ADSORPTIVE AND SWELLING PROPERTIES OF CLAY-WATER SYSTEM

By Isaac Barshad *

INTRODUCTION

The subject of the adsorption and swelling properties of the clay-water system may be divided into three parts: (1) clay-water vapor system, (2) clay-liquid water system in the gel state, and (3) clay-liquid water system in the fluid state, i.e. pastes and sols.

In studying the swelling of clays in relation to hydration, it is necessary to distinguish between the two kinds of swelling encountered; namely, the intramicellar swelling which involves the expansion of the crystal lattice itself, commonly known as the interlayer or interlamellar expansion, as found in montmorillonite, vermiculite-like, and in some of the hydrous mica clay minerals; and intermicellar swelling which involves an increase in volume due to adsorption of water molecules between individual clay particles. Intramicellar swelling can be identified and measured only by x-ray analysis, whereas the intermicellar swelling can be determined from a measurement of the total increase in volume of the clay body or of the clay-bearing material with apparatus designed for this purpose (Freundlich et al. 1932; Keen and Raczkowski 1921; von Ensline 1933; Winterkorn and Baver 1934).

The common feature among the clay minerals is their platy surfaces which consist either of oxygen ions organized into an hexagonal network, or of hydroxyl ions organized into a closely packed network. The oxygen surfaces characterize the montmorillonitic and the micaceous clay minerals, whereas both oxygen and hydroxyl surfaces characterize the kaolinitic and the chloritic clay minerals.

One of the fundamental differences among the clay minerals lies in the amount and kind of exchangeable cations present on their surfaces, and in the seat of the excess negative charge of the crystal lattice which these cations neutralize (Hendricks 1945; Ross and Hendricks 1945). The scarcity of the exchangeable cations relative to the number of the surface oxygen ions which bear the negative charge (the ratio of the oxygen ions to the cations may range from 3 to 1, as in the micas, to 18 to 1, as in some of the montmorillonites) has been advanced as the possible cause for the polarization of these surfaces and consequently for their reactivity with polar molecules (Barshad 1952).

One of the important features, insofar as water adsorption is concerned, by which the various clay minerals may be differentiated, is the extent of the absorbing surface. Table 1 is a summary of the extent of the external surfaces of several of the clay minerals as measured by N_2 and ethane gas adsorption, and of the extent of the internal surfaces of montmorillonite as measured by glycol adsorption (Dyal and Hendricks 1950; Keenan et al. 1951; Mooney et al. 1952, 1952a; Nelson and Hendricks 1942). The external surfaces of the mica-like clay minerals and those of montmorillonite are in the same range of values, but that of kaolinite is somewhat less; the ratio of the internal to the external surface in the montmorillonites ranges from 9 to 40.

*Table 1. External and internal surface areas of some clay minerals.**

Clay mineral	External surface: By ethylene glycol adsorption	External surface: By ethane or N_2 adsorption	Internal surface by ethylene glycol adsorption	Ratio of internal to external surfaces
	sq. m/g	sq. m/g	sq. m/g	
Montmorillonite				
Range	20–80	30–90	700–800	9–40
Average	50	48	750	15
Micalike				
Range	75–180	50–100	0	0
Average	130	80	0	0
Kaolinite				
Range	22–37	18–44	0	0
Average	30	29	0	0
Halloysite	37	44		

* Data taken from the following: Dyal and Hendricks, 1950; Keenan, et al., 1951; Mooney, et al., 1952, 1952a; Nelson and Hendricks, 1942.

CLAY-WATER VAPOR SYSTEMS

Early studies of the degree of hydration of clay bearing materials or clays upon exposure to a given vapor pressure disclosed that it is affected by the degree of hydration of the adsorbent prior to exposure (that is, whether the adsorbent gains or loses water during the exposure) (Thomas 1921, 1921a), the aggregate structure of the adsorbent (Thomas 1928), the kind and amount of exchangeable cations on the adsorbent (Anderson 1929, Kuron 1932, Thomas 1928a), the kind and amount of salts and oxides present within the adsorbent (Thomas 1928), and the nature and amount of the clay minerals present in the adsorbent (Alexander and Haring 1936, Keen 1921, Kuron 1932, Puri 1949).

The usefulness of these early studies is somewhat limited because the precise mineralogical composition of the clay minerals studied was not recognized. However, they laid the foundation for later investigations which deal with the specific clay-mineral species of the montmorillonitic and kaolinitic groups. The present review deals mainly with the later investigations.

Many investigators contributed to the elucidation of the relation between intramicellar swelling (that is, the interlayer expansion) and the degree of hydration (Barshad 1949, 1950; Bradley et al. 1937; Hendricks and Jefferson 1938; Hendricks et al. 1940; Hofmann and Bilke 1936; Mering 1946; Mooney et al. 1952, 1952a). The discussion that follows is based on these investigations, but the data presented are taken from Hendricks and Jefferson (1938), Hendricks et al. (1940), and Mooney et al. (1952, 1952a).

The relation between hydration and interlayer expansion can be shown most clearly by expressing the degree of hydration on adsorption isotherms in terms of water molecules per unit cell (i.e. 12 oxygen ions) of the crystal lattice, and indicating the course of expansion by lines drawn across the adsorption isotherms: one line representing expansion equivalent to a unimolecular

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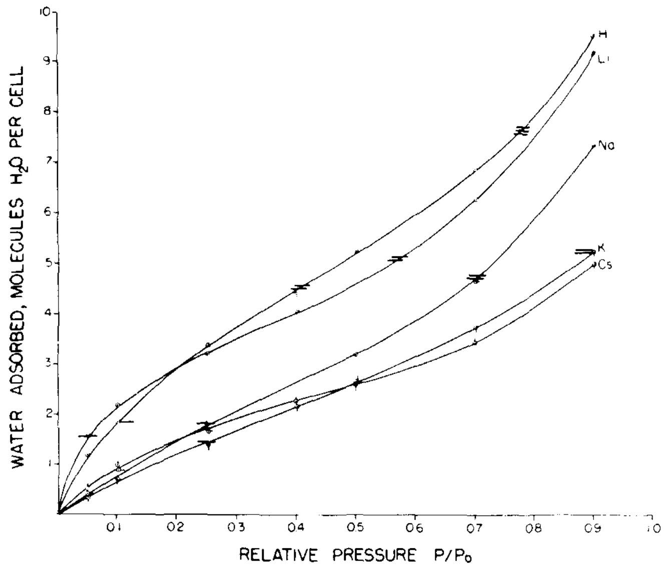

Figure 1. Adsorption isotherms at 30°C of a Mississippi montmorillonite saturated with various monovalent cations.

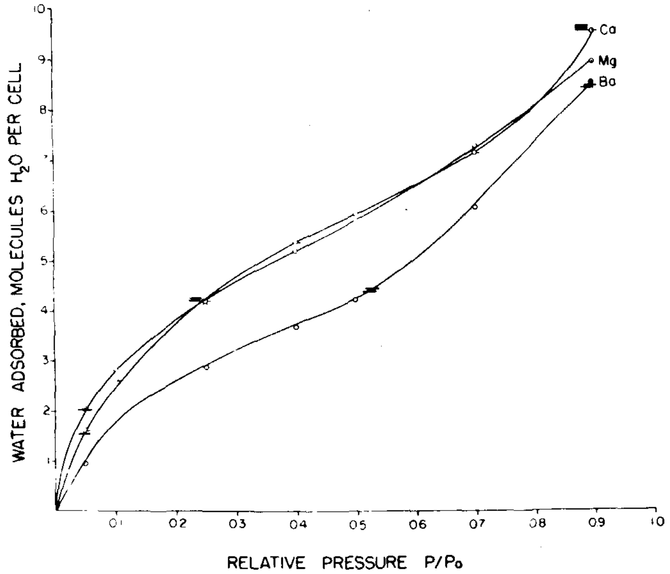

Figure 2. Adsorption isotherms at 30°C of a Mississippi montmorillonite saturated with various divalent cations.

layer of water, two lines representing a dimolecular layer, and three lines representing a trimolecular layer. The possible number of water molecules per unimolecular layer when related to the unit cell may vary from 2 to 4, depending on the nature of the organization of the water molecules with respect to the hexagonal network of the oxygen surfaces (Barshad 1949). Furthermore, the process of interlayer expansion, apart from hydration, may be described as occurring in two distinct steps: the first step consisting in a separation of the oxygen surfaces during the course of which the interlayer cations remain attached to the surfaces; and the second step consisting in a detachment of the cations from the oxygen surfaces through their interaction with water molecules.

Interlayer Expansion in Relation to Hydration. Any one of the adsorption isotherms, as shown in figures 1, 2, 3 and 4, may be chosen to illustrate the course of expansion in relation to hydration. This course is also depicted schematically in figure 5.

The course of hydration and interlayer expansion of dehydrated and contracted montmorillonite particles (1 of fig. 5) along the adsorption isotherm may be described as occurring in five distinct steps.

The first step consists of hydration of the exterior surfaces of the particles to the extent of about 1 to 1.5 water molecules per unit cell of the crystal lattice, which is equal to 50 and 75 mg of water per gram of clay, or 180 and 270 sq. meters of a unimolecular layer of water. As the extent of the external surface of montmorillonite

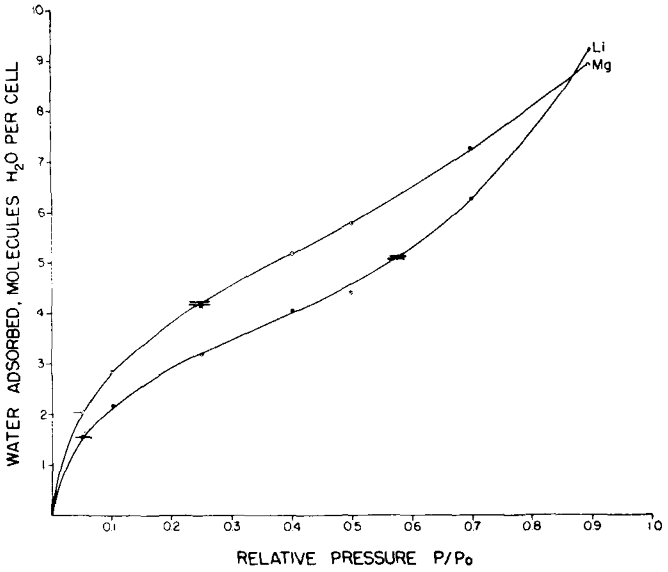

Figure 3. Adsorption isotherms at 30°C of a Mg and a Li saturated Mississippi montmorillonite.

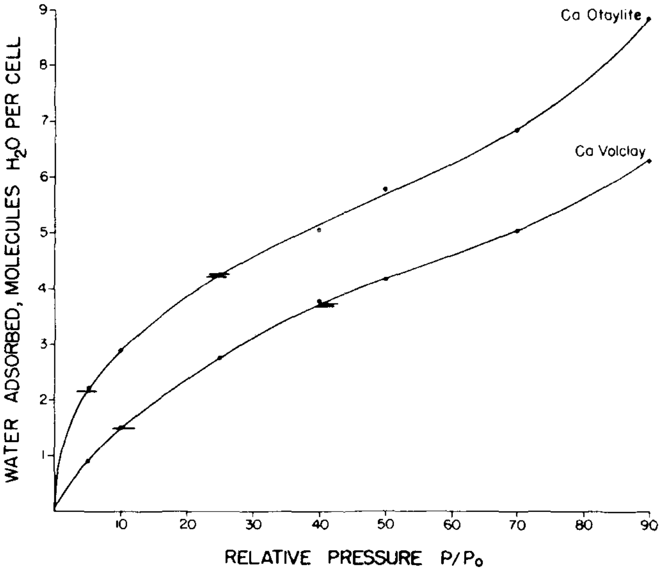

Figure 4. Adsorption isotherms at 30°C of two Ca^{++} saturated montmorillonites of varying cation exchange capacity: Otaylite with 120 me. and Volclay with 90 me. per 100 gm oven dry (100°C) clay.

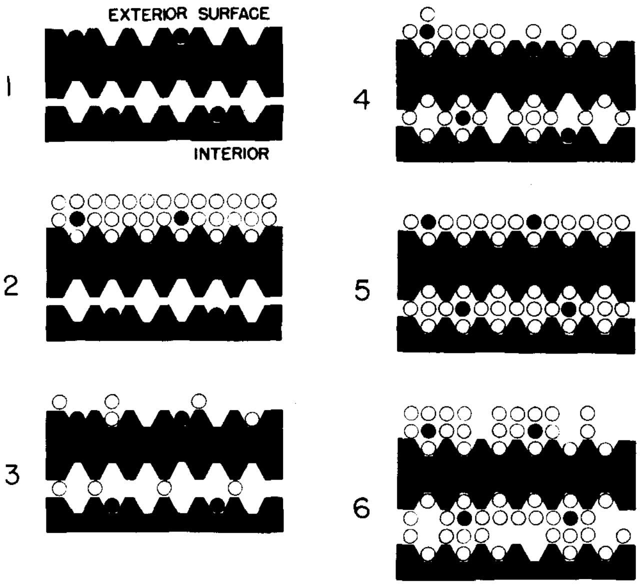

Figure 5. Schematic representation of the hydration and interlayer expansion processes of montmorillonite. Black o = exchangeable cation. White o = water molecules. 1, Anhydrous and contracted stage; 2, the initially hydrated stage; 3, the initially expanded stage; 4 and 5, advanced stages of hydration after the initial expansion; 6, beginning of the second stage of expansion.

particles of the Na^+ form, for example, is about 33 sq. meters per gram (Mooney et al. 1952), it follows that the thickness of the initial water layer on the outside surfaces of the particles in terms of water molecules is from 6 to 9. The exact thickness of this water layer may vary from one form to another but in all cases the initial hydration consists of a building up of a multimolecular water layer prior to interlayer expansion (2 of fig. 5).

The second step consists of an expansion at the interlayer position which is equivalent to a thickness of a unimolecular layer of water; it occurs after the formation of the multimolecular layer of water on the exterior of the particles. The expansion is accompanied by a distribution of the water from the exterior to the interlayer positions of the particles and results in the formation of a discontinuous unimolecular water layer at the interlayer position. The interlayer cations at this stage of hydration still remain attached to the oxygen sheets (3 of fig. 5).

The third step consists of a completion of the interlayer unimolecular water layers, accompanied by detachment of some of the interlayer cations from the oxygen sheets (the extent of the latter varies with the form), and by a reformation of the multimolecular water layer on the exterior surfaces of the particle (4 and 5 of fig. 5).

The fourth step consists of another expansion at the interlayer position which is equivalent to a unimolecular water layer. As in the second step, the expansion is accompanied by a redistribution of the already existing interior unimolecular and the exterior multimolecular water layers with the formation of a discontinuous dimolecular water layer in which the water molecules are grouped around the interlayer cations (6 of fig. 5).

The fifth step consists of a completion of the interior dimolecular water layer and of the reformation of a multimolecular water layer on the exterior of the particles.

The data available at present indicate that no further expansion occurs through adsorption of water vapor. However, as will be shown later, further expansion does occur when the clay is immersed in liquid water.

The appearance during the second and fourth steps of d(001) spacings which do not correspond to a thickness of either a uni- or dimolecular water layer has been interpreted to represent the average thickness of mixed layer structures consisting of either unexpanded and expanded zones or zones of both uni- and dimolecular water layers (Hendricks and Jefferson 1938; Mering 1946).

Interlayer Expansion and Hydration as Affected by the Interlayer Cations. The effect of the interlayer cations becomes apparent when the expansion is considered in relation to the vapor pressure or humidity at which it occurs. In samples saturated with cations of equal charge but varying in size, the larger the ionic radius the higher the relative humidity at which expansion occurs; but the degree of hydration at the beginning of expansion is about equal for all sizes of ions. It is interesting to note that expansion beyond a unimolecular water layer does not take place in the montmorillonites saturated with K^+, Rb^+, or Cs^+ ions. In samples saturated with cations of equal radius but varying charge, the larger the charge the lower the relative humidity at which expansion occurs; but, again, the degree of hydration at the beginning of expansion is about equal for all of the ions (figs. 1, 2, and 3). In samples saturated with the same cation but varying in amount, the larger the number of the cations, the lower the relative humidity at which expansion occurs; but here too, when expansion has taken place, the degree of hydration is about equal for the different montmorillonites (fig. 4).

The importance of the relationship between the vapor pressure, or the relative humidity, and expansion is that it offers a means of evaluating the interlayer attractive forces which hold together the individual lattice layers (Cornet 1950; Katz 1933).

The course of hydration and expansion as outlined above implies that the adsorbed water molecules are in a constant state of motion—particularly during the existence of incomplete uni- or dimolecular water layers. This is also implied by the fact that the adsorbed water present on internal surfaces must enter the interior of the particle by way of its edges. The significance of this mode of entry in relation to adsorption appears when the water adsorption properties of montmorillonite and kaolinite are compared.

WATER ADSORPTION BY KAOLINITE

From tables 2 and 3 it may be seen that the degree of hydration of kaolinite at any given vapor pressure is very much less than that of montmorillonite when the degree of hydration is expressed on a unit-weight basis; but it is considerably higher when expressed on a unit-area basis—particularly in the range where montmorillonite is in an expanded state. The unit-area expression, however, is the more valid one, as water adsorption is a surface reaction. This greater reactivity of the kaolinite surfaces with water may be attributed to two causes:

Table 2. Water adsorption by a Ca-kaolinite and a Ca-montmorillonite at various relative humidities.†

Relative humidity (percent)	Adsorption area m²/g clay		d(001) spacing (Å)	Water adsorption				Exchange cations (me.-/1000m²)	
				(mg/g clay)		(mg/1000m²)			
	K*	M*	M	K	M	K	M	K	M
	27.6	437	12.9	5.5	80	199	183	1.56	1.11
1	27.6	810	14.5	6.5	100	235	124	1.56	1.11
18	27.6	810	14.8	7.9	125	286	154	1.56	1.11
25	27.6	810	15.2	9.3	165	337	204	1.56	1.11
33	27.6	810	15.4	10.8	185	392	228	1.56	1.11
37	27.6	810	15.4	11.5	200	417	247	1.56	1.11

† Data derived from Keenan, Mooney, and Wood (1951) and from Mooney, Keenan, and Wood (1952, 1952a).
* K = kaolinite; M = montmorillonite.

(1) all of the adsorbing surface in kaolinite is on the exterior of the particles, and as a result the water molecules in the vapor phase impinge directly on it; whereas in montmorillonite the larger portion of the absorbing surface is an interior one, and as a result the water molecules in the vapor phase must first be adsorbed on the edges of the particle and then migrate to the interior —a process which tends to retard adsorption; and (2) the larger water adsorbability per unit surface area of the kaolinite could also be attributed, in part, to the larger cation charge per unit area (tables 2 and 3), if it be true that the ability of a surface to adsorb water is proportional to the cation exchange capacity per unit area.

Table 3. Water adsorption by a Na-kaolinite and a Na-montmorillonite at various relative humidities.†

Relative humidity (percent)	Adsorption area (m²/g clay)		d(001) spacing (Å)	Water adsorption				Exchange cations (me.-/1000m²)	
				(mg/g clay)		(mg/1000m²)			
	K*	M*	M	K	M	K	M	K	M
8	18.6	33	10	3.0	20	161	606	1.93	1.11
14	18.6	33	10	4.2	45	226	1364	1.93	1.11
19	18.6	33	10	4.9	65	263	1970	1.93	1.11
24	18.6	440	12.4	5.4	80	290	182	1.93	1.11
32	18.6	440	12.5	6.4	100	344	227	1.93	1.11
38	18.6	440	12.6	7.2	115	387	261	1.93	1.11
60	18.6	810	14.2	8.0	170	430	386	1.93	1.11
70	18.6	810	15.0	10.0	215	534	489	1.93	1.11
80	18.6	810	15.2	13.0	240	698	545	1.93	1.11
90	18.6	810	15.4	20.0	280	1075	636	1.93	1.11
95	18.6	810	15.4	25.0	365	1345	830	1.93	1.11

† Data derived from Keenan, Mooney, and Wood (1951) and from Mooney, Keenan, and Wood (1952, 1952a).
* K = kaolinite; M = montmorillonite.

THERMODYNAMICS OF WATER ADSORPTION AND DESORPTION OF MONTMORILLONITE

Thermodynamic data relating to water adsorption and desorption reflect the course of the changes which the water and the clay undergo during hydration or dehydration.

The thermodynamic values which reflect the changes of the water system in going from the adsorbed state to the free liquid state or vice versa are as follows:

$\Delta\bar{F}_1$ = partial free energy change per gram of water
$\Delta\bar{H}_1$ = partial net heat of desorption or adsorption per gram of water
$\Delta\bar{S}_1$ = partial entropy change per gram of water.

The thermodynamic values which reflect the changes of the clay system in going from the expanded state to the contracted state or vice versa during hydration or dehydration are as follows:

$\Delta\bar{F}_2$ = partial free energy change per gram of clay
$\Delta\bar{H}_2$ = partial net heat of desorption or adsorption per gram of clay.

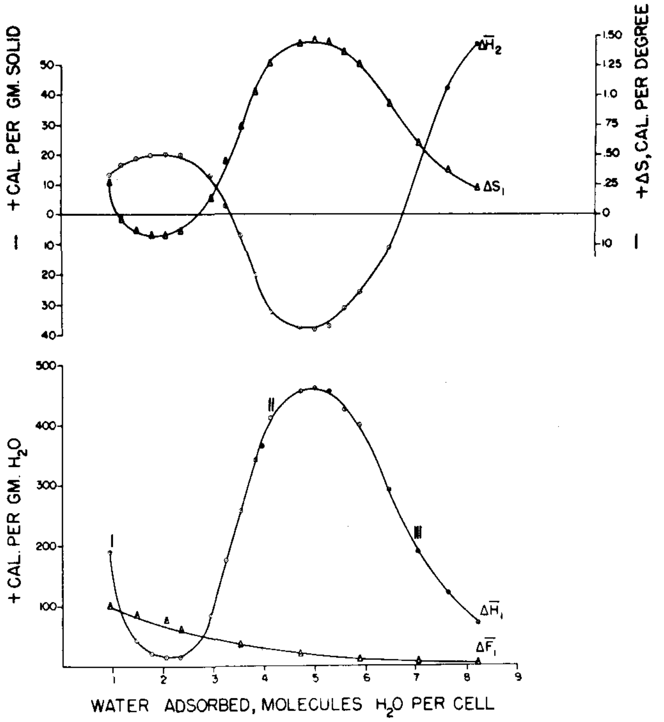

Figure 6. Thermodynamic quantities relating to the desorption of water from a Ba^{++} saturated Mississippi montmorillonite at various stages of hydration and expansion (see text for definition of the quantities).

A definition of these quantities may be found in texts on thermodynamics. Figures 6, 7, and 8 illustrate the type of thermodynamic data obtainable.

The data presented in figure 6, the desorption values for a Ba^{++}-saturated Mississippi montmorillionite, are believed to reflect the course of hydration and expansion as already described. The high $\Delta\bar{H}_1$ value at the moisture content just prior to expansion (end of step 1) reflects an external water layer of well organized water molecules, a large proportion of which are grouped around

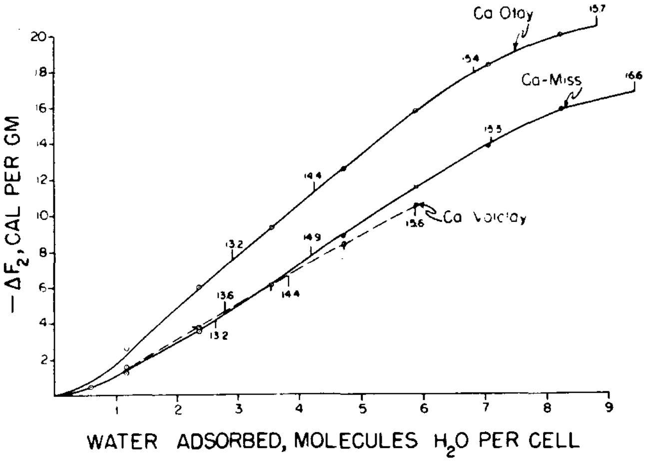

Figure 7. Partial free energy change per gram of the solid of three Ca^{++} saturated montmorillonites of varying cation exchange capacity at various stages of hydration and expansion. The numbers on the curves represent d(001) spacings in Å. The exchange capacities are as follows: Ca (Otay) = 120; Ca (Mississippi) = 110; Ca (Volclay) = 90 me./100 g of dry (110°C) clay.

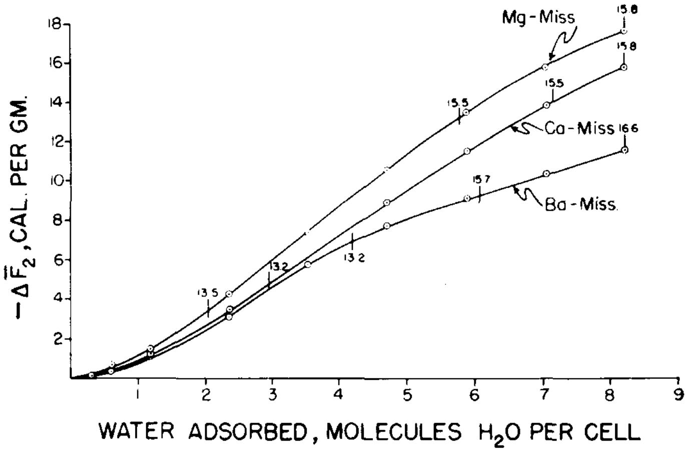

Figure 8. Partial free energy change per gram of solid of a Mg^{++}, a Ca^{++}, and a Ba^{++} saturated Mississippi montmorillonite at various stages of hydration and expansion. The numbers on the curves represent d(001) spacings in Å.

the externally held exchangeable cations. The sudden drop in $\Delta\overline{H}_1$ which follows expansion is believed to reflect the condition resulting from the redistribution of the externally adsorbed water (step 2) with the formation of a discontinuous internal unimolecular layer in which the water molecules are not associated directly with exchangeable cations; that is, the exchangeable cations are still attached to the oxygen surfaces within the cavities of the hexagonal network of oxygen ions (3 of fig. 5). The increase in the $\Delta\overline{H}_1$ which follows an increase in water content reflects the interaction of the water molecules with the exchangeable cations. The decrease that follows the maximum $\Delta\overline{H}_1$ reflects a proportional increase in water molecules which are not associated directly with the exchangeable cations.

The changes in entropy of the water, $\Delta\overline{S}_1$, in going from the adsorbed state to the free liquid state (fig. 6), support the depicted changes in the state of organization of the water molecules presented earlier. For according to the third law of thermodynamics, an increase in entropy reflects an increase in randomness of the water molecules in going from the adsorbed state to the free liquid state, whereas a decrease in entropy reflects a decrease in randomness. Thus the maximum increase in entropy during desorption indicates that the water molecules at that state of hydration were at the maximum state of organization, that is, when grouped around the exchangeable cations; and the maximum decrease in entropy indicates that the adsorbed water molecules were at the lowest state of organization, that is, having a considerable freedom of motion on the adsorbing surface.

The changes in $\Delta\overline{H}_2$, the partial net heat of desorption for the solid state (fig. 6), are believed to reflect the heat of reaction associated with contraction. The positive heat values are interpreted as reflecting the contraction or the coming together of the oxygen sheets, whereas the negative heat values reflect the readsorption of the exchangeable cations by the oxygen

Table 4. Integral net heat of water desorption from two montmorillonites and a vermiculite as affected by total charge on the crystal lattice and water content.

Sample	Cation exchange capacity (me.*)	Water content (g*)	Mean integral net heat (cal/g H_2O)	Integral net heat (cal/g)	
				Wet clay	Dry clay
Na-Vermiculite	200	4.32	670	28	29
Na-Otaylite	120	4.32	450	18	19
Na-Volclay	95	4.32	280	11	12
Na-Vermiculite	200	8.64	555	44	48
Na-Otaylite	120	8.64	295	24	26
Na-Volclay	95	8.64	125	11	12
Ca-Vermiculite	200	17.28	440	65	76
Ca-Otaylite	120	17.28	290	43	50
Ca-Volclay	95	17.28	145	21	25

* Per 100 g. dry (120° C.) material.

Table 5. Mean integral net heat of water desorption from a Mississippi montmorillonite at a given state of hydration as affected by the exchangeable cation.

Exchangeable cation	Water content (g.*)	Mean integral net heat (cal/g H_2O)
Mg^{++}	8.64	360
Ca^{++}	8.64	330
Ba^{++}	8.64	245
H^{+}	8.64	190
Li^{+}	8.64	90
Na^{+}	8.64	100
K^{+}	8.64	40

* Per 100 g. dry clay (120° C.).

sheets; that is, the re-entry of the cations into the cavities of the oxygen layers. Thus at low moisture contents, when the contraction involves the coming together of the oxygen surfaces without involving the readsorption of the exchangeable cations, $\Delta\bar{H}_2$ is positive. Zero $\Delta\bar{H}_2$ reflects the occurence of contraction associated with the readsorption of a part of the exchangeable cations, with the result that the positive and negative heat reactions cancel one another. The negative $\Delta\bar{H}_2$ values indicate that the heat of readsorption of the cations exceeds the heat of contraction.

Since $\Delta\bar{F}_2$ values during water adsorption (figs. 7 and 8) may be interpreted to represent the work done in bringing about expansion and the detachment of the exchangeable cations from the oxygen surfaces, it is not surprising to find that the greater the interlayer charge (fig. 7), the greater is the work done during expansion. The effect of the cation on $\Delta\bar{F}_2$ (fig. 8) appears as follows: For the initial expansion to a thickness equivalent to a unimolecular water layer but without the detachment of the cations from the oxygen surface, the work done is larger the larger the cation, since as pointed out by the author (Barshad 1952), the interlayer attractive forces are larger the larger the exchangeable cation. On the other hand, since expansion equivalent to a dimolecular water layer represents not only the work done in separating the oxygen sheets but also the work done in detaching the exchangeable cation from the oxygen sheets, it is not surprising to find that the total work in the overall process is greater the smaller the cation, since the smaller the cation the stronger the force with which it is attached to the oxygen sheets (Barshad 1952); and consequently the work in detaching the cation is also greater.

The *integral net heat of desorption,* which may be determined by differential thermal analysis (Barshad 1952a), is a useful thermodynamic value as a measure of the total change in energy during water desorption. The effect on this value of such factors as the nature of the exchangeable cation, and the total interlayer charge on the crystal lattice at identical states of hydration and expansion are shown in tables 4 and 5.

CLAY-LIQUID WATER SYSTEM IN THE GEL STATE

The differences among the clays in their capacity to absorb water from the liquid state are as pronounced as from the vapor state.

Several methods are in use for measuring water adsorption and volume changes of a clay or clay-bearing material when brought in contact with liquid water. The apparatus designed by Winterkorn and Baver (1934), Freundlich and co-workers (1932), and von Ensline (1933) is particularly useful for measuring both water adsorption and volume change for small amounts of clay materials, and the Keen-Raczkowski box (1921; Russell and Gripta 1934) is useful for measuring volume changes and water adsorption for large amounts of soil.

The water content at onset of gelation of clays which can be brought into stable suspension may also be determined by evaporating the suspension at a temperature of about 40°-50°C until it sets into a rigid gel. The water and solid contents are then determined by drying a known weight of the gel. From the density of the water and of the clay the total volume, as well as the ratio of the volume of the liquid to that of the solid, may be calculated—assuming that the density of the water is the same as in the free state. The data reported in tables 6, 7, and 8 were obtained in this manner.

Water adsorption and swelling data for two montmorillonite clays are given in tables 6, 7, and 9. The data in table 6 show that gels of montmorillonite, at onset of gelation, contain from 5 to 30 times as much water as solid. The montmorillonite gels saturated with the divalent cations contain from 50 to 100 percent more water than those saturated with the monovalent cations. A striking difference between the two montmorillonites studied appears in their capacity to retain water at onset of gelation. The Wyoming montmorillonite retained nearly twice as much water as the California montmoril-

Table 6. Water content at onset of gelation of two montmorillonites saturated with various cations, in grams H_2O per gram of clay.

Saturating cation	Source of montmorillonite	
	Wyoming*	California**
H^+	13–15	13–15
Li^+	18–20	9–10
Na^+	18–20	9–10
K^+	18–20	9–10
NH_4^+	18–20	9–10
Rb^+	12–14	5–6
Cs^+	12–14	5–6
Mg^{++}	26–30	11–12
Ca^{++}	26–30	11–12
Ba^{++}	26–30	11–12

* Clay Spur, Wyoming.
** Otay, California.

Table 7. Ratio of liquid volume to solid volume at onset of gelation of two montmorillonites saturated with various cations.

Saturating cation	Source of montmorillonite	
	Wyoming	California
H^+	35–40	35–40
Li^+	48–53	24–27
Na^+	48–53	24–27
K^+	48–53	24–27
NH_4^+	48–53	24–27
Rb^+	32–37	13–16
Cs^+	32–37	13–16
Mg^{++}	69–80	29–32
Ca^{++}	69–80	29–32
Ba^{++}	69–80	29–32

Table 8. Water content at onset of gelation of two Na-saturated illites and a Na-saturated kaolinite of varying particle size, in grams H_2O per gram clay.

Sample	Water content
Fithian illite <0.3μ	1.5
Fithian illite 1-0.5μ	0.9
Grundy illite <0.3μ	1.4
Grundy illite 1-0.5μ	1.2
S. C. kaolinite <0.16μ	1.0
S. C. kaolinite 0.3μ-0.5μ	0.7
S. C. kaolinite 1μ-2μ	0.7
S. C. kaolinite >2μ	0.5

S. C. = South Carolina.
μ = micron.

Table 9. Interlayer spacing d(001) at onset of gelation of two montmorillonites saturated with various cations.

Saturating cation	Source of montmorillonite	
	Wyoming	California
	Å	Å
H^+	20.9	19.8
Li^+	diff.*	diff.*
Na^+	diff.*	diff.*
K^+	diff.*	16.9
NH_4^+	diff.*	15.7
Rb^+	15.9	16.0
Cs^+	14.6	12.8
Mg^{++}	19.8	19.5
Ca^{++}	19.4	19.3
Ba^{++}	19.3	19.4

* diff. = diffused and of extremely weak intensities.

lonite in all of its forms, except the H^+-saturated form. In that form the water retained by both montmorillonites was nearly the same.

The swelling associated with water adsorption at onset of gelation is shown in tables 7 and 9. It may be seen from the data of table 9 that the intramicellar swelling for several of the montmorillonite forms is limited to about 10 Å. This represents only about one-fold increase in volume. In some of the forms the intramicellar swelling is less, whereas in others it may be considerably more, as indicated possibly by the diffused d(001) spacing. From these data and those in table 7 it may be concluded that the large macroscopic swelling at point of gelation of some of the forms is mainly a manifestation of intermicellar swelling rather than intramicellar swelling, and that the exterior surfaces of the particles rather than the interior surfaces make the macroscopic swelling possible.

Further data which indicate that the hydration of the exterior surfaces of the particles is the cause for the macroscopic swelling are (1) those of Baver and Winterkorn (1935) on water intake and hydration of a Wyoming montmorillonite (Winterkorn and Baver 1934), and (2) those of Freundlich et al. (1932) and Mattson (1932) and the author (1950, and table 10 herein), which show the effect of free base and salt on water content and intramicellar swelling of pastes of montmorillonites prepared either from stable suspensions or from the air-dried forms.

Baver and Winterkorn found that the hydration and the macroscopic swelling of montmorillonite are several times larger in gels prepared from suspensions than in gels prepared from the air-dried forms. On the other hand, the data on intramicellar swelling of montmorillonite in excess water (tables 9 and 10 herein; Barshad 1950, table 3) show that for most montmorillonite forms drying has no effect on the extent of the intramicellar swelling. This would indicate, therefore, that the decrease in macroscopic swelling and hydration of montmorillonite upon drying must be due mainly to its effect on the hydration properties of the external surfaces of the particles.

Both Freundlich's (1932) and Mattson's (1932) data show that the macroscopic swelling of montmorillonite in salt solutions and in solutions containing free base is smaller the greater the concentration of the solutions. On the other hand, the data of table 10 show that the intramicellar swelling in several of the montmorillonite forms is not affected by the presence of soluble salts. It may be concluded, therefore, that the reduction in the macroscopic swelling in the presence of salts is a manifestation of the effect of the salt on the water adsorption properties of the exterior, rather than on the interior surfaces of the particles.

A proper evaluation, therefore, of the over-all water adsorption and swelling properties of montmorillonite should account not only for the nature of the internal surfaces but also for the nature of the external surfaces of the montmorillonite particles.

Table 10. Interlayer spacing d(001) in water suspensions and in pastes made with normal chloride salt solution of the saturating cation of two montmorillonites saturated with various cations.

Saturating cation	Water suspensions		Salt pastes	
	Wyoming montmorillonite	California montmorillonite	Wyoming montmorillonite	California montmorillonite
	Å	Å	Å	Å
H^+	20.7	19.8	20.9	19.7
Li^+	diff.	diff.	19.1	19.1
Na^+	diff.	diff.	19.3	19.7
K^+	diff.	16.7		16.7
NH_4^+	diff.	15.7		16.7
Rb^+	15.9	16.2		
Cs^+	14.6	12.8		
Mg^{++}	19.8	19.5	19.5	19.0
Ca^{++}	19.4	19.3	19.3	19.2
Ba^{++}	19.3	19.4	19.3	19.4

Data relating to water adsorption and swelling of other identified clay minerals are presented in table 8. It is seen that both illite and kaolinite "gels", at onset of gelation, contain several times less water than any of the montmorillonite gels (compare tables 6 and 8).

CLAY-LIQUID WATER SYSTEMS IN THE FLUID STATE

The type of data useful for differentiating the clays in such systems include measurements of viscosity, thixotropy, plasticity, stability, and flocculation (Freundlich et al. 1932; Marshall 1949). Such measurements, however, will not be presented in the present discussion.

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