

THERMAL ANALYTIC STUDY OF THE ADSORPTION
OF CRYSTAL VIOLET BY MONTMORILLONITE

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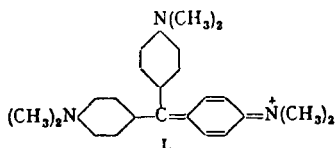
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ABSTRACT

The adsorption of crystal violet by montmorillonite was investigated by visible spectroscopy, X-ray diffraction and thermal analysis. DTA, TG and DTG curves were run in air. The evolved H₂O, CO₂, NO₂, CH₃ and C₂H₆ were simultaneously determined by mass-spectrometry. The spectroscopic study showed that the adsorption of crystal-violet may result in four different types of adsorption. In one type π interactions occur between the dye cation and the aluminosilicate layer. This type of interaction increases the thermal stability of the dye cation. The oxidation of this dye cation occurs only together with or after the dehydroxylation of the montmorillonite, whereas the oxidation of other adsorbed dye species occurs at lower temperatures. The oxidation gives rise to exothermic peaks and to CO₂ evolution peaks.

INTRODUCTION

The adsorption of crystal violet (CV, I) by various homoionic montmorillonites was recently investigated by Ghosh, Hepler and Yariv [1] using spectrophotometric methods. From the location of the principal $\pi \rightarrow \pi^*$ absorption band they identified four different types of adsorption of CV by montmorillonite. Type A is identified by an absorption band located at 590 nm (band α).



This absorption band characterizes monomeric cations located on the particle surfaces at the solid-liquid interface. Type B is identified by an absorption band at wavelengths longer than 590 nm (perturbed band α). This absorption band characterizes monomeric cations located inside the interlayer space of the montmorillonite. Type C is identified by a metachromic band at wavelengths shorter than 590 nm (band β), ranging from 526 to 570 nm. This absorption band characterizes monomeric cations located in the interlayer space and bound to the clay surface by π interactions. Type D is identified by an absorption band located below 510 nm (band γ). This absorption band characterizes aggregated cationic entities (quasi-micelles) which are located in the interparticle space of a floc. Possible models for the four types of adsorption of CV with the alumino-silicate layers of montmorillonite are shown in Fig. 1.

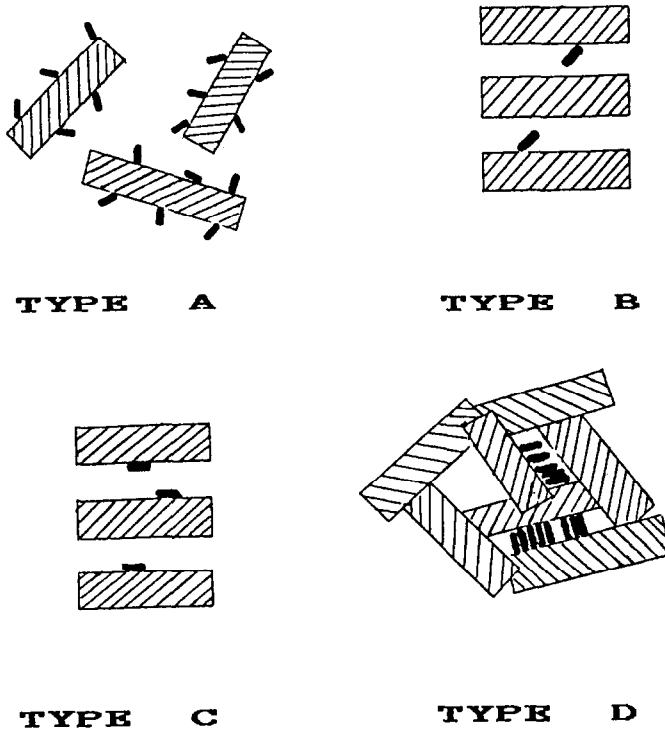


Fig.1. Possible models for the four types of adsorption of CV by montmorillonite.

DTA has been widely used for the study of adsorption of organic materials by clay minerals [2]. In most studies the DTA curves are applied as fingerprints for the identification of different types of interactions which are obtained between the organic entity and the clay mineral. Recently, we showed that it is possible to make a reliable interpretation of the peaks in the DTA and DTG curves if they are supplemented by gas evolution curves [3, 4]. In this method the combustion products are mass-spectrometrically analyzed simultaneously with the DTA and TG runs. In these publications we described the thermal analysis of montmorillonite and laponite treated with the cationic dyes rhodamine 6G and acridine orange. From spectrophotometric studies it was found that the adsorption of acridine orange by montmorillonite is accompanied by π interactions between the oxygen plane and the aromatic entity [5]. On the other hand, due to steric hindrance the adsorption of rhodamine 6G by montmorillonite is not accompanied by π interactions of this kind [6]. In the case of laponite, the adsorption of both dyes is not accompanied by π interactions between the clay and the dye cation. The shapes of the gas evolution curves of rhodamine 6G treated montmorillonite or laponite and those curves of acridine orange treated laponite are not affected by the degree of saturation of the clay. On the other hand, gas evolution curves of acridine orange treated montmorillonite showed that the shapes of the different curves and the appearance of several peaks depend on the degree of saturation of the clay. This is an indication of the presence of several types of association between the dye and montmorillonite, one of which comprises the π interactions between the clay layers and the dye cation.

In the present investigation the adsorption of CV by montmorillonite was studied by thermal analysis. Different types of adsorption were identified by the spectrophotometric method supplemented by X-ray diffraction. A correlation was made between the thermal analysis and the spectroscopic data.

EXPERIMENTAL

CV was supplied by BDH. Montmorillonite (Wyoming bentonite) was supplied by Ward's Natural Science Establishment, Inc. Air-dried clay samples (250 mg) were dispersed in 20 ml of water. After an aging period of 24 hours, various amounts of the dye solution were added dropwise to the well-stirred clay suspension. The suspension was kept in the dark and after 24 hours the organo-clay was separated by centrifugation. Samples were washed six times with distilled water to remove excess dye.

Oriented samples of CV treated montmorillonite were prepared for X-ray diffraction by drying the suspension on glass slides. X-ray diffraction patterns were recorded on a Philips PW 1730 diffractometer.

Thermoanalytical experiments were carried out under a flow of air on Mettler TA-1 thermal analysis instrument coupled with a Balzers quadrupole mass-spectrometer [7]. Samples of 20 mg 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. The following atomic masses were used for the gas evolution curves: H₂O, 18; CO₂, 44; NO₂, 46; CH₃, 15 and C₂H₆, 30.

For spectrophotometric measurements suspensions containing a constant amount of dye (4.0×10^{-6} M) and increasing amounts of clay in the concentration range of $2-400 \times 10^{-4}$ wt% were used. Spectra were recorded at room temperature, using a Cary 219 double-beam spectrophotometer, in the 700-400 nm range.

RESULTS AND DISCUSSION

Visible Spectrophotometry

Spectra of an aqueous solution of CV and of aqueous montmorillonite suspensions treated with CV are shown in Fig. 2. With degrees of saturation of 4, 25 and 50 mmole dye per 100 g clay, band α , which is the principal absorp-

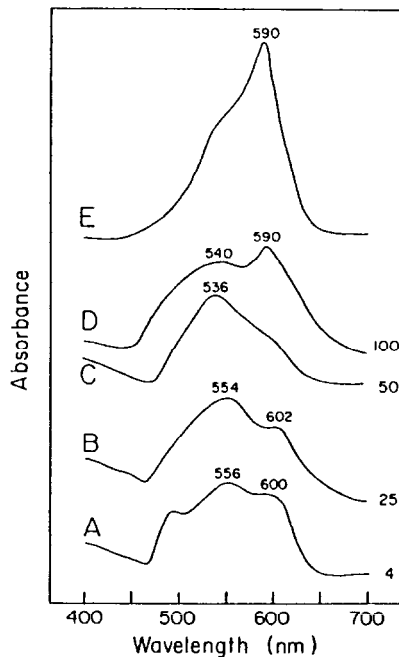


Fig.2. Electronic spectra of (E) an aqueous solution of CV (4×10^{-6} M) and of the same solution in the presence of different amounts of montmorillonite. (A) 4, (B) 25, (C) 50 and (D) 100 mmole CV per 100 g clay.

tion band in the spectrum of the dilute dye solution, is very weak in the spectra of the suspensions. Instead, the metachromic band β appears, indicating the occurrence of adsorption type C. From the location of band α (>590 nm) it is obvious that in addition to adsorption type C, type B is also present, but in small amounts relative to type C. Only when the degree of saturation is 100 mmole CV per 100 g clay, does band α become the principal band. It is located at 590 nm which is characteristic for type A. At this stage the adsorption by the type C mechanism becomes small relative to that of type A. Type D is obtained in trace amounts. The contribution of this type to the thermal analysis can be neglected.

X-ray study

Oriented specimens of clay samples treated with various amounts of CV were examined by X-ray diffraction under ambient conditions (Table 1). Heating natural montmorillonite at 195°C for six days results in a c-spacing of 1.0 nm due to dehydration. However, in the presence of CV only minor changes in the c-spacing due to dehydration by the same thermal treatment 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. Up to a degree of saturation of 40 mmole dye per 100 g clay the c-spacing is <1.5 nm, a monolayer of CV is formed in the interlayer space with the aromatic rings parallel to the silicate layer. Since the spectrophotometric study shows metachromasy, the blue shift at this stage must be the consequence of π interaction between the aromatic entity and the oxygen plane of the alumina-silicate layer. With a higher degree of saturation, the c-spacing is greater than 1.6 nm, indicating a bilayer or tilting of the cationic dye relative to the silicate layer.

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

m mole CV per 100 g clay	Basal Spacings
0	1.28
4	1.44
25	1.45
50	1.65
100	2.06

Thermal analysis

Representative DTA curves of montmorillonite saturated with various amounts of CV are shown in Fig. 3. The H_2O , CO_2 and NO_2 evolution curves are also shown in the figure. All these curves differ from those of pure CV. As with R6G and AO treated montmorillonite, according to the directions of the various peaks, the DTA curves of the organo-clay can be divided into three regions. From the DTG curves (not shown) it is obvious that the three regions are associated with three stages of weightloss. In the first region (region A), up to $200^\circ C$, the endothermic dehydration of the clay is the major thermal reaction. The second region (region B) is between $200-550^\circ C$. The exothermic oxidation of the adsorbed CV is the principal thermal reaction of this region. The DTG curves show that this region can be further divided into three subregions. The third region (region C) occurs at temperatures above $550^\circ C$. The major thermal reaction of this region is the dehydroxylation of the smectite mineral and the last stages of the oxidation of organic matter. This

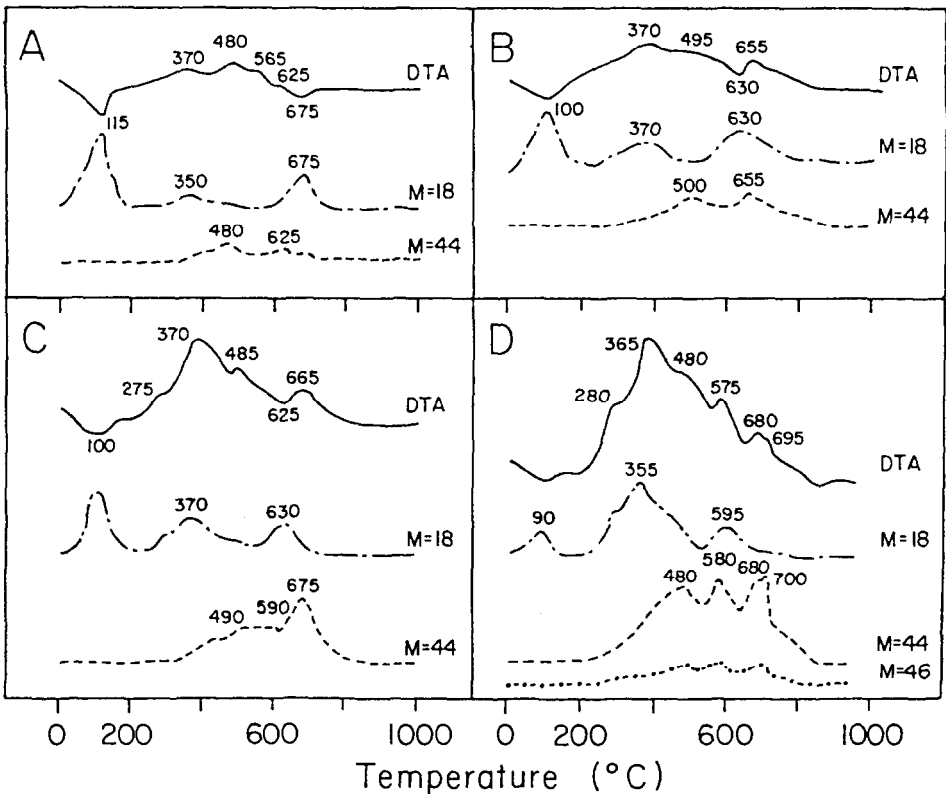


Fig.3. DTA and gas evolution curves of montmorillonite treated with CV. (A) 4, (B) 25, (C) 50 and (D) 100 mmole CV per 100 g clay. M = 18, 44 and 46 are gas evolution curves of H_2O , CO_2 and NO_2 .

region can be divided into two sub-regions. Weightloss occurring in the different regions was determined from TG curves (Table 2).

TABLE 2
Weightloss (%) obtained by TG of montmorillonite treated with various amounts of CV in three regions (A, B and C) of the thermal analysis.

mmole CV per 100 g clay	REGIONS OF THE THERMAL ANALYSIS					
	A	B			C	
	25-200°C	200-300°C	300-425°C	425-550°C	550-625°C	625-1000°C
0	6.60	0.00	0.10	0.20	0.20	3.20
4	5.00	0.00	0.55	0.95	1.25	2.25
25	3.00	0.25	1.00	3.00	2.50	6.00
50	3.00	0.50	1.75	3.50	3.00	9.00
100	1.75	1.25	3.00	8.50	6.00	11.50

The first region

According to the H₂O evolution curves the first region represents the dehydration of the clay. At this stage the interlayer water is evolved. 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 to 90°C with increasing degrees of saturation of montmorillonite. At the same time the amount of evolved water decreases (see H₂O evolution curves and Table 2). The shift in the peak temperature and the decrease in weightloss are probably associated with increasing hydrophobicity of the interlayer space as a result of an increase in the amount of adsorbed dye. As a consequence of increasing hydrophobicity the amount of interlayer water decreases.

The second region

In the curves of CV treated montmorillonite peak maxima appear at 355-370 and 480-500°C. A shoulder is observed at 280°C only when the degree of saturation is >25 mmole dye per 100 g clay. These exothermic peaks, which do not appear in the DTA curves of untreated montmorillonite, result from the oxidation of the adsorbed CV. These peaks are associated with weightloss which increases with increasing degrees of saturation (Table 2). The H₂O which is evolved in this region results from the combination of hydrogen atoms of the CV cations with oxygen atoms of air. The H₂O evolution curves of CV treated

montmorillonite show a single intense peak at 355-370°C and a shoulder at 280°C. The degree of saturation has an effect on the location of the principal peak of the H₂O evolution curve of CV-montmorillonite. It appears at 370°C up to 50 mmole CV per 100 g clay and shifts to 355°C with 100 mmole dye per 100 g montmorillonite. The intensity of this peak in the H₂O evolution curve and the weightloss that is associated with this peak (200-425°C) are proportional to the degree of saturation.

The evolution of CO₂ and NO₂ results from the oxidation of the carbon and nitrogen atoms, respectively, originating from the CV cations. The evolution curves of these two gases are very similar. They both show a great dependency on the degree of saturation. The evolution of CO₂ starts below 300°C. An intense CO₂ or NO₂ evolution peak appears at 480°C. The intensity of this peak increases with each increasing degree of saturation.

Weightloss in the temperature range of 425-550°C is due to the combination of carbon atoms with oxygen atoms of air. At up to 50 mmole CV per 100 g montmorillonite there is almost no correlation between weightloss and the degree of saturation. Above 50 mmole CV per 100 g montmorillonite weightloss increases very much with increasing degrees of saturation. Only part of the carbon is oxidized at this stage. In the discussion at the third region of the DTA curve, it will be shown that the oxidation of the residual carbon in montmorillonite occurs above 550°C.

Correlation of the DTA curve with the H₂O and CO₂ evolution curves reveals that the profile of the DTA curve is determined by the amounts of hydrogen and carbon which are oxidized. The shoulder at 280°C and the first exothermic peak at 355-370°C are the consequence of the oxidation of hydrogen atoms. The second peak at 480-500°C is due to the oxidation of carbon.

The third region

This region is controlled by the dehydroxylation of the smectite mineral. The DTA curve of untreated montmorillonite shows an endothermic peak at 695°C.

The temperature of the dehydroxylation of CV-treated montmorillonite can be determined from the H₂O evolution curve. It is located at 695°C in the H₂O evolution curve of untreated montmorillonite. Fig. 3 shows that the dehydroxylation peak shifts to lower temperatures with increasing degrees of saturation. It is located at 675 and 595°C with 4 and 100 mmole dye per 100 g montmorillonite, respectively.

Table 2 shows that the weightloss during the third region increases with each increasing degree of saturation, indicating that the oxidation of organic matter has not been completed in the second region but continues into the third region. In agreement with this, the CO₂ and NO₂ evolution curves of montmorillonite show two peaks at 565-580 and 625-680°C. However, weightloss

associated with the latter peak increases only up to a degree of saturation of 50 mmole CV per 100 g montmorillonite. With higher degrees of saturation the increment in weightloss becomes small and a large portion of carbon is already oxidized at a lower temperature with the appearance of the 580°C peak in the CO₂ and NO₂ evolution curves.

In CV treated montmorillonite the exothermic oxidation reaction overlaps the endothermic dehydroxylation reaction (compare H₂O and CO₂ evolution curves in Fig. 3). An endothermic peak is shown in DTA curves of montmorillonite saturated with 4 mmole CV per 100 g clay. On the other hand, with 25, 50 and 100 mmole CV per 100 g montmorillonite exothermic peaks are detected in this region (Fig. 3).

CH₃ and C₂H₆ evolution curves

Mass 15 represents CH₃ radicals. They are characteristic of methane. The identification of these radicals in the evolved gases may serve as proof of the pyrolysis of CV. Peak maxima are located at 270°C in the evolution curves of montmorillonite and laponite, respectively, before the maxima of peaks which characterize oxidation reactions of carbon atoms.

Mass 30 represents C₂H₆ and NO. The identification of the former among the evolved gases may serve as a proof of pyrolysis. NO is obtained due to the incomplete oxidation of nitrogen atoms of the CV. Peaks in the gas evolution curves of mass 30 are much more intense than those of mass 15. The first peak in the gas evolution curves of montmorillonite is located at 330°C slightly above the temperatures of the peak in the CH₃ evolution curve and below those of the peaks of the oxidation reactions. It probably characterizes the pyrolysis of CV. The last peak in these evolution curves is located at 640°C. It may represent, at least in part, the incomplete oxidation of the nitrogen. The temperature of this peak is slightly below that of the last peak of the CO₂ evolution curve.

CONCLUSIONS

Although the spectrophotometric study was carried out in suspensions and the thermal analysis was done on the solid phase, the present data demonstrate that the CO₂ evolution curves are dependent on the mechanism of adsorption of CV by montmorillonite. It seems that the peak at 625-680°C is characteristic for type C whereas the peak at 580°C is characteristic for type A. The peak at 480°C seems to be characteristic for types A and B. The spectrophotometric study showed that with 4, 25 and 50 mmole dye the adsorption is mainly of type C, with small amounts of type B. The relative amount of the former increases with increasing degrees of saturation. This is indeed illustrated by the

intensity of the 625-680°C peak relative to the intensity of the 480°C peak. The spectrophotometric study also showed that with 100 mmole CV per 100 g montmorillonite considerable amounts of associations of type A are present. This is illustrated by the appearance of the CO₂ evolution peak at 580°C.

From the present results it seems plausible to assume that the π interactions between the aromatic entity and the oxygen plane contribute to the thermal stability of the carbon skeleton of the organic matter, and consequently, the exothermic peak appears together or after the dehydroxylation reaction of the clay. Laponite does not form π interactions with the aromatic entity. During a thermal analysis of laponite treated with CV we found that the CO₂ evolution peak is located at 515°C (paper in preparation). In conclusion, thermal analysis by means of CO₂ evolution curves seems to be promising for the identification of π interactions between clay minerals and organic matter.

ACKNOWLEDGEMENT

The authors wish to thank Dr. Harold Cross for reading the manuscript and for his useful discussions and suggestions. The X-ray diffractions were recorded by Mr. Shlomo Meiri of the Department of Geology at the Hebrew University of Jerusalem. His assistance is gratefully acknowledged.

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