

## STUDIES ON PROPERTIES OF MONTMORILLONITE-AMINO ACID COMPLEXES

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### ABSTRACT

Three montmorillonite-amino acid complexes (montmorillonite-glicine, montmorillonite-arginine and montmorillonite-lysine) were prepared. The complexes were studied by DTA, X-ray and IR-spectroscopy.

DTA measurements indicate a strong interaction between montmorillonite and organic material. There is a mutual stabilization as evidenced by the shift of peak temperatures of both the structural decomposition of the montmorillonite and the decomposition of the organic material. X-ray measurements support the results obtained by other methods. IR-spectra support the existence of the montmorillonite-organic material interactions. Complex formation brings about such conjugational relationships which result in the appearance of a new absorption band in the IR-spectra.

### INTRODUCTION

The well known characteristic of clay minerals is that they readily take up organic matter [EGLINTON, 1969]. Montmorillonite especially features that habit. Montmorillonite stabilizes the absorbed organic material against bacterial degradation, and — under favourable conditions — catalyzes the alteration of the organic substance. However, in the course of the transformation of the organic material, montmorillonite itself turns into a more "illite-like" material [ROLOFF, 1965].

TSUNASHIMA *et al.* [1975] carried out hydrothermal synthesis of montmorillonite-lysine, montmorillonite-glicine and ammonium-mica complexes, respectively. It was proved that the organic component can play an important role in clay formations during the sedimentation and the following diagenetic phases.

This paper reports on the preparation of montmorillonite-amino acid complexes. In the course of the work the amino acid uptake of a given montmorillonite, the type of changes effected by the built-in organic material upon the structure of the montmorillonite, the presence and type of interactions between the clay mineral and the organic matter and their effects upon the thermic properties of the materials involved were studied.

### EXPERIMENTAL

Experiments were started with Mád-Koldu (Hungary) bentonite as raw material. X-ray diffractometric and DTA measurements revealed that this material was a mixture of kaolinite and montmorillonite. The raw material was subjected to repeated sedimentation and centrifugation resulting in a practically pure montmorillonite fraction, with grain size of  $<0.5$  micron. Complexes were prepared from that montmorillonite and analytical grade amino acids.

The cation-exchange capacity of montmorillonite was determined by the  $\text{NH}_4\text{Cl}$ -method according to HOFMANN and GIESE. Absorption isotherms were obtained at constant pH, equilibration period, temperature, and amount of the absorbent and only the amino acid concentrations were changed. 2 g absorbents were weighed, mixed with 40 ml distilled water, then agitated for 20 hours on a shaking machine. Different amounts of amino acids corresponding to the different concentration levels were weighed and dissolved in distilled water, then, in turn, added to the montmorillonite suspension. The pH was adjusted and the volume of the suspension was brought to 100 ml. The pH values of the montmorillonite-glycine; montmorillonite-arginine and montmorillonite-lysine complexes were 3, 2, 8 and 9 respectively. This procedure was followed by a 24 hours mechanical agitation-equilibration procedure on the shaking machine. The complex was centrifuged, the supernatant phase separated and sampled for an automatic amino acid analyser to determine the amounts of the unreacted amino acids. The complex obtained was washed four times with 60 ml portions of distilled water. Part of the complex was subjected to DTA, the other part to X-ray investigations. A suspension of 0.5% of the complexes was prepared and the clay mineral-amino acid complex was sedimented onto a sample holder to obtain an oriented sample.

Having determined the conditions of the greatest amino acid uptake on the basis of adsorption isotherms, larger quantities of the complexes were prepared and their DTA curves were recorded. Transformation temperatures of the complexes were determined from the DTA curves, then 2 g samples of the respective complexes were subjected to heat treatment.

Complexes were heated for an hour in  $\text{N}_2$  or air stream in tube furnaces at predetermined temperatures. DTA curves of the heat-treated samples were also recorded.

Infrared spectra of both the montmorillonite, the original and heat treated complexes were recorded. 800 mg spectral grade KBr and 3 mg material to be tested were mixed, homogenized and pelletized.

## RESULTS

The cation-exchange capacity of montmorillonite was found to be 96 meq/100 g. Based on the adsorption isotherms the maximum amounts of amino acids adsorbed 250 meq/100 g; 560 meq/100 g and 585 meq/100 g in the case of montmorillonite-glycine, montmorillonite-arginine, and montmorillonite-lysine complexes, respectively. However, it should be noted that only apparent absorbed quantities can be spoken about. That means that only a part of these amounts are bound by chemisorption and incorporated into the clay-structure.

The greater part of amino acids is bound only by physical absorption forces to the surfaces. It is evidenced by the fact that having subjected the complexes to vigorous agitation and repeated washings, most of the originally absorbed amino acid is removed. The considerable amount of amino acid thus returned into the solution stabilizes the suspension, so the complex can not be separated during the usual centrifugation time.

### *X-ray diffraction studies*

X-ray diffraction measurements support the results of DTA measurements to be discussed below. The  $d_{001}$  values are 12.44 Å; 13.38 Å and 13.48 Å in the case of the montmorillonite-glycine, montmorillonite-arginine and montmorillonite-lysine complexes, respectively. These figures agree well with data in the literature.

### DTA measurements

When the complexes obtained by determining the absorption isotherms experiments were studied, it was observed that only a part of the absorbed amino acid is incorporated into the montmorillonite structure. The amount of organic material could be evaluated from the weight losses observed on the TG curves. These calculations may be to a certain extent imprecise, yet this fact does not effect the usefulness of the data obtained. The following cation-exchange capacity values could be derived from the DTA measurements: 33 meq/100 g; 77 meq/100 g and 88.3 meq/100 g in the case of montmorillonite-glicine, montmorillonite-arginine and montmorillonite-lysine complexes, respectively.

DTA measurements made on complexes obtained at different points of the absorption isotherms revealed that due to the 24 hours long shaking process the amount of the absorbed amino acid did more or less approach the exchange capacity value at quite low amino acid concentrations. Based on the DTA curves of the untreated complexes it can be concluded that there is a strong interaction between the montmorillonite and the organic material (*Fig. 1*). In the case of the montmorillonite-glicine complex the temperature of the second endothermic peak is shifted from 560° C to 590° C, while that of the peak denoting the final structural decomposition is shifted from 870° C to 890° C. Furthermore, an other exothermic peak, so far undetected on the DTA curves of the original montmorillonite, appeared at 920° C.

On the DTA curves of the montmorillonite-arginine and montmorillonite-lysine complexes the endothermic effect corresponding to the decomposition of the montmorillonite structure is almost totally distorted and covered by two intense exothermic peaks appearing between 630° C and 730° C.

The exothermic effect, however, can well be observed at each these complexes at 930° C and 970° C, -respectively.

It can be seen from the DTA curves of the heat-treated samples that the peak temperature values corresponding to the structural decomposition of montmorillonite are shifted towards higher temperatures.

The montmorillonite-organic matter interaction manifests itself in increased thermal stability of the organic material. The DTA curves-based thermal stability order is as follows: glicine, lysine and arginine. Thermal cracking of the organic substance bound in the complex occurs at a significantly higher temperature than that derived from the melting point.

### IR-measurements

Infrared spectra of the montmorillonite samples agree well with those published by MOENKE [1962], shown in Table 1. It can be seen, that bands belonging to the organic material do not occur equally frequently in the case of different substances (*Fig. 2 and 3*). Organic bands can best be identified in the case of the montmorillonite-lysine complex, while in the IR-spectra of the other two complexes only one band in each can be identified. The organic bands are as follows:

$\gamma_s > \text{CH}_2$	at 1342 $\text{cm}^{-1}$
$\beta_s > \text{CH}_2$	at 1405 $\text{cm}^{-1}$
$\beta\text{-NH}_3^+$ and amide II	at 1510 $\text{cm}^{-1}$
$\nu_s\text{-NH}_3^+$	at 2950 $\text{cm}^{-1}$ and
$\nu_{as}\text{-NH}_2$	at 3290 $\text{cm}^{-1}$ .

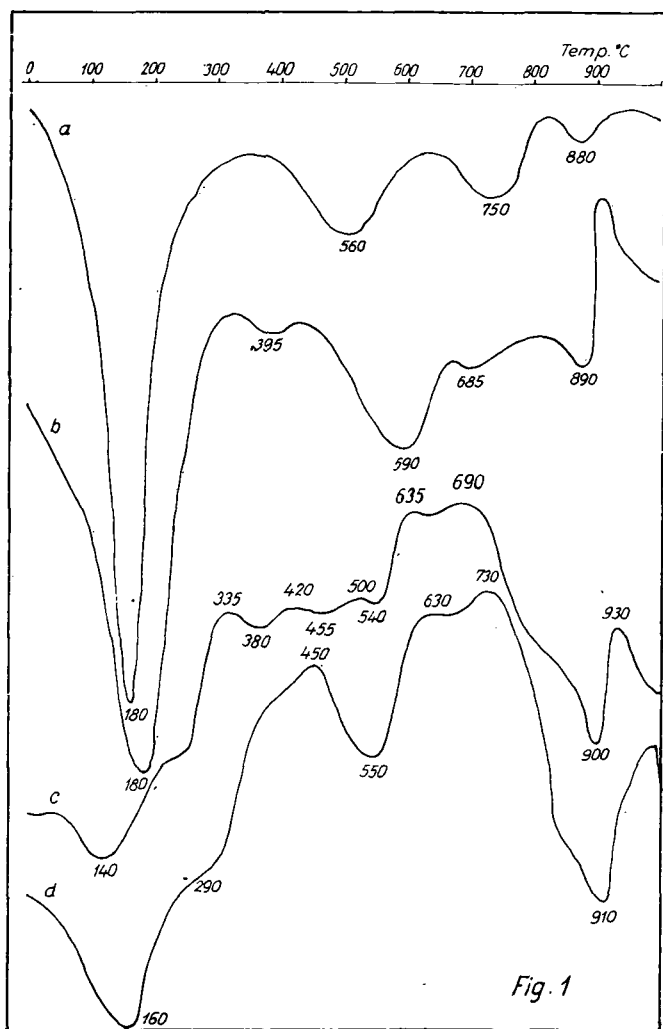


Fig. 1. DTA curves of montmorillonite-amino acid complexes

- a) montmorillonite, Mád-Koldu (Hungary)
- b) montmorillonite-glycine
- c) montmorillonite-arginine
- d) montmorillonite-lysine

Bands assigned to the organic substance disappeared in samples subjected to heat treatment at elevated temperatures. Treating the samples at 600° C and 800° C for 1 hour a number of bands corresponding to montmorillonite fundamental vibrations disappeared (at 430  $\text{cm}^{-1}$ , 353  $\text{cm}^{-1}$ ; 925  $\text{cm}^{-1}$ , and 3635  $\text{cm}^{-1}$ ), while new bands appeared (at 740  $\text{cm}^{-1}$ , and 810  $\text{cm}^{-1}$ ).

There is a doublet at 2370 and 2350  $\text{cm}^{-1}$  in the IR spectra of each complex; a peak nonexistent in the IR spectrum of the original montmorillonite but always present in the complexes. It is probably due to the special conjugation conditions brought about by the complex formation.

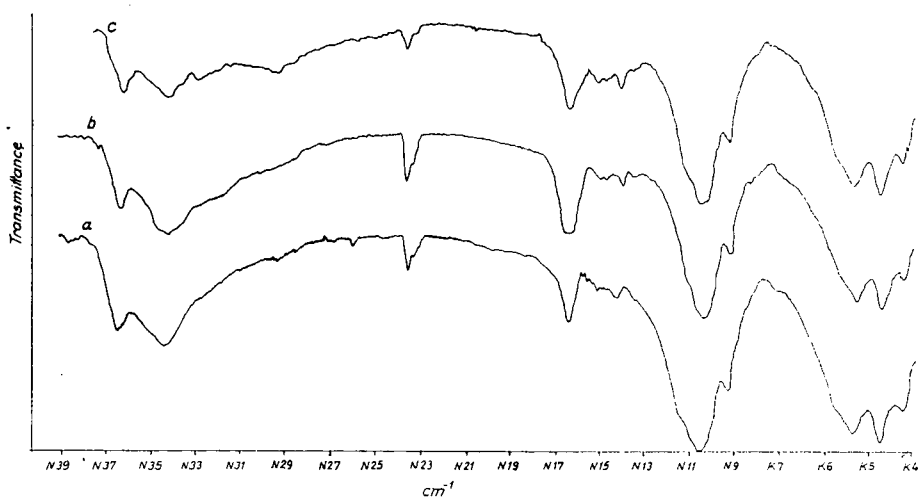


Fig. 2. Infrared spectra of montmorillonite-amino acid complexes

- a) montmorillonite-glycine  
b) montmorillonite-arginine  
c) montmorillonite-lysine

TABLE I

*Major bands in the IR-spectra of montmorillonites*

Group; type of vibration	Wave number range cm <sup>-1</sup>	Montmorillonite bands in	
		MOENKE's cm <sup>-1</sup>	MÁD-KÖLDÜ- samples cm <sup>-1</sup>
Fundamental vibrations of the SiO <sub>4</sub> tetrahedron and AlO <sub>6</sub> octahedron	(600—350)	470	426
		525	475
		630	530
$\nu_s$ (Si—O)—Si	850—800	850	810
$\nu_{as}$ (Si—O)—Al <sup>(6)</sup>	1000—830	920	920
$\nu_{as}$ (Si—O)—Al <sup>(4)</sup>	1055—980	1040	1040
$\nu_{as}$ (Si—O)—Si	1120—1070	1100	1100
$\beta$ —OH	1680—1600	1650	1650
$\nu$ H—O—H	3600—3000	3430	3470
$\nu$ —OH	3760—3520	3628	3630

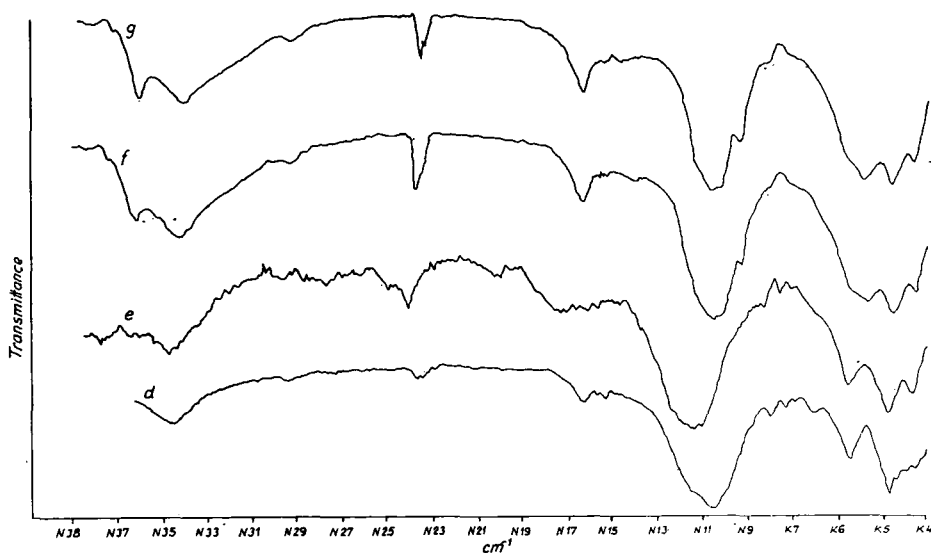


Fig. 3. Infrared spectra of heat treated samples

d) montmorillonite-lysine (800 °C)

e) montmorillonite-lysine (600 °C)

f) montmorillonite-arginine (420 °C)

g) montmorillonite-arginine (320 °C)

#### SUMMARY

Results of DTA and IR measurements yield valuable information relating to the montmorillonite-amino acid complexes. There is a mutual stabilization between the organic substance and montmorillonite resulting in 20–40° C higher temperature values for the structural changes of montmorillonite and increased thermal stability of the amino acids. Since the remaining products and none of the gases evolved could be studied by the DTA investigations, it would be proper to extend these tests and to study the gases evolved as well.

Bands corresponding to the organic material and montmorillonite occur at separate wave numbers. There are vibrations in the 2370–2350  $\text{cm}^{-1}$  range, which can be assigned to the complex formation.

#### REFERENCES

- EGLINTON, G., MURPHY, M. T. J. [1969]: Organic Geochemistry. Springer-Verlag, Berlin—Heidelberg—New York.
- ROLOFF, E. K. [1965]: Über die Rolle glimmerartigen Schichtsilicaten bei der Entstehung von Erdölen und Erdöllagerstätten. Diss., Heidelberg.
- TSUNASHIMA, A., KANAMARU, F., UEDA, S., KOIZUMI, M., MATSUSHITA, T. [1975]: Hydrothermal Synthesis of Amino Acid-Montmorillonites and Ammonium-Micas. Clay and Clay Minerals 23, 2.
- MOENKE, H. [1962]: Mineralspektren. Akademie-Verlag, Berlin.
- KISS—ERÖSS, K. [1974]: Az infravörös spektroszkópia analitikai alkalmazása. (Analytical Application of Infrared Spectroscopy), Műszaki Könyvkiadó, Budapest.

Manuscript received, July 10, 1977

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