acetone) to the water solution, but increases very much on a further addition of these solvents. The maximum velocity is reached in solutions containing from 30 to 50% organic solvent. At higher concentrations the decomposition of the blue compound slows down more and more. It was assumed that the blue intermediate yields coördinated compounds with the organic solvents as well as with water molecules, which are most stable in the corresponding pure solvent and are unstable when deprived of the coördinating partner.

5. In highly concentrated alcoholic solutions of dichromate and hydrogen peroxide mixtures, the velocities of formation and decomposition of the violet compound are small and co-measurable. The photometric curves are composed of two symmetrical halves with the maximum extinction in the middle.

6. The relation between the violet and blue compound is that of an anion to its undissociated acid form, both being formed from the dichromate ion and hydrogen peroxide. The resulting compound depends on the pH: above pH 4.5 the violet anion exists chiefly; below pH 4 the undissociated blue form is dominant. The velocity of decomposition of the blue form below pH 4 does not vary with the pH of the solution.

7. The mechanism of the catalytic decomposition of hydrogen peroxide below pH 4 was explained by assuming the existence of three successive reactions: the formation of the blue perchromate, its decomposition, and the regeneration of hexavalent chromium. Above pH 4.5 the catalysis is simpler, consisting of two successive reactions only: the formation and the decomposition of the violet perchromate.

JERUSALEM, PALESTINE RECEIVED JULY 24, 1944

[CONTRIBUTION FROM THE ILLINOIS STATE GEOLOGICAL SURVEY]

Molecular Associations between Montmorillonite and Some Polyfunctional Organic Liquids[1]

BY W. F. BRADLEY

The considerable amounts of data which have been available on the nature of montmorillonite and its relationship with water,[1a,2,3] have suggested that some interest might attach to the more or less analogous instances of association between the clay mineral and organic liquids of the types illustrated below. Attention has previously been directed to the activity of organic bases in base exchange, and to the value of such reactions in estimations of van der Waals thicknesses.[4,5] More recently, MacEwan[6] has called attention to the value of polyhydric alcohols for the identification of montmorillonite.

The organic liquids employed in the present study are chiefly of these two related types: (1) the aliphatic di- and polyamines and (2) the glycols, polyglycols and polyglycol ethers. Members of the two groups tend to differentiate themselves both in the nature of the clay complexes which they form and in the fact that the amines are active in base exchange, but the glycols are not. A few incidental unrelated liquids were also included.

The better established details of the structure of the montmorillonite type mineral, to which Dr. S. B. Hendricks had contributed heavily, can probably be best enumerated with reference to Fig. 1. The salient feature of the structure is the four-high packing of oxygen and hydroxyl ions coördinated about three layers of cations as shown. A "triple layer" configuration of this sort can be electrostatically neutral, as illustrated by the common mineral pyrophyllite, or can carry a residual negative charge due to substitution of lesser valent cations into either of the two types of coördination positions. In mica this charge is regularly distributed and arises from the substitution of aluminum for one-fourth of the silicon ions in the tetrahedrally coördinated positions. It is balanced by the presence of one potassium ion in each of the positions of 12-fold coördination which occur between adjacent triple layers. The structure is stable and three dimensional, marked only by the familiar perfect basal cleavage, and those potassium ions not actually in a cleavage surface are fixed. In the montmorillonite minerals this residual charge is less regularly distributed, arises in the main from the substitution of magnesium for aluminum ions in octahedrally coördinated positions, and occurs considerably less frequently than do the comparable charges of mica. Interlayer ions, usually sodium or calcium, again balance the total electrostatic charge, but under these conditions of reduced interlayer attraction, water is observed to interleave between layers effectively making each triple layer surface equivalent to an exterior surface, and the balancing interlayer ions are exchangeable.

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(1) Published with the permission of the Chief, Illinois State Geological Survey, Urbana, Illinois.

(1a) W. F. Bradley, R. E. Grim and G. L. Clark, *Z. Krist.*, **97**, 216–222 (1937).

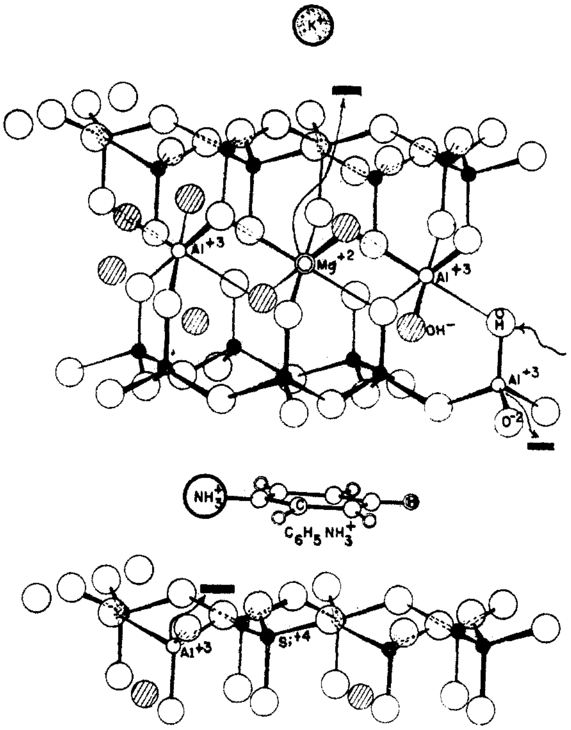
(2) S. B. Hendricks and M. E. Jefferson, *Am. Mineral.*, **23**, 863–875 (1938).

(3) U. Hofmann and A. Hausdorf, *Z. Krist.*, **104**, 265–293 (1942).

(4) J. E. Gieseking, *Soil Sci.*, **47**, 1–13 (1939).

(5) S. B. Hendricks, *J. Phys. Chem.*, **45**, 65–81 (1941).

(6) D. M. C. MacEwan, *Nature*, **154**, 577–578 (1944).



Exchange cations only on external surfaces of mica KAl$_2$(AlSi$_3$)O$_{10}$(OH)$_2$.

Layer in pyrophyllite Al$_2$Si$_4$O$_{10}$(OH)$_2$.

Exchange cations between layers in montmorillonite Al$_{1.67}$Mg$_{.33}$Si$_4$O$_{10}$(OH)$_2$.

Fig. 1.—The structural relationships of the montmorillonite type mineral with mica and pyrophyllite (after Hendricks).

The interlayer water is itself disposed in layers. These water layers are described by Hendricks[2] as hexagonal groups of water molecules joined in an extended hexagonal net. Protons are approximately tetrahedrally distributed about each oxygen ion. Each oxygen ion is thus bonded through hydrogen to three oxygen neighbors in the plane, and the one-fourth of the protons not so utilized are available for bonding to oxygen ions of the silicate framework or to other water molecules above or below the plane. The configuration is approximately illustrated by the positions of silicon ions in Fig. 1, if Si be considered equivalent to O and O equivalent to H, remembering that extra protons are available only on alternate oxygens. Under the influence of excess water, large quantities of water are imbibed by the structure, excessive swelling occurs, and exchange reactions involving the inorganic interlayer cations are a familiar phenomenon.

The interlayer surface area associated with each exchange ion is of the order of 50 to 100 sq. Å. Under these circumstances, neither the number of the inorganic ions nor their volume is great enough to afford direct observation by diffraction methods. Upon the introduction, by exchange, of large organic bases, however, water is excluded from a certain portion of each triple layer surface, and the periodic distance from layer to layer can be altered. In addition the attraction of a surface for the ion is stabilized by the van der Waals forces associated with the large organic molecules,[5] and excessive swelling in water may be inhibited.

A few additional relevant features are readily observed, but less clearly understood. 1. Natural montmorillonites which occur as the Na$^+$ salt apparently tend to associate with themselves one layer of hydrogen bonded water; those which occur as the Ca^{++} salt, two layers. 2. Hydrogen bonded water is readily removed by desiccation or mild oven drying (at least by about 200°) and is regained semi-reversibly. 3. Significant ignition losses at about 400 to 600°, thought of as elimination of water from the hydroxyl groups coördinated with Al, etc., in Fig. 1 are somewhat reversible but once the clay has reached such a temperature, hydrogen bonded water layers no longer enter the structure spontaneously. 4. The dehydrated mineral tends to "burn dead" on ignition to 700 or 800°. Some sort of rearranged skeleton layer persists after ignition to slightly higher temperatures, recognizable by a distinctive X-ray diffraction diagram but lacking about one oxygen ion in each twelve, and not significantly active in absorbing moisture from the air. The indefinite nature of these processes is apparent in the many published thermal analysis diagrams.[7] Figure 2 illustrates the loss of weight plotted against temperature rise compared with the "hygroscopic" gain after one day.

Materials and Methods.—Preliminary tests with several assorted montmorillonites indicated that no significant differences in the complexes formed were to be ascribed to individual montmorillonites. In most cases either Wyo-

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(7) R. E. Grim and R. A. Rowland, *Am. Mineral.*, **27**, 746–761 (1942).

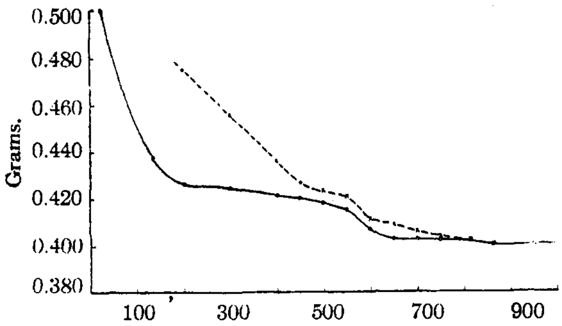

Fig. 2.—Water lost from 0.5 g. of Ca-montmorillonite (full line) and regained in twenty-four hours at room temperature (dotted line) after ignition to indicated temperatures. The relative humidity throughout is about 50%.

ming bentonite as furnished commercially by the American Colloid Company or a pink montmorillonite from Tatatila, Vera Cruz, Mexico, U. S. Nat. Mus. 101,836, was used. These represent, respectively, a predominantly Na$^+$ and a predominantly Ca^{++} salt, and the layer thicknesses in Table I refer to either or both. Occasional discrepancies of 0.1 or 0.2 Å. have been disregarded.

Organic solvents of both the above groups yielded characteristic complexes whether they were employed as the pure liquids or as water solutions as weak as molal or one-half molal for the glycols, weaker for the amines. For Table I the solvents were applied directly (except the solid compounds). Substantially the same thicknesses were observed in preparations from water solutions. Small amounts of clay were simply soaked in the solvent, the solvent poured off, the clay washed superficially by decantation, and permitted to air dry. X-Ray diffraction diagrams of the powder were then registered using either filtered Fe or Cu radiation.

Also in several instances clays were mounted on a blotting paper wick and the wick kept immersed in the organic liquid during exposure. Such diffraction diagrams did not differ from those of the equivalent preparations above for the stable complexes. Among the incidental liquids of high vapor pressure, however, the wick was necessary to keep the clay from reverting to a water system. Pyridine was unique among the liquids tried in that it formed a stable complex when dry but swelled excessively when wet.

Supplemental analytical information established the following relations:

FOR WYOMING BENTONITE

Base exchange capacity	0.8 me. per gr.
Nitrogen in ethylenediamine complex	0.8 me. per gr.
Nitrogen in diethylenetriamine complex	1.1 me. per gr.
Nitrogen in triethylenetetramine complex	1.5 me. per gr.
Nitrogen in tetraethylenepentamine complex	1.8 me. per gr.
Na$^+$ displaced by NH$_4$Cl	0.6 me. per gr.
Na$^+$ displaced by triethylenetetramine	0.6 me. per gr.

Gypsum known to be present in the bentonite displaces 0.2 or 0.3 me. per gr. of Na$^+$ by either a water or glycol extraction.

FOR Ca MONTMORILLONITE

Ca^{++} displaced by NH$_4$Cl	0.4 me. per gr.
Ca^{++} displaced by ethylenediamine	0.3 me. per gr.
Ca^{++} displaced by ethylene glycol	None

For one-half gram samples as in Fig. 3	Na-Montmorillonite	Ca-Montmorillonite
Water displaced by ethylene glycol	0.05 g.	0.10 g.
Apparent weight of glycol in complex	0.14 g.[a]	0.18 g.
Water displaced by dimethyl ether of tetraethylene glycol	.....	0.10 g.

[a] Other estimates have indicated that the amount of montmorillonite in Wyoming bentonite is about 80 to 85%.

Analysis of the complexes formed established the fact each of the aliphatic polyamines as well as the diamines entered into exchange reaction essentially as dibasic ions. The ratios of recoverable nitrogen to the exchange capacity were essentially 1, 1.5, 2, and 2.5 for amines with 2, 3, 4, and 5 nitrogen atoms, respectively. The actual displacement of inorganic ions was checked by the recovery of displaced sodium in the case of the bentonite and displaced calcium in the case of the Ca-montmorillonite. Accessory minerals present in the natural materials (gypsum in the bentonite and calcite (?) in the Ca montmorillonite) preclude the possibility of precise agreements.

Complexes with glycol or glycol derivatives were not analyzed directly, but the failure of these liquids to displace exchange ions was checked as noted. To arrive at an estimate of the degree of displacement of water by the oxygen containing compounds, advantage was taken of the different magnitude of the vapor pressures of water, ethylene glycol, and the dimethyl ether of ethylene glycol. One-half gram samples of clay were wetted with small weighed doses of the respective liquids, and the pastes were placed in desiccators over calcium chloride. Figure 3 diagrams the course of the loss of weight as the pastes were weighed intermittently during a period of several weeks. In each case loss of weight during the first few hours was equal to the known molecular water content of the respective clays. It is probably significant that these losses are faster and more complete than losses by desiccation of the mineral alone. Glycol treated specimens lost weight progressively over an extended period, finally attaining a stable

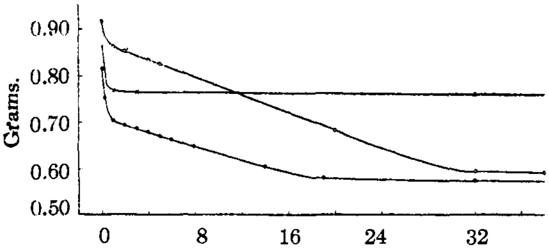

Fig. 3.—Displacement of water from montmorillonite by glycols and polyglycols: O, 0.5 g. of Wyoming bentonite with ethylene glycol; ×, 0.5 g. of Vera Cruz montmorillonite with dimethyl ether of tetraethylene glycol; , 0.5 g. of Vera Cruz montmorillonite with ethylene glycol.

weight which is taken to be the weight of the respective montmorillonite–glycol complexes. The high molecular weight ether did not evaporate appreciably. Inspection of the curves indicates that approximately one mole of glycol displaces two moles of water from the two-water layer configuration, and one mole of water from the one-water layer configuration. The density of the glycol in such a packing is about equal to, or slightly above, the density of the liquid itself.

The X-ray diffraction diagrams of the various complexes commonly showed a sufficient sequence of orders not only to permit one to calculate thicknesses of the complexes from higher orders but also to distinguish clearly that they constituted a rational sequence from a regularly repeated configuration as distinguished from the irrational sequences arising from random mixed layers.[8] In Figure 4 are five representative diagrams. Numerals indicate the more prominent orders of the basal reflections.

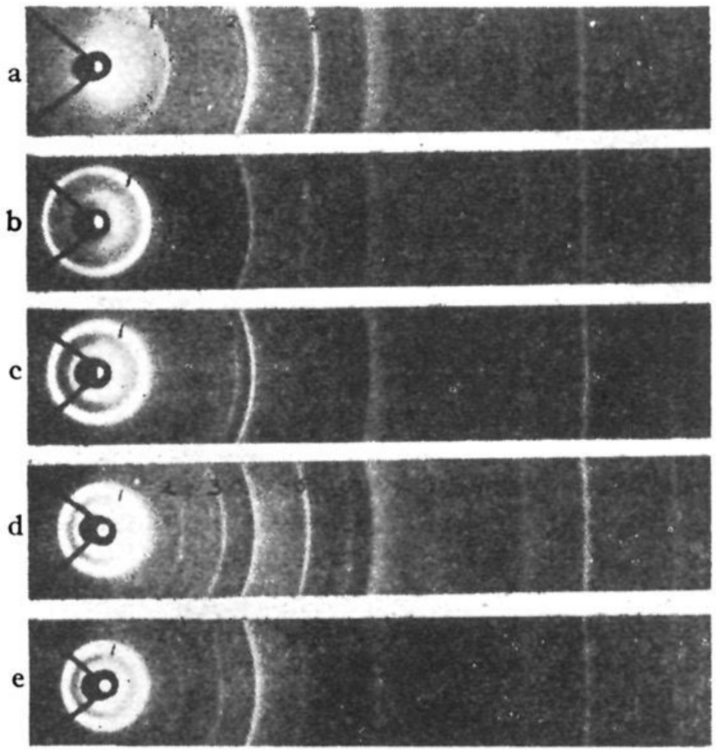

Fig. 4.—Representative diffraction diagram for the Vera Cruz montmorillonite: a, ignited at 550°; b, with ethylenediamine; c, untreated; d, with ethylene glycol; e, with dimethyl ether of tetraethylene glycol.

In Table I it is noted that the amine complexes exhibit similar thickness between 13 and 13.5 Å. and that most of the oxygen compounds run about 17 or 18 Å. The former figure suggests at once that one layer of the organic molecules separates adjacent clay layers with the zig-zag of the chain parallel to the clay surface. The second figure is not so directly indicative. As many as ten orders for 001 were evident on some films, however, and although these represent no d spacing under 1.8 Å., one would feel that they should locate the organic molecules fairly well, particularly if, as was indicated, those molecules lay parallel to the clay surface. Visually estimated intensities and signs based on the inorganic skeleton were therefore used for a one dimensional Fourier series, and electron density curves were sketched after adjustment to comparable scales. In arriving at these estimates intensities of the powder diffraction rings were weighted for one of the more complete sequences (with ethylene glycol), and reduced as for F-values. To help compensate for the comparative shortness of the separate observed sequences they were then fur-

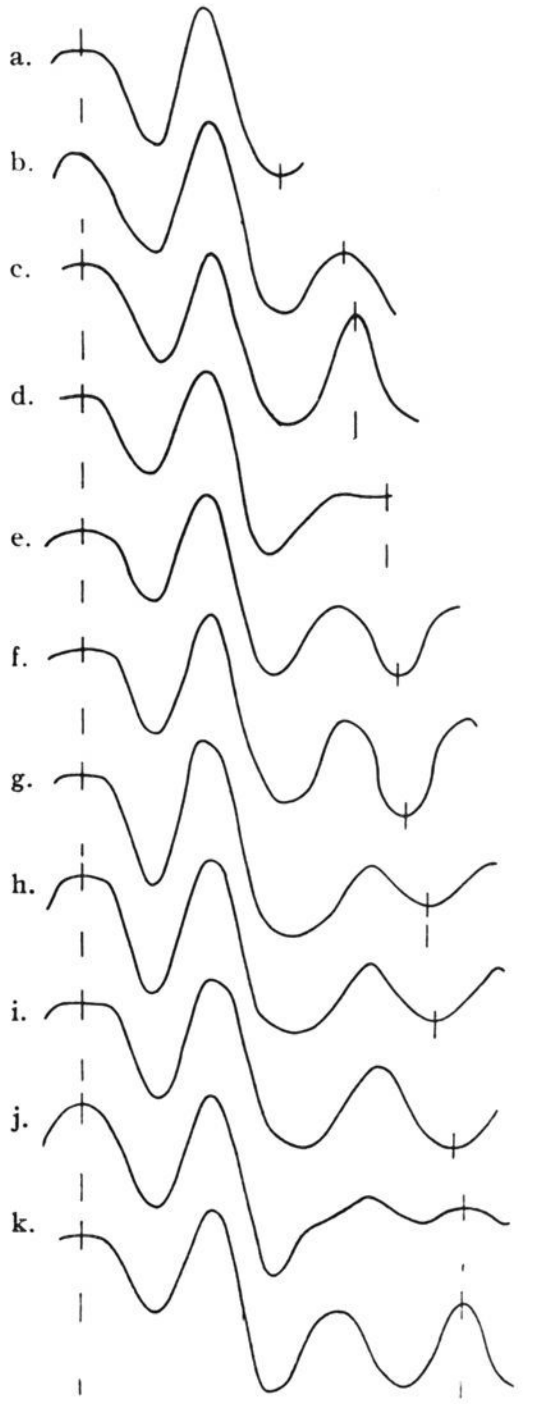

Fig. 5.—Fourier sketches illustrating the types of complexes observed: a, the montmorillonite "Skeleton"; b, water (1 layer); c, ethylenediamine; d, 1,4-dioxane; e, benzidine; f, water (2 layers); g, ethoxytrimethylene glycol; h, ethylene glycol; i, dimethyl ether of tetraethylene glycol; j, sucrose; k, water (3 layers). Each sketch extends from 0 to $^1/_2$ of d_{001}.

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[8] S. B. Hendricks and E. Teller, *J. Chem. Phys.*, **10**, 147–166 (1942).

TABLE I

COMPLEX FORMATIONS BETWEEN MONTMORILLONITE AND ORGANIC LIQUIDS

Compound employed	Cell height observed, Å.	Apparent $O-CH_2$ contract, Å.	Apparent interlayer distance for double layers, Å.
Ethylenediamine	13.1	3.3	
Propylenediamine	13.4	3.4	
Hexamethylenediamine	13.2	3.3	
Diethylenetriamine	13.2	3.3	
Triethylenetetramine	13.3	3.4	
Tetraethylenepentamine	13.4	3.4	
Methylamine	12.7	...	
Ethylene glycol	17.0	3.5	3.4
Propylene glycol	18.1	3.6	4.2
Tetramethylene glycol	17.9	3.6	4.1
Pentamethylene glycol	13.7	3.6	
Decamethylene glycol	13.5	3.5	
Ethoxy-pentamethylene glycol	14.3	3.8	
Ethoxy-trimethylene glycol	16.7	3.4	3.3
Carbitol	16.9	3.5	3.4
Methoxy-triethylene glycol	17.4	3.6	3.6
Di-methyl ether of ethylene glycol	17.0	3.5	3.4
Di-methyl ether of triethylene glycol	17.5	3.6	.3.7
Di-methyl ether of tetraethylene glycol	17.7	3.6	3.9
Ethanol	17.3	3.6	3.5
Glycerol	17.7	...	
Sucrose	18.3	...	
1,4-Dioxane	14.7	...	
Pyridine	14.8	2.6[a]	3.0
Benzene	15.1	2.7[a]	3.1
Benzidene	15.2	2.7[a]	3.2

[a] Oxygen ring contact.

ther arbitrarily reduced according to diffraction angle in a manner equivalent to the introduction of a temperature factor. · "F-coefficients" for the entire series of complexes were then estimated directly by comparison with this single set. Estimated intensities and the corresponding "F-coefficients" for the glycol complex are listed in Table II, together with a tabulation of the "F-coefficients" used in sketching the density curves illustrated in Fig. 5.

The inorganic ends of the curves are of course unresolved, the shortest observed spacing being greater than any projected interionic distance in the individual triple layers. The peaks at the origin represent the octahedrally coördinated ions and the oxygen associated with them, and the peaks at about 3 Å. represent the tetrahedrally coördinated ions and the surface oxygen. The general resemblances of these ends of the curves indicate that the smaller interlayer peaks are also probably real. These smaller interlayer peaks, involving molecular approaches of 3 or 4 Å., are much better resolved. The examples 5a, b, f, and k, illustrating water relationships previously established,[1,2,3] are included for comparison. Curve 5c, representing the complex with ethylenediamine, is equally typical of the other di- and polyamines and of the deca- and pentamethylene glycols. Curves 5g, h, and i are typical of the other glycols, ethanol, the polyglycols, and the various ethers. Of particular interest in establishing the validity of these peaks is a comparison of curves 5i and k, which differ but little in cell height represented, but clearly indicate two layers of interlayer liquid for the ether and three layers for the water. It is also no doubt significant that curves 5d and j, representing molecules without planar configurations, are not readily interpreted.

TABLE II

ESTIMATED "F-COEFFICIENTS" FOR DIFFRACTION DIAGRAMS FROM TYPICAL MONTMORILLONITE COMPLEXES

	With ethylene glycol		Estimated coefficients for:									
Order	Estimated intensity	Corresponding coefficients	Dehydrated skeleton	Water (1 layer)	Ethylenediamine	1,4-Dioxane	Benzidene	Water (2 layers)	Ethoxy-trimethylene glycol	Di-methyl ether of tetraethylene glycol	Sucrose	Water (3 layers)
1	Very strong	+5	+2	+4	+4	+5	+5	+4	+5	+5	+6	+5
2	3	+1	−1	−2	...	...	...	...	+1	+1.5	+2	+1
3	6	−2	+5	...	−1	−3	−2	−1	−3	−2	−1	−1
4	..	...	...	+5	+5	+1	...	+0.5	...	...	−2	−1
5	15	+5	−1	...	−0.5	+4	+4	+4	+5	+5	+3	+0.5
6	3	+2		−1	−1	...	...	...	+2	+2	+6	+5
7	..	...			−1	−1	−1	−1	...	...	+1	−1
8	1	−1.5					−1	−1	−1.5	−1	−1	−1
9	0.5	−1							−1	−1	−2	−1
10											+1	

Discussion

The present investigation was originally undertaken as a supplement to a series of studies of the influence of hydrogen bonding on solubilities,[9] and was suggested by the presumedly strong donor properties of oxygen populated surfaces as illustrated in Fig. 1; the thought being that O—H · · · O and N—H · · · O bonds between the

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(9) G. F. Zellhoefer, M. J. Copley and C. S. Marvel, THIS JOURNAL, 60, 1337-1343 (1938).

organic and inorganic portions respectively should exercise strong influence on the associations. Extension of the classes of solvents to molecules such as those with exclusively ether oxygens, and considerations of the distances concerned have however both raised serious objections to such a picture.

For the aliphatic di- and polyamines the association does not clearly distinguish itself from the similar associations with other organic bases. An anticipated d value would be about 13.2 Å. (6.6 Å. for O–O thickness for the inorganic layer +2 (1.3 + 2) Å., the van der Waals radii, respectively, of O and CH_2). The surface area per exchange ion for the Wyoming bentonite is about 70 sq. Å., which is sufficient to accommodate any of the amines, on a dibasic basis. For the largest, tetraethylenepentamine, for example, nearly half of the surface would not be utilized, and would be available to water or excess liquid without alteration of the observed d value. The combination of Coulomb and van der Waals forces as described by Hendricks would have seemed to account adequately for the stability of the configurations.

Those of the complexes, as the oxygen compounds, which have not involved displacement of the inorganic bases, present a different sort of picture. Not only are the configurations assumed without the benefit of Coulomb forces (indeed, in opposition to those of the inorganic exchange ions), but these organic molecules may be withdrawn by the clay from rather dilute solutions, and in becoming adsorbed on the clay surfaces, displace hydrogen bonded water. Complete displacement is indicated in Fig. 3.

It is uncertain to what degree reliance can be placed in the resolution of peaks in the electron density sketches. Center to center distances from the aliphatic chain to the oxygen surface run about 3.3 to 3.6 Å., considerably too long for strong O—H · · · O bonding, and such distances do not vary significantly, for example, for glycol or for a given polyglycol where such bonds were anticipated and for their respective dimethyl ethers, where no such bonds were possible.

One is led then to the conclusion that the interaction between hydrogen atoms of the aliphatic chain with oxygen ions of the silicate surface involves energy comparable in magnitude with that of the O—H · · · O bonds of a natural water system. For the glycol and polyglycol chains employed, about four such interacting pairs are possible per 45 sq. Å. of surface as compared with two O—H · · · O bonds between a water layer and an equivalent surface area as postulated by Hendricks. The 3.3 to 3.6 Å. distances indicated are plainly about what would be expected for an O—CH_2 van der Waals contact, but the energies which apparently must be associated with these interactions suggest an augmented attraction of the nature of an actual C—H · · · O bond, with hydrogen atoms from the aliphatic chain directed at negative surface areas. The stability of the complexes with the polyfunctional compounds employed, as compared with possible complexes with hydrocarbons, is presumably a consequence of the high proportion of α-carbons, which should be more susceptible to attraction by the negative areas.

Indicated distances between organic layers range from about 3.4 up to 4.0 Å. or more, and seem to increase with increasing chain length. These probably represent the 4.0 Å. CH_2—CH_2 van der Waals contact, foreshortened by some degree of packing for the shorter molecules.

Looking back from this, now, to the single layer polyamine complexes it would seem that for these, too, a major contribution to their stability could be the same C—H · · · O bonding, with the Coulomb forces merely adding to the stability.

In the matter of the arrangement of liquid molecules in the plane of a clay surface, no information is made available. Alcoholic ends would, however, be free to associate normally. It was noted that for larger numbers of methylene links per functional group, the glycols assumed a single layer configuration.

A short consideration of aromatic molecules is not inconsistent with the foregoing concept. Hendricks observed both adsorption in excess of exchange capacity, with increased interplanar spacings, and rather ready hydrolysis for phenylenediamine clay salts, whereas aliphatic amine complexes here described have maintained the same physical appearance and c axis length both in the presence of excess amine and after intermittent washings for a year's duration. More pronounced "over saturation" and greater increased c axis lengths are also observed for clays kept wet with pyridine. Aromatic molecules such as these could hardly exhibit the same sort of hydrogen-oxygen interaction suggested above, but apparently are subject to some weaker attraction involving polarization of the rings as a whole. The three cases, benzidene, pyridine and benzene yield substantially the same configuration, which must be geometrically independent of Coulomb forces, although the stabilities plainly vary. In this configuration, not only is it true that the total space available is insufficient to accommodate the normal van der Waals ring thicknesses, but the Fourier sketches suggest that the foreshortened approach is between the oxygen surfaces and the adjacent organic layers rather than between the two organic layers.

A consideration of heat treated montmorillonites points also to higher energies for the organic complexes than for the water systems. Although it is not clear what factors have been effective, it is readily observed that montmorillonites heated to some 400 or 500° (lower in some instances) assume a water-free configuration of about 9.5 Å. layer thickness, and stand indefinitely in humid air or under water without again developing the water layers characteristic of the natural materials. Both the nitrogen and the oxygen containing liquids, however, swell these roasted materials with assumption in each case of their characteristic complex configurations. The glycols and glycol derivatives can then be washed out with water, regenerating the natural mineral.

"Dead burned" materials (about 700 or 800°) have not been observed to swell with any of the agents employed.

Acknowledgment.—The author is indebted to Dr. M. J. Copley of the Eastern Regional Research Laboratory, who suggested the probable existence of associations between clays and the types of liquids employed, and who furnished the various polyamines and glycol derivatives.

Summary

The association of a number of polyfunctional saturated aliphatic chains with montmorillonite surfaces gives evidence of augmented attraction of the nature of a C—H · · · O bond between methylene groups and the oxygen surfaces of the clay.

The same oxygen surfaces exercise a lesser but similar influence on some aromatic rings.

RECEIVED JANUARY 15, 1945

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MANITOBA]

The System Aniline–Phenol–Water

BY A. N. CAMPBELL

An exhaustive treatment of the equilibrium of three liquids, both with and without the formation of two (or three) layers, has been given by F. A. H. Schreinemakers in the *Z. physik. Chem.*, between 1897 and 1903. In **23**, 649 (1897), he discusses the equilibrium of two liquid layers; in **25**, 305 (1898), the occurrence of a solid phase in the above equilibrium; in **29**, 577 (1899), the system aniline–phenol–water; in **30**, 460 (1899), the occurrence of solid phases in the system aniline–phenol–water; in **35**, 459 (1900), the vapor pressures of binary and ternary liquid mixtures of aniline–phenol–water; in **36**, 257 (1901), he gives a theoretical discussion of the vapor pressures of ternary mixtures; in **36**, 413, 710 (1901), and **37**, 129 (1901), further theory, including the distillation curves; in **38**, 227 (1901), the occurrence of three liquid layers; in **43**, 671 (1903), some concluding remarks.

Schreinemakers' experimental work on the ystem aniline–phenol–water (except the vapor pressure) was done by the method of Alexejeff, that is, mixtures of known composition were made up and the temperature of homogeneity observed. This isobaric method becomes indirect when applied to the investigation of isotherms and there is serious objection to it wherever the curvature of the isotherm is great. Thus, for example, Schreinemakers finds for the critical composition at 95°: 69.9% water, 26.6% phenol, 3.5% aniline, whereas, I find by direct analysis of equilibrium layers, at 96.7°, 59.8% water, 35.5% phenol, and 4.7% aniline. The slope of the tie-lines leaves little doubt as to the general correctness of my result, and this therefore illustrates the danger of the method used by Schreinemakers. He was probably forced to use this method through lack of an analytical method. I found an excellent analytical procedure in the conductimetric method and have determined the isotherms directly by analysis of equilibrium layers. In addition, I have also investigated the equilibrium with solid phases, and the conditions of the various eutectics. Finally, I have investigated the vapor pressures over the whole field of the diagram at different temperatures and, in some typical cases, found the composition of the vapor given off by boiling mixtures.

The Component Binary Systems

These are phenol–water, aniline–water, and aniline–phenol. The system water–phenol is too well known,[1] to require discussion, except to point out that it has been found[2] that in the stable system a solid hydrate of phenol makes its appearance, but this hydrate is never observed under ordinary circumstances.

The data on the system aniline–water are due to Alexejeff[3] who determined the mutual solubility curve; no compound is formed.

The equilibrium data for aniline–phenol are due to Schreinemakers[4] although the existence of a compound 1 aniline:1 phenol, had previously frequently been observed.[5]

The compound has a congruent melting point and there are therefore two eutectics.

Experimental Details

The analytical method was the conductimetric, which is recommended for this purpose by Kolthoff[6]; the attainable accuracy is for both substances about 0.5% of the total quantity estimated.

Samples of 20–30 g. were made up to 2 liters and 500-cc. portions titrated with normal acid and normal alkali,

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[1] Rothmund, *Z. physik. Chem.*, **26**, 443 (1898); Timmermans, *ibid.*, **58**, 184 (1907); *J. Chem. Phys.*, **20**, 491 (1923); Hill and Malisoff, THIS JOURNAL, **48**, 918 (1926); Campbell and Campbell, *ibid.*, **59**, 2481 (1937).

[2] Rhodes and Markley, *J. Phys. Chem.*, **25**, 530 (1921).

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