

POTENTIAL-DISTANCE RELATIONSHIPS OF CLAY-WATER SYSTEMS CONSIDERING THE STERN THEORY

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Abstract—This paper deals with the use of Stern theory as applied to a clay-water electrolyte system, which is more realistic to understand the force system at micro level than the Gouy-Chapman theory. The influence of the Stern layer on potential-distance relationship has been presented quantitatively for certain specified clay-water systems and the results are compared with the Gouy-Chapman model. A detailed parametric study concerning the number of adsorption spots on the clay platelet, the thickness of the Stern layer, specific adsorption potential and the value of dielectric constant of the pore fluid in the Stern layer, was carried out. This study investigates that the potential obtained at any distance using the Stern theory is higher than that obtained by the Gouy-Chapman theory. The hydrated size of the ion is found to have a significant influence on the potential-distance relationship for a given clay, pore fluid characteristics and valence of the exchangeable ion.

Key Words—Cation Size, Clay Minerals, Diffuse Double Layer, Electric Potential, Stern Theory.

INTRODUCTION

Several investigators have studied the diffuse double layer theory (Verwey and Overbeek 1948; Bolt 1956; Low 1959; van Olphen 1963; Mitchell 1976; Sridharan and Jayadeva 1982) to understand better the behavior of a clay-water electrolyte system. Many of these researchers have used the Gouy-Chapman theory to explain their experimental observations (Bolt 1956; Olsen and Mesri 1970; Mitchell 1976; Sridharan and Jayadeva 1982). However, the Gouy model of an electric double layer contains some unrealistic elements. For example, the ions are treated as point charges and any specific effects related to the ion size are neglected. However, in the vicinity of particle surface, where the concentration is high, the distance of the closest approach to the surface is important and the size of the ions must be considered to give an accurate description of the status of cations adsorbed on clay particles as in the Stern model. An attempt was made here to study the effect of various parameters on the potential-distance relationship assuming the Stern model and compared the effect to the Gouy-Chapman model.

DOUBLE LAYER AS PER STERN THEORY

In the Stern theory, the distance of the closest approach of counter-ions to the charged clay surface is limited by the size of these ions. The counter-ions charge is separated from the surface charge by a layer of thickness, δ in which there is no charge (van Olphen 1963). A molecular condenser is formed by the surface charge and the charge in the plane of the centers of the closest-ions (Figure 1). Beyond the molecular condenser, the remainder of the counter-ion charge is distributed as in a diffuse Gouy atmosphere. A low dielectric constant is assigned to the medium within the Stern layer (van Olphen 1963). Many investigators

have discussed the dielectric constant of the medium next to the charged plate (Conway et al. 1951; Cownie and Palmer 1952; Palmer 1952; Palmer et al. 1952). Sridharan (1968) discussed the variation of a dielectric constant with distance, closer to the clay platelet as brought out by the above investigators and concluded that there is a general agreement between different approaches and could be taken as 3 to 6.

Single Platelet (van Olphen 1963)

Clay particles carry net negative charges on their surfaces (Grim 1962; Lambe and Whitman 1969; Mitchell 1976). These negative charges are primarily due to isomorphous substitution. These charges depend upon the type of the clay and the environmental conditions in which they are formed. They can be treated as constant charged platelets.

$$\sigma = \sigma_1 + \sigma_2 \quad [1]$$

where σ = Total surface charge = BEC/S, σ_1 = Charge in the Stern layer, σ_2 = Charge in the Gouy layer, where BEC = Base exchange capacity of soil and S = Specific surface area of soil.

According to the Stern theory, σ_1 and σ_2 are given as:

$$\sigma_1 = \frac{N_1 v e}{1 + (N_A / M n) \exp(-ve\Phi_\delta + \Psi) / kT} \quad [2]$$

$$\sigma_2 = \left(\frac{\epsilon n k T}{2\pi} \right) \sinh \left(\frac{ve\Phi_\delta}{2kT} \right) \quad [3]$$

where N_1 = No. of adsorption spots on 1 cm² area of the surface, N_A = Avogadro Number, M = Molecular weight of the solvent, n = Concentration of ion electrolyte, v = Valence of cation, e = Unit electrostatic charge, Φ_δ = Potential on the border of Stern and Gouy layers (Stern Potential), ψ = Specific adsorption po-

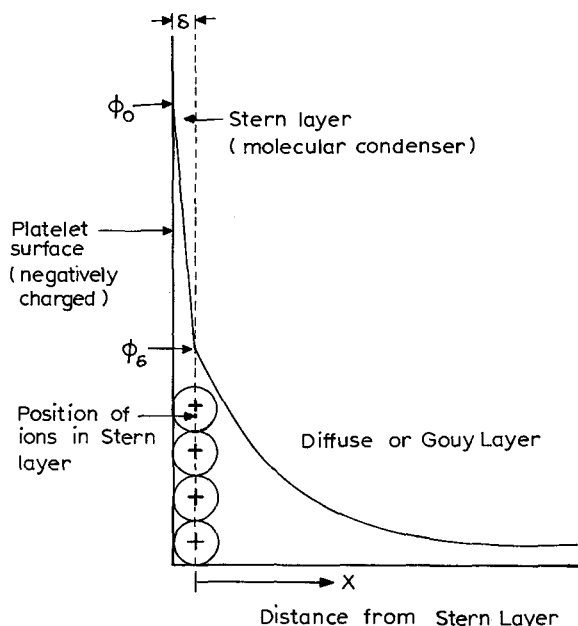


Figure 1. Schematic figure of Stern and Gouy layers.

tential of the counter-ions at the surface, k = Boltzmann constant, T = Absolute temperature and ϵ = Dielectric constant of the pore medium.

The surface charge is related to the Stern potential and surface potential as:

$$\sigma = \frac{\epsilon'}{4\pi\delta} (\Phi_0 - \Phi_\delta) \tag{4}$$

where ϵ' = Dielectric constant of the medium within the field of the molecular condenser (that is, within the Stern layer), δ = Thickness of the Stern layer, ϕ_0 = Potential at the surface of the clay platelet and ϕ_δ = Stern potential.

Substituting the Equations [2] and [3] into [1], one can get the relation between σ and ϕ_δ as

$$\sigma = \frac{N_1 ve}{1 + (N_A/Mn)\exp(-(ve\Phi_\delta + \Psi)/kT) + \left(\frac{\epsilon nkT}{2\pi}\right) \sinh\left(\frac{ve\Phi_\delta}{2kT}\right)} \tag{5}$$

By solving Equation [5], one can get the value of ϕ_δ . By knowing the value of ϕ_δ , using Equation [4], surface potential, ϕ_0 can be calculated.

POTENTIAL-DISTANCE RELATIONSHIP. Within the literature, the potential-distance relationship for clays using the Stern theory has been dealt with qualitatively, but not quantitatively. Therefore within this paper, an attempt was made to give a quantitative picture. For the Stern layer, the potential drops linearly with distance from a value of ϕ_0 at the surface to a value of ϕ_δ (Stern

Table 1. Values of valence, hydrated radius and N_1 for various ions.

Ion	Valence	Hydrated radius (Å)	N_1 (ions/cm ²)
K	1	3.8	1.731×10^{14}
Na	1	7.9	4.006×10^{13}
Li	1	10.3	2.357×10^{13}
Ca	2	9.6	2.713×10^{13}

potential) at a distance, δ . Beyond the Stern layer, the potential distribution, which follows the Gouy distribution, considering ϕ_δ as the starting potential of the Gouy layer, is given by:

$$e^{y/2} = \frac{e^{z_0/2} + 1 + (e^{z_0/2} - 1)e^{-\xi}}{e^{z_0/2} + 1 - (e^{z_0/2} - 1)e^{-\xi}} \tag{6}$$

where $y = ve(\Phi/kT)$ (Non-dimensional potential at a distance x) $z_0 = (ve\Phi_\delta/kT)$ and $\xi = Kx$, in which $K = \sqrt{8\pi n e^2 v^2 / \epsilon kT}$. Thus, for any given soil and pore fluid, ϕ_δ can be determined from Equation [5], ϕ_0 from Equation [4], and potential, ϕ at any distance, x beyond the Stern layer using Equation [6].

Parametric Study

The influence of various parameters, such as, the number of adsorption spots on 1 cm² area of the plate, N_1 , the thickness of Sternlayer, δ , specific adsorption potential, ψ , the value of dielectric constant of pore fluid within the Stern layer, and ϵ' on potential-distance relationships have been studied. Also, the distribution of potential according to the Stern theory is compared to the Gouy-Chapman theory.

The thickness of the Stern layer was taken as the radius of the hydrated ion. The number of adsorption spots on 1 cm² area of the plate, N_1 depends upon the hydrated radius of the ion. The value of N_1 is determined as the number of equivalent squares of size equal to the diameter of the hydrated ion of those can be accommodated on 1 cm² area of the platelet. Hence, the thickness of the Stern layer and the number of adsorption spots per cm² of the plate are interdependent.

Table 1 presents the type of ion, valence, hydrated radius (Mitchell 1976) and corresponding value of N_1 . When the type of ion is specified, corresponding values of δ , N_1 , and v were used.

Table 2 gives the values of BEC, Base Exchange Capacity, and S, Specific Surface Area, for the three types of clays, which were used in this study (Sridharan and Jayadeva 1982).

Table 3 gives the assumed values of dielectric constant of the pore fluid in the Gouy atmosphere, ϵ , dielectric constant of the fluid in the Stern layer, ϵ' and the molecular weight of the solvent, M , which were used in this study. The values were taken at a room temperature of 25 °C.

Table 2. Clay properties.

Clay type	BEC (meq/100 gm)	S (m ² /gm)
Montmorillonite	100	800
Illite	40	100
Kaolinite	3	15

EFFECT OF N_1 . Figure 2 hypothetically shows the effect of N_1 on the potential-distance relationship, beyond the Stern layer, for a fixed value of δ of 6 Å. As N_1 is increased, the Stern potential is decreased at any distance. Beyond the value of $N_1 \approx 10^{16}$ ions/cm², the potential at any distance by the Stern theory is less than that obtained by the Gouy-Chapman theory. Figure 3 shows the potential-distance relationship for Na and Ca montmorillonites, with corresponding values of N_1 , δ and v (Table 1). For both Na and Ca montmorillonites, it was seen that the potential at any point that is obtained using the Stern model is higher than that is calculated by using the Gouy-Chapman model throughout.

EFFECT OF ϵ' . From Equations [4] and [5], it can be seen that the change in the value of ϵ' does change the value of ϕ_s , but not ϕ_0 . The relation between ϕ_0 and ϵ' is given by Equation [6]. Figure 4 gives the varia-

Table 3. Values of dielectric constants in Gouy and Stern layers and molecular weights for various pore fluids

Pore fluid	Dielectric constant in Gouy layer (ϵ)	Dielectric constant in Stern layer (ϵ')	Molecular weight of pore fluid (M)
Water	78.54	6	18
Ethanol	24.3	3	46
Carbon tetrachloride	2.28	2.28	154

tion in surface potential with ϵ' . It can be observed that the increase of the value of ϵ' decreases the surface potential, ϕ_0 significantly. Since ϕ_s was not affected by ϵ' , beyond the Stern layer, the potential distribution was the same for a given soil and pore fluid characteristic and was independent of ϵ' .

EFFECT OF ψ . The relation between the specific adsorption potential, ψ , thickness of Stern layer, δ , and surface negative charge, σ , is given by Equation [5]. The change within the value of ψ causes change within the Stern potential. Figure 5 gives the potential-distance relationship for Li and K montmorillonites for $\psi = 0$ and $\psi = 0.1$ eV. Corresponding values of N_1 and δ given in Table 1 were used. It is observed that the increase of ψ reduces the Stern potential significantly that is for K, especially when N_1 is large.

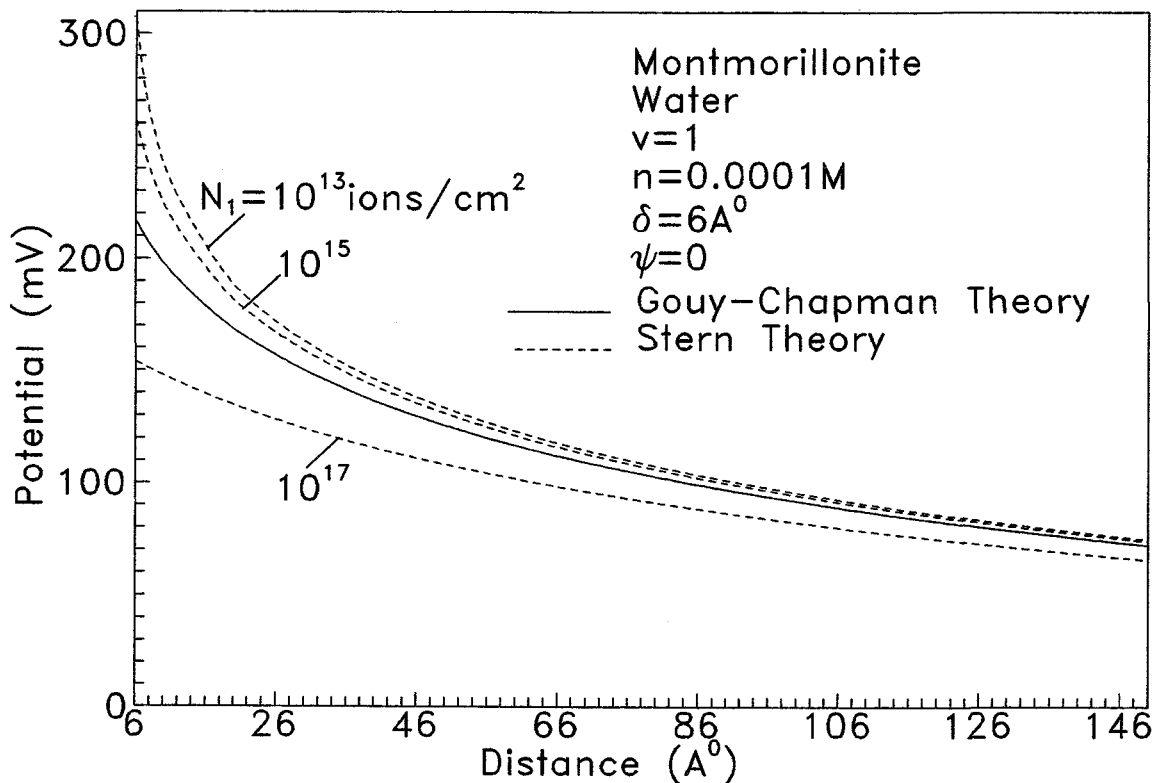


Figure 2. Effect of N_1 on potential-distance relationship.

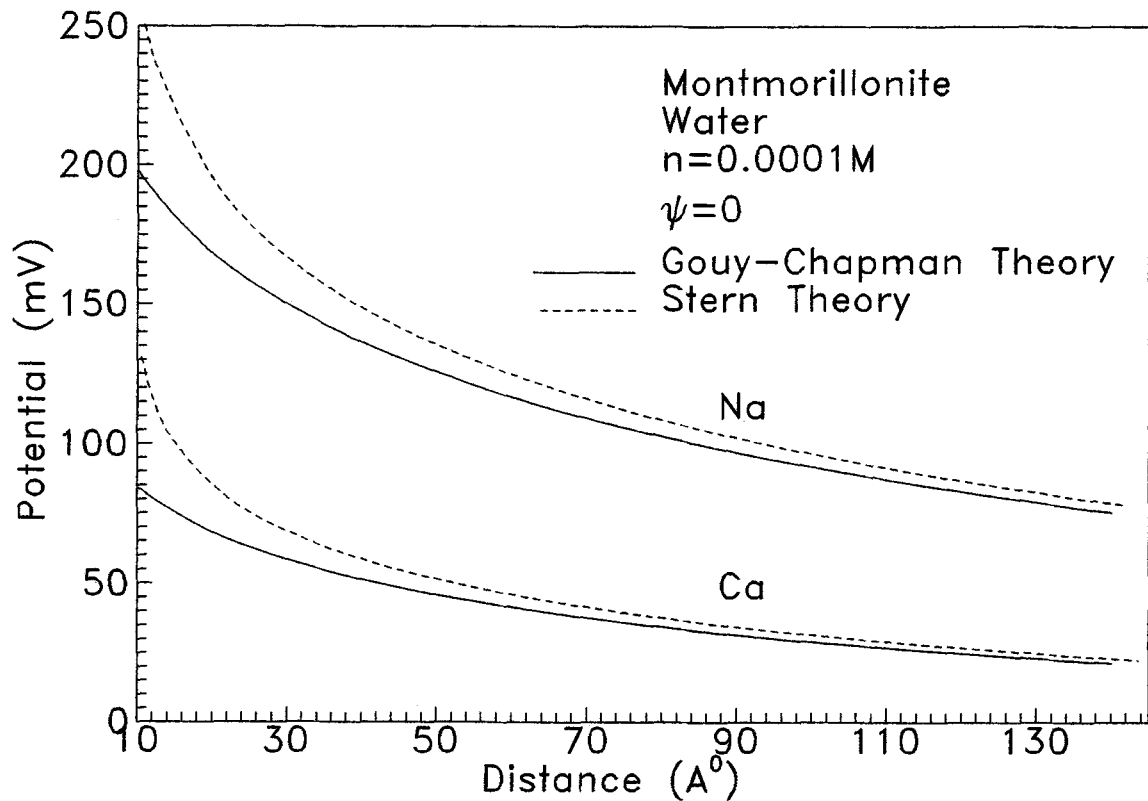


Figure 3. Potential vs distance curves for Na and Ca montmorillonites.

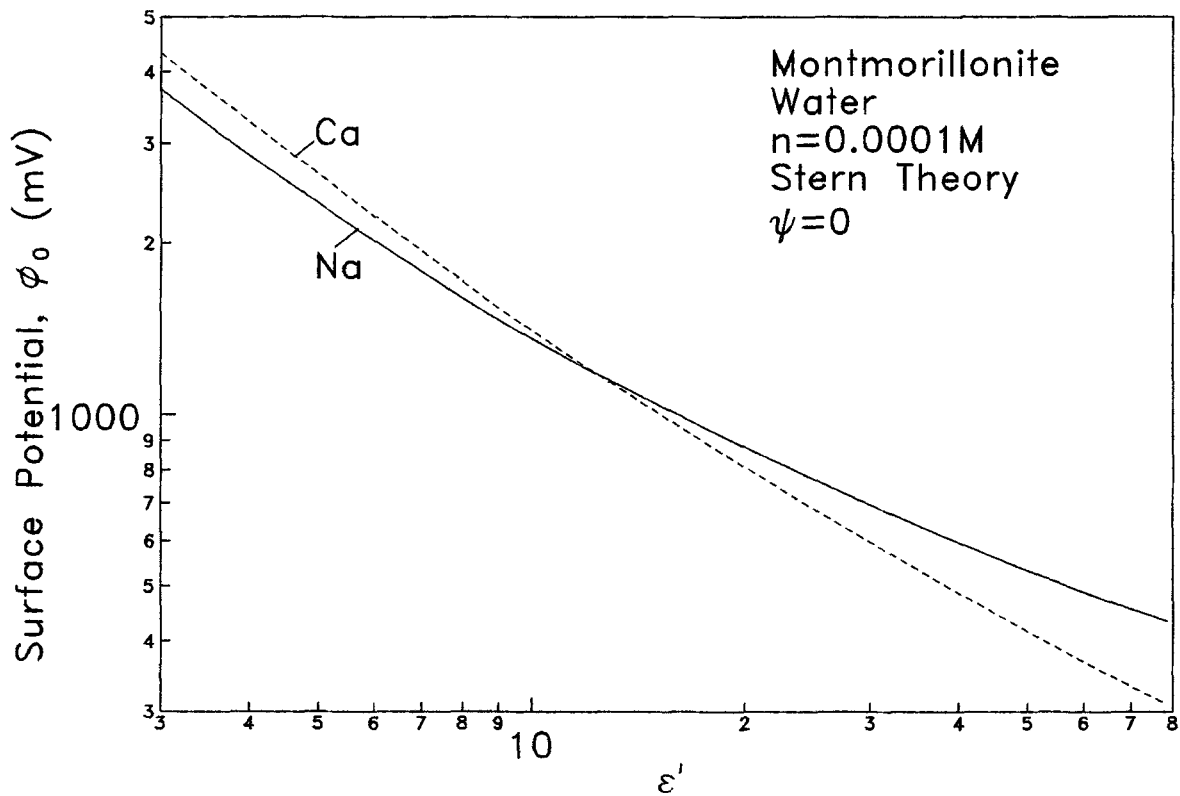


Figure 4. Effect of ϵ' on surface potential.

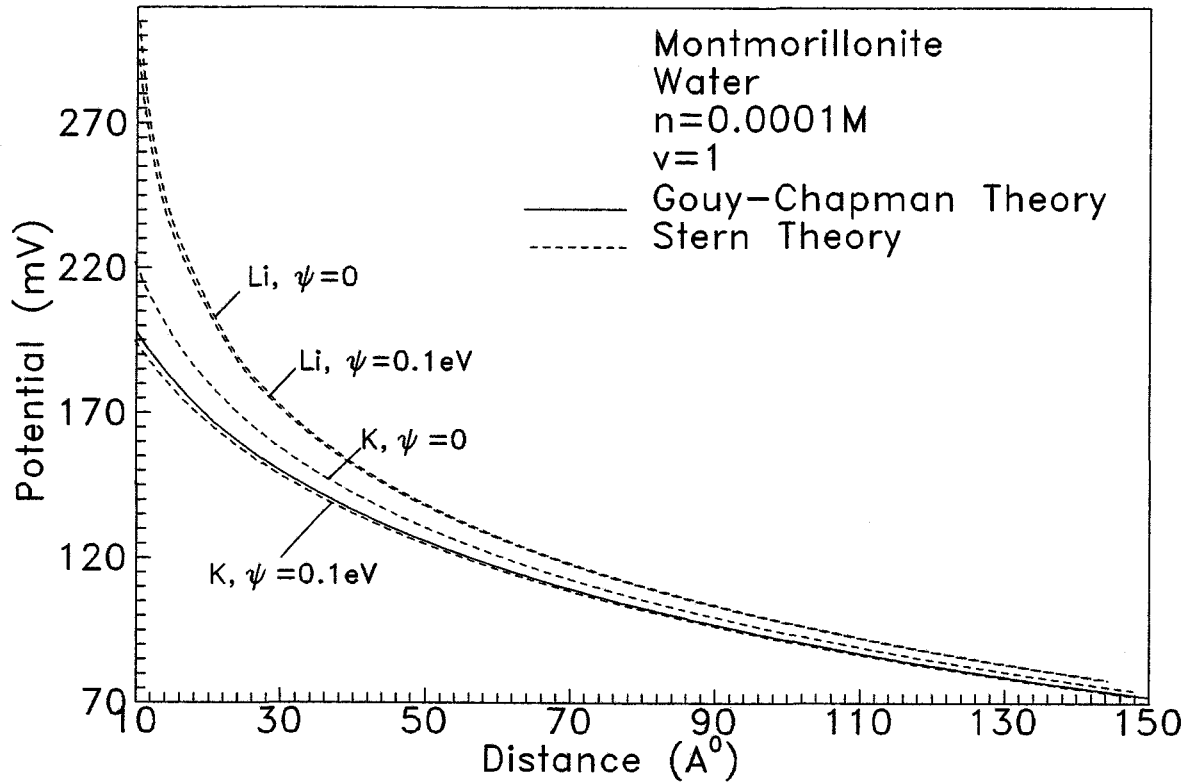


Figure 5. Effect of specific adsorption potential on potential-distance relationship.

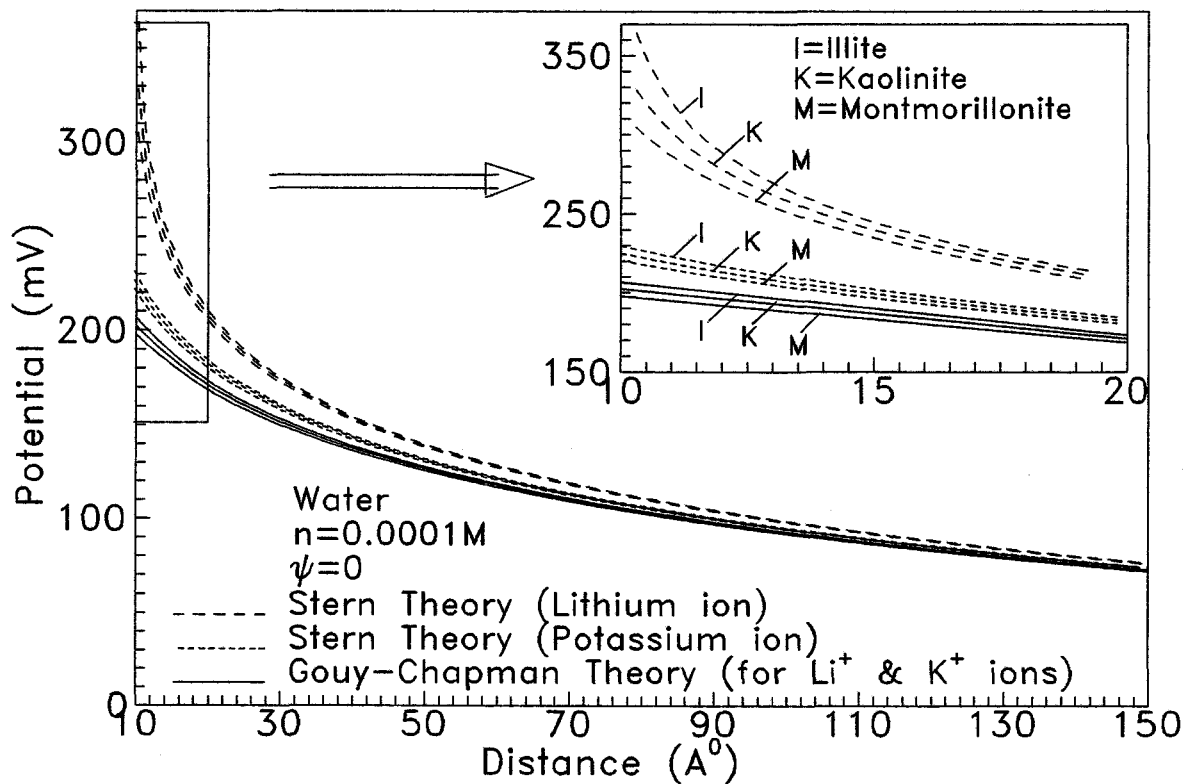


Figure 6. Potential-distance curves for three types of clays.

EFFECT OF CLAY TYPE. Figure 6 shows the potential-distance relationship for the three types of clays. For a given pore fluid, the differences in potentials at any distance for the three types of clays is negligible. But, the type of exchangeable ion has a significant effect on the potential-distance relationship for a given clay and pore fluid, although the valence is the same.

CONCLUSIONS

A detailed quantitative study of the Stern theory, which is more realistic for use within the clay-water system since it takes the size of the ion into consideration, has been carried out. A quantitative study has been completed using the Stern theory. The Stern theory is compared with the Gouy-Chapman theory. This detailed parametric study determined the influence of the various parameters affecting the surface and Stern potentials. The potentials obtained at any distance from the clay surface using the Stern theory are higher than those obtained by the Gouy-Chapman theory. The size of ion is found to have a significant influence on the potential-distance relationship for a given clay, pore fluid characteristics and valence.

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