NOTE ON THE INTERCALATION OF KAOLINITE, DICKITE AND HALLOYSITE BY DIMETHYL-SULFOXIDE

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Abstract—Various kaolinites, a dickite and halloysites have been treated by DMSO in presence of D_2O and subsequently washed by D_2O. This procedure allowed to record OD stretching bands which are due specifically to the intercalated fraction and, for the washed samples, to the fraction of the solid which has been intercalated and has subsequently collapsed.

No structural difference is found between the intercalated materials prepared from the various minerals. Washing usually restores the starting mineral; however, for a non-tubular halloysite, DMSO intercalation and subsequent washing gave a product similar to kaolinite.

INTRODUCTION

Intercalation of dimethyl-sulfoxide between the sheets of kaolinite has been described in the literature (Sanchez Camazano and Gonzalez Garcia, 1966; Gonzalez Garcia and Sanchez Camazano, 1965; Olejnik *et al.*, 1968; Jacobs and Sterckx, 1970).

The intercalating ability of DMSO has been compared with that of other organic reagents and the expandibility of various kaolin minerals has also been investigated (Olejnik *et al.*, 1970; Range *et al.*, 1969; Alietti, 1970).

The aim of this paper is to compare structural aspects of complexes made from different minerals of the kaolinite family and the products obtained after destruction of these complexes. For that purpose, extensive use has been made of infrared spectroscopy combined with selective deuteration.

EXPERIMENTAL

The samples studied are listed in Table 1. The main characteristics of their morphology, as observed by electron microscopy, and the Hinckley index of kaolinites, deduced from the X-ray powder diffraction patterns, are also presented.

Intercalation by dimethyl sulfoxide (DMSO) was realized by mixing 250 mg of clay with 25 ml of DMSO (Merck) and 3 ml of D_2O in glass tubes, which were sealed immediately and left for 30 days at room temperature with occasional stirring (Olejnik *et al.*, 1968).

The clay–DMSO complexes were decomposed by washing five times with D_2O. For that purpose, the samples were agitated with fresh D_2O and centrifuged; for the last washing, the mixture of clay and D_2O was maintained at 90°C in a sealed tube for 1 day.

The infrared spectra were recorded by a Perkin–Elmer 180 or a Karl Zeiss Jena UR.10 spectrograph. Oriented films (~ 0.5 mg clay/cm^2) were prepared by depositing the clay suspension on a KRS5 window and letting it dry. KBr pellets were also prepared with the untreated clay and with the clay recovered from dry films of the washed complexes. Measurements dealing with films were made in polarized light at

Table 1. Mineralogical characteristics of the samples

| Name	Details	Morphology	Hinckley index Untreated	Hinckley index Washed after DMSO treatment	Degree of intercalation by DMSO
Kaolinite Zettlitz	< 2 μm fraction well crystallized	Mosaic pseudohexagonal plates	0.80	0.42	Almost complete
Kaolinite Pugu	< 2 μm fraction well crystallized	Well-developed pseudo-hexagonal plates	1.26	1.10	Partial
Kaolinite P. Avram	*b*-axis disordered	Rounded small particles	0.38	0.13	Almost complete
Dickite San Juanito	2–5 μm fraction	Thick pseudohexagonal crystals			Partial
Halloysite B	7 Å halloysite hydrothermal alteration in Neogene volcanic andesite Baia Mare–Romania	Tubes			Almost complete
Halloysite BM	*idem.*	Platy crystals with rolled edges and not completely rolled tubes			Almost complete
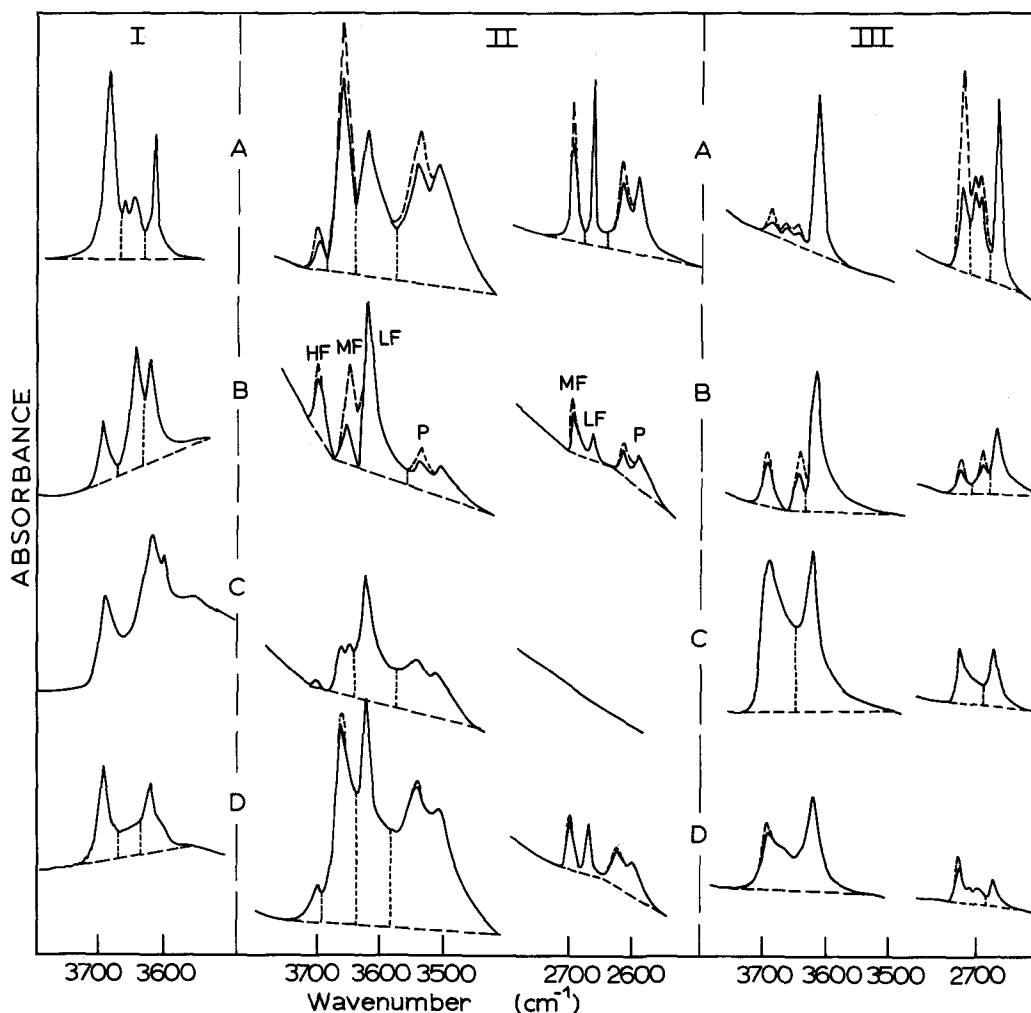
Figure 1. Infrared spectra in the OH and OD stretching region: A, kaolinite Zettlitz; B, dickite San Juanito; C, halloysite B; D, halloysite BM; I, untreated (KBr pellet); II, treated by DMSO (film); III, treated by DMSO and washed (film). Full line: normal incidence; interrupted line: incidence angle of 35°.

various incidence angles obtained by rotating the film around an axis perpendicular to the polarization plane. The X-ray powder diffraction patterns were recorded by a Philips diffractometer (CuK$_\alpha$, 40 kV); the diagrams presented are for non-oriented specimens, but diffraction patterns were also used to control the oriented films.

The electron micrographs were obtained by using a AEI-EM6G electron microscope; one drop of suspension was deposited on a support sieve and after drying, the sample was covered by a thin carbon film.

RESULTS AND DISCUSSION

Material treated with DMSO

Table 1 gives the degree of intercalation of the various clays, roughly estimated from the relative intensity of the 7.2-Å and the 11-Å X-ray diffraction peaks. Three samples of fire-clays, studied by Herbillon *et al.* (1976), were also investigated; however, they were practically not affected by DMSO, in agreement

with literature data (Alietti, 1970) and will not be considered further.

The infrared spectra of the natural clays present the expected pattern in the OH stretching region (Figure 1, set I). All of them have a band at 3620 cm^{-1} (LF), which is due to inner hydroxyls. For well-crystallized kaolinites, the band at high frequency (HF, ~3695–3700 cm^{-1}) and the adjacent band (~3670 cm^{-1}) are attributed to coupled vibrations of inner-surface hydroxyls (2 per unit cell) nearly perpendicular to the sheet; the band at about 3655 cm^{-1} is due to inner-surface hydroxyls (1 per unit cell) lying close to the sheet (Rouxhet *et al.*, 1977). For the kaolinite of P. Avram, the ratio of the absorbance at 3670 cm^{-1} to the absorbance at 3655 cm^{-1} is slightly smaller than for the Pugu and Zettlitz kaolinites. This may be due to the lower ordering of that specimen. Dickite (Figure 1, B) shows only one band in the intermediate frequency range (HF), at about 3650 cm^{-1} (Farmer, 1974). The absorption of halloysite in the region between the HF and LF bands (MF

Table 2. Data derived from the intensity of infrared bands recorded on films (i = incidence angle), except when KBr pellet is indicated

| | Clay treated by DMSO | | | | | | Treated by DMSO and washed | | Natural clay |
| | $\dfrac{2A_P^{OD}}{A_P^{OH} + 2A_P^{OD}}$ | $1 - \dfrac{(A_{HF}/A_{LF})_{DMSO}}{(A_{HF}/A_{LF})_{washed}}$ a | $\dfrac{A_P^{OH} + 2A_P^{OD}}{A_{LF}^{OH} + 2A_{LF}^{OD}}$ | | A_P^{OD}/A_{MF}^{OD} | | $\dfrac{2A^{OD}}{A^{OH} + 2A^{OD}}$ for MF and HF | A_{HF}^{OD}/A_{MF}^{OD} KBr pellet | A_{HF}^{OH}/A_{MF}^{OH} KBr pellet |
			$i = 0°$	$i = 40°$	$i = 0°$	$i = 40°$			
Kaolinite Zettlitz	0.40	0.83	2.0	2.1	2.6	2.2	0.80–0.90	2.26	2.28
Kaolinite Pugu	0.67	0.20	1.2	1.3	2.2	2.0	0.40–0.60	2.00	2.09
Kaolinite P. Avram	0.54	0.91	2.0	1.8	2.4	1.6	0.70–0.80	1.82	2.32
Dickite	0.54	0.22	0.8	1.0	1.7	1.5	0.45–0.65	0.84	0.50
Halloysite B	—	0.98	1.0	1.0	—	—	~ 0.40	—	—
Halloysite BM	0.08	0.80	1.9	1.9	—	—	0.40–0.80	—	—

a $A_{HF}/A_{LF} = (A_{HF}^{OH} + 2A_{HF}^{OD})/(A_{LF}^{OH} + 2A_{LF}^{OD})$

range) does not give distinct features. The shoulder observed at $3600\,cm^{-1}$ probably is due to inner-surface hydroxyls perturbed by interlamellar water (Yariv, 1975). The importance of this shoulder, the absorption at lower wavenumber due to water, and the intensity ratio of the HF and LF bands indicate that sample BM is less hydrated than sample B (Farmer, 1974; Rowland, 1973).

Spectra of films of treated clays are presented in Figure 1 (set II). Deuteration of non-expanded kaolinite or dickite would require high temperature and pressure. Therefore the OD region of the spectra is due only to the fraction of the clay which is intercalated, without contribution of the unreacted part. The LF band is not modified after intercalation but the HF band is absent. In the intermediate frequency range (MF) one intense band is observed around $2700\,cm^{-1}$. In addition, there are two bands at 2596 and $2622\,cm^{-1}$ which are attributed to hydroxyls perturbed by H bonding and will be called P bands (Olejnik et al., 1968; Jacobs and Sterckx, 1970). In the OH region, bands of the DMSO complex and of the unreacted clay are superposed.

The intensity of the various types (HF, MF, LF, P) of both OH and OD bands has been evaluated by measuring their integrated absorbance A. The base line was drawn and the various components were roughly separated as indicated in Figure 1. The degree of deuteration of inner-surface hydroxyls in the intercalated part may be estimated by the ratio $2A_P^{OD}/(A_P^{OH} + 2A_P^{OD})$ which is given in Table 2. The factor 2 is due to the fact that the integrated absorption coefficient for an OD group is twice smaller than that of an OH group (Rouxhet, 1969). The degree of deuteration of inner hydroxyls given by $2A_{LF}^{OD}/(A_{LF}^{OH} + 2A_{LF}^{OD})$ is smaller.

As there is no HF band for the clay–DMSO complex, the non-intercalated fraction of the clay may be roughly estimated by the ratio $(A_{HF}^{OH} + 2A_{HF}^{OD})/(A_L^{OH} + 2A_{LF}^{OD})$, characteristic of the clay treated by DMSO, divided by the same ratio measured for a film of clay washed after DMSO treatment. Table 2 gives the degree of intercalation of the various clays

estimated by that procedure; the results are in agreement with the X-ray powder diffraction data.

The values of $(A_P^{OH} + 2A_P^{OD})/(A_{LF}^{OH} + 2A_{LF}^{OD})$, given in Table 2, are close to 2 when the intercalation degree is high; this observation has been repeated for various films of Zettlitz kaolinite. Therefore the intensity ratio of P bands with respect to the LF band is another way to estimate the degree of intercalation.

The OD bands are similar for complexes originating from kaolinite, dickite and halloysite. In contrast to what was reported by Jacobs and Sterckx (1970) the MF band and the high-frequency component of P bands show a weak but quite clear pleochroism; this is observed for all the complexes prepared from the various kaolinites and from dickite. The similarity between different types of complexes also is illustrated by the ratio A_P^{OD}/A_{MF}^{OD} which is given in Table 2. For halloysite complexes, the pleochroism is less marked or absent, as the morphology of the particles does not allow complete orientation along the ab plane.

Figure 2 shows also the similarity of powder X-ray diffraction patterns, especially in the region of 20–$24°2\theta$, for complexes prepared from kaolinite and from halloysite.

Figure 3 presents the low-frequency region of the infrared spectrum of a well-crystallized kaolinite, a dickite from Romania and halloysite BM, and also the same clays after submission to an increasing degree of intercalation by DMSO. It is interesting to note that the intensity of the band at $795\,cm^{-1}$, decreasing for the natural samples following the sequence dickite–kaolinite–halloysite, is markedly reduced after intercalation by DMSO. This reflects a perturbation by DMSO and, at the same time, confirms the assignment by Farmer and Russell (1964) to vibrations involving octahedral cations and hydroxyls groups. The shift to $550\,cm^{-1}$ of the band at $540\,cm^{-1}$ due to Si–O–Al^{VI} vibrations, supports the supposition of Jones et al. (1974) that DMSO intercalation perturbs the coordination sphere of Al ions. The other modifications of the spectra resulting from intercalation have been discussed by Olejnik et al. (1968) and Jacobs and Sterckx (1970).
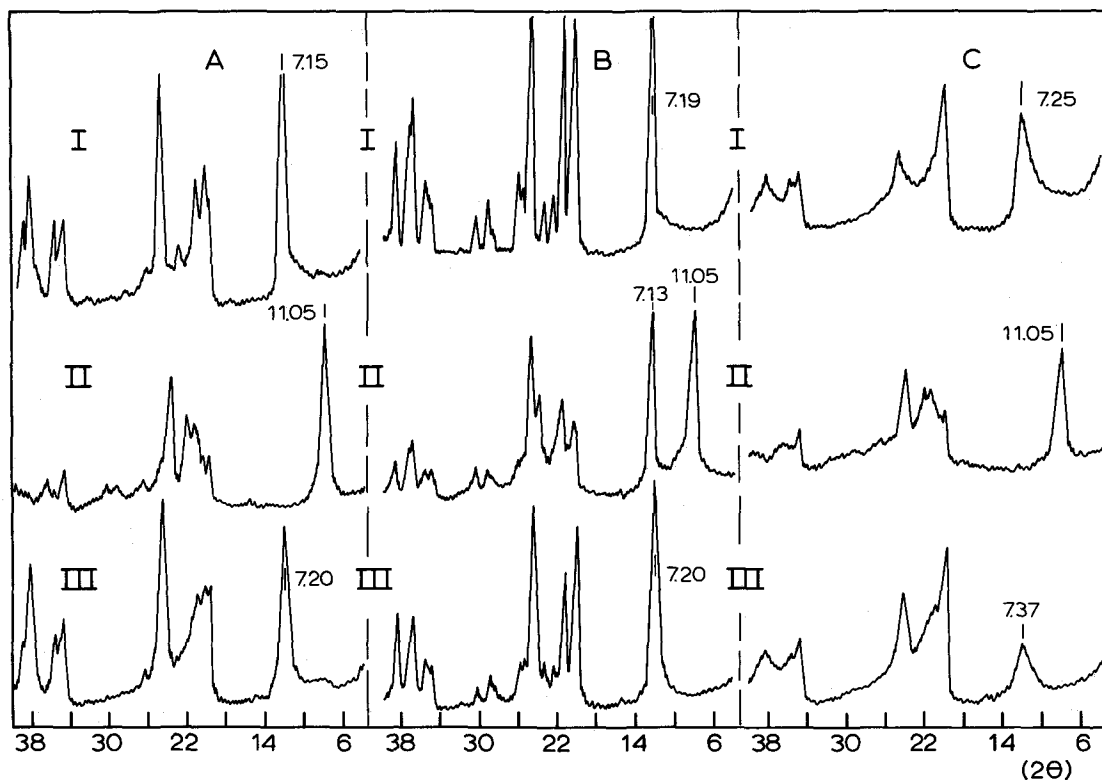
Figure 2. X-ray powder diffraction diagrams of: A, kaolinite Zettlitz; B, dickite San Juanito; C, halloysite BM; I, untreated; II, treated by DMSO; III treated by DMSO and washed. The numbers indicated are *d* spacings (Å).

Material washed after DMSO treatment

Figure 1 (set III) presents spectra of films of the clays treated by DMSO and subsequently washed by D_2O; spectra of KBr pellets have also been recorded. In the OD region, the P bands are no longer visible and therefore the bands characteristic of inner-surface OD groups are due only to the fraction of the solid which has been intercalated by DMSO and has really collapsed as a result of washing. A minimum estimation of the fraction concerned is provided by the ratio $2A^{OD}_{MF}/(A^{OH}_{MF} + 2A^{OD}_{MF})$ or $2A^{OD}_{HF}/(A^{OH}_{HF} + 2A^{OD}_{HF})$. For kaolinite and dickite a good agreement is obtained between these two ratios measured on films and KBr pellets. The average value is given in Table 2. For halloysites, the values given are only a rough figure because of perturbation by the adsorbed water.
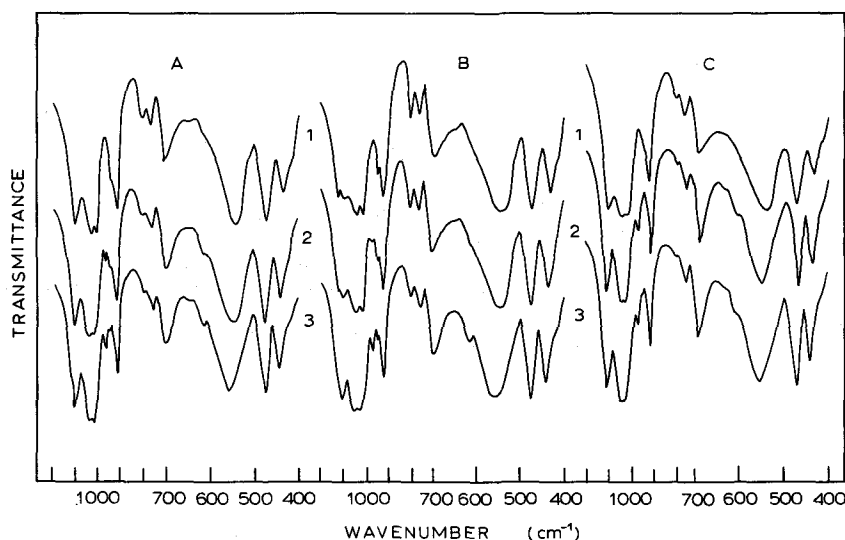

Figure 3. Infrared spectra of untreated clays (1) and of clays with increasing degree of intercalation by DMSO (2,3): A, well-crystallized kaolinite; B, dickite; C, halloysite BM.

Figure 2 shows that destruction of a complex prepared from kaolinite gives a kaolinite with a slightly lower Hinckley index (Table 1); the OD bands are typical of well-crystallized kaolinite.

Washing the complex prepared from dickite restores also the X-ray powder diffraction pattern of dickite. The OD bands are similar to the OH bands of dickite if the isotopic shift is taken into account and has the same pleochroism (Farmer, 1974). These observations have been repeated with a dickite originating from Romania.

As the ratio of the intensity of the HF band with respect to the bands in the MF range is quite sensitive to the polymorphic form, it has been measured for KBr pellets of the untreated clay (OH region) and of the clay treated by DMSO and washed (OD region). The results, listed in Table 2, confirm the similarity between the starting clay and the product obtained after washing the complex.

The OD bands of halloysite B, treated and washed, correspond to a dehydrated halloysite, while the OH bands indicate that some hydrated material or DMSO complex is also present.

Halloysite BM has a rather peculiar behaviour. The OD bands of the washed complex present OD bands typical of a well-crystallized kaolinite, with a pleochroic HF band. This might be due to discrimination of a kaolinite coexisting with halloysite in the specimen. However, according to the X-ray pattern and the infrared spectrum of the untreated clay, the presence of 40–80% (Table 2) kaolinite seems unlikely. The appearance of kaolinite-like infrared bands after washing may be attributed to rearrangement of the sheets with respect to each other. This is supported by the X-ray diagrams which present more features around 20–$24°2\theta$ for the washed complex than for the starting material (Figure 2). The electron micrographs of halloysite BM are also very different from those of halloysite B and indicate the presence of many particles which are platelets, eventually with curved edges, or not completely formed tubes. Rearrangement of the sheets must indeed be easier for such particles than for well-formed tubes.

CONCLUSION

Deuteration of kaolin minerals treated by DMSO has allowed selective observation of the OD bands of the intercalated fraction of the material. The OD bands observed for the DMSO-complexes washed with D_2O are due to the fraction of the solid which has been intercalated and has really collapsed as a result of washing.

These infrared data, and X-ray powder diffraction measurements, indicate no structural difference between complexes made from kaolinite, dickite or halloysite. However, washing the complexes usually restores the original mineral. For a non-tubular halloysite, it seems that DMSO intercalation and subsequent washing transformed part of the material into a product similar to kaolinite.

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