A Study on Potential—Distance Relationship of Clays

by

M.S. Jayadeva*

A. Sridharan**

Introduction

It is clearly known that clay particles carry net negative charges on their surface (Grim 1962, Lambe and Whitman, 1969, Mitchell, 1976). Gouy-Chapman developed a theory for the diffusion of electric potential ϕ (which is normally a negative quantity) with the distance from the clay surface. In the case of parallel plates, the diffused double layers interact causing a midplane potential ϕ_d. Number of investigators, Verwey and Overbeek, 1947, Bolt, 1956, Lambe, 1958, Low, 1959, van Olphen, 1963, Mitchell, 1976, to name a few have contributed to better understanding the behaviour of clay-water electrolyte system. It can be seen further from literature that an understanding of the macro behaviour of clay water system primarily depends on the better understanding of the force system controlling at micro level. With this in view this paper reports the results obtained on a study on the effect of various factors affecting the electric potential at the surface and at a distance from clay platelet based on the Gouy-Chapman theory. Since bentonite, is one of the very active clay minerals and since it is extensively used in practice as slurry, the results are obtained with particular reference to bentonite. For comparison, other typical clay minerals like kaolinite and illite have also been included.

Theoretical considerations :

Single clay platelet :

Surface Potential—ϕ_o

From Gouy-Chapman theory the surface change is given as

$$\sigma = \frac{BEC}{S} \qquad \dots (1)$$

where, BEC = Base exchange capacity usually expressed in meq/100 gm.

S = Specific surface usually expressed in m²/gm.

Substituting the required values, Equation 1 can be written as,

$$\sigma = 289104 \times \frac{BEC}{S} \text{ in esu/cm}^2$$

*Research Scholar, Civil Engineering Department, Indian Institute of Science, Bangalore 560012, India.

**Associate Professor, Civil Engineering Department, Indian Institute of Science, Bangalore-560012 India.

The surface charge is constant for a clay and is independent of the surrounding fluid property.

If $Z = \dfrac{V_e\,\phi_o}{kT}$

Where k = Boltzmenn Constant = 1.38×10^{-16} ergs/° k

T = Absolute temperature in °K

V = Valency of the cation

e = unit electrostatic charge = 4.8×10^{10} esu

ϕ_o = Electric potential at the surface of the clay platelet,

then the relation between ϕ_o and σ is given by

$$\text{Sinh}\left(\frac{V_e\,\phi_o}{2kt}\right) = \text{Sinh }\frac{Z}{2} = \frac{\sigma}{2}\sqrt{\frac{2\pi}{\varepsilon nkT}} \qquad \ldots (2)$$

where,

n = concentration of ion in the electrolyte

ε = dielectric constant.

Thus, for a constant surface charge, it can be seen that ϕ_o, the surface potential is not a constant but a dependent on the electrolyte properties.

This aspect has not been reported in the literature clearly.

Equation 2 can be rewritten as

$$\text{Sinh }\frac{Z}{2} = 1256.81 \frac{P}{\sqrt{n\varepsilon P}} = A \qquad \ldots (3)$$

where, $P = \dfrac{\text{Base exchange capacity in meq/100 gm}}{\text{specific surface in m}^2\text{/gm}}$

= the soil property in $\dfrac{\text{meq}}{100\,\text{m}^2}$, n is in molar and T is in Kelvin.

Equation 3 can be rewritten as,

$$\frac{Z}{2} = Ln\,(A + \sqrt{A^2+1}\,] \qquad \ldots (4)$$

The exact solution for ϕ_o is

$$\phi_o = 0.1725 \frac{T}{V}\left(\text{Sinh}^{-1}\frac{1256.81P}{\sqrt{n\varepsilon T}}\right) \text{ in } mV \qquad \ldots (5)$$

where T is in °K

P is in meq/100 m²

n is in molar

When A is large, Equation 4 can be rewritten as

$$\frac{Z}{2} = Ln\,[2\,A]$$

and

$$\phi_o = \frac{T}{V}\left[\; 1.351 + 0.397\log_{10}\left(\frac{P}{\sqrt{n\varepsilon T}}\right)\right] \qquad \cdots (6)$$

Thus, it can be seen that ϕ_o is inversely linearly proportional to the valency and directly related to logarithm of the soil property represented by $P\,(= BEC/S)$. The Concentration, temperature and the dielectric constant of the fluid also influence the magnitude of ϕ_o.

It can thus be seen that ϕ_o is not a constant for a particular clay. More often it is reported in the literature (for example Leonards, 1962, Lambe and Whitman 1969) that ϕ_o is essentially a constant for a particular clay not affected by the fluid properties. This aspect is brought out in more detail further.

The exact solution of ϕ_o (Equation 5) is represented in Figure 1. Knowing the soil and the fluid properties, the value of ϕ_o V/T and/or Z could be directly found out. It could be seen that the relationship is linear when $\dfrac{P}{\sqrt{n\varepsilon T}} > 2\times10^{-3}$. The error involved in using Equation 6 is less than 3 per cent when $P/\sqrt{n\varepsilon T}$ is greater than 2×10^{-3}. This usually happens for most of the soils when the concentration n is less than 0.1M at room temperature.

The effect of various parameters viz., V, ε, n and BEC/S, or the surface
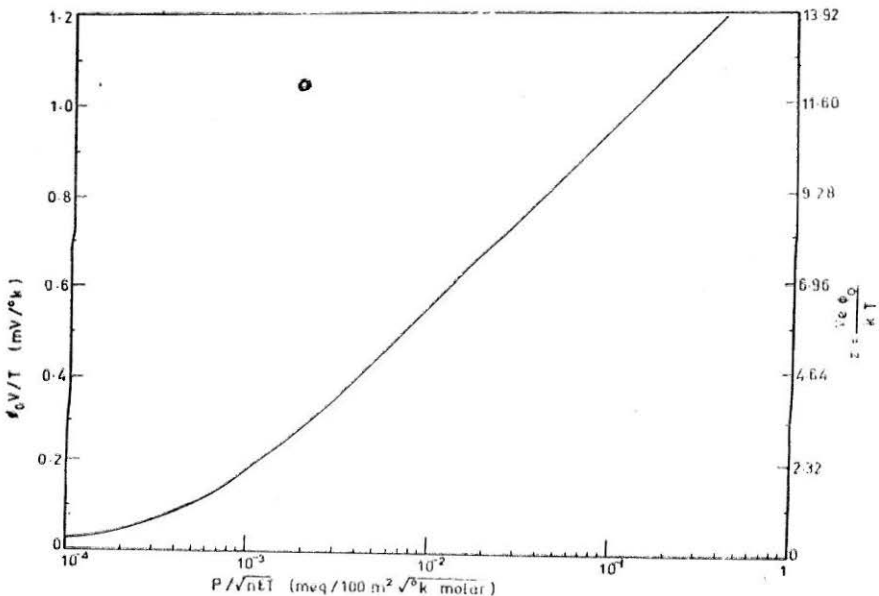

FIGURE 1

potential of a bentonite clay using Equation (5) is analysed. Figures 2a to 2d clearly brings out the dominant influence of the fluid properties on the surface potential.

Potential-Distance Relationship : The variation of the potential (ϕ) with distance (x) is given by (Babcock 1963)

$$\tanh \frac{V}{4} = \left(\tanh \frac{Z}{4} \right) e^{-Kx} \qquad \text{... (7)}$$

where $\quad y = \dfrac{Ve\phi}{KT}$ and $K = \sqrt{\dfrac{8\ \pi n e^2\ v^2}{\varepsilon\ kT}}$

when Z is small, it can be shown that (Van Olphen 1963)

$$\phi = \phi_o\, e^{-Kx} \qquad \text{... (8)}$$

Although, Equation 8 is simple, most often this is not applicable to clay-water system. Equation 8 is valid only when ϕ_o is less than 25 mV. Even under extreme conditions, the values will not be less than 25 mV. Eventhough, Equation 8 is most often quoted in literature, its usefulness in clay-water system perhaps is very much limited or nil.

Thus σ can be determined from Equation 1, ϕ_o or Z from Equation 5 and ϕ Vs distance x, from Equation 7 for given values of BEC, S, n, V. ε and T.
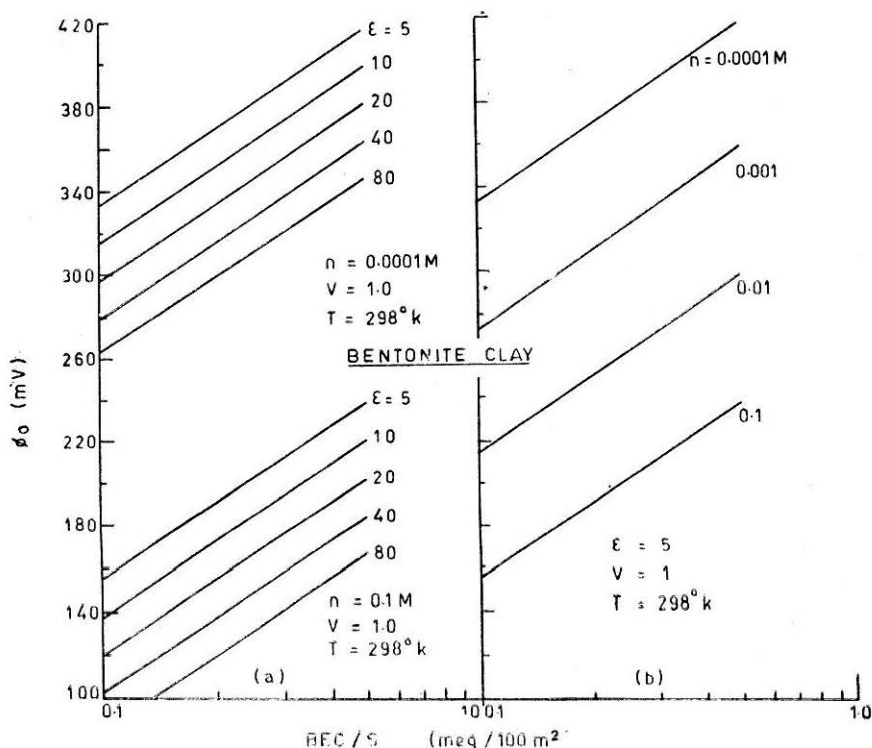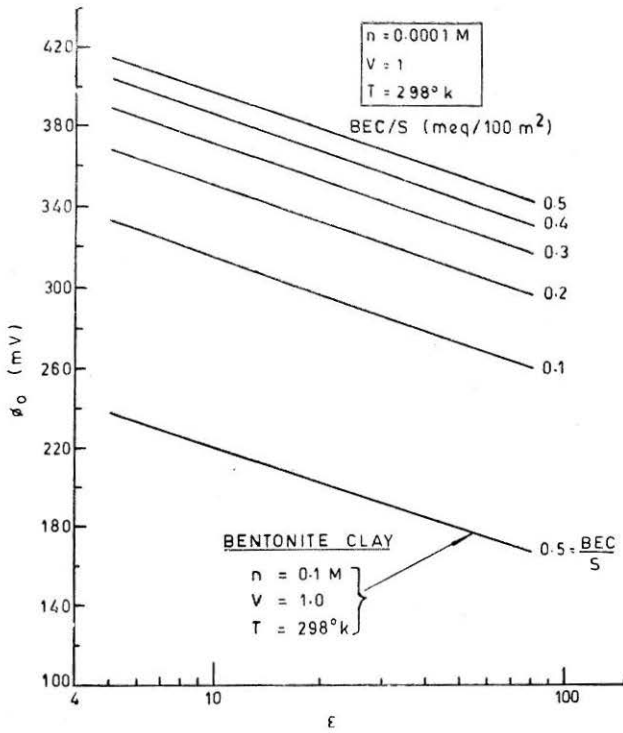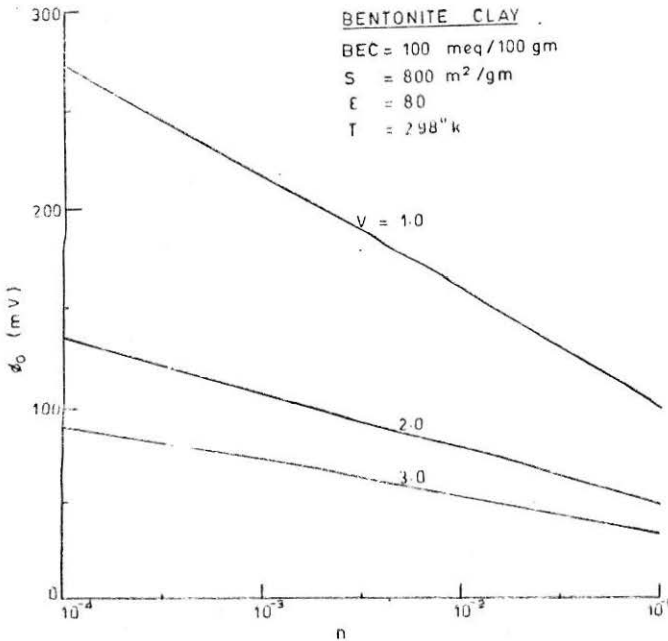

FIGURE 2

FIGURE 2c

FIGURE 2d

Parametric Study

The influence of the parameters, viz., salt concentration n, valency V, dielectric constant ε, Temperature T, and type of clay on the potential-distance relationship has not been brought out clearly in the literature. The following paragraphs bring out the significance of some of the parameters on the surface potential and on the variation of potential with distance for bentonite and other typical clay minerals.

Effect of salt concentration

For the purpose of this study a bentonite (montmorillonite) clay of $BEC = 100$ meq$_l$100 gms : and surface area $= 800$ m^2/gm with water as electrolyte ($\varepsilon = 80.36$) containing monovalent ions ($V = 1$) of varying concentrations ($n = 0.001$M. 0.01M and 0.1M) has been considered at a temperature of $T = 293°$K. The corresponding K values at the three concentrations are 1.037×10^6 cm^{-1}, 3.276×10^6 cm^{-1} and 1.036×10^7 cm^{-1} respectively.

Using Equation 5, the surface potential ϕ_o can be calculated and using Equation 7 the potential Vs. distance relation could be evaluated. Figure 3
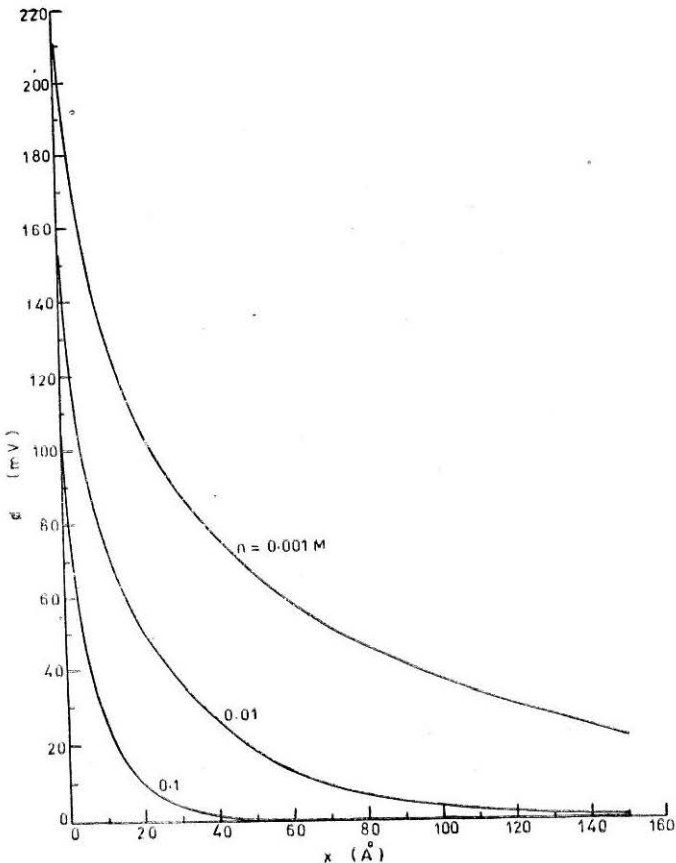

FIGURE 3

illustrates the effect of salt concentration on the surface potential and the decay of potential with distance. It is seen that the surface potential is significantly influenced by the electrolyte properties. The surface potential varies from 95.6 to 210.8 mV for the change in the concentration of 0.1M to 0.001M. Further, the dominant influence of concentration on the diffusion of potential with distance is evident.

Effect of Valency

The effect of valency on ϕ_o and ϕ Vs. distance relation in brought out in Figure 4. For this, the values as used above with $n = 0.001$M and valency of 1, 2 and 3 have been used in the computation. Although the surface potential is linearly inversely proportional to the valency with distance the potential ϕ diffuses more rapidly with increase in valency of ion. The corresponding K values at the three valencies are 1.036×10^6 cm^{-1}, 2.072×10^6 cm^{-1}, and 3.108×10^6 cm^{-1} respectively.
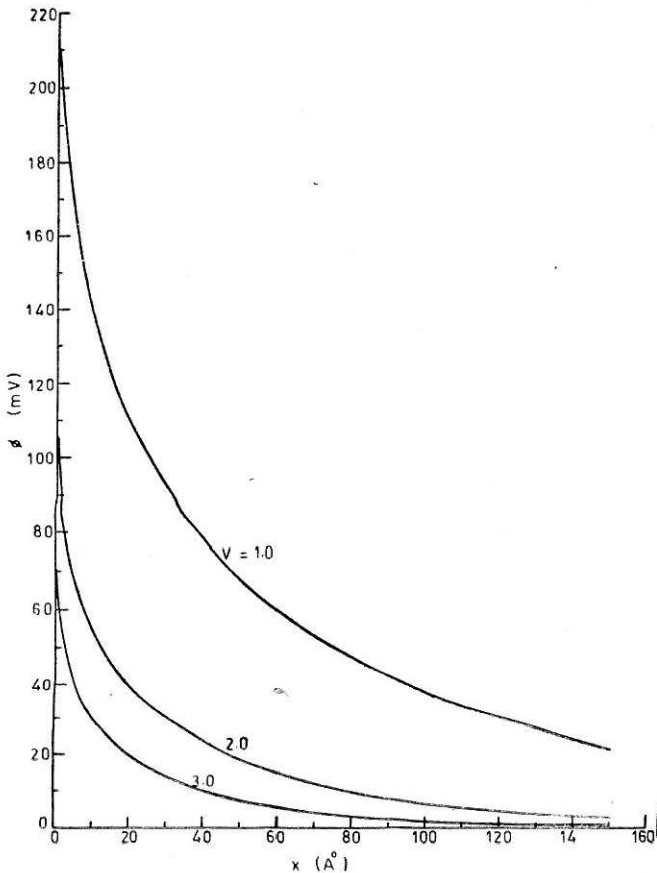

FIGURE 4

Effect of dielectric constant

Figure 5 show the influence of dielectric constant on ϕ_o and ϕ Vs. x relation for the bentonite clay. For this, values $n = 0.001M$, $V = 1$ and dielectric constant of 78.54 (water), 24.3 (Ethyl alcohol) and 2.284 (carbon tetrachloride) at a temperature of T 298° K have been used for computation. The corresponding K values are 1.039×10^6 cm^{-1}, 1.868×10^6 cm^{-1} and 6.094×10^6 cm^{-1} respectively. It is seen that ϕ_o is significantly affected by the dielectric constant of the electrolyte and increases with decrease in dielectric constant and that the diffusion of the potential with distance is much faster for electrolyte of lower dielectric constant. It should be mentioned here that ϕ decreases with decrease in dielectric constant beyond a very small value of x.
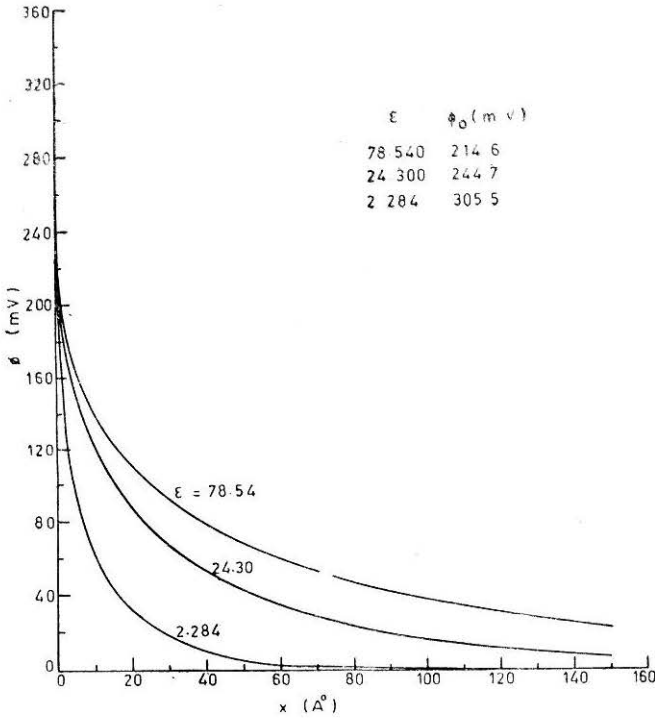

| ε	ϕ_0 (m v)
78 540	214 6
24 300	244 7
2 284	305 5

FIGURE 5

Effect of temperature

The effect of temperature on the potential should be studied taking into consideration the temperature effect on dielectric constant. As temperature increases, dielectric constant of water decreases and the product εT decreases slowly as can be noted from Table 1. For a change in temperature of 273°K to 320°K, the change in the value of εT is less than 6 per cent. Figure 6 bringout the negligible influence of temperature on the potential for the bentonite clay. For this, values of $n = 0.001M$, $V = 1$ have been used. The corresponding K values (Eqn. 7) obtained are 1.0304×20^6 cm^{-1}, 1.036×13^6 cm^{-1} and 1.0425×01^6 cm^{-1}. As the distance x increases the temperature effect gets reduced.

TABLE 1

Variation of the product (εT) with temperature

T in $°K$	Dielectric constant ε	$\varepsilon T(°K)$
273	88.00	24024
278	86.04	23919
283	84.11	23803
288	82.22	23679
293	80.36	23545
298	78.54	23405
303	76.75	23255
308	75.00	23100
313	73.20	22937
318	71.59	22766
323	69.94	22591
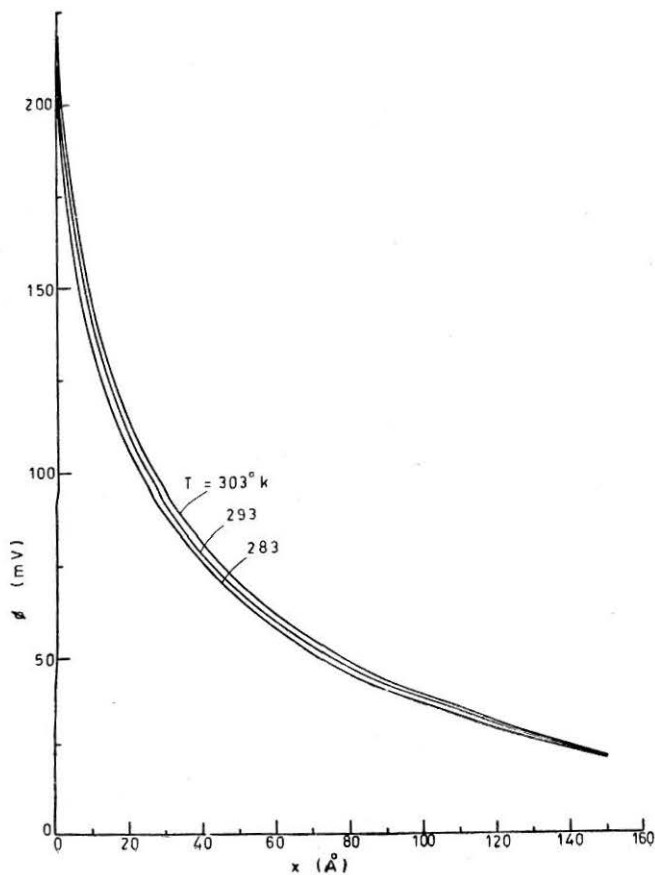
FIGURE 6

It it reported in the literature (Lambe 1958, Leonards 1962, Craig 1978) that after having taken into consideration the effect of temperature on dielectric constant, the potential decreases with increase in temperature at any distance. This is contrary to what is obtained from Gouy-Chapman theory. It can be seen from Figure 6 that potential increases with increase in temperature at any distance. However, as stated earlier, this variation is marginal.

Types of Platelet

The potential distance relationship for different clay types bring out very interesting observation. Three typical types of clays viz. Bentonite (Montmorillonite), Illite and Kaolinite have been considered. Their relevant properties are listed in Table 2. The pore fluid properties used are $n = 0.001M$, $V = 1$, $\varepsilon = 80.36$, $T = 293°K$ resulting in $K = 1.036 \times 10^6$ cm^{-1}. Figure 7 and Table 6b brings out the potential distance relationship for the three typical clays. It is rather interesting to note that there is essentialy no difference among the clays studied, when x is about 20°A or more. However, the difference in ϕ_o do exist and the difference could be quite large when n is low (Figure 2).

TABLE 2

Some properties of three clay minerals

Type of soil	Bentonite	Illite	Kaolinite
Base exchange capacity in meq./100 gm.	100	40	3
Surface area in m²/gm	800	100	15
B.E.C./surface in meq./100 M²	0.125	0.4	0.2
Surface charge σ in esu/cm²	36138	115641.6	57820.8
Z	8.342	10.667	9.281
ϕ_o in mV	210.8	269.6	234.6

This insignificant effect of clay type on ϕ Vs. x relationship (when x is about 20°A or more) is primarily due to the following. Although the clay type varies to extreme limits, (surface area from 15 to 800 m²/gm and *BEC* from 3 to 100 meq/100 gm. Table 2) what is more important is the ratio of base exchange capacity to specific surface (Equation 2). The difference in this ratio is not much, it varies from 0.125 meq/100 m² to 0.4 meq/100 m² (Table 2) and for kaolinite this ratio is in between Bentonite and Illite. This is the reason why the curve for kaolinite in between Bentonite and Illite (Figure 7). The Gouy-Chapman theory brings out the potential at the surface or at any point away from the clay platelet. From this view point, the theory is concerned about the charges/unit area and does not take into account how many such charges exist per unit mass of soil. The macro behaviour is greatly influenced by the number of charges per unit mass also. This is evident from the literature that abentonite clay is
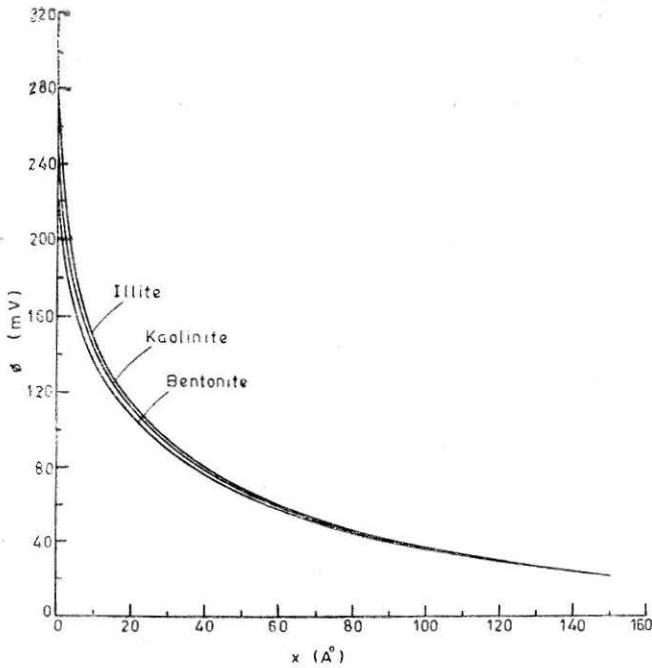
FIGURE 7

relatively more active compare to the kaolinite clay. From this consideration, Gouy-Chapman theory relating potential and distance. will not bring out the physical behavior truly; whereas the same theory extended to the interaction of double layers will predict the engineering behaviour of clays (Sridharan and Jayadeva, 1981).

Graphical solution for obtaining ϕ Vs. distance

The potential-distance relationship could be obtained by calculating ϕ_o using Equation 5 or Figure 1 (or Table 1) and ϕ at any distance, x using Equation 7. However, numerial calculation of these equations is usually laborious. To simplify the calculations graphical solutions have been prepared to obtain ϕ Vs. x relationship knowing all other values. For this, the following steps should be followed.
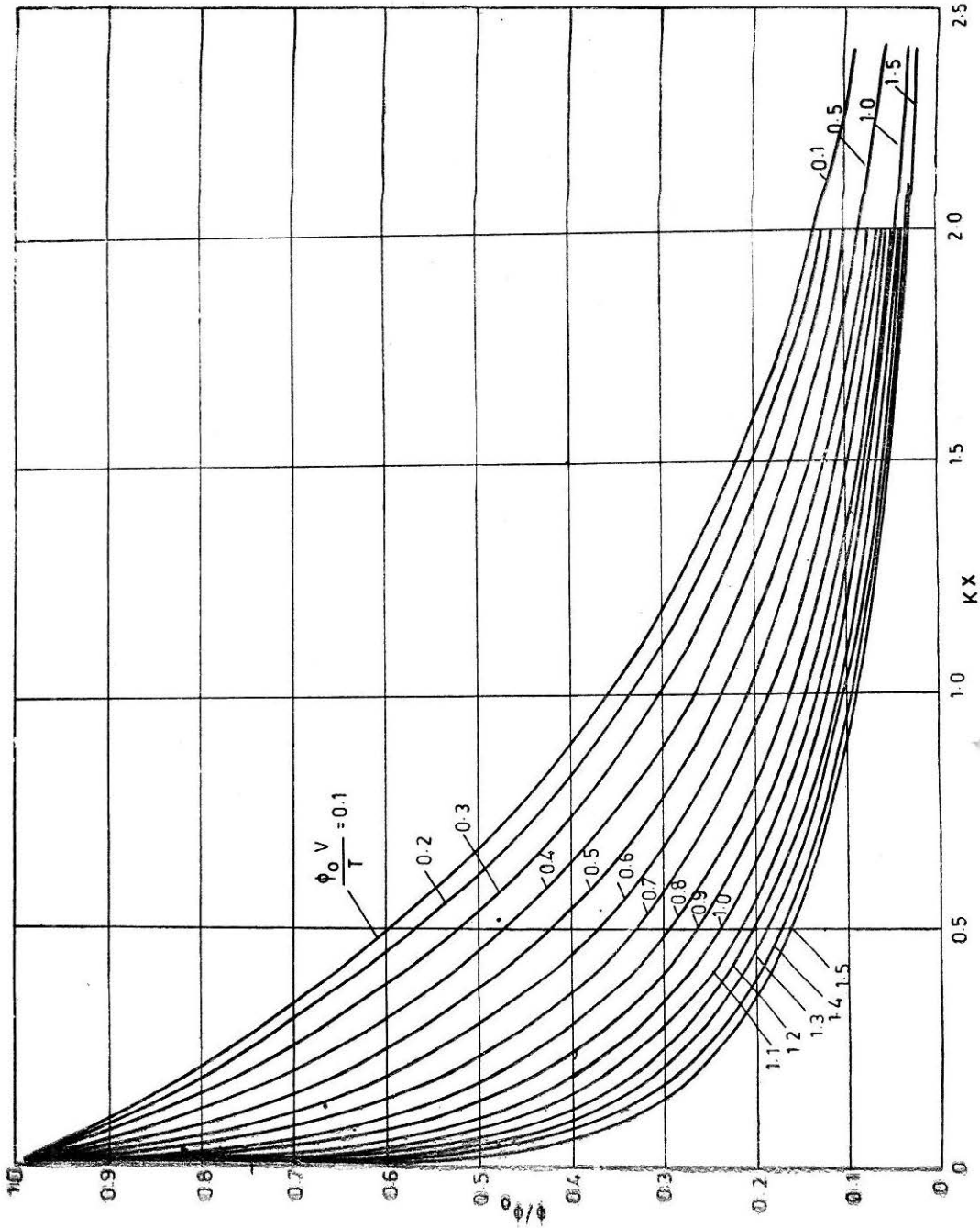
1. Using Figure 1 or Table 1.

$\dfrac{\phi_o V}{T}$ could be obtained for known values of $\dfrac{P}{\sqrt{n\varepsilon T}}$.

2. Value of K is obtained by Equation 9.

$$K = 50.272 \times 10^8 \ V\sqrt{n/\varepsilon T} \ldots \text{cm}^{-1} \ldots \qquad \ldots (9)$$

where $V =$ valency of cation, $n =$ concentration of ions in molar, $\varepsilon =$ dielectric constant, $T =$ temperature in Kelvin.

3. Unsing Figure 8 or Table 7, ϕ/ϕ_o (hence ϕ) could be obtained for known values of Kx and $\phi_o V/T$.
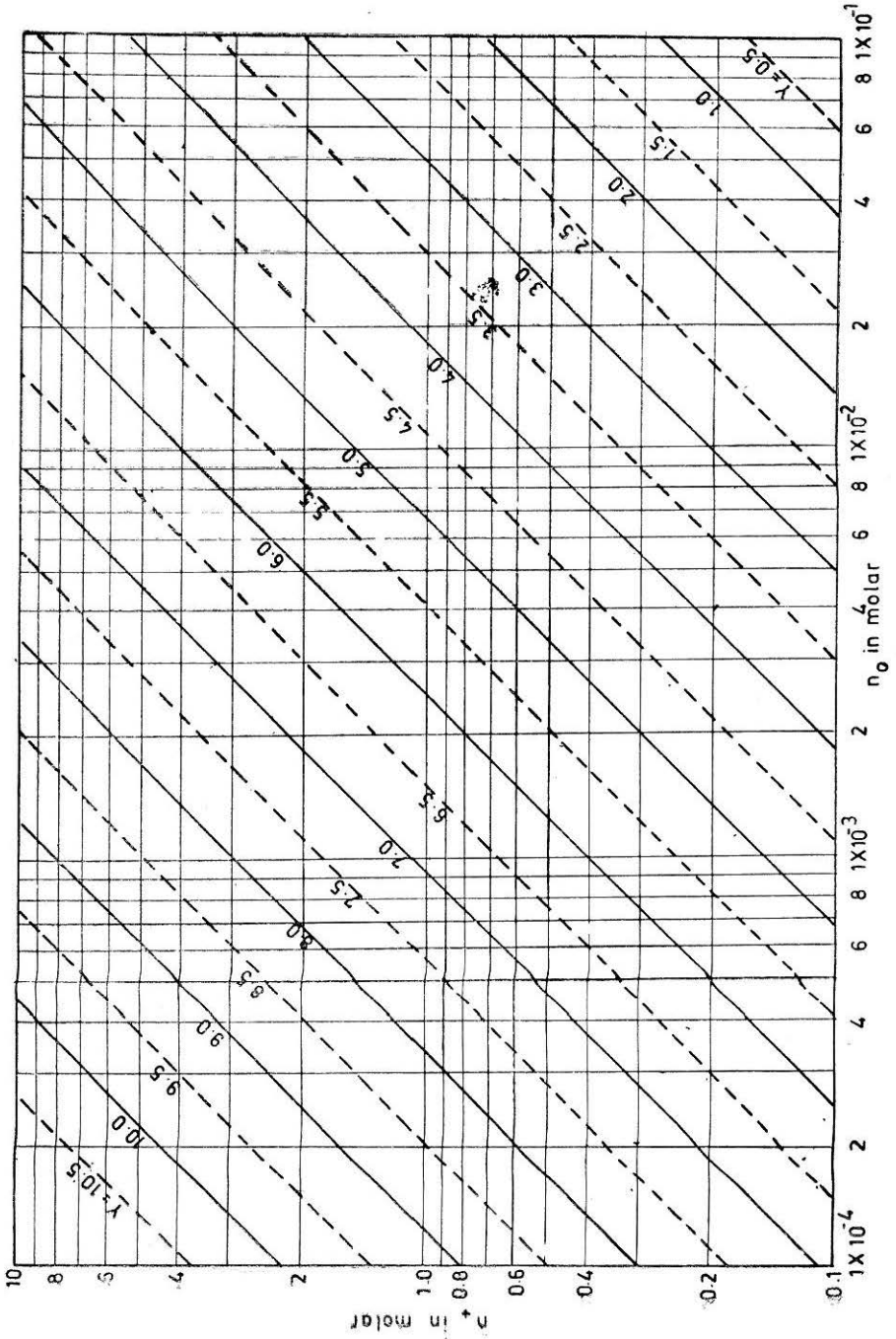
FIGURE 9

Ion distribution next to the clay mineral surface

It could be shown that the ion ($+$ion or $-$ion) is distributed as per the Boltzman equation.

$$n_+ = n_0\, e^{+y}$$

$$n_- = n_0\, e^{-y} \qquad\qquad \ldots (10)$$

Equation 10 could be presented graphically as shown in Figure 9. From Figure 9, knowing n_0 and p values one can directly determine the value of n_+, the concentration of cation at any distance x. Both the axes could be multipled by $10b$ where b may be negative or positive in case the scale has to be extended on either side.

To determine the concentration of anion, n_-, the vertical axis (n_+ axis) of Figure 9 is used for measuring n_0 and the horizontal axis (n_0 axis) gives concentration of anion Appendix I illustrates the use of Figure 9 with a worked out example.

Summary and Conclusions

Realising the importance of force system at micro level in controlling macro behavior, a detailed study of Gouy-Chapman theory has been made. The importance of the electrolytic properties in influencing the surface potential has been clearly broughtout. A detailed parametric study has been made bringing out lucidly the influence of various parameters, affecting the surface potential and the potential distance relationship. In the theory, the soil is represented by the ratio, base exchange capacity to surface area (number of charges per unit area) and since this ratio varies over a limited range for extreme clay mineral types (0.125 to 0.4 meq/100 m^2), the potential-distance relationship is not affected significantly (and essentially same) for different types of clays. It is brought out that macro behavior of clays is controlled by the interaction of diffused double layers. This basic study enables to better understand the behavior of clays, especially very active clays like bentonite.

Graphical solutions have been presented to obtain the surface potential, the potential at any distance from clay platelet and the concentration of cations and anions at the surface as well as any distance.

References

BABCOCK, K.L., (1963), 'Theory of the chemical properties of soil colloidal systems at equilibrium', Hilgardia, 34, pp. 417-542.

BOLT, G.H., (1956), 'Physico-chemical analysis of the compressibility of pure clays', Geotechnique, Vol. 6, No. 2, pp. 86-93.

CRAIG, R.F., (1978), 'Soil Mechanics', 2nd Edition, Van Nostrand Reinhold Company Ltd., London.

GRIM, R.E., (1962), 'Applied Clay Mineralogy', McGraw Hill Book Co.

LAMBE, T.W., (1958), 'The Structure of compacted clay', Journal of the Soil Mechanics and Foundations Division, ASCE, Vol. 84, No. SM2, p. 1654.

LAMBE, T.W., and WHITMAN, R.V., (1969), 'Soil Mechanics', Wiley-Eastern Reprint 1973, New Delhi.

LEONARDS, G.A., (1962), *Engineering Properties of Soils*, Foundation Engineering, edited by Leonards, G.A., McGraw-Hill Book Co.

LOW, P.F., (1959), Discussion of paper by A.W. Taylor, 'Physico-chemical properties of soils : ion exchange phenomena,' *Journal of the Soil Mechanics and Foundations Divisions*, ASCE, Vol. 85, No. SM2, p. 79.

MITCHELL, J.K. (1976), *'Fundamentals of Soil Behaviour'*, John Wiley, New York.

SRIDHARAN, A. and JAYADEVA, M.S., (1981), "Double Layer Theory and Compressibility of Clays" Submitted for Publication.

VAN OLPHEN, H., (1963), *An Introduction to Clay Colloid Chemistry*, Inter-science Publishers, New York, London.

VERWEY, E.J.W. and OVERBEEK, J.T., 1948), *'Theory of the Stability of Lyophobic Colloids*, Elsevier, New York.

Appendix 1

Use of Figure 9

To determine the concentration of Cation (n_+) and anion (n_-) given the following data :

Bulk concentration $n_o = 2 \times 10^{-3}$ molars, and potential function $y = 6.0$

Solution : From Figure 9 for $n_o = 2 \times 13^{-3}$, and $y = 6$, the value of n_+ is read as 0.8 molar.

To obtain u_-, n_o is to be read on the vertical axis and n_- on the horizontal axis.

Since $n_v = 2 \times 10^{-3}$ Molar, the multiplying factor for the axes is 10^{-3}. The value of n_- corresponding n_o of $2M$ and $y = 6$ is $5 \times 10^{-3} M$ which should be further multiplied by the multiplying factor of 10^{-3}. Hence the value of n_- is $5 \times 10^{-6} M$.

Guide for Submission of Discussion

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