CHAPTER II

THEORY

2.1 Mineral-Solution Interface [13]

The interfacial region between the mineral surface and solution is marked by a discontinuity density, composition, and structure of the two phases. A mineral is made up of three dimensional arrays of ions in a crystal structure and varieties of surface groups, while an aqueous solution consists of polar, water molecules and chemical elements. These elements in natural waters may be present in many different forms such as cations, anions, neutral molecules and complexes.

Mineral surfaces commonly have a non-zero electrical charge, producing the electrostatic forces that can be modified by the arrangement of water dipoles and aqueous species near the interface as ions accumulate at the mineral surface to preserve net electrical neutrality. A net charge at the interface may also be produced by chemical reactions between ions in solution and those at the mineral surface. In metal(hydr)oxides, for example, the oxygens at the interface may bind with protons in two steps forming OH^- and OH_2^0 ligands. This can be written as:

$$O^{-2} + 2H^+ \leftrightarrow OH^- + H^+ \leftrightarrow OH_2^0 \qquad (1)$$

This means that the oxide surface may contain O^{-2}, OH^- and OH_2^0 groups. Hydroxyl group is so reactive that a proton may be accepted from the adjacent solution phase or removed from the mineral surface by chemical reactions :

$$\equiv X\text{-}OH + H^+ \leftrightarrow \equiv X\text{-}OH_2^+ \qquad (2)$$

$$\equiv X\text{-}OH + OH^- \leftrightarrow \equiv X\text{-}O^- + H_2O \qquad (3)$$

where ≡XOH is the surface hydroxyl group(X represents a metal ion on the surface forming bond with the surface hydroxyl groups and other ions in the bulk structure). Reaction(2) shows that the metal(hydr)oxides surface favors positive charge in acid solution while in basic solution a proton may be lost from the hydroxyl group and the surface carries a negative charge as in reaction(3).

Because of these reactions, mineral surface charge can change signs from positive to negative with increasing pH. The pH at which the mineral surface charge becomes zero is called a point of zero charge (PZC) or **pH_{PZC}**. At pH lower than pH_{PZC} value mineral surface has a net positive charge due to reactions such as reaction (2) and for higher pH the mineral has a net negative charge due to reaction (3).

The number of oxygen atoms exposed at the mineral surface and the charge on the surface control the types of aqueous species that accumulate on the mineral surface and the ability to exchange with other ions in solution.

2.2 Complexation at the Oxide - Solution Interface [13,30]

There are varieties of chemical reactions occuring at the oxide-solution interface. These reactions involve uptake of species from the aqueous solution phase in the presence of a mineral which are termed **sorption.**

Sorption occurs by three processes (Figure 2.1). First, the formation of a surface precipitate having a structure or composition different from the host mineral. The second process is absorption or coprecipitation whereby a chemical species is removed from the aqueous solution and penetrates the crystal lattice of the mineral surface. The third process is adsorption whereby chemical species are taken up from the solution and are chemically bound in a monolayer at the oxide water interface. In this study, **adsorption** reactions will be focused.

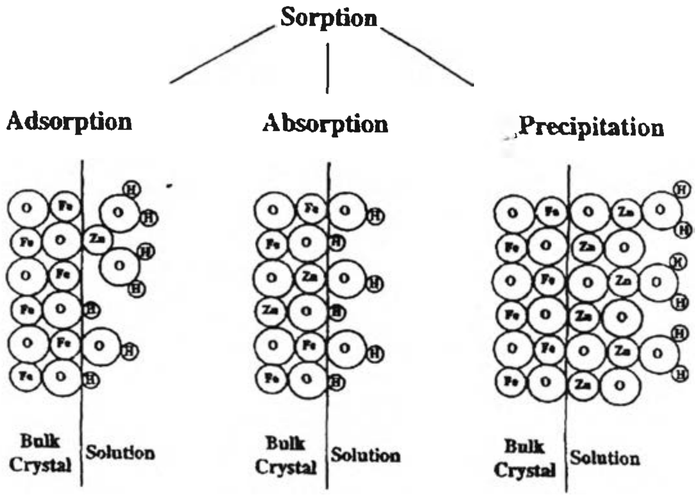


Figure 2.1 Representation of the adsorption,absorption and precipitation of Zn on goethite surface. All three processesare described by the general term sorption.

The adsorption takes place by reactions between the solute species and the mineral surface forming surface complexation. There are two types of adsorption based on atomic arrangement and bonds formed between solute and oxide surface (Figure 2.2). The first type is the inner-sphere complex with ionic or covalent bonds formed. This kind of complex has no water molecules positioned between the mineral surface and the adsorbed species. The second one is the outer-sphere complex whereby the solute species is attached to the mineral surface by electrostatic interaction with water molecules located between the mineral and the solute species.

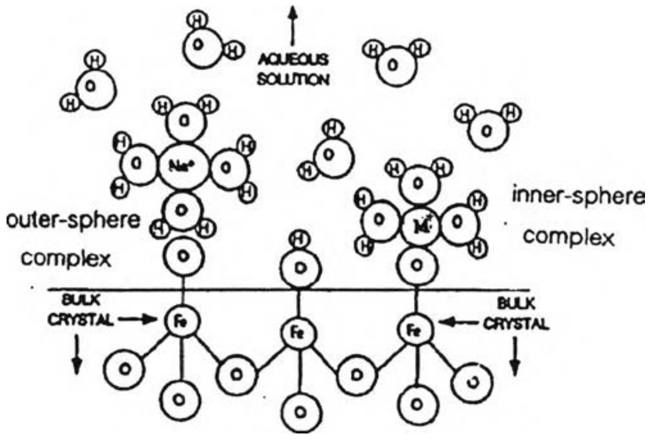


Figure 2.2 Representation of inner-sphere and outer-sphere complexation.

The amount of adsorption depends primarily on the initial concentrations of adsorbate and adsorbent, surface area of mineral, temperature, pressure and the pH of solution which is the most important factor controlling the adsorption. Other factors which can affect the adsorption processes are the ionic strength of the solution and the extent of hydrolysis or complexation of the metal ions.

In the oxide-solution system, the mineral surface, metal ions and complexing ligands (e.g. organic acids or anions) can interact in a number of ways: (1) metal ions and ligands may compete directly for surface sites; (2) metal ions and ligands may influence each other indirectly by altering charges (electrostatic properties) at the oxide-solution interface; (3) non-adsorbing or weakly adsorbing metal-ligand complexes may be formed in solution, thereby reducing adsorption of metal ions; (4) metal-ligand complexes may be adsorbed strongly on the surface (ternary surface complexes), thereby enhancing adsorption of metal ions, ligands or both compared to single sorbated systems.

2.3 Ferric (hydr)oxide : Goethite [6,21,30]

Goethite is a common mineral and abundant in soils that has long been known as having large reactive surface area. In nature, it is decomposed from iron ore such as pyrite or siderite by the oxidation reactions :

$$2FeS_2 + 7.5O_2 + 4H_2O \leftrightarrow Fe_2O_3 + 4H_2SO_4$$

Pyrite Hematite

or

$$2FeCO_3 + 0.5O_2 + 2H_2O \leftrightarrow Fe_2O_3 + 2H_2CO_3$$

Siderite Hematite

then

$$Fe_2O_3 + H_2O \leftrightarrow 2FeOOH$$

Hematite Goethite

Goethite forms a reddish-brown or yellowish-brown surface coating on other less reactive mineral during weathering and hydrothermal alteration. The physical characteristics of goethite are summerized in table 2.1.

Table 2.1 Goethite characteristics

Goethite property	Goethite characteristics
Chemical formula	α-FeOOH*
Empirical formula	Fe^{+3} OOH, -FeOH, ≡FeOH
Composition	62.85% Fe, 36.1% O, 1.13% H
Crystal system	Orthorhombic
Crystal shape	Needles, laths

* The α denotes hexagonal close-packing of O(H) atoms

The crystal of goethite has a size range of 10-100 nm . High resolution transmission electron microscopy and X-ray line broadening show dominant crystal planes of goethite on the surface to be 110 and 021 as shown in figure2.3. The lesser extent planes are 100, 010, and 001.

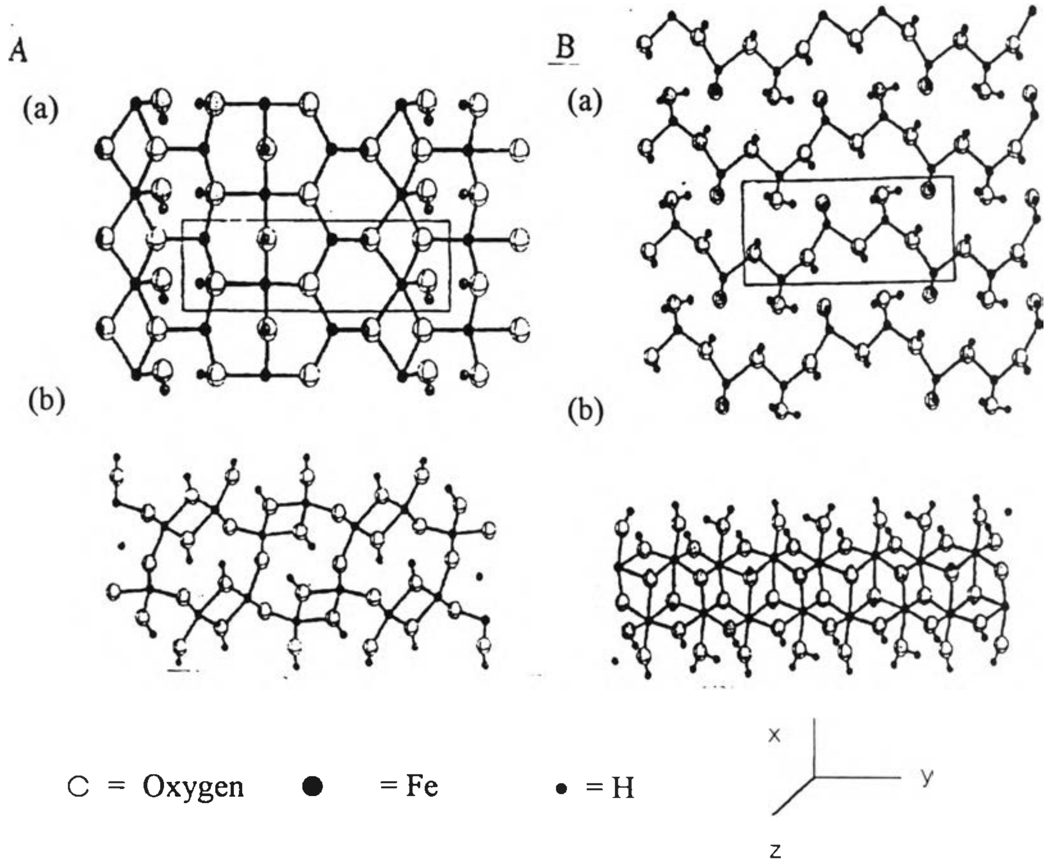


Figure 2.3 A is the 110 surfaces and B is the 021 surfaces.

(a) top view of the surface atoms.

(b) slab viewed perpendicular to the z direction.

From the infrared spectroscopy data,the amphoteric goethite surfaces are likely to be populated by three types of surface hydroxyl groups due to the surface oxygens being coordinated to either one, two or three iron atoms in the bulk. This leads to singly, doubly, and triply coordinated groups, respectively. The singly coordinated groups are the most reactive surface sites capable of undergoing protonation-deprotonation and complexation reactions. While, the doubly and triply coordinated groups are thought to be unreactive and inert. These types of hydroxyl groups are shown in figure 2.4.

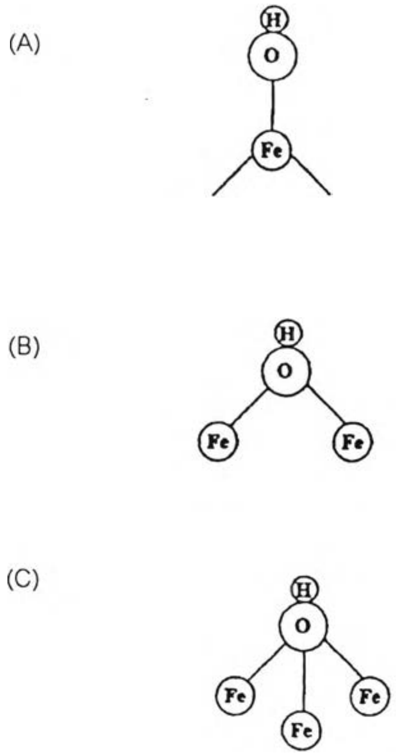


Figure 2.4 Representation of (A) singly, (B) doubly, and(C) triply coordinated surface oxygen atom on goethite.

2.4 Surface Complexation Models [14,29,30]

The adsorption reactions on mineral surface play an important role in controlling the concentrations of most reactive elements in soil and natural water system. In order to understand these reactions in a manner similar to real natural system, various surface complexation models (SCMs) have been developed to describe ion adsorption behaviors on mineral surfaces. Surface complexation models provide molecular descriptions of ion adsorption using equilibrium approach defining surface species, chemical reactions, mass balances and charge balances.

All SCMs share at least four common characteristics [30]. First, it is assumed that mineral surfaces can be described as a flat plane of surface hydroxyl sites. To describe the reactions at these specific sites, for example, the surface ionization reactions can be written as,

$$\equiv XOH_2^+ \rightleftharpoons \equiv XOH^0 + H^+ \qquad : K_1^{app} \qquad (4)$$

$$\equiv XOH^0 \rightleftharpoons \equiv XO^- + H^+ \qquad : K_2^{app} \qquad (5)$$

where K_1^{app} and K_2^{app} are apparent equilibrium constants.

The second assumption is that the reactions at the mineral surfaces may be described using mass law equations, in other word, these reactions are assumed to be in a state of local equilibrium. For reactions (4) and (5), therefore the mass law equations can be written as,

$$K_1^{app} = \frac{\{\equiv XOH^0\}\{H^+\}}{\{\equiv XOH_2^+\}} \qquad (6)$$

$$K_2^{app} = \frac{\{\equiv XO^-\}\{H^+\}}{\{\equiv XOH^0\}} \qquad (7)$$

where { } represents an activity of the species.

The third assumption adopted in all SCMs is that variable charges on the mineral surface are the direct results of chemical reactions occuring at the surface.

Finally, it is also assumed that the apparent equilibrium constant of such a mass law is the product of two terms: a constant 'intrinsic' term corresponding to the chemical free energy of binding to a specific surface site, and a variable 'coulombic' term corresponding to the coulombic free energy of binding contributed by the electrostatic charge at the surface. The surface charge is caused by the ionization of all surface sites, mostly by proton exchange reactions. The distinction of intrinsic constant from apparent constant using coulombic correction factor can be written as,

$$K^{\text{int}} = K^{\text{app}} \exp\left(\frac{\Delta zF\,\psi}{RT}\right) \tag{8}$$

where K^{int} is the intrinsic equilibrium constant, K^{app} is the apparent equilibrium constant, Δz is the net change in charge of the surface species due to the adsorption reactions, F is the Faraday constant, ψ is the electrical potential of the surface, R is the gas constant, and T is the temperature. The mass law of reactions (4) and (5) can thus be separated as,

$$K_1^{\text{int}} = \frac{\{\equiv XOH^0\}\{H^+\}}{\{\equiv XOH_2^+\}}.\exp(-F\psi/RT) = K_1^{\text{app}}.\exp(-F\psi/RT) \tag{9}$$

$$K_2^{\text{int}} = \frac{\{\equiv XO^-\}\{H^+\}}{\{\equiv XOH^0\}}.\exp(-F\psi/RT) = K_2^{\text{app}}.\exp(-F\psi/RT) \tag{10}$$

The surface complexation models differ in the number of layers that are used to represent surface charges, as well as the types of species that are permitted to adsorb in each layer, and the description of the electrical potential profile. Four models of the most commonly employed SCMs are Diffuse Double Layer Model, Constant Capacitance Model, Basic Stern Model, and Triple-Layer Model. These models will be discussed briefly.

In the Diffuse Double Layer and Constant Capacitance Models (figure 2.5), a single surface layer referred to as the 0-layer accepts all adsorbing ions including potential determining ions (H^+ and OH^-). This is accompanied by a diffuse outer layer, called the d-layer. The difference between them is how they relate surface potential (ψ_0) to surface charge (σ_0).

For the Diffuse Double Layer Model:

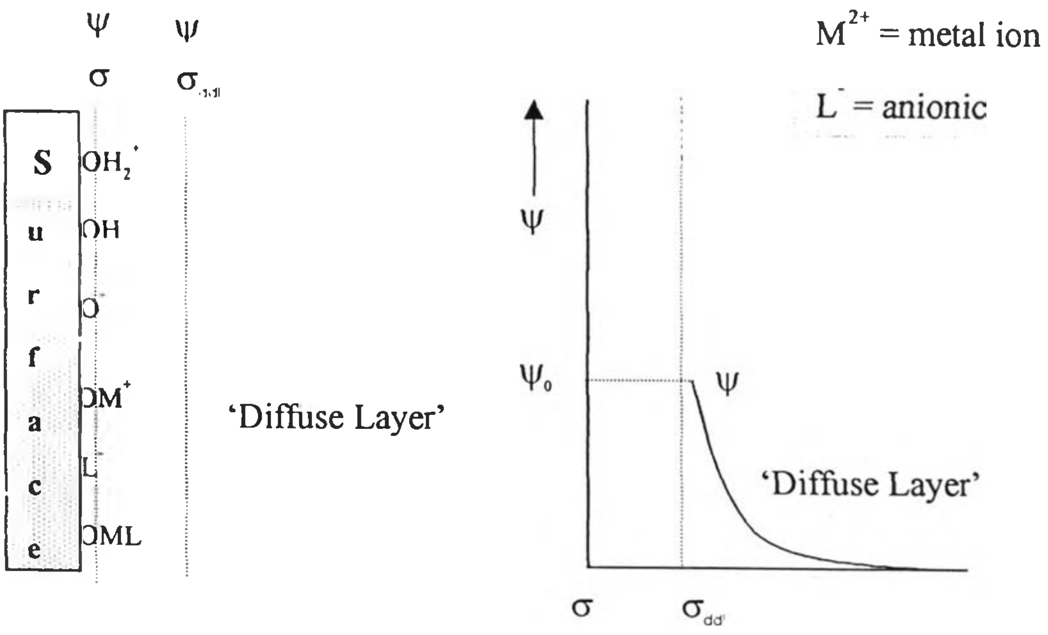
$$T_{\sigma_0} = 0.1174\sqrt{I}\sinh\left(\frac{\Psi_0 F}{2RT}\right)\cdot\frac{A}{F} \tag{11}$$

For the Constant Capacitance Model :

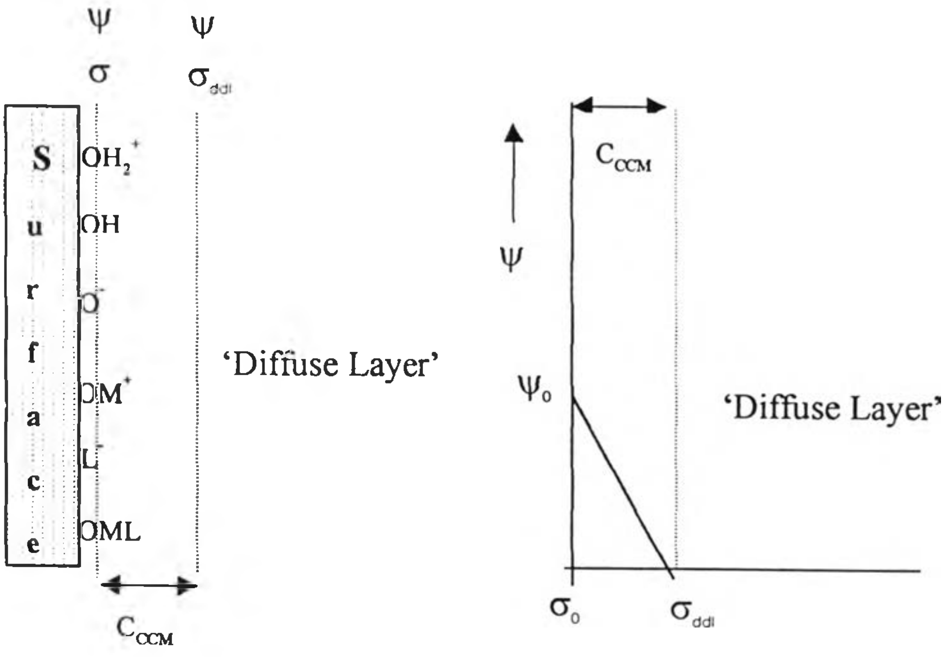
$$T_{\sigma_0} = C\psi_0 \cdot \frac{A}{F} \tag{12}$$

$$\psi_0 = \frac{\sigma_0}{C} \tag{13}$$

where T_{σ_0} is the total charge at 0-layer, I is the ionic strength (mol/L), ψ_0 is the surface potential at 0-plane, A is the total surface area (m^2/g), C is the capacitance, σ_0 is the net surface charge density (C/m^2), T is the temperature (K), F is the Faraday constant (96,485 C/mol) and R is the Gas constant (8.314 J/K-mol) .



(A) Diffuse Double Layer Model



(B) Constant Capacitance Model

Figure 2.5 The schematic illustration of (A) Diffuse Double Layer Model and (B) Constant Capacitance Model.

In the Basic Stern Model (figure 2.6), the interface model is extended with a charge free layer called Stern layer . Stern layer is limited by two electrostatic planes which can be treated as plate condenser. Protons are adsorbed in the surface plane called 0-plane, whereas the specificially adsorbing ions can be located either 0-plane or 1-plane. The electrostatic plane at the head end of the diffuse double layer is called 1-plane. The sum of the charge in the two electrostatic planes ($\sigma_0 + \sigma_1$) is neutralized by the charge in the double layer (σ_{ddl}) according to

$$\sigma_0 + \sigma_1 = -\sigma_{ddl} \tag{14}$$

The value of ψ_{ddl} in the Stern model equals the potential at the outer plane (ψ_1). Because the Stern layer is free of charge, there is a linear relationship between ψ_0 , ψ_1 and σ_0 according to

$$\sigma_0 = C_{Stern} (\psi_0 - \psi_1) \tag{15}$$

where C_{Stern} is the capacitance of the Stern layer

The surface potential (ψ_0) can be related to pH by Nernst'equation, recently used and described in detail by Fokkink and Lyklema [19] as :

$$PZC - pH = \log e . \left(\frac{F}{RT} \psi_0 \right) \tag{16}$$

where PZC is the point of zero charge, log e = 0.43, and ψ_0 is the potential at the surface.

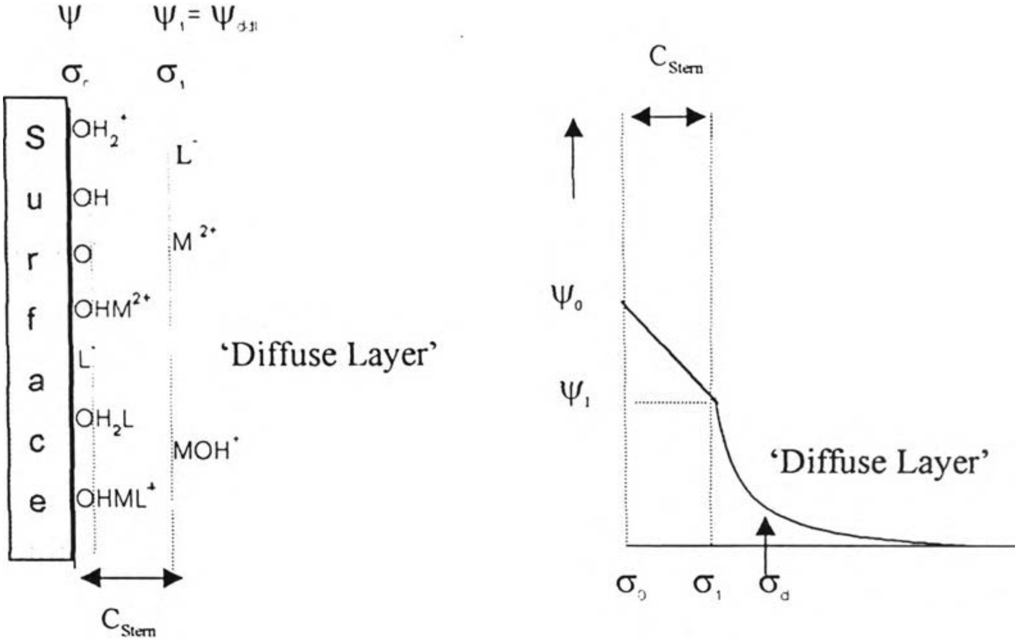


Figure 2.6 The schematic illustration of Basic Stern Model.

In the triple layer model(figure2.7), the adsorbing surface is defined by 2 layers : an inner 0-layer and a middle 1-layer. The outermost diffuse layer is referred to as the d-layer. Protons are located in the surface plane(0-plane). Metal ions can be located in either surface plane or in 1-plane. Ions in background electrolyte are located in 1-plane. Applying the principle of electroneutrality, the sum of the charge in the three electrostatic planes ($\sigma_0 + \sigma_1 + \sigma_2$) is compensated by the charge of the diffuse double layer according to,

$$\sigma_0 + \sigma_1 + \sigma_2 = -\sigma_{ddl} \qquad (17)$$

the relation between the potentials and surface charge (σ_0) is

$$\sigma_0 = C_{inner}(\psi_0 - \psi_1) \quad (18)$$

$$\sigma_0 + \sigma_1 = C_{outer}(\psi_1 - \psi_2) \quad (19)$$

where C_{inner} and C_{outer} are the capacitance of the inner and outer layer, respectively.

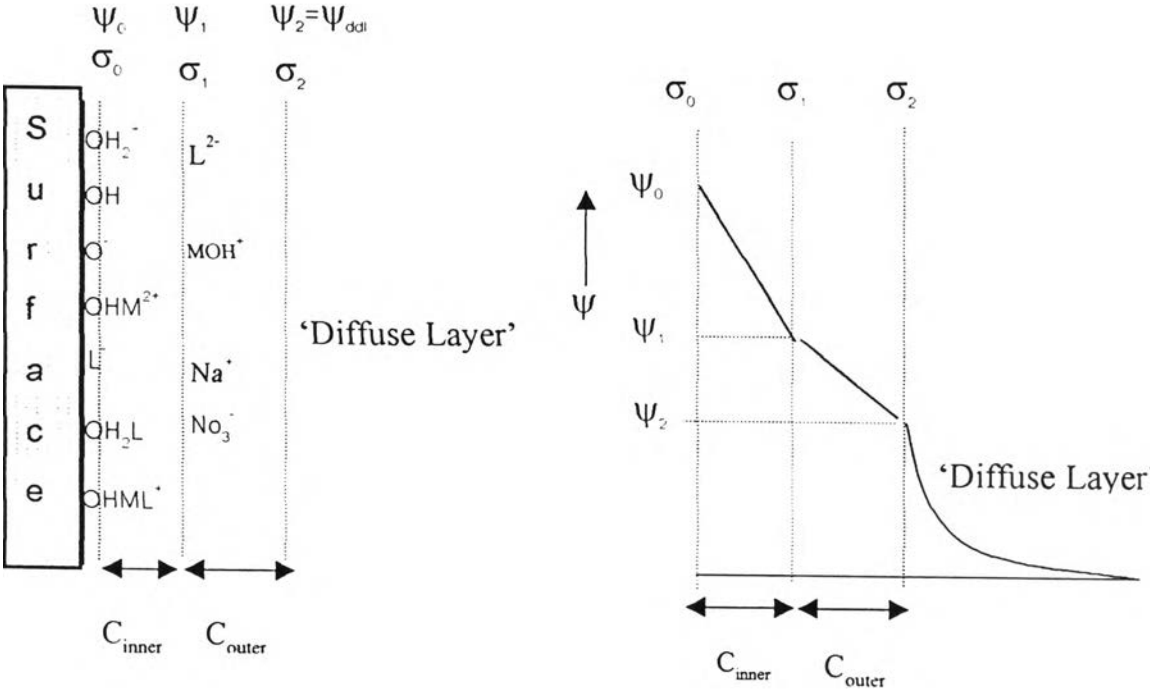


Figure 2.7 The schematic illustration of Triple Layer Model.

2.5 Determination of the Equilibrium Constant : Potentiometry

Potentiometric Titration is the method used to measure the change in potential of the cell during titration. The resulting titration curve shows the relation between the volume of titrant and the measured potential. This method has been used for the determination of equilibrium constants by means of the relationship between the measured potentials and the concentrations of the species in solution, the Nernst's equation:

$$E = E^{0} - \frac{RT}{nF} \ln Q \qquad (20)$$

where E is the measured potential

E^0 is the standard potential at 25 ^{0}C

R is gas constant (8.314Jk^{-1} mol^{-1})

T is the absolute temperature (K)

F is the Faraday constant (96,485 $Cmol^{-1}$)

n is the number of moles of electrons involved in the reaction

Q is the product concentrations of the species in solution

In this study, the glass calomel electrode is used for measuring the concentration of free H^+. The Nernst's equation thus becomes,

$$\begin{aligned} E &= E^0 - \frac{RT}{F}\ln\left[H^+\right] \\ &= E^0 - \left(\frac{RT}{F}\ln 10\right)\log\left[H^+\right] \\ &= E^0 + \left(\frac{RT}{F}\ln 10\right)pH \qquad (21) \end{aligned}$$

which is a linear equation. For complex system, however, a non linear equation of Nernst type is usually employed :

$$E = E^0 + \left(\frac{RT}{F}\ln 10\right)pH + a\frac{1}{H^+} + b\left[H^+\right] \qquad (22)$$

where a, b is the correction factors

The concentrations of species in solution and the protonation-deprotonation constants are related in the following acid-base equilibria,

$$LH + H^+ \rightleftharpoons LH_2^+ \qquad : K_{a1} = \frac{\left[LH_2^+\right]}{\left[LH\right]\left[H^+\right]}$$

$$LH_2^+ + H^+ \rightleftharpoons LH_3^{2+} \qquad : K_{a2} = \frac{\left[LH_3^{2+}\right]}{\left[LH_2^+\right]\left[H^+\right]}$$

$$\vdots \qquad\qquad \vdots \qquad\qquad \vdots$$

$$LH_n^{(n-1)+} + H^+ \rightleftharpoons LH_{n+1}^{n+} \qquad : K_{an} = \frac{\left[LH_{n+1}^{n+}\right]}{\left[LH_n^{(n-1)+}\right]\left[H^+\right]} \qquad (23)$$

Another way of expressing the equilibria relations can be shown as follows

$$LH + H^+ \rightleftharpoons LH_2^+ \qquad : \beta_{a1} = \frac{[LH_2^+]}{[LH][H^+]}$$

$$LH + 2H^+ \rightleftharpoons LH_3^{2+} \qquad : \beta_{a2} = \frac{[LH_3^{2+}]}{[LH][H^+]^2}$$

$$\vdots \qquad \vdots \qquad \vdots$$

$$LH + nH^+ \rightleftharpoons LH_{n+1}^{n+} \qquad \beta_{an} = \frac{[LH_{n+1}^{n+}]}{[LH][H^+]^n} \qquad (24)$$

The K values are called stepwise protonation constants and the β values called the overall or cumulative protonation constants. The mass balance equations for these equilibria can be expressed as,

$$[LH]_T = [LH] + [LH_2^+] + [LH_3^{2+}] + \ldots + [LH_{n+1}^{n+}] \quad \text{and}$$

$$[H]_T = [H] + [LH_2^+] + 2[LH_3^{2+}] + \ldots + n[LH_{n+1}^{n+}] \qquad (25)$$

Similarly, the concentrations of the species in solution and the stability constants for metal(M)-ligand(LH) system can be described by stepwise or overall ligand additions as,

$$M + LH \rightleftharpoons ML + H^+ \qquad : K_1 = \frac{[ML][H^+]}{[M][L]}$$

$$ML + LH \rightleftharpoons ML_2 + H^+ \qquad : K_2 = \frac{[ML_2][H^+]}{[ML][LH]}$$

$$\vdots \qquad \vdots \qquad \vdots$$

$$ML_{n-1} + LH \rightleftharpoons ML_n + H^+ \qquad : K_n = \frac{[ML_n][H^+]}{[ML_{n-1}][LH]} \qquad (26)$$

or

$$M + LH \rightleftharpoons ML + H^+ \quad : \beta_1 = \frac{[ML][H^+]}{[M][L]}$$

$$M + 2LH \rightleftharpoons ML_2 + 2H^+ \quad : \beta_2 = \frac{[ML_2][H^+]^2}{[M][LH]^2}$$

$$\vdots \qquad \vdots \qquad \vdots$$

$$M + nLH \rightleftharpoons ML_n + nH \quad \beta_n = \frac{[ML_n][H^+]^n}{[M][LH]^n} \qquad (27)$$

where

$$\beta_1 = K_1$$

$$\beta_2 = K_1.K_2$$

$$\vdots \qquad \vdots$$

$$\beta_n = K_1.K_2...K_n$$

The K values are stepwise stability constants and the β values are the overall or cumulative stability constants. The mass balance equations for these equilibria can be expressed as,

$$[LH]_T = [LH] + [ML] + [ML_2] + ... + [ML_n]$$

$$[M]_T = [M] + [ML] + [ML_2] + ... + [ML_n] \qquad (28)$$

In the computation process, the $[H^+]$ are calculated from the values of E and E^0 according to equation (22). These values were then used in equations (24) and (27) to determine the equilibrium constants and the species concentrations based on mass balance equations (25)and (28).