

A MODEL OF CLAY SWELLING AND TACTOID FORMATION

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Abstract—An electrostatic model for the stability of clay tactoids (stacks of parallel clay platelets at ~ 10 Å separation) in an aqueous solution has been developed. The counter ions located in the interstitial water layers are assumed to be in equilibrium with the bulk solution. Generally, the counter-ion charge density is slightly different in magnitude from the platelet charge density. Approximating the discrete charges by homogeneously charged planes, a one-dimensional potential distribution can be calculated. From this the Gibbs energy of electrostatic interaction (using single platelets as a reference) can be computed. The model predicts that clay minerals with high (vermiculite, mica) and low (pyrophyllite, talc) degrees of cationic substitution form stable tactoids. For smectites, charge density, electrolyte concentration, and counter-ion species determine the swelling characteristics. At a particular charge density, lower valences of the counter ions and lower electrolyte concentrations lead to increased swelling. If tactoids are formed, the number of platelets is governed by a dynamic equilibrium between electrostatic forces, van der Waals forces, and external forces, such as shear forces due to hydrodynamic flow.

Key Words—Electrostatic forces, Mica, Pyrophyllite, Tactoid, Talc, Swelling, Vermiculite.

INTRODUCTION

Since the discovery of the crystalline structure of clay minerals in the early 1930s, knowledge of the interaction between clay platelets in an aqueous medium has increased rapidly. It has been found that clays with both high (e.g., mica) and low (e.g., pyrophyllite, talc) degrees of cationic substitution never swell in an aqueous medium, whereas vermiculites swell to a very limited extent, and smectites swell vigorously under certain conditions. The swelling properties of the smectite group vary with counter-ion species, ionic strength, and temperature.

Because clay platelets are electrically charged, their interaction has been described in terms of the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory on the interaction of colloidal particles in suspension (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948). The DLVO theory describes the interaction of two surfaces resulting from overlapping Gouy electric double layers (Gouy, 1910) and van der Waals forces. The theory predicts the swelling behavior of moderately charged minerals (such as smectites) in specific cases.

However, the DLVO theory cannot explain why highly charged clay minerals, such as mica and vermiculite, do not swell. These minerals form quasi-crystals composed of packets of many individual clay platelets with a fixed, small interlayer space between them. The small spacing results in conditions which strain the assumptions used in the DLVO theory. Childs (1955) showed that the usual assumption that the Gouy layer charge per unit surface is equal for both sides of a clay platelet does not introduce a significant error in the pre-

dictions of the DLVO theory when two clay platelets interact in an aqueous solution. However, asymmetry in charge distribution around clay platelets will be shown below to be important in clay tactoids.

The DLVO theory is satisfactory in predicting swelling behavior of Na-illite if one allows for "dead" water volume (Bolt and Miller, 1955). The "dead" water volume does not change during compression, being located at the edges of the (large) illite particles. Good agreement with the DLVO theory was found for Na-montmorillonite (Warkentin *et al.*, 1957). For Ca-montmorillonite, quasi-crystals are formed (Blackmore and Miller, 1961) that consist of stacks of parallel, equally spaced clay platelets and are called *tactoids* (Blackmore and Miller, 1961). For Ca-montmorillonite in an aqueous solution, the platelets are separated by about 9 Å of interstitial water (Norrish, 1954). Blackmore and Miller (1961) found that the DLVO theory predicts the swelling pressure accurately if the tactoids and not the single platelets are considered as the elemental particles in the suspension.

Callaghan and Ottewill (1974) concluded that the electrostatic forces described by the DLVO theory are responsible for the long-range interactions in Na-montmorillonite gels. Israelachvili and Adams (1978) found that the DLVO theory described the interaction of two mica surfaces in a KNO_3 solution well at low concentrations (10^{-3} , 10^{-4} M), but that the decay length of the repulsion forces deviated by about 25% for high concentrations (10^{-2} , 10^{-1} M). For bivalent cations, the DLVO theory was found to be more erroneous (20 to 45%), even in dilute solutions. Israelachvili and Adams

(1978) stated that forces due to structural water are present at short range (<50 Å). Low and Margheim (1979) concluded from the data of Callaghan and Ottewill (1974) that forces due to structural water, and not electric double-layer forces, dominate the swelling behavior of montmorillonite platelets. This opinion has been disputed (Barnes, 1980).

At small separations (<10 Å), different models have been used. Giese (1978) calculated the interaction energies of clay platelets by treating the system of clay platelets and counter ions as one large crystal. A vacuum was assumed to exist between the platelets. In the Giese model, the location of the counter ions must be well defined. It is difficult to make the transition from the Giese model at small separations to the DLVO model at large separations because of the requirement of a well-defined, counter-ion location in the former and because of the medium effects in the latter. The Giese model does not take into account effects due either to the medium between the platelets or to van der Waals forces. According to Farmer and Russell (1971), the medium plays a major role in the interaction between clay platelets at small separations. These authors gave a qualitative evaluation of the Gibbs energy of interaction as a function of the length of the dipole chains between the platelets and the counter ions.

It is well known that the interlayer spacing of clay platelets changes in discrete steps at small separations (e.g., Norrish, 1954). Apparently, the Gibbs energy of interaction has discrete minima for certain spacings that depend upon the species of the counter ions (Norrish, 1954). Recently obtained neutron-scattering data for montmorillonite indicate that the counter ions have well-defined hydration shells (Hall *et al.*, 1978). Interstitial water, not located in hydration shells, was shown to have a similar structure to that of bulk water (Hall *et al.*, 1979; Hawkins and Egelstaff, 1980). Only about half of the first layer of water molecules is associated with the silicate structure of the clay minerals (Hawkins and Egelstaff, 1980). Additional evidence for liquid-like ordering was provided by Stigter (1980), who showed that observed decreases in the viscosity of water in clay plugs could be explained by the boundary conditions imposed on the flow by the clay surfaces. Thus, the minima in the Gibbs energy of interaction appear to be related to the different sizes of the hydration shells of the different counter ions. In line with this argument is the observation of the phenomenon of demixing (Glaeser and Mering, 1954; McAtee, 1956; Levy and Francis, 1975; Inoue and Minato, 1979). Only one species of counter ion is found in a particular interlayer region—this region has a thickness characteristic of the counter ion.

In a clay suspension, strong, short-range attraction can result in the formation of tactoids. Ca-montmorillonite forms small tactoids (5 to 20 platelets) at low concentrations (about 10^{-4} M or less) (Blackmore and Mil-

ler, 1961; Shainberg and Otoh, 1968; Levy, 1976; Shomer and Mingelgrin, 1978). Considering the results of Norrish (1954), it appears that Ca-montmorillonite forms tactoids containing more platelets at higher electrolyte concentrations. Na-montmorillonite forms tactoids at electrolyte concentrations larger than about 0.2 M (Norrish, 1954). According to Blackmore and Miller (1961), the number of platelets per tactoid is governed by a dynamic equilibrium between two forces—a tendency to form tactoids containing an infinite number of platelets, and mechanical forces between the platelets due to imperfect orientation. Shomer and Mingelgrin (1978) reported that the standard deviation of the number of platelets per tactoid is rather small.

The recent data on the water structure inside clay tactoids (Hall *et al.*, 1978; Hawkins and Egelstaff, 1980) led us to conclude that electrostatic forces are the dominant form of clay platelet interaction, even at small separations. In this paper, a simple electrostatic model which contains macroscopic parameters but no adjustable parameters is developed for clay tactoids. The approximate magnitude of the van der Waals forces is also evaluated. The results of these computations are compared to experimental results.

THEORY

An electrostatic model must be developed that will predict the stability or instability of clay tactoids as a function of the number of clay platelets per tactoid, the species of counter ion, and electrolyte concentration. The model must also describe simplified electrostatic interactions that occur in a tactoid containing parallel clay platelets at small (<10 Å) separation.

The electric charges in the proposed model are divided into three groups: the charges located inside the clay platelets, caused by cationic substitution; the charges of the counter ions located inside the tactoid within the interstitial water layers; and the charges located in the diffuse double layer on the outer surfaces of the tactoid. Macroscopic parameters simplify the calculations. The diffuse double layer is modeled with the Gouy theory (Gouy, 1910). The cationic substitution charge and the charge created by the counter ions in the interstitial water layers are smeared out in planes. These assumptions make the calculations one dimensional. The micro-potentials caused by discrete-charge effects are neglected as they are in most ion-adsorption models (e.g., Healy and White, 1978). In addition to increasing the computational complexity of the problem, a discrete-charge model requires knowledge of the lateral location of both cationic substitution charges and counter-ion charges. At present, there is no certainty about the lateral location of these charges.

The location of the cationic substitution charges along the *c*-axis is known. For example, in the montmorillonite subgroup, the cationic substitution charge is located in the octahedral sheet; in vermiculite, the

cationic substitution charge is located in the tetrahedral sheet. The principal model in this paper has the montmorillonite type of cationic substitution, with a smeared out set of charges in the symmetry plane of the clay platelet. A model that features the vermiculite charge arrangement has also been developed. The counter ions in either case are located in a central plane between the clay platelets. This seems appropriate because of the assumption that the hydration shells of the counter ions determine the separation of the clay platelets. In reality, some counter ions might be located at the clay surface, forming inner-sphere complexes. Because no clear experimental data are available on the location of the counter ions, inner-sphere complexes have not been considered, however the present models may be easily modified to allow for inner-sphere complexes.

If the potential distribution over the tactoid as a function of cationic substitution charge is known, the average Gibbs energy of electrostatic interaction can be calculated from the following equation:

$$G_e \equiv \int_1^2 dG/n = \sum_{i=1}^n \int_0^\sigma (\psi_{2i} - \psi_{1i}) d\sigma/n, \quad (1)$$

where the sum is over the n platelets in the tactoid, the integral is over the cationic substitution charge, σ , and the potentials, ψ_{2i} and ψ_{1i} , refer to the electric potential at the location of the cationic substitution charge in the actual state (2) and a reference state (1). As a reference state, single platelets are taken, and, therefore, the values of ψ_{1i} are identical for all values of i . Eq. (1), which is applicable to constant charge surfaces, calculates the electrostatic contribution to the Gibbs energy only. If the surface charges are not constant (e.g., constant potential surfaces), Eq. (1) is not valid because it lacks a chemical term. For a more detailed discussion on this subject, see Verwey and Overbeek (1948).

To solve Eq. (1), the relations among ψ_{2i} , ψ_{1i} , and σ must be known. For a certain clay species, the cationic substitution-charge density, σ , is known. The charge densities of the counter ions are a function of the potential at their location, ψ_c . The concentration of a given species i of interstitial counter ions per unit surface area, c_{ic} , is dependent on the concentration of the species in the bulk electrolyte solution via the Boltzmann distribution factor on the electrical potential in the counter-ion plane, ψ_c , and the "rest" energy term, Φ_c , which contains all nonideal interactions affecting the counter ions:

$$c_{ic} = Dc_{ib} \cdot \exp(-zq\psi_c/kT) \cdot \exp(-zq\Phi_c/kT). \quad (2)$$

In Eq. (2), D is the thickness of the interfacial region, c_{ib} is the bulk solution concentration of ion species i , z is the valence of the counter-ion species i , k is the Boltzmann constant, q is the protonic charge, and T is the absolute temperature. The size of the "rest" term Φ_c will depend upon the magnitude of the discreteness

of charge effect (including image effects) and the non-electrostatic interactions of the counter ions with the clay surface. In this first attempt to use the model, Φ_c is assumed to be insignificant and, therefore, the second Boltzmann factor can be deleted in Eq. (2). The concentration of counter ions, c_{ic} , is thus:

$$c_{ic} = Dc_{ib} \cdot \exp(-zq\psi_c/kT). \quad (3)$$

To have electroneutrality at zero cationic substitution charge, anions are introduced into the interstitial region. (The case of zero cationic substitution charge is needed for evaluation of Eq. (1).) For simplicity, the anions are assumed to be identical to the cations except for the sign of its charge. As in the diffuse double layer, the effect of the anions is small, and the valence is not of great importance. Thus, the following equation for the interstitial counter-ion charge density, σ_c can be obtained:

$$\sigma_c = 2FzDc_{ib} \cdot \sinh(-zq\psi_c/kT) \quad (4)$$

where F is the Faraday constant. It should be noted that anions do not necessarily have to be introduced to the interstitial region to preserve electroneutrality at zero cationic substitution charge. If no anions are introduced, the electric double layer at the outside of the tactoid is negative and cancels the charge in the interstitial regions for small cationic substitution charge. However, in this model, anions are introduced to the interstitial layer.

The potential distribution is calculated using Gauss' law, which relates the electric field through a closed surface to charge inside the surface. To use Gauss' law, the integral capacitance between the plane of cationic substitution and the plane of counter-ion charge must be known. The capacitance, C , is a function of the effective dielectric constant in the clay mineral (ϵ_1), the interfacial water layer, ϵ_2 ; and the respective thicknesses of these regions, d_1 and d_2 . Thus,

$$C = [d_1/\epsilon_0\epsilon_1 + (d_2/\epsilon_0\epsilon_2)]^{-1}, \quad (5)$$

where ϵ_0 is the permittivity of vacuum (SI units are used). The layer between the outer surface of the tactoid and the diffuse double layer is assumed to have properties similar to the interstitial water layer (including a thickness d_2).

To calculate the potential distribution, its symmetry over the tactoid is used. Using the tactoid shown in Figure 1 as an example, the boundary potential of the diffuse layer to the left of the tactoid is labeled ψ_d . For an arbitrary value of ψ_d , the charge of the diffuse layer to the left of the tactoid can be calculated. Knowing the cationic substitution-charge density, the charge density of the counter ions in the interstitial locations can be calculated from Eqs. (4) and (5) and Gauss' law. Thus, the boundary potential of the diffuse layer at the right-hand side of the tactoid can be obtained. In general, this potential will not be equal to ψ_d . An iterative procedure

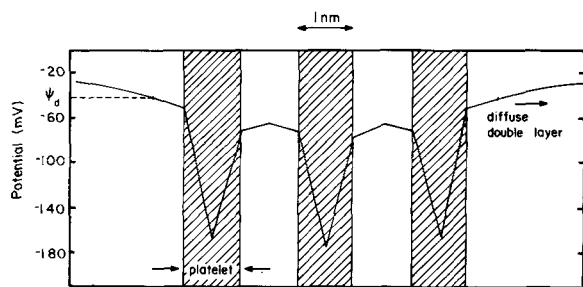


Figure 1. The potential distribution over a tactoid at 0.017 C/m^2 cationic substitution charge.

can now be used to find the suitable value for the cationic substitution-charge density for which the potential distribution is symmetric over the tactoid.

The potential distribution has values which are not identical to those found in single platelets at the locations of the cationic substitution charges. The differences between these potentials are typically of the order of 1 to 10 mV. In Figure 1, a schematic potential-distribution function over a three-platelet tactoid is shown. The charge density in the interstitial layer σ_e generally differs only slightly in magnitude from the cationic substitution charge density, σ . The difference is less than 5.10^{-4} C/m^2 for clay minerals. This small difference is unimportant for most purposes, but it determines G_e through the resulting potential-distribution function.

To apply the models described above, computer algorithms were developed to solve the systems of equations numerically. Numerical integrations of Eq. (1) were made in these programs. For each step of integration, the potential distribution over the tactoid and the potentials in a single platelet were evaluated. The equation that determined the potential distribution over the tactoid was solved with a modified Newton-Raphson procedure. Modifications of the Newton-Raphson method were necessary to prevent computer overflow for the initial estimates of ψ_d . Depending on the size of the cationic substitution charge, 5 or 6 platelets within a tactoid is the maximum capacity of the program. Statistical errors in the potential distribution were kept smaller than 0.001 mV. The accuracy of the integration was judged from the change of the results with the step size.

An additional program was developed to evaluate the G_e for a tactoid having an infinite number of platelets. This program uses the symmetry over the platelets for its boundary conditions (therefore no diffuse double layer is involved). The infinitely large tactoid provides a useful limit for our purposes.¹

Van Olphen's (1977) equation to calculate the van der

Waals interaction energy between two clay platelets was used to obtain an approximate value for the van der Waals interaction energy. Because van der Waals forces are essentially "short range forces," only the effect of neighboring platelets was considered. This is not a very accurate method (Ninham and Parsegian, 1970), but it provides a rough estimate of the magnitude of the van der Waals forces, as compared to the electrostatic forces. The average Gibbs energy of van der Waals interaction, G_w (in mJ/m^2), is thus:

$$G_w = 0.675(n - 1)/n, \quad (6)$$

where n is the number of platelets in the tactoid. For the computation of Eq. (6), the spacing of the platelets (between the central planes) was taken to be 18.9 \AA , as was found experimentally for Na- and Ca-montmorillonite (Norrish, 1954). The Hamaker constant was taken to be 10^{-19} J , following van Olphen (1977). It appears that a slightly larger value is more reasonable in vacuum (Tabor and Winterton, 1969); however, the water layer between the platelets results in a reduction of the Hamaker constant (as compared to vacuum) by a factor of about 1.77 (Gregory, 1969). Therefore, it is assumed that the value given by van Olphen (1977) gives a fair estimate.

RESULTS

With the computer model, G_e was calculated for several cases. For the computations, a capacitance of 0.07375 F/m^2 was used for the regions between the central planes of the platelets and the central planes of the neighboring water layers. If the dielectric constant of the clay mineral is assumed to be 5, this corresponds to an effective dielectric constant of 20 in the interstitial water layers. The sensitivity of G_e to the dielectric constant of the water layers was found by varying it from 5 to 78. It was found that the change of G_e over this range of dielectric constant was too small to be discerned from the computer plots and was, therefore, insignificant to the electrostatic interaction. This result implies that the exact value of the dielectric constant in the water layer need not be known. Thus, the dispute about the water structure within the tactoid is of no concern to the present electrostatic model.

The location of the cationic substitution charge is also of minor importance to G_e . It was found that a vermiculite-type charge arrangement led to G_e values that are generally lower than a montmorillonite-type arrangement. However, the trends for both charge arrangements were similar. For more highly charged clay minerals, such as vermiculite itself, the two charge arrangements led to essentially the same results ($<0.1 \text{ mJ/m}^2$ difference was observed). Therefore, only the montmorillonite-type charge arrangement will be discussed.

Two types of counter ions were considered in the electrostatic model: bivalent and monovalent ions. Differences in the interaction behavior of different ions of

¹ All computer programs, with the necessary information, can be obtained by writing to the authors.

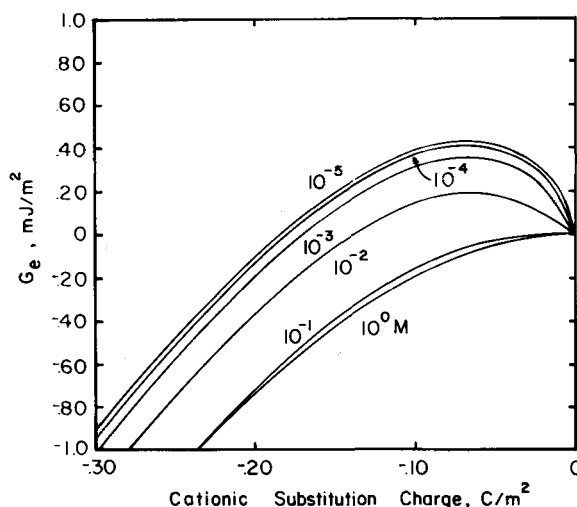


Figure 2. G_e of a tactoid consisting of two platelets as a function of cationic substitution charge with calcium as counter ion at different electrolyte concentrations.

equal valences result from different values of the "rest" term Φ_c in Eq. (3). The rest term is likely to change with the spacing of the platelets and, therefore, the hydration radius of the ions. In addition, the spacing of the platelets is important because of its effect on the van der Waals forces. G_w becomes more negative for shorter separations. In this paper, an observed spacing of 18.9 Å for Ca- and Na-montmorillonite tactoids is used.

In Figure 2, G_e is shown for a tactoid consisting of two platelets with bivalent counter ions for different values of the ionic strength. G_e is more attractive at higher ionic strength. G_e is repulsive at low cationic substitution-charge densities for all concentrations except the highest concentrations (0.1 M, 1 M). For high cationic substitution-charge densities, G_e is always attractive. This behavior of G_e is in agreement with experimental observations, as will be shown later, but has not been predicted by previous models, to the best of our knowledge. The key to the behavior of G_e lies in Eq. (4). At low cationic substitution-charge densities, the interstitial counter-ion charge density, σ_c , is smaller than the cationic substitution-charge density σ . The mutual repulsion of the negative clay platelets is only partly cancelled by the attractive forces generated by the positive counter ions and, therefore, swelling results. At high cationic substitution-charge densities, the value of σ_c is larger than σ . Then the attractive forces generated by the positive counter ions are larger than the mutual repulsion of the negative clay platelets and, therefore, stable tactoids can be formed. Thus, in a tactoid where the interstitial counter ions are in equilibrium with the bulk solution, excess negative charge results in repulsion while excess positive charge results in attraction. As mentioned above, these excess

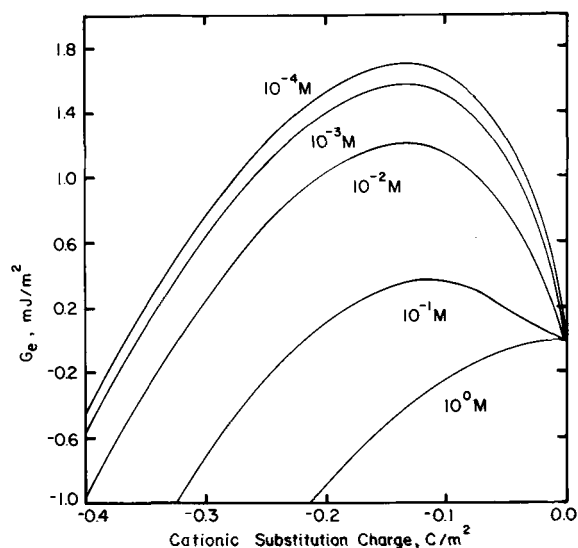


Figure 3. G_e of a tactoid consisting of two platelets as a function of cationic substitution charge with sodium as counter ion at different electrolyte concentrations.

charges of the tactoid (which are canceled in the diffuse layer at the outer surfaces of the tactoid) are extremely small.

Figure 3 shows a plot similar to Figure 2 for the monovalent counter-ion case. For monovalent counter ions, trends similar to those of bivalent counter ions are apparent. However, the range of cationic substitution where repulsion occurs is much larger and the repulsion is stronger.

For comparison with the results of Figures 2 and 3, the cationic substitution-charge densities for different clay groups are listed in Table 1. The repulsive G_e values are limited to the smectite group. Experimentally, this is the only group capable of significant swelling (Grim, 1968). It has also been shown that monovalent counter ions result in more swelling than bivalent counter ions (Warkentin *et al.*, 1957; Norrish, 1954). Vermiculites do not swell beyond approximately 10 Å, and micas do not swell at all (Grim, 1968).

Figure 4 shows G_e as a function of the cationic substitution charge for tactoids with 2, 3, 4, and an infinite number of platelets suspended in a solution with biva-

Table 1. The approximate charge densities per clay platelet for different clay groups.

Clay group	Charge density (C/m ²)
Pyrophyllite-talc	0
Smectite	0.175–0.35
Vermiculite	0.35–0.525
Illite	0.70
Mica	0.70
Brittle mica	1.40

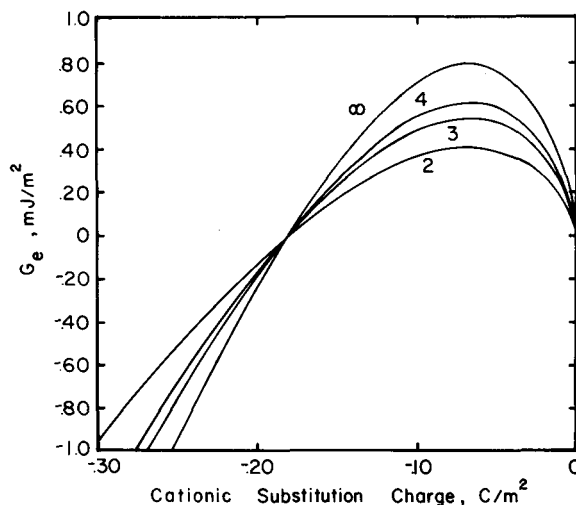


Figure 4. G_e at an electrolyte concentration of 10^{-4} M as a function of cationic substitution charge with calcium as a counter ion for tactoids of varying size.

lent cations at an electrolyte concentration of 10^{-4} M. With an increase in the number of platelets per tactoid, the absolute value of the G_e becomes larger. All tactoid sizes have zero G_e for an identical value of the cationic substitution charge. In Figure 5, the G_w is shown as a function of the number of platelets per tactoid. Because of the approximations made, the values of the G_w are not very precise.

The sum of G_w and G_e , labeled G , is the important parameter with which one can predict the size of the tactoid. The tactoid size for which G is a minimum will be preferred. Tactoid sizes for which G has a maximum are the least likely to occur. G was calculated as a function of the number of platelets per tactoid for several cationic substitution densities. For all cases studied, G was found to be a continuously increasing or decreasing function of the number of platelets per tactoid. Variation of the Hamaker constant did not change this apparently general qualitative result. Thus, either a single platelet or a tactoid containing an infinite number of platelets results in a minimum value of G .

As can be seen from Figures 4 and 5, the value of G does not depend strongly on the number of platelets per tactoid for tactoids consisting of more than about 4 platelets. When the decrease of G for an extra platelet in the tactoid approaches kT , the tactoid has attained its maximum size. The size of the tactoid is limited by thermal movement. However, mechanical forces can break up the tactoid before this maximum size is reached. This is the point of view taken by Blackmore and Miller (1961). In the laboratory system where the experiments were done, these mechanical forces were likely to be shear forces caused by hydrodynamic flow. A dynamic equilibrium between G and the shear forces due to shaking results in finite tactoids which may have

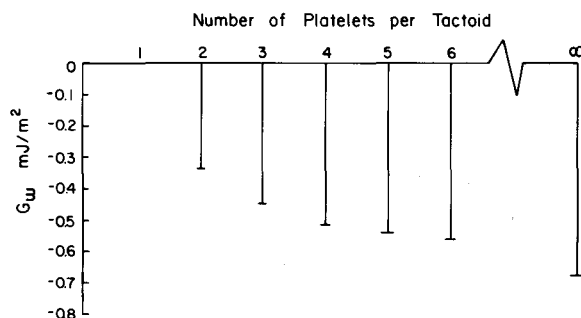


Figure 5. G_w as a function of the number of platelets per tactoid at a basal spacing of 18.9 Å.

the rather uniform size distribution observed by Shomer and Mingelgrin (1978). This tactoid size can increase irreversibly in a swelling experiment where no stirring or shaking occurs, as was observed by Blackmore and Miller (1961).

The numerical results obtained by the model in this form are in agreement with existing experimental data. Consider a montmorillonite with a charge density of 0.23 C/m^2 , which corresponds to a cation-exchange capacity of 95 meq/100 g . From the model, it follows that the Na-montmorillonite will form tactoids at electrolyte concentrations of about 0.05 M or higher. This result is in reasonable agreement with the experimental results obtained by Norrish (1954). Ca-montmorillonite tactoids are predicted to be stable for concentrations considered (10^0 – 10^{-5} M). The attraction between the platelets decreases with decreasing electrolyte concentration. Thus, Ca-montmorillonite tactoids exposed to external forces are more likely to break up at lower electrolyte concentrations. Norrish (1954) did not observe small tactoids at higher ($>10^{-3}$ M) concentrations, while many other authors (Blackmore and Miller, 1961; Levy, 1976; Shainberg and Otoh, 1968; Shomer and Mingelgrin, 1978) observed small tactoids at lower ($<10^{-4}$ M) concentrations. For evaluation of the current model in more detail, a comprehensive study on the number of platelets per tactoid as a function of electrolyte concentration, hydrodynamic shear forces, and counter-ion species is clearly needed.

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REFERENCES

- Barnes, C. J. (1980) The swelling of clay: *Soil Sci. Soc. Amer. J.* **44**, 658–659.
- Blackmore, A. V. and Miller, R. D. (1961) Tactoid size and osmotic swelling in calcium montmorillonite: *Soil Sci. Soc. Amer. Proc.* **24**, 169–173.

- Bolt, G. H. and Miller, R. D. (1955) Compression studies of illite suspensions: *Soil Sci. Soc. Amer. Proc.* **18**, 285–288.
- Callaghan, I. C. and Ottewill, R. H. (1974) Interparticle forces in montmorillonite gels: *Faraday Disc. Chem. Soc.* **57**, 110–118.
- Childs, E. C. (1955) The space charge in the Gouy layer between two plane, parallel non-conducting particles: *Trans. Faraday Soc.*, 1356–1362.
- Derjaguin, B. V. and Landau, L. D. (1941) Theory of strongly charged lyophobic soils and of the adhesion of strongly charged particles in solutions of electrolytes: *Acta Physicochim. USSR* **14**, 633–662.
- Farmer, V. C. and Russell, J. D. (1971) Interlayer complexes in layer silicates: *Trans. Faraday Soc.* **67**, 2737–2749.
- Giese, R. F., Jr. (1978) The electrostatic interlayer forces of layer structure minerals: *Clays & Clay Minerals* **26**, 51–57.
- Glaeser, R. and Mering, J. (1954) Isothermes d'hydratation des montmorillonites bi-ioniques: *Clay Min. Bull.* **12**, 188–193.
- Gouy, G. (1910) Sur la constitution de la charge électrique à la surface d'un électrolyte: *Ann. Phys. (Paris) Série 4*, **9**, 457–468.
- Gregory, J. (1969) The calculation of Hamaker constants: *Adv. Colloid Int. Sci.* **2**, 396–417.
- Grim, R. E. (1968) *Clay Mineralogy*: McGraw-Hill, New York, 234–277.
- Hall, P. L., Ross, D. K., Tuck, J. J., and Hayes, M. H. B. (1979) Neutron scattering studies of the dynamics of interlamellar water in montmorillonite and vermiculite: in *Proc. Int. Clay Conf., Oxford, 1978*, M. M. Mortland and V. C. Farmer, eds., Elsevier, Amsterdam, 121–130.
- Hawkins, R. K. and Egelstaff, P. A. (1980) Interfacial water structure in montmorillonite from neutron diffraction experiments: *Clays & Clay Minerals* **28**, 19–28.
- Healy, T. W. and White, L. R. (1978) Ionizable surface group models of aqueous interfaces: *Adv. Colloid Int. Sci.* **9**, 303–345.
- Inoue, A. and Minato, H. (1979) Ca-K exchange reaction and interstratification in montmorillonite: *Clays & Clay Minerals* **27**, 393–401.
- Israelachvili, J. N. and Adams, G. E. (1978) Measurement of forces between two mica surfaces in aqueous electrolyte solutions in the range of 0–100 nm: *J. Chem. Soc. Faraday Trans. I.* **74**, 975–1001.
- Levy, R. and Francis, C. W. (1975) Demixing of sodium and calcium ions in montmorillonite crystallites: *Clays & Clay Minerals* **23**, 475–476.
- Levy, R. (1976) Size of sodium-calcium montmorillonite crystallites: *J. Colloid Int. Sci.* **57**, 572–574.
- Low, P. F. and Margheim, J. F. (1979) The swelling of clay. I. Basic concepts and empirical equations: *Soil Sci. Soc. Amer. J.* **43**, 473–481.
- McAtee, J. L. (1956) Determination of random interstratification in montmorillonite: *Amer. Mineral.* **41**, 627–631.
- Ninham, B. W. and Parsegian, V. A. (1970) Van der Waals interaction in multilayer systems: *J. Chem. Phys.* **53**, 3398–3402.
- Norrish, K. (1954) The swelling of montmorillonite: *Discussions Faraday Soc.* **18**, 120–134.
- Shainberg, I. and Otoh, H. (1968) Size and shape of montmorillonite particles saturated with Na/Ca ions (inferred from viscosity and optical measurements): *Isr. J. Chem.* **6**, 251–259.
- Shomer, I. and Mingelgrin, U. (1978) A direct procedure for determining the number of plates in tactoids of smectites: The Na/Ca montmorillonite case: *Clays & Clay Minerals* **26**, 135–138.
- Stigter, D. (1980) Self-diffusion and viscosity of water in clays: *Soil Sci.* **130**, 1–6.
- Tabor, D. and Winterton, R. H. S. (1969) The direct measurement of normal and retarded van der Waals forces: *Proc. Roy. Soc. A.* **312**, 435–450.
- van Olphen, H. (1977) *An Introduction to Clay Colloid Chemistry*: Wiley Interscience, New York, 292–293.
- Verwey, E. J. W. and Overbeek, J. Th. G. (1948) *Theory of the Stability of Lyophobic Colloids*: Elsevier, Amsterdam, 51–65.
- Warkentin, B. P., Bolt, G. H., and Miller, R. D. (1957) Swelling pressure of montmorillonite: *Soil Sci. Soc. Amer. Proc.* **21**, 495–497.

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Резюме—Была развита электростатическая модель стабильности глинистых тактоидов (групп параллельных глинистых пластинок, отделенных 10 Å) в водном растворе. Предполагается, что противоионы, расположенные в промежуточных водных слоях, находятся в равновесии со всем раствором. Обычно, плотность заряда противоионов отличается немножко по величине от плотности заряда пластинок. Одномерное распределение потенциала может быть вычислено, заменяя дискретные заряды равномерно заряженными площадями. Из этого можно вычислить энергию Гиббса электростатического взаимодействия (используя отдельные пластинки как базу). Модель предсказывает, что глинистые минералы с высокой (вермикулит и слюда) и низкой (пиррофиллит, тальк) степенью катионной подстановки образуют стабильные тактоиды. Плотность заряда, концентрация электролита и противоионы определяют характеристики набухания смектитов. При определенной плотности заряда низшие валенции противоионов и низшие концентрации электролита приводят к увеличению набухания. Если формируются тактоиды, число пластинок определяется динамическим равновесием между силами: электростатическими, Ван дер Ваальса и внешними, такими как срезающие силы, возникающие при гидродинамическом течении. [E.C.]

Resümee—Es wurde ein elektrostatisches Modell für die Stabilität von Ton-Taktoiden (Pakete von parallelen Tonplättchen mit ~ 10 Å Abstand) in einer wässrigen Lösung entwickelt. Dabei wird angenommen, daß die Gegenionen im Zwischenschichtwasser im Gleichgewicht mit der Gesamtlösung sind. Im allgemeinen ist die Größe der Ladungsdichte der Gegenionen etwas verschieden von der der Lagerungsdichte der Tonschichten. Betrachtet man die einzelnen Ladungen annähernd als homogen geladene Ebenen, so kann eine eindimensionale Potential-Verteilung berechnet werden. Daraus kann die Gibbs'sche Energie der elektrostatischen Wechselwirkung berechnet werden, wobei einzelne Tonschichten als Bezug verwendet werden. Das Modell sagt voraus, daß Tonminerale mit einem hohen (Vermiculit, Glimmer) und einem niedrigen (Pyrophyllit, Talk) Kationenaustausch stabile Ton-Taktoide bilden. Bei Smektiten bestimmen Ladungsdichte, Elektrolytkonzentration und Art des Gegenions die Art der Quellung. Bei einer bestimmten Ladungsdichte führen niedrige Wertigkeiten der Gegenionen und niedrige Elektrolytkonzentrationen zu einer Zunahme der Quellbarkeit. Wenn Ton-Taktoide gebildet werden, wird die Zahl der Tonschichten durch ein dynamisches Gleichgewicht Zwischen elektrostatischen Kräften, Van der Waals'schen Kräften und äußeren Kräften, wie z.B. Scherkräften, aufgrund hydrodynamischen Fließens, bestimmt. [U.W.]

Résumé—On a développé un modèle électrostatique pour la stabilité de tactoïdes argile (empilements de plaquettes d'argile parallèles à ~ 10 Å de séparation) dans une solution aqueuse. Les contre-ions situés dans l'eau interstitiale sont supposés être en équilibre avec la solution en masse. Généralement la densité de charge du contre-ion diffère légèrement en magnitude de la densité de charge de la plaquette. On peut calculer une distribution potentielle à une dimension en approximant les charges discrètes par des plans chargés de manière homogène. A partir de ceci, l'énergie d'interaction électrostatique Gibbs (utilisant des plaquettes simples comme référence) peut être calculée. Le modèle prédit que des minéraux argile ayant de hauts (vermiculite, micas) et bas (pyrophyllite, talc) degrés de substitution cationique forment des tactoïdes simples. Pour les smectites, la densité de charge, la concentration d'électrolyte, et l'espèce de contre-ion déterminent les caractéristiques d'enflément. A une densité de charge particulière, des valences de contre-ions plus basses, et de plus basses concentrations d'électrolyte, mènent à un accroissement d'enflément. Si des tactoïdes sont formés, le nombre de plaquettes est gouverné par un équilibre dynamique entre les forces électrostatiques, les forces van der Waals, et des forces externes telles des forces dues au flot hydrodynamique. [D.J.]