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## WETTING PROPERTIES OF Fe AND Ca HUMATES

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### SUMMARY

Contact angle determinations were carried out on Ca, Fe and H-humates in order to assess their wettability. The two liquids method (ref. 7) was suitably employed to characterize polar and dispersive interactions. Fe and H-humates displayed large contact angle with water and behaved as low surface energy polymers, whereas Ca-humate was quite hydrophilic.

### INTRODUCTION

Humic substances play an important part in aggregation and water stability of soils. One mechanism involves organic polymers bound to inorganic constituents through polyvalent cations thus acting as effective cementing agents among clay mineral particles (ref. 1). The soil organic compounds influence the stability of soils aggregates through two processes :

- they increase the cohesion of the particles within the aggregates ;
- they decrease the wettability of the soil constituents, thus decreasing the pressure of trapped air during immersion in water.

Several authors (refs. 2-4) have suggested that humic acids display hydrophobic character in soils.

### MATERIALS

Humic acids extracted with a 0.5 N NaOH solution, from a peat (P) and from the A<sub>1</sub> horizon of a Podzol (A) were treated with Fe and Ca solutions. The flocs were washed in order to eliminate the salts and the soluble complexes, then freeze-dried. The conditions of preparation and the composition of the different humates are given in Table 1. The products were characterized through Differential Thermal Analysis (D.T.A.) and I.R. Spectroscopy.

### D.T.A.

D.T.A. curves (Fig. 1) are characteristic of insoluble organo-metallic associations. The main decomposition peak appears at a temperature progressively lower when the amount of fixed Fe increases ; in contrast Ca increases the thermic stability of the humate (Refs. 5-6).

## I.R.

I.R. spectra (Fig. 2) show the abundance of oxygen containing functional groups and they reveal the existence of metal-carboxylate linkages. The  $3200\text{ cm}^{-1}$  band is characteristic of the H-humates whereas it is absent at pH 7 for Fe-humates where OH groups could complex together with the COOH (ref. 6).

TABLE 1  
Characteristics of the different humates

| Sample | Conditions of preparation | % M             | % C             |
|--------|---------------------------|-----------------|-----------------|
|        |                           | (g/100g humate) | (g/100g humate) |
| P1     | Fe, pH 3, 900 meq./100g   | 12              | 31              |
| P2     | Ca, pH 7, 900 meq./100g   | 7               | 43              |
| P3     | H, pH 1.5                 | -               | 51              |
| A1     | Fe, pH 3, 900 meq./100g   | 12              | 44              |
| A2     | Fe, pH 7, 900 meq./100g   | 13              | 40              |
| A3     | Fe, pH 7, 2700 meq./100g  | 26              | 23              |
| A4     | H, pH 1.5                 | -               | 56              |

TABLE 2  
Contact angle, polar and dispersive interactions, and surface free energy

| Sample | $\theta_{SW}$ | $I_{SW}^P$               | $I_{SW}^D$               | $\gamma_S$               |
|--------|---------------|--------------------------|--------------------------|--------------------------|
|        | (°)           | (ergs.cm <sup>-2</sup> ) | (ergs.cm <sup>-2</sup> ) | (ergs.cm <sup>-2</sup> ) |
| P1     | 62            | 57                       | 17                       | 43                       |
| P2     | 0             | 80                       | 42                       | 88                       |
| P3     | 68            | 69                       | 31                       | 64                       |
| A1     | 83            | 47                       | 11                       | 29                       |
| A2     | 74            | 52                       | 17                       | 40                       |
| A3     | 74            | 61                       | 13                       | 47                       |
| A4     | 73            | 69                       | 26                       | 62                       |

## METHOD

The wettability of the humates was determined from advancing contact angle measurements of a sessile drop of water (W) on a flat and smooth surface (S), performed with a tele-goniometer; such surfaces were prepared from dry humate powder pressed into pellets, two methods are used in that purpose:

- the  $\theta_{S\ W/V}$  contact angle of water is measured in the air; at the equilibrium, the system is described by Young's model.

- the  $\theta_{S\ W/H}$  contact angle of water is measured under several non-polar hydrocarbons (H). This 2 liquids method set by Tamai et al. (1967),

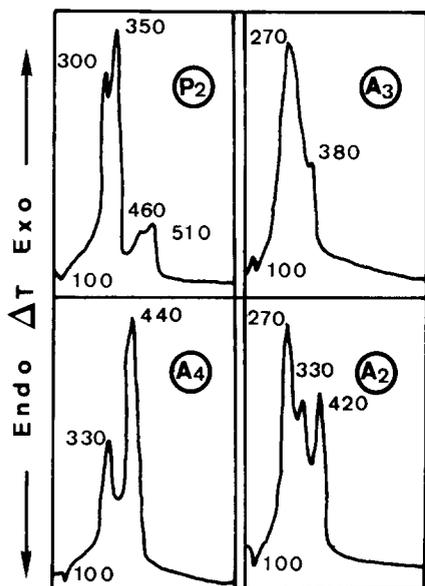


Fig. 1 D.T.A. curves

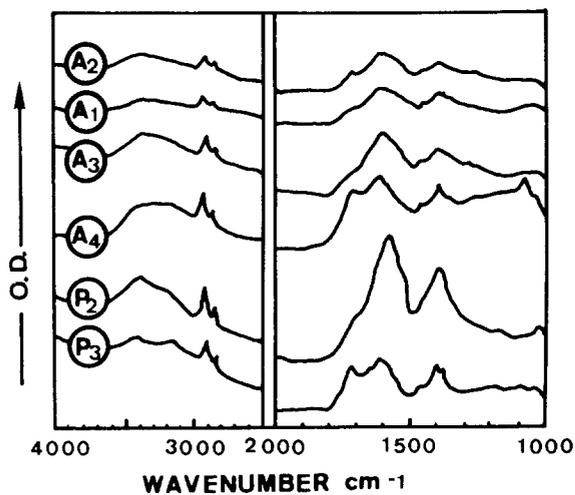


Fig. 2 I.R. spectra

(ref. 7) provides the polar and dispersive energies of interaction between and the solid:  $I_{S W}^D$  and  $I_{S W}^D$ , respectively; also, it makes possible the determination of  $\gamma_S$  for high surface energy solids (which do not exhibit a finite contact angle in a Solid-Water-Vapor system), (ref. 8).

## RESULTS

Humic acids and their salts were observed to display different affinities with water, according to the nature of the cation (Table 2):

- H and Fe humates exhibited quite high contact angles with water. It was concluded that they interact with it mainly through dispersive forces and have  $\gamma_S$  values similar to those of low energy polymers (polyethylene or polypropylene for instance). The amount of Fe complexed did not influence significantly the  $\theta$  angle or  $\gamma_S$ .

- Ca-humate was demonstrated to be quite wettable ( $\theta \neq 0^\circ$ ) and shows high polar interactions with water.

## CONCLUSION

Both methods used to characterize the wettability of the humates were found to be suitable; each gave similar results. Although humic acids contain a large number of hydrophilic oxygen-containing functional groups (OH, COOH, C=O) when complexed with Fe, they display hydrophobic properties. Upon flocculation, then drying, strains are exerted, and the Fe and H-humates exhibit their non-polar ( $\text{CH}_2$ ,  $\text{CH}_3$ ) groups at the surface. In contrast, Ca-humate retains its hydrophilic, polar surface.

It is likely that in the soil, insoluble Fe-organo metallic complexes, coating hydrophilic inorganic constituents (clays, oxides) change their wetting properties, and will prevent slaking and disaggregation through their water-proofing action.

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