



Micro-organization of humic acids in aqueous solutions



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ABSTRACT

The methods of dynamic light scattering and micro-rheology were used to investigate the molecular organization of humic acids in solutions. The obtained results were supplemented by ultraviolet/visible spectrometry and measurement of the zeta potential. Particle tracking micro-rheology was used for the first time as a novel method in humic research. Solutions of humic acids were prepared in three different mediums: NaOH, NaCl, and NaOH neutralized by HCl after dissolution of the humic sample. The molecular organization of humic acids was studied over a wide concentration range ($0.01\text{--}10\text{ g dm}^{-3}$). Two breaks were detected in the obtained concentration dependencies. The rearrangements were observed at concentrations around 0.02 g dm^{-3} and 1 g dm^{-3} . Changes in the measured values observed at around 0.02 g dm^{-3} were less noticeable and were related to the formation of particles between 100 and 1000 nm in size and the strong bimodal character of humic systems diluted by NaCl. The “switch-over point” at around 1 g dm^{-3} indicated changes in the secondary structure of humic acids connected with the increase in colloidal stability (decrease of zeta potential), the decrease in polydispersity, and minimal values of viscosity.

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1. Introduction

The term “organic matter seems to invoke a simple straightforward meaning, which is “matter arising from living matter”, and in chemistry and soil science referring more specifically to “matter relating to or containing carbon compounds”. In basic soil science, it is a general term to describe a mixture of fresh and dead organisms, composed of carbonaceous remains of organisms that once occupied the surface of the earth. It then qualifies to be called natural organic matter [1,2]. The natural organic matter of soils and waters consist of a mixture of plant and animal products in various stage of decomposition, of substances synthesized biologically and/or chemically from the breakdown products and of microorganisms and small animals and their decomposing remains [3]. Organic matter contributes to plant growth through its effect on the physical, chemical, and biological properties of the soil. It has a nutritional function in that it serves as a source of N, P, and S for plant growth, a biological function in that is profoundly affects the activities of microflora and microfaunal organisms, and a physical function in that is promotes good soil structure, thereby improving tilth, aeration, and retention of moisture [4,5]. Natural organic

matter consists of heterogeneous components with a wide range of molecular weights and diverse functionality, ranging from nonpolar polymethylene chains to highly polar carboxylic groups [6]. Individual compounds in natural organic matter can be bridged via water molecule bridges or cation bridges [7]. To simplify this very complex system, natural organic matter, is usually divided into two groups: nonhumic substances, and humic substances. The bulk of the organic matter in most soils and water consist of humic substances. These are amorphous, acidic, polydisperse substances with various molecular weights. Natural organic matter is usually fractionated on the basis of solubility characteristics. The fractions commonly obtained include humic acids (soluble in alkali and precipitated by acid), fulvic acids (soluble in aqueous solutions, not precipitated by acid), and humin (insoluble), other fractions include humatmelanic acids (soluble in alkali and precipitated by acid, soluble in alcohol) and the gray and brown humic acids. Gray humic acids unlike brown ones coagulate in the presence of electrolyte [1,3,8].

A number of studies have shown that humic substances are very complex and heterogeneous molecular systems [3,8]. A variety of structural models for humic matter have been suggested [9–12]. Schulten [9] suggested for the structure of humic acids many aromatic residues, considerable degree of cross-linking and in three dimensions a fairly open structure. Del Rio and Hatcher [10] presented the network structure. They revealed the presence of a

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series of benzenecarboxylic acid methyl esters as well as long-chain fatty acid methyl esters and dimethyl esters. Published average molecular weights of humic acids vary from a few thousand to a few hundred thousand with high polydispersity [11]. Stevenson [4] suggested that the highest values may have been affected by aggregation, which is plausible in view of the high concentrations of humic material ($>1 \text{ g dm}^{-3}$) used in experiments. Wershaw [5] proposed that humic acids are not inherently large, and that the apparently high molecular weights reflect aggregation of small units. Similarly, Conte and Piccolo [13] claimed, that humic acids comprise primary units of low molecular weight. The construction of molecular structure of humic acids is a more complex and difficult problem. All of the theories suggested on molecular structures based on aromatic constituents or phenol obtained by a variety of degradation analyses of humic substances. These small units are then rearranged into a structural unit to represent a humic acid structure [1,12]. Essington [14] suggested the structural models “pseudostructures”, which was defined as hypothetical structures containing elemental and chemical components and functional group features consistent with the observed composition, mass, and other properties obtained from several analytical methods [1].

Humic substances have a colloidal character, whose size and negative charge are strictly dependent on surface functional groups [15]. Humic substances exhibit different structures at different conditions [13,16–21]. Chen et al. [18] observed, that humic substances form coils in acidic solutions, and in strong electrolyte solutions, but elongated structures are formed in dilute alkaline solutions. They behave as rigid spherocolloids or compacted networks at high humic concentrations, low pH values, or high neutral electrolyte concentrations, but as flexible linear colloids at low humic concentrations and high pH values. They can form linear structures as pH is increased and the ionic strength is decreased. The physicochemical properties of humic substances, such as their biopolymer chain structure and colloidal character, are closely related to the solution chemistry, e.g. the electrolyte and pH. The ionized and protonated states of functional groups significantly influence metal complexation, surface charge, and supramolecular structure [13,16,17,19–21]. Wilson et al. [22] reported that humic substances are able to rearrange and restructure themselves in response to environmental changes such as changes in pH, ionic strength, and moisture. The significance of the secondary structure of dissolved humic substances in their interactions in nature has been attributed to entrapment in structural voids, adsorption on surfaces, and partitioning into the hydrophobic interiors of micelle-like structures and humic aggregates [21,23–25]. The formation of micelles depends on the number and nature of hydrophobic association sites in humic solutions and on the origin and concentration of humic acids at a given pH value. At lower pH values, the possibility of humic molecules forming pseudo-micelles increases due to a combination of neutralized and dissociated charged sites. At high ionic concentrations, organizational rearrangements result in a salting-out effect, i.e. the formation of a hydrophobic colloid. At lower salt concentrations, the formation of pseudo-micelles precedes intermolecular interactions [26–28]. A significant secondary structure of humic acids was identified also by Jansen et al. and Varga et al. [29,30].

While many authors [13,17,20,22,31] confirmed that humic molecules in solution are organized in supramolecular associations of relatively small molecules loosely bound together by dispersive interactions and hydrogen bonds, Baigorri et al. [32] reported the presence of both macromolecules and supramolecules in humic substances in solution. They investigated the presence of stable molecular aggregates in different selected humic substances and identified the possible presence of different molecular behaviours (macromolecular and supramolecular) in these humic substances.

These results were supported by the research of Esfahani et al. [33]. They detected the existence of two submicrometer-sized particle size distributions, specifically 10–100 nm and 100–1000 nm, and a supramicrometer-sized particle size distribution of less than 1 μm .

In this research, dynamic light scattering, zeta potential measurements, UV/VIS spectrometry, and micro-rheology were used in order to investigate secondary structure and conformational changes in humic systems. The dynamic light scattering method is frequently used for the investigation of changes in aggregate sizes and micellization [15,16,20,32–35]. Wang et al. [20] studied the coagulation behaviour of humic acid aggregates in electrolyte solutions with different pH values, valences, and concentrations of electrolyte cations. Alvarez-Puebla and Garrido [34] investigated the effect of pH on the aggregation of gray humic acids in colloidal and solid states. They observed that the decrease in the size of colloids was affected more by the ionization of phenolic acidic groups, than by that of carboxylic ones, which was probably because, in the case of ionized carboxylic groups, humic colloids were still capable of generating H-bonds. In the solid state, aggregation effects were illustrated by a decrease in surface area, and the disappearance of certain micro-pores, with increasing pH. Baiggorri et al. [32] stated that humic substances appeared to be composed of two main fractions: one which exhibited clear macromolecular behaviour in solution, with macromolecules and/or very stable molecular aggregates present; and another fraction that was principally formed by molecular aggregates (supramolecular associations), which also included molecules of low molecular weight and an unclear macromolecular nature. Therefore, macromolecules, small molecules, and supramolecular associations all seem to coexist in humic systems. Angelico et al. [15] studied particle size, charge, and colloidal stability in humic acids coprecipitated with Ferrihydrite. Their results showed a bimodal size distribution for this system at acidic pH values, and a slow aggregation process that was observed at very low pH. Palmer and von Wandruszka [16] studied particle size development in aqueous humic materials at relatively low concentrations ($15\text{--}30 \text{ mg dm}^{-3}$). They detected the intramolecular contraction and intermolecular aggregation of humic substances. Jovanovic et al. [35] concluded that humic acids in sols behaved as molecular aggregates or supramolecular structures from small individual moieties (sizes $< 10 \text{ nm}$) at higher pH values. On the other hand, no particles smaller than 10 nm were observed by Esfahani et al. [33].

The Zeta potential showed a decrease with increasing humic concentration [33], a decrease with decreasing pH values [34], or a minimum in the 5–7 pH range [35].

In this work, particle tracking micro-rheology was used for the first time as a novel method in humic research. It is an emerging experimental technique which utilizes the Brownian motion of embedded particles to probe the local dynamics of studied materials. Macroscopic (bulk) rheology, which studies the deformation and flow of materials in the presence of stress at a particular time, has proven to be an important and useful tool with major practical significance for studying the rheological properties of colloids. However, bulk rheological measurements describe the overall mechanical response of a material on a macroscopic scale. They do not provide any information on local variations in the microstructure or their contribution to the overall mechanical response of a material [36]. Passive micro-rheology is based on the thermal motion of particles embedded in the investigated sample. The driving force is thermal, with a known energy scale corresponding to $k_{\text{B}}T$ (k_{B} is the Boltzmann constant and T is temperature). An advantage of this method is that no external driving force is required. Because the thermal driving force is small, no sample deformations that exceed equilibrium thermal fluctuations occur [37]. This technique uses video microscopy to track the position-

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