

INTERCALATION OF SALTS IN HALLOYSITE

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Abstract—Several new salt intercalation complexes of halloysite have been prepared and characterized using X-ray powder diffraction techniques taking into account both the position and the shape of the d_{001} peaks. The amount of intercalated ion in some fully complexed halloysites has been directly determined using conventional analytical techniques. The results show that less than half of the theoretical amount of salt is intercalated into the clay; the amount of salt depending on its nature and, where hydrolyzable ions are present, on the pH. Infrared spectra taken of some complexes give an indication of the nature of the interaction within interlayer space and elsewhere. The interactions are weak and are either dipolar attractions or hydrogen bonds. The ions which show the greatest tendency to intercalate with halloysite are water structure-breaking cations or hydrogen-bonding anions.

Key Words—Halloysite, Intercalation, Interlayer, Kaolinite.

INTERCALATION OF SALTS IN HALLOYSITE

The phenomenon of the formation of clay complexes with organic compounds has been known for many years. Organic complexes of smectites have received much attention but in recent years the kaolin minerals, kaolinite and halloysite, have been investigated. Inorganic salts are known to form complexes with some clay minerals, notably halloysite and kaolinite.

Throughout this paper the following terminology is used: hydrated halloysite = halloysite (10 Å); dehydrated halloysite = halloysite (7 Å). Hydrated halloysite is defined as a clay mineral with a kaolin layer structure which contains interlayer water in its natural state (Churchman and Carr, 1975). This mineral is recognized from its X-ray powder diffraction pattern which contains a strong reflection at, or near, 10.1 Å together with mainly broad bands at smaller spacings. On heating at 110°C the 10.1 Å peak disappears and is replaced by a reflection at 7.2 Å (Brindley, 1961).

The penetration of ammonium fluoride into the interlayer regions of an halloysite was reported by Weiss et al. (1956). Salt complexes of halloysite were first extensively studied by Wada (1958, 1959a, 1959b) who showed that certain inorganic salts of some alkali metals were intercalated within the halloysite structure by replacing interlayer water. Wada prepared complexes with the chlorides, nitrates, acetates, and monohydrogen phosphates of potassium and ammonia but did not observe any interactions between the clay mineral and the corresponding salts of lithium and sodium. Several other ammonium salts, rubidium chloride, and cesium

chloride were observed to form complexes but intercalation of salts of divalent cations such as magnesium, calcium, and barium was not demonstrated. In all cases hydrated halloysite was regenerated when the complexed clay was washed with water. Wada concluded that the intercalation process depended on the size and charge of the ions and, in some cases, on hydrogen bonding. He estimated that 200–300 m mol of salt intercalates with 100 g of clay, i.e., up to two molecules of salt per unit cell $[Al_4Si_4O_{10}(OH)_8]$. Later, an estimate based on weight loss data for an halloysite-potassium acetate complex showed the amount of intercalated salt to be very much smaller viz. 14 m mol/100 g clay (Wada, 1965).

Independently, Garrett and Walker (1959) obtained a value of 9.0–9.5 meq/100 g for the cation exchange capacity of halloysite and demonstrated that the anomalously high value of about 50 meq/100 g reported by Riviere (1948) probably was due to the formation of salt complexes. Their investigation showed that complexes could be formed with KCl, KNO₃, KBr, KOOCCH₃, NH₄Cl, RbCl, and CsCl but not with LiCl, NaCl, and BaCl₂. Their results suggested that the ability of certain salts to intercalate with halloysite was related to their concentrations in solution and to the hydration energy of the cation. The effect of cationic potential (charge/size) was also noted; only low potential salts forming intercalation complexes.

Another investigation by Wada (1961) showed that partially hydrated halloysites, both on exposure to salt solutions and especially on grinding with solid salt, would form complexes with potassium acetate. A more

dehydrated halloysite (7 Å) was almost completely resistant to complex formation. Hofmann and Reingraber (1969) reported that intercalation compounds were formed by halloysite (7 Å) with potassium and ammonium acetates as well as with some organic compounds. In all cases halloysite (10 Å) could be regenerated from the complexes by washing with water.

In view of the limited number of different salts tested, the lack of analytical data for the intercalation complexes, and the difficulties encountered in explanation of the phenomenon, this further investigation of halloysite-inorganic salt intercalation compounds was undertaken.

EXPERIMENTAL

Equipment

Grinding was effected with a Fritsch pulverisette. X-ray powder diffraction patterns were obtained with Philips equipment using Ni filtered Cu K α radiation and a diffractometer. Infrared spectra were obtained with a Perkin-Elmer (model 357) grating spectrophotometer. Electron microscopic examination was conducted with a Siemen's instrument using samples sedimented onto collodian discs.

Materials

Halloysites from three localities viz. Te Puke, Kauri Mountain, and Matauri Bay, New Zealand, were used. All were almost fully hydrated. The Kauri clay was essentially free from impurities whereas quartz was present in both the Matauri Bay and Te Puke samples while the latter contained a little cristobalite, traces of iron and some organic matter. The Te Puke clay consisted of mainly tabular particles but some rolled material was present (Hughes, 1966; McKee et al., 1973). Electron microscope examination indicated the presence of many tubular particles in the Kauri and Matauri Bay samples.

Salts were usually of laboratory grade purity and no special effort was made to purify them.

Procedure

In all cases small samples (~0.5 g) of halloysite (10 Å) were exposed to aqueous salt solutions (≥ 1 ml) usually of concentration 2.5 mol l⁻¹. In the case of sparingly soluble salts e.g., silver nitrate, solution concentrations were lower. Exposure times varied from about 30 minutes to several days and reaction mixtures were usually agitated periodically by stirring. After exposure, moist and oven-dried (110°C) clay samples were examined by X-ray powder diffraction; the diffraction data being compared with that obtained from hydrated samples unexposed to salt solutions but similarly treated.

To confirm the presence or absence of intercalation complexes all samples were subjected first to a dehydration process to distinguish between interlayer water

and intercalated salt, and then to a rehydration process to differentiate between partial dehydration and partial intercalation. Most samples were heated at 105–110°C for 40 hours before being washed repeatedly with water and examined by X-ray powder diffraction. Those samples containing volatile or unstable salts, e.g., lithium acetate and ammonium citrate respectively, were held in a vacuum desiccator for at least 24 hours prior to washing.

Chemical analysis

All intercalation complexes for chemical analysis were prepared from the available halloysite of highest purity viz. the Kauri clay. Potassium acetate complexes were prepared for analysis from aqueous solutions in the pH range 2.50–10.30; adjustment being made to pH with acetic acid or potassium hydroxide. In all cases the potassium ion concentration in aqueous solution was 3 mol l⁻¹ while the acetate ion concentration varied between 3 and 6 mol l⁻¹. For potassium chloride solutions the pH was adjusted in the range 0.20–13.20 with hydrochloric acid and potassium hydroxide. Other complexes for analysis were prepared using unbuffered aqueous solutions of potassium bromide, ammonium fluoride, and ammonium chloride of concentration 2.5–6 mol l⁻¹. In each case about 2 g of clay was soaked and thoroughly stirred for 10 minutes in a concentrated solution of the salt before being vacuum filtered, complex formation being confirmed by X-ray powder diffraction.

Since the total salt uptake of halloysite is due both to intercalation and to ion exchange (surface phenomenon), blanks were prepared by subjecting samples of halloysite (7 Å) to the same preparative procedure (halloysite (7 Å) was obtained by heating halloysite (10 Å) at 100°C for several days). It was assumed first, that intercalation does not occur in halloysite (7 Å), and second, that the surface ion exchange capacities of equal masses of hydrated and dehydrated halloysite would be equal. Hence any differences in values for salt ion composition would be due to intercalation. The validity of the first assumption was demonstrated by X-ray powder diffraction analysis; halloysite (7 Å) showed no c axis expansion after being subjected to the preparative procedures described below. Chemical analysis of hydrated and dehydrated halloysites after treatment with sodium acetate (the latter shows a very slight tendency only to intercalate) indicated similar sodium and acetate contents thus demonstrating the validity of the second assumption within the limits of experimental error. Although it has been assumed that the intercalation process is confined to interlayer regions of the halloysite structure it is by no means certain that this is true since the presence of pore space (in which salt ion pairs could readily be occluded) has been demonstrated both in Te Puke halloysite (McKee et al., 1973) and in a Guatemalan clay (Askenasy et al., 1973).

Samples (0.5 g) of intercalation complexes and blank clays were washed (agitation followed by centrifugation) five times with 50 ml aliquots of aqueous ammonium acetate (1 mol l^{-1}) and then with distilled water. All washings were collected and made up to 500 ml; 3 ml of this solution being diluted to 50 ml. The potassium ion content of this resulting solution was determined against a standard solution flame photometrically. The solid residues were heated at 110°C overnight and weighed to provide a dry-weight basis for the analytical results.

Acetate ion was determined in air-dried samples by combustion at $800\text{--}900^\circ\text{C}$ in a carbon-hydrogen analyser. Liberated carbon dioxide and water were absorbed and weight increases in absorbents measured. The amount of carbon dioxide provides a measure of the amount of acetate ion present in the clay sample. Small samples of the air-dried complex were washed free of potassium acetate prior to determination of the dry weight. Similar dry weight procedures were adopted for other anions.

Chloride ion was determined by burning the samples in oxygen at $750\text{--}800^\circ\text{C}$. The liberated chlorine gas was absorbed in aqueous sodium borohydride which was then neutralized with perchloric acid and titrated with a standard mercury(II) nitrate solution. The same procedure was used for the estimation of bromide ion. For fluoride ion, the combustion product was dissolved in isopropanol and titrated with thorium nitrate (Oliver, 1966).

Nitrogen in ammonium complexes was determined by burning the clay in a stream of carbon dioxide at $750\text{--}800^\circ\text{C}$. The gaseous products were passed through aqueous potassium hydroxide to remove carbon dioxide, and the volume of liberated nitrogen was measured, thus providing a measure of the amount of ammonium ion present.

CRITERIA FOR COMPLEX FORMATION

The manner in which the formation of a salt intercalation complex of halloysite may be recognized is based on the following observations:

- (1) All reported halloysite-salt complexes have $d_{001} \geq 10.1 \text{ \AA}$ (Wada, 1959a; Garrett and Walker, 1959). This means that the process is usually accompanied by *c* axis lattice expansion or, in terms of MacEwan's (1948) Δ value

$$\Delta_{\text{complex}} \geq \Delta_{\text{H}_2\text{O}}$$

where $\Delta_{\text{H}_2\text{O}}$ is approximately 2.9 \AA .

- (2) The replacement of interlayer water by salt is reversible in halloysite, i.e., halloysite (10 \AA) can be regenerated from oven-dried salt complexes (Wada, 1959a) by water washing.
- (3) Fully hydrated halloysite (10 \AA) exhibits a d_{001} X-

ray powder diffraction peak with a symmetric profile; asymmetry in this peak being diagnostic, through interstratification effects, of partial hydration (Churchman et al., 1972).

Since halloysite (10 \AA) is the water complex of halloysite (7 \AA) then the assumption that the diffraction peak profiles of salt complexes will provide information on the degree of intercalation must be valid. The use of diffraction profiles in providing additional information has been discussed for halloysite-organic complexes (Carr and Chih, 1971). In this investigation d_{001} diffraction profiles have been used qualitatively to distinguish partial and complete intercalation. It follows from criterion (3) above that a symmetric profile in a diffraction peak where d_{001} is between 10.1 and 7.2 \AA would indicate the presence of intercalated material other than water. On the other hand an asymmetric peak in the same d_{001} range could be due either to water or to some other material. Hence it is possible to recognize a fully complexed halloysite in which *c* axis contraction has occurred.

RESULTS AND DISCUSSION

Most of the salts used by Wada (1958, 1959a, 1959b) and Garrett and Walker (1959) were tested with Kauri halloysite (10 \AA) and, in most cases, similar results were obtained. To gain a better understanding of the mechanism of intercalation several other salts containing univalent, divalent, and trivalent cations were tested. In Table 1 positive results of this and previous investigations are listed.

It should be noted that complexes of several salts including $\text{NH}_4\text{OOCCH}_3$, $\text{NH}_4\text{OOCCH}_2$, NH_4Cl , KOOCCCH_3 , and KCl were prepared from each of the halloysite samples. No significant differences either in reaction rate or in *c* axis expansion were observed. Several of the salts listed e.g., KH_2PO_4 , NaOOCCH_3 , $(\text{NH}_4)_2\text{HC}_6\text{H}_5\text{O}_7$ (citrate), $\text{Ba}(\text{OOCCH}_3)_2$; exhibit only a limited tendency to intercalate with halloysite. In general any discrepancies between Δ values fall into two categories viz. $<0.5 \text{ \AA}$ or $>2 \text{ \AA}$. The smaller discrepancies probably are due to both the experimental error and differences in the nature of the clays used in the various investigations. In earlier studies X-ray powder diffraction patterns were obtained using powder cameras and experimental errors were as large as $\pm 0.1 \text{ \AA}$ in Wada's (1959) investigations. Δ values in the present study could be subject to errors of similar magnitude due to thickness variations in the mounted samples required for counter detection of diffracted radiation. The Δ values represent average interlayer spacing which may change slightly (up to 0.2 \AA) from sample to sample due to varying small amounts of dehydrated layers. Large discrepancies were observed in the behavior of five salts viz. $\text{NH}_4\text{H}_2\text{PO}_4$, $(\text{NH}_4)_2\text{C}_2\text{O}_4$, NaOOCCH_3 , KH_2PO_4 , and $\text{Ba}(\text{OOCCH}_3)_2$. Wada (1959a) listed Δ val-

Table 1. Comparison with previous results.

Salt	Δ observed	Δ previously observed
NaOOCCH ₃ *	3.0	n.c. W
KCl	3.0	3.0 W, 3.1 G
KBr	3.3	3.4 G
KNO ₃	2.9	2.9 W, 3.4 G
K ₂ CO ₃	6.1	6.4 G
KH ₂ PO ₄ *	4.4	n.c. W
K ₂ HPO ₄	5.8	6.1 W
KOOCCH ₃	6.8 - 7.0	7.1 W, 6.4 - 6.8 H
NH ₄ Cl	3.2	3.3 W, 2.9 G
NH ₄ Br	3.6	3.4 W
NH ₄ F	2.9 - 3.2	2.7 Ws
NH ₄ NO ₃	4.4	4.4 W
NH ₄ HSO ₄	n.t.	6.0 W
(NH ₄) ₂ SO ₄	5.8	6.2 W
(NH ₄) ₂ HPO ₄	5.8	6.0 W
NH ₄ H ₂ PO ₄	0.2	2.9 W
NH ₄ OOCCH ₃	4.2	4.4 W
NH ₄ OOCCH ₃	7.1	7.2 W, 7.0 - 10.1 H
(NH ₄) ₂ C ₂ O ₄	0.3	2.9 W
(NH ₄) ₂ HC ₆ H ₅ O ₇	6.2	5.8 W
(NH ₄) ₂ HAsO ₄	n.t.	5.9 W
RbCl	3.1	3.1 G
CsCl	3.3	3.5 G
Ba(OOCCH ₃) ₂ *	3.6	n.c. W

n.t. not tested.

n.c. no complex

* Listed as new complexes in Table 2.

Ws = Weiss, Mehler, Koch and Hofmann (1956)

W = Wada (1959a)

G = Garrett and Walker (1959)

H = Hofmann and Reingraber (1969)

ues for NH₄H₂PO₄ and (NH₄)₂C₂O₄ identical to that for halloysite (10 Å) but made no specific reference to heat treatment which may have distinguished the product salt intercalation compound from the reactant hydrated clay. It is possible, then, that Wada may not have demonstrated the unequivocal formation of complexes with those salts which have been shown to cause partial dehydration of halloysite (10 Å) in the present investigation. Some evidence has been obtained (see Table 2) to suggest that KH₂PO₄, NaOOCCH₃, and Ba(OOCCH₃)₂ show a slight tendency to intercalate with halloysite contrary to Wada's observations. The observed effects are small and may be due to differences, perhaps arising from variations in stacking disorder, among the samples used.

Garrett and Walker reported that KClO₃, K₂SO₄, KClO₄, LiCl, and NaCl did not form intercalation compounds and Wada listed negative results for LiCl, LiNO₃, NaCl, NaNO₃, Na₂SO₄, Na₂HPO₄, NaH₂PO₄, K₂SO₄, MgCl₂, Mg(NO₃)₂, CaCl₂, Ca(NO₃)₂, Ca(OOCCH₃)₂, BaCl₂, and Ba(NO₃)₂. Most of these negative results were confirmed in the present study.

Positive results were obtained with several salts not previously tested and the details, including descriptions

Table 2. New complexes.

Salt	Intercalation data		Rehydration data	
	Δ	d ₀₀₁ profile	d ₀₀₁ profile	extent
LiOOCCH ₃	4.7	sym	broad	partial
NaOOCCH ₃	3.0	broad	broad	slight
KF	3.0	broad (w)	asym	partial
KI	2.9	broad	asym	partial
KOH	3.1	broad (w)	sym	complete
KHCO ₃	3.0	sym (w)	asym	partial
K ₃ C ₆ H ₅ O ₇	5.6	sym	sym	complete
K ₂ C ₄ H ₄ O ₆	2.8	sym	asym	slight
KOOCCH ₃	3.0	sym	sym	complete
KCN	3.0	sym	asym	partial
KOCN	3.4	sym	sym	complete
KNCS	4.6	sym	sym	complete
KNO ₂	3.5	sym	sym	complete
KH ₂ PO ₄	4.4	broad (w)	broad	slight
KAsO ₂	2.9	sym	asym	partial
KHSO ₄	2.5	broad (w)	broad	partial
K ₂ S ₂ O ₃	2.6	broad	asym	slight
K ₂ S ₂ O ₅	2.9	sym	asym	slight
K ₂ S ₂ O ₇	2.6	broad	broad	partial
(NH ₄) ₃ PO ₄	5.0	sym	asym	partial
(NH ₄) ₂ S ₂ O ₈	4.9	broad	asym	complete
NH ₄ SO ₃ NH ₂	4.7	sym	asym	partial
C ₉ H ₈ O ₃ NNH ₄	9.4	sym	asym	partial
(NH ₄) ₂ Ce(NO ₃) ₆	3.0	broad (w)	asym	slight
TlOOCCH ₃	2.7	broad (w)	asym	slight
Ba(OOCCH ₃) ₂	3.6	sym (w)	asym	slight
Pb(NO ₃) ₂	2.8	asym	broad	slight
Pb(OOCCH ₃) ₂	2.5	sym (w)	broad	slight

* All new complexes were prepared with

Kauri halloysite.

(w) = weak

sym = symmetric

asym = asymmetric

of the d₀₀₁ X-ray powder diffraction peak profiles for both the complexes and the corresponding rehydrated halloysites are listed in Table 2.

Of the 26 salts listed only K₃C₆H₅O₇ (citrate), KOOCCH₃ (formate), KOCN (cyanate), KNCS (thiocyanate), and KNO₂ (nitrite) show marked tendencies to intercalate with halloysite. Most of the other salts show a variable but noticeably smaller affinity for the clay mineral. It is of importance to note that limited complex formation is claimed for eight salts where $\Delta \ll 2.9$ Å. These claims are based either on the symmetric profiles of the (001) diffraction peaks for the KAsO₂ (arsenite) and K₂S₂O₅ (metabisulphite) complexes, or on the tendency (albeit slight but nevertheless real in some cases) for the complexes formed from KI, K₂C₄H₄O₆ (tartrate), KHSO₄, K₂S₂O₃ (thiosulphate), K₂S₂O₇ (pyrosulphate), and TlOOCCH₃ (thallium(I) acetate) to rehydrate. Several complexes exhibit inconsistencies with respect to the d₀₀₁ profile of the intercalation complex and the extent of rehydration. The salts, KOH and (NH₄)₂S₂O₈ (peroxodisulphate), caused c axis expansion accompanied by disordering (broad d₀₀₁ profiles) which was reversed on rehydration (symmetric, sharp profiles). On the other hand LiOOCCH₃, KHCO₃,

$K_2C_4H_4O_6$ (tartrate), KCN, $KAsO_2$ (arsenite), $K_2S_2O_5$ (metabisulphite), $(NH_4)_3PO_4$, $NH_4SO_3NH_2$ (ammonium sulphamate), $C_9H_8O_3NNH_4$ (ammonium hippurate), and $Ba(OOCCH_3)_2$ appeared to intercalate effectively, but the corresponding complexes did not rehydrate completely. Some of these inconsistencies may have been due to disordering effects induced through chemical attack of the halloysite samples by alkaline solutions (several of the above salts are alkaline by hydrolysis in aqueous solution) but this possibility was not investigated experimentally.

Negative results were obtained in intercalation tests with 39 salts in addition to those listed in Tables 1 and 2 and reference to these will be made below.

Nature of cation

In general the results of this investigation, which confirm previous findings, indicate that many potassium and ammonium salts together with the only rubidium and cesium ones tested form intercalation complexes whereas lithium, sodium, and several other cations do not appear to enter the interlayer regions in halloysite. In addition to those given above, negative results were obtained using aqueous solutions of Li_2SO_4 , $NaOOCCH_3$, $Na_2C_2O_4$, Na_2SO_3 , $NaNO_2$, NaI , $NaHCO_3$, $Na_2S_2O_3$, $Cu(NO_3)_2$, $CuSO_4$, $Cu(CH_3COO)_2$, $AgNO_3$, Ag_2SO_4 , $TiCl_3$, $Mg(CH_3COO)_2$, $MgSO_4$, $CaBr_2$, $BaBr_2$, $Ba(NO_3)_2$, $Hg_2(NO_3)_2$, Hg_2Cl_2 , $AlCl_3$, $LaCl_3$, $La(NO_3)_3$, $CeCl_3$, $MnCl_2$, $FeCl_3$, $FeSO_4$, and $NiCl_2$. It is obvious then that intercalation usually occurs only with those salts which contain large univalent cations viz. K^+ , NH_4^+ , Rb^+ , and Cs^+ . Wada (1959a) related the size of the cation to the size of the cavity in the oxygen network of the silicate layer and concluded that complexes did not form if the cation was sufficiently small to occupy the cavity. The nonintercalation of Ba^{2+} which is almost identical in size to K^+ was noted but not adequately explained. The validity of the size factor as a significant parameter in salt intercalation is challenged by the negative results obtained with other barium salts, $AgNO_3$, Ag_2SO_4 , and $TiCl_3$. The Ag^+ -ion with a radius of 1.26 Å is slightly smaller than K^+ (1.33 Å) but Tl^+ is larger ($r = 1.40$ Å). On the basis of size, both La^{3+} (1.15 Å) and Ce^{3+} (1.11 Å) would not necessarily have been expected to penetrate the interlayer regions. It is possible that the silver and thallous salts, did not form complexes because their low solubilities did not allow preparation of solutions of sufficiently high concentrations. Both Wada and Garrett and Walker had observed that relatively high salt concentrations are required for effective intercalation. However, it is concluded that the cationic size factor alone is not entirely satisfactory as the intercalation-determining parameter.

The observation that ions other than K^+ , NH_4^+ , Rb^+ and Cs^+ do not normally intercalate with halloysite may suggest a more satisfactory parameter. Garrett and Walker related this type of observation to the hydration

energy of the cation which is low for those ions which form complexes, and is relatively high for all polyvalent ions. Unlike the surface-solution interface in an aqueous clay suspension the interlayer regions of halloysite are relatively water deficient and so are unlikely to attract highly or strongly hydrated ionic species. It is quite reasonable, therefore, to suggest that intercalation may be possible only for cations which have low hydration energies. Examination of the single ion hydration energies calculated by Verwey (1942) indicates that intercalating cations, with the exception of NH_4^+ which is not listed, have energies between -73.0 kcal mol^{-1} (i.e., K^+) and -59.2 kcal mol^{-1} (i.e., Cs^+). Clear distinctions between the behavior of these ions and for example Na^+ (-93.2 kcal mol^{-1}) or Ca^{2+} (-373.2 kcal mol^{-1}) are obvious but Tl^+ with a single ion hydration energy of -74.2 kcal mol^{-1} would be expected to behave more like K^+ than Na^+ which was contrary to observation. It has long been known that the viscosity of aqueous salt solutions is related to the hydration behavior of ions. Entropy data has been used to distinguish between structure formers and structure breakers; intercalating cations in general falling into the second category. The structure-breaking tendency of ions is related to their field strength, the lower the field strength the greater the structure breaking due to the ions. This involves the size and charge of the ion, as the larger the size and smaller the charge, the smaller the field strength. Bingham (1941) measured the viscosities of aqueous salt solutions and presented his data in terms of ionic elevations for 25 cations including all of the alkali, alkaline earth, and several transition metal elements. Positive values denoting fluidities higher than that of pure water were reported for Cs^+ , Pb^{2+} , Rb^+ , NH_4^+ , and K^+ . The values for Ag^+ , Na^+ , Li^+ , Ba^{2+} , Ca^{2+} , and all other polyvalent ions tested were negative. In general, cations with negative ionic elevations do not appear to intercalate with halloysite. The exceptions, viz. Li^+ , Na^+ , Tl^+ , and Ba^{2+} , underwent intercalation in the form of their acetates only and this is attributed to the nature of the anion (see below). The only divalent cation observed to intercalate was Pb^{2+} and although the extent of the process was far from complete it was, nevertheless, real for both the nitrate and the acetate. Hence it appears that cation intercalation behavior closely parallels fluidity in aqueous salt solutions; the relatively hydrophobic cations (water structure breakers) occupying the water deficient regions (interlayer) in the halloysite-water system. It is important to note that no account has been taken in the above discussion of the exact nature of the intercalated species e.g., whether simple cation or complex ion, because this has not been determined.

Nature of anion

The ability of the salt, potassium acetate, to interpenetrate partly hydrated and even dehydrated halloy-

Table 3. Infra-red absorption bands in halloysites.

Assignments and wave number (cm ⁻¹) range*	Kauri halloysite complexes									
	7Å	10Å	KH ₂ PO ₄	KCl	KBr	KI	KOOCCH ₃	NH ₄ F	NH ₄ Cl	
OH stretch	3700 - 3690	✓	✓	✓	✓	✓	✓	✓	✓	✓
	3640 - 3620	✓	✓	✓	✓	✓	✓	✓	✓	✓
OH ...H	3614 - 3608	-	-	✓	✓	✓	✓	-	-	✓
H ₂ O interlayer	3570 - 3520	-	✓	✓	✓	✓	✓	✓	✓	✓
H ₂ O voids	3470 - 3200	-	✓	✓	✓	✓	✓	✓	✓	✓
Fermi resonance band	3180 - 3105	-	-	✓	-	-	✓	-	-	✓

✓ denotes presence of band

- denotes absence of band

* Some of the variation in absorption frequencies is probably due to the use of samples mullied with Nujol.

A few spectra were taken from sample films sedimented onto calcium fluoride windows and were not significantly different from those mullied samples.

sites was first reported by Wada (1961). This observation has led to the view that KOOCCH₃ has greater complex-forming tendencies than other tested salts due to the presence of the acetate ion. The limited complex formation observed with the acetates of lithium, sodium, thallium(I), and barium confirms the above view since none of those cations in the form of other salts shows any tendency to intercalate. Although KOOCCH₃ appears to be the only salt which will penetrate halloysite (7 Å) from aqueous solution its behavior in the solid state is not unique as shown by Wada (1959b) who observed the partial penetration of ammonium chloride after 10–15 minutes grinding. Experiments have been conducted in the present investigation in which Kauri halloysite (7 Å) has been ground with ammonium fluoride, ammonium chloride, potassium acetate, potassium chloride, and potassium fluoride for periods of up to 2 hours. In all cases the 7.2 Å diffraction maximum was replaced with a broad or moderately sharp maximum at larger interlayer spacings which confirmed that salt penetration into interlayer space had occurred. Potassium acetate as expected, intercalated more extensively than the other salts.

Many potassium and ammonium salts were tested and most showed some tendency to form complexes with halloysite (10 Å). Ammonium carbonate, potassium sulphite, potassium arsenate, and the dichromates of both ammonium and potassium did not complex. If

the assumption that the cations, potassium and ammonium are readily intercalated is true then it follows that differences in salt behavior are due to the anions. The experimental observations seem to indicate that the very large anions (e.g., C₁₂O₇²⁻ and Ce(NO₃)₆²⁻) and those of moderate size but high charge (e.g., AsO₄³⁻, S₂O₅²⁻, S₂O₃²⁻) show extremely limited tendencies to penetrate interlayer space. On the other hand the behavior of ions such as PO₄³⁻, S₂O₇²⁻, and SO₄²⁻ seems to invalidate the suggested size and charge relationships.

Infrared spectra

Infrared absorption spectra were recorded for intercalation complexes formed with seven salts viz. KH₂PO₄, KOOCCH₃, KCl, KBr, KI, NH₄F, and NH₄Cl, and were compared with those obtained from halloysite (10 Å) and halloysite (7 Å). All samples showed absorptions at frequencies near 3695 cm⁻¹ and 3620 cm⁻¹ arising from OH stretching modes. Variations in the spectral profiles of these bands were evident; the absolute peak height of the 3695 cm⁻¹ band being much smaller than that of the 3620 cm⁻¹ absorption in the hydrated sample, slightly larger in the dehydrated material, and a little smaller in intercalation complexes. This effect has been noted by other investigators including Serratos et al. (1963) and Yariv and Shoval (1975), the latter claiming from extrapolations

Table 4. Composition of intercalation complexes.

Salt	Ions per unit cell		Salt composition (m mol per 100 g clay)
	cation	anion	
KOOCCH ₃	1.2 ± 0.1	1.3 ± 0.2	242
KCl	0.6 ± 0.1	0.7 ± 0.1	126
KBr	0.7 ± 0.1	0.7 ± 0.1	136
NH ₄ Cl	1.4 ± 0.1	1.3 ± 0.1	262
NH ₄ F	1.5 ± 0.1	1.7 ± 0.1	310

which seem quite arbitrary that the change in profiles is not accompanied by significant changes in absorption intensities. It is significant that the spectral profiles of air-dried complexes are similar to those of halloysite (10 Å) whereas profiles of dehydrated complexes (heated at 110°C) resemble those of halloysite (7 Å). The changing profile thus appears to be related to the interlayer water content of the clay mineral.

Absorption bands of lower intensity and greater breadth were observed for all samples in the frequency range 3615–3100 cm⁻¹. The assignments listed in Table 3 were made on the basis of Yariv and Shoval's interpretations. All absorptions other than those due to OH stretching vibrations were usually weak and ill defined. It should be noted that Yariv and Shoval observed several additional weak absorptions in the 3500–3700 cm⁻¹ range for an halloysite from Te Puke, New Zealand. Since the nature of the voids in the halloysite structure can be so variable (McKee et al., 1973) it is not unreasonable to assign absorptions over a relatively large energy range (3470–3200 cm⁻¹) to water in this environment. The distinction between such absorptions and the Fermi resonance band is quite arbitrary but it seems unlikely that hydrogen-bonded water molecules would absorb at frequencies below 3200 cm⁻¹. Spectra of some of the complexes showed two absorption bands assigned to interlayer and void regions e.g., KCl at 3570, 3520, 3380, and 3220 cm⁻¹; KBr at 3560 and 3512 cm⁻¹; KI at 3450 and 3300 cm⁻¹. These absorptions could arise from variations caused by structural irregularities in the numbers of layers of water molecules trapped in those regions. The above results tend to support Yariv and Shoval's conclusion that the intermolecular forces between interlayer water and kaolin-like layers in halloysite are not due to hydrogen bonds but to dipole attraction. On the other hand there is some evidence from absorptions in the 3614–3620 cm⁻¹ spectral region that hydrogen bonding does contribute to interactions between water molecules within intercalation complexes.

Chemical composition

Analytical data for complexes prepared from Kauri halloysite and unbuffered aqueous salt solutions (6 mol l⁻¹) are shown in Table 4. Compositions are expressed in terms of the number of interlayer ions per dehydrated unit cell, i.e., Al₄Si₄O₁₀(OH)₈, together with the cor-

Table 5. pH effect on intercalation compositions.

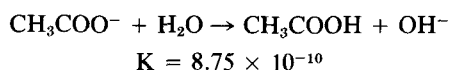
pH	ions per unit cell		pH	ions per unit cell	
	K ⁺	CH ₃ COO ⁻		K ⁺	Cl ⁻
2.50	0.0	0.7 ± 0.1	0.90	1.1 ± 0.1	1.0 ± 0.1
5.45	0.7 ± 0.1	0.4 ± 0.1	5.30	0.6 ± 0.1	0.7 ± 0.1
6.70	0.6 ± 0.1	0.7 ± 0.1	7.00	1.0 ± 0.1	1.0 ± 0.2
10.30	1.2 ± 0.1	1.3 ± 0.1	13.20	1.0 ± 0.1	1.0 ± 0.2

responding average values for the salts expressed as m mol per 100 g of dehydrated clay. The experimental errors listed represent the normal variations in values obtained from repeated determinations.

An examination of the halloysite literature indicates that the data presented above is probably the first to be obtained by direct chemical analysis of intercalated salts. The composition of the potassium acetate and ammonium chloride complexes may be compared with previously reported values. Wada (1959a) roughly estimated a retention of 200–300 m mol or more of salt per 100 g of air-dried clay, and implied that the kind of salt was not critical. In another investigation (Wada, 1959a) he estimated the amount of intercalated NH₄Cl by X-ray powder diffraction (185 m mol), DTA (240 m mol), and from water loss (220 m mol). The discrepancies between the diffraction value and the others were attributed to the experimental observation that dehydrated halloysite on grinding may intercalate 40 m mol of salt. It may be significant that the value Wada obtained from water loss determination during NH₄Cl intercalation bears no relationship to the details of the calculation which, in itself, is rather obscure. Wada concluded that two molecules of NH₄Cl per unit cell of halloysite are intercalated. In a later thermogravimetric investigation Wada (1965) estimated that 0.07 molecules of potassium acetate were intercalated in each unit cell of halloysite (i.e., 12 m mol per 100 g of air-dried clay) but did not comment on the major discrepancy between this and earlier estimates. Wada's values are reasonably close to the values listed in Table 4. These values indicate significant differences between salts, which may arise from variations in the nature of the interactions between ions and clay surfaces. Such interactions are known to be markedly affected by changes in pH and this variable was investigated for potassium acetate and potassium chloride. The experimental data is given in Table 5.

Of all the salts which form complexes with halloysite, potassium acetate and ammonium chloride appear to have the highest affinity for the interlayer spaces as indicated by both the high symmetry and high intensity of the d₀₀₁ X-ray powder diffraction peaks of the complexes. It is a little surprising, therefore, that the maximum amount of potassium acetate intercalated not only is a little less than that of ammonium fluoride but also is significantly less than the two molecules per unit

cell as measured by Wada or the theoretical four molecules assuming a 1:1 replacement of interlayer water molecules. All of the above analytical data provides strong evidence for the proposal that salt molecules do not completely replace water molecules during the formation of interlayer complexes and, further, that the quantities which are intercalated are dependent on the nature of the salt. The variation in composition of the potassium acetate complex is readily explained in terms of the behavior of the acetate ion in aqueous solution, viz.,



At low pH the acetate ion is extensively hydrolyzed with the result that acetic acid molecules rather than salt ions participate in the intercalation process. The preparation of an halloysite-acetic acid complex has already been reported (Carr and Chih, 1971). At pH = 5.45 there is disparity between the K^+ and CH_3COO^- contents which falls just outside the limits of experimental error. This difference could be due to the intercalation of some hydroxide ions formed by the replacement of OH groups in the clay structure with CH_3COO groups. This process must be confined to interlayer space since any OH^- ions released on clay surfaces would be neutralized by the acid solution. Hence the mechanism would not necessarily involve a pH change and none was observed. This proposal is analogous to the reported behavior of F^- and PO_4^{3-} which have been shown to replace OH groups in kaolinite (Dickman and Bray, 1941; Buswell and Dudenbostel, 1941). Under still higher pH conditions the aqueous concentration of acetate ion increases further as the degree of hydrolysis decreases and hence the amount which is intercalated increases; the ionic charge being balanced by potassium ions.

The amount of interlayer water remaining in two of the potassium acetate complexes has been estimated from hydrogen analyses. The sample prepared at pH = 5.45 has a unit cell interlayer composition of $(\text{H}_2\text{O})_{1.9}(\text{K}^+)_{0.7}(\text{CH}_3\text{COO}^-)_{0.4}$ and the sample formed from unbuffered solution of pH = 10.30 contained $(\text{H}_2\text{O})_{2.3}(\text{K}^+)_{1.3}(\text{CH}_3\text{COO}^-)_{1.2}$ per cell. It is obvious that the data does not support a 1:1 replacement of water either by ion pairs or by single ions. This could be a direct consequence of the structure-breaking properties of the cation, more water molecules being expelled than salt ions or ion pairs being intercalated.

As expected, potassium chloride intercalation shows no observed pH dependence. The anomalously low values at pH = 5.30 can be attributed to the zero point of charge. Clay particles normally have a slight electrostatic charge arising from a very small imbalance between anions and cations caused by bonding energy differences on surface exchange sites. The sign of this charge can be measured by a simple electro-osmotic

test in which a direct current is passed through a moist clay-electrolyte paste (Cashen, 1959). Using this test an halloysite-KCl paste at pH = 5.1 was shown to carry a negative charge whereas an halloysite- $\text{NH}_4\text{OOCCH}_3$ paste at pH = 7.0 was positively charged. Hence it is proposed that the anomaly at pH = 5.30 can be attributed to the zero point of charge.

Conclusions

The ease of formation of intercalation complexes and their facile destruction by water washing indicate low stability and hence weak bonding within the interlayer space. Electrostatic forces of attraction appear to constitute the affinity between salt and clay. Since these forces are quite small then it follows that one entity present in high concentration may readily be able to replace another present in low concentration. If the interlayer space of halloysite, which may contain up to one layer of water molecules, is regarded as a region of low water concentration and the 2.5–3 molar salt solutions used are considered to be of high concentration then salt intercalation could be said to proceed because of concentration gradients. On the other hand the process may be regarded as an osmotic phenomenon where water molecules move from the dilute interlayer environment to the concentrated bulk aqueous solution, some of the interlayer water being replaced with salt. Since the detailed structure of the halloysite interlayer regions has not been precisely determined, and the exact nature of the intercalated ionic species is not known, together with the situation that interactions between species within such confined spaces are not clearly understood, it is impossible to propose a detailed mechanism.

Despite the above imperfections in our knowledge of the system under investigation it is possible to draw some positive conclusions. The ability of cations to enter interlayer space appears to be related to their so-called structure-breaking effect on water. In some cases certain anions, e.g., acetate, exhibit such a strong tendency to intercalate that they carry 'structure-forming' cations, e.g., lithium, sodium, and barium, into interlayer space. This phenomenon may be caused by the formation of hydrogen bonds between anion and clay rather than dipole interactions. Whether the intercalation proceeds because of the structure-breaking cation or the hydrogen-bonding anion the charge is balanced by the accompanying ion of the salt molecule.

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Резюме— Были получены несколько новых комплексов галлуазита, переслаивающегося с солью, которые охарактеризованы с использованием порошкового метода рентгеноструктурного анализа, причем во внимание принимались как положение, так и форма пиков d_{001} . Количество внедрившихся ионов в некоторых полностью укомплектованных галлуазитах определялось с использованием обычных аналитических методов. Результаты показывают, что менее, чем половина теоретического количества соли внедрилась в глину. Количество соли зависит от ее природы и, если присутствуют ионы, поддающиеся гидролизу, от pH. Инфракрасные спектры некоторых комплексов указывают на природу взаимодействия в межслойном пространстве и других местах. Взаимодействия слабы и являются или дипольным притяжением, или водородными связями. Ионы, которые проявляют наибольшую тенденцию к внедрению в галлуазит, являются водными структуро-разрушающими катионами или водородо-связующими анионами.

Kurzreferat— Etliche neue Salzeinbettungskomplexe von Halloysit wurden prepariert und durch Röntgenpulverdiagramme charakterisiert, indem sowohl die Position wie auch die Form der d_{001} Signale in Betracht gezogen wurden. Die Menge von eingebetteten Ionen wurde unmittelbar mit konventionellen, analytischen Techniken in einigen vollkomplexierten Halloysiten bestimmt. Die Resultate zeigen, daß weniger als die Hälfte der theoretischen Menge des Salzes in den Ton eingebettet ist. Die Menge des Salzes hängt von ihrer Natur, und falls die Ionen hydrolisierbar sind, von dem pH ab. Infrarotspektren, welche von einigen Komplexen aufgenommen wurden, geben Anhaltspunkte über die Natur der Wechselwirkung in der Zwischenschicht ab. Diese Wechselwirkungen sind schwach und entweder dipolare Anziehungen oder Wasserstoffbindungen. Diejenigen Ionen, die die größte Tendenz zur Einbettung in Halloysiten zeigen, sind Wasserstruktur- brechende Kationen oder Wasserstoff- bindende Anionen.