Characterization and Three-Dimensional Structural Modeling of Humic Acid Using Molecular Dynamics

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Abstract The humic acid (HA) that was obtained from an alluvial soil from the experimental station under conservation tillage in Luancheng County, Hebei Province, China, is the object of this study. HA was characterized by elemental composition and infrared and ^{13}C-nuclear magnetic resonance (NMR) spectroscopy. ChemBioOffice was used to construct the two-dimensional molecular structure of the HA monomers. By comparing the actual and simulated spectra, we determined that the two-dimensional structure of the HA molecular model had better suitability. This study also used HyperChem to simulate the three-dimensional molecular structure of the monomers, which was optimized by the molecular mechanics of the MM+, AMBER, and OPLS force fields. After optimization, the bond energy, bond-angle energy, dihedral-angle energy, van der Waals energy, electrostatic energy, and total potential energy were all found to have changed, which show no rules during the variation. At the same time, a molecular dynamics simulation was also used. Under the OPLS force field, the three-dimensional structure of the HA monomers had the smallest heat of formation ($-1{,}485.99$ kJ mol^{-1}), which indicates that it is the most stable of the three force fields. The molecular structure and total potential energy in the simulated environment changed after optimization, but all of the various energy states were generally stable.

Keywords Alluvial soil • Humic acid • Molecular simulation • Three-dimensional structure • OPLS force field

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Introduction

In recent years, with the development of computer science and modern quantum chemistry, molecular-modeling studies of polymer systems have become increasingly more common (Liu et al. 2004a). Humic acid (HA) is an organic compound with several special properties and a loose mixture that plays a very important role in the regulation of migration, transformation, and bioavailability within the environment (Li et al. 2004). HA consists of nitrogen-containing compounds, aromatic compounds, and a large number of oxygen atoms and active, amine-containing functional groups. Its molecular weight is 400–100,000 Da, but it does not have a defined molecular structure. Molecular simulation methods could solve the problem which the experiments have not been able to do. By using molecular simulations to determine the three- dimensional structure and explore the relationship between HA's structure and its properties, we were able to apply a reasonable theory to explain the experimental results (Liu et al. 2004b). In 2003, Diallo et al. (2003) used electrospray ionization quadrupole time-of-flight mass spectrometry to analyze the structure of HA and perform three-dimensional simulations in order to determine the three-dimensional structure of HA with the lowest energy. In 2007, Niederer et al. (2007) applied ^{13}C-NMR data to build a model of the HA monomers of weathered lignite that contained 31 carbon atoms. In 2008, Albers et al. (2008) proposed an average structural model for S1A HA of clay topsoil, and the size of the model's units is in agreement with the present understanding of the average molecular size of HA.

Materials and Methods

HA was obtained from the alluvial soil of the experimental station of conservational tillage in Luancheng County, Hebei Province, China (114°40′ E, 37°50′ N). The altitude of the station is 50.1 m, and it is located in the eastern monsoon region of China. Luancheng station has a semi-humid, warm, temperate climate. The annual average temperature is 12.2°C. The mean annual rainfall is 536.8 mm, and the frost-free period is about 200 days. Samples from the upper 0–20 cm of soil were collected, air-dried, and passed through a 2-mm sieve. HA was purified according to the standard IHSS method. The soil samples were pretreated with hydrogen chloride, extracted with sodium hydroxide, and freeze-dried. At last, each sample was grinded, desiccated, and stored. The amount of carbon, hydrogen, and nitrogen in HA were measured using a Vario EL III elemental analyzer (Elementar, Germany). The oxygen content was obtained by subtraction. The microinfrared testing method was performed using a Nicolet 750 microinfrared instrument with KBr beam. One hundred and twenty-eight scans were collected at a resolution of 8 cm^{-1}. The test range was 400–5,000 cm^{-1}, and the detector was MCT/A. The ^{13}C-NMR spectra were obtained using a BRUKER DSX 2300 instrument at a

Table 1 Elemental compositions and ratios of HA

	Elemental content (%)				Molar ratio		
Sample	C	H	N	O	H/C	O/C	C/N
Alluvial soil	51.91	5.29	5.66	37.14	1.22	0.54	10.70

frequency of 5 kHz. The molecular structures of the samples were determined from the results of the elemental analysis, infrared spectroscopy, and NMR spectroscopy. The structures of the monomers and simulation spectra were constructed using ChemBioOffice.

Results and Discussion

HA is mainly composed of carbon, hydrogen, nitrogen, oxygen, sulfur, phosphorous, and various other elements. The elemental composition is more fixed. The nitrogen content reflects the protein content of HA, while the oxygen content and O/C reflect the carbohydrate and carboxylic acid content of HA, respectively. The H/C reflects the fat characteristics of HA. The results in Table 1 show that HA has a small H/C, which indicates a high fat content in humic acid.

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