Journal of Thermal Analysis and Calorimetry, Vol. 56 (1999) 865-884

THERMAL INTERCALATION OF ALKALI HALIDES INTO KAOLINITE*

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Abstract

Solid state intercalation of alkali halides into kaolinite takes place by heating pressed disks of dimethylsulfoxide (DMSO)-kaolinite complex ground in different alkali halides. This reaction involves diffusion of the DMSO outside the interlayer space and the alkali halide into the interlayer space. IR and Raman spectroscopy reveal two types of intercalation complexes: (i) almost non-hydrous, obtained during thermal treatment of the DMSO complex; and (ii) hydrated, obtained by regrinding the disk in air. The strength of the hydrogen bonds between intercalated water or halide anions and the inner surface hydroxyls decreases in the order $Cl^->Br^->I^-$. Chlorides penetrate the ditrigonal holes and form hydrogen bonds with the inner OH groups.

Keywords: alkali halides, intercalation, kaolinite intercalation complexes, mechanochemical intercalation, thermal intercalation

Intercalation complexes of kaolin-type minerals

Kaolin-type minerals intercalate a variety of organic compounds [1–5]. The penetrating species overcome the strong electrostatic and van der Waals interactions between the kaolin-like layers and the basal spacing expands from 0.72 to about 1.00–1.44 nm. Intercalating compounds may form hydrogen bonds with components of the TO layer by accepting protons from inner-surface hydroxyls and donating protons to inner-surface oxygens, as was first inferred by comparing calculated and experimental basal spacings, and later proved by infrared spectroscopy [6–12]. Basal

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* Plenary lecture.

1418-2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

hydroxyls are poor proton donors and form hydrogen bonds only with very strong basic groups, such as NH_2 in urea or hydrazine, C=O in urea and several other amides, NO in pyridine-N-oxide (PNO) and S=O in dimethylsulfoxide (DMSO). The latter are bound to inner-surface hydroxyls through either the sulphur or the oxygen atoms. In all these cases the proton acceptor groups point to the hydroxyl surfaces and hydrogen bonds are obtained, in which these groups accept protons from the hydroxyls. The inner-surface O–H stretching bands in the kaolinite IR spectrum are perturbed and shifted to lower wavenumbers. The characteristic absorption bands of the adsorbed proton acceptor groups are also shifted.

Strong proton donor groups, such as NH_2 in urea or amides, may form hydrogen bonds with oxygens located on the tetrahedral sheet surface. Since the oxygen plane is a poor electron donor, these hydrogen bonds are very weak. Their existence was inferred from perturbation of the Si–O stretching vibrations of the kaolinite and of the NH_2 stretching vibrations of the organic molecule [8].

Three main groups of polar organic compounds were distinguished by their mode of intercalation [13, 14]. 'Group A' includes species which are directly intercalated from the liquid, melt or concentrated aqueous solution. 'Group B' consists of species which are indirectly intercalated by means of an 'entraining agent', and 'group C' includes species which are intercalated by displacement of previously intercalated compounds.

In contrast with halloysite, which forms intercalates with many organic compounds [4], kaolinite and dickite directly intercalate only a few compounds. Small molecules with a large dipole moment (3.71–5.37 Debye) may serve as group A compounds, and are intercalated directly by batch treatment, without any pretreatment of the clay [5]. This includes molecules which act simultaneously as proton donors and acceptors, such as urea [2], hydrazine [13], hydroxylamine, imidazole, form-amide [15], acetamide (and mono- or dimethyl derivatives of the amides) [8, 10, 12, 16], small molecules with a betain-like mesomeric structure which serve as proton acceptors, such as DMSO, dimethylselenoxide and PNO [14, 17–23] and salts of short-chain fatty acids with large monovalent cations, such as K^+, Rb^+, Cs^+ and NH_4^+ [1, 14].

When the intercalating compound is liquid, a trace amount of water is sometimes essential for the intercalation process; however, increasing amounts of water may decrease the extent of intercalation [22]. Similarly, if the intercalating compound is adsorbed from aqueous solution, this solution must be highly concentrated. For example, in the case of urea or hydrazine, below a limiting concentration (10–11 M) the solute is highly solvated and relatively few unsolvated molecules are present or available for intercalation [2]. Increasing the solute concentration will initially raise the intercalation rate until a point is reached beyond which this rate falls. This phenomenon is attributed to self-association of the organic molecules at high concentrations, leaving very few monomers for intercalation. The liquid structure can be disrupted by raising the temperature, hence an increase in temperature gives rise to a faster rate of intercalation. However, the batch temperature cannot be too high, because the intercalated molecules escape from the interlayer space in these conditions.

Most known intercalation complexes of group A are not stable. They exist as long as contact with the pure liquid is maintained [16, 17]. Moreover, these complexes are destroyed by water: the kaolinite hydrates on eluting the intercalated species with water and recollapses with intense washing. Several of these compounds, particularly hydrazine and ammonium acetate, act as entraining agents. Hydrazine can entrain any neutral molecule or salt (group B), the only requirement being that the entrained species is soluble in aqueous hydrazine solution. Some of these compounds, studied by Weiss *et al.* [14], are benzidine, *n*-octylamine, glycerol and the following organic salts: sodium acetate, potassium salts of glycine, alanine, lysine, oxalate and lactate. Intercalation of sodium and potassium salts of the fatty acids, lauric, palmitic, elaidic, oleic and 12-hydroxystearic acid via hydrazine, was recently carried out [24, 25]. The appropriate complex with the entrained compound may then be obtained by selectively removing the hydrazine by evaporation, exposure to air, or heat treatment. Compounds such as nitrobenzene, acetonitrile, glycol and long chain alkylamines (group C) may penetrate the mineral interlayers by replacing other intercalated compounds, such as ammonium acetate [13, 14] or DMSO [18].

The size of adsorbed molecules affects the intercalation rate: the rate usually increases with a decrease in size [12, 16, 17]. From X-ray data it appears that a single layer of organic molecules is obtained with a considerable amount of 'keying' in most cases. This also includes kaolinite treated with long chain (up to 18 carbons) carboxylic acids [24, 25]. There were only a few cases in which a double layer of molecules was obtained, with the plane of an aromatic ring or the axis of an aliphatic chain lying parallel to the kaolinite surface. These XRD results could also indicate that a single layer was obtained with the ring or chain perpendicular to the silicate layer and the oxygen of the organic molecule in contact with the inner-surface hydroxyls [14]. However, the c-spacing was too short for this orientation and the authors suggested that some keying took place. On the other hand, pleochroic IR data led to the conclusion that the molecules were tilted with respect to the silicate surface [8].

Kaolinite-fatty acid salt intercalation complexes are of particular interest, because in the presence of water, a very large c-spacing is obtained. As shown by Seto *et al.* [26], a stepwise intercalation of ammonium propionate resulted in a spacing in the range 1.2–2.55 nm, with a high degree of order along the c axis.

Intercalating ability differs from one mineral to the next [27, 28]. There are also differences in reactivity between kaolinites themselves, and from sample to sample. For example, all batch experiments to form intercalation complexes of fire clay (b-axis disordered kaolinite) with DMSO failed. Well crystallized kaolinite from Georgia (USA) forms a stable DMSO complex and the degree of intercalation is almost 100%. On the other hand, kaolinite S-5 from Makhtesh Ramon (Israel) intercalates DMSO only in part, and the complex is stable only in the presence of excess DMSO. When the sample is dried in ambient atmosphere, the organic molecule escapes from the interlayer (unpublished results).

Kristóf *et al.* [29] showed that the stability of the intercalation complex towards washing with water depends on the degree of disorder of the kaolinite. Intercalation complexes of ordered kaolinites collapse to 0.72 nm upon washing, whereas complexes of disordered kaolinites form hydrates similar to halloysite. The thermal behaviour of intercalation complexes also depends on the degree of order of the kaolinite. The DTG curve of an ordered kaolinite-potassium acetate complex showed two separate peaks due to dehydroxylation and acetate decomposition, whereas the DTG curve of the disordered complex showed a single peak indicating that both reactions occur simultaneously.

In addition to hydrazine and hydroxylamine, a few other inorganic compounds were directly or indirectly intercalated into kaolinite. Costanzo *et al.* [30–33] reported the synthesis of four different intercalation hydrates of kaolinite, obtained by replacing DMSO by H_2O. Weiss *et al.* [14] intercalated different inorganic alkali halides into kaolinite using aqueous solutions of the salts and hydrazine or ammonium acetate as an entraining agent. The intercalation of the alkali halide was verified by X-ray determination of the basal spacing. In our laboratories intercalation complexes of alkali halides have been investigated for about thirty years. RbCl, CsF, CsCl and CsBr complexes are obtained directly either (i) after long periods at 60°C in concentrated aqueous solutions in sealed glass ampoules or as slurry, followed by long ageing in a damp atmosphere, or (ii) by mechanochemical treatment (grinding). Other alkali halides penetrate into kaolinite interlayers by replacing DMSO that has been previously intercalated into kaolinite. Thus, the first four alkali halides are classified as group A intercalating compounds, whereas the other halides belong to group C. In the present paper the work which was carried out in our laboratories is reviewed.

Direct intercalation of caesium halides

Three different grinding techniques were employed in our laboratory [34–47]. The first was manual grinding (2–30 min) of mixtures containing kaolinite and the appropriate caesium salt, in different mass ratios. In the second, the same mixtures were ground for 15–30 min by a mechanical grinder, comprising a mortar and pestle. Samples were prepared by 'air grinding', in ambient air, or by 'wet grinding', where 5–7 drops of water were added every 3–5 min to keep the mixture moist. In the third technique, the mixtures were ground in a centrifugal ball-mill equipped with an agate cell and several agate balls. In this grinding system the mixture was isolated from the atmosphere. The term 'dry grinding' is used for grinding in a ball mill with no addition of water. The different ground samples were examined after being aged in an oven at 100°C, in a desiccator under air saturated with water vapour, or in ambient atmosphere for different periods. In a non-mechanochemical preparation method, unground kaolinite was suspended in a concentrated aqueous caesium halide solution or mixed with the salt and water to form a slurry. After different ageing periods in sealed glass ampoules at 60°C, the excess water was evaporated. The dried mixture was aged in air saturated with water vapour.

The interaction of CsF with kaolinite by any of these methods resulted in a complex mixture of caesium silicates, caesium aluminum silicates, caesium aluminum fluoride and aluminum fluoride. Three types of intercalation complexes (A, B and C) were also identified [34, 35]. Small amounts of complex A were detected in samples obtained by drying CsF–kaolinite slurries. This complex was identified by its X-ray diffraction peak at 0.99 nm. IR spectroscopy showed that this complex is hydrated. However, the characteristic bands of kaolinite were not perturbed, indicating that there were no interactions between functional groups of the kaolinite layer surface (OH or Si–O groups) and the intercalated molecules [34]. Adsorbed water molecules form intermolecular H-bonds between themselves, which is similar to the intermolecular interactions of water in natural halloysite [36]. It appears that some of the inner-surface hydroxyls were replaced by fluorides during this treatment. According to the calculations of Wolfe and Giese [37] substitution of F for OH groups dramatically weakens the interlayer bonding of kaolinite. Complex A is probably obtained by the intercalation of water clusters into the space between weakly bonded kaolinite layers.

Complex B was identified by XRD (0.84 nm) after evaporating a kaolinite–CsF suspension in the presence of excess salt. The intensity of this peak relative to the 0.72 nm peak was initially weak, but it increased with ageing. The 0.84 nm peak disappeared when the sample was washed with water or heated at 260°C. The keying of F^- is obvious from the spacing of 0.84 nm. On the other hand, Cs^+ is large and cannot be located in the interlayer space. We therefore suggested that HF (or $[H(H_2O)_x]F$) was the intercalated species. A hydrated proton was identified by an IR band at 1725 cm^{-1} [34].

Complex C was identified by IR after grinding kaolinite–CsF mixtures [35]. The X-ray diffractogram of this complex did not show any characteristic basal spacing, but the 0.72 nm peak of untreated kaolinite became very weak. The diminution of the 001 reflection indicates that due to grinding the kaolinite is delaminated and becomes amorphous in the c-direction. CsF is hygroscopic and the kaolinite–CsF mixture adsorbs water from the atmosphere during grinding. Thus, grinding in open systems can be regarded as wet grinding. In the presence of excess Cs^+, which is a water structure breaker, the adsorbed water becomes non-structured and single H_2O molecules form hydrogen bonds with active sites on the layers of mechanically delaminated kaolinite. This gives rise to changes in the IR spectrum. Band A, an inner-surface OH stretching vibration of kaolinite located at 3692 cm^{-1}, becomes weak. A new band appears at 3600 cm^{-1}, attributed to perturbed band A. The extinction of band A and appearance of the new band provide evidence for the interaction of intercalated water with exposed inner surface hydroxyls. Band D, the inner hydroxyl stretching vibration at 3620 cm^{-1}, diminishes slightly immediately after grinding and further decreases with ageing. This extinction is accompanied by the appearance of a new band at 3518 cm^{-1}, attributed to a perturbed inner hydroxyl vibration. This perturbation of about 100 cm^{-1} is strong and must be due to hydrogen bonds between inner hydroxyls and F^-, which can occur only if the fluoride ions penetrate the ditrigonal holes of the oxygen planes. This keying effect will be discussed in the last part of this review.

The grinding of minerals of the kaolin subgroup with CsCl in air leads to their delamination and the formation of an intercalation complex in which CsCl, together with water adsorbed from the atmosphere, is located between the layers of the minerals [38–47]. Kaolin-type minerals that have been studied until now are kaolinite [38–40], halloysite [41], fire clay and dickite [42]. In these intercalation complexes hydrogen bonds are formed between inner-surface hydroxyls of the octahedral sheets of the kaolin-like layers and oxygens of adsorbed water molecules, as well as between protons of adsorbed water molecules and inner-surface oxygens of the tetrahedral sheets. Delamination and intercalation occur during the grinding of the mineral with CsCl. However, the intercalation reaction associated with the adsorption of water from the atmosphere is much slower than the delamination, and an ageing period longer than a month is sometimes needed to complete the reaction. This is especially noticeable for kaolinites, where the partial intercalation observed immediately after grinding gradually increased. The long time was probably necessary for the hydroxyls to become reoriented. Intercalation of dickite was observed for the first time one day after grinding [42]. Fire clays, on the other hand, formed complexes mainly during the grinding process, and their spectra remained unchanged for at least six weeks [42]. Halloysite is an expanded mineral and intercalation, although gradual, begins with grinding and is fast [42]. The three serpentine-type minerals antigorite, lizardite and chrysotile did not react with CsCl during the grinding process [42]. The surface acidity of their inner-surface hydroxyls is weaker than that of the dioctahedral kaolins and the surface basicity of their inner-surface oxygens is also weaker than that of the kaolin minerals. They do not form hydrogen bonds with intercalated water molecules and consequently this kind of intercalation does not occur. To the best of our knowledge intercalation complexes of serpentines are not reported in the literature.

The IR spectrum of the complex is characterized by the diminution of inner surface hydroxyl absorption bands (designated A, B and C, at 3692, 3666 and 3653 cm^{-1}, respectively) and the appearance of new bands at 3599 and 3582 cm^{-1}, attributed to a perturbed clay inner-surface OH group (A′) and intercalated H_2O, respectively. The intercalation is also accompanied by shifts of framework Si–O and Al–O stretching and bending bands as well as AlO–H deformation bands. These significant changes in the infrared spectra of the intercalation complexes indicate the formation of hydrogen bonds between OH groups of the octahedral sheets and adsorbed water molecules, and between the latter water molecules and basal siloxane oxygens of the tetrahedral sheets [42, 43].

Orientation of hydroxyls in the different minerals of the kaolin subgroup varies [48]. As a result there are differences in the locations and relative intensities among the inner surface OH stretching bands in the IR spectra of the untreated kaolin-type minerals. Band A is the most intense for some kaolins, whereas others, like dickite, show band C to be more intense, relative to band D. Halloysite exhibits only bands A and D. Similar intensity differences are not observed in the IR spectra of the intercalation complexes of the various kaolin-type minerals. These data suggest that there are no structural differences between intercalation complexes obtained from kaolinite, dickite, fire clay or halloysite [41, 42].

Delamination of CsCl intercalated minerals of the kaolin-type subgroup has been proven by deuteration [42]. The inner-surface hydroxyls of the kaolin sub-group minerals were deuterated without any difficulty by washing the CsCl complexes six times with D_2O. A new band A_D at 2725 cm^{-1}, accompanied by two shoulders B_D and C_D at 2710 and 2698 cm^{-1}, respectively, appeared in the IR spectrum. Simultaneously, bands A, B and C showed considerable reduction in their intensities. A weak shoulder D_D at 2675 cm^{-1} indicates that the inner hydroxyls were deuterated to a very small extent. This is indeed what one would expect from a delaminated kaolin-type mineral.

Deuteration also supported the idea that water molecules were adsorbed by the kaolin-type clay from the atmosphere during its grinding with CsCl. The different clays were already deuterated after the first washing with D_2O, but their spectra differed from those obtained after six washings. A very broad absorption, which comprises shoulders at 2600 and 2663 cm^{-1} and a maximum at 2610 cm^{-1}, in addition to a very weak band A_D, was observed in the spectra of kaolin-type CsCl complexes after they were washed twice with D_2O. The intensity of the 2663 cm^{-1} band was dependent on the orientation of the clay film, indicating that it was due to a vibration perpendicular to the kaolin-like layer. It was denoted A'_D and attributed to deuterated band A′. Band A'_D is thus equivalent to perturbed band A_D. The broad band at 2610 cm^{-1} was attributed to intercalated D_2O. Simultaneously bands A, B and C showed considerable reduction, whereas band A′ and the intercalated water band at 3582 cm^{-1} disappeared. These data indicate that intercalated water in the kaolin–$CsCl–H_2O$ complex was replaced by D_2O [42]. The kaolin-type $CsCl–D_2O$ complexes are very stable and spectra of samples left at room humidity for 48 h were similar to spectra recorded immediately after the preparation of the complex. After six washings the intercalated CsCl is removed and the clay framework collapses [42].

The degree of intercalation of CsCl was least with mixing, intermediate with air grinding and greatest with wet grinding [43]. With the latter the extent of intercalation was almost complete. Water seems to be essential in the mechanochemical intercalation process. The specific activity of caesium salts may be due to the fact that this cation breaks the water cluster structure and in the first stage of the process, monomeric species are adsorbed on the external surfaces of the kaolinite [40]. These molecular species should be more active compared with clustered water (Fig. 1a). No peak was observed in the X-ray diffraction curve of samples obtained by wet grinding for 30 min [40, 46, 47]. The samples obtained after air grinding showed a peak at 0.72 nm which gradually disappeared after ageing 2–4 weeks in air or 1–2 days in a humid atmosphere [47]. The IR spectra of the air ground mixtures showed that the intercalation started with the grinding process. It is possible that at this stage hydrated CsCl penetrated into the edges of the interlayer space (Fig. 1b). The disappearance of the 0.72 nm peak, which is characteristic of non-intercalated kaolinite, indicates that the sample was delaminated and became amorphous in the c-direction. In this assemblage the kaolin-like layers are not arranged in any preferred orientation (card house structure) with Cs^+, Cl^- and water in the space between the layers. (Fig. 1c). The sample was heated for 2 h at 250°C, in order to eliminate the intercalated water. The diffractogram of this sample contained a very intense peak at 1.06 nm.

IR spectroscopy and DTA-TG curves showed that this thermal treatment resulted in an almost complete dehydratation of the sample. It is therefore concluded that a spacing of 1.06 nm characterizes the anhydrous CsCl–kaolinite intercalation complex. Water molecules were evolved during heating, and new assemblages were formed by reorganization with parallel TO layers intercalated by Cs and Cl ions (Fig. 1d) [46].

X-ray diffractograms, IR spectra and thermal curves obtained from samples prepared by suspending the ground sample or untreated KGa-1 kaolinite in an aqueous 8 M CsCl solution for 3 weeks at 60°C in sealed glass ampoules were diagnostic for an anhydrous intercalation complex [46, 47]. Although these samples were obtained from an aqueous phase, it should be noted that the resulting CsCl intercalation complex was almost anhydrous, which shows that a system with inter-water hydrogen bonds is more stable than one with hydrogen bonds between water molecules and kaolinite siloxane and hydroxyl groups. The aging of the CsCl–kaolinite ground sample for 2–3 months in a humid atmosphere also resulted in the anhydrous intercalation complex [47]. Clustered water molecules are more restricted in their translational and rotational motion than monomers weakly bonded to the kaolinite silox-

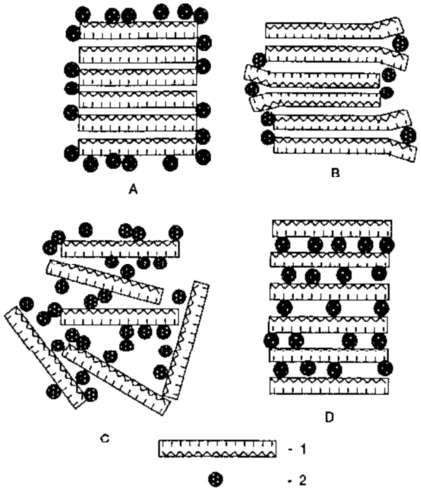

Fig. 1 Four stages in the mechanochemical intercalation of CsCl and H_2O by kaolinite. A – First stage: adsorption of molecular H_2O on the external surfaces of a kaolinite assemblage (the *c*-spacing is 0.72 nm and the IR spectrum is that of kaolinite); B – second stage: penetration of CsCl and H_2O into frayed edges of the interlayers of kaolinite assemblages (the c-spacing is 0.72 nm, but the IR spectrum shows weak bands of the intercalation complex); C – third stage: delamination of the kaolinite assemblage by the grinding process, the intercalation of hydrated Cs and Cl ions and their interaction with inner-surface hydroxyls and oxygens (XRD does not show any peak for basal spacing but the IR spectrum is characteristic for the intercalation complex); D – fourth stage: thermal dehydration of the intercalation complex at 250°C and rearrangement of the TO layers (a new XRD peak is obtained at 1.05 nm and the IR spectrum is significantly changed compared with those of the previous stages). 1, Kaolin-type TO layer; 2, Adsorbed CsCl and/or H_2O species

anes and hydroxyls, and therefore have lower entropy. Thus during the mechanochemical treatment, when the water content is low and non-clustered due to the Cs, intercalation of kaolinite by water is favored by entropy. In aqueous systems, where the water content is high, enthalpy stabilization of water clusters occurs, as in halloysite [41].

Dry grinding of CsBr or CsI with kaolinite in the ambient atmosphere did not result in any intercalation [43]. Ageing, which improves the intercalation in a CsCl–kaolinite system, did not affect the CsBr– and CsI–kaolinite systems. However, IR and thermal mass loss study proved that CsBr and water (but not CsI and water) formed a kaolinite intercalation complex during wet grinding [43]. The CsBr–H_2O–kaolinite intercalation complex was studied by simultaneous DTA-TG, supplemented by IR spectroscopy [44]. TG curves show six stages of mass loss. The first stage, in the room temperature–170°C range, is accompanied by an endothermic DTA peak at 75–115°C. This corresponds to the desorption of surface and interparticle water, located mainly at the interface between the mineral and the salt. Untreated kaolinite does not show any peak or mass loss in this temperature range. The second stage of mass loss (170–400°C), is due to desorption of intercalated water.

Reexamination of the IR spectrum of thermally treated samples showed that the CsBr complex obtained at this stage is almost anhydrous. The third mass loss stage 400–590°C) is due to the dehydroxylation of the clay and simultaneous thermal hydrolysis of the intercalated CsBr. Mass loss of mixtures that do not contain excess CsBr is smaller than that of untreated kaolinite in the same temperature range; this s due to the fact that the dehydroxylation of the former, which is delaminated, has already started during the second stage. These reactions give rise to an endothermic peak at 485–500°C. The dehydroxylation DTA peak of natural kaolinite appears at a slightly higher temperature, i.e., 530°C.

The fourth-sixth stages depend on the initial salt/clay ratio. In the absence of excess non-intercalated salt, mass loss is relatively small, resulting from the dehydroxylation of the clay which started at the second or third stages but continues at the fourth stage. A weak exothermic peak due to the recrystallization of the dehydroxyated kaolinite phase appears at above 950°C (sixth region). This peak decreases with ncreasing CsBr content and is not observed with excess salt. During the dehydroxyation of the kaolinite a phase is obtained in which the salt is incorporated into the TO framework. The thermal properties of the Cs-bearing meta-kaolinite differ from hose of normal meta-kaolinite by not exhibiting an exothermic reaction at ~1000°C. The presence of a non-adsorbed CsBr phase is confirmed in the corresponding DTA curves by two endothermic peaks at 605–640 and 825–1040°C, arising from melting and boiling of this salt. The fourth mass loss stage (590–685°C) represents partial sublimation of the excess salt, which starts in this temperature range. In the fifth mass loss stage (685–950°C) the boiling salt evaporates. In the sixth stage (950–1170°C) a very small mass loss is recorded, associated with the recrystallization of the meta-clay. Mixtures with more than 140 mmol/100 g kaolinite show the presence of a non-adsorbed CsBr phase. Below this saturation point, all of the CsBr occurs in the intercalation complex. This saturation concentration is lower than the >297 mmol/100 g kaolinite obtained for CsCl by a similar DTA method [45].

Indirect intercalation of alkali halides

The DMSO–kaolinite intercalation complex was the starting material for the preparation of the alkali halides complexes. It was prepared by stirring kaolinite with a solution containing 75% DMSO and 25% H_2O for one week. After this treatment, the separated slurry was aged at 60°C for one week. The DMSO intercalation complex was identified from a basal spacing of 1.11 nm in X-ray diffraction. 200 mg of this complex were ground with 200 mg of each alkali halide and pressed into 12.5 mm diameter disks using a mass of 10 tons for 10 min. Each disk was reground and repressed before it was thermally treated. In the thermal treatment the disk was gradually heated in air from room temperature to above 300°C for different durations, after which X-ray diffractograms and IR spectra were recorded. The disks were repressed without grinding each time before they were returned to the furnace n order to avoid fast evolution of the released DMSO [49]. The activation energies for the thermal decomposition of the DMSO intercalation complex and the evolution of DMSO were found from isothermal and dynamic studies by Breen and Lynch [50] to be 85±2 and 72±4 kJ mol^{-1}, respectively, or 78 kJ mol^{-1} by Adams and Waltl [51].

At room temperature the IR spectra of all samples showed characteristic DMSO bands [52–54]. These bands became weak and disappeared when the disks were heated, indicating that DMSO was gradually evolved. The IR spectra of the thermally treated samples differed from that of kaolinite and from each other. The spectra of the CsCl and CsBr complexes were similar to those of the thermally treated complexes obtained by direct intercalation. It was therefore concluded that the alkali halide ions diffused into the swollen mineral interlayers, replacing the organic compound. Such a solid state exchange may take place only if the thermal diffusion of the penetrating species is faster than the evolution of the intercalated DMSO. For this reason the mixtures were pressed into disks and each disk was repressed after each thermal treatment. All attempts to replace DMSO with any of the alkali halides without pressing the mixture into a disk failed. Furthermore, we did not find appropriate conditions for intercalating NaI, and only a small amount of NaCl and intermediate amounts of NaBr were intercalated [49]. Lithium and fluoride salts could not be studied because these salt-kaolinite mixtures are hygroscopic and it is impossible to press them into disks. It appears that the intercalation ability of the alkali cation increases with decreasing hydration energy. It is possible that the anhydrous cation is essential for the intercalation process. This requires further study.

After heating the disks at 100°C, in addition to the 1.11 nm XRD peak indicating that the DMSO complex persisted, two new peaks at 0.72 and 1.00–1.17 nm appeared, due to non-intercalated collapsed kaolinite and kaolinite intercalated by alkali halide, respectively [49]. The latter peaks increased at 150°C and became dominant at 200 or 250°C. At higher temperatures the complexes started to decompose and the 0.72 nm peak intensified to some extent. In some cases longer thermal treatment at 100–150°C gave optimal intercalation. With NaCl maximum intercalation was obtained at 150°C, but as mentioned previously, it occurred to a very small extent. The replacement of DMSO by CsCl was almost complete at 100°C, but CsBr and CsI required temperatures of 250 and 200°C, respectively, for the complete reaction. Considerable amounts of KBr displace DMSO at 200°C. For KCl and KI, only trace amounts of the alkali halide replaced DMSO at 200°C and higher temperatures were required for an efficient exchange [49]. Basal spacings corresponding to optimal intercalation, are summarized in Table 1. The basal spacings observed in the work of Weiss *et al.* [14], mentioned earlier, are similar to our data and are also shown in Table 1. It may be concluded that similar intercalation complexes were obtained by both techniques, although the complexes of Weiss et al. were obtained from aqueous solutions, whereas our complexes were obtained in solid state thermal reactions [49].

After grinding the thermal treated discs (330°C), the XRD peaks which characterize intercalation became weak [53]. It was suggested that during grinding kaolinite was delaminated and became disordered. Water molecules from the atmosphere together with alkali and halide ions penetrated into the vacancies between the disordered layers. This assemblage is similar to that obtained by grinding kaolinite with CsF or CsCl (Fig. 1c) [53]. As is shown by IR spectroscopy two different groups of intercalation complexes are present [52, 53]. The thermally treated freshly prepared complexes are almost anhydrous, whereas the ground samples are gradually hydrated. The 001 spacings in the diffractograms of the ground disks should be considered to arise from the remaining anhydrous complex in the samples.

IR spectroscopy supplemented by curve fitting calculations, is established as a reliable tool for the characterization of intercalation complexes. In conventional IR absorption spectroscopy of clays, samples are pressed into disks with alkali halides as matrices. Possible reactions between the mineral and the salt during the preparation of the disk may affect the recorded spectra. We therefore employed photoacoustic and diffuse reflectance FT-IR spectroscopy for the reground mixtures in addition to the conventional technique. These techniques yield spectra of powders without the requirement that they be pressed into disks. The IR spectra showed that the alkali halide intercalation complexes are obtained together with water initially present in the disk in the first stages of the thermal treatment [52, 53]. At elevated temperatures most of the water was removed, and almost non-hydrous intercalation complexes of alkali halides were obtained. The spectra also showed that after two months storage in air and grinding the disks, the water bands increased substantially relative to all others. This suggests a rehydration of the intercalation complexes previously obtained at high temperatures. The IR spectra of the two groups of samples were used to characterize both almost anhydrous and hydrous varieties of these intercalation complexes. Representative spectra of freshly prepared and reground potassium halides-kaolinite intercalation complexes are shown in Fig. 2.

The positions of the stretching bands due to kaolinite hydroxyl groups and adsorbed H_2O in the spectra of potassium and caesium halide complexes (determined in part by curve fitting) are summarized in Table 2. In the curve fitting calculations Lorentzian shape bands were attributed to OH bands and Gaussian shape bands to water bands [43]. For comparison, data for untreated kaolinite are also included. Two of the bands in the spectra of the intercalation complexes were designated A′ and A″ and attributed to perturbed band A in the spectrum of untreated kaolinite.

Table 1 The 001 spacings of kaolinite-alkali halide intercalation complexes obtained from diffractograms of thermally treated disks [49] (a) and of complexes obtained from aqueous salt solutions in the presence of hydrazine or ammonium acetate as an entraining agent [14] (b)

Alkali halide	001 spacing (nm)	
	a	b
NaCl	1.00	1.01
KCl	1.05	1.01
RbCl	1.01	1.01
CsCl	1.05	1.03
NaBr	1.07	1.07
KBr	1.03	1.04
CsBr	1.09	1.08
KI	1.09	1.08
RbI	1.15	1.14
CsI	1.17	–

Table 2 Location of OH and H_2O stretching bands (in cm^{-1}) in the IR spectra of potassium and caesium halide-kaolinite intercalation complexes

Assignment	Symbol	Natural clay	Complexes											
			KCl		KBr		KI		CsCl		CsBr		CsI	
			a	b	a	b	a	b	a	b	a	b	a	b
Inner surface OH	A	3692	3694	3695	3693	3693	3694	3696	3692	–	3693	3694	3696	3697
Inner surface OH	Z	3686	–	3690	–	3679	–	3689	–	3672	–	3683	–	3690
Inner surface OH	B	3668	3668	3668	3668	3668	3669	3669	–	–	–	3663	–	3670
Inner surface OH	C	3653	3648	3648	3648	3648	3648	3648	–	–	–	3645	–	3646
Inner OH	D	3620	3618	3618	3620	3620	3621	3621	–	3616	3619	3618	3618	3618
Inner surface OH	A′	–	3605	3604	3597	3597	3591	3590	3600	3599	3592	3594	3591	3591
Inner OH	D′	–	3562	3588	–	–	–	–	3576	–	–	–	–	–
Inner surface OH	A″	–	3524	3523	3540	3551	3561	3561	3502		3541	3545	3552	3560
Intercalated water		–	351	3561	3605	3610	3606	3606	–	3582	–	3596	–	3600
Adsorbed water		–	–	–	3583	3582	3576	3576	–	–	–	3568	–	3576
Intercalated water		–	3502	3502	3554	3531	3549	3548	–	3508	–	3530	–	3545
Adsorbed water		–	3458	3454	3501	3501	3528	3528	–	3466	–	3500	–	3517

(a) Samples heated in alkali halide disks to 330°C (almost dehydrated); (b) Thermal treated disks ground in ambient atmosphere (rehydrated)

Band A appears in some of the spectra of the intercalated kaolinite, but is very weak; this peak arises from that fraction of the kaolinite which does not form an intercalation complex. The weakening of the original inner-surface hydroxyl stretching bands, and the concomitant appearance of new bands due to perturbed inner surface hydroxyls, prove that these groups form hydrogen bonds with intercalated species. Comparison between freshly prepared, almost dry samples and ground, hydrated samples, proves that the intercalated species that accept protons from inner-surface hydroxyls are water molecules and halide anions. Band A′ is weak in the spectra of the anhydrous samples but intense in the spectra of the hydrated samples. This band was attributed to surface hydroxyls bound to water. Band A″ is weak in the spectra of hydrated samples but intense in spectra of almost anhydrous complexes. This band was attributed to inner-surface hydroxyls bound to the halide anion. The fact that the location of band A′ and of the H_2O stretching bands depend on the alkali halide, indicates that the intercalated water molecule is bonded to both ions of the salt,

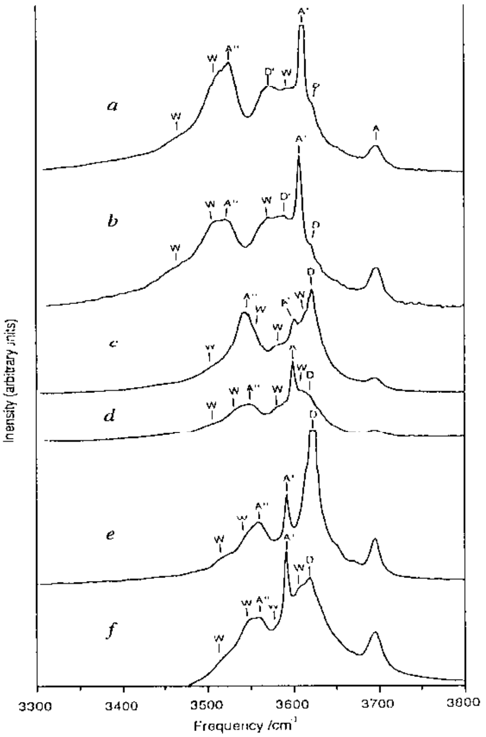

Fig. 2 Infrared spectra of thermally treated disks of DMSO kaolinite in a – KCl, heated at 330°C; b – KCl-kaolinite, after regrinding and rehydration; c – KBr disk heated at 330°C; d – KBr-kaolinite, after regrinding and rehydration; e – KI heated at 330°C; f – KI-kaolinite, after regrinding and rehydration

the alkali and the halogen. The cation is bound to the H_2O oxygen by electrostatic dipole-ion interaction whereas the anion is bound through a hydrogen bond in which the water molecule acts as the proton donor as follows M...O(H)–H...X where *M* is the alkali cation and *X* is the halide anion.

In the spectra of bromides and iodides the frequency of band D, which arises from inner hydroxyls, is very similar to that of untreated kaolinite [43, 52, 53]. However, in the spectra of the freshly prepared chlorides this band shifts to lower frequencies [46, 47, 52, 53]. The perturbed band is designated D′. Curve fitting shows that both bands D and D′ are present in the spectra. 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 hydration diminished. The perturbation of band D′ is due to the hydrogen-bonding between inner hydroxyls and chlorides which occurs after the chlorides penetrate the ditrigonal cavities. This penetration reverses in the presence of intercalated water. It should be mentioned here that band D′ was observed when the hydrous CsCl/kaolinite complex, which had been obtained by the wet grinding technique, was heated at 250°C [46, 47]. Table 2 shows that the perturbation of band A to band A″ (171 and 191 cm^{-1} in the spectra of KCl and CsCl complexes, respectively) is much higher than that of band D to band D′ (58 and 44 cm^{-1}, respectively). This is an indication that the hydrogen bonds between the chlorides and the inner-surface OH groups are much stronger than those between the chlorides and the inner OH groups. The penetration of Cl^- and its interaction with the inner OH group will be discussed in the last part of this review. It should be mentioned that the penetration of F^- results in a higher perturbation of band D to 3518 cm^{-1} (a perturbation of 102 cm^{-1}) [35].

Frequencies and assignments of IR absorption bands below 1200 cm^{-1} in spectra of freshly prepared intercalation complexes obtained by thermal treatment of disks, and the same samples after they had been reground and hydrated, are summarized in Table 3 together with the corresponding bands in the spectrum of untreated kaolinite. The Si–O stretching and deformation vibrations are modified in spectra of the intercalation complexes: they shift from their positions in the spectrum of untreated kaolinite, and their shapes are changed. These effects are a consequence of several factors, such as the cation, the anion, and the degree of intercalation and hydration. The data suggest that hydrogen bond formation between intercalated water molecules and atoms of the oxygen plane affects the perturbation. The shifts of the Si–O frequency with the halogens indicate that these bonds are weak in the presence of Cl^-, but are stronger with Br^- and still stronger with I^-. This is due to the strengths of the bonds formed between a water molecule and Cl, Br or I ions. The water molecules serve as proton donors in these bonds, the strength of which decreases with increasing atomic number of the halogen. Consequently the ability of the water molecule to donate its second proton to an oxygen atom of the silicate layer increases in the sequence opposite to its tendency to donate a proton to the halogen.

The two AlO–H deformation bands (H and I) and the Al–O deformation band (*M*) are also perturbed in the complexes with respect to their frequencies in the spectrum of the original kaolinite. Bands H and *M* shift to higher frequencies and their locations depend on the halogen, whereas band I shifts to lower frequencies.

Table 3 Location of Si–O stretching and deformation bands, AlO–H deformation and Al–O deformation bands (in cm^{-1}) in the IR spectra of potassium and caesium halide-kaolinite intercalation complexes

Assignment	Symbol	Natural clay	Complexes											
			KCl		KBr		KI		CsCl		CsBr		CsI	
			a	b	a	b	a	b	a	b	a	b	a	b
Si–O stretching	E	1117	1107	1108	1108	1108	1109	1109	1117	1111	1112	1113	1113	1113
Si–O stretching	P	1099	–	–	–	–	–	–	–	–	–	–	–	–
Si–O stretching	F	1040	1026	1025	1023	1021	1019	1018	1032	1030	1023	1021	1019	1020
Si–O stretching	G	1013	1002	1002	999	999	997	996	1005	1009	1002	1004	995	1000
AlO–H deformation	H	939	987	–	970	969	956	956	987	–	968	977	959	963
AlO–H deformation	I	918	905	903	905	905	905	905	903	903	903	905	902	905
	J	–	793	793	787	789	790	788	780	779	–	–	–	–
	K	756	757	757	759	760	761	761	759	760	759	759	759	760
	L	694	693	692	707	707	702	702	590	690	707	703	705	698
		–	–	651	674	674	672	670	–	–	–	673	–	–
Al–O deformation	M	552	565	563	560	560	558	557	570	565	–	559	–	556
		–	–	515	–	513	511	510	–	510	–	510	–	510
Si–O deformation	N	476	475	475	475	475	473	472	474	471	–	469	–	468
Si–O deformation	O	434	435	435	436	436	436	435	443	440	–	439	–	440

(a) Samples heated in alkali halide disks to 330°C (almost dehydrated);
(b) Thermal treated disks ground in ambient atmosphere (rehydrated).

The 50–1000 cm^{-1} region of the Raman spectra of five alkali halide–water–kaolinite intercalation complexes was studied and compared with both the Raman spectrum of a reference kaolinite and far-IR spectra of the complexes [54, 55]. Most of the 26 Raman bands observed for the complexes can be correlated with Raman and IR frequencies of uncomplexed kaolinite, permitting assignments based on previously published data. New Raman bands detected in the spectra of the chloride complexes probably arise from the keying of this ion through the ditrigonal hole into the TO layer.

In general, band A′ (Table 2) shows that weak H-bonds are obtained between inner-surface OH groups and I^-, stronger bonds occur with Br^- and the strongest are obtained with Cl^-. This sequence agrees with the fact that basic strength of the halide ion increases with decreasing atomic number. As one would expect, the acid behaviour of the water molecules coordinated to the anions (second proton donation ability to the siloxanes) follows the opposite order. From the locations of bands F, G and N (Table 3) it is obvious that strong Si–O...H–OH hydrogen bonds are obtained with I^-, weaker bonds are obtained with Br^- and the weakest are obtained with Cl^-. Surprisingly, the basic behaviour of the water molecules coordinated to the anions (proton accepting ability from inner-surface hydroxyls) is in the opposite sequence. From the location of band A′ (Table 2) it is obvious that strong $OH...OH_2$ hydrogen bonds are obtained with hydrated I^-, weaker bonds result with hydrated Br^- and the weakest are obtained with hydrated Cl^-. This behaviour is probably associated with steric interference upon the free movement and rotation of the intercalated water molecule, which is simultaneously involved in four bonds. Table 1 shows that the swelling of the kaolinite is the highest with iodide salts and decreases with decreasing size of the halide. In I^- intercalates, the water molecule is free to take the best location for accepting a proton from the inner-surface OH group. In bromide intercalates this ability decreases and it further decreases in chloride intercalates.

The inductive effect of the alkali cation on the basic and acidic properties of the water molecules is also noteworthy. K^+ is a stronger acid than Cs^+. Consequently water coordinated to K^+ is a stronger acid than water coordinated to Cs^+, and Si–O groups in potassium salts are more perturbed than in caesium salts (Table 3). Similarly, water coordinated to K^+ is a weaker base than water coordinated to Cs^+, and OH groups in potassium salts (band A′) are less perturbed than in caesium salts (Table 2).

The involvement of the oxygen plane in complex formation may occur through the interaction of partially negatively charged oxygens with the positively charged cations, but it could also be due to the keying of the different ions in the ditrigonal holes. There is no problem accepting the slight keying of K^+ and Cs^+, which are positively charged and have a diameter similar to that of the ditrigonal hole (0.276 and 0.334 nm, respectively). The classical model of fixation of ions by clay minerals [56] cannot be used to explain the penetration of chloride into the ditrigonal cavity for two reasons: (1) electrostatic repulsion occurs between negatively charged chlorides and the negatively charged oxygens; and (2) the ditrigonal hole which has approximately the diameter of the oxygen is too small to enable the penetration of an atom with a non-bonded van der Waals radius larger than that of oxygen (~0.3 nm) [57]. In the classical picture, atoms are considered as dense spheres. This approach is incorrect for the situation under discussion, because of the positive field that is induced by the inner hydroxyls. The IR spectra show that these groups are involved in

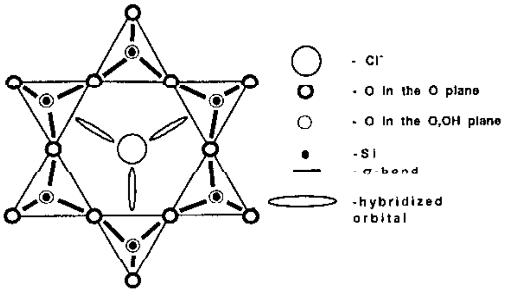

Fig. 3 Keying of chloride ion in ditrigonal cavity. Sizes of atoms and orbitals are arbitrary. The plane of the edges of the three represented hybridized orbitals is not parallel to the plane of the page; the fourth orbital is perpendicular to the plane of the other three and is not shown in the figure

hydrogen bonds with the chlorides, which requires that hybridization of the latter takes place (hydrogen bonds are formed by partial electron pair donation from the chloride to the proton, and this can occur only from hybridized orbitals). Consequently the negative charge density around the anion has directional character, namely that of the hybridized orbitals. It can be assumed that the hybridization of the chloride is sp^3. The three hybridized orbitals not involved in the hydrogen bond with an inner-surface hydroxyl would then be directed towards three of the six silicon nuclei, which are the centres of the six tetrahedra that form the ditrigonal cavity. The electrons of the valence shells of the silicons and oxygens of these tetrahedra are located mainly in the σ (and to some extent also in the π) bonding orbitals between the nuclei of these atoms. Consequently, the directions between the centre of the cavity and the silicons can be considered as voids, because of their low electron densities (Fig. 3).

Inner electron shells are not involved in the hybridization and should always be taken as spherical. The number of inner shells for both bromides and iodides is higher than the total number of shells for oxygen. Consequently, these ions can penetrate only slightly into the ditrigonal cavity and cannot form hydrogen bonds with inner hydroxyls.

The diameters of Cl^-, Br^- and I^- anions are 0.36, 0.39 and 0.44 nm, respectively. Spacings of 1.08, 1.11 and 1.16 nm allow these anions to be located in the interlayer without keying. According to Table 1 smaller basal spacings are obtained with all Na and K salts, which may indicate some keying of the anions. In chloride salts the anion penetrates the ditrigonal cavity and reaches the inner OH groups. The basal spacing should be determined by the alkali cation and the water which are present in the interlayer space.

No keying of I^- was observed in the case of CsI; keying was very slight with RbI or CsBr (RbBr was not studied), but considerable with KBr and KI. Cs^+ and I^- are, respectively, a soft acid and a soft base [57]. We assume that the strong interaction between the soft acid and the soft base in the CsI system prevents the penetration of this anion into the ditrigonal hole. K^+, and to some extent also Rb^+, are harder acids and their interaction with I^- is weaker. Consequently, a very small keying of I^- from RbI and a more considerable keying from KI are observed. The small keying of Br in CsBr should also be associated with the hardening of bromide in comparison with iodide.

The indirect intercalation of CsI is remarkable. This complex was not formed by air or wet grinding, in contrast to the other caesium salts. We previously suggested two possible reasons for this observation: (1) I^- is too large and cannot penetrate the interlayer space of kaolinite, and (2) hydrogen bonds between inner surface hydroxyls and sorbed water molecules or intercalated anions, essential for intercalation, are very weak with I^- [43]. The assumption that I^- is too large and cannot intercalate kaolinite is disproven by indirect intercalation. Therefore, the primary reason for the inertness of CsI during mechanochemical treatment must be the weak hydrogen bonds formed between intercalated I^- and inner-surface hydroxyls, and between the anion and intercalated water; this is consistent with the frequencies of band A″ and the HOH bands, respectively. The inertness of CsI in the mechanochemical treatment can be attributed to the strong interaction between the soft acid (Cs^+) and the soft base (I^-). Similar nonreactivity was observed during a mechanochemical study of caesium and sodium halides [58].

In conclusion, three types of intercalation complexes of alkali halides were identified. The first is a hydrated variety (Fig. 4a), in which hydrated alkali and halide ions are located between disordered kaolinite TO layers (card house structure. See also Fig. 1c). The water molecule forms two hydrogen bonds by donating protons, to the halide ion and to the surface oxygen of the siloxane group of the kaolinite layer. A third hydrogen bond involving the water molecule is obtained when it accepts a proton from an inner-surface hydroxyl of the kaolinite layer. An ion-dipole electrostatic interaction occurs between the alkali halide and the water molecule. The sec-

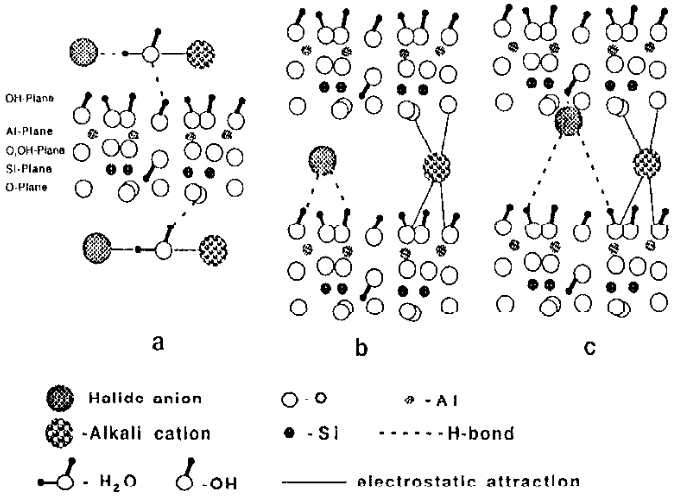

Fig. 4 Schematic representation of the fine structures of three types of alkali-halide kaolinite intercalation complex and the bonding between the active groups on the kaolinite layers and the intercalated species. a – hydrated, with halide anions, alkali cations and water molecules located between disordered layers of kaolinite; b – anhydrous, with halide anions and alkali cations located between layers of kaolinite; and c – anhydrous, the halide anions penetrating the ditrigonal cavity of the oxygen plane

nd type of intercalation complex is anhydrous (Fig. 4b). The halide ion forms hydrogen bonds by accepting protons from the inner surface hydroxyls. The alkali cat- on electrostatically interacts with the partially negatively charged oxygens of the in- er-surface OH-plane and the O-plane. The third type of intercalation complex is pecific for the small anions F^- and Cl^- (Fig. 4c). These anions penetrate through the itrigonal holes of the O-plane to form H-bonds with the inner hydroxyls of the O, H-plane of the kaolinite layer.

References

1 K. Wada, Amer. Mineral., 46 (1961) 78.
2 A. Weiss, Angew. Chem., 73 (1961) 736.
3 A. Weiss, W. Thielepape, G. Goering, W. Ritter and H. Schaefer, Proc. Intern. Clay Conf., Stockholm, 1 (1963) 287.
4 R. M. Carr and H. Chih, Clay Miner., 9 (1971) 153.
5 B. K. G. Theng, The chemistry of clay-organic reacions, Adam Hilger, London 1974, pp. 239–274.
6 R. L. Ledoux and J. L. White, Science, 143 (1964) 244.
7 R. L. Ledoux and J. L. White, Proc. Intern. Clay Conf., Jerusalem, 1 (1966) 361.
8 R. L. Ledoux and J. L. White, J. Colloid Interface Sci., 21 (1966) 127.
9 M. Cruz, A. Laycok and J. L. White, Proc. Intern. Clay Conf., Tokyo, 1 (1969) 775.
10 S. Olejnik, A. M. Posner and J. P. Quirk, Spectrochim. Acta, 27A (1971) 2005.
11 S. Olejnik, A. M. Posner and J. P. Quirk, Clays Clay Miner., 19 (1971) 83.
12 S. Olejnik, A. M. Posner and J. P. Quirk, J. Colloid Interface Sci., 37 (1971) 536.
13 A. Weiss, W. Thielepape, W. Ritter, H. Schaefer and G. Goering, Z. anorg. allgem. Chem., 320 (1963) 183.
14 A. Weiss, W. Thielepape, W. Ritter and H. Schaefer, Proc. Intern. Clay Conf., Jerusalem, 1 (1966) 277.
15 J. M. Adams, P. I. Reid, J. M. Thomas and M. J. Walters, Clays Clay Miner., 24 (1976) 267.
16 S. Olejnik, A. M. Posner and J. P. Quirk, Clay Miner., 8 (1970) 421.
17 S. Olejnik, L. A. G. Aylmore, A. M. Posner and J. P. Quirk, J. Phys. Chem., 72 (1968) 241.
18 M. S. Camazano and S. G. Garcia, An. Edafol. Agrobiol., 25 (1966) 9.
19 J. G. Thompson and C. Cuff, Clays Clay Miner., 33 (1985) 490.
20 M. Raupach, P. F. Barron and J. G. Thompson, Clays Clay Miner., 35 (1987) 208.
21 C. Breen and S. Lynch, Clays Clay Miner., 35 (1988) 19.
22 A. Mata-Arjona, A. Ruiz-Amil and E. Martin Inaraja, Reunion Hispano-Belga Miner. Arcilla, Madrid 1970, p. 115.
23 P. M. Costanzo and R. F. Giese, Jr., Clays Clay Miner., 34 (1986) 105.
24 P. Sidheswaran, S. V. Ram Mohan, P. Ganguli and A. N. Bhat, Indian J. Chem., 26A (1987) 994.
25 P. Sidheswaran, A. N. Bhat and P. Ganguli, Clays Clay Miner., 38 (1990) 29.
26 H. Seto, M. I. Cruz and J. Fripiat, Amer. Mineral., 63 (1978) 572.
27 K. J. Range, A. Range and A. Weiss, Proc. Intern. Clay Conf., Tokyo, 1 (1969) 3.
28 O. Anton and P. G. Rouxhet, Clays Clay Miner., 25 (1977) 259.
29 J. Kristóf, M. Tóth, M. Gábor, P. Szabó and R. L. Frost, J. Thermal Anal., 49 (1997) 1441.
30 P. M. Costanzo, R. F. Giese, Jr. and M. Lipiscas, Clays Clay Miner., 32 (1984) 419.
31 M. Lipiscas, C. Straley, P. M. Constanzo and R. F. Giese, Jr., J. Colloid Interface Sci., 107 (1985) 221.
32 R. F. Giese, Jr. and P. M. Costanzo, 'Geochemical processes at mineral surfaces', Am. Chem. Soc. Symposium Series, 323 (1986) 37.

33 P. M. Costanzo and R. F. Giese, Jr., Clays Clay Miner., 33 (1985) 415; 38 (1990) 160.
34 I. Lapides, S. Yariv and N. Lahav, Clay Miner., 30 (1995) 287.
35 I. Lapides, S. Yariv, N. Lahav and I. Brodsky, Colloid Polym. Sci., 276 (1998) 601.
36 S. Yariv and S. Shoval, Clays Clay Miner., 23 (1975) 473.
37 R. Wolfe and R. F. Giese, Jr., Clays Clay Miner., 26 (1978) 76.
38 S. Yariv, Powder Technol., 12 (1975) 131.
39 S. Yariv, Clays Clay Miner., 23 (1975) 80.
40 S. Yariv, J. Chem. Soc. Faraday Trans. I, 71 (1975) 674.
41 S. Yariv and S. Shoval, Clays Clay Miner., 24 (1976) 253.
42 S. Yariv, Intern. J. Trop. Agric., 4 (1986) 310.
43 K. H. Michaelian, S. Yariv and A. Nasser, Can. J. Chem., 69 (1991) 749; K. H. Michaelian, W. I. Friesen, S. Yariv and A. Nasser, Can. J. Chem., 69 (1991) 1786.
44 S. Yariv, A. Nasser, Y. Deutsch and K. H. Michaelian, J. Thermal Anal., 37 (1991) 1373.
45 S. Yariv, E. Mendelovici and R. Villalba, in B. Miller, (Ed.) Proc. Seventh Intern. Conf. Thermal Anal., Kingston, Canada, John Wiley, Chichester 1982, Vol 1, p. 533.
46 S. Yariv, A. Nasser, K. H. Michaelian, Y. Deutsch and N. Lahav, Thermochim. Acta, 234 (1994) 275.
47 I. Lapides, S. Yariv and N. Lahav, Intern. J. Mechanochem. Mechanical Alloying, 1 (1994) 79.
48 C. T. Johnston, S. F. Agnew and D. L. Bish, Clays Clay Miner., 38 (1990) 573; C. T. Johnston, J. Helsen, R. Schoonheydt, D. L. Bish and S. F. Agnew, Amer. Miner. 83 (1998) 75.
49 I. Lapides, N. Lahav, K. H. Michaelian and S. Yariv, J. Thermal Anal., 49 (1997) 1423.
50 C. Breen and S. Lynch, Clays Clay Miner., 36 (1988) 19.
51 J. M. Adams and G. Waltl, Clays Clay Miner., 28 (1980) 130.
52 K. H. Michaelian, I. Lapides, N. Lahav, S. Yariv and I. Brodsky, J. Colloid Interface Sci., 204 (1998) 389.
53 S. Yariv, I. Lapides, A. Nasser, N. Lahav, S. Yariv, I. Brodsky and K. H. Michaelian, Clays Clay Miner., submitted for publication.
54 K. H. Michaelian, K. L. Akers, S. L. Zhang, S. Yariv and I. Lapides, Microchim. Acta, 14 (1997) 211.
55 K. H. Michaelian, S. L. Zhang, S. Yariv and I. Lapides, Appl. Clay Sci., 13 (1998) 233.
56 B. L. Sawhney, Clays Clay Miner., 20 (1972) 93.
57 J. E. Huheey, E. A. Keiter and R. L. Keiter, Inorganic Chemistry, 4th ed., Harper Collins College Publishers, New York 1993, pp. 344–355.
58 S. Yariv and S. Shoval, Appl. Spectrosc., 39 (1985) 599.