

MONTMORILLONITE-POLYALCOHOL COMPLEXES¹

by

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ABSTRACT

Some montmorillonites may be differentiated by complexing them with polyalcohols having a CH₂ group that is not connected to an oxygen atom. Montmorillonites with a low layer charge and high valence interlayer cations have larger basal spacings for their complexes than do those with a high layer charge and low valence interlayer cations. The basal spacings of these complexes are relatively larger if the clay has a large initial water content. The spacings for some complexes which are initially equilibrated at very low humidities are small, indicative of little penetration by polyalcohol molecules. Polyalcohol molecules may have difficulty replacing water molecules that are associated with the interlayer cations. The spacings of complexes with ethylene glycol and glycerol do not depend upon the initial interlayer water content. Water molecules may be an essential component of montmorillonite-polyalcohol complexes.

The polyalcohol molecules probably are associated with the clay surface through weak C—H···O interactions although virtually no shortening of this bond distance occurs. The C—H···O interaction is enhanced by the presence of higher valence interlayer cations. OH groups increase the thermal stability of complexes probably by interacting with the exchangeable cations. Longer chain molecules are held more tightly between the silicate sheets. One layer of polyalcohol molecules between silicate sheets is more stable than two layers. One layer of organic molecules is more stable with higher valence interlayer cations. Small molecules such as those of ethylene glycol may pack down somewhat into the "hexagonal holes" in the silicate surface.

INTRODUCTION

Preliminary Statement

Many of the present techniques for quantitative identification of clay minerals by X-ray diffraction, staining, surface area determination, cation exchange capacity, and differential thermal analyses involve the use of clay-organic complexes. Investigations of reactions between clay minerals

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and organic compounds have led to conclusions regarding the detailed nature of the structure and composition of clay minerals. The study of clay-organic reactions and analyses of the complexes provide an approach to the investigation of the shape of the adsorbed organic molecules and the bond between the reactants. The existence of clay-organic combinations in Recent and ancient sediments has been postulated and is being investigated. The resistance of some clay-organic complexes to both chemical and biological decomposition; the possible connection between clay minerals and the origin, accumulation, and migration of oil; and the use of clay-organic complexes in the manufacture of greases, paints, varnishes, lacquers, medicines, rubber products, and for decolorizing oils indicate the importance of fundamental clay-organic research.

Objectives

This investigation evaluates some of the physical and chemical characteristics of the complexes formed by a series of layered silicates of the montmorillonite clay mineral group and a series of polyhydric (more than one OH group per molecule) alcohol compounds. The primary objective of this investigation is to discriminate more precisely between members of the montmorillonite group by employing a group of polyhydric alcohols as complexing agents. A second objective is to characterize the bond between the montmorillonites and these organic molecules and to determine the orientation and configuration of the polyalcohol molecules on the silicate surface. In particular, the effect on the montmorillonite-polyalcohol complex of the following variables is investigated: (1) chemical composition and layer charge of the montmorillonite; (2) size and structure of the organic molecules; (3) valence of the exchangeable cation; (4) amount of interlayer water initially present; and (5) the overall amount of water in the clay-water-organic system.

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REVIEW

Organic molecules can be adsorbed on the basal planes between the unit sheets of montmorillonite (Grim, 1953, pp. 250-277). Furthermore, it has been shown that organic compounds thus adsorbed may be classified into

two groups: ionic compounds (such as the guanidinium ion) which replace exchangeable inorganic cations often irreversibly, and polar compounds (such as ethylene glycol) which displace the water normally held in inter-layer positions. These latter do not necessarily displace the inorganic cations originally present on the surface of clay minerals. The organic liquids employed in this investigation are polar compounds. The bond between montmorillonite units and polar organic molecules is relatively weak as indicated by the labile nature of the complexes; a given complex may be converted to another by washing with an excess of another miscible liquid.

Bradley (1945) and MacEwan (1948) were the first to show definitely that nonionic molecules of polar character could be adsorbed by clay minerals. These investigators also considered the kind of bond between these substances and concluded (from X-ray spacing measurements and Fourier syntheses) that polar organic molecules were held to the clay surface through a $C-H \cdots O$ (clay mineral surface) bond. Their data agreed with those of Hendricks (1941) and indicated that organic molecules tend to lie flat between the clay layers.

Greene-Kelly (1955) studied the complexes formed when a wide variety of aromatic organic compounds were reacted with montmorillonite. He interpreted his X-ray data to indicate that two orientations of the organic molecules between the silicate sheets were common. The first orientation was generally stable at low surface concentrations and had the plane of the ring of the organic molecule parallel to that of the silicate surface. At higher surface concentrations the molecules seemingly reoriented so that their planes were perpendicular to that of the silicate sheet and facilitated a closer packing on the surface. His evidence with cyclic compounds apparently confirmed the observation of Bradley and MacEwan that the $C-H \cdots O$ distance in the montmorillonite-organic complexes was shorter than would be expected if the normal van der Waals binding was in effect. He suggested, however, that the shortening did not vary as much between complexes as originally assumed.

Using benzene as a complexing agent, Barrer and MacLeod (1955) and Barrer and Reay (1957) concluded that better agreement with expected results for monolayer values from adsorption isotherm studies was obtained if the benzene molecules were standing on edge between the silicate sheets. They further suggested an upright configuration, perhaps even at low surface concentrations for benzene-clay complexes. Emerson (1957) suggested that the orientation of the simple alcohols also might be perpendicular to the plane of the silicate sheets and not parallel as had been originally assumed by Bradley (1945) and MacEwan (1948). He further postulated that the alcohol-clay bond might be an $O-H \cdots O$ bond instead of the $C-H \cdots O$ bond originally conceived.

The previous work on clay-organic relationships was carried out mainly by X-ray analyses with some isotherm studies. It seemed likely at the outset of this study that a more direct analysis of the type of bond between clay units and organic molecules and the energy of this bond might be provided by infrared investigations.

Oscillating-heating X-ray studies also provide data on the bond energy between montmorillonites and polyalcohols. Applications of the oscillating-heating technique to clay-organic studies are given by Rowland, Weiss, and Bradley (1958). The oscillating-heating technique is superior to that of differential thermal analysis because phase changes not only are recorded but also may be followed and identified.

Allaway (1948) and Byrne (1954) showed that montmorillonites treated with various organic substances and analyzed by DTA gave a series of curves which differed from one another. They showed that differences in the curves may be related to differences in composition of the montmorillonites. A comparative study of various clay-organic complexes by the oscillating-heating method might provide better data on variations between montmorillonites in addition to providing data on the clay-organic bond.

Clay complexes with polar organic substances differentiate swelling clays from various nonswelling clay mineral groups. Ethylene glycol was suggested by Bradley (1945) and glycerol by McEwan (1946) for this purpose. Other organic liquids might be employed to distinguish one montmorillonite from another—a much more subtle test than has been heretofore realized. The influence of water molecules in montmorillonite-polyalcohol complexes should be determined because both clays and polyalcohols are hydrophilic. Variations in the water in the clay-organic-water system might distort the interpretations.

SAMPLES INVESTIGATED AND PRELIMINARY PROCEDURES

The following three montmorillonites, selected from a variety of samples, represent the purest obtainable materials which cover a considerable range of compositional variations within the montmorillonite group: (1) hectorite, Hector, California; (2) montmorillonite, San Juan, Argentina; and (3) montmorillonite, Cheto, Arizona. Additional samples within the montmorillonite group, such as relatively iron-rich nontronite and beidellite-nontronite, also were examined in detail but X-ray patterns from these materials were poor and difficult to interpret. Complexes with poorly crystalline clays or with clays containing impurities do not give results analogous to those reported herein.

Variations in chemical composition, exchange capacities and high-temperature phases (Grim and Kulbicki, 1960), thermal behavior and infra-

red spectra provided the evidence of chemical differences from sample to sample; namely, the Hector clay is trioctahedral with some lithium in octahedral positions while the other two clays are dioctahedral; the Hector clay has no aluminum in either octahedral or tetrahedral coordination, the Cheto clay has very little tetrahedral aluminum, and the Argentina clay has considerable tetrahedral aluminum; the Cheto clay has the highest layer charge and the Hector clay has the lowest layer charge, the respective exchange capacities are 130 meq/100 g for Cheto, 105 meq/100 g for Argentina, and 80 meq/g for Hector.

Portions of the $< 2 \mu$ fraction of each sample were made homoionic with Na and Ca ions with exchange resins. In some instances, however, the clays were treated with excesses of the chloride of the proper cation and the excess salt washed out. Oriented aggregates were used for X-ray analysis and silver chloride platelets for infrared absorption analysis. The oriented clay aggregates were saturated with the organic compounds up to two months under controlled humidity conditions and analyzed frequently by X-ray analysis during this period. The slides for the oscillating-heating X-ray studies were sprayed with excess of the organic liquids 24 hr before, and again about 1 hr before analysis. The initial interlayer water content of the clay was not controlled in these instances.

DISCUSSION OF X-RAY RESULTS

The X-ray analyses of these complexes under a variety of conditions have shown that the basal spacings of some montmorillonite-polyalcohol complexes depend upon the layer charge of the clay and the valence (Rowland, 1960, personal communication, suggested the term "charge density") of the interlayer cation, initial interlayer water content, amount of water in the system surrounding the complex, and number and position of the OH groups of the organic molecules.

Layer Charge of Clays and Valence of Interlayer Cation

Basal spacings of these montmorillonite-polyalcohol complexes depend upon the layer charge of the clay and the valence of the interlayer cation, in agreement with the conclusions of Barshad (1952). A relatively larger basal spacing is obtained with montmorillonites having a low layer charge and with higher valence cations in interlayer positions. For example, the basal spacing for the Na Hector clay complexed with 1,4-butanediol (column 6 of Table 1) is 18.4–17.8- I^1 , indicating that most of the silicate sheets in this sample are associated with two layers of organic molecules.

¹ All the numbers that refer to basal spacings represent $d(001)$ values in Ångstrom units. I = irrational sequence of basal reflections.

In contrast a more highly charged clay such as the Na Argentina sample has a spacing of 13.6-I which indicates that most of the clay layers are associated with only one layer of organic molecules. The effect of the higher valence cations in promoting a larger amount of expansion is illustrated in column 8 of Table 1 for the Argentina samples which are complexed with 1,5-pentanediol. The Na Argentina sample has a spacing of 13.6-I

TABLE 1.—BASAL SPACINGS IN ÅNGSTRÖM UNITS FOR CLAY SAMPLES COMPLEXED WITH VARIOUS ORGANIC LIQUIDS AT 15 PERCENT R.H.

	(1) Ethylene Glycol	(2) Glycerol	(3) 1,2-Propanediol	(4) 1,3-Propanediol	(5) 1,3-Butanediol	(6) 1,4-Butanediol	(7) 1,2,4-Butanetriol	(8) 1,5-Pentanediol	(9) TEGDE
Na Hector	17.0-I	17.8-I	18.4- 18.0-I	18.0- 13.6-I	18.4- 17.8-I	18.4- 17.8-I	17.8	13.6-I	17.8
Ca Hector	17.0-I	17.8-I	18.4	18.0- 13.6-I	18.4- 17.8-I	18.4- 17.8-I	18.0- 17.8-I	13.6-I	17.8
Na Argentina	17.0	17.8-I	18.4	13.6-I	14.3- 14.0-I	13.6-I	17.8-I	13.6-I	17.8
Ca Argentina	17.0	17.8	18.4	13.6-I	18.4- 14.3-I	13.6-I	17.8-I	14.3-I	17.8
Na Cheto	17.0	17.8-I	14.3-I	13.6	14.6-I	13.6	18.0- 14.3-I	13.6	17.8
Ca Cheto	17.0-I	17.8	14.3-I	13.6-I	14.6-I	13.6-I	18.0- 17.8-I	14.3-I	17.8

The clays originally were equilibrated at 30 percent R.H.

I = irrational sequence of basal reflections.

while the Ca Argentina has a spacing of 14.3-I. The data in Table 1 indicate that the layer charge of the clay exerts a greater influence on the basal spacing of the complex than does the valence of the exchange cation.

The foregoing conclusions concerning the amount of expansion in relation to the layer charge of the clay and the valence of the cation apply to only those complexes with polyalcohols which have at least one CH₂ group which is not directly connected to an oxygen atom. Polyalcohols such as ethylene glycol and glycerol, and also the dimethyl ether of tetraethylene glycol (TEGDE) expand the varieties of each clay the same amount (17.0 for ethylene glycol and 17.8 for glycerol and TEGDE). These three organic substances are not suited to distinguish one montmorillonite from another.

It may be significant that the TEGDE molecules apparently are adsorbed more regularly than those of ethylene glycol or glycerol, because the X-ray diffraction patterns show a rational sequence of orders related to an 001 spacing of 17.8.

Initial Interlayer Water Content

Basal spacings of clays that have a high initial water content are equal to or larger than spacings for the same clays with a smaller initial water content when equilibrated and complexed with polyalcohols having at least one CH₂ group which is not connected to an oxygen atom. For example, compare the results for the Ca Cheto clay with 1,3-propanediol in column 1

TABLE 2.—BASAL SPACINGS IN ÅNGSTRÖM UNITS FOR CLAY SAMPLES COMPLEXED WITH 1,3-PROPANEDIOL AND 1,5-PENTANEDIOL AT APPROXIMATELY ZERO PERCENT R.H.

Sample	(1)	(2)	(3)	(4)
	1,3-Propanediol	1,5-Pentane-diol	1,3-Propanediol	1,5-Pentane-diol
Na Hector	18.4-18.0-I	13.6-I	18.4-18.0-I	13.6
Ca Hector	18.4-18.0-I	17.8-13.6-I	18.0-I	17.8-13.6-I
Na Argentina	14.0-13.6-I	13.6	14.3	13.6-I
Ca Argentina	18.0-13.6-I	17.8-13.6-I	18.4-14.3-I	17.8-13.6-I
Na Cheto	13.6-I	13.6	14.3-I	13.6
Ca Cheto	13.6-I	14.0-I	14.5	14.3

The clays in columns 1 and 2 originally were equilibrated at 15 percent R.H.; those in columns 3 and 4 originally were equilibrated at 30 percent R.H.

I = irrational sequence of basal reflections.

of Table 2 (13.6-I) to column 3 of Table 2 (14.5). The clays listed in columns 1 and 2 were equilibrated at 15 percent R.H. (relative humidity) before the clay and organic liquids were brought together, while the clays listed in columns 3 and 4 were equilibrated at 30 percent R.H. A wider range of humidities at which the clays are equilibrated promotes larger differences in the spacings of some complexes. Spacings for complexes with organic compounds such as ethylene glycol and glycerol are not affected by differences in the initial interlayer water content.

Not only do some polyalcohols bring out differences between various montmorillonites but they also can bring out differences between the individual layers of a given clay at certain humidities. A value of 18.0-13.6-I indicates that some of the silicate layers are associated with one layer of polyalcohol molecules and others with two layers and suggests that there are differences between the individual layers of a montmorillonite. A value of 18.4-18.0-I, for the same clay with the same organic compound but complexed at a different humidity, suggests that there are few differences

between the individual clay layers as nearly all of them expand the same amount.

Some clays equilibrated at very low humidities (15 percent or less) have small spacings with little penetration by polyalcohol molecules between silicate layers. This result is especially evident on X-ray patterns that are recorded soon after the clay and organic compounds are complexed. For example, compare the spacings listed for the Na Hector and Ca Argentina samples in column 1 of Table 3 with the spacings in the last few columns for the same clays. The small spacings of Na Hector and Ca Argentina in

TABLE 3.—BASAL SPACINGS IN ÅNGSTRÖM UNITS FOR CLAY SAMPLES COMPLEXED WITH 1,3-BUTANEDIOL AT APPROXIMATELY ZERO PERCENT R.H. FOR INCREASING INTERVALS OF TIME

Sample	(1) 27 hr	(2) 52 hr	(3) 95 hr	(4) 9 days 11 hr	(5) 31 days
Na Hector	14.3 and ¹ 10.0-I	18.4-14.3-I	18.4-14.3-I	18.4-14.3-I	18.4-14.3-I
Ca Hector	18.4-17.8-I	18.4-17.8-I	18.4-17.8-I	18.4-17.8-	18.4-17.8-I
Na Argentina	15.0-14.7-I	15.0-14.7-I	15.0-14.7-I	15.0-14.7-I	15.0-14.7-I
Ca Argentina	15.0 and ¹ 12.5-I	18.0-14.3-I	18.0-14.3-I	18.0-14.3-I	18.0-14.3-I
Na Cheto	14.6-I	14.6-I	14.6-I	14.6-I	14.6-I
Ca Cheto	14.0-I	14.0-I	14.0-I	14.6-I	14.6-I

¹ Two distinct 001 peaks present.

The clays were originally equilibrated at 15 percent R.H.

I = irrational sequence of basal reflections.

column 1 may be a result of the fact that some of the silicate units in these clays have very little water associated with them initially. The small amounts of water may be more intimately associated with the exchange ions than with the basal oxygen surfaces. Molecules of polyalcohols with CH₂ groups which are not connected to an oxygen atom may not replace (or may replace with difficulty) water molecules bound to the exchange cations and have difficulty penetrating between some of the silicate sheets. These polyalcohol molecules may replace easily the more loosely held water associated with the basal oxygen surfaces. These data show that molecules of water may often be an essential part of montmorillonite-polyalcohol complexes. In contrast ethylene glycol- and glycerol-clay complexes quickly develop a stable maximum spacing, which suggests that they are more "miscible" with or more readily replace pre-existing interlayer water molecules.

Water in System

The relative humidity inside the desiccators in which some clay-organic complexes were allowed to equilibrate has an effect on the spacing of the complexes. The relative humidities listed in Table 4 were obtained with supersaturated solutions of NaCl for 25 percent R.H., $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ for 50 percent R.H., and NH_4Cl for 75 percent R.H. A humidity of approxi-

TABLE 4.—BASAL SPACINGS IN ÅNGSTRÖM UNITS FOR CLAY SAMPLES COMPLEXED WITH 1,3-PROPANEDIOL FOR INCREASING INTERVALS OF TIME AND MAINTAINED AT VARIOUS RELATIVE HUMIDITIES

Sample	R.H.	(1) 8 hr	(2) 81 hr	(3) 11 days
Ca Hector	approx. zero	18.0-I	18.0-I	18.0-I
	25	18.0-I	18.0-13.6-I	13.6-I
	50	18.0-I	18.0-13.6-I	13.6-I
	75	18.0-13.6-I	13.6-I	13.6-I
	100	18.0-I	13.6-I	13.6-I
Na Argentina	approx. zero	14.3-I	14.3-I	14.3-I
	25	16.4 and 13.6-I ¹	13.6	13.6
	50	13.6	13.6	13.6
	75	13.6	13.6	13.6
	100	—	—	—
Na Cheto	approx. zero	13.6	13.6	13.6
	25	13.6	13.6	13.6
	50	13.6	13.6	13.6
	75	13.6	13.6	13.6
	200	13.6	13.6	13.6

¹ Two distinct 001 peaks present.

The clays originally were equilibrated at 30 percent R.H.

I = irrational sequence of basal reflections.

mately zero was obtained with Linde Molecular Sieves. Clay complexes saturated with polyalcohols were placed in large desiccators containing these saturated salt solutions or Linde Sieves and analyzed by X-ray diffraction at three time intervals. Water molecules displace the polyalcohol molecules from the interlayer positions because montmorillonites and these organic substances are hydrophilic. As the humidity of the system increases, complexes which show a spacing equivalent to two layers of polyalcohol molecules at lower humidities give way to a spacing of a mixture of one and two layers of polyalcohol molecules at higher humidities and finally to a spacing equivalent to a monomolecular layer of polyalcohol molecules. (See Table 4, especially for the Ca Hector sample.) Spacings smaller than

those expected for a monomolecular layer of polyalcohol molecules are not observed. A monomolecular layer of polyalcohol molecules may be more stable than two layers because effective contact can be made with adjacent silicate sheets. Larger differences in spacing between clays result when as much water as possible is eliminated from the system (Table 4).

Position and Number of OH Groups in Polyalcohol Molecules

The position of OH groups in the organic molecules has an important effect on the basal spacings of the complexes. The smallest spacings observed for complexes with 1,2-propanediol and 1,3-butanediol are larger than the smallest spacings observed for complexes with 1,3-propanediol and 1,4-butanediol, respectively. For example, the Na Cheto sample in Table 1 has a 14.3-I spacing with 1,2-propanediol compared to a 13.6 spacing with 1,3-propanediol and has a 14.6-I spacing with 1,3-butanediol compared to a 13.6 spacing with 1,4-butanediol. Probably the main reason for this is the steric effect produced by the OH group in the middle of the 1,2-propanediol and 1,3-butanediol chains which prevents closer packing between the silicate sheets.

A comparison of the data in Table 1 for complexes with 1,2,4-butanetriol with the data for complexes with glycerol, 1,2-propanediol, and 1,3-butanediol illustrates the effect of the organic molecules on the resultant spacings. Compared to the results with glycerol, spacings with 1,2,4-butanetriol complexes are less regular and are affected slightly by differences in the composition of the silicate sheets and the exchange cations. For example, the spacing for Na Cheto with 1,2,4-butanetriol is 18.0–14.3-I, indicative of the presence of both one and two layers of organic molecules. The two layer situation is predominant for Ca Cheto as shown by the 18.0–17.8-I spacing. The presence of the extra OH group in 1,2,4-butanetriol as compared to 1,2-propanediol probably causes a better fit between the layers of butanetriol molecules or between the butanetriol molecules and the exchange cations; this may account for the somewhat smaller spacing for the two layer state observed with the Hector and Argentina clays. A comparison of the spacings of complexes with 1,2,4-butanetriol to those for 1,3-butanediol shows fewer variations between clays for complexes with 1,2,4-butanetriol. In other words, 1,2,4-butanetriol molecules act more like those of glycerol probably because of the extra OH group. The somewhat larger spacing for most of the two layer complexes with 1,3-butanediol may reflect a poorer fit between the two organic layers which contain molecules with fewer OH groups, or a poorer interaction of the 1,3-butanediol molecules with the exchange cations.

All the X-ray results discussed thus far are summarized in Table 5 with examples illustrating each and a reference to a discussion in the text.

TABLE 5.—SUMMARY OF FACTORS CONTRIBUTING TO LARGER SPACING OF COMPLEXES

Factor Contributing to Larger Spacing	Table	Column in Table	Example	
			Large Spacing	Small Spacing
Small Layer charge of clay	1	6	Na <i>Hector</i> and 1,4-butanediol at 15% R.H. Clay originally at 30% R.H. (18.4–17.8-I)	Na <i>Argentina</i> and 1,4-butanediol at 15% R.H. Clay originally at 30% R.H. (13.6-I)
Large Valence of inter-layer cation	1	8	Ca <i>Argentina</i> and 1,5-pentanediol at 15% R.H. Clay originally at 30% R.H. (14.3-I)	Na <i>Argentina</i> and 1,5-pentanediol at 15% R.H. Clay originally at 30% R.H. (13.6-I)
Large Initial interlayer water content	2	3 and 1	Ca <i>Cheto</i> and 1,3-propanediol at about zero % R.H. Clay originally at 30% R.H. (14.5)	Ca <i>Cheto</i> and 1,3-propanediol at about zero % R.H. Clay originally at 15% R.H. (13.6-I)
Small Amount of water in system	4	3	Ca <i>Hector</i> and 1,3-propanediol at about zero % R.H. Clay originally at 30% R.H. (18.0-I)	Ca <i>Hector</i> and 1,3-propanediol at 50% R.H. Clay originally at 30% R.H. (13.6-I)
OH groups in middle of chain	1	3 and 4	Na <i>Cheto</i> and 1,2-propanediol at 15% R.H. Clay originally at 30% R.H. (14.3-I)	Na <i>Cheto</i> and 1,3-propanediol at 15% R.H. Clay originally at 30% R.H. (13.6)
Small number of OH groups for organic molecules of the same chain length	1	3 and 2	Ca <i>Argentina</i> and 1,2-propanediol at 15% R.H. Clay originally at 30% R.H. (18.4)	Ca <i>Argentina</i> and <i>glycerol</i> at 15% R.H. Clay originally at 30% R.H. (17.8)

Italics indicate the agent causing the differences in spacing for each factor. Numbers in parentheses represent basal spacings in Ångström units.

I = irrational sequence of basal reflections.

Orientation of Polyalcohol Molecules

Molecular models were used in an effort to determine the orientation of the organic molecules in the clay-organic complexes. The lack of rational series of reflections on the X-ray patterns of many of the complexes precluded detailed structural analysis. The flat-lying position of the organic molecule models gives the best comparison between observed and calculated two-layer spacings. The relationships are shown in Table 6. Polyalcohols with a relatively high OH/C ratio per molecule give slightly larger calculated

spacings than observed spacings, while organic compounds with a larger number of CH_2 groups that are not connected to an oxygen atom give somewhat smaller calculated spacings than observed spacings (Table 6). More OH groups per organic molecule may promote a better fit between the organic molecules themselves or between the organic molecules and the exchange cations or interlayer water molecules. Virtually no shortening of the $\text{C}-\text{H}\cdots\text{O}$ bond distance occurs because there is close correspondence between calculated and observed values.

TABLE 6.—DATA ON THE ORIENTATION OF ORGANIC MOLECULES IN THE CLAY-ORGANIC COMPLEXES

Organic Molecule	Smallest Width (Å)	Calculated Two-layer Spacing ¹ (Å)	Largest Observed Spacing (Å)	OH/C Ratio
Ethylene glycol	3.9	17.4	17.0	1.00
Glycerol	4.2	18.0	17.8	1.00
1,2,4-Butanetriol	4.3	18.2	18.0	0.75
1,2-Propanediol	4.3	18.2	18.4	0.67
1,3-Propanediol	4.0	17.6	18.4	0.67
1,3-Butanediol	4.3	18.2	18.4	0.50
1,4-Butanediol	4.0	17.6	18.4	0.50
1,5-Pentanediol	4.0	17.6	17.8	0.40
TEGDE	3.9	17.4	17.8	—

¹ Values are for two layers of organic molecules plus 9.6 Å for the silicate sheets.

Complexes with ethylene glycol show the largest difference between observed and calculated two-layer spacings, when the calculated spacing is larger than the observed spacing (Table 6). Ethylene glycol molecules have a small enough size to permit packing down into the hexagonal holes in the silicate surfaces. This packing argument is supported by data for complexes with TEGDE (Table 6). The two-layer spacing calculated for complexes with TEGDE is the same as for ethylene glycol but the observed spacing is larger, in spite of the fact that every carbon atom in the TEGDE chain is connected to an oxygen which would presumably enhance $\text{C}-\text{H}\cdots\text{O}$ bonding to the clay surface and, perhaps, result in a shorter $\text{C}-\text{H}\cdots\text{O}$ bond distance. The difference between the observed spacings for TEGDE and ethylene glycol complexes may be explained by the fact that the large size of the TEGDE molecules prevents them from packing down into the silicate surface as effectively as the ethylene glycol molecules. An alternative is that the layers of glycol molecules pack together better to give a smaller observed spacing.

DISCUSSION OF INFRARED RESULTS

Infrared spectra in the 2–5 μ region were obtained on various polyalcohol liquids and also on polyalcohols complexed with the Na and Ca varieties of the Argentina clay. Special emphasis was given to an analysis of the bands representing the C–H and O–H stretching vibrations. Several small and apparently new C–H bands are evident on the clay–organic spectra which might suggest a C–H...O interaction, but band shifts are absent. Band shifts would be expected if strong C–H...O interaction and large shortening of the bond distance occurred.

A pronounced feature in the clay–organic spectra is a decrease in the height or broadening, or both, of the peak representing the symmetrical CH₂ vibration compared to the peak representing the asymmetrical CH₂ vibration. This may indicate weak C–H...O interaction between the polyalcohol molecules and the clay surface. A general correlation exists between the extent the peak representing the symmetrical CH₂ vibration is changed and an increase in the valence of the interlayer cation. This might be expected because of the “higher interlayer dipole moments” (Barshad, 1952) created with highly charged exchange cations. These “high interlayer dipole moments” promote a stronger bond between the basal oxygens and the hydrogens of the CH₂ groups in the polyalcohol molecules. The peak representing the symmetrical CH₂ vibration is altered with an increase in the number of CH₂ groups that are not connected to an oxygen atom and with an increase in chain length. The CH₂ groups that are not directly connected to an oxygen atom may be active in C–H...O bonding to the clay surface (MacEwan, 1948), and longer chain molecules are associated more strongly than shorter chain molecules.

The O–H band is unchanged when the spectra of the organic liquids are compared to the spectra of the clay–organic complexes. However, the O–H band is very broad and small changes are easily overlooked. The O–H groups in a polyalcohol molecule probably are associated with other organic molecules, the exchange cations, or water molecules in the interlayer positions. Clay complexes with TEGDE molecules were examined by infrared absorption. The C–H vibration peaks could not be completely resolved, but changes in the C–H stretching region of the spectra may indicate a weak C–H...O interaction.

DISCUSSION OF OSCILLATING-HEATING RESULTS

The oscillating–heating X-ray technique (Rowland, Weiss, and Bradley, 1956) was used to study the clay–polyalcohol complexes. The factors that contribute to the thermal stability of complexes and a strong clay–polar organic molecule interaction are: large interlayer dipole moments of the

clays which are enhanced by the presence of high valence interlayer cations; a large number of OH groups on the organic molecules; and organic molecules with long chain length.

Two layers of organic molecules persist to higher temperatures in the clay that has the lowest layer charge, *i.e.* Hector, regardless of the interlayer cation, with the exception of the Na Cheto-glycerol complex (Table 7). Oscillating-heating patterns are shown in Fig. 1 for Ca Hector and Ca Cheto complexed with ethylene glycol. Variations in the temperature at which the first of two layers of organic molecules is lost are independent of the valence of the exchangeable cation (Table 7). Molecules that are most easily lost from the two-layer state at elevated temperatures probably are those held near the edges of the platelets or those not directly associated with the exchange cations. Polar organic molecules that are directly associated

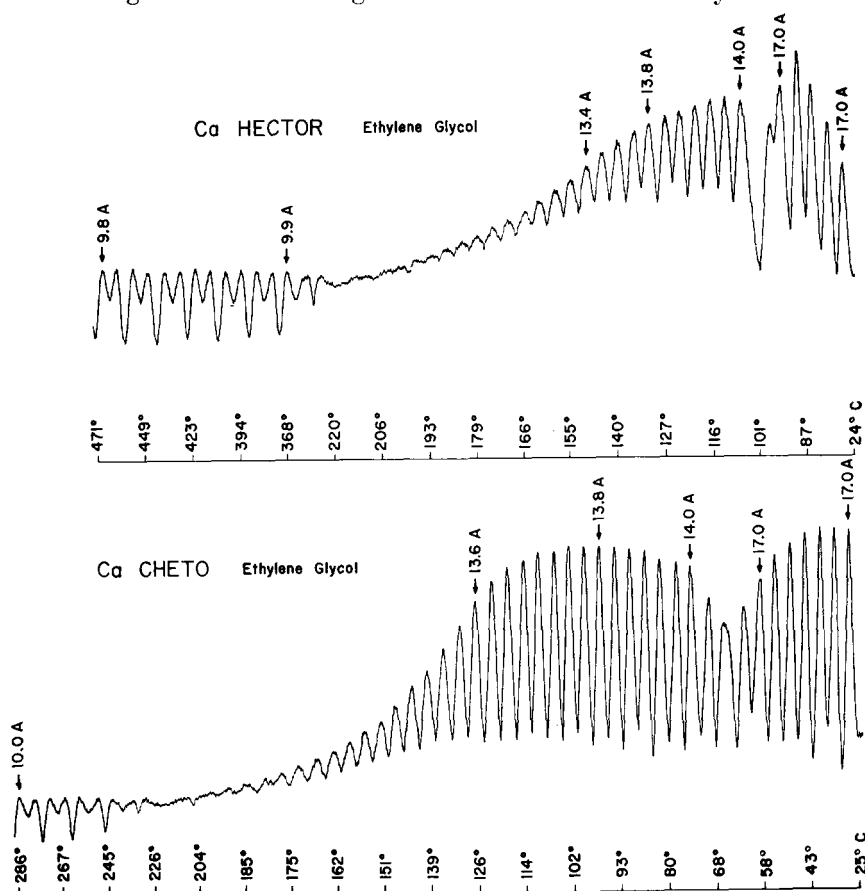


FIGURE 1.—Continuous records of position and intensity of first-order maxima from liquid-saturated products with increasing temperature.

with the exchange cations may neutralize the effect of variations in the interlayer dipole moments of the clays which are caused by differences in the valence of the cations. Organic molecules that fill the remaining interlayer space are all bonded with about the same energy.

The importance of OH groups on the polyalcohols in increasing thermal stability of the two-layer state may be illustrated by comparing the patterns for Na Hector with glycerol and 1,2-propanediol (Fig. 2). The OH groups on the polyalcohols may increase the thermal stability because they provide

TABLE 7.—TEMPERATURE (°C) AT WHICH FIRST LAYER OF ORGANIC MOLECULES IS REMOVED

Organic Compound	Hector		Argentina		Cheto	
	Na	Ca	Na	Ca	Na	Ca
Ethylene glycol	110	110	75	80	75	70
Glycerol	150	135	115	120	170	120
1,2-Propanediol	90	90	60	< 25	< 25	70
1,3-Butanediol	85	90	< 25	< 25	< 25	< 25
1,4-Butanediol	95	105	< 25	80	< 25	< 25
1,2,4-Butanetriol	150	160	120	160	130	150
1,5-Pentanediol	105	110	< 25	< 25	< 25	< 25
TEGDE	135	150	115	90	120	95

more effective contacts with the exchange cations or interlayer water molecules, or because oxygen atoms increase the effective positive charge on the hydrogens which mutually share a carbon atom (Bradley, 1945).

Two separate experiments (Tables 8 and 9) were performed to study the thermal stability of complexes with a single layer of organic molecules. The first experiment was a factorial study (Table 8) covering the three clays with both Na and Ca complexed with seven polyalcohols and TEGDE. A second experiment (Table 9) checked the reproducibility of measuring the temperature for the thermal stability of the single-layer complexes. The random error (residual) from the factorial study is equal to the averaged error from the separate replication and operator experiment. The latter experiment used six complexes replicated four times in blocks and employed four operators. Operators tabulated the temperature at which the organic molecules were completely removed from the complexes. The six complexes covered the entire temperature range for complete removal of organic molecules. There was no significant difference between operators but the variances of the six selected complexes were heterogeneous. The heterogeneity could not be related to temperature or to any other apparent characteristic of the complexes, but probably is the result of experimental error in running samples and reading temperatures during the run. Precisions (variances) that are heterogeneous cannot be averaged to obtain a

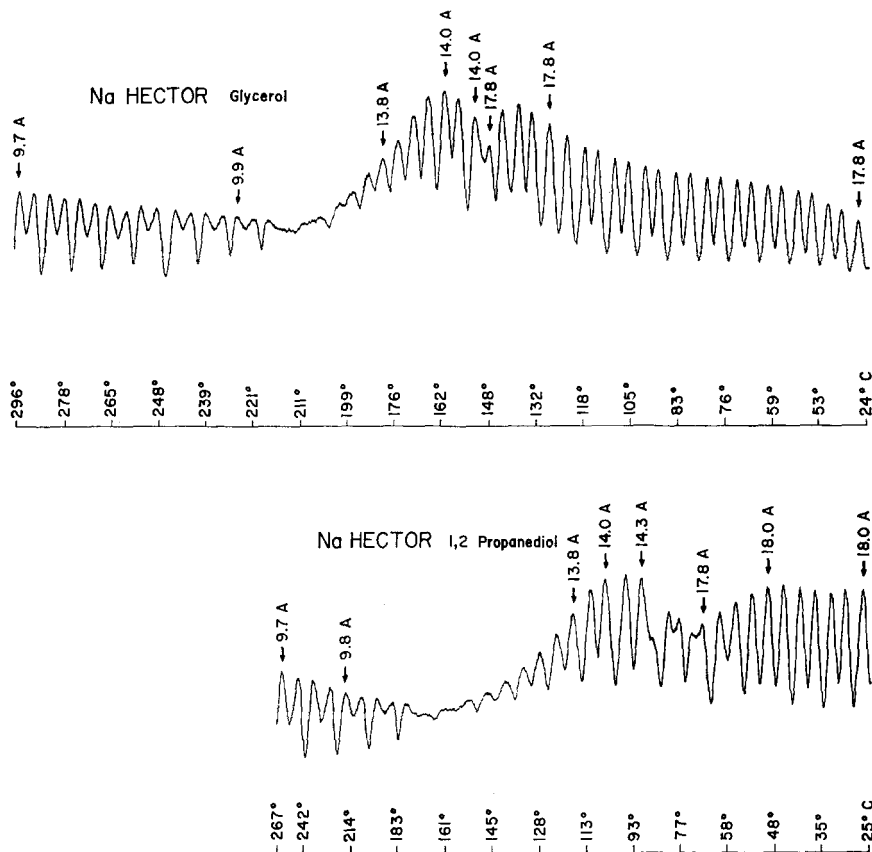


FIGURE 2.—Continuous records of position and intensity of first-order maxima from liquid-saturated products with increasing temperature.

TABLE 8.—FACTORIAL EXPERIMENT: TEMPERATURE (°C) AT WHICH 001 PEAKS ARE COMPLETELY DISORGANIZED OR EXHIBIT LOWEST INTENSITY BEFORE DEVELOPMENT OF A COLLAPSED 10 Å PEAK

Organic Compound	Hector		Argentina		Cheto	
	Na	Ca	Na	Ca	Na	Ca
Ethylene Glycol	155	210	105	210	120	200
Glycerol	210	260	160	250	210	300
1,2-Propanediol	165	230	105	220	135	255
1,3-Butanediol	175	245	115	230	110	210
1,4-Butanediol	185	245	200	230	140	215
1,2,4-Butanetriol	280	300	300	450	220	400
1,5-Pentanediol	220	240	160	240	150	245
TEGDE	235	340	265	350	235	280

single plus or minus value applicable to each individual complex, therefore no limits of precision can be calculated for all the temperatures in Table 8 from the results of Table 9. The factorial experiment (Table 8) shows that the thermal stability of complexes having a single layer of organic molecules depends on the valence of the exchangeable cation and the organic com-

TABLE 9.—REPLICATION EXPERIMENT: TEMPERATURES (°C) AT WHICH 001 PEAKS ARE COMPLETELY DISORGANIZED OR EXHIBIT LOWEST INTENSITY BEFORE DEVELOPMENT OF A COLLAPSED 10 Å PEAK

Operator	Block	Na Cheto 1,2-propane- diol	Na Hector glycerol	Na Argentina 1,2,4-butane- triol	Ca Hector glycerol	Ca Argentina TEGDE	Ca Hector 1,2,4-butane- triol
1	1	124	195	302	252	347	306
	2	128	172	219	275	295	308
	3	130	163	229	207	310	269
	4	124	175	206	250	290	293
2	1	126	198	306	254	340	294
	2	133	174	220	279	295	307
	3	130	166	220	205	305	266
	4	123	177	201	250	289	298
3	1	125	222	305	234	343	317
	2	116	168	210	276	290	283
	3	130	160	225	220	310	285
	4	123	178	204	250	291	290
4	1	128	200	306	253	348	310
	2	130	175	218	280	295	306
	3	128	166	219	210	305	266
	4	126	177	206	254	292	300

ound. The layer charge of the clay does not significantly affect the thermal stability of a single layer complex.

Calcium clays retain one layer of organic molecules to a higher temperature than do respective sodium clays (Fig. 3), probably owing to the increase in the interlayer dipole moments of the clays when the exchange ion has a larger valence. The increase in thermal stability from Na to Ca clays is less pronounced with Hector (Fig. 3), the clay with the lowest layer charge. A valence change from Na to Ca on high layer charge clays is expected to increase the interlayer dipole moments of the clays and thermal stability of the complexes more than the same change on clays with a low layer charge. The thermal stability of one-layer complexes increases proportionally to the chain length and the number of OH groups of the organic molecules (Fig. 4).

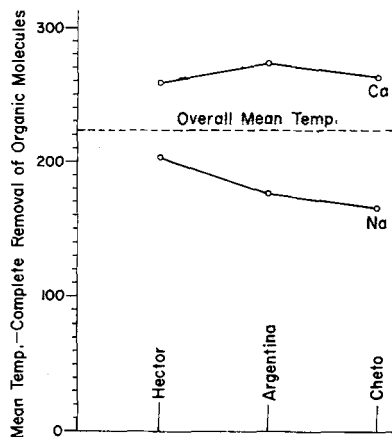


FIGURE 3.—Graph of mean temperatures for complete removal of organic molecules from various clay-organic complexes. Each point represents the average of eight clay-organic combinations.

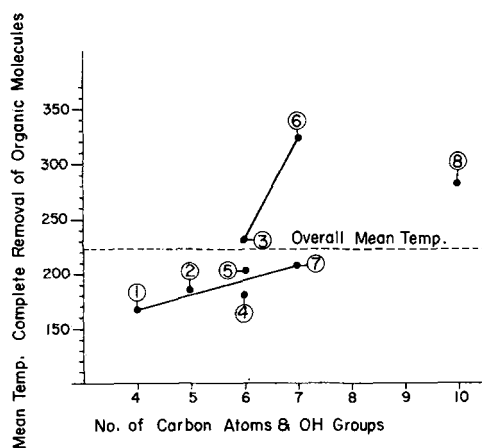


FIGURE 4.—Graph of mean temperatures for complete removal of organic molecules from various clays. Each point represents the average of six clay-exchangeable cation combinations. (1) ethylene glycol; (2) 1,2 propanediol; (3) glycerol; (4) 1,3 butanediol; (5) 1,4 butanediol; (6) 1,2,4 butanetriol; (7) 1,5 pentanediol; (8) TEGDE

CONCLUSIONS

(1) In certain instances expandable clay minerals within the montmorillonite group can be differentiated by employing one or more polyalcohols as complexing agents. The basal spacings for complexes with polyalcohols having a CH_2 group which is not connected to an oxygen atom depend upon the layer charge of the clay and the valence of the exchange cation.

Relatively larger basal spacings for these complexes are shown with montmorillonites that have a low layer charge and higher valence cations in interlayer positions.

(2) The basal spacings of montmorillonite-polyalcohol complexes that have a large initial water content are generally larger compared to the same complexes with a small initial water content, when polyalcohols are employed which have at least one CH_2 group which is not connected to an oxygen atom. Some complexes that do not have much interlayer water initially have small spacings and little penetration by polyalcohol molecules. The organic molecules may not replace easily water molecules that are associated with the interlayer cations. The spacings of clay complexes with ethylene glycol and glycerol do not depend upon the initial interlayer water content.

(3) The two-layer basal spacings of montmorillonite-polyalcohol complexes decrease as the humidity of the system increases. Water molecules commonly may be an essential component in montmorillonite-polyalcohol complexes.

(4) The basal spacings of the complexes are dependent upon the shape of polyalcohol molecules. Relatively larger monolayer spacings are observed for complexes with organic substances whose molecules have OH groups in the middle of the chain compared to those which have OH groups on the ends of the chain.

(5) One layer of polyalcohol molecules between silicate sheets is more stable than two layers of polyalcohol molecules. Two layers of organic molecules are more stable in clays that have a low layer charge. One layer of organic molecules is more stable with higher valence interlayer cations.

(6) The polyalcohol molecules probably are associated with the clay surface through weak $\text{C}-\text{H}\cdots\text{O}$ bonds and virtually no shortening of this distance occurs. The $\text{C}-\text{H}\cdots\text{O}$ interaction is enhanced by the presence of high valence interlayer cations. Long chain molecules probably are held more tightly between the silicate sheets.

(7) A high OH/C ratio promotes smaller observed spacings than calculated spacings. This high OH/C ratio promotes a better fit or packing between the organic molecules, or between organic molecules and exchange cations, or interlayer water molecules. A larger number of OH groups in the polyalcohol molecules increases the thermal stability of the complexes.

(8) Small polyalcohol molecules may pack down somewhat into the "hexagonal holes" in the silicate surface.

REFERENCES

- Allaway, W. H. (1948) Differential thermal analysis of clays treated with organic cations as an aid in the study of soil colloids: *Soil Sci. Soc. Amer. Proc.*, v. 13, pp. 183-188.
- Barrer, R. M. and MacLeod, D. M. (1955) Activation of montmorillonite by ion exchange

- and sorption complexes of tetraalkylammonium montmorillonites: *Trans. Faraday Soc.*, v. 51, pp. 1290–1300.
- Barrer, R. M. and Reay, J. S. S. (1957) Sorption and intercalation by methylammonium montmorillonites: *Trans. Faraday Soc.*, v. 53, pp. 1253–1261.
- Barshad, I. (1952) Factors affecting the interlayer expansion of vermiculite and montmorillonite with organic substances: *Soil Sci. Soc. Amer. Proc.*, v. 16, pp. 176–182.
- Bradley, W. F. (1945) Molecular associations between montmorillonite and some polyfunctional organic liquids: *J. Amer. Chem. Soc.*, v. 67, pp. 975–981.
- Byrne, P. J. S. (1954) Some observations on montmorillonite–organic complexes: in *Clays and Clay Minerals*, Natl. Acad. Sci.—Natl. Res. Council, pub. 327, pp. 241–253.
- Emerson, W. W. (1957) Organo-clay complexes: *Nature*, v. 180, pp. 48–49.
- Greene-Kelly, R. (1955) Sorption of aromatic organic compounds by montmorillonite, I. Orientation studies: *Trans. Faraday Soc.*, v. 51, pp. 412–424.
- Grim, R. E. (1953) *Clay Mineralogy*: McGraw-Hill Book Co., Inc., New York, 384 pp.
- Grim, R. E. and Kulbicki, G. (1960) Montmorillonites: high temperature phases and classification (manuscript).
- Hendricks, S. B. (1941) Base exchange of the clay mineral montmorillonite for organic cations and its dependence upon adsorption due to van der Waals forces: *J. Phys. Chem.*, v. 45, pp. 65–81.
- MacEwan, D. M. C. (1946) The identification and estimation of the montmorillonite group of clay minerals with special reference to soil clays: *J. Soc. Chem. Ind.* v. 65, pp. 298–304.
- MacEwan, D. M. C. (1948) Complexes of clays with organic compounds, I. Complex formation between montmorillonite and halloysite and certain organic liquids: *Trans. Faraday Soc.*, v. 44, pp. 349–367.
- Rowland, R. A., Weiss, E. J. and Bradley, W. F. (1956) Dehydration of monoionic montmorillonites: in *Clays and Clay Minerals*, Natl. Acad. Sci.—Natl. Res. Council, pub. 456, pp. 85–95.