# Colloidal Chemistry

## Soil Chemistry (Soil 503)

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# Colloidal Chemistry

- Physical chemistry of soil is essentially a study of the most reactive fractions of soils or the so called colloidal phase

- Colloid size particles play an important role in determining the physical & physico chemical properties and reactions that occur in soils

- Colloidal particles consists of mineral and organic matter intimately associated and held together by various forces

- Under certain circumstances, mineral & organic phases may exist separately

- In general, as the colloidal content increases, soils tend to lose friability to retain more water against loss by drainage and evaporation and to increase storage capacity for plant nutrient elements in the forms available for plant use

# Colloidal properties of soil colloids and clay minerals

**Colloidal sized particles of soil exhibit characteristics of the colloidal state, such as light scattering, osmotic effects and charge**

## Iso electric point (pH) of some soil colloids and the point of minimum migration rates of clay minerals

| Soil colloid/clay mineral | Iso electric pH | pH of minimum migration |
|---|---|---|
| Bentonite | - | 3.10 |
| Kaolinite | - | 3.05 |
| Illite | - | 3.45 |

- Data indicates that colloidal sized particles of clay minerals are never isoelectric, and must be considered as strongly electronegative colloids

- Soil colloids depending on their $SiO_2/R_2O_3$ ratios, have various isoelectric points, which indicates that they are in most cases amphoteric.

- The amphoteric nature of soil colloids is associated with the presence of iron, aluminium and manganese which coat the crystalline nucleus.

# Surface chemistry of soil clays

Clay surfaces can be divided into 3 categories.

1.  Surfaces formed by Si-O-Si linkages(Siloxane) - 2:1 type clays

2. Surfaces formed by O-Al-OH linkages of alumina octahedrons(Oxy-hydroxide surfaces)- 1:1 type clays

3. Surfaces formed by Si-OH or Al-OH of amorphous compounds( Si-OH -Silanol surfaces, Al-OH- Aluminol surfaces)- soils containing large amount of amorphous minerals or allophane.

# Surface areas

The surface area or specific surface area can be measured by two types of methods.

1. Electron microscopy

2. Group of methods based on compounds in the vapour or gas phase.

# Origin of negative charges in soil clays

Soil carry an electronegative charge, which gives rise to cation exchange reactions.

Two major sources are :

## 1. Isomorphous substitution

- Major source of –ve charges in 2:1 layer clays.

- Part of silicon in the tetrahedral layer is subject to replacement of ions of similar size usually, $Al^{3+}$.

- Part of Al in the octahedral sheet may be replaced by $Mg^{2+}$, without disturbing the crystal structure & such a process of replacement is called isomorphous substitution. The resulting –ve charge is considered a permanent charge since it will not change with changing pH.

## 2. Dissociation of exposed hydroxyl groups (pH dependent charge)

- **Appearance of OH groups on crystal edges or on exposed planes can also give rise to –ve charges.**

- **At high pH, hydrogen of these hydroxyls dissociates slightly and the surface of the clay is left with –ve charge of the oxygen ions & this type of –ve charge is called variable or pH dependent charge.**

- **Magnitude of the variable charge varies with pH and type of colloid.**

- **It is important type of charge for 1: 1 layer, iron and aluminium oxide clays and organic colloids.**

# Positive charges and zero point of charge

- Soil colloids may also exhibit +ve charges as well as –ve charges

- +ve charges make possible anion exchange reactions and are very important in $PO_4$ retention. These charges are thought to arise from protonation or addition of H+ ions to hydroxyl groups

- This mechanism depends on pH and the valence of the metal ions

- It is usually of significance in Al and Fe oxide clays, but it is of lesser importance in Si-oxides. For ex. Gibbsite is +vely charged at pH 7.0 or at lower pH.

- Gibbsite and other soil colloids may be characterised by a particular pH at which the surface charge is electrically neutral. This point or pH value is called zero point of charge $pH_0$ .

- At pH values above $pH_0$, the colloid is –vely charged. At pH values below $pH_0$, the colloid is positively charged.

# Surface potential

- If the H+ and OH- are the potential determining ions of reversible interfaces, adsorption of protons produces positive charge surfaces, whereas adsorption of OH$^-$ yields – ve charges.

These reactions can be summarised in the following relationship(Gast, 1977 ; Van Raij & Peech, 1972):

$$- Al\text{-}OH\ 0.5 + H^+ \rightleftharpoons -Al\text{-}OH\ ^{0.5}_2$$
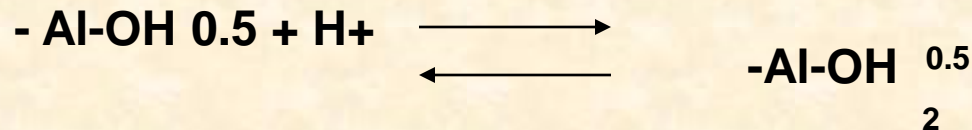
- This relationship of course dependent on pH, while at $pH_0$ (ZPC) in order to maintain electro neutrality, the amount of + ve charges must be equal to that of – ve charges.

- Because of the presence of opposite charges on the colloid surface and in the liquid interface, called the surface potential. The magnitude of the surface potential is given by the Nernst equation :

$$\Psi = \dfrac{RT}{nF} \ \ln \ \dfrac{(H^+)}{(H^+)_{ZPC}}$$

**Changing into common log gives**

$$\Psi = 0.059 \left[ \log (H^+) - \log (H^+) \right]_{ZPC}$$

(or)

$$\Psi = 0.059 \ (ZPC\text{-}pH) \ \text{Volts at } 25^0 \ C$$

# Electrical Double Layer

- **Because of the presence of an electronegative charge, clay in suspension can attract cations.**

- **These positively charged ions are not distributed uniformly throughout the dispersion medium.**

- **They are held on or near the clay surface.**

- **Some are free to exchange with other cations.**

- **The –ve charge of the clay surface is thus screened by an equivalent swarm of counter ions that are positive.**

- **-ve charge on the clay surface and the swarm of positive counter ions are called the electric double layer.**

- **First layer of the double layer is formed by the charge on the surface of the clay.**

- **Technically the charge is a localized point charge & however we consider this charge to be distributed uniformly over the clay surface**

- **Second layer of the double layer is in the liquid layer adjacent to the clay surface.**

- **-ve counter ions in this zone are attracted to the clay surface, but at the same time they are free to distribute themselves evenly throughout the solution phase**

- **Two processes will come to equilibrium, and the resulting distribution zone is like the distribution of gas molecules in the earth's atmosphere.**

## Helmholtz Double layer theory

- One of the oldest theories

- -ve charge on the colloid is considered to be evenly distributed over the surface(charge density Φ)

- Total counter charge in the second layer is concentrated in a plane parallel to the surface at distance x.

- If the medium has a dielectric constant D, then the electro kinetic potential is the same as the total potential

$$\Psi = \frac{4\pi\Phi x}{D}$$

Electrochemical potential is maximum at the colloid surface and drops linearly at locations with increasing distance (x) from the surface within the double layer

Clay

Soil solution

Ψ

Ψ =0

Distance

Line represents the potential distribution with distance
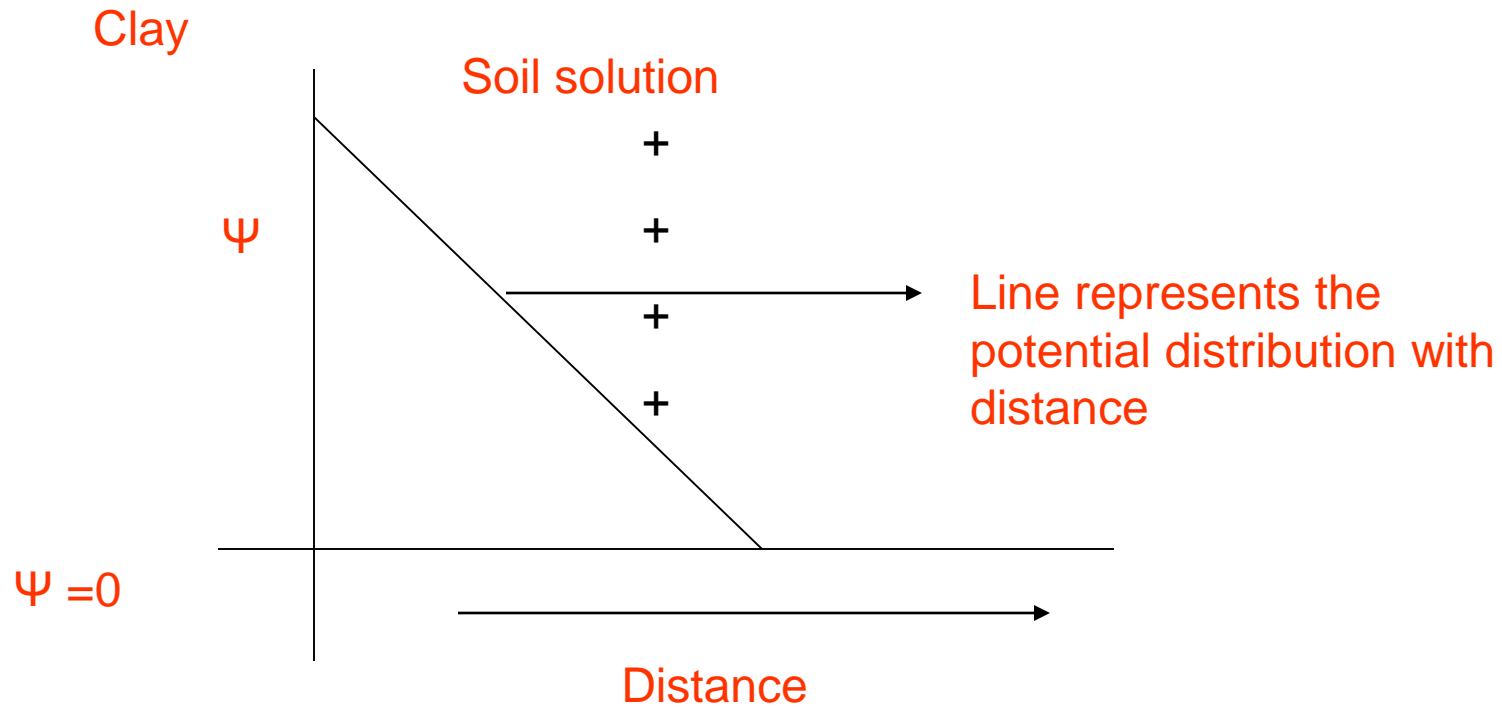
# Gouy-Chapman Double layer theory

- -ve charge is again considered to be distributed evenly over the colloid surface

- However, the counter ions are dispersed in the liquid layer as in the case of gas molecules in the earth atmosphere

- This theory is also called the diffuse double layer theory of Gouy and Chapman

**Concentration distribution in the liquid zone follows the Boltzmann equation :**

$$Cx = C^o_x \exp(-ze\Psi / kT)$$

**Where**

$C_x$ = Concentration of cations at distance x from surface
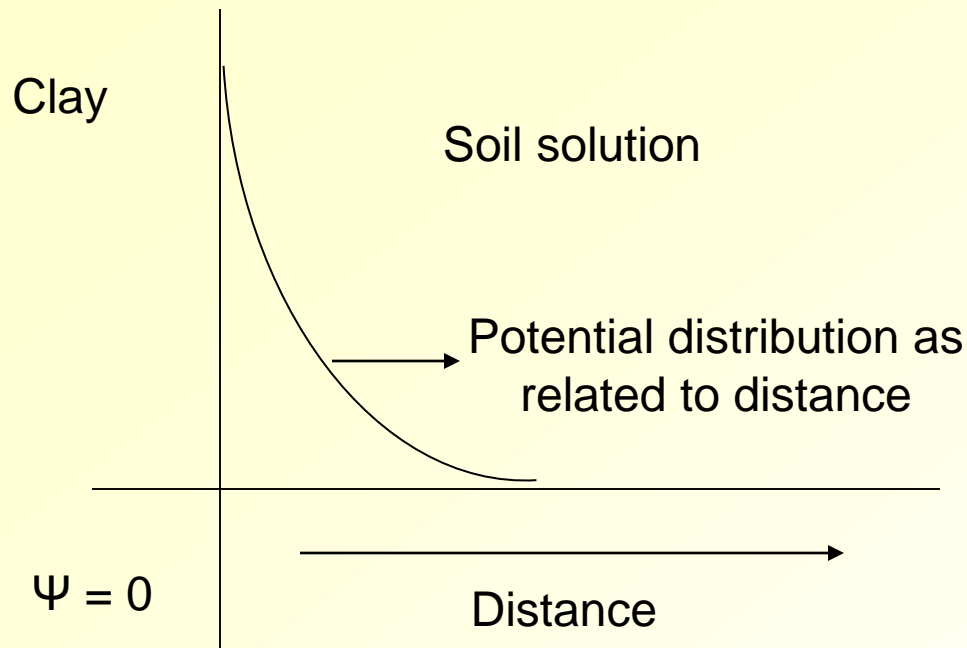
$C^O_X$ = Concentration of cations in the bulk solution

z    =  valence

e    =  electronic charge

$\Psi$    =  electrical potential

k    =  Boltzmann constant

T    = absolute temperature

Clay

Soil solution

Potential distribution as related to distance

$\Psi = 0$

Distance

**Because of the attraction by the –vely charged surface, cations in the soil solution phase tend to distribute themselves over the colloid surface so that electroneutrality is maintained, while the tendency for these ions to diffuse away is counteracted by Van der waals attracation**

Deficit of anions is usually present in the liquid interphase, and the total charge of the surface is considered to be balanced by excess cations.

Initial electric potential at the colloid surface is maximum and decreases exponentially with distance from the surface as follows:

$$\Psi_x = \Psi_o \exp(-K_x)$$

Where

$\Psi x$ = electric potential at distance x

$\Psi o$ = surface potential

K = constant associated with concentration, valence of ions, dielectric constant and temperature

**At room temperature,**

$$K = 3 \times 10^7 \, z^{\pm} \, \sqrt{C}$$

**Where**

**Z = valence of the ion**

**C = conc. of the bulk solution in moles/lit.**

# Limitations of Gouy-Chapman Diffuse Double layer theory

- **Gouy-Chapman Diffuse Double layer theory was developed by Guoy(1910) and Chapman(1913) for the application on flat surfaces, but it may apply equally to rounded or spherical surfaces.**

- **-ve charge was considered to be evenly distributed over the surface.**

- **Since the counter ions are assumed to be point charges, and therefore occupy no spaces, they may reach excessively high conc. at the liquid interface.**

- **Modification to this theory was given by Stern(1924) - who stated that ions of finite sizes cannot approach the colloidal surface more closely than allowed by their effective radii.**

# Stern Double Layer theory

- **Stern made corrections in the double layer theory by taking into consideration the ionic dimensions.**

- **Influence of ionic dimension is greatest near the colloid.**

- **In the Stern theory, the first layer is similar to that of previous theories.**

- **However, the second layer is divided into :**

1. **a sub layer nearest the colloid surface**
2. **a diffuse layer**
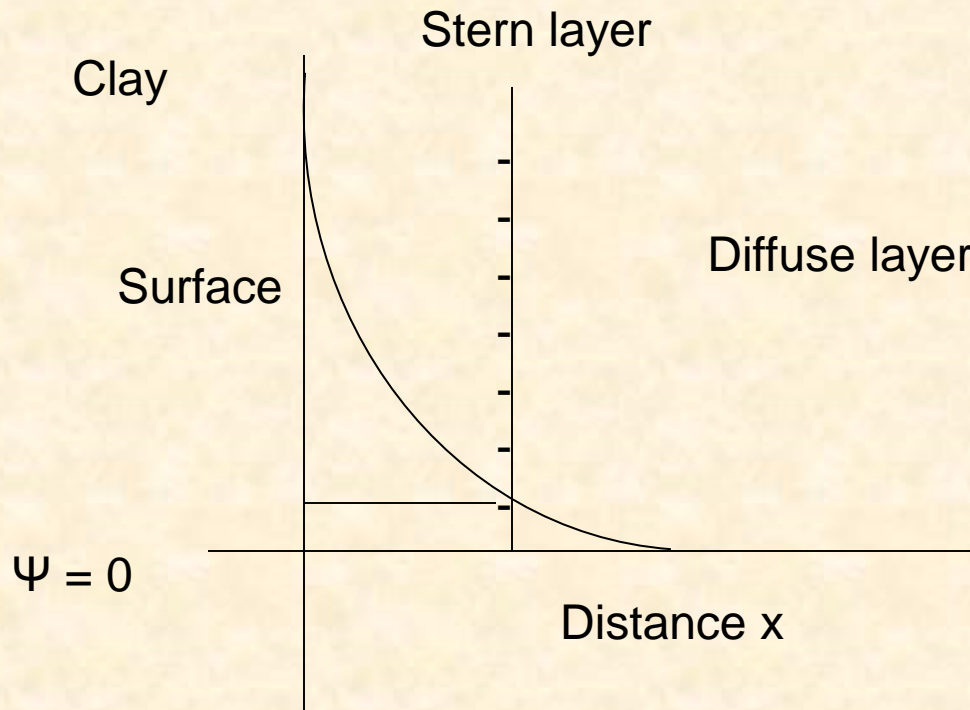
- **First sub layer is tightly packed with cations, and is called the stern layer. The potential distribution appears to be a combination of the Helmholtz and Gouy-Chapman diffuse layer. The decrease in potential is also divided into two parts :**

- **In the stern layer, potential decrease with distance from the surface according to Helmholz theory**

- **From in the diffuse layer, the decrease in potential with distance follows the Gouy-Chapman theory**

# Effect of electrolytes on the thickness of Diffuse Double layer

| Electrolyte concentration (mol/l) | Thickness of diffuse double layer (cm) | |
|---|---|---|
| | Monovalent ions | Divalent ions |
| $1 \times 10^{-5}$ | $1 \times 10^{-5}$ | $0.5 \times 10^{-5}$ |
| $1 \times 10^{-3}$ | $1 \times 10^{-6}$ | $0.5 \times 10^{-6}$ |
| $1 \times 10^{-1}$ | $1 \times 10^{-7}$ | $0.5 \times 10^{-7}$ |

# Effect of valency of cations on the thickness of Diffuse Double Layer

- Thickness of Double layer is also affected by the valency of the exchangeable cations.

- Monovalent cations in exchange position yield thicker diffuse double layer than divalent cations

- Trivalent cations will decrease the thickness strongly than divalent ions.

- This is due to the tendency of ions to diffuse away from the colloidal surface being the order :

- Monovalent ions > Divalent ions > trivalent ions

- Na and K ions – responsible for thicker double layer than Ca & Mg.

- Double layers formed by Al ions are the thinnest.

## Zeta potential

- When a colloidal suspension is placed in an electric field, the colloidal particles move in one direction (towards positive pole). The counter ions move into another direction (towards – ve pole)

- The electric potential developed at the solid-liquid interface is called the zeta potential.

- The seat of zeta potential is shearing plane or slipping plane between the bulk liquid and an envelope of water moving with the particle.

- Since the position of the shearing plane is not known, the potential represents the electric at an unknown distance from the colloidal surface.

- Van Olphen(1977) stated that zeta potential is not equal to the surface potential. It is less than the electrochemical potential on the colloid. Perhaps, it is comparable with the Stern potential.

**Effect of Electrolytes on zeta potential**

- Thickness of the double layer affects the zeta potential

- Increasing the electrolyte conc. results in decreasing the thickness of the double layer

- Compression of double layer will also occur by increasing the valence of ions in the solution.

- Zeta potential decreases with increasing electrolyte conc.

- It reaches the critical value, at the point at which the zeta potential equals zero & this point is called iso electric point.

- At the iso electric point, double layer is very thin and particle repulsive forces are at a minimum.

- At and below this point, repulsion would no longer be strong enough to prevent flocculation of colloidal particles.

- Zeta potential is not a unique property of soil colloid, but depends on the surface potential of the clay particle.

It is determined from the electrophoretic mobility of the suspension using the formula

$$V_e = \frac{D \pounds E}{4 \pi \eta}$$

Where

Ve  = eletrokinetic velocity

D  = Dielectric constant

E  = Applied emf

η  = Viscosity of the fluid