

INFRARED STUDY OF THE INTERCALATION OF POTASSIUM HALIDES IN KAOLINITE

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Abstract—KCl-, KBr-, and KI-kaolinite intercalation complexes were synthesized by gradually heating potassium-halide discs of the dimethylsulfoxide (DMSO)-kaolinite intermediate at temperatures to 330°C. Two types of complexes were identified by infrared spectroscopy: almost non-hydrous, obtained during thermal treatment of the DMSO complex; and hydrated, produced by regrinding the disc in air. The former showed basal spacings with integral series of 00 l reflections indicating ordered stacking of parallel 1:1 layers. Grinding resulted in delamination and formation of a disordered “card-house” type structure. The frequencies of the kaolinite OH bands show that the strength of the hydrogen bond between the intercalated halide and the inner-surface hydroxyl group decreases as Cl > Br > I. The positions of the H₂O bands imply that halide-H₂O interaction decreases in the same order. Consequently, the strength of the hydrogen bond between H₂O and the oxygen atom plane increases in the opposite sequence.

In the non-hydrous KCl-kaolinite complex the inner hydroxyl band of kaolinite at 3620 cm⁻¹ is replaced by a new feature at 3562 cm⁻¹, indicating that these OH groups are perturbed. It is suggested that Cl ions penetrate through the ditrigonal hole and form hydrogen bonds with the inner OH groups. In contrast, Br and I ions are too large to pass into the ditrigonal holes and do not form hydrogen bonds with the inner hydroxyls.

Key Words—CMS Clay KGa-1, Infrared Spectra, Intercalation Complexes, Kaolinite, Potassium Halide-Kaolinite Complexes, X-ray Diffractograms.

INTRODUCTION

In previous studies, we showed that CsCl and CsBr-kaolinite intercalation complexes, where alkali halides and H₂O intercalate kaolinite, can be prepared by grinding clay-salt mixtures with a limited amount of water; intercalation was proven by infrared (IR) spectroscopy (Michaelian *et al.*, 1991a, 1991b) and thermal analysis (Yariv *et al.*, 1982, 1991). Anhydrous complexes were prepared by evaporation of aqueous clay suspensions containing Cs salts, followed by aging the samples in air saturated with water vapor (Lapides *et al.*, 1994). The RbCl-kaolinite complex can also be synthesized by the latter method.

Our curve-fitting analysis of diffuse-reflectance IR spectra of kaolinite and CsCl-kaolinite complexes (Michaelian *et al.*, 1991b) showed that the hydroxyl band at 3620 cm⁻¹, which arises from inner OH groups, becomes weaker and nearly disappears as the degree of intercalation increases. Concomitantly, the band shifts to slightly lower frequencies. These results are surprising because an inner hydroxyl group, in contrast with an inner-surface hydroxyl group should not be affected by intercalation.

Recently, we showed by IR spectroscopy and thermal analysis that the hydrated CsCl-kaolinite intercalation complex obtained by grinding can be dehydrated by thermal treatment (Yariv *et al.*, 1994). With the evolution of intercalated H₂O, hydrogen bonds existing between these H₂O molecules and inner-surface

hydroxyl groups are partially replaced by bonds between intercalated chlorides and these hydroxyls. Consequently, the band arising from inner hydroxyl groups disappears and a new band appears at a lower frequency. These changes develop gradually with heat treatment. Yariv *et al.* (1994) and Lapides *et al.* (1995) suggested that penetration of Cl⁻ into the ditrigonal cavity of the oxygen atom plane (“keying”) may lead to an interaction between this ion and the inner hydroxyl group, thereby perturbing this band.

The hydrated CsCl-kaolinite complex does not show long-range periodicity and thus no $d(00l)$. The $d(00l)$ -value of the anhydrous phase is 1.05 nm. After heat treatment at 250°C and dehydration, an ordered stacking with parallel 1:1 layers is obtained.

Preparation of other alkali halide-kaolinite complexes by grinding is problematic. In the earlier studies, grinding K or Na salts with kaolinite did not yield intercalation complexes (Michaelian *et al.*, 1991a). Indeed, when kaolinite is ground with most alkali halides, particle size decreases owing to delamination of the kaolinite tactoids and, to some extent, breaking of the layers. Thermal diffusion of protons (prototropy) eventually leads to amorphization of the clay, with this process being slower in the presence of alkali halides than in their absence (Yariv, 1975a, 1975b).

The latter results conflict with those of Thompson *et al.* (1992, 1993) who sought to prepare alkali halide-kaolinite complexes by dry grinding. When alkali

halides other than RbCl, CsCl, and CsBr are ground together with kaolinite, the definition of the IR bands of kaolinite improves, but there is no evidence of intercalation (Yariv, 1975a, 1975b). Weiss *et al.* (1966) intercalated several alkali halides into kaolinite indirectly by treating ammonium acetate or hydrazine-kaolinite complexes with saturated aqueous solutions of different salts.

The objective of the present study is to understand better these alkali halide-kaolinite complexes. Kaolinite intercalation complexes were prepared with KCl, KBr, and KI by an indirect thermal method previously described by Lapides *et al.* (1997). In this procedure, kaolinite intercalated with dimethylsulfoxide (DMSO) is ground together with the required alkali halide, pressed into a disc, and gradually heated to temperatures $>200^{\circ}\text{C}$. Under these conditions, the DMSO evolved to form discs containing potassium halide-kaolinite intercalation complexes, together with small amounts of water. Grinding and re-pressing the discs produced hydration of the intercalation complexes, even after treatment at higher temperatures. In the present study, the IR spectra after heating at various temperatures to 330°C were used to characterize both near anhydrous and hydrous varieties of these intercalation complexes. Comparable results for the CsBr and CsI-kaolinite complexes are discussed elsewhere (Michaëlian *et al.*, 1998).

EXPERIMENTAL

Materials

Low-defect Georgia kaolinite (KGa-1, previously referred to as "well-crystallized"), supplied by the Source Clay Minerals Repository (The Clay Minerals Society), was gently ground to 80 mesh. Analytical-grade alkali halides (Merck, Darmstadt, Germany) were used without further purification.

Preparation of DMSO-kaolinite intercalation complex

The DMSO-kaolinite complex was used for the synthesis of the alkali halide-kaolinite intercalation complexes. The DMSO-kaolinite was prepared as follows: 5 g of kaolinite was stirred for 1 wk in a closed bottle containing 150 mL of DMSO and 50 mL of H_2O . The mixture was centrifuged and the separated slurry was aged at 60°C . After 1 wk, X-ray diffraction (XRD) results showed an intercalation complex of DMSO in kaolinite with a $d(001)$ -value of 1.11 nm, similar to that obtained by Olejnik *et al.* (1968). From the intensities of the 1.11 and 0.72-nm peaks, the intercalation was nearly complete.

Preparation of potassium halide-kaolinite complexes and XRD

Fifty mg DMSO-kaolinite was manually ground in an agate mortar for ~ 30 min with 100 mg of the ap-

propriate potassium halide. Ground mixtures were pressed into 12.5-mm discs under vacuum, by applying 10 tons of pressure for 10 min. Each disc was reground and re-pressed before heat treatment and examination by XRD. The discs were gradually heated in air between 50 – 330°C for different times and X-ray diffractograms were recorded; in a few cases the discs were heated at 400 and 500°C , as stated below. The discs were re-pressed each time before additional heat treatment to avoid rapid release of DMSO. After heating at 330°C , the discs were reground. They remained at ambient conditions for 1 h and then X-ray powder diffractograms were recorded between 4 – $40^{\circ}2\theta$.

Infrared spectra

IR absorption spectra of the re-pressed discs were recorded for unground and ground samples using a Bruker IFS 113v FT-IR spectrometer. Standard Bruker software was used for curve-fitting.

RESULTS

X-ray diffractions

Lapides *et al.* (1997) described $d(001)$ -values of the alkali halide-kaolinite complexes. In addition, however, we present new XRD data on the potassium halide-kaolinite complexes. When KCl, KBr, and KI discs of the DMSO-kaolinite complex were treated at 150°C , a very weak and broad peak was observed at 0.84 – 0.90 nm, which may characterize the formation of one or more hydrated varieties (without alkali halide) of kaolinite. This was not mentioned in Lapides *et al.* (1997) but is seen in Figures 1, 2, and 3 of that paper. Similar complexes were described by Costanzo *et al.* (1984, 1990) and by Tunney and Detellier (1994). The intensity of this peak decreased in the order $\text{KCl} > \text{KBr} > \text{KI}$ discs. In some samples, a trace of the peak was observed at 100°C . At 200°C , this peak did not occur.

The $d(001)$ -value of the KCl, KBr, and KI intercalation complexes were 1.00, 1.03, and 1.09 nm, respectively. The corresponding peaks were observed at 70°C but were very weak. They increased in size with temperature, whereas the intensity of the 1.11 nm-peak of the DMSO-kaolinite complex decreased. Note that the diffractograms of the intercalated kaolinite, after each thermal treatment, showed an integral series of $00l$ reflections, indicating well-ordered stacking of 1:1 layers.

For discs heated at 250°C , the X-ray diffractograms showed the presence of potassium halide intercalation complexes and small amounts of non-intercalated kaolinite. The relative amount of the non-intercalated kaolinite increased as $\text{KI} > \text{KBr} > \text{KCl}$. The peak at 0.72 nm for the non-intercalated kaolinite was very broad and asymmetric compared to the original kaolinite, indicating that the non-intercalated kaolinite in

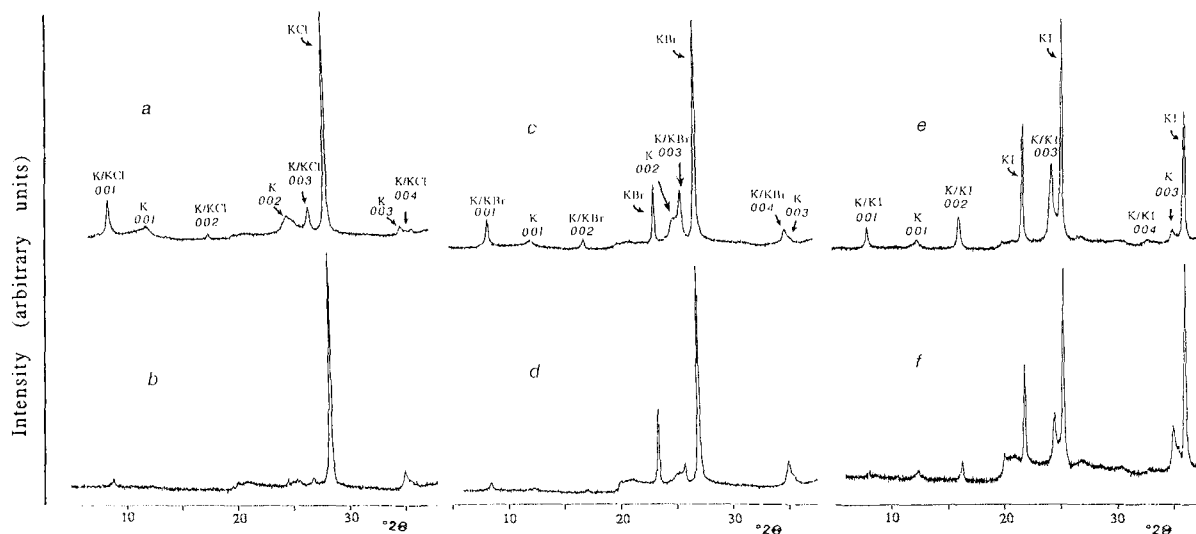


Figure 1. X-ray diffractograms of discs from mixtures of 100 mg kaolinite-DMSO and 200 mg potassium halide gradually heated to 330°C (upper curves) and of powders obtained by grinding the thermally treated discs (lower curves), (a, b) KCl, (c, d) KBr, and (e, f) KI.

the product material was disordered. In addition, excess potassium halide was observed. The DMSO-kaolinite complex was not detected after heating at 250°C. No significant changes were observed after heating to 330°C (Figure 1).

After grinding the heat-treated (330°C) discs, those peaks characterizing intercalation became weak relative to the peaks of potassium halide. The peak of non-intercalated kaolinite also became weak upon grinding. The non-intercalated kaolinite decreased in the order $KI < KBr < KCl$. In the present study, potassium halide is used as an internal standard. The weakening of the peaks of intercalated and non-intercalated kaolinite after grinding, relative to the intensity of the peaks of potassium halides, indicates that the grinding caused delamination.

Based on studies on grinding of CsCl-kaolinite mixtures (Lapides *et al.*, 1994, Yariv *et al.*, 1994), we suggest that during grinding of the disc delaminated kaolin-like layers form a "card-house" type structure and potassium halide together with H_2O adsorbed from the atmosphere are located in vacancies between the disordered layers.

The ground heat-treated discs were washed with distilled water until the salt was removed. The XRD patterns (Figure 2) showed the basal spacing of kaolinite at 0.72 nm, although the $d(001)$ peak was broad relative to the unreacted KGa-1. The Hinckley "crystallinity" index (Hinckley, 1963) of the untreated KGa-1 clay is 0.94. After washing the three intercalated samples, the Hinckley index for each decreased to <0.2 . These results indicate that the kaolinite is preserved during intercalation and heat treatment of the samples, but the degree of crystallinity of the clay is

reduced. Similar results were observed by Heller-Kalai *et al.* (1991) for washed DMSO-kaolinite intercalation complexes without heat treatment.

Infrared spectra

Thermal reactions between potassium halides and DMSO-kaolinite complex. The changes to the OH and Si-O vibrations resulting from heat treatment of potassium halide discs are similar to changes observed during heat treatment of the hydrous CsCl-kaolinite intercalation complex (Yariv *et al.*, 1994). Figure 3 shows the OH-stretching region in the IR spectra of KBr discs of untreated kaolinite and the DMSO-kaolinite intercalation complex after heating. A sharp IR band occurs at 3663 cm^{-1} for DMSO-kaolinite. This feature apparently replaces a band at 3693 cm^{-1} of untreated kaolinite. The 3693-cm^{-1} band arises from inner-surface hydroxyl stretching. The perturbation of this band in the spectrum of the DMSO complex implies that the inner-surface hydroxyl groups form hydrogen bonds with the intercalated-DMSO molecules by donating protons to the S-O groups (Olejnik *et al.*, 1968). Thus, the 3663-cm^{-1} band is characteristic of the DMSO-kaolinite intercalation complex and serves as an indicator of its presence. This band appears in the spectrum of the unheated disc and of those heated at 100 and 150°C, but is weak for the disc heated at $>150^\circ\text{C}$.

Similarly, bands at 3505 and 3540 cm^{-1} for the DMSO-kaolinite intercalation complex gradually disappear during thermal treatment at $>150^\circ\text{C}$. These bands were also attributed to perturbed inner-surface hydroxyl groups hydrogen bonded to the DMSO (Johnston *et al.*, 1984; Lipsicas *et al.*, 1986; Raupach

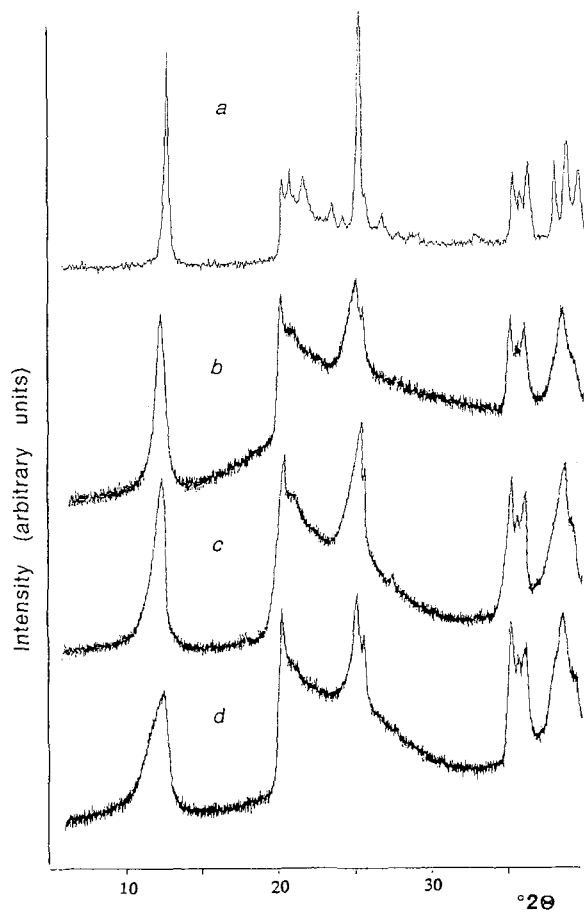


Figure 2. X-ray diffractograms of kaolinites (a) KGa-1, untreated and (b–d) obtained after washing kaolinite-intercalation complexes with distilled water, (b) KCl-, (c) KBr-, and (d) KI-kaolinite.

et al., 1987). New bands, which appear at $>200^{\circ}\text{C}$ display an increase in intensity with temperature, as shown in Figure 3 (curves c and d at 250 and 330°C , respectively), suggesting that they arise from perturbed OH groups. These bands become slightly weaker at 400°C and disappear after heating at 500°C , indicating that the kaolinite is dehydroxylated and has transformed into new dehydroxylated silicate phases at that temperature (Heller-Kallai, 1978).

The Si-O stretching bands change gradually with heat treatment. Differences between intercalated and untreated kaolinite arise from perturbed Si-O bonds. Bands at 1013 and 1040 cm^{-1} at room temperature of untreated kaolinite are replaced at 500°C by a single, broad absorption at 1000 cm^{-1} , further indicating that transformation of kaolinite occurred and dehydroxylated silicate phases formed.

When discs of the DMSO-kaolinite intercalation complex and KCl or KI were heat treated, similar changes in the spectra were obtained (Figures 4 and 5), but the locations of the IR bands differed and var-

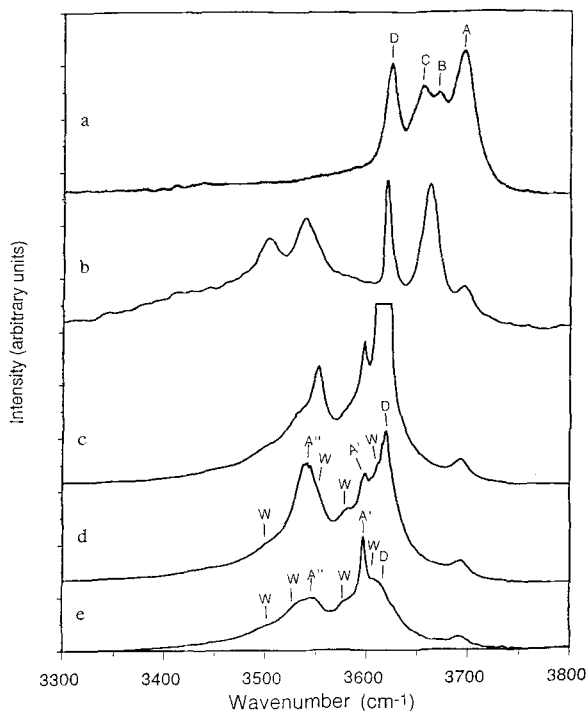


Figure 3. Infrared spectra of (a) kaolinite; DMSO-kaolinite in a KBr disc heated at (b) 100°C , (c) 250°C , and (d) 330°C . (e) KBr-kaolinite, after re-grinding and rehydration.

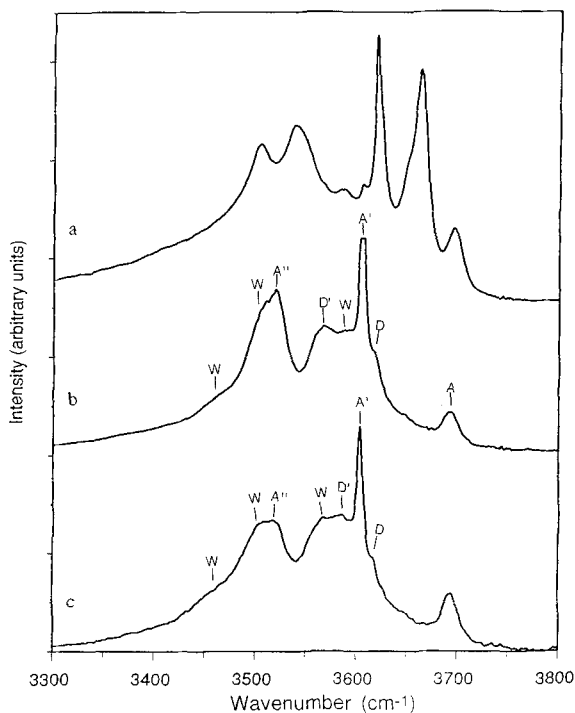


Figure 4. Infrared spectra of DMSO-kaolinite in a KCl disc heated at (a) 200°C and (b) 330°C . (c) KCl-kaolinite, after re-grinding and rehydration.

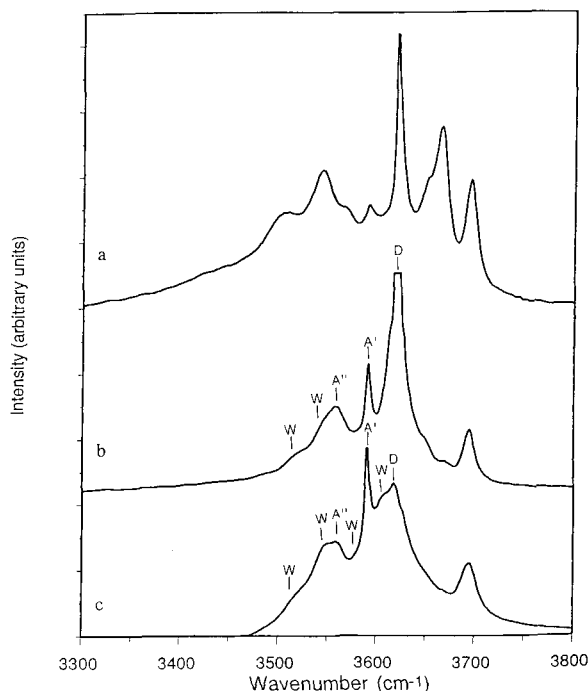


Figure 5. Infrared spectra of DMSO-kaolinite in a KI disc heated at (a) 200 and (b) 250°C. (c) KI-kaolinite, after re-grinding and rehydration.

ied with the halide (Table 1). We conclude that intercalated DMSO is replaced by the potassium halide during heat treatment. However, at 200°C, only some of the DMSO was replaced by KCl or KI, whereas at 250°C the exchange was nearly complete.

As noted above, the XRD patterns for samples heated to 150°C showed small amounts of hydrated kaolinite (without potassium halide). The shift of the 3620-cm⁻¹ band to 3612 cm⁻¹ was used to identify this complex by IR spectroscopy by Constanzo *et al.* (1990), but this band was not identified in our spectra, probably because the complex is below the detection limit of the experiment.

Infrared spectra of freshly prepared potassium halide-kaolinite complexes. Table 1 summarizes frequencies and assignments of bands in the spectra of potassium halide-kaolinite intercalation complexes obtained during heat treatment of DMSO-kaolinite discs containing different potassium halides. For comparison, data for untreated kaolinite are included. The positions of the bands in the 3300–3800-cm⁻¹ region are based on curve fitting. Lorentzian and Gaussian peaks were attributed to OH and H₂O vibrations, respectively (Michaëlian *et al.*, 1991b).

The most significant result in the spectra (Figures 3–5) is the diminution of bands owing to inner-surface hydroxyl-stretching vibrations (bands A, B, and C), and the appearance of two new bands (A' and A''),

which are attributed to perturbed inner-surface hydroxyl vibrations. Water-related bands are detected after heat treatment in the fitted curves, but they are very weak and their intensities decrease with higher temperature. These bands appear as shoulders to the principal bands.

According to Ledoux and White (1964, 1966), the perturbation of band A of the intercalated complexes indicates that the inner-surface hydroxyl groups participate in hydrogen bonding by donating protons to the intercalated species. In the present study, the relative intensity of band A' increased with heat treatment and that of A' decreased. Since heat treatment results in intercalated-H₂O loss, we attribute bands A' and A'' to hydroxyl groups involved in hydrogen bonds with intercalated H₂O and with halide, respectively. The positions of the OH bands depend on the halide: band A' shifts to slightly lower wavenumbers with increasing atomic number of the anion, whereas A'' displays the opposite trend. The shift of band A'' to higher wavenumbers indicates that the strength of the bond between the hydroxyl group and the halide decreases according to Cl > Br > I, as expected based on the electronegativity of these elements. The changes in the spectra due to dehydration are similar to changes described for the CsCl-kaolinite intercalation complex (Yariv *et al.*, 1994).

Band D arises from stretching vibrations of inner hydroxyl groups. Its presence depends on the halogen; the band persists with KBr and KI, but disappears with KCl. The absence of band D of KCl-intercalated kaolinite occurs with the appearance of a band at 3562 cm⁻¹. This latter band, which is not in the spectra of KBr and KI intercalation complexes, appears to be a perturbed vibration of the inner hydroxyl groups, and is designated D'. Changes to band D were observed previously during thermal dehydration of hydrated CsCl-kaolinite (Yariv *et al.*, 1994). Band D occurred in the spectrum of ground hydrated CsCl-kaolinite, but disappeared when the sample was thermally dehydrated. Simultaneously, a band occurs at 3576–3577 cm⁻¹ and was attributed to perturbed inner hydroxyl groups. Consequently it was assigned as band D'.

The two AIO-H deformation bands (designated H and I) are also perturbed in the complexes in comparison to untreated kaolinite. The location of band H depends on the halogen: it occurs at higher wavenumbers for the bromide ion (968 cm⁻¹) than for the iodide ion (956 cm⁻¹); consistent with this trend, it is not observed for chloride ions, where it is presumably masked by Si-O stretching bands. However, in the KCl complex obtained by heating to 200°C, a band located at 994 cm⁻¹ is attributed to perturbed band H. Band I shifts to lower wavenumbers (903–905 cm⁻¹) and is identifiable in the spectra of all three complexes. The Si-O stretching vibrations are shifted significantly and the bands change shape in the spectra of the interca-

Table 1. Infrared spectra of potassium halide-kaolinite complexes.

Assignment	Symbol	Natural clay	Complexes					
			KCl		KBr		KI	
			a ¹	b ¹	a ¹	b ¹	a ¹	b ¹
Inner-surface OH	A	3692	3694	3695	3693	3693	3694	3696
Inner-surface OH	Z	3686 ²	—	3690	—	3679	—	3689
Inner-surface OH	B	3668	3668	3668	3668	3669	3669	3669
Inner-surface OH	C	3653	3648	3648	3648	3648	3648	3648
Inner OH	D	3620	3618	3618	3620	3620	3621	3621
Inner-surface OH	A'	—	3605	3604	3597	3597	3591	3590
Inner OH	D'	—	3562	3588	—	—	—	—
Inner-surface OH	A''	—	3521	3524	3540	3551	3561	3561
Intercalated water	—	—	3591	3561	3605	3610	3606	3606
Adsorbed water	—	—	—	—	3583	3582	3576	3576
Intercalated water	—	—	3502	3502	3554	3531	3549	3548
Adsorbed water	—	—	3458	3454	3501	3501	3528	3528
Si-O stretching	E	1117	1107	1108	1108	1108	1109	1109
	P	1099	—	—	—	—	—	—
	F	1040	1026	1025	1023	1021	1019	1018
	G	1013	1002	1002	999	999	997	996
AIO-H deformation	H	939	987 ³	—	970	969	956	956
	I	918	905	903	905	905	905	905
	J	—	793	793	787	789	790	788
	K	756	757	757	759	760	761	761
	L	694	693	692	707	707	702	702
	—	—	—	651	674	674	672	670
Al-O deformation	M	552	565	563	560	560	558	557
	—	—	—	515	—	513	511	510
Si-O deformation	N	476	475	475	475	475	473	472
	O	434	435	435	436	436	436	435

¹ a = almost dehydrated (freshly prepared); b = rehydrated.

² From micro-Raman experiment.

³ Observed in spectrum of the concentrated disk.

lation complexes in comparison to untreated kaolinite. The data suggest that several factors, such as the keying of anhydrous ions (mainly potassium), hydrogen-bond formation between intercalated H₂O and oxygen atoms of the basal plane, and thermal diffusion of atoms within the 1:1 layers during the preparation of the complexes, affect the perturbation of bands.

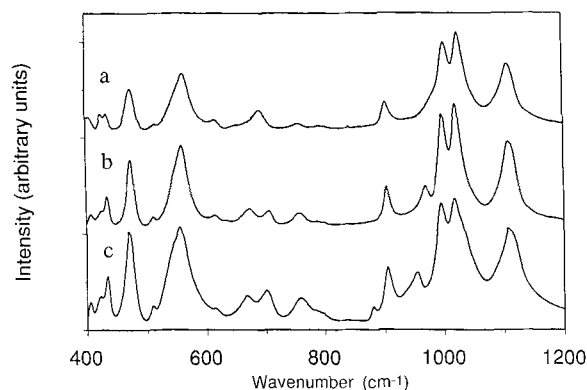


Figure 6. Infrared spectra from 400–1250 cm⁻¹ for kaolinite-intercalation complexes with (a) KCl, (b) KBr, and (c) KI, after regrinding and rehydration.

Infrared spectra of reground potassium halide-kaolinite complexes. Figures 3e, 4c, and 5c show the 3300–3800-cm⁻¹ region, whereas Figure 6 illustrates the 400–1250-cm⁻¹ region of the IR spectra of the reground potassium halide-kaolinite intercalation complexes. These samples contain considerable H₂O, and consequently the bands owing to H₂O, which appear as shoulders in spectra of freshly prepared complexes, become distinct in the present spectra.

Frequencies and assignments of bands of hydrated complexes, obtained by regrinding the potassium halide-kaolinite complexes and preparing discs, are summarized in Table 1, together with the corresponding bands of freshly prepared complexes and untreated kaolinite. The positions of the bands between 3300–3800 cm⁻¹ are determined from curve fitting. In general, the spectra show features similar to the freshly prepared samples, and there is little change in the frequencies of absorption bands associated with OH or H₂O. Only the relative intensities of the bands associated with hydration are increased. Like the fresh samples, bands associated with the inner-surface hydroxyl groups of kaolinite (A, B, and C) become very weak or disappear due to the intercalation reaction; new bands A' and A'' appear, indicating that the inner-surface hy-

droxyl groups donate protons to intercalated H₂O or halogen ions. In contrast to the fresh samples, the presence of substantial intercalated H₂O causes an increase in intensity of band A' relative to A".

Band D occurs as a weak shoulder in the spectrum of the ground KCl sample. Curve fitting shows that bands D and D' are present in the spectrum of the ground sample, at 3618 and 3588 cm⁻¹, respectively. The shift of the latter from 3562 cm⁻¹ in the spectrum of the near anhydrous sample is associated with stacking disorder of the particle. The relative intensity D'/D depended on the degree of hydration of the sample. In spectra of highly hydrated samples, this ratio was very small, but increased as the H₂O content decreased. Note that D' bands at 3562 and 3588 cm⁻¹ are Lorentzian, whereas the H₂O bands at 3591 cm⁻¹ in the fresh sample and the band at 3561 cm⁻¹ in the ground sample are Gaussian in shape. Band D' is caused by perturbed inner hydroxyl groups which accompany the penetration of the Cl ion into the ditrigonal cavity, and this suggests that the penetration reverses in the presence of intercalated H₂O. In the spectra of KBr and KI intercalation complexes, band D superposes with H₂O bands, and this is quantified by curve fitting.

The locations of the intercalated-H₂O bands are dependent on the halogens, thus suggesting that intercalated-H₂O molecules are coordinated to halogen ions. As expected, the lowest frequencies of both H₂O bands, and hence the highest perturbation of H₂O, are obtained with Cl, owing to the strong interaction between this anion and H₂O. The perturbation is weaker with other halogens. Note also that the frequencies of the two bands arising from intercalated H₂O in each complex are separated by ~60 cm⁻¹.

The two AlO-H deformation vibrations (bands H and I) in the spectra of the reground intercalation complexes are similar to those in the fresh complexes. In particular, they shift to higher and lower frequencies, respectively, relative to data for untreated kaolinite.

The Si-O stretching vibrations (bands E, P, F, and G) are also modified in the spectra of the hydrated intercalation complexes, but not as much as in the fresh samples; this is probably owing to the penetration of anhydrous ions into the ditrigonal cavities, which is limited in the presence of H₂O. In each case, the bands occur at lower frequencies than in untreated kaolinite. The location of band E, although changed, does not depend on the halide, whereas bands F and G occur at lower frequencies with increasing atomic number of the halogen. The data suggest that the basal-oxygen planes form hydrogen bonds with the intercalated H₂O, the latter serving as proton donors. The shifts in Si-O frequencies with the halogens indicate that these bonds are weak in the presence of Cl, but become stronger with Br and still stronger with I. This is due to the strength of the bonds formed between

H₂O and Cl, Br, or I ions. Moreover, H₂O serves as proton donors in these bonds, the strength of which decreases with increasing atomic number of the halogen. Consequently the ability of H₂O to donate the second proton to an oxygen atom of the 1:1 layer increases in opposite sequence as its tendency to donate a proton to the halogen ions.

DISCUSSION

Four different phases were identified during and after heating the DMSO-kaolinite complex. XRD data showed non-intercalated kaolinite, an ordered non-hydrated potassium halide-kaolinite intercalation complex, and at 150°C, a hydrated kaolinite without alkali halide. IR spectra identified non-intercalated, anhydrous, and hydrated potassium halide intercalation complexes. IR spectroscopy failed to identify the hydrated kaolinite (without salt) because the amounts obtained at 150°C were very small, and at higher temperatures this complex decomposed. XRD spectroscopy cannot identify the hydrated potassium-halide intercalated kaolinites because these complexes are delaminated and do not apparently produce XRD data.

Variations observed in the XRD and IR spectra of the DMSO-kaolinite complex when heated with various alkali halides arise from the intercalation of the clay mineral by these salts. The loss in intensities of the inner-surface hydroxyl-stretching bands, and the concomitant appearance of new bands owing to perturbed inner-surface hydroxyl and AlO-H bands, indicates that the inner-surface hydroxyl groups form hydrogen bonds with intercalated species. Comparison between freshly prepared, nearly dry samples and ground, hydrated samples shows that the H₂O and halide anions accept protons from inner-surface hydroxyl groups. The perturbation of band A owing to the interaction of the inner-surface hydroxyl groups with H₂O or with halide anions gives rise to bands A' or A", respectively.

The shift of the Si-O bands to lower frequencies is an indication that the inner-surface oxygen atoms are involved also in the formation of intercalation complexes. The involvement of the oxygen atom plane may occur by the interaction of the negatively charged oxygens with the positively charged cations, but it may also be due to keying of the different ions in the ditrigonal holes. The perturbation of the stretching vibration of the inner hydroxyl groups is probably associated with the keying of the halides. Thus the Cl anion penetrates into the ditrigonal cavity of the tetrahedral sheet, reaching the inner hydroxyl group and resulting in a hydrogen bond. This produces the perturbation of band D and the occurrence of band D'. The Br or I anions, due to their greater size, enter the hexagonal hole partially and induce a weak electric field on the inner hydroxyl group, leading to a slight weakening of the OH bond and minor changes in the

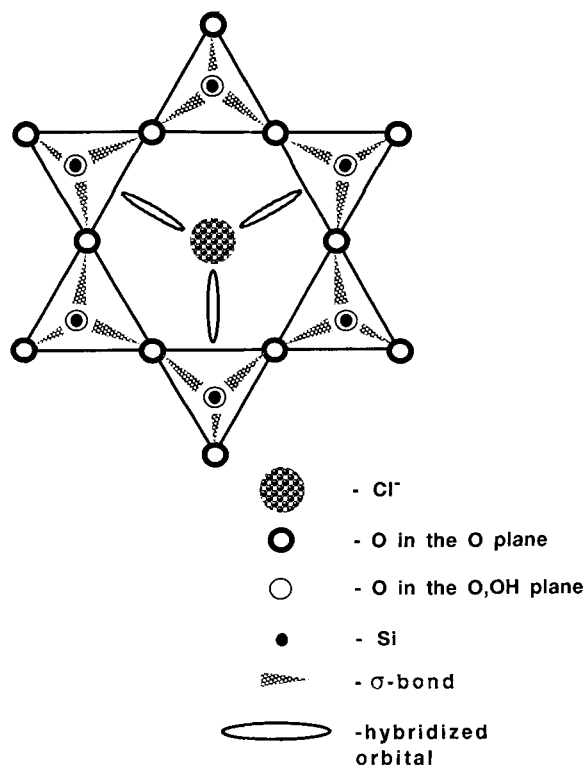


Figure 7. Keying of chloride ion in ditrigonal cavity. Sizes of atoms and orbitals are arbitrary.

IR spectra. Keying of CsF and CsCl (and to a small extent CsBr) was shown previously by X-ray studies (Lapides *et al.*, 1995).

The classical model of fixation of ions by clay minerals (Sawhney, 1972) cannot explain the penetration of the Cl anion into the ditrigonal cavity for two reasons: (1) electrostatic repulsion occurs between the negatively charged Cl anions and the negatively charged oxygen atoms (due to the polar nature of the Si-O bond); and (2) the ditrigonal hole is too small to enable the penetration of an atom with a non-bonded van der Waals radius larger than that of an oxygen atom. In the classical model, atoms are considered as dense spheres. This model is incorrect in the present case, because of the positive field that is induced by the inner-surface hydroxyl groups. The IR spectra show that these groups are involved in hydrogen bonds with the Cl anions, which requires that a hybridization of the latter takes place (hydrogen bonds are formed by partial electron-pair donation from the chloride to the proton, and this happens only from hybridized orbitals). Consequently, the negative charge of the anion has directional character based on the hybridized orbitals. Assuming that the hybridization of the chloride is sp^3 , the three hybridized orbitals not involved in hydrogen bonding with an inner-surface hydroxyl group would be directed towards three of the six sili-

con nuclei, located at the center of the tetrahedra forming the ditrigonal cavity. The electron density owing to the valence shell of the oxygen atoms is at a maximum along the Si-O bonds and is at a minimum between the center of the "cavity" and the silicon atoms (Figure 7). Thus, the hybridized orbitals of the Cl ion penetrate relatively unimpeded. A similar approach was used to determine the shapes and sizes of molecules (Meyer, 1986), as well as molecular crystals. The approach was also used to determine shape selectivity in zeolites and carbon (Csicsery, 1984). Inner-electron shells are not involved in the hybridization and are spherical. The numbers of inner shells of bromides and iodides are higher than the total number of shells of oxygen. Consequently, these ions do not penetrate the ditrigonal cavity and do not form hydrogen bonds with inner hydroxyls.

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