

ADSORBED WATER ON CLAY: A REVIEW

by

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ABSTRACT

Current knowledge of clay mineralogy and changing concepts of clay behavior have suggested a re-examination of the experimental data concerning adsorbed water. Data published between 1935 and 1959 have been studied and evaluated. In some instances this requires a reinterpretation of data that may lead to inferences or conclusions not intended by the original author. The intention of the re-evaluation of data is to clarify understanding of the nature of adsorbed water and to suggest fruitful avenues for future research. While all literature on the subject has not been included, a concerted effort has been made to include representative data from all viewpoints and experimental methods. Data reviewed come under the following headings: X-ray and electron diffraction, density, dielectric and magnetic, thermodynamic, diffusion and fluid flow, freezing, and rigid water films.

Utilizing present knowledge of crystal and surface chemistry of clay leads to the following conclusions: (a) Positions of the oxygen atoms of the adsorbed water molecules have been established by X-ray diffraction of vermiculite. These positions preclude both the ice structure and the Hendricks-Jefferson net structure even after modification to accommodate the exchangeable ions, (b) Density of water sorbed on Na montmorillonite has a minimum value of about 0.97 g/cm^3 at a water content of $0.7 \text{ g H}_2\text{O/g}$ clay (approximately the plastic limit). For water contents less than 0.7 the density rapidly rises to about 1.4, and for water contents greater than 0.7 the density gradually rises until at about $6.5 \text{ g H}_2\text{O/g}$ clay the density of the adsorbed water equals that of normal liquid water. (c) The differential entropy of water adsorbed on kaolinite has a minimum value approximately that of ice; however, (1) this minimum occurs at about 0.7 of a monolayer, and (2) the integral entropy is greater than that for normal liquid water up to at least two molecular layers. The apparently contradictory entropy of sorbed water on montmorillonitic clay has not been resolved but is believed to be at least partially associated with clay swelling. (d) Diffusion and fluid flow phenomena are shown to be extremely sensitive to clay fabric; therefore, it is the writer's opinion that diffusion and fluid flow data on loosely compacted clay are of little help in ascertaining the structure of the adsorbed phase. (e) Adsorbed water is easily supercooled and an appreciable fraction of the adsorbed water remains unfrozen after ice has once formed.

The two major hypotheses indicate that the nature of the adsorbed water is: (1) a solid-like substance, or (2) a two-dimensional fluid. In the writer's opinion the only data that cannot be adequately explained by both of the hypotheses are the integral entropy data on kaolinite. The integral entropy data favor the two-dimensional fluid hypothesis; however, the paucity of data requires that this be a very tentative conclusion.

The major difficulty encountered in the re-examination of data for this review was that a rather poorly defined clay surface was employed by various investigators. If progress is

to be made in unraveling the water-clay complex, it is deemed absolutely essential that experiments be carried out on very carefully defined and controlled clay surfaces. The nature of adsorbed water as interpreted from physico-chemical data on water-clay systems is no better than the purity of the clay surface regardless of the accuracy and precision of the measurements.

INTRODUCTION

There is complete unanimity among different investigators that water adsorbed on clay surfaces differs in structure and physical properties from bulk liquid water. Unfortunately, there is considerable uncertainty concerning even the direction, let alone the magnitude, of the deviations from bulk liquid water. For the present discussion, adsorbed water is defined as the entire interfacial region between the oxygen or hydroxyl surface of the clay crystal and bulk liquid water. The thickness of the adsorbed water layer is therefore a variable ranging from only a fraction of the surface being covered by one molecular layer up to many tens of molecular layers, depending upon the water content and the type of clay.

The importance of adsorbed water to soil engineering is immediately obvious when one realizes that adsorbed water includes virtually all water at any moisture content less than approximately the liquid limit. The present ambiguous state of knowledge concerning adsorbed water precludes a satisfactory explanation of many soil engineering phenomena because adsorbed water properties form a vital link to the understanding of shear strength, compression (particularly secondary compression), and the apparently anomalous fluid flow behavior of clay soils.

This paper attempts an objective examination of the experimental data relative to adsorbed water in light of current knowledge of clay. In some instances this requires a reinterpretation of data that may lead to inferences or conclusions not intended by the original author. This re-evaluation of data is undertaken with the intention that it may clarify the nature of adsorbed water or at least suggest fruitful avenues for future research.

While all the literature reviewed has not been discussed herein, a real effort has been made to include representative data from all viewpoints and experimental methods. It is possible that some contributions were inadvertently overlooked; the author apologizes for any such omissions.

After presentation of the data for various physical and chemical properties of adsorbed water along with some discussion as to their reliability and significance, the various hypotheses concerning the nature of adsorbed water will be examined for adequacy within the framework of available data. Interpretation of the data consists of opinions, those of the writer and those of others. They are presented in this juxtaposition not to belittle scientific effort or to offend the individuals. The publications in the field

of water sorbed on clay have become an overwhelming morass, and this paper, it is hoped, will provide a guide through it.

This paper is a contribution from the M. I. T. Soil Engineering Division. The writer gratefully acknowledges the financial assistance of the sponsoring organizations and the advice and constructive criticism offered by his colleagues. Special thanks are due Professor Barshad of the University of California and Professor Low of Purdue University for their splendid cooperation in supplying detailed facts concerning their experiments. While the writer frequently finds himself at odds with Professor Low over interpretation, he maintains a very high regard for Professor Low's genius as an experimentalist.

ELECTRON AND X-RAY DIFFRACTION

Forslind (1948) presented Laue-type electron diffraction photos taken down the *c*-axis of moist (?) hydrogen (electrodialyzed) montmorillonite and kaolinite. McEwan (1951, p. 110) has questioned the tacit assumption that the clay remains hydrated under the high vacuum required for electron microscopy. At equilibrium there can be no doubt that the clay would be very nearly anhydrous. That it is possible to obtain electron diffraction photos before complete dehydration is supported by Forslind's data. He obtained good agreement between calculated and observed intensities of *hk* spots for a $d_{00l} = 15 \text{ \AA}$ and the Edelman-Favejee structure model for montmorillonite. Forslind mentions that

similar calculations were carried out for the Hofmann structure, under the assumption of specific adsorption of water molecules in "holes" of silica layers, but failed to give agreement with experimental observations.

This latter computation would seem to imply a d_{00l} of from 10 to 11 \AA .

The really significant point, which is casually mentioned by Forslind, is that agreement between calculated and observed intensity of the *hk* spots would be obtained by use of $d_{00l} = 15 \text{ \AA}$ with either the Edelman-Favejee or Hofmann-Marshall-Hendricks structure model and completely neglecting the interlamellar water molecules; i.e. the electron diffraction effects are to a first approximation determined wholly by the clay crystals. Since Forslind could observe only a few orders of reflections, any conclusion regarding the structure of interlamellar water must be considered as largely speculative.

By the use of vermiculite single crystals Mathieson and Walker (1954) were able to observe as many as sixty-two orders of X-ray reflections; the data thus obtained permitted them to examine in some detail the positions of the interlamellar exchangeable ions and water molecules. Further elucidation of the interlayer water-exchangeable ion structure as a function of water content has been given by Walker (1956). Mathieson and Walker

(1954) conclude that in Mg-vermiculite the location of water sites is determined by the surface configuration of the silicate layers and, equally important, by the requirement for octahedral coordination of water around the Mg cations.

While the data clearly indicate a hexagonal pattern for the interlayer water molecules, Mathieson and Walker (1954) specifically state:

The structure derived for the interlamellar region in Mg-vermiculite, even in its less specific form, excludes the hypothetical water-layer structure proposed by Hendricks and Jefferson (1938) for vermiculite and later modifications made to take account of the exchangeable ions.

The purely statistical character of this highly ordered arrangement for the interlayer space is emphasized by Mathieson and Walker (1954):

... the interlamellar region must be regarded as a dynamic system in which constant rearrangement and adjustment is taking place.

The very excellent data available for Mg-vermiculite (Walker, 1956) afford a unique opportunity for calculation of the adsorbed water density, since the number and position of the water molecules are known. For the 14.81 Å, 14.36 Å, and 11.59 Å phases, the adsorbed water densities are 1.27, 0.92 and 1.43 g/cm³, respectively. These density values are noteworthy in two respects: (1) the adsorbed water density goes through a minimum value, and (2) the minimum value corresponds to the density of ice or the Hendricks-Jefferson net; however, Walker (1956) and Mathieson and Walker (1954) repeatedly emphasize that there is continual migration of water molecules and cations. Therefore, it is obvious that a low density for adsorbed water may occur for both "ice-like" and "two-dimensional liquid" models [see MacEwan (1948, p. 366) and Martin (1960, p. 108) for discussion of two-dimensional liquid].

DENSITY

The only unambiguous adsorbed water density (ρ) data are the data of Anderson and Low (1958). These density values involve no assumptions and are limited, therefore, only by any possible experimental error. Briefly, Anderson and Low measured the partial specific volume (V) of water by more or less standard physical-chemical methods. Since $\rho = 1/V$, the data give a direct measure of the incremental change in ρ at a particular water content. Data in Table 1 give the range of water contents investigated and ρ values interpolated from Anderson and Low's graphs.

Mackenzie (1958) in his criticism of Anderson and Low presents some scant pycnometer data of his own, along with selected data from DeWit and Arens (1950). As shown by Fig. 1, the data of Mackenzie are in a different water content range from the ρ data of Anderson and Low.

TABLE 1.—DENSITY OF ADSORBED WATER AT 25 °C¹

Water Content (g H ₂ O/g Clay)	Adsorbed Water Density (g/ml)		
	Na	Li	K
0.60	—	—	0.980
0.78	0.9715	—	—
1.00	0.9731	—	0.983
1.214	—	0.977	—
2.00	0.980	0.984	0.988
3.00	0.986	0.989	0.993
3.35	—	—	0.994
4.00	0.991	0.992	—
4.61	—	0.993	—
4.80	0.995	—	—
6.70	0.9971	0.9971	0.9971

¹ Data from Anderson and Low (1958) and Low and Anderson (1958a).

DeWit and Arens (1950) determined the density of clays as a function of water content using a pycnometer technique with a petrol fraction as the suspension medium. The adsorbed water density data in Table 2 were calculated from DeWit and Arens' data employing the clay densities given

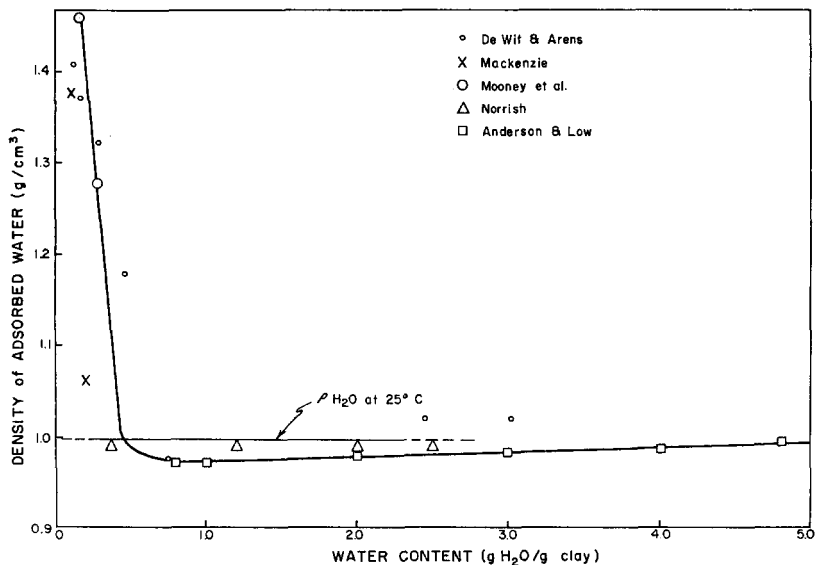


FIGURE 1.—Adsorbed water density on Na-montmorillonite.

TABLE 2.—ADSORBED WATER DENSITY ON CLAY¹

Mineral	Relative Humidity (percent)	Water Content (mg/g)	Density of Adsorbed Water (g/cm ³)
Montmorillonite	25	116	1.41
	50	166	1.37
	75	284	1.32
	100	460	1.16
	—	2440	1.02
	—	3010	1.02
Kaolinite	25	4	1.68
	50	8	1.12
	75	9	1.03
	100	65	0.99
Illite	25	30	1.36
	50	49	1.17
	75	69	1.08
	100	188	1.04
	—	1038	1.00

¹ Calculated from DeWit and Arens (1950).

by them. At low water content there is good agreement between Mackenzie's¹ and DeWit and Arens' data. There appears to be a sizable difference between the adsorbed water density data of DeWit and Arens and that of Anderson and Low in the 2–3 g H₂O/g clay range; however, it must be borne in mind that whereas DeWit and Arens measured the average value of ρ for a given water content, Anderson and Low measured the incremental change in ρ at a given water content.

Hauser and le Beau (1938) concluded from their pycnometer data that the ρ was greater than one. However, by re-examination of these data in terms of the expression given by Low and Anderson (1958a) (which involve no assumptions) one finds that the data of Hauser and le Beau are virtually identical with the data of Low and Anderson. Fig. 2 compares the recalculated data of Hauser and le Beau with the straight line extrapolation of Low and Anderson's line for Na-montmorillonite.

Nitzsch (1940) reported ρ values of 0.25–0.96 for water contents of 0.005–0.08 g H₂O/g clay. These data are at such low water contents that they do not conflict with any of the data in Fig. 1; however, the data have been omitted because Nitzsch used an air pycnometer and there are ample

¹ Mackenzie erroneously gives $\rho = 0.997$ g/cm³ for DeWit and Arens' point at 284 mg H₂O/g clay. It should also be mentioned that some investigators have mistaken DeWit and Arens' volume of 0.73 cm³/g as a density of 0.73 g/cm³.

data in the literature demonstrating that water can penetrate many spaces in a clay that exclude penetration of air; hence, low ρ values. This error becomes more serious as the water content is lowered.

The adsorbed water density (ρ) also can be calculated from measurement of c -axis spacing and water content plus the assumptions that the surface area is known and that the water is spread uniformly over the area. It can be shown easily that the surface area of Na-montmorillonite must be

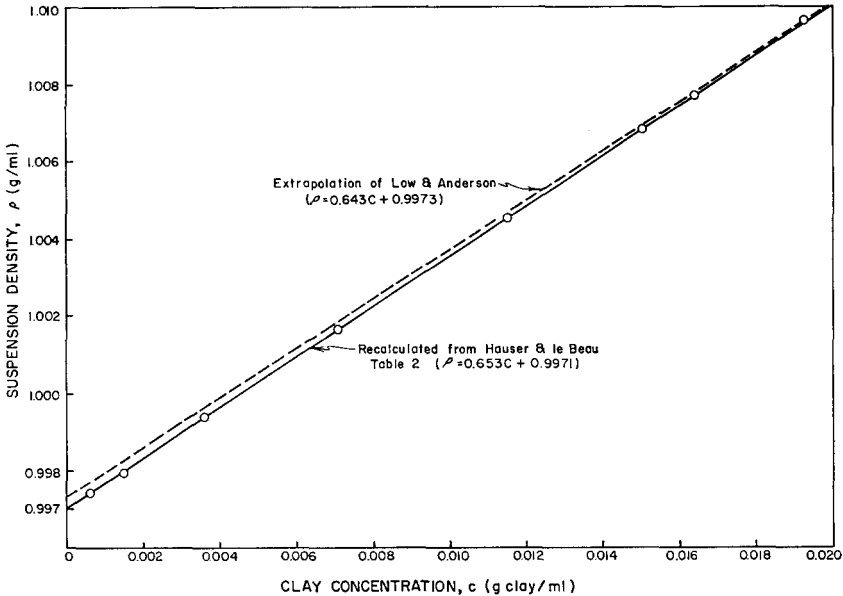


FIGURE 2.—Suspension density as a function of clay concentration.

$790 \pm 20 \text{ m}^2/\text{g}$. Since edge area is likely to be only 2 percent of the total, the major uncertainty (except at extremely low water content) is whether the interlayer voids are full. If one takes the water content just before a jump in c -axis spacing to compute the ρ , the interlayer voids undoubtedly are filled.

The stepwise hydration of montmorillonite is accepted as a well verified experimental fact (Bradley *et al.*, 1937; Hendricks, Nelson and Alexander, 1940; Mering, 1946; Mooney, Keenan and Wood, 1951; and Norrish, 1954). The data of all these authors are in substantial agreement at water contents below $0.3 \text{ g H}_2\text{O/g}$ clay; however, for ease in obtaining numerical data for ρ computations, the data of Mooney *et al.* and Norrish will be used.

The data in Table 3 were calculated from the equation

$$\rho = \frac{W}{SA}$$

A pessimistic estimate of errors (water content, $W \pm 0.01$ g H₂O/g clay; surface area, $S \pm 20$ m² per g; and half the interlayer distance, $\Delta \pm 0.2$ Å) yields $\rho \pm 10$ percent. Therefore, by the use of the water content just before a jump in *c*-axis spacing, the density calculated from X-ray data should be reliable to within a few percent. As seen in Fig. 1, the agreement between the ρ values calculated from the X-ray data of Norrish and the ρ values of Low show very satisfactory agreement. Méring (1946) did not observe the

TABLE 3.—DENSITY OF ADSORBED WATER CALCULATED FROM X-RAY DATA

	Experimental Data		Calculated Adsorbed Water Density ¹ (g/ml)
	d_{001} (Å)	Water Content (g H ₂ O/g clay)	
Mooney <i>et al.</i> (1952)	8.8	0	—
	12.4	0.10	—
	12.4	0.15	1.46
	15.4	0.20	—
	15.4	0.28	1.27
Norrish (1954)	9.5	0	—
	19.0	0.37	0.986
	40.0	1.19	0.986
	61.0	2.0	0.986
	73.5	2.5	0.99-

¹ See text for method of computation.

large d_{001} values found by Norrish (1954); however, in view of the experimental difficulties in obtaining equilibrium, it seems quite likely that Méring simply failed to reach equilibrium.

Three important conclusions are shown by the available adsorbed water density (ρ) data for Na-montmorillonite. First, at the same temperature there are no contradictory data pertaining to ρ 's being greater or less than that of normal liquid water. Second, at water contents below 0.3 g H₂O/g clay the ρ exceeds ρ_0 , while at water contents above 1.0 g H₂O/g clay the adsorbed water density is within 2–3 percent of that of normal liquid water. Third, at no water content does the ρ approach the density required for ice (0.90) or for the hexagonal net theory (0.92).¹

¹ Bradley (1959) has presented another interpretation of some of the density data discussed herein.

THERMODYNAMIC PROPERTIES

For physical sorption upon an inert adsorbent it has been amply demonstrated (Hill, 1950) that the integral entropy and energy (adsorption thermodynamics) are the proper thermodynamic functions to be used for interpreting the assembly of water molecules alone in terms of intermolecular interactions, configurations of the assembly, rotation of the molecules, etc. If adsorbent perturbations are appreciable, as is certainly the case for clay surfaces where the exchangeable ions move out from the adsorbent surface as the water vapor pressure is increased, the integral thermodynamic functions are still well-defined quantities but extra thermodynamic data are necessary for elucidation of their physical significance. For dilute clay suspensions the differential thermodynamic functions (solution thermodynamics) are appropriate. There is no clear-cut point in the transition region between adsorption thermodynamics and solution thermodynamics where adsorption thermodynamics loses its advantage.

A simple example of NaCl and water illustrates this point: (1) Region 1—at any low vapor pressure, water is adsorbed on the NaCl crystals; (2) Region 2—at some intermediate vapor pressure, a saturated solution of NaCl is in equilibrium with NaCl crystals; and (3) Region 3—above this vapor pressure, all the salt is dissolved and water vapor is in equilibrium with an unsaturated salt solution. Solution thermodynamics is the logical choice for application to Region 3, but there is no easy way to extend solution thermodynamics down to the low vapor pressures of Region 1 (Hill, 1951). The integral thermodynamic functions of adsorption thermodynamics require solution of the Gibbs equation, eq. (1), for evaluation.

$$\varphi = RT \int_0^p \Gamma d \ln p \quad (1)$$

where φ = spreading pressure,

R = gas constant,

T = absolute temperature,

p = equilibrium vapor pressure for surface concentration of adsorbate Γ .

The Gibbs equation applies to the entire range in vapor pressure and is relatively easy to evaluate with adequate data. Obviously, adsorption thermodynamics is the natural choice to cover Region 1 or all three regions. The integral functions have the additional advantage that ideally they are of direct physical significance.

Martin (1960) obtained water vapor adsorption isotherms in a high-vacuum system at three temperatures on Li and Na kaolinite surfaces that did not change during the course of the experiment. Earlier work (Martin, 1958) had shown that extreme care in sample preparation is essential in

order to have a constant surface for study, and that even then experiments on any particular specimen must be completed within a few weeks. The measurements of vapor pressure, p , and weight of water sorbed, X , were sufficiently precise that a fairly reliable extrapolation to $p = 0$ and $X = 0$ was possible; thereby giving a reasonable solution to eq. (1) for the different temperatures. The integral entropy of adsorption ($S_a - S_l$) is calculated in a straightforward manner:

$$(S_a - S_l) = \frac{\Delta H - \Delta G}{T} \tag{2}$$

where ΔH is the molal enthalpy calculated from the Clapeyron equation at constant φ for various values of φ and ΔG is the molal Gibbs free energy.

The liquid water reference phase was taken at $p = 17.53$ mm Hg and $T = 293$ °K. The differential entropy of adsorption ($\bar{S}_a - S_l$) was calculated from an expression similar to eq. (2) except that molal quantities are replaced by partial molal quantities and the computations are at constant X instead of constant φ . Typical data for Na-kaolinite are shown in Fig. 3. Li-kaolinite gave similar results.

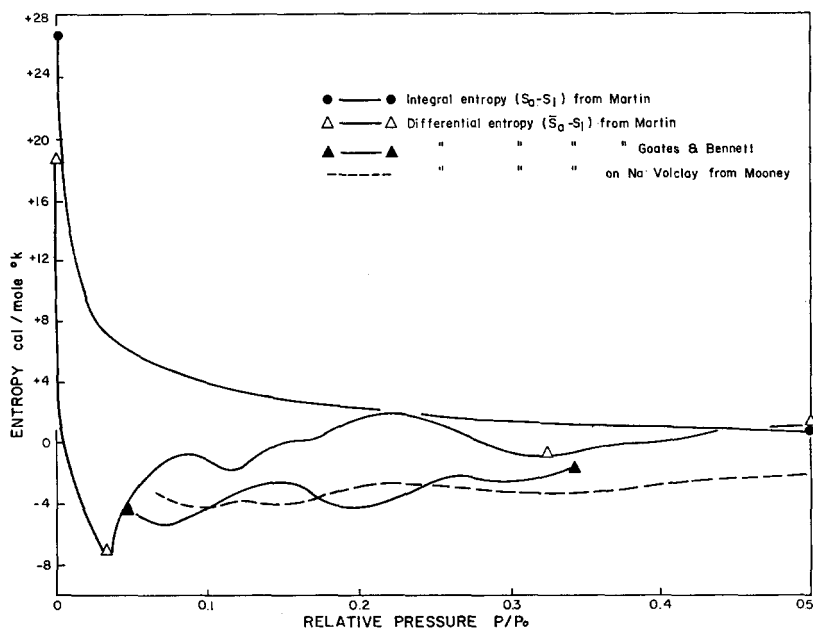


FIGURE 3.—Entropy of water adsorbed on kaolinite.

Goates and Bennett (1957) also employed a high-vacuum sorption system to obtain water vapor isotherms at three temperatures on an H-kaolinite.¹ In order to compare more directly the entropy data, the Goates and Bennett isotherm data have been recalculated to a constant reference phase where $p = 23.75$ mm Hg and $T = 298$ °K. The result (Fig. 3) reveals very satisfactory agreement between the two kaolinites, particularly when one considers the rather marked difference in the exchangeable ion.

The entropy data (Fig. 3) very clearly show that the integral entropy, S_a , for water sorbed on Na-kaolinite is greater than the entropy of bulk liquid water at the same temperature and pressure at least to a relative pressure of 0.5. The differential entropy curve for Na-kaolinite shows a fairly deep minimum; however, this minimum persists over a very limited pressure range and beyond $p/p_0 \approx 0.2$, approximately monolayer coverage, the differential entropy differs little from bulk liquid water. Based upon the present data, it would seem that the difference between the Na and H kaolinite ($\bar{S}_a - S_l$) curves is most logically attributed to the change in exchangeable ion. Since the integral entropy, S_a , is a measure of the randomness of the water molecules in the sorbed phase, one is forced to conclude that the water molecules in the sorbed phase on kaolinite have *greater* randomness than water molecules in bulk liquid water. Considering the sorbed phase as a two-dimensional fluid adequately accounts for both the S_a and \bar{S}_a data.

Employing a high vacuum system, Mooney (1951) obtained desorption isotherms at two temperatures on Na-montmorillonite. The homoionic clay was prepared by neutralization with NaOH of electrodialed Volclay. Later research (Mathers, Weed and Coleman, 1955; and Low, 1955) has shown that the Na-montmorillonite surface used by Mooney probably was heavily contaminated with alumina. The differential entropy ($\bar{S}_a - S_l$) was calculated for a constant reference phase at $p = 9.21$ mm Hg and $T = 283$ °K, and the Clapeyron equation was employed to compute the differential enthalpy. The resultant entropy curve is in Fig. 4, and for comparison with the kaolinite entropy the lower pressure range is reproduced in Fig. 3. The remarkable similarity in the ($\bar{S}_a - S_l$) curves for H-kaolinite and Na-montmorillonite seems to confirm the suspicion that both these clays are contaminated with alumina.

Barshad (1960) has investigated some thermodynamic functions for water sorbed on a number of montmorillonites saturated with various exchangeable ions. The preparation procedure was the same as that used by Mooney. Water content determinations on samples from different relative humidity desiccators held at constant temperature gave a sorption isotherm at 30 °C.

¹ In view of the instability of even Li and Na kaolinite it seems quite likely that Goates and Bennett's H-kaolinite was probably a mixed H-Al-kaolinite.

Other samples from the desiccators were subjected to DTA, and from the area of the low temperature water loss peak the enthalpy was computed (Barshad, 1952). This method of obtaining the enthalpy is equivalent to a calorimetric method. The extremes in the data are shown in Fig. 4.

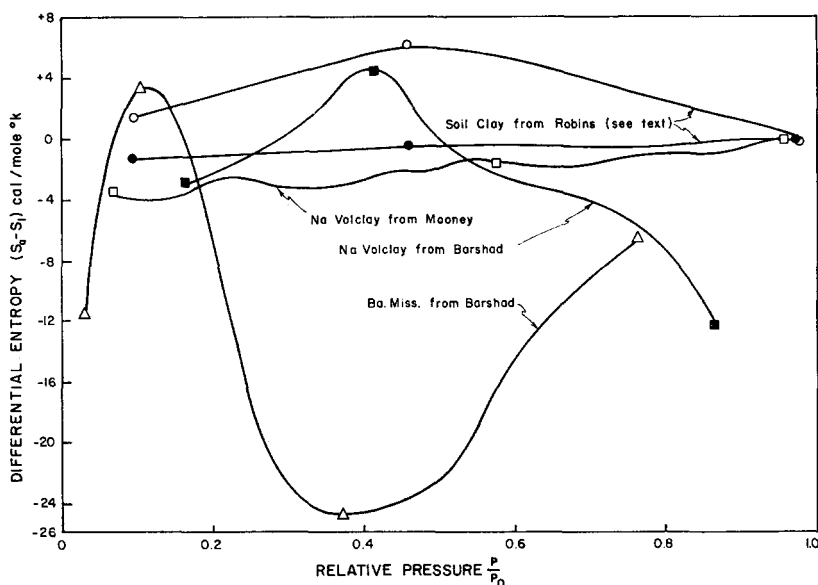


FIGURE 4.—Differential entropy of water adsorbed on montmorillonite.

The $(\bar{S}_a - S_l)$ curves for the two Na-Volclays can hardly be compared. Most of the 20 °C reference temperature difference should be accounted for by the fact that the entropy is plotted *vs.* relative pressure. Whether or not there could be enough variation in surface contamination to account for the large variation in the entropy curves is not known. Another possibility is that where Mooney calculated the enthalpy from isotherm data, Barshad in effect used calorimetric data for obtaining the enthalpy. The writer knows of no reason why the method of obtaining the enthalpy should make any difference; however, the fact remains, the data are clearly very different.

A similar anomaly occurs in the data of Robins (1952) on a montmorillonitic soil clay. The solid black circles in Fig. 4 are a recalculation of Robins' data to a constant reference phase where the enthalpy was obtained from calorimetry (heat of wetting). Although he did not make the calculation, Robins gave adequate data for computation of $(\bar{S}_a - S_l)$ where the enthalpy was ascertained wholly from isotherm data. The open circles in Fig. 4 are the result of this calculation. Again, there is no similarity.

While the discrepancy between the data of Mooney and Barshad may be explained as a difference in surface contamination or other unknown experimental details, it seems doubtful that this explanation will account for the data of Robins. Until this dilemma is resolved, there seems to be little point in discussing the entropy data on montmorillonite. In fact, one may well question the entropy data on kaolinite surfaces. Careful direct calorimetric determination of the enthalpy on controlled clay surfaces appears to be absolutely essential. The discrepancy must lie somewhere in the experimental procedure because theoretically the differential enthalpy is the same whether obtained from calorimetric or isotherm data.

At the other water-content extreme, Kolaian (1960) measured the temperature coefficient of the osmotic pressure for a Li-montmorillonite suspension (water content 1200 percent). For each temperature the suspension was stirred vigorously and the osmotic pressure measured as a function of time until the osmotic pressure became constant. Employing the calculation procedure outlined by Low and Anderson (1958b) the differential entropy of the water ($\bar{S}_a - S_l$) was found to be -3×10^{-4} cal/mole °K.

The writer willingly accepts this small negative entropy as significant; however, as already discussed for low water contents the physical significance of the result may be obscured owing to experimental difficulties. In Kolaian's experiment where the entropy difference is exceedingly small, clay fabric, the geometrical arrangement of the clay particles, is temperature sensitive, and would thereby be expected to have an effect on the water.

To recapitulate, the entropy data for sorbed water show that: (1) on kaolinite the water molecules in the sorbed phase have *greater* randomness (a positive integral entropy) than water molecules in bulk liquid water for at least the first two molecular layers; (2) on montmorillonite the data are inadequate to reach any definite conclusion concerning the water molecules *per se*; (3) on montmorillonite the nature of the exchangeable ion has a profound influence upon the differential entropy changes which are both positive and negative; and (4) on montmorillonite a negative differential entropy change in the water associated with the clay is measurable at a water content of 1200 percent.

DIELECTRIC AND MAGNETIC PROPERTIES

Muir (1954) presents data for the dielectric loss, ϵ'' , of water adsorbed on kaolinite at several different relative humidities, R.H., as a function of frequency (Fig. 5a). The 0 percent R.H. is for kaolinite dried over P_2O_5 at 20 °C, which Muir arbitrarily calls a monomolecular layer. Quirk (1955) in his review of water vapor adsorption data on clays finds that a R.H. of 20 percent corresponds very closely to a monomolecular layer. Drying four

different kaolinites over P_2O_5 showed that the water content was approximately equivalent to one-third of a monolayer.¹ Therefore, it seems that Muir's dielectric loss data are for surface coverages, θ , of from 0.3 to 1.3.

The very low value of ϵ'' maximum is to be anticipated for such low water contents; however, any interpretation in terms of the adsorbed phase may be largely obscured by the dielectric loss for the clay crystals themselves. Keymeulen and Dekeyser (1957) found the maximum in $\tan \delta$ to be 0.05 at a frequency of 10^3 c/s for clay heated to 60 °C. As a first approximation this would give a maximum in ϵ'' of 0.12 which is quite close to the maximum in ϵ'' displayed in Fig. 5 (a). Because of the powdery nature of kao-

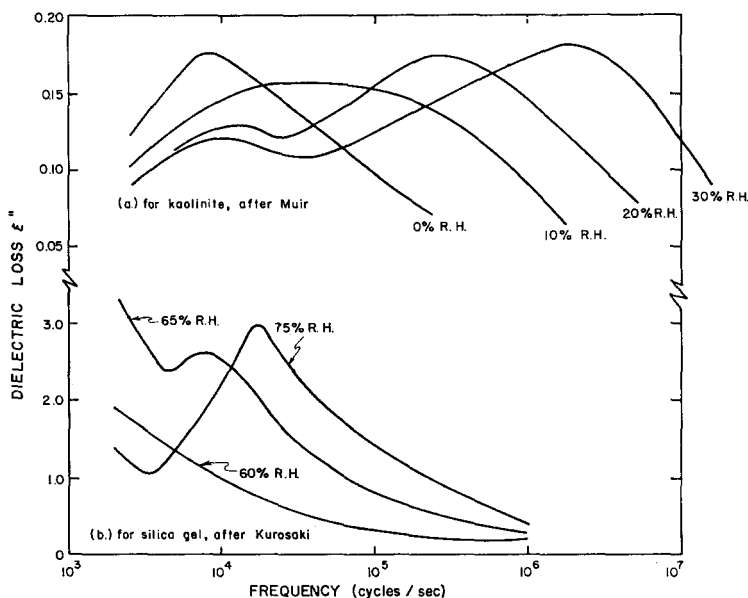


FIGURE 5.—Dielectric loss of adsorbed water for different relative humidities as a function of frequency.

linite, whether the shift in frequency of the ϵ'' peak should be attributed to the adsorbed water, to a different state of aggregation in the clay, or to both is problematical.

At the other water content extreme are the data of Deeg and Huber (1955). From dielectric measurements of decimeter wavelength, they showed that the dielectric properties of water in kaolinite-water and montmorillonite-water can be treated as those of pure water for any water content greater than approximately the plastic limit (40 percent for kaolinite

¹ Unpublished data, Soil Engineering Laboratory, Massachusetts Institute of Technology.

and 60 percent for montmorillonite). Dielectric dispersion, ϵ' , which is the real part of the complex dielectric constant, of kaolinite-water systems was constant at 2.5 up to a water content of 18 percent or at least twenty to thirty molecular layers. For the montmorillonite-water system, the dielectric dispersion began increasing significantly at a water content of 8 percent or less than one molecular layer (Fig. 6a).

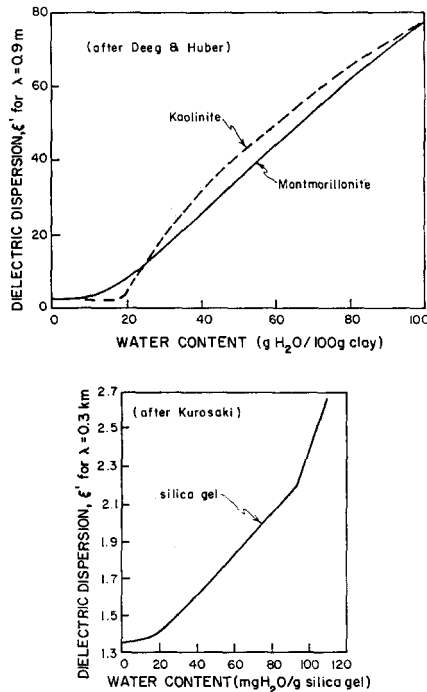


FIGURE 6.-- Dielectric dispersion of adsorbed water as a function of water content.

Pickett and Lemcoe (1959) employed nuclear magnetic resonance for the study of adsorbed water. Fig. 7 shows that beyond a couple of molecular layers the clay surface has only a small effect on the line width. In fact, for Na-montmorillonite at $\theta = 0.5$, the line width is 350 mG, which is still less than one-tenth that of ice. Another feature of Pickett and Lemcoe's data is that samples stored at constant moisture content:

exhibited no change in line width despite noticeable changes in strength properties (caused by thixotropic behavior and remolding) which resulted from quiescent aging for periods of as long as six months and from agitation.

The fact that no change was observed may simply reflect that the method is not particularly sensitive.

From the meager data presented above, any conclusion must be somewhat tentative; however, detailed investigations of dielectric properties and nuclear magnetic resonance on silica gel have demonstrated that dielectric and magnetic properties of sorbed phases can give useful information concerning the nature of the sorbed phase. Further, the fact that both types of data substantiate one another strengthens the major conclusion that the first couple of molecular layers of adsorbed water on silica gel has properties quite different from normal bulk water and that the sorbed water does not have an "ice-like" structure.

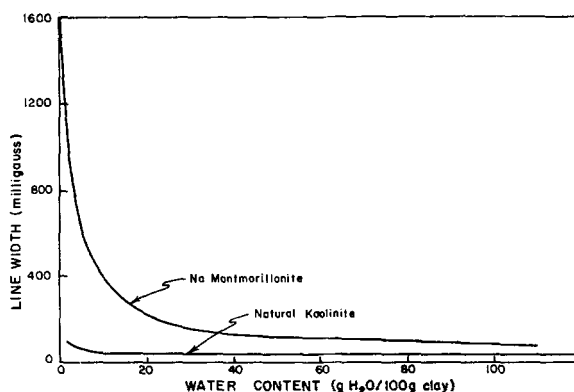


FIGURE 7.—Nuclear magnetic resonance line width with water adsorbed on clay (after Pickett and Lemcoe, 1959).

The detailed nuclear magnetic resonance study of water sorbed on silica gel made by Zimmerman and co-workers (1956, 1958) is summarized in Fig. 8. For comparison, the correlation time, τ , of liquid water at 25 °C is 8.6×10^{-12} sec and that of ice at 0 °C is 2.2×10^{-5} sec, or if adjusted by the equation for τ of ice (Auty and Cole, 1952), one finds τ of ice at 25 °C is 2.5×10^{-6} sec. At monolayer coverage, $\theta = 1.0$, $\tau = 6 \times 10^{-10}$ sec, which the present writer would prefer to consider as energetically more "liquid-like" than "ice-like." For $\theta = 0.2$, $\tau = 3 \times 10^{-7}$ sec, which energetically approaches ice; however, the surface coverage is so low that to attribute an "ice-like" structure to the sorbed phase is a highly artificial condition.

Typical dielectric data for water adsorbed on silica gel (Figs. 5b and 6b) indicate the qualitative similarity between the dielectric properties of water adsorbed on clay and on silica gel. McIntosh, Rideal and Snelgrove (1951) clearly demonstrated that even detailed dielectric data are open to several interpretations. They showed that the data for adsorbed vapors on silica gel could be explained adequately by assuming either that there is free rotation in the plane of the sorbent surface with no rotation normal to the

surface, *i.e.* a two-dimensional liquid, or that there is restricted three-dimensional rotation.

Since the data for clays show the same general trends as the data for silica gel, it would seem that, qualitatively at least, the first couple of molecular layers of sorbed water on clay and on silica gel are similar. From

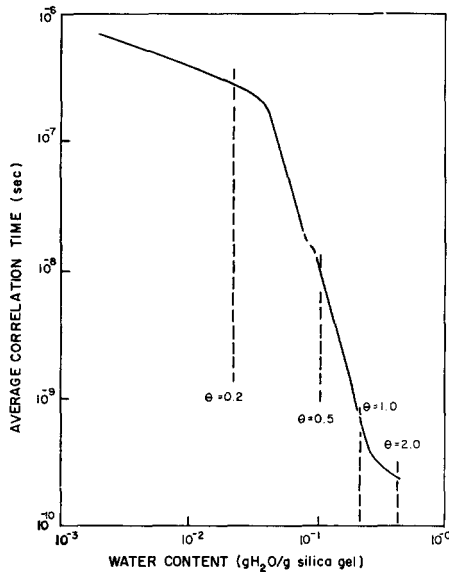


FIGURE 8.—Variation in nuclear correlation time with water content for water adsorbed on silica gel (after Zimmerman and Lasater, 1958).

the combination of dielectric and nuclear magnetic resonance data, a two-dimensional liquid model for the sorbed phase seems to allow a more consistent interpretation of the data than a fixed adsorption site model. The meager dielectric and magnetic data available for clay-sorbed water systems would be consistent with either the two-dimensional liquid or the fixed adsorption site model.

DIFFUSION AND FLUID FLOW

Diffusion and fluid flow have been grouped together because in the study of water self-diffusion and viscosity appear to be closely related (Ottar, 1955; Wang, 1951). Of far greater significance to clay-water systems is the fact that interpretation of diffusion and fluid flow experiments requires some assumption, either explicit or implied, concerning the flow path. The effective flow path or tortuosity is controlled for a given particle size by the geometrical arrangement of the particles, *i.e.* the clay fabric. Since clay fabric is particularly sensitive to environment (Mitchell, 1956; Pacey,

1956; Rosenqvist, 1955), the clay fabric must be either rigidly controlled or carefully considered as a possible factor that will account for experimental diffusion and fluid flow data.

The experiments of Michaels and Lin (1954) were specifically designed to investigate whether permeability abnormalities in clay systems are due primarily to abnormal fluid properties or to fabric changes. They measured the permeability of kaolinite beds to different fluids as a function of void ratio. The experimental error in permeability was estimated to be ± 10 percent. The usual way to show that flow through clay is abnormal is to relate the results to the Kozeny-Carman equation which relates the permeability coefficient, k ,¹ for randomly packed porous beds consisting of spherical or nonspherical particles to void ratio, e , and specific surface, S , of the porous solid

$$k = \frac{1}{k_0 S^2} \frac{e^3}{1 + e} \tag{3}$$

The value of k_0 depends on pore shape and the ratio of length of actual flow path to bed thickness.

Fig. 9 adopted from Michaels and Lins' data clearly shows that the

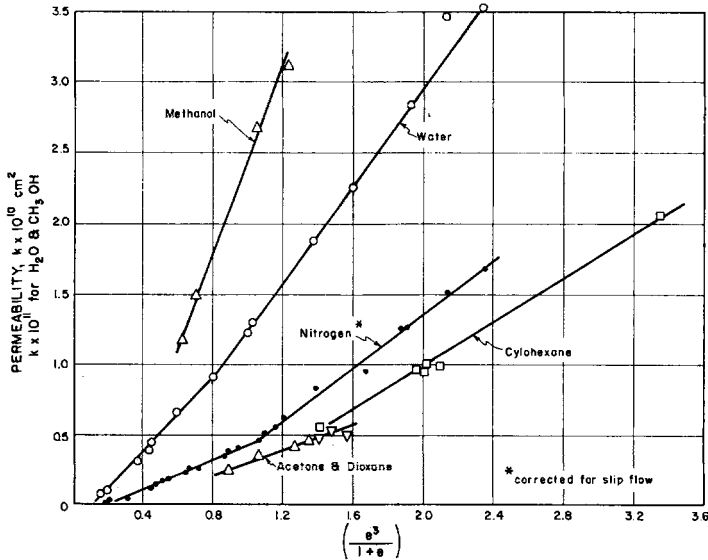


FIGURE 9.—Permeability of kaolinite to various fluids as a function of the void ratio, e , Term $(e^3/1+e)$ (after Michaels and Lin, 1955).

¹ The cgs unit of permeability, k , is cm^2 . The cgs units of conductivity, C , are $\text{cm}^3 \text{ sec g}^{-1}$. The usual engineering hydraulic conductivity or permeability, K , has units cm/sec , and when multiplied by the viscosity of fluid and divided by the product of fluid density times acceleration of gravity yields the permeability k .

permeability decreases with increasing polarity of the permeant. The plots indicate that the Kozeny-Carman equation is obeyed over a considerable void ratio range for all permeants; however, deviations from the Kozeny-Carman relation occur for all permeants because none of the straight lines in Fig. 9 pass through the origin.

Another procedure for revealing deviations from the Kozeny-Carman relation is obtained by calculating the value

$$V(k_0)S = \left[\frac{1}{k} \frac{e^3}{1+e} \right]^{1/2}$$

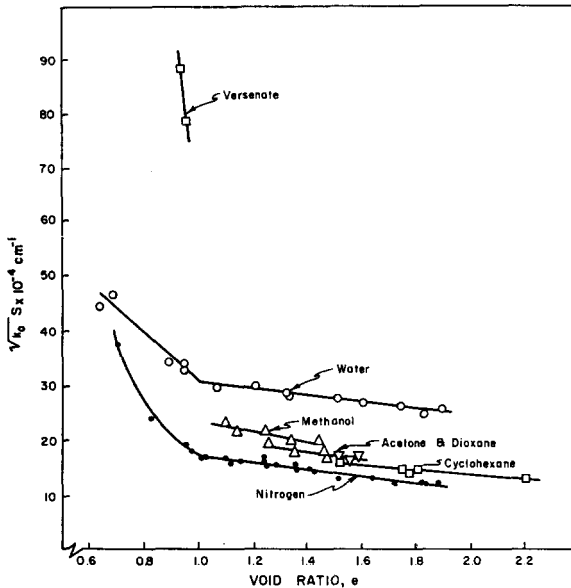


FIGURE 10.—Kozeny-Carman coefficient, $V(k_0)S$, for various fluids through kaolinite beds as a function of void ratio (after Michaels and Lin, 1955).

and plotting as a function of void ratio. All fluids have the same general trend (Fig. 10). Whether these trends reflect changes in k_0 , in S , or in both cannot be determined from these data alone; however, they strongly suggest that the factors responsible for the changes in $V(k_0)S$ with void ratio are the same, irrespective of the permeant. This renders it somewhat difficult to ascribe the low permeability (or high $V(k_0)S$) of water-permeated kaolinite solely to the existence of abnormal fluid properties not occurring in the presence of a gaseous permeant such as nitrogen.

To examine more carefully the factors responsible for the observed differences in permeability with different fluids, Michaels and Lin (1954) measured dry nitrogen gas permeability of kaolinite beds formed initially

in the presence of liquid permeants and dried without mechanical disturbance. For kaolinite initially sedimented in water the desolvation was accomplished by permeating with progressively less polar solvents ($H_2O \rightarrow$ dioxane \rightarrow acetone $\rightarrow N_2$). The method is effective in desolvating the clay because the weight loss after desolvation is less than 0.1 percent, which is less than one-third of a monomolecular layer.

Compared at the same void ratio, nitrogen permeability after desolvation of kaolinite beds initially formed in cyclohexane, acetone, or methanol is the same as the permeability for the liquid permeants. Since the specific

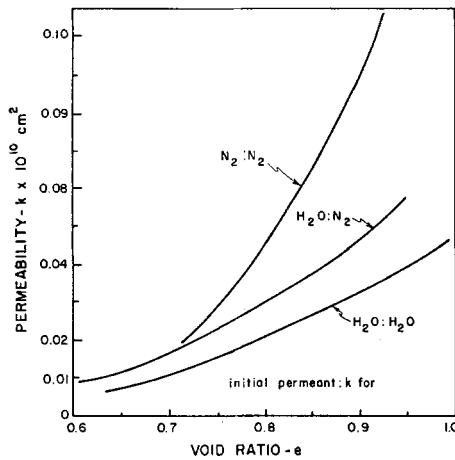


FIGURE 11.—Effect of initial permeant on nitrogen permeability of kaolinite (after Michaels and Lin, 1955).

effects that the liquid permeants exert upon the kaolinite persist when the clay is thoroughly dried in a confined state, the permeability differences from the different fluids most likely result from changes in clay fabric that arise from different polarity of the initial suspending media.

Even when water is the initial permeant, the major factor controlling the dry nitrogen permeability as a function of void ratio is the initial condition of the clay bed (Fig. 11). There is a 10–30 percent permeability decrease for aqueous permeants that may be either individually or collectively attributed to abnormal viscosity, counter electroosmosis, or immobile films. Michaels and Lin computed that an immobile water film 45–90 Å thick would account for the lower permeability of the aqueous permeants. In a subsequent investigation, Michaels and Lin (1955) showed that counter electroosmosis could account for no more than 5 percent permeability reduction. Inasmuch as the Michaels and Lin data clearly demonstrate

that the clay fabric alone can alter the permeability at a given void ratio, by 1000 percent, one can hardly rule out microscopic fabric changes that would account for the 10–30 percent additional permeability reduction for aqueous permeants.

Michaels and Lin (1954, 1955) provide ample data for their major conclusions that: (1) clay fabric is the primary factor for the change in permeability with different permeants; and (2) abnormal fluid properties contribute less than 30 percent toward the total resistance to fluid flow through kaolinite beds.

Fluid flow through solids high in sand apparently is very sensitive to fabric changes of the fines within the fixed fabric provided by the sand. Massachusetts Institute of Technology (1955, 1956) has found that the water permeability of a silty sand containing 3 percent minus 20 μ can be changed by a factor of 10 depending upon whether the water permeability measurement follows a dispersant permeant (0.5 percent sodium tetraphosphate solution) or a flocculant permeant (0.2 N CaCl_2 solution). Water permeation following the dispersant solution lowers the permeability still further while water permeation after the CaCl_2 solution does not alter the permeability. Therefore, it seems likely that the major cause of the ten-fold permeability change is aggregation or dispersion of the fines. This void plugging, and unplugging, is reversible through at least five cycles. On the assumption that the fines are in the voids formed by the skeleton of the larger particles, one finds that the void ratio of the fines for the above sample is 16 although the void ratio of the sample as a whole is 0.49. The loose condition of the fines readily explains the reversible ten-fold permeability change. Data of this kind have been observed on a number of natural soils and on sand-clay mixtures containing up to 20 percent clay (M.I.T., 1955, 1956).

The reported nonlinearity of flow rate with head loss for aqueous flow through sandstone cores (von Engelhardt and Tunn, 1955) would seem to be explained more logically as clay fabric changes. A water viscosity of 4–9 for sandstone cores containing less than 5 percent clay and at clay void ratios between 5 and 15 is, in the opinion of the writer, unreasonable. The permeability changes observed by von Engelhardt and Tunn are well within the range discussed above, and therefore may arise from changes in fabric of the fines within the fixed fabric of the coarser material.

Macey (1942) studied consolidation and aqueous conductivity of a number of ceramic clays that were presumably high in kaolinite. At the time of Macey's monumental work, methods of clay mineralogy did not recognize that minor mineralogical variation could result in major changes in soil properties. The clay sample approximately 1/8 in. thick and 2 in. in diameter was placed between two filter papers backed by metal plates having 1/32 in. holes on 1/8 in. centers and a cross grid of channels 1/32 in. deep connecting

the holes on the side next to the filter paper. The cell was held in a frame so that pressures of 1–50 atm could be applied. The volume change and aqueous conductivity were measured at ten different pressures. The data were plotted as water content versus log pressure and water content versus aqueous conductivity curves. In order to compare Macey’s data with those of other investigators his water contents were converted to void ratios assuming that: (1) the samples were saturated (implied by the data since he measured aqueous conductivity), and (2) the specific gravity of the clays was 2.60 g/cm³. Any error in the specific gravity gives appreciable

TABLE 4.—COMPRESSION INDICES FOR KAOLIN CLAYS

Sample	Source	C_c	
Clay No. 28	Macey (1942)	0.10	
Clay No. 29	Macey (1942)	0.08	
Clay No. 33	Macey (1942)	0.05	
Clay No. 34	Macey (1942)	0.11	
Clay No. 36	Macey (1942)	0.14	
Kaolinite		} 0.10 ± 0.04	
8 different exchangeable ions	Cornell (1951)		0.24 ± 0.02
Kaolinite	Roberts (1960)		0.30 ± 0.02
Kaolinite	Lambe (1953)		0.33
Kaolinite	Waidelich (1958)		0.20
Kaolinite, — 1 μ			
5 different exchangeable ions	Samuels (1950)	0.50 ± 0.1	
Kaolinite, — 0.5 μ	Cornell (1951)	0.59	

error in the absolute values of void ratios but the relative void ratios for a particular clay are not affected.

The compression indices, C_c (Δ void ratio ÷ Δ log pressure), of Macey’s clays are very low for kaolinite (Table 4). The low C_c values found by Macey are due either to appreciable nonclay mineral in the samples or to experimental difficulties arising from the rather thin samples used because C_c of illite and of montmorillonite are much larger than C_c of kaolinite.

Macey (1942) reported the fluid flow as absolute aqueous conductivity with the units given as cm³ sec⁻¹ cm⁻¹ dyn⁻¹, which reduces to reciprocal viscosity, η^{-1} . The present writer has been unable to rationalize these units with Macey’s definitions of aqueous conductivity. Macey states “. . . rate of water flow is $C \frac{dP}{dx}$ ” where C is the conductivity and $\frac{dP}{dx}$ is the pressure gradient. The cgs units of C are then cm³ sec g⁻¹ or cm² η^{-1} . Later Macey gives

$$C = \frac{Nr^4\pi}{8\eta}$$

where N is the number of capillary tubes per unit area, r is the average pore radius, η is the viscosity, and C is the conductivity in absolute units. The units of the right-hand side of this equation are $\text{cm}^2 \eta^{-1}$, so that whereas both definitions of C agree with accepted terminology, Macey's stated units of $C \text{ cm}^3 \text{ dyn}^{-1} \text{ cm}^{-1} \text{ sec}^{-1}$ must be in error.

If the numerical values reported by Macey are absolute conductivities, then the absolute permeability, k , which equals $C\eta$ and has the dimensions, cm^2 , has extremely low values for kaolinite (Fig. 12). If Macey's conduc-

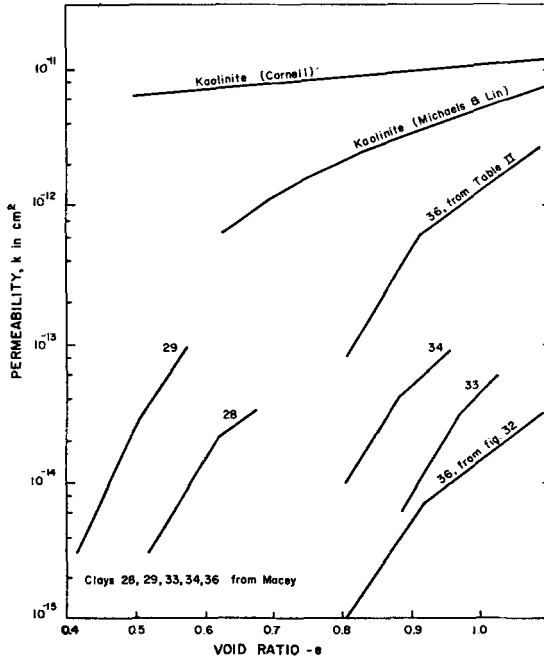


FIGURE 12.—Variation in the permeability of clays with void ratio.

tivities are really absolute permeabilities, they fall in the same region as the k values of Michaels and Lin (1954). The large change in permeability for a small change in void ratio on Macey's samples is completely inconsistent with other data on kaolinite. The possibility that the clay is high in illite or in montmorillonite is ruled out because, (1) the C_e values are too low, and (2) the $\log k$ versus e plot for illite and for montmorillonite is much flatter, not steeper, than the $\log k$ versus e plot for kaolinite.

Macey (1942) also made flow measurements to organic liquids about which he says:

... All these liquids (benzene, nitrobenzene, and pyridine) pass through the clay with great rapidity, the conductivities being estimated to be of the order of, and not less

than, 10^{-6} or 10^{-7} . This is 100,000 to 1,000,000 times greater than the rate of flow of water through the same clay.

Again, Macey's data are completely at odds with data for pure kaolinite. The maximum permeability change due to the permeant found by Michaels and Lin (1954) occurred for nitrogen permeability which was five times larger than the water permeability at a void ratio of 1.9.

The natural clays examined by Macey very likely contained appreciable sand that would readily account for the low compression indices, C_c . While pure montmorillonite has a large C_c , a very small amount, 1 percent, would have a negligible effect upon C_c but could greatly reduce the permeability of the clay bed by plugging the pores. Such pore plugging might also be expected to be very sensitive to void ratio changes. Organic liquids would be expected to have a much larger effect upon the permeability of montmorillonite than upon kaolinite. Waidelich (1958) calculated permeabilities from his consolidation data and found that the permeability of montmorillonite to nitrobenzene was 200,000 times larger than the permeability of montmorillonite to water at the same void ratio. This explanation is offered as one possibility that makes Macey's data consistent with other literature.

In an attempt to explain his conductivity and consolidation data Macey proposed the ice structure for the adsorbed water. While the ice hypothesis for adsorbed water may be a perfectly good theory, Macey's interpretation of his data in support of the ice hypothesis must be seriously questioned.

Before discussing diffusion, mobility, and viscosity data for clay systems, brief mention of data for true solutions will be considered. Selected data from studies by Wang (1954) on the self diffusion of water have been cited as proof that the adsorbed water has a more coherent structure (more order implied) than pure water (Leonards, 1958). All of Wang's data are indeed pertinent to the present discussion.

Wang (1951) determined the influence of temperature on the self-diffusion coefficient of water, D in cm^2/sec , employing both O^{18} and H^2 as tracers. At 25 °C, D using O^{18} was 17 percent larger than D using H^2 . The activation energies, E , for self-diffusion of water calculated from the slope of $\log D$ versus $1/T$ were 4410 cal/mole for O^{18} and 4580 cal/mole for H^2 , a difference of less than 4 percent. From these data Wang concluded that self-diffusion, viscous flow, and dipole orientation of liquid water all involve essentially the same activation mechanism (or the same activation energy).¹

Wang (1954) also investigated the effects of ions on the water structure. The deviations from constant $D\eta/T$ with temperature (Fig. 13) give the relative distortion to the free water structure outside the hydrated ion. A schematic presentation of the hydrated Li and Cs ions is shown in Fig. 13

¹ Parenthetical insert by writer.

where the dotted circles represent the hydrated ion size. The gross distortion (a structure breakdown) for the simple electrolyte systems studied showed that for cations $\text{Li} < \text{Na} < \text{K} < \text{Cs}$ and for anions $\text{Cl} < \text{Br} < \text{I}$.

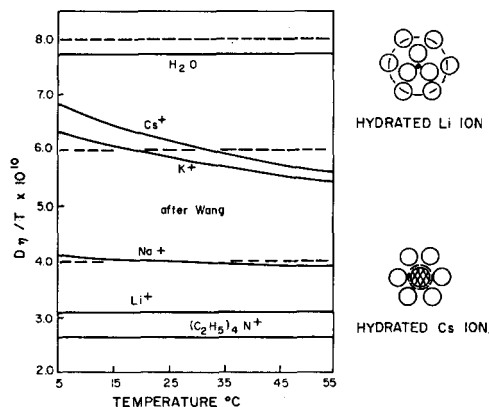


FIGURE 13.—Variation in the limiting diffusion coefficient, D , of ions and viscosity, η , with temperature T .

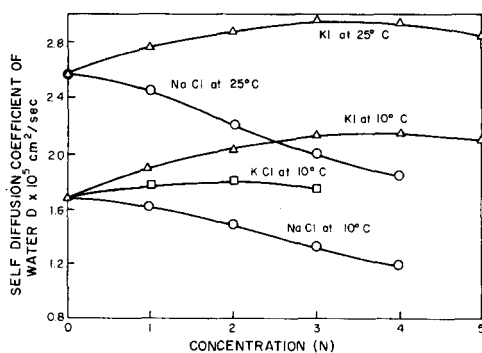


FIGURE 14.—Variation in self-diffusion coefficient of water with electrolyte type and concentration, and temperature (after Wang).

These effects are also evident in Fig. 14 where the self-diffusion coefficient of water is plotted against electrolyte concentration for different electrolytes and for two temperatures. Apparently the KI breaks down the normal water structure thereby permitting easier self-diffusion of water molecules, while the NaCl builds up a more coherent water structure than normal water which slows down self diffusion of water molecules.

One would expect the activation energy for self-diffusion of water to reflect the differences in water structure inferred from the data in Fig. 14. The activation energy for self diffusion of water in KI and NaCl solutions

was calculated on the assumption that $\log D$ versus $1/T$ is linear over the temperature range 10–25 °C (Fig. 15). The activation energy for pure water also was calculated from the data at 10° and 25 °C in order to have a better relative comparison between pure water and the salt solutions. It is readily apparent that the activation energy for self-diffusion of water in both the KI and NaCl solutions is less than the activation energy for self-diffusion of water in pure water for all concentrations less than 3.5 N. This cannot be

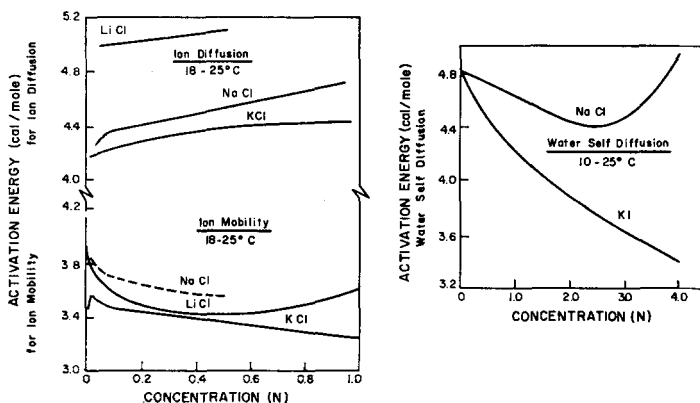


FIGURE 15.—Variation in activation energy calculated from different properties of electrolyte solutions with ion type and concentration.

considered as an isolated anomaly, because similar anomalous behavior is shown by activation energies calculated from ionic diffusion coefficients, equivalent conductance, and viscosity of salt solutions¹ (Figs. 15 and 16). The specific viscosity of a NaCl solution continuously increases as salt is added while the specific viscosity of KCl and KI solutions first decreases and then increases; yet the activation energies for viscous flow of all three decrease as salt is added. The relative positions of the alkali ions are $Li > Na > K$ for activation energies calculated from water diffusion coefficients, from ion diffusion coefficients, or from viscosity of the salt solutions; however, for activation energies calculated from equivalent or specific conductance data of the salt solutions at all salt concentrations larger than 0.005 N, the order of activation energy is $Na > Li > K$. A detailed theoretical discussion of these activation energies is beyond the scope of this paper; however, it should be mentioned that the above activation energy computations assumed that the entropy of activation remained constant.

Husted and Low (1954) studied the counter diffusion of ions through montmorillonite gels and calculated that the presence of the clay reduced

¹ Calculated from data given by Robinson and Stokes (1955) and I.C.T. (1926).

the diffusion constants to $1/2.7$ that of the ions in solution. This calculation assumes that the length of the diffusion path equals the macroscopic length of the montmorillonite plug. The clay concentration in the plugs was about 10 percent by weight. A tortuosity factor of 2.7 for a 10 percent montmorillonite gel would seem to be very small; therefore, since there is no way of estimating the effective diffusion path, the lower diffusion constants in the clay plugs relative to true solution can have no physical significance.

Schofield and Dakshinamurti (1948) demonstrated that the amount of clay required to alter significantly the properties of electrolyte solutions is small. They found that the electrical conductivity of 0.1 N KBr solution was reduced 16 percent when 0.91 percent montmorillonite was added

TABLE 5.—ACTIVATION ENERGY
FOR ION MOVEMENT FROM LOW (1958)

Montmorillonite	Water	Cation	Water ¹
4035	3435	K ⁺	3450
4485	3920	Na ⁺	3880
4360	4205	Li ⁺	4060

¹ Calculated from Robinson and Stokes (1955, p. 454). Cal/mole for 18°–25 °C and infinite dilution.

and that the electrical conductivity of 0.25 N KBr solution was increased 3 percent when 0.57 percent montmorillonite was added. The first suspension formed a thixotropic gel and the latter was completely dispersed. That the montmorillonite reduces the electrical conductivity mainly by a process of obstruction due to gel formation is the obvious conclusion; however, the possibility of a change in water structure caused by the thixotropic gel is an equally plausible explanation.

Employing a direct current conductivity method, Low (1958) measured apparent mobilities of exchangeable ions in clay–water systems. Experiments were performed at several temperatures so that the activation energy for adsorbed ion movement could be evaluated. It is assumed that the “close packed clay particles” do not contribute to the conductance. The clay, montmorillonite, was at a water content of about 1.6 g H₂O/g clay and a void ratio of 4.4. The activation energies are given in Table 5 along with activation energies for the ions in pure water. Apparently Low’s value for the activation energy of the Li ion in water is in error. Low (1958) attributes the higher activation energies in the clay system to a more coherent water structure in the clay, or to the breaking of electrostatic bonds between the ions and the clay, or both.

Potassium ions in solution produce a breakdown of the water structure¹; therefore, one could attribute Low's increased activation energy for the K-clay to the fact that the K^+ , being held by electrostatic bonds to the clay, causes *less* disruption of the water structure with the result that the water structure is more like that of pure water in a K-clay-water system than in a K-water system. In fact, from Wang's data (Fig. 13) and from the activation energy for viscous flow (Fig. 16), it would appear reasonable

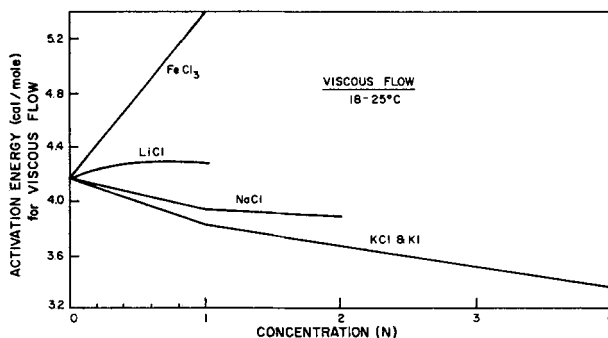


FIGURE 16.—Variation in activation energy for viscous flow with electrolyte type and concentration.

to assign an activation energy for ion movement of 3950 ± 100 cal/mole to an ideal ion which has no effect whatever on the water structure. In these terms, the K-clay has no significant effect upon the water structure; *i.e.* the water structure in the K-clay is essentially that of pure water.

The Na-Li-clay gave an increase in activation energy; however, the cause of this increase is far from clear. Low (1958) found that the activation energy for Na-montmorillonite prepared from an electrodialed H-clay was 5155 cal/mole or 15 percent higher than for the Na-clay prepared from a resin-exchanged H-clay. As mentioned earlier, there is abundant evidence that electro dialysis produces appreciable quantities of high-alumina amorphous material; therefore, the 15 percent increase in activation energy probably should be attributed to the alumina gel and not to the crystalline clay. Low and Anderson (1958a) mention that even the resin-exchanged clays contain aluminum hydroxide impurities, thus raising the question as to whether or not all the activation energies simply reflect differences in kind or amount, or both, of alumina gel.

The montmorillonite crystals may have an effect upon the water structure independent of any exchangeable ion effects; however, it is the opinion of the writer that the present data for contaminated clay surfaces make it

¹ See excellent review article by Frank and Wen (1957) on this topic.

impossible to assess the relative importance of exchangeable ions, the crystalline clay, and the amorphous alumina.

Rosenqvist (1955) measured the self-diffusion coefficient of water, D , in clay-water systems employing deuterium as tracer. For the three illitic soil clays studied, D was $0.05 \pm 0.01 \times 10^{-5}$ cm²/sec at 20 °C. The computed D values need to be corrected because, as noted by Rosenqvist, the volume of water is only a fraction of the total volume and the platy clay particles lengthen the diffusion path (sinuosity). Rosenqvist gives the porosity as 40 percent and estimates the sinuosity factor as $\sqrt{2}$, which gives a corrected diffusion coefficient of 0.18×10^{-5} cm²/sec. Michaels (1959) points out that a tortuosity (the total diffusional restriction, sinuosity plus areal effects) of 20 is as probable as the factor of $\sqrt{2}$ chosen by Rosenqvist; therefore, since Wang (1951) found $D = 2.2 \times 10^{-5}$ cm²/sec at 20 °C for deuterium as tracer, the diffusion coefficient of water in the clay-water system is anywhere between one-tenth that of pure water to about the same as pure water. Obviously, the diffusion coefficients calculated for clay-water systems have questionable physical significance for interpretation of water structure per se.

For one of his clays Rosenqvist (1955) also measured D as a function of temperature and found a seven-fold increase in D for a 30 °C temperature increase. Unfortunately, details are lacking as to whether these measurements were made on one sample or on separate samples each prepared at the testing temperature. The activation energy for water diffusion obtained from the plot of $\log D$ versus $1/T$ is 11 ± 3 kcal/mole, which is 2.5 times the activation energy for water diffusion in pure water (Wang, 1951). From the available data it is impossible to assess how much of the change in the diffusion coefficient with temperature results directly from a change in the water per se and how much from changes in the clay fabric. Accordingly, the meaning of the activation energy is obscure.

In a later publication, Rosenqvist (1959) computed the viscosity of adsorbed water from the self diffusion coefficients of water in a clay-water system presumably obtained in the manner just described. The equation of Ottar (1955) for the relation between diffusion, D , and viscosity, η , is equivalent to Wang's expression $D\eta/T = 7.73$, discussed earlier. Since the absolute value of D is unknown, the calculated η is very uncertain.

Low (1960) calculated the activation energy for viscous flow from measurements of the rate of water flow through a clay plug at different temperatures. The clay was confined between two rigidly fixed porous discs so that when air pressure was applied to the water at one end, the water outflow at the other end could be measured in a microburette. The dry Na-montmorillonite in the cell was degassed 24 hr and then allowed to take up water. After various wetting times flow rates were obtained at 57.0 ± 0.1 lb/in² and at five or six temperatures within the range 25° to

36 °C. The clay contained 2.0 g H₂O/g clay, giving a void ratio of 5.5 or an 85 percent porosity. The volume of flow per each activation energy determination was about 1 cm³ which for the total cell volume of 1.5 cm³ means approximately three-fourths of the void volume was replaced. The sample thickness was 0.3 cm so that the hydraulic gradient was 16.7 atm/cm.

The error in reading the microburette was about 0.5 percent. Low (1960) gives a plot of flow rate, *Q*, versus pressure to show that Darcy's law is valid in the pressure range 50–80 psi. From the slope of this line, 0.11 × 10⁻³ cm³ min⁻¹ psi⁻¹, the error in *Q* from the uncertainty in the applied pressure, ± 0.1 psi, is about 1.5 percent for the range of flow rates observed. Since 10–20 readings were taken at each temperature the experimental error in the best slope, *Q*, for the plot of volume *vs.* time probably amounts to no more than 0.3 or 0.4 percent.

The slope of the plot log *Q* versus 1/*T* permits computation of an activation energy (Low, 1960).

$$\log Q = \log \left(\frac{k}{B} A i \right) - \frac{E}{4 \cdot 575 T} \tag{4}$$

Q is the flow rate (cm³/min), *k* is the permeability (cm²), *B* is a function of the entropy of activation, *A* is the area for flow, *i* is the hydraulic gradient, *E* is the activation energy for viscous flow, and *T* is the absolute temperature. The data obtained by Low (1960) are summarized in Table 6. These data indicate that the activation energy for viscous flow in the clay–water system is as much as 13 percent larger than the activation energy for viscous flow of pure water.¹

TABLE 6.—FLOW RATES AND ACTIVATION ENERGIES FOR FLOW WATER THROUGH NA MONTMORILLONITE

Sample	Days after Wetting	Flow Rate at 25 °C (cm ³ /min × 10 ⁴)	Activation Energy* (cal/mole)
Pure water	—	—	3860
Clay No. 1	6	10.85	3840
Clay No. 2	13	6.80	3890
Clay No. 3	7	7.27	3840
Clay No. 3	14	6.84	4270
Clay No. 3	15	6.84	4260
Clay No. 4	7	6.62	3990
Clay No. 4	14	6.45	4050
Clay No. 4	21	6.25	4360

* Low (1960) states that the experimental error in *E* is ± 1 percent; this is ± 40 cal/mole; therefore, the *E*'s have been rounded off to the nearest 10 cal/mole.

¹ This result may be compared to the 250 percent increase cited by Rosenqvist (1959).

Low (1960) shows that the plot of $\log \eta$ versus $1/T$ for pure water is a good straight line in the temperature range 25° – 36° C; however, there is a definite curvature to the line (Table 7) which amounts to a 7 percent change in slope between 25° and 35° C. On the assumption that the data in Table 7 can be represented by a straight line and employing the method of least squares, one finds that the standard derivation for η is about 0.1 percent¹. This error is indeed very small and a straight line gives a good re-

TABLE 7.—VISCOSITY OF WATER¹ AND SLOPE OF $\log \eta$ vs. $1/T$

Temperature		Viscosity		Slope
t (°C)	$1/T \times 10^{-3}$	$\eta \times 10^{-3}$ (P)	$\log \eta - 3$	$\left(\frac{\Delta \log \eta}{\Delta 1/T} \right)$
24	3.36519	9.142	0.96104	
26	3.34269	8.737	0.94136	> 874.7
28	3.32049	8.360	0.92221	> 862.6
30	3.29859	8.007	0.90347	> 855.7
32	3.27697	7.679	0.88530	> 840.4
34	3.25563	7.371	0.86742	> 832.7
36	3.23457	7.085	0.85034	> 816.2

¹ Data from Lang (1956, p. 1668). $E = 3880$ cal/mole.

presentation of the data; however, this does not alter the fact that the slope at 25° C is 7 percent larger than the slope at 35° C. The value obtained for the activation energy of pure water depends somewhat upon the source of the viscosity data. The data in Table 7 were taken from Lange (1956) and are the same as those given by Robinson and Stokes (1955); however, if one uses the η data from Lange (1944) or I.C.T. (1926) the activation energy for the same temperature range is 3950 cal/mole or 2 percent larger.

Returning to the data in Table 6 and accepting the stated experimental error in E , one finds if the activation energy of water is taken as 3950 cal/mole, half of the activation energy values are less than that of pure water. There is a general trend toward increasing activation energy with days after wetting as evidenced by the average activation energies in Table 8. The activation energies of Table 8 agree with Low's conclusion that initially the activation energy is essentially the same as liquid water but increases with time.

Low (1960) attributes the increase in activation energy to the time-dependent development of a clay-induced water structure or to the increase in order and coherence of said structure as the clay particles reorient. The

¹ Calculated according to method outlined by Worthing and Geffner (1943, p. 249).

clay sample probably is responsible for the change in the calculated activation energy; however, whether this change arises from the clay surface per se or not is another matter.

Low (1955) and others (Mathers, Weed and Coleman, 1955) have shown that H-montmorillonites spontaneously convert rather quickly to Al-montmorillonite. This conversion also has been clearly demonstrated for Li-kaolinite-water systems (Martin, 1958). Therefore, the author feels that since Li-kaolinite will spontaneously convert to Al-kaolinite, monovalent montmorillonites will behave similarly. Reference to Fig. 16, which gives the activation energy for viscous flow, E , of different electrolytes as a

TABLE 8.—AVERAGE ACTIVATION ENERGY FOR FLOW OF WATER THROUGH Na-MONTMORILLONITE (AFTER LOW, 1959)

Days after Wetting	Activation Energy (cal/mole)
Pure water	3920 ± 50 ¹
6-7	3890 ± 50 ¹
13-15	4120 ± 130 ¹
21	4360

¹ Maximum deviation from mean.

function of electrolyte concentration, reveals that: (1) the cation is the major ion controlling E , and (2) Na⁺ lowers E slightly while Fe³⁺ causes a sharp rise in E . Unfortunately, data for Al³⁺ could not be found; however, the behavior of Fe³⁺ and Al³⁺ compounds is generally quite similar. On the assumption that the exchangeable ions are completely dissociated, the normality of the pore fluid is ≈ 0.5 N, so that if, during the 21 days, one-third of the exchange capacity became Al³⁺ saturated, the expected E value would be just that observed by Low.

Reorientation of the clay particles undoubtedly occurs; however, to attribute the erratic fluctuations in E , for the same time after wetting, to changes in clay fabric is believed unnecessary in view of the fact that any particular E does not vary significantly from its mean of Table 8. The trend in E with time after wetting may well be due to changing clay fabric. To interpret the activation energy so calculated in terms of the molecular organization of the water molecules per se from the data presented is in the writer's opinion extremely hazardous. For pure water the term in brackets on the right-hand side of eq. (4) is only a function of the entropy of activation. The B term for pure water is 20 percent larger at 35 °C than at 25 °C; therefore, even though the data can be described accurately by a straight line, which leads to an activation energy and implies a constant

intercept, B , there is no proof that the observed constant is temperature independent.¹ Inspection of eq. (4) shows that if the permeability or entropy, or both, have any temperature dependence this temperature dependence is included automatically in the E term. So that, while one can easily obtain an apparent activation energy, to interpret this activation energy in terms of a molecular model requires that the temperature coefficients of permeability and of entropy be accurately known.

In conclusion, fluid flow and diffusion measurements in clay-water systems provide no clear-cut evidence concerning the nature of adsorbed water.

FREEZING

There are two aspects to the freezing of any substance. The first is supercooling, ΔT , which means that upon cooling the liquid remains metastable below the melting point. The second is freezing point depression, which is a change in the temperature at which the liquid freezes or melts. Since both occur in clay-water systems, one can conclude that the water in clay-water systems differs from normal liquid water.

Supercooling may be very significant in fairly large glass capillaries (Fig. 17). The "spontaneous freezing temperature" of Hosler and Hosler (1955) is predominantly supercooling and not freezing point depression because when freezing occurred the entire mass of water immediately changed to ice. Hosler and Hosler (1955) froze water in capillaries varying

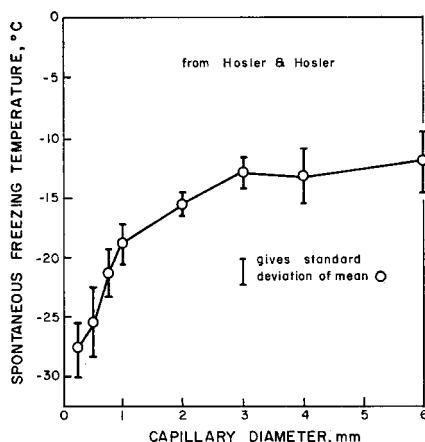


FIGURE 17.—Spontaneous freezing temperature as a function of capillary diameter (from Hosler and Hosler, 1955).

¹ The theoretical derivation of Glasstone, Lardler and Eyring (1941, pp. 485–486) shows that the factor B cannot be independent of temperature.

in length from 1 to 102 mm and used tapered as well as straight bore capillaries. Their data clearly show that the supercooling is independent of the volume and of the interface area. Therefore, the supercooling of pure water is a function only of the maximum capillary radius.

The amount of ΔT necessary to induce freezing may be either increased or decreased by the addition of electrolytes.¹ Table 9 gives representative data from the twelve electrolytes used by Hosler and Hosler. The magnitude and sign of the change in ΔT is a function of the type of ion, the ion concentration, and the capillary radius. The effect of electrolytes upon the

TABLE 9.—DEVIATIONS OF THE MEAN SPONTANEOUS FREEZING TEMPERATURES OF VARIOUS SOLUTIONS FROM THOSE OBTAINED WITH DISTILLED WATER¹

Solution	Molar Concentration	Capillary Diameter		
		3 mm	0.5 mm	0.25 mm
H ₂ O	—	0	0	0
KI	7.4×10^{-3}	+ 2.4	—	+ 14.5
NH ₄ I	8.3×10^{-3}	+ 4.9	+ 16.9	+ 14.4
NH ₄ I	1.0	— 5.5	+ 1.0	—
CaCl ₂	2.3×10^{-3}	+ 0.5	—	+ 0.7
NaCl	4.4×10^{-3}	— 0.6	— 1.1	— 1.1
NaCl	1.0	— 11.2	+ 0.3	—

¹ Data taken from Hosler and Hosler (1955).

water structure is fairly well established (Frank and Wen, 1957). For the water structure in low-concentration electrolyte solutions relative to normal liquid water one would expect KI to give less order, NaCl to give more order, and CaCl₂ to give still more order. Table 9 reveals that CaCl₂ and NaCl have an opposite effect upon supercooling while CaCl₂ and KI change the supercooling in the same direction; therefore, supercooling apparently can be increased by either more or less order in the water structure.

The fact that supercooling is very commonly observed in clay-water systems clearly indicates that the water differs from normal liquid water; however, the direction of the change is indeterminant from supercooling data. It is also a well documented fact that an appreciable fraction of the water in a clay-water system remains unfrozen to temperatures of at least -40 °C. Again, whether the change in water structure is more or less ordered is indeterminant because a change in either direction obviously will account for a portion of the water remaining unfrozen.

¹ This statement would include the limited data given by Dorsey (1948).

"RIGID" WATER FILMS

Grim and Cuthbert (1945) investigated the "green strength" and bulk density at various water contents for different amounts of clay in sand-clay mixtures. The conclusions of this investigation have been used repeatedly as evidence for the rigidity of the adsorbed water structure. Grim and Cuthbert accept as a well-established fact that the water held on the basal surfaces of montmorillonite is made up of water molecules that tend to be arranged in a definite pattern. The reference cited for this "fact" is the clearly stated "hypothesis" advanced by Hendricks and Jefferson in 1938 even before it had been established that the basal surfaces contained exchangeable ions. For this reason alone, reexamination of the data appears to be warranted.

Varying amounts of Na- or Ca-montmorillonite were mixed with sand, and a water content-green compressive strength curve was obtained for each clay percentage. In every instance, as the amount of water increased, the strength increased to a maximum and then as more water was added the strength dropped off. Grim and Cuthbert (1945) calculated the number of hexagonal net water layers from the water content at maximum strength for each clay percentage. One-tenth of a gram of water per gram of montmorillonite gives one water layer between two montmorillonite sheets (Hendricks, Nelson and Alexander, 1940). These data are shown in columns 1 and 3 of Tables 10 and 11. Grim and Cuthbert's tables I and II give the

TABLE 10.—ADSORBED WATER FILMS ON Na-MONTMORILLONITE

Sand-Clay Mixtures ¹		3 No. of Molecular Water Layers ²	Basal Spacing d_{001} (Å)	
1 g Dry Clay per 100 g Mixture	2 g H ₂ O per 100 g Mixture		4 Calculated From (3)	5 Experimentally Observed ³
1.84	0.95	5.2	25	18.5
2.77	1.25	4.5	25	18.5
3.69	1.35	3.7	22	17.0
4.61	1.49	3.2	19	16.0
5.55	1.65	3.0	19	15.5
6.45	1.85	2.9	19	15.5
7.35	2.10	2.9	19	15.5
7.80	2.375	3.1	19	16.0
9.20	2.60	2.8	19	15.5
11.10	3.30	3.0	19	15.5
13.85	4.125	3.0	19	15.5

¹ From data of Grim and Cuthbert (1945).² Based on 0.1 g H₂O/g montmorillonite = 1 water layer.³ From data of Foster *et al.* (1955).

grams of dry clay per 2000 g of mixture, permitting computation of the true dry clay percentage in any of their mixtures. The calculation assumes that all the water is associated with the clay—a satisfactory assumption.¹ The data in Tables 10 and 11 contain the results for all the mixtures presented in Fig. 1 of Grim and Cuthbert.

TABLE 11.—ADSORBED WATER FILMS ON Ca-MONTMORILLONITE

Sand-Clay Mixtures ¹		3	Basal Spacing d_{001} (Å)	
1	2		4	5
g Dry Clay per 100 g Mixture	g H ₂ O per 100 g Mixture	No. of Molecular Water Layers ²	Calculated From (3)	Experimentally Observed
1.84	1.125	6.1	28	19 ³
3.69	1.70	4.6	25	17 ⁴
5.55	2.25	4.1	22	17 ⁴
7.35	2.70	3.7	22	16.5 ⁵
9.20	3.20	3.5	22	16.5 ⁵
11.20	3.88	3.5	22	16.5 ⁵
13.85	4.70	3.4	18	16.5 ⁵

¹ From data of Grim and Cuthbert (1945).

² Based on 0.1 g H₂O/g montmorillonite = 1 water layer.

³ Ca-montmorillonite in excess of water (Norrish, 1954).

⁴ Ca-montmorillonite $d_{001} = 16.8$ at 0.45 g H₂O/g clay, Méring (1946).

⁵ Mooney *et al.* (1952) for water contents of column 3 (see text).

A comparison between the d_{001} spacing calculated from the number of water layers according to Grim and Cuthbert and the d_{001} spacing experimentally observed by various investigators at the water contents given by column 3² reveals that the observed d_{001} is always less than the calculated value. Further, Mooney (1951) showed that d_{001} for Na-montmorillonite changes abruptly at 0.075 g H₂O/g clay, which is not enough for one hexagonal net layer, and again changes abruptly at 0.16 g H₂O/g clay. The d_{001} for Ca-montmorillonite jumps to 15 Å before the water content reaches 0.1 g H₂O/g clay; *i.e.* already two apparent layers of water but only enough water for *one* hexagonal net layer. Since one-third of Grim and Cuthbert's data do not give the required fixed number of water layers and all the calculated water layers are larger than those observed experimentally, the conclusion that the water is rigidly held in a hexagonal net configuration has not been proved.

¹ Quartz ground to -74μ adsorbs less than 0.001 g H₂O/g quartz at 25 °C and 99 percent relative humidity.

² Since 0.1 g H₂O/g clay = 1 water layer; number of water layers/10 = g H₂O/g clay.

Table IV of Grim and Cuthbert (1945) gives strength and water content data after various curing times on duplicate samples of different clays. From these data the conclusion is reached that kaolinite and halloysite develop strength by air-set with little change in water content while illite and montmorillonite show no appreciable strength gain without an accompanying loss of water. All the data from Grim and Cuthbert's table IV have been plotted on Fig. 18. Starting at the right, the points on each

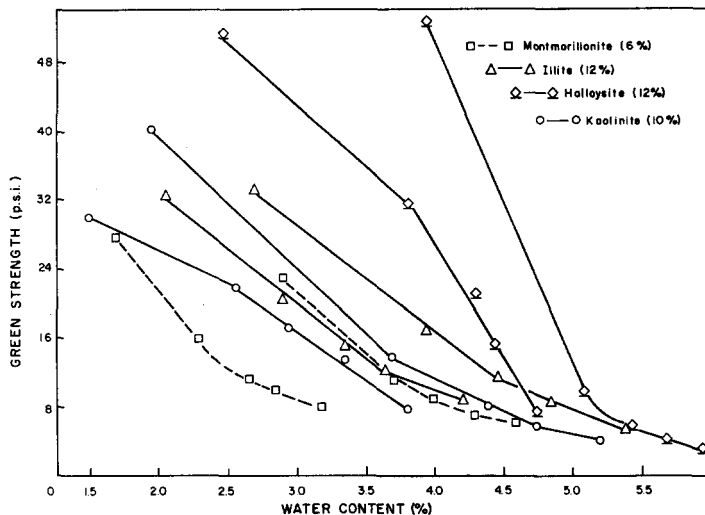


FIGURE 18.--Change in strength of sand-clay mixtures with time and water content for different clays (after Grim and Cuthbert, 1945).

curve are for time: 0, 0.25, 0.5, 1, and 3 hr, respectively. Obviously all the clays show the same trend, from which the writer would conclude that the major factor for increase in strength with time for all the clays was the decrease in water content.

SUMMARY AND RECOMMENDATIONS

Starting from normal liquid water the adsorbed water may vary in any number of ways; two models that have been mentioned are: (1) solid¹ and (2) two-dimensional fluid. The solid model does not mean that the water molecules are rigidly fixed into a well ordered lattice but only that there is more "order" than in normal liquid water. One may infer that each bond is stronger than in normal liquid water owing to the polarization of

¹ The term "ice-like" has been purposely avoided even in its most general sense because the structure definitely must differ from that of ice.

the clay surface. Presumably, this water would resist both normal and shear forces to a larger degree than normal liquid water. The two-dimensional fluid model recognizes the constraint due to the clay surface slightly differently. As in the solid model each bond that forms would be stronger than in normal liquid water; however, because of the surface constraint, the number of bonds that can form between the polar water molecules is considerably reduced from what it would be in normal liquid water. The result is that the two-dimensional fluid will resist appreciable normal stress but will shear perhaps even more easily than normal liquid water. The available data are, for the most part, consistent with either the two-dimensional fluid or the solid model.

Unfortunately one may reasonably question virtually all the data cited for various reasons; hence the nature of adsorbed water remains unknown. The only data that cannot be completely explained on both the solid and two-dimensional fluid models for the adsorbed phase are the integral entropy data on kaolinite which favor the two-dimensional model. The writer considers the data inadequate to prove whether the adsorbed phase is a solid or a two-dimensional liquid. While the data on clay-water systems are inconclusive, the writer favors the two-dimensional liquid model. There is ample evidence that for simple electrolytes the high electric field about an ion disrupts the strongly hydrogen bonded water structure and, since there are no data to the contrary, the writer sees no reason for postulating a reversal of this effect for polyelectrolytes (clays). A detailed discussion of the various hypotheses concerning adsorbed water is considered unwarranted because of ambiguities in the available data. There are, however, several points that should be helpful in future research and therefore worth mentioning.

X-ray and density data are inconsistent with the ice structure (Macey, 1942) and the hexagonal net structure (Hendricks and Jefferson, 1938) for adsorbed water. The behavior of clay-water systems below 0 °C provides additional evidence against the ice structure. In addition to the evidence against these theories there are no data to support them; therefore, based upon all available data, the ice structure and the hexagonal net structure should be stricken from the probable hypotheses for the adsorbed water structure.

The entropy of ideal two-dimensional water approximates that of normal ice; therefore, an entropy less than normal liquid water does not prove that the water molecules are more solidlike than normal liquid water. The water molecules actually may be nearly completely free to move around over the surface, and the lower entropy simply results from the surface constraint. Conversely, the entropy observed larger than normal liquid water is not conclusive proof that the water molecules have greater freedom of movement than normal liquid water. Nevertheless, thermodynamic data on carefully

defined surfaces will provide a powerful check point for interpretation of any model. More complete thermodynamic data, both integral and differential functions and their temperature coefficients, are urgently needed.

Ideally, the activation energies are thermodynamic functions so that just as with the entropy, extra thermodynamic data are required for complete elucidation of the adsorbed water in terms of a molecular model. Disregarding the experimental and other difficulties already discussed concerning activation energies, one wonders whether it is worthwhile to attempt to refine the various activation energy experiments since the activation energy obtained is even further removed from direct interpretation in terms of a molecular model than are the entropy data.

Adsorbed water density data show that the water is different from normal liquid water; however, a low density can be obtained either from a solid or a compressed gas. The temperature coefficient of the adsorbed water density over a water-content range should prove to be very helpful in deciding between different molecular models. Anderson and Low (1958) give data for K-montmorillonite which show a decrease in adsorbed water density with decreasing temperature which would favor the solid model.

For fairly rigid microporous solids, such as silica gel, dielectric data have provided valuable aid toward elucidation of the molecular structure of the adsorbed phase. If some way can be found to form clay into a rigid macroporous mass or to correct reliably the experimental data for the contribution of the clay particles themselves, then dielectric measurements on clays would provide valuable data concerning the adsorbed phase. However, blind application of this technique to clay systems will only add to the confusion that already exists. Molecular structure as interpreted from nuclear magnetic resonance data is usually in terms of the Bloembergen-Purcell-Pound three-dimensional model. Theoretical investigation as to the adequacy of this model for an adsorbed phase is needed.

A continually recurring stumbling block to the interpretation of adsorbed water literature for clays was the problem of contaminated clay surfaces. The difficulty of obtaining clean surfaces has always plagued those who study surface phenomena, and the problem is particularly troublesome for clays because of the instability of clean clay surfaces. If progress is to be made in interpretation of physico-chemical data for clay-water systems in terms of any molecular model, clean surfaces, which either do not change or change in a known manner during the course of an experiment, are absolutely essential. It is all too easy to lose sight of the fact that the significance of any data regardless of the accuracy and precision of the measurements is almost universally limited by the sample itself. Such limitation is particularly true for clean clay surfaces because a clean clay surface will change spontaneously. Therefore, the investigator has two choices: he can perform his experiments upon either, (1) a clean clay surface, taking

care that the surface does not change measurably during the experiment; or (2) a clay surface in equilibrium with its environment which generally implies appreciable surface contamination by alumina or silica gel, or both. The writer believes that data for clean clay surfaces have more direct physical significance than data for contaminated clay surfaces. An adequate knowledge of the clay surface investigated and due allowance for this factor when interpreting the experimental data will go a long way toward furthering our understanding of adsorbed water.

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