

MONOIONIC MONTMORILLONITES TREATED WITH CONGO-RED

Differential thermal analysis study

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Abstract

The adsorption of the anionic dye congo-red (CR) by Na-, Cs-, Mg-, Al- and Fe-montmorillonite was studied by simultaneous DTA-TG. Thermal analysis curves of adsorbed CR were compared with those of neat CR. The oxidation of neat CR is completed below 570°C. Thermal analysis curves of adsorbed CR show three regions representing dehydration of the clay, oxidation of the organic dye and dehydroxylation of the clay together with the oxidation of residual organic matter. The oxidation of the dye begins at about 250°C with the transformation of organic H atoms into water and carbon into charcoal. Two types of charcoal are obtained, low-temperature and high-temperature stable charcoal. The former gives rise to an exothermic peak in the second region of the thermal analysis and the latter in the third region. The exchangeable metallic cation determines the ratio between the low-temperature and high-temperature stable charcoal, which is formed. With increasing acidity of the exchangeable metallic cation higher amounts of high-temperature stable charcoal are obtained. It was suggested that aromatic compounds π bonded to the oxygen plane of the clay framework are converted into charcoal, which is burnt at about 550–700°C. With increasing surface acidity of the clay more species of CR are protonated. Only protonated dye species can form π bonds with oxygen plane and are converted to high-temperature stable charcoal during the thermal analysis. The thermal behavior of the dye complex of Cu-montmorillonite is different probably due to the catalytic effect of Cu.

Keywords: charcoal, congo-red, DTA, montmorillonite, organo-clay complex, thermogravimetry

Introduction

Thermal analysis curves of most organo-montmorillonite complexes, recorded either in an oxidizing or an inert atmosphere, can be divided into three regions: (1) the region of dehydration of the clay, (2) the region of the thermal reactions of the organic material and (3) the region of the dehydroxylation of the clay [1, 2].

The shape of the first region does not depend on whether the DTA is recorded in an oxidizing or inert atmosphere. The thermal dehydration of the clay usually occurs in the same temperature range in which clay samples, not treated with organic materi-

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als (untreated clays), lose most of their adsorbed water that is below 200 or 250°C. With polyvalent exchangeable cations some water evolved at higher temperatures. The dehydration is shown by an endothermic peak [3–5].

The shape of the second region depends on whether the DTA is recorded under an oxidizing or inert atmosphere. In air this region represents the oxidation of the organic substances and the evolution of H₂O, CO₂ and NO₂. The DTA curves show several exothermic peaks, which are not observed under an inert atmosphere. Under the latter conditions, broad endothermic peaks of pyrolysis are recorded [1, 2, 6].

The third region of the DTA curves of most organo-montmorillonites (above 550°C) is determined by the endothermic dehydroxylation of the clay, which is followed by a small exothermic peak of the recrystallization of the meta-clay.

In some cases the oxidation of the organic matter is not completed in the temperature range of the second region and is traced in the third region by giving rise to new peaks, which overlap the dehydroxylation of the clay mineral. Exothermic peaks of DTA curves recorded in air are applicable for the study of the adsorption of organic compounds by clay minerals. In most studies the DTA curves were used merely as fingerprints for the identification of different associations obtained on the clay surface [1, 2, 6].

Simultaneous DTA-EGA study of cationic dyes adsorbed by Laponite and montmorillonite showed that the oxidation of the organic matter in air started about 200°C with the evolution of H₂O and CO₂ and the formation of charcoal inside the interlayer space [7].

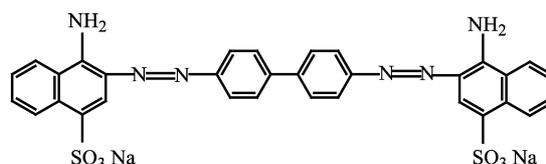
In our laboratory characteristic DTA curves of montmorillonites loaded with ionic and molecular aliphatic and aromatic amines were recorded. Aromatic amines are characterized by their tendency to develop an exothermic peak in the third region in addition to exothermic peaks in the second region. Unlike 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 [2, 7–10]. Aromatic compounds might be involved in π interactions with the oxygen plane of montmorillonite by accepting lone-pair electrons from O atoms into the π anti-bonding orbitals of the aromatic rings [11].

From the collection of data of the thermal analysis of organo-montmorillonites, it appears that two types of charcoal are obtained in the interlayer space. One type is a low-temperature stable charcoal thermally oxidized in the second region of the thermal analysis, below 550°C. The second type is a high-temperature stable charcoal oxidized in the third region of the thermal analysis, above 550°C [2].

It has been suggested that during the first step of the oxidation reaction when organic H is converted into water, the type of interactions between the adsorbed organic compound and the adsorbing sites on the clay surface is responsible for the type of charcoal, which is formed. Aromatic compounds π bonded to the framework oxygen plane of the clay are converted into charcoal, which is burnt only at about 550–700°C.

In the present investigation we wish to examine the contribution of the π interactions between the oxygen plane and the aromatic rings and relate it to the appearance, size and shape of an exothermic peak in the third region of the DTA curve.

Congo-red (CR, Diphenyl-4,4¹-bis azo-2-naphthylamine-1-1-sulphonic acid-4), shown in Scheme 1, was chosen for this purpose. In previous studies we showed that this anionic bis-azo dye is adsorbed into the interlayer space of montmorillonite in considerable amounts [12]. We also showed that in the interlayer space the dye appears in different varieties, e.g. anionic varieties, which may also be hydrogen bonded to water molecules and in protonated varieties [13]. It is expected that the protonated variety will, in part, form π bonds by accepting lone-pair electrons from O atoms of the clay oxygen plane [11].



Scheme 1

The differentiation between acidic and basic varieties was done by visible spectroscopy study. The ratio between the anionic and the protonated varieties depends on the exchangeable metallic cation. In the spectrophotometric study we showed that this ratio increases in the order Na, Mg, Cs, Cu, Al and Fe. According to Yariv [11], the anionic variety does not form π bonds with the oxygen plane of the clay framework. Since the net charge of the anionic-aromatic ring is slightly negative it cannot accept electron pairs from the oxygen atoms into the π anti-bonding orbitals. For these interactions to occur the aromatic species should be in part positively charged. This can be achieved by the protonation of the anion. In conclusion, we will expect that the surface acidity of the clay and the protonation of CR will affect the shape of the DTA curve of the CR-clay complex. With stronger acidity one would expect that the high temperature exothermic peak would be more pronounced.

Experimental

Materials

Congo-red (for microscopic grade) was supplied by Merck. According to the supplier the dye content in the sample is 75% and the impurities are sodium sulfate and water. No other impurities were detected by ICP and TLC analyses. Wyoming bentonite (Na-montmorillonite) was supplied by Wards National Science Establishment, Inc. It was ground and sieved to 80 mesh and the non-clay fraction was separated by sedimentation. The original sample contained 74 mmol Na⁺ and 18 mmol Mg²⁺ plus Ca²⁺ per 100 g clay. Almost monoionic montmorillonites saturated with Na⁺, Cs⁺, Mg²⁺, Cu²⁺, Al³⁺ and Fe³⁺ were prepared as follows: a portion of 10 g Wyoming bentonite was dispersed in 800 mL water and stirred during two days. The stable clay suspension was separated from the sedimented micas, quartz and feldspar and 200 mL of 0.2 M aqueous solution of the respective chloride salt was added and the suspension

was stirred. After two days the clay was washed several times by distilled water until it was free of chloride (examined by AgNO_3 solution).

Method

Preparation of CR-montmorillonite complexes

Each monoionic montmorillonite was treated with 65.0 mmol CR per 100 g clay (air-dried). For this loading 4.0 mL of $9.75 \cdot 10^{-3}$ M CR aqueous solution were added into the 5.0 mL of the clay suspensions. Each suspension was treated for ten minutes in ultrasonic bath before and after adding the dye. After 24 h the suspensions were centrifuged for 30 min (8.000 rpm) and the supernatants were separated from the sedimented clays.

Washing of CR-montmorillonite complexes

The separated clay sample was washed four times by adding 10 mL distilled water. The mixture was shaken thoroughly and the water was separated by centrifugation. The sediment was dispersed in 25 mL of water. After three months the aqueous phase was separated. A new portion of 25 mL of water was added and the dispersed sediment was poured on a glass plate, on which it was air-dried for two days.

Thermal analysis

The dried CR-montmorillonite complexes were scratched from the glass plate. Simultaneous DTA–TG curves of 10 mg powdered samples were recorded in air using a Shimadzu ‘DTG–50’ Instrument. Heating rate was 10°C per minute. To simplify peak area determination, the baseline was corrected in such a way that the dehydroxylation endothermic peak was included in the exothermic area. This treatment makes the dehydration peak area non-reliable.

Results

Thermal analysis of congo-red

Figure 1 shows the TG and DTG curves of neat CR. Water (9 mass%) is lost upon heating up to 200°C , but most of it is evolved below 100°C , with a DTG peak at 70°C . The DTA curve demonstrates that this water-evolution reaction is endothermic. Mass loss (70 mass%) in the range 250 – 570°C , is due to the oxidation of the organic matter. The DTG curve shows five peaks indicating that this mass loss occurs in five stages. The DTA curve proves that all these stages are exothermic. The residue which remains at 570°C (20.5 mass%) is composed mainly of the salt Na_2SO_4 and also Na_2O obtained from the oxidation of CR, which is a sodium salt. A very slow mass loss (0.5 mass%), which continues at higher temperatures is probably due to the thermal decomposition of this salt.

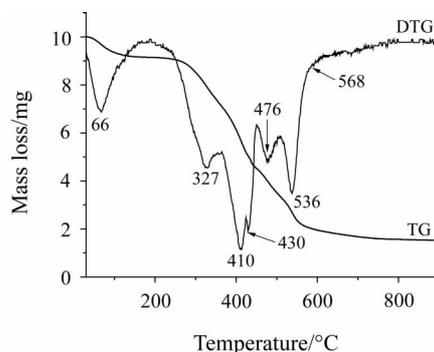


Fig. 1 TG and DTG curves of neat CR

Thermal analysis of montmorillonites treated with congo-red

In the present paper we shall focus our attention on the second and third regions of the DTA curves. The dehydration process, as effected by the adsorption of the anionic dye, will be treated in a later paper.

Figures 2–6 show the DTA curves of CR complexes of Na-, Cs-, Mg-, Al- and Fe-montmorillonite recorded in air atmosphere. The temperature range of each peak and the maxima of the exothermic peaks are given in the figures. The figures demonstrate that the thermal behavior of these montmorillonites shows significant similarities but that the locations of the exothermic peaks depend on the exchangeable metallic cation. All these curves can be divided into three regions, the dehydration region below 225°C represented by an endothermic peak at about 74–90°C, the region of the combustion reactions up to 550–595°C, represented by two exothermic peaks (labeled *A* and *B*) and the dehydroxylation region represented by an endothermic reaction and three exothermic peaks (*C*, *D* and *E*). Peaks *C* and *D* probably are associated with one exothermic reaction but they overlap the endothermic dehydroxylation of the clay and appear therefore as two separate peaks.

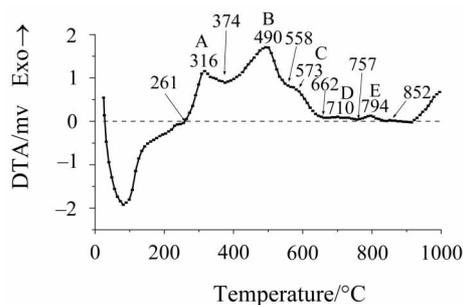


Fig. 2 DTA curve of CR treated Na-montmorillonite

The TG curves of these samples show that mass loss continues after the dehydroxylation process indicating that the oxidation of the organic matter continues at this

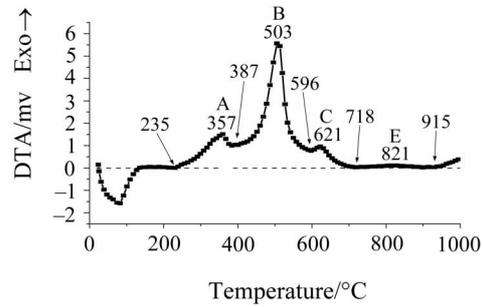


Fig. 3 DTA curve of CR treated Cs-montmorillonite

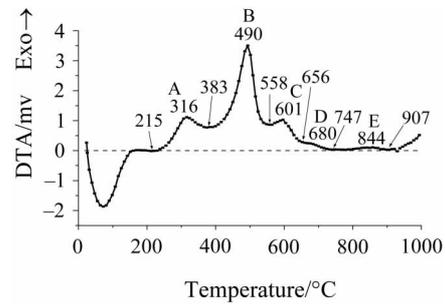


Fig. 4 DTA curve of CR treated Mg-montmorillonite

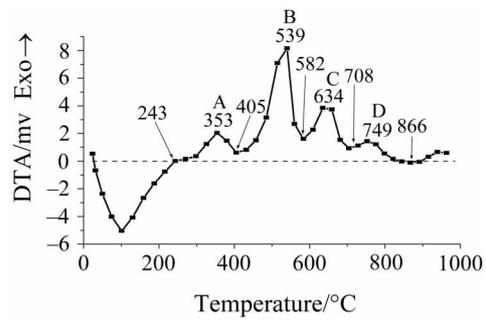


Fig. 5 DTA curve of CR treated Al-montmorillonite

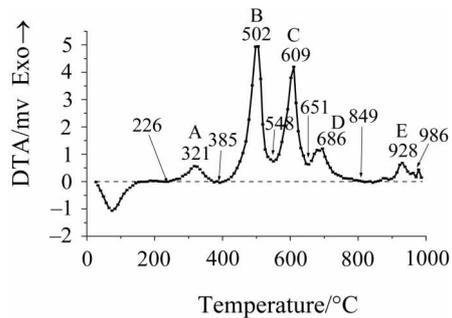


Fig. 6 DTA curve of CR treated Fe-montmorillonite

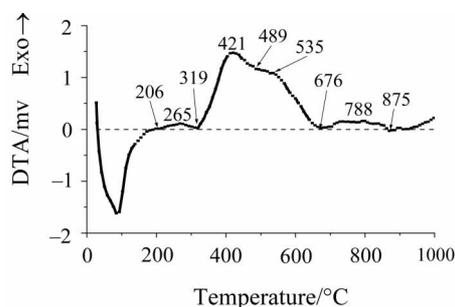


Fig. 7 DTA curve of CR treated Cu-montmorillonite. (There are no assignments of peaks since the shape of this DTA curve differs from the shapes of the other curves)

stage (peak *E*). The thermal behavior of the CR complex of Cu-montmorillonite is different (Fig. 7) probably due to the catalytic effect of Cu and will be described separately.

Table 1 Areas of exothermic peaks *A*, *B*, *C*, *D* and *E* (in %) relative to the total area of these peaks

Exchangeable cation	Peaks				
	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>E</i>
Na	24.4	60.9	11.1	2.0	1.6
Cs	19.8	69.4	8.7		2.1
Mg	21.0	59.3	14.8	3.0	1.9
Al	12.6	51.9	25.8	9.7	
Fe	5.6	42.6	34.9	14.0	2.9

In Table 1 the relative areas of the exothermic peaks are collected. By relative areas it is meant the absolute area of the peak divided by the total area of all the exothermic peaks. The table shows that the relative area of peak *A* decreases in the order Na, Mg, Cs, Al and Fe. Peak *B* decreases in the order Cs, Na, Mg, Al and Fe whereas the relative area of peaks *C* and *D* decreases in the reverse order. Peak *A* represents the first step of the oxidation of the organic matter. At this step the organic hydrogen is combined with the air oxygen to form water [2, 7]. Only part of the carbon and nitrogen are combined with the air oxygen at this stage. The other part is condensed to form charcoal or petroleum coke. The decrease in the relative exothermic peak area from Na to Fe through Mg, Cs and Al clay is equivalent to a decrease in the relative exothermic energy. We suggest that at this stage a very small part of the carbon is oxidized to CO₂ in Fe-montmorillonite and the rest forms charcoal, whereas much of the carbon is oxidized to CO₂ in Na-montmorillonite and smaller amounts of charcoal are obtained. In the second and third steps of the exothermic reaction, the charcoal is oxidized to CO₂. Peak *B* represents the oxidation of low-temperature stable charcoal whereas peaks *C*, *D* and *E* represent the oxidation of the high-temperature stable charcoal. From Table 1 it is concluded that in the thermal analysis of CR complexes of Na-, Cs- and Mg-montmorillonite the low-temperature stable charcoal is the principal carbon product whereas in the thermal analysis of CR complex

of Fe-montmorillonite the high temperature stable charcoal is the principal product. Al-montmorillonite shows an intermediate behavior.

Table 2 Mass loss (in mass%) during dehydration (first region of the DTA curves) and during the air oxidation of the adsorbed congo-red and the dehydroxylation of the clay (second and third regions of the DTA curves). Percentage was calculated on the basis of the final mass of each sample at the end of peak *E*

Exchangeable cation	Mass loss/%				Total organic matter	Calculated organic matter/ mmol/100 g
	Dehydration	Peak		Peaks <i>C+D+E</i> and dehydroxylation		
		<i>A</i>	<i>B</i>			
Na	15.4	3.0	4.5	10.7	14.9	25.3
Cs	11.2	3.2	13.7	14.6	28.2	43.9
Mg	19.2	5.5	12.2	16.9	31.3	48.0
Al	15.8	5.7	12.1	24.8	39.3	59.1
Fe	19.2	5.7	17.5	38.0	57.9	84.2

Thermal mass losses in mass percent were calculated from TG curves and are presented in Table 2. Since each sample contains a different amount of organic matter and a different amount of water, the percentage of mass loss was calculated on the basis of the mass of each calcined samples obtained at the end of peak *E*. Total mass loss in the second and third regions is mainly due to the oxidation of the organic matter. In addition to the dehydration of montmorillonite in the first region, a small amount of interlayer water is evolved in the second region. This occurs mainly with the polyvalent exchangeable cations. At about 650°C the clay dehydroxylates. In Table 2 the mass loss associated with peaks *C*, *D* and *E* are presented in one column because these peaks overlap together with the endothermic dehydroxylation mass loss. It should be taken into consideration that the dehydration in the second region and dehydroxylation in the third region are also responsible for the mass loss during the oxidation of the organic matter. The information in Table 2 on the total organic matter from mass loss in the second and third regions can give a rough estimation on the amount of the adsorbed dye. It is difficult to estimate the water-loss in the second region of the thermal analysis, because the water content changes with the organic matter. The dehydroxylation, on the other hand, can be determined from TG curves of montmorillonites which were not treated with organic matter. We determined mass loss of Na-montmorillonite non-treated with CR at 570–700°C and concluded that the mass loss due to the dehydroxylation was 3.3% on the basis of dry-calcined montmorillonite. We assume a similar mass loss due to the dehydroxylation of the other monoionic montmorillonites. This percentage was subtracted from the mass loss during the third region of the thermal analysis. The calculated mass loss due to total organic matter is depicted in Table 2. Based on these data the loadings of the different montmorillonites by CR (in mmol per 100 g clay) were calculated and are given in

the Table (last column). The table shows that adsorption increases in the order Na, Cs, Mg, Al and Fe. There are significant differences between the adsorption capacity of the different montmorillonites obtained in the present study and those obtained previously [12, 13]. As we mentioned previously, since CR is an anion and its adsorption takes place by a complicated mechanism, the adsorption capacity changes very much with the experimental conditions.

Table 2 shows an increase in mass loss of the third thermal region in the order Na, Cs, Mg, Al and Fe indicating that the amount of the high-temperature stable charcoal increases in the same order. The Table shows that mass loss associated with peak *A* is higher with the polyvalent cations compared with the monovalent cations. This is not in agreement with our observations on the relative peak area (Table 1). We attribute this difference to the fact that the polyvalent cations keep the interlayer water to higher temperatures and it appears that at this stage interlayer water is evolved together with the CR-oxidation products.

In Table 3 the mass loss percentage was calculated relative to the estimated organic matter. That means that the total mass loss of the organic matter was equal to 100 percent. The Table shows that CR complexes of Na-, Cs- and Mg-montmorillonite lost more than 50 percent of the organic matter in the second region whereas CR complexes of Al- and Fe-montmorillonite lost more than 50 percent of the organic matter only in the third region of the thermal analysis. This trend is similar to the trend represented in Table 1 where the relative exothermic peak areas are collected.

Table 3 Mass loss (in mass%) of organic matter (associated with exothermic peak) calculated from TG curves on the basis of the final mass of each sample at the end of peak *E* relative to the total mass loss of organic matter

Exchangeable cation	Peaks		
	<i>A</i>	<i>B</i>	<i>C+D+E</i>
Na	20.1	30.2	49.7
Cs	11.4	48.6	40.0
Mg	17.6	39.0	43.4
Al	14.5	30.1	55.4
Fe	9.8	30.2	60.0

The thermal behavior of the CR complexes of Cu-montmorillonite is completely different from that of other CR complexes of montmorillonite [12]. The DTA curve does not show any separation between the second and third regions of the thermal analysis. A very small exothermic peak appears at 265°C accompanied by a very small mass loss of 1.1%. The onset temperature of the principal exothermic reactions appears at 319°C. This reaction continues up to 680°C with a peak at 421°C and a shoulder at 535°C. Mass loss percentage on the basis of calcined sample (determined at the end of the highest temperature exothermic peak) are as follows: 318–361°C, 0.4%; 361–487°C, 4.4%; 487–676°C, 7.9%; 676–711°C, 1.4%; 711–875°C, 1.5%

Discussion

The shape of the thermal curves of the neat CR depends on whether the dye anion is non-adsorbed or adsorbed by the clay mineral. Comparing the thermal curves of the neat CR with those of CR adsorbed on montmorillonite demonstrates that as a result of adsorption the final oxidation of CR takes place at higher temperatures.

In previous studies of a combined EGA–DTA of montmorillonite complexes of the cationic dyes acridine–orange and crystal–violet we showed that montmorillonite treated with 100 mmol acridine–orange per 100 g clay gave a CO₂ evolution curve with two broad peaks at 480 and 670°C and CV treated montmorillonite showed three CO₂ evolution peaks at 490, 590 and 675°C [14–16]. The latter peaks belong to the third region of the DTA curve, occurring together with the dehydroxylation of the clay. These peaks are very intense in the evolution curves of dye–montmorillonite complexes and are weak shoulders in the evolution curves of dye–Laponite complexes. π interactions are obtained between the oxygen plane of montmorillonite and cationic dyes but not between the oxygen plane of Laponite and the cationic dyes. It was therefore concluded that this high temperature peak belongs to the oxidation of charcoal associated with these π interactions. It is possible that the precursor of this high-temperature stable charcoal, namely the cationic dye that was oxidized to give this fraction of charcoal, was π bonded with the clay. By careful examination of the CO₂ evolution curves published by Yariv *et al.*, [14–16] one can see that the increase in loading of the clay by the dye up to 50 mmol dye per 100 g clay was mainly shown by increase of the peaks belonging to the third stage of the DTA curves. Increase in loading above 50 mmol dye per 100 g clay showed only a small effect on the evolution peak at temperature above the dehydroxylation of the clay but significant increase of the peaks belonging to the second stage. It is now known that several types of interaction occur between the cationic dyes and the clay mineral. π interactions between the cationic dyes and the oxygen plane of montmorillonite occur mainly when the adsorption of the cationic dye is below 30–40 mmol dye per 100 g montmorillonite. With higher loadings, other types of interaction between the cation and functional groups on the clay surface are obtained. These data support our suggestion that peak *B* at the second region of the thermal analysis is due to the oxidation of charcoal, which was formed from aromatic compounds not associated with the oxygen plane by π interactions, whereas the peaks in the third region (*C*, *D* and *E*) are due to the charcoal obtained from aromatic compounds which were associated with π interactions.

In the present study there is a very good correlation between the surface acidity of the different clay samples, as determined by the electronic spectroscopy study of the CR complexes of montmorillonite, and the intensity of the exothermic peaks in the third region of the DTA curves. These observations support the idea that π interactions between adsorbed aromatic compounds and O atoms from the oxygen plane are essential to the formation of the high-temperature stable charcoal and the appearance of exothermic peaks in the third region of the DTA curves of aromatic–montmorillonite complexes.

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