STUDY OF THE ADSORPTION OF ORGANIC MOLECULES ON CLAY MINERALS BY
DIFFERENTIAL THERMAL ANALYSIS

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ABSTRACT

DTA was adapted to study the types of associations between water mole-
cules, exchangeable metallic cations and organic molecules or ions formed
on clay surfaces. Comparison between curves recorded in the absence or
presence of air show that in the latter case strong diagnostic exothermic
peaks are obtained and the analysis is more sensitive for identification
of the different associations. The location of the peaks serves to differen-
tiate between adsorbed and non-adsorbed organic matter, a neutral free
organic molecule, cationic organic matter or a neutral molecule coordinated
to transition metal. DTA study of the adsorption of aliphatic and aromatic
amines by montmorillonite is described in detail, in order to demonstrate
how this technique is applicable for the study of surface reactions.

INTRODUCTION

The application of DTA as a tool for the study of the adsorption of
water by different colloidal and surface active materials is well known.
Recently it was shown that DTA and DSC can also be useful for the identifica-
tion of different types of hydroxyl groups on surfaces of goethite [1]. In
the past twenty years thermal analysis was adapted to study the types of
associations between water, metallic cations and organic molecules or ions on
clay surfaces. The methods which were employed in our laboratory included
DTA, thermogravimetry and IR spectroscopy of thermally treated organo-clay
complexes. The present communication will demonstrate the possible contribu-
tion of DTA to the study of the adsorption of organic materials by clay
minerals.

DTA of organo-clay complexes

Although DTA has been very widely used in the study of clay minerals
[2], it has been applied relatively very little to the study of adsorption
of organic materials by clay minerals. Already in 1949, Jordan [3] demonstra-
ted that DTA curves of amine treated montmorillonite can give useful informa-
tion on the effect of the adsorbed organic molecule on the hydration of the
clay. These curves show a progressive decrease in the height of the low-
temperature endothermic peak with an increase in the size of the aliphatic
chain. This endothermic peak characterizes the thermal loss of interlayer
water and it may be concluded that the adsorption of amines is associated
with increasing hydrophobic character of the clay surface and the loss of
adsorbed water. Water-loss increases with the size of the aliphatic chain.

DTA curves of organic substances show exothermic and endothermic peaks which are principally associated with combustion, decomposition, dehydration, sublimation, vaporization, fusion and solid-state transitions [4]. Since the adsorption process of organic materials by clay minerals will have an influence on the enthalpies as well as on the activation energies of the reactions that produce endothermic or exothermic peaks, it is to be expected that adsorption of the organic molecules by any sorbent will lead to different DTA curves from those recorded before the adsorption. Using this technique together with spectroscopic and potentiometric methods, enables one to obtain information about the interactions which occur during the adsorption of the organic matter by the clay mineral. The data were obtained mostly for minerals of the smectite group, especially for montmorillonite, and will be dealt with in the present paper. Very little DTA work has been done on the adsorption of organic materials by other minerals. DTA data for organomontmorillonite complexes was reviewed in 1957 by Green-Kelly [5]. No comprehensive review has been published since.

When DTA is carried out in air atmosphere, the adsorbed organic material is oxidized, giving rise to intensive exothermic peaks. On the other hand, in inert atmosphere weak endothermic peaks are observed, due to pyrolysis and liberation of the organic material. Eltantawey [6] recorded DTA curves of several organoclay complexes in nitrogen, oxygen and air. Since the oxidation reaction was very strong and dominated the resulting curve, he concluded that only very little information could be obtained from such curves. On the other hand, it will be shown in the present communication that because of the high intensities of the exothermic peaks, it is more convenient to apply exothermic reactions for the study of the adsorption mechanism. DTA shows that oxidation of most interlayer organic cations proceeds in two stages, in the range 200-350°C and 500-750°C respectively. The peak temperatures of the exotherms depend on the type of clay mineral on one hand, and on the organic compound on the other hand. DTA curves of organic complexes of smectites were used to distinguish between the different minerals [7-9]. Allaway [7] used the piperidine complex for this purpose. During the recording of DTA curves in an air atmosphere he obtained the following diagnostic exothermic peaks, for montmorillonite, beidelite and nontronite at 700, 600 and 400-500°C, respectively. Another exothermic reaction (a single peak or a doublet) occurs in the temperature range 200-320°C. On the basis of the results of IR absorption studies, a sooty residue containing some carbon groups is left after the decomposition of the piperidine during the first stage of the oxidation. This residue disappears only after the final exothermic peak [9].

In a comprehensive study of the DTA of twelve different cyclohexylammonium smectites a correlation was found between features of the DTA, Ir and X-ray patterns but not between the amounts of cyclohexylammonium exchanged [10]. The nature of the smectite mineral determines the types of bonding in which the interlayer cyclohexylammonium ion takes part. Different types of bonding are obtained in the different smectites which may result from differences in hydrophilic properties of the minerals. These properties depend on: (a) the electric charge of the silicate layer, (b) the exchangeable metallic cation which initially occupies the exchange position of the clay and of which traces remain after the preparation of the ammonium-smectite, and (c) the surface acidity of the oxygen plane of the silicate layer [11]. Oxidation of interlayer organic material occurs in two stages, at 285-340°C and at 530-680°C. Whenever a single exothermic peak appears in the lower temperature region, a single peak also occurs at a temperature in the higher range. Conversely, when two peaks appear at lower temperatures, two are also observed at higher temperatures. A reasonable correlation is obtained between the temperatures of the two stages of reactions. If the first takes place below 310°C the second occurs below 600°C. If the first exotherm is observed above 310°C, the second occurs above 600°C. The two sets of peaks, 275-305°C and 530-600°C on the one hand, and 310-355°C and 600-680°C on the other hand, will be denoted as Group A and Group B respectively. The present results are most

readily interpreted if it is postulated that various forces bind cyclohexyl-ammonium ions in the clay interlayers. Some types of interaction give rise to lower temperature exotherms (Group A), NH_3^+ bending frequencies of 1493 and 1499 cm^{-1} in the absorption spectrum and an interlayer spacing of 1.47 - 1.48nm. Others cause higher temperature exotherms (group B), NH_3^+ bending frequencies of 1503-1508cm^{-1} in the IR absorption spectrum and a basal spacing of about 1.38nm. In some of the samples several types of bonding occur simultaneously. The differences between the various types of interaction have not yet been clarified.

When organic ammonium smectite is exposed to excess amine, the latter is adsorbed and a change in the character of bonding of the ammonium cation to the clay mineral is obtained [12,13]. Various types of structure can occur, e.g. $(R-NH_2-H-NH_2-R)^+$ or $(R-NH_2-H_3O-NH_2-R)^+$ complex cations. The poorly defined IR spectrum and the absence of coherent x-ray scattering indicate that the material is non-homogeneous and comprises various ammonium-amine associations. The DTA curves of the samples are correspondingly complex, showing a mutilplicity of small exothermic peaks and a very strong base-line drift. In conclusion, a change in the character of bonding of a certain organic species to a smectite mineral leads to a new DTA curve.

The Exothermic Peaks

Two basically different theories have been proposed to account for the low and high temperature exothermic peaks on DTA curves of organo-clay complexes. The first theory was proposed by Allaway [7] and Bradley and Grim [14]. They assumed that the peaks were entirely due to the oxidation of interlayer material, occurring in successive stages. Allaway inferred complete oxidation of hydrogen at low temperatures, leaving a graphite layer, which is burnt off only on dehydroxylation of the clay. Bradley and Grim, however, postulated the initial formation of "petroleum coke" composed largely of carbon with some hydrogen which is subsequently oxidized. The second theory, proposed by Ramachandran, Kacker, Patwardham and Garg [8] attributes the low and high temperature exothermic peaks to oxidation of organic molecules attached to broken bonds and to silicate layers, respectively. Some experimental data show that the latter theory is not always valid: (a) there are many sorbed organic molecules which are proved to be located in the interlayer space of the montmorillonite and give only a single exothermic peak. For example, DTA curves of copper montmorillonite saturated with ethylenediamine or 1.3 propylenediamine, with amine copper ratios of 1 (curves will be shown later) do not show high temperature exothermic peaks. Since it has been established that these complexes contain amine in the interlayer space [15] it is evident that high temperature exothermic peaks are not exclusively due to oxidation of interlayer organic material. Also, Fe-montmorillonite saturated with pyrocatechol, gives a single exothermic peak at 330°C [16]. (b) Fig. 1 shows DTA curves of copper montmorillonite saturated with ethylenediamine (En) with amine: Cu molar ratio of 2, diluted with alumina in proportions of 1:30 to 15:30. The DTA were carried out in the presence of air. Combustion commenced at the same temperature, whatever the dilution, but the second exothermic peak shifted to higher temperatures on increasing the concentration of the organo-clay. The peak at 500°C, which first appeared as a slight hump at the 5:30 clay to alumina ratio, increased considerably at the expense of the lower temperature peaks when this ratio was raised to 15:30 [17]. When more oxygen was circulated through the heating cell during the thermal treatment, the first exothermic peak increased whereas the second became very small. Samples were removed from the heating cells after they had been heated to 500°C. When the thermal treatment was carried out with pure oxygen circulating through the heating cell the samples became light grey in color. On the other hand, when the thermal treatment was carried out in air the sample became black, indicating incomplete combustion.

Allaway [7] is of the opinion that the position of the high temperature exothermic peak depends on the dehydroxylation temperature of the clay. This
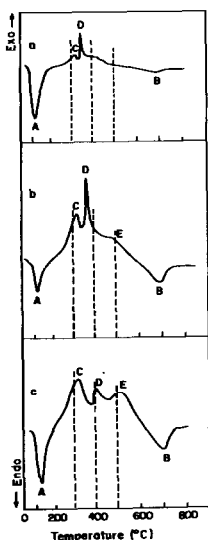
peak corresponds to the final loss of the carbonaceous material, and according to Allaway, the opening up of the clay structure on dehydroxylation enables the organic residue to be oxidized completely. Our results do not confirm this contention. Moreover, there are many sorbed organic molecules and cations giving DTA curves with the last exothermic peaks at temperatures below that of the dehydroxylation reaction. For example, diethylenetriammonium-, triethylenetetraammonium- and tetraethylenepentammonium-montmorillonite, having the final exothermic peaks at 610, 615, and 585°C, respectively (Fig. 2). However, the oxidation reaction is not complete at the temperature of the exothermic peak, and continues at higher temperatures. Consequently, the endothermic peak of dehydroxylation at 680°C is verv small, especially for triethylenetetramine and tetraethylenepentamine [18,19]. In many cases the dehydroxylation peak is masked by the exothermic reaction.

In order to explain the above phenomena, the following mechanism was suggested for the occurrence of two distinct stages during the exothermic oxidation reaction [17]. Combustion commences at a temperature which is independent of the amount of material present, but is dependent on the activation energy of the combustion reaction. The clay mineral serves as a positive or negative catalyst to the combustion reaction and the peak temperatures should be affected by the type of bonding reaction which is formed between the sorbate and the sorbent. If the total concentration of the
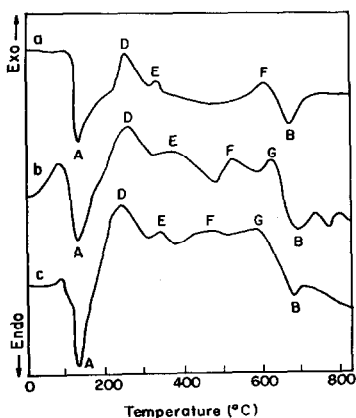
Fig. 1:

DTA curves of [CuEn$_2$]-Mont diluted with calcined alumina in the ratio (a) 1:30; (b) 5:30; (c) 15:30, recorded in air on equipment supplied by Stone (Heating rate 10°C/min).

Fig. 2:

DTA curves of (a) diethylenetriammonium-; (b) triethylenetetrammonium- and (c) tetraethylenepentammonium-montmorillonite, (Wyoming-bentonite), recorded in air, using a thermal system which was described in Ref. [32]. Samples were diluted 1:1 with calcined alumina.
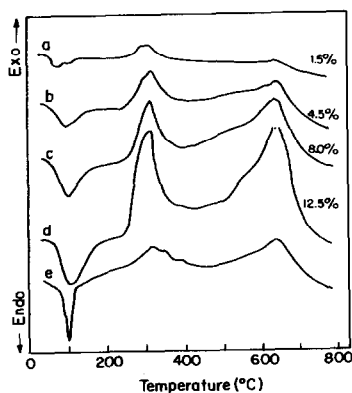
Fig. 3:

DTA curves of (a-d) cyclohexylammonium montmorillonite (Camp Berteau) diluted with calcined alumina and (e) cyclohexylammonium-cyclohexylamine-montmorillonite, recorded in air using a Stone instrument (heating rate 10°C/min).

organic material in the DTA cell is low, oxidation will be complete at a relatively low temperature. If the concentration is high, the amount of oxygen in the system is insufficient for complete combustion. Partial oxidation of hydrogen to water and of carbon to "petroleum coke" occurs at the first stage of the exothermic reaction. Oxidation can be completed only at the higher temperature. The combustion temperature of the petroleum coke depends on the degree of cross-linking of this complex material and on the size of the polymeric species from which it is composed. These are affected by (a) the composition, size and shape of the parent organic molecule and (b) the type of clay mineral, which acts as a catalyst.

If the above reaction mechanism is correct, then the absolute concentration of the organic matter in the DTA cell should affect the DTA curves and in some cases wrong interpretations can be made. To avoid this error, it is suggested to dilute the organic-clays with inert material and to record curves in several clay concentrations, in order to be able to differentiate between the effects of absolute concentration of the organic material in the heating cell and the intrinsic thermal properties of the organo-clay complex. Increasing the concentration of the clay sample profoundly influences the nature of the DTA curves. Fig. 3 shows DTA curves of cyclohexylammonium-montmorillonite from Camp Berteau. The figure demonstrates the effect of clay concentration on the DTA curve when the clay is diluted with calcined alumina. At low concentrations the exothermic peak corresponding to the second oxidation stage is less intense, than that corresponding to the first oxidation stage. It increases with increasing concentration until it becomes the dominant exothermic peak. Conversely, at high clay concentrations, some lower temperature exothermic effects are obscured by adjacent peaks. Some peaks cannot be detected unless the concentration is very low. Endothermic peaks are shifted to higher temperatures when the clay concentrations are increased. On the other hand, the positions of the maxima of exothermic peaks are not affected by changes in concentration, unless there are endothermic peaks in their vicinity [10].

The Mechanism of Adsorption of Organic Matter by Smectite Minerals

Adsorption of organic matter by smectite minerals is the process in which organic species (such as molecules or ions) are accumulated either in the interlayer space or on the broken bond surface of the mineral [11,20]. Adsorption results from the high activity of the solid surface. It involves either short-range chemical valence bonds, including coordination and H bonds and to some extent also π interactions, or long-range physical interactions through electrostatic or van der Waals forces.

Adsorption of cations: Organic cations may be adsorbed by smectite minerals through cation exchange reaction, in which the inorganic cation which is initially present in the clay mineral, is replaced by an organic cation. For example, if Na-montmorillonite is equilibrated with an aqueous solution of ethylammonium chloride, the following cation exchange reaction occurs:

$$C_2H_5NH_3Cl(aq) \ + \ M\text{-Mont}(s) \ \rightleftarrows \ MCl(aq) + C_2H_5NH_3\text{-Mont}(s)$$
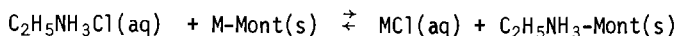
(where Mont is montmorillonite and M is an exchangeable cation). Organic cations in the interlayer space are also obtained by the protonation of adsorbed organic basic molecules. Due to the polar effect of exchangeable cations in the interlayer on the adsorbed water, the latter is very acidic and may donate protons to organic bases. For example, adsorbed ethylamine is protonated in the interlayer space as follows:

$$(C_2H_5NH_2...H\underset{\underset{H}{|}}{-}O-M^{m+})\text{-Mont} \quad \rightarrow \quad (C_2H_5NH_3^+...[(OH)M]^{(m-1)+})\text{-Mont}$$

With increasing size of the adsorbed cation, the contribution of van der Waals forces to the adsorption process becomes important. In addition to the long-range electrostatic forces in which the cation is attracted to the clay surface,

short-range interactions such as H-bonds occur between organic cations and residual water or the oxygen plane of the silicate layers [12, 13, 21, 22]. With aromatic cations π interaction may occur between the aromatic ring and the oxygen plane [23]. DTA curves of adsorbed organic cations were described in the first sections of the present communication.
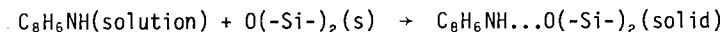
Adsorption of anions: Under certain conditions anions are adsorbed on the broken-bond surface. In the presence of polyvalent metallic cations, anions are adsorbed due to short-range interaction of the basic anions with the acidic metallic cations. Anions may be sorbed from aqueous solutions by clay minerals if they are able to form stable coordination species that are positively charged [17,24]. Adsorbed anions can be obtained in the interlayer space of smectites from the ionic dissociation of adsorbed organic acids. The ratio between the two varieties of the adsorbed organic material depends on the nature of the exchangeable metallic cation. Polyvalent cations stabilize the anionic variety whereas Cs stabilizes the acidic variety [25]. DTA of adsorbed organic anions is now under investigation in our laboratory.

Adsorption of organic polar molecules: A central role in the adsorption process of organic polar molecules is played by the nature of the exchangeable cation and the hydration state of the clay. The polarizing power of the cation on its associated water molecules, determines the acidity of the clay surface. Sorbed hydrated cations are better proton donors than hydrated cations in an aqueous solution, since the dielectric constant of the solvent in the inter-layer space is lower than that in the bulk solution [26]. Adsorption may occur via the mechanism of proton transfer or via the formation of coordination cations.
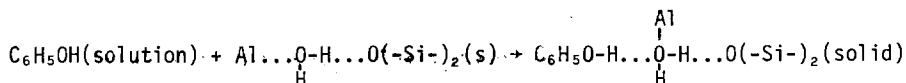
1) <u>Adsorption via the mechanism of proton transfer</u>: Strong bases are protonated during adsorption, yielding positive ions. The extent of this reaction depends on the basic strength of the organic compounds and the polarizability of the metallic cation [27]. The protonation of aliphatic amine in the interlayer of smectite was formulated above. With decreasing basic strength of the organic compounds or decreasing acidic strength of exchangeable metallic cations, association species are obtained with hydrogen bondings, wherein a water mole-cule acts as a proton donor. This can be illustrated by the adsorption of aro-matic amines which are weak bases, such as aniline [28,29], as follows:

$$C_6H_5NH_2 + H_2O...M\text{-Mont} \rightarrow C_6H_5\overset{H}{\underset{H}{N}}...H\overset{H}{O}...M\text{-Mont}$$
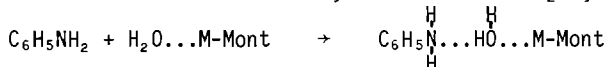
where M is an exchangeable metallic cation and Mont is montmorillonite. In this adsorption reaction the nitrogen atom serves as the nucleophilic site. If the adsorbed molecule is a proton donor it may react with two different surface sites: (i) basic sites in the oxygen plane and (ii) negative poles of water molecules in the hydration spheres of cations. These can be illustrated by the sorption of indoles, which are very weak acids, by Cs-montmorillonite [30], and by the sorption of phenol by Al-montmorillonite [31], which may be illustrated as follows:

$$C_8H_6NH(\text{solution}) + O(-Si-)_2(s) \rightarrow C_8H_6NH...O(-Si-)_2(\text{solid})$$

and

$$C_6H_5OH(\text{solution}) + Al...\overset{}{\underset{H}{O}}-H...O(-Si-)_2(s) \rightarrow C_6H_5O-H...\overset{Al}{\underset{H}{O}}-H...O(-Si-)_2(\text{solid})$$

In the following sections it will be demonstrated how DTA is applied to differ-entiate between adsorbed and free organic matter, as well as between ionic and molecular adsorption.

2) <u>Adsorption via the formation of coordination ions</u>: Transition metals in the interlayer space may form stable coordination complexes with electron pair donors such as amines [18,19,32,33,34]. With di- and polyamines, which may coor-dinate to form 5- or 6- member chelates, complexes stable to hydrolysis are

obtained in the interlayer space. Coordination compounds of monoamines are un-
stable and are easily hydrolyzed by water. They are obtained only under dry
conditions. DTA data on adsorption reactions were obtained mostly for amines
and will be dealt with in the following sections. The locations of the exotherm-
ic peaks are diagnostic and may serve to identify adsorbed organic molecules,
coordinated to metallic cations and to differentiate them from adsorbed mole-
cules which are not coordinated to metallic cations. It will be demonstrated
how DTA is useful to differentiate between the various associations which are
formed between adsorbed organic species, water molecules and exchangeable
cations, which occur in the interlayer space of montmorillonite. It should be
mentioned that DTA is often used for the study of non-adsorbed coordination
compounds of transition metals with organic bases [34].

ADSORPTION OF ALIPHATIC AMINES BY MONTMORILLONITE

Potentiometric titration

A quantitative study of the adsorption of amines by monoionic montmorillo-
nites from aqueous systems was carried out by potentiometric titration [18,19,
32,33,35]. Aqueous suspensions of the clay samples were titrated potentiometric-
ally with solutions of various amines. Na, Mg and Ca clays gave an immediate
jump in pH on addition of small quantities of the amine solution. Clays with
transition metal cations which can form complexes with amines, showed at the
beginning of the titrations practically no changes, and only after larger
additions of the amine solution did the pH jump, indicating a distinct inflec-
tion point. Before reaching the inflection point, the supernatant liquid does
not show any remaining amine, proving that it has all been adsorbed by the clay.
Three different types of titration curves have been observed for clays
saturated with transition metal cations.
  (1) A single very sharp inflection-point is obtained. Free amine can be
      detected in the supernatant immediately after reaching the inflection-
      point.
  (2) Two inflection-points are obtained. The second inflection-point is
      reached after an addition of a little more than twice the quantity
      which corresponds to the first inflection-point. Free amine is detected
      in the supernatant solution only after the second inflection-point.
  (3) A single inflection-point is obtained which is not sharp. The pH
      increases gradually after this inflection-point, indicating further
      adsorption of the amine by the clay, until the final pH of the amine
      solution is reached. Free amine is detected in the supernatant solution
      only when the latter stage of the titration is reached.
As will be shown later, there is a correlation between the potentiometric
titration and the DTA curves of the organo-clay complexes. DTA curves of clay
samples which were separated from the system at different stages of the poten-
tiometric titration will be described and discussed.

DTA of monoionic montmorillonites treated with ethylenediamine

The thermal behaviour of montmorillonite treated with various amounts of
ethylenediamine will be described in detail, in order to demonstrate the effect
of complex formation on the DTA curves of the samples. As will be shown, the
exothermic peaks are generally diagnostic rather than the endothermic peaks and
the former will therefore be emphasized.

1. Natural montmorillonite-ethylenediamine (ethylenediammonium montmorillonite):
When amines are adsorbed by montmorillonite either from organic solvents or from
concentrated aqueous solutions (e.g., 50v%) ammonium cations in addition to
neutral amine molecules are detected in the interlayer space [36,37]. It was
shown by IR spectroscopy that neutral amine molecules, but not ammonium cations
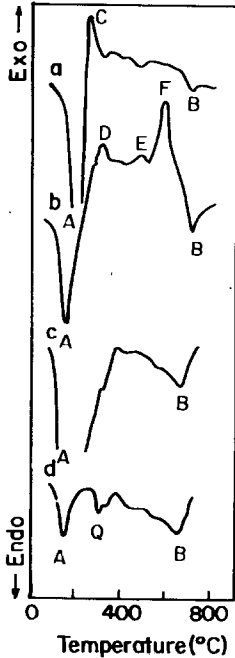can be leached out by repeated washings with water.

Fig. 4 shows the DTA curves of natural montmorillonite saturated with ethylenediamine, carried out in air and in an inert atmosphere (argon). Curves recorded in air show exothermic peaks, in addition to the endothermic peaks A and B which are diagnostic for dehydration and dehydroxylation of the montmorillonite. On the other hand, curves recorded in an inert atmosphere show only endothermic peaks. The suppression of the exothermic peaks in the inert atmosphere supports the suggestion that they correspond to the oxidation of the organic material. Dehydroxylation of the clay (peak B) in the inert atmosphere occurred at a lower temperature than in air, 620-640°C instead of 680-700°C. This is caused by the constant stream of gas, which removes the water liberated and thus reduces the temperature of dehydroxylation.

Considerable differences appear between washed and unwashed samples. DTA curves of the unwashed samples either in air or in the inert atmosphere, show a large endothermic peak at 165°C. This may be attributed to the vaporization of molecular amines at relatively low temperature. Peak A of washed samples is located at 125°C, which is the normal location of this peak in the untreated clay. According to the IR spectrum, amines are present in washed samples mainly in the form of ammonium cations, and to some extent also as ammonium-amine cations. The DTA curves of washed samples show three exothermic peaks, assigned in the figure as D, F and G, located at 290, 480 and 550°C respectively.

On the other hand, the exothermic reaction starts at a lower temperature in the DTA curves of unwashed samples. An exothermic peak is located at 220°C. This peak is regarded to be diagnostic for the presence of free amine. Other exothermic peaks are broad and not well defined, although they seem to be similar to those of the washed sample.
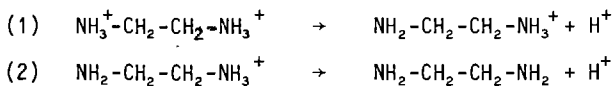

Fig. 4:

DTA curves of Wyoming bentonite (natural montmorillonite) saturated with ethylenediamine, (a) and (c) unwashed, (b) and (d) washed; (e) and (b) recorded in air; (c) and (d) recorded in inert atmosphere (argon).

In the inert atmosphere there is a series of endothermic peaks in the range 250-600°C. The principal peak is located at 280°C (compare to peak D in the DTA curve of samples recorded in air). After the liberation of molecular amine only ionic amine remains in the interlayer space and at elevated temperatures the following thermal deprotonation reaction is thought to occur in two stages as follows:

$$(1) \quad NH_3^+-CH_2-CH_2-NH_3^+ \quad \rightarrow \quad NH_2-CH_2-CH_2-NH_3^+ + H^+$$

$$(2) \quad NH_2-CH_2-CH_2-NH_3^+ \quad \rightarrow \quad NH_2-CH_2-CH_2-NH_2 + H^+$$

Liberation of amine will occur only at the second stage.

It is possible that the different peaks correspond to different binding

energies of various exchange positions or to stages in the decomposition of the diammonium cation. Other pyrolytic reactions involving the ammonium cation may also be responsible for the several endothermic peaks.

2. Sodium, magnesium and calcium-montmorillonite: When these monoionic mont-morillonites are equilibrated with dilute aqueous solutions of ethylenediamine (∿0.02M) only negligible amounts of the amine are adsorbed by the clay. For example, Mg-montmorillonite which was equilibrated with a solution containing 140mM amine per 100g clay (pH of suspension 9.3) adsorbs ∿5mM amine per 100g clay. The adsorption takes place by the mechanism of cation exchange. IR spectroscopy confirms the presence of ammonium cation in the interlayer space of the various montmorillonites. The low degree of cation exchange is due to the low concentration of the ammonium cation in the highly alkaline aqueous solution used in the present equilibrium systems.
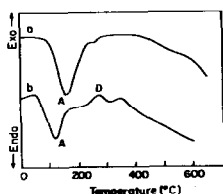

Fig. 5:

DTA curves of Mg-montmorillonite equilibrated with dilute aqueous solutions of ethylenediamine, (a) 60mM amine; (b) 140mM amine per 100g clay in equilibrium system. Ammonium content in (a) traces in (b) <5mM per 100g clay.

Representative DTA curves of Mg-montmorillonite equilibrated with aqueous dilute solutions of ethylenediamine are shown in Fig. 5. Only small exothermic peaks are observed at 280 and 330°C. The difference between these curves and those of Fig. 4 should be noted. In both cases the ammonium cation is the principal organic species which is present in the interlayer space. Nevertheless, the degree of saturation of the clay determines the shape of the DTA curve. The exothermic reaction is completed at a relatively low temperature and peaks E and F are not detected. A similar DTA curve was recorded for washed samples of the natural montmorillonite treated with ethylenediamine, after it had been highly diluted with alumina. It may therefore be concluded that when small amounts of ammonium cation are involved, peak D alone can be considered as the indicator for the presence of this species.

3. Copper and zinc-montmorillonite: When these clays are potentiometrically titrated by ethylenediamine, a titration curve of type I is obtained. The amine is totally adsorbed by the clay up to the amine:metal molar ratio of 2. The color of the pale blue copper clay changes first to deep blue and then to violet due to the formation of the coordination cations $[CuEn]^{2+}$ and $[CuEn_2]^{2+}$ in the interlayer (En = ethylenediamine), in which the neutral amine molecules are directly coordinated to the copper cations. In the presence of excess of amine the following cation exchange reaction occurs to a small extent.

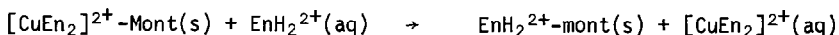$$[CuEn_2]^{2+}-Mont(s) + EnH_2^{2+}(aq) \rightarrow EnH_2^{2+}-mont(s) + [CuEn_2]^{2+}(aq)$$

Fig. 6 shows DTA curves of samples of copper montmorillonite equilibrated with various amounts of ethylenediamine. The exchange capacity of the montmorillonite was 76 meq per 100g (or 38mM Cu^{2+} per 100g clay). The endothermic peaks A and B at 130°C and 700°C respectively are characteristic for the dehydration and dehydroxylation of the clay. Exothermic peaks K and M appear at 320 and 500°C. The latter increases with the amount of amine. They are indicative for amine coordinated to copper. Peak L is observed in DTA curves of untreated Cu-montmorillonite. It may be due to the oxidation of the traces of organic matter which are originally present in the clay. When the molar ratio amine: Cu is above 2, an additional exothermic peak D appears at 280°C, which is
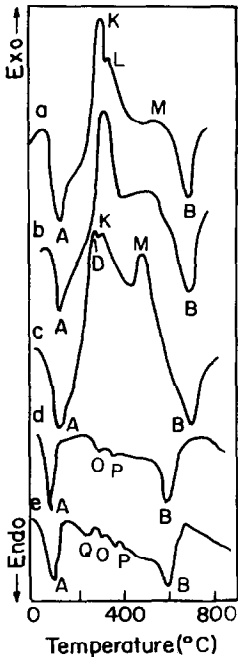
Fig. 6:
DTA curves of Cu-montmorill-
onite equilibrated with di-
lute aqueous solutions of
ethylenediamine (a) 20mM
amine, (b) and (d) 60mM
amine, (c) and (e) 100mM
amine per 100g clay in
equilibrium system; (a),
(b) and (c) recorded in air,
(d) and (e) recorded in inert
atmosphere. CEC of Cu-mont-
morillonite is 38mM Cu per
100g clay.

indicative for ethylenediammonium montmorillonite.
No additional peaks are observed when the ratio
amine:Cu is above 3. As will be shown later, this
may serve as proof that no complex is formed in
the interlayer space in which 3 molecules of
ethylenediamine are coordinated to one copper ion.

In the inert atmosphere the complex is char-
acterized by two endothermic peaks O and P at
325 and 380°C respectively. An additional peak
observed in DTA curves of samples collected after
the inflection-point at 280°C is due to the
presence of small amounts of ammonium cations
(compare to the curves obtained for ethyelenedi-
ammonium, Fig. 4).

The DTA curves of samples of Zn-montmorillo-
nite saturated with different amounts of the
amine (Fig. 7) are similar to those obtained for
Cu-montmorillonite. As long as the amine:Zn
molar ratio is less than 2 the curves show a
single peak K at 325°C, diagnostic for the coor-
dinated ethylenediamine. When this ratio is above
2, an additional exothermic peak D appears at
280°C which may characterize the presence of
ammonium cation.

4. Nickel and cadmium-montmorillonite: When
these clays are potentiometrically titrated by
ethylenediamine, a titration curve of type III
is obtained. The amine is totally adsorbed by the
clay up to the amine:metal molar ratio of 3,
although a slight pH jump is observed when this
ratio is equal to 2. Following this observation
it was postulated that the complex cations
$[NiEn_2]^{2+}$ and $[CdEn_2]^{2+}$ are stable, whereas the
cations $[NiEn_3]^{2+}$ and $[CdEn_3]^{2+}$ are unstable in
the interlayer space of montmorillonite.

Fig. 7 shows DTA curves of samples of Ni-
montmorillonite saturated with various amounts of
ethylenediamine. An exothermic peak is located at
350°C for samples with small amounts of amine,
shifts to 400°C when the amine:Ni molar ratio
approaches 3. An additional peak located at 250°C
appears when the amine:Ni ratio exceeds 2. These
two peaks represent the complex ions $[NiEn_2]^{2+}$
and $[NiEn_3]^{2+}$ respectively. When the amine:Ni
ratio exceeds 3, a new sharp peak C appears at
220°C which is indicative for free amine. The
appearance of the latter peak only when the amine
Ni ratio is above 3 may indicate complexation of
the amine up to this ratio.

Cadmium montmorillonite shows a single exo-
thermic peak at 350°C up to amine:Cd molar ratio
of 3. This peak is diagnostic for coordinated
amine. When the molar ratio is above 3 an addi-
tional exothermic peak C appears at 230°C which may characterize free amine in
the interlayer space.

DTA of copper-montmorillonite treated with 1,3 propylenediamine

The titration of Cu-montmorillonite by this amine gives a type II curve. The
first and second inflection points appear, as the molar ratio amine:Cu reaches
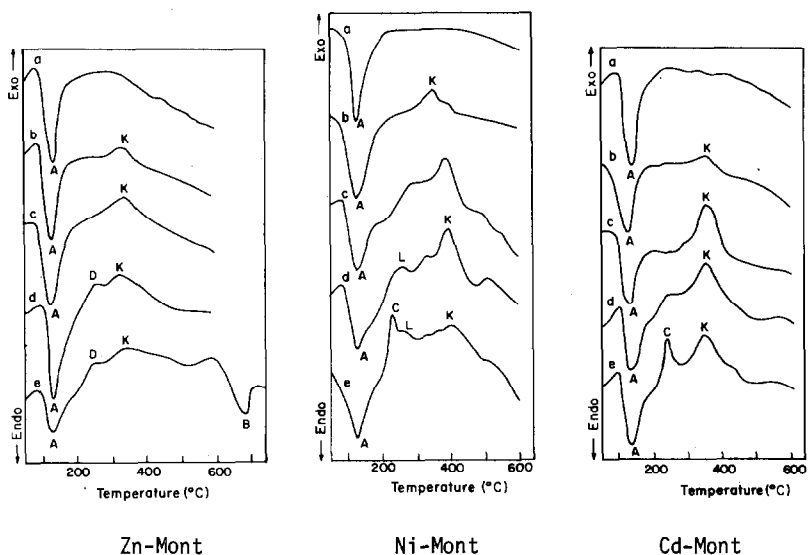
Zn-Mont   Ni-Mont   Cd-Mont

Fig. 7:

DTA curves of Zn-, Ni- and Cd-montmorillonite equilibrated with dilute aqueous solutions of ethylenediamine (a) 0 mM amine, (b) 20mM amine, (c) 60mM amine, (d) 100mM amine, (e) 140mM amine per 100g clay in equilibrium system, recorded in air. CEC of montmorillonites is 38mM Zn, Ni or Cd per 100g clay.
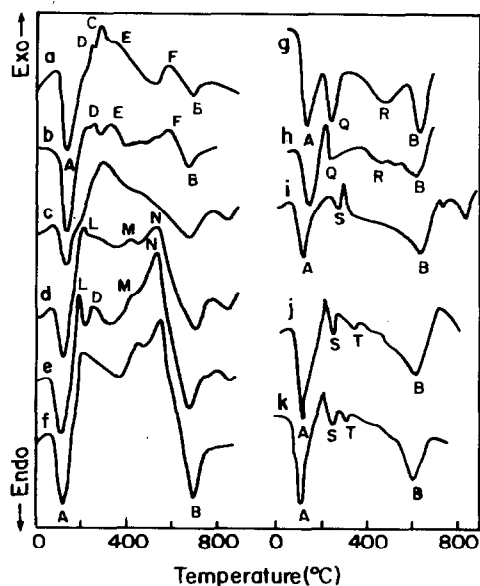

Fig. 8:

DTA curves (a), (b), (g) and (h) of natural montmorillonite saturated with 1.3 propylenediamine, and (c)-(f) and (i)-(k) of Cu-montmorillonite equilibrated with dilute aqueous solutions of 1.3 propylenediamine, (c) and (i) 20mM amine; (d) and (j) 60mM amine; (e), (f) and (k) 100mM amine per 100g clay. Samples (a), (f) and (g) are unwashed. Other samples are washed. Curves (a)-(f) recorded in air. Curves (g)-(k) recorded in inert atmosphere. CEC of Cu-montmorillonite is 38mM Cu per 100g clay.

0.9 and 2 respectively. Fig. 8 shows DTA curves of propylenediammonium montmorillonite and of Cu montmorillonite saturated with different amounts of amine, recorded in air and in an inert atmosphere. Liberation of free amine from unwashed and washed propylenediammonium montmorillonite occurs at 250°C, and is represented by an endothermic peak Q in the curves recorded in inert atmosphere. An additional endothermic peak R is observed in inert atmosphere at 450-460°C. Exothermic peaks in the curve of washed ammonium clay recorded in air are located at 250°C, 320 and 570°C. An additional peak C appears in the curve of unwashed samples at 280°C. This strong peak overlaps with exothermic peaks of the ammonium, making it difficult to verify the presence of the ionic species together with free amine.

The DTA curves of Cu-montmorillonite treated with propylenediamine differ from those of propylenediammonium clay. In curves recorded in inert atmosphere, the first endothermic peak of the Cu clay characterizing the liberation of the amine, is located at a higher temperature (285°C instead of 205°C for the ammonium clay). In general, DTA curves of copper-diamine-clay complexes containing an excess of amine recorded in inert atmosphere showed additional endothermic peaks. In the case of propylenediamine, an additional peak at 360°C was observed as soon as the first inflection-point was passed (peak T) and no further peaks appeared beyond the second inflection-point, but the latter shifted to 330°C.

More striking effects are observed when DTA curves are recorded in air. The curves obtained for samples with less amine than that required to reach the first inflection-point showed only one exothermic peak K at 300°C. When the first inflection-point was exceeded this peak gradually disappeared, being replaced by three peaks L, M and N at 200, 450 and 500°C respectively. This drastic change in the DTA curve is assumed to be associated with drastic structural changes as a result of the transformation from $[CuPen]^{2+}$ to $[CuPen_2]^{2+}$ (Pen = propylenediamine) in the interlayer space of the mineral. After the second inflection-point an additional exothermic peak is detected at 250°C. It may represent small amounts of propylenediammonium. The unwashed sample may contain free amine as well, giving rise to minor differences between curves of washed and unwashed samples, collected after the second inflection-point.

DTA of copper-montmorillonite treated with monoamines

Adsorption of alkyl monoamines by Cu-montmorillonite has been described [27,33,35,38,39]. When Cu-montmorillonite is potentiometrically titrated by aliphatic amines, a titration curve of type I is obtained. A pH jump is observed with amine:Cu molar ratios ranging from 1.26 to 1.52. The ratio of 2, so readily reached with many diamines, was never attained with monoamines. The amine is totally adsorbed by the Cu clay up to this ratio, but copper is not released into the solution. Only after the inflection-point are slight amounts of Cu^{2+} detected in the supernatant, probably due to cation exchange reaction. On the other hand, mono-amines are only slightly adsorbed by Na- or Mg-montmorillonite from dilute aqueous solutions, probably by cation exchange mechanism.

Copper complexes of monoamines are unstable. From IR spectroscopy it was concluded that the amine adsorbed by Cu-montmorillonite is protonated in the interlayer space, resulting in the formation of alkylammonium cations. In this respect the monoamines differ from the di- and polyamines.

Fig. 9 shows DTA curves obtained for (a) hexylammonium montmorillonite, (b)Cu-montmorillonite after addition of insufficient amine to reach the inflection-point, and (c) after addition of amine in excess of that required to reach this point. More DTA examples are given in Table 1. Similarly to di- and polyamine complexes of Cu-montmorillonite previously described, monoamine complexes give rise to characteristic DTA curves which differ markedly from those of the ammonium clay in the absence of copper. In the latter, combustion of organic material, as reflected by the exothermic peaks, commences at a higher temperature and is more drawn out, frequently reducing or obscuring the characteristic
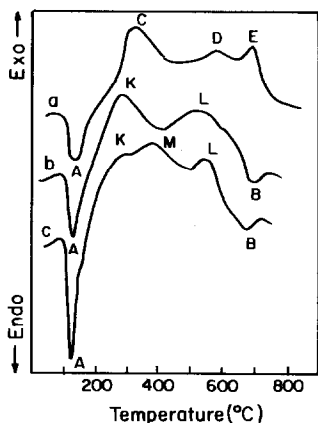
endothermic dehydroxylation peak of the
clay. In the presence of copper the peaks
are considerably sharper. Copper appears
to act as a combustion catalyst. DTA
curves of Cu samples with quantities of
amines exceeding the inflection-point,
resemble curves of samples with amine less
than the inflection-point, with one or
more additional exothermic peaks, indicat-
ing the appearance of new species, in add-
ition to those previously noted.
     The results of the DTA seem to con-
tradict the IR observations. One would
expect that the catalytic effect of Cu on
the combustion of the amine would be due
to some kind of coordination between Cu
and the amine. On the other hand, IR spectra do not show that the amine is co-
ordinated to the copper ion. Indeed, IR study shows that by the thermal dehy-
dration a complex ion is formed in the interlayer space [39] as follows:

$$([CuOH]^+ + H_3N^+R)Mont \rightarrow [CuNH_2R]^{2+}-Mont + HOH$$
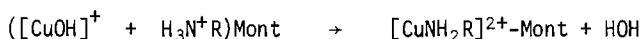
A similar reaction very probably occurs during the recording of the DTA curve.
     If the thermal analysis of Cu-monoamine-montmorillonite complex is com-
pared to the thermal analysis of ethylenediamine complexes one is surprised
that the alkyl ammonium cation in the DTA curve of Cu-montmorillonite does not
show the same peaks as those observed in the DTA curves of alkylammonium-mont-
morillonite whereas ethylenediammonium cation in Cu-montmorillonite shows the
same peak observed in the DTA curve of ethylenediammonium montmorillonite. We
believe that this is attributable to the fact that in Cu-En-montmorillonite
after the inflection-point all the copper ions are coordinated by two molecules
of ethylenediamine, whereby all the four coordination valencies of Cu are
occupied. In Cu-monoamine-montmorillonite, after the inflection-point less than
half of the coordination valencies of Cu are occupied by amino groups. During
the DTA run most of the alkylammonium cations which are present in the inter-
layer may become coordinated to Cu, and thereby the oxidation reactions will be
catalyzed by this metal.

DTA of montmorillonites treated with polyamines

     DTA curves of Cu-, Ni- and Hg-montmorillonite complexes of diethylenetri-
amine (dien), triethylenetetramine (trien) and tetraethylenepentamine (tepa)
have been described [18,19]. These polyamines form coordination complex cations
with transition metals in the interlayer. For most polyamines the curves are
compatible with the potentiometric titration and IR spectroscopic data. The lo-
cations of the exothermic peaks obtained for Cu-montmorillonite saturated with
the three polyamines are given in Table 1. With all polyamines the titrations
of Cu-montmorillonite had inflection-points at amine:Cu molar ratio of less
than 1. Namely, after the inflection-point not all the coordination valencies
of Cu are occupied by amino groups. By comparing peak temperatures recorded
with samples below and above the inflection-point it is obvious that the amine
present below this point is largely involved in complex formation.

TABLE 1. Exothermic peak maxima in DTA curves of natural (N) and
Cu-montmorillonite (Wyoming bentonite) treated with various amines
(Clay: alumina ratio in heating cell is 1)

Amine	Clay	Amine: Cu ratio	Peak temperature (°C)
Ammonia	N	--	330 m
Ammonia	Cu	1.2	275 s
Ammonia	Cu	2.5	275 s; 330 s
Methylamine	N	--	330 s; 575 s
Methylamine	Cu	1.2	265 s
Methylamine	Cu	2.5	265 s; 485 s
Ethylamine	N	--	260 s; 320 sh
Ethylamine	Cu	1.2	230 m; 285 m; 330 m
Ethylamine	Cu	2.5	230 m; 290 sh; 340 m; 400 w; 450 w
n-Propylamine	N	--	245 m; 350 s; 440 sh; 580 sh
n-Propylamine	Cu	1.2	230 s; 325 s
n-Propylamine	Cu	2.5	245 s; 350 s; 565 s
iso-Propylamine	N	--	340 s; 580 s
iso-Propylamine	Cu	1.2	280 s; 335 sh; 525 m
iso-Propylamine	Cu	2.5	310 s; 550 s
n-Hexylamine	N	--	315 s; 585 m; 690 m
n-Hexylamine	Cu	1.2	275 s; 530 s
n-Hexylamine	Cu	2.5	265 m; 380 s; 530 m
Trimethylamine	N	--	300 w; 625 w
Trimethylamine	Cu	1.2	265 s
Trimethylamine	Cu	2.5	265 s
Triethylamine	N	--	300 m; 400 s; 590 m; 700 s
Triethylamine	Cu	1.2	310 sh; 380 s; 550 s
Triethylamine	Cu	2.5	265 s; 310 s; 380 m; 550 m

./.

TABLE 1 (contd.) Exothermic peak maxima in DTA curves of natural (N) and
Cu-montmorillonite (Wyoming bentonite) treated with various
amines (Clay: alumina ratio in heating cell is 1)

Amine	Clay	Amine: Cu ratio	Peak temperature (°C)
Diethylamine	N	--	340 s; 600 m; 660 m
Diethylamine	Cu	1.2	290 s; 430 m
Diethylamine	Cu	2.5	290 s; 525 s
Tributylamine	N	--	340 s; 430 sh; 625 sh; 715 m
Tributylamine	Cu	1.0	300 s; 575 s
Tributylamine	Cu	2.5	300 sh; 355 s; 575 s
Diethylenetriamine	N	--	255 s; 330 w; 610 m
Diethylenetriamine	Cu	0.6	245 w; 305 s
Diethylenetriamine	Cu	1.5	190 s; 300 w; 350 w; 430 m; 535 s
Diethylenetriamine	Cu	2.5	160 s; 190 m; 300 w; 350 w; 430 m; 535 s
Triethylenetetramine	N	--	260 s; 340-373 m; 515 m; 615 m
Triethylenetetramine	Cu	0.6	355 s
Triethylenetetramine	Cu	1.5	355 s; 430 m; 550 s
Triethylenetetramine	Cu	2.5	355 s; 430 m; 550 s
Tetraethylenepentamine	N	--	240 s; 335 m; 450-485 m; 565-585 m
Tetraethylenepentamine	Cu	0.6	255 s; 355 s
Tetraethylenepentamine	Cu	1.5	255 s; 355 s; 435 s; 550 s
Tetraethylenepentamine	Cu	2.5	255 s; 355 s; 435 s; 550 s

s - strong;   m - medium;   w - weak;   sh - shoulder

Trien and tepa form with Cu only one type of complex, with amine:Cu ratio of 1. These are [CuTrien]$^{2+}$ and [CuTepa]$^{2+}$. On the other hand, dien may form with Cu two types of complex ions, with amine:Cu ratio of 1 and 2, [CuDien]$^{2+}$ and [CuDien$_2$]$^{2+}$ respectively. The additional trien or tepa taken up by the Cu clay beyond the inflection-point gives IR spectra similar to, but more intense than, those of complexes deficient in amine, and so must be present largely as complexed or intercalated neutral amine. Accordingly, the additional high temperature exothermic peaks which are observed in the DTA curves of trien and tepa beyond the inflection points, do not represent a new phase, but are characteristic for the presence of big amounts of complexed amine in the heating cell. It should be noted that if the additional amine is involved in the formation of a new phase, it is to be expected that at least one new exothermic peak will appear in the low temperature range (below 350°C). Table 1 shows that the additional peaks of amine added beyond the inflection-point are located at higher temperatures.

The dien-Cu-montmorillonite differs from the other two amines in showing a distinct change of DTA curves above the inflection-point. Samples collected before the inflection-point which contain the single complex ion [CuDien]$^{2+}$ give rise to two exothermic peaks. Distinct changes are observed after the inflection point as some peaks are replaced by others, in addition to the appearance of new peaks. The appearance of new peaks in the low temperature range (below 350°C) may be attributed to the formation of a new phase [CuDien$_2$]$^{2+}$. The curve obtained with amine:Cu molar ratio of 2.5 can be interpreted as a mixture of the latter complex and an additional phase. This additional phase presumably corresponding to free neutral or ionic amine, only appears with a large excess of amine.

ADSORPTION OF AROMATIC AMINES BY MONTMORILLONITE

The most striking difference between DTA curves of montmorillonite complexes of aliphatic and aromatic amines is the tendency of the latter to develop an exothermic peak at about 700°C. Unlike aliphatic complexes, small exothermic peaks at this temperature persisted with the aromatic complexes even when the total organic matter in the heating cell was very small. It was previously stated that aromatic compounds may be involved in π interactions with the oxygen plane of montmorillonite [23]. It appears that during the first stages of the oxidation reaction the clay catalyzes the formation of some kind of charcoal which is burnt only at about 700°C (see also ref. [8]).

Aniline

The data concerning the adsorption mechanism of aniline by different mono-ionic montmorillonites has been obtained mainly from infrared spectroscopy [28, 29]. Adsorbed aniline molecules react either directly or through water bridges with exchangeable metallic cations. The first type of interaction occurs with transition metals, to a considerable extent already at room temperature, but mainly after thermal dehydration of the clay. Cations of the main groups of the Periodic Table react with aniline molecules through water bridges. DTA curves of some representative samples are given in ref. [28]. The DTA curve of liquid aniline mixed with alumina powder shows that aniline vaporizes below 200°C. The evaporation gives rise to a sharp endothermic peak at 185°C. No peaks are observed above this temperature. In the clay interlayers, on the other hand, aniline is retained to much higher temperatures. Exothermic peaks are observed in three ranges of temperature, 220-340, 440-450 and 650-750°C. The mechanism of oxidation of adsorbed aromatic compounds differs from that of the adsorbed aliphatics. These compounds may form π interactions with the oxygen plane of the clay mineral [23] and it is to be expected that these interactions will affect the oxidation reaction. The contribution of π interactions to the adsorption forces increases with the acid strength of the exchangeable cation. This is associated with shifting and broadening of the peaks in the 220-300°C range. With monovalent exchangeable cations (Na, K and NH$_4$) they are sharp, located at

220°C. With di- and trivalent cations several small exothermic peaks appear between 260 and 300°C. Oxidation is completed at about 700°C, even with small amounts of aniline, except in the presence of Cr, when catalytic effects seem to occur. In this case the last exothermic peak is observed at 530°C. The peak at 700°C is very intense in the DTA curves of divalent cations whereas the two at the lower temperatures are very small. On the other hand, the three exothermic peaks in the DTA curves of Na-, K- and Cs-montmorillonite are of a similar size.

The endothermic peaks (or shoulders) at 125 and 185°C correspond to water and loosely held aniline. The peak at about 125°C is decreased, but not eliminated on more prolonged exposure to aniline, confirming that water is slowly, but incompletely, displaced by aniline.

The relative sizes of exothermic and endothermic peaks give some indication of the amounts of aniline loosely and firmly bound, respectively. It is evident from the small size of the exothermic peaks that Na-, K- and Cs-montmorillonites sorb aniline less firmly than the other samples. Mg-, Ca- and Al-montmorillonites, like those substituted by transition metal cations, bind aniline more firmly.

Indole, 2-methylindole, 3-methylindole

The data concerning the mechanism of adsorption of these indoles by different monoionic montmorillonites has been obtained mainly from IR spectroscopy [30]. Some DTA curves are also shown in the same publication. The different associations which were identified in the interlayer are shown in Fig. 10.
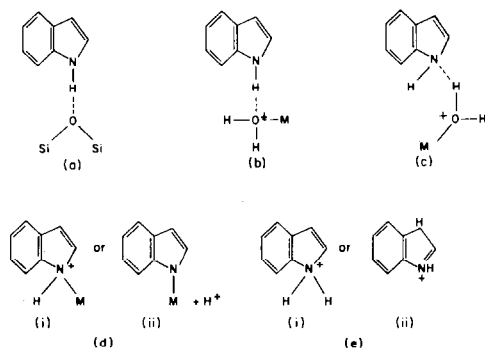

Fig. 10:

Possible configurations of indole-water-cation assemblages in montmorillonite interlayers. M = cation.

DTA peak maxima of some representative samples are shown in Table 2. The DTA curves differ from each other, showing that the type of interlayer assemblage affects the thermal stability. There are many similarities between the DTA curves of anilines and indoles and the effects of exchangeable cations on these curves.

The endothermic peaks in the temperature range 65-130°C represent the liberation of water together with some "free" indole. When configuration (b) comprises the principal association in the interlayer space (as with 2-methylindole) this endothermic reaction tends to be resolved into two peaks or to show a distinct shoulder. On the other hand, when configuration (c) comprises the principal association (as with indole or 3-methylindole) a single endothermic peak is obtained.

There are very small peaks in the temperature range 200-310°C. However, it is difficult to differentiate between exothermic and endothermic peaks and to define them. In this range several reactions occur simultaneously, e.g., release of water and organic material from the organo-clay complex, the beginning of the oxidation process and polymerization. This stage determines the nature of the residual charcoal and the shapes and locations of the high

temperature peaks. For example, Cs montmorillonite holds indoles in the form of association (a) and the exothermic peaks in the range 380-600°C are strong whereas Mg montmorillonite holds it mainly in the forms of association (b) and (c) the peaks in this region are weak or absent and the principal exothermic peak appears at 670-690°C. That is to say, associations (b) and (c) lose water during the thermal treatment giving rise to the formation of association (d), the latter protects the organic matter from oxidation. Na resembles Cs rather than Mg, due to the relative ease with which Na samples form association (a) after losing water on heating. Cd montmorillonite treated with indole resembles Cs montmorillonite and most of the organic matter is oxidized at 490°C. On the other hand, with 2- and 3-methylindole Cd resembles Mg and the principal exothermic peak appears at 650-690°C.

The two curves of Cs montmorillonite saturated with 2- and 3-methylindole resemble each other very much. They differ from that of the indole saturated Cs clay by having a broad exothermic peak at 390-500°C. The first two have a strong peak at 690°C as well, whereas the latter has only a weak peak at this location. Since all three indoles form association (a) in Cs-montmorillonite,

TABLE 2. Dominant species and exothermic peak maxima in DTA curves of various monoionic montmorillonites (Wyoming bentonite) treated with indole (I), 2-methylindole (2MI) and 3-methylindole (3MI)

Cation	Amine	Dominant species	Exothermi- peaks (°C) 00°C	
			300-600°C	600-700°C
Cs	I	a	360 sh; 500 vs	680 mm
Cs	2MI	a	390-490 s	690 vs
Cs	3MI	a	390-510 m	690 vs
Na	I	a,b,c	500 m,br	620-670 s
Na	2MI	a,b	380 w	660 vs
Na	3MI	a,b,c	380 w; 510 w; 580 vw	650 vs
Mg	I	b,c	310 w; 520-570 w	690 vs
Mg	2MI	b	320 vw	670 vs
Mg	3MI	c	380 vw; 580 vw	680 vs
Cd	I	a,b,c	490 s, br	665 m
Cd	2MI	a,b	320 sh; 390 w	650 vs
Cd	3MI	c	370 vw; 500 vw; 570 vw	690 vs
Cr	I	c	450 vs	--
Cr	2MI	c	425 vs	--
Cr	3MI	c	450 vw; 530 sh, 580 s	620 vs

w - weak;   m - medium;   s - strong;   v - very;   br - broad

the difference between 2- and 3-methylindole on the one hand and indole on the other, is attributable to their chemical composition. The peak at 390°C is probably associated with the beginning of the oxidation of the methyl group. This oxidation is completed at 690°C.

Cr in clay interlayers acts as a catalyst, reducing the temperature at which the oxidation of the indoles occurs. This behavior of Cr towards indoles is similar to its behavior towards aniline.

THE ADSORPTION OF STEARIC ACID BY VARIOUS CLAY MINERALS

The study of the adsorption of fatty acids by clay minerals raises some technical difficulties due to the fact that both components, the adsorbent and the adsorbate are solids. Most investigated minerals have only a low surface area and the degree of adsorption is low. We found that DTA can serve as a useful tool to establish whether adsorption complexes are formed or whether the clay and organic material are present merely as mechanical mixtures (papers in preparation and ref. [40]). In this technique DTA curves of the pure acid on one hand and of the clay mineral-stearic acid mixtures on the other hand, are recorded either in nitrogen or in oxygen atmosphere. The curves of the mixtures show all the peaks that occur in the curve of the pure acid, but, additional peaks appear indicating that another phase is present. It is reasonable to infer that the additional peaks which are not due to the clay minerals themselves, arise from adsorbed stearic acid. When DTA is carried out together with TGA, semiquantitative information on the adsorption can be obtained.

CONCLUSIONS

The present communication demonstrates that the exothermic peaks of DTA curves recorded in air are applicable for the study of the adsorption of organic compounds by clay minerals. The curves are used as finger-prints for the identification of the different associations which are obtained on the clay surface. The catalytic effect of the clay on the DTA curve is so big that we could not recognize any correlation between the behaviour of non-adsorbed, either free or complexed amine, and adsorbed amine. Sophisticated thermal methods and analyses of the combustion products are now in progress in order to obtain a better understanding of the different peaks.

REFERENCES

1 R.C. Mackenzie, E. Paterson and R. Swaffield, J. Thermal Anal. 22 (1981) 269.
2 W. Smykatz-Kloss, Differential Thermal Analysis. Application and Results in Mineralogy. Springer Verlag, Berlin 1974.
3 J.W. Jordan, Mineral. Mag., 28 (1949) 598.
4 B.D. Mitchell and A.C. Birnie, in R.C. Mackenzie (Ed.), Differential Thermal Analysis, Academic Press, London, 1970, p. 611.
5 R. Greene-Kelly, in R.C. Mackenzie (Ed.), The Differential Thermal Investigation of Clays, Mineralogical Society, London, 1957, p. 140.
6 I.M. Eltantawy, Bull. Groupe Franc. Argiles, 26 (1974) 211.
7 W.H. Allaway, Proc. Soil Sci. Soc. Am., 13 (1949) 183.
8 V.S. Ramachandran, S.P. Gorg and K.P. Kacker, Chem. Ind. (1961) 790.
  V.S. Ramachandran, K.P. Kacker and N.K. Patwardhan, Nature (London), 191 (1961) 696; V.S. Ramachandran and K.P. Kacker, J. Appl. Chem., 14 (1964) 455.

K.P. Kacker and V.S. Ramachandran, 9th Inter. Ceram. Congress, Trans. (1964) 483.

9 J.M. Oades and W.M. Townsend, Clay Miner. Bull. 5 (1963) 177; A.R. Carthew, Soil Sci., 80 (1955) 337; R.C. Mackenzie, in R.C. Mackenzie (Ed.), Differential Thermal Analysis, Academic Press, London, 1970, p. 497.

10 S. Yariv, L. Heller, Y. Deutsch and W. Bodenheimer, Thermal Analysis, Proc. 3rd ICTA Davos, Birkhauser Verlag, Basel 1971, Vol. 3, p. 663.

11 S. Yariv and H. Cross, Geochemistry of Colloid Systems, Springer Verlag, Berlin 1979.

12 L. Heller and S. Yariv, Isr. J. Chem., 8 (1970) 391.

13 S. Yariv and L. Heller, Isr. J. Chem., 8 (1970) 935.

14 W.F. Bradley and R.E. Grim, J. Phys. Chem., 52 (1948) 1404.

15 L. Heller-Kallai and S. Yariv, J. Colloid Interface Sci., 79 (1981) 479.

16 S. Yariv, W. Bodenheimer and L. Heller, Isr. J. Chem., 2 (1964) 201.

17 W. Bodenheimer, L. Heller and S. Yariv, Clay Minerals 6 (1966) 167.

18 W. Bodenheimer, L. Heller, B. Kirson and S. Yariv, Isr. J. Chem. 1 (1963) 391

19 W. Bodenheimer, L. Heller, B. Kirson and S. Yariv, Proc. Inter. Clay Conf. Stockholm 2 (1963) 351.

20 B.K.G. Theng, The Chemistry of clay-organic reactions, Adam Hilger, London 1974.

21 M. Lacher, S. Yariv and N. Lahav, Thermal Anal. Proc. Intern. Conf. Bayreuth 2 (1980) 313.

22 M. Shoval and S. Yariv, Clays Clay Minerals, 27 (1979) 29.

23 R. Cohen and S. Yariv, J. Chem. Soc., Faraday Trans. 1, 80 (1984) 1705.

24 S. Yariv and W. Bodenheimer, Isr. J. Chem. 2 (1964) 197.

25 S. Yariv and S. Shoval, Isr. J. Chem. 22 (1982) 259.

26 M.M. Mortland, 9th Int. Cong. Soil Sci. Adelaide, Trans. 1 (1968) 691.

27 R.D. Laura and P. Cloos, Clays Clay Miner. 23 (1975) 61.

28 S. Yariv, L. Heller, Z. Sofer and W. Bodenheimer, Isr. J. Chem., 6 (1968) 741

29 S. Yariv, L. Heller and N. Kaufherr, Clays Clay Miner. 17 (1963) 301.

30 Z. Sofer, L. Heller and S. Yariv, Isr. J. Chem., 7 (1969) 697.

31 S. Saltzman and S. Yariv, Soil Sci. Soc. Am. Proc., 39 (1975) 474.

32 W. Bodenheimer, B. Kirson and S. Yariv, Isr. J. Chem., 1 (1963) 78.

33 W. Bodenheimer, L. Heller, B. Kirson and S. Yariv, Clay Miner. Bull. 5 (1962) 145.
R.D. Laura and P. Cloos, Reunion Hispano-Belga de Minerales de la Arcilla, Madrid (1970) 76.

34 J.L. Bear and W.W. Wendlandt, J. Inorg. Nucl. Chem. 17 (1961) 286.
W.W. Wendlandt, J. Inorg. Nucl. Chem. 25 (1963) 833.
W.W. Wendlandt, S. Iftikhar Ali and C.H. Stembridge, Anal. Chim. Acta, 30 (1964) 84.
D.H. Bronen, R.H. Nuttal and D.W. Sharp, J. Inorg. Nucl. Chem., 26 (1964) 1151.
P.B. Boneman and L. Rogers, J. Inorg. Nucl. Chem., 28 (1966) 2215.
A. Beltran-Porter, E. Martinez-Tamayo and F. Caturla, Thermochim. Acta 75 (1984) 303.

35 W. Bodenheimer, L. Heller and S. Yariv, Proc. Intern. Clay Conf., Jerusalem, 1 (1966) 251.

36 E.F. Vansant and J.B. Uytterhoeven, Clay Miner., 10 (1973) 61.

37 S. Yariv and L. Heller-Kallai, Clay Miner., 10 (1975) 479.

38 V.C. Farmer and M.M. Mortland, J. Phys. Chem., 69 (1965) 683.

39 W. Bodenheimer, L. Heller and S. Yariv, Proc. Intern. Clay Conf., Jerusalem 2 (1966) 171.

40 S. Yariv and L. Heller-Kallai, Chem. Geol. 45 (1984) 313.