

SWELLING OF SOME VERMICULITE-ORGANIC COMPLEXES IN WATER

by

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ABSTRACT

Complexes formed by macroscopic vermiculite crystals and *n*-alkylammonium ions with alkyl chains of 3-4 carbon atoms swell unidimensionally in water until the silicate layers are several hundred Ångströms apart.

The initiation of swelling is thought to involve the development of "icebergs" of the Frank-Evans type around the alkylammonium ions. Hydration of the oxygen surfaces of the silicate layers may also be a significant factor in the swelling process.

Cataphoresis experiments on finely dispersed aqueous suspensions indicate the presence of diffuse double layers of positive ions around negatively charged silicate particles. Further swelling on applying an electric field to individual swollen crystals immersed in water and dilute solutions also has been observed.

INTRODUCTION

Complexes formed by organic substances with expanding-lattice layer silicates have been the subject of both basic and applied studies for several years. From the review of the early literature on this subject by Grim (1953, pp. 250-271), it is apparent that these complexes may be cationic or molecular depending on the nature of the interaction between the intercalated organic substance and the mineral. The present communication is concerned mainly with the formation and properties of the cationic complexes produced when vermiculites are treated with certain *n*-alkylammonium ions, and is an extension of the work on the macroscopic swelling of butylammonium-vermiculite crystals in water reported by Walker (1960).

Jordan (1949) observed a relationship between alkyl chain length and basal spacing of *n*-alkylammonium-montmorillonite complexes, and noted that the organophilic nature of the complexes increased with increasing chain length. The free energy change occurring on exchange of *n*-alkylammonium ions for Na⁺ in montmorillonite has also been found to increase with increasing alkyl chain length (Cowan and White, 1958). X-ray diffraction studies on batavite and the Kropfmuhl vermiculite have enabled

Weiss, Mehler and Hofmann (1956) to make deductions regarding the orientation of interlayer alkylammonium ions in these vermiculites, in the dry state and after immersion in various liquids.

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RESULTS AND DISCUSSION

The localities of the vermiculite specimens used in the current work and their estimated layer charge in equivalents per $O_{10}(OH)_2$ unit of structure are as follows:

Young River, West Australia	0.6
Kenya	0.65
West Chester, Pennsylvania	0.7
Macon County, North Carolina	0.8

Small rectangular flakes were cut from larger natural crystals of vermiculite and treated with 1 N alkylammonium chloride solutions at 80 °C until no further change in basal spacing could be detected by X-ray diffraction. Replacement was usually complete within a few days and was in general more rapid the longer the alkyl chain.

Basal spacings of the four vermiculites after treatment with a series of *n*-alkylammonium ions are listed in Tables 1–3. Values are given for samples

TABLE 1.—BASAL SPACINGS IN ÅNGSTRÖM UNITS FOR VERMICULITES IMMERSED IN 1 N ALKYLAMMONIUM SOLUTIONS

Alkyl Group	Vermiculite Locality			
	Young River	Kenya	West Chester	Macon County
methyl	12.3	12.2	12.3	12.1
ethyl	12.7	12.6	12.7	12.6
<i>n</i> -propyl	13.1	13.1	13.3	18.4
<i>n</i> -butyl	19.0	19.2	19.0	19.2
isoamyl	18.8	19.0	19.0	19.0
<i>n</i> -amyl	19.1	19.2	19.9	19.5
<i>n</i> -hexyl	17.4	21.0	21.2	17.4
		22.9	26.3	20.5
<i>n</i> -heptyl	22.8	26.8	27.2	27.0
<i>n</i> -octyl	—	27.7	—	27.6

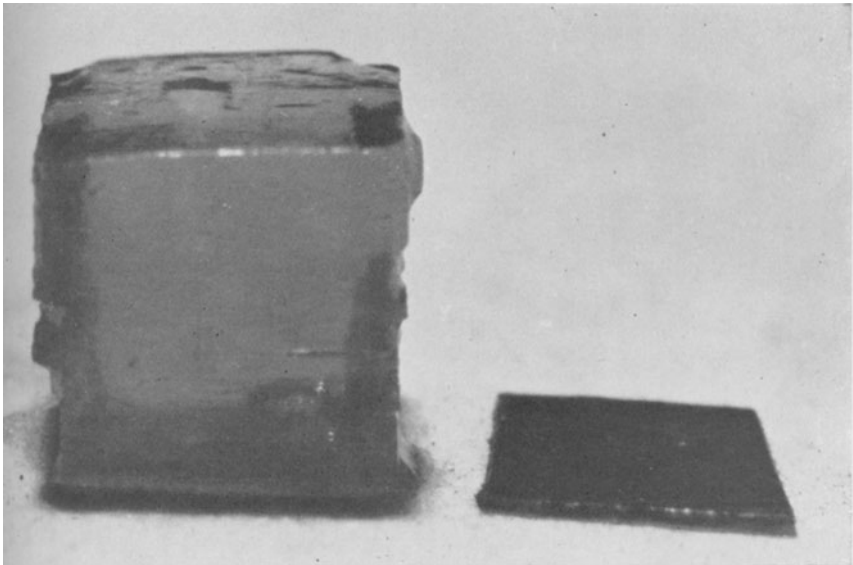


PLATE 1.—Butylammonium-vermiculite (Kenya) crystals before and after swelling in water (lateral dimensions of crystals approximately $2\frac{1}{2} \times 2\frac{1}{2}$ mm).

TABLE 2.—BASAL SPACINGS IN ÅNGSTRÖM UNITS FOR VERMICULITES TREATED WITH ALKYLAMMONIUM IONS AND IMMERSED IN WATER

Alkyl Group	Vermiculite Locality			
	Young River	Kenya	West Chester	Macon County
methyl	12.2	12.2	12.3	12.2
ethyl	12.6	12.6	12.7	12.6
<i>n</i> -propyl	MS	MS	MS	MS
<i>n</i> -butyl	MS	MS	MS	MS
isoamyl	MS	MS	MS	MS
<i>n</i> -amyl	19.8	20.2	20.0	19.3
<i>n</i> -hexyl	21.2	—	—	21.4
<i>n</i> -heptyl	22.2	22.6	22.3	22.0

MS = Macroscopic swelling.

TABLE 3.—BASAL SPACINGS IN ÅNGSTRÖM UNITS FOR VERMICULITES TREATED WITH ALKYLAMMONIUM IONS, WASHED WITH WATER (OR ALCOHOL WHERE MACROSCOPIC SWELLING IN WATER OCCURS) AND DRIED AT 80 °C

Alkyl Group	Vermiculite Locality			
	Young River	Kenya	West Chester	Macon County
methyl	12.2	12.2	12.3	12.4
ethyl	12.6	12.3	12.6	12.6
<i>n</i> -propyl	13.1	13.0	13.2	13.0
<i>n</i> -butyl	14.7	14.6	14.6	14.6
isoamyl	15.2	15.2	15.2	15.4
<i>n</i> -amyl	16.4	—	16.6	16.0
<i>n</i> -hexyl	17.3	17.1	17.3	17.2
<i>n</i> -heptyl	22.2	22.9	22.7	22.6

X-rayed while still in the salt solution, after washing with water, and after washing with water or alcohol and drying at 80 °C. In the preliminary tests, irrational basal spacings frequently were encountered and these could not always be exactly duplicated. Investigation showed that a number of factors were involved, and that rational and reproducible spacings usually could be obtained if suitable procedures were followed. Some examples are given below.

Introduction of methylammonium, ethylammonium and *n*-propylammonium ions into a Mg-vermiculite is only partial even after very prolonged treatment at 80 °C. Intercalation of the alkylammonium ions is facilitated

if the interlayer Mg^{2+} ions are first replaced by Na^+ , and complete, or almost complete, exchange can be obtained in this way.

A second source of irrational spacings, particularly noticeable with the longer chain ions, lies in the intercalation of variable amounts of the cation in excess of the exchange capacity, electroneutrality being preserved by simultaneous intercalation of the anion. For any given alkylammonium chloride, the amount of salt entering the interlayer regions increases with the concentration of the solution, and the concentration at which the effect becomes noticeable is less the longer the alkyl chain. The excess salt can be removed by washing the crystals with water or alcohol.

Variations in basal spacing associated with a color change in the vermiculite crystals from the normal yellow or brown color to green were also observed. The development of the green color, which is particularly marked with the *n*-butylammonium, *n*-amylammonium and *n*-hexylammonium complexes, becomes noticeable when the crystals are treated for longer periods than are necessary for exchange to be complete. Examination of the absorption spectra of the brown and green crystals indicates that the former have an appreciably higher content of ferric iron. The change in color from brown to green appears, therefore, to be related to the conversion of ferric to ferrous iron in the octahedrally coordinated positions at the centers of the silicate layers, and implies that electrons are being transferred from the interlayer organic material to the silicate layers. (A similar color change also is produced in vermiculites by the introduction of stannous ions into the interlayer exchange positions.) Reversal of this process can subsequently be effected by treatment with oxidizing agents, such as hydrogen peroxide, when the green crystals revert to their original color and the absorption spectrum shows a corresponding increase in ferric iron content.

Oxidation processes occurring on montmorillonite surfaces have frequently been reported (*e.g.* Hauser and Leggett, 1940; Dodd and Ray, 1960) and similar phenomena have been noted in vermiculite (Walker, 1950), but the strong color of the oxidized organic substance normally obscures any color change taking place within the silicate layers. It is evident, however, that an oxidation process occurring on the crystal surfaces requires concomitant reduction elsewhere in the complex and that lattice iron would be a likely electron acceptor.

The basal spacings listed in Tables 1 and 3 suggest that in general the interlayer *n*-butylammonium ions and higher homologs are oriented with their long axes perpendicular or at high angles to the silicate layers, when the crystals are immersed in their solutions. In the propylammonium series, this is true only for the Macon County specimen, which is the vermiculite of highest layer charge. In the complexes formed by propylammonium with the other three vermiculites, the alkyl chains apparently lie at an

the interlayer surfaces, and this also occurs with all the ethylammonium complexes.

A remarkable feature of the complexes studied is the macroscopic swelling which some of them exhibit when they are placed in water (Table 2). This swelling is most marked in the *n*-butylammonium series, but also develops to a lesser extent in the *n*-propylammonium complexes. Although X-ray data are not given in the tables for alkyl chain lengths greater than 7 carbons, complexes were also produced with primary *n*-alkylammonium ions containing 8, 10, 12, 14, 16 and 18 carbon atoms. None of these complexes showed macroscopic swelling in water. Swelling in the *n*-alkylammonium complexes, therefore, appears to be restricted to those with alkyl chains of 3 or 4 carbons. Moreover, the corresponding isoamylammonium complexes, which also contain a linear 4-carbon chain, also swell in water although not so markedly as the butylammonium complexes.

Inspection of the *n*-propylammonium, *n*-butylammonium and isoamylammonium crystals before and after swelling indicates that the swelling is anisotropic, being confined to the direction normal to the silicate layer planes. Butylammonium-vermiculite (Kenya) crystals in the unswollen and swollen states are illustrated in Plate 1. The swollen crystals are coherent and gel-like in consistency. Their shape suggests that the silicate layers are effectively parallel to one another after swelling, and that they are separated by some hundreds of Ångström units. Considerable distortion of the crystals may occur *during* the swelling process, since water entering at the edges of the layer planes tends to force them apart, while the central portions are still unexpanded. This distortion is more marked the larger the flake, because of the finite rate of penetration of the water molecules. Eventually, when water has penetrated to the center of the crystal, the distortions disappear and further swelling becomes uniform.

Many of the crystals tend to break into several pieces along cleavage planes during swelling, and X-ray examination sometimes shows significant scattering in the 19 Å region indicating that a proportion of the interlayer regions have remained unexpanded. These characteristics vary considerably with the different complexes, but appear to be at a minimum with the butylammonium complexes, particularly those formed with the vermiculite from Kenya.

Low-angle X-ray examination of several swollen crystals of the butylammonium-vermiculite (Kenya) complex, enclosed in cellulose capillary tubes in the presence of excess water, confirmed that interlayer separations of several hundred Ångström units are involved, and indicated that individual interlayer distances do not deviate markedly from the mean value. In view of these results, it seemed justifiable in the case of this particular complex to derive the mean interlayer distances in the swollen crystals directly from measurements of the change in thickness on swelling. Crystals

that cleaved during swelling or showed X-ray evidence of layers remaining unexpanded were rejected in making these measurements. The data in Fig. 1 were obtained in this way, and show that the amount of swelling is related to the concentration of butylammonium ions in the external solution. At high concentrations, basal spacings of 19.2 Å are observed by X-ray methods, indicating an interlayer separation of some 10 Å. When the concentration is reduced to about 0.06 N, marked swelling develops rather suddenly and spacings of the order of 170 Å are calculated from the change in thickness of the crystal. Further dilution results in continuous swelling, which is

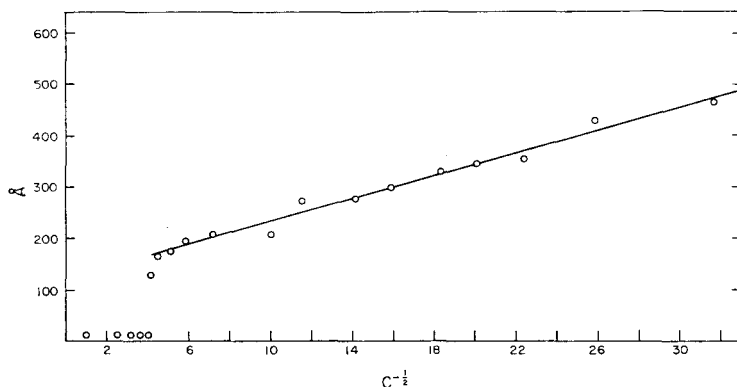


FIGURE 1.—Relationship between interlayer distance of butylammonium-vermiculite and concentration of butylammonium chloride in external solution (c = moles/l.).

linear with respect to the reciprocal of the square root of solution concentration. In the linear region of the curve, the swelling is reversible; however, increasing the concentration to a value above 0.06 N does not normally produce complete and uniform contraction of the swollen crystals, although X-ray measurements indicate the development of strong scattering in the vicinity of 19 Å showing that parts of the lattice have contracted under these conditions. Swelling is fully reversible if water-swollen crystals are allowed to dry out at room temperature.

Macroscopic swelling of Li-vermiculite crystals has been noted previously by Walker and Milne (1950), although they gave no detailed information. In this system, swelling is again generally less uniform than for the Kenya butylammonium complexes, so that estimates of interlayer distance based on macroscopic changes in thickness of Li saturated flakes are less reliable, and are not given here in detail. Some tentative conclusions, however, may be drawn. The shape of the curve relating the interlayer distance in Li-vermiculite to solution concentration appears to resemble in its general form that shown in Fig. 1 for butylammonium-vermiculite, and the maximum

separation (*i.e.* at infinite dilution) is also about the same. The discontinuity on the curve, however, occurs at a different and somewhat higher concentration, and is much smaller.

The swelling behavior of both Li-vermiculite and butylammonium-vermiculite recalls that observed by Norrish (1954) in his X-ray diffraction studies of the swelling of H-, Na- and Li-montmorillonites. With Li-montmorillonite, Norrish found a "step" of about 20 Å on the swelling curve, and attributes this to hydration of the interlayer cations. Our measurements on Li-vermiculite suggest that the corresponding step may be of the same order of magnitude as this, while with butylammonium-vermiculite it is clearly very much larger.

Butylammonium ions in aqueous solution would not be expected to form hydration shells similar to those around a small ion, such as Li. Frank and Evans (1945), however, have shown that alkylammonium ions can have ordered water structures around them. These water structures, which they called "icebergs," while making it clear that the type of order envisaged is *not* that of ordinary ice, belong to the group of clathrate compounds in which water acts as host. Guest molecules in such clathrates do not impose an orientation on the surrounding water dipoles as in normal ionic hydration shells, but act rather as supports for the water, allowing it to overcome its high internal pressure and so to take up an ordered structure. If we assume that, at the discontinuity on the swelling curve (Fig. 1), all the interlayer butylammonium ions dissociate from the silicate layer surfaces and allow double shells of "iceberg" water to form around them, the space requirement for a regular distribution of the ions in the interlayer regions approximates the silicate layer separation observed.

The thermal stability of "icebergs" should be less than that of hydration shells around small ions like Li⁺ (Frank and Evans, 1945; Frank and Wen, 1957; Masterton, 1954), and it is perhaps significant that immersion of unswollen butylammonium-vermiculite crystals in water held at temperatures of 50 °C and higher almost completely inhibits the development of swelling. Li-vermiculite crystals on the other hand swell apparently as readily at 90 °C as they do at room temperature.

Since butylammonium ions, in spite of their low energy of interaction with water (Frank and Evans, 1945), lead to swelling in vermiculites, it seems possible that a not insignificant contribution to the swelling energy of the crystals may arise from the hydration of the oxygen surfaces of the silicate layers. The influence of the silicate surface on the first sheet of water adsorbed in vermiculite is shown by the observed arrangement of the interlayer water in Mg-vermiculite (Mathieson and Walker, 1954), where each water molecule site is related in a specific and similar fashion to an individual oxygen in the surface. There is, however, no direct evidence regarding the extent to which this influence is propagated away from the surfaces,

although the specificity of the swelling lattice for certain cations may seem to imply some type of long-range order.

Measurements on the swelling in water of butylammonium-treated samples of the Macon County, West Chester and Young River vermiculites, when compared with the Kenya data, suggest that the rate and maximum amount of swelling are less the higher the layer charge of the minerals. These data, however, which are again based on measurements of changes in crystal thickness, are not entirely conclusive, and it is evident that confirmation will have to await direct determination of interlayer separations by means of low-angle X-ray diffraction techniques. Butylammonium-phlogopite crystals, which should have a still higher charge, swell less than any of the vermiculites, although the swelling is still quite apparent. On the other hand, the relatively very fine-grained montmorillonites, which have a lower layer charge than the vermiculites and which on this account might have been expected to swell more in water, failed to swell at all. Moreover, powdering the vermiculite and mica crystals, either by filing or by grinding to particles of less than $50\ \mu$ maximum diameter, largely inhibited the swelling of the minerals in water, irrespective of whether they were treated with butylammonium chloride solution before or after powdering. The same is not true for powdered Li-vermiculite or for the naturally fine-grained Li-montmorillonite, both of which show a marked increase in gel volume when immersed in water. The swelling behavior of the butylammonium complexes with respect to particle size argues that the very extensive planar surfaces obtainable only with macroscopic crystals are necessary for swelling to occur in this system. Tests with butylammonium-vermiculite crystals of various sizes indicate that inhibition of swelling does not appear suddenly at any particular size, but that a gradual reduction of swelling ability develops in particles of the order of $100\ \mu$ maximum diameter and becomes more marked with further decrease in size.

Replacement of the interlayer butylammonium ions is relatively easy and rapid if water-swollen crystals are used. Most cations, however, both organic and inorganic, cause an irreversible contraction of the lattice in the *c*-direction, inhibiting further swelling in water. Apart from those already mentioned, *viz.*, *n*-propylammonium, isoamylammonium and Li, only a few other cations of a large number tested give swelling complexes, for example, dibutylammonium and the cationic forms of some amino acids. Immersion of water-swollen crystals in organic liquids, such as ethanol, leads to complete contraction which, however, is reversible since subsequent immersion in water causes the crystals to swell again to their original size.

When a strong aqueous solution of butylamine is used instead of butylammonium chloride for the original treatment of the vermiculite crystals, the resulting complex fails to swell in water. This behavior seems to be related to the presence in the interlayer regions of physically adsorbed

butylamine molecules between the butylammonium ions. The adsorption of the butylamine is apparently strong enough to prevent subsequent access by water molecules to the interlayer surfaces so that swelling does not occur. Moreover, crystals treated originally with butylammonium chloride and subsequently swollen in distilled water, contract in dilute butylamine solutions to a greater extent than they would in butylammonium chloride solutions of the same concentration.

The relationship between interlayer distance in butylammonium-vermiculite and concentration of the external solution in the linear part of the swelling curve (Fig.1) is consistent with the behavior expected from a swelling system in which diffuse electrical double layers are present (Norrish,

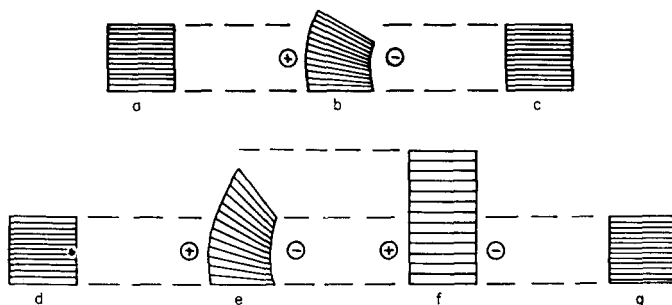


FIGURE 2.—Dimensional changes occurring in water-swollen butylammonium-vermiculite crystal placed in an electric field (schematic). *a-c*, in distilled water or dilute butylammonium chloride; *a*, before; *b*, during; and *c*, after application of field. *d-g*, in dilute aqueous butylamine; *d*, before field applied; *e*, in field for about 2 min; *f*, in field for about 10 min; *g*, after removal of field.

1954). In this region of swelling, dissociated butylammonium ions are envisaged as distributing themselves as counter ions between the silicate layers in accordance with double-layer theory. If an aqueous suspension of butylammonium-vermiculite, prepared by dispersing macroscopic water-swollen crystals in a high speed stirrer, is subjected to an electric field in the range 2–10 V per cm, an accumulation of silicate particles is observed around the anode of the cell. This result indicates that, under these conditions at least, butylammonium ions have dissociated from the silicate surfaces leaving the latter with exposed negative charges.

If, on the other hand, a single macroscopic crystal, prepared by treatment with butylammonium chloride solution, is swollen in water and placed in a weak electric field so that the plane of the silicate layers lies in the direction of the field, migration does not occur but the crystal shows dimensional changes which are illustrated diagrammatically in Fig. 2 *a-c*. Fig. 2 *a* represents the water-swollen crystal. On first applying the field, that side of the crystal proximate to the anode expands, while the other side shrinks (Fig. 2 *b*), the magnitude of the change being dependent on the field strength.

When the field is removed the crystal recovers almost completely (Fig. 2c). After a few cycles, however, an irreversible contraction of the crystal gradually develops, particularly at the edges, due perhaps to interference by H^+ ions from the water. If dilute butylammonium chloride is used instead of distilled water as immersion medium, similar phenomena are observed. In this instance, the initial silicate layer separation is less than in distilled water by an amount depending on the concentration of electrolyte present (*cf.* Fig. 1). In the presence of dilute aqueous butylamine, swelling of the side of the crystal nearer the anode is followed after a few minutes by swelling on the cathode side until the layer planes are again parallel to the field, as depicted in Fig. 2 *d-g*. The maximum amount of swelling obtainable under these conditions increases with the field strength. On removal of the field, the crystal slowly reverts to its original state. This type of swelling behavior is fully reversible over a number of cycles.

Li-vermiculite crystals under similar conditions, *i.e.* immersed in distilled water or in dilute lithium chloride or hydroxide solutions, generally respond in a similar fashion to that described for the butylammonium crystals, but their behavior is less reproducible. The significance of these changes in the butylammonium and Li-vermiculite crystals under electrical stimulation is not understood, although the phenomenon appears to be basically electro-osmotic in origin.

Although it is evident from this preliminary study that a great deal still remains to be done in defining the swelling characteristics of the complexes described herein, it is already apparent that their behavior is similar in some respects to that found in clay gels. Moreover, analogies undoubtedly exist with the swelling behavior of a variety of other layer systems, both inorganic and organic. Recently Hofmann (1960) has drawn attention to similarities in the swelling behavior of several such systems, using as examples such widely divergent materials as collagen, polyphosphates, layer silicates and nucleic acids.

It is perhaps pertinent to observe that highly oriented liquid crystals such as those described in this communication are likely to be amenable to types of experimental approach not directly, or less readily, applicable to other aqueous swelling systems. Their further study may, therefore, help to provide fresh information on the properties of the water and the nature of the forces operating in such systems.

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