

WATER SORPTION PROPERTIES OF HOMOIONIC MONTMORILLONITE *

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ABSTRACT

Homoionic samples of four montmorillonite clays, selected on the basis of the properties which control their economic uses, were prepared by treating with two normal neutral solutions of ammonium acetate, lithium, sodium, potassium, calcium, and magnesium chloride. Atterberg plastic and liquid limits, slopes of the liquid limit curves, and water sorption curves were determined. Among the results suggested, the following are particularly considered:

1. The plastic state is reached when enough water is put into the system to fill all the pore space and to supply all the montmorillonite layers with water adequate for rigid layers plus a slight additional amount.

2. The type of cation is not the only factor which controls the properties of montmorillonite.

3. The structure of the lattice also appears to determine the properties of montmorillonite.

INTRODUCTION

In recent years there has been considerable discussion in the literature concerning the nature of the water surrounding the particles in clay-water systems. One school of thought considers that adsorbed cations hydrate and that the water is held to the surface primarily by van der Waal's forces. The other school of thought is that the first layers of water take on a crystalline structure, perhaps with a configuration similar to that of ice, and are held to the surface of the clay mineral by hydrogen bonding.

The purpose of this study was to obtain a better understanding of the clay-water relationships with the various cations on the exchange positions of the montmorillonites and their effect on the properties of the various montmorillonites studied.

Definitions

Plasticity. — According to Grim (1953, p. 1) plasticity is “the property of a moistened material to be deformed under the application of pressure, with the deformed shape being retained when the deforming pressure is removed.”

Atterberg Limits. — The Atterberg limits of a soil or clay are the liquid limit, plastic limit, and plastic index. Allen (1942, pp. 263-265) defines them as follows:

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1. "Liquid limit is the moisture content, expressed as a percentage by weight of the oven-dry soil, at which the soil will just begin to flow when jarred slightly."

2. "Plastic limit is the lowest moisture content expressed as a percentage by weight of the oven-dry soil, at which the soil can be rolled into threads $\frac{1}{8}$ -inch in diameter without breaking into pieces. Soils which cannot be rolled into threads at any moisture content are considered non-plastic."

3. "Plastic index is the difference between the liquid limit and the plastic limit. . . . It is the range of moisture content through which a soil is plastic. When the plastic limit is equal to or greater than the liquid limit, the plastic index is recorded as zero."

Water Sorption.—Water sorption is absorption and adsorption by physical and chemical means.

1. Absorption of water is the taking up of water by capillary suction.

2. Adsorption of water is the adhesion of water molecules to the surface of the clay minerals by bonding processes.

Materials

Four samples of montmorillonite with different properties were selected to illustrate variations of properties within the group.

1. Montmorillonite-1, from Pontotoc, Miss., is a high-iron montmorillonite with some substitution of Al^{+++} for Si^{++++} (personal communication, R. E. Grim). It is used as a bonding clay for molding sand and, after acid treatment, for removing color from oil. The exchangeable cations are calcium and hydrogen, and the cation exchange capacity is 93 me./100 gms. (Grim and Cuthbert 1945a, p. 10). Montmorillonite-1 does not swell appreciably in water.

2. Montmorillonite-2, from Cheto, Ariz., is a low-iron montmorillonite with little substitution of Al^{+++} for Si^{++++} (personal communication, R. E. Grim). It is used for the manufacture of catalysts and as a bleaching clay after acid treatment. Calcium is the chief exchangeable cation, and the cation exchange capacity is over 100 me./100 gms. Montmorillonite-2 does not swell appreciably when placed in water.

3. Montmorillonite-3, from Belle Fourche, S.D., has a slightly higher aluminum content than do the other montmorillonites. Some aluminum is replaced by magnesium, but very little is replaced by iron (personal communication, R. E. Grim). Sodium is the exchangeable cation (Grim and Cuthbert, 1945a, p. 10). There is some substitution of Al^{+++} for Si^{++++} (Greene-Kelley, 1953, p. 53). The clay has a cation exchange capacity of 93 me./100 gms. (Grim and Cuthbert, 1945a, p. 10) and swells in water to several times its volume. Its thixotropic properties make it well suited for use as a drilling mud; it is also used as a bonding clay for molding sands in foundries.

4. Montmorillonite-4, from Olmsted, Ill., is low in aluminum, but even so, iron and magnesium are substituted for some aluminum. The clay has

TABLE I. — CHEMICAL ANALYSIS OF THE FOUR MONTMORILLONITES

	M-1 ¹	M-2 ²	M-3 ¹	M-4 ¹
SiO ₂	57.55	66.75	64.41	61.06
TiO ₂	0.32	0.29	0.19	—
Al ₂ O ₃	19.93	19.85	20.80	15.99
Fe ₂ O ₃	6.35	2.25	3.65	4.50
FeO	0.95	—	—	0.12
MgO	3.92	6.98	2.33	2.00
CaO	1.94	3.21	0.83	0.96
K ₂ O	0.59	0.18	0.39	1.43
Na ₂ O	0.33	0.84	2.86	0.07
Ign.	8.53	—	4.86	13.36
Total	100.41	100.91	100.32	99.96
H ₂ O—	8.51	—	—	5.88
H ₂ O+	7.43	—	—	13.36

¹ Analysis made under the supervision of O. W. Rees, Illinois State Geol. Survey.

² File of W. F. Bradley, Illinois State Geol. Survey.

a low cation exchange capacity for montmorillonite, 37 me./100 gms. The exchangeable cations are calcium, magnesium, and hydrogen, and the clay is slightly acid in nature. The potassium content, as indicated by chemical analysis (Table I), suggests that about 20 percent of the layers are mica layers. This montmorillonite differs from the others in that it was probably transported and deposited as montmorillonite instead of being a devitrification product of volcanic ash. It is a natural fuller's earth and does not swell appreciably when placed in water.

PROCEDURE

The homoionic montmorillonite samples were prepared by leaching 150 grams with 1 liter of neutral 2N salt solutions of ammonium acetate and potassium, sodium, lithium, calcium, and magnesium chlorides. Then the clays were washed free of the salt solutions with distilled water.

Plastic Limits

The Atterberg plastic limits are determined by rolling a ball of clay into a thread $\frac{1}{8}$ -inch in diameter, using just enough water to keep it from breaking into pieces.

In preparing montmorillonite for liquid-limit determinations, I have found (1949, p. 509) that water cannot be added as with other clays; the process has to be started with dilute suspensions, the water allowed to evaporate, and the suspension stirred every few hours to insure an even moisture distribution.

The liquid limits were determined by the method described by Casagrande (1932, pp. 122-126). The sample is placed in the liquid-limit machine and a groove 2 mm. wide at the base, 11 mm. wide at the top, and

8 mm. deep is made in the sample. The cup containing the sample is dropped 1 cm. as many times as is required to cause the clay to flow together for $\frac{1}{4}$ -inch. For 10 different moisture contents the numbers of taps between 15 and 35 were determined. The moisture is plotted, on semilogarithmic paper, along the arithmetic scale (ordinate) and the taps on the logarithmic scale (abscissa). A straight line is drawn through these points; the moisture content at the point where the lines cross the 25-tap line is considered the liquid limit.

Plastic index equals the liquid limit minus the plastic limit.

Slope of the Liquid-Limit Line

The slope of the liquid-limit line is determined as an angle. To obtain the angle α (Fig. 1), the 10-tap line is considered tangent to a circle whose radius originated where the liquid-limit curve crosses the 100-tap line. The liquid-limit curve is the hypotenuse of the right triangle made by the radius and the tangent. The angle of slope can be derived from the following equation:

$$\tan \alpha = \frac{y}{x}$$

let $\tan \alpha =$ angle of slope

$x =$ radius, or $100 - 10$ taps $= 90$

$y =$ difference in moisture content between the points where the radius x and the hypotenuse r cut the tangent y (Fig. 1).

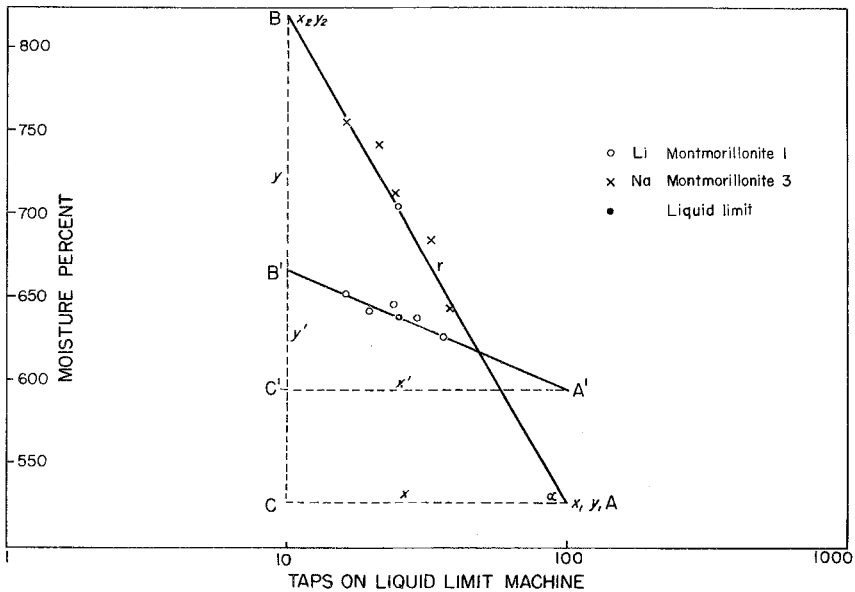


FIGURE 1. — Method of obtaining slopes.

The angle of slope of the liquid-limit line is a measure of thixotropy at the liquid limit. The steeper the slope the greater the ability of the montmorillonite to set into a gel.

Water Sorption

Water sorption apparatus used in the experiment was similar to that used by Enslin (1933, p. 147) consisting of a 3-way stopcock, U-tube, porous filter, a male and a female ground-glass joint, and a 5 ml. pipette, as illustrated in Figure 6.

Before running an adsorption analysis the funnel is filled with water, which is allowed to flow through the U-tube until it makes contact with the porous plate. As much air as possible is forced from under the porous plate to give maximum surface contact with the liquid. The pipette is filled until the meniscus of the water along the top side reads about 4 ml. The stopcock is turned so that there is a water contact between the pipette and the U-tube. The evaporation curves are determined by taking readings, beginning with 15 seconds and doubling the time for each reading, until about two days have passed.

Because clays of different particle sizes give different sorption curves (Pichler, personal communication), the samples were ground and the 120-230 mesh material was selected for analysis in preference to that cut greater than 120 mesh or the material that remained on the pan after passing through the 230-mesh screen.

The moisture content of the clay was then determined and calculations were made to determine the amount of air-dried clay that would equal $\frac{1}{2}$ gram of oven-dried clay (the amount used).

When the clay was poured into the Enslin sorption apparatus, it was poured against a spatula so that it would be fairly evenly distributed over the surface of the porous plate. The ground-glass joint was tapped with the spatula to level off the ridges. The cover was placed over the ground-glass joint to reduce evaporation to a minimum. The readings were taken from the pipette at 0, $\frac{1}{4}$, $\frac{1}{2}$, 1, 2, 4, 8, 15, 30, 60, 120, 240, 480, 900, etc., minutes and made to the nearest 0.01 ml., as the accuracy of the reading would be ± 0.01 ml. The time was plotted logarithmically and the adsorbed moisture was plotted arithmetically on semilogarithmic paper. At the end of the adsorbing period, in order to check the accuracy of the method, the clay was taken from the Enslin apparatus and the moisture content was measured. The moisture as determined by the gravimetric method and the moisture as determined from the sorption curve were within a few percent of each other, the latter usually being slightly higher.

ANALYTICAL DATA

Plastic Limits

The plastic limits for the homoionic montmorillonites range from 51 percent moisture for magnesium montmorillonite-2 to 97 percent for sodium

TABLE II.—ATTERBERG PLASTIC LIMITS

Adsorbed cations	M-1	M-2	M-3	M-4
Ca ⁺⁺	65	65	63	79
Mg ⁺⁺	59	51	53	73
K ⁺	57	57	60	76
NH ₄ ⁺	75	75	60	74
Na ⁺	93	89	97	86
Li ⁺	80	59	60	82

montmorillonite-3. The order of plastic limits (Table II) for homoionic montmorillonites with various cations is $\text{Na} > \text{NH}_4 \geq \text{Li} \geq \text{Ca} > \text{Mg} \geq \text{K}$. The plastic limits for homoionic montmorillonites vary as follows: Montmorillonite-1, $\text{Na} > \text{Li} > \text{NH}_4 > \text{Ca} > \text{Mg} \geq \text{K}$; montmorillonite-2, $\text{Na} > \text{NH}_4 > \text{Ca} > \text{Li} > \text{K} > \text{Mg}$; montmorillonite-3, $\text{Na} > \text{Ca} \geq \text{NH}_4 = \text{K} = \text{Li} > \text{Mg}$; and montmorillonite-4, $\text{Na} > \text{Li} > \text{Ca} > \text{K} \geq \text{NH}_4 \geq \text{Mg}$. The plastic limits for montmorillonite-4 homoionic samples vary less than those of the other three. M-4 has a variation of only 13 between the high and low limits, whereas M-1, M-2, and M-3 vary 36, 38, and 44 units, respectively. Calcium and sodium give consistently higher limit values than magnesium and lithium, respectively. Ammonium tends to give higher limits than potassium. M-1, M-2, and M-3 have about the same plastic limits for calcium, magnesium, and potassium.

The boundary between the plastic state and the non-plastic state was not as sharp for sodium and lithium montmorillonites as for the other homoionic montmorillonites, indicating that the transition from nonplastic to plastic is not as sharp.

Liquid Limits

The liquid limits of the montmorillonites (Table III) range from 180 for potassium montmorillonite-4 to 700 for sodium montmorillonite-3. The liquid limits have the following order for the homoionic samples: Montmorillonite-1, $\text{Li} > \text{Na} > \text{NH}_4 > \text{Ca} > \text{K} \geq \text{Mg}$; montmorillonite-2, $\text{Li} > \text{Na} > \text{Mg} \geq \text{Ca} \geq \text{K} > \text{NH}_4$; montmorillonite-3, $\text{Na} > \text{Li} > \text{NH}_4 > \text{K} > \text{Ca} > \text{Mg}$; and montmorillonite-4, $\text{Li} > \text{Na} > \text{NH}_4 \geq \text{Mg} \geq \text{Ca} > \text{K}$.

TABLE III.—ATTERBERG LIQUID LIMITS

Adsorbed cations	M-1	M-2	M-3	M-4
Ca ⁺⁺	166	155	177	123
Mg ⁺⁺	158	199	162	138
K ⁺	161	125	297	108
NH ₄ ⁺	214	114	323	140
Na ⁺	344	443	700	280
Li ⁺	638	565	600	292

Montmorillonite-3 has the widest range of liquid limits — 162 for Mg to 700 for Na. For montmorillonite-1, the liquid limit range is 158 for Mg to 638 for Li. For montmorillonite-2, the liquid limits range from 114 for NH_4 to 565 for Li. For montmorillonite-4, which has the least spread between the high and low liquid limits, the values are 108 for K to 292 for Li. The liquid limit for lithium montmorillonite-1 is almost twice as great as that for sodium montmorillonite-1, and the liquid limit for montmorillonite-2, for the lithium sample is one-fourth higher than that for the sodium sample. In contrast, for montmorillonite-3, the liquid limit of the sodium sample is higher by 100 units than that for the lithium sample. The data in Table III show that lithium montmorillonites tend to give higher liquid limits than the sodium samples; ammonium higher than potassium; and calcium and magnesium about the same. Most calcium and magnesium montmorillonites have liquid limits which range around 175 ± 25 percent moisture. The range for potassium and ammonium is 100 to 300; for sodium it is 300 to 700, and for lithium it is 600 ± 100 percent moisture.

When the suspensions were prepared for the various homoionic montmorillonites, one important difference was observed between sodium and lithium montmorillonites-2 and -3. Montmorillonite-3 sodium and lithium suspensions set into gel immediately, whereas montmorillonite-2 sodium and lithium suspensions took several days to gel. When stirred, the montmorillonite-3 suspensions set up gels immediately, but montmorillonite-2 sodium and lithium suspensions took several days to set up gels again, even with the loss of water by evaporation. This same phenomenon occurred several times until enough water had been lost by evaporation so that some rigidity remained, after stirring, in montmorillonite-2 sodium and lithium suspensions.

Plastic Indices

The plastic indices (Table IV) range from 32 for potassium montmorillonite-4 to 603 for sodium montmorillonite-3. The plastic indices for the various homoionic montmorillonites have the following order: Montmorillonite-1, $\text{Li} > \text{Na} > \text{NH}_4 > \text{K} > \text{Ca} \approx \text{Mg}$; montmorillonite-2, $\text{Li} > \text{Na} > \text{Mg} > \text{Ca} > \text{K} > \text{NH}_4$; montmorillonite-3, $\text{Na} > \text{Li} > \text{NH}_4 > \text{K} > \text{Ca} > \text{Mg}$; and montmorillonite-4, $\text{Li} > \text{Na} > \text{NH}_4 \approx \text{Mg} > \text{Ca} > \text{K}$. For montmorillonite-1,

TABLE IV. — ATTERBERG PLASTIC INDICES

Adsorbed cations	M-1	M-2	M-3	M-4
Ca^{++}	101	90	114	44
Mg^{++}	99	148	109	65
K^+	104	68	237	32
NH_4^+	139	39	263	66
Na^+	251	354	603	194
Li^+	558	506	540	210

the plastic indices range from 99 for magnesium to 558 for lithium; for montmorillonite-2, from 39 for ammonium to 506 for lithium; for montmorillonite-3, from 109 for magnesium to 603 for sodium; and for montmorillonite-4, from 32 for potassium to 210 for lithium. Lithium montmorillonite-1 has a plastic index about 2.2 times greater than sodium montmorillonite-1, and for montmorillonite-2, lithium gives a plastic index 1.4 times higher than sodium. However, for montmorillonite-3, sodium gives a plastic index which is 1.1 times higher than lithium; and for montmorillonite-4, the plastic index for lithium is 17 units higher than that for sodium. The tendency is for ammonium montmorillonites to have higher plastic indices than the potassium montmorillonites.

Montmorillonite-4, which has a low cation-exchange capacity, has much lower plastic indices than do the other montmorillonites when comparing samples with the same cations. Montmorillonite-3, which is the naturally high-swelling montmorillonite, has much higher plastic indices for NH_4 and K than the montmorillonites which do not swell appreciably in the natural state.

The plastic indices for most lithium montmorillonite are probably 525 ± 35 units; for sodium, 400 ± 200 ; for potassium, 125 ± 100 ; for ammonium, 150 ± 125 ; for magnesium, 125 ± 25 ; and for calcium, 100 ± 25 .

Slopes for the Liquid-Limit Lines

The slope angles for homoionic montmorillonites (Table V) range from 4° for calcium montmorillonite-4 to 74° for lithium montmorillonite-3. Three samples, sodium, ammonium and lithium montmorillonite-3, have slopes between 70° and 75° . Only three other samples have slopes greater than 45° : they are sodium and lithium montmorillonite-2 and lithium montmorillonite-4. Four others have slopes greater than 35° — sodium, lithium, and calcium montmorillonite-1 samples, sodium montmorillonite-4.

The slopes for the homoionic samples of each montmorillonite are as follows:

Montmorillonite-1: $\text{Li} > \text{Na} > \text{Ca} > \text{Mg} = \text{K} > \text{NH}_4$

Montmorillonite-2: $\text{Li} = \text{Na} > \text{Mg} > \text{Ca} > \text{NH}_4 > \text{K}$

Montmorillonite-3: $\text{Li} > \text{Na} > \text{NH}_4 > \text{Ca} > \text{Mg} > \text{K}$

Montmorillonite-4: $\text{Li} > \text{Na} > \text{Mg} > \text{NH}_4 > \text{K} > \text{Ca}$

TABLE V. — ANGLE SLOPE OF LIQUID-LIMIT LINE

Adsorbed cations	M-1	M-2	M-3	M-4
Ca^{++}	39°	20°	26°	4°
Mg^{++}	17°	32°	23°	11°
K^+	17°	5°	19°	6°
NH_4^+	13°	9°	70°	8°
Na^+	35°	59°	73°	44°
Li^+	37°	59°	74°	48°

Lithium and sodium montmorillonites tend to have slope angles greater than 35° ; potassium and ammonium montmorillonites, less than 20° ; and calcium and magnesium montmorillonites, between 20° and 40° .

Water Sorption

The sorption curves are plotted as semilogarithmic graphs, time along the logarithmic (abscissa) scale and adsorbed moisture along the arithmetic (ordinate) scale. A straight line indicates that the average sorption rate is equal to one-half the sorption rate of the time interval preceding it and twice the average sorption rate of the time interval following it. If a curve turns toward the vertical, either the average sorption rate has increased or the sorption rate did not decrease to half the average sorption rate of the preceding time interval. If a curve turns toward the horizontal, the average rate of sorption is less than half the average rate of the preceding time interval.

For descriptive purposes, normal sorption rate will herein be considered as that decrease in rate which will give a straight line with one scale logarithmic and the other scale arithmetic. Sorption rates which cause the curves to turn toward the vertical (ordinate) will be considered above normal, and sorption rates which cause the curve to turn toward the horizontal (abscissa) will be considered below normal.

The curves for montmorillonite-1 (Fig. 2) indicate that for the various homoionic samples the sorption rate is slow at first, having insignificantly different rates of sorption; but after two minutes the rates of sorption begin to vary, calcium having a faster rate than the other cations. After two minutes the relative rates of sorption for montmorillonites-1 samples are: $\text{Ca} > \text{Li} > \text{Mg} > \text{K} > \text{NH}_4 > \text{Na}$. Calcium montmorillonite-1 has an almost normal rate of sorption from 1 to 15 minutes; then it decreases to a considerably slower rate. The sorption rate for lithium montmorillonite is above normal from 2 to about 30 minutes, when the line becomes almost straight (normal). Almost normal sorption takes place between 30 and 120 minutes, which is between 144 and 346 percent moisture. Then the sorption rate decreases, but establishes a new normal sorption rate which is less than the one preceding. The sorption rate for magnesium montmorillonite-1 is slightly above normal from $\frac{1}{2}$ to 80 minutes, after which it drops to below normal.

For the potassium montmorillonite-1, the water sorption was about the same as that for the magnesium from 1 up to 60 minutes; the curve remained normal from 60 to about 150 minutes, when the sorption rate decreased slightly below normal. The sorption rates for sodium and ammonium montmorillonite-1 were about the same up to 30 minutes and 60 percent moisture, when the sorption rate for ammonium became a little more rapid. The ammonium curve was about normal from 120 minutes and 134 percent moisture to 480 minutes and 268 percent moisture, when

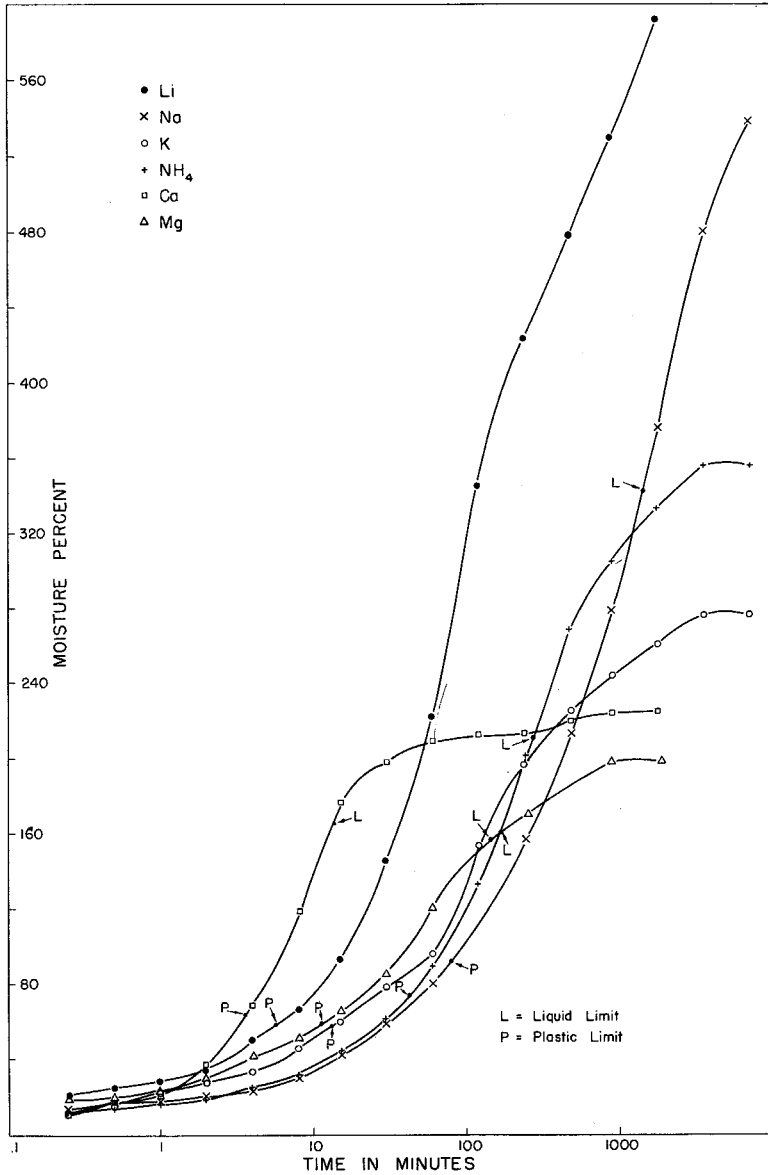


FIGURE 2.— Water sorption curves for homoionic montmorillonites — 1.

its sorption rate decreases below normal. The curve for sodium becomes normal at about 240 minutes and 150 percent moisture.

The total percentage of moisture taken up by homoionic montmorillonite-1 at the end of 900 to 14,400 minutes is $\text{Li} > \text{Na} > \text{NH}_4 > \text{K} > \text{Ca} > \text{Mg}$.

The curves in Figure 3 indicate that the initial water sorption was much more rapid for homoionic montmorillonite-2 than for homoionic montmorillonite-1. The curves for calcium and magnesium montmorillonite-2 are almost normal for the first 30 seconds, and then the sorption rate is above normal from $\frac{1}{2}$ to 2 minutes. After 2 minutes and moisture content of 149 percent the rate of water sorption for calcium montmorillonite-2 decreases slightly below normal to 30 minutes and 247 percent moisture; then the sorption rate decreases rapidly, the line becoming almost horizontal. After 4 minutes and a moisture content of 189 percent, the magnesium montmorillonite-2 has a much faster decrease in the rate of sorption than its calcium equivalent. The sorption rate for sodium montmorillonite-2 is slower than for its calcium and magnesium equivalents and the curve indicates that above normal sorption begins at 1 minute and continues to 15 minutes and a moisture content of 225 percent. Below normal sorption begins after 15 minutes and continues to 60 minutes, when above normal sorption begins again and continues to 1,190 percent moisture and 14,400 minutes. The ammonium, lithium, and potassium montmorillonites adsorbed about the same quantity of moisture for the first minute and then they began to adsorb above normal amounts of moisture, but at different rates, ammonium having the most rapid rate, followed by potassium and then by lithium with a much slower rate. The relative rates of sorption for homoionic montmorillonite-2 (Fig. 3) are $\text{Ca} > \text{Mg} > \text{Na} > \text{NH}_4 > \text{K} > \text{Li}$. The ammonium curve is slightly below normal at 15 minutes and 200 percent moisture, and the rate decreases to 288 percent moisture and 120 minutes, when the rate of sorption again turns above normal. The potassium curve turns below normal between 15 and 30 minutes and continues to 440 minutes and 222 percent water, when it turns to above normal again, to 760 minutes and 278 percent moisture. The total sorption for the homoionic montmorillonites is $\text{Na} > \text{Li} > \text{NH}_4 > \text{Ca} > \text{K} > \text{Mg}$.

For all samples of montmorillonite-3 (Fig. 4), the initial sorption rate is slow for the first 2 to 4 minutes. After 2 minutes the sorption rate for lithium montmorillonite-3 increases greatly above the normal and establishes a new normal from which it deviates only a little, first decreasing slightly and then increasing. After 4 minutes the sorption rate for magnesium montmorillonite-3 increases above normal less sharply than its lithium equivalent to establish a new normal. Beginning after about 60 minutes the sorption rate begins to decrease below the second normal, but the new normal line is steeper than the initial curve. Sodium, ammonium, potassium, and calcium montmorillonite-3 begin increasing the normal sorption rate between 2 and 4 minutes, the increase being more gradual than for the lithium and magnesium equivalents. At the end of 240 minutes, the rate for calcium

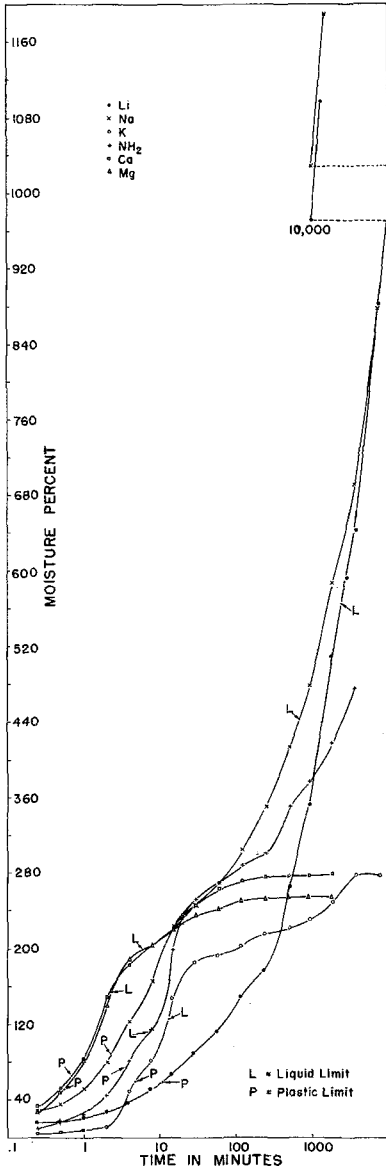


FIGURE 3. — Water sorption curves for homoionic montmorillonites — 2.

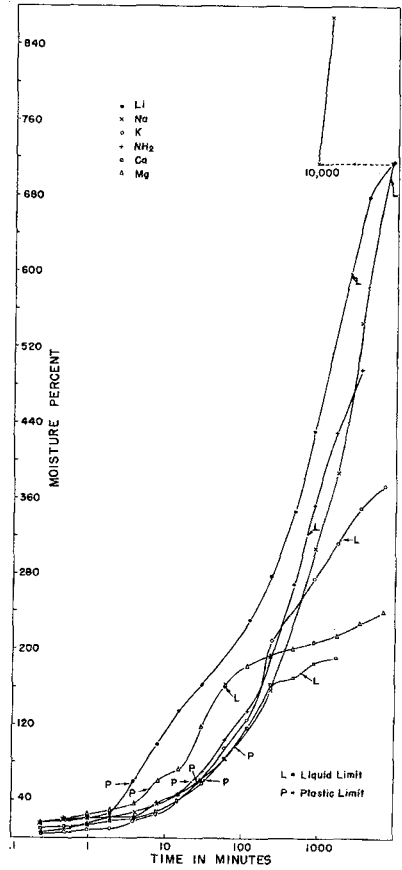


FIGURE 4. — Water sorption curves for homoionic montmorillonites — 3.

montmorillonite-3 decreases rapidly. The relative rates of sorption for homoionic montmorillonite-3 and the total sorption is $Na > Li > NH_4 > K > Mg > Ca$.

For homocationic montmorillonite-4 (Fig. 5), the sorption rates were rapid at first, taking up more than half the moisture in the first minute, except for lithium and sodium montmorillonite-4. In the first minute the rates of sorption are $Ca > Na > NH_4 > Mg > K > Li$. Calcium montmorillonite-4 sorption decreases considerably to establish a new normal after 15 seconds; ammonium montmorillonite-4, after 30 seconds; and mag-

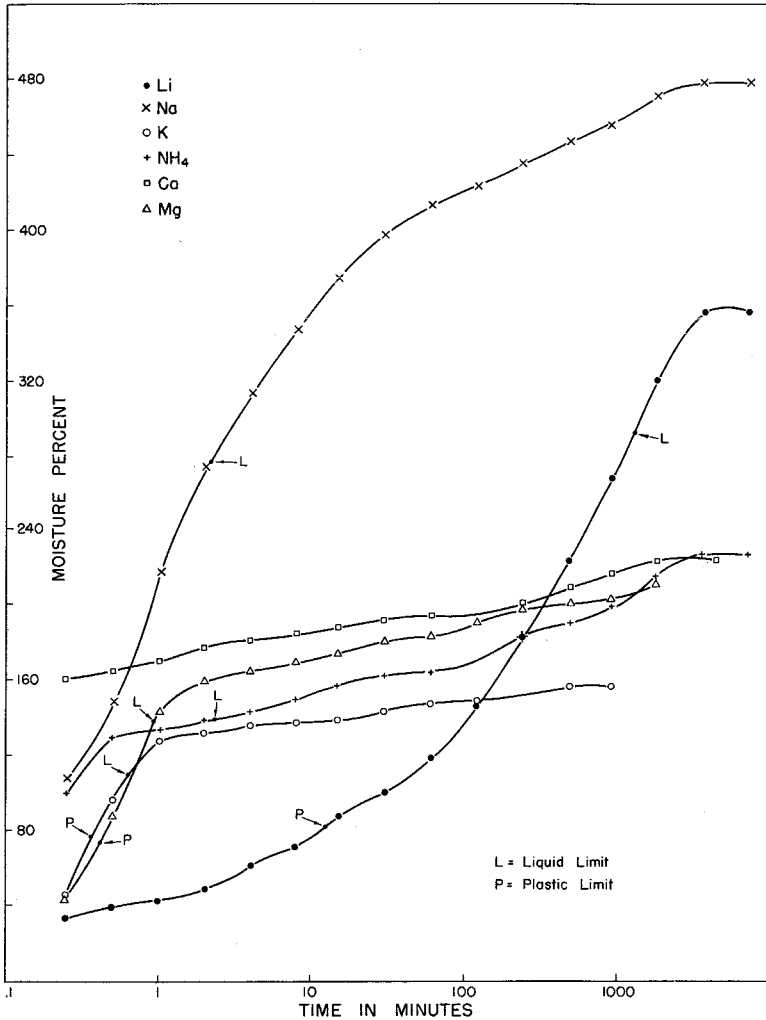


FIGURE 5.—Water sorption curves for homoionic montmorillonites—4.

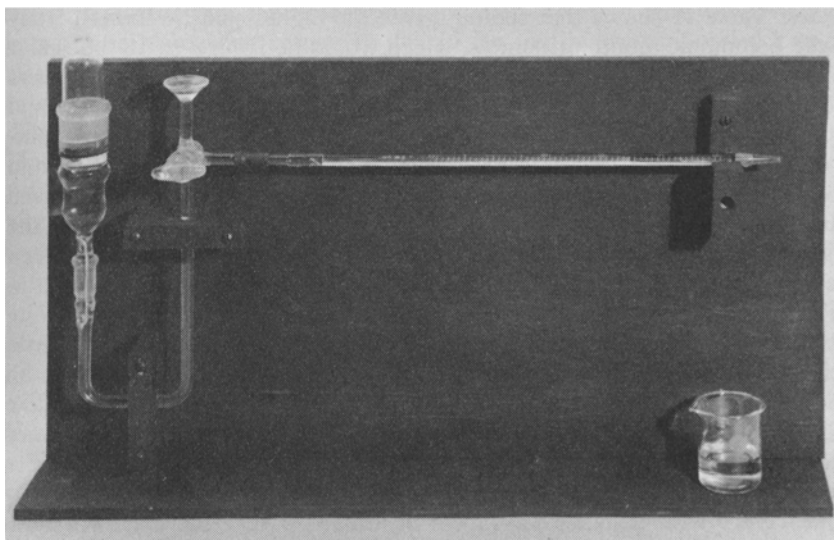


FIGURE 6. — Enslin water sorption apparatus.

nesium and potassium montmorillonite-4, after 1 minute. Sodium montmorillonite-4 adsorbs water at a much faster rate than lithium montmorillonite-4. The total amount of water taken up in 900 minutes by homoionic montmorillonite-4 is $\text{Na} > \text{Li} > \text{Ca} > \text{Mg} > \text{NH}_4 > \text{K}$.

DISCUSSION

Plastic Limit

If it is assumed that all the water adsorbed between the clay mineral flakes, the plastic limit data (Table II), according to the values used by Hendricks, Nelson and Alexander (1940, p. 1459), are calculated to be between 5 and 10 molecular water layers,† depending on the cations. From the data in Table II, the plastic limits for sodium montmorillonites are calculated to be about 9 or 10 water layers; on the other hand, for such cations as calcium and magnesium, they range from 5 to 8. These values are high, as some water would be required to fill voids.

Norrish (1954, p. 256) has found that lithium montmorillonites take up water one molecular layer at a time up to 4 molecular water layers and then jump to 9 molecular water layers, and that sodium montmorillonites take up water stepwise to 3 water layers and then jump to 10 water layers. This can explain the higher plastic limits for sodium and lithium montmoril-

† Hendricks, Nelson and Alexander (1940, p. 1459) state that 0.1 gram of water for each gram of clay is equivalent to a single molecular water layer per unit cell of montmorillonite.

lonites. Table II shows that sodium gives the highest plastic limits of any of the homoionic montmorillonites, which would be from 8 to 10 molecular layers thick if all the water was adsorbed between the montmorillonite layers and evenly distributed between them. From the data in Table II, it would appear that there is not enough water for every sheet of sodium montmorillonite to have 10 molecular water layers and for every sheet of lithium montmorillonite to have 9 molecular layers of water between them, even considering that the void spaces were not occupied with water. Since the void spaces are present and are filled, there is less absorbable water between the layers. Therefore, from Norrish's data (1954, p. 256) and the data in Table II, it would appear that the plastic limits for sodium montmorillonite are obtained when just enough of the montmorillonite sheets have 10 molecular water layers between them to produce continuous liquid water film when shear stresses are applied (which causes the montmorillonite to flow plastically) and the remaining montmorillonite layers contain 3 rigid molecular water layers. There are probably some lithium montmorillonite sheets which have 4 rigid molecular water layers and enough montmorillonite layers with 9 molecular layers of water so that the clay will flow plastically when stresses are applied.

Norrish (1954, p. 257) also found that for magnesium and calcium montmorillonites the spacing increases from 2 to a maximum of 3 molecular water layers, and that potassium and ammonium montmorillonites do not increase in spacings above 2 water layers even in a large excess of water.

Hendricks, Nelson and Alexander (1940, p. 1464) postulated that for magnesium and calcium montmorillonites, the first step is the hydration of the magnesium and calcium ions with 6 molecules of water, which was followed by the completion of the water layer, that lithium hydrated with 3 molecules of water, and that sodium and potassium did not hydrate.

It appears that with their higher hydration energies, calcium and magnesium montmorillonites should make the same jump that sodium and lithium make if all the cations were hydrated. From the data, it would appear that calcium and magnesium ions, which fit into the hydration network on the surface of the clay lattice, have used up so much of their hydration energy by hydrating at the same time the clay surface hydrated that the jump is not possible; or another possibility might be that the divalent ions would tend to hold the flakes together with their high charge. On the other hand, sodium did not hydrate when the first 3 layers of water entered between the montmorillonite layers, and this being true, the jump from 3 to 10 water layers could be explained by the hydration of the sodium ion. Since lithium has a higher hydration energy than sodium, it would appear that it should make just as large a jump, but because it is already partially hydrated it may not have the energy to do so. Because potassium and ammonium have lower hydration energies, they may not have enough energy to overcome the attracting forces after the clay surface has hydrated.

Hendricks and Jefferson (1938, pp. 863-870) and Macey (1942, pp. 117-

118) postulated that the first layers of water are rigid with the structure, in a manner somewhat similar to that of ice, and hydrogen-bonded ‡ to the clay surface. The electron diffraction data of Forslund (1948, p. 13) indicate an ice structure on the surface of the montmorillonite, and the density data of de Wit and Arens (1950, p. 62) suggest that the ice structure of Macey (1942, p. 118) is most likely. According to Grim and Cuthbert (1945b, p. 90), the rigid water has a definite thickness. From Norrish's work (1954, pp. 256-257), it would appear that the rigid layers would be 4 molecules thick for lithium, 3 for sodium, magnesium, and calcium, and 2 for potassium and ammonium.

Thiemecke (1936, p. 69) points out that the transition from the nonplastic to plastic state is rather sharp. Grim (1948, p. 9) gives further evidence to support Thiemecke's observations by showing that the consumption of power to extrude illite and kaolinite clays in the nonplastic state is high. When the plastic limit is reached, the power consumption drops sharply with a slight addition of water. According to Grim (1948, p. 9), "the plastic condition develops in a clay-water system when there is enough water to supply all the rigid water that can develop on available surfaces and a little more water that has poor or no orientation to act as a lubricant between the flakes."

Grim (1948, p. 9) also points out that the transition between the rigid and nonrigid water may be abrupt or somewhat gradual. During this study it was found that the plastic limit was not as sharp for the sodium and lithium montmorillonites as for the other homoionic montmorillonites. It is believed that the reason for the less abrupt transition for lithium and sodium montmorillonites is that after the rigid water requirements are satisfied 5 more water layers are required for lithium montmorillonites and 7 more for the sodium ones. Also more water is required for the void spaces other than those between the montmorillonite layers. The transition of calcium, magnesium, potassium, and ammonium montmorillonites should be rather sharp (owing to the fact that only one water layer is required), which was borne out by the observations made while measuring the plastic limits.

Another factor in raising or lowering the plastic limit, though only slightly, is the degree of orientation of the particles. If the particles are well oriented and their surfaces parallel, less water will be required because the less well oriented samples will have more void space other than that between the clay flakes.

In summary, the data indicate that the plastic state begins when enough water is put into the system to fill all the pore space and to supply all the montmorillonite layers as well as the rigid layers, plus a slight additional amount.

‡ Waring and Custer (1954, p. 2060) indicate that magnetochemical evidence suggests that the hydrogen bond occurs as simple electrostatic attraction. In my opinion the hydrogen bond is a van der Waal's bond, which can be defined.

The Plastic State and Swelling

The data on the plastic and swelling properties suggest that the clay-water system consists of the clay mineral with its flat surfaces, rigid water only a few molecular layers thick which has the structure of ice, water which has the properties of both rigid water and fluid water, and the cations which lie somewhere on or between the clay minerals in the water structure.

The data indicate that the layers of water which make up the plastic range have both rigid and fluid properties. For sodium and lithium montmorillonites, Norrish (1954, pp. 256-257) has found that after the jump from 3 to 10 and 4 to 9 water layers, respectively, water then entered stepwise between the surfaces. He did not observe this phenomenon for the other homoionic montmorillonites, but the data suggest that water enters between at least some of the clay mineral surfaces. Norrish considers that the second stepwise sorption of water is the development of the diffuse double layer and that the water enters as a result of the osmotic forces associated with the cations. Macey (1942, p. 118), on the other hand, considers that the ice structure of the first layer of water is almost perfectly crystalline because it fits almost perfectly on the hexagonal oxygen network of the Si-O sheet; that there will be a tendency for the structure to build outward; and that this tendency will be opposed by the thermal agitation of the water molecules and by the ions present. According to Forslund (1948, p. 9), the effects of the ions are twofold: they cause a break of the hydrogen bonds and deformation of the ice lattice structure.

Both the plastic and swelling data (Table III and IV, and Figs. 2, 3, 4, and 5) indicate that the water up to the limit of swelling has some rigidity. It seems logical that this water would have a structure tending to be a continuation of the rigid ice structure on the surface of the clay minerals and that the water layers are either added by osmotic forces by the cations, as suggested by Norrish (1954, p. 257) or that they tend to grow outward in the ice structure and are hindered by thermal agitation, as suggested by Macey (1942, p. 118), and by cations, as suggested by both Macey (1942, p. 118) and Forslund (1948, p. 10).

Slopes of the Liquid-Limit Lines

The slopes of the liquid-limit lines (Table V) indicate that the steeper or greater the angle of the slope, the more readily the clay will set up into a gel. In general, sodium and lithium montmorillonites gel readily and the slopes are 70° and more. There is considerable variation between different montmorillonites in this property; sodium and lithium montmorillonite-2 form a gel, but the formation is very slow, requiring several days, ammonium montmorillonite-2 does not appear to have any appreciable gelling properties, and ammonium montmorillonite-3 gels rapidly.

The gelling properties of the other homoionic montmorillonites are quite low, and their liquid-limit slope angles are small.

It is suggested that the angle of slope of the liquid-limit line is a measure of the thixotropic properties of a clay.

Structure and Properties of Montmorillonites

The data (Table III, IV, and V, and Figs. 2, 3, 4, and 5) indicate that the structure of the clay minerals is one of the more important factors in determining the clay-water systems. If the cations were the sole factors influencing the properties of clay minerals, two clays with the same cation exchange composition and capacity should have the same properties, but they do not.

Thus, montmorillonite-3, which is a sodium montmorillonite in the natural state, has very high water-sorption, thixotropic, and plastic properties when it carries either sodium, lithium, or ammonium; whereas montmorillonite-1, which has the same cation exchange capacity, has much lower water-sorption, thixotropic, and swelling properties when it carries the same cations.

The data suggest that the montmorillonites are different structurally and that the structural aspect of the clay particle is at least as important as the cation in determining the properties of the clay. Structure is probably determined by the location of the substitutions within the lattice, and by the distribution of the substitutions. For example, the substitutions may be concentrated in certain sheets, in certain areas of the sheet, or evenly distributed in the sheet and evenly distributed throughout the sheets. Certain substitutions in a sheet could produce lengthening of certain parts of the sheet. The substitution of Al^{+++} for Si^{++++} would have a tendency to lengthen the tetrahedral layer, and the substitution of Mg^{++} , Fe^{+++} , and/or Fe^{++} for Al^{+++} would have a tendency to lengthen the octahedral layer, thus putting more strain on the tetrahedral layers. Substitution in both layers would probably tend to equalize the strain but would tend to lengthen the lattice. The strain on the tetrahedral layer might interfere with the orientation of the water. The ideal structure on which water layers have the most perfect fit is probably sodium and lithium montmorillonite-3, on which the water layers can build outward from the clay mineral surface with amazing rapidity.

CONCLUSIONS

1. The structure of the clay minerals seems to be the most important factor in determining the properties of clay-water systems and the cation exerts a secondary influence by which it can only act to alter the properties established by the structure of the clay mineral.
2. The plastic state begins when enough water is put into the clay-water system to fill all the pore space and to supply all the montmorillonite layers with water adequate for the rigid layers plus a slight additional amount.
3. The first layers of water on the surface are rigid and have a definite structure.

4. The structure of the water layers in the plastic and in the viscous liquid regions probably is similar to that of the rigid water but has more defects (the farther from the surface, the more defects), making these structures less rigid.

5. The structure can be easily broken by shearing stresses, but can set up immediately at low concentrations of water, more slowly at higher concentrations. The length of time would depend on the concentration of the clay-water system and the structure of the clay mineral.

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