Journal of Thermal Analysis and Calorimetry, Vol. 97 (2009) 1, 19–25

THERMO-X-RAY-DIFFRACTION ANALYSIS OF DIMETHYLSULFOXIDE–KAOLINITE INTERCALATION COMPLEXES

I. Lapides[*] *and S. Yariv*

Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

DMSO-kaolinite complexes of low- and high-defect Georgia kaolinite (KGa-1 and KGa-2, respectively) were investigated by thermo-XRD-analysis. X-ray patterns showed that DMSO was intercalated in both kaolinites with a *d*(001)-value of 1.11 nm (type I complex). The samples were gradually heated up to 170°C and diffracted by X-ray at room-temperature. With the rise in temperature, due to the thermal evolution of the guest molecules, the relative intensity of the 1.11 nm peak decreased and that of the 0.72 nm peak (neat kaolinite) increased indicating that the fraction of the non-intercalated tactoids increased. The 1.11 peak disappeared at 130–140°C. During the thermal treatment of both complexes two additional peaks appeared at 110 and 120°C, respectively, with *d*-values of 0.79–0.94 and 0.61–0.67 nm in DMSO-KGa-1 and 0.81–0.86 and 0.62–0.66 nm in DMSO-KGa-2, indicating the formation of a new phase (type II complex). The new complex was obtained by the dehydration of type I complex and was composed of intercalated DMSO molecules which did not escape. The new peaks disappeared at 150–160°C indicating the complete escape of DMSO.

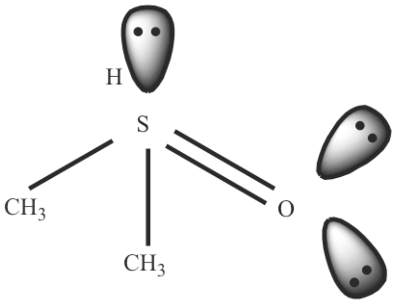
Keywords: *dimethylsulfoxide, DMSO, intercalation complexes, kaolinite, X-ray diffraction*

Introduction

Some inorganic and organic compounds may penetrate into a newly formed interlayer space of kaolin-like layers and the tactoids expand from 0.72 to 1.00–1.47 nm [1]. The penetrating species that break the strong electrostatic and van der Waals types of interactions between the kaolin-like layers may form H-bonds with inner surface hydroxyls and inner surface oxygens. This was first inferred by comparing calculated and experimental basal spacing and later proved by IR and Raman spectroscopy [2–5].

The intercalation of dimethylsulfoxide (DMSO, Scheme 1) into kaolinite has been widely studied by X-ray diffraction (e.g. [6–9]). Diffractograms recorded after treating kaolinite in DMSO showed two peaks with *d*(001)-values of 1.11 and 0.72 nm characterizing kaolinite tactoids with intercalated DMSO and non-intercalated tactoids. Intensity ratios of these two peaks depend on the degree of intercalation [1].

Several investigators showed that small amounts of water were essential for this intercalation (e.g. [10]). In spite of the fact that the resulting complex forms ordered structure [8, 9], the contribution of water is not clear. Kristóf *et al.* [11] studied the thermal behavior of DMSO–kaolinite complex by TG-DTA-EGA and TG-MS. Evolution of DMSO occurred in two steps, at 117 and 173°C. Most of the water was lost up to 80°C during the first step of decomposition but some water was released at 173°C. From the thermal evolution patterns of DMSO they suggested that the guest molecules were bonded at least in two different ways in the interlayer space.



Scheme 1 Dimethylsulfoxide (DMSO)

Recently DMSO–kaolinite intercalation complexes of low- and high-defect Georgia kaolinite (KGa-1 and KGa-2, respectively) were studied by thermo-IR-spectroscopy analysis in our laboratory [12]. The results showed that the location of the Si–O vibrations depended on the temperature of the thermal treatment. Below 130°C Si–O stretching and deformation bands were perturbed, mainly in the spectra of DMSO-KGa-1 and to a smaller extent in those of DMSO-KGa-2, implying the presence of H-bonds between the basal oxygens and the guest molecules. Since the O-plane is a very poor electron pair donor, H-bonds are formed only with strong proton donors [13, 14]. DMSO is aprotic and is not a proton donor. Taking into account the thermal analysis of

---

[*] Author for correspondence: isaak8@hotmail.com

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Kristóf *et al.* [11] who identified by MS a thermal release of water, we concluded that below 130°C water molecules were present in the interlayer, forming bridges between DMSO and the O-plane, by donating one proton to sulfur atom of DMSO and a second proton to oxygen of the clay-O-plane. Two bands at 3538 and 3503 cm^{-1} were attributed to asymmetric and symmetric H–O–H stretching vibrations. After 130°C no perturbations of the Si–O bands were observed and the water bands disappeared. Bands which were associated with DMSO, e.g. methyl bands and perturbed inner-surface hydroxyls, became weak with the rise in temperature due to its thermal evolution, but persisted and disappeared only at 160°C.

Based on the thermo-IR-spectroscopy study we concluded that the intercalation of DMSO into kaolinite resulted in two types of complex, hydrated and non-hydrated, labeled type I and II, respectively. The new type II complex was obtained by the thermal dehydration of type I. The new complex was obtained by the dehydration of type I complex and was composed of intercalated DMSO molecules which did not escape at that thermal stage [12]. Thermo-XRD-analysis is a reliable tool to examine this conclusion. Although XRD was used by several investigators to study the structure of DMSO–kaolinite complex most attention was given to type I complex or to the crystallinity of the deintercalated clay [15].

Experimental

Materials

Low- and high-defect Georgia kaolinite (KGa-1 and KGa-2, previously referred to as well- and poorly-crystallized, respectively), supplied by the Source Clay Minerals repository (The Clay Minerals Society), were gently ground to 80 mesh. Chemical pure DMSO supplied by Merck, Germany, was used without further purification.

Preparation of DMSO–kaolinite intercalation complexes [16]

The complexes were prepared as follows: 5 g of KGa-1 or KGa-2 was stirred for one week in a closed bottle containing 150 mL DMSO and 50 mL H_2O. After centrifugation the separated slurry was aged at 70°C for another week and air-dried.

Methods

Carbon and sulfur determinations

Percentage of C in the DMSO–kaolinite complexes before any thermal treatment and after heating the samples 3 h at 140°C was determined by a PerkinElmer 2400 C, H and N Analyzer at the Laboratory of Microanalysis at the Hebrew University of Jerusalem. Percentage of S in the DMSO–kaolinite complexes before any thermal treatment was determined by ICP measurements with a Perkin-Elmer Optima 3300 instrument at the Analytical Laboratory of the Geochemistry Department at the Israel Geological Survey in Jerusalem. From C and S determinations the adsorbed DMSO (in mass percent and mmol per 100 g clay) was calculated.

Thermal mass loss

For the determination of total mass loss due to the thermal escape of the guest molecules 100 mg samples were heated 3 h at 250°C. Gradual mass losses were determined by heating 100 g samples at 120, 130 and 140°C.

Thermo-XRD-analysis [17]

Two series of experiments were performed. In both series 100 mg of powdered DMSO complexes were gradually heated in glass beakers with a diameter of 15 and a height of 30 mm. In the first series samples were heated at 40, 60, 80, 100, 110, 120, 130, 140, 150, 160 and 170°C, 3 h at each temperature. In the second series they were gradually heated from room temperature to 120°C (≈30 min) and left at this temperature for several days. Diffractograms were recorded at room temperature and at ambient atmosphere, using a Philips Automatic Diffractometer (PW 1710) with a Cu tube anode. Peak positions and intensities were obtained by Philips Automatic Powder Diffraction (PW1877/43) software, version 3.5 [18].

Results and discussion

X-ray diffractograms of DMSO-KGa-1 and DMSO-KGa-2

X-ray diffractograms of DMSO complexes of both kaolinites are shown in Figs 1a and 2a, respectively. Both diffractograms show two peaks with *d*(001)-values of 0.72 and 1.11 nm, characterizing tactoids of neat and expanded kaolinite, respectively. The expansion of the basal spacing from 0.72 to 1.11 nm proves that the adsorption of the guest molecules occurred by intercalation into newly formed interlayer spaces. A *d*(001)-value of 1.11 nm (type I complex), is similar to the spacing obtained by previous investigators (e.g. [6, 8]) for the intercalation DMSO–kaolinite complex. From the intensities of these peaks it appears that the intercalation of DMSO by KGa-1 is higher than by KGa-2 and is nearly complete. This is

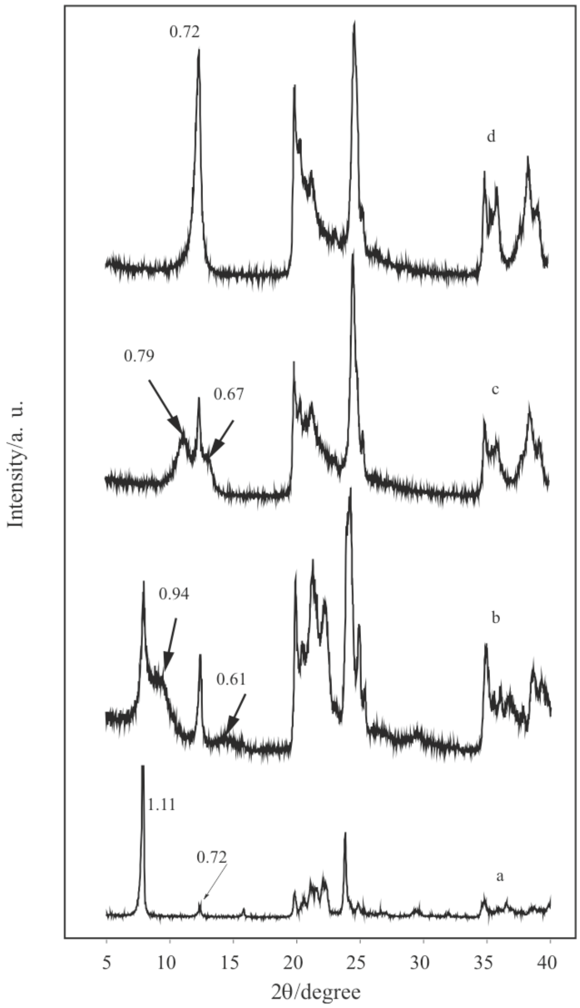


Fig. 1 X-ray diffractograms of DMSO-KGa-1 a – before thermal treatment, b – heated at 110°C, c – heated at 140°C, d – heated at 160°C

in agreement with the results of C or S determinations which are discussed in the next paragraph.

Carbon and sulfur analyses and thermal mass loss

DMSO-KGa-1 and DMSO-KGa-2 were subjected to C and S analyses and percentages of adsorbed DMSO were calculated. According to C analyses they were 14.2 and 7.2% DMSO (or 182 and 93 mmol DMSO per 100 g clay), respectively. According to S analyses they were 13.0 and 6.3% DMSO (or 167 and 81 mmol DMSO per 100 g clay), respectively. From our previous experience with determinations of organic matter in organo-clay complexes the correlation between the different determinations seems to be reasonable. After heating the samples 3 h at 140°C, C analyses showed that they contained 4.3 and 4.2% DMSO (or 55 and 53 mmol DMSO per 100 g clay), respectively.

Heating DMSO-KGa-1 and DMSO-KGa-2 at 250°C resulted in mass losses of 20.1 and 17.3%, respectively, due to the thermal evolution of DMSO and water. Percentages of evolved water were calculated by subtracting those of adsorbed DMSO from the total mass loss. They were 5.8 and 10.1%, respectively. DMSO-KGa-1 and DMSO-KGa-2 heated 3 h at 140°C lost 16.7 and 14.9%. Loss in the temperature range 140–250°C is calculated by subtracting this loss from the total mass loss of the sample at 250°C. From the subtraction it appears that the loss in the temperature range 140–250°C was 3.4 and 2.4%, respectively. These percentages are smaller than those of DMSO determined by C analyses indicating that no water was evolved. This is in agreement with the thermo-IR-spectroscopy study which showed at 140°C the presence of type II complex composed of DMSO with no water [12].

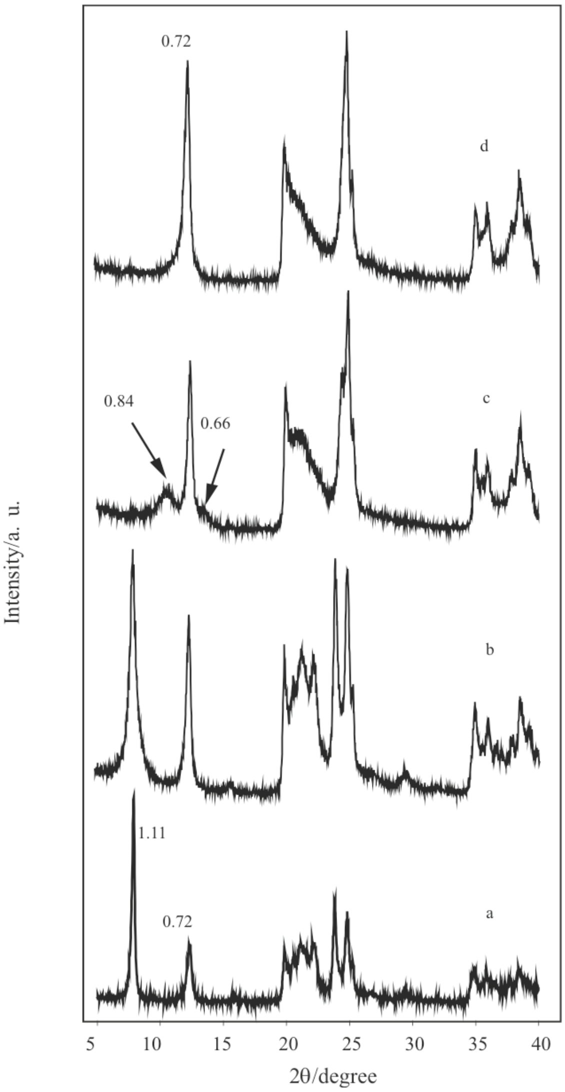


Fig. 2 X-ray diffractograms of DMSO-KGa-2 a – before thermal treatment, b – heated at 110°C, c – heated at 140°C, d – heated at 160°C

Thermo-XRD-analysis of DMSO-KGa-1 and DMSO-KGa-2

Preliminary experiments

Representative diffractograms of thermal treated DMSO-KGa-1 are shown in Fig. 3. For each thermal treatment 100 mg of the clay was placed in a glass beaker with a 15 mm diameter and a 30 mm height or on a Petri glass plate with a 50 mm diameter. Because of the larger diameter, a very thin layer of dispersed clay occurred in the latter and a thicker layer in the former. Complex-peak *d*-values, intensity ratios of the complex-peaks relative to those of the 0.72 nm peaks (neat kaolinite) and thermal mass losses are summarized in Table 1. Curve a depicts a diffractogram of a sample heated in a glass beaker at 40, 60, 80, 100, 110 and 120°C, 3 h at each temperature. Curve b depicts a diffractogram of a sample heated in about 30 min from room temperature to 120°C and then left 3 h at this temperature. Curves c and d depict diffractograms of samples heated 3 h at 120°C in a beaker and a Petri plate, respectively. It appears that the thermal reactions are faster in the Petri plate than in the beaker. Comparing between these four curves shows that in these experiments reproducibility is not perfect but depends on the thermal treatment. Curves e and f depict diffractograms of a sample heated in beakers five days at 120°C or 3 h at 140°C, respectively. The diffractograms show four peaks characterizing type I complex, type II complex, neat kaolinite and again type II complex, respectively.

Representative diffractograms of thermal treated DMSO-KGa-2 are shown in Fig. 4. Complex-peak *d*-values, intensity ratios of the complex-peaks relative to those of the 0.72 nm peaks (neat kaolinite) and thermal mass losses are summarized in Table 2. A sample of 100 mg was heated in a glass beaker at 120°C (curves a and b) and 130°C (curves c and d). 3 h at 120°C resulted in a mass loss of 6.0%. Curve a does not show the formation of type II complex. The behavior of this sample differed from that of DMSO-KGa-1 that under the same thermal treatment lost only 0.6% but showed the presence of small amounts of type II complex (Fig. 3c). Longer thermal treatments at 130°C were required for the disappearance of the 1.11 nm peak (Fig. 4d).

Shorter times were required for the completion of the thermal reactions with clay amounts smaller

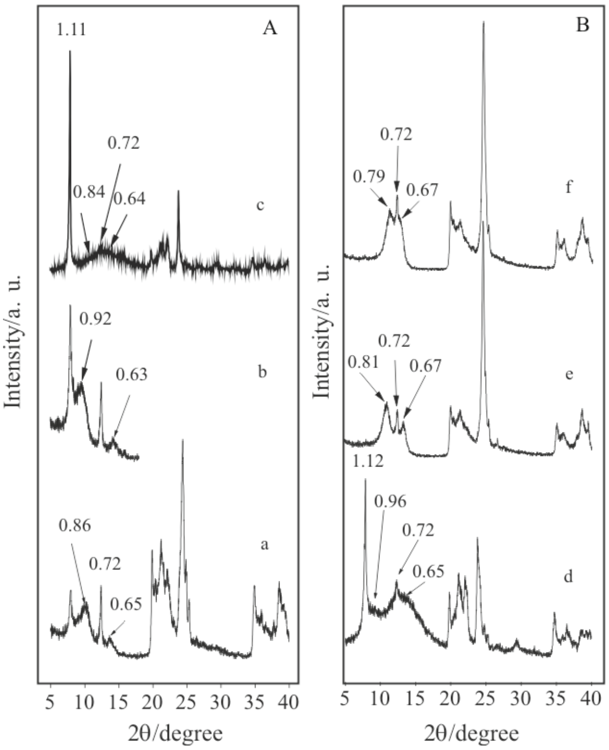


Fig. 3 A and B – X-ray diffractograms of DMSO-KGa-1 a – heated in a glass beaker at 40, 60, 80, 100, 110 and 120°C, 3 h at each temperature, b – gradually heated in a beaker from room temperature to 120°C (≈30 min) and left 3 h at that temperature, c – heated in a beaker 3 h at 120°C, d – heated in a Petri glass plate 3 h at 120°C, e – heated in a beaker 5 days at 120°C, f – heated in a beaker 3 h at 140°C

Table 1 Complex-peak *d*-values (in nm) and intensity ratios of the complex–peaks relative to those of the 0.72 nm peak (neat kaolinite) in the diffractograms of representative samples of KGa-1 and thermal mass losses of the samples

Sample No.	Type I complex		Type II complex		Type II complex		Mass loss/ %
	d/nm	Intensity ratio	*d*/nm	Intensity ratio	*d*/nm	Intensity ratio	
1	1.11	1.32	0.86	0.76	0.65	0.19	n.d.
2	1.11	3.25	0.92	0.98	0.63	0.14	n.d.
3	1.11	26.32	0.84	0.60	0.64	0.63	0.6
4	1.12	7.69	0.96	0.48	0.65	0.48	5.2
5	–	–	0.81	1.12	0.67	0.58	15.2
6	–	–	0.79	0.82	0.67	0.55	16.7

n.d. – not determined, 1. Heated in a glass beaker at 40, 60, 80, 100, 110 and 120°C, 3 h at each temperature, 2. Gradually heated in a beaker from room temperature to 120°C (≈30 min) and left 3 h at that temperature, 3. Heated in a beaker 3 h at 120°C, 4. Heated in a Petri glass plate 3 h at 120°C, 5. Heated in a beaker 5 days at 120°C, 6. Heated in a beaker 3 h at 140°C than 100 mg but longer times were required with higher amounts. It may be concluded that mass loss and X-ray diffractograms are affected by the amount of the heated DMSO–kaolinite complex, the thickness of the clay layer and the stages of the thermal treatment. It seems therefore that the thermal treatment of a certain series must be carried out under a strict control of the experimental conditions in order to obtain reliable trends of the thermal reactions.

First series

Representative X-ray diffractograms of DMSO-KGa-1 and DMSO-KGa-2 recorded after gradual heating the clays, 3 h at each temperature are shown in Figs 1 and 2 (curves b–d). Intensity ratios of the 1.11 nm peak relative to those of the 0.72 nm peak in diffractograms of non-heated DMSO–kaolinites were 52.63 and 5.75, respectively. They decreased to 50.00, 50.00, 34.48, 17.54, 6.13 and 1.32 in the diffractograms of DMSO-KGa-1 and to 5.52, 5.75, 5.85, 4.13, 2.08 and 0.57 in those of DMSO-KGa-2 after heating at 40, 60, 80, 100, 110 and 120°C, respectively. At 130 or 140°C the 1.11 nm peak disappeared. These results show that during the thermal treatment intensities of the 1.11 nm peak decreased and those of the 0.72 nm peak increased, indicating that the fraction of non-intercalated tactoids increased due to a thermal evolution of the guest molecules DMSO and H_2O.

After 110 or 120°C two new peaks appeared in the diffractograms of DMSO-KGa-1 and DMSO-KGa-2, respectively, indicating the appearance of a new phase (type II complex). In the former, the *d*-value of one peak shifted with the rise in temperature from 0.94 to 0.78 nm and that of the second peak from 0.61 to 0.67 nm. In the latter they shifted from 0.86 to 0.81 and from 0.62 to 0.65 nm. With the rise in temperature these peaks intensified up to 130 or 140°C but at higher temperatures they became weak and disappeared at 150 or 160°C. The intensity ratios of the 0.94–0.78 nm peaks relative to those of the 0.72 nm peaks in the diffractograms of DMSO-KGa-1 were 0.69, 0.76, 0.85, 0.60 and 0.21 and those of the 0.61–0.67 nm peaks were 0.06, 0.13, 0.30, 0.31 and 0.00 after heating the complex at 110, 120, 130, 140 and 150°C, respectively. The intensity ratios of the 0.86–0.81 nm peaks relative to those of the 0.72 nm peaks in the diffractograms of DMSO-KGa-2 were 0.12, 0.22, 0.19, and 0.16 and those of the 0.62–0.65 nm peaks were 0.02, 0.04, 0.07 and 0.00 after heating the

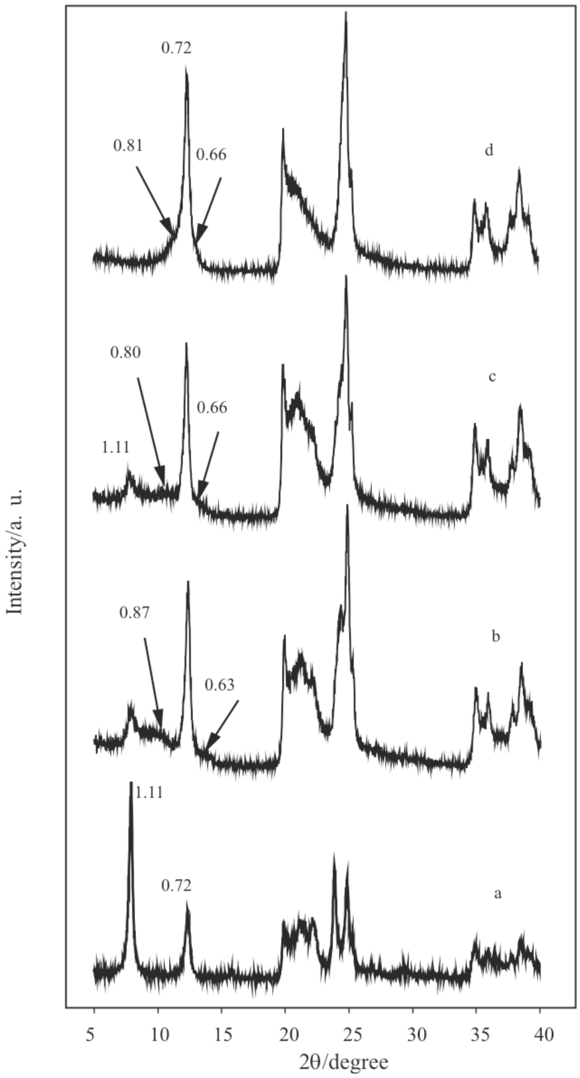


Fig. 4 X-ray diffractograms of DMSO-KGa-1 a – heated 3 h at 120°C, b – sample a heated 8 h at 120°C, c – sample b heated 3 h at 130°C, d – sample c heated 8 h at 130°C

Table 2 Complex-peak *d*-values (in nm) and intensity ratios of the complex-peaks relative to those of the 0.72 nm peak (neat kaolinite) in the diffractograms of representative samples of KGa-2 and thermal mass losses of the samples

Sample No.	Type I complex		Type II complex		Type II complex		Mass loss/ %
	d/nm	Intensity ratio	*d*/nm	Intensity ratio	*d*/nm	Intensity ratio	
1	1.11	4.72	–	–	–	–	6.0
2	1.11	0.33	0.87	0.11	0.63	0.04	10.2
3	1.11	0.21	0.80	0.09	0.66	0.04	11.3
4	–	–	0.81	0.13	0.66	0.10	14.6

1. Heated 3 h at 120°C, 2. Sample 1 heated 8 h at 120°C, 3. Sample 2 heated 3 h at 130°C, 4. Sample 3 heated 8 h at 130°C

complex at 120, 130, 140 and 150°C, respectively. At higher temperatures only the 0.72 nm peak was detected, indicating the complete escape of DMSO molecules and collapse of the clay.

Second series

DMSO-KGa-1 was heated at 120°C for 3 days. Each day a small fraction was diffracted by X-ray at room temperature. During the thermal treatment the intensity of the 1.11 nm peak (type I complex) decreased whereas that of the 0.72 nm peak (neat kaolinite) increased. Intensity ratios of the 1.11 nm peaks relative to those of the 0.72 nm peaks were 3.08, 3.32, 0.17 and 0.14 after 3 h, 1, 2 and 3 days of thermal treatment, respectively. Two new peaks appeared implying the formation of type II complex. One peak initially appeared at 0.92 nm but gradually shifted to 0.80 during the three treatment days. The intensity ratio of the 0.92–0.80 nm peak relative to that of the 0.72 nm peak was 0.98, 1.09, 0.72, and 0.33 nm after heating the sample for 3 h, 1, 2 and 3 days suggesting that the type II complex was formed mainly during the first day of the thermal treatment but with longer treatments it decomposed with the evolution of DMSO. The second new peak initially appeared at 0.63 nm but gradually shifted to 0.66. The ratios of the intensity of the 0.63–0.66 nm peak relative to that of the 0.72 nm peak were 0.14, 0.12, 0.36, and 0.22 nm after heating the sample for 3 h, 1, 2 and 3 days at 120°C, respectively.

During the thermal treatment of DMSO-KGa-2 at 120°C intensity ratios of the 1.11 nm peaks relative to those of the 0.72 nm peaks were 0.81, 0.27 and 0.04 after heating 3 h, 1 and 4 days, respectively. Intensity ratios of the 0.86–0.80 nm peaks relative to those of the 0.72 nm peaks were 012, 0.13 and 0.06, suggesting that the type II complex was obtained mainly during the first day and decomposed after longer thermal treatments. The 0.65 nm peak was not detected in these diffractograms.

Conclusions

The formation of a new phase (type II complex) during the thermo-XRD-analysis of DMSO–kaolinite complexes was clearly recognized from the appearance of two new peaks at 110–120°C, persisting up to 150°C. The C analysis proved the presence of carbon in samples heated at 140°C probably in the form of DMSO, whereas the thermal mass loss experiments showed that water was absent. We showed by thermo-IR-spectroscopy that type II complexes were obtained by the thermal dehydration of type I complexes. The presence of small amounts of DMSO in type II complexes was proved by the persistence of the methyl group absorption bands in the IR spectra recorded after heating the complexes at 140°C. Water bands, which were identified in the spectra of the complexes heated at lower temperatures, disappeared at 130 or 140°C. On the other hand, the inner-surface hydroxyl band was perturbed at this thermal stage indicating that the remaining DMSO was located in the interlayer.

The classical method to calculate the *d*(001)-value of intercalation complexes is by adding the height of the intercalated molecule to 0.72 nm (e.g. [19]). In the case of the DMSO–kaolinite complex the calculated value should be higher than 1.11 nm and it was suggested that methyl groups were keying into ditrigonal holes of the O-planes [8]. In the present study *d*-values of the peaks characterizing type II complex are 0.96–0.79 and 0.61–0.67 nm in the diffractograms of DMSO-KGa-1 and 0.86–0.81 and 0.62–0.66 nm in those of DMSO-KGa-2. These spacings, and especially the later, are too short for being 001 reflection. It was previously shown that the intercalation of cesium halides by kaolinite is accompanied by delamination [20]. It might be possible that in the present study during the thermal treatment some of the intercalated tactoids undergo delamination which is followed by critical changes in the packing of the layers and reflections other than 001 are recorded. This requires further investigation.

References

1 S. Yariv, Organo-clay Complexes and Interactions, S. Yariv and H. Cross, Eds, Marcel Dekker, New York 2002, p. 90.

2 A. Weiss, W. Thielepape, G. Goring, W. Rieter and H. Schafer, Proc. 1st Intern. Clay Conf., Stockholm, 1963, I. T. Rosenquist, Ed., 2 (1963) 67.

3 A. Weiss, W. Thielepape, W. Rieter, H. Schafer and G. Goring, Z. Anorg. Allg. Chem., 320 (1963) 183.

4 A. Weiss, W. Thielepape and H. Orth, Proc. 2nd Intern. Clay Conf., Jerusalem 1966, A. Weiss and L. Heller, Eds, 1 (1966) 277.

5 R. L. Frost, J. Kristóf, G. N. Paroz and J. T. Kloprogge, J. Phys. Chem. B, 102 (1998) 8519.

6 S. Olejnik, L. A. G. Aylmore, A. M. Posner and J. P. Quirk, J. Phys. Chem., 72 (1968) 241.

7 C. T. Johnston, G. Sposito, D. F. Bocian and R. R. Birge, J. Phys. Chem., 88 (1984) 5959.

8 J. G. Thompson and C. Cuff, Clays Clay Miner., 33 (1985) 490.

9 M. Raupach, P. F. Barron and J. G. Thompson, Clays Clay Miner., 35 (1987) 208.

10 A. Mata-Arjona, A. Ruiz-Amil and E. Inaraja-Martin, Proc. Reunion Hispano-Belga de Minerales de la Arcilla, Consejo Superior de Investigaciones Cientificas, Madrid 1970, p. 115.

11 J. Kristóf, R. L. Frost, J. T. Kloprogge, E. Horváth and M. Gábor, J. Therm. Anal. Cal., 56 (1999) 885.
12 S. Yariv and I. Lapides, J. Therm. Anal. Cal., 94 (2008) 433.
13 S. Yariv, Int. Rev. Phys. Chem., 11 (1992) 345.
14 S. Yariv and K. H. Michaelian, Schriftenr. Angew. Geowiss., 1 (1997) 181.
15 L. Heller-Kallai, E. Huard and R. Prost, Clay Miner., 26 (1991) 245.
16 S. Yariv, I. Lapides, A. Nasser, N. Lahav, I. Brodsky and K. H. Michaelian, Clays Clay Miner., 48 (2000) 10.
17 S. Yariv and I. Lapides, J. Therm. Anal. Cal., 80 (2005) 11.
18 Z. Yermiyahu, I. Lapides and S. Yariv, Appl. Clay Sci., 30 (2005) 33.
19 B. K. G. Theng, The Chemistry of Clay-organic Reactions, Adam Hilger, London 1974, p. 239.
20 S. Yariv, I. Lapides, K. H. Michaelian and N. Lahav, J. Therm. Anal. Cal., 56 (1999) 865.

ICTAC 2008

DOI: 10.1007/s10973-008-9622-x