 100% in 0.100, 0.010 and 0.005 M $NaNO_3$ were reached at pH~5. The concentration of this species decreases slowly above pH~5 and the hydrolyzed species $\equiv$FeOZn(OH)$_2$SO$_4^{3-}$ was initially formed at pH~5 in 0.500 M $NaNO_3$ and at pH~5.5 in 0.100 to 0.005 M $NaNO_3$. This species dominates above pH~7 and is the only species found in the basic range. In comparison to the system of goethite($\equiv$FeOH) - H^+ - Zn^{2+} (section4.4.2), adsorption of Zn^{2+} ion on goethite surface in the presence of SO_4^{2-} ion occurred at lower pH with higher tendency of adsorption.
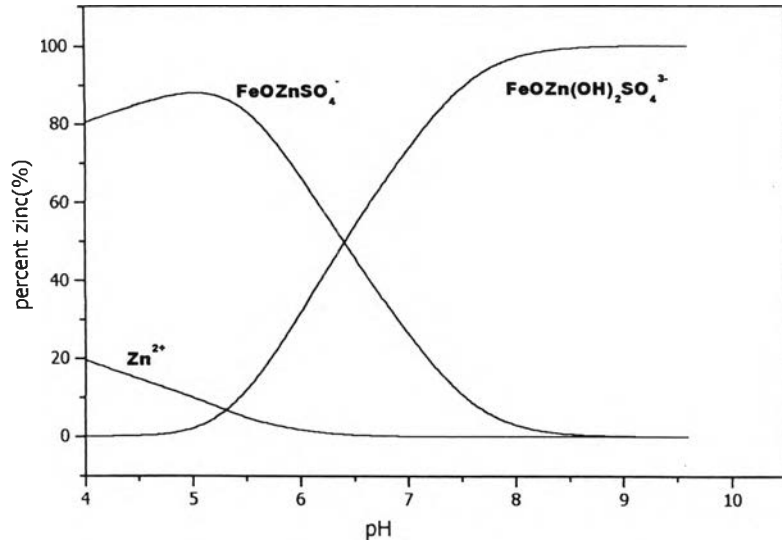
Figure 4.20 The distribution diagram of Zn^{2+}-SO_4^{2-} surface complexes system in 0.500 M $NaNO_3$
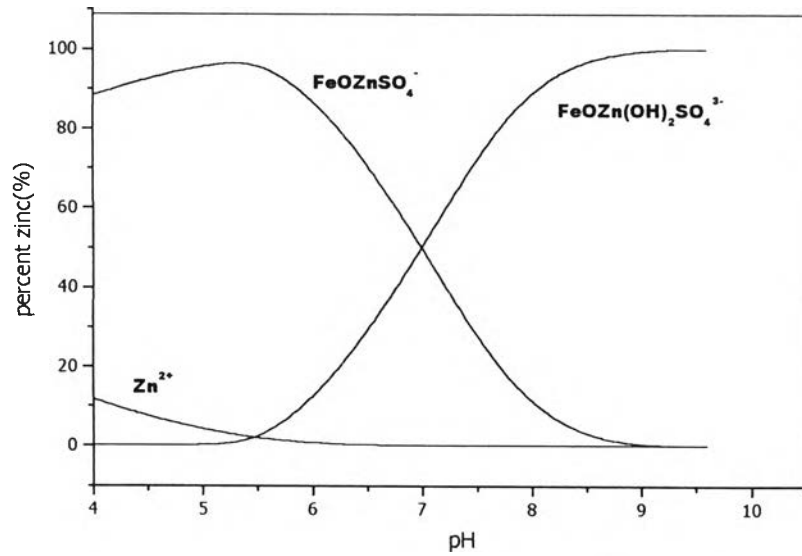

Figure 4.21 The distribution diagram of Zn^{2+}-SO_4^{2-} surface complexes system in 0.100 M $NaNO_3$
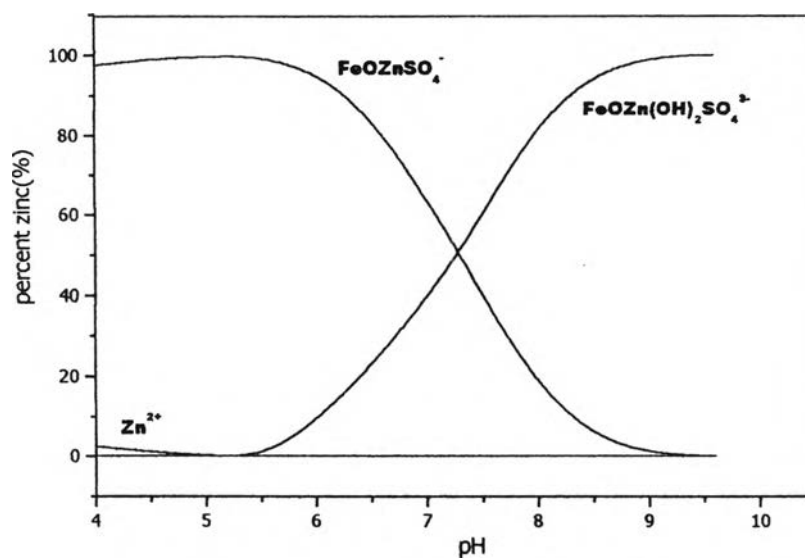
Figure 4.22 The distribution diagram of Zn^{2+}-SO_4^{2-} surface complexes system in 0.010 M $NaNO_3$
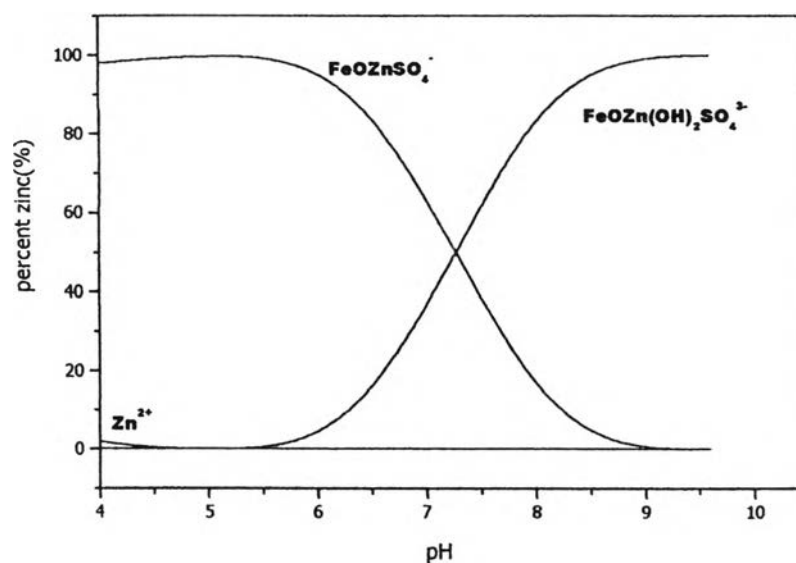

Figure 4.23 The distribution diagram of Zn^{2+}-SO_4^{2-} surface complexes system in 0.005 M $NaNO_3$