

**THERMAL ANALYTIC STUDY
OF THE ADSORPTION OF CRYSTAL VIOLET
BY LAPONITE**

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The adsorption of crystal violet on laponite was investigated by X-ray diffraction and thermal analysis. DTA, TG and DTG curves were recorded in air. The evolved H₂O, CO₂, NO₂, H₂ and C₂H₆ were simultaneously determined by mass spectrometry. The thermal analysis curves were compared on one hand with the thermal analysis curves of laponite and on the other hand with thermal analysis curves of non-adsorbed crystal violet and of crystal violet adsorbed on montmorillonite. The thermal analysis curves of crystal violet adsorbed on laponite show similarities to the curves of the non-adsorbed crystal violet, but differ from the curves of crystal violet adsorbed on montmorillonite. The differences in the thermal behaviour were attributed to π interactions which do not occur between crystal violet and laponite but do occur between this dye and montmorillonite.

The adsorption of organic aromatic dyes by montmorillonite has been extensively studied (see e.g. Ref. 1–8] because of the importance of this reaction in various industrial, environmental and agricultural processes. In recent years laponite, a synthetic hectorite, has replaced montmorillonite in some of its industrial applications, and consequently, the adsorption of organic aromatic dyes by this mineral has been investigated by several authors (see e.g. Ref. 9–10). Since both minerals belong to the smectite family, most authors believe that they react very similarly. Recently, it has been shown by visible spectroscopy that the two minerals adsorb cationic dyes by different adsorption mechanisms. The difference is shown by their ability to produce metachromasy of the adsorbed dye [11].

In aqueous solutions metachromic dyes are characterized in that the location of the maximum of the $\pi \rightarrow \pi^*$ absorption band depends on the concentration of the dyes. In dilute solutions the maximum of this absorption (band α) is at a longer wavelength compared with its location in the more concentrated solutions (band β).

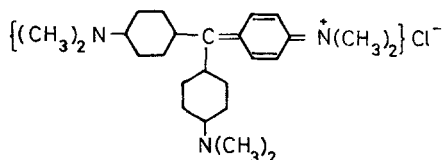
With increasing concentrations this absorption is shifted to still shorter wavelengths (band γ). Metachromasy in aqueous solutions results from the association of two or more dye cations and the blue shift is the consequence of π interactions between the aggregated aromatic entities.

When a metachromic dye is adsorbed by montmorillonite with tetrahedral substitutions, part of it undergoes metachromasy as a result of π interactions between surface oxygens of Si–O–Al tetrahedral groups and the aromatic rings. Consequently, metachromasy in montmorillonite systems is detected even at very low degrees of saturation. In laponite systems the situation is different and metachromasy is detected only after saturation of the clay with considerable amounts of the metachromic dye.

The adsorption of crystal violet (CV, I) by laponite has recently been investigated by normal and differential electronic spectroscopy [12]. The following spectroscopic phenomena were observed: with degrees of saturation below 44 mmol CV per 100 g laponite the clay was peptized and band α showed a red shift, indicating the adsorption of monomeric CV into the interlayer space; with degrees of saturation between 44 and 130 mmol CV per 100 g clay, metachromasy and flocculation were observed. Metachromasy is characteristic for the adsorption of dimeric CV species. Since metachromasy appeared together with the flocculation of the clay it was assumed by the investigators that the dimers were located in the interparticle space of the floc. With higher saturation laponite repeptized and band α again appeared but was not shifted to longer wavelengths as before the flocculation of the laponite. At this stage the monomeric cations were adsorbed in excess of the cation exchange capacity. Consequently the clay was peptized and the adsorbed cations were located at the water solid interface.

DTA was used by several investigators for the study of the adsorption of organic matter by smectite minerals [13, 14]. A combined DTA–EGA technique was recently used for the study of the adsorption of rhodamine 6G by montmorillonite and laponite [15]. In this technique the evolved gases were determined by mass spectrometry together with the recording of the DTA, and thus, a better understanding was obtained of the thermal reactions. In that study it was found that the exothermic peaks of the DTA curves recorded in air were 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. In a recent publication we described the thermal analysis of CV adsorbed by montmorillonite [16]. In the present publication the thermal analysis of CV adsorbed by laponite is described. Samples containing 4 and 25 mmol CV per 100 g clay (monomeric CV) and 50 and 75 mmol CV per 100 g clay (dimeric CV) were examined. We will show that as a result of different adsorption mechanisms

between montmorillonite and laponit e, different thermal analysis curves are obtained.



Experimental

CV was supplied by BDH. Laponite XLG (a synthetic Na hectorite) was kindly donated by Laporte Industries, Ltd., UK. Air-dried clay samples (250 mg) were dispersed in 20 ml of water. After an aging period of 24 hours, various amounts of CV 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 laponite 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 a Mettler TA-1 thermal analysis instrument coupled with a Balzer quadrupole mass spectrometer [17]. Samples of 20 mg CV, laponite or CV treated laponite were used for each run. The rate of the air flow was 1.9 l.p.H. Heating rate was 10 deg · min⁻¹. Calcined kaolinite was used as a reference material. Total pressure in mass spectrometer was 4 × 10⁻⁶ mbar. Partial pressures of the various gases are indicated in the legends to figures given for the most intense peak in the appropriate curve. The following atomic masses were used for the gas evolution curves: H₂O, 17 and 18; CO₂, 22 and 44; NO₂, 46; CH₃, 15 and C₂H₆, 30.

Results

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 untreated laponite at 195 °C for six days resulted 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

Table 1 Colloidal and spectroscopic characterizations and basal spacings of air-dried laponite treated with different amounts of CV

mmol CV per 100 g clay	Colloidal characterization	Spectroscopic characterization	Basal spacings, nm
0	—	—	1.34
4	Dispersed	No metachromasy	1.46
25	Dispersed	No metachromasy	1.39
50	Flocculated	Metachromasy	1.47b
75	Flocculated	Metachromasy	1.61vb

b: broad; vb: very broad.

presence of the organic cation in the interlayer space. A c -spacing smaller than 1.5 nm is a proof that dimerization of the dye in the interlayer space does not occur. This is the case with samples containing 4 and 25 mmole CV per 100 g clay which do not show metachromasy. Electronic spectra of these samples show a red shift of band α . This is an indication that the cationic dye is located in an acidic environment. According to the X-ray determination the interlayer space should be the acidic environment for the adsorbed dye.

The spectrum of the sample containing 50 mmol CV per 100 g clay shows metachromasy which may account either for π interactions between the clay oxygen plane and the organic cation or between CV dimers. The first possibility is ruled out because metachromasy was not observed with 4 and 25 mmol CV per 100 g clay, in the event that the dye is also present in the interlayer space. Metachromasy of CV in laponite should result from dimerization of the cation. However, a c -spacing smaller than 1.5 nm which was determined for this sample, may indicate that the dimerization of CV occurs outside the interlayer space. In the spectroscopic study of the adsorption of CV by laponite it was found that metachromasy is always detected together with flocculation. It was therefore concluded that dimerization of CV occurs in the interparticle space of the floc [12].

Thermal analysis of untreated laponite

DTA, TG, and DTG curves of untreated laponite together with H₂O, CO₂ and H₂ evolution curves are shown in Fig. 1. The endothermic peak at 135 °C is accompanied by a weight loss of 12.8% in the temperature range 25–350°. This is mainly due to the dehydration of interlayer and interparticle water. Weight loss in the temperature range 350–620° is 1.2%. The second endothermic reaction at 730° is due to the dehydroxylation of the clay and the formation of an amorphous meta laponite phase. This endothermic reaction is followed immediately by an exothermic recrystallization of the amorphous phase at 755°. A weight loss of 3.3%

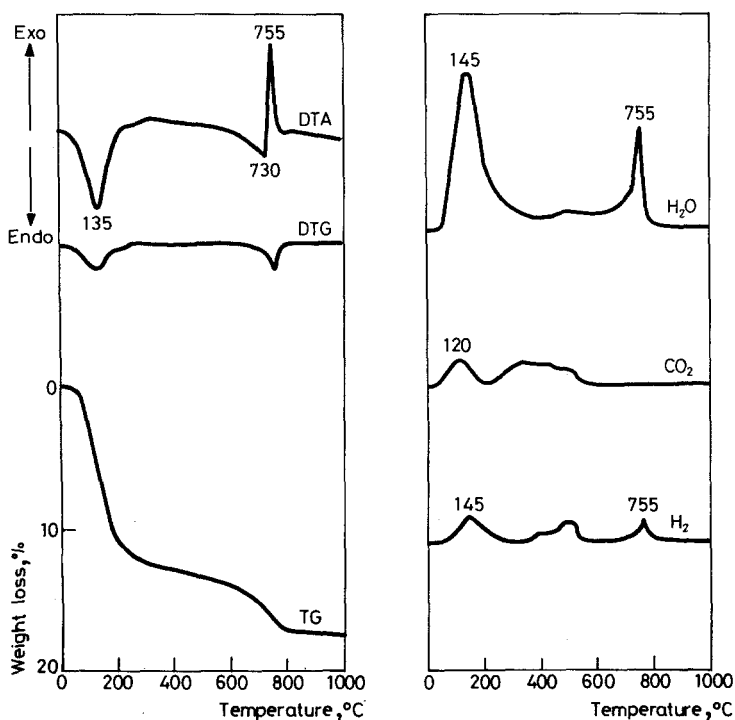


Fig. 1 DTA, TG, DTG and gas evolution curves of laponite. Partial pressures for the most intense peaks in the gas evolution curves are as follows: H_2O , 1.6×10^{-10} ; CO_2 , 1.2×10^{-12} ; H_2 , 1.6×10^{-13}

in the temperature range 620–790° is due to the evolution of H_2O originating from lattice hydroxyls.

The CO_2 evolution curve shows that very small amounts of this gas are evolved below 525°. The CO_2 , and especially that fraction which gives an evolution peak at 120°C, probably originates from the atmosphere, being adsorbed during the synthesis of the laponite. The broad evolution peak between 315 and 525° may result from the oxidation of trace organic impurities.

The H_2 evolution curve shows small peaks with maxima at temperatures similar to those of the H_2O evolution curve, which may be associated with decomposition of water. A small evolution peak at 475° may be due to the decomposition of organic impurities.

Thermal analysis of non-adsorbed crystal violet

DTA, TG, and DTG curves of CV together with H_2O , CO_2 , NO_2 and H_2 evolution curves are shown in Fig. 2. The first broad endothermic peak with a

maximum at 125° is associated with a peak in the H₂O evolution curve and is due to the drying of the dye. This endothermic peak is followed by a very small exothermic peak at 215° (the start of the oxidation of the organic hydrogen), followed by a small endothermic peak at 245° (melting of the organic salt and fast dehydration), and another endothermic peak at 410° (pyrolysis of the organic matter). Above this temperature the oxidation of the carbon and the formation of CO₂ leads to a very strong exothermic reaction with two sharp maxima at 520 and 550°. The DTG curve, on the other hand shows three steps for the reaction which occurs at this stage, at 495, 520 and 550°, the latter being a shoulder. The appearance of two peaks and a shoulder is in agreement with the peaks which are observed in the CO₂ and NO₂ evolution curves. The discrepancy between the DTA, on one hand, and the DTG or CO₂ and NO₂ evolution curves, on the other hand, is probably due to the fact that this exothermic reaction occurs together with the endothermic pyrolysis reaction which is strong below 500°. The resulting peaks are the sum of both reactions. Expected peaks of exothermic reactions occurring at 465° (H₂O

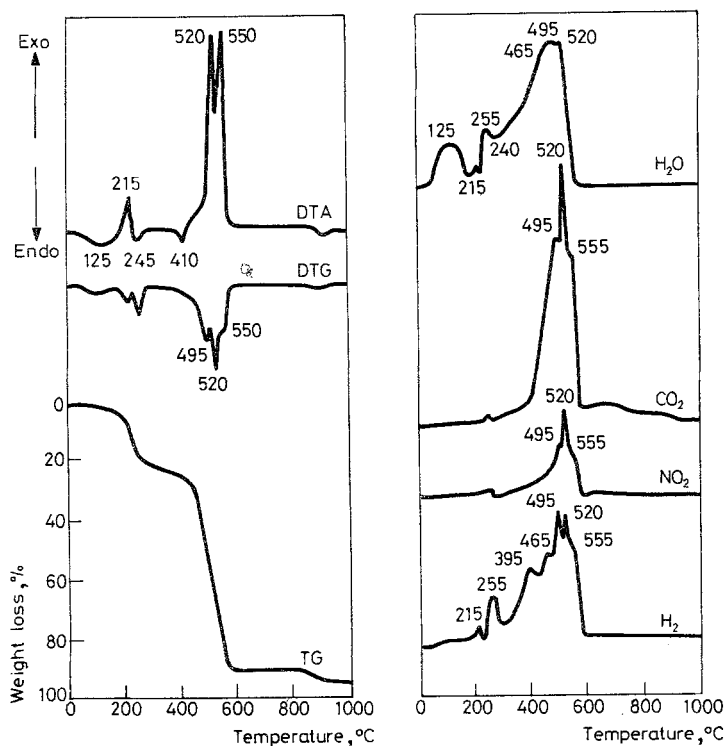


Fig. 2 DTA, TG, DTG and gas evolution curves of CV. Partial pressures for the most intense peaks in the gas evolution curves are as follows: H₂O, 1×10^{-10} ; CO₂, 1×10^{-9} ; NO₂, 1×10^{-12} ; H₂, 8×10^{-12}

evolution) and 495° (H₂O, CO₂ and NO₂ evolutions) do not appear in the DTA curve.

A very small endothermic peak appears at 900° and is associated with a weight loss of about 4%. The CO₂ evolution curve shows that only very small amounts of this gas is evolved at this stage. We assume that an evolution of various pyrolysis products which were not examined in our mass spectroscopy studies, is responsible for the 4% weight loss. The H₂ evolution curve shows maxima at the same temperatures at which the H₂O, CO₂ or NO₂ evolution curves show maxima as well as at those temperatures at which the DTA curve shows melting and pyrolysis. The ash content of CV is 4%.

Thermal analysis of laponite treated with crystal violet

Representative DTA curves of laponite saturated with various amounts of CV are shown in Fig. 3. The H₂O, CO₂ and NO₂ evolution curves are also shown in the figure. According to the directions of the various peaks, the DTA curves of CV laponites can be divided into three regions. In the first region (region A), up to 200°,

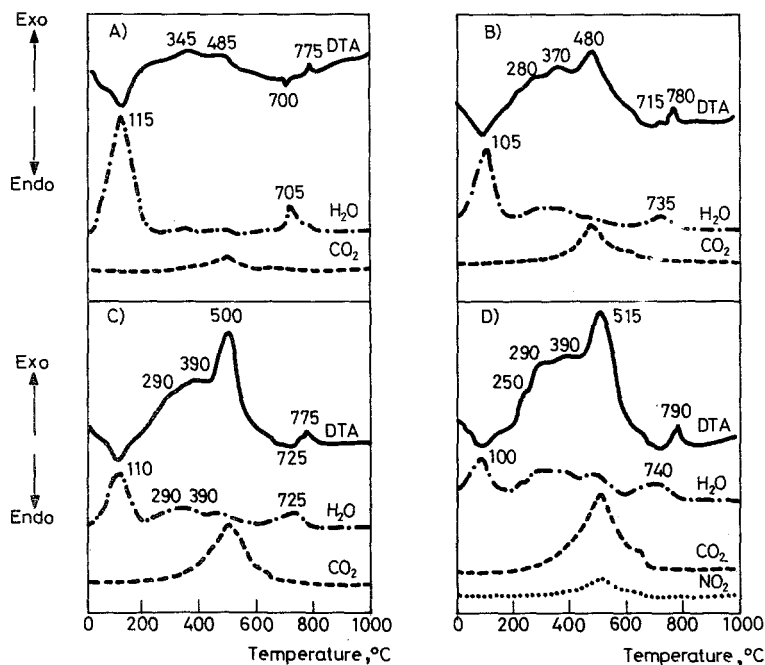


Fig. 3 DTA and gas evolution curves of laponite treated with various amounts of CV, (A) 4, (B) 25, (C) 50 and (D) 75 mmole CV per 100 g laponite. Partial pressures for the most intense peaks in the gas evolution curves are as follows: (A) H₂O, 7.8×10^{-11} ; CO₂, 6×10^{-12} ; (B) H₂O, 5.3×10^{-11} ; CO₂, 2.7×10^{-11} ; (C) H₂O, 4.1×10^{-11} ; CO₂, 4.4×10^{-11} ; (D) H₂O, 3.3×10^{-11} ; CO₂, 5.6×10^{-11} ; NO₂, 6×10^{-13}

Table 2 Weight loss (%) determined by TG of laponite treated with different amounts of CV in three regions (A, B and C) and sub-regions of the thermal analysis

mmol CV per 100 g clay	Regions of the thermal analysis				
	A	B		C	
	25–200 °C	200–420 °C	420–600 °C	600–670 °C	670–1000 °C
0	11.10	2.00	0.70	1.10	2.40
4	13.20	1.60	2.00	1.00	2.50
25	9.20	3.00	7.70	1.30	2.70
50	7.00	3.50	11.50	2.50	3.50
75	4.50	3.50	13.40	3.20	2.80

the endothermic dehydration of the clay is the major thermal reaction. The second region (region B) is between 200 and 600°. The exothermic oxidation of the adsorbed CV is the principal thermal reaction of this region. The DTG and EGA curves show that this region can be further divided into two subregions, from 200 to 420° and from 420 to 600°. The third region (region C) occurs at temperatures above 600°. It can also be divided into two sub-regions, from 600 to 670 and from 670 to 1000°. The major thermal reaction of this region is the dehydroxylation of the smectite mineral and the last stages of the oxidation of organic matter. Weight losses occurring in the different regions were determined from TG curves (Table 2).

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 135 to 100–115°. The exact location of this peak depends on the degree of saturation, it shifts to lower temperatures with increasing degree of saturation. At the same time the amount of evolved water decreases (Table 2). An increase in weight loss is observed with 4 mmol CV per 100 g clay, but this is due to the fact that some of the interlayer water which in the reference untreated clay was evolved at higher temperatures, such as 200–420°, is already evolved from the organo-laponite complex below 200°. The shift in the peak temperature and the decrease in the amount of adsorbed water result from increasing hydrophobicity of the interlayer space as a result of increase in the amount of adsorbed dye.

The second region

In the DTA curves of CV treated laponite, two exothermic peaks are traced. The first peak is very broad, located at 345° with 4 mmol CV per 100 g clay. This peak shifts to higher temperatures with increasing degrees of saturation (e.g. 390° with ≥ 50 mmol CV per 100 g clay) but at the same time a shoulder appears at 290°. The exothermic reaction which occurs at this stage is the oxidation of the organic hydrogen and the evolution of H₂O. It appears in the EGA curves as a plateau extending from 290 to 390° when the degree of saturation is ≥ 25 mmol CV per 100 g clay, or as a single broad peak at 350° when the degree of saturation is 4 mmol CV per 100 g clay.

The second exothermic peak shifts from 480 to 515° with 4 and 75 mmol CV per 100 g clay, respectively. The exothermic reaction which occurs at this stage is the oxidation of the organic carbon and nitrogen. Evolution peaks of CO₂ and NO₂ appear in the respective EGA curves at a similar temperature, which is the temperature of the exothermic peak. Small amounts of hydrogen are also oxidized at this stage, but the H₂O evolution peaks appear at temperatures which are slightly lower than those of the CO₂ evolution peaks or the respective exothermic peaks.

Weight loss in the temperature range 200–420° is in part due to desorption of strongly bound interlayer water which did not escape below 200°, and in part due to the combination of the organic hydrogen with air oxygen. Except for the sample containing 4 mmol CV per 100 g clay, weight loss in this temperature range increases only slightly with increasing degree of saturation. This is due to the fact that some of the strongly bound water has already escaped at below 200°.

Weight loss in the temperature range 420–600° is mainly due to the oxidation of the carbon, and to some extent also due to the oxidation of organic nitrogen which behaves similarly to carbon, and hydrogen which has not been oxidized below 420°. At this region weight loss increases significantly with increasing degree of saturation (Table 2).

The third region

It is very difficult to determine a definite temperature for the end of region 2 and the beginning of region 3, because dehydroxylation starts at 620° whereas the oxidation of the organic matter and the evolution of CO₂ is completed above 670°. The DTA and the CO₂ evolution curves show a shoulder at 645–670°.

The dehydroxylation and recrystallization peaks of laponite are affected by the presence of the organic matter. The DTA peaks and the H₂O evolution peaks are shifted and their shapes are modified (Fig. 3). There is no explanation for this phenomenon which demands further study.

Table 2 shows that in the 600–670° temperature range thermal weight loss

increases with increasing degree of saturation. At this sub-region weight loss results from the evolution of H_2O (dehydroxylation, mainly above 670°) and the evolution of CO_2 (oxidation of the organic matter, mainly below 670°). As one would expect, weight loss between 600 and 670° increases with increasing adsorption, whereas above 670° weight loss is not affected by the degree of saturation.

C_2H_6 and/or NO evolutions curves

Mass 30 represents C_2H_6 and, to some extent also NO. The identification of the former among the evolved gases may serve as proof of pyrolysis. NO is obtained due to the incomplete oxidation of nitrogen atoms of the CV. The first peak in the gas evolution curve of mass 30 is located at 290° , the temperature at which the broad H_2O evolution peak begins. It probably characterizes the pyrolysis of CV. A second peak appears at 560° , slightly above the CO_2 evolution peak. It may represent, at least in part, the incomplete oxidation of the nitrogen. It should be noted that the intensities of these peaks are very small relative to those of the CO_2 evolution peaks.

Mass 15 which represents CH_3 radicals was not detected by the mass spectrometer. It should be mentioned that this radical was detected in the thermal analysis of CV adsorbed by montmorillonite [16].

Discussion

The thermal analysis curves of CV adsorbed by laponite show great similarities to those of non-adsorbed CV. The CO_2 and NO_2 evolution curves of adsorbed CV are very similar to those of the non-adsorbed CV, namely in that the principal evolution occurs at about 500° . The only difference is the very small shoulder at 645 – 670° which appears in the evolution curves of adsorbed CV but does not appear in the curves of non-adsorbed CV. Water evolution curves of both varieties of CV show that oxidation of hydrogen starts at about 200° but continues up to about 600° . The EGA curve of non-adsorbed CV showed that the evolution of H_2O above 420° was higher than that below this temperature whereas that of adsorbed CV showed that H_2O evolution was equal or almost so, below and above 420° . However, this may be due to the fact that the amount of the non-adsorbed CV which was employed for the analysis was equal to 20 mg whereas the total amount of the CV-laponite sample used for the thermal analysis was also equal to 20 mg but the amount of the organic material was only a few percent of the total 20 mg.

The DTA curves of the adsorbed CV also reveal similarities to that of the non-adsorbed CV with the exception that the endothermic peaks do not appear. These are the melting of the non-adsorbed salt at 245° and the pyrolysis at 410° . The

melting peak is not expected because the organic matter does not exist as a solid salt but is adsorbed. The pyrolysis peak is not observed and since the exothermic zone below 500° is very pronounced for the adsorbed CV, it is suggested that the catalytic effect of the clay is manifested by the lowering of the activation energy of this reaction, thus leading to an early gradual pyrolysis.

Thermal analysis curves of CV adsorbed on montmorillonite, which were described in a previous publication [16] differ from those of CV adsorbed on laponite or of non-adsorbed CV. Moreover, the shapes of the different curves of CV adsorbed on montmorillonite, the number and size of the various peaks as well as the temperatures of the peak maxima change with the degree of saturation.

From the comparison of the thermal curves of CV treated montmorillonite with those of CV treated laponite it appears that π interactions between the aromatic entity and the oxygen plane of montmorillonite contribute to the thermal stability of the carbon skeleton of the organic matter, and consequently, a higher temperature is required for the oxidation of CV adsorbed on montmorillonite than the temperature needed for the oxidation of the dye when it is adsorbed on laponite or when the non-adsorbed dye is analyzed. In montmorillonite the principal exothermic peak appears together with or after the dehydroxylation reaction of the clay. Laponite does not form π interactions with the aromatic entity and therefore does not contribute to the thermal stability of CV. Consequently, the principal exothermic peak appears before the dehydroxylation reaction of the clay.

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Zusammenfassung – Mittels Röntgendiffraktion und thermischer Analyse wurde die Adsorption von Kristallviolett an Laponit untersucht. Es wurden die DTA-, TG- und DTG-Kurven in Luft registriert. Freigesetztes H₂O, CO₂, NO₂, H₂, und C₂H₆ wurde gleichzeitig mittels eines Massenspektrometers bestimmt. Die thermoanalytischen Kurven wurden einerseits mit denen von Laponit und andererseits mit denen von nichtadsorbiertem Kristallviolett bzw. mit denen von an Montmorillonit adsorbiertem Kristallviolett verglichen. Die thermoanalytischen Kurven von an Laponit adsorbiertem Kristallviolett und nichtadsorbiertem Kristallviolett zeigen Ähnlichkeiten, unterscheiden sich aber von denen von an Montmorillonit adsorbiertem Kristallviolett. Die Unterschiede im thermischen Verhalten werden damit erklärt, daß zwischen Kristallviolett und Laponit keine π -Wechselwirkungen auftreten, zu denen es jedoch aber wohl zwischen diesem Farbstoff und Montmorillonit kommt.

Резюме — Рентгенодифракционным методом и термическим анализом изучена адсорбция кристаллического фиолетового на лапоните. Кривые ДТА, ТГ и ДТГ были измерены в атмосфере воздуха. масс-спектрометрическим методом были одновременно определены выделяющиеся вода, углекислый газ, двуокись азота, водород и этан. Термические кривые были сопоставлены с таковыми для чистого лапонита, чистого кристаллического фиолетового и кристаллического фиолетового, адсорбированного на монтмориллоните. Термические кривые адсорбированного на лапоните кристаллического фиолетового были подобны таковым для неадсорбированного кристаллического фиолетового, но отличались от таковых для кристаллического фиолетового, адсорбированного на монтмориллоните. Эти различия в термическом поведении были отнесены за счет π взаимодействия, происходящего между кристаллическим фиолетовым и монтмориллонитом, но не происходящего между этим красителем и лапонитом.