

INTERLAYER FORCES IN BENTONITE¹

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ABSTRACT

An attempt is being made to analyze the forces between unit layers of a bentonite particle and between the flat surfaces of two particles from colloid chemical data and theory. The electric double-layer interaction, the van der Waals attraction, and the hydration energies are considered.

From experimental observations the general qualitative shape of the net potential curve of interaction may be derived.

In a quantitative discussion, first the long-range interaction is considered by applying the theory of Verwey and Overbeek in which the net interaction curve is found as the sum of the double-layer repulsion and van der Waals attraction. The fact that the layers do not spontaneously dissociate in solution despite the high charge density of the surfaces points to a considerable specific adsorption potential of the counter ions (the exchangeable ions) to the surface (~ 0.2 ev). The consequences for ion exchange are briefly discussed.

Next, two possibilities for the status and position of the counter ions are considered: the cations are either unhydrated and located in or close to the holes in the tetrahedral sheet in six coordination with the oxygen six rings or they are partly or completely hydrated and with their hydration shell adsorbed on top of the oxygen sheet.

Then the short-range interaction of the unit layers is considered. In the case of bentonite there is the fortuitous situation that the net short-range potential curve for the layer interaction can be found experimentally from adsorption isotherms and x-ray diffraction. This net interaction energy is the sum of three contributing energies: the van der Waals attraction, the electrostatic interaction, and the hydration energies. Therefore, on computing the first two for either model mentioned above, the hydration term can be evaluated and its order of magnitude may decide between the two possibilities since ion hydration energy would be expected to be much higher than surface hydration energy.

For the model of unhydrated ions the van der Waals attraction is relatively small and partly compensated by the rather small electrostatic repulsion (repulsion of two finite layers of dipoles). Thus the net repulsion energy measured is practically the hydration energy in this case. This hydration energy figure is of the right order of magnitude if interpreted as hydrogen bonding of a Hendricks water layer to the oxygen surface.

For the model of the at least partly hydrated cations the van der Waals attraction is small, the same as in the first model, but the electrostatic interaction is now an appreciable attraction since the cations take up a midway position between the negative bentonite layers for at least the mono- and dilayer adsorption complex. This makes the computed hydration energy higher; this is readily explained by the

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availability of the higher ion hydration energy as compared with the surface hydration energy.

Thus the analysis shows both pictures to be acceptable within the limits with which the adsorption isotherms and therefore the net potential curve can be evaluated. More elaborate adsorption data at very low relative humidities would be required to obtain a better estimate of the energies involved in the removal of the last layer of water where the major portion of the ion hydration energy would enter the picture if ion hydration would indeed take place and be the primary cause of interlayer swelling of bentonite.

There is a correlation of bentonite hydration energy with the hydration energy of the counter ions present, but this correlation does not constitute positive evidence of ion hydration. A secondary effect of the ions on the formation of ideal Hendricks' layers (and thus on their bonding energy to the clay surface), which also depends on ion size, is possible.

Other experimental and theoretical approaches to the problem are briefly mentioned and finally the differences between swelling and nonswelling clays are dealt with.

INTRODUCTION

A quantitative colloid chemical approach to the problem of the interlayer forces in bentonite clays will be presented. First, therefore, a few remarks will be made about the general colloid chemical characteristics of bentonite suspensions.

According to the classical distinction between lyophobic and lyophilic colloids, bentonites might have been considered an intermediate case, particularly because of their swelling and gelation properties. However, in modern terms they are preferably treated as lyophobic colloids: the particles which are observed ultramicroscopically are in the crystalline phase (as shown from x-ray analysis of suspensions) and are protected by an electric double layer (as indicated by their electrophoretic mobility). Therefore, the modern theories of particle interaction in lyophobic sols developed by Verwey and Overbeek (1948) may be applied, keeping in mind that the peculiarities of bentonite may require certain modifications. Some specific properties of bentonite particles are:

i) They show interlayer swelling with water; obviously, therefore, some degree of surface hydration should be taken into account.

ii) The particles are large thin flakes which expose two crystallographically different surfaces — the flat surface and the edge surface. Thus, the electric double layer at these two surfaces may be expected to be different, and the three possible types of particle association — edge to edge, edge to flat surface, and flat surface to flat surface — may be governed by three different potential curves.

iii) The charge of the electric double layer on the flat surface, which is assumed to be equivalent to the amount of isomorphous substitution in the lattice, is rather high.

Therefore, when drawing conclusions from colloid chemical data to be applied to flat surface or unit layer association, one should be careful to separate the effects of the other types of association.

It has, for example, been shown in earlier work (Van Olphen, 1950, 1951, 1951a) that such phenomena as the development of a rigid structure in clay suspensions, as well as the breakdown of such structure by various anions—as used in drilling muds—can be consistently explained by considering the association of the edges of the clay flakes and the prevention of this association by charging due to anion adsorption on these edges. There appears to be no need to introduce any improbably far-reaching orientation effects on the water, or any stabilization effect of water of hydration. Flat-surface association plays only a secondary role in these phenomena so that this item of colloid chemical information is rather irrelevant to our problem.

The layer surface interaction will first be discussed qualitatively on the basis of colloid chemical experience, and a quantitative analysis will then be made. The Hofmann structure of bentonite, as well as the concept of isomorphous substitution as the cause of ion exchange, will be adopted.

QUALITATIVE ANALYSIS OF LAYER SURFACE INTERACTION

On the basis of x-ray studies of suspensions, ultramicroscopical counting, and relative viscosity data, the following concept of layer association in an individual bentonite particle was previously developed (Mering, 1946; Van Olphen, 1950, 1951, 1951a; Barber, 1952; in particular Van Olphen, 1951a, p. 41-45).

The persistence of the basal reflections in the x-ray pattern in suspensions of several bentonites, and estimates of the thickness of the particles as derived from their hydrodynamic behavior, indicate that the individual particle in most bentonite sols consists of a packet of a few unit aluminum hydro-silicate layers. According to the increase of the number of particles with increasing dilution as well as with time, as counted ultramicroscopically, the average number of associated layers per particle—which may be different for different types of bentonites—appears to vary with the sol concentration. Apparently there is a dynamic layer association-dissociation equilibrium, the position of which depends on the sol concentration. This suggests that all layer surfaces and the planar surfaces of the particles behave identically. This is also borne out by ion exchange with both inorganic and very large organic cations to which not only the surface-exposed cations but also the interlayer cations contribute. The exchanging cations may either penetrate between the layers, or all the layer surfaces may be exposed in turn so that ion exchange can take place on them.

Thus, in a discussion of flat-surface association, single-layer association may be considered; in other words, the clay particles may be treated as parallel flocs of unit layers. In this respect the bentonite clay sols behave like association colloids (such as soaps), the smallest kinetic unit being the single layer.

If these concepts are right, the following conclusions can be drawn concerning the general shape of the potential curves governing both inter-layer and flat-surface interaction.

It is shown from x-ray studies of concentrated bentonite suspensions that the equilibrium distance between the outer surfaces of the oxygen sheets is of the order of 10 Å, sometimes a few Å more or less. This means in terms of potential curves, in a plot of the energy of interaction versus the half-distance between the layers, that there must be a minimum with net attraction in the curve at about 5 Å half-distance. The fact that the layers can dissociate because of their thermal energy indicates that if this minimum is adjoined by a maximum at some larger interlayer distance, the maximum should be shallow. The energy difference between this maximum and the minimum as well as between the maximum and the position of infinite separation should be only a few times kT in order to explain both the thermal dissociation and association.

The spontaneous swelling of bentonite particles, as shown by the increase of the layer spacing of the dry particle when placed in contact with water or water vapor, indicates that there is net repulsion in the range of zero to approximately 10 Å separation, where the repulsion curve decreases monotonically, although some shallow barrier may occur in the descending curve.

Thus the general qualitative shape of the net potential curve for single-layer or flat-surface interaction in bentonites may be represented by the curve of Figure 1.

Differences are observed in the average degree of layer association in different bentonites or in different ion forms of the same bentonite. In some cases the estimates average 4 to 5 layers per particle; sometimes dissociation to units of, on the average, two layers may take place [e.g. see Schofield's (1947) results from negative adsorption determinations].

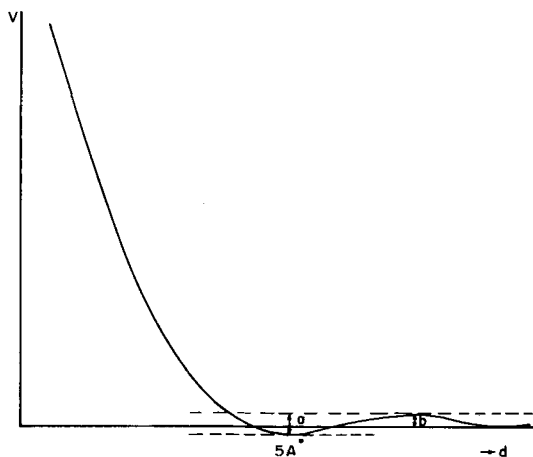


FIGURE 1.—Qualitative potential curve for flat surface or layer interaction.

Such differences in average degree of association might be interpreted statistically by taking into account varying values for the depth of the minimum. This will, however, not be attempted here since more detailed data on the association-dissociation equilibrium would be required for such an analysis.

An attempt will be made to account for the shape of the net potential curve for layer interaction by analyzing the forces acting between the layers and their repulsive and attractive potentials. The "long-range" interaction part beyond 10 Å and the "short-range" part will be treated separately. The long-range interaction is calculated by combining Stern-Gouy double-layer repulsion with van der Waals attraction. The short-range interaction can be found experimentally and will be interpreted by combining electrostatic, van der Waals, and hydration energies.

QUANTITATIVE DISCUSSION OF LAYER AND FLAT SURFACE INTERACTION AND HYDRATION

a) Long-Range Interaction. Combination of Stern-Gouy Layer Repulsion with van der Waals Attraction

For thin crystal layers the decay of the van der Waals attraction should be calculated from the full equation given by Verwey and Overbeek (1948, eq. 48). The thickness of the plates was taken as 6.60 Å, and the plate distance was measured between the planes of the centers of the oxygen atoms of the tetrahedral sheets. A was chosen equal to 10^{-12} erg. The results are plotted in the lower part of Figure 2, where V_A , the attraction potential, is a function of the half-distance of the plates.

In the upper part of Figure 2 the Stern-Gouy double-layer repulsive energy is plotted for various compositions of the intermicellar liquid. The calculation was carried out as follows:

The constant charge density on the surface is given by the base-exchange capacity, and amounts for a b.e.c. of 100 meq/100 g to a charge density of 3.8×10^4 esu/cm², an unusually high value for hydrophobic colloids. Applying the condenser formula (Verwey and Overbeek, 1948, eq. 18), the potential drop in the Stern layer can be computed at 1.2 volt for a Stern-layer thickness of 5 Å and a dielectric constant of 6 (Verwey and Overbeek, 1948, p. 44). The Boltzmann distribution function for the ions in Stern and Gouy layer gives the relation between Stern-layer charge and Stern-layer potential (ψ^δ), assuming a zero specific adsorption potential (Verwey and Overbeek, 1948, eq. 17-21 where $\varphi = 0$). The relation between the Gouy-layer charge and the Stern-layer potential ψ^δ (Verwey and Overbeek, 1948, eq. 19) is derived from the Poisson equation, and since the total charge is the sum of Stern- and Gouy-layer charge (Verwey and Overbeek, 1948 eq. 20), the value of the Stern potential ψ^δ can be computed. With reasonable assumptions for the available positions of the ions in Stern and Gouy layer ($N_1 = 10^{15}$, eq. 21), a value of 200 mv is, for example, found for ψ^δ in a 0.001 N solution of a 1-1 electrolyte.

In the region of weak interaction the minimum repulsion energy for the approach of two layers can then be calculated from the Gouy-layer interaction with constant

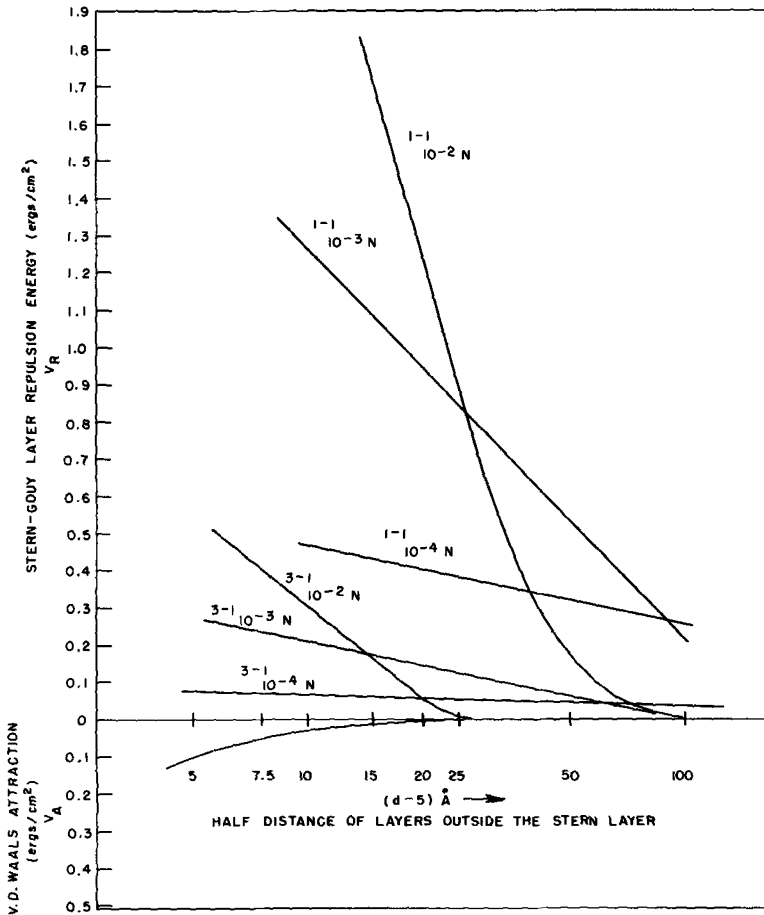


FIGURE 2. — Long-range potential curves.

potential equal to $\psi\delta$, as shown by Mackor (1951). (If the particle surface charge is constant, as is the case in clays, the repulsive energy will be higher than this minimum; for constant surface potential it is equal to this minimum.) From eq. 43 (Verwey and Overbeek, 1948), the values plotted in the graph are found.

The curves in Figure 2 show that the combination of van der Waals attraction with Stern-Gouy layer repulsion results in very high long-distance energy barriers. This is not surprising in view of the rather high double-layer charge together with the comparatively rapid decay of the van der Waals attraction energy for the thin layers. The required shallow energy barrier, however, should be less than $10 kT$; this is of the order of approximately 0.001 erg/cm^2 or less for plates with a radius of about 1000 \AA or more, which is the most likely order of magnitude for the size of the bentonite plates (Verwey and Overbeek, 1948, p. 123).

Another factor which tends to reduce the energy barrier is the possible presence of traces of Al^{3+} or Fe^{3+} ions in the intermicellar liquid; but this reduction is still not sufficient, as is seen from the curve for a tri-valent electrolyte in 0.0001 *N* solution (Fig. 2).

Therefore, the fact that despite the high double-layer charge the particles do not spontaneously split up in single layers leads to the assumption of some specific adsorption potential of the counter ions. This shifts the equilibrium distribution of the ions to the Stern layer and thus reduces $\psi\delta$ and the repulsive potential. This specific adsorption potential is estimated to be of the order of 0.2 ev in order to account for the required shallow barrier, or possibly the absence of a barrier.

The existence of a specific adsorption potential also ties in with the peculiarities observed in cation exchange. Ion exchange would be predominantly Stern ion exchange. When the exchange equation for monovalent cations is written in the mass law form, the equilibrium constant may be seen as an expression for the differences in the specific adsorption potentials ψ_1 and ψ_2 by putting:

$$K = e^{(\psi_1 - \psi_2)/kT}$$

The equilibrium constant often varies with the occupation ratio on the clay. If this change, for example, amounts to an increase of from 1.5 to 2.0, the difference in adsorption potentials of the ions increases from 0.011 to 0.018 ev, which is an increase of only 5 to 9 percent of the average total adsorption potential. If the change of equilibrium constant with occupation ratio on the clay is attributed to nonidentical exchange sites, such small percentage changes in the adsorption potentials may quite possibly occur.

b) Status and Position of the Cations in the Stern Layer

Next the status and position of the adsorbed cations in the Stern layer will be discussed. There is sufficient evidence that ions in the presence of water are hydrated and this would certainly be the case for the cations in the Gouy layer. However, their hydration status close to a solid surface may be different, inasmuch as the structure of the water at the interface may be different from that in the bulk phase, owing to the action of surface forces.

Therefore, a priori, two possibilities should be considered; the Stern ions are either unhydrated or they are at least partially hydrated. The required total adsorption potential and the position of the cations at the interface in either case will be evaluated.

If the cations in the Stern layer were in an unhydrated state, their total adsorption potential would have to exceed the ion hydration energy (which would be gained in their transference to the Gouy layer) by the net specific adsorption potential of approximately 0.2 ev as calculated above. This would amount to total adsorption potentials of from 5.1 ev for Li to 2.8 ev for Cs ions, which are of the order of the energy of a chemical bond.

If the cations in the Stern layer were in at least partially hydrated state, the total adsorption potential would only have to outweigh the difference in hydration energy of Stern and Gouy cations by 0.2 ev. In this case the total adsorption potential would be of a comparatively small order of magnitude.

Unhydrated ions either may be fixed to the oxygen sheet of the tetrahedral silica sheet or may at least partly fill the holes in this sheet. In view of the large total adsorption potential required, the hole position seems more likely since there the ions would be in 6-coordination with oxygen. Moreover, this potential would be expected to depend on the size of the cations: the geometry of the coordination position governs the total coordination energy.

Hydrated ions would not be able to penetrate into the holes and they should be considered fixed to the oxygen surface, either in a two-dimensional state of hydration (buried in the first monolayer of water on the surface) or in a three-dimensional state of hydration, e.g., by octahedral coordination (buried in the first two water layers on the surface). Their small adsorption potential may be a result of hydrogen bonding between the surface and the hydrated ion (every hydrogen bond may be of the order of 0.35 ev). Since on drying of the bentonite the observed layer spacing does not leave room for the ions between the oxygen faces of the layers, they must be in the hole position under these conditions. Consequently, if they hydrate and leave the holes when the bentonite is brought into contact with water, the ion hydration energy of the Stern ions must be large enough to overcome the higher electrostatic potential of the ions when in hole position; but this is possible.

Therefore, either possibility—unhydrated ions in hole position or hydrated ions on the surface—is conceivable: the first requires an appreciable total adsorption potential, the second a relatively small one. Whether or not experiments can lead to a decision will be discussed in the next paragraph.

c) *Stern Layer Interaction, Combination of Electrostatic, Hydration, and van der Waals Energy*

The net repulsion between the layers in the region where Stern layers overlap can be obtained from water adsorption isotherms. These give the relation between mgs of water adsorbed per gram of dry bentonite (n) with equilibrium water vapor pressure p : $n = f(p)$. The net repulsion as a function of the amount of water between the layers as compared with the repulsion at about 10 Å separation (or practically infinite separation) when the layers are immersed in water at a saturation pressure p_o can be obtained by the following relation:

$$V_R = \frac{RT}{18000\Sigma} \left[\int_p^{p_o} \frac{n}{p} dp + n_p \ln \frac{p}{p_o} \right],$$

where Σ is the total number of opposite square centimeters of layer surface per gram, or half the total layer surface per gram, neglecting the outer surfaces of the individual particles. (As shown by the nitrogen adsorption isotherms of the material used in the following data, this is only a small fraction of the total layer surface area. See Appendix.)

The integral can be evaluated graphically by plotting n/p versus p (Fig. 3). The data were taken from the adsorption isotherms published by Mooney, Keenan, and Wood (1951, 1952). Unfortunately the data at very low pressures, as well as those near the saturation pressure, are scarce and do not allow accurate integration in most cases. However, in Figure 3 surface areas corresponding to a value of the integral term of 50 and 100 ergs/cm² are indicated, which enables an estimation of the orders of magnitude involved. These curves suggest that the total change of potential energy between zero and saturation pressure, which is given by the integral term only (the other term being zero at both pressures), varies between 100 and 300 ergs/cm² for the different ion forms of bentonite.

In Figure 4, for both sodium and calcium bentonite the repulsive potential V_R calculated from the full equation is plotted versus the amount of water adsorbed expressed in either mg/cm² or molecules per unit cell. In order to show the difference between the full equation and the integral term only, both are evaluated and plotted for Na bentonite. The upper curve represents the integral term, whereas the lower curve is obtained by adding the $-nRT \ln (p_0/p)$ term. The extrapolation to zero adsorption is doubtful, whereas the integral term is only evaluated from a relative pressure of approximately 0.95 downwards. Therefore the total curve should be raised to a slightly higher level by the amount of the value of the integral term between 0.95 and 1.0 relative pressure, which will possibly be not more than 10 ergs/cm².

Some discontinuities in these curves are observed, indicating a sudden change in the rate of change of potential energy.¹ These are most pronounced at a water content of 4-5 molecules per unit cell. Here the first so-called Hendricks' layer (Hendricks and Jefferson, 1938; Hendricks, Nelson, and Alexander, 1940) (4 molecules per unit cell) may be completed, allowing for some additional water which may find a place near the vacant tetrahedral holes. Then the change in potential energy between zero and one water-layer separation would be of the order of 90 ergs/cm² for Na and 130 ergs/cm² for Ca bentonite, although it should again be emphasized that the extrapolation is doubtful. Assuming that another four molecules per unit cell are required to reach

¹ Unfortunately, insufficient x-ray data are available for an energy-distance plot instead of the energy—water-content plot. The former would make the discontinuities more pronounced since the limited data on the water-content—layer-spacing relation in the quoted paper (Mooney, Keenan, and Wood, 1951, 1952) show sharp discontinuities.

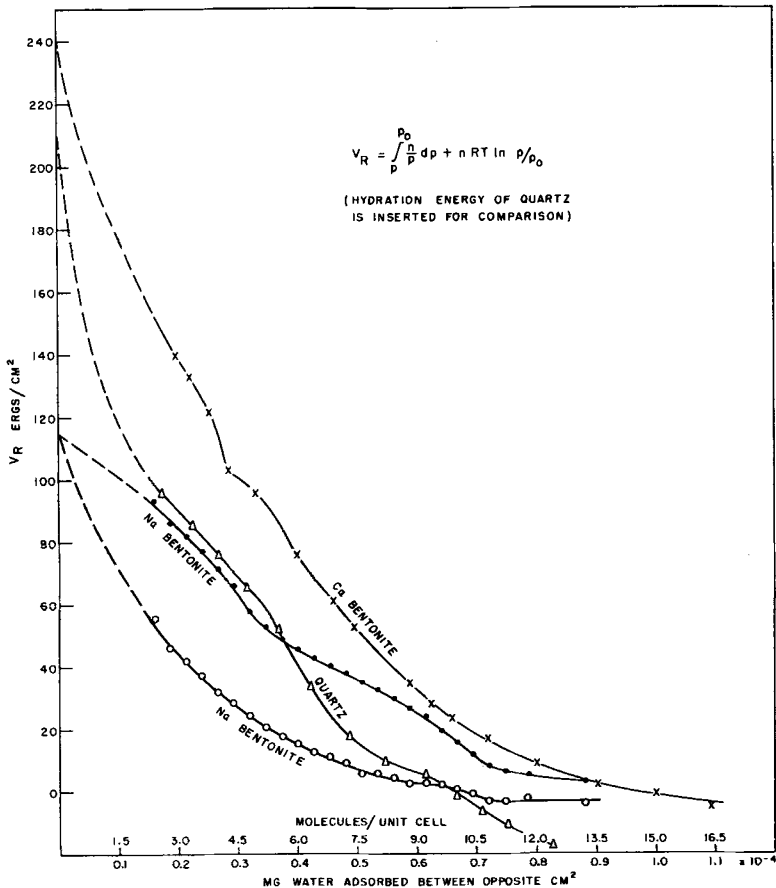


FIGURE 4.— Potential energy of Ca and Na bentonite layers as a function of the amount of interlayer water.

two-layer separation as supported by x-ray analysis, the potential energy difference between one- and two-layer separation amounts to about 25 and 60 ergs/cm² for Na and Ca bentonite, respectively. These energy differences are still less for the third and the fourth layer.

These potential curves as derived from the adsorption isotherms are the net result of three contributions: electrostatic, van der Waals, and hydration energy.

The van der Waals attraction energy computed from eq. 48 (Verwey and Overbeek, 1948) for one and two water-layers separation amounts to 6.7 and 2.4 ergs/cm² respectively. However, at such close separations (a few atomic diameters) the equation should no longer be applied as such; the action of the atom pairs can no longer be treated on the basis

of a continuous average atom density. Also no direct information as to the distance dependence of the van der Waals attraction in this region is known. As shown later, the van der Waals attraction in this region is probably smaller and thus amounts to a quite small potential energy contribution compared with the net repulsion energies arrived at above.

The electrostatic and hydration contribution is different for the two possibilities discussed for the status and position of the cations in the Stern layer.

Case 1 — Unhydrated cations in hole position. — Since it was necessary to assume that the major part of the cations were in the hole position, the electrostatic interaction energy may be seen as the repulsion of dipole layers, the dipoles being the combination of the cation and the negative charge center of the clay lattice. For finite plates, $a \times a$ cm, the total dipole repulsion energy can be computed to be

$$E(x) = -\frac{8\mu^2 a}{\epsilon} \left[0.773 - \ln a - \frac{s}{a} - 1 - \frac{x}{a} - 0.5 + \frac{x^2}{2s^2} \ln \frac{(x+2s)x}{(x+s)^2} - \frac{2x}{s} \ln \frac{(x+2s)}{(x+s)} + \ln \frac{(x+2s)^2}{(x+s)} \right],$$

where μ is the dipole moment per unit area, x the separation of the plane of the closest poles of the dipole, s the pole distance of the dipole, and ϵ the dielectric constant (~ 6).¹

In order to make an estimate of the repulsive energy, the negative charge is assumed to be concentrated in the OH groups underneath the cations. It must be kept in mind that when two bentonite layers interact there are four interacting dipole layers, two pairs being attractive and two pairs repulsive. For the most likely plate sizes the net repulsion of the dipole layers is then found to be less than about 0.01 erg/cm².

Thus the electrostatic repulsion combined with the van der Waals attraction amounts to a comparatively small work term. Consequently, the net potential energy change is mainly due to the hydration energy, which in this case is surface hydration energy. To determine whether surface hydration energy can be of the required order of magnitude it can be compared with surface hydration energy of other silica surfaces having a much smaller coverage with ions, where the other work terms may be neglected, e.g., quartz. In Figures 3 and 4 data of Boyd and Livingston (1942) for water adsorption on quartz have been inserted, taking into account the difference of surface areas of quartz and bentonite by expressing the results per cm² surface. These hydration energies are of the same order as those found for the bentonite system. Also the shape of the curve is analogous with an inflection point at monolayer coverage as obtained from the B.E.T. plot of the quartz-water isotherm.

¹ The author is indebted to Dr. A. S. Ginzburg for this calculation.

In Hendricks' picture (Hendricks and Jefferson, 1938; Hendricks, Nelson, and Alexander, 1940) for interlayer adsorption of water where two hydrogen bonds per unit cell are available to form the link between two layers, the surface hydration energy is roughly of the order of about 80 ergs/cm² (depending on the strength of the hydrogen bond) which is of the right order of magnitude.

Therefore the concept of the unhydrated ions can account for the observed energy relations. However, the alternative picture can be shown to be equally good in this respect:

Case 2 — Hydrated ions attached to the surface.— If the ions are two-dimensionally hydrated they will occupy midway positions between the plates at monolayer separation; if they are three-dimensionally hydrated the same position will still be held at two water-layers separation. Beyond this separation the hydrated ions would, for the major part, stick to the surface. This picture is analogous to that postulated by MacEwan (1948) for rearrangement of position of the ions with plate separation for methanol complexes.

When the ions are in the midway position the electrostatic energy is attractive and quite appreciable. The potential energy of one plate with respect to the other as a function of the separation $2x$ is given by

$$E(x) = + \frac{4\pi\sigma^2x}{\epsilon},$$

where σ is the surface charge density and ϵ the dielectric constant of the medium (~ 6).

For the computation of the change in electrostatic energy when the plates are brought together from about 10-Å separation, work will be gained only during removal of the last two layers in the case of three-dimensional hydration. This work amounts to approximately 30 ergs/cm² per layer. The combination of this electrostatic attraction plus the van der Waals attraction and the hydration energy should result in a net energy change as derived above from the adsorption isotherms. It is quite possible that the higher hydration energy, which would be required in this case to compensate the higher attraction, can be supplied by ion hydration energy. Unfortunately the energy change involved in removing the very last layer of water, where the bulk of the ion hydration energy enters (several hundreds ergs/cm²) cannot be evaluated with sufficient accuracy from the adsorption isotherms, so that it is not possible to arrive at a more accurate energy balance.

It may be concluded, therefore, that although the adsorption isotherms supply some information concerning the magnitude of the net energy changes in Stern layer interaction, they do not supply a definite answer as to the status of the Stern ions within the limits of the experiment.

d) *Stern Layer Interaction for Layer Separations between Zero and One Water-Layer. Swelling and Nonswelling Clays*

As mentioned before, a better chance for evaluation of the hydration energies involved in interlayer swelling should be obtained from analysis of the energies required to remove the last monolayer of water. Here we touch upon the problem of the difference between expanding and nonexpanding clays. Is ion hydration energy responsible for interlayer swelling, or is surface hydration energy sufficient? Why do some clays not swell?

The mineral pyrophyllite can be considered the closest nonswelling relative to the montmorillonoids. This mineral has only a very small base-exchange capacity, if any. At first sight, therefore, its nonswelling character might be seen as a consequence of the lack of cations between the layers so that no ion hydration energy is available to open up the layers. Although surface hydration energy is still available to overcome the van der Waals attraction between the plates, this energy is apparently insufficient. This is explainable since the van der Waals attraction between the layers is very high because of their close approach: x-ray analysis indicates close contact (001 spacing 9.14 Å). In reversibly dried montmorillonoids, however, this spacing is still about 9.6–9.8 Å so that the layers are about 0.6 Å farther apart than those of pyrophyllite, and the van der Waals attraction is thus lower. Unfortunately the van der Waals attraction at such small separations cannot be evaluated properly; hence we are not in the position to decide whether in bentonite the high ion hydration energy is required to exceed the van der Waals attraction or whether the smaller surface hydration will do. One argument, however, seems to favor the concept that surface hydration energy, and not ion hydration energy, is responsible for the swelling of bentonite. This argument is as follows:

By moderate heat treatment bentonites are known to collapse; they do not swell again, although no structural water is lost in the operation. It is surprising, however, that alcohol compounds can still expand the collapsed bentonite structure (Bradley, 1945). Since *ion* alkanolization energy is likely to be smaller than *ion* hydration energy, it is rather the higher *surface* alkanolization energy which can exceed the attraction where a lower *surface* hydration energy fails. The higher surface alkanolization energy can be seen as a result of the formation of a larger amount of hydrogen bonds per unit area compared with water according to the Hendricks structure of the water layers, as pointed out by Bradley (1945). However, the above argument is not entirely conclusive since in the formation of the first water layer both ion and surface hydration or alkanolization energy may contribute simultaneously.

By collapse, the layer spacing of Na bentonite is reduced to about 9.4 Å which is a wider basal spacing than that of the mineral pyrophyllite. One

can account for this reduction by assuming that before collapse, some water is still present in the reversibly dried bentonite, which is indeed the case. These last molecules of water could find a place between opposite tetrahedral holes which are not occupied by the counter ions. In the collapsed bentonite these last traces of water are removed, allowing the plates to come closer together.

The reason why the pyrophyllite spacing is not obtained may be sought in the presence of counter ions in the bentonites. Possibly these ions rearrange themselves in such fashion as to attain a position midway between the plates where two tetrahedral holes are opposite. Although this position will certainly be a labile position from the electrostatic point of view, the reason for this rearrangement could be that energetically the 12 coordination of the midway ions with the two opposite oxygen 6 rings of the two plates is more favorable than the 6 coordination realized in the hole position. Thus the collapsed bentonite may have the same basic structure as that postulated for the illites. Also, in the illites the basic layer spacing is not reduced to that of pyrophyllite. Such a midway arrangement of the counter ions would substantially increase the attraction, since an electrostatic attraction must be added to the van der Waals attraction, making the expansion of the collapsed bentonites more difficult.

e) Stern Layer Interaction, Summary

Assuming ion hydration, the differences in hydration energy between the various ion forms of bentonite (demonstrated by Figs. 3 and 4), may be explained in a rather straightforward way: the hydration energy of the clay would run parallel with hydration energies of the exchangeable ions present (Mackenzie, 1950). If, on the other hand, the cations are assumed to be dehydrated in the Stern layer, the differences in hydration energies of the various bentonite forms should be seen as the result of some secondary effect of the various ions on the formation of ideal Hendricks' layers, owing to geometrical effects (Forslind, 1950).

In conclusion, no final decision as to the status of the Stern ions can be made. Hendricks' (Hendricks and Jefferson, 1938; Hendricks, Nelson, and Alexander, 1940) interpretation of the resolution of the low-temperature dehydration peaks in the differential thermal analysis points to ion hydration in the case of Mg, Ca, Sr, Ba, and Li bentonite and no ion hydration for H, Na, K, and Cs bentonite. If this interpretation is correct, it would imply that either possibility may be realized, depending on the type of cation. For kaolinite, Mooney et al. (1951, 1952), suggests that, owing to its fit in the tetrahedral holes, Li is the only ion which may be present in a dehydrated condition.

f) The Short-Distance Minimum

As to the shallow minimum at about 10 Å separation, where we have arbitrarily set the borderline between Stern and Gouy layer, the following

speculative estimates may be made about the balance of the potential energies at this equilibrium separation.

The occurrence of this minimum may be the consequence of the increase of the van der Waals attraction on approach, which may just exceed the electrostatic repulsion at this distance before the stronger hydration repulsion makes itself felt. The electrostatic repulsion on the basis of dipole repulsion has been shown to be rather small, probably less than 0.01 erg/cm^2 . Consequently the van der Waals attraction should be of the same order of magnitude, but should exceed the repulsion by a few thousandths of one erg/cm^2 , the required magnitude of the depth of the minimum. However, on the basis of the van der Waals attraction formula, a value of about 0.5 erg/cm^2 would be found. Therefore, either a much lower value for the van der Waals attraction must be assumed, or alternatively a higher repulsion energy, possibly still due to some hydration energy, should be postulated. The latter assumption is unlikely, because for proper balance the hydration repulsion at the equilibrium distance should be of the order of 0.5 erg/cm^2 also, and should be just a few thousandths of one erg/cm^2 smaller than the van der Waals attraction; this seems rather accidental. On the other hand, it should also be kept in mind that the estimate of the depth of the minimum is based on the assumption of the association of the plates over their whole surface. Probably only a fraction of the surfaces associates in reality, making the estimated depth of the minimum proportionally higher. Certainly insufficient information is available at present to do more than speculate about the balance of the forces in the minimum.

The possibility that a secondary long-range minimum occurs, owing to the difference in decay of van der Waals attraction and Gouy layer repulsion, is not to be excluded. This might show up in long-distance spacings in clay suspensions (Verwey and Overbeek, 1948, p. 184).

Finally a few remarks about some aspects of the above considerations for the understanding of the behavior of hydrophobic colloids in general. In the first place, the hydration of Stern ions in colloids other than clay may be questioned. In the second place, the general importance of the hydration energy in Stern layer interaction may be emphasized. Since the hydration energies of quartz are of the same order as those of bentonite, there is sufficient reason to assume that in hydrophobic quartz sols also (and probably in many other hydrophobic sols), close approach of the particles is prevented by the hydration energy. Consequently, on flocculation, the deep van der Waals attraction minimum is probably not realized. This may be of importance in the interpretation of repectization phenomena in hydrophobic sols. In fact, the association-dissociation equilibrium of clay layers might be seen as a special case of simultaneous flocculation and repectization.

ACKNOWLEDGMENT

The author is indebted to Dr. W. F. Bradley and Prof. Dr. J. Th. G. Overbeek for their stimulating discussions.

APPENDIX

POTENTIAL ENERGY OF BENTONITE LAYERS
IN STERN LAYER INTERACTION

As a reference separation for the potential curve the 10 Å equilibrium spacing will be chosen, which according to the former discussions has no appreciable potential energy compared with infinite separation.

Imagine two parallel bentonite layers at the equilibrium distance immersed in water, the partial pressure of which is the saturation pressure at the temperature chosen. The potential curve to be computed is found from the work required to bring the plates toward each other.

In order to link this potential energy with the data available from the adsorption isotherm, the following isothermal, reversible cycle is considered (Fig. 5) :

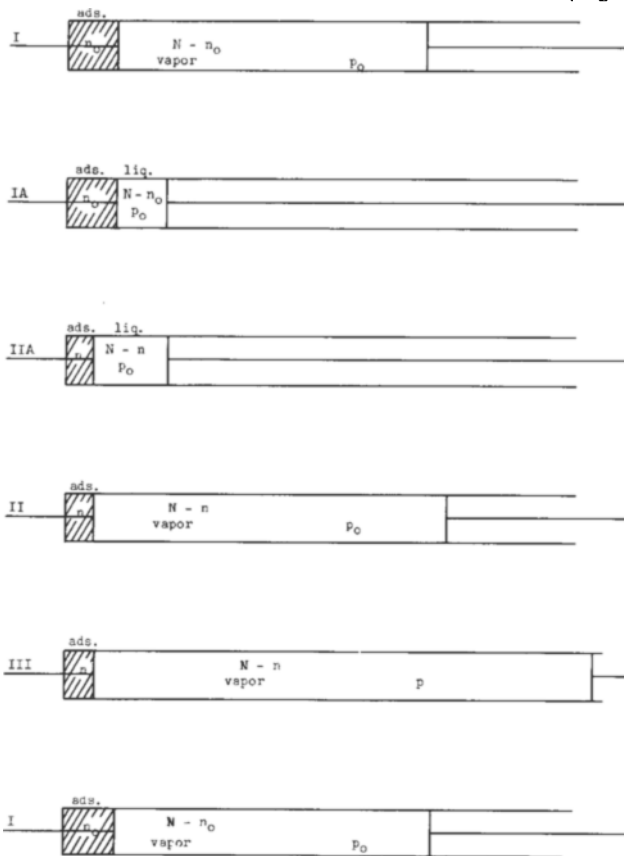


FIGURE 5. — Isothermal reversible cycle.

System I consists of a cylinder with a piston at the righthand side, which can move without friction. The base of the cylinder at the left consists of a bentonite layer. A second piston can move without friction in the cylinder (left-hand piston), its rod being guided through the base of the cylinder. The surface of the piston opposite the base of the cylinder is a bentonite layer. No surface phenomena are supposed to take place at the other side of this piston.

In system I the bentonite layers are at the equilibrium distance ($\sim 10 \text{ \AA}$) for saturated vapor (pressure p_0) outside, and n_0 moles of water are adsorbed between the plates. The total amount of water in the system is N moles; thus there are $N - n_0$ moles of water in the vapor phase in this case.

Going from system I to system IA the water is isothermally and reversibly condensed by moving the right-hand piston to the left until all the water is in the condensed state and the bentonite plates are thus immersed in water.

Subsequently the left-hand piston is moved to the left in infinitesimal steps, allowing the expelled water to go to the liquid phase outside the bentonite layers in infinitesimal amounts. The result is system IIA, with only n moles between the layers.

Now the total amount of liquid water ($N - n$) moles, is completely evaporated isothermally and reversibly, keeping the left-hand piston fixed with n moles of water between the bentonite layers. The vapor pressure is maintained at saturation pressure p_0 . The volume of the vapor phase will now be slightly higher than that in system I. System II results from this change.

System II is transformed to system III by keeping the distance and amount of water between the layers fixed, and isothermally and reversibly expanding the vapor by moving the right-hand piston to the right to the pressure p , which is the equilibrium pressure when n moles are adsorbed between the layers as given by the adsorption isotherm.

Finally system III is transformed to system I by moving the right-hand piston to the left, thus compressing the vapor in infinitesimal steps, after each step allowing the left-hand piston and the amount of water adsorbed between the layers to adjust itself to the equilibrium situation, which means that here the adsorption isotherm is followed.

It will be clear that the work done by the left-hand piston between systems IA and IIA constitutes the potential energy which should be computed.

In performing the cycle mentioned above the sum of the external work should be zero, since the total free energy change and the total entropy change are zero, as are the total heat changes; heat would otherwise have been transformed into work during a reversible isothermal process, which is against the second law of thermodynamics. Indicating the work terms with W the following equation will thus apply:

$$W(I \rightarrow IA) + W(IA \rightarrow IIA) + W(IIA \rightarrow II) + W(II \rightarrow III) + W(III \rightarrow I) = 0.$$

The total work done by the system is zero. The work done by the system in going from IA to IIA is $\int_R V$ where \int_R equals the repulsion potential of the plates in system IIA with respect to their position in system IA. The vapor may be considered an ideal gas in the region of pressure studied.¹

¹ The deviation from ideal gas behavior of saturated water vapor at 24°C is given by

$$pV = RT + \frac{b}{V} \left[RT - \frac{a}{b} \right]$$

$R = 0.003662$ for p and V measured at standard conditions.
 $a = 0.01089$, $b = 0.001362$.

At the saturation pressure (22.37 mm Hg) $V = 37$, then $RT = 1.09$ and the correction term is 0.0026 or about 0.02 percent.

The various work terms in the above equation amount to:

$$W(I \rightarrow IA) : -p_o V_I \quad (\text{neglecting the volume of the condensed water})$$

$$W(IA \rightarrow IIA) : -V_R$$

$$W(IIA \rightarrow II) : +p_o V_{II}$$

$$W(II \rightarrow III) : + \int_{V_{II}}^{V_{III}} p \, dV$$

for the right-hand piston. The number of moles in the vapor phase is constant ($N - n$). dV is positive. The left-hand piston does no work since the layer distance is constant.

$$W(III \rightarrow I) : \int_{V_{III}}^{V_I} p \, dV$$

for the right-hand piston and taken along the adsorption isotherm, the number of moles in the vapor phase being variable. dV is negative. The left-hand piston does no work since there is no force on the layers (equilibrium positions).

Substituting these work terms in the above equation gives the result:

$$\int_{V_{II}}^{V_{III}} p \, dV = - (N - n) RT \int_{p_o}^p \frac{1}{p} dp ;$$

$$\left[dV = - \frac{(N - n) RT}{p^2} dp \right]$$

$$\int_{V_{III}}^{V_I} p \, dV = p V \int_{V_{III}}^{V_I} \frac{1}{V} dV - \int_{p_o}^{p_o} V dp = p_o V_I - p V_{III} - \int_p^{p_o} V dp$$

Thus

$$V_R = + p_o V_{II} - p_o V_I - NRT \int_{p_o}^p \frac{1}{p} dp + nRT \int_{p_o}^p \frac{1}{p} dp + p_o V_I - p V_{III} - \int_p^{p_o} V dp$$

$$\text{Since } p_o V_{II} = p V_{III},$$

$$\begin{aligned} + V_R &= - NRT \int_{p_o}^p \frac{1}{p} dp + nRT \ln \frac{p}{p_o} - \int_p^{p_o} V dp \\ &= - RT \int_p^{p_o} \frac{N - n}{p} dp \end{aligned} \quad (III-1)$$

Taking the integrals together

$$+ V_R = + nRT \ln \frac{p}{p_o} + RT \int_p^{p_o} \frac{n}{p} dp ,$$

the relation $n = f(p)$ being given by the adsorption isotherm.

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DISCUSSION

Rustum Roy. — From the author's discussion it would appear that the chief objection to one of the two current theories is the fact that pyrophyllite and talc do not "swell" or admit interlayer water into their structures. As a matter of fact, from our phase equilibrium data for the system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ it will be seen that pyrophyllite is not stable in the

presence of water at low temperatures ($<420^{\circ}$ C) and hence if the pyrophyllite had been brought to equilibrium (which would require drastic methods to overcome the energy barrier) it would indeed have been seen to have admitted inter-layer water. In the case of talc the same is true although the pure magnesium montmorillonite is not as well characterized as its aluminum counterpart.

J. W. Jordan. — Ethylene glycol brings about interlayer separation in some bentonites which do not swell in water. How does this fit in with your picture?

H. Van Olphen. — Glycol tends to confirm the theory involving hydrogen bonding of the swelling agent with the clay surface rather than with the interlayer cations.