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THERMAL ANALYSIS OF THE ADSORPTION OF RHODAMINE 6G BY SMECTITE MINERALS

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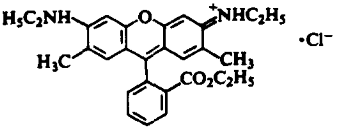
ABSTRACT

DTA, TG and DTG curves of montmorillonite and laponite treated with various amounts of rhodamime 6G were run in air. The evolved gases were simultaneously determined by mass spectrometry and gas evolution curves of H_2O, CO_2, NO_2, H_2, CH_3 and C_2H_6 were recorded. Each thermal analysis curve can be divided into three regions. The first region represents the dehydration of the clay. The second region represents the oxidation of the organic cation and is characterized by two or three exothermic peaks. The first peak is due to the oxidation of H atoms. The second and third peaks are mainly due to the oxidation of C and to some extent also N atoms. The third region represents the dehydroxylation of the smectite mineral. The resulting DTA curve of montmorillonite in this region is affected by the oxidation of organic matter which remains in the heating cell throughout the second region, whereas with laponite only traces of the organic material remain.

INTRODUCTION

DTA is used in many laboratories for the study of adsorption of organic materials by clay minerals [see e.g. 1-3]. The thermal analysis is carried out either in air or under a flow of nitrogen (inert atmosphere). When DTA is performed in air, the adsorbed organic material is oxidized, giving rise to intensive exothermic peaks. At the present time the interpretation of these peaks and the reactions which are attributed to the various exothermic peaks are speculative and the DTA curves are used only as fingerprints for the identification of the different associations which are obtained on the clay surface. In the present communication we shall describe an improved thermal analysis method for the study of organo-clay complexes. In this method the combustion products are mass spectrometrically analyzed with the DTA and TG runs [4]. The use of gas evolution curves, together with DTA and TG curves, enables correct interpretation of the exothermic peaks. For the present study the adsorption of the non-volatile cationic dye rhodamime 6G (R6G,1) by the smectite minerals montmorillonite and laponite was examined. The adsorption characteristics of organic dye cations by montmorillonite and laponite have been described [5-11]. The adsorption proceeds, principally, by the mechanism of cation exchange. In addition to the cation exchange reaction the adsorption of most dyes on



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montmorillonite results in π interactions between the oxygen planes of the clay and the aromatic rings of the organic dye. On the other hand, the adsorption of R6G is not accompanied by this kind of π interaction due to steric hindrance [8,12]. Because of the lack of π interactions between montmorillonite and R6G this dye was chosen for the present study.

EXPERIMENTAL

R6G supplied by Aldrich was recrystallized [8]. Laponite XLG (a synthetic Na-hectorite) was kindly donated by Laporte Industries, Ltd., U.K. Montmorillonite (Wyoming bentonite) was supplied by Ward's Natural Establishment, Inc.. 250 mg of air-dried clay were dispersed in 20 ml of water. After 24 hours, various amounts of the dye solution were added dropwise to the well-stirred clay suspension. After 24 hours the organo-clay was separated by centrifugation. Samples were washed three times with distilled water to remove excess dye. According to Grauer et al. [8] montmorillonite and laponite become saturated with 60 and 45 mmole R6G per 100 g clay. Additional amounts of R6G are only in part adsorbed by the clay.

Oriented samples were prepared for X-ray diffraction by drying the suspension on glass slides. X-ray diffraction patterns were recorded on a Phillips PW 1730 diffractometer. Thermoanalytical experiments were carried out under a flow of air on a Mettler TA-1 thermal analysis instrument coupled with a Balzers quadrupole mass spectrometer [4]. 20 mg samples were used for each run. The rate of the air flow was 1.9 l.p.H. Heating rate was 10°C per minute. Calcined kaolinite was used as a reference material.

RESULTS AND DISCUSSION

X-ray study

Oriented specimens of clay samples treated with various amounts of R6G were examined by X-ray diffraction at ambient conditions (Table 1). Heating natural montmorillonite or laponite at 195°C for six days results in a c-spacing of 1.0 nm due to dehydration. In the presence of R6G only minor effects of the thermal treatment on the c-spacing due to dehydration were observed. From these results it may be concluded that the c-spacing is principally determined by the presence of the organic cation in the interlayer space.

Thermal analysis

Representative DTA curves of montmorillonite and laponite saturated with various amounts of R6G are shown in Figs. 1 and 2. The DTA curves of both organo-clays can be divided into three regions. In the first region, up to 250°C, the endothermic dehydration of the clay is the major thermal reaction. The second region is between 250-580°C and 250-640°C in the curves of montmorillonite and laponite, respectively. The exothermic oxidation of the adsorbed R6G is the principal thermal reaction of this region. The third region occurs at temperatures above 580 and 640°C for montmorillonite and laponite, respectively. The major thermal reactions of this region are the dehydroxylation and recrystallization of the smectite minerals and the last stages of the oxidation of organic matter. Weightloss occurring in the different regions were calculated from TG curves (Table 2).

The first region

The first region represents the dehydration of the clay and the evolution of interlayer water. It is characterized by a single endothermic peak in the DTA curve and a single peak in the DTG curve. The peak maximum in the DTA or

DTG curves shifts from 115 or 135 to 100°C with increasing degrees of saturation of montmorillonite or laponite, respectively.

TABLE 1
Basal spacings (in nm) of air-dried montmorillonite and laponite treated with different amounts of R6G.

mM R6G per 100 g clay	**Montmorillonite**	**Laponite**
3	1.50	1.46
20	1.55	1.54
40	1.64	1.57
60	----	1.61
80	1.88, (1.97 sh)	----

The second region

In the DTA curves of R6G-laponite, three exothermic peaks are traced at 365-370 (shoulder), 405-410 and 490-510°C. The relative intensity of the latter increases with increasing degrees of saturation of the clay. In the curves of R6G-montmorillonite peak maxima appear at 390-395, 415-420 and 505°C. The last peak is clearly observed only when the degree of saturation is 80 mmole dye per 100 g montmorillonite, but it appears as a shoulder at 525°C with lower degrees of saturation. These peaks are associated with weightloss which increases with increasing degrees of saturation (Table 2).

Figs. 3 and 4 bring representative thermal gas evolution curves recorded by mass spectrometry for various masses. Mass 18 represents evolved H_2O. The H_2O which is evolved in this region results from the oxidation of hydrogen atoms of the R6G cations. The H_2O evolution curves of R6G-montmorillonite differ from those of laponite, the former showing an intense peak at 390°C and a shoulder at 420°C, whereas the curves of the latter show an intense peak at 375°C followed by a weak peak at 490°C. The degree of saturation has no effect on the shape of the H_2O evolution curves of either montmorillonite or laponite in the temperature range of the second region.

Mass 44 represents CO_2. The evolution of CO_2 results from the oxidation of the carbon atoms originating from the R6G cations. All evolution curves show one peak at 410-420°C (assigned as peak A) and a second peak at 500-525°C (peak B). The latter peak is very broad in the evolution curves of R6G-montmorillonite. The intensity ratios of these two peaks as a function of the degrees of saturation of the clay by R6G are given in Table 3. The table shows that in the case of laponite, this ratio decreases with increasing saturation. It is possible that in this case the amount of oxygen which is supplied by the flowing air (during peak A) is not sufficient to oxidize all the carbon which is present in the DTA cell. Residual carbon forms polymeric structures and is oxidized at peak B. The ratio between carbon which is oxidized at this stage (peak B) relative to that which is oxidized at peak A becomes greater with increasing initial amount of R6G. In the case of montmorillonite, on the other hand, the degree of saturation has no effect on this ratio. It should be mentioned here that in the discussion of the third region of the DTA curve, we shall show that the oxidation of the residual carbon in montmorillonite occurs above 600°C.

Correlation of the DTA curve with the H_2O and CO_2 evolution curves reveals that the shape of the DTA curve is determined by the amounts of hydrogen and carbon which are oxidized. In the case of montmorillonite the first exothermic peak at 390°C is the consequence of the combination of hydrogen atoms with oxygen atoms from air. The second peak at 420°C is due to the oxidation of both elements simultaneously and consequently is the most intense. The third peak is associated with the broad peak at 525°C in the CO_2 evolution curve. No hydrogen is oxidized at this stage. Furthermore, the endothermic dehydroxylation of montmorillonite starts at 525°C. Consequently, the intensity of this exothermic peak is very weak compared with the intensities of the other exothermic peaks. In the case of laponite the first exothermic peak at 370°C is the consequence of the oxidation of hydrogen atoms. The second and third exothermic peaks at 410 and 490°C are due to the oxidation of carbon atoms.

Mass 46 represents NO_2. The evolution of NO_2 results from the oxidation of the nitrogen atoms of R6G. The evolution curves are very similar to those of CO_2. It may, therefore, be concluded that the oxidation of nitrogen contributes to the intensification of the exothermic peaks at 410-420 and 490-525°C.

Mass 15 represents CH_3 radicals. They are characteristic of methane. The identification of these radicals in the evolved gases may serve as a proof for pyrolysis of R6G. Peak maxima are located at 375 and 350°C in the evolution curves of montmorillonite and laponite, respectively, before the appearance of peaks which characterize oxidation reactions. It is supposed that pyrolysis occurs at higher temperatures as well, but due to the fast oxidation of the products, mass 15 is not detected by the spectrometer.

Mass 30 represents C_2H_6 and NO. The identification of the former among the evolved gases may serve as a proof for pyrolysis. The latter is obtained by the incomplete oxidation of nitrogen atoms of the R6G. The first peak in the gas evolution curves of montmorillonite and laponite are located at 380 and 365°C, respectively, which are slightly above the temperature of the peaks in the CH_3 evolution curves but below those of the peaks of the oxidation reactions. It probably characterizes the pyrolysis of R6G. The last peak at 665 and 525°C, respectively, may represent, at least in part, the incomplete oxidation of the nitrogen. Its location corresponds to the last peak of the NO_2 evolution curve.

Mass 2 represents H_2. Hydrogen is usually evolved during the thermal char formation in an inert atmosphere by aromatization and condensation. The identification of H_2 in the presence of air is due to incomplete oxidation of the evolved hydrogen atoms. H_2 evolution curves were recorded only in some of the thermal analysis runs. Fig. 4 shows that H_2 is detected in the temperature range in which oxidation reactions occur. From the gas evolution curves it may be concluded that the thermal char formation, oxidation and pyrolysis occur simultaneously in the temperature range of the second region.

The third region

This region represents the dehydroxylation of smectite minerals. The DTA curve of untreated montmorillonite shows an endothermic peak at 695°C. In the presence of organic matter this peak shifts to lower temperatures [Fig. 1]. In the case of untreated laponite the dehydroxylation occurs simultaneously with a recrystallization reaction. A broad endothermic peak is recorded at 730°C, followed by a sharp exothermic peak at 755°C. The presence of organic matter has an effect on the dehydroxylation and recrystallization of the laponite. The DTA peaks and the H_2O evolution peaks are shifted and their shapes are modified (Figs. 2 and 4).

Table 2 shows that the degree of saturation of the clay by the dye has almost no effect on the thermal weightloss of R6G-laponite at temperatures of the third region, but affects the thermal weightloss of R6G-montmorillonite. Weightloss of montmorillonite during the third region increases with increasing degrees of saturation, indicating that the oxidation of organic matter has not been completed in the second region but continues in the third region. In agreement with this conclusion the CO_2 and NO_2 evolution curves of montmorillonite show two peaks at 610-650 and 680-665°C.

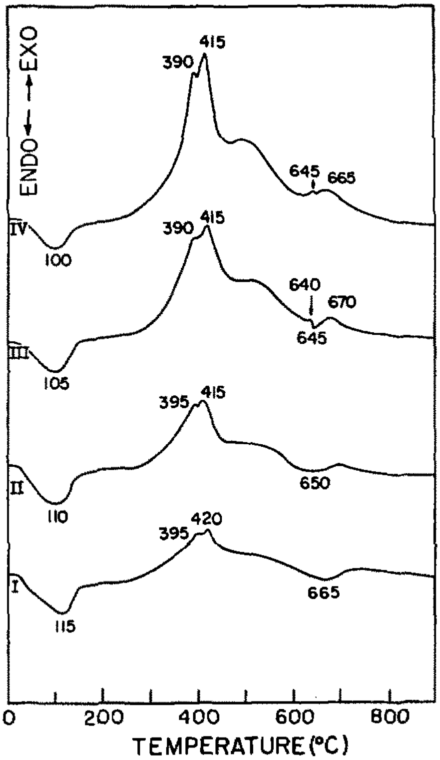

Fig 1

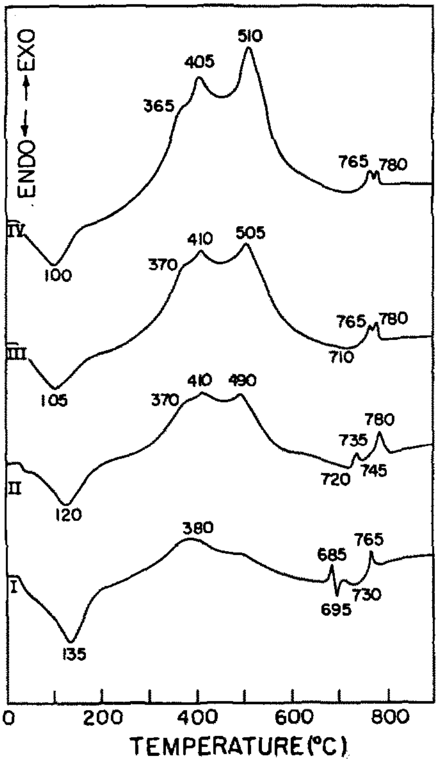

Fig 2

Fig. 1. Differential thermal analysis (DTA) curves of montmorillonite treated with R6G; (I) 3, (II) 20, (III) 40 and (IV) 80 mmole R6G per 100 g montmorillonite

Fig. 2. Differential thermal analysis (DTA) curves of laponite treated with R6G; (I) 3, (II) 20, (III) 40 and (IV) 60 mmole R6G per 100 g laponite.

The exothermic oxidation reaction of R6G-montmorillonite overlaps the endothermic dehydroxylation reaction (compare H_2O and CO_2 evolution curves in Fig. 3). An endothermic peak occurs in DTA curves of montmorillonite saturated with 3 and 20 mmole R6G per 100 g clay. With 40 and 80 mmole R6G per 100 g montmorillonite small exothermic peaks are detected (Fig. 1). However, one should realize that in the present system, according to the shapes of the gas evolution curves which do not change with the degree of saturation, the new exothermic peaks in the third region of the DTA curves of montmorillonite treated with 40 and 80 mmole R6G, as compared to those with 3 or 20 mmole R6G per 100 g montmorillonite, do not characterize new types of adsorption. No peaks are observed in the CO_2 or NO_2 evolution curves of R6G-laponite in the temperature range of the third region (Fig. 4). The CO_2 evolution curves show that very small amounts of CO_2 are evolved at temperatures between 640 and 800°C. The amounts of evolved CO_2 increase with the degree of saturation.

TABLE 2

Weightloss (%) obtained by TG of montmorillonite and laponite treated with various amounts of R6G in three regions (A, B and C) of the thermal analysis

mM R6G per 100 g clay	Montmorillonite			Laponite		
	A^{1}	B^{1}	C^{1}	A^{11}	B^{11}	C^{11}
3	4.75	3.00	4.37	14.25	5.25	2.75
20	4.00	4.37	5.00	7.63	7.10	3.50
40	4.85	6.50	6.50	11.25	11.23	3.00
60	----	——	----	7.00	18.27	3.50
80	3.23	10.35	8.50	----	----	----

A^{1}= 25-200°C B^{1}= 250-580°C C^{1}= 580-900°C
A^{11}= 25-200°C B^{11}= 250-640°C C^{11}= 640-900°C

CONCLUSIONS

1. The exothermic peaks of DTA curves of montmorillonite or laponite treated with R6G and recorded in air are due to the oxidation of H, C and N atoms. The first exothermic peak is the result of the oxidation of the H atoms whereas the other peaks result from the oxidation of C and N atoms.
2. The shapes of the gas evolution curves of R6G treated montmorillonite or laponite are independent of the degree of saturation of the clay. This may serve as an indication that only one type of association is obtained between R6G and montmorillonite and one type is obtained between R6G and laponite, which is independent of the degree of saturation.
3. During the thermal analysis of R6G-laponite most of the organic matter is oxidized before the dehydroxylation of the clay whereas with R6G-montmorillonite a large portion of the organic matter is oxidized together with the dehydroxylation of the clay.
4. Pyrolysis products such as CH_3, C_2H_6 and H_2 were detected in the gaseous phase, in spite of being thermal analyzed in an oxidizing atmosphere.

TABLE 3

Effect of degree of saturation of montmorillonite and laponite on ratios between intensities of peaks A (maximum at 410-420°C) and B (maximum at 500-525°).

mM R6G per 100 g clay	Intensity ratio (peak A/peak B)	
	Montmorillonite	Laponite
3	1.12	0.90
20	1.10	0.66
40	1.18	0.61
60	----	0.50
80	1.14	----

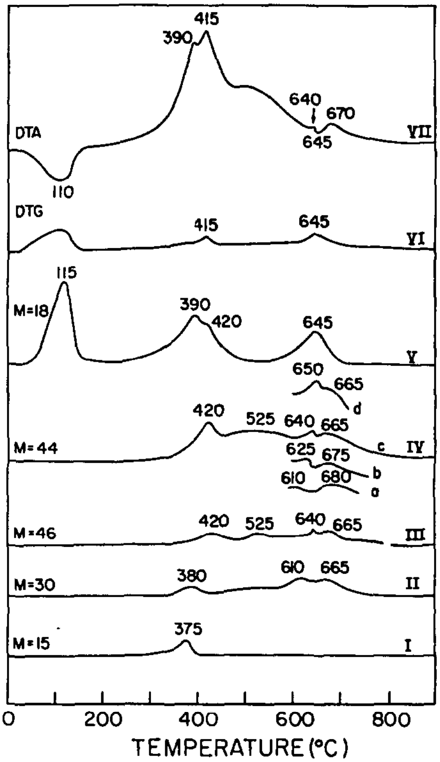

Fig 3

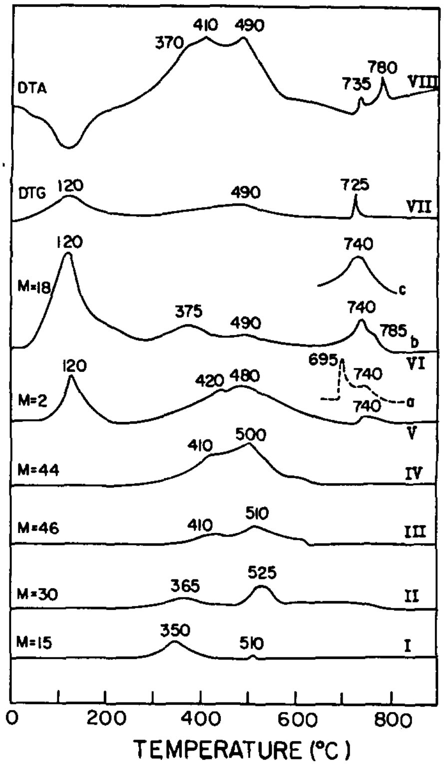

Fig 4

Fig. 3. Gas evolution curves of masses (I) 15, (II) 30, (III) 46, (IVc) 44, (V) 18, and DTG and DTA curves (VI and VII, respectively) of montmorillonite treated with 40 mmole R6G per 100 g clay. (IVa, b and d) saturations are 3, 20 and 60 mmole R6G per 100 g montmorillonite, respectively.

Fig. 4. Gas evolution curves of masses (I) 15, (II) 30, (III) 46, (IV) 44, (V) 2, (VIb) 18 and DTG and DTA curves (VII and VIII, respectively) of laponite treated with 20 mmole R6G per 100 g clay. (VIa and d) saturations are 3 and 40 mmole R6G per 100 g laponite, respectively.

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