An X-ray diffraction study of alkylammonium humate complexes

E. Tombácz, K. Varga1), and F. Szántó

Department of Colloid Chemistry, Attila József University, Szeged, Hungary

1) Department of Applied Chemistry, Attila József University, Szeged, Hungary

Abstract: By exchange of cations of different humates (synthetic, brown coal and compost humates) with an equivalent amount of long-chain organic cations, derivatives with the following alkylammonium ions were prepared: n-decyl, n-dodecyl, n-tetradecyl, n-hexadecyl and n-octadecyl ammonium ions. X-ray diffraction of the humic acids and the alkylammonium humates revealed a behaviour similar to that of smectite-type clay minerals. The results seem to support the layer structure of humic substances. The layers of synthetic, brown coal and compost humate are about 0.60, 0.45 and 0.84 nm thick, and the bilayers of alkylammonium cations are bound to the carboxyl and phenolic hydroxyl groups. The chain tilt is 41-45°.

Key words: Humic acid, alkylammonium humates, organophilic humates, cation exchange.

Introduction

Humic substances are of natural origin. They are dark brown, hydrophilic, acidic, polydisperse substances of high molar mass. They contain carboxyl and phenolic hydroxyl groups which dissociate to varying degrees depending on the pH of the solution and the concentration of the electrolyte. They display features of both polyelectrolytes [1], and association colloids [2].

Several research workers [3] have examined the chemical structures of humic substances using different methods for a long time. Due to the chemical complexity of humic substances, no exact structure can be given. Various conceptions have been put forward. Burges et al. [4] consider that the structure is similar to that of other natural macromolecules and is a polycondensate of a random collection of phenolic units. Haworth [5] assumes that the basis of the structure is a complex aromatic nucleus, to which polysaccharides, proteins, simple phenols and metal ions are attached physically or chemically. According to Schnitzer [3], fulvic acids (a group of humic substances) are built up of aromatic oxycarboxylic acids. These “building blocks” are attached to each other through hydrogen bonds.

The steric structure of the particles of humic substances is questionable. Are they linear, flexible chains which, depending on the dissociation of the functional groups, roll up to various extents? Do they form a random coil? Or are they planar aromatic ring systems with a partially ordered structure?

From examination of humic acids by ultracentrifugation, Fläig and Beutelspacher [6] concluded that the acids form spherical colloids. On the basis of small angle X-ray scattering, Wershaw et al. [7] proposed that larger particles of humic acid are elliptical, while smaller ones are spherical. Humic substances, as examined by viscosity measurements by several authors [3], behaved like polyelectrolytes. However, it could not be decided whether polyanions of humic substances are linear chains and/or spherical colloids.

Solid humic substances of natural origin are not crystalline [3]. In the X-ray diffraction pattern of a powder specimen of fulvic acid, Kodama and Schnitzer [8] found a diffuse band at about 4.1 Å. This pattern was similar to that of carbon black which contains graphite-like layers. They stated that the carbon skeleton of fulvic acid is a network of poorly condensed aromatic rings. From X-ray examination, Kasatochkin et al. [9] concluded that humic substances contain a flat
condensed aromatic network, to which side-chains and functional groups are attached.

The X-ray examinations reported in the literature, which were interpreted by assuming linear or globular shapes of the molecules of humic substances or by a planar structure of condensed aromatic ring systems, are not convincing. In all cases, diffuse diffraction patterns are formed, since the linear or planar units ("molecules"), even if they exist in solution, are not arranged in the solid sample in sufficient regular manner.

Alkylammonium ions can increase the order of disordered materials [10]. They may even transform amorphous materials into an ordered state so that X-ray diffraction patterns are obtainable. In fact, Pfirrmann and Weiss [11, 12] observed sharp reflections after reacting humic materials with alkylammonium ions. So, it seems to be worthwhile to study the reaction of alkylammonium ions with humates in some detail.

**Experimental**

The samples of humic acid were extracted from brown coal of miocene age (Steinberg, German Federal Republic) and compost soil (Klärslammm, German Federal Republic) with a 0.1 mol dm$^{-3}$ NaOH solution after Rochus and Sipos [19]. Purification of the crude humic acids was carried out in the usual way, as described by Schnitzer and Khan [3]. Synthetic humic acid was prepared from hydroquinone after Rochus, following the procedure of Eller [20]. The total acidity of humic acids was determined by conductometric titration [3]. The number-average molar mass of synthetic and brown coal humic acids was measured by vapour pressure osmometry using a correction method of Hansen and Schnitzer [21]. The molar mass of compost humate was measured in the same way, since an acidic solution of this material could not be prepared. The properties of humic acids are summarized in Table 1.

### Preparation of n-alkylammonium organocomplexes

Humic acid was dissolved in an equivalent quantity of sodium hydroxide (calculated from the total acidity of the sample, Table 1) to produce a 1 g/100 cm$^3$ sodium humate solution. The alkylammonium chlorides were made by dissolution of alkylamines in an equivalent quantity of HCl. With increasing chain length, the alkylammonium salts become less soluble in water, so 0.1 mol dm$^{-3}$ (n-decyl, n-dodecyl and n-tetradecylammonium chloride), 0.05 mol dm$^{-3}$ (n-hexadecylammonium chloride) and 0.03 mol dm$^{-3}$ (n-octadecylammonium chloride) solutions were used. The organon humate complexes were prepared at 60 °C. Calculated quantities of alkylammonium salts were added to the sodium humate solutions. The amounts of alkylammonium salts were equivalent to the acidic groups (carboxyl and phenolic hydroxyl ones) of the humic acid samples. The suspensions were kept at 60 °C for 1 day, then filtered and washed free of chloride with distilled water at approx. 60 °C. The substances were dried under infrared light and then ground.

The powder samples were examined by X-ray diffraction with a DRON-3 (USSR) diffractometer. The scanning rate was 0.5 °/min.

### Results and discussion

Diffractograms of humic acids and the various alkylammonium humates for 2θ = 1–6 ° can be seen in Figs. 1–3. It seems that the small shoulders in the range 2θ = 4–6 ° are reflections of the second order. The alkylammonium humates, especially those with longer alkyl chains, give sharp reflections of high intensity in contrast to the amorphous character of the starting humic acids. With increasing chain length, the reflections shift to lower 2θ values and become even sharper.

The diffraction patterns of humic acids of different origin (Figs. 1–3) show that the structure becomes more ordered after reaction with alkylammonium ions when the molar mass and the ash content of the humic acid are smaller (cf. Table 1). For example, the dodecylammonium salt of synthetic humic acid has a very sharp reflection (Fig. 1), but the derivative of compost humic acid reveals a more diffuse diffraction pattern (Fig. 3).

The basal reflections exhibit some resemblance to those of alkylammonium montmorillonites [13–16]. Therefore, one may conclude that the humate anions form layered structures. In this case, the basal spacing

### Table 1. Properties of humic acids

<table>
<thead>
<tr>
<th>Humic acid</th>
<th>Molar mass $M_n$ g/mol</th>
<th>Total acidity C mmol/g</th>
<th>Elementary composition</th>
<th>Ash content %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic</td>
<td>1050</td>
<td>5.27</td>
<td>53.3</td>
<td>42.0</td>
</tr>
<tr>
<td>Brown coal</td>
<td>1200</td>
<td>6.70</td>
<td>56.1</td>
<td>30.6</td>
</tr>
<tr>
<td>Compost</td>
<td>2200</td>
<td>5.10</td>
<td>47.5</td>
<td>36.0</td>
</tr>
</tbody>
</table>