INTERACTIONS BETWEEN MONTMORILLONITE AND A SOIL HUMIC COMPOUND

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ABSTRACT

INTERACTIONS between montmorillonite and fulvic acid* extracted from a Podzol soil were investigated by X-ray and chemical methods.

Adsorption of fulvic acid by montmorillonite strongly depended on the pH of the system and the amount of added fulvic acid. 40 mg of Na–montmorillonite ($< 0.2\ \mu$) adsorbed 31 mg of fulvic acid at pH 2.5, but only 15.8 mg of fulvic acid at pH 6.0 from 100 mg of fulvic acid added. *D*-spacings of the organo–clay complexes were 17.6 Å and 10.5 Å, respectively, under the condition of 1% relative humidity. The steepest decrease in spacing occurred between pH 4 and 5 when the ionization of the functional groups in the fulvic acid increased rapidly. At pH < 4, relatively few of these groups had ionized, so that the fulvic acid behaved like a neutral molecule that could penetrate the interlamellar spaces of montmorillonite.

Fulvic acid gave a diffuse X-ray pattern typical of non-crystalline substances. The pattern consisted of a broad maximum at about 4.0 Å, accompanied by a few minor humps. Radial-distribution analysis of the diffuse pattern suggested that the structure of fulvic acid was basically similar to that of carbon black. Since analytical data indicated that one molecular weight of fulvic acid ($M \cdot W_n = 670$) contained aromatic rings, possibly an aliphatic chain or an alicyclic ring between aromatic rings, and functional groups such as COOH, OH, CH_3, and C=O, the spacing of 4.0 Å may correspond to the distance between sheets of rings and chains. On the basis of this, the expansion of montmorillonite at pH 2.5 ($17.6 - 9.6 = 8.0$ Å) was considered to be equivalent to a double layer of fulvic acid. On the other hand, the molecular volume of fulvic acid as estimated from its molecular weight and density was 690 Å^3. The resulting cross-sectional area of 172.5 Å^2 conformed to those of various models of plane molecules. The net amount of interlamellar-adsorbed fulvic acid was possibly of the order of 15 ~18 mg/40 mg clay. Provided that the surface area of montmorillonite was 500 m^2/g, the fulvic acid adsorbed in the interlamellar spaces was approximately one molecule per 172.5 Å^2.

In the presence of various metal cations, similar interaction between montmorillonite and fulvic acid took place. X-ray data suggested that the complexes contained up to three layers of fulvic acid. Adsorption of higher amounts of fulvic acid could be explained by the formation of metallo–organic complexes on the external surface of montmorillonite.

* Organic matter soluble in both base and acid.

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