

## EXCHANGE REACTIONS IN SOILS

We have already demonstrated that soil colloids exhibit charges at the mineral surface, which arise from structural defects and protonation reactions. Since charge balance must be maintained counter ions of opposite charge satisfy most of the surface charges. The interaction varies from covalent bonding (specific adsorption) to weak electrostatic interactions. Ions attracted by weak electrostatic interactions can be replaced by other similarly charged ions. This process of stoichiometric replacement has been termed exchange. Interaction of positive ions is called cation exchange and conversely, negatively charged ions participate in anion exchange.

Exchange reactions are rapid, if the site is solution accessible, stoichiometric, reversible, and exhibits preferences (selectivity) among ions of differing charge and size. This section details the exchange process. Stronger covalent interactions will be covered in the adsorption section.

Since exchange is a chemical reaction, it can be treated like any other mass action expression and an equilibrium constant can be defined for the reaction. The equilibrium expression  $K$  has been named the selectivity coefficient, exchange coefficient and other terms.

For the reaction:  $AX + B \rightleftharpoons BX + A$

We may define the following selectivity coefficient:

$$\text{Selectivity coefficient} = K_B^A = \frac{(BX)(A)}{(AX)(B)}$$

If the value of the selectivity coefficient is  $>1$ , this implies that B is preferred over A and if  $K < 1$  then A is preferred over B. There are several reasons that one ion may be more strongly attracted to the surface than another ion.

### ION EXCHANGE SELECTIVITY

The following is a discussion of some of the reasons for differential preference.

**VALENCE** - The general rule is that the exchanger prefers the ion of higher valence (more properly, the charge on the ion). However, we will see later that under some conditions, this rule can be violated.

**ION SOLVATION** - The exchanger will prefer the ion that is less solvated with water molecules. This rule also takes the form of the "lyotropic series". Another formulation is that the exchanger will prefer an ion which is a (water) structure "breaker" over one which is a structure "maker".

**CHELATION BY EXCHANGER** - Some exchangers such as proteins, humates, fulvates and polyuronides have vicinal functional groups that can form a multidentate complex with ions. Since divalent (and higher valent) ions generally form chelate structures whereas monovalent ions do not, the above environmental materials are likely to show additional preference for higher valent ions.

**van der WAAL'S FORCES** - The exchanger will prefer the ion with the greater number of "exposed" atoms which can form dipole-induced dipole attractive forces between the exchanger and the ion. An example of this is the inability of mineral salts to displace polynuclear aluminum hydroxides from the interlayer of smectites and vermiculites.

**SIEVE ACTION BY EXCHANGER** - Zeolites are aluminosilicate exchangers with internal channels of sizes that permit small ions to enter but which exclude larger ions.

### **The Exchange Process**

A number of expressions have been proposed to quantitatively describe the equilibrium between ions in bulk solution (pore water) and ions in aqueous solution immediately adjacent to charged colloid surface (interface). The first type is referred to as "solution phase" ions that are no different in concept from ions that have come into solution from dissolution of salts while the second type is called "exchangeable" ions. Some of these types of ions are thought to be loosely bound to the surface by forces in addition to electrostatic forces while others are clearly dissociated from the surface and fully hydrated but still held in the area by electrostatic forces. We will learn later that the boundary between the exchange "phase" in solution and the "solution" is not sharp or distinct; hence the term diffuse layer to describe the zone in solution which includes all of the exchange ions. Although there is a distressing vagueness to this general picture, we use a pragmatic experimental approach which says that solution phase composition for a column of soil or sediment in a cylinder is the salt composition of an aqueous solution that passes into the top of the column and exits the bottom of the column without change. By definition, the exchange phase is at equilibrium with a solution of exactly known ionic composition. Next, we extract all of the pore water (including its salt) as well as all the exchangeable ions. By subtracting the quantity of salt ions from the total quantity of ions, the quantity of exchange ions in the sample is estimated. Obviously, this simple approach assumes there is one type of charge in the sample, cation exchange capacity or anion exchange capacity but not both.

Solution phase ion activities are expressed as usual:

$$(Ca^{2+}) - \text{Calcium ion activity} = \gamma_{Ca}[Ca^{2+}].$$

where  $\gamma_{Ca}$  = the activity coefficient of calcium ion in that particular solution and  $[Ca^{2+}]$  = the concentration of free calcium ion in solution.

Many different nomenclature conventions are used throughout the literature to represent the exchange phase composition in equilibrium expressions:

$$\bar{C}_a, CaX, Ca_x, Ca\text{-Clay}$$

In addition to these obvious but unimportant differences, one must be careful to note that different expressions have quite different dimensions. For instance, the selectivity coefficient of Helfferich ( $K_B^A$ ), includes terms for A and B in dimensions of moles A (and B) per liter of exchange phase fluid. It is fairly easy to estimate the volume of water inside a bead of swollen synthetic organic resin exchanger, and since most of the exchange capacity (the sum of the functional groups) of the bead is inside the bead, it is possible in this special exchanger to express AX (or BX) in the dimensions given above. Obviously, it is very difficult unless one makes some very arbitrary assumptions to estimate (in a soil-water system) an exchange phase fluid volume. When estimated, this volume is sometimes termed an "exclusion volume", again because salt is virtually excluded from this zone of water in the pores. Note in the selectivity coefficient expression, values of AX and [A] are both given in moles per liter but the exchange solution is a different compartment than the salt solution compartment (pore water). In making measurements on real columns of resin bead exchangers, the total volume of water inside all the beads in the column,  $V_{BT}$  is likely to be different from the total volume of all the water in the pores,  $V_{PT}$  between the beads. In order to calculate [A], one uses a chemical estimate of the total quantity of salt A,  $Q_A$ , and  $V_{PT}$ :

$$[A] = Q_A/V_{PT}.$$

Note that later in the simplified dynamic exchanger model, Farmer Fillipi, we make the assumption that  $V_{PT} = V_{BT}$ .

This difficulty (knowing  $V_{BT}$ ) is eliminated by the Vanselow convention which uses the mole fractions of the ions in the exchanger,  $N_A$  and  $N_B$ , as the representing dimensions:

$$N_A = \frac{Q_A}{Q_A + Q_B}$$

This does introduce another minor difficulty when the valences of the two ions,  $z_A$  and  $z_B$  are not equal because the total exchange capacity in the column, CEC, in dimensions of equivalents is:

$$\text{CEC} = z_A Q_A + z_B Q_B$$

Therefore, when  $z_A \neq z_B$ ,  $Q_A + Q_B \neq \text{constant}$  at different  $Q_A/Q_B$ , even when CEC is constant.

Following are statements and definitions about some of the exchange expressions that have been proposed. Their relative quality has been or can be Judged on two bases. Some expressions are preferred by chemists because they have a solid basis in thermodynamics, *i.e.*, they can be derived by formal chemical thermodynamic arguments very similar to those invoked to derive expressions for acid-base dissociation, ion-pair formation, chelation, complex formation, or solubility "products". (It is not expected at the level of this class that the student has knowledge of chemical thermodynamic theory, but it is expected that you have already had some experience with the working expressions derived from thermodynamics for these equilibria.)

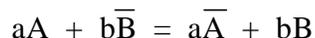
A second criteria used to judge quality of an expression is the degree to which the expression describes equilibria over a wide range of chemical compositional space, *i.e.*

$$\text{from } Q_A/(Q_A + Q_B) \sim 0 \text{ to } Q_A/(Q_A + Q_B) \sim 1.$$

None of the expressions given below are really good when judged on both criteria simultaneously. From a practical standpoint, the second criterion is certainly the most important.

## THERMODYNAMIC EXPRESSIONS

A general stoichiometric reaction is.



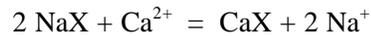
(Note: this does not give the valences of A and B but the integer values of (a) and (b) are based on the integer values of these valences. The main reason we write the above expression is to see what the values of (a) and (b) should be and it is not important whether the expression is written as above or from right to left with  $\bar{A}$  and  $B$  as "reactants" rather than as "products".)

The equilibrium thermodynamic expression is:

$$K = \frac{(\bar{A})^a (\bar{B})^b}{(\bar{B})^b (\bar{A})^a}$$

where ( ) = activity of the ion in the phase.

A specific example of monovalent-divalent cation exchange in soil represented by the symbol X is:



$$K = \frac{(\text{CaX})(\text{Na}^+)^2}{(\text{NaX})^2 (\text{Ca}^{2+})}$$

Note that the thermodynamic  $K$  has no subscripts or superscripts. Also note that the activity of the participant ions can be calculated with standard techniques using total concentrations of the free ions and the ionic strength of the solution. However, there are no generally accepted techniques to calculate the activity coefficients of ions in the exchanger phase,  $\bar{g}$ , so that for example:

$$(\bar{A}) = \bar{g} [ \bar{A} ]$$

One of the first suggestions to deal with this problem was that of Vanselow who suggested that mole fraction,  $N_i$ , of an ion in the exchange phase might be proportional to activity in the exchange phase by analogy with the known behavior of two different elements in solid solutions such as copper and zinc in brass. Thus.

$$(\bar{A}) = \bar{g}_A N_A$$

where

$$N_A = \frac{Q_A}{Q_A + Q_B}$$

Without calculating the  $\bar{g}$ 's, the Vanselow exchange coefficient,  $K_V$ , is given by:

$$K_V = \frac{N_A^a (B)^b}{N_B^b (A)^a}$$

Therefore,

$$K = \frac{\bar{g}_A^a}{\bar{g}_B^b} K_V$$

For the specific case of Na-Ca exchange:

$$K_V = \frac{N_{Ca} (\text{Na}^+)^2}{N_{Na}^2 (\text{Ca}^{2+})}$$

Initially, it was probably hoped that  $K_V$  would be relatively constant at different values of the ratio  $\frac{(B)^b}{(A)^a}$ . This turned out to be true but only over narrow ranges of the ratio. Therefore, one would expect this

to be the death of the Vanselow expression. It was not, for two reasons. First, a mole fraction is an easy parameter to calculate from experimental data because it does not involve the additional uncertainty of the value of  $V_{PT}$  in a given system. Second, Gaines and Thomas developed a theory based on further thermodynamic

arguments that lead to the estimation of  $K$  from many measurements of  $K_v$  at many selected experimental values of  $\frac{(B)^b}{(A)^a}$ . We will not study this theory because even though we may know  $K$  for a particular sample of a soil or a sediment, it is not possible to use  $K$  to predict the exchange behavior of that material in the field without also knowing each of the exchange phase activity coefficients as functions of exchange phase composition. The cost of doing this for a soil profile by standard techniques would be exorbitant. Sparks details the methods of deriving  $K$  from  $K_v$  because the theoretical applications of exchange equations are problematic, less rigorous formulations have been developed to describe cation exchange in soils.

### Empirical or Semi-Theoretical Expressions

#### 1. Gapon.

$$K_G = \frac{[Ca_{1/2}X] [Na^+]}{[NaX] [Ca^{2+}]^{0.5}}$$

As ordinarily applied, the cation concentrations in solution are inserted in dimensions of mmol/L (concentration, not activity), while the exchange composition is inserted in dimensions of meq/100 g of sample. Note that the expression includes both exchangeable sodium and exchangeable calcium with a unitary exponent. This equation was adopted by workers at the USDA Salinity Laboratory at Riverside, California to describe the exchange behavior of Western United States soils. They then collected many soils with a variety of salinity and Na-Ca-Mg compositions. Soluble and exchange ion compositions of each were measured. Then, the data were plotted with  $NaX/(CaX + MgX)$  on the Y-axis and  $(Na^+)/(Ca^{2+} + Mg^{2+})^{0.5}$  on the X-axis. The parameter on the Y-axis was dubbed Exchangeable Sodium Ratio (ESR) while that on the X-axis was called the Sodium Adsorption Ratio (SAR). The "best" straight line was fitted through the data graphically giving the equation:

$$ESR = - 0.01 + 0.015 (SAR)$$

This expression is sometimes called the statistical regression equation (see Agricultural Handbook No. 60.). Note that the slope  $\sim 1/K_G$  and that this form is tantamount to assuming that

$$K = 1 = \frac{CaX [Mg^{2+}]}{MgX [Ca^{2+}]}$$

The equation applies reasonably well to saline or saline-alkali soils dominated by smectite clay minerals, but should not be applied without calibration to variable charge soils.

There are a number of other exchange equations in the literature that have been used to describe cation exchange in soils. However, the discussion above will suffice to introduce you to the concept of exchange equations and selectivity. Application of exchange equations to soil systems produce some interesting results in relation of changes in soil moisture, and salt levels.

### Dilution (or alternatively, desiccation)

Lets calculate the effect of changing salt level (dilution or desiccation) on composition of the exchange and solution phase.

**Assume:**

1.  $K_v = 1 = \text{constant} = \frac{N_{Ca} (Na^+)^2}{N_{Na}^2 (Ca^{2+})}$
2. **ESP** = % of exchange phase occupied by  $Na^+$ .  
**E<sub>Ca</sub>P** = % of exchange phase occupied by  $Ca^{2+}$ .
3. **All ? = 1**

Solution phase ( $Ca^{2+}$ )/( $Na^+$ )	ESP	Exchange phase E <sub>Ca</sub> P
.001/.001	1.58	98.4
.01/.01	4.99	95.0
0.1/0.1	15.6	84.4
1.0/1.0	44.7	55.3
10/10	84.5	15.5

The result is that exchangeable sodium percentage is not constant. The exchanges shows increasing preference for the lower valent ion as the concentration of both ions increase. The phenomenon has been formalized by Schofield as the "Ratio Law".

### Exchange Composition During Desiccation of Solution Phase.

The following graphs were constructed from calculations resulting from the following models, assumptions and protocol:

1. Initially the soil is saturated at  $\theta = 0.385$  L H<sub>2</sub>O/kg soil. This solution is considered to have two different initial compositions ( $m_i$ ):
  - a. Case 1.  $[\text{Na}^+] = [\text{Ca}^{2+}] = 0.005$  moles/L =  $m_i$
  - b. Case 2.  $[\text{Na}^+] = [\text{Ca}^{2+}] = 0.015$  moles/L =  $m_i$ .
2. The exchange equation used is that due to Vanselow arranged in the following form:

$$\frac{[\text{Ca}_X + \text{Na}_X] (\text{Na}^+)^2}{[\text{Na}_X]^2 (\text{Ca}^{2+})} = K_v$$

where:

$(\text{Na}^+) =$  moles Na<sup>+</sup>/L solution phase

$(\text{Ca}^{2+}) =$  moles Ca<sup>2+</sup>/L solution phase

$[\text{Ca}_X] =$  moles Ca<sup>2+</sup> in the exchange phase / kg O.D. soil

$[\text{Na}_X] =$  moles Na<sup>+</sup> in the exchange phase / kg O.D. soil

- a. Two cases are considered:
  1.  $K_v = 1$
  2.  $K_v = 5$ .
3. Exchange capacity of the soil is constant at 150 mmol (+)/kg O.D. soil.
4. After the first computation is performed at  $\theta = 0.385$ , the soil is dried without gain or loss of electrolyte from the system.
5. One special case is considered where  $K_v = 1$ ,  $m_i = 0.015$ , but where the concentration of Ca<sup>2+</sup> in solution remains constant during drying due to the precipitation of gypsum.
6. Two parameters are calculated during the drying process which are defined as:
  - a.  $f_{\text{Na}}$  in solution = equivalent fraction of Na<sup>+</sup> in solution

$$f_{\text{Na}} = \frac{(\text{Na}^+)}{2 (\text{Ca}^{2+}) + (\text{Na}^+)}$$

- b.  $f_{\text{NaX}}$  - equivalent fraction of Na in exchange phase

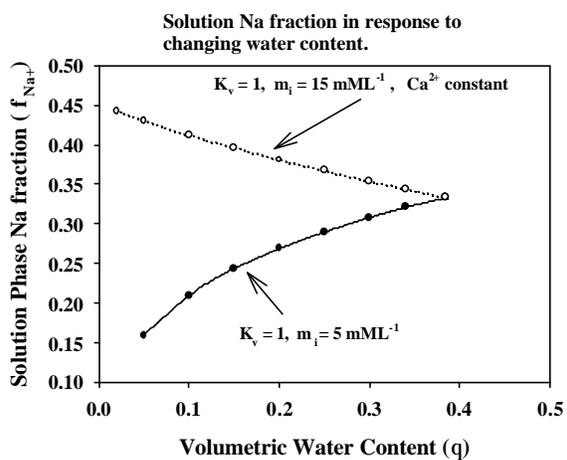
$$f_{\text{NaX}} = \frac{(\text{Na}_X)}{2 (\text{Ca}_X) + (\text{Na}_X)}$$

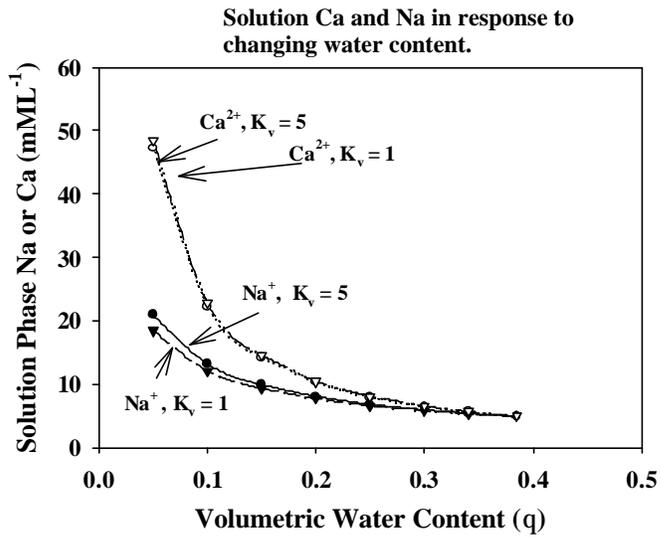
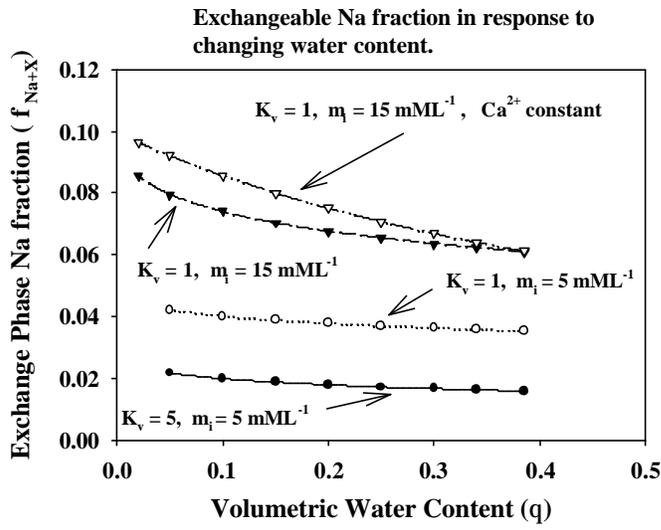
Calculated changes in exchanger and solution phases during *in situ* drying.

$K_v = 5$ $Ca_i^{2+} = Na_i^+ = 0.005$					$K_v = 1$ $Ca_i^{2+} = Na_i^+ = 0.005$			
?	$Na^+$	$Ca^{2+}$	$f_{Na^+}$	$f_{NaX}$	$Na^+$	$Ca^{2+}$	$f_{Na^+}$	$f_{NaX}$
0.385	.00500	.00500	.333	.0158	.00500	.00500	.333	.0353
0.340	.00549	.00575	.323	.0162	.00545	.00577	.321	.0358
0.300	.00603	.00661	.313	.0166	.00593	.00666	.308	.0363
0.250	.00690	.00810	.299	.0171	.00671	.00820	.290	.0370
0.200	.00812	.01040	.281	.0178	.00778	.01050	.269	.0378
0.150	.00997	.01430	.259	.0187	.00940	.01460	.244	.0388
0.100	.01320	.02230	.229	.0198	.01210	.02280	.210	.0401
0.050	.02100	.04720	.182	.0216	.01850	.04850	.160	.0420

$K_v = 1$ $Ca^{2+} = 0.015 = \text{constant}$ $Na_i^+ = 0.015$					$K_v = 1$ $Ca_i^{2+} = Na_i^+ = 0.015$			
?	$Na^+$	$Ca^{2+}$	$f_{Na^+}$	$f_{NaX}$	$Na^+$	$Ca^{2+}$	$f_{Na^+}$	$f_{NaX}$
0.385	.0150	.015	.333	.0611	.0150	.0150	.333	.0611
0.340	.0157	.015	.344	.0640	.0164	.0173	.322	.0624
0.300	.0164	.015	.354	.0668	.0180	.0199	.311	.0636
0.250	.0174	.015	.367	.0707	.0205	.0244	.296	.0655
0.200	.0184	.015	.381	.0750	.0240	.0313	.277	.0676
0.150	.0197	.015	.396	.0800	.0293	.0431	.254	.0703
0.100	.0210	.015	.412	.0856	.0385	.0674	.222	.0740
0.050	.0227	.015	.43	.092	.0604	.1430	.174	.0795
0.020	.0237	.015	.442	.0965	.106	.3800	.122	.0855





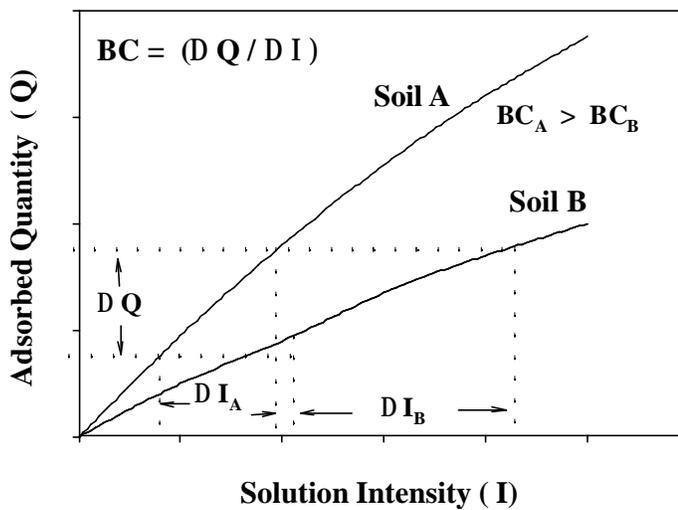
**BECKETT - Q/I RELATIONSHIPS**

Exchange reaction and exchange capacity in soils are sources of plant nutrient such as K, Ca and Mg. However, it is difficult to visualize how the complex interaction between ions, exchange capacity and extraction of nutrients by plant affect nutrient supplies. Beckett developed a technique and theory to examine the buffer capacity of soils with respect to potassium. The theory is based on exchange reactions between Ca, Mg, and K. Beckett called the buffering capacity of the soil with respect to potassium quantity-intensity relations. In this concept Q stands for quantity, I stands for intensity. Although the following from Beckett was derived for assessing potassium status in soils, it can be generalized to a large number of other systems. These are summarized and presented in the following table.

**Summary Table of Quantity-Intensity Buffering Relationships.**

System	Q	I	Buffer Index (dQ/dI)
Acid-base	$C_a$ or $C_b$	pH	$dC/dpH$
thermal	calories	temperature	$dQ/dT$
soil water	% water in soil	vapor pressure	$d?/dP_{H_2O}$
soil nutrient - $K^+$	$\bar{K}$	$AR^K$	$\frac{d \bar{K}}{d AR^K}$

The following graph illustrates the concept of Q/I for soil solution ions and soil buffering capacity as derived from the changes in Q in relation to changes in solution ion levels.



Beckett's proposal for evaluation of soil potassium status is based on a mass action exchange equation:

$$K_{K^+}^{M^{2+}} = \frac{[\overline{Ca^{2+}} + \overline{Mg^{2+}}] (K^+)^2}{[K^+]^2 (Ca^{2+} + Mg^{2+})}$$

where ( ) = activities, and [ ] = concentrations. Take the square root and rearrange:

$$[\overline{K^+}] = \frac{(K^+) [\overline{Ca^{2+}} + \overline{Mg^{2+}}]^{0.5}}{(Ca^{2+} + Mg^{2+})^{0.5} (K_{K^+}^{M^{2+}})^{0.5}}$$

In the above, the Q or quantity term for potassium =  $[\overline{K^+}]$  while  $\left( \frac{(K^+)}{(Ca^{2+} + Mg^{2+})^{0.5}} \right) = AR^K$  the activity ratio in solution is the I or intensity term for potassium.

If Q is plotted as a function of I, the slope should represent the ratio of exchangeable calcium plus exchangeable magnesium divided by the square root of the selectivity coefficient.

However, Beckett added an additional feature permitting the examination of the change in exchangeable potassium and obviating the need to directly measure  $[\overline{K^+}]$ . Suppose that  $AR^K$  is changed so that  $AR^K$  increases. The equation predicts an increase in  $[\overline{K^+}] = \Delta \overline{K^+}$ . This new condition could be represented as follows:

$$[\overline{K^+}] + \Delta[\overline{K^+}] = \frac{(K^+) \left[ \overline{Ca^{2+}} + \overline{Mg^{2+}} - \frac{\Delta K^+}{2} \right]^{0.5}}{(Ca^{2+} + Mg^{2+})^{0.5} (K_{K^+}^{M^{2+}})^{0.5}}$$

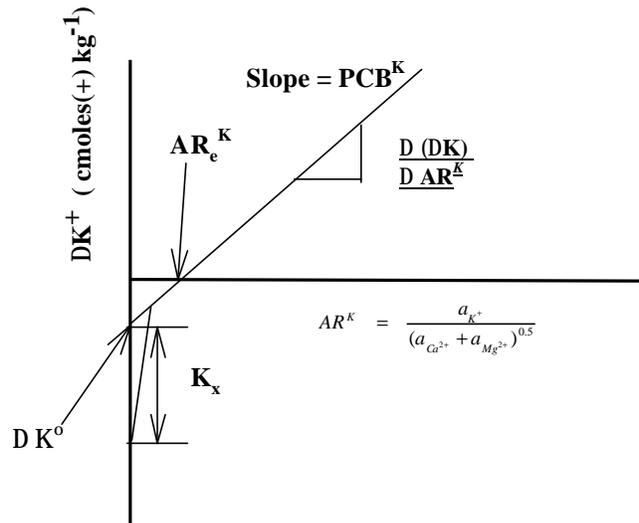
Rearranging:

$$\Delta[\overline{K^+}] = \frac{(K^+) \left[ \overline{Ca^{2+}} + \overline{Mg^{2+}} - \frac{\Delta K^+}{2} \right]^{0.5}}{(Ca^{2+} + Mg^{2+})^{0.5} (K_{K^+}^{M^{2+}})^{0.5}} - [\overline{K^+}]$$

If  $\frac{[\Delta \overline{K^+}]}{2} \ll [\overline{Ca^{2+}} + \overline{Mg^{2+}}]$  then the slope of a plot of  $[\overline{K^+}]$  versus  $AR^K$  should be approximately constant and this function should approximate a straight line with a negative intercept equal to exchangeable potassium in the original sample.

The procedure is to weigh out several 5 g soil samples. To each is added a KCl and CaCl<sub>2</sub> solution of designed potassium and calcium concentration. Fifty mL of solution is added to each soil sample and the flask

is shaken. Then it is centrifuged or filtered and  $K^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$  are measured. Ionic strength ( $\mu$ ) is calculated and activity coefficients for the three cations are calculated from by the extended Debye-Hückel (or other) equation. These values are used to calculate  $AR^K$ . Differences between the final equilibrium solution  $K^+$  and the initial solution  $K^+$  are  $\frac{D(K)}{AR^K}$  due to adsorption or desorption of exchangeable K. The x axis value is a measure of available  $K^+$  or the intensity of labile K in a soil. The potential buffering capacity ( $PBC^K$ ) is a measure of the ability of the soil to maintain the intensity of K in soil solutions. It is proportional to CEC. Low  $PBC^K$  indicates a need for frequent fertilization.  $K_x$  is a measure of specific sites for K, and  $K^0$  is the labile or exchangeable K.



**A typical Quantity/Intensity (Q/I) plot from Sparks and Liebhardt 1981. Effects of Long-term Lime and Potassium Applications on Quantity-Intensity Relationships in Sandy Soil. SSSAJ 45:786-790.**

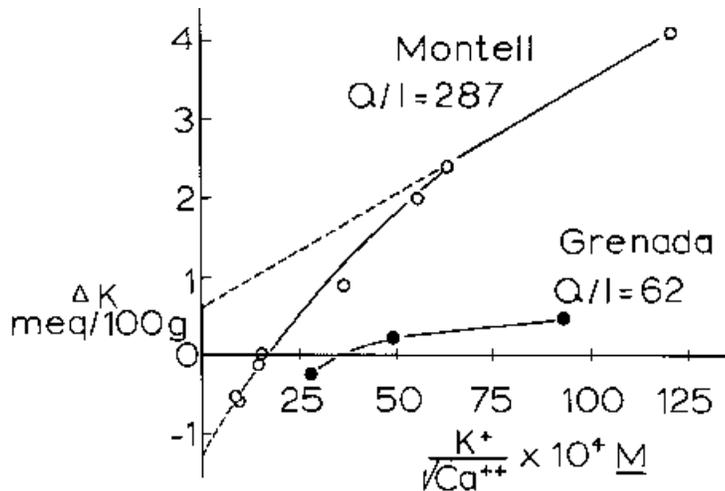


Fig. 16.4. "Beckett" plot of potassium equilibrium data from two soils. (Montell: from W. G. J. Knibbe, Ph.D. Thesis, Texas A & M University, 1968; Grenada: from S. Yimprasert, M. S. Thesis, University of Kentucky, 1969)

The figure on the left illustrates the difference between two soil with very different potassium buffering capacities.

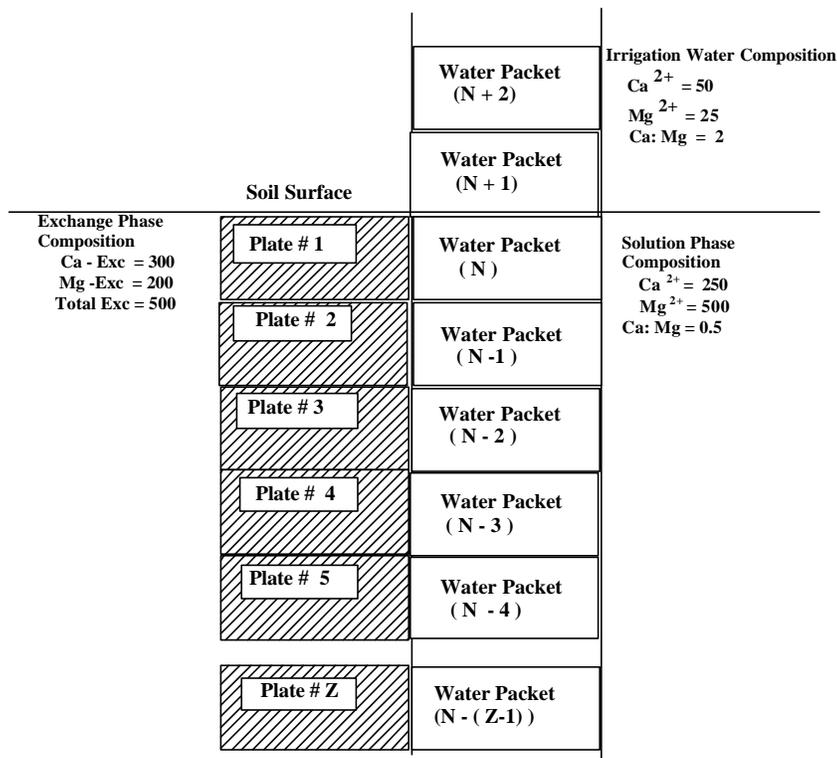
[Note that this older data uses meq/100g and that Mg is not included in the AR].

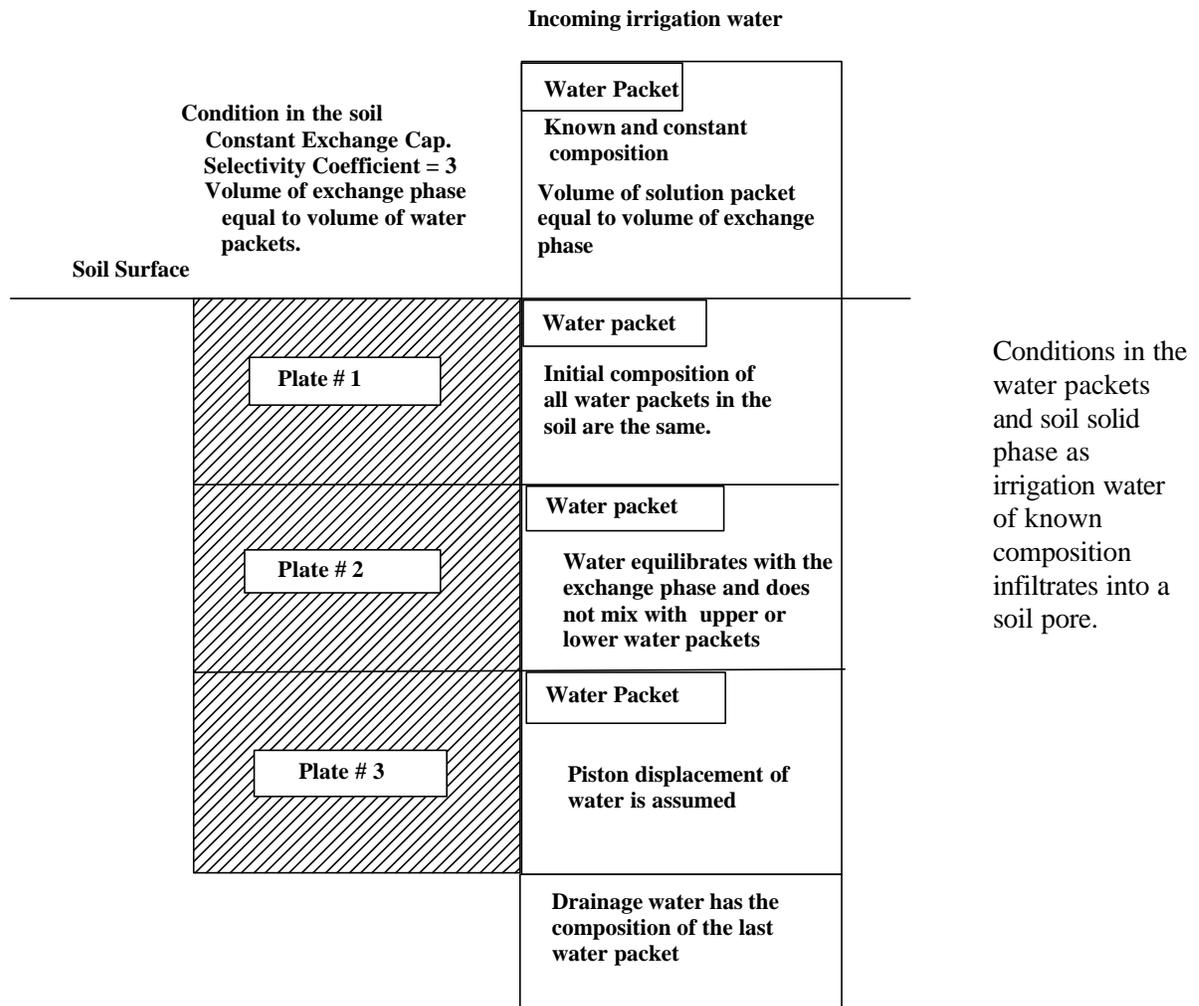
Source: G. W. Thomas (1974)-**Chemical Reactions Controlling Soil Solution Electrolyte Concentration.** *IN Carson the Plant Root and Its Environment.*

**CATION EXCHANGE BY CARTOON STRIP**

The following presentation describes the interaction of a soil via exchange with an irrigation water containing only  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in a hypothetical cotton field owned by Farmer Filippi. The physical picture of this interaction is to treat the soil a number of small soil volumes which are very thin. (In essence this is the formulation similar to plates in a condenser or in a chromatographic column.) The figure below depicts the system under discussion. Each frame for the cartoon strip represents a small increment in time as the initial solution infiltrates downward in the soil. The solutions are not allowed to mix and therefore piston displacement is assumed for all of the water in the system. A selectivity of 3 for Ca is assumed along with an irrigation water composition of 50 Ca and 25 Mg.

A schematic representation of irrigation water interacting with thin plates of soil.





## Explanation

Frame 1	
<b>Plate 1</b> <b>Ca-Ex = 300</b> <b>Mg-Ex = 200</b>	<b>Soil Solution</b> <b>Ca = 250</b> <b>Mg = 500</b>
<b>Plate 2</b> <b>Ca-Ex = 300</b> <b>Mg-Ex = 200</b>	<b>Soil Solution</b> <b>Ca = 250</b> <b>Mg = 500</b>

Frame 2	
	<b>Water Packet 2</b> <b>Ca = 50</b> <b>Mg = 25</b>
<b>Plate 1</b> <b>Ca-Ex = 300</b> <b>Mg-Ex = 200</b>	<b>Soil Solution ( WP 1)</b> <b>Ca = 250</b> <b>Mg = 500</b>

Frame 3	
	<b>Water Packet 3</b> <b>Ca = 50</b> <b>Mg = 25</b>
<b>Plate 1</b> <b>Ca-Ex = 300</b> <b>Mg-Ex = 200</b>	<b>Water Packet 2</b> <b>Ca = 50</b> <b>Mg = 25</b>
	<b>Soil Solution ( WP 1)</b> <b>Ca = 250</b> <b>Mg = 500</b>

Exchanger phase (left ) is at equilibrium with the solution phase (right) in the surface of a field about to be irrigated with with water containing 50 Ca and 25 Mg.  $K_{Mg}^{Ca} = 3 = (CaX)(Mg) / (MgX)(Ca)$

Farmer Fillipi applies water to the field. Note that this water is more dilute than the soil water and that Ca/Mg in the irrigation water is 2.0 while in the soil water it is 0.5. The incoming water is called water packet 2 (WP2). The thin layer of soil is called plate 1 (PL 1). A plate is of the order of 3-4 mm thick

The packet of water displaces an equal volume of soil water without mixing. No exchange or reaction has occurred (yet) between the incoming water and the exchangeable ion on the soil. The equilibrium values of the exchangeable and solution ions can be calculated knowing the selectivity coefficient and including a mass balance statement. The derivation is shown on the following pages.

## Explanation

**Frame 4**

<b>Plate 1</b> <b>Ca-Ex = 321.8</b> <b>Mg-Ex = 178.2</b>	<b>Water Packet 2</b> <b>Ca = 28.2</b> <b>Mg = 46.8</b>
<b>Plate 2</b> <b>Ca-Ex = 300</b> <b>Mg-Ex = 200</b>	<b>Soil Solution ( WP 1)</b> <b>Ca = 250</b> <b>Mg = 500</b>

The system comes to equilibrium. Values in Frame 3 must be used to solve equation 8 of the Ca-Mg derivation sheet to give these equilibrium values.

**Frame 5**

	<b>Water Packet 3</b> <b>Ca = 50</b> <b>Mg = 25</b>
<b>Plate 1</b> <b>Ca-Ex = 321.8</b> <b>Mg-Ex = 178.2</b>	<b>Water Packet 2</b> <b>Ca = 28.2</b> <b>Mg = 46.8</b>

A new water packet (WP 3) is position to infiltrate into the soil displacing WP2 to the next soil plate PL 2.

**Frame 6**

<b>Plate 1</b> <b>Ca-Ex = 321.8</b> <b>Mg-Ex = 178.2</b>	<b>Water Packet 3</b> <b>Ca = 50</b> <b>Mg = 25</b>
<b>Plate 2</b> <b>Ca-Ex = 300</b> <b>Mg-Ex = 200</b>	<b>Water Packet 2</b> <b>Ca = 28.2</b> <b>Mg = 46.8</b>
	<b>Soil Solution ( WP 1)</b> <b>Ca = 250</b> <b>Mg = 500</b>

The water packet (WP3) has entered and displaced the previous equilibrated packet. The displace packet is now opposite another volume of exchanger having the same composition as Plate 1 before infiltration of water packet 2 (WP2). The system is not at equilibrium

## Explanation

## Frame 7

<b>Plate 1</b> <b>Ca-Ex = 340.6</b> <b>Mg-Ex = 159.4</b>	<b>Water Packet 3</b> <b>Ca = 31.2</b> <b>Mg = 43.8</b>
<b>Plate 2</b> <b>Ca-Ex = 302.8</b> <b>Mg-Ex = 197.2</b>	<b>Water packet 2</b> <b>Ca = 25.39</b> <b>Mg = 49.6</b>

Both layers come to equilibrium.

## Frame 8

<b>Plate 1</b> <b>Ca-Ex = 356.6</b> <b>Mg-Ex = 143.4</b>	<b>Water Packet 4</b> <b>Ca = 34</b> <b>Mg = 41</b>
<b>Plate 2</b> <b>Ca-Ex = 321.8</b> <b>Mg-Ex = 178.2</b>	<b>Water Packet 3</b> <b>Ca = 26.1</b> <b>Mg = 48.9</b>
<b>Plate 3</b> <b>Ca-Ex = 340.6</b> <b>Mg-Ex = 159.4</b>	<b>Water Packet 2</b> <b>Ca = 25.04</b> <b>Mg = 49.95</b>
<b>Plate 4</b>	<b>Water Packet 1</b> <b>Ca =</b> <b>Mg =</b>

A third packet enters and all layer have come to a new equilibrium

What is the composition of plate 4 and water packet 1 in Frame 8 ?

---

**DERIVATION OF THE Ca-Mg EXCHANGE FUNCTION**

A. Selectivity coefficient:

$$K_{Mg}^{Ca} = \frac{[\overline{Ca}][Mg^{2+}]}{[Mg][Ca^{2+}]} \quad (1)$$

B. Mass balance:

$$[Ca]_T = [\overline{Ca}] + [Ca^{2+}] \quad (2)$$

$$[Mg]_T = [\overline{Mg}] + [Mg^{2+}] \quad (3)$$

C. Exchange capacity of the exchanger  $[\overline{R}]_T$  is constant, and therefore:

$$[\overline{R}]_T = [\overline{Ca}] + [\overline{Mg}] \quad (4)$$

D. (1), (2), (3) and (4) can be rearranged into a polynomial in  $[Ca]$  by rearranging (2), (3), and (4):

$$[Mg^{2+}] = [Mg]_T - [\overline{R}]_T + [Ca]_T - [Ca^{2+}] \quad (5)$$

$$[\overline{Mg}] = [Mg]_T - [Mg^{2+}] \quad (6)$$

$$[\overline{Mg}] = [Mg]_T - ([Mg]_T - [\overline{R}]_T + [Ca]_T - [Ca^{2+}]) \quad (6a)$$

$$[\overline{Ca}] = [Ca]_T - [Ca^{2+}] \quad (7)$$

E. Substituting (5), (6a), and (7) into (1) and rearranging:

$$A [Ca^{2+}]^2 + B [Ca^{2+}] + C = 0 \quad (8)$$

where:

$$A = (K_{Mg}^{Ca} - 1) \quad (9)$$

$$B = [K_{Mg}^{Ca} - 1][\overline{R}]_T - [K_{Mg}^{Ca} - 2][Ca]_T + [Mg]_T \quad (10)$$

$$C = (([\overline{R}]_T - [Mg]_T) - [Ca]_T)[Ca]_T \quad (11)$$

**DERIVATION OF THE Ca-Na EXCHANGE FUNCTION**

A. Selectivity coefficient:

$$K_{Na}^{Ca} = \frac{[\overline{Ca}] [Na^+]^2}{[\overline{Na}]^2 [Ca^{2+}]} \quad (1)$$

B. Mass balance:

$$[Ca]_T = [\overline{Ca}] + [Ca^{2+}] \quad (2)$$

$$[Na]_T = [\overline{Na}] + [Na^+] \quad (3)$$

C. Exchange capacity of the exchanger  $[\overline{R}]_T$  is constant, and combined with the electrical neutrality condition:

$$[\overline{R}]_T = 2 [\overline{Ca}] + [\overline{Na}] \quad (4)$$

D. (1), (2), (3) and (4) can be rearranged into a polynomial in  $[Na]$ . This is arbitrary. It could also be rearranged into a polynomial in any of the other variables. Equation (2), (3), and (4) are first rearranged into:

$$[\overline{Ca}] = \frac{[\overline{R}]_T - [\overline{Na}]}{2} \quad (5)$$

$$[Na^+] = [Na]_T - [\overline{Na}] \quad (6)$$

$$[Ca^{2+}] = [Ca]_T - 0.5 [\overline{R}]_T + 0.5 [\overline{Na}] \quad (7)$$

E. Substituting (5), (6), and (7) into (1) and rearranging:

$$A [\overline{Na}]^3 + B [\overline{Na}] + C [\overline{Na}] + D = 0 \quad (8)$$

$$\text{where: } A = 0.5 (K_{Na}^{Ca} + 1) \quad (9)$$

$$B = K_{Na}^{Ca} [\overline{Ca}]_T - 0.5 K_{Na}^{Ca} [\overline{R}]_T - 0.5 [\overline{R}]_T - [Na]_T \quad (10)$$

$$C = [\overline{R}]_T [Na]_T + 0.5 [Na]_T^2 \quad (11)$$

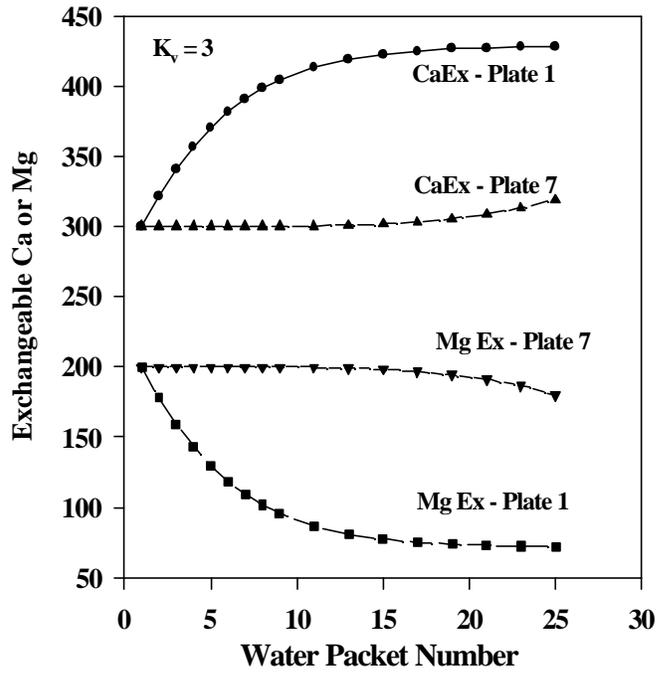
$$D = -0.5 [\overline{R}]_T [Na]_T^2 \quad (12)$$

**Ca -Mg EXCHANGE by FARMER FILLIPI****Behavior in Plates 1 & 2.**

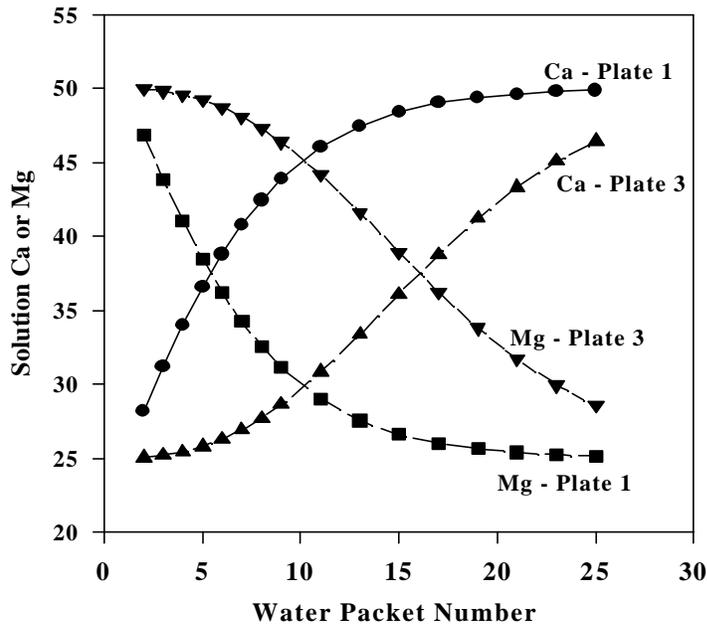
Water Packet #	Plate 1			
	CaX	MgX	[Ca]	[Mg]
1	300	200	250	500.
2	321.8	178.2	28.2	46.8.
3	340.6	159.4	31.2	43.8.
4	356.6	143.4	34.0	41.0.
.				
.				
4	428.6	71.4	50	25

Water Packet #	Plate 2			
	CaX	MgX	[Ca]	[Mg]
0	300	200	250	500.
1	300	200	250	500
2	302.8	197.2	25.39	49.6
3	307.9	192.1	26.1	48.9
.				
.				
.				
4	428.6	71.4	50	25

Plate #	Behavior of Water Packet #2			
	CaX	MgX	[Ca]	[Mg]
0			50	25
1	321.8	178.2	28.2	46.8
2	302.8	197.2	25.4	49.6
3	300.3	199.7	25.04	49.96
.				
.				
.				
4	300	200	25	50.00



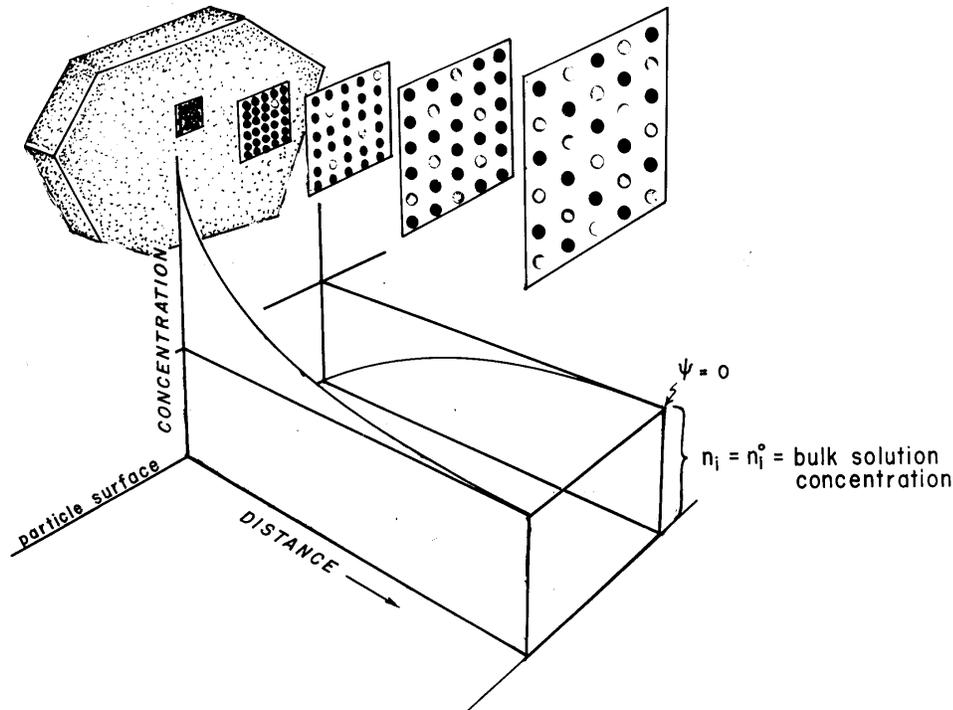
Solution Ca or Mg in relation to Water Packet Number



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**QUANTITATIVE DESCRIPTION OF SOIL SOLUTION - COLLOID INTERFACE**


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The figure above illustrates the general concepts of a cation distribution around a charged particle. Assuming that the particle is negatively charged, anions are repelled from the surface and cations are attracted to the surface. This attraction and repulsion extend outward into the solution bathing soil colloids to a greater or lesser extent depending on the charge on the colloid, the ionic strength of the bathing solution, the nature of the interaction between the cations, the anions and the surface, and the valence of the cations and anions. At some distance from the colloid, the field of the colloid is not expressed and the repulsion and attraction of cations and anions is zero. This point is called bulk solution. Since electrical neutrality must be maintained in bulk solution the charge in any volume element from negative ions is equal to the charge in this volume element from positively charged ions.

Numerically this is:  $z_i^+ m_i^+ = z_i^- m_i^-$  and if we use the politically incorrect notation of equivalents then  $z_i m_i = n_i$  and  $n_i^+ = n_i^-$ . If we use the notation that in the bulk solution  $n = n_0$ , then relative to  $n_0$ ,  $n^+$  increases as we approach the negative colloid and  $n^-$  decreases.

This behavior is analogous too and well illustrated by for the distribution of gases in a gravitational field. To help us develop a feel for the colloidal system, we will examine the behavior of gases in the earth's gravitational field. In this case gases decrease in relation to the distance from the earth's surface. If we designate  $n_0$  as the value of the gas concentration at the earth's surface, we can develop a model of the gas distribution.

### The Barometric Formula and Analogy

$$n = n_0 \exp\left(-\frac{mgh}{kT}\right) \quad (1)$$

$n$  = the number of gas atoms per cubic centimeter at height  $h$

$n_0$  = the number of gas atoms per cubic centimeter at  $h = 0$ , (earth's surface)

$m$  = the mass of the atoms

$g$  = the gravitational constant

$k$  = the Boltzmann constant

$T$  = absolute temperature (  $K^\circ$  )

$mgh$  = the gravitational potential of the gas atoms

$kT$  = the thermal or kinetic energy of the gas atoms (escaping energy)

Thus gases are distributed in around the earth in relation to their thermal energy ( $kT$ ) or escaping tendency and the gravitational attraction ( $mgh$ ). By a similar analogy, ions are distributed in an electrical field around a charged colloid in relation to two opposing forces.

### The Boltzmann Expression for Ions in an Electrical Field

$$n_+ = n_0 \exp\left(-\frac{z_+ c y}{kT}\right) \quad (2)$$

$$n_- = n_0 \exp\left(\frac{|z_-| c y}{kT}\right) \quad (3)$$

$n_+$  = local cation concentration

: ions  $\text{cm}^{-3}$

$n_-$  = local anion concentration

: ions  $\text{cm}^{-3}$

$n_0$  = concentration of cations and anions where  $\psi = 0$

: ions  $\text{cm}^{-3}$

$z_+$  = cation valence

: electrons  $\text{ion}^{-1}$

$|z_-|$  = absolute value of the anion valence

: electrons  $\text{ion}^{-1}$

$e$  = the charge on the electron = 1 unit of charge =

$4.8 \times 10^{-10}$  statvolts  $\text{electron}^{-1}$

$\psi$  = local electrical potential, the sign of  $\psi$  is negative for negatively charged particles.

: statvolts

Note 1 statvolt = 300 volts

$z_i e \psi$  = electrical potential of the ion

: ergs  $\text{ion}^{-1}$

Note: 1 statvolt\* statcoulomb = 1 erg

Define a convenience parameter ( $y$ ):

$$y = \left( \frac{z_i e \psi}{kT} \right) \quad (4)$$

then from (2) and (3):

$$n^+ = n_0 \exp(-y) \quad \text{or} \quad n_+ = n_0 e^{-y} \quad (5)$$

$$n^- = n_0 \exp(y) \quad \text{or} \quad n_- = n_0 e^y \quad (6)$$

Introduce the Poisson equation from classical electrostatic theory:

$$\frac{d^2 \psi}{dx^2} = - \frac{4\pi r}{D} \quad (7)$$

$x$  = the normal distance from a flat surface

$D$  = the dielectric constant  $\epsilon_0$

: statcoulombs  $\text{cm}^{-1}$  statvolts $^{-1}$

? = local net charge density

? = is defined as the difference in charge in any volume element found by summing the positive and negative charges in that volume element.

$$= \sum (z_i c \eta_i) \quad (8)$$

: statcoulombs  $\text{cm}^{-3}$

substituting for ? in (7) yields:

$$\frac{d^2 \mathbf{y}}{d x^2} = - \frac{4 \mathbf{p}}{D} \sum z_i c n_o \exp\left(- \frac{z_i c \mathbf{y}}{kT}\right) \quad (9)$$

If we assume that the solution contains a single symmetrical electrolyte we may rewrite (9) to give:

$$\frac{d^2 \mathbf{y}}{d x^2} = - \frac{4 \mathbf{p} |z_i| c n_o}{D} \left[ \exp\left(- \frac{|z_i| n_o \mathbf{y}}{kT}\right) - \exp\left(\frac{|z_i| c \mathbf{y}}{kT}\right) \right] \quad (10)$$

Introducing  $y$  from (4) after finding  $\frac{d^2 y}{d x^2}$  and recalling that  $\sinh y = \frac{\exp(y) - \exp(-y)}{2}$  we can

rewrite (10) as:

$$\frac{d^2 y}{d x^2} = \frac{8 \mathbf{p} c^2 z_i^2 n_o \sinh(y)}{D k T} \quad (11)$$

Since there are a number of constants in equation (11), it is convenient to introduce the convenience parameter kappa squared:

$$\mathbf{k}^2 = \frac{8 \mathbf{p} z_i^2 c^2 n_o}{D k T} \quad (12)$$

having units of  $\text{cm}^{-1}$

$$\frac{d^2 y}{d x^2} = \mathbf{k}^2 \sinh (y) \quad (13)$$

Applying an integrating factor to both sides and using the boundary conditions that at  $x = \infty$ ,  $y = 0$  and

$dy/dx = 0$  it can be shown:

$$\frac{dy}{dx} = 2 \mathbf{k} \sinh \left( \frac{y}{2} \right) \quad (14)$$

Adding that  $y = y_o$  at  $x = 0$ , and after some manipulations (14) may be integrated to the working equation:

$$y = 2 \ln \left[ \frac{a + \exp(\mathbf{k} x)}{-a + \exp(\mathbf{k} x)} \right] \quad (15)$$

$$\text{where } a = \tanh \left( \frac{y_o}{4} \right) \text{ and } y_o = \left( \frac{|z_i| c y_o}{kT} \right)$$

we proceed by introducing the space charge ( $s$ ) which is equal and opposite to the surface charge, and has units of: statvolts  $\text{cm}^{-2}$

$$s = \int_0^{\infty} \mathbf{r} dx \quad (16)$$

Substituting for (?) from (7) into equation (16) yields:

$$s = - \int_0^{\infty} \frac{D}{4\mathbf{p}} \frac{d^2 y}{dx^2} dx \quad (17)$$

which after some manipulations integrates to:

$$s = - \frac{4 c |z_i| n_o}{\mathbf{k}} \sinh \left( \frac{y_o}{2} \right) \quad (18)$$

If we again introduce a convenience parameter  $J$  defined as :

$$J = \frac{4 |z_i| c}{\left( \frac{8 \mathbf{p} z_i^2 c^2}{DkT} \right)^{0.5}} \quad (19)$$

introducing the constant makes it easier to examine the relation between ( $s$ ) and surface potential.

Remember that surface potential is contained in the  $y_o$  term.

$$s = -J \sqrt{n_o} \sinh \left( \frac{y_o}{2} \right) \quad (20)$$

It has been shown that for variable charge surfaces:

$$y_o = \frac{kT}{z c} \ln \left( \frac{a_{\text{PDI}}}{a_{\text{PDI}_{\text{zpc}}}} \right) \quad (21)$$

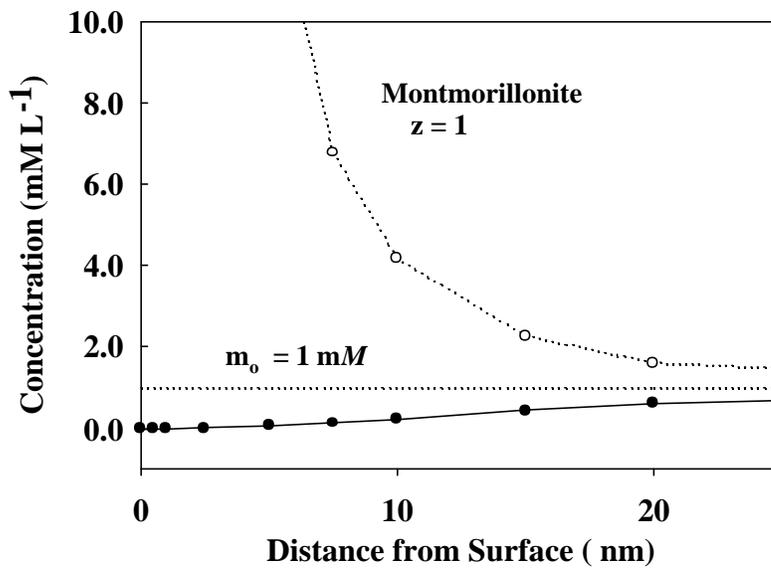
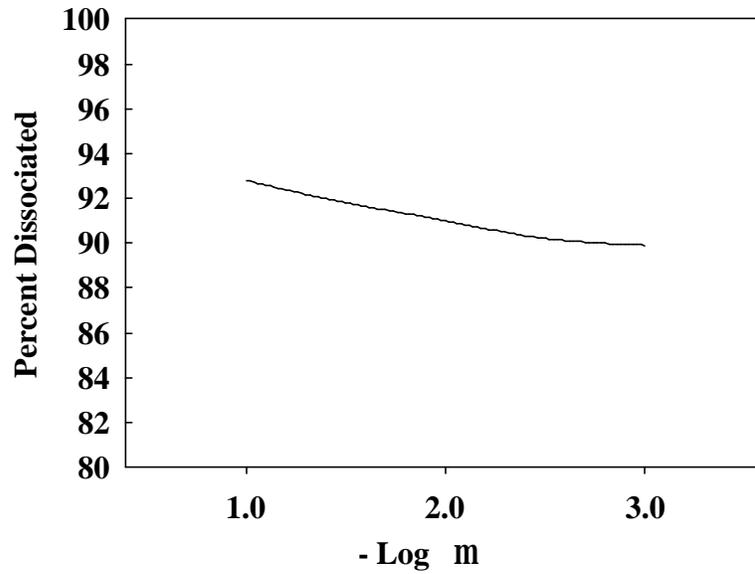
where

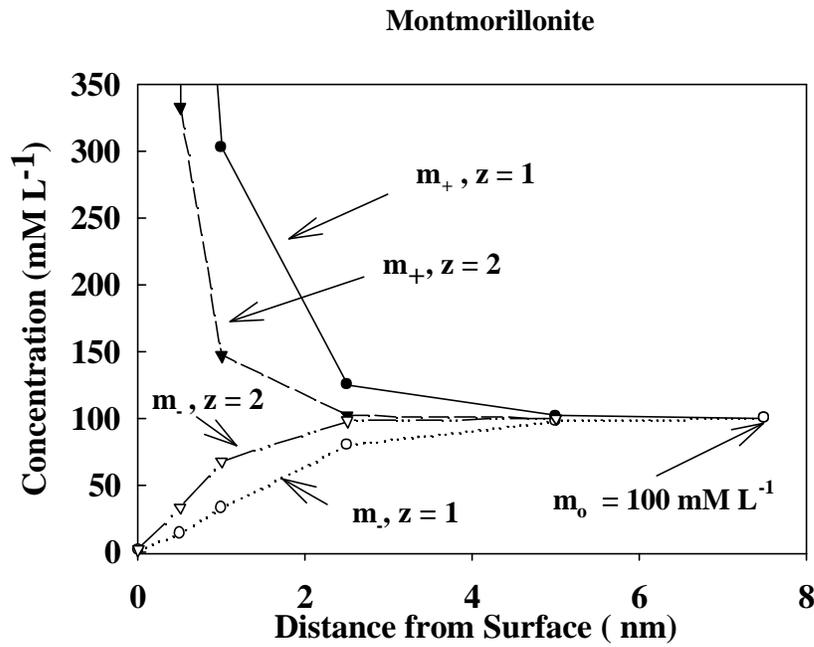
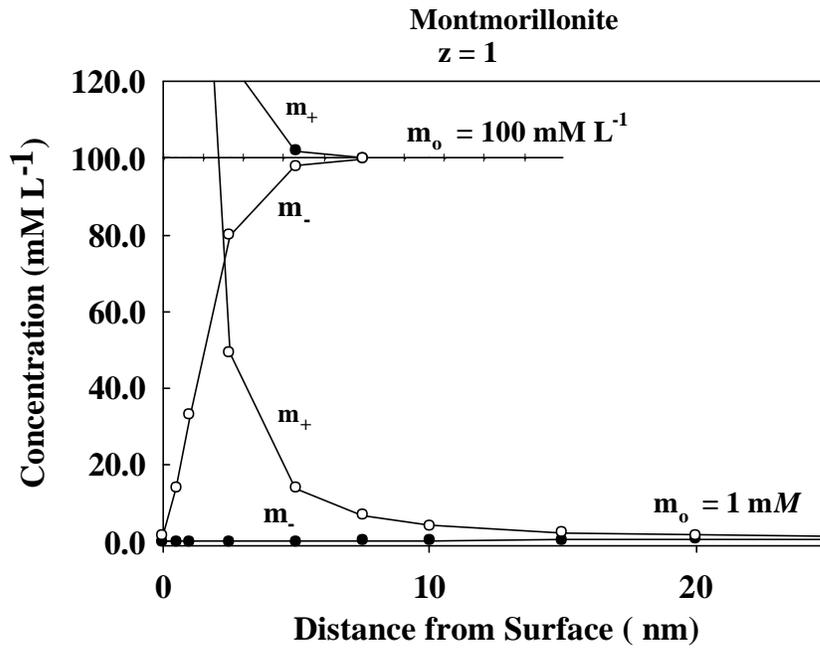
$y_o$  = surface potential of the colloid

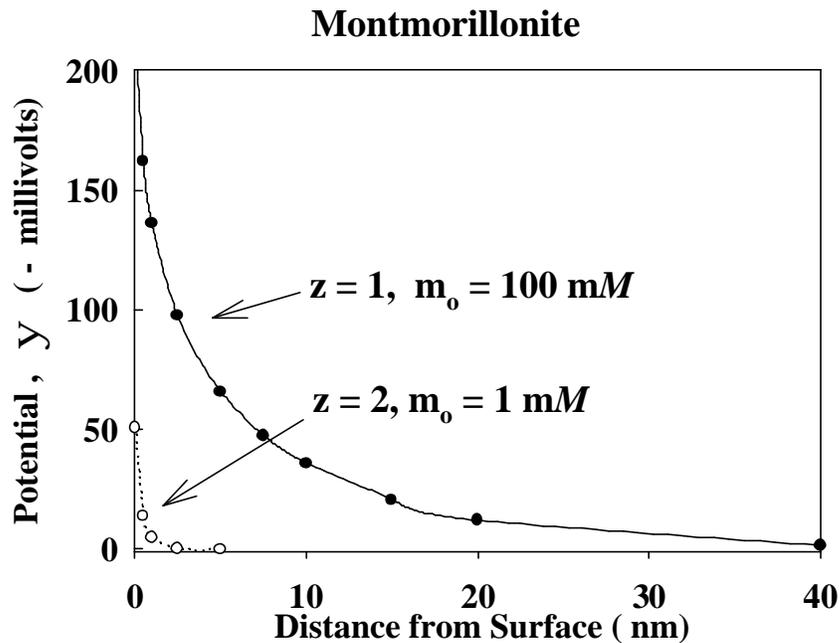
$a_{\text{PDI}}$  = solution activity of the potential determining ion

$a_{\text{PDI}_{\text{zpc}}}$  = the solution activity of the potential determining ion at the point of zero charge (zpc)

**I. S. Effect on Acetic Acid Dissociation**





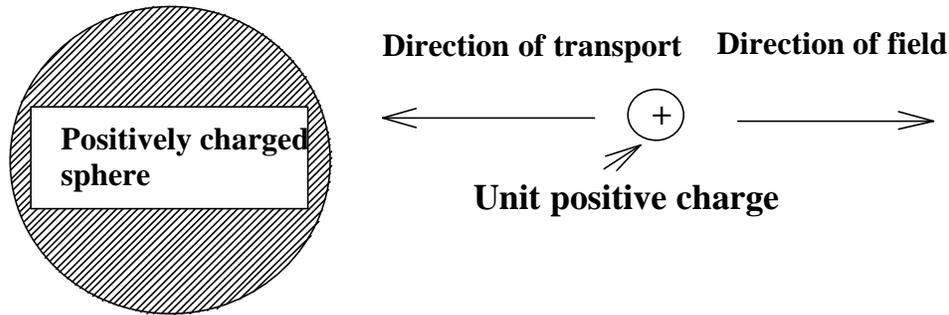


#### APPENDIX FOR DDL

An understanding of soil electrical properties necessitates a recollection and understanding of some basic physical science concepts. This review section is designed to reacquaint you with some concepts from physics which are important for an understanding of DDL and other related surface phenomena.

#### ELECTRICAL POTENTIAL

Electrical potential (?) is a measure of the work required to move a charge in an electrical field. More precisely, electrostatic potential at any point in space is defined as the work done to transport a unit positive charge from infinity (a point outside the electrical field) to a point within the field. Work is done when the unit charge is transported near a charged particle because the particle exerts an electrical force on the charge being transported. This situation is illustrated in the following diagram:



For a charged particle where  $E$  is the electric field or force operating on a unit charge and  $x$  is the distance of transport, the electrical potential ( $y$ ) is the product of the field ( $E$ ) and the displacement  $x$ .

$$|y| = \bar{E} * \bar{x} \quad (1)$$

where:  $x$  = the displacement

$E$  = the electrical field

$y$  = the electrical potential

If the particle is positive then work is done by some external agent and the potential is taken to be positive. Conversely, for a negative particle (the common soil situation) the potential is taken to be negative. Potential is developed when charges are separated. Any separation of charge requires work and therefore develops a potential.

An example taken from Newman (1973) [*Electrochemical Systems*, Prentice Hall] illustrates the point well. Newman estimates the 2 (1 cm in radius) metal spheres separated by 10 cm and charged to an average capacity of  $10 \mu\text{C cm}^{-2}$  develop a potential of  $2 * 10^8$  volts.

Since both the electric field and displacement are vector quantities, the product  $\bar{E} \bar{x}$  is negative (*i.e.*  $\bar{A} \bar{B} = A B \cos \theta$  where  $\theta$  is the angle between the vectors. In this case the angle is  $+ 180$  and  $\cos \theta = -1$ ). Therefore, in a uniform electrical field:

$$y_x = - E x \quad (2)$$

If  $E$  is functionally dependent on  $x$ , and the relationship is known equation (2) becomes:

$$y_x = - \int_{\infty}^x E dx \quad (3)$$

The relationship between  $E$  and distance can be derived from Coulomb's Law. In a vacuum Coulombs law takes the form:

$$F = K \left[ \frac{q_1 q_2}{x^2} \right] \quad (4)$$

where:  $q_1 =$  the charge on particle # 1  
 $q_2 =$  the charge on particle # 2  
 $x =$  the distance of separation between the charges  
on  $q_1$   $q_2$

In solvent the dielectric constant  $D$  is included to account for the energy dissipated by orientation of the solvent molecules (see also Parker, 1982) :

$$F = K \left[ \frac{q_1 q_2}{D x^2} \right] \quad (5)$$

alternatively, the static diabativity ( $\beta$ ) can be used in place of  $K$  and  $D$  where  $\beta = \frac{D}{K}$  :

$$F = \left[ \frac{q_1 q_2}{\beta x^2} \right] \quad (6)$$

For the specific case of a unit charge, *i.e.*  $q_2 = 1$ , the force is equal to the charge on the first particle expressed by Coulomb's Law. Since  $E$  is defined as the force on a unit charge, then for this specific case  $F = E$ :

$$F = \left[ \frac{q_1 (1)}{\beta x^2} \right] \text{ or } E_x = \frac{q_1}{\beta x^2} \quad (7)$$

Substituting for  $E$  in (3) shows that the potential is equal to the integral evaluated over the distance of transport (from outside the electrical field  $x = \infty$ , to the point of interest  $x$ ):

$$y_x = - \frac{1}{\beta} \int_{\infty}^x \left( \frac{q}{x^2} \right) dx \quad (8)$$

$$= - \frac{1}{\beta} \left[ \frac{q}{x} \Big|_{\infty} - \frac{q}{x} \Big|_x \right] \quad (9)$$

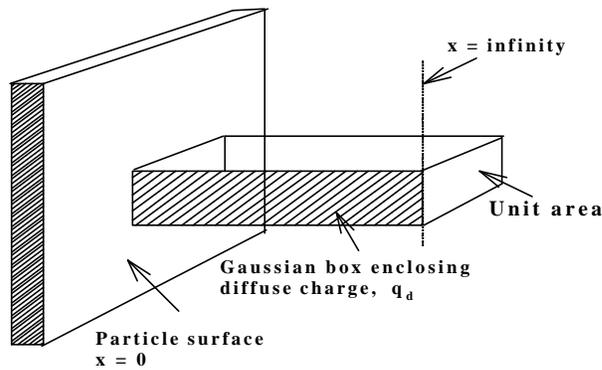
$$= \frac{1}{\beta} \frac{q}{x} \quad (10)$$

We now turn our attention to the distribution of charge around a particle. Gauss's Law (11) describes the distribution of charge emanating from a charged body. The charge is contained in a closed surface or Gaussian box. This charge is equal to the  $(D / 4 \pi)$  times the area of the surface and the component of the field  $(dE/dx)$  normal to the surface.

$$q = - \frac{D}{4\mathbf{p}} (A) \frac{d}{dx} \quad (11)$$

where A = the Gaussian area

Schematically, the model for Gauss's Law applied to a flat particle is shown below (after Bockris and Reddy, 1970) [*Modern Electrochemistry* Plenum Press, New York].



Choosing the enclosed area to be a unit value and rearranging gives:

$$\frac{d \mathbf{y}}{d x} (1) = - \frac{4 \mathbf{p}}{D} q \quad (12)$$

In ionic media ( $q$ ) is equal and opposite to the charge imbalance caused by excess of counter-ions (ions of charge opposite to the surface) over co-ions (ions of the same charge as the surface). Total charge is equal to the summation of charge imbalance for each volume element of the Gaussian box.

$$q = - \int_{\infty}^{x=0} \mathbf{r} d x \quad (13)$$

Substituting from (12) for  $q$  and rearranging yields:

$$\frac{d \mathbf{y}}{d x} = \frac{4 \mathbf{p}}{D} \int_{\infty}^{x=0} \mathbf{r} d x \quad (14)$$

Differentiating both sides of the equation yields Poisson's Equation in one dimension that describes the divergence of the electrical potential gradient in relation to charge density.

$$\frac{d^2 \mathbf{y}}{d x^2} = - \frac{4 \mathbf{p}}{D} \mathbf{r} \quad (15)$$

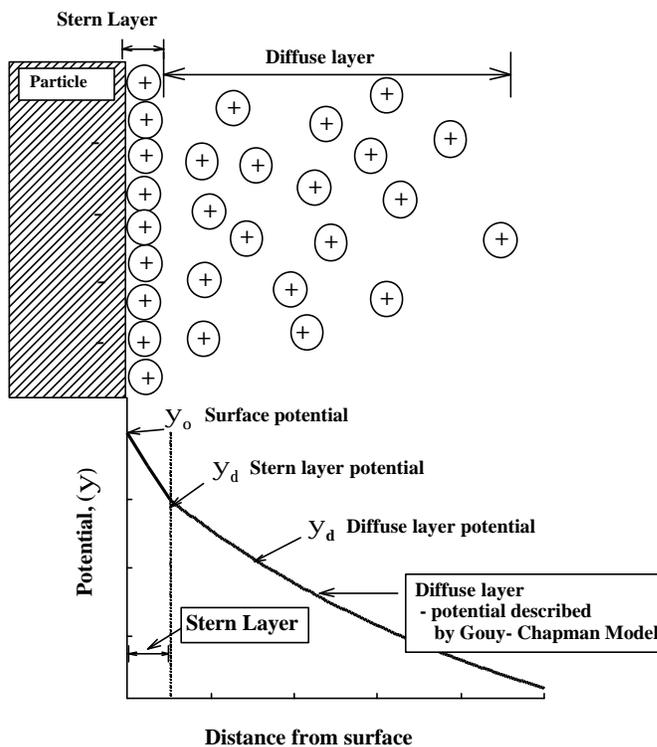
Poisson's Equation describes the behavior of electrical potential around a charged particle. Poisson's Equation is also used in the derivation of the Debye-Hückel Theory of ion-ion interaction. [see K.L. Babcock. 1963. Theory of the Chemical Properties of Soil Colloidal Systems at Equilibrium, *Hilgardia* 34: 417-542.]

As you know from lecture and the previous material, Poisson's Equation along with the Boltzmann Equation are the fundamental equations used in the Gouy-Chapman derivation of DDL.

## MODIFICATIONS TO DDL

There are several assumption inherent in the Gouy-Chapman model which limit its application. For example, the dielectric constant is assumed to be constant from bulk solution up to the particle surface. Poisson's equation is derived for point charges; therefore, ion crowding at the surface can not be accommodated and ridiculously high concentrations are predicted for some conditions. Adamson (1976, p. 201) (*Physical Chemistry of Surfaces 3 Ed.* Wiley-Interscience NY) calculates that given a surface potential of 300 mV and a bulk concentration of  $1 \text{ mM L}^{-1}$ , the surface concentration would be  $160 \text{ M L}^{-1}$ . Specific chemical interactions between the surface and the counter ions are not build into the model. These limitations and others have been discussed by Bolt (1955). (*Analysis of the Validity of the Gouy-Chapman Theory for the Electric Double Layer.* J. Colloid. Sci.10: 206-218.) Bolt found that many of the assumption in the model compensated for one another. However, in many situations, refinement of the basic Gouy-Chapman model is necessary.

In 1924, Stern proposed a modification which incorporates a layer of strongly adsorbed ions next to the surface. These adsorbed ions (specifically sorbed ions) may be partially or completely dehydrated. The Stern Layer is visualized to behave like a molecular condenser and the potential drop across the layer is linear. Beyond the Stern Layer, the ion swarm is described by the Gouy-Chapman model. A simple Stern Model is illustrated below.



## Review Questions

1. What is SAR and  $SAR_{free}$ ? How are SAR and ESR related?
2. What assumption about the behavior of Ca and Mg is inherent in the SAR formulation?
3. What is the idea behind the Q/I relationship of Beckett? How are Ca and Mg related in this model?
4. As a soil solution is diluted, the higher valent ion is preferred by the solid phase. What predicts this result?
5. What factors control the solid phase composition during exchange reactions?
6. What is the suggestion of Vanselow relative to exchange equations?
7. In relation to exchange reactions, what is hydrolysis?
8. In some CEC procedures alcohol is used to remove the excess soluble salts why alcohol and not water?
9. What is a selectivity coefficient?
20. How are  $K_{Ca-Mg}$  and  $K_{Mg-Ca}$  related?
21. Do all exchange sites exhibit the same affinity for  $H^+$ ?
22. What are the general steps in measuring CEC? Why is it called an operationally defined measurement?
23. What two forces are acting on an ion in the Gouy-Chapman model of the double layer?
24. How does ionic strength and charge affect the double layer thickness and flocculation dispersion behavior of a colloidal system?
25. How are anions and cations distributed near a charged surface?
26. How do charge and potential vary with respect to solution concentration for constant charge and constant potential surfaces?
27. How will CEC vary with ionic strength and pH in soils systems.
28. What is bases saturation? What is abhorrent about the term?
29. Why is there confusion about the place of  $H^+$  in the replacement series?
30. CEC is not equal to the space charge sigma ( $\sigma$ ). Why?