

EFFECT OF THE DIELECTRIC CONSTANT ON THE DOUBLE LAYER ON CLAYS

A. K. HELMY AND I. M. NATALE

Universidad Nacional del Sur, 8000 Bahia Blanca, Argentina

Abstract—Electric potentials as a function of distance were calculated for a model of the double layer on clays in which a surface zone a few water molecules thick has a low dielectric constant. This zone is followed by bulk water with a normal dielectric constant. The double layer potentials were found to be lower than those obtained from the Gouy model, in which water has a normal dielectric constant throughout the double layer.

Key Words—Dielectric constant, Double layer potential, Gouy model, Montmorillonite, Water.

INTRODUCTION

Most workers agree that the water layers in contact with oxygen-hydroxyl surfaces, such as those found in phyllosilicates and oxides, have a much lower dielectric constant than the value of 78.3 for bulk water. In other words, the inner zone of the double layer on clay minerals is characterized by a low dielectric constant which is at least one order of magnitude lower than the corresponding bulk water value. Opinions, however, differ on the thickness of that water. Measurements of the dielectric properties of adsorbed water on clays and oxides by Mamy (1968), Nelson *et al.* (1969), McCafferty and Zettlemoyer (1971), Hoekstra and Doyle (1971), and Hall and Rose (1978) show beyond doubt that the dielectric constant of water at and below monolayer coverages is very low, about 4, but that the values increase abruptly as the number of water layers increases. Recent studies by Fripiat *et al.* (1983) concluded that the thickness of the water which is under the direct influence of the surface fields is less than 10 Å in clays.

Some time ago, a study was carried out by Helmy (1973) on the influence of the presence of a layer of liquid with a low dielectric constant at a clay surface on the electric potential-distance curve. The study examined both high and low double layer potentials. In the present study a general solution is presented that is valid for all potential values and for all distances between the particles.

THEORY

Consider two interacting clay plates as shown schematically in Figure 1. Each plate has a surface charge density σ . In contact with the clay surface is a liquid layer of thickness l having a dielectric constant D_1 (zone 1 in Figure 1). This layer is followed by more layers of liquid having a dielectric constant D_2 (zone 2 in Figure 1). The charged plate at the left is placed at $x = 0$. The electrolyte concentrations are C_1 and C_2 in zones 1 and

2, respectively. At any point in the system the Poisson equation is valid; hence in zone 1:

$$d^2\psi_1/dx^2 = -4\pi\rho_1/D_1, \quad (1)$$

and in zone 2:

$$d^2\psi_2/dx^2 = -4\pi\rho_2/D_2, \quad (2)$$

where ρ_1 and ρ_2 are the respective charge densities and ψ_1 and ψ_2 are the respective potentials in the zones. For the system as a whole, the electroneutrality condition is given by:

$$\int_0^l \rho_1 dx + \int_l^h \rho_2 dx = -\sigma. \quad (3)$$

Furthermore, the following boundary condition is valid at $x = l$:

$$D_1(d\psi_1/dx) = D_2(d\psi_2/dx). \quad (4)$$

Substitution of Eq. (1) and Eq. (2) into Eq. (3) and integrating (knowing that $(d\psi/dx)$ vanishes at the midway distance between the plates, where $x = h$) gives after using Eq. (4) the relation:

$$D_1(d\psi_1/dx)_0 = -4\pi\sigma. \quad (5)$$

Limiting the treatment to a system containing a symmetric-type electrolyte, a first integration of Eq. (1) and Eq. (2) gives:

$$(d\psi_1/dx)^2 = (16\pi RTC_1/D_1) \cdot (\cosh(zF\psi_1/RT) + K_1) \quad (6)$$

and

$$(d\psi_2/dx)^2 = (16\pi RTC_2/D_2) \cdot (\cosh(zF\psi_2/RT) + K_2). \quad (7)$$

To evaluate K_2 , the condition $(d\psi/dx)_h = 0$ must be assumed in Eq. (7) to yield:

$$K_2 = -(16\pi RTC_2/D_2)\cosh y_h. \quad (8)$$

To evaluate K_1 , the condition given by Eq. (4) must be imposed upon Eqs. (6) and (7) to yield:

$$2K_1 = (D_2^2 \kappa_2^2 / D_1^2 \kappa_1^2) (2 \cosh y_l - 2 \cosh y_h) - 2 \cosh y_b \quad (9)$$

where

$$\kappa = \sqrt{8\pi F^2 Z^2 C / RTD} \quad \text{and} \quad y = zF\psi / RT.$$

Eq. (6) may now be written as:

$$\int_{y_0}^{y_l} dy / \sqrt{2 \cosh y + 2K_1} = - \int_0^l \kappa_1 dx; \quad (10)$$

and similarly, Eq. (7) may be written as:

$$\int_{y_l}^{y_h} dy / \sqrt{2 \cosh y - 2 \cosh y_h} = - \int_0^{X_h} \kappa_2 dx, \quad (11)$$

where X_h is the distance from the point where $y = y_l$ to $y = y_h$.

The solution of Eq. (10) valid for $K_1 \geq 1$ may be written as:

$$\kappa_1 l = 2/b \{ F[\sqrt{1 - (1/b^4)}, \tan^{-1}(b \exp(y_0/2))] - F[\sqrt{1 - (1/b^4)}, \tan^{-1}(b \exp(y_l/2))] \}, \quad (12)$$

where $b = \sqrt{K_1 + \sqrt{K_1^2 - 1}}$ (Devereux and de Bruyn, 1963).

For $-1 \leq K_1 \leq 1$, the solution of Eq. (10) may be written as:

$$\kappa_1 l = F[\sqrt{(1 - K_1)/2}, \sin^{-1}(1/(\cosh(y_l/2)))] - F[\sqrt{(1 - K_1)/2}, \sin^{-1}(1/(\cosh(y_0/2)))] \quad (13)$$

The solution of Eq. (11) when the slope of the potential-distance curve is negative, may be written as (Devereux and de Bruyn, 1963):

$$\begin{aligned} \kappa_2 X_h &= 2 \exp(-y_h/2) \\ &\cdot \{ F[\exp(-y_h), \pi/2] \\ &- F[\exp(-y_h), \sin^{-1}(\exp((y_h - y_l)/2))] \}. \end{aligned} \quad (14)$$

$F[k, \phi]$ is the elliptic integral of the first kind, and $F[k, \pi/2]$ is the complete elliptic integral of the first kind.

To obtain a relation between the surface charge density σ and the surface potential, the condition given by Eq. (5) is imposed on Eq. (6) to yield:

$$2 \cosh y_0 = (2\pi\sigma^2)/(RTD_1 C_1) - 2K_1. \quad (15)$$

CALCULATIONS

Non-interacting system at constant surface-charge density

The following values for the different quantities were used in the calculations: $\sigma = 2.788 \times 10^4$ esu/cm², $C_1 = C_2 = 0.01$ M, $D_1 = 7.83$, and $D_2 = 78.3$. The calculations were made as follows: by assuming $y_h = 0$ in Eq. (9), K_1 was calculated using assumed values for y_l .

The values of y_0 were then obtained from Eq. (15) using the known values of K_1 and σ . The value of l , i.e., the thickness of zone 1, was obtained from Eq. (12) and/or Eq. (13) using the known values of y_0 , y_b and K_1 . When the arguments of the elliptic integrals were both near 90°, the integrals were evaluated by the methods given by Franklin (1944) and Jahnke *et al.* (1966).

The value of l was also calculated using the following equation (Helmy, 1973):

$$l = \frac{RT/F}{\sqrt{k_1 k_2}} \ln \left[\frac{k_2 + 0.5 \exp y_0]^{1/2} - \sqrt{k_2}}{[k_2 + 0.5 \exp y_0]^{1/2} + \sqrt{k_2}} \cdot \frac{[k_2 + 0.5 \exp y_l]^{1/2} + \sqrt{k_2}}{[k_2 + 0.5 \exp y_l]^{1/2} - \sqrt{k_2}} \right],$$

where

$$k_1 = 16\pi RTC_1 / D_1 \quad \text{and}$$

$$k_2 = ((D_2/D_1) - 1) \cosh y_l - (D_2/D_1).$$

The results of the calculations are given in Figures 2 and 3.

Interacting system at constant charge density

The minimum potential was calculated using Eqs. (9), (12), (14), and (15). The thickness of zone 1 (l) was taken as constant and equal to 3 Å. The minimum potentials obtained are plotted as a function of the distance from the clay surface in Figure 4. For comparison, the values obtained when the double layer has the same dielectric constant throughout are shown in the same figure. Values calculated from experimental data from Barclay *et al.* (1972) are also plotted in Figure 4.

DISCUSSION

It is generally believed that the effective dielectric constant in the aqueous phase increases with distance from a charged surface, from a low value (probably <10) compared with its bulk value (~80) over a distance of several water molecular diameters. The profile of this dielectric change is an important characteristic on which depend many properties of the electric double layer, such as the energy of an adsorbed ion (Levine and Robinson, 1972) and the electric potential distribution (*vide infra*). This profile can be continuous, discontinuous, or a combination of both. The discontinuities may be placed at the outer Helmholtz plane or at the inner one or at both. Levine *et al.* (1974) and Levine and Fawcett (1979) preferred a continuous profile, though the function that represents the variation of the dielectric constant was chosen arbitrarily (e.g., hyperbolic cosine, circular cosine, elliptic functions) and the problem remains for further study.

In the present work a discontinuous profile has been assumed for the dielectric constant in the double layer,

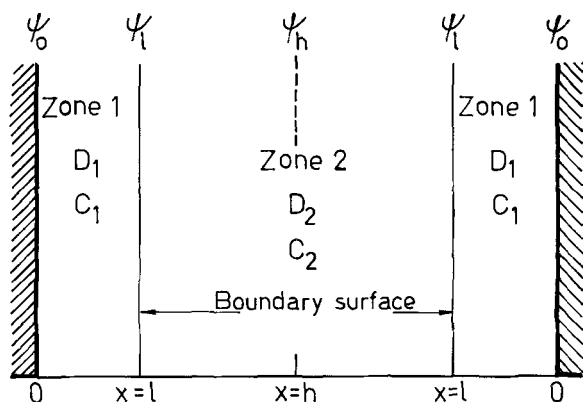


Figure 1. Schematic representation of the model of liquid water near charged clay surfaces. The dielectric constant in zone 1 is much smaller than in zone 2. The potentials are: ψ_0 at $x = 0$, ψ_l at $x = l$, and ψ_h at $x = h$.

because most of the studies on clays cited above show that only below few water layers coverage is the dielectric constant of water lower than the bulk value. Furthermore, the discontinuity in the dielectric profile was not confined to any specific zone of the double layer because we wanted to know the effect of the thickness of the liquid layer with low dielectric constant on the properties of the double layer on clays.

Non-interacting system

For the non-interacting system, the dependence of the surface potential (ψ_0) on the potential at the boundary between the two solvent phases (ψ_l) is shown in Figure 2 for a zone in contact with the charged clay surface (zone 1) having a dielectric constant 1/10, the value in the subsequent zone, and for a (1-1) type electrolyte at a concentration of 0.01 M in both zones. It may be seen from Figure 2 that if the thickness of zone 1 is zero, as in the Gouy model, $\psi_0 = \psi_l = 142$ mV. If the thickness of the zone is 3 Å, the approximate thickness of a monolayer of water, the surface potential reaches 200 mV. This value remains almost constant as the thickness of zone 1 increases, reaching finally the value of 201 mV obtained when all of the double layer is present in a single medium having a dielectric constant of 7.83. In other words, once one layer of solvent with a low dielectric constant is formed on the surface, more layers of the same solvent hardly affect the value of the surface potential.

Though the effect on the surface potential of the presence of a layer of a low dielectric constant near a clay surface was found to be small, it is very pronounced on the potential-distance curve, as shown in Figure 3. As these data show, the Gouy model gives a much slower decay in the values of the potential as a function of the distance than the multimedia model presented in this paper. For example, at a distance of

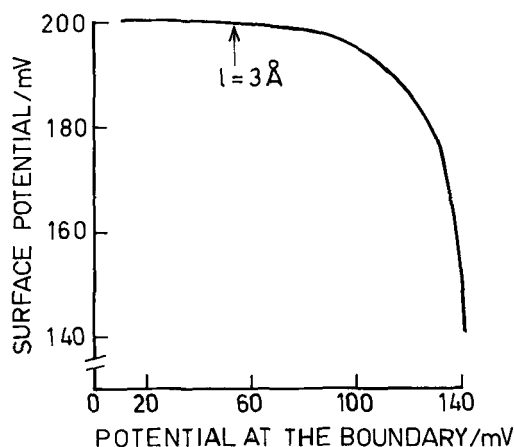


Figure 2. Dependence of the surface potential on the potential at the boundary between the two dielectric solvents. Arrow points to the values when the low dielectric zone is 3 Å thick. To the left of the arrow, the thickness of the low dielectric zone increases to infinity.

3 Å, the potential has the value of 56 mV compared to 113 for the Gouy model. At a distance of 6 Å the values are 26 mV for the multimedia model and 98 mV for the Gouy monomedium model. If the zeta potentials of clay particles, which are of the order of 30 to 40 mV (Hauser and Le Beau, 1941; Oakes, 1960; Swartzen-Allen and Matijevic, 1975) represent the potential at a plane of shear separated by thicknesses of one or two water molecules from a clay surface, the values of the potential obtained from the present model are more in line with the experimental values of clays than the Gouy model.

For the purpose of comparison, the results of calculations carried out using an equation given earlier by Helmy (1973) and representing the high potential approximation of Eq. (12) and Eq. (13) are given in Figure 3. As may be seen from the figure, the high potential approximation gives values slightly greater than those obtained by the mentioned equations.

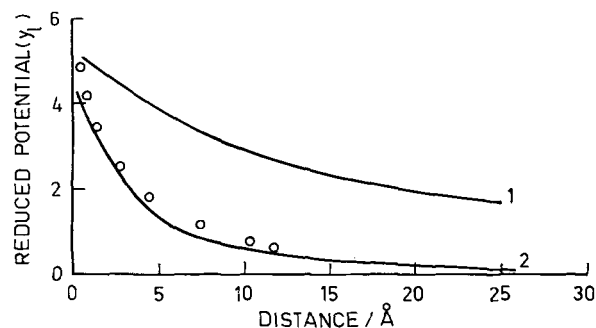


Figure 3. Potential-distance curves, according to Gouy (curve 1) and according to the multimedia model (curve 2). Circles represent the high potential approximation.

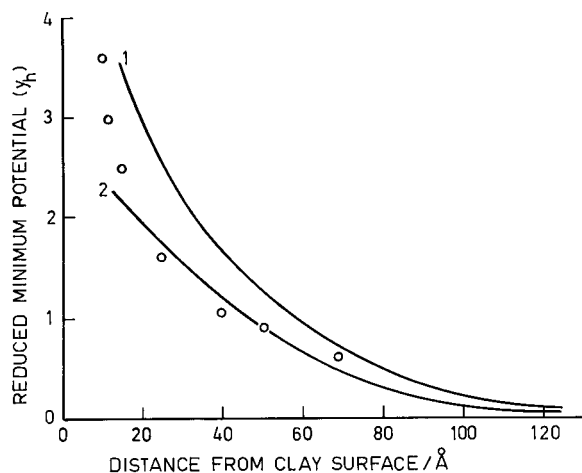


Figure 4. Reduced minimum potential between two interacting particles as a function of the midway distance. Curve 1—water has a normal dielectric constant throughout the double layer; curve 2—the innermost zone has a lower dielectric constant than the rest of the double layer. Circles represent data calculated from Barclay *et al.* (1972) for 0.0001 M NaCl.

Interacting systems

For interacting double layers wherein a zone of low dielectric constant of thickness 3 Å is found near the solid surface, the calculations show that under the condition of constant surface-charge density, the potentials at the boundary between zone 1 and zone 2 as well as the surface potentials, change little as the distance between the particles increases. Thus, at a separation distance between the particles of 30.4 Å, $y_1 = 2.82$ and attains the value of 2.60 at infinite distance of separation. The corresponding values of y_0 are 7.808 and 7.708, respectively.

With respect to the values of the minimum potential between two interacting particles, the data given in Figure 4 show that the minimum potentials are smaller where a zone of low dielectric constant is present near the surface than where it is absent. The distance between the two curves in Figure 4 increases as the distance between the particles decreases. This result may have an important effect on the value of the energy of repulsion, swelling pressure, and other properties of clay suspensions in which the values of the minimum potential are needed.

Furthermore, for the inner region of the double layer, the Stern correction of the Gouy model is inadequate for surfaces characterized by a constant charge density, because the rate of change of the potential with the distance at the diffuse region boundary (see Eq. (5)) is a constant due to the constancy of the surface-charge density. Hence, according to Bell and Peterson (1972),

the potential distribution and the energy of repulsion are not affected by the presence of a Stern layer. This, however, does not occur for the correction of the Gouy model presented above where important changes in the potentials take place as a result of the presence of a layer of low dielectric constant near the surface.

REFERENCES

- Barclay, L., Harrington, A., and Ottewill, R. H. (1972) The measurement of forces between particles in disperse systems: *Kolloid Z. Z. Polym.* **250**, 655–666.
- Bell, G. M. and Peterson, G. C. (1972) Calculation of the electric double layer force between unlike spheres: *J. Colloid Interface Sci.* **41**, 542–565.
- Devereux, O. F. and de Bruyn, P. L. (1963) *Interaction of Plane-Parallel Double Layers*: M.I.T. Press, Massachusetts Institute of Technology, Cambridge, Massachusetts, 361 pp.
- Franklin, P. (1944) *Methods of Advanced Calculus*: McGraw-Hill, New York, 479 pp.
- Fripiat, J., Cases, J., Francois, M., and Letellier, M. (1983). Thermodynamic and microdynamic behavior of water in clay suspensions and gels: *J. Colloid Interface Sci.* **89**, 378–400.
- Hall, P. G. and Rose, M. A. (1978). Dielectric properties of water adsorbed by kaolinite clays: *J. Chem. Soc. Faraday I* **74**, 1221–1233.
- Hauser, E. and Le Beau, D. S. (1941) Studies in colloidal clays: *J. Phys. Chem.* **45**, 54–65.
- Helmy, A. K. (1973) Electric double layer across two media: *J. Chem. Phys.* **59**, 3101–3104.
- Hoekstra, P. and Doyle, W. T. (1971) Dielectric relaxation of surface adsorbed water: *J. Colloid Interface Sci.* **36**, 513–521.
- Jahnke, E., Emde, F., and Losch, F. (1966) *Tables of Higher Functions*: Teubner Verlags., Stuttgart, 322 pp.
- Levine, S. and Fawcett, W. R. (1979) Some aspects of discreteness of charge and ion size effects for ions adsorbed at charged metal-aqueous electrolyte interfaces: *J. Electroanal. Chem.* **99**, 265–281.
- Levine, S. and Robinson, K. (1972) The discreteness of charge effect at charged aqueous interfaces: *J. Electroanal. Chem.* **38**, 253–269.
- Levine, S., Robinson, K., and Fawcett, W. R. (1974) The self image potential and its role in electrode kinetics: *J. Electroanal. Chem.* **54**, 237–252.
- Mamy, J. (1968) Recherches sur l'hydratation de la montmorillonite: propriétés diélectriques et structure du film d'eau: *Ann. Agron.* **19**, 175–292.
- McCafferty, E. and Zettlemoyer, A. C. (1971) Adsorption of water on Fe₂O₃: *Disc. Faraday Soc.* **52**, 239–254.
- Nelson, S. M., Huang, H. H., and Sutton, L. E. (1969) Dielectric study of water, ethanol and acetone adsorbed on kaolinite: *Trans. Faraday Soc.* **65**, 225–243.
- Oakes, D. T. (1960) Solids concentration effects in bentonite drilling fluids: in *Clays and Clay Minerals, Proc. 8th. Natl. Conf.*, Ada Swineford, ed., Pergamon Press, New York, 252–273.
- Swartzen-Allen, S. L. and Matijevec, E. (1975) Colloid and surface properties of clay suspensions: *J. Colloid Interface Sci.* **50**, 143–153.

(Received 26 January 1984; accepted 19 November 1984; Ms. 1330)