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October, 1966

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TITLE: Phosphorus Adsorption by Selected Clay Minerals

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PHOSPHORUS ADSORPTION BY
SELECTED CLAY MINERALS



A thesis

Submitted to the Faculty of Graduate Studies
in Partial Fulfilment of the Requirements
for the Degree of
Master of Science
in the Department of Soil Science
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by

Andreas Savva Pissarides

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ABSTRACT

The structure of the ionic atmosphere surrounding the clay particles has been presented to show the theoretical effect of certain cations on the adsorption of phosphorus by clay minerals. The various diffuse double layer and Donnan equilibrium theories were used in this theoretical treatment.

Three standard clay minerals, a kaolinite, an illite and a montmorillonite were used in the investigation of the effect of exchangeable cations on phosphorus adsorption in dilute phosphorus solutions.

The clays were first treated to remove the surface coatings and impurities with the least possible alteration of the clay lattice. The purified clays were then saturated with Li^+ , Na^+ , K^+ , Mg^{++} , Ca^{++} , Sr^{++} and Ba^{++} by salt leaching techniques. The clays were then equilibrated with very dilute phosphorus solutions. Preliminary experiments with representative clay samples showed that equilibrium between adsorbed phosphorus and the phosphorus in solution was reached in 72 hours. Each of the three clays saturated with a specific cation was shaken with dilute NaH_2PO_4 solutions (2-40 $\mu\text{g P/ml}$). The pH of these suspensions were measured and were found to vary in the range of 6.0-7.2.

From the final and the initial phosphorus concentration in solution, the amount of phosphorus adsorbed per unit weight of clay was determined. Phosphorus adsorption maxima were calculated from the Langmuir adsorption isotherm. The values of the constants derived from the plot of these isotherms was shown to follow the general order predicted from theoretical considerations.

Phosphorus adsorption changed with the saturating cation in the following order:

for kaolinite $\text{Li}^+ < \text{K}^+ < \text{Na}^+ \ll \text{Mg}^{++} < \text{Ca}^{++} = \text{Sr}^{++} < \text{Ba}^{++}$

for illite $\text{Li}^+ < \text{Na}^+ < \text{K}^+ \ll \text{Mg}^{++} < \text{Ba}^{++} < \text{Ca}^{++}$

for montmorillonite $\text{Mg}^{++} < \text{Sr}^{++} = \text{Ba}^{++} < \text{Ca}^{++}$

Phosphorus adsorption maxima were smaller than values previously obtained for similar clay-phosphorus mixtures. Theoretical and practical considerations proved that Al and Fe ions were responsible for higher phosphorus adsorption values.

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1. GENERAL INTRODUCTION

An outstanding property of the soil colloids is their ability to adsorb ions from the equilibrating solution. They may do this with varying degrees of reversibility, and in amounts by far in excess of those present in the equilibrium solution (10). Thus, the soil colloids may be visualized as a reservoir, which releases nutrient ions into solution upon depletion of ions from solution by plant uptake, drainage or precipitation. For an adequate evaluation of the nutrient status of the soil, it is necessary to estimate not only the adsorption capacity but also the rate at which nutrient ions are released into solution by the soil colloids.

Cation adsorption in soils is in part due to the negative charges on the planar surface of clay minerals arising from isomorphous substitution (10, 37). As a result of these charges cations are adsorbed on clay surfaces by electrostatic attraction. The adsorption capacity of clays for cations is determined by the specific surface in contact with the solution and the accessible charge, and by the valency and hydrated size of the cation. The electrostatic nature of this attraction creates a type of ionic atmosphere around the particles which can be described by various double layer models and the Donnan equilibrium theory.

Anion adsorption is entirely different. Anion adsorption can be attributed to a positive, pH dependent charge which is thought to be located on edge surfaces and on lattice imperfections of clay minerals. However, the major cause of anion adsorption is considered to be of a chemical nature for many anions including the phosphate

ion (10). Anion adsorption is also controlled by the repulsion effect exerted on anions by the predominant negative charge of the planar surfaces. This repulsion effect is modified by the degree of effectiveness with which the negative charge of the clay particles is neutralized by the adsorbed cations.

The purpose of the study reported in this manuscript, is to show the effect of the adsorbed cations on the phosphate ion adsorption by clay minerals. For this purpose an extensive theoretical section has been included in order to indicate the type of the ionic atmosphere around the clay particles which is influenced by the type of the clay and the adsorbed cation. The theoretical effect of the ionic atmosphere, so created, on the adsorption of anions has been outlined prior to presenting the results of experiments designed to illustrate phosphate ion adsorption by clay minerals saturated with different cations.

2. THE CLAY SYSTEM

2.1 General consideration

The crystalline alumino-silicate clay minerals may have been subjected to ionic substitution giving rise to a more or less uniform negative charge density. The edge surfaces carry variable charges due to unsatisfied bonds, and the charge density of these edges is related to the pH of the system. The extent of edge surfaces and the magnitude of their charge is much lower than that of the flat surfaces (10). As a result of the attraction of the cation towards and the repulsion of the anions away from the negative clay surfaces, the surrounding ionic atmosphere around a clay particle is positively charged. The negatively charged clay surface with the ambient ionic atmosphere is called electrical double layer (37).

The suspension of clay mineral particles in a dilute electrolyte solution is defined as a clay system for the purpose of this discussion.

Different geometric models have been proposed to illustrate this double layer, the major ones being the Helmholtz, the Gouy or diffuse double layer, and the Stern double layer. These models are discussed in turn.

2.2 The Helmholtz model

Helmholtz in 1879 advanced the original theory on electrokinetic phenomena. On the basis of this work Perrin developed a picture of a double layer which is usually called "The Helmholtz Layer" (31). According to this model, the charged particle surface with the

counterions around it, was assumed to behave like a micro condenser with rigid and parallel plates. The inner wall of the condenser consisted of the negatively charged clay surface while a rigid layer of cations formed the outside plate (Fig. 2.2-1). Beyond the condenser, the ionic atmosphere was uniform and was commonly known as the free electrolyte. As a result of the two oppositely charged layers, an electrical potential was established which dropped linearly with distance from the clay surface (39). When the Helmholtz's theory, based theoretically on macro bodies, was applied to micro bodies such as clay minerals, serious discrepancies were found between the theoretical and observed results (23). This was mainly due to the mobility of ions in solution which rendered the strict application of the concept of parallel condenser plates unsuitable for clay suspensions.

2.3 The Gouy double layer

Gouy in 1910 replaced the idea of an electrical condenser having fixed plates with the concept of a diffuse layer; but he pointed out that this layer as a whole could be equivalent to the outside plates of an imaginary condenser (23), (Fig. 2.2-1). The diffuse type of the double layer supports the observation that, in a clay system the ionic mobility is relatively high. As a result of this mobility, the terminals of the outside wall of the imaginary condenser is at a considerably greater distance from the clay surface than that described in Helmholtz model. This diffused layer is referred to as the inner solution or micellar solution in contrast to the solution of the free electrolyte which is called the outer solution

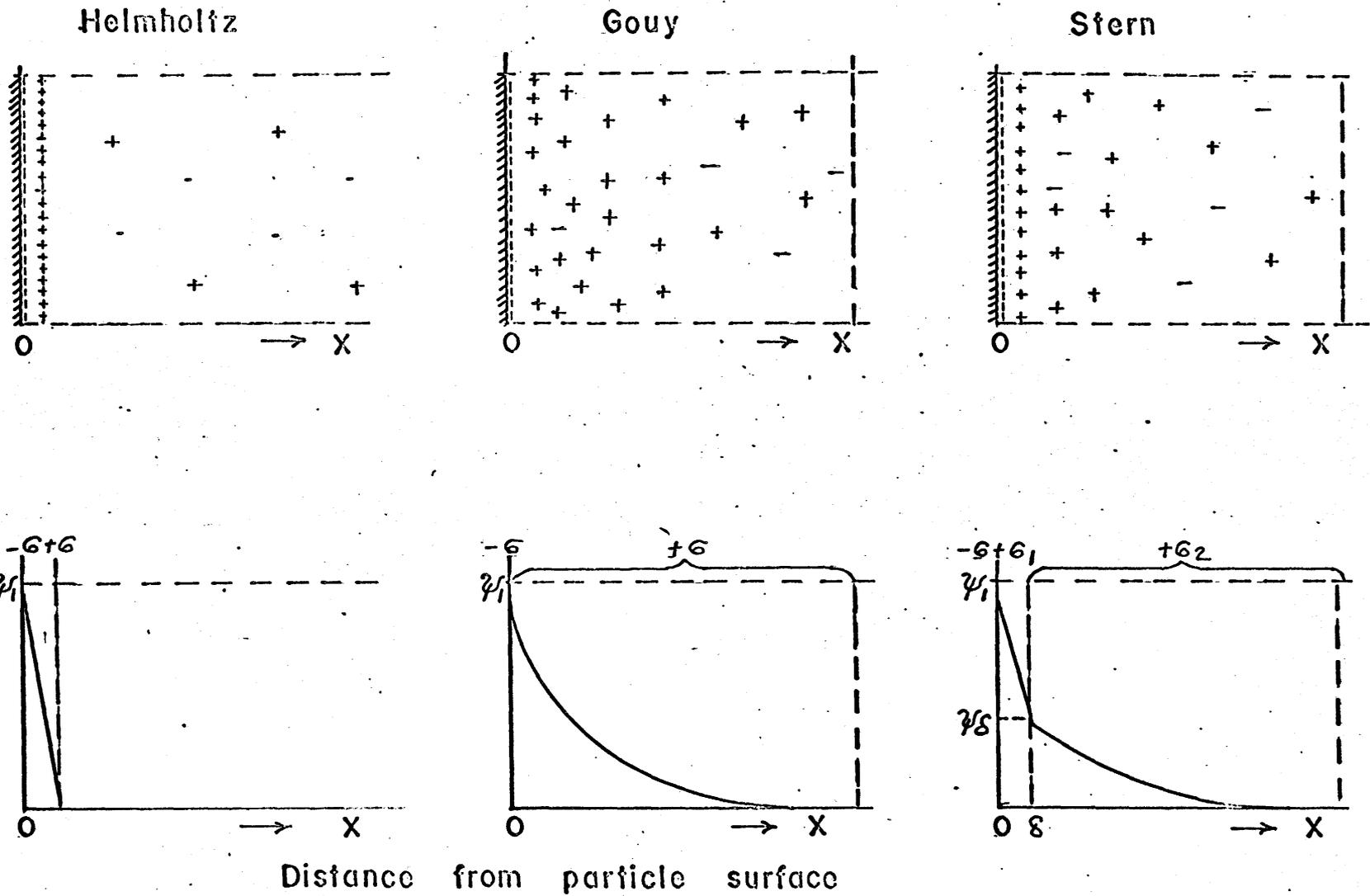


Figure: 2.2-1 Schematic representation of ion and potential distribution in the double layer according to the theories of Helmholtz, Gouy, and Stern. ψ_1 denotes total potential; ψ_2 , zeta potential; x , distance from particle surface; σ , surface charge density; δ , thickness of Stern layer, (39).

or intermicellar solution. More specifically the distribution of ions around the clay particles, at equilibrium, is governed by the action of two types of forces, the coulombic forces, and the diffusion forces (osmotic). Thus the cations tend to move towards the charged clay surface as a result of coulombic attraction and away from the surface as a result of a diffusion potential gradient or osmotic pressure. On the other hand, the anions tend to move away from the negatively charged surfaces as a result of coulombic repulsion and towards the negatively charged surface as a result of a diffusion potential gradient (37). At constant temperature, a dynamic equilibrium in the motion of the ions is established with cation concentration being highest at the surface of the clay particles and decreasing exponentially from the clay surface. Anions are almost absent at the clay surface and their concentration gradually increases until at an indefinitely large distance their concentration becomes equal to that of the cations. This is the distance where the micellar (inner) solution ends and the intermicellar (outer) solution begins (37, 39).

The mathematical treatment of the Gouy layer concept is given by the combination of the Boltzmann's and Poisson's equations under conditions which maintain the electroneutrality on the system. Imposing conditions of small surface potential ($\phi_0 = 25\text{mv}$) as is the case with the clay minerals (3), and considering infinitely large plane surfaces, the following equations are derived (2, 31, 37, 39):

$$\phi = \phi_0 \exp. (-kx)$$

Equation 2.3-1

where:

ϕ = electrical potential at distance x from the clay surface

ϕ_0 = surface potential

x = distance from the clay surface

k = a constant numerically considered as the reciprocal of the thickness of the diffuse double layer

$$x_{ddl} \approx \frac{1}{3.10^7 v \sqrt{n}} \quad \text{Equation 2.3-2}$$

where:

x_{ddl} = thickness of the diffuse double layer (ddl) at room temperature

v = valency of the exchangeable cation

n = concentration of the free electrolyte solution

$$\sigma = (\epsilon k / 4\pi) \phi_0 \quad \text{Equation 2.3-3}$$

where:

σ = surface charge density

ϵ = the dielectric constant of the medium

Equation 2.3-1 explains the exponential drop of electrical potential (ϕ) with distance (x). Equation 2.3-3 shows that the surface potential (at x = 0) is proportional to the surface charge density. It appears also from Equation 2.3-2 that the thickness of the diffuse double layer decreases with increasing valence of the exchangeable cation and increasing concentration of the equilibrium solution.

Basic assumptions for the application of the Gouy layer concept are that: the attraction between ion and colloid is caused

by electrostatic forces, the charge of the colloid is homogeneously distributed over the surface, the behavior of the ions in the diffuse double layer is ideal, and the ions are assumed to be point charges (10).

The above assumptions restrict the application of Gouy layer concept to the flat surfaces of the clay particle where the charge density is more or less uniform and the surfaces of attraction or repulsion are coulombic and not chemical. The Gouy layer model can not be applied to the edges and corners of the clay particles due to the non uniformity of surface which excludes the possibility of uniform charge density. Also, the acting forces are not purely coulombic but to a certain extent chemical as a result of unsatisfied bonds.

2.4 The Stern model

The basic drawback of the Gouy double-layer-theory is the "point charge" character of the ions which disregards the ionic dimensions (37). Thus, according to the Gouy layer concept, the ions can approach quite near the particle surface. As a result of this "closest approach theory" impossibly high counterion concentrations are theoretically possible.

In the Stern double layer model, (Fig. 2.2-1), the crowding of the counterions is avoided by assuming that the ions, as a result of their ionic dimensions, can not reach the clay surfaces. Thus the closest ions are separated from the surface by a distance, δ , which although small, is large enough to prevent the infinitely high ion concentration at the clay surface which are permitted by the Gouy formula (31, 37). A molecular layer identical to that of the Helmholtz's

type is assumed to be formed by the plane of surface charge and the plane of the centers of the closest ions (37, 39). The space between the "walls" is occupied by water molecules and has a thickness, δ , which is dependent on the hydrated radius of the counterions (37, 39). In this layer, which is called the Stern layer, the electrical potential drops linearly from (ϕ_i) at the surface to a lower value (ϕ_δ) at a distance equal to the hydrated radius of the cations. Beyond the Stern layer and up to the free electrolyte the ion distribution in the second part of the double layer is of the Gouy type (37, 39).

The total charge density of the counterions is divided: in the Stern layer charge density (σ_1) and the Gouy layer charge density (σ_2). The surface charge density (σ) is then given by (37):

$$\sigma = \sigma_1 + \sigma_2 \quad \text{Equation 2.4-1}$$

The electric potential and the charge distribution in the Stern layer are determined by an approximate statistical treatment which combines the electrostatic theory and adsorption statistics; specific adsorption forces, if necessary, between the surface and the counterions are also considered. In mathematical terms (37):

$$\sigma_1 = \frac{N_i v e}{1 + (N_A/Mn) \exp(-(ve\phi_\delta + \psi)/kT)} \quad \text{Equation 2.4-2}$$

where:

- N_i = number of adsorption spots on 1 cm^2 of the surface
- v = valency of the ion
- e = elementary charge in esu units
- N_A = Avogadro's number
- M = Molecular weight of solvent
- n = Local ion concentration in number of ions/ cm^3
- kT = Boltzmann's constant x absolute temperature
(2.3×10^{-3} erg at room temperature)

$\phi\delta =$ Potential at border between Stern and Gouy layers
(Stern potential)

$\Psi =$ Specific adsorption potential of the counterions on the
surface

$$\sigma_2 = (\epsilon k/4\pi)\phi\delta \quad \text{Equation 2.4-3}$$

where k is the same as in equation 2.3-1

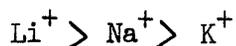
From Equation 2.4-2 it is evident that σ_1 increases with increasing "adsorption spot density", valency of the counterion and specific adsorption potential. It is also obvious from Equations 2.4-1 and 2.4-3 that if σ_1 increases, the Stern Potential ($\phi\delta$) decreases.

Under these conditions the whole micellar solution tends to be compressed and the model approaches the Helmholtz model.

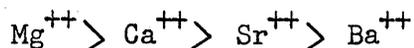
As the above mentioned variables (adsorption spot density, valency of the cation, and specific-adsorption-potential) decrease, the charge density of the molecular condenser diminishes. This results in an increase of the Gouy layer charge density and an increase of the Stern Potential. Under these conditions, the thickness of the Gouy layer increases and the model of the Stern double layer approaches that of the Gouy double layer (39).

The ionic dimensions affect the distance to which the nearest counterion approach. This in turn affects the specific adsorption potential and the charge density of the molecular condenser. Consequently, the larger the hydrated radius of the counterion the smaller the specific adsorption effect; the charge of the molecular condenser (σ_1) also decreases with a corresponding increase in the charge density of the Gouy layer (σ_2) and increase of the thickness of the whole micellar solution. Thus the expanding effect on the micellar solution

by the monovalent cations should follow the order:



and by the divalent ions:



Basic principles involving ionic equilibrium between "inner" and "outer" solution are outlined in the following discussion.

2.5 The Donnan equilibrium

When two solutions are separated by a membrane which is impermeable to at least one of the ion species present, an unequal ion distribution of the other ions occurs. The equilibrium state of this system has been described by Donnan, in 1911, and is known as the Donnan equilibrium or distribution (31).

Wiklander (39) considers that an electrically charged colloidal particle, such as a clay particle, with its surrounding ionic atmosphere can be looked upon as a micro Donnan system where the coulombic attraction between the clay surface and the cations imposes a restraint in the motion of the cations thus acting as an imaginary semipermeable membrane.

Thermodynamically, the equilibrium condition of a clay system containing a strong electrolyte M^+A^- is characterized with respect to chemical potential between the inner (i) and the outer solution (o) as (39):

$$\mu(\text{MA})_i = \mu(\text{MA})_o \quad \text{Equation 2.5-1}$$

Through the relationship between chemical potential and activity it can be easily proved that:

$$(MA)_i = (MA)_o \quad \text{Equation 2.5-2}$$

Further (MA) can be characterized as:

$$(MA) = (M) (A) \quad \text{Equation 2.5-3}$$

Therefore Equation 2.5-2 can be transformed to:

$$(M)_i (A)_i = (M)_o (A)_o \quad \text{Equation 2.5-3}$$

All through the above equations "i" denotes the "inner" and "o" denotes the "outer" solutions respectively.

For an electrolyte $M_n^{m+} A_m^{n-}$ Equation 2.5-3 becomes:

$$(M)_i^n (A)_i^m = (M)_o^n (A)_o^m \quad \text{Equation 2.5-4}$$

If distinction is made between the activities of the ions originating from the colloid (Z), the free salt inside the micellar (inner) solution (Y) and the outer solution (X), Equation 2.5-4 can be transformed to:

$$\frac{(X_A)}{(Y_A)} = \left[\frac{(Z_M) + (Y_M)}{(X_M)} \right]^{\frac{n}{m}} \quad \text{Equation 2.5-5}$$

and Equation 2.5-3:

$$\frac{(X_A)}{(Y_A)} = \frac{m \cdot \frac{CEC}{v} + (Y_M)}{(X_M)} \quad \text{Equation 2.5-6}$$

where:

m = Weight of clay (g)

v = Volume of micellar solution (ml)

CEC = Cation exchange capacity of clay in meq per g of clay.

The following can be concluded from the inspection of the above

equations:

(i) Although the activity of the ions is not constant in the Donnan system, the ion product of the cations and the anions is kept constant through the entire system (Equation 2.5-2 and 2.5-3). This can be ascribed to the coulombic forces acting between the clay particles and the ions in solution. Thus the activity of the cations increases with decreasing distance from the clay surface and the activity of the anions decreases in the same direction.

(ii) From statement (i) it is obvious that there exists an unequal distribution of ions, the measure of which is given by the ratio:

$$\frac{X_A}{Y_A}, \text{ or } \left[\frac{(Z_M) + (Y_M)}{(X_M)} \right]^{\frac{n}{m}} \quad \text{or} \quad \frac{m \cdot \frac{CEC}{v} + (Y_M)}{(X_M)}$$

Since Z_M does not change with dilution, $Y_M = Y_A$ and both are very low, X_M decreases proportionally with dilution, it can be shown from Equation 2.5-5 that dilution causes an increase of uneven ion distribution. Salt addition should cause the opposite effect.

(iii) Since the clay particles are negatively charged they induce higher cation concentration in the micellar than in the intermicellar solution, therefore:

$$(Z_M) + (Y_M) > X_M, \text{ and } \frac{(Z_M) + (Y_M)}{(X_M)} > 1$$

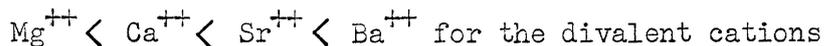
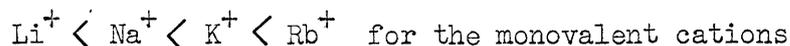
and the ion distribution as exemplified in the ratio $\frac{X_A}{Y_A}$ (Equation 2.5-5) increases with the increase in the valence of the anion but decreases with increase of cation valency.

(iv) From Equation 2.5-6 it can be concluded that the unequal distribution of ions increases with increase in the CEC of the clay mineral.

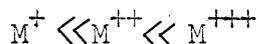
3. CATION ADSORPTION

3.1 The relative replacing power of cations

The adsorption of the cations by clay particles in suspension is governed by many factors, the most important of which are: the type of cation, the electrolyte concentration, the nature of the anion in solution, and the type of the colloidal particle (36). The effect of the type of the cation is readily illustrated through its power to replace other ions on the surface of the clay particles. Other factors being equal, the higher the valency of the cation the greater is its replacing power. The cations are adsorbed on the clay surfaces in their hydrated form (23, 39). The degree of hydration of the ion is proportional to the valency and inversely proportional to its dimensions. This can be attributed to the effect of the polarizing power of the ion on the water molecules. Thus the replacing power of the cations follow the lyotropic series:



and with a small range of radius differences:



Although the nature of the colloid and the concentration of the solution has an effect on the displacing power of the cation, a general confirmation of the above series has been reported (14, 23, 39).

Mattson and Larsson (26) showed that at low ionic concentrations the replacing power of the cations tends to magnify the difference

between monovalent and divalent cations. The opposite effect is observed at high concentrations. This is in accordance with Jarusov's rule which states that the colloidal system tends to acquire the lowest possible free energy level (23). This can be accomplished by the most effective neutralization of the negative charge on the surface. At low electrolyte concentration the divalent ions are much more effective in neutralizing the surface charge on the clay surface than the monovalent ions; hence the divalent ions are preferably adsorbed to the monovalent ones by the clay surfaces. At high concentrations, the effect of valency loses importance in comparison with the effect of concentration and both the monovalent and divalent cations are adsorbed in almost equal amounts. This can be deduced by the inspection of the mathematical relationships of the Gouy and Stern double layer models. More specifically, it can be stated that the higher the compressing power of the added electrolyte on the thickness of the diffuse double layer, the higher will be the replacing power of the cations of the electrolyte. From Equation 2.3-2 it can be seen that the thickness of the diffuse double layer is inversely proportional to the valency of the cation in the diffuse double layer. If the thickness of the Stern layer is (δ), and the thickness of the diffuse layer is (x), then the thickness of the whole diffuse double layer is ($\delta + x$). From Equation 2.3-2 it can also be shown that the thickness of the diffuse layer with a divalent cation on the exchange complex is double the thickness of the diffuse layer with a monovalent cation on the exchange complex. Since $x \gg \delta$ at low concentrations, δ can be neglected so that the thickness of the whole double layer with a monovalent cation on the exchange

complex is twice the thickness of the diffuse double layer with a divalent cation on the exchange complex. This relationship holds where the concentration of the free electrolyte is very low and is the same in both cases.

As the concentration of the free electrolyte of both clay suspensions increases, x decreases exponentially and approaches the dimension of δ which is being considered to be approximately equal to $5\overset{\circ}{\text{A}}$ (3, 37). Under these conditions the thickness of the layer with divalent cations tends to approach, in dimensions, the thickness of the layer with monovalent cations (Table 3.1-1).

The same conclusion can be derived from the Donnan equilibrium theory. Marshall (23) showed through the application of the Donnan equilibrium that:

$$\frac{[M^+]_i (f_M)_i}{\sqrt{[M^{++}]_i (f_{M^{++}})_i}} = \frac{1}{\sqrt{v_o}} \cdot \frac{(M^+)_o (f_{M^+})_o}{\sqrt{(M^{++})_o (f_{M^{++}})_o}}$$

where:

M^+ = monovalent cations

M^{++} = divalent cations

() = moles of M^+ or M^{++} only

[] = concentration in moles/l

i = inner solution

o = outer solution

f = activity coefficient

v_o = outer volume

By disregarding variation in f values and keeping $(M^+)_o$ and $(M^{++})_o$ constant, $(M^+)_i / \sqrt{(M^{++})_i}$ is proportional to $1/\sqrt{v_o}$. Dilution which results in an increase of v_o corresponds to a decrease in the

ratio: $(M^+)_{i} / \sqrt{(M^{++})_{i}}$. Therefore the exchanger tends to take on more divalent and less monovalent cations as the dilution proceeds (23).

The characteristics of the exchanger, in particular the CEC, also affects the relative adsorption of the divalent and monovalent cations by the exchanger. As the CEC increases it has been shown that the degree of uneven ion distribution increases (Equation 2.5-6).

This effect is similar to the dilution effect which results in an
 Table 3.1-1. Variation in the thickness of the diffuse double layers* (x) at different concentrations of monovalent and divalent cations in the free electrolyte solution.

Normality of the free electrolyte solution	Thickness of the diffuse double layer in Å	
	Monovalent cations	Divalent cations
	o A	o A
10^{-5}	1000.0	500.0
10^{-3}	100.0	50.0
10^{-1}	10.0	5.0
1	3.3	1.6

*Calculated through the application of the approximate equation 2.3-2.

increase of the ratio, the divalent : monovalent ion on the exchanger. Hence it is expected that the increase in the CEC of the exchanger should result in an increase in the divalent : monovalent ion ratio. The above observation suggests that there exists a higher adsorptive specificity of divalent ions as the CEC of the exchanger increases. Thus, when equivalent solution concentrations are used, the ratio of the divalent : monovalent cations is higher for montmorillonite than Kaolinite (39).

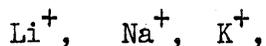
3.2 The Flocculating power of cations

The stability against flocculation of clay particles in suspension is directly related to the thickness of their diffuse double layer. As the thickness of the diffuse double layer increases, the particle collisions, arising from the thermal motion of the clay particles, will not cause any appreciable agglomerate formation. Agglomerate formation or flocculation is the result of Van der Waals forces which are effective at very short distances between or among colliding particles. These forces are ineffective where the thickness of the diffuse double layer is relatively large. Upon the addition of an electrolyte to the suspension the diffuse double layer is compressed and at a critical point the Van der Waals forces become effective in causing flocculation.

The relative flocculating ability of an electrolyte can be measured by the ionic concentration required to show the first sign of clay flocculation. The higher the valency and the lower the hydrated radius of the counterion the lower is the critical concentration required to produce flocculation. The increase of valency is more



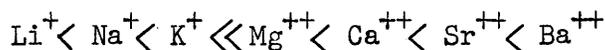
effective in flocculation than the decrease of the hydrated size of the cations (23). This is in accordance with the Schulze-Hardy rule, which states that the important factor in flocculating ability of a cation is its valency. The hydrated radius of the cation is of secondary importance (37). The above rule can be explained through the great dependence of Stern surface charge density (σ_1) on the charge of the counterion (Equation 2.4-2). As σ_1 increases, σ_2 (the surface charge density of the diffuse layer) decreases rapidly suppressing the whole double layer. The Schulze-Hardy rule is valid only if the radius differences of the selected counterions do not vary considerably as in the case of the alkali metals:



and the alkaline earths:



In summary, the flocculating effect of an electrolytic solution is an indication of the ability of its cations to reduce the thickness of the diffuse double layer. The general trend of the flocculating ability of a cation should then follow the lyotropic series:



which is generally observed with clay minerals.

3.3 The bonding energy of the cation on the clay surface in relation to the structure of the diffuse double layer

The bonding energy of a cation attached to a colloidal surface

is dependent, among other factors, upon the density of the clay negative charge and the valency of the cation. Thus a divalent cation with the same hydrated radius and at the same solution concentration as a monovalent cation, is expected to be associated with two charged surface sites and in ideal cases to be held with twice the energy with which the monovalent ion is held. If ΔF is the mean free bonding energy of the cation to the surface, c , the cation concentration, \bar{a} the mean ionic activity of the electrolyte, f , the active portion of the cation (analogous to the mean ionic activity coefficient) then for the monovalent ion the relationship will be (23):

$$(\Delta F)_1 = RT \ln \frac{c_1}{a_1} = RT \ln \frac{1}{f_1} \quad \text{Equation 3.3-1}$$

for the divalent ion:

$$(\Delta F)_2 = 2RT \ln \frac{1}{f_1} = RT \ln \frac{1}{f_2} \quad \text{Equation 3.3-2}$$

and for a cation of valency n :

$$(\Delta F)_n = nRT \ln \frac{1}{f_1} = RT \ln \frac{1}{f_n} \quad \text{Equation 3.3-3}$$

From the above relationship it is seen that:

$$f_n = f_1^n \quad \text{Equation 3.3-4}$$

The above relationships lead to the conclusion that the bonding energy increases proportionally with the valency or decreasing active portion of the cation. As the bonding energy increases the Stern charge density increases (Equation 2.4-2) with the consequent decrease of the charge density of the diffuse layer (σ_2) and Stern potential (ϕ_s). The variation of the above factors in the stated direction tend to suppress the thickness of the diffuse double layer or from Donnan equilibrium considerations, to minimize the uneven distribution of the ions. Under

these conditions the replacing power and the flocculating power of the cation increases.

The statement that $f_n = f_1^n$ was based on the assumption that the cations under discussion were identical except for the charge. Where both the charge and the radius are different the variation of bonding energy with the activity coefficient is given through the application of the complete Debye-Hückel equation (39):

$$-\log f_M = \frac{aZ_M^2 \cdot \sqrt{I}}{1 + b \cdot d \sqrt{I}} \quad \text{Equation 3.3-5}$$

where:

Z_M = the valency of the cation

a and b are constants

I = the ionic strength*

d = the effective mean diameter of the hydrated cations.

The above relationship (Equation 3.3-5) shows that f_M decreases with increasing valence of the cation, electrolyte concentration and decreasing hydrated radius of the cation. The relative effect of the valence of the cation on f_M , therefore on ΔF and the structure of the diffuse double layer, is higher than the effect of the radius. This is in line with the Stern layer theory, the Schulze-Hardy rule and experimental evidence.

$$* I = \frac{1}{2} \sum m_i z_i^2$$

where:

\sum = summation

m_i = concentration of each individual ion present in solution

z_i = valency of each individual ion present in solution

4. ANION ADSORPTION

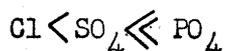
4.1 General consideration

The equilibrium concentration of anions in the micellar or outer solution of a clay system is primarily dictated by:

(i) The movement of anions into the micellar solution which is restricted by the repulsive forces between the anion and the colloid. Thus, if no or very slight adsorption occurs, the equilibrium solution sustains a higher anion concentration than the initial solution. This effect is termed negative adsorption (37, 39). Since clay minerals are negatively charged they exhibit the effect of negative adsorption of the anions. This, in turn, implies that the effect of negative adsorption may prevent or mask positive adsorption.

(ii) Where positive adsorption occurs, this must result from direct physical and chemical bonding (10). The latter implies high anion specificity due to chemical affinity between the adsorbant and the adsorbate. Electrostatic attraction at positively charged sites may also account for positive anion adsorption. This mechanism may be considered as the initial stage leading to chemical adsorption. Since the charge at the clay edges is pH dependent it follows that anion adsorption by clay minerals is pH dependent. The anion adsorption capacity decreases with a rise in pH.

(iii) The presence of another anion in solution may also affect the adsorption of a specific cation (10). The specificity of soil and soil colloids for the main soil anions follow the order (39):



The anion adsorption capacity of various soil types increases with a decrease in the $\text{SiO}_2 : \text{R}_2\text{O}_3$ ratio (39). Such an observation points out the importance in anion adsorption of Fe and Al oxides and hydroxides and clay edge surfaces. Thus lateritic soils which are high in R_2O_3 adsorb higher amounts of $\text{SO}_4^{=}$ than podzols which are low in R_2O_3 (39).

Certain anions form complex compounds or precipitates with soluble cations (Al, Fe, Ca, Mg). These factors render the distinction between anion adsorption and precipitation difficult. This is particularly true for the phosphate ion.

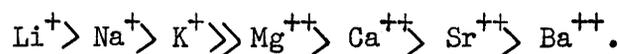
4.2 Negative adsorption of anions

The factors which tend to increase the thickness or the volume of the diffuse double layer will increase the extent of anion exclusion or negative adsorption. It has been estimated that the anion concentration in the micellar solution or diffuse double layer is 1-4% of the anion concentration in the equilibrium solution (10). If the anion exclusion is measured in meq per g of clay, it can be shown that the anion exclusion is proportional to CEC if the latter is measured also in meq per g of clay. This can be concluded from the fact that if n meq of adsorbed cation per g of clay are necessary to neutralize the equivalent amount of negative charge of 1 g of clay, n meq of anions must be excluded from the micellar solution in order to preserve the electroneutrality of the system. Since the micellar solution is almost depleted of anions it can be characterized also as the volume of anion exclusion (V_{ex}). Thus V_{ex} can serve as a reliable measure of negative adsorption. V_{ex} can be experimentally determined

from the meq of excluded anion per g of clay (γ^-) determined by ordinary chemical or radiochemical techniques and the normality of the equilibrium solution (N_o) as follows (10):

$$V_{ex} = \frac{\gamma^-}{N_o} \left(\frac{cm^3}{g} \right) \quad \text{Equation 4.2-1}$$

With different cationic saturations V_{ex} is expected to vary the same way as the diffuse double layer. Various cationic saturations (type of clay and electrolyte concentrations being kept constant) affect V_{ex} in the following order:



It can also be stated that:

- (i) As V_{ex} increases the positive adsorption is masked. This effect will be highest with Li^+ and lowest with Ba^{++} on the exchanged complex.
- (ii) The effect of valency on V_{ex} is expected to be higher than the effect of radius. Thus one expects larger differences in V_{ex} between heterovalent cations with the same radius than between homovalent cations of different size.
- (iii) V_{ex} will increase with decrease of electrolyte concentration.

The effect of the type of the cation, the electrolyte concentration and the nature of the colloid on V_{ex} have been deduced so far from the structure of the diffuse double layer in a very qualitative way.

Negative adsorption is used to measure the surface area of clay particles. The direct dependence of negative adsorption on surface area is evident from the relationship (34):

$$\gamma = \bar{\Gamma} x \quad S \text{ meq of excluded anion per gram of clay} \quad \text{Equation 4.2-2}$$

where:

Γ^- = meq of excluded anion/cm² of clay surface, and

S = surface area of clay mineral in cm²/g.

Schofield and Talibudeen (34, 37) proved mathematically through the Boltzmann-Poisson equation that:

$$\frac{\Gamma^-}{N_0} = \frac{q}{\sqrt{v\beta N_0}} - \frac{4}{v\beta\Gamma} \quad \text{Equation 4.2-3}$$

where:

β = a constant depended mainly on the dielectric constant and the temperature of the suspension

Γ = surface charge density of the colloid

v = valence of the cation

q = a variable which depends on the valence of the ions of the electrolyte present (being 2 for a 1 : 1 electrolyte)

combining Equations 4.2-1, 4.2-2 and 4.2-3, Equation 4.2-4 is derived:

$$V_{ex} = S \cdot \frac{q}{\sqrt{v\beta N_0}} - \frac{4S}{v\beta\Gamma} \quad \text{Equation 4.2-4}$$

If V_{ex} is plotted against $q/\sqrt{v\beta N_0}$ a straight line relationship is obtained. The slope of this line will be equal to S.

In developing Equation 4.2-3 the assumptions were made that there is only a single electrolyte in solution and the diffuse double layer interaction does not occur among the adjacent particles (10). DeHaan improved the above equation so as to include the case of multiple electrolyte content. This improvement was reflected mainly in changes of the variable q. Expressions were also derived to include the case of diffuse double layer interaction (10).

The improved form of equation 4.2-3 brought about by de Haan for non interacting diffuse double layers is (10):

$$d = \frac{Q}{\sqrt{\beta N_0}} - \delta$$

where:

$$d = \frac{\Gamma}{N_0}$$

Q = the improved form of variable q ;

β and N_0 are the same as in Equation 4.2-3 and

δ = a correction factor introduced for mathematical convenience in the theoretical derivations being proved to be approximately equal to $\frac{4}{\sqrt{\beta \Gamma}}$ for illite, kaolinite and montmorillonite (10).

A plot of V_{ex} against $\frac{Q}{\sqrt{\beta N_0}}$ gives a straight line with slope equal to S and intercept equal to δ for each clay mineral (10).

The variation of V_{ex} with CEC can be illustrated in Figure 4.2-1 which is based on the work of deHaan (10) for the determination of surface area via negative adsorption.

Let point A (Fig. 4.2-1) correspond to the thickness of the diffuse double layer with a divalent cation on the exchange complex and point B to the thickness of the diffuse double layer with a monovalent cation on the exchange complex. In both cases the electrolyte concentration is kept constant. The variation in V_{ex} between monovalent and divalent saturations for the clay with the higher CEC is given by the line segment DC and for the clay with the lower CEC by the segment C' D'. Since $DC > C'D'$ it can be concluded that: The variation between V_{ex} with a divalent cation on the exchange complex and V_{ex} with a monovalent cation on the exchange complex increases as the CEC increases. If ΔV_{ex} expresses this variation then:

$$(\Delta V_{ex})_{\text{montmorillonite}} > (\Delta V_{ex})_{\text{illite}} > (\Delta V_{ex})_{\text{kaolinite}} \quad 4.2.5$$

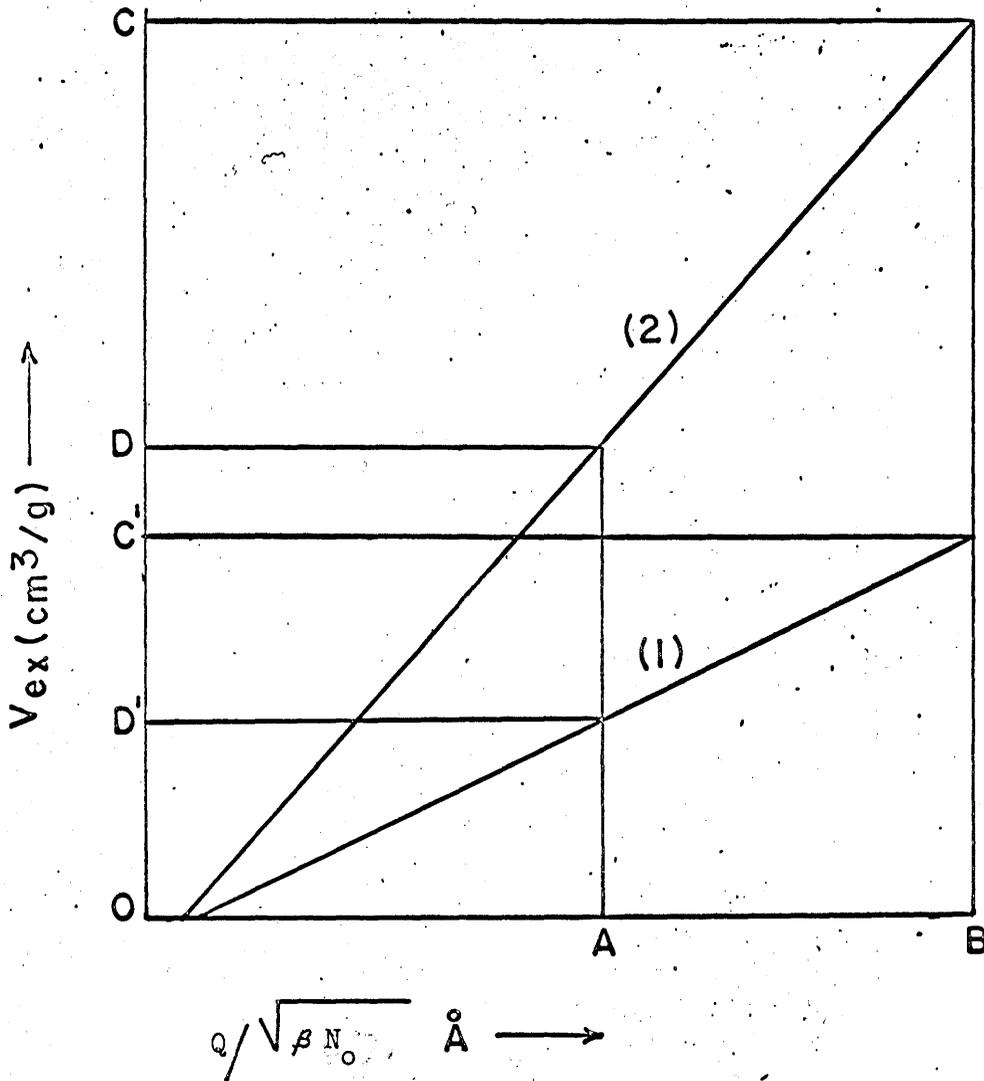


Figure 4.2-1. Variation of V_{ex} with clay minerals differing in CEC exemplified in curves (1) and (2) with CEC of clay (2) higher than CEC of clay (1).

The same relationship is also obtained by keeping valency values constant and varying the concentration of the free electrolyte solution.

The above assumed variations of V_{ex} with changes in valency of cation and concentration of the electrolyte solution for different clay mineral suspensions have been experimentally verified (3, 10).

Equation 4.2-4 is valid only where positive anion adsorption does not occur. If positive adsorption occurs, low values of V_{ex} compared with the theoretically expected ones were obtained (4). The expected values were restored after the addition of very small amount of a polyanion (such as polymetaphosphate). This is attributed to the reversal of edge surface charge by the adsorption of the polyanion which prevented positive adsorption. The reversal of charge has been demonstrated by electron microscope techniques using kaolinite and colloidal gold. Particles of colloidal gold were preferentially adsorbed at the edges of kaolinite (23, 37). Polyphosphates were also strongly adsorbed at the edges leading to increase in CEC. Such modified edges no longer adsorbed gold particles (23).

4.3 Positive anion adsorption

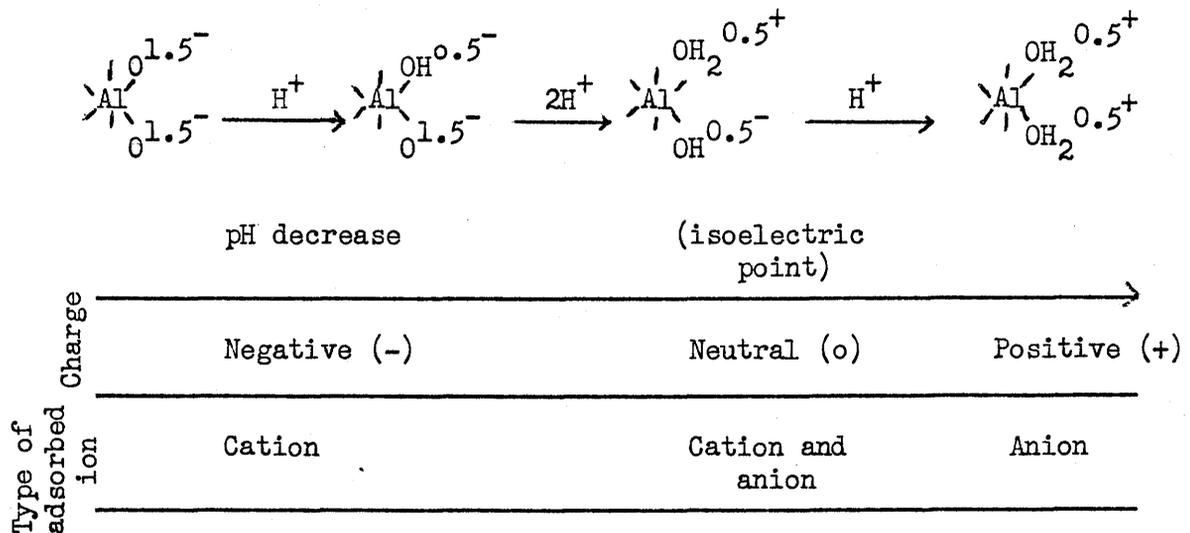
4.3.1 Electrostatic attraction on positively charged sites

This mechanism can be considered of the same character as the cation adsorption phenomenon except for the inversion of the sign of the charges on the adsorbant and the adsorbate. The positively charged sites on soil clays arise from the activation of basic groups by increased acceptance of protons as the pH becomes lower (39). The main functional group which is responsible for this mechanism is the

Al(OH)_n group (39) which exist at the edges of the clay minerals and the surface of the aluminum sesquioxides.

The role of Fe-(OH)_n (39) and possibly of Mg(OH)_n is similar to that of the Al-(OH)_n. At high pH values these groups are proton donors and become negatively charged. These groups can also be used as a cation exchange site. This is a reason why CEC varies with pH (21).

The changes which the Al-(OH)_n group undergoes with pH changes can be summarized as follows (21);



The above diagram is generally applicable to all exposed Al surfaces. The important factor is the pH value at which the Al surfaces attain the isoelectric point. This depends on the element with which the surface Al is associated and on the crystalline state of the mineral (21). On the positively charged Al-OH₂ or R-OH₂ edges, anions, such as: OH⁻, NO₃⁻, Cl⁻, SO₄⁼ and H₂PO₄⁻ are considered to be electrostatically bound in an exchangeable form. The anions bound in this way are said by Mattson (39) to be saloid bound and occur in Pedalfer soils (rich in hydrous oxides of Fe and Al at low pH

This type of reaction explains the dispersing effect of phosphate ion on clay minerals due to the reversion of edge charge from positive to negative. A similar reaction is reported to occur between phosphate ions, and the surface Al and Fe of the amorphous hydrous oxides (17).

(ii) Isomorphous replacement of surface OH by the anion

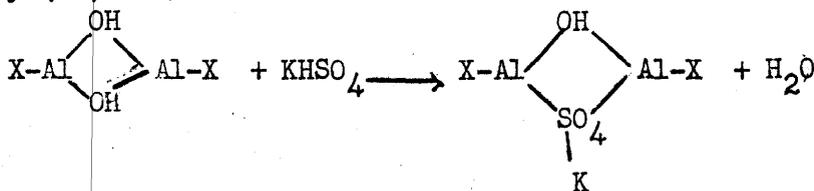
Fluoride ion with about the same radius as OH⁻ displaces OH from the surface of hydrous oxides and clay minerals in the following way (21, 39):



The above mechanism has been challenged by Huang and Jackson (18a). The release of OH⁻ in solution was attributed to the disruption of the clay minerals by F⁻ to form complex ions with lattice Fe and Al. There is some evidence (11, 39) that the phosphate ion, though not of the same size as OH⁻, can also displace lattice OH. The similarity of substitution between OH and phosphate may explain the fact that hydroxides have a strong replacing power for phosphate. Phosphate adsorbed in this way is classified under the term "colloid bound" by Mattson (39). This type of bonding can take place above the isoelectric point. Arsenate can be similarly bonded.

(iii) Anion penetration

This mechanism is similar as (ii) except that the OH⁻ replacement occurs not on the surface but in the interior of the soil colloid. Both phosphate and sulfate ions are assumed to react in this way (21):



(iv) Replacement of silicon tetrahedron by phosphate ion

The above mechanism has been explained by the fact that phosphate ion and silicon tetrahedron are approximately of the same size (14, 39). The reversible exchangeability between these two ions has been shown experimentally (10). Hendricks (14, 39) also suggested that phosphate and arsenate due to their similarity with the silicate tetrahedron may extend the clay lattice by adsorption of these ions on the edges of the silicon tetrahedron layer.

5. CHEMICAL PRECIPITATION

Certain anions, especially phosphate, are retained in soil or clay systems by chemical precipitation. The phosphate ion reacts with Fe and Al at low pH forming insoluble compounds belonging to the variscite-strengite isomorphous series (12). At higher pH values phosphate ions may be precipitated by calcium and magnesium present in the soil or clay solution (40, 41). It is generally believed that both chemical adsorption and chemical precipitation are basically the same mechanism. Due to the complexity of the soil system, in the nearly neutral and alkaline region of pH, the determination of the activity of the various ions in solution responsible for the phosphate fixation is extremely difficult. This restricts the application of the solubility product principle, as a means of investigation of the phosphate fixation, to the region of very acid pH values or in soil and clay systems high in exchangeable Al. This is due to the fact that at pH values < 5 the Al^{+++} ion added or dissociated from the soil colloids is on the exchange complex or in solution in its monomeric form: $\text{Al}(\text{H}_2\text{O})_6^{3+}$ (35). Its activity can be then easily determined in this pH region; the precipitation of phosphate by Al is considered as the main source of phosphate fixation and can be verified through the solubility product principle. However, at higher pH values Al ions polymerize with consequent sharp decrease of activity of the monomeric form. The monomeric Al can not, therefore, be considered as the main source of phosphate fixation. However, phosphate can still be fixed on the surface of the polymeric Al and Fe hydrous oxides and on clay edge surfaces by the residual activity arising from unsatisfied bonds (16, 17). The amorphous hydrous

oxides may exist in the free state or as coatings on the surface of the clay minerals (both planar and edges). As the pH increases further phosphate can be fixed by Ca and Mg ions, if present in sufficient amounts, or by the surface of Ca CO₃ (8).

6. EXPERIMENTAL AND RESULTS

Three standard clay minerals were first purified, then saturated with specific monovalent and divalent cations prior to equilibrating with dilute phosphorus solutions. The equilibrium phosphorus concentration was then determined colorimetrically and the amount of phosphorus adsorbed per g of clay was calculated. The results were then arranged and plotted according to a linear form of Langmuir isotherm (32, 33). The phosphorus adsorption maximum, (b), and a constant related to the bonding energy, (k), were then calculated from the plot of these isotherms.

6.1 Preparation of standard clay minerals

The standard clay minerals used in this study included a kaolinite sample supplied by R. T. Vanderbilt Co. Inc., New York (A.P.I.* No. 6) and an illite (A.P.I.* No. 36), and a montmorillonite (A.P.I.* No. 24) purchased from Wards Limited, Rochester, N.Y. Specific physical and chemical characteristics of these clays are outlined in Table 6.1-1. The clay minerals were first purified and then saturated with monovalent or divalent cations prior to equilibrating with dilute phosphorus solutions.

6.1.1 Purification of clays

An attempt was made to remove "coating substances" and other impurities such as iron oxides, aluminum hydrous oxides and amorphous silicates from the clay minerals with the least possible alteration of

*"The American Petroleum Institute Clay Mineral Standards - Project 49"

Table 6.1.1 Some of the physical and chemical characteristics of the standard clay samples

Characteristics	Clay minerals		
	Kaolinite	Illite	Montmorillonite
Cation exchange capacity (Ca - saturated clays)*	4.2 meq/100 g	30.6 meq/100 g	120.0 meq/100 g
Surface area*	31.0 m ² /g	235.8 m ² /g	876.0 m ² /g
Purity ⁺	96%	89.9%	97.5 - 96%

* Data supplied by J. W. B. Stewart.

+ Data reported in "The American Petroleum Institute Clay Mineral Standards - Project 49"

the clay structure. For this purpose the dithionite-citrate-bicarbonate method (1, 19, 27) which has been found to be effective in removing iron oxides (amorphous and crystalline) was used. However, hydrous aluminum oxides and amorphous silicates are not completely removed (19). None of the many known extracting methods can claim complete removal of coatings or impurities, without prolonged treatment which significantly alters the structure of the clay minerals (29).

6.1.2 Saturation of purified clays with different cations

Approximately 5 g of each of the clay minerals, suspended in dilute sodium chloride solutions, were saturated with the chloride salts of lithium, sodium, potassium, magnesium, calcium, strontium and barium respectively: The original clay suspension was centrifuged in 250 ml plastic bottles and the supernatant sodium chloride solution was removed. About 200 ml of 2 M solution of the chloride salt of the cation intended to saturate the clays was added and the stoppered bottles were shaken for ten minutes. The clay suspension was then centrifuged and the supernatant solution removed. The above process was repeated twice. To remove the excess salt the clays were shaken once with distilled water and the supernatant liquid was removed after centrifugation. The last traces of the salt were removed by successive washings with 95% ethyl alcohol until the supernatant liquid gave no visible precipitate of silver chloride upon the addition of few drops of concentrated silver nitrate solution.

6.2 Phosphorus adsorption studies

The three clay minerals saturated with the respective cations were equilibrated with phosphorus solutions of varying concentrations. Prior to carrying out these adsorption studies, it was necessary to investigate different colorimetric methods for determining phosphorus in dilute solution.

6.2.1 Comparison of colorimetric methods for determining phosphorus in dilute solutions

As error in phosphorus determination, even though small, invalidate adsorption studies, it was first necessary to investigate selected colorimetric methods for determining phosphorus in dilute solution. Comparisons were made between the isobutyl alcohol method which has not only shown to be unaffected by the presence of colloidal organic matter, but also gives very stable colored solutions (38); the phosphomolybdic acid method (20) which is perhaps the most universal method used for phosphorus determination; and the ascorbic acid method which has recently been developed (30). The criteria used to select the method for this study were: the reproducibility of results, the stability of color with time, the sensitivity, and the time required for the analysis. A Beckman adsorption spectrophotometer and a Klett-Summerson photoelectric colorimeter were used to measure the intensity of color.

The stability of the colored solution was highest with the ascorbic acid method, the intensity of color remaining unchanged up to one hour after preparation. The isobutyl alcohol method rated second in this respect, the color remaining unchanged up to half

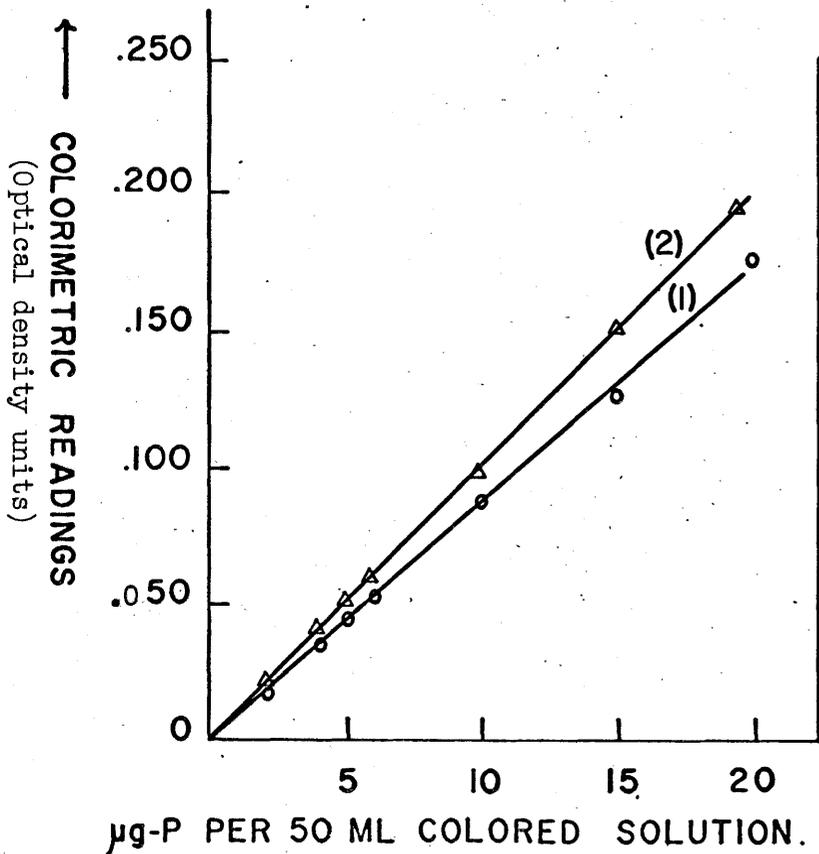


Figure 6.2.1-1. Standard colorimetric curves of phosphorus by the ascorbic acid (I) and the isobutyl alcohol (2) methods on the Beckman spectrophotometer at 625 mu setting.

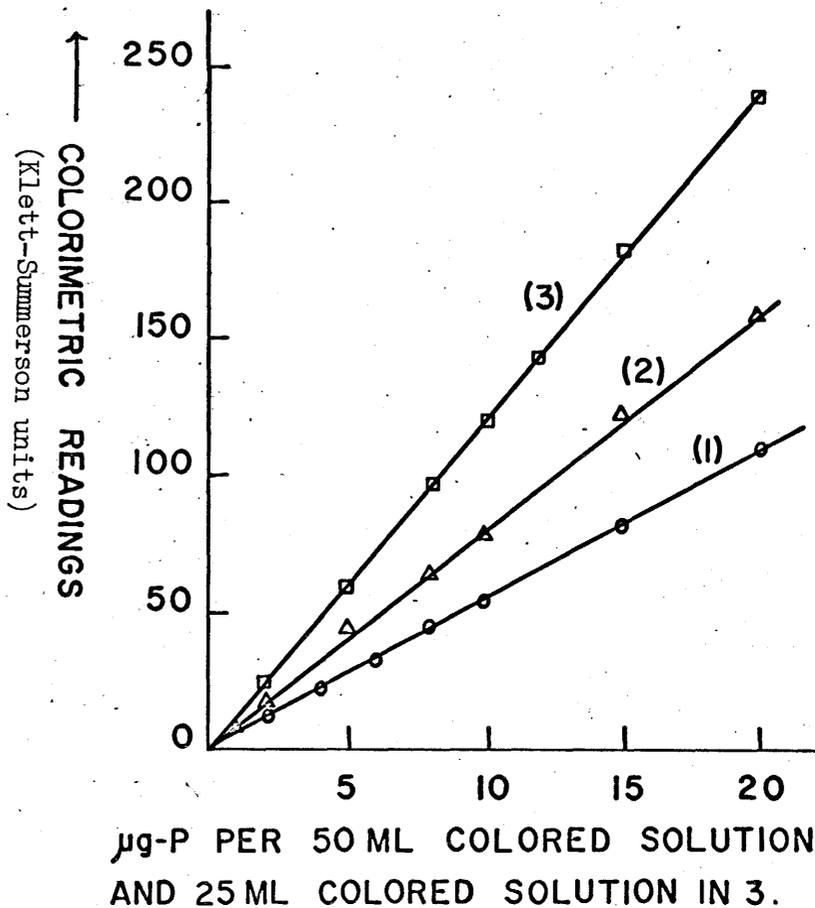


Figure 6.2.1-2. Standard colorimetric curves of phosphorus by the phosphomolybdic acid (2) and the ascorbic acid (1 & 3) methods on a Klett Summerson photoelectric colorimeter with filter No. 660.

an hour. The intensity of colored solution with the phosphomolybdic acid method remained stable up to 20 minutes only. The sensitivity of the three methods was found to be similar (Figures 6.2.1-1 and 6.2.1-2), (Appendix Table 1).

The simplest and quickest method was found to be the ascorbic acid method while the isobutyl alcohol method required much more time in the laboratory.

The ascorbic acid method eliminates the use of the chlorostannous reductant solution, the instability of which affects the reproducibility of results especially in the phosphomolybdic acid method. As well as this, the reproducibility of results of the ascorbic acid method was quite satisfactory as can be judged from Appendix Table 2. From the above comparison the ascorbic acid method was regarded as the most suitable one to be used in this study. To raise the sensitivity of the ascorbic acid method the final volume of colored solution used was 25 ml instead of 50 ml (Figure 6.2.1-2, Appendix Table 1).

The Klett-Summerson photoelectric colorimeter was found to be precise and sensitive enough to be used in this work. The handling of this instrument is also faster and simpler than that of the Beckman adsorption spectrophotometer.

6.2.2 Equilibrium between adsorbed and solution phosphorus

To establish the approximate time for the initial rapid removal of phosphorus, suspensions were shaken for a period of 48, 72, and 96 hours on an end-over-end shaker. Fifty ml of sodium dihydrogen phosphate solution (NaH_2PO_4) containing 400, 2,000 and 4,000 μg of P were equilibrated in 100 ml plastic tubes with 0.5 g of calcium kaolinite. The tubes were then centrifuged at a speed of 2,000 rpm for 20 minutes,

Table 6.2.2.1 Time-adsorption data of Ca-kaolinite suspensions.

Initial amount of phosphorus added $\mu\text{g P/g clay}$	Amount of phosphorus adsorbed by Ca- Kaolinite $\mu\text{g P/g clay}$ after the specified time		
	48 hr	72 hr	96 hr
400	80.4	87.2	87.1
2000	145.5	150.0	150.0
4000	153.1	155.4	155.5

and an aliquot was removed from the clear supernatant solutions for phosphorus determinations (Table 6.2.2-1). Similar experiments were conducted with illite suspensions saturated with both mono- and divalent cations respectively and montmorillonite suspensions saturated with divalent cations (Appendix Table 3). In all the above cases an overall positive phosphorus adsorption has been obtained. Suspensions of montmorillonite saturated with monovalent cations showed an overall negative adsorption which did not alter even after 120 hours of shaking (Appendix Table 4).

It can be concluded from the adsorption data given for various times of shaking that equilibrium has been generally reached after 72 hours.

6.2.3 Adsorption of phosphorus by clays saturated with various cations

Fifty ml of sodium dihydrogen phosphate solutions, ranging in concentration from 2 to 40 ug of P per ml, were added to 0.5 g (ODB) of the air-dried clays, previously placed in 100 ml plastic tubes. The tubes were shaken for 72 hours on an end-over-end shaker, then centrifuged at 2,000 rpm for 20 minutes. With some samples, a further centrifuging at 12,000 rpm for 10 minutes was necessary to obtain a clear supernatant solution.

All samples were duplicated. The colorimetric determinations reported in Appendix Tables 5, 6 and 7 are the arithmetic average of the duplicate data. Where the duplicate determinations differed by more than 5%, the experiment was repeated.

pH measurements were made on the potassium kaolinite-phosphorus suspensions after 0, 6 and 72 hours of shaking. The pH values of the supernatant solution of various phosphorus-clay samples after 72 hours

Table 6.2.3-1. pH values of ^{supernatant} / solutions of different clay-phosphorus suspensions after 72 hr of shaking.

<u>Mg - illite</u>		<u>Sr - illite</u>		<u>Li - illite</u>		<u>Sr - kaolinite</u>	
Initial P conc. ($\mu\text{g P/ml.}$)	pH	Initial P conc. ($\mu\text{g P/ml.}$)	pH	Initial P conc. ($\mu\text{g P/ml.}$)	pH	Initial P conc. ($\mu\text{g P/ml.}$)	pH
4	6.60	2	7.0	2	7.10	2	6.55
10	6.40	10	6.8	6	6.90	6	6.25
20	6.35	15	6.70	10	6.75	10	6.10
40	6.30	20	6.55	20	6.60	20	6.00
		40	6.50	40	6.55		

<u>Sr - montmorillonite</u>		<u>Li - montmorillonite</u>		<u>Li - kaolinite</u>	
Initial P conc. ($\mu\text{g P/ml.}$)	pH	Initial P conc. ($\mu\text{g P/ml.}$)	pH	Initial P conc. ($\mu\text{g P/ml.}$)	pH
2	7.20	2	6.20	2	7.00
4	7.15	10	6.10	4	6.70
6	7.10	20	6.10	6	6.80
8	7.00	30	6.00	8	6.60
10	6.90	40	6.00	10	6.30
15	6.60				
20	6.40				

Table 6.2.3-2. pH values of K - kaolinite-phosphorus suspensions after 0, 6 and 72 hr. of shaking.

Initial P conc. ($\mu\text{g P/ml}$)	pH values		
	0 hr.	6 hr.	72 hr.
4	6.95	6.96	6.97
10	6.45	6.47	6.55
20	6.16	6.20	6.20
40	6.00	6.10	6.10

of shaking were also determined. In all instances, after 72 hours of shaking (Table 6.2.3-1), the pH values of the supernatant solution decreased as the initial phosphorus concentrations increased. The data given for the potassium-kaolinite suspensions (Table 6.2.3-2) suggest that this decrease in pH can be attributed directly to the sodium dihydrogen phosphate rather than to any adsorption or precipitation reaction occurring in the system. This observation is based on the data of Table 6.2.3-2 which indicates a remarkably constant pH value with time for all initial phosphorus concentrations.

6.2.4 Langmuir adsorption isotherm

The Langmuir adsorption isotherm was originally developed to describe the mode of physical adsorption of gases on solid surfaces (22), but also has been extensively used in describing the adsorption of ions, including phosphate ion, from solution on solid bodies (5, 10, 12, 13, 16, 18, 32, 33, 35). Although the agreement of results with the Langmuir adsorption isotherm does not necessarily imply adsorption reaction (15, 18, 32), the constants derived from the plot of this isotherm have been correlated with actual properties of the reacting species (5, 10, 32, 33, 35). The formal equivalence of the Langmuir adsorption isotherm with the law of mass action (5, 12, 15) permits the plot of data of chemical reactions according to this isotherm.

The values of equilibrium phosphorus concentrations in $\mu\text{g P per ml (c)}$ versus the corresponding values of phosphorus adsorbed by clay in micrograms of P per g of clay $(\frac{x}{m})$ have been plotted and the curve passing through these points is given (Figures 6.2.4(-1, -2, -3, -4, -5)).

Values of $\frac{c}{\frac{x}{m}}$ times 10^2 corresponding to various integer values of c were then calculated (Appendix Tables 8, 9 and 10) and the corresponding Langmuir adsorption isotherm plotted (Figures 6.2.4-1, -2, -3, -4, and -5).

The Langmuir adsorption isotherm can be presented in the following equation:

$$\frac{c}{\frac{x}{m}} = \frac{c}{b} + \frac{1}{kb} \quad (32, 33) \quad \text{Equation 6.2.4-1}$$

where c is the final solution concentration ($\mu\text{g P/ml}$), b is the phosphorus adsorption maximum ($\mu\text{g P/g clay}$), and k is a constant related to the bonding energy of phosphorus on the clay surface ($\mu\text{g P/ml}$)⁻¹

From the equation of Langmuir adsorption isotherm and the way the data have been plotted b and k can be determined as follows:

$$b = \frac{1}{\text{slope}} \times 10^2 \quad \text{Equation 6.2.4-2}$$

$$k = \frac{\text{slope}}{\text{intercept}} \quad \text{Equation 6.2.4-3}$$

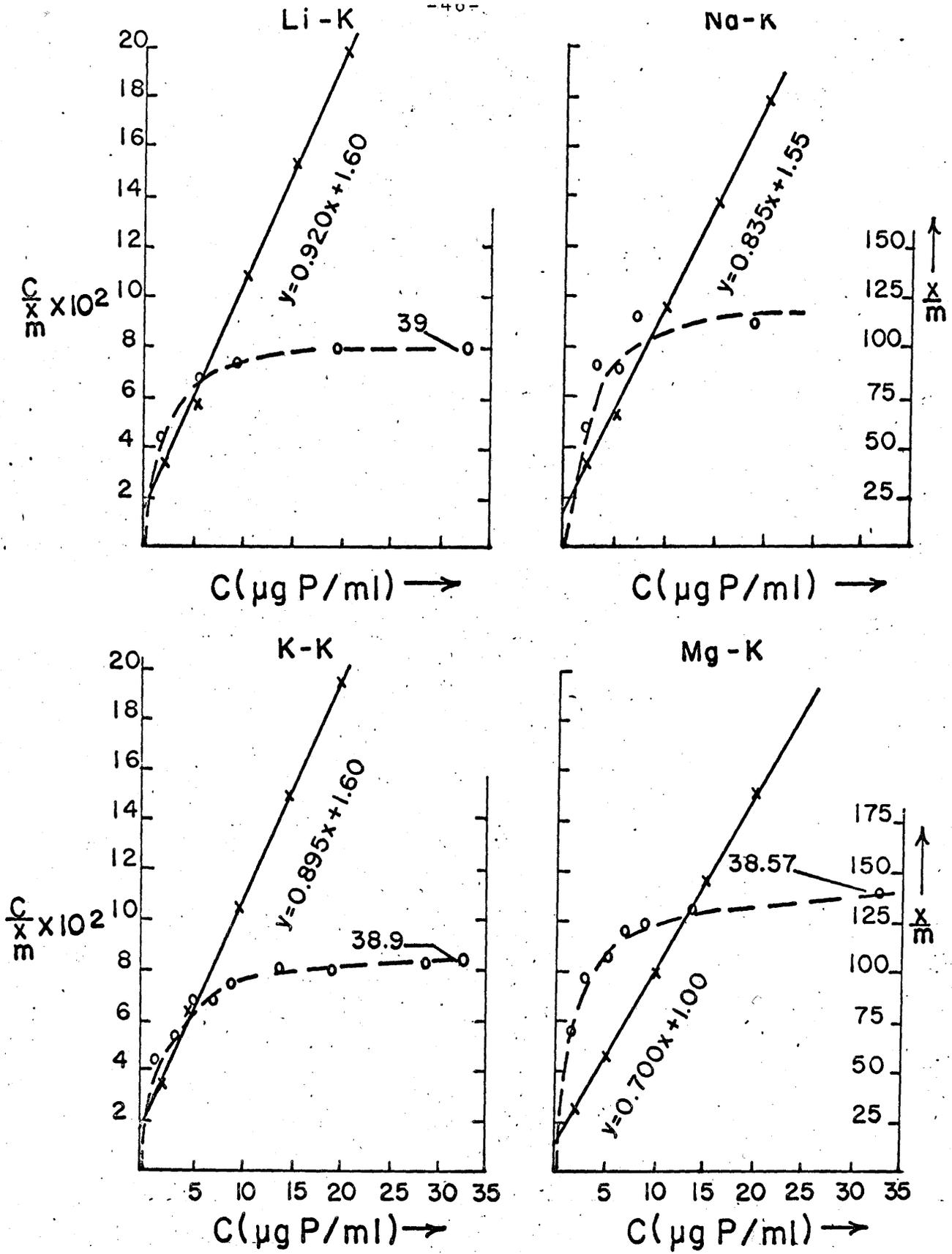


Figure 6.2.4-1. Plot of the Langmuir isotherms for phosphorus adsorption by lithium kaolinite (Li-K), sodium kaolinite (Na-K), potassium kaolinite (K-K), and magnesium kaolinite (Mg-K).

o-o = c vs. $\frac{x}{m}$
 x-x = c vs. $\frac{c}{x/m} \times 10^2$

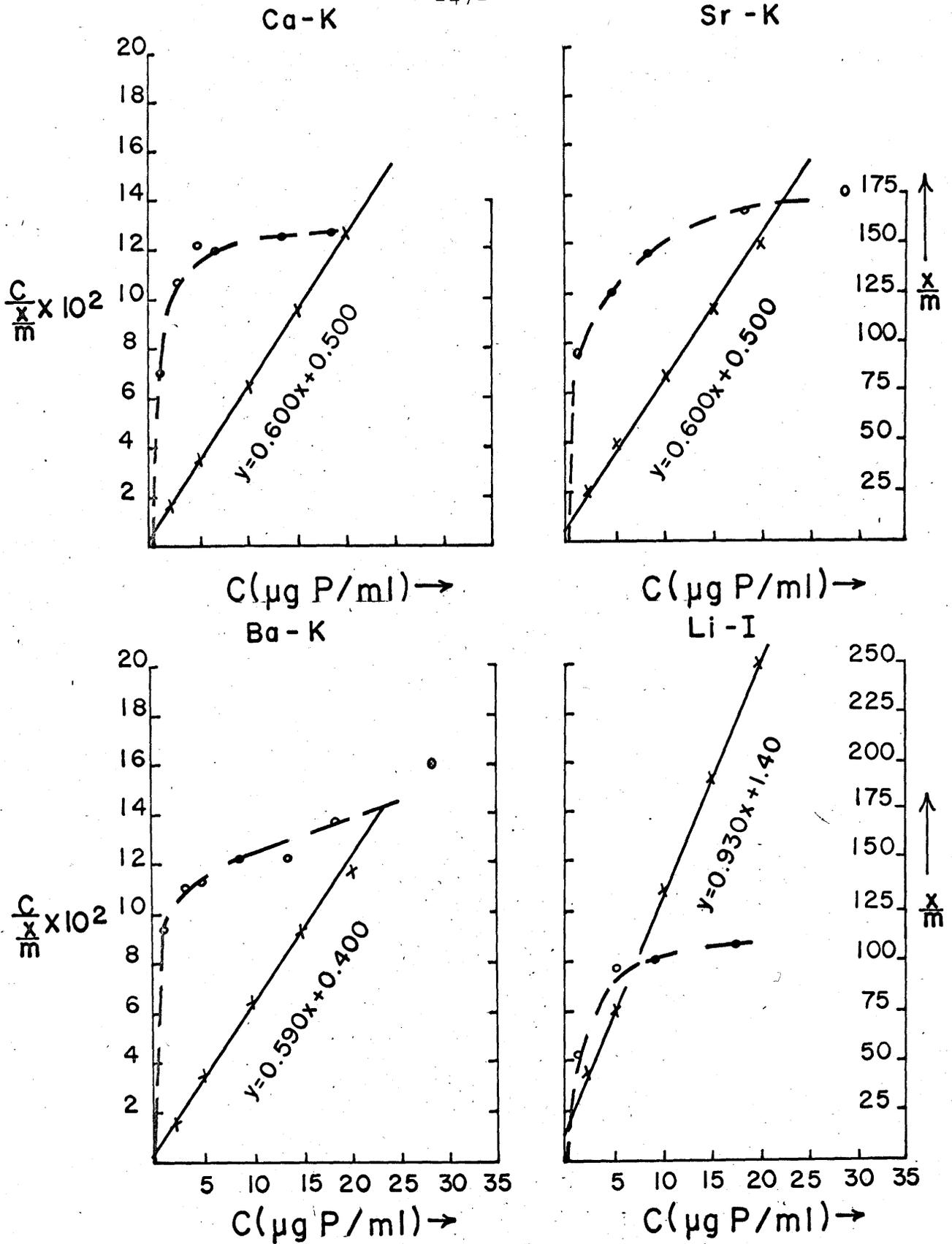


Figure 6.2.4-2. Plot of the Langmuir isotherms for phosphorus adsorption by calcium kaolinite (Ca-K), strontium kaolinite (Sr-K), barium kaolinite (Ba-K), and lithium illite (Li-I).

o-o = c vs. $\frac{x}{m}$

x-x = c vs. $\frac{c}{x/m} \times 10^2$

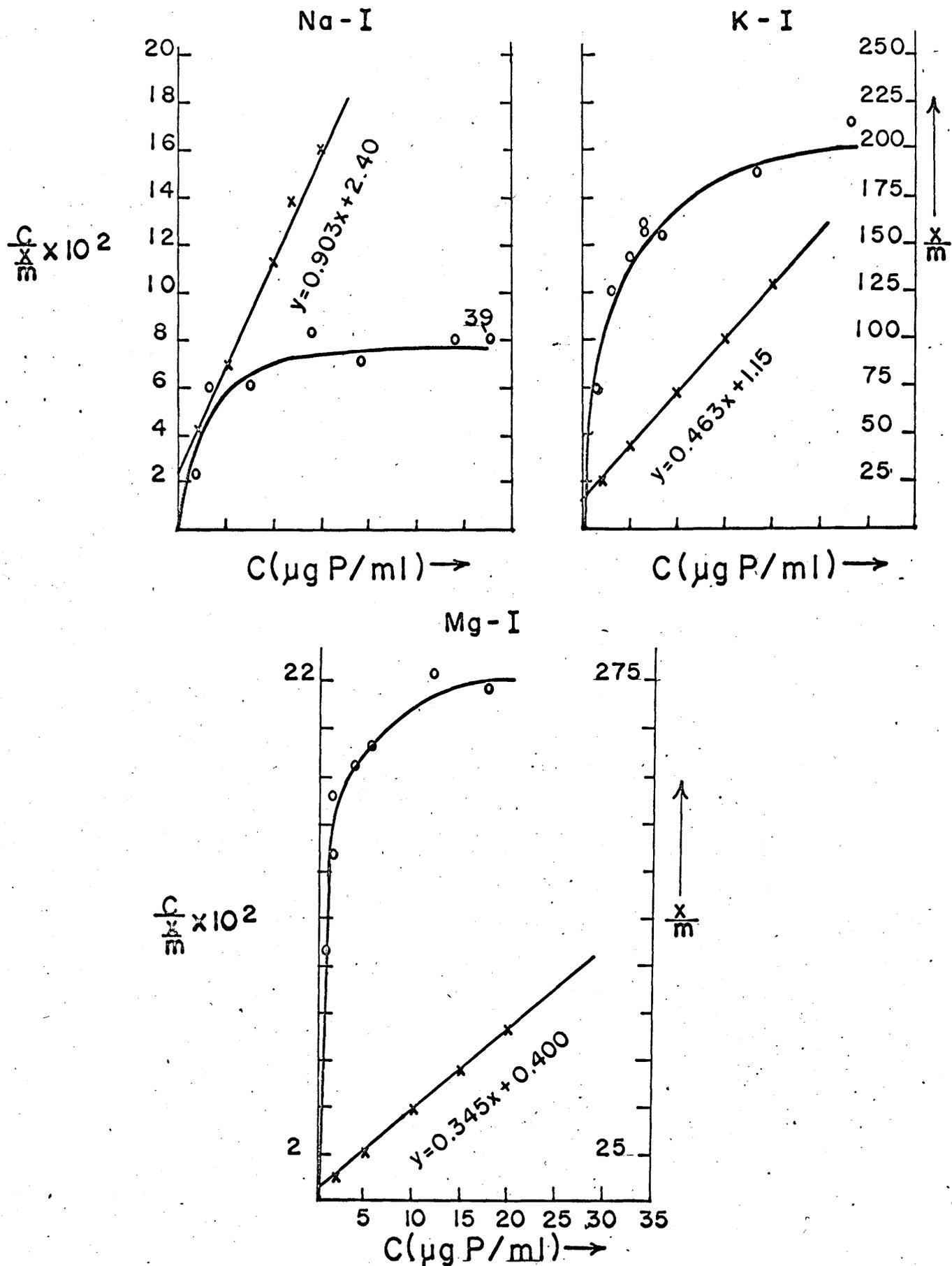


Figure 6.2.4-3. Plot of the Langmuir isotherms for phosphorus adsorption by sodium illite (Na-I), potassium illite (K-I), and magnesium illite (Mg-I).

o-o = c vs. $\frac{x}{m}$

x-x = c vs. $\frac{C}{c} \times 10^2$

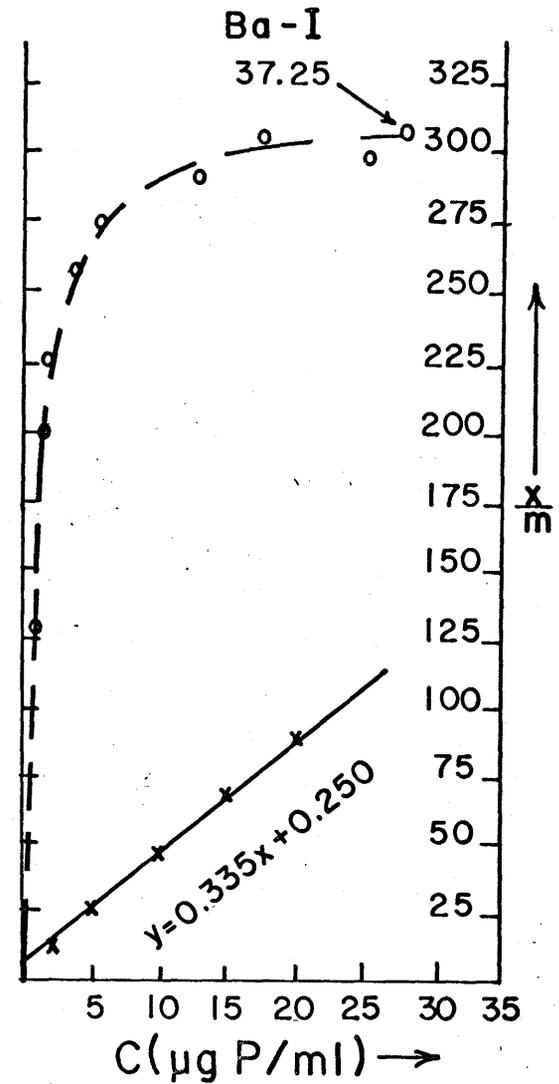
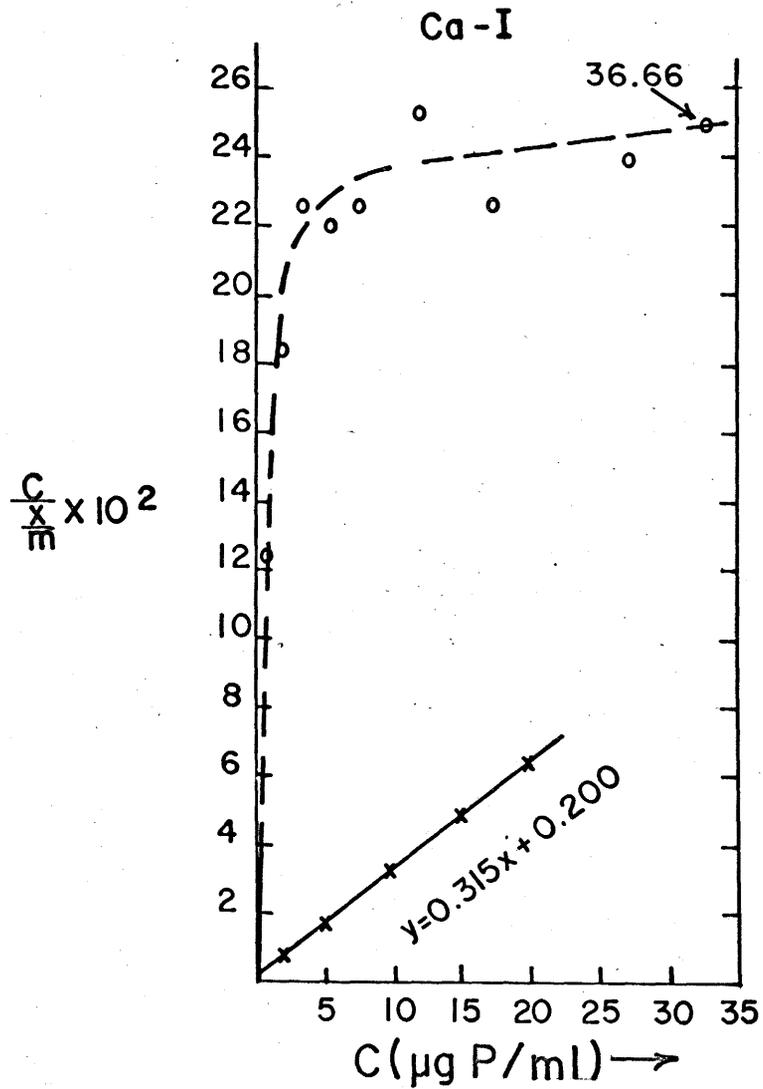
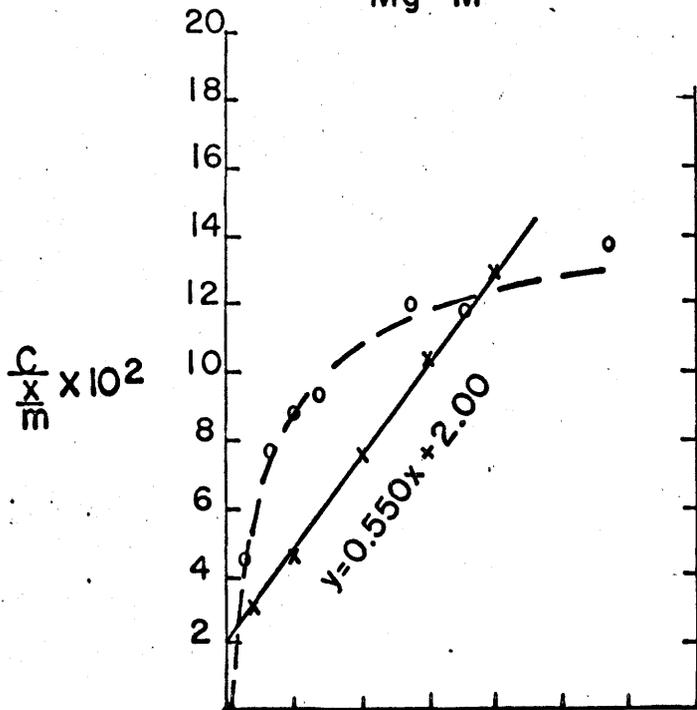


Figure 6.2.4-4. Plot of the Langmuir isotherms for phosphorus adsorption by calcium illite (Ca-I), and barium illite (Ba-I).

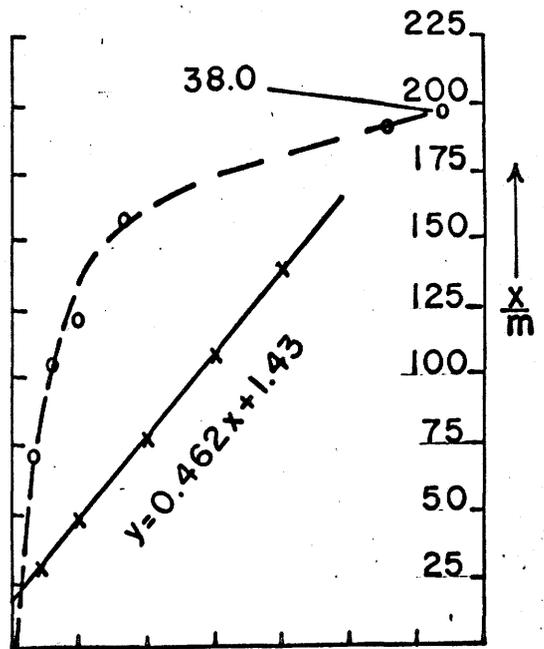
o-o = c vs. $\frac{x}{m}$

x-x = c vs. $\frac{c}{x/m} \times 10^2$

Mg - M



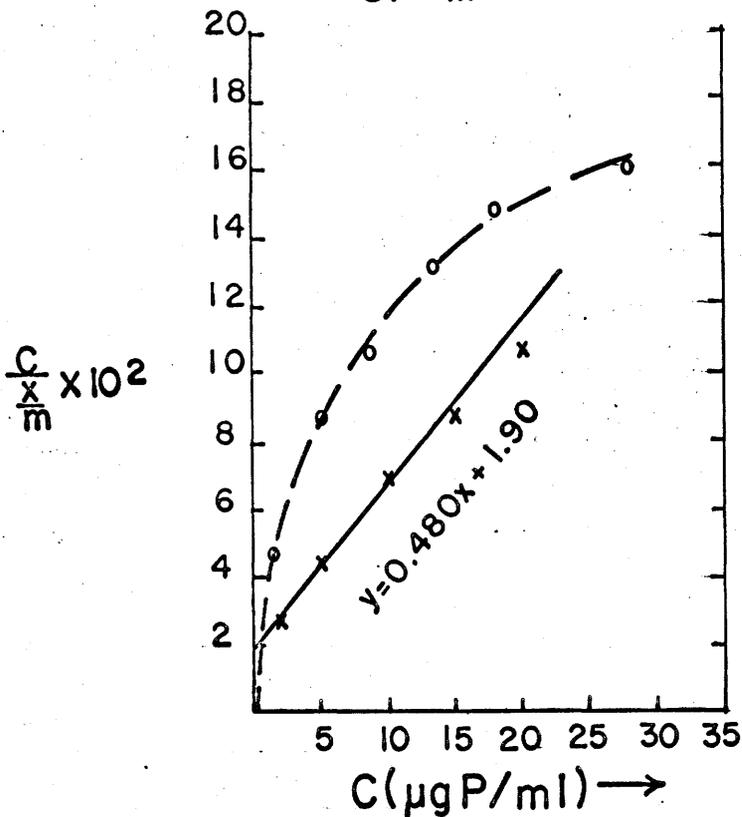
Ca - M



$C (\mu\text{g P/ml}) \rightarrow$

$C (\mu\text{g P/ml}) \rightarrow$

Sr - M



Ba - M

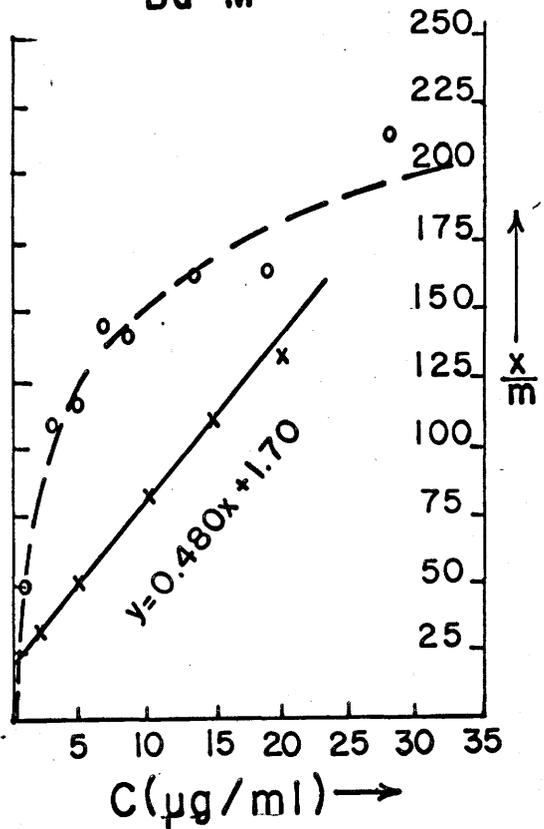


Figure 6.2.4-5. Plot of the Langmuir isotherms for phosphorus adsorption by magnesium montmorillonite (Mg-M), calcium montmorillonite (Ca-M), strontium montmorillonite (Sr-M), and barium montmorillonite (Ba-M).

o-o = $\frac{x}{C}$ vs. $\frac{x}{m}$

x-x = $\frac{x}{C}$ vs. $\frac{C}{x/m} \times 10^2$

6.2.4.1 The equilibrium constant (k)

While k is a constant related to bonding energy of phosphorus of a specific clay mineral on the clay surface/through the equation (13):

$\Delta F = RT \ln k$ Equation 6.2.4.1-1

where:

ΔF = bonding energy

R = the gas constant and

T = the absolute temperature

it can also be referred to as the equilibrium constant in the relationship:

activity of adsorbate + activity of unoccupied sites of adsorbant = activity of the occupied sites

Therefore $k = \frac{(a_{\text{occupied sites}})}{(a_{\text{adsorbate}})(a_{\text{unoccupied sites}})}$ Equation 6.2.4.1-2

If θ is the fraction of the available surface of the adsorbant covered by the adsorbate, c the activity or concentration of adsorbate in very dilute solution, the relationship (6.2.4.1-2) becomes (13):

$k = \frac{\theta}{c(1 - \theta)}$ Equation 6.2.4.1-3

From the relationship (6.2.4.1-2) it can be seen that as the reaction goes to the right, due to increasing affinity of the adsorbant for the adsorbate, k increases too. Inversely, an increase in k suggests an increasing affinity of the adsorbant for the adsorbate. From Equation 6.2.4.1-2 it can also be shown that:

$k = \frac{1}{c}$, at $\theta = 1/2$ (or at 1/2 P adsorption maximum) Equation 6.2.4.1-4

This then implies that the higher the k, the lower is the equilibrium

concentration of the adsorbate at half coverage or half maximum adsorption. Inversely the lower the equilibrium concentration at which half adsorption maximum is achieved the higher is the equilibrium constant (k).

It can be stated that as the thickness of the diffuse double layer decreases and the average activity of the phosphate ion increases, as a result of the increase of the valency of the saturating cation, the adsorption of the phosphate ion on the clay surface is facilitated. It is then implied that under these conditions the half adsorption maximum can be achieved at lower phosphate ion activity in the equilibrium solution. According then to relationships (6.2.4.1-1) and (6.2.4.1-4) under the above conditions, the equilibrium constant (k) and the bonding energy (ΔF) increase. It can be then deduced that the equilibrium constant, and the bonding energy of phosphorus on the clay surface is higher when the clay is saturated with a divalent and lower when saturated with monovalent cation.

Table 6.2.4.1-1 shows that the equilibrium constant (k), varies as was expected.

6.2.4.2 Phosphorus adsorption maximum (b)

The adsorption maxima values given in Table 6.2.4.2-1 have a function not only of the type of clay, but of the saturating cation. The cation on the clay, in particular, markedly influenced the amount of phosphorus adsorbed. These results can be explained through the Stern double layer and the Donnan equilibrium theories:

According to the Stern double layer theory, as the valency increases and the hydrated radius of the cation decreases, the

thickness of the diffuse double layer decreases; the Donnan equilibrium theory dictates that the average activity of the phosphate ion in the micellar (inner) solution increases as a result of the suppression of the uneven ion distribution occurring under the above conditions. It can then be understood that the properties of exchangeable cation as stated above will result in conditions favoring the increase of the phosphorus adsorption and hence of the phosphorus adsorption maximum. From Table 6.2.4.2-1, as is anticipated from theoretical considerations, it can be seen that, in general, the lower the hydrated radius and the higher the valency of the exchangeable cation, the higher is the phosphorus adsorption maximum for the same type of clay mineral.

It has been shown that the effect of the size of the cation is less effective than the effect of valency in suppressing the diffuse double layer (Sections 3.2 and 3.3); hence it can be expected that the effect of valency is higher than that of the hydrated radius of the exchangeable cation on phosphorus adsorption maximum. Thus, the values of phosphorus adsorption maxima of the clays when saturated with different divalent cations do not differ much from one another, but they are considerably higher than the adsorption maxima of the clays with monovalent cations on the exchange complex. The adsorption maxima values in the latter case are very close to each other except for the K-illite whose adsorption maximum deviates considerably from the rest of the adsorption maxima with monovalent saturations. This difference can be attributed to the interlayer adsorption of K by illite (14) leading to a further neutralization of negative charge and suppression of the diffuse double layer.

Table 6.2.4.1-1. Values of equilibrium constants (k) in $(\mu\text{g/ml})^{-1}$

Exchangeable cation	Kaolinite	Illite	Montmorillonite
Li ⁺	0.57	0.66	Overall negative
Na ⁺	0.54	0.38	
K ⁺	0.56	0.40	adsorption
Mg ⁺⁺	0.70	0.86	0.27
Ca ⁺⁺	1.20	1.57	0.32
Sr ⁺⁺	1.20	-	0.25
Ba ⁺⁺	1.70	1.34	0.38

Table 6.2.4.2-1. Values of phosphorus adsorption maximum (b) in $\mu\text{g P/g}$ clay

Exchangeable cation	Phosphorus adsorption maxima (b) in $\mu\text{g P/g}$ clay		
	Kaolinite	Illite	Montmorillonite
Li^+	108.6	107.5	Overall negative adsorption
Na^+	119.7	110.9	
K^+	112.0	216.0	
Mg^{++}	143.0	289.8	182.0
Ca^{++}	166.0	317.0	216.4
Sr^{++}	166.0	-	208.3
Ba^{++}	169.4	298.5	208.3

The effect of the exchangeable cation among different types of clays can be best illustrated through the use of volume of exclusion (V_{ex}). It has been shown in section 4.2 that the higher the CEC the higher will be the variation of V_{ex} ; for example if the clays are suspended in 0.01 N NaCl and 0.01 N $CaCl_2$ respectively, then:

$$(\Delta V_{ex})_{\text{montmorillonite Na-Ca}} > (\Delta V_{ex})_{\text{illite Na-Ca}} > (\Delta V_{ex})_{\text{kaolinite Na-Ca}} \quad 6.2.4.2-1$$

where:

$$(V_{ex})_{\text{clay Na-Ca}} = (V_{ex})_{\text{Na-clay}} - (V_{ex})_{\text{Ca-clay}}$$

The higher the V_{ex} , the higher will be the volume in which the phosphate ion is excluded and also the higher will be the thickness of the diffuse double layer; under these conditions phosphorus adsorption and the phosphorus adsorption maximum of the clay minerals will be lower. Therefore, the higher the variation in V_{ex} the higher will be the variation in phosphorus adsorption and hence the higher the variation of the phosphorus adsorption maximum but in the opposite direction:

$$(\Delta P \text{ ads. max})_{\text{illite Ca-Na}} > (\Delta P \text{ ads. max})_{\text{kaolinite Ca-Na}} \quad 6.2.4-2-2$$

An inspection of Table 6.2.4.2-1 confirms the above relationship. Montmorillonite saturated with alkali metals shows an overall negative adsorption of phosphorus and can not be compared with kaolinite and illite which show an overall positive adsorption.

Similar cationic effects on phosphorus adsorption were reported

by A. Wild (41) although he used different experimental techniques. He found that the cationic effect on phosphorus adsorption at varying pH values up to pH 9 by montmorillonite and kaolinite followed the order: $Ca^{++} > Cs^{+} > Na^{+}$. A. Wild explained the above cationic effect through the influence of the cation on the structure of the diffuse double layer which in turn influences the phosphate ion activity in the micellar solution.

6.2.5 The effect of salt addition on the phosphorus adsorbed by the prepared clays

Added salt should compress the diffuse double layer thus leading to an increase in phosphorus adsorption. To demonstrate the effect of addition of salt on phosphorus adsorption, 0.1 N NaCl was added concurrently with dilute NaH_2PO_4 solution in 0.5 g Na-montmorillonite. For the rest of the experiment the procedure followed was the same as described in Section 6.2.3. The results presented in Table 6.2.5-1 confirm the theoretical predictions. ^{But} the addition of 0.1 N sodium chloride to the barium kaolinite suspensions resulted in a decrease of phosphorus adsorption. The addition of sodium chloride to this barium system would cause an immediate replacement of barium by sodium on the exchange complex. This would induce an increase rather than a decrease in the thickness of the diffuse double layer. The increase of the salt concentration in the intermicellar solution seems not to be strong enough to counter-balance the effect of substitution of Ba by Na; thus the overall effect will be the increase of the thickness of the diffuse double layer. Under these conditions the phosphorus adsorption on the clay should decrease, as

Table 6.2.5 - 1. The effect of the addition of 0.1 N NaCl on phosphorus adsorption by Ba-kaolinite and Na-montmorillonite systems.

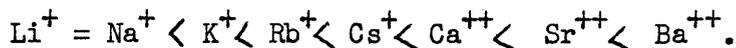
<u>Ba - kaolinite</u>		<u>Ba-kaolinite in 0.1 N NaCl</u>		Na - montmorillonite (no salt added)	<u>Na-montmorillonite in 0.1 N NaCl</u>	
c ($\mu\text{g P/ml}$)	$\frac{x}{m}$ ($\mu\text{g P/g clay}$)	c ($\mu\text{g P/ml}$)	$\frac{x}{m}$ ($\mu\text{g P/g clay}$)		c ($\mu\text{g P/ml}$)	$\frac{x}{m}$ ($\mu\text{g P/g clay}$)
0.83	116.7	3.08	91.6	Overall negative adsorption	2.83	108.3
2.62	137.5	4	100		7.83	216.7
4.58	141.7					

is evidenced in the data in Table 6.2.5-1.

This variable effect of the added salt on the thickness of the diffuse double layer is supported by de Haan's work (10). For example, he found that the volume of exclusion (V_{ex}) in montmorillonite systems decrease with increase in concentration of the electrolyte solution in systems containing only NaCl or $CaCl_2$. In mixed Ca-Na montmorillonite systems, containing $CaCl_2$ and NaCl in equal proportions the volume of exclusion tends to be appreciably lower than in the Ca-montmorillonite systems in spite of the fact that the electrolyte concentration in the Na-Ca-montmorillonite system can be many times higher than in the Ca-Montmorillonite system. However, the volume of exclusion in the mixed Na-Ca-montmorillonite is lower than that in the Na-montmorillonite systems at equal electrolyte concentration levels. De Haan also showed that the lower the V_{ex} as a result of increasing salt concentrations in a homionic system the higher is the phosphorus adsorption.

SUMMARY AND CONCLUSIONS

Wild (41) investigated the effect of exchangeable cations on the fixation of phosphate by kaolinite, montmorillonite and Rothamsted subsoil clay. He first converted the clays to acid clays by leaching with dilute HCl. The pH of the clay suspensions were adjusted by titrating with acid or base, containing a specific cation prior to equilibrating with very dilute phosphorus solution (2.3×10^{-4} moles H_3PO_4 per l). The titration of the clay suspensions with a base served a dual purpose, first, it adjusted the pH of the system and, secondly, saturated the clay with a specific cation. All clays showed much higher retention of phosphorus in the presence of Ca^{++} than in the presence of Na in the pH range of 4-9. Above pH 9 the amount of phosphorus retained by Ca-clays increased even more, while that of Na-clays decreased to zero. With the Rothamsted clay at pH 5.5, the effect of the cations on the amount of phosphorus retained by the clay was in the order of:



Above pH 9.5, the order with the alkaline earths was reversed. This indicated a precipitation reaction of phosphorus with the alkaline earths as Ca^{++} in solution has a greater effect on phosphate precipitation than Ba^{++} in solution (solubility product criteria).

Due to the presence of Al on the exchange complex prior to saturating these clays with a specific cation, Wild concluded that $Al(OH)_2H_2PO_4$ had been formed. The exchangeable cation was thought to have two effects on the formation of the above compound:

1. The added cation determined the amount of reactive Al by replacing it from the exchange complex.

2. The cation determined the distribution of phosphate ions within the Gouy layer.

Both effects could have occurred at the same time.

Coleman et al. (9a) used Granville and Cecil soils and showed that Al-montmorillonite bound quantities of phosphate equivalent to the exchangeable Al, but only under conditions favoring Al hydrolysis. The Granville, a soil containing relatively large amounts of exchangeable Al bound far more phosphate when titrated with $\text{Ca}(\text{OH})_2$ than when Ca-saturated by salt leaching. In the former case, the products of hydrolysis remained in the soil and in the latter, the hydrolysis products were leached out. On the other hand, the amount of phosphate sorbed by the Cecil soil, although appreciable, was independent of the method of saturating the soil. The Cecil soil contained virtually no exchangeable Al. It was suggested (9a) that phosphate was bound in the Cecil soil through a reaction involving the clay and oxide minerals. The high fixing capacity of hydrous Al compounds has been demonstrated by Coleman (9) and others (33a,39). In a similar study clays coated with hydroxy Al-polymers adsorbed approximately 100 times more phosphate than uncoated clays (35).

The methods that were used in the present work to clean and to saturate the clays with exchangeable cations were deliberately chosen to exclude the possibility of the presence of Al or Fe in any appreciable amounts on the exchange sites. Therefore, the effect of the saturating cation on the phosphorus adsorption (Tables 6.2.4.1-1, 6.2.4.2-1, and 6.2.5-1) cannot be attributed to the release of Al^{+++} ion from the exchange sites, and the effect of the saturating cation can be evaluated without the Al^{+++} ion interference.

It is still possible, however, that Al^{+++} may be released by

decomposition of the clay lattice during the equilibration period with phosphorus. This Al^{+++} may occupy exchange sites and, in part, enter into solution where it would react with the phosphate ion. Through solubility product criteria, Hemwall, /^(14a) proved that the Al dissociating from the clay lattice was precipitated as $\text{Al}(\text{OH})_2(\text{H}_2\text{PO}_4)$ at pH 4 and could account for the observed phosphorus fixation. However, he did not try these calculations at higher pH values. Since Al^{+++} at pH 5 polymerizes to positively charged hydroxy polymers (21), it is reasonable to assume that at nearly neutral pH values the Al^{+++} which originates from the decomposition of the clay lattice is for all practical purposes in the form of hydroxy polymers. These polymers, being positively charged (21), are most likely attached on clay surfaces where they can fix phosphorus. Since the pH values of the systems in this study are kept between 6.0-7.2, Hemwall's explanation of phosphorus fixation by clays is inapplicable in this study.

Another explanation of phosphorus fixation by clays is precipitation by divalent cations dissociating from the exchange sites of the clay. Wild (41) showed that when standard clays and Rothamsted subsoil clay were suspended in 0.02 N CaCl_2 solution, fixation increased rapidly as the pH values increased to pH 9 and higher, indicating the formation of a calcium-phosphate precipitate. The method used for saturating the clays with exchangeable cation in this study excludes the possibility of the saturating cation existing in any appreciable amount in the clay suspensions. Calculations showed that, if all the exchangeable Ca^{++} on montmorillonite dissociated from the clay surface, it would not furnish a Ca^{++} ion concentration under the chosen experimental conditions higher than 0.01 N. Moreover, Ca^{++} concentration in this solution is approximately equal to $5 \cdot 10^{-5}$ N (14). Application of solubility product criteria showed that Ca^{++} ion

cannot precipitate phosphorus at this low concentration level. The data obtained from the addition of 0.1 N NaCl to the Ba-kaolinite-phosphorus solution also suggest that the saturating cation does not exist in any appreciable amount in the clay suspension. Under these conditions Ba^{++} ion concentration in solution should increase. If precipitation of Ba^{++} and phosphate had occurred, the amount of phosphorus fixed would be greater than the amount fixed by the Ba-kaolinite system without an addition of 0.1 N NaCl. This was not the case (Table 6.2.5-1). Therefore, the precipitation of phosphorus by divalent cations released into solution from the exchange complex can be disregarded as a possibility in this work.

Phosphorus adsorption changed with the saturating cation in the following order:

For kaolinite: $Li^+ < K^+ < Na^+ \ll Mg^{++} < Ca^{++} = Sr^{++} < Ba^{++}$,

For illite: $Li^+ < Na^+ < K^+ \ll Mg^{++} < Ba^{++} < Ca^{++}$,

For montmorillonite: $Mg^{++} < Sr^{++} = Ba^{++} < Ca^{++}$

The cationic effect on phosphorus adsorption in Wild's work (41) followed the order:

For kaolinite and montmorillonite: $Na^+ \ll Ca^{++}$ at pH 5

For Rothamsted subsoil clay: $Li^+ = Na^+ < K^+ \ll Ca^{++} < Sr^{++} < Ba^{++}$ at pH 5.5

The amount of phosphorus adsorbed in Wild's experiments was greater (41) than values obtained in this study. He also obtained a value of phosphorus adsorption by Na-montmorillonite which exhibited negative adsorption in the present study.

A comparison of the two studies shows in general the same trends.

The effect of cations on phosphorus adsorption through the release of Al^{+++} by the exchangeable cations cannot be applied in this work as has been discussed. The effect of cations on phosphorus adsorption through the influence of phosphate concentration in the Gouy layer (diffuse double layer) in the absence of Al^{+++} , can be regarded as the only possibility which can be applied.

As the thickness of the diffuse double layer increases, the volume of the micellar solution increases and the volume from which phosphate ions are excluded becomes larger (Section 6.2.4). Under these conditions, the accessibility of the reactive clay sites to the phosphate ions decreases with the result that there is a decrease of phosphorus adsorption. This effect is more pronounced in montmorillonite when saturated with monovalent cations than when saturated with divalent cations (Table 6.2.4.2-1). With monovalent cation saturations, an overall negative adsorption of phosphorus was observed. The addition of 0.1N NaCl to this system resulted in a positive phosphorus adsorption which reached the magnitude of phosphorus adsorption exhibited by Ca-montmorillonite (Table 6.2.5-1).

In the absence of exchangeable Al and of any divalent cation in solution that could cause precipitation, the above increase in phosphorus adsorption can only be explained through the contraction of the diffuse double layer by an increased salt concentration through the addition of 0.1 N NaCl.

The effect of valency and hydrated radius of the exchangeable cation on phosphorus adsorption has been discussed in Section 6.2.4. It has been shown that as the valency of the cation increases and the hydrated radius of the exchangeable cation decreases, both the

adsorption maximum and the equilibrium constant increase for the same clay mineral. However, the ratio valency: hydrated radius of the exchangeable cation is not a simple function of the Langmuir adsorption constants. If that was the case, K-clays (with hydrated radius of $K^+ = 1.5 \overset{\circ}{\text{A}}$) and Ca-clays (with hydrated radius of $Ca^{++} = 3 \overset{\circ}{\text{A}}$) (Table App. 11) should have exhibited the same Langmuir adsorption constants. An inspection of Table 6.2.4.1-1 and 6.2.4.2-1 shows that this was not the case. It has been shown that the effect of the valency of the exchangeable cations is greater than the effect of hydrated radius on the thickness of the diffuse double layer (Sections 3.2 and 3.3). The effect of the hydrated radius would not be so noticeable in the very dilute solutions employed in this work. In this case, the ionic atmosphere around the clay particles approached the Gouy type of diffuse layer where the dimensions of the ions are neglected (Section 2.4). Under these conditions, the characteristics of the diffuse double layers with homovalent cations on the exchange complex are almost identical. It is then expected that the values of the phosphorus adsorption constants (b and k) with homovalent cations on the exchange complex should be numerically very close to one another. The values of phosphorus adsorption constants (b and k) are also expected to be significantly greater when the clay is saturated with divalent cations, as compared with the values of these constants (b and k), when the clay is saturated with monovalent cations. These theoretical predictions are verified in Tables 6.2.4.1-1 and 6.2.4.2-1.

The adsorption maxima obtained with Ca^{++} , Sr^{++} and Ba^{++} saturated clays are close to one another and larger than the adsorption maxima

obtained with Mg saturation. These variations can be explained by the fact that the hydrated radius of Ca^{++} , Sr^{++} and Ba^{++} (3.0 to 2.5 Å) are very close to one another, as compared to the hydrated radius of Mg^{++} (4.0 Å).

The phosphorus adsorption maximum obtained with K-illite is also considerably higher than the adsorption maxima obtained with the other monovalent cation saturations. This difference has been explained through the interlayer fixation of K^+ by illite (Section 6.2.4). This fixation is assumed to be brought about during dehydration with ethyl alcohol and drying.

The purification and saturation of the clays with exchangeable cations were carried out so that the effect of exchangeable cations could be investigated without the precipitation of phosphate by Al and Fe. It was therefore possible to evaluate the effect of the exchangeable cations on phosphorus fixation through their influence on the structure of the micellar solution around the clay particles. Other workers (9a, 41) have not eliminated the interference of Al and Fe.

The very low phosphorus adsorption maxima obtained in this work agree with numerous reports that phosphorus adsorption by standard clay minerals is rather small when compared to the amount of phosphorus fixed by Al and Fe oxides or by precipitation with Fe, Al and Ca ions (36).

The question still remains as to where phosphorus has been bound in this work. Van Olphen has hypothesized that clays in addition to the double layer due to the negative charge on the planar surfaces possess a positive double layer at their edge surfaces which may be

capable of adsorbing anions even at neutral pH values (37). This assumption has been used by Hemwall to explain the mechanism of adsorption by a montmorillonite (14a). De Haan assumed that the phosphorus fixed by an illite and a montmorillonite was adsorbed at the clay edge surfaces (10). He showed from data obtained from electron micrographs that all phosphorus fixed by these clays could fit spatially on the clay edges. Since the amount of phosphorus fixed by this mechanism is very small (14a), it is reasonable to assume that phosphorus in this work has been fixed at the edge surfaces.

A complete understanding of the chemistry of soil phosphorus cannot be attained unless the behavior of phosphorus with the individual soil components has first been elucidated. These individual effects can then be interrelated in a unifying principle of soil phosphorus. This study has attempted to investigate the behavior of phosphorus with clay minerals saturated with certain monovalent and divalent cations. The effect of hydroxy aluminum polymers on the phosphorus adsorption maximum of clay minerals is concurrently being investigated by a colleague. This type of research work should continue until enough data has been obtained to identify the phosphorus compounds and their behavior in any soil.

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9. APPENDIX

Table 1. Colorimetric readings of phosphorus colored solutions produced by three methods.

Klett Summerson filter No. 660						Beckmann Spectrophotometer at 625 mμ.			
Ascorbic Acid method		Phosphomolybdic Acid method		Ascorbic Acid method		Isobutyl alcohol method		Ascorbic Acid method	
μg P/ 50 ml	Reading	μg P/ 50 ml	Reading	μg. P/ 25 ml	Reading	μg P/ 50 ml	Reading	μg P/ 50 ml	Reading
0	0	0	0	0	0	0	0	0	0
2	11	1	7	2	24	2	0.020	2	0.017
4	22	2	16	5	60	3	0.032	4	0.035
6	33	5	44	8	97	4	0.040	5	0.044
8	46	8	65	10	120	5	0.050	6	0.052
10	56	10	78	12	143	6	0.060	10	0.087
12	67	15	122	15	182	7	0.68	15	0.125
15	81	20	158	20	239	10	0.093	20	0.175
20	110					15	0.152		
						20	0.195		

Table 2. Reproducibility of results with the ascorbic acid method on a Klett-Summerson photoelectric colorimeter using the same standard phosphorus solution every time.

Phosphorus concentration of the colored solution in $\mu\text{g P}/25 \text{ ml}$	Colorimetric readings of colored solutions in different experiments at an interval of fifteen days			
2	23.5	24.0	24.0	23.4
5	60.0	61.0	59.5	58.3
10	120.0	120.0	120.0	120.0
20	240.0	240.0	239.0	240.0

Table 3. Time adsorption data for Na - illite, Ca - illite and Ca - montmorillonite suspensions.

Initial amount of phosphorus in suspension $\mu\text{g/g}$ clay	Phosphorus adsorbed in $\mu\text{g P/g}$ of clay at the specified time and at different cation saturations					
	Na - illite		Ca - illite		Ca - montmorillonite	
	72 hr	120 hr	72 hr	120 hr	72 hr	120 hr
200	28.33	28.00	154.0	155.0	70.83	71.00
600	75.00	75.50	283.0	283.5	120.8	120.5
2000	87.5	87.2	283.3	284.5		

Table 4. Overall negative adsorption of phosphorus in $\mu\text{g P/g}$ clay exhibited by Na- and K - montmorillonite suspensions at the specified time of shaking and at different initial phosphorus levels.

Initial amount of phosphorus in suspension $\mu\text{g/g}$ clay	Overall negative adsorption of phosphorus in $\mu\text{g P/g}$ clay					
	Na - montmorillonite			K - montmorillonite		
	72 hr	96 hr	120 hr	72 hr	96 hr	120 hr
200	7.00	6.90	7.00	6.50	5.30	6.25
600	23.0	23.4	23.5	22.7	22.8	22.7
2000	75.00	74.9	75.10	71.5	71.7	71.6

Table 5. Adsorption of phosphorus by kaolinite saturated with various cations (phosphorus adsorption is given in micrograms of P per gram of clay $\left(\frac{x}{m}\right)$ and the equilibrium concentration (c) given in micrograms of P per ml.

Li - K*		Na - K*		K - K*		Mg - K*		Ca - K*		Sr - K*		Ba - K*	
c	$\frac{x}{m}$	c	$\frac{x}{m}$	c	$\frac{x}{m}$	c	$\frac{x}{m}$	c	$\frac{x}{m}$	c	$\frac{x}{m}$	c	$\frac{x}{m}$
1.46	54.17	1.46	58.40	1.46	54.16	1.31	68.8	1.12	87.93	1.08	91.66	0.83	116.7
5.17	83.3	3.09	91.00	3.33	66.60	3.03	97.0	2.67	132.7	4.75	125.0	2.62	137.5
9.03	96.70	5.10	89.65	5.17	83.30	4.93	107.0	4.48	151.7	8.55	145.0	4.58	141.7
19.0	100.0	6.86	113.9	7.17	83.30	6.82	118.0	6.51	149.1	18.3	166.0	8.46	154.2
39.0	100.0	18.88	112.0	9.06	93.70	8.77	123.0	13.45	155.2	28.25	175.0	13.46	154.2
				13.98	102.0	13.69	131.1	18.44	155.5			18.29	170.8
				19.00	100.0	38.57	142.8					28.00	200.0
				28.96	104.1								
				38.91	109.1								

* Kaolinite

Table 6. Adsorption of phosphorus by illite saturated with various cations (Phosphorus adsorption is given in micrograms of P per gram of clay ($\frac{x}{m}$) and with the equilibrium concentration (c) given in micrograms of P per ml)

Li - I*		Na - I*		K - I*		Mg - I*		Ca - I*		Ba - I*	
c	$\frac{x}{m}$	c	$\frac{x}{m}$	c	$\frac{x}{m}$	c	$\frac{x}{m}$	c	$\frac{x}{m}$	c	$\frac{x}{m}$
1.45	55	1.72	28.33	1.27	72.91	.678	132.2	0.46	154.0	.708	129.2
5.08	91.66	3.25	75.00	2.77	122.9	1.86	213.5	1.67	233.3	2	200
9.00	100.00	7.25	75.00	4.57	143.7	3.69	231.35	3.17	283.3	3.77	222.9
18.91	108.3	13.96	104.0	6.42	158.3	5.59	240.7	5.25	275.0	5.67	233
		19.12	87.5	6.45	154.1	7.50	250.0	7.17	283.0	7.58	241.7
		29.50	100.0	8.46	154.1	12.20	279.66	11.83	316.7	12.50	250.0
		37.50	100.0	18.12	187.5	17.29	271.18	17.16	283.3	17.31	268.7
				27.87	212.5			27.00	300	27.50	250
								36.66	333	37.25	275

*Illite

Table 7. Adsorption of phosphorus by montmorillonite saturated with various cations (Phosphorus adsorption is given in micrograms of P per gram of clay($\frac{x}{m}$) and the equilibrium concentration (c) is given in micrograms of P per ml)

Li - M*	Na - M*	K - M*	Mg - M*		Ca - M*		Sr - M*		Ba - M*	
			c	$\frac{x}{m}$	c	$\frac{x}{m}$	c	$\frac{x}{m}$	c	$\frac{x}{m}$
Overall negative			1.43	56.65	1.29	70.83	1.42	58.33	1.50	50
adsorption			3.04	96.25	2.95	104.2	4.92	108.3	2.92	108.3
			4.92	108.3	4.79	120.8	8.67	133.3	4.83	116.6
			6.84	116.4	8.42	158.3	13.33	166.7	6.54	145.8
			13.72	127.5	28.08	191.6	18.17	183.3	8.56	141.7
			18.51	148.9	38.0	200.0	27.83	216.7	13.37	162.5
			28.28	172					18.35	164.5
									27.67	233.3

*Montmorillonite

Table 8. Integer values of equilibrium phosphorus concentrations (c) in $\mu\text{g P/ml}$ and the corresponding values of $\frac{c}{\frac{x}{m}} \times 10^2$ for the plot of the Langmuir isotherms of phosphorus adsorbed by kaolinite in the different cationic saturations.

c	Li - K*	Na - K*	K - K*	Mg - K*	Ca - K*	Sr - K*	Ba - K*
				$\frac{c}{\frac{x}{m}} \times 10^2$			
2	3.33	3.33	3.47	2.42	1.66	1.95	1.57
5	5.71	5.31	6.45	4.65	3.40	3.92	3.47
10	10.81	9.61	10.55	8.00	6.45	6.62	6.41
15	15.43	13.79	15.00	11.55	9.57	9.23	9.20
20	20.0	17.02	19.55	15.10	12.74	11.90	11.59

* Kaolinite

Table 9. Integer values of equilibrium phosphorus concentrations (c) in $\mu\text{g P/ml}$ and the corresponding values of $\frac{c}{\frac{x}{m}} \times 10^2$ for the plot of the Langmuir isotherms of phosphorus adsorbed by illite with different cationic saturations.

C	Li - I*	Na - I*	K - I*	Mg - I*	Ca - I*	Ba - I*
			$\frac{c}{\frac{x}{m}} \times 10^2$			
2	3.50	4.19	2.00	1.00	0.80	1.00
5	6.02	6.90	3.44	2.10	1.73	2.02
10	10.80	11.26	5.78	3.85	3.38	3.70
15	15.38	16.06	8.00	5.55	4.96	5.40
20	19.90		10.25	7.25	6.58	7.10

* Illite

Table 10. Integer values of equilibrium phosphorus concentration (c) in $\mu\text{g P/ml}$ and the corresponding values of $\frac{c}{x} \times 10^2$ for the plot of the Langmuir isotherms of phosphorus adsorbed by montmorillonite with different cationic saturations.

c	Mg - M*	Ca - M*	Sr - M*	B - M*
	$\frac{c}{x} \times 10^2$			
2	3.07	2.35	3.76	2.66
5	4.54	3.85	4.54	4.00
10	7.58	6.15	6.89	6.66
15	10.30	8.69	8.76	8.82
20	12.93	11.11	10.69	10.66

*Montmorillonite

Table 11: Most probable hydration numbers according to Ulich,
and mean effective diameters (d) in Angstrom as given
by Kielland (39)

Ion	H ⁺	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Mg ²⁺	Ca ²⁺	Ba ²⁺
H ₂ O/ion	4	6	4	2.5	2	9-13	8-10	6-8
d	9	6	4.3	3	2.5	8	6	5

