

Interlamellar Adsorption of a Blackearth Humic Acid on Na-Montmorillonite

By *F. Martin Martinez**) and *J. L. Perez Rodriguez*

Centro de Edafologia y Biologia Aplicada del Cuarto C.S.I.C. Sevilla (España)

(Eingegangen: 24. 4. 1969)

Interaction between clay and organic compounds has been extensively studied and a considerable amount of literature is available. So, for example, reaction with glycerol (1), ethyleneglycol (7) and dimethylsulfoxide (3) are very well known. But there are not many papers dealing with the reaction between clay and organic matter of soil. Recently, Greenland (4) has made an interesting review of this event. Reactions between clay minerals and fulvic acid have been reproduced in a number of publications, but there are very little papers about interaction between clay minerals and humic acid, probably due to the difficulty to get humic acid in solution. *Schnitzer* and *Kodama* (10) have been made an intensive study on the reaction between a Podzol fulvic acid and Na-Montmorillonite, and they have found that the fulvic acid was adsorbed in the interlamellar spaces of the clay. They found also, that the adsorption was dependent on pH, clay mineral/fulvic acid ratio and time of contact.

Former X-ray studies have shown that humic acid do not penetrate the interlamellar regions of montmorillonite (2, 5, 11) although *Kononova* (6) states that *Khan* has observed such penetration. *Evans* and *Russell* (2), *Martin* and *Reeve* (8) believe that such effect is not produced unless the clay mineral is first made acid and Al enters the exchange sites.

The purpose of this paper is to describe the penetration of humic acid between the clay layers, and to this end we have followed the method described by *Schnitzer* and *Kodama* (10).

Materials and Methods

The montmorillonite used in this study was Na-saturated Wyoming bentonite, fraction $< 2 \mu$.

The humic acid was extracted from the upper horizon of a Blackearth, typical of West Andalusia, with 0.5 N NaOH solution, precipitated with

*) *Dr. F. Martin Martinez*, Centro de Edafologia y Biologia Aplicada del Cuarto, Cortijo de Cuarto, Sevilla/Spainien.

Table 1

Analytical characteristics of the Blackearth humic acid

Elementary composition (Calculated as ash free)		Oxygen-containing functional groups (meq/g)	
C	59.09 %	Total acidity	6.9
H	4.17 %	Carboxyl	3.91
N	3.26 %	Total hydroxyl	4.08
O	33.48 % (by difference)	Phenolic hydroxyl	3.00
Ash	1.32 %	Alcoholic hydroxyl	1.08
		Carbonyl	2.5

2 N sulfuric acid, redissolved and centrifuged at 15.000 r. p. m., three times dissolved and precipitated, and then dialyzed against distilled water, changed at frequent intervals until sulfate test in the distilled water outside the dialysis bag was negative. Following dialysis, the humic acid was dried at 70° C. The characteristic of humic acid are presented in table 1.

For the experiment, 10 to 100 mg of humic acid (H. A.) were dissolved in 0.5 N NaOH (10 to 35 mg of H. A. dissolved in 2.5 ml NaOH solution and 35 to 100 mg of H. A. dissolved in 4 ml of NaOH solution) and then was eluted through anion exchange resin (Dowex-2, OH form) and after through cation exchange resin (Dowex 50-W, H-form), thus the H. A. became soluble, with an original pH of 2.75.

For checking a possible loss of H. A. during the solubilisation, a quantity of (50 mg) was eluted through both exchange resins and evaluated after, the amount being identical.

The original volume was about 15 ml. In experiments done at other pH values, this was adjusted with NaOH, prior to the addition of clay, and the final volume raised to 20 ml with distilled water. To this solution, 10 mg of clay were added and then centrifuged for 1 hour at 600 r. p. m. To evaluate the possibility of H. A. precipitation during the centrifugation, a sample of H. A. was dissolved and centrifuged, checking that there was no precipitation. The supernatant solution of H. A. was decanted, dried, and analysed for C by the chromic sulfuric method.

Measurements of d_{001} spacing were made by extending a thin layer of clay-humic complexes on a glass slide and used directly in diffractometer. The conditions were: Cu $K\alpha$ radiation, 36 kV, 20 mA, scanning speed 1°/min. During the running of the X-ray pattern, dry nitrogen was passed to keep the relative humidity constant.

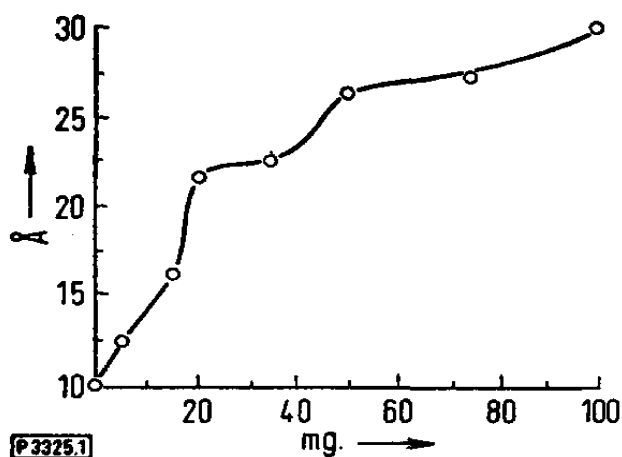


Figure 1

Changes in d_{001} spacing of Na-montmorillonite with increasing amounts of humic acid

Veränderungen des $d(001)$ -Wertes von Na-Montmorillonit durch steigende Mengen sorbierter Huminsäure

Results and discussion

Figure 1, shows the change in d_{001} spacing of Na-montmorillonite with increased quantity of H. A. at the original pH of 2.75.

We have observed, like *Schnitzer* and *Kodama* (10) that there is an initial slope of the curve until ratio 20/10 (mg H. A./mg clay), a second slope until a ratio 50/10 and then the curve becomes asymptotic. In table 2, the relationship of d_{001} spacing of Na-montmorillonite with the increase of the H. A. / clay ratio is shown.

The time of shaking was also studied in relation with d_{100} spacing. The ratio was always 35/10 and the results are in figure 2 (in this time is not included the one hour of centrifuging).

Increase in pH of the H. A. solution on the interlamellar adsorption gives a decrease in the d_{001} spacing as in fulvic acid (9). The steepest decrease occurred

Table 2
Relationship of increasing d_{001} spacing with increase H. A. per 10 mg Na-montmorillonite

d_{001}	H. A. (mg) added per 10 mg clay	H. A. not adsorbed by clay
9.87	—	—
12.44	5	4.64
14.71	10	9.00
16.20	15	12.30
21.53	20	14.55
22.07	35	26.5
26.30	50	36.00
27.00	75	60.70
30.00	100	79.50

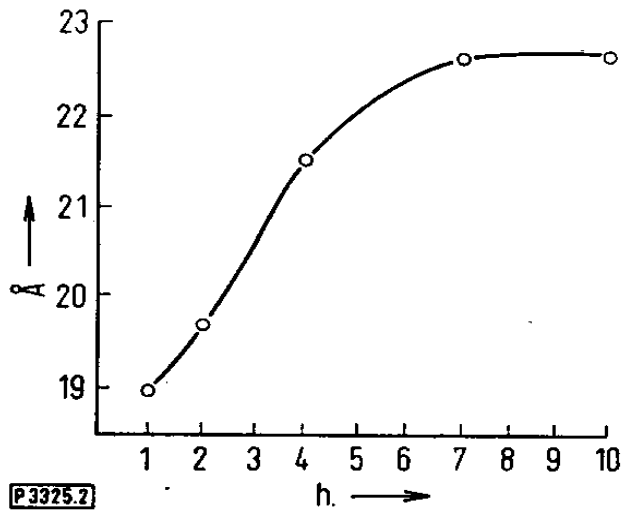


Figure 2

Effect of time of shaking on the d_{001} spacing of Na-montmorillonite (35 mg humic acid/10 mg clay)

Einfluß der Schüttelzeit auf den $d(001)$ -Wert von Na-Montmorillonit bei Zugabe von 35 mg Huminsäure pro 10 mg Ton

between pH 3 and 4 (fig. 3) and the cause of that, may be, as in fulvic acid, related with the ionized group of H. A., but the slope of the curve is different to that of fulvic acid.

The amounts of H. A. in the interlamellar spaces have been calculated from figure 1 in which the steepest slope is between the ratio 20/10 and the ratio 15/10, which means that the complex formation began at the ratio 2:1. The difference between d_{001} spacing at ratio 20/10 and ratio 15/10 is ($21.53 - 16.20 = 5.33$ A) and the difference in mg of H. A. adsorbed ($5.45 - 2.70 = 2.75$ mg) which suppose 1 A approximately for 0.5 mg of H. A. if we assume that the 2.75 mg are interlayer humic acid.

If we suppose that at the ratio 50/10 and 75/10 the complex between H. A. and clay are entirely formed, we can made the following consideration: the difference in A between the complex formed at the ratio 50/10 and the

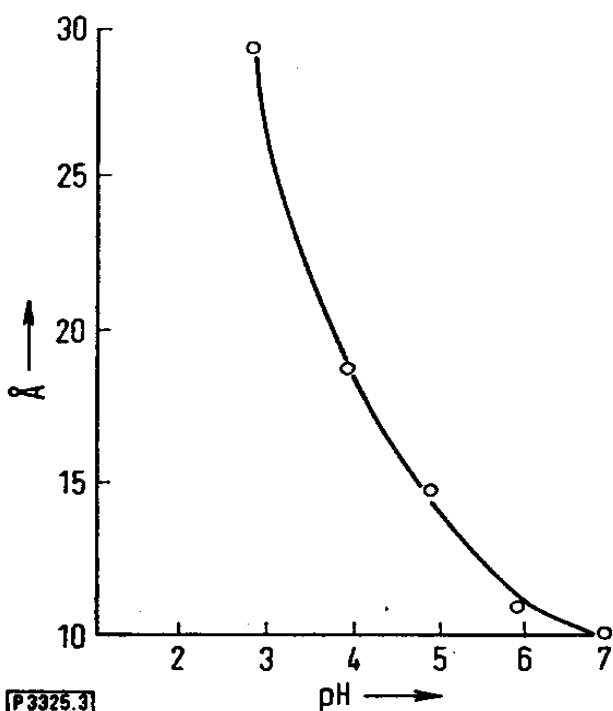


Figure 3

Effect of pH of the humic acid solution on the d_{001} spacing of Na-montmorillonite

Einfluß des pH der Huminsäure auf den $d(001)$ -Wert von Na-Montmorillonit

original clay is $26.30 - 9.87 = 16.43$ Å, this expansion of the lattice corresponds to 8.2 mg of H. A. adsorbed by clay in the interlamellar spaces. As the total H. A. taken was 14 mg the difference ($14 - 8.2 = 5.8$ mg) is externally adsorbed. The same consideration can be made with the complex formed at the ratio 75/10 ($d_{001} = 17.38$ Å) which corresponds to 8.68 mg of H. A. adsorbed and an external adsorption of 5.62 mg.

In the complex formed at ratio 100/10 the H. A. concentration is very high in relation with the clay present, and it is possible that since the interlamellar complex is completely formed, there is a more external adsorption (probably two layers around the surface area of montmorillonite).

The IR-spectra of original clay mineral, original H. A., H. A./clay complex and a mechanical mixture made by grinding solid H. A. with clay at ratio 1:1, are in figure 4. We have not found in the C=O frequency of carboxyl group any difference between the complex and the mixture, to that the interaction is through the carboxyl group of H. A., but that is due to the lower content in carboxyl group of H. A. which prevent its determination by IR.

We have observed that heating at 110° C for several days produces a decrease in the d_{001} spacing. This phenomenon may be motivated by decomposition of the carboxyl group with evolution of CO_2 , since the lability of H. A. at this temperature is known. Schnitzer and Kodama (10) suppose part of the fulvic acid adsorbed in and on the clay were undissociated or slightly dissociated and to some extent Na-fulvic acid. As the H. A. behave themselves, like fulvic acid, the loss of CO_2 is due to the undissociated form.

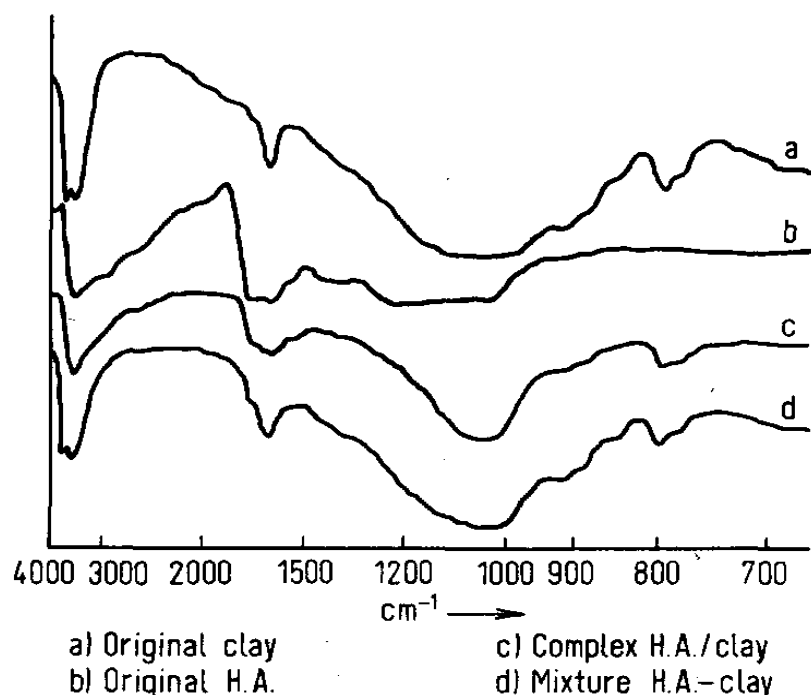


Figure 4

Infrared spectra of a) original clay (2 mg/200 mg KBr); b) original humic acid (1 mg/200 mg KBr); c) complex humic acid/clay (2 mg/200 mg KBr); d) mixture humic acid/clay (1 mg humic acid 1 mg clay/200 mg KBr)

Infrarotspektren von a) Ausgangston (2 mg/200 mg KBr), b) Ausgangshuminsäure (1 mg/200 mg KBr), c) Huminsäure-Ton-Komplex (2 mg/200 mg KBr), d) Huminsäure-Ton-Mischung (1 mg/200 mg KBr)

S u m m a r y

Interaction between Wyoming Na-bentonite and humic acid has been studied. The humic acid from a Blackearth increases the interlayer spacing up to 30.00 Å. The relationship with pH, humic acid/clay mineral ratio and time of shaking has been also studied. Increase in pH of the humic acid solution supposes a decrease in the d_{001} spacing. Increasing humic acid/Na-montmorillonite ratio increases the d_{001} spacing and the same occurs with the time of shaking, but after eight hours does not show more appreciable change.

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Zwischenschichtadsorption einer Schwarzerde-Huminsäure an Na-Montmorillonit

Von *F. Martin Martinez* und *J. L. Perez Rodriguez*

Die Huminsäure einer Schwarzerde erhöht den Zwischenschichtabstand von Na-Montmorillonit bis auf 30 Å. Mit steigendem pH der Huminsäurelösung sinkt der $d(001)$ -Wert, während er mit steigendem Huminsäure/Montmorillonit-Verhältnis und steigender Schütteldauer bis zu 8 Std. ansteigt. [3325]