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Expansion of Montimorillonite Due to Adsorption of Water Vapor

G. L. Roderick and Turgut Demirel[1]

Abstract. Expansions of pure sodium and calcium montmorillonites due to absorption of water vapor were studied and the results were correlated with X-ray diffraction and free swelling studies. Specimens of various porosities were used. Results indicate that the uptake of water is a multimolecular physical adsorption phenomenon which justifies application of BET theory. Porosity of specimens did not appreciably affect their expansions due to adsorption of water vapor. Sodium montmorillonite expanded appreciably more than calcium montmorillonite. At near saturation vapor pressure, calcium montmorillonite has attained practically its maximum swelling, while sodium montmorillonite will expand further if exposed to liquid water. Free energies of wetting, calculated from adsorption isotherm data, do not directly reflect the extent of swelling but do reflect the uplift pressures developed. Sodium montmorillonite presents the more serious problem with respect to settlement, and calcium montmorillonite presents the more serious problem with respect to uplift pressures.

Two types of swelling, intermicellar and intramicellar, have been recognized in clay-water systems. These two types are due to interpositioning of water between the clay particles and between the lattice units comprising the particles, respectively (1 pp 87-95, 5). Marshall (5) points out that only the intermicellar swelling occurs in kaolinites and micas and does not lead to entensive expansion; both types of swelling take place in montmorillonites and lead to extensive expansion. This explanation conforms with the results obtained from free swelling tests (4, 6) and X-ray diffraction studies (2). This, however, should not be considered as implying that the intramicellar swelling is more important than intermicellar swelling (1). For clarity, intramicellar swelling will be termed interlayer swelling in this paper.

It is believed that both intermicellar and interlayer swellings of montmorillonite free from electrolytes are brought about by the adsorption, on the solid mineral surfaces, of water which reaches film thicknesses exceeding the separation distance of the surfaces. Therefore, the swelling depends mainly on the affinity of the solid surface for water. This affinity for water may be expressed in terms of the free energy change accompanying the adsorption process. The free enery change accompanying the adsorption of water at saturation vapor pres-

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sure by clay minerals can be expressed by the following equation (3):

$$\triangle F = \gamma_{sf} - \gamma_{so} + \alpha \triangle V \text{------------}(1)$$

where $\triangle F$ is the free energy of wetting of the clay mineral by liquid water, γ_{sf} is the solid-fluid interfacial tension, γ_{so} is the surface tension of the solid in vacuum, α is the interlayer surface area per cm² of the total surface and $\triangle V$ is the change in the free energy per cm² of the interlayer surface due to separation of particles against the force of interaction.
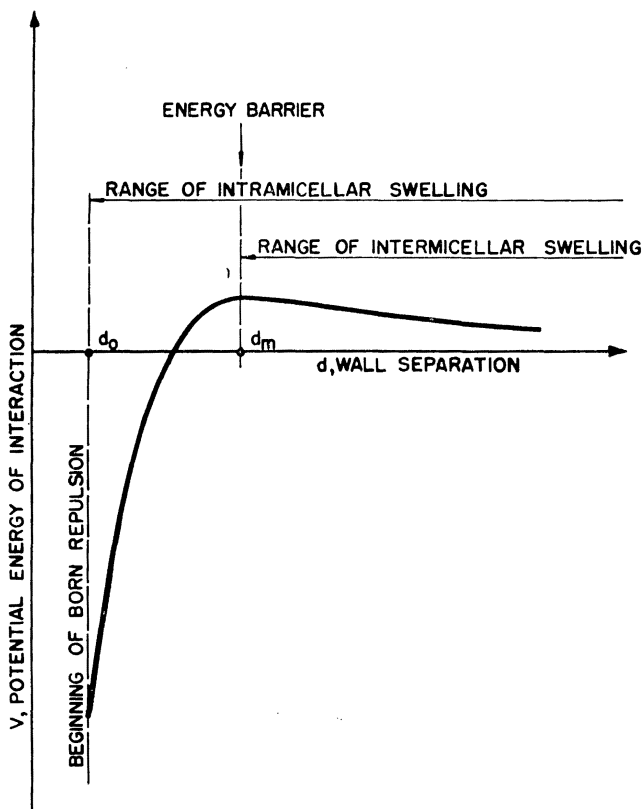

Figure 1. A schematic representation of the potential energy of interaction between solid walls of clay particles facing each other.

A schematic representation of the potential energy of interaction between solid walls of clay particles facing each other in a well dialized clay-water system is shown in figure 1. In a completely dried montmorillonite, the interlayer wall separation is d_o, which corresponds to the minimum free energy attainable by the system as water is evaporated while maintaining themodynamic equilibrium. On the other hand, the intermicellar wall separation has a value larger than d_m which corresponds to a

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thermodynamically unstable, but kinetically stable, state attain-
ed as water is evaporated; the kinetic stability is due to the
existence of the energy barrier at a wall separation of d_m. When
the completely dried montmorillonite is gradually brought in
contact with water vapor of increasing vapor pressure, water is
adsorbed on the wall surfaces. If the thickness of the water film
thus formed exceeds the separation distance of the walls, swell-
ing takes place. This swelling takes place from the very begin-
ning of adsorption on the interlayer walls since these walls were
in contact with each other before adsorption began. The driving
force for interlayer adsorption is the free energy change accom-
panying this process and may be expressed as:

$$\triangle F = \alpha \left(\gamma_{sf}\text{-}\gamma_{s0} \right) + \alpha \triangle V \text{————————(2)}$$

per cm² of total montmorillonite surface. On the other hand,
adsorption on intermicellar walls proceeds without swelling
taking place, since these walls are already separated from each
other. The driving force for adsorption on these walls may be
expressed as:

$$\triangle F = (1 - \alpha) \left(\gamma_{sf}\text{-}\gamma_{s0} + \gamma_f \right) \text{————————(3)}$$

where γ_f is the surface tension of water against its vapor and
all other terms have the same meaning as in equation 1. When
the intermicellar pores are completely filled with water due to
capillary condensation taking place in fine pores, the free
energy change becomes:

$$\triangle F = (1 \text{-} \alpha) \left(\gamma_{sf}\text{-}\gamma_{s0} \right) \text{————————(4)}$$

At this point intermicellar swelling may start taking place
due to the possibility of attaining by expansion a low energy
position on the potential energy of interaction curve (figure 1).
However, the portion of the interaction potential curve corres-
ponding to wall separations larger than d_m is rather flat in the
neighborhood of d_m and almost flat for larger separations,
which means the intermicellar swelling contributes but little
to the free energy of wetting. Therefore, use of equation 1,
which is the sum of equations 2 and 4, for expressing the free
energy of wetting of montmorillonite does not introduce any
appreciable error.

The objective of the present investigation was to correlate
the swelling due to adsorption of water vapor with the results
of X-ray diffraction studies indicating interlayer swelling (2 p.
170) and the results of free swelling due to adsorption of liquid
water (6). The results obtained from X-ray diffraction studies
have been interpreted as indicating stepwise (discontinuous)
adsorption of water molecules on interlayer walls of montmor-
illonites, i.e., a sudden uptake of a maximum number of layers
of water molecules at a certain relative pressure and the number
of layers remaining unchanged for a range of relative pressures.

On the other hand, a brief study conducted at the Iowa Engineering Experiment Station Soil Research Laboratory on correlating the first order basal spacing (d_{oo1}) changes upon adsorption of water with line broadenings has indicated a rather continuous nature of interlayer uptake of water with development of a maximum number of layers predominating only at certain relative pressures (3). Either a stepwise or a continuous uptake of water was expected to be reflected in the swelling of compacted specimens of montmorillonites due to adsorption of water vapor. A continuous uptake of water justifies the application of multimolecular adsorption theory (BET theory) adsorption isotherm studies.

The difference between the amount of swelling caused by adsorption of water vapor near the saturation pressures and the amount of free swelling caused by absorption of liquid water reflects the additional factors contributing to further swelling. If interlayer wall separations are in the neighborhood of d_m (figure 1) at saturation vapor pressure, slight increases in temperature, as might be caused by heat of wetting, may expand the interlayer water and cause a separation of these walls past the energy barrier. Then the walls which have passed the energy barrier, as well as intermicellar pores, keep separating further in presence of water available for capillary absorption. This water may be squeezed out when external pressure is applied, causing the primary consolidation of fine disperse systems. Extraction of the water by external pressures becomes progressively more difficult as the energy barrier is approached and the primary consolidation changes into secondary consolidation.

According to Terzaghi (7), in coarse disperse systems physical factors outweigh the physio-chemical factors; and a purely mechanical treatment, without thermodynamic considerations, becomes sufficient for determining the state of these systems. On the basis of this theory, Terzaghi has shown that the surface tension of water and the elastic properties of coarse disperse systems cause swelling when exposed to additional liquid water and cause primary consolidation when external pressures are applied.

<div align="center">LABORATORY INVESTIGATION</div>

Materials

The montmorillonite used was a commercially available Wyoming bentonite known by the trade name Volclay-SPV produced by the American Colloid Company. According to the producer it consists of 90 per cent montmorillonite, essentially sodium montmorillonite, and 10 per cent other minerals such as feldspar, quartz and volcanic glass. This material was freed from impurities by a repeated sedimentation process.

Sodium montmorillonite was prepared by mixing a saturated sodium chloride solution with the suspension obtained from the sedimentation process. This mixture was stirred for 24 hours and the clay was then separated by means of a super-centrifuge. This process was repeated five times to assure replacement by sodium ions of all the cations associated with the montmorillonite. The free electrolyte was removed from the sample by dispersing and centrifuging. This was repeated several times until the material was free of chloride ions.

The calcium montmorillonite was prepared by the same method except that a calcium chloride solution was used for ion exchange.

X-ray diffraction analyses on the samples prepared showed that they were pure sodium and calcium montmorillonite. The physical and chemical properties are listed in Table 1.

Table 1. Properties of the minerals used.

Mineral	Sodium montmorillonite	Calcium montmorillonite
Physical properties		
Liquid limit, %[a]	968	341
Plastic limit, %[b]	51	46
Plasticity index, %	917	295
Shrinkage limit, %[c]	17	34
Centrifuge moisture equivalent, %[d]	882	173
Chemical properties		
Cation exchange capacity, m.e./100 gm[e]	94	103
pH[f]	7.55	6.60

[a] ASTM method D423-54T.
[b] ASTM method D424-54T.
[c] ASTM method D427-61.
[d] ASTM method D425-39.
[e] Ammonium acetate method.
[f] Glass electrode method using suspension of 1 gm soil in 30 cc distilled water.

Sample Preparation

Four samples each of the sodium montmorillonite and calcium montmorillonite were prepared by compressing the material into a mold by static loading. About 0.08 gram of the material was placed in a cylindrical mold having a diameter of 0.4902 cm. The four samples were compacted by pressures of 9.6, 28.2, 62.3 and 120.2 kg/cm^2, respectively. Weights of the specimens were determined to 0.001 gm immediately after molding. Moisture samples taken at time of molding showed the sodium montmorillonite contained 7.62% hygroscopic moisture and the calcium montmorillonite contained 16.07%, which corresponded to a p/p_0 ratio of 0.4.

Apparatus

The adsorption chamber was connected to a vacuum train by means of a mercury sealed stopcock, and immersed in a water

thermostat at 24.3°C. The vacuum train consisted of a rotary single stage forepump, a single stage mercury diffusion pump, a cold trap containing liquid nitrogen, and a McLeod gauge. The thermostat was made of plexiglass and was equipped with a Beckman thermometer reading to 0.01°C, a motor stirrer, a tap water cooling coil, a continuous heater and an intermittent heater. The heaters were two 110 volt, 100 watt, light bulbs. Optical glass observation windows were provided.

A permanent water reservoir was connected to the adsorption chamber through a simple mercury manostat-manometer combination by which water vapor was transferred to the chamber and vapor pressures were measured.

Procedure

The test specimens were placed on small stainless steel platforms fastened to a stainless steel wire by which they were suspended in the adsorption chamber. The wire was hooked to a support attached to a mercury-sealed ground glass stopper in the top of the adsorption chamber.

After being placed in the chamber, the initial heights of the specimens were measured by means of an optical reader whose objective field is divided into 1000 divisions by means of a filar micrometer eyepiece containing a movable cross line. One division on the reader corresponds to 0.005 mm length.

The adsorption chamber was then pumped down to 10^{-5} mm Hg for several days to evacuate (de-gas) the specimens. The heights of the specimens were again measured with the optical reader. Assuming the the lateral dimensions of each sample changed by the same ratio as the heights, the volume of each after evacuation was calculated. By using this volume and the oven dry weight of each sample, and assuming the specific gravity of the minerals to be 2.7, the porosity of each specimen at its evacuated volume was determined.

Water vapor was then introduced into the adsorption chamber in small increments through the manostat arrangement. After each increment was introduced, a period of 24 hours was allowed for the system to attain equilibrium. At the end of this period the pressure difference on the manometer was measured with a cathetometer and the change of the heights of the test specimens were measured with the optical reader. The pressure range up to near saturation was investigated by transferring more and more vapor into the adsorption chamber.

The temperature of the thermostat was maintained at 24.3°C during the entire test period.

PRESENTATION AND DISCUSSION OF RESULTS

Results obtained are presented in figures 2 and 3 in the form

of expansion isotherms. The portions of these isotherms be-
tween relative pressures of 0 to 0.4 do not represent the true
expansion; since specimens were molded at a relative pressure
of 0.4, and evacuation to 0 relative pressure did not produce
any overall shrinkage but evidently increased the intermicellar
por space. Therefore, adsorption up to the relative vapor pres-
sure of 0.4 evidently proceeds mainly with interlayer expansion
into the intermicellar pores available. For relative pressures
above 0.4, the expansion isotherms show a rather continuous
and smooth trend without the formation of steps which would
be expected in case of a sudden uptake of water.

On the basis of this trend and changes in line broadenings
observed in X-ray diffraction studies (3), it is believed that the

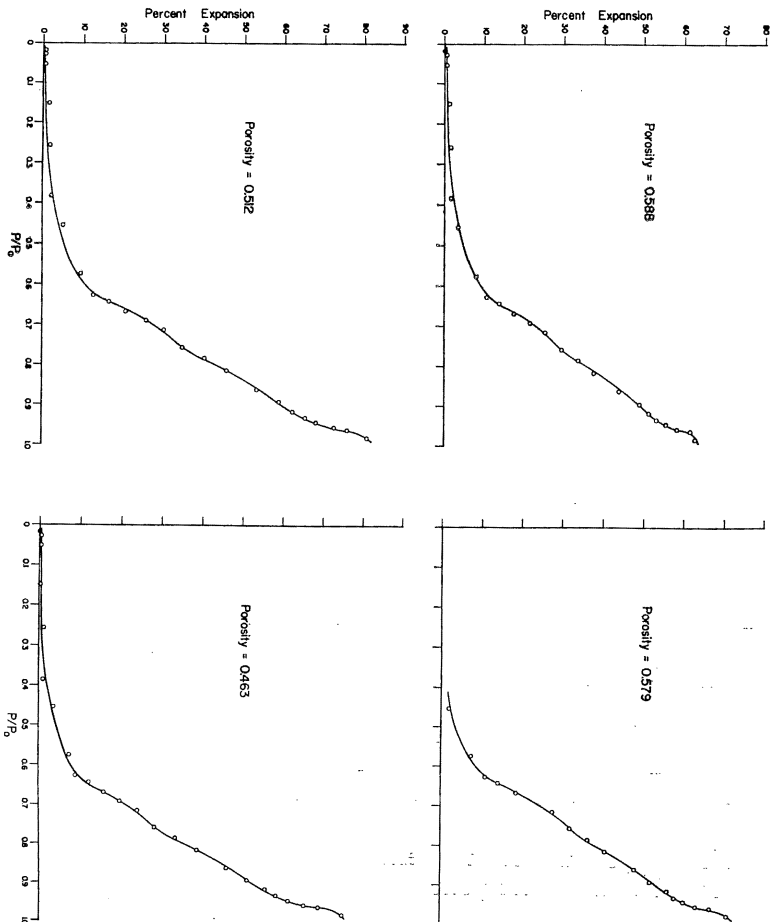Figure 2.   Expansion   isotherms   of   sodium   montmorillonite   compacted   to   various
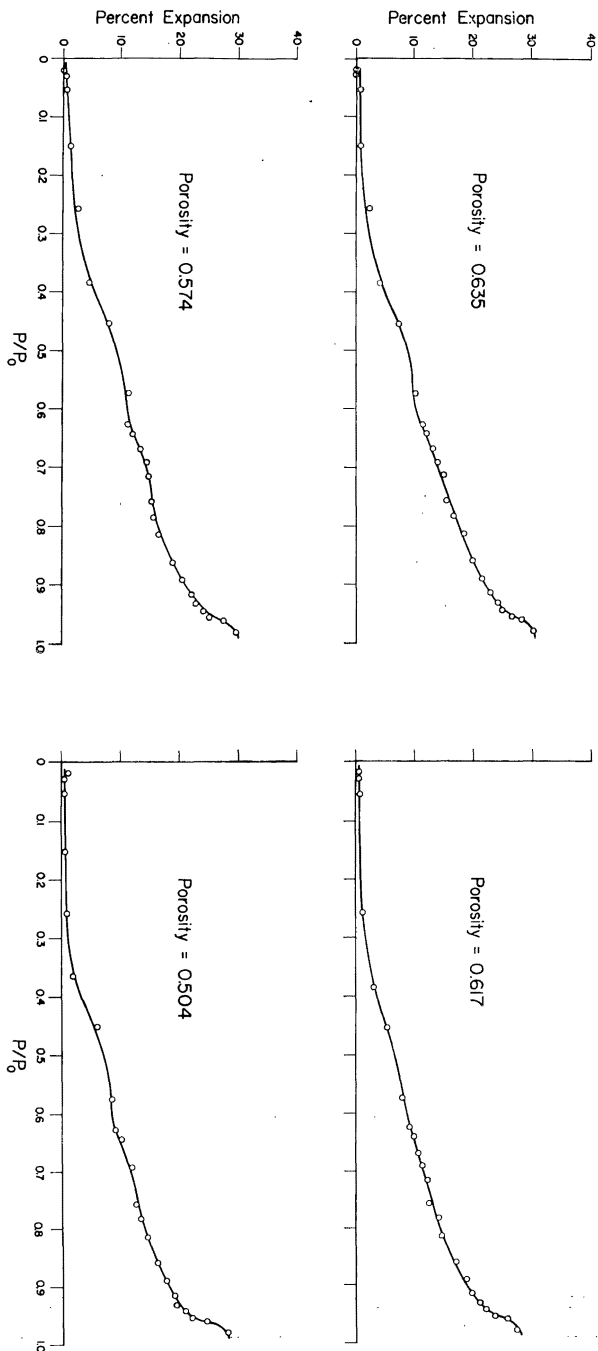   porosities.

Figure 3.   Expansion isotherms of calcium montmorillonite compacted to various porosities.

water molecules enter between the interlayer walls and form layers of various thicknesses simultaneously, i.e., the uptake of water is a multimolecular physical adsorption phenomenon justifying the application of BET theory in adsorption isotherm studies. Certain thicknesses evidently dominate at certain vapor pressures, causing slight slope changes in expansion isotherms (figures 2 and 3). This agrees with the conclusion from X-ray studies (3).

The free energies of wetting of sodium and calcium montmorillonites calculated from adsorption isotherms by using Bangham's free energy equation, were found to be -76.6 erg/cm^2 for calcium montmorillonite and -34.8 erg/cm^2 for sodium montmorillonite (3). There appears to be no direct correlation between free energies of wetting and swelling. The uplift pressures, however, seem to correlate with free energy data. The uplift pressures reported by Mielenz and King (6) range from 2.0 to 11.0 ton/ft^2 for sodium montmorillonite and from 4.9 to 15.9 ton/ft^2 for mixed cation montmorillonites.

The porosity of specimens of montmorillonite having the same exchangeable cation does not seem to have an appreciable effect on swelling due to adsorption of water vapor (figures 2 and 3).

The average linear swelling due to adsorption of water vapor near the saturation vapor pressure was found to be 80 per cent for sodium montmorillonite and 30 per cent for calcium montmorillonite. These values correspond to volumetric expansions of 480 per cent and 120 per cent for sodium and calcium montmorillonites, respectively. The above is true despite a smaller X-ray basal spacing of sodium montmorillonite at most values of p/p_o (3). Therefore, the much greater expansion of the sodium clay from adsorption of water vapor is not so much a result of interlayer swelling as intermicellar swelling.

Data from Mielenz and King (6) indicate that in the presence of liquid water the volumetric expansion of calcium montmorillonite is 125 per cent, indicating little or no further expansion beyond what occurs from adsorption from the vapor phase. Their free swelling data for sodium montmorillonite, however, give values 3 to 3.3 times the volumetric expansion obtained in this study near the saturation vapor pressure. X-ray data indicate that this additional swelling is the presence of liquid water is due to lattice expansion of sodium montmorillonite (3).

CONCLUSIONS

1. In the relative vapor pressure range 0.4 to near 1.0, calcium montmorillonite expands volumetrically about 120 per cent, largely from interlayer swelling. Apparently there is very little additional swelling in the presence of liquid water.

2. In the relative vapor pressure range 0.4 to near 1.0, sodium montmorillonite expands volumetrically about 480 per cent, largely as a result of intermicellar swelling. An additional three-fold expansion in liquid water may be attributed to interlayer swelling.

3. Continuity of the clay expansion curves indicates that the uptake of water is a multimolecular physical adsorption phenomenon which justifies the application of BET theory.

4. Porosity of compacted homoionic montmorillonite specimens does not have an appreciable effect on swelling due to adsorption of water vapor.

5. The free energies of wetting do not reflect the extent of swelling directly; however, they do reflect the uplift pressures which develop upon swelling.

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