SIMULTANEOUS DTA-TG STUDY OF MONTMORILLONITE MECHANOCHEMICALLY TREATED WITH CRYSTAL-VIOLET

I. Lapides[1], S. Yariv[1] and D. Golodnitsky[2]

[1]Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel
[2]Wolfson Applied Material Research Center, School of Chemistry, Sackler Faculy of Exact Sciences, Tel Aviv University, Tel Aviv 69978, Israel

Abstract

The mechanochemical solid-state adsorption of the cationic dye crystal violet (CV) by montmorillonite was investigated by XRD and simultaneous DTA-TG. Solid CV was ground with the clay for 5 min and four different varieties of CV mechanochemically treated clay were investigated. X-ray and DTA data were compared with those of CV-montmorillonite obtained from an aqueous suspension. X-ray and DTA studies of a ground mixture and a ground mixture heated at 110°C suggest that the mechanochemical adsorption of organic cations takes place on the external surfaces of the clay. The study of a ground mixture washed with water, and washed with water and acetone reveal that water is essential for the penetration of CV into the interlayer space.

Keywords: crystal violet, DTA, mechanochemical adsorption, montmorillonite, organo-smectites

Introduction

The adsorption of cationic dyes by montmorillonite has been the subject of many investigations. In most cases, the adsorption was carried out from aqueous solutions, and adsorption isotherms and visible spectra of the suspensions were studied [1, 2]. Thermal analysis was also applied for the study of dye-clay complexes but the complexes were obtained from aqueous suspensions [3]. The adsorption of cationic dyes by montmorillonite from aqueous solution takes place in several stages. In the first stage (up to ~25% of the total CEC) the adsorption takes place through the mechanism of cation exchange in which the inorganic exchangeable cation is replaced by the organic dye cation. At this stage, the adsorbed organic cations are intercalated inside the interlayer space where they may form π bonds with oxygens from the O-plane. The second stage (up to ~100% of the total CEC) is also a cation exchange reaction, but at this stage, the clay flocculates and the adsorbed organic cations penetrate into the interparticle space where they may undergo dimerization. With higher saturations, when the clay particles are neutral, an organophilic adsorption takes

place, the clay is repeptized and the organic cations reside on the water-solid interface at the edges of the layers. At this stage the platelets become positively charged [4].

This is the first publication in a series of studies on the mechanochemical adsorption of cationic organic dyes by smectite minerals. For this purpose, crystal violet (CV, Fig. 1) was chosen [5–8]. Most studies on the adsorption of CV by clay minerals have been from aqueous solutions and adsorption isotherms have commonly been applied. Ghosal and Mukherjee [9] and Rytwo *et al.* [10] showed that in aqueous suspensions, CV is adsorbed by montmorillonite in amounts greater than the exchange capacity. De *et al.* [11, 12] studied the adsorption of CV by montmorillonite, kaolinite and vermiculite, all of which were in the H-form (their CEC were: 105, 5.5 and 133 mmol per 100 g clay, respectively). In the case of montmorillonite, the amount of dye adsorbed (131 mmol per 100 g clay) exceeded the cation exchange capacity. The maximum amount adsorbed by kaolinite was 3.6 mmol CV per 100 g clay, slightly less than its exchange capacity. Vermiculite adsorbed much smaller amounts than its exchange capacity. The adsorption was 27 mmol CV per 100 g clay. Except for the adsorption of CV onto vermiculite, all other adsorption isotherms fit the Langmuir equation well.
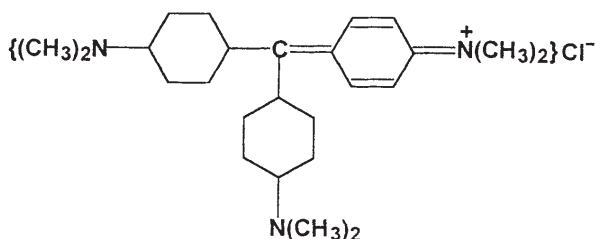

Fig. 1 Chemical structure of the cationic dye crystal violet

Nir *et al.* [13] studied adsorption isotherms of CV by montmorillonite saturated with Na^+, Mg^{2+}, Ca^{2+} and Cd^{2+}. The binding coefficients of these cations to montmorillonite were calculated from the adsorption isotherms of the organic cationic dyes and the desorption isotherms of the released inorganic cations. The calculations showed that the organic dye cation is characterized by binding coefficients at least six orders of magnitude larger than those of Na^+, Mg^{2+}, Ca^{2+} and Cd^{2+}. Due to the strong binding affinity of CV to the clay, its addition in small concentrations results in an essentially complete displacement of inorganic cations from the clay. Calculations also showed that saturation of montmorillonite by organic dye cations could be 140–200% of the exchange capacity of the clay and the adsorption of the dye in excess of the CEC would cause charge reversal.

The adsorption of CV from aqueous solutions by smectites and kaolinite was previously studied by electrophoresis [4], spectrophotometric techniques [14, 15], calorimetry [16], electric dichroism [17], DTA [18–20] and combined mass spectrometry-DTA [21, 22].

Recently, we used mechanochemical techniques for the adsorption of phenols by several smectites [23–25]. Adsorption of non-ionic organic molecules by clay

minerals is usually carried out from organic solvents. Some polar compounds are adsorbed from organic solvents by smectites in considerable amounts, but many are adsorbed in very small amounts – even after long treatments. In mechanochemical adsorption, high amounts of organic matter are usually adsorbed during grinding periods of a few minutes. In the case of smectites, we assume that the clay is first delaminated by the grinding process which is followed by the formation of new tactoids with organic matter in the new interlayer space. The objective of this study is to investigate the mechanochemical interaction between smectite and organic salt. For this purpose the adsorption of an organic cationic dye (crystal violet by montmorillonite) was investigated. A mixture containing the solid dye and the clay was ground for 5 min and the ground product was analyzed by X-ray, DTA and TG. The analyzes were carried out on the ground mixture and on the grinding product after they had been washed by water and acetone. XRD, DTA, and TG data were compared with those obtained from CV-montmorillonite complexes synthesized in aqueous suspensions.

Experimental

Materials

Wyoming bentonite (Na-montmorillonite) was supplied by Wards' Natural Science Establishment, Inc. It was ground and sieved to 80 mesh. The original sample contained 74 mmol Na^+ and 18 mmol Mg^{2+} plus Ca^{2+} per 100 g clay. The chloride salt of crystal violet was purchased from Merck and used as supplied.

Methods

Five different varieties of CV-montmorillonite associations (samples I–V) were prepared as follows: A mixture containing 1.0 g of clay and 0.2 g of CV was manually ground with a mortar and pestle for 5 min in air atmosphere. During grinding drops of distilled water were added from time to time. This sample is labeled 'I'. Part of sample I (200 mg) was heated under vacuum for 3 h at 110°C. The thermal treated sample is labeled 'II'. Another part (half a gram) of sample I was washed 7 times with 40 mL distilled water. The clay fraction was separated from the supernatant by centrifugation. The sample was labeled 'III'. 30 mL acetone were added to 200 mg of air-dried sample III. After thoroughly stirring, the solid clay was separated from the liquid and then air-dried (sample IV). The fifth sample was separated from an aqueous suspension (sample V). The procedure for the preparation of this CV-clay complex was previously described [22]. The loading of samples I–IV was 50 mmol, and that of sample V, 100 mmol CV per 100 g clay. The air-dried complexes were studied by X-ray diffraction and simultaneous DTA-TG.

X-ray analysis of powdered samples was carried out by means of a Philips Automatic Powder Diffractometer (PW 1710) with a Cu tube anode.

The simultaneous differential thermal analysis and thermogravimetric (DTA-TG) tests were carried out with a TA Instruments module SDT 2960. The sample compart-

ment was flushed with UJP oxygen at all times. DTA-TG runs were recorded at a scan rate of 10°C min^{-1} up to 1000°C. Mass loss (in percents) was calculated from TG curves, based on the mass of the calcined sample.

Results and discussion

Washing sample I with distilled water

Sample I was washed seven times. Due to the peptization of the colored clay, the first supernatant was a very pale violet. The amount of peptized clay was very small. After four months, the CV-clay was completely flocculated and the supernatant was colorless. These observations suggest that during grinding, the cationic dye was adsorbed by the clay.

With further washing (up to five times), the supernatant became dark violet due to the extensive peptization of colored CV-montmorillonite. The sixth washing was only slightly violet; the seventh washing was almost colorless.

X-ray diffraction data

The X-ray diffractogram of ground CV is shown in Fig. 2. The time of grinding up to 5 min did not show any effect on the diffractogram. The following basal spacings were recorded for air-dried montmorillonites loaded with 4, 25, 50 and 100 mmol CV per 100 g clay prepared in aqueous suspensions, 1.44, 1.45, 1.65 and 2.06 nm, respectively [22]. Diffractograms of air-dried natural montmorillonite and montmorillonite ground with CV (unwashed sample I), and heated for 3 h at 110°C under vacuum (sample II) are depicted in Fig. 2, left side. The basal spacings are: 1.21, 1.28 and 1.29 nm. These data cannot be regarded as proof that the adsorbed CV is located inside the interlayer space. Sample I does not show any residual non-adsorbed CV, indicating that most CV is adsorbed. Sample II shows an additional medium size peak at 1.01 nm, indicating that at 110°C, many of the interlayers became dehydrated. The appearance of the latter peak proves that crystals of the ground sample contain interlayers free of CV cations.

X-ray diffractograms of samples III–V are depicted in Fig. 2, on the right side. The diffractogram of sample V (CV-montmorillonite obtained from aqueous suspension) shows a basal spacing of 2.00 nm, similarly to the spacing shown previously by montmorillonite with a loading of 100 mmol CV per 100 g clay [22]. This basal spacing indicates that the dye is located inside the interlayer space. The ground samples washed with water (sample III) or with water and acetone (sample IV) show broad peaks, extending from 1.62 and 1.84 nm, respectively, to lower spacings, indicating that CV cations are located in the interlayers. However, washing with these solvents resulted in non-homogeneous systems.
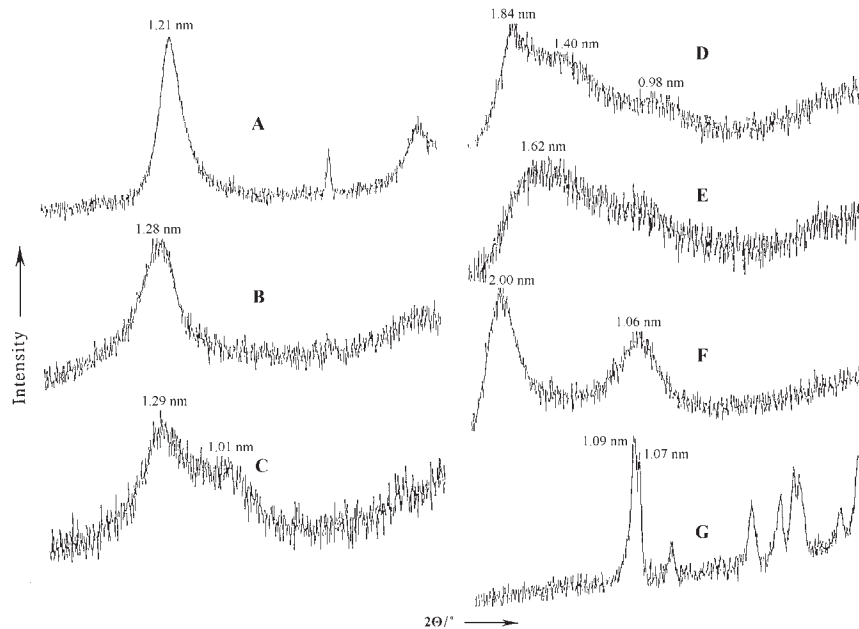
Fig. 2 X-ray diffractograms of A – untreated Wyoming bentonite (Na-montmorillonite);
B – Sample I, Na-montmorillonite ground 5 min with CV; C – Sample II,
Na-montmorillonite ground 5 min with CV and heated 3 h at 110°C under vacuum;
D – Sample III, Na-montmorillonite ground 5 min with CV and washed with dis-
tilled water; E – Sample IV, Na-montmorillonite ground 5 min with CV and
washed with distilled water and acetone; F – Sample V, CV-montmorillonite ob-
tained from aqueous suspension; G – powder CV

Thermal analysis

The DTA curve of untreated montmorillonite, recorded by the instrument used in the
present study, shows two endothermic peaks, at 95 and 675°C which represent dehy-
dration and dehydroxylation of the clay, respectively. In the DTG curve the two
peaks are at 89 and 679°C and are associated with mass loss of 8.8 and 3.7% of the
mass of the calcined sample.

DTA, TG, DTG and gas evolution curves of CV powder were previously stud-
ied. The evolved gases were H_2O, CO_2, NO_2 and H_2 and were measured by mass spec-
trometry [21]. In that study, the DTA curve showed a very weak exothermic peak at
215°C, the start of the oxidation of the organic hydrogen, and the formation of H_2O.
Very strong and sharp exothermic peaks appeared at 520 and 550°C, the latter due to
the oxidation of the organic carbon and nitrogen which forms CO_2 and NO_2, whereas
the former was also due to the hydrogen oxidation. Very weak endothermic peaks
were observed at 125, 245 and 410°C due to the evolution of adsorbed water and py-
rolysis of the organic cation, respectively. Peaks in the H_2O evolution curve appeared
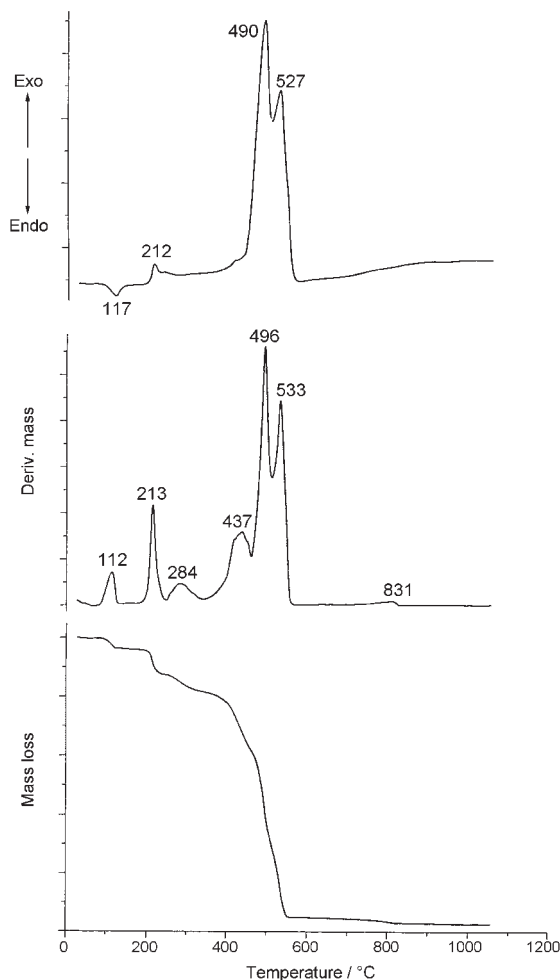
Fig. 3 DTA, TG and DTG curves of crystal violet

at 255 (weak), 495 and 520°C and in the CO_2 or NO_2 evolution curves at 495 (shoulder), 520 (strong and sharp) and 555°C (shoulder). The DTA curve of CV crystals recorded in the present study (Fig. 3) shows exothermic peaks at 212, 490 and 527°C. In the DTG curve, peaks are located at 112 (moisture), 213, 284, 437 (several small peaks), 496, 533 and 831°C and are associated with mass loss of 4.0, 8.0, 6.0, 20.0, 23.0, 34.0, and 2.5% of the total mass. The total mass loss at 850°C is 97.5% from total mass before the thermal treatment.

DTA, TG, DTG and gas evolution curves of CV-montmorillonite, obtained from aqueous suspensions with increasing amounts of dye, were previously studied [22]. The evolved gases H_2O, CO_2 and NO_2 were measured by mass spectrometry. The
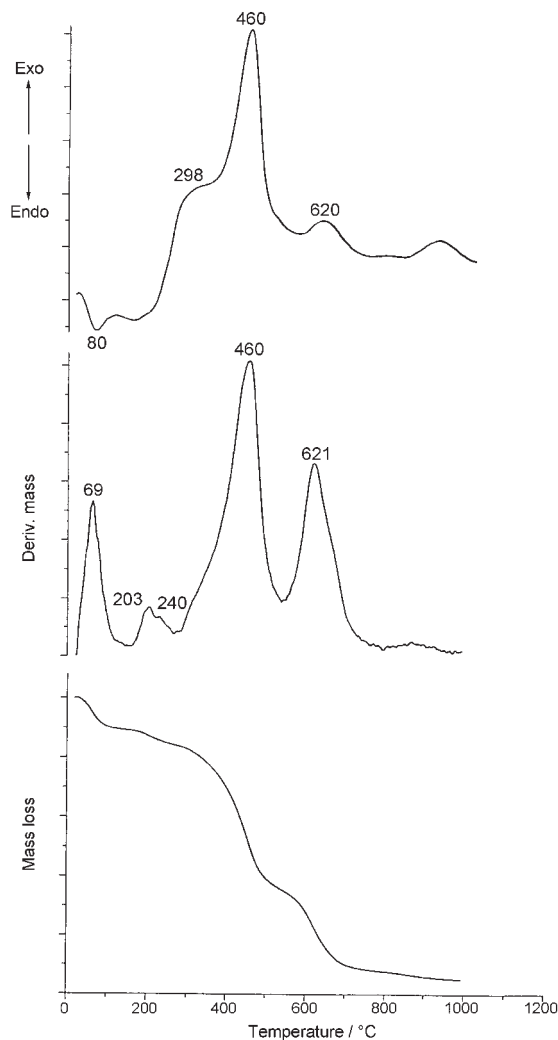
Fig. 4A DTA, TG and DTG curves of sample I, Na-montmorillonite ground 5 min with CV

evolved CO_2 and NO_2 gases resulted from the oxidation of organic carbon and nitrogen, respectively. The evolved H_2O resulted in part from the dehydration and dehydroxylation of the clay (named 'inorganic water') and, in part, from the oxidation of organic hydrogen (named 'organic water'). The thermal analysis curves were divided into three regions, labeled 'A–C'. In region A (up to 200°C), the endothermic dehydration of the clay was the major thermal reaction evolving 'inorganic water'. Region B was between 200 and 550°C. The exothermic oxidation of the adsorbed CV was the principal thermal reaction of this region. Water evolved in this region originated from the oxidation of the organic cation ('organic water'). Region C occurred above

550°C. The last stages of the oxidation of the adsorbed CV and the dehydroxylation of the montmorillonite were the principal thermal reactions of this region. Water evolved in this region was mainly 'inorganic water'.
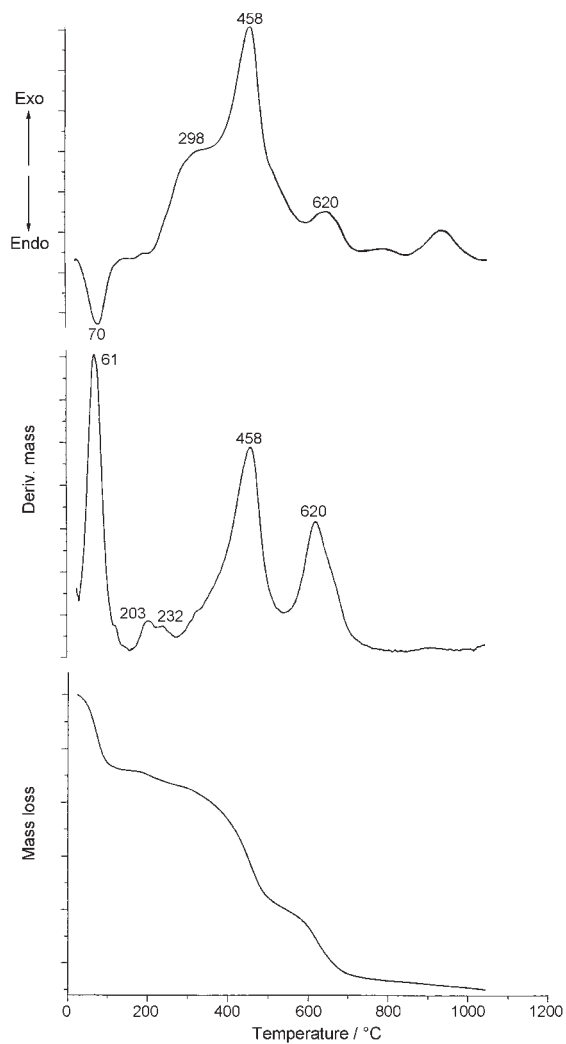

Fig. 4B DTA, TG and DTG curves of sample II, Na-montmorillonite ground 5 min with CV and heated 3 h at 110°C under vacuum

Region A

It was previously shown that the peak maximum in the DTA or DTG curves and in the H_2O evolution curves shifts to lower temperatures with increasing loading of the clay by CV [22]. At the same time the amount of evolved water decreases. The shift

in the peak temperature and decrease in water mass loss are attributed to the increasing hydrophobicity of the interlayer space as a result of an increase in the amount of CV inside the interlayer. In the present study, the endothermic peak maxima of samples I, II, III, IV, and V appear at 80, 70, 57, 65 and 58°C, respectively (Fig. 4). Mass loss below 200°C is: 9.7, 3.5, 10.0, 4.8 and 3.2% of the calcined sample, respectively. The high mass loss and peak temperature of sample I suggest that most of the adsorbed CV in this sample, which was obtained by grinding, was not located in the interlayer. Sample V contains the highest amount of CV inside the interlayer and the smallest amount of water suggesting that this sample is highly hydrophobic.
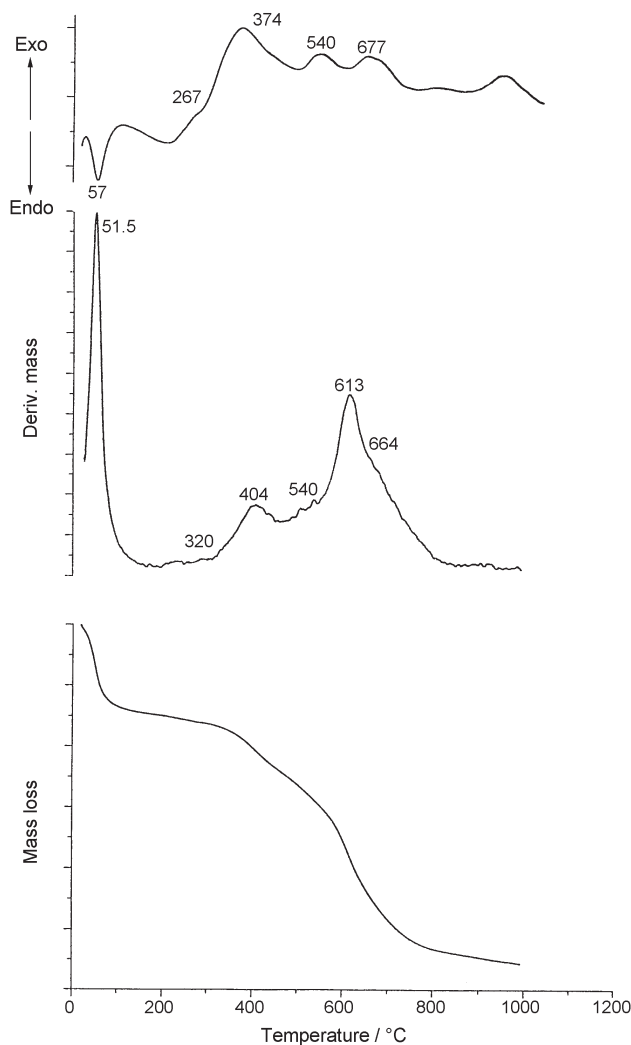

Fig. 4C DTA, TG and DTG curves of sample III, Na-montmorillonite ground 5 min with CV and washed with distilled water
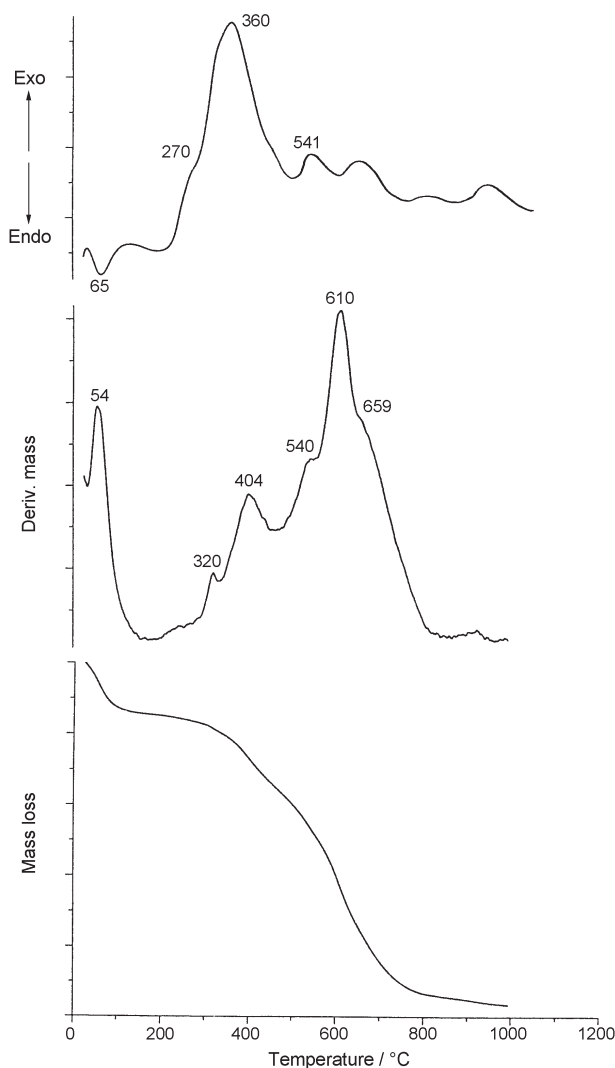
Fig. 4D DTA, TG and DTG curves of sample IV, Na-montmorillonite ground 5 min with
        CV and washed with distilled water and acetone

Region B

According to Yariv *et al.* [22], peak maxima in the DTA curves of CV-treated mont-
morillonite in aqueous suspensions appeared at 355–370 and 480–500°C. A shoulder
was observed at 280°C only when loading was >25 mmol CV per 100 g clay. Evolu-
tion of H_2O resulted from the oxidation of hydrogen atoms of the CV cations ('or-
ganic water'). H_2O evolution curves of CV-montmorillonite determined by mass
spectrometer showed a shoulder at 280°C and an intense peak at 355–370°C. The

evolution of CO_2 and NO_2 resulted from the oxidation of the CV-carbon and -nitrogen, respectively. The evolution curves of these two gases were determined by mass spectrometer and were very similar, both showing an intense CO_2 or NO_2 evolution peak at 480°C.
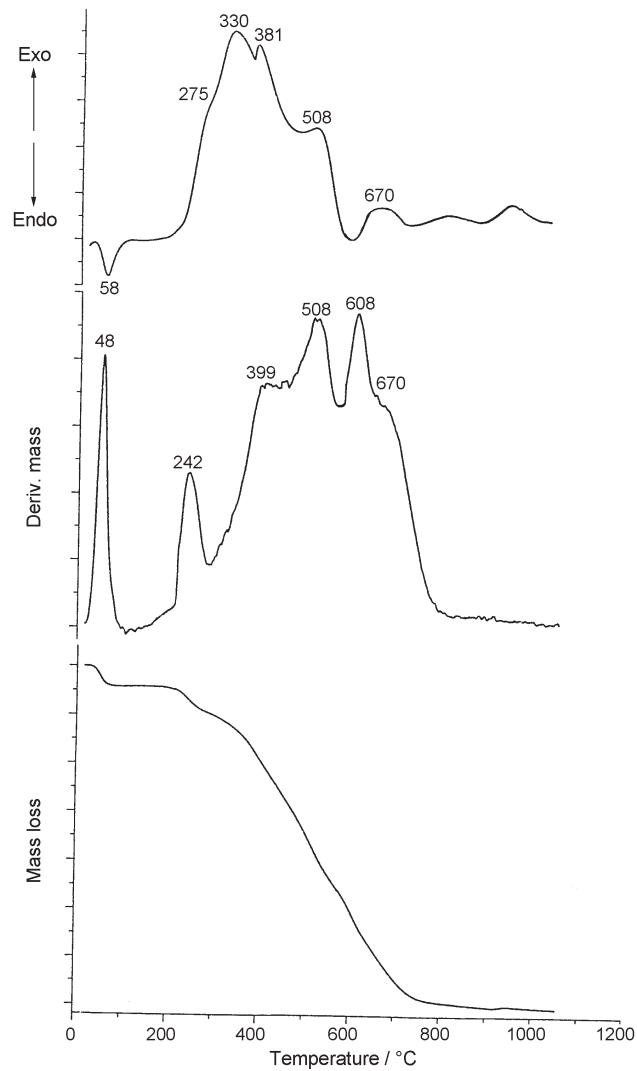

Fig. 4E DTA, TG and DTG curves of sample V, CV-montmorillonite obtained from aqueous suspension

In the present study the DTA curve of sample V (Fig. 4 E) shows similarities to those obtained previously by Yariv *et al.* [22]. A shoulder at 275°C, attributed to the first stage of hydrogen oxidation, is accompanied by mass loss of 4.1% in the

200–290°C temperature range. An intense peak appears at 242°C in the DTG curve. The fact that the DTA peak appears at a higher temperature than the DTG peak suggests that in addition to the oxidation of organic H and the formation of organic water, some adsorbed inorganic water is also evolved with a maximum rate at 242°C.

The major exothermic peak at 330 is accompanied by a weak peak at 381°C. These two peaks represent the oxidation of hydrogen, but above 300°C, some carbon is also oxidized. Both peaks are accompanied by mass loss of 13.1% in the 290–460°C temperature range. An additional exothermic peak at 508°C is accompanied by a DTG peak at the same temperature and mass loss of 14.2% in the 460–560°C temperature range. This peak represents carbon and nitrogen oxidation.

The TG curves of sample I and II (Fig. 4 A, B) show a mass loss of 1.9% in the 170–250°C temperature range. The DTG curves show two small peaks at 203 and 232–240°C. The principal exothermic peaks in this region appear at 295 (medium) and 460°C (very strong). In the DTG curves of this region, there is only one peak at 460–458°C. Mass loss in the 250–550°C temperature range is 15.8%.

In the DTA curves of samples III and IV (Fig. 4 C, D), there is a weak exothermic shoulder at 267–270°C accompanied by a mass loss of 0.9 and 1.1%, respectively, in the 200–300°C temperature range. The principal exothermic peaks in this region appear at 360–374°C (very strong) and about 540°C (weak). In the DTG curves of this region there is a peak at 404°C and a shoulder at 540°C. The DTG curve of sample IV shows an additional small peak at 320°C. Mass losses are 5.5 and 4.9% in the 300–450°C, and 3.8 and 4.3% in the 450–550°C range, in samples III and IV, respectively.

The difference in mass loss between sample I–IV and V is mainly due to the fact that the former ones are loaded by 50 mmol and the latter by 100 mmol CV per 100 g clay. A CV-montmorillonite complex loaded with 50 mmol CV per 100 g clay, prepared from aqueous suspension, lost 0.6, 2.2 and 4.4% of mass (calculated per calcined sample) in the 200–300, 300–425 and 425–550°C temperature ranges, respectively [22]. The total mass loss of this sample in region B is smaller than the loss of samples I–IV.

Region C

This region is controlled by the dehydroxylation of the clay mineral. The DTA curve of the untreated montmorillonite shows an endothermic peak at 680°C. The temperature of the CV-montmorillonite dehydroxylation was determined by Yariv et al. [22] from the H_2O evolution curve. This peak shifted to lower temperatures with increasing loadings. It was located at 675 and 595°C with 4 and 100 mmol dye per 100 g clay, respectively.

Evolution curves of CO_2 and NO_2 indicated that the oxidation of organic carbon and nitrogen had not been completed in the second region but continued into the third region. These curves showed a peak at 625–680°C. The area of this peak increased only up to a degree of saturation of 50 mmol CV per 100 g clay. With higher loadings, the increments in area became small and a large portion of carbon was already oxi-

dized at a lower temperature with the appearance of an additional peak at 560–580°C in the CO_2 and NO_2 evolution curves. It should be noted that Yariv *et al.* [15] showed an exothermic peak at 575°C only when the loading was 100 mmol CV per 100 g clay. This peak was not detected with smaller loadings.

In CV treated montmorillonite, the exothermic oxidation reaction overlaps the endothermic dehydroxylation reaction. An endothermic peak was shown in the DTA curve of montmorillonite loaded with small amounts of CV (4 mmol CV per 100 g clay). Exothermic peaks were detected in this region with higher loadings (25, 50 and 100 mmol CV per 100 g clay). In the present study (Fig. 3 A–E) exothermic peaks appear at 620, 620, 672, 680 and 670°C in the DTA curves of samples I–V, respectively.

The DTG curves of samples I–V show a peak at 621, 620, 613, 610 and 608°C, respectively. Samples III–V show a shoulder at about 659–670°C, which is very weak in sample III but becomes significant in samples IV and V. In samples I and II, mass loss at about 620°C is due to both reactions — the dehydroxylation of the clay and the final oxidation of the charcoal. Total mass loss in the third region is 10.4 and 10.0%, respectively, of which 3.7% is 'inorganic water'. In samples III, IV and V the dehydroxylation peak occurs at about 610°C, and the final peak oxidation of charcoal occurs at about 659–670°C. Mass loss in the 550–630°C temperature range is 10.6, 8.3, and 10.9% and in the 630–700°C temperature range 7.7, 7.3, and 7.8 in the TG curves of samples III, IV, and V, respectively. For comparison mass loss in CV-montmorillonite loaded with 50 mmol CV per 100 g clay, prepared in aqueous suspension is 3.8 and 11.4% in the 550–625 and 625–700°C temperature ranges, respectively [22].

Conclusions

The present thermal analysis curves show that samples I–V can be divided into three groups. Samples I and II belong to one group, samples III, and IV to a second, and sample V to a third group. Sample V was prepared in aqueous suspension and it is therefore expected that its structure is similar to the structure of the samples previously described by Schramm *et al.* [4]. It contains CV cations located in the interlayer space, in addition to CV cations at the external surfaces. Samples I and II were prepared by a mechanochemical treatment and the adsorbed CV cations are probably located at the crystal edges. Washing the ground samples by water and acetone assists the penetration of CV cations into the interlayer space. Samples III and IV exhibit CV cations in the interlayer, replacing the Na^+ cations initially present in the clay.

Yariv *et al.* [22] showed that π interactions between the aromatic entity and the oxygen plane contributes to the thermal stability of the carbon skeleton of the organic cation; consequently, the exothermic oxidation reactions appear after the dehydroxylation reaction of the clay. The present results show that the penetration of the CV cation into the interlayer space through washing the ground sample, increases the thermal stability of the charcoal obtained during the DTA run. Total mass loss of non-washed and washed samples from 200 to 550°C is 17.7 and 10.2%, respectively. Mass loss from 550 to 800°C is about 10 and 16–18% in TG curves of non-washed

and washed samples, respectively. The CV-montmorillonite which contains 50 mmol CV per 100 g clay and was prepared from aqueous suspension shows mass loss of 7.2 and 15.2% at 200–550 and 550–700°C, respectively.

In conclusion, the present results show that water is essential for the penetration of the CV into the interlayer space. The penetration probably occurs by a cation exchange reaction which requires the presence of water.

References

1 S. Yariv, Intern. J. Tropic. Agric., 6 (1988) 1.
2 S. Yariv, Proc. 2nd Mediterranean Clay Meeting, Aveiro 1998, (C. S. F. Gomes, Ed.), 1 (1998) 99.
3 S. Yariv, J. Thermal Anal., 36 (1990) 1953.
4 L. L. Schramm, S. Yariv, D. K. Ghosh and L. G. Hepler, Can. J. Chem., 75 (1997) 1868.
5 D. K. De, J. L. Das Kanungo and S. K. Chakravarti, J. Indian Soil Sci., 27 (1979) 85.
6 D. N. Ghosal and S. K. Mukherjee, Indian J. Chem., 10 (1972) 569.
7 S. Nir, G. Rytwo, U. Yermiyahu and L. Margulies, Colloid Polymer Sci., 272 (1994) 619.
8 G. Rytwo, S. Nir, L. Margulies, B. Casal, J. Merino, E. Ruiz-Hitzky and J. M. Serratosa, Clays Clay Minerals, 46 (1998) 340.
9 D. N. Ghosal and S. K. Mukherjee, Ind. J. Chem., 10 (1972) 835.
10 G. Rytwo, S. Nir and L. Margulies, Clay Miner., 28 (1993) 139.
11 D. K. De, J. L. Das Kanungo and S. K. Chakravarti, Indian J. Chem., 12 (1974) 165.
12 D. K. De, J. L. Das Kanungo and S. K. Chakravarti, Indian J. Chem., 12 (1974) 1187.
13 S. Nir, G. Rytwo, U. Yermiyahu and L. Margulies, Colloid Polymer Sci., 272 (1994) 619.
14 S. Yariv, A. Nasser and P. Bar-On, J. Chem. Soc. Faraday Trans., 86 (1990) 1593.
15 S. Yariv, D. K. Ghosh and L. G. Hepler, J. Chem. Soc. Faraday Trans., 87 (1991) 1201.
16 C. Dobrogowska, L. G. Hepler, D. K. Ghosh and S. Yariv, J. Thermal Anal., 37 (1991) 1347.
17 Z. Chernia, D. Gil and S. Yariv, Langmuir, 10 (1994) 3988.
18 V. S. Ramachandran and K. P. Kacker, J. Appl. Chem., 14 (1964) 455.
19 V. S. Ramachandran, S. P. Gart and K. P. Kacker, Chem. Ind., (1961) 790.
20 V. S. Ramachandran, K. P. Kacker and N. K. Patwardhan, Nature, 191 (1961) 696.
21 S. Yariv, M. Mueller-Vonmoos, G. Kahr and A. Rub, J. Thermal Anal., 35 (1989) 1941.
22 S. Yariv, M. Mueller-Vonmoos, G. Kahr and A. Rub, Thermochim. Acta, 148 (1989) 457.
23 D. Ovadyahu, S. Shoval, I. Lapides and S. Yariv, Thermochim. Acta, 282/283, (1996) 369.
24 D. Ovadyahu, S. Yariv and I. Lapides, J. Therm. Anal. Cal., 51 (1998) 415.
25 D. Ovadyahu, S. Yariv, I. Lapides and Y. Deutsch, J. Therm. Anal. Cal., 51 (1998) 431.