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NEGATIVE ADSORPTION IN CLAY–WATER SYSTEMS WITH INTERACTING DOUBLE LAYERS

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Abstract—A relation was derived which describes negative adsorption (salt exclusion) in systems in which double layer interaction takes place but where the surface potential remains finite, such as in clay pastes and sediments. Exclusion volumes calculated for montmorillonite pastes in equilibrium with 1:1 type electrolytes were found to compare favorably with data obtained by F. A. M. de Haan in an earlier study.

Key Words—Adsorption, Clay–water systems, Double layer, Negative adsorption, Salt exclusion.

INTRODUCTION

Where a charged surface is in equilibrium with an electrolyte solution, ions of the same charge as the surface (co-ions) are repelled from the interface zone. This phenomenon is known as negative adsorption, or salt exclusion or rejection, and plays an important role in the permeability of membranes to salts and in desalinization (Teorell, 1956; Helfferich, 1962; Dresner and Kraus, 1963), as well as in processes associated with biological systems, such as salt uptake and movement in plant roots (Shone and Barber, 1966).

The earliest quantitative treatment of negative adsorption was given by Mattson (1929) and was based on the Donnan theory (Helfferich, 1962). This was followed by the application of the Gouy theory of diffuse double layers (Schofield, 1947; Overbeek, 1956; Bolt and Warkentin, 1958; Helmy, 1963; Edwards *et al.*, 1965; van den Hul and Lyklema, 1967). One interesting application of negative adsorption phenomena is in the determination of specific surface area of colloids, clays, and fibers (Schofield and Talibudeen, 1948; van den Hul and Lyklema, 1968; Lyklema and van den Hul, 1970) and of materials of biological origin (Shone, 1966) whose surface properties change upon drying or on exposure to liquid nitrogen temperatures or to chemicals and procedures used in other methods of specific surface area determination. All theoretical treatments of negative adsorption are based on the equation first introduced by Schofield (1947) which deals with dilute colloidal systems or systems ". . . in which the distance between opposing surfaces considerably exceeds the distance between neighboring point charges on the surfaces." When the distance between opposing surfaces is small, double layer interaction takes place, and negative adsorption decreases. Negative adsorption in cases with interaction of double layers has been so far only evaluated by de Haan (1964), who assumed that the surface potential of the particles is infinite. This assumption was used to evaluate the elliptic integrals involved in the treatment.

In the present study, negative adsorption phenomena have been reexamined in systems with interacting double layers but where the surface potential remains finite, such as in concentrated clay pastes.

THEORY

A schematic representation of co-ion and counter-ion distributions in a concentrated suspension in which the double layers (pertaining to charge particles with flat surfaces) interact, is shown in Figure 1. The negative adsorption is indicated by the shaded area in the figure and is equal to the difference between the area under the horizontal line (the line traces the co-ion concentration as a function of distance, assuming no charge on the particles) and the area under the curve representing the concentration of co-ions as a function of distance. The shaded area (or negative adsorption) is thus given by (van den Hul and Lyklema, 1967):

$$\Gamma = \int_0^d [C - C \exp(-zF\Psi/RT)]\, dx \qquad (1)$$

where Γ is the negative adsorption in mole/cm^2, C is the electrolyte concentration in mole/cm^3, Ψ is the electric potential in volts, F is the faraday charge in coulombs per mole, z is the valence of the co-ions, R is the gas constant, and T is the absolute temperature. The limits of integration are from the surface where $x = 0$ and the surface potential $= \Psi_0$, to $x = d$, where d is half the distance between two plate particles. At the distance d, the electric potential is Ψ_d. Eq. (1), after integration of the first part on the right hand side, becomes:

$$\Gamma = Cd - C \int_0^d \exp(-zF\Psi/RT)\, dx \qquad (2)$$

The integral in Eq. (2) can be transformed from an integral over the distance to an integral over the potential; hence Eq. (2) can be written in the form:

$$\Gamma = Cd - C \int_{\Psi_0}^{\Psi_d} \exp(-F\Psi/RT)(dx/d\Psi)\, d\Psi \qquad (3)$$

In Eq. (2), z is eliminated since only monovalent co-

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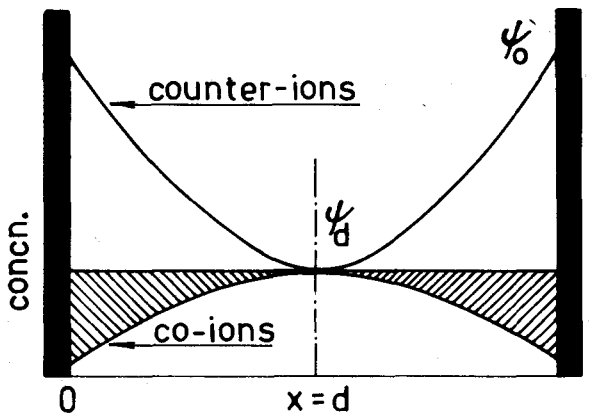


Figure 1. Schematic distribution of counter ions and of co-ions in the space between two interacting flat double layers. The shaded area represents the amount of co-ions excluded from the mentioned space.

and counter-ions are of interest here. For a system of interacting double layers and in the presence of 1:1 type electrolyte ($d\Psi/dx$) was given by Verwey and Overbeek (1948) as follows:

$$(d\Psi/dx) = -k(RT/F)[2\cosh(F\Psi/RT) - 2\cosh(F\Psi_d/RT)]^{1/2} \quad (4)$$

where $k = [8\pi CF^2z^2/RTD]^{1/2}$, and D is the dielectric constant. Combination of Eq. (4) with Eq. (3) gives:

$$\Gamma = Cd - [C/(kRT/F)]\int_{\Psi_d}^{\Psi_0} \exp(-F\Psi/RT)\, d\Psi/[2\cosh(F\Psi/RT) - 2\cosh(F\Psi_d/RT)]^{1/2} \quad (5)$$

Eq. (5) is similar to an earlier one derived by Overbeek (1956).

In a system where strong double layer interaction takes place, the potentials attain high values, and the following relation becomes valid:

$$\cosh(F\Psi/RT) = \tfrac{1}{2}\exp(F\Psi/RT) \quad (6)$$

Eq. (6) transforms the integral (I) in Eq. (5) into:

$$I = -[C/(kRT/F)]\int_{\Psi_d}^{\Psi_0} \exp(-F\Psi/RT)\, d\Psi/[\exp(F\Psi/RT) - \exp(F\Psi_d/RT)]^{1/2} \quad (7)$$

Eq. (7) integrates to:

$$I = -(C/k)\Big\{\exp(-3F\Psi_d/2RT)\tan^{-1}\cdot\Big[[\exp(F\Psi_0/RT) - \exp(F\Psi_d/RT)]^{1/2}/\exp(F\Psi_d/2RT)\Big] + \Big[[\exp(F\Psi_0/RT) - \exp(F\Psi_d/RT)]^{1/2}/[\exp(F\Psi_d/RT)][\exp(F\Psi_0/RT)]\Big]\Big\} \quad (8)$$

According to Verwey and Overbeek (1948), the surface charge density σ is related to Ψ_0 and Ψ_d by:

$$\sigma = [RTCD/2\pi]^{1/2}[2\cosh(F\Psi_0/RT) - 2\cosh(F\Psi_d/RT)]^{1/2} \quad (9)$$

Taking Eq. (6) into consideration, Eq. (9) may be written as:

$$\sigma[2\pi/RTCD]^{1/2} = [\exp(F\Psi_0/RT) - \exp(F\Psi_d/RT)]^{1/2} \quad (10)$$

$$= Q \quad (11)$$

In Eq. (11) let both sides of Eq. (10) be equal to Q for the purpose of simplification. Furthermore, Ψ_d is related to the surface charge density σ by the following relation given by Helmy *et al.* (1979):

$$\tan^{-1}\{\exp(-F\Psi_d/2RT)\sigma[2\pi/RTCD]^{1/2}\} = (kd/2)\exp(F\Psi_d/2RT) \quad (12)$$

Combination of Eqs. (11), (12), and (8) and rearrangement gives:

$$I = -(C/2k)\exp(-F\Psi_d/RT)\cdot\{[kdQ^2 + kd\exp(F\Psi_d/RT) + 2Q]/[Q^2 + \exp(F\Psi_d/RT)]\} \quad (13)$$

From Eq. (5) and Eq. (13),

$$\Gamma = Cd - (C/2k)(\exp(-F\Psi_d/RT))\cdot\{[kdQ^2 + kd\exp(F\Psi_d/RT) + 2Q]/[Q^2 + \exp(F\Psi_d/RT)]\} \quad (14)$$

To use Eq. (14) for surface area determinations it must be transformed. First, the following relations are defined:

$$\Gamma = \Gamma'/S \quad (15)$$

$$\sigma = \sigma'/S \quad (16)$$

$$d = w/S \quad (17)$$

$$q = Q/S \quad (18)$$

where Γ' is the negative adsorption in mole/g, σ' is the surface charge density of the particles in esu/g, S is the surface area in cm^2/g, w is the water content of the paste or suspension in cm^3/g, and q is a parameter that depends on the surface charge density as given in Eq. (11).

Introducing Eqs. (15), (16), (17), and (18) in Eq. (14) and rearrangement gives:

$$2[(w - (\Gamma'/C)] = \exp(-F\Psi_d/RT)\cdot\{[wq^2 + wS^2\exp(F\Psi_d/RT) + (2q/k)S^2]/[q^2 + S^2\exp(F\Psi_d/RT)]\} \quad (19)$$

Eq. (19) may also be written in the form:

$$S^2 = q^2[b\exp(F\Psi_d/RT) - w]/[(2q/k) + w\exp(F\Psi_d/RT) - b\exp(2F\Psi_d/RT)] \quad (20)$$

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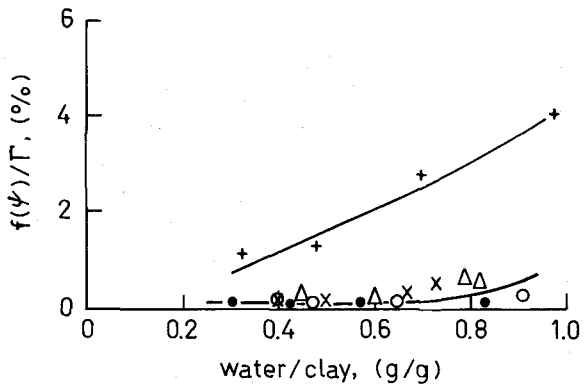


Figure 2. The percent contribution of the second term of Eq. (14) to the negative adsorption (f(Ψ)/Γ) plotted as a function of the water/clay ratio. The symbols represent the following: + NH_4-montmorillonite from Cerro Bandera in 0.2 M NH_4Cl. ○ NH_4-montmorillonite from Cerro Bandera in 0.01 M NH_4Cl. △ Na-montmorillonite from Cerro Bandera in 0.01 M NaCl. ● Na-montmorillonite from Wyoming in 0.01 M NaCl. × Li-montmorillonite from Wyoming in 0.01 LiCl.

where $b = 2[w - (\Gamma'/C)]$

It is worth mentioning that Eqs. (19) and (20) are valid for systems of interacting double layers in the presence of 1:1 type electrolyte, and that for calculating purposes the positive values of Ψ_d and q must be used in both equations.

MATERIALS AND METHODS

To examine the validity of the equations derived, the midway potential in a clay paste was obtained through experimental determinations of freezing temperatures using a low temperature, differential scanning calorimeter (DSC). The freezing temperature T of water in a paste permits the calculation of the midway potential Ψ_d from the relation given by Helmy *et al.* (1979):

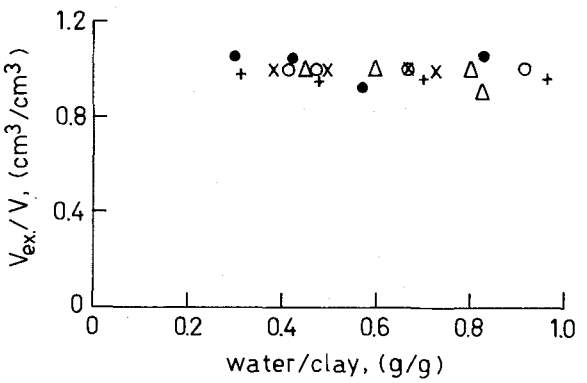


Figure 3. The volume of exclusion relative to the total water for different cation saturated clays, plotted as a function of the water/clay ratio. Symbols represent the same as in Figure 2.

$$(T_0/T) - 1 = (2CRT_0v/L)[\cosh(F\Psi_d/RT) - 1] \quad (21)$$

where T_0 is the freezing temperature of pure water (273.15°K), v is the molar volume of water (18 cm^3), and L is the molar heat of fusion (1434.18 cal/mole).

Low temperature differential thermal analysis curves were obtained for the clay pastes and plotted in Figure 2 as a function of their water content, using a Perkin-Elmer DSC, model DSC-1B. Different amounts of electrolyte were added to about one gram of clay to give a final water content of 0.3–1 g/g and a final salt concentration of 0.01 M or 0.2 M. The samples were well mixed and left to equilibrate 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 placed in the sample holder assembly of the calorimeter. The sample was then frozen. After thermal analysis, the sample pan was withdrawn, weighed, and dried at 110°C to constant weight. The moisture content of the sample was then calculated. The freezing temperatures were read from the thermal curves using a procedure given by the manufacturer (O'Neill, 1964).

Montmorillonites from Wyoming (Volclay, SVP obtained from the American Colloid Company), and from Cerro Bandera, Argentina (Peinemann *et al.*, 1972) were used in this study. Particles smaller than 2 μm in diameter were separated by sedimentation and were saturated with Na, Li, or NH_4 by repeated washing with 0.1 M chloride solutions. Excess salt was washed out using distilled water and a high speed centrifuge. The clays were then dried over a water bath. The specific surface areas of the clays were determined by orthophenanthroline adsorption (Lawrie, 1961) and found to be 564 and 588 m^2/g for the Wyoming and the Cerro Bandera clays, respectively. Cation-exchange capacities, determined by the ammonium acetate method, are 0.82 and 0.92 meq/g for the above mentioned clays, respectively. The surface charge density for the two clays are therefore 4.2×10^4 esu/cm^2 and 4.5×10^4 esu/cm^2, respectively.

The values of Ψ_d and σ thus obtained were used in Eq. (14) for the evaluation of the relative contributions of each of the two principal parts of the equation and for comparisons with the data of de Haan (1964). The results are given in Figures 2, 3, and 4.

RESULTS AND DISCUSSION

Eq. (14), which describes negative adsorption in systems in which double layer interaction takes place, is composed of two principal parts. The first, which is the main term, was obtained without making mathematical approximations. The second term was obtained using the approximation given by Eq. (6). The error in calculating negative adsorption from Eq. (14) is therefore expected to be small, especially for systems with considerable double layer interaction and where the elec-

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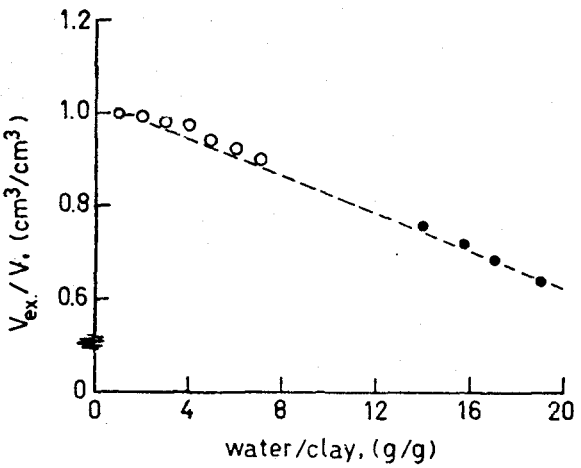


Figure 4. The volume of exclusion relative to the total water present in Na-montmorillonite (V ex./V), plotted as a function of the water/clay ratio; filled circles (●) represent the experimental data from de Haan (1964), open circles (○) represent values obtained from Eq. (14).

tric potentials attain high values. To assess the relative importance of each term of Eq. (14), the value of the second term was calculated using the midway potential values (Ψ_d) obtained from the freezing experiments. The values obtained were then divided by the corresponding values of negative adsorption. These ratios represent the contributions of the second term to the overall values of negative adsorption and are plotted as a function of water content in Figure 2. As can be seen, f (Ψ_d) contributes little to the overall values of negative adsorption in systems with strong double layer interaction and low electrolyte concentration. Its contribution, however, increases as the water content in the paste increases and becomes important when the electrolyte concentration is high.

For a closer examination of Eq. (14), in Figures 3 and 4 the exclusion volume relative to the total volume of water in the systems is plotted as a function of the water content of the pastes. The exclusion volume is the volume of solvent which may be considered as void of coions, and is given by:

$$V_{ex} = (\Gamma/C)S$$

It can be seen from Figure 3 that the exclusion volume is almost equal to the volume of water present in the pastes when the water/clay ratio ≤ 1. This is the limit expected in both the present treatment and that of de Haan (1964). As the water/clay ratio increases, the volume of exclusion decreases as shown in Figure 4.

Furthermore, Figure 3 shows that no significant differences exist between the two clays or between the three saturating cations. This is probably due to the fact that the water/clay ratios lie within the range in which the exclusion volumes become almost equal to the volume of water present in the paste.

Finally, in Figure 4 are plotted data obtained by the present treatment together with experimental values given by de Haan for Na-montmorillonite. It may be seen from the Figure that good agreement is observed between the two sets of data.

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Резюме—Было выведено отношение, которое описывает отрицательную адсорбцию (удаление соли) в системах, в которых происходит взаимодецствие двойных слоев, но, где поверххностный потенциал остается ограниченным, как в глинистых пастах и отложениях. Удаленные объемы, высчитаные для монтмориллонитовых паст, находящихся в равновесии с электролитами типа 1:1, оказались сходными с данными, полученными ранее Ф. А. М. де Хааном. [N.R.]

Resümee—Es wurde eine Beziehung abgeleitet, die die negative Adsorption (Salzausschluß) in Systemen beschreibt, in denen Doppelschichtwechselwirkungen stattfinden, in denen aber das Oberflächenpotential begrenzt bleibt, wie z.B. in Tonpasten und Sedimenten. Die Ausschlußvolumen, die für Montmorillonitpasten im Gleichgewicht mit 1:1 Typ Elektrolyten berechnet wurden, ließen sich gut mit den Ergebnissen einer früheren Untersuchung von F. A. M. de Haan vergleichen. [U.W.]

Résumé—On a derivé une relation qui décrit l'adsorption negative (exclusion de sel) dans des systèmes dans lesquels l'interaction à couche double se passe mais où le potentiel de surface reste fini, tel que dans des pâtes argileuses et des sediments. Des volumes d'exclusion calculés pour des pâtes de montmorillonite en équilibre avec des électrolytes du type 1:1 pouvaient être favorablement comparés aux données obtenues par F. A. M. de Haan dans une étude précedente. [D.J.]

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