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ORIENTED PENETRATION OF IONIC COMPOUNDS BETWEEN THE SILICATE LAYERS OF HALLOYSITE

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ABSTRACT

Drying hydrated halloysite from certain salt solutions results in reversible lattice expansion ranging from 5 to 45 per cent of the basal spacing. The reaction occurred with K^+, NH_4^+, Rb^+ and Cs^+, whose ionic diameters are of the order of 2.7 Å or more, whereas smaller cations such as Li^+ and Na^+, and divalent cations Mg, Ca and Ba gave no evidence of the reaction. The increase in the basal spacing of halloysite is clearly related to the kind of anion. There was no evidence of this type of expansion for montmorillonite. About 200 to 300 m. mols. of the ionic compound were estimated to be retained on the basal plane surfaces per 100 gm. of the air-dried clay.

It is concluded that the cation and anion penetrate between the silicate layers of halloysite, probably forming a unimolecular layer of the ionic compound, replacing the interlayer water.

INTRODUCTION

The phenomenon described here is concerned with oriented penetration of ionic compounds between the silicate layers of halloysite, resulting in reversible one-dimensional swelling. Similar phenomena are known with halloysite and some minerals of the montmorillonite group in the formation of interlayer complexes with certain organic and inorganic liquids. Although a type of complex of montmorillonite with inorganic molecules, e.g., $Mt^-NH_4^+(AgCl)$ was reported by Bloch (2); a chlorite-like mineral, $Mt^-NH_4^+Mg(OH)_2$ was obtained on treating Mg-montmorillonite with NH_4OH by Caillère and Hénin (3), relatively little is known of the oriented penetration of ionic compounds between the layers of clay minerals. It is suggested, however, from a study by the author on the reaction of halloysite with phosphates (10), that $(NH_4)_2HPO_4$ orients between the silicate layers of halloysite and forms a type of interlayer complex.

The first aim of the present study is to show that this type of reaction is possible between halloysite and some ionic compounds under certain conditions. The second is to study the factors affecting the reactions, to determine the stability of the resulting complexes and to assess the mechanism of the reaction. The technique used in this study is direct x-ray examination of the air-dried specimens obtained by treating clay minerals with salt solutions, without removing the excess salt.

MATERIALS AND METHODS

The clay minerals employed were hydrated halloysite from Yoake, Oita, Japan (1), and montmorillonite from Osage, Wyoming, U.S.A. One-half gram samples of the clay (<150 mesh, saturated predominantly with Na^+) were soaked in 1 ml. H_2O with 0.5 to 2.5 m. mols of an appropriate salt, allowed to dry at 30° C. (R.H. 36.5 to 60%) for several days, and ground in an agate mortar for *x*-ray analysis. Some specimens were subjected to ethylene glycol (E.G.) treatment; wetting with E.G. for 24 hours and heating at 100° C. for an appropriate time to remove the excess liquid.

X-ray diffraction patterns were obtained using Co radiation with Fe filter and a camera with a diameter of 80 mm., and employing a fine rod of the specimen in an *oblate* tube. Reported spacings were probably accurate to ±0.1 Å in the *d*-values higher than 10 Å, and intensity was measured visually.

EXPERIMENTAL RESULTS

Sodium, potassium, and ammonium chloride, nitrate, sulfate, phosphate, and acetate were tentatively divided into the following two groups on the basis of the effect of the treatment on the 10.1 Å spacing of hydrated halloysite (Table 1):

1. The treatment of the first group with the salts did not affect the basal spacing of hydrated halloysite. After heating at 100° C., the basal spacing of halloysite was reduced to the 7.2–7.4 Å spacing of metahalloysite.
2. The treatment of the second group with the salts clearly affected the basal spacing of hydrated halloysite, and after heating at 100° C. the basal spacing of halloysite was not reduced to 7.2–7.4 Å.

The interaction of halloysite with the salts belonging to the second group was shown by alteration in spacing between the layers and in the relative intensities of higher order basal reflections, excepting for the KCl and KNO_3 treated halloysites, where the basal spacing of hydrated halloysite was not significantly affected (Table 2 and 3). No essential alteration was found apart from these basal reflections.*

TABLE 1. EFFECT OF THE TREATMENT WITH SALTS ON THE BASAL SPACING OF HYDRATED HALLOYSITE

(5.0 m.mols of the salt per gm. of clay)

Cation	Anion					
	Cl	NO_3	SO_4	H_2PO_4	HPO_4	CH_3COO
Na	−	−	−	−	−	−
K	+	+	−	−	+	+
NH_4	+	+	+	−	+	+

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* Recently it has been shown by *x*-ray diffractometer methods that (*hk*) bands of halloysite are a little affected as the result of the reaction in some cases (unpublished).

On heating at 100° C., the basal reflections of all specimens treated with these salts, except for NH_4CH_3COO which sublimates at this temperature, were either not affected at all or merely diffused (Table 2 and 3). In either case the 7.2–7.4 Å spacing corresponding to that of metahalloysite was not shown. On the other hand, on washing with excess water, the 10.1 Å spacing of hydrated halloysite was readily restored in every specimen.

FACTORS AFFECTING THE REACTION

(*a*) *Kind of cation*

No alteration in the basal spacing of halloysite was found with the specimens treated with the sodium salts in contrast to those with the potassium and ammonium salts (Table 1). The similarity in the behavior of some of the latter is noted in view of the similarity of the ionic radii of K^+ and NH_4^+. This suggests the importance of the size of the cation in relation to the structure of the interlayer surface of halloysite in allowing the reaction, although the absence of the reaction with some ammonium and potassium salts should also be noted.

TABLE 2. *X*-RAY DIFFRACTION PATTERNS OF HALLOYSITE TREATED WITH POTASSIUM SALTS

(5.0 m.mols of the salt per gm. of clay)

(00*l*) or (*hk*)	Salt									
	None		KCl		KNO_3		K_2HPO_4		KCH_3COO	
	d	I	*d*	I	*d*	I	*d*	I	*d*	I
001	10.1	vs	10.2	s	10.1	s	13.3	m	14.3	vs
002							6.9	bv	7.2	bv
02, 11	4.42	s	4.38	ms	4.38	ms	4.42	w	4.33	mw
003	3.36	m	3.46	vw	3.38	bv				
004									3.51	mw
20, 13	2.56	m	2.55	w	2.53	w	2.55	vw	2.55	mw
	2.34	vw	2.34	bv			2.34	bv	2.34	bv
04, 22	2.23	vw	2.20	bv	2.16	bv	2.21	bv	2.23	vw
24, 31, 15	1.68	bv	1.69	bv	1.68	bv	1.67	bv	1.67	vw
	1.64	vw	1.65	bv	1.65	bv	1.64	bv	1.64	vw
33, 06	1.48	ms	1.48	w	1.48	w	1.48	mw	1.48	m
001*	7.4	m	10.1	s	10.1 7.2	w w	diffuse		14.3	vs

d in Å.

Reflections due to the presence of the excess salt were omitted.

* (001) reflection after heating at 100° C.

TABLE 3. *X*-RAY DIFFRACTION PATTERNS OF HALLOYSITE TREATED WITH AMMONIUM SALTS

(5.0 m.mols of the salt per gm of clay)

(00*l*) or (*hk*)	Salt									
	NH_4Cl		NH_4NO_3		$(NH_4)_2HPO_4$		$(NH_4)_2SO_4$		NH_4CH_3COO	
	d	I	*d*	I	*d*	I	*d*	I	*d*	I
001	10.5	vs	11.6	vs	13.2	vs	13.4	s	14.4	vs
002					6.65	w	7.1	bv	7.2	w
02, 11	4.43	mw	4.43	s	4.43	s	4.45	vs*	4.45	s
003	3.51	m	3.87	m						
004									3.57	w
20, 13	2.57	w	2.58	w	2.58	w*	2.56	vw*	2.58	w
			2.34	vw	2.30	bv*	2.34	vw*	2.36	bv
04, 22	2.23	vw	2.22	vw			2.20	vw*	2.23	vw
24, 31, 15	1.69	bv	1.68	bv	1.69	bv	1.69	bv	1.69	bv
	1.65	bv	1.64	bv	1.64	bv	1.64	bv	1.64	bv
33, 06	1.48	m	1.48	w	1.48	m	1.48	m	1.48	mw
001†	10.5	vs	11.6	vs	diffuse		diffuse		7.4	m

d in Å.

Reflections due to the presence of the excess salt were omitted.

* Reflection due to the presence of the excess salt was superposed.

† (001) reflection after heating at 100° C.

In order to clarify the relation of the size and the valence of the cation to the nature of the reaction, the following experiment with some alkali and alkaline earth chlorides, nitrates, and acetates was carried out. The specimens treated with the salts were placed in a desiccator over $CaCl_2$, heated at 100° C., washed with H_2O, air-dried, and then *x*-rayed. It is assumed that if the altered spacing is maintained on heating at 100° C., and the 10.1 Å spacing is readily obtained by washing with H_2O as was shown above with some specimens, the resulting 10.1 Å spacing may be considered an evidence that the reaction occurred, and the 7.2–7.4 Å spacing that it did not (Table 4). This procedure was adopted because of difficulties in obtaining clear *x*-ray diffraction patterns with some treated specimens, due to the deliquescent nature of some salts and the strong *x*-ray absorption of some cations.

The occurrence of the reaction seems to depend on the size of the cation involved. No reaction on halloysite was found with any salt involving a cation smaller than Na^+. A limiting value of ionic size might be estimated at approximately that of K^+. This is of interest in relation to the size of the cavity in the oxygen network of the silicate layer, because K^+ is assumed to fit into this cavity. Thus, so far as the monovalent cation is concerned, the reaction seems to occur only with the salt involving a cation not falling into the cavity of the oxygen network, suggesting a positive role of the cation for allowing the reaction. That is, the geometrical fitting of the cation into the surface structure of the oxygen layer of clay minerals seems to have prime importance in the reaction. The salts involving the divalent cation give no evidence of the reaction, in spite of the similarity of Ba^{++} to K^+ in ionic radii. These limitations in size and valency of cation are noted from the viewpoint of the mechanism of the reaction.

TABLE 4. EFFECT OF THE TREATMENT WITH CHLORIDES, NITRATES, AND ACETATES OF ALKALI AND ALKALINE EARTH METALS ON THE BASAL SPACING OF HALLOYSITE

(5.0 m.mols of salt per gm. of clay)

Anion	Cation								
	Li	Na	K	NH_4	Rb	Cs	Mg	Ca	Ba
Cl	−	−	+	+	+	+	−	−	−
NO_3	−	−	+	+			−	−	−
CH_3COO		−	+	+				−	−

Observed differences in the behavior between some corresponding potassium and ammonium salts—generally the latter are clearly liable to induce the reaction—would be accounted for by either the minor difference in the geometry of K^+ and NH_4^+, or the effect of hydrogen bonding that might be assumed between the H atom of NH_4 and the oxygen atom of the silicate layer. Also, it would be considered that the difference in solubility is of importance.

(*b*) *Kind of anion*

The variation in the basal spacing of halloysite between the specimens treated with some ammonium salts, or those treated with the potassium salts, and the similarity between the specimens treated with some corresponding ammonium and potassium salts indicate clearly the existence of anions between the silicate layers (Tables 2 and 3). Here, again, the absence of the reaction with some ammonium and potassium salts should be noted, because the occurrence is supposed to be limited by the type of anion involved in the reaction. However, there is no evidence to show the specific relation between the type of anion and the absence of the reaction or to suggest the positive role of the anion for causing the reaction, as was shown with the cation.

The effect on the basal spacing of halloysite treated with ammonium salts of different anions is shown in Table 5. The resulting variation in basal spacing may be due to the difference in the geometry of the anions. The validity of this view is also supported by the striking similarity in the basal spacing of halloysite treated with phosphate, sulfate, and arsenate, suggesting that the size and shape of the tetrahedra affect the basal spacing of the treated halloysite.

TABLE 5. BASAL SPACING OF HALLOYSITE TREATED WITH AMMONIUM SALTS

Anion	Basal spacing in Å	Δ-value* in Å
Without treatment	10.1	2.9
H_2PO_4	10.1	2.9
$(COO)_2$	10.1	2.9
Cl	10.5	3.3
Br	10.6	3.4
NO_3	11.6	4.4
HCOO	11.6	4.4
$HC_6H_5O_7$	13.0	5.8
$HAsO_4$	13.1	5.9
HSO_4	13.2	6.0
HPO_4	13.2	6.0
SO_4	13.4	6.2
CH_3COO	14.4	7.2

* Δ-value = basal spacing − 7.2 Å.

While HPO_4^{--} and CH_3COO^- afford practically the same increments of basal spacing associated either with K^+ or NH_4^+, Cl^- and NO_3^- do not, although the reason for this is not clear at present. Rather small clearance space for the KCl and KNO_3 treated halloysites is of interest, because it raises the question whether the anions penetrate between the silicate layers.

(c) *Amount of salt*

Up to a certain point, the basal spacing obtained with the treated specimens increased with the amount of the added salt, but above this, showed a definite value (Fig. 1). The shift of the (001) reflection position followed approximately what would be expected from random interlayer stratification. That is, the movement of the position of the (001) reflection relates to the separation in basal spacing between the reaction product and the original halloysite. When the separation is smaller, such as in the case of hydrated halloysite and NH_4Cl, the reflection position moves almost linearly; widely separated ones, as NH_4NO_3 and NH_4HCOO, show S-shaped curves. When they are far apart, $(NH_4)_2HPO_4$ and $(NH_4)_2HC_6H_5O_7$, the reflection position follows a markedly S-shaped curve with a steep central portion, where the reflection itself becomes very diffuse, and an almost horizontal end portion. Finally the separation becomes still greater, and with KCH_3COO the two reflections cease to form a pair and become isolated. This suggests the random interlayer stratification of the layers with a hydrated halloysite spacing and one with a unique spacing of the reaction product.

The rate of the salt addition required for the development of a unique spacing of the reaction product is 300 to 400 m. mols per 100 gm. of clay and seems not to depend so critically on the kind of the salt (Fig. 1). The reflections due to the excess salt were barely perceptible unless the salt was added at the above rate or more. The rate was found to be 50 to 100 m. mols per 100 gm. of clay in the corresponding experiment with the baked clay. Thus, it might be estimated roughly that 200 to 300 m. mols or more of the salt per 100 gm. of clay participates in the reaction. Since the cation exchange capacity of this clay is about 20 m.e. per 100 gm. of clay, the rather high figure of 200 to 300 m. mols is significant from the viewpoint of the forces exerted on the interlayer surface of halloysite.

(*d*) *Kind of clay minerals*

In view of a common peculiarity in the crystal structure in connection with interlayer swelling, it was of interest to determine whether montmorillonite also gives the same reaction. No evidence of variation in basal spacing was found with montmorillonite treated with some ammonium salts in contrast with halloysite (Table 6). The rather uniform 12.8 Å spacing may be attributed to the presence of the interlayer NH_4^+ and water. The difference between montmorillonite and halloysite is ascribed to the difference in the charge density on the interlayer surface and the atomic configuration of the exposed silicate layer. The higher interlayer charge and the lack of the exposed hydroxyl layer of the former would induce a stable configuration of NH_4^+ and a contraction of the silicate layers, that probably hinder further absorption of cation and anion With halloysite, on the contrary, the low interlayer charge and the existence of the exposed oxygen and hydroxyl layers seem to favor the

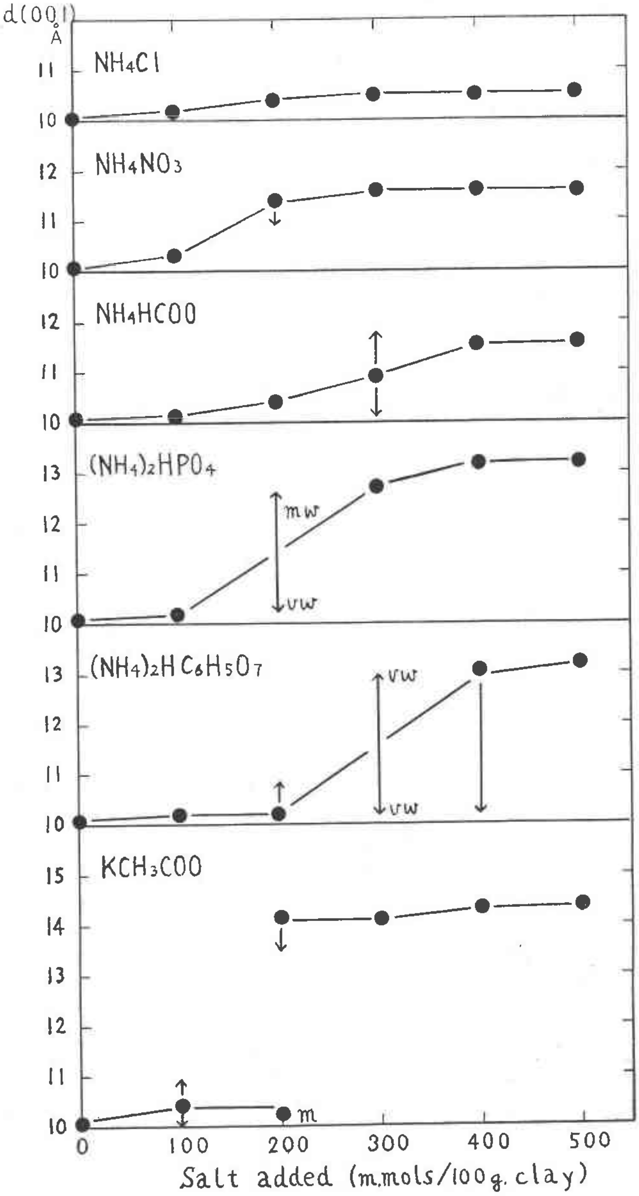

FIG. 1. Variation of basal spacing of halloysite with the amount of salt added.

TABLE 6. BASAL SPACING OF MONTMORILLONITE AND HALLOYSITE TREATED WITH AMMONIUM SALTS

(5.0 m.mols of salt per gm. of clay) in Å

Mineral	Anion				
	Cl	NO_3	HPO_4	SO_4	CH_3COO
Montmorillonite	12.7	13.8 ~11.7	12.8	12.8	12.8
Halloysite	10.5	11.6	13.2	13.4	14.4

reaction. Besides this, a possible weak polarizability of the silicate layer itself would support the reaction.

STABILITY OF THE REACTION PRODUCTS

The reversibility of the reaction is ascertained from the ready restoration of the 10.1 Å spacing of hydrated halloysite by washing the reaction product with water. It is suggested that the progress of the reaction depends on the moisture condition of the salt-halloysite system. The reaction may occur appreciably only after some diminution of moisture in the system.

In connection with this, the effect of the following tests of dry intimate mixing of hydrated halloysite and salt on the basal spacing of halloysite is of interest. On grinding hydrated halloysite with NH_4Cl, NH_4NO_3, NH_4HCOO, or KCH_3COO in an agate mortar for 5 to 10 minutes, the resulting alteration in the basal spacing of halloysite was identical with that observed previously by drying from these salt solutions (Table 7).

TABLE 7. RELATIVE STABILITY OF THE REACTION PRODUCT OBTAINED BY TREATING HALLOYSITE WITH SALTS

Salt	Basal spacing of halloysite dried from salt solution in Å	Basal spacing of halloysite after dry mixing in Å	Basal spacing of the reaction product after E.G. treatment in Å
NH_4Cl	10.5	10.5	10.5
NH_4NO_3	11.6	11.6	11.6
NH_4HCOO	11.6	11.6	11.1
NH_4CH_3COO	14.4	—	11.1
KCH_3COO	14.3	14.4	14.3
$(NH_4)_2SO_4$	13.4	Not clear	11.1
$(NH_4)_2HPO_4$	13.2	Not clear	11.1

However, with $(NH_4)_2HPO_4$ and $(NH_4)_2SO_4$, no clear basal reflection was obtained on this treatment, suggesting some difference in the stability of the reaction product.

As regards the relative stability of the reaction product, the result of the E.G. treatment shows a tendency similar to that observed above. Under this experimental condition, the resulting spacing may be considered a manifestation of the stability of the reaction product relative to the E.G.-halloysite complex. That is, the NH_4Cl, NH_4NO_3, or KCH_3COO treated halloysite each showed its own spacing after this treatment (Table 7). On the contrary, with $(NH_4)_2HPO_4$ or $(NH_4)_2SO_4$, the resulting spacings were identical with that of the E.G.-halloysite complex, indicating interlayer penetration of E.G. molecules, because these treated halloysites have shown only diffuse basal reflections on heating without E.G. at 100° C. (Table 3). Although the 11.1 Å spacing of the E.G.-halloysite complex was observed with NH_4HCOO and NH_4CH_3COO, it could be interpreted as the result of the sublimation of these salts at this temperature, not as the manifestation of their relative stability to the E.G.-halloysite complex.

DISCUSSION

Several possible explanations for the alteration of hydrated halloysite observed in *x*-ray patterns may be listed as follows:

a. Cation exchange reaction between halloysite and salt.
b. Anion exchange reaction between halloysite and salt.
c. Chemical combination of salt with halloysite, resulting in a breakdown of halloysite, as has been shown by several workers for the phosphate fixation by clay minerals (4, 5, 6, 7, 9).
d. Oriented penetration of neutral ionic compounds between the silicate layers of halloysite resulting in a type of the interlayer complex.

Explanations (a) and (b) would not account for the dependence of the reaction on the kind of cation and anion. Explanation (c) could be applied to the alteration in *x*-ray pattern as the result of the reaction of halloysite with ammonium phosphate in acidic solution, as was found by Stout (9) and by the present author in his preceding study (10). However, it seems very difficult to account for many results obtained here, particularly for the following:

(1) The alteration in *x*-ray pattern was found only on (00*l*) reflections of halloysite, essentially not on (*hk*) bands.
(2) There was no specific relation between the type of anion and the

reaction, that is expected from the viewpoint of the breakdown of the silicate layers.

(3) On washing with excess water, the complete *x*-ray pattern of the original halloysite, and only that, reappeared.

(4) Merely by intimately mixing halloysite and salt, similar alteration in *x*-ray pattern was found with certain salts.

The results obtained, including the ones just described, are overwhelmingly in favor of the oriented penetration of neutral ionic compounds between the silicate layers.

The limitation in geometry and valence of cation associated with those of the anion for the reaction may be interpreted in terms of the stability of the resulting configuration of the salt layer at the interlayer region. The difference between montmorillonite and halloysite can also be accounted for by this supposition

The increment in basal spacing suggests two-dimensional one or two molecular salt layer formation as was shown in Table 4. If the cation is trapped in the cavity of the oxygen network at the interlayer surface, as is presupposed from the geometrical fitting into that cavity, the position of the anion which orients to balance the excess positive charge, and consequently the configuration of the salt layer would also be fixed to the silicate layer of halloysite, indicating that the orienting force is sufficiently strong to induce the polymorphism of the salt.

Although the obtained spacings give no conclusive evidence on the disposition of the anion, some information would be obtained (Table 5). For example, a packing effect of Cl^- and Br^- into the hollows of the interlayer surface is suggested from comparison of the Δ-value for each NH_4Cl- and NH_4Br-halloysite complex (3.3 and 3.4 Å) with the diameter of each anion (3.6 and 3.9 Å). Also, since the Δ-value is obviously too high for a single anion layer formation of the tetrahedral type of anion ($\Delta = 13.4 \sim 13.4 - 7.2 = 6.0 \sim 6.2$ Å, the height of the tetrahedra $= 4.9$ Å), a triple cation-anion-cation layer formation is likely to occur, though the spacing of NH_4HSO_4-halloysite complex is not accounted for. The organic anion may dispose itself in some complicated manner. Further study is needed on this point.

It was estimated roughly that 200 to 300 m. mols or more of the salt orients onto 100 gm. of clay. The magnitude of this value is comparable with the theoretically expected value, 330 m. mols per 100 gm. of clay, assuming the formation of mono-molecular layer of the salt and the orientation of two molecules of the salt per unit cell of halloysite. Also, the random interlayer stratification of the layer with a hydrated halloysite spacing and one with a unique complex spacing was suggested, so that the salt is supposed to become regular within any one given interlayer region, rather than partially filling all the interlayer regions to an equal extent. This is also expected from the concept of the layer formation of the ionic compound.

If nearly 300 m. mols of the salt orients between the silicate layers, the interlayer water, or a part of it at least, should be replaced with the penetrating ions. Hence it might be considered from the view of the bond energy that the added stability of the system consisting of the halloysite, water, and salt, due to the salt halloysite bond formation, is greater than that due to the water-halloysite bond formation at least in the condition of air-drying . This also seems to be evident from the positive penetration of some salts, as the result of the intimate mixing in air-dry state.

It might be concluded from the experiments on the stability of the salt-halloysite complex, that the strength of the bond between the oriented salt and halloysite depends on the kind of the ionic compounds, particularly of the type of anion, suggesting the importance of the geometrical relationship between the interlayer material and the surface structure of clay minerals, and is much the same as that of the bond between water or E.G. and halloysite, in which the hydrogen bond is usually assumed to have prime importance. The small activation energy expected from this small bond energy agrees with the observed reversible complex formation occurring readily at normal temperature. The weak electrostatic forces may act between the ionic compound and the silicate layers of halloysite with a weak polarizability, as has been indicated by MacEwan for the formation of the interlayer complex between halloysite and some polar organic molecules (8), but the van der Waals forces may act mainly in the complex formation. Besides this, with ammonium salts, one may consider the effect of NH-O hydrogen bond formation.

SUMMARY AND CONCLUSION

Variation in the basal spacing of halloysite results from the interaction of halloysite with some K^+, NH_4^+, Rb^+, and Cs^+ salts. The alteration in x-ray pattern was found only in the $(00l)$ reflections and was reversible. Although the increment in basal spacing varied with the type of anion, there was no specific relation between the type of anion and the occurrence of the reaction. The reaction has not been shown for montmorillonite. It is concluded that the neutral ionic compound penetrates and orients between the silicate layers of halloysite.

Through this mechanism, halloysite would be able to retain 200 to 300 m. mols of the ionic compound on the basal plane surfaces per 100 gm. of air-dried clay state, and it is probable that the interlayer water is replaced. The stability of the resulting complex may be determined by the geometry and valency of anion in combination with those of the cation. The geometrical fitting between the interlayer material and halloysite as substrate is of prime importance in this type of complex formation.

The observed phenomenon is important in that it presupposes a type of physical adsorption peculiar to the surface structure of clay minerals and to the combination of ion species in solution. The technique used in this work should permit more positive identification and characterization of hydrated halloysite with *x*-ray diffraction.

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