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Thermo–IR–spectroscopy analysis of the interactions between organic pollutants and clay minerals[1]

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Abstract

A short description of thermo–IR–spectroscopy analysis is given together with some examples of the interactions between hazardous organic pollutants and clay minerals. Self-supported films of organo–montmorillonite and laponite complexes can be heated in a vacuum cell and the IR spectra of the samples recorded at different temperatures. Organo complexes of other clay minerals can be heated as alkali-halide disks. In this case the effect of the alkali halides on the stability of the organo–clays and on thermal reactions should be taken into consideration. This method is useful for determination of the fine structures of organo–clay complexes. It can be applied to obtain information on the adsorption mechanism of organic pollutants by clay minerals and on the types of bond which are obtained between adsorbed hazardous species and functional sites on the clay surfaces.

Keywords: Adsorption mechanism; Clay minerals; Organic pollutants; Organo–clay complexes; Thermo–IR–spectroscopy

1. Introduction

Information on the adsorption of hazardous organic pollutants by clay minerals is essential for forecasting the migration of these molecules through soils and sediments and in running water. The organic molecules migrate in the direction of ground water together with irrigation, drainage, or rain water. Their migration can be slowed down as a consequence of their adsorption by different components of soils and sediments

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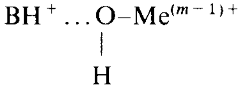
[1,2]. The adsorption of organics by clay minerals affects the mechanical properties of soils and sediments and their morphology [3–5]. This is due to the effect of adsorption on the colloid dispersibility and surface properties of minerals and on their flocculation or peptization states. Consequently, it plays a major role in the sedimentation and erosion processes which occur in sedimentary systems. Adsorption may change the activation energy of the decomposition of the hazardous organics and thus their lifetime is changed. As a result, it plays a major role in the geochemical diagenesis of the buried organic matter [6–10]. Hazardous materials can also be removed from the environment, e.g., from ground water or from the atmosphere, etc., by adsorption on a substrate which can be buried in any isolated place. The substrate should be cheap with adsorption properties which are specific towards a certain material. Clay minerals are cheap adsorbing materials with high surface areas and specific basic and acidic properties which depend on the composition of the mineral [8, 11–13]. It is, therefore, supposed that they can be used for this purpose.

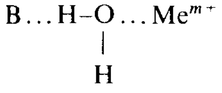
This information is also important in solving many industrial problems. Clay minerals are used as fillers in different products [14]. For example, kaolinite is used in the paper industry where interactions take place between the clay and the cellulose giving stability to the organic web. Smectites and sepiolite are used as fillers for pesticides and herbicides. Smectites are added to dye and paint suspensions and often the use of these additives leads to changes in the colors of the dyes due to π interactions between the aromatic compounds and the oxygen plane of the clay [15]. Several clays are common fillers in the cosmetic industry, where interaction between the clay and hydrophobic molecules is expected. Synthetic clays are added to laundry powders as fillers and for water softening. There are many other industrial products in which clays occur together with organic matter, such as in the pharmaceutical, plastics, rubber, and agricultural industries, etc.

During the last sixty years much study of the interactions between clays and organic matter was carried out with the purpose of determining the structures and stability of the organo–clay complexes and the types of bond between the clay component and the adsorbed organic species [16–18]. The clay surface and its interlayer space are populated by Brönsted and Lewis acidic and basic sites [12,19,20]. The principal interactions between the clay and the adsorbed organic species are of the acid–base type [21–33]. In the interlayer space of smectites and vermiculites adsorbed water molecules which are coordinated to exchangeable metallic cations (Me^{m+}), serve as proton donors (Brönsted acid) [21–23]. Depending on the polarizing power of the metal and the basic strength of the adsorbed organic species (B), the organic base may be protonated by accepting a proton from a water molecule, thus gaining a positive charge (association I), or it may form a hydrogen bond with the polar water molecule (association II).



$$\mathrm{BH^+\ldots\underset{\underset{\displaystyle H}{|}}{O}{-}Me^{(m-1)+}}$$

(I)



$$\mathrm{B\ldots H{-}\underset{\underset{\displaystyle H}{|}}{O}\ldots Me^{m+}}$$

(II)

In many clay systems both associations are obtained simultaneously.

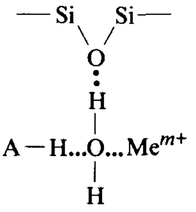
After thermal dehydration, the exchangeable cations may serve as Lewis acids and adsorbed bases become coordinated directly to the cations (III). Alkali metal cations do not form stable hydrates and in several cases direct coordination with B is obtained at room temperature. The bond between the alkali metal cation and B is mainly electrostatic, ion–dipole attraction. With certain exchangeable transition metal cations and certain ligands direct coordination of B to Me^{m+} is obtained at room temperature [27–30]. In this case the bond between the transition metal and B is semipolar with a high contribution of covalency. Here B donates an electron pair to the metallic cation.

$B\ldots Me^{m+}$

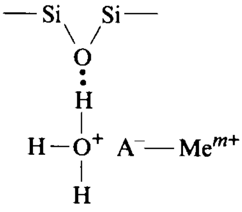
(III)

In many clay systems associations II and III are obtained simultaneously.

In the interlayer space of smectites with tetrahedral substitutions, and of vermiculites, adsorbed water molecules which form hydrogen bonds with the oxygen plane (Si–O–Si) may serve as proton acceptors and form hydrogen bonds with adsorbed organic proton donors (A–H, IV) [28]. If the coordination of the anionic part of A–H to Me^{m+} has a considerable contribution of covalency, an anionic species A^- is obtained in the interlayer space as a result of deprotonation of the acid (V). Anionic species were detected mainly in the presence of polyvalent exchangeable cations [26].



(IV)



(V)

Many papers have been published on the IR spectra of organo–clays and on the study of the mechanism of adsorption of organic compounds by IR spectroscopy. Only part of these publications deal with thermal effects on the IR spectra. IR spectroscopy enables the identification of bonds which are formed between functional organic groups and active sites on the clay surfaces. Bond formation and its strength can be estimated from the perturbation of characteristic IR absorption bands of the active organic groups. No attempt will be made here to consider the details of IR spectroscopic analysis of organo–clays, nor to review the vast literature which covers this subject.

Thermo–IR–spectroscopy is used to determine the fine structure of organo–clay complexes. In thermo–IR–spectroscopy the IR spectrum of the sample is recorded against the temperature, while the temperature of the sample, in a specified atmosphere, is programmed [34]. The sample, either as a disk or as a film, is heated at different temperatures and after a certain heating period the spectroscopic properties are examined. This review article will briefly describe the effect of temperature on IR spectra of several samples which represent the principal functional groups in hazardous pollutants and will demonstrate how from changes in the spectra the fine structure of the organo–clay can be established. Some examples of hazardous pollutant–clay complexes which have been studied in our laboratory will be discussed here, in order to clarify what can be achieved from this method and also to clarify some of the technical requirements which must be fulfilled in order to obtain reliable results. The following requirements will be treated: (i) the saturation of the clay with considerable amounts of organic matter in order to obtain reliable IR spectra, (ii) the preparation of the sample for the thermo–IR–spectroscopy study, and (iii) the protection of the thermally treated sample from any effect of cooling, so that the recorded spectrum will represent the effects of the thermal treatment.

This method was used to study the thermal desorption of adsorbed organic compounds from montmorillonite and oxidation of adsorbed compounds [35–37]. It was widely used in the study of dehydration of clays (see, e.g., [38, 39]) and of pillared clays [40], and in the study of other thermal reactions of clay minerals (e.g., thermal proton migration [41, 42]). Thermo–IR–spectroscopy is also useful in the study of thermal reactions of organic and inorganic materials on clay surfaces, such as polymerization of acrylonitrile on hectorite [43], formation of monosaccharides with five or six carbons from glyceraldehyde on Na–montmorillonite [44], decomposition of alkylammonium on montmorillonite [45] or on vermiculite [46] and the decomposition of cobalt complexes on montmorillonite [47, 48]). Thermo–IR–spectroscopy was applied in the synthesis of organic derivatives of attapulgite [49] and of intercalation complexes of kaolinite [50]. It was used to identify substitution of iron for aluminum in kaolinites [51].

To obtain reliable IR spectra of organo–clays, the amount of adsorbed organic matter should be high, so that the characteristic absorption bands of the functional organic groups will be seen in the presence of the bands of the clay minerals. This method is, therefore, very reliable for complexes of expanding clays such as smectites and vermiculites with high surface areas and high adsorption capacities, but not for complexes of kaolin–serpentine or talc–pyrophyllite minerals which have very low adsorption capacities. The adsorption of the organic molecules should be carried out from the gaseous or liquid state, and of solids, from solvents which give high adsorption. Adsorption of molecules with a low polarity should be carried out from organic solvents.

2. Preparation of clay samples for infrared spectroscopy

IR absorption spectra of clay minerals are usually obtained from (1) self-supporting films, (2) films sedimented on IR-transparent windows, (3) alkali-halide disks (e.g. KBr), or (4) from oil mulls (the most common mulling agent is Nujol—paraffin oil) [52, 53]. Modification of the spectra of some organo–clays may occur in alkali halide disks or Nujol because they may react either with the clay (e.g. cation exchange with the alkali halides [54], intercalation of the alkali halides [55], grinding [56, 57] or pressure [58] effects) or with the organic matter (e.g. extracting the organic matter from the clay by Nujol, replacing of adsorbed organic matter by alkali halide).

In many of our studies the disks were prepared in the presence of excess organic matter which was evolved during the thermal treatment. Self-supporting films of montmorillonite, hectorite, or laponite can be prepared by drying 1–2 ml of dilute clay suspensions (1–2%) on a piece of smooth plastic (polyethylene or Mylar). These films can be peeled from the piece of plastic. They are stable and can be immersed in organic liquids for the preparation of self-supporting films of organo–clays. They are thermally stable and are used for thermo–IR–spectroscopy analysis of organo–clays in a heated vacuum cell. Organo–clays of other minerals can be sedimented on infrared-transparent windows, such as AgCl, ZnS (irtran), or Si. The clay, as a film or a sediment, has a preferred orientation. With a polarized IR beam it is possible to observe the orientation of the organic molecule in the interlayer space of smectite or vermiculite.

3. Thermal treatment of organo–clay complexes

3.1. *Heating of organo-clays in alkali-halide disks*

The disks can be heated up to 450°C. At higher temperatures alkali halides partly sublime and the disks may disintegrate. During the thermal treatment water and organic molecules are evolved. Consequently, the disks become opaque and must be carefully re-pressed (without re-grinding) with care taken not to damage them in the process. Clay samples cannot be heated as powder because, if they are heated below 300–500°C they readsorb water as soon as they are taken out of the oven. As well, the desorption of the weakly adsorbed organic matter is faster in powder than in disks. The disk protects the organo–clay from atmospheric humidity and from ligand exchange which may occur between the adsorbed organic molecules and atmospheric water. The thermal reactions are slower in the disks than in powder. This must be considered when the heating time is monitored. The alkali halide may take part in the thermal reactions [59] and it is sometimes necessary to study the effects of the alkali halides on the thermal reactions of the organo–clays.

3.2. *Vacuum cell for heating clay films*

A vacuum heating cell for heating clay films is shown schematically in Fig. 1. This cell, used in our laboratory, was constructed for measuring IR absorption spectra. Usually the spectrum of the film is first recorded in air and then under vacuum at room temperature and at 50, 100, 150 and 200°C, after heating the sample for half an hour at each temperature. The spectrum is recorded again after cooling the sample in the vacuum cell to room temperature and after equilibrating it in air for 24 h. A cell and optical configuration for measuring diffuse reflectance FTIR spectra of adsorbed species, which may be heated to 600°C and evacuated to 10^{-6} Torr, has been described [60]. Recently a vacuum system connected to an FTIR spectrophotometer was described [61] for the study of the interactions between organic and inorganic pollutants in the clay interlayer. By adapting a suitable heater, this sytem can be adjusted for thermo–IR–spectroscopy.

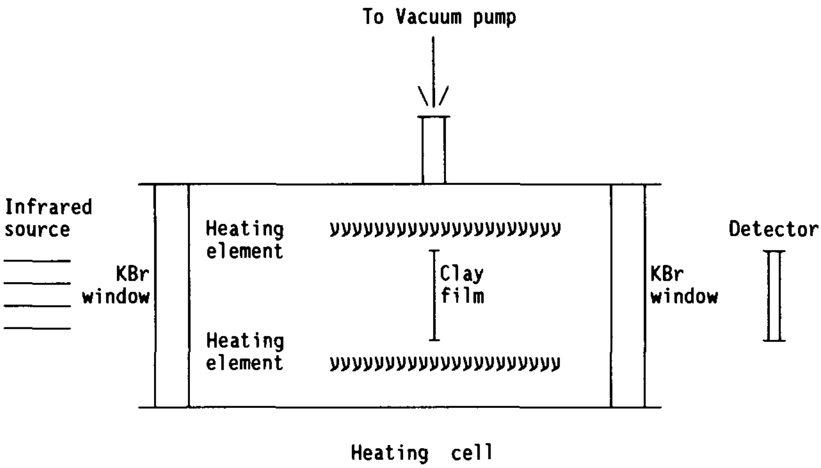
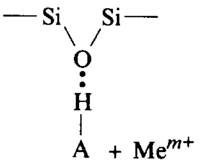


Fig. 1. A schematic presentation of a vacuum heating cell for heating a clay film (consists of a stainless steel tube, two KBr windows, heating element, and a sample holder).

The thermal reactions of organo–clays below 200°C are mainly water loss and other reactions which are associated with the dehydration of the clay. Polymerization and carbonization of the organic matter also occur to some extent. Important examples are the dehydration of exchangeable metallic cations and the thermal hydrolysis of hydrated polyvalent cations. In the presence of adsorbed organic bases, ligand exchange between the water molecules of association II and molecules of the organic base takes place, leading to a direct linkage between the organic molecule and the metallic cation (association III) as follows [26]:

$$Me^{m+}\ldots OH_2 + B \rightarrow Me^{m+}\ldots B + H_2O$$

In the presence of an adsorbed organic acid (association IV), after the thermal evolution of water, a direct linkage between the organic molecule and the oxygen plane can be obtained (association VI) [30, 31]:



(VI)

4. Adsorption of benzoic acid onto montmorillonite

Benzoic acid is effective in inhibiting the growth of microorganisms and is added to foods, fats, and fatty oils as a preservative. It is an important chemical in the food industry and in the manufacture of dyes, pharmaceuticals, synthetic perfumes, plasticizers, synthetic resins, and coatings and mordants.

IR spectra of a Ca–montmorillonite film saturated with benzoic acid, recorded at different temperatures, are shown in Fig. 2 [26]. The thermo–IR–spectroscopy analysis was carried out in a vacuum heating cell. The COOH stretching band, which is located at 1690 cm^{-1} in the spectrum of a solid benzoic acid in a KBr disk, is shifted to 1684 cm^{-1} in the spectrum of benzoic acid in Ca–montmorillonite, at room temperature. The coupled C=O stretching and O–H in-plane bending vibrations, which lie at 1425 and 1294 cm^{-1} in the spectrum of the solid acid, shift to 1415 and 1275 cm^{-1} in

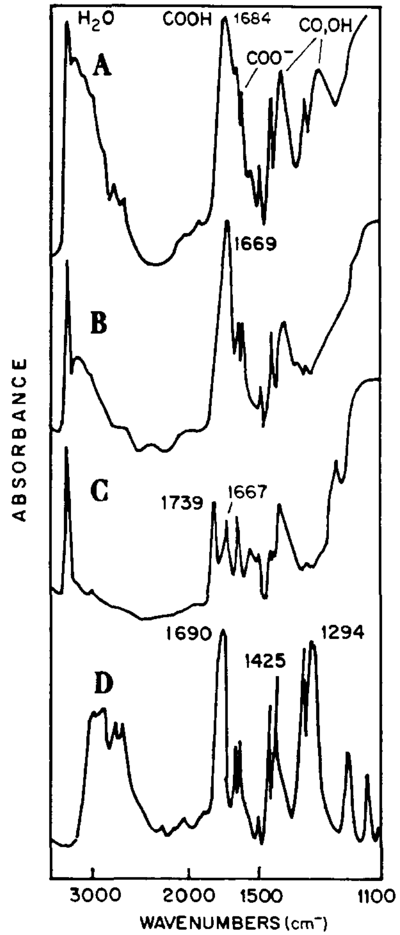


Fig. 2. Thermo–IR–spectroscopy analysis of Ca–montmorillonite–benzoic acid complex: (a) IR spectrum of a film, recorded in air; (b) IR spectrum of the same film, recorded after heating in a heating cell under vacuum at 70°C; (c) after heating in vacuum at 150°C; (d) IR spectrum of crystalline benzoic acid in a KBr disk (after [26]).

the adsorbed acid. The shifts of these three bands to lower frequencies as a result of adsorption is an indication of an increase in the strength of the hydrogen bonds in which this functional group is involved. In the solid state the acid forms dimers with hydrogen bonds between two COOH groups. In the adsorbed state at room temperature hydrogen bonds occur between the C=O groups (proton acceptors) and water molecules (proton donors). A water bridge exists between the C=O group and the metallic cation (association II in the Introduction).

The broad HOH stretching and bending absorption bands, located at ≈ 3500 and 1630 cm^{-1}, respectively, in the spectrum of Ca-montmorillonite saturated with benzoic acid, recorded before the thermal treatment (Fig. 2A), decreased at 70°C and were not observed in the spectrum recorded after the thermal treatment at 150°C (Figs. 2B and 2C, respectively). This is an indication of the evolution of the interlayer water during the thermal treatment. The figure also shows that the evolution of water is associated with drastic changes in the location of the COOH vibrations.

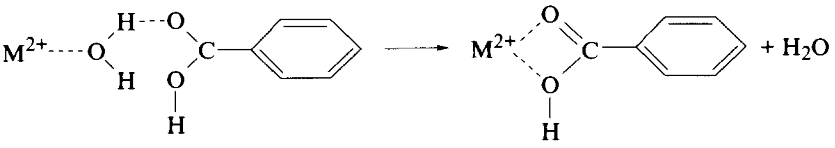
The spectra of benzoic acid in Ca-montmorillonite recorded in different stages of the thermal analysis are largely typical of those of samples containing other exchangeable cations. The dependence of the COOH stretching frequency on the cation and on the hydration state is shown in Table 1. In the anhydrous complexes, studied under vacuum at 50-100°C, there is a continuous decrease in the COOH frequency in the series Na, Li, NH_4, Ca, Mg, Cu, Al, corresponding to increased perturbation of the C=O vibration by the cation. In air at room temperature, benzoic acid associated with Ca, Mg, Cu, or Al gives a frequency which is independent of the cation and higher than those given in the vacuum conditions. The COOH frequency of benzoic acid, associated with the monovalent ions, is unaffected by the hydration state. From these observations it was concluded that the acid can enter the interlayer space as a neutral polar molecule, forming hydrogen bonds with water molecules which are directly coordinated to the more polar cations, displacing water from the outer spheres of the coordination. The difference between the hydrated and the anhydrous state for

Table 1
Carbonyl frequencies (in cm^{-1}) of intercalated benzoic acid in montmorillonite saturated with various cations obtained during thermo-IR-spectroscopy analysis (after [26])

	Exchangeable cation							
	Na	K	Li	NH_4	Ca	Mg	Cu	Al
Air	1706	1706 1689	1695	1689	1684	1684	1684	1684
Vacuum; 50-100°C	1706	1706	1695 1724 w[a]	1689	1669	1664	1639	1625
Vacuum; 150°C	vw[a]	vw	vw	lost	1739 1667	1740 w 1712 1661	1650	1660- 1620

[a] w—weak, vw—very weak.

polyvalent cations could be accounted for by the following dehydration reaction:



The anhydrous variety is equivalent to association III in the Introduction.

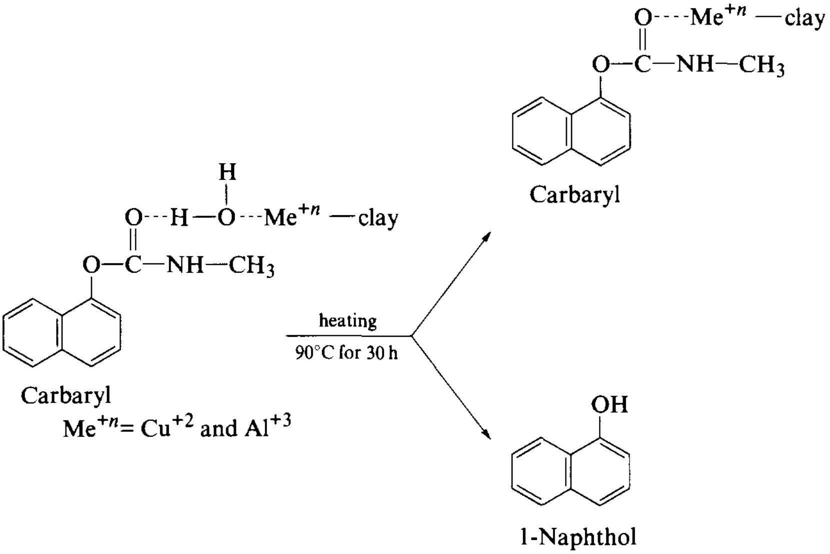
Benzoic acid was lost from NH_4–montmorillonite and little remained in Na–montmorillonite in vacuum at 100°C. More benzoic acid was retained by the more polar cations. Benzoic acid associated with the divalent cations underwent further reaction between 100 and 150°C with the loss of all or nearly all hydroxyl absorption, the appearance of one or more higher frequency carbonyl bands between 1650 and 1740 cm^{-1}, and of one or two sharp bands near 1230 cm^{-1} indicating the formation of benzoic acid anhydride. The crystalline anhydride has a strong band at 1214 cm^{-1} and carbonyl frequencies at 1770 and 1706 cm^{-1}. The low shift of the upper carbonyl frequency shows that the anhydride is coordinated to the cations through its carbonyl groups and the increasing displacement of this band in the series Ca, Mg, and Cu is consistent with their polarizing power. Vacuum conditions were necessary for the formation of significant amounts of anhydride, as little or none was formed at 200°C in air.

An absorption band of benzoate ion near 1550 cm^{-1} was present in the spectra of the benzoic acid complexes of polyvalent cations but of the monovalent cations only Li showed a weak band due to benzoate. As the frequency, sharpness, and intensity of this band was dependent on the interlayer cation, the benzoate ion must be associated primarily with the interlayer cation, and not with the silicate lattice. Further, the position of the bands were not identical with those of the benzoate salts of the cations, so that it cannot be in the form of a discrete crystalline phase. The absorption bands of benzoate ion appeared more strongly in spectra of Cu and Al complexes, and the intensity of these bands increased when the complexes of the polyvalent cations were examined in vacuum at 100–150°C. This conversion of interlayer benzoic acid to benzoate ion was partially reversed when the complexes rehydrated at room temperature.

4.1. Carbonyl group

Compounds containing C=O groups, such as aldehydes, ketones, carboxylic acids, esters, acid anhydrides, and amides, etc., behave similarly when adsorbed on swelling clay minerals. The C=O group is bound to the exchangeable metallic cation either through a water molecule bridge or by being directly linked to the cation. When the interaction between the C=O group and the cation is through a water bridge, the shift to lower frequencies of the C=O stretching band, relative to the location of this band in the spectrum of the neat compound, is less than 40–50 cm^{-1} [62]. When the C=O group is directly coordinated to the cation, the shift of the C=O stretching band depends on the strength of the bond. As the degree of covalency of this bond increases, this band appears at a lower frequency.

The fine structures of most smectite complexes of pollutants which are derivatives of benzoic acid, show similarities to the complexes of benzoic acid. For example, the carbamate insecticide "carbaryl" (1-naphthylmethyl carbamate) was adsorbed on montmorillonite at room temperature via a water bridge between the C=O group and the exchangeable cation [63]. At 90°C the C=O stretching vibration shifted to lower frequencies which were dependent on the exchangeable cations, indicating that the C=O group became directly coordinated to the cation. In the case of Cu– and Al–smectite some of the insecticide decomposed. The thermal reactions can be formulated as follows:



$$+ \mathrm{CH_3{-}NH_3^+{-}Me^{+n}(OH^-){-}clay} + \mathrm{CO_2} + \text{Dark colored compounds–}$$

The herbicides fluazifop (2-[4-(5-trifluoromethyl-2-pyridyloxy)phenoxyl]propionic acid) and fluazifop-butyl were adsorbed on montmorillonite at room temperature by forming both associations: (1) direct coordination of C=O group to exchangeable metallic cation (stretching band at about 1675 or 1652 $\mathrm{cm^{-1}}$) and (2) through a water bridge between the C=O group and the cation (stretching band at about 1725–1705 $\mathrm{cm^{-1}}$) [64]. The extent and strength of the bond depend on the nature of the exchangeable cation and on the thermal treatment. On heating more organic molecules coordinated directly to the cations. Upon rehydration a band due to bonding through a water bridge reappeared. With Al– or Fe–smectites, which are highly acidic, the adsorbed herbicides were protonated at the nitrogen of the pyridine ring (in-plane N–H bending band at 1552–1560 $\mathrm{cm^{-1}}$, association I).

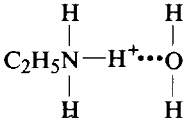
The adsorption of the nonionic polymer poly(vinylpyrrolidone) (PVP) on several clay minerals was investigated by thermo–IR–spectroscopy [65]. The IR data on thermal changes in the C=O absorption band were difficult to interpret and were inconclusive in determining if any specific chemical reaction was responsible for adsorption. Carbon–H–O–clay bonding was hypothesized to occur because the CH deformation band at 1430 cm^{-1} was increased considerably by polymer-to-clay adsorption. In general, adsorption of nonionic polymers to surfaces is a result of van der Waals forces.

5. Adsorption of aliphatic amines onto smectites and vermiculites

Amines are widely used in various industries as primary materials, e.g. for pharmaceuticals, rubber chemicals, special soaps and detergents, and insecticides. They are used as surface-active materials and emulsifiers and as anticorrosive materials. Organic ammonium cations and cationic detergents are held by the negative silicate layers through electrostatic attractions. They are adsorbed on smectites and vermiculites by the mechanism of cation exchange, in which inorganic cations initially present in the mineral are replaced by the organic cations. For example, the cation exchange reaction between Me–smectite and ethylammonium chloride in an aqueous solution is described by the following chemical equation:

$$C_2H_5NH_3Cl(aq) + Me\text{–}Smec(s) \rightarrow MeCl(aq) + C_2H_5NH_3\text{–}Smec(s)$$

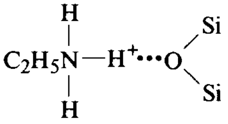
where Me is the exchangeable cation and Smec is the mineral. The ammonium cations are located in the interlayer space of smectites and vermiculites. In addition to the long-range electrostatic forces in which the cations are attracted to negatively charged clay platelets, short-range interactions, such as hydrogen bonds, occur between organic cations, which are proton donors, and residual water or the oxygen planes of the silicate layers [66–71].



$$C_2H_5NH_2\text{—}H^{+}\cdots OH_2$$

VII

and

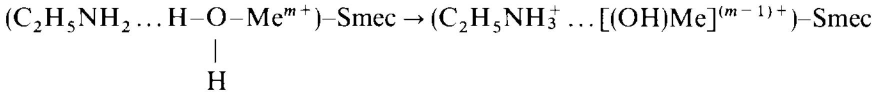


VIII

The location of the NH_3^+ band shifted as a result of the evolution of water. In the case of cyclohexylammonium smectites at room temperature, samples gave rise to NH_3^+ bending modes at 1503–1508 cm^{-1} and 1619–1625 cm^{-1}. On heating the samples at 150–180°C, these bands were shifted to 1511–1513 cm^{-1} and 1604–1605 cm^{-1}, respectively, together with the diminution of the characteristic water bands. Before the thermal treatment the ammonium cations were hydrated (VII). The NH_3^+ group was hydrogen-bonded to the water molecules by donating protons to the latter. During the thermal treatment the ammonium cations were dehydrated and the NH_3^+ groups became hydrogen-bonded to the oxygen planes (VIII) [68].

Butylammonium Wyoming montmorillonite showed an NH_3^+ deformation band at 1500 cm^{-1}. Butylammonium Beni–Buxera vermiculite and Llano vermiculite showed this band at 1532 and 1572 cm^{-1}, respectively. In both vermiculites this band was dichroic. In montmorillonite the ammonium group was hydrated, whereas in vermiculite it was not hydrated. There is a keying of this group into the ditrigonal cavities and a disposition of their C_3 axis normal to the layers [67].

Organic ammonium cations in the interlayer space are also obtained by the protonation of adsorbed amines [25, 32, 66, 69–72]. In the interlayer, water molecules coordinated to metallic cations are highly acidic and may donate protons to organic bases (association I). For example, adsorbed ethylamine is protonated in the interlayer space as follows:



$$(C_2H_5NH_2\ldots H\text{–}\underset{\substack{|\\ H}}{O}\text{–}Me^{m+})\text{–Smec} \rightarrow (C_2H_5NH_3^{+}\ldots[(OH)Me]^{(m-1)+})\text{–Smec}$$

Amine herbicides, such as “Asulam”, $H_2N–SO_2–NH–CO–O–CH_3$, are adsorbed at room temperature by protonation of the $-NH_2$ group [73].

There are also van der Waals forces acting between the flat oxygen planes and the organic species in the interlayer space. With increasing size of the organic cation, the contribution of the van der Waals forces to the adsorption process becomes more significant [74, 75]. Due to increasing van der Waals interactions, smectites show a high affinity towards long-chain organic cations leading to fixation of long-chain ammonium cations.

Thermo–IR–spectroscopy study of the adsorption of cyclohexylamine ($C_6H_{11}NH_2$) by montmorillonites saturated with different cations was carried out in order to understand the adsorption mechanism of aliphatic amines [32]. All exchangeable cations except Cs and Na led to protonation of the amine immediately upon exposure to liquid or to atmosphere saturated with the amine. This tendency depended upon the exchangeable cation and decreased in the order Al, Mg, Ca, Co, Zn, Cd, Cu. Protonation also depended on the origin of the lattice charge. It was more pronounced for Camp Berteux montmorillonite, with no tetrahedral substitution, than for Wyoming montmorillonite, with little tetrahedral substitution. On further exposure to the amine increasing amounts of molecular amine were sorbed. Various associations were formed in the interlayer space between hydrated cations, hydroxides, cyclohexylammonium, and cyclohexylamine.

After short periods of exposure the NH_3^+-bending frequencies were the same as those of cyclohexylammonium montmorillonite (1510 and 1620 cm^{-1}), but the intensities were very weak. Upon prolonged exposure the intensities of the bands increased and there were shifts of asymmetric and symmetric modes to lower and higher frequencies, respectively. At this stage the location of the band maximum depended on the exchangeable cations. This was interpreted as follows. When adsorption of the amine started, the amount of ammonium ion was small and it was hydrated (VII). With further adsorption of the amine, the amount of the cationic variety increased as a result of protonation, together with the formation of hydroxides. At this stage some interaction took place between the ammonium cations and the OH^- anions, leading to shifts in the NH_3^+-bending frequencies. These shifts are characteristic of hydrogen bonds and may indicate that in the interlayer space ammonium cations donate protons to the hydroxyl oxygens. Most clays, after being washed with water, gave a spectrum identical with that of cyclohexylammonium montmorillonite. Washing removed not only the neutral amine, but also hydroxy cations which are soluble in ammoniacal solution. With Al, which gives rise to an insoluble hydroxide, the NH_3^+ frequencies remained unchanged on washing with water.

Protonation did not occur when cyclohexylamine was adsorbed by Na or Cs montmorillonite. Na Wyoming bentonite developed a small shoulder at 1540 cm^{-1}, indicating partial hydrolysis. Na Camp Berteau montmorillonite did not show this band. With Cs-montmorillonite the water band at 1635 cm^{-1} was weakened as sorption progressed. The band due to NH_2 stretching was very small relative to the amount of organic material sorbed and that due to NH_2 bending was very broad, suggesting hydrogen bonding, probably to the oxygen plane of the aluminosilicate layer.

Ammonium ions in the interlayer space of montmorillonite obtained either by cation exchange or by protonation of adsorbed amines, may associate with molecular amines, giving rise to ammonium-amine complex [66, 68, 69, 76].

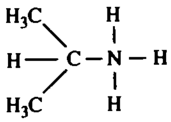
Isopropylammonium is common in various agrochemicals. Its adsorption on montmorillonite from aqueous and ethanolic solutions of "Roundup" was investigated by thermo-IR-spectroscopy [77]. The adsorption occurs by two different mechanisms: (1) the ammonium ion exchanges metal cations in the interlayer space, and (2) the ammonium ion exchanges protons originating from the dissociation of interlayer water. In the latter process, which takes place from concentrated solutions of Roundup, protons are transferred from the interlayer space to the solution. Mechanism (1) gives rise to the adsorption of amounts not greater than those equivalent to the cation exchange capacity of the clay whereas the amount of ammonium adsorbed by mechanism (2) is much higher. The maximum of the NH_3^+ symmetric bending absorption band at 1490-1520 cm^{-1} can give information on the character of the ammonium ion in the interlayer space. The characteristic maxima of the various associations of isopropylammonium are summarized in Scheme 1.

5.1. *Adsorption of molecular amines via the formation of coordination ions*

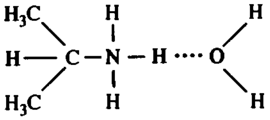
In the interlayer space of smectites, transition metal cations form stable coordination complexes with amines. Thermo-IR-spectroscopy was applied to study the formation of ethylenediamine (NH_2-CH_2-CH_2-NH_2) complexes of various transition metals [78-81] and of copper-polyamine complexes [81, 82]. With di- and polyamines, such as propylenediamine (NH_2-CH_2-CH_2-CH_2-NH_2) and diethylenetriamine (NH_2-CH_2-CH_2-NH-CH_2-CH_2-NH_2) which form 5- or 6-membered chelates, stable complexes are obtained with transition metals in the interlayer space; these are similar to those formed in aqueous solutions. These complexes do not undergo hydrolysis. They can be identified by the appearance of asymmetric and symmetric NH_2-stretching vibrations at 3250-3350 cm^{-1} and NH_2-scissoring at 1595 cm^{-1}. Coordination cations of transition metals and ammonia or aliphatic amines, which do not form chelates (monoamines), are obtained only under dry conditions or with excess amine [66, 68]. They undergo hydrolysis in the presence of water, resulting in ammonium or

1. Adsorption in the range of the CEC of montmorillonite.

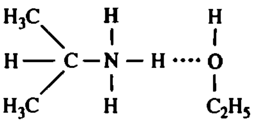
A. 1492 cm^{-1}—anhydrous.



B. 1500 cm^{-1}—hydrated.

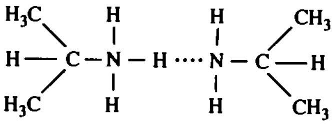


C. 1510 cm^{-1}—solvated by ethanol.

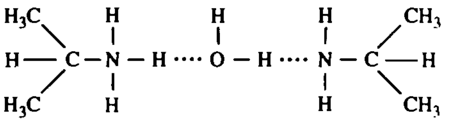


2. Adsorption of amounts in excess of the CEC of montmorillonite.

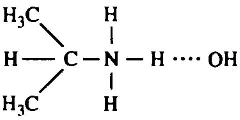
A. 1507 cm^{-1}—ammonium amine formation.



and/or

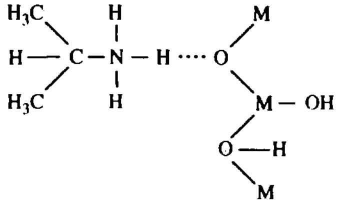


B. 1512 cm^{-1}—hydrogen bonds with hydroxylions.



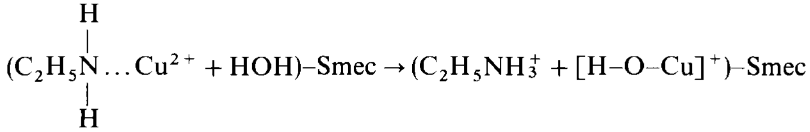
Scheme 1. The associations formed by isopropylammonium in the interlayer space of montmorillonite and the characteristic frequencies (in cm^{-1}) of the NH_3^+ symmetric deformation band (after [77]).

C. 1518 cm^{-1}—hydrogen bonds with polymeric AlOH and FeOH cations.



Scheme 1. (*Continued*)

alkyl ammonium as follows:



$$(C_2H_5\overset{H}{\underset{H}{N}}\ldots Cu^{2+} + HOH)\text{-Smec} \rightarrow (C_2H_5NH_3^+ + [H\text{-}O\text{-}Cu]^+)\text{-Smec}$$

6. Adsorption of anilines and benzidine onto montmorillonite

Aniline, $C_6H_5NH_2$ and its derivatives are used in the manufacture of dyes, pharmaceuticals, photographic chemicals, rubber accelerators, antioxidants, herbicides, and fungicides and are highly toxic when absorbed through skin or accidentally inhaled or swallowed. Aniline is a much weaker base than cyclohexylamine (pK_a cyclohexylamine $= 10.6$, pK_a aniline $= 4.6$).

Anilines are amphiprotic compounds which may react as proton acceptors or donors. Aniline is protonated by strong Brönsted acids and becomes a cation ($ArNH_3^+$, type D, association I in the Introduction). With weak acids aniline forms hydrogen bonds by accepting protons from the weak acids (type A, association II in the Introduction). IR spectroscopy is used to identify protonated and molecular anilines. The spectrum of protonated aniline (anilinium) shows deformation and rocking NH_3^+ absorptions at 1520–1575 and ≈ 1350 cm^{-1}. The presence of anilinium in montmorillonite treated with liquid or vapor aniline is proof for the presence of strong Brönsted acid sites in the clay interlayer. In contrast to aliphatic amines, protonation of anilines in the interlayer space of smectites occurs to a very small extent. With exchangeable Al, which has a high polarizing power, the IR spectrum shows considerable amounts of anilinium.

Concerning molecular anilines, IR spectroscopy may give information on whether they are proton acceptors or donors (named types A and B, respectively, associations II and IV in the Introduction). Type A contains a free NH_2 group and type B a free NH. Two bands, corresponding to asymmetric and symmetric NH_2 frequencies appear for type A, at 3400 ± 100 cm^{-1}, but only one band for type B. The presence of types A and B in the interlayer of montmorillonite treated with liquid or vapor anilines is an indication for the presence of weak Brönsted acid sites and basic sites, respectively, in the clay interlayer. In most cases, both structures occur simultaneously in varying proportions and the NH-stretching frequency of type B either coincides with the asymmetric NH_2 frequency of type A or is too close to it to be resolved. The ratio between types A and B depends on the exchangeable cations. Relative values and general trends are obtained from the intensity ratios of the asymmetric to symmetric NH_2 vibrations. Whenever the band corresponding to the asymmetric vibration is intense, so also is a broad band at 3130–3210 cm^{-1}, which was assigned as a combination band of NH_2 deformation vibration and ascribed to N–H...O vibration. This band is diagnostic for type B. The CN-stretching band in pure anilines is located at 1250–1300 cm^{-1}. In type B this band has much more double-bond character than that in type A. The CN-stretching band of type A appears at a lower frequency than the frequency of CN band of the pure liquid, while that of type B is similar or higher.

Fine structures of montmorillonite complexes of several anilines have been investigated by thermo–IR–spectroscopy [27–29, 84–88]. With major elements anilines are bound to interlayer cations through water molecules, except in Cs–montmorillonite, where bonding to the oxygen planes of the aluminosilicate layers seems to predominate. Different types of water are present in the interlayer space. Water of hydration of the interlayer cations is acidic. The oxygen plane is basic and water molecules which are hydrogen-bonded to this plane acquire a basic character. Except with Cs, where most adsorbed water is nonstructured, acidic water predominates. In K–, Na–, Mg–, H– and Al–montmorillonites, where aniline and its derivatives are bound to the cations through water bridges, the oxygen planes compete with the weak organic bases for protons of the water molecules. Consequently, anilines act as proton acceptors (type A) or proton donors (type B). Type B is favored by increasing polarizing power of the interlayer cation and by steric hindrance arising from *ortho* substitution of the organic base.

IR spectroscopy can differentiate between anilines bound to Brönsted and those bound to Lewis acid sites (types A and C, respectively, associations II and III in the Introduction). Both types are identified from the locations of the NH_2- and CN-stretching vibrations. In type C the displacements of these bands to lower frequencies are more significant than in type A. An NH_2 symmetric stretching band appears at a frequency below 3300 cm^{-1} and the CN band appears below 1250 cm^{-1}. Type A is characterized by an NH_2 asymmetric stretching band at 3380–3400 cm^{-1}.

Two types of association are formed between anilines and interlayer transition metal cations; the N of the aniline molecule is either directly coordinated to the cation (type C), or bonding occurs through a water bridge (type A). The frequencies of NH_2-stretching bands in the IR spectra of montmorillonite saturated with different cations and treated with different anilines are given in Table 2, from which it is obvious that type C complexes are not obtained at room temperature between anilines and major elements. Cd–montmorillonite forms type C complexes with all the anilines which are mentioned in the table, in addition to type A complexes. From the relative intensity of the bands it is obvious that, except for *o*-chloroaniline, type C predominates. By heating the samples at 50–100°C under vacuum, type A almost disappears.

Table 2

Frequencies of NH_2 stretching bands (in cm^{-1}) in IR spectra of Na–, Mg–, Al–, Mn–, Co–, Ni–, Zn– and Cd–montmorillonite saturated with anilines. Spectra recorded at room temperature (after [90–92])

Aromatic amine	Exchangeable cation							
	Na	Mg	Al	Mn	Co	Ni	Zn	Cd
Aniline	–	–	–	3270	3265	3270	3245	3260
	3320	3320	3315	3320	3315	3320	3315	3325
	3390	3390	3385	3385	3380	3385	3385	3385
o-Toluidine	–	–	–	–		3260vw[a]	3245	3265
	3320	3320	3310	3315	3315	3320	3315	3320
	3390	3390	3385	3385	3390	3395	3390	3390
m-Toluidine	–	–	–	3255sh[b]	3255sh[b]	3260	3240w[c]	3260
	3320	3320	3310	3315	3315	3320	3330[c]	3310
	3390	3390	3385	3385	3390	3395	3420[c]	3380
p-Toluidine	–	–	–	–	3270	3270	3225	3260
	3320	3315	3310	3310	3320	3330	3300	3320
	3390	3385	3385	3375	3380	3390vw	3380	3385
2,5-Dimethylaniline	–	–	–	–	–	–	3250[d]	3260
	3315	3315	3310	3305	3305	3315	3300	3315
	3385	3385	3385	3385	3385	3385	3385	3385
2,6-Dimethylaniline	–	–	–	–	–	–	–	3260
	3335	3335	3325	3325	3325	3330	3305	3325
	3400	3400	3395	3395	3395	3395	3385	3395
2,4,6-Trimethylaniline	–	–	–	–	–	–	–	3255
	3335	3335	3325	3325	3320	3330	3335	3315
	3400	3400	3395	3395	3390	3385	3390	3395
o-Chloroaniline	–	–	–	–	–	3270vw[d]	3220	3250
	3330	3330	3315	3330	3320	3325	3315	3320
	3400	3395	3390	3395	3390	3390	3390	3390
m-Chloroaniline	–	–	–	3270vw	3260sh[b]	3265	3235	3265
	3330	3330	3315	3325	3320	3320	3320	3325
	3395	3395	3385	3390	3385	3385	3385	3390
Benzidine	–	–	–	3270vw	3280	3275	3235m	3275
	3325	3325	3315	3330	3335	3335	3310w	3335
	3390m	3390m	3375	3390sh	3400w	3395sh	3390w	3400sh

[a] v—very, w—weak band, m—medium band, sh—shoulder.

[b] —This band was detected only after vacuum treatment at 100°C.

[c] —After vacuum treatment at 100°C bands change to 3230, 3305, 3385 cm^{-1}.

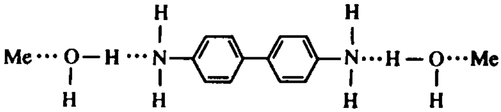
[d] —Band disappears after vacuum treatment at 100°C.

Zn–montmorillonite forms type C complexes with most of the anilines which are mentioned in the table, but not with 2,6-dimethyl- and 2,4,6-trimethylaniline, probably due to steric hindrance. Mn–, Co– and Ni–montmorillonites form largely type A complexes and only some of the anilines produce type C. From the location of the *sym* NH_2-stretching band it appears that the strongest Me–N bond is obtained with Zn. However, the tendency to form type C complexes decreases in the order Cd > Zn > Ni > Co > Mn. The type of the coordination complex which is formed with the transition metal cations depends more on the tendency of the particular cation to hydrate than on the strength of the Me–N bond.

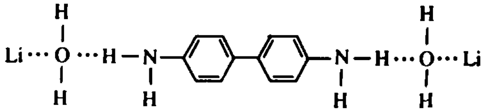
Benzidine, $C_{12}H_{12}N_2$, is an important industrial chemical, mainly for the synthesis of dyes and rubber chemicals. It is used as a detecting agent for blood pigments and for liquidification measurements. Recently we studied its adsorption by montmorillonite films and the effect of the exchangeable cations on the adsorption products. The purpose of that study was to identify acidic and basic sites on the clay surface at elevated temperatures, to differentiate between Brönsted and Lewis sites and to obtain relative information on their strength. Benzidine is a suitable reagent for study of surface acidity at elevated temperatures up to 200°C, because it is not evolved from the clay. The classical reagents for this purpose, pyridine and aniline, are not reliable at these temperatures, because of their high vapor pressure and ease of evaporation. Adsorption was carried out from a 5% CCl_4 solution [89–92]. Excess amine was removed by immersing the films for very short periods in pure CCl_4. X-ray study showed that the adsorbed benzidine was located in the interlayer space. The thermo–IR–spectroscopy analysis showed that benzidine molecules interact with interlayer water, with the exchangeable metallic cations and with the oxygen planes. Some molecules also undergo protonation to give the benzidinium cation and the dimerization product benzidinium–benzidine. Several types of association are obtained with each metallic cation, but the percentage of each type relative to the total amount depends on the exchangeable cation and on the heating temperature. Different associations which were identified, are shown in Scheme 2. The location of the absorption bands which were used to identify the different associations are also given in the scheme. With major elements, at room temperature, the benzidine molecules are bound to the cations through water bridges (Fig. 3a). After the thermal treatment and water evolution, they become directly bound to the cations (Fig. 3b). With transition elements most of the benzidine is bound directly to the cation before the thermal treatment. The thermal dehydration at 50°C increased the fraction of benzidine which was directly coordinated to the cation (Fig. 3, c and d). Except for Na–montmorillonite, heating the clay to 200°C increased the fraction of protonated benzidine, indicating that the Brönsted acidity of the interlayer space increases with the rise in temperature.

7. Adsorption of phenols onto smectites

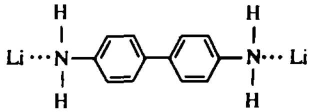
Phenol and substituted phenols are important chemicals in the manufacture of synthetic resins, dyes, pharmaceuticals, and agrochemicals. Chlorophenols are used as



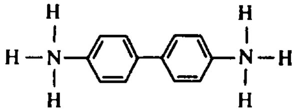
Association type A: Linkage to exchangeable cation through a 'water bridge'. Benzidine is proton acceptor.
Characteristic absorption bands: NH$_2$ stretching 3390, 3325 cm^{-1}
NH$_2$ bending 1610–1620 cm^{-1}; C—N stretching 1250 cm^{-1}



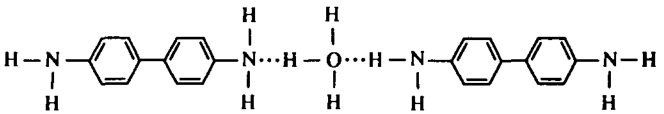
Association type B: Linkage to exchangeable cation through a 'water bridge'. Benzidine is proton donor.
Characteristic absorption bands: N(H)—H···OH$_2$ combination band 3200 cm^{-1}
NH$_2$ bending 1610–1620 cm^{-1}; C—N stretching 1320 cm^{-1}



Association type C: Direct linkage between the NH$_2$ group and an exchangeable cation. Characteristic absorption bands: NH$_2$ stretching 3360, 3300 cm^{-1} (Li-mont after dehydration) 3310, 3235 cm^{-1} (Zn-mont)
NH$_2$ bending 1613 cm^{-1} (Li-mont after dehydration); 1578 cm^{-1} (Zn-mont)
C—N stretching 1243 cm^{-1} (Li-mont after dehydration); 1215 cm^{-1} (Zn-mont)

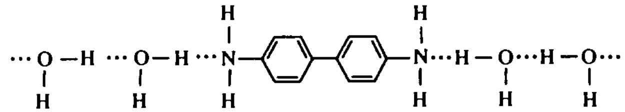


Association type D: Protonation of benzidine. NH$_3^+$ is hydrated(I); NH$_3^+$ is linked to oxygen plane(II).
Characteristic absorption bands: NH$_3^+$ stretching 2930 cm^{-1} (D-I), 3150 cm^{-1} (D-II)
NH$_3^+$ bending 1570, 1550, 1530 cm^{-1}; C—N stretching 1208 cm^{-1}

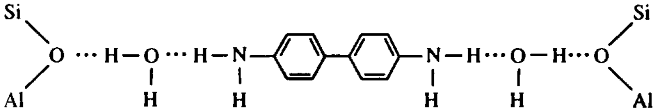


Association type E: Benzidinium-benzidine.
Characteristic absorption bands: NH$_2$ stretching 3390, 3325 cm^{-1} (E-I); N(H)-H··OH$_3^+$ combination band 3210 cm^{-1} (E-II)
NH$_2$ bending 1620 cm^{-1} (E-I); 1610–1620 cm^{-1} (E-II)
C—N stretching 1250 cm^{-1} (E-I); 1320 cm^{-1} (E-II)

Scheme 2. The associations between benzidine, water, exchangeable cations, and the oxygen plane in the interlayer space of montmorillonite and the characteristic frequencies (in cm^{-1}) of the NH$_2$ stretching and bending bands, NH$_3^+$ stretching and bending bands, and C–N stretching band (after [90–92]).



Association type F: Linkage between NH_2 group and non-structured water. Characteristic absorption bands: NH_2 stretching 3375, 3315 cm^{-1}
NH_2 bending 1620 cm^{-1}; C—N stretching 1265 cm^{-1}



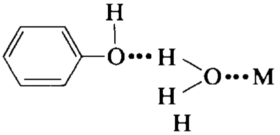
Association type G: Linkage to oxygen plane through a 'water bridge'. Benzidine is proton acceptor. Characteristic absorption bands: N(H)—H ··· O(H)—H ··· OSi combination band 3235 cm^{-1}
C—N stretching 1320 cm^{-1}

Scheme 2. (*Continued*)

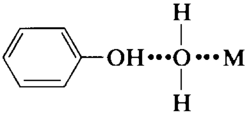
pesticides. Their toxicity is high and they accumulate in the environment. Sorption of phenol from the vapor phase by hectorite has been investigated by thermo–IR–spectroscopy [93]. The only direct phenol cation interaction occurred with Cu– and Ag–hectorite. With other inorganic cations bonding of phenols through water bridges to exchangeable cations was observed. In these associations water molecules were hydrogen-bonded to the phenols by donating protons to the phenolic O atoms. Weak π electron interactions with the oxygen planes of the silicate layers were also observed. This was inferred from the fading or disappearing of the ring vibration at 1595–1606 cm^{-1}.

Sorption of phenol and *p*-nitrophenol from organic solvents onto montmorillonite was investigated by thermo–IR–spectroscopy [31]. Phenol is a weak acid ($K_a = 1.3 \times 10^{-10}$). The electrophilic NO_2 substituent increases the acid character, due to the conjugation effect ($K_a = 6.5 \times 10^{-8}$). When adsorbed by montmorillonite, phenols reveal their amphiprotic nature. They may donate or accept protons. The following configurations were inferred for the phenolic group in the interlayer space:

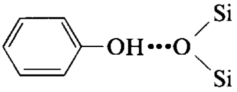
I



II



III



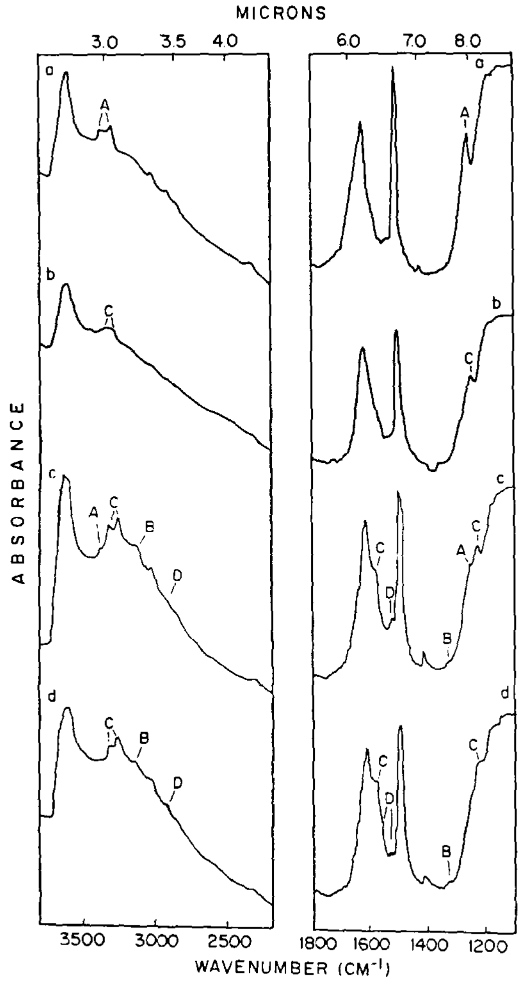


Fig. 3. Thermo-IR-spectroscopy analysis of Li- and Cd-montmorillonite-benzidine complexes: (a) IR spectrum of a Li-montmorillonite-benzidine film recorded in air; (b) IR spectrum of the same film recorded after heating in a heating cell under vacuum at 150°C; (c) IR spectrum of a Cd-montmorillonite-benzidine film recorded in air; (b) IR spectrum of the same film recorded after heating in a heating cell under vacuum at 50°C (after [92]).

where M is the exchangeable inorganic cation and O of the Si–O–Si group is an atom belonging to the oxygen plane of the tetrahedral sheet. Under ambient conditions the exchangeable metallic cations are hydrated. Due to the inductive effect of the cation, the water molecules may behave as Brönsted acids. In configuration I the phenol forms a hydrogen bond with the water molecule by accepting a proton from this acidic species. Such bonding implies a reduction in the delocalization energy of the benzene ring. This gives rise to shifts of the ring vibrations from 1595 and 1498 cm^{-1} in the spectrum of a benzene solution of phenol to higher and lower frequencies, respectively, in the spectrum of the adsorbed phenol. The C–O stretching vibration is located at 1186 cm^{-1} in the spectrum of phenol in benzene solution. It is expected that in configuration I, due to the involvement of the lone pair of electrons of the phenolic oxygen in the hydrogen bond which is formed with the water molecule, the C–O band is shifted to lower frequencies. In most spectra this band cannot be detected, since it overlaps the Si–O absorption band of the clay. The thermal stability of this association is very low and the phenol escapes together with water during the thermal treatment.

In configuration II phenol reveals acidic character. It forms hydrogen bonds with water molecules by proton donation. Such bonding implies a slight increase in the localization energy of the benzene ring and there should be only small shifts of the ring vibrations. More significant for this structure is the increase in the double bond character of the C–O band. In the phenol–montmorillonite complexes this band shifts from 1186 cm^{-1} to higher frequencies (1220–1240 cm^{-1}). The thermal stability of this association is higher than that of configuration I.

Montmorillonite complexes of nitrophenol were more stable than those of phenol. Phenol was desorbed almost completely when saturated samples were left for 1 week at 40% relative humidity. Almost no nitrophenol was desorbed under the same conditions. Also, when the samples were heated under vacuum, much phenol was lost, but not nitrophenol. Montmorillonite saturated with monovalent cations lost greater amounts of phenol compared to divalent cations.

Recently the mechanochemical adsorption of phenol by laponite, saponite, montmorillonite, beidellite, and vemiculite was investigated by thermo-IR-spectroscopy [94, 95]. In this study the clay was ground with the phenol. The spectra of the phenol–clay complexes were recorded in KBr disks. The disks were left for 3 d in a vacuum furnace at 115°C and the excess phenol was evolved. Depending on the clay mineral and on the time of grinding, two types of association between phenol, water molecules, and exchangeable cations (configurations I and II) were

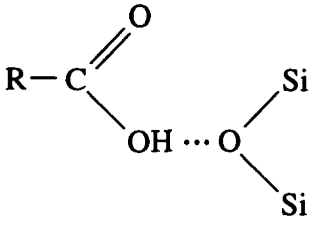
Table 3
Characteristic features of infrared spectra (in cm^{-1}) of phenol and phenol–smectite complexes (after [95])

Vibration type	Phenol		Phenol–smectite complexes	
	Benzene solution	KBr disk	Type I	Type II
OH Stretching	3550	3400	o.w.[a]	o.w.
Ring stretching	1595	1596	1606	1596–1600
	1498		1487–1493	1500
	1470	1470	1470–1472	1470–1472
OH Deformation	1342	1366	1435	≈ 1350
CO Stretching	1186	1228	1165–1180	1220–1240

[a] Overlapping with stretching water bands.

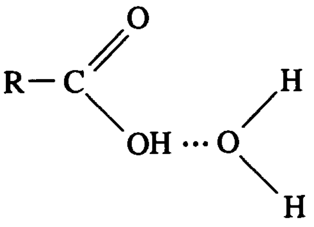
(1) *Molecular Carboxylic Acid*

Linkage between a COOH group and an oxygen sheet of silicate layer.



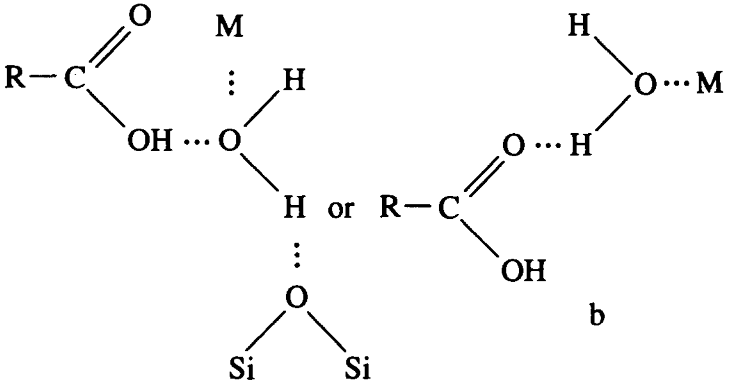
I

Linkage between a COOH group and hydrophobic structured water.



II

Linkage to exchangeable cation through a 'water bridge', in which the COOH group is either proton donor (IIIa) or proton acceptor (IIIb).



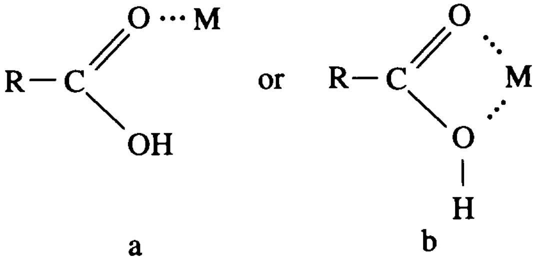
a

b

III

Scheme 3. The associations between fatty acids, water, exchangeable cations, and the oxygen plane in the interlayer space of montmorillonite (after [96]).

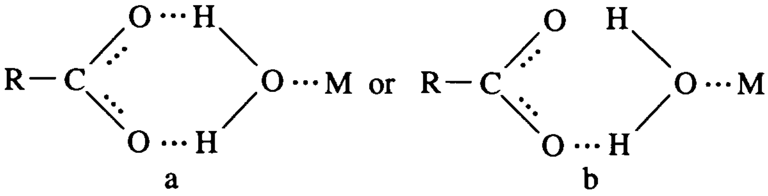
Direct linkage between the COOH group and an exchangeable cation.



IV

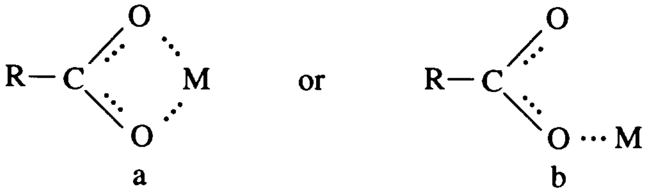
(2) *Carboxylate Anion*

Linkage between a COO^- group and an exchangeable cation through a 'water bridge'.



V

Direct linkage between a COO^- group and an exchangeable cation.



VI

Scheme 3. (*Continued*).

identified from the IR spectra. The characteristic features of the spectra are shown in Table 3.

8. Adsorption of fatty acids by different clay minerals

Fatty acids are used as raw materials in the manufacture of surfactants, metallic soaps, resins, cosmetics, and insecticides. Stearic acid is also used in the rubber industry, for candles, lubricating oil, and as a plasticizer for polymers. The study of adsorption of fatty acids by clay minerals is important for solving serveral environmental problems, because these acids are decomposition products of biopolymers.

8.1. Montmorillonite

Adsorption of acetic (CH_3COOH), lauric ($C_{11}H_{23}COOH$), and stearic ($C_{17}H_{35}COOH$) acids by montmorillonite from 1.5% CCl_4 solutions and the effect of the exchangeable cations on the adsorption products, were investigated by thermo–IR–spectroscopy [96]. Two distinct species were identified. One is the acidic form, RCOOH, characterized by an absorption band between 1650 and 1725 cm^{-1}. The other is the anionic form, $RCOO^-$, characterized by two absorption bands between 1420 and 1610 cm^{-1}. The appearance of anionic species indicates that adsorbed acid dissociated in the interlayer space, thus producing carboxylate anion. It also indicates that basic sites are found in the interlayer space. Intensity ratios of the various bands, the ion versus the acid, can give information on the tendency of the acid to dissociate in the interlayer space. Stearic acid shows the highest tendency to dissociate.

Associations which were determined by thermo–IR–spectroscopy are shown in Scheme 3. They were identified from the locations of the appropriate absorption bands. The adsorbed acid molecules which are located in the interlayer space, react with water, with the exchangeable cations, and with the oxygen plane. When films of Cs–montmorillonite treated with the different acids were evacuated at 200°C, they were dehydrated and the H_2O band at 1640 cm^{-1} disappeared. With acetic and lauric acids the COOH band maxima were not shifted after dehydration and it was therefore concluded that these acids were not bound to the clay through water bridges, but were directly bound to the oxygen plane (association I, Scheme 3). With stearic acid, there was a small shift of the COOH band due to the thermal treatment and it became very sharp. Probably, before the thermal treatment there was some kind of interaction between the COOH group and hydrophobic structured water molecules (association II, Scheme 3) and this species was transformed into an anhydrous species (association I) during the thermal treatment. In Mg– and Ca–montmorillonite the acids were bound to the exchangeable cations through water bridges (association III, Scheme 3). With acetic and lauric acids, thermal dehydration at 200°C under vacuum resulted in anhydrous species with the cation directly coordinated to the acid (association IV). This is shown from the shifts of the COOH group to lower frequencies. With stearic acid, most of the acid was evolved during the thermal treatment. The acid which remained in the interlayer space was bound directly to the oxygen plane, as in Cs–montmorillonite. Li–, Na–, and K–montmorillonites gave extremely broad bands with several maxima, shoulders, or inflections, which may indicate the presence of several types of association (I–IV). The acidic variety is very small in Al–montmorillonite (association III). It was transformed into association IV at 100°C and disappeared at higher temperatures. Fe–montmorillonite behaved similarly to Al–montmorillonite but association IV was stable at 200°C.

One would expect that the basic strength of the interlayer space will decrease with increasing positive charge of the exchangeable cation. Surprisingly, the intensity ratios of the absorption bands of the carboxylic and carboxylate groups showed that the anionic species was obtained mainly with Cu, Al and Fe(III) as exchangeable cations and to a small extent with Ca and Mg. Exchangeable Cs stabilized the acidic variety. In Cs–montmorillonite the locations of the COOH absorption bands were not shifted after dehydration of the clay samples, indicating that these acids were not bound to the clay through water bridges. A possible interaction may be a direct association of COOH with the oxygen plane.

Other clay minerals were treated with stearic acid and investigated by thermo–IR–spectroscopy. These minerals do not form stable films and the organo–clays were heated as a alkali-halide disks [97–99]. The organo–clays were prepared in the following way. Mixtures of one part clay with five parts stearic acid by weight, were heated in closed vessels at 100°C for 72 h, cooled and washed five times with hexane to remove nonadsorbed acid. Disks were prepared with NaCl, KCl, and CsCl. Each disk was crushed, reground, and re-pressed an additional four times. The disks were heated for 10 d at 110°C, 50 d at 190°C and 18 h at each subsequent temperature: 250, 300, 350, 400, and 450°C. After each thermal treatment, the disks were cooled in a desiccator and pressed, with care taken not to damage them in the process. IR spectra were recorded at every stage of the grinding and thermal treatment of the various disks. Disks of stearic acid, without addition of a clay mineral, were similarly prepared and treated.

8.2. Sepiolite and palygorskite

These two minerals contain two types of adsorbed water: “bound water” molecules coordinating Mg atoms at the broken bond surfaces of the channels, and “zeolitic water” clusters which fill the empty space in the channels and are hydrogen-bonded to the bound water. Sepiolite and palygorskite both showed two bands in the H_2O deformation region, an unsymmetrical band at $\approx 1620\ \mathrm{cm}^{-1}$, assigned to “bound water” and structural hydroxyls, and a band at 1650–1660 cm^{-1}, assigned to “zeolitic water” [100]. From the thermo–IR–spectroscopy study the following conclusions were made [97]:

1. Spectra of freshly prepared disks of the sepiolite– or palygorskite–stearic acid complexes showed very broad COOH absorption bands at 1680–1715 and 1705–1715 cm^{-1}, respectively, each band comprising several maxima. The COOH bands became sharper after partial dehydration of the alkali-halide disks at 115°C, with the main absorption located at 1693 and 1710 cm^{-1} in the spectra of sepiolite and palygorskite, respectively. In addition to the principal absorption, a series of weak shoulders appeared at 1705, 1710, 1722, and 1738 cm^{-1} in the spectra of both minerals. After heating at 190°C, much of the acid was lost and the COOH regions of the two minerals became very similar with several shoulders. The various shoulders and peaks must be attributed to different types of bonding of the acid. Association of stearic acid with differently bonded water molecules could give rise to the various absorptions.

2. The locations of the absorption bands or shoulders are the same for both minerals but their relative intensities differ. It may, therefore, be concluded that

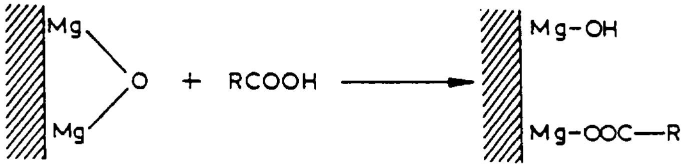


Fig. 4. A mechanochemical break of an Mg–O bond in sepiolite or palygorskite and interaction between the new exposed functional groups and stearic acid (after [97]).

the bonding is similar but that the proportions of the species formed differ in the two minerals.

3. The nature of the alkali halides had no effect on the positions of the absorption band maxima.

4. During the grinding of the organo–clay complex with the alkali halide, absorption bands due to the anionic stearate were observed in the 1540–1600 cm^{-1} region, in addition to the stearic acid. The intensity of these absorptions increased with continuous grinding. The formation of the anionic stearate in a mechanochemical process is associated with the breaking of bonds such as Mg–O in the silicate framework. As a result of the grinding, new functional oxygens were exposed and they could accept protons from the acid molecules. According to this model the ionic species are located on the mineral surfaces, probably near the Mg at the broken bonds (Fig. 4). It should be mentioned that the stearate was not obtained when stearic acid was ground in alkali halides in the absence of clay.

5. Although the organo–clay was washed repeatedly, it contained excess acid during the preparation of the disk. This prevented the alkali halide from replacing the acid in the organo–clay complex. The excess acid which was not adsorbed, evolved during the ten days of the heating of the disks at 110°C.

6. The molten acid was adsorbed by the clay minerals, penetrating into the channels and exchanging zeolitic water. This was shown by a decrease in the intensity of the zeolitic water band relative to its intensity in the spectra of untreated clays.

7. Inside the channels the acid molecules were hydrated. In sepiolite, which has broad channels, COOH groups formed hydrogen bonds with zeolitic water. In palygorskite, which has narrow channels, hydrogen bonds were formed with "bound water"; these are more acidic than those formed with the zeolitic water.

8. The anionic species were linked to "bound water" molecules which formed bridges between the COO^- groups and the Mg. Consequently, these water molecules persisted during the thermal treatment up to relatively high temperatures.

9. The effect of the alkali chloride on the thermal reactions was observed only at high temperatures, after the clay crystal had lost water and became folded. With CsCl, the folding took place at lower temperatures than with NaCl or KCl.

10. When the organo–clay complex was heated as powder (not as a disk) or in NaCl disk, the acid escaped at lower temperatures, before it decomposed. In KCl and CsCl disks the acid was retained at high temperatures where it decomposed.

8.3. *Talc and pyrophyllite*

These minerals do not swell and the adsorption of stearic acid took place at the layer edges [98]. At 250°C, the acid was coordinated directly to the Mg or Al atoms located at the layer edges (broken bonds). Consequently, the locations of the COOH absorption band in the spectra of these minerals appeared at different frequencies (1705 and 1660 cm^{-1}, respectively). As with sepiolite and palygorskite, the grinding of the disks gave rise to the development of anionic species. The basicity of talc is higher than that of pyrophyllite, and consequently, the thermal stability of the stearic acid–talc complex is greater than that of stearic acid–pyrophyllite complex.

8.4. *Alophane*

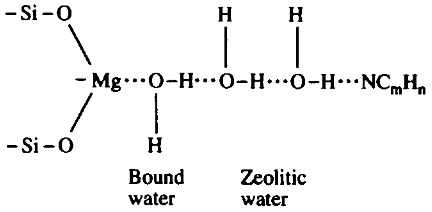
The reaction between stearic acid and this mineral, which is an amorphous aluminosilicate, is different from the previous reactions [99]. The surfaces of this mineral are basic and, consequently, most of the acid is adsorbed by deprotonation, resulting in an adsorbed anionic species, without any grinding of the mixture. The COO^- is shown in the IR spectrum by absorption bands at 1600–1575 and 1470–1460 cm^{-1}. At 115°C, in NaCl or KCl disks, alophane holds water molecules very firmly and the acid is bound to the mineral surface through water bridges. The hydrated COOH is shown in the IR spectrum by an absorption band at 1710 cm^{-1}. Cs is a water structure breaker. In the presence of CsCl the hydration of the surface of alophane is hydrophobic and the acid is directly coordinated to the Al at the edges of the particles. The anhydrous COOH which is directly coordinated to Al, is shown in the IR spectrum by a perturbed absorption band at 1660 cm^{-1}. Alophane adsorbs great amounts of stearic acid in the presence of CsCl, and the organo–clay complex which is obtained in the presence of CsCl is more stable than that obtained in the presence of NaCl or KCl, and it persists at higher temperatures.

9. Adsorption of amines by sepiolite and palygorskite

The adsorption of butylamine (aliphatic), pyridine (aromatic), and trimethylpyridine (aliphatic and aromatic) by these minerals has been studied [101]. Adsorption was carried out by reflux. A mixture containing clay powder and the liquid pure amine was heated to boiling point. After 1d the powder was separated from the liquid and dried under a vacuum of 0.01 Torr. The thermo–IR–spectroscopic study was carried out in KBr disks. From the intensities of the water bands it was obvious that the amounts of water in the organo–clays were much smaller than the amounts found in the untreated clays. The spectra in the different temperatures were different from clay to clay. These two observations indicate that the amines were located inside the channels of both minerals.

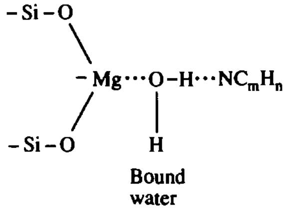
For the interpretation of the thermo–IR–spectroscopy analysis we proposed six possible associations as a model for adsorption (Scheme 4). In four of these model associations the sepiolite or palygorskite donate protons to the amine. The spectra

Association type A



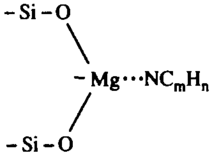
Possible association between amine (proton acceptor) and zeolitic water (proton donor) via hydrogen bond.

Association type B



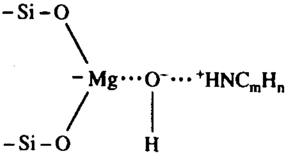
Possible association between amine (proton acceptor) and bound water (proton donor) via hydrogen bond.

Association type C



Possible association between amine (electron pair donor) and octahedral magnesium exposed to the channel (electron pair acceptor).

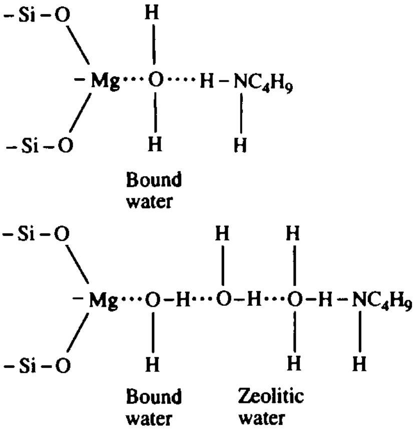
Association type D



Possible protonation of amine. Bound water serves as proton donor.

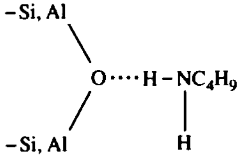
Scheme 4. Possible associations between amines and zeolitic water, bound water (proton donation via hydrogen bond), and octahedral magnesium exposed to the channel (electron pair acceptor) (after [101]).

Association type E



Possible association between butylamine (proton donor) and zeolitic or bound water (proton acceptor) via hydrogen bond.

Association type F



Possible association between butylamine (proton donor) and siloxane group at the surface of the channel (proton acceptor) via hydrogen bond.

Scheme 4. (*Continued*).

reveal that the adsorbed amines form hydrogen bonds with the zeolitic water. In sepiolite hydrogen bonds are also formed between butylamine or pyridine and the bound water. Pyridine replaces some of the bound water in sepiolite. The other amines do the same to a very small extent only. During the thermal treatment the amines become protonated. At 200°C most of the water has escaped and direct coordination of Mg by the amine is obtained.

Above 300°C both clays are folded. In the presence of organic matter this folding occurs at lower temperatures than in its absence. The product of the thermal treatment at 400°C in the case of palygorskite with organic matter is similar to the product obtained in its absence. Sepiolite–organo complexes at 400°C differ from those of the natural sepiolite at this temperature.

In two of the model associations which are shown in Scheme 4 (associations E and F), the minerals accept protons from the amine. In our case this can happen with the butylamine only. The spectra did not show the formation of associations E or F and it seems that there are no basic sites on the surfaces of these two minerals.

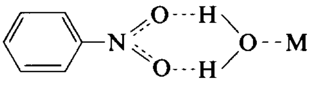
10. Miscellaneous

Pyridine is a relatively strong base and is used to differentiate between Brönsted and Lewis acid sites in solid surfaces. Inside the interlayer space of a swelling clay, pyridine forms hydrogen bonds with water molecules in the hydration shells of the highly polarizing cations. The dehydration of the clay resulted in direct coordination of the organic molecule with the metallic cation. Part of the adsorbed pyridine is protonated giving the pyridinium cation. The degree of protonation depends on the polarizability of the exchangeable cation. Associations I, II, III, and ammonium–amine were formed when this base was adsorbed on montmorillonite [22].

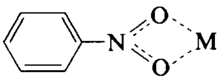
Indoles are amphiprotic compounds. Associations I, II, III, IV, V, and VI were formed when some derivatives of this compound were adsorbed on montmorillonite [30]. Complexes of 27 different *s*-triazines and of 3-aminotriazole with montmorillonite were studied by IR spectroscopy. The adsorption was attributed to protonation of heterocyclic nitrogen atoms of these molecules. The degree of protonation depended on the exchangeable cation. Upon protonation these molecules were transformed into cations [102, 103]. The influence of substitution at the 2-, 4- and 6- positions on the protonation of *s*-triazines by Ca–montmorillonite was investigated [104].

The nitro group, which acts as a base, is an important component of many hazardous pollutants. Inside the interlayer space of air-dried smectite films nitrobenzene and its derivatives are coordinated to the metallic cations through water bridges or directly. When the films were thermally dehydrated, the following configurations involving the nitro group bondings were identified by thermo–IR–spectroscopy [26, 31]:

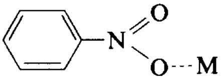
A



B



C



The herbicide nisulam (4-nitrobenzenesulfonylmethylcarbamate) is sorbed to montmorillonite at room temperature by linking the NO_2 group to the exchangeable cations through water bridges. One oxygen of the nitro group is involved in this coordination. The decomposition of the complex to 4-nitrobenzenesulfonamide begins at 75°C but is completed at 90°C [105].

The adsorption of the organophosphorus insecticide parathion (the diethylthionophosphoric acid ester of *p*-nitrophenol) by montmorillonite saturated with different cations has been investigated by thermo–IR–spectroscopy [106].

Both functional groups of parathion, NO_2 and P=S, interact with the clay. The nitro group in parathion is less basic than in nitrobenzene or in *p*-nitrophenol. In air-dried films they all behave similarly, being involved in hydrogen bonding with water associated with the cations. Unlike nitrobenzene and nitrophenol, with which both oxygens of the NO_2 group were involved in this interaction, with parathion only one oxygen is H-bonded to the clay. In air-dried films, only in Mg- and Al-clays is the P=S group bound to the metallic cation through a water bridge. With other cations no interaction between this group and the cation was observed at room temperature.

In dehydrated clay–parathion complexes of monovalent cations there is direct interaction between the metallic cation and the organic molecule. Both nitro-stretching bands shifted to lower frequencies, indicating that both oxygens were involved in the bonding. With divalent cations heated under vacuum, the frequencies for the NO_2 group were similar to those of free parathion. This suggests that no interaction occurred between the cations and the nitro group. At the same time the P=S band shifted to lower frequencies, indicating direct interaction between the P=S group and the divalent cations.

The adsorption of the organophosphorus pesticide "phosdrin" by montmorillonite saturated with different cations has been investigated by thermo-IR-spectroscopy [107]. Two types of complex were identified, with basal spacings of 1.605 and 2.006 nm. The complex formed depended on the hydration status and the interlayer cation of the sample, the nature of the solvent, and the concentration of phosdrin. The location of the P=O vibration shifted from 1275 cm^{-1} in the spectrum of neat phosdrin to lower frequencies (1250–1270 cm^{-1}) which were dependent on the exchangeable cations. These locations did not change when the samples were thermally dehydrated, indicating that at room temperature and after dehydration the P=O group was directly coordinated to the cation. The location of the C=O vibration, on the other hand, was changed by thermal dehydration of the samples. In the spectra which were recorded at room temperature, this band appeared at 1710 cm^{-1} with all exchangeable cations. After thermal dehydration this band shifted to lower frequencies (1675–1700 cm^{-1}) which were dependent on the exchangeable cations. This thermal effect indicates that at room temperature the C=O group is coordinated to the cation through a water bridge. After the dehydration the C=O group became directly coordinated to the cation.

11. Conclusions

This paper shows that thermo-IR-spectroscopy can be successfully used for the determination of the fine structure of organo-clay complexes. Most of the examples described in the article concerned small organic molecules. Large and complicated organic hazardous pollutants can be successfully studied by the same technique.

Acknowledgments

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