

ELECTRICAL POTENTIAL BETWEEN DISSIMILAR CLAY DOUBLE LAYERS

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Abstract—A model describing the electric double layers in clay-electrolyte systems containing particles with different surface charge densities was developed and used to calculate the film thickness of water present in a clay paste. The average water film thicknesses ($\sim 18 \text{ \AA}$) calculated by considering the clay to contain 9 groups of particles of different charge densities did not differ from those calculated by assuming one average charge density; provided the minimum potential between particles remained constant. These values, however, were higher than those obtained from gravimetric water determinations by about 30%. The overestimation of the average thickness of the water films by the theoretical model is most likely due to the assumption of a complete parallel arrangement of particles in the paste and the validity of the Gouy theory for double layers on clays.

Key Words—Double layer, Electrolyte, Film thickness, Montmorillonite, Surface charge, Water.

INTRODUCTION

Many properties of solid dispersions are dependent on whether a simple surface-charge density or a spectrum of charge densities characterizes the dispersed phase. Examples of such properties include suspension stability, coagulation behavior of the particles and their sedimentation volumes (Hogg *et al.*, 1966; Harding, 1972), adsorption and retention of organic solutes (Lagely and Weiss, 1971), clay-water interactions, and particle mobility (Beavers and Larson, 1953). It has been established by electrophoresis of clay suspensions (Beavers and Larson, 1953) and by saturation of clay with certain organic compounds (Lagaly *et al.*, 1976) that natural clays are mixtures of particles having different electric charge densities. Such mixtures of charge densities raise interesting questions about the validity of theories that assume complete homogeneity of a clay with respect to its surface charges. Existing theoretical treatments deal with binary systems (two colloidal species) and employ some approximate form of the Poisson-Boltzmann equation suitable for low potentials in the system (Hogg *et al.*, 1966; Kar *et al.*, 1973; Ohshima, 1974) and/or require tedious graphical or numerical integrations (Derjaguin, 1954; Devereux and de Bruyn, 1963). These techniques are not easily applicable to clay systems where surface potentials are not known and elude experimental evaluation.

In the present work an attempt is made to describe the electric double layers in a clay-electrolyte system containing more than two groups of particles having different charge densities. A condition of high electrostatic potential is used which, in addition to producing considerable mathematical simplification, is perhaps more appropriate to clays known to have high cation-exchange capacities. From this theory the thickness of water films in a clay paste containing particles with

varying charge densities is calculated and compared with experimentally determined film thickness.

THEORY

Consider a suspension of a clay in an electrolyte solution. The clay consists of groups of particles, with each group characterized by a certain average density of surface charge. Wyoming bentonite, for example, consists of 9 such groups as shown by Stul and Mortier (1974). In the well-stirred suspension and under equilibrium conditions, the particles will arrange themselves such that the system attains its lowest free energy of interaction between the particles, i.e., under such conditions the resultant of attraction and repulsion forces between any two particles stays at a minimum value and is constant throughout the suspension. At particle surface-to-surface distances greater than about 20 \AA , the attraction forces are negligible in comparison with the repulsive ones, especially when the particles possess high surface-charge densities. In such a case, the minimum electrical potential between the particle surfaces, ψ_h , is a measure of the free energy of interaction, and its value is the same throughout the suspension. When the two clay particles are identical, ψ_h is then known as the midway potential (Verwey and Overbeek, 1948). For two dissimilar particles, ψ_h is not at the midpoint of the surface-to-surface distance (Figure 1).

When ψ_h is the same throughout the system, as is required by the condition of minimum free energy of interaction, the surface-to-surface distance between any two interacting particles should differ according to the surface-charge density of each particle. Particles with high values maintain larger distances than those between particles with lower surface-charge densities. The value of ψ_h is in principle accessible from experi-

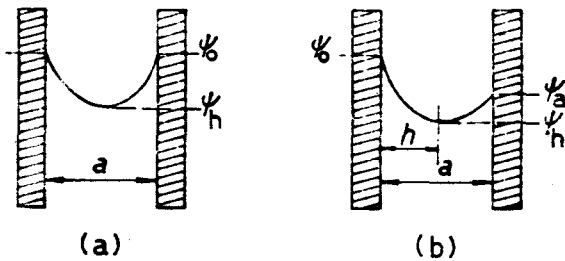


Figure 1. Schematic representation of the electric potentials in the system of two interacting particles having: (a) identical surface charge densities and (b) unequal surface charge densities.

mental measurements of such properties as osmotic pressure (Barclay *et al.*, 1972), disjoining pressure (Peschel and Belouschek, 1977), and freezing point depression of water in clay pastes (Helmy *et al.*, 1979). The distances between particles may be obtained from X-ray diffraction methods (Norrish, 1954), and the average water film thickness, i.e., the average distance between the particles, is in turn available from water content measurements if the specific surface area of the sample is also known.

Based on the Gouy-Chapman theory of electric double layers, relations can be derived between ψ_h and the surface-to-surface distance, a , between any two particles of known surface-charge densities that are immersed in an electrolyte solution of the (1-1) type. First, the case of two types of particles with surface-charge densities σ_1 and σ_2 may be considered. In the suspension three interactions are possible; namely that between particles with dissimilar surface-charge densities and those between particles with similar charge densities.

For the double layer interaction between two parallel dissimilar plates, the plates are separated by a distance, a , as shown in Figure 1. Only double layers of the Gouy type are to be considered. As mentioned above, the same problem has been treated by many authors in the Debye-Hückel approximation. In the present paper the case with high surface and in-between particle potentials is treated. Such conditions are more appropriate for clay double layers at low electrolyte concentrations.

According to the Gouy theory, the potential in the system under consideration, ψ , satisfies the Poisson-Boltzmann equation:

$$(d^2\psi/dx^2) = (8\pi FC/D)\sinh(F\psi/RT) \quad (1)$$

where F is the faraday charge in coulombs, C is the electrolyte concentration in mole/cm³, R is the gas constant, and T is the absolute temperature. At a certain distance, h , between the plates, the potential is at a minimum, ψ_h , hence with the boundary conditions:

$$\begin{aligned} \text{at } x = 0, \quad \psi &= \psi_0, \\ \text{at } x = h, \quad \psi &= \psi_h, \quad \text{and } (d\psi/dx) = 0. \end{aligned}$$

Eq. (1) can be integrated to obtain

$$(d\psi/dx) = \pm(16\pi CRT/D)^{1/2}[\cosh(F\psi/RT) - \cosh(F\psi_h/RT)]^{1/2}. \quad (2)$$

Eq. (2) with a minus sign is valid for the space between zero and h (see Figure 1), and with a positive sign for that between h and a . This is because the field intensity decreases from zero to h and increases from h to a . Furthermore, the surface charge densities are given by:

$$\int_0^h \rho \, dx = -\sigma_1 \quad (3)$$

and

$$\int_h^a \rho \, dx = -\sigma_2, \quad (4)$$

where the net charge density ρ at any point is given by the Poisson equation:

$$\rho = -(d^2\psi/dx^2)(D/4\pi). \quad (5)$$

Substitution of Eq. (5) in Eqs. (3) and (4) and integrating gives:

$$\sigma_1 = (D/4\pi)(d\psi_0/dx - d\psi_h/dx), \quad \text{and} \quad (6)$$

$$\sigma_2 = (D/4\pi)(d\psi_a/dx - d\psi_h/dx). \quad (7)$$

Substitution of Eq. (2) in Eq. (6) and knowing that $(d\psi_0/dx) = 0$, gives:

$$\sigma_1 = (DCRT/\pi)^{1/2}[\cosh(F\psi_0/RT) - \cosh(F\psi_h/RT)]^{1/2}. \quad (8)$$

If the potentials are high throughout the system, the following relation is valid:

$$\cosh(F\psi/RT) = 1/2 \exp(F\psi/RT). \quad (9)$$

Eq. (9) transforms Eq. (8) into:

$$\sigma_1 = (DCRT/2\pi)^{1/2}[\exp(F\psi_0/RT) - \exp(F\psi_h/RT)]^{1/2}. \quad (10)$$

Similarly, the surface-charge density of the other plate is:

$$\sigma_2 = (DCRT/2\pi)^{1/2}[\exp(F\psi_a/RT) - \exp(F\psi_h/RT)]^{1/2}. \quad (11)$$

At this step, it is interesting to note that when $\sigma_1 = \sigma_2$, Eqs. (10) and (11) are identical.

Eq. (9) transforms Eq. (2) into:

$$\pm(d\psi/dx) = (8\pi CRT/D)^{1/2} \cdot [\exp(F\psi/RT) - \exp(F\psi_h/RT)]^{1/2}. \quad (12)$$

Integration of Eq. (12) between the limits h and zero and the corresponding potential limits ψ_h and ψ_0 gives:

$$\frac{2}{(F/RT)\sqrt{\exp(F\psi_h/RT)}} \cdot \tan^{-1}\left(\frac{\sqrt{\exp(F\psi_0/RT) - \exp(F\psi_h/RT)}}{\sqrt{\exp(F\psi_h/RT)}}\right) = \left[\sqrt{8\pi CRT/D}\right]h. \quad (13)$$

Similarly, integrating Eq. (12) between the limits a and h and the corresponding electric potentials ψ_a and ψ_h gives:

$$\frac{2}{(F/RT)\sqrt{\exp(F\psi_h/RT)}} \cdot \tan^{-1}\left(\frac{\sqrt{\exp(F\psi_a/RT) - \exp(F\psi_h/RT)}}{\sqrt{\exp(F\psi_h/RT)}}\right) = \left(\sqrt{8\pi CRT/D}\right)(a - h). \quad (14)$$

Substitution of Eq. (10) in Eq. (13) and Eq. (11) in Eq. (14), respectively, and summation after rearrangement gives:

$$\exp(F\psi_h/2RT) = (2/x)a \left[\tan^{-1}\left(\frac{\sigma_1\sqrt{2\pi/CRTD}}{\exp(F\psi_h/2RT)}\right) + \tan^{-1}\left(\frac{\sigma_2\sqrt{2\pi/CRTD}}{\exp(F\psi_h/2RT)}\right) \right], \quad (15)$$

where: $x = (8\pi F^2 C/DRT)^{1/2}$.

Noting that when $\sigma_1 = \sigma_2$, $h = a/2$, which is the case for two similar plates, Eq. (15) reduces to:

$$\exp(F\psi_h/2RT) = \frac{2}{xh} \tan^{-1}\left(\frac{\sigma\sqrt{2\pi/CRTD}}{\exp(F\psi_h/2RT)}\right), \quad (16)$$

where σ is the surface charge density of any two similar plates.

Because, as mentioned above, ψ_h is the same throughout the system in a suspension, the following relations can be written for the suspension which contains two types of particles having charge densities σ_1 and σ_2 :

$$\begin{aligned} \exp(F\psi_h/2RT) &= (2/x)a(\tan^{-1}W + \tan^{-1}V) \\ &= (2/xd_1)(\tan^{-1}W) \\ &= (2/xd_2)(\tan^{-1}V), \end{aligned} \quad (17)$$

where d_1 is the midway distance between two interacting particles with charge σ_1 , and d_2 is that for particles with charge density σ_2 ; a is the surface-to-surface distance defined above, $W = \sigma_1\sqrt{2\pi/CRTD}/\exp(F\psi_h/2RT)$, and $V = \sigma_2\sqrt{2\pi/CRTD}/\exp(F\psi_h/2RT)$. From Eq. (17) it follows that:

$$a = d_1 + d_2. \quad (18)$$

Eqs. (17) and (18) can be generalized for any number of groups of particles of different σ that may be found in a clay sample. Eq. (18) is important because it solves the impossible problem of knowing which particles are

interacting with which particles in a clay suspension or paste.

MATERIALS AND METHODS

Wyoming montmorillonite (Volclay SVP obtained from the American Colloid Company) was used in the present study. Particles smaller than $2\ \mu\text{m}$ in diameter were separated by sedimentation and were saturated with Na^+ , NH_4^+ , and Li^+ by repeated treatment with 0.1 M chloride salts. Excess salt was washed out using distilled water and a high speed centrifuge until the supernatant liquids gave no reaction to chloride. The clays were then dried over a water bath. The following values of exchangeable Li^+ , Na^+ , and NH_4^+ were obtained by chemical analysis: 0.77, 0.82, and 0.77 (meq/g) respectively. Under the conditions of the experiment the specific surface area of the clay was determined by orthophenanthroline adsorption (Lawrie, 1961) to be $564\ \text{m}^2/\text{g}$. The cation-exchange capacity of the clay was determined by the usual ammonium acetate method to be 0.82 meq/g. The calculated surface charge density is therefore $4.21 \times 10^4\ \text{e.s.u./cm}^2$, equivalent to $14.0\ \text{microcoulomb/cm}^2$.

Low-temperature, differential scanning calorimeter (DSC) curves were obtained for the clays as a function of their water contents using a model DSC-1B Perkin-Elmer instrument. The apparatus was first calibrated using *n*-octanol (melting point 256.7°K). The procedure used for obtaining the freezing temperatures of the water in the clays was as follows: different amounts of electrolyte were added to about 1 g of clay to give a final water content of 0.3–0.9 g/g and a final chloride concentration of 0.01 M. The samples were mixed and equilibrated for one week in weighing bottles. A clay sample of 10–30 mg, depending on its water content, was placed in a preweighed aluminum sample pan which was then put in the sample holder assembly of the calorimeter. The sample was then subjected to freezing during which the thermal curve was obtained. The sample pan was withdrawn, weighed, and placed in an oven at 110°C until constant weight was obtained. The moisture content of the sample was then calculated. The freezing temperature was read from the thermal curve after adopting a procedure given by the manufacturer of the calorimeter which corrects for problems of heat transfer between sample and holder (O'Neill, 1964).

The freezing temperature, T , in degrees Kelvin, is related to the minimum potential between particles, ψ_h , through the relation given by Helmy *et al.* (1979) as follows:

$$[(T_0/T) - 1] = k[\cosh(F\psi_h/RT') - 1], \quad (19)$$

where T_0 is the freezing temperature of the pure water (273.16°K), T' is the room temperature to which ψ_h refers, and k is a constant equal to 1.3619×10^{-4} when the electrolyte concentration is 0.01 M.

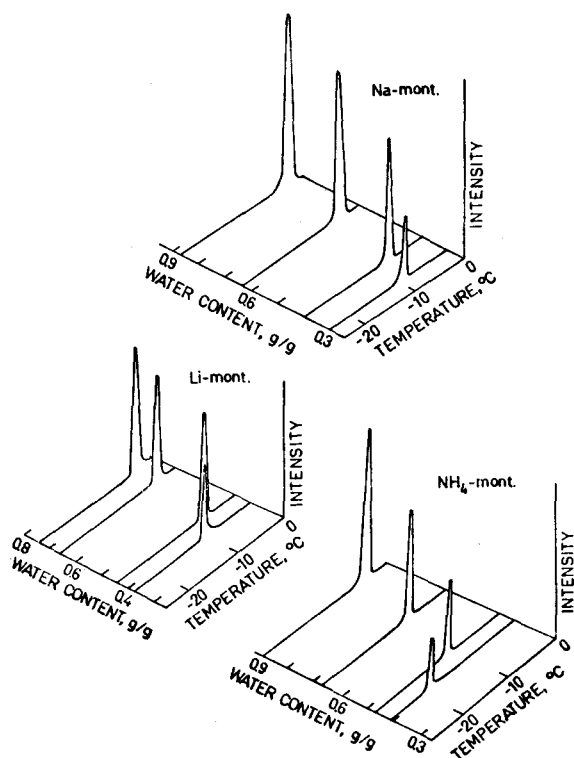


Figure 2. Low temperature, differential thermal curves for Na-, NH_4 -, and Li-montmorillonite. The electrolyte concentration was 0.01 M.

RESULTS

The experimental low-temperature DSC curves are shown in Figure 2. The values of ψ_h for the different cation-saturated clays at different water contents were obtained from the experimentally determined freezing temperatures through the use of Eq. (19).

The water film thicknesses were then calculated using Eq. (16) along with these ψ_h values and the average σ value of 4.2×10^4 e.s.u./ cm^2 . The dotted lines in Figure 3 give freezing point depressions (ΔT) as a function of the water film thickness calculated in this way. The continuous lines in the plots of Figure 3 which almost coincide with the dotted lines represent the average water film thicknesses as calculated by considering that the clay sample contains 9 groups of particles, each group having the relative percentage and the charge density given in Table 1. This relative percentage is the same as that given by Stul and Mortier (1974) for Wyoming montmorillonite.

The methods of calculation of the film thickness was as follows: for example, for a water content of 0.829 g/g, the ΔT value obtained for Na-montmorillonite was 3.8°K. This gives a value of $\psi_h = 133$ mV calculated using Eq. (19). Putting this ψ_h value in Eq. (16) a value

Table 1. Surface-charge densities, relative percentages of the 9 groups of particles in Wyoming Na-montmorillonite, and film thickness for a water content of 0.829 g/g.

Surface charge density (e.s.u./ cm^2)	Percent of group	Film thickness (Å)
5.49×10^4	3	18.1
5.07×10^4	7	18.0
4.71×10^4	27	17.9
4.40×10^4	5	17.7
4.14×10^4	18	17.6
3.91×10^4	11	17.5
3.70×10^4	8	17.3
3.50×10^4	12	17.3
3.33×10^4	9	17.2

of d for each σ given in Table 1 can be calculated. According to Eq. (18), the average water film thickness in the sample (\bar{d}) is then given by:

$$0.03d_1 + 0.07d_2 + 0.27d_3 + \dots + 0.09d_9 = \bar{d}. \quad (20)$$

This type of calculation is repeated for the other water contents and cations. Some results are given in Table 1. The average film thickness (\bar{d}) calculated from the gravimetric water content (w) and the specific area are also given in Figure 3. These are related through the equation:

$$d = (w/S)10^4, \quad (21)$$

where w is in cm^3/g , S is in m^2/g , and d is in Å.

DISCUSSION

The results obtained in this work show that the average water film thickness calculated by considering the clay to contain 9 groups of particles of different surface-charge densities is not significantly different from the average film thickness calculated by considering all the clay particles to be identical, with an average surface-charge density obtained from the cation-exchange capacity and the specific surface area of the sample. This result can perhaps be associated with the fact that the mixture model is rather insensitive to variations in the surface-charge density of the clay, provided that the minimum potential between particles remains constant. For example, as seen in Table 1, a 60% decrease in charge density produces about 5% decrease in film thickness. The mixture model has the advantage, however, of describing the fine structure, i.e., the film thicknesses present in the paste as well as their relative percentages.

It appears also from the results plotted in Figure 3 that the two ways of calculating the water film thickness mentioned above give rise to values larger than the average values obtained from the water content of the pastes. This is true for all the cation-saturated clays at all water contents. This overestimation of the water film thickness is thought to be a direct consequence of

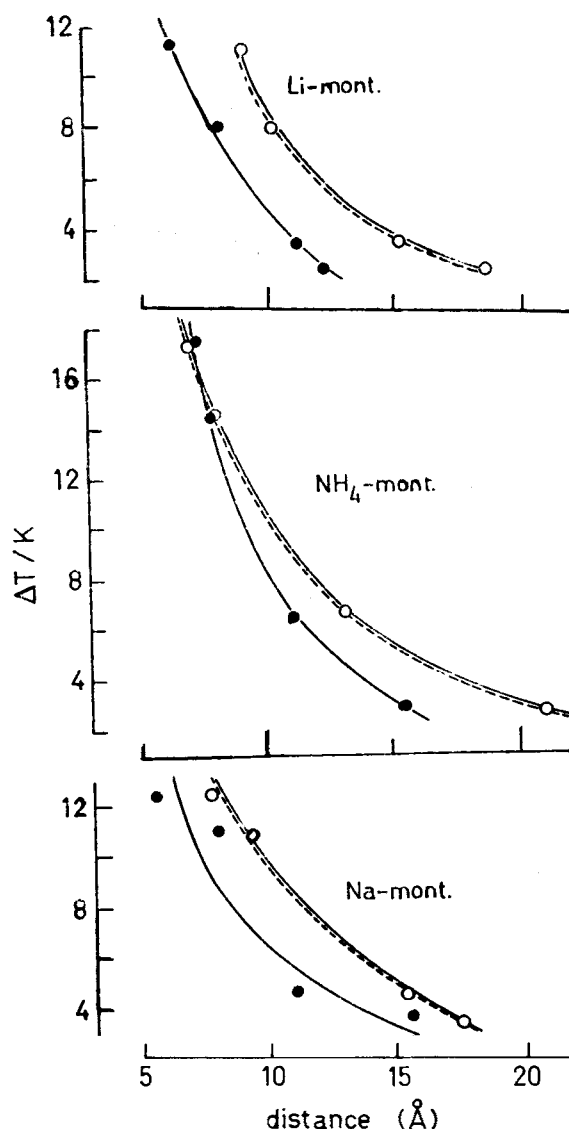


Figure 3. Freezing point depression of montmorillonite paste (ΔT) as a function of the water film thickness. Open circles represent theoretical data using Eq. (20) from text; solid circles represent data obtained from gravimetric water contents. The dotted lines in the figure represent data calculated using the average surface-charge density.

the adoption of the Gouy model and of Eq. (9), which give rise to high values of surface and midway potentials (Helmy *et al.*, 1966; Helmy, 1973; Helmy *et al.*, 1979). Added to this, is the fact that the model assumes a complete parallel arrangement of particles in the paste, a geometry which is probably too ideal to obtain in practice. Both of these factors, namely the high potentials and the geometry, can be handled within the framework of the mixture model so that further improvement seems likely.

Finally, the experimental observations presented here and the results reported by Anderson and Hoekstra (1965), Anderson and Tice (1971), and others are in agreement with the model presented here in that a single freezing temperature is obtained for Na-, NH_4 -, Li- and other montmorillonite pastes at water contents that are greater than about 30% and at low salt concentration. This observation gives credence to the present mixture model, which postulates the presence of only one midway potential in each well-homogenized paste. The similarities in the theoretical and experimental curves shown in Figure 3 lend support to the model. However, the differences observed between clay samples saturated with different cations cannot be explained because ions of the same valence are not distinguished by the model. The differences in the theoretical curves arise, however, from using in the calculations potentials between the particles that were different for each cation, as obtained from Eq. (19).

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Резюме—Модель, описывающая электрические двойные слои в системах глина-электролит, содержащих частицы с разными плотностями поверхностного заряда, была разработана и использована для вычислений толщины фильма воды, присутствующей в глинистой пасте. Средняя толщина фильма воды (~18 Å), вычисленная на основе предположения, что глина содержит 9 групп частиц с разными плотностями заряда, не отличалась от величины, вычисленной на основе одной средней плотности заряда предполагая, что минимальный потенциал между частицами остается постоянным. Эти величины, однако, были больше около 30% от тех, которые получались путем гравиметрического определения содержания воды. Переоценка средней толщины фильмов воды на основе теоретической модели, наиболее вероятно, является результатом предположения полностью параллельного расположения частиц в пасте и законности теории Гуи для двойных слоев в глинах. [E.C.]

Resümee—Es wurde ein Modell entwickelt, das die elektrischen Doppelschichten in Ton-Elektrolyt-Systemen beschreibt, das Teilchen mit unterschiedlichen Oberflächenladungsdichten enthält. Dieses Modell wurde verwendet, um die Filmdicke des Wassers zu berechnen, die in einer Tonpaste vorhanden ist. Die durchschnittliche Wasserfilmdicke (~18 Å), die unter der Annahme berechnet wurde, daß der Ton 9 Teilchengruppen von verschiedener Ladungsdichte enthält, unterschied sich nicht von den Wasserfilmdicken, die unter der Annahme berechnet wurden, daß eine durchschnittliche Ladungsdichte vorhanden ist. Dies gilt unter der Voraussetzung, daß das minimale Potential zwischen den Teilchen konstant bleibt. Diese Werte waren jedoch um etwa 30% höher als die Werte, die aus gravimetrischen Wasserbestimmungen erhalten wurden. Die überschätzung der durchschnittlichen Dicke der Wasserfilme durch das theoretische Modell hängt wahrscheinlich von der Annahme ab, daß die Teilchen in der Paste vollständig parallel angeordnet sind und von der Gültigkeit der Gouy-Theorie für Doppelschichten auf Tonen. [U.W.]

Résumé—Un modèle décrivant les doubles couches électriques dans des systèmes argile-électrolyte contenant des particules ayant des densités de charge de surface différentes a été développé et utilisé pour calculer l'épaisseur du film d'eau présent dans une pâte argileuse. Les épaisseurs moyennes du film d'eau (~18 Å) calculées en considérant que l'argile contient 9 groupes de particules ayant des densités de charge différentes n'ont pas différé de celles calculées en assumant une densité de charge moyenne; pourvu que le potentiel minimum entre les particules reste constante. Ces valeurs étaient cependant à peu près 30% plus élevées que celles obtenues des déterminations d'eau gravimétrique. La surestimation de l'épaisseur moyenne des films d'eau par le modèle théorique est probablement due au fait que l'on suppose un arrangement parallèle complet des particules dans la pâte, et la validité de la théorie Gouy pour les couches doubles sur les argiles. [D.J.]