

THERMAL ANALYSIS OF ALOH POLYMER/MONTMORILLONITE/HUMIC ACID COMPLEXES

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ABSTRACT

Hydroxy Al polymer/montmorillonite complexes were prepared in the presence of humic acid extracted from Canadian soils. DTG analyses as well as isothermal heating studies of these complexes suggest that some organic material from the humic acid may have penetrated the interlayer spaces of the montmorillonite, together with the aluminum. Also, the presence of the humic acid appears to have decreased ALOH polymer interlayering in montmorillonite.

The DTG curve of pure HA shows the greatest weight loss at 525°C, attributable to the decomposition of aromatic compounds, with minor losses at 95°C and 288°C. In the ALOH/montmorillonite complex, the greatest weight losses occur at 95°C (loss of adsorbed water) and 192°C (dehydration of the ALOH polymer). In the ALOH/montmorillonite/HA complex, the temperature of the major pyrolytic reaction, that of the decomposition of the aromatic compounds, had increased from 525°C in the pure HA to 575°C in the complex. This increase suggests that some of the humic matter in the complex must have been present in more protected sites, presumably in interlayers.

Carbon determinations were carried out on samples heated at 3 different temperatures (300, 400, 500°C) for 24 hours. Pure HA loses only a small fraction of its C up to 300°C, but then nearly all of it is eliminated with increase of temperature to 400°C. Elimination of C from HA in the ALOH/montmorillonite/HA complexes at 400°C is substantially lower than from the pure HA. This phenomena seems to suggest that a fraction of the humic matter in the complex had been less exposed to the pyrolysis process, possibly as a result of interlayering with the montmorillonite.

INTRODUCTION

Hydroxy-Al interlayered expansible phyllosilicates are among the most common interaction products of Al with clay minerals in soils (Barnhisel, 1977). The

stability of Al interlayers is influenced by many factors, such as Al/clay ratios, type of phyllosilicate and OH/Al molar ratios. Rich (1968) when summarizing optimum conditions for hydroxy-Al interlayer formation in soils, mentions low organic matter content. That organic acids may affect the stability of Al-interlayers in the alkaline range has been suggested by studies of Violante and Violante (1978).

Humic substances are the principal organic components of soils, in which they interact, among others, with clay minerals to form associations of widely differing chemical and biological stabilities. Among the humic substances, humic and fulvic acids are major components.

Work of Kodama and Schnitzer (1980) suggests that fulvic acid extracted from soil apparently so strongly Al complexes that it greatly inhibits its hydroxylation and crystallization into aluminum hydroxides.

While it is accepted that humic acids, because of their higher molecular weight, have a considerably lower acidity and COOH reactivity than fulvic acid, their conspicuous representation in the organic matter of nearly all soils, makes the study of the effect they might exert on Al interlayer formation of considerable interest. Moreover, in Black Soils (Vertisols) where humic acids dominate in the humic matter and montmorillonite in the clay fraction, the intimate relationship between the humic matter and the clay fraction has been suspected for a long time (Martinez and Jimenez, 1973; Rodriguez et al., 1977; Pezerat and Vallet, 1972 and Bernard et al., 1984). The objective of the present study was to examine by thermal analysis the effect of a humic acid, extracted from a Saskatchewan soil, on Al interlayer formation in a montmorillonite.

EXPERIMENTAL

Humic acid was extracted from an Orthic Black Chernozemic soil from Southwestern Saskatchewan; extraction was according to the recommendation of the International Humic Substances Society. The humic acid with 1.29% ash, contains 54.1% C, 32.7% O, 4.6% H, 4.23% N, and 0.75% S. The E_4/E_6 extinction coefficient ratio is 4.2. The freeze-dried humic acid was turned into a 200 ppm Na-humate solution by slow additions of 0.1 M NaOH to pH 6. This solution, when kept refrigerated, was stable for weeks.

The clay used for the adsorption studies is a Wyoming Na-montmorillonite (SWY-1, Source Clay Minerals Repository, Clay Minerals Society). Monoionic (Na^+) $<2 \mu\text{m}$ suspensions with a concentration of 2000 ppm were used.

Organic carbon was determined by an improved method of dry combustion (Tiessen et al., 1981). Thermal analysis was performed on a Stanton Redcroft model STA

781 combined DTA & TGA apparatus.

Preparation of complex

40 mL of $2 \times 10^{-3} \text{M}$ Al, at an initial pH of 4.10, were titrated against 0.1 M NaOH to pH 4.8, at a titration rate of 1 mL/h, and with constant and vigorous stirring; to this were added slowly (0.5 mL/min) 200 ppm humic acid solutions; unless a ratio of 40 mL HA/40 mL Al was exceeded, no (visible) flocculation occurred in the system at this stage; finally 20 mL of 2000 ppm Na-montmorillonite suspension was added; pH remained stable during these additions; a few minutes after clay addition, visible flocculation occurred; the systems were left agitated for 24 hours, and without agitation for another 24 hours centrifugation at 2000 g for 20 minutes followed; precipitates were separated from supernatants and then washed with 5 mL water.

In these systems, designated as Al/OH/HA/cl, Al/cl ratio was constant and equal to 0.24 meq/40 mg (600 meq/100 g clay); HA/cl varied between 2-8 mg/40 mg (in one instance 20 mg/40 mg), while OH/Al ratio was constant at 2.25. For reference purposes, Al-polymer-clay systems (Al/OH/cl) were prepared in a similar way, but in the absence of humic acid.

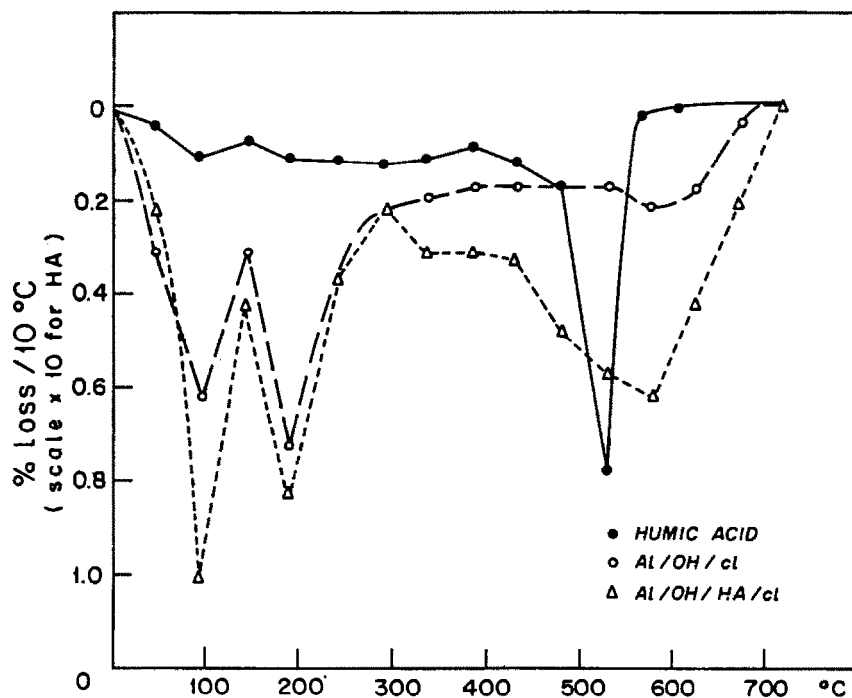


Fig. 1

RESULTS AND DISCUSSION

In Fig. 1 are shown the differential thermogravimetric curves of pure humic acid, hydroxy-Al-montmorillonite and hydroxy-Al-humic acid-montmorillonite complex. With the HA, the weight loss rates are greatest at 525°C. Minor weight losses occur at 95°C and 288°C. In their study of the thermal decomposition of fulvic acid, Kodama and Schnitzer (1970) attribute the weight loss at 100°C to dehydration, that at 280°C to decarboxylation of more stable COOH groups, while the principal weight loss at 465°C is attributed to the decomposition of the aromatic nucleus. The aromatic nucleus in HA is more pronounced and more stable than in FA. Thus, the 525°C weight loss in the HA is attributable to the decomposition of aromatic compounds.

In the Al/OH/cl complex two low-temperature weight-loss peaks can be observed. The greatest weight losses occur at 95°C (loss of adsorbed water) and 192°C (dehydration of the hydroxy-Al polymer). The relatively low temperature of the hydroxy-Al dehydroxylation indicates the low stability of this polymer. The slight weight loss at 576°C may be attributed to the dehydroxylation of the montmorillonite.

The DTG curve of the Al/OH/HA/cl complex combines features of curves of HA and Al/OH/cl with some significant differences. The size of the second low-temperature weight-loss peak, associated with the dehydroxylation of the hydroxy-Al polymer, in relation to the first peak, had decreased, compared to the ratio between these two peaks in the curve for the Al/OH/cl complex. This suggests a relative decrease in Al-polymer interlayering in the complex that contains also humic acid. Significance can also be assigned to the shift in the temperature of the major pyrolytic reaction of the organic matter, from 525°C in the pure humic acid to 575°C in the Al/OH/HA/cl complex. Kodama and Schnitzer (1969) interpreted the appearance of thermic reactions at 670°C (DTA) or 610°C (DTG) in a fulvic acid-montmorillonite complex as indications for the combustion of interlamellar fulvic acid, as opposed to lower temperature reactions, at 400-500°C (DTA) or 270-530°C (DTG), attributed to the oxidation of the externally adsorbed fulvic acid. They proposed to use thermic analysis as a means for differentiation between externally adsorbed and interlayered humic matter. No such distinct separation of combustion maxima was observed in the present study.

Rather oxidation appeared to start at about 330°C and to obtain its maximum at about 575°C in the Al/OH/HA/cl complex, as opposed to the rather sharp maximum at 525°C observed in the pure humic acid. The shift to a higher maximum of the main pyrolysis reaction suggests that some of the humic matter must have been present in more protected sites, presumably in interlayers.

A similar interpretation was given to results obtained from isothermal heating

studies. In order to separate weight-loss reactions associated with the pyrolysis of humic matter from those attributable to montmorillonite dehydration and/or dehydroxylation, carbon determinations were carried out on samples heated at 3 different temperatures for 24 hours (Table 1).

Table 1 Combustion losses of C by isothermal heating of humic acid (HA), HA-montmorillonite mechanical mixture (1:10) and Al/OH/HA/cl complexes.*

<u>Material</u>	<u>Heating temperatures (C°)</u>		
	<u>300</u>	<u>400</u>	<u>500</u>
	%		
HA	17.1	91.9	100.0
HA-Na-montmorillonite	72.9	88.0	95.0
Al/OH/HA/cl (4 mg HA)	37.7	73.0	92.0
Al/OH/HA/cl (8 mg HA)	30.1	80.8	90.0

* Hydroxy-Al was mixed with HA, the pH was adjusted to 4.8 and then Na-montmorillonite was added.

Pure humic acid loses only a small fraction of its C up to 300°C, but then nearly all humic matter is eliminated with increase of temperature to 400°C. When added in a mechanical mixture to Na-montmorillonite, loss of C up to 300°C is very much greater than in the pure HA. This effect of clay acting as a catalyst for the low-temperature combustion of organic matter has been observed by others (Kodama and Schnitzer, 1969). Losses at 300°C for C from HA in complexes with hydroxy-Al-montmorillonite are also considerably higher than from the pure HA, probably also due to some catalytic effects of the clay fraction on low temperature combustion of organic C. At the higher temperature of 400°C, however, elimination of C from HA in the Al polymer-montmorillonite complex is substantially lower than from the pure HA and from the HA in a mechanical mixture. About 20% less C had been pyrolysed in the Al/OH/HA/cl complex with 4

mg HA compared to pure HA. This may be taken to indicate that a fraction of the humic matter had been less exposed to the pyrolysis process, probably as a result of interlayering and complexation with hydroxy Al-polymers. A smaller proportion of the added C had been eliminated at 400°C from the Al/OH/HA/cl complex at the lower HA addition level. This suggests that at the higher addition level of HA, the proportion of humic matter in those protected sites is lower.

In conclusion, thermal analysis suggests that (1) the presence of HA decreases ALOH polymer interlayering in montmorillonite (2) some organic material from the humic acid may have penetrated the interlayer spaces of montmorillonite, together with the aluminum polymer in the course of the formation of the ALOH/montmorillonite/humic acid complex.

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