



Binding affinity of terrestrial and aquatic humics toward organic xenobiotics



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ABSTRACT

This paper presents study of binding affinity of seven aquatic and terrestrial molecular models of fulvics (**FA-i**, $i = \text{I-VII}$) and six models of humics (**HA-i**, $i = \text{I-VI}$); their polydeprotonated and polyprotonated forms towards the organic xenobiotics amitrole, anilazine, pyridine, toluene and, 4-chlorophenol, respectively. The humics–xenobiotics covalent interactions are discussed as well. Eighty one models of bonded molecular/ionic complexes are presented. The molecular scaffolds of humics and fulvics have significant ability to connect xenobiotics within the frame of many possible structural residues, which are also shown. We have chosen as quantitative parameters for elucidation of the binding affinity the natural bond orbital charges and electrostatic potentials. And nevertheless, that there are numerous studies of coordination ability of humics towards xenobiotics, it has not consensus about their molecular structures. The understanding of the coordination/bonding behaviour is rather obscure. Given that, our work presents for the first time comprehensive analysis of molecular level interactions of different models of organic matter accounting for those structural factors contributing to the thermodynamic stability of the molecular/ionic complexes. On this view we can conclude our research contributions emergence as an interdisciplinary study, blending of environmental analytical chemistry, geochemistry, agricultural chemistry, and the fourth.

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1. Introduction

Knowledge about the coordination ability of humics to organic xenobiotics is of significant importance, because their binding affinity governs environmental bioavailability of organic and inorganic xenobiotics [1]. The complexation with organic matter is major competitive processes determining adsorption/desorption behavior onto inorganic matter. Humics are major competitive ligands towards environmental migration of inorganic xenobiotics, including radionuclide and other toxic heavy metals as well [1i,j]. Furthermore, has been proposed that humics take part in process

of methyl-/ethylation of Hg^{II} , yielding to methyl-/ethyl-mercury; among most toxic substances [1k]. In this context, studies like this one are highly justified due to the following major reasons: (i) Soil organic matter, originating from plants and dead microorganisms contains humics; (ii) More than 50–90% of organic matter in surface and ground water with terrestrial origin represents humics; (iii) Humics are found even in deep underground, where nuclear wastes are disposed; and (iv) Mineral bonded organic matter represents significant part of organic carbon [1]. In spite of enormous effort concentrated to understand the behavior of xenobiotics in presence of humics upon environmental conditions, there is a lack of consensus about their molecular structures. This fact, causes for an obscure knowledge about molecular level coordination ability of those substances. A significant progress has been achieved employing mass spectrometry, determining humic substances. Those studies have shown that humics are spacial and temporal heterogeneous composition of self-assemblies of interacting relatively low molecular weight analytes with molecular masses $\in m/z$ 100–800 [1c,2]. This concept about the structure of humics as molecular mixture of low molecular weight analytes, rather than a polymeric macromolecular substance has justified series proposed models of molecular scaffolds of humics and

Abbreviations: B3PW91, hybrid functional (quantum chemical method); DFT, density functional theory (quantum chemical method); ESI, electrospray ionization (mass spectrometry); ESPs, electrostatic potentials; FAs, fulvic acids; HAs, humic acids; MP2, second-order Møller–Pleset perturbation theory (quantum chemical method); NBO, natural bond orbital (analysis); NEC, natural electron configuration; PCM, polarizable continuum model (quantum chemical method); SDD, Stuttgart–Dresden pseudopotential; T, temperature; TNB, Temple–Northeastern–Birmingham (model).

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fulvics. There is significant difference of molecular structure, which is associated with different environmental conditions governing the decayed process of animals, plants and microbes tissues. The two step degradation procedure for structural analysis of aquatic humics [2b] yields to derivatives containing aromatic dicarboxylic acidic residues and n -(C₂₃)-(n-C₃₂) fatty acids. The coordination centers, thereby, are numerous —COOH and OH— phenolic functional groups, amine N-atoms, and aniline —NH₂— ones, such as for example TNB model of humic acids **HA-IV** [2d,3]. The formation of five-membered chelate ring with two adjacent phenolic OH-groups is one of the leading possible processes of interaction of **HA-IV** and **HA-V** with actinide ions [1e,f,2b]. The suitable disposition of phenolic —OH and —COOH groups in benzene ring of **FA-VII** or **HA-I** molecular scaffold enables formation of six membered chelate structure as a stable geometry of metal-organic complexes with transition metal ions [3]. This coordination model would be, therefore, also leading to interaction of HAs and FAs with actinides in the environment. There are assigned a series HA, H₂A and H₃A models, on the base on fact that there is not experimental evidence to H₂A₂, H₂A₃ or HA₃ molecules. For this reason, our theoretical analysis involves study of coordination ability of corresponding mono-, di- and polyanions of FAs and HAs [3]. Particularly important for the behaviors of organic mater in the environment are redox processes, involving transition metal ions such as, for example, Cu^{II}-ion, yielding to complexes of Cu^I and Cu⁰ [4]. In the presence of Ag^I-ions, there is found that humics affect photo-reduction of the metal ion [5]. The mechanism includes a ligand-to-metal charge transfer and/or a formation of intermediate of super-oxide type. A production of H₂O₂ as a result of photochemical transformation of humics has also been reported [11]. A preliminary stabilization of super-oxide O₂⁻ occurs, which under acidic conditions yields to H₂O₂. But, it has not information about chemical transformation at molecular level of humics under the shown reactions. Nevertheless complexity of environmental processes, where humics take part, the understanding of their coordination ability and interaction behavior is of primary goal, investigating environmental processes. A major part of experiments carried out of development of ligand exchange separation and concentration approaches for analysis of heavy metals and, particularly radionuclides, using similarly functionalized polymer materials and/or examination of stability constants of the processes has involved simple equilibrium models or independent de-/protonation or coordination sites, interacting with metal ions and/or protons. They cannot take into account for, however, (a) A possible formation of covalent bonds, which has been evidenced experimentally, as a possible process of interaction between HAs/FAs and organic xenobiotics; (b) Change of the molecular conformation of naturally occurring ligands within the frame of wide dynamic range experimental conditions, involving, pH, photochemical reactions, temperature depending on photochemical and/or microbiological degradation and/or induced chemical transformations by other environmental factors. The point (b) has involved different conformations of neutral organic matter components (i.e. their fully protonated forms) and their mono- and polyanionic forms (i.e. corresponding deprotonated polyanions), too. It has included as well as possible charge redistribution as a result of deprotonation process; stabilization of different tautomers such as, for example, those typical for **FA-I-C** (Appendix). A possible stabilization of —COO⁻···H—O(CO)— bonds between structurally disposed functional groups, is often proposed in HAs and FAs. An example is anionic forms of **FA-III**. Such as intramolecular hydrogen network, however, prevents the application of simple model of protonation/deprotonation processes, because of the protonation is associated with an intramolecular proton transfer; and/or (c) Ligand exchange within the frame of real complex system of mineral-bonded organic matter

(see point (iv) above), which molecular level mechanistic engineering, can be changed, during complexation with inorganic radionuclide forms and/or organic xenobiotics [3,4]. Such as processes, however, lead to different molecular level coordination modes, effecting the thermodynamics of systems, involving both enthalpy and entropy of the systems. Furthermore, if we have performed a parallel between polyprotonation (or coordination) ability of humics, calling attention on carboxylate-COO⁻ molecular sites with protonation of titrable sites in proteins, than each protonation stages can be described as an independent chemical reaction [5]. The process of organic xenobiotic/humic substances interaction may involve photochemical degradation of both organic matter and pollutants, too, because of, as it was written above the ability of humics to act as photosensitizers has resulted to possible formation of O₂⁻, O₂^{-•}, •OH and/or CO₃^{-•}, respectively. Those ions/radicals have great reactivity either organic xenobiotic and humic components [5b]. Our paper makes attempt to provide answers to these questions, comparing quantitatively the coordination behavior of **HAs** and **FAs** with organic xenobiotics. The minimum of the free Gibbs energy (ΔG in this paper) of a molecular system is a macroscopic quantity determining the most stable conformation, depending on molecular structural and environmental factors, so that comparing free Gibbs energies of sets possible models of interacting ensembles, in our case humics/xenobiotics we can deduce at a high level of probability, which ones can be observed under real environmental conditions [3b]. We have treated, for first time, molecular level structure and binding properties of a set of **HAs** and **FAs** models, evaluating those structural factors causing for selective coordination to different type of organic xenobiotics. We have chosen series low molecular weight xenobiotics [6], on the base on our past and ongoing experience on adsorption/desorption of organic pollutants in aquatic and terrestrial systems, which has shown that these substances can interact with components of organic matter via non-covalent π -interactions (**Mode VI**) and/or forming covalently bonded systems (**Modes IV, V, X–XII, XVII and XVIII**), which we have evidenced by solid-state cross polarization magic angle spinning ¹⁵N NMR spectroscopy [6b,c]. In addition amitrole can participate in classical hydrogen bonding interactions of type —NH₂···OCO or —NH₂···NH₂— with the organic matter components [6c]. Those interactions have been also involved in our model study.

Before we go onto consider theoretical analysis in this paper [8–10], we should point out that, this is the first study providing comprehensive information about the protonation/deprotonation ability as well as covalent- and non-covalent interactions of humics with xenobiotics. Because of there are known scarce reports devoted to application of computational quantum chemical approaches in this topic. The known effort is limited to semi-empirical and/or MM/MD simulations of TNB (**HA-IV-A**), Leenhoeer's (**HA-II-A**) and Stevenson's (**HA-VI-A**) models (Figs. A5–A9; Schemes A.1–A.18) providing an information about molecular geometry in solution [11]. Or those simulations are associated with surface interaction phenomena to inorganic metal ions, reduced, however, to ligand centers mainly in inner coordination sphere or very simple organic models representative to known proposed molecular scaffolds [11]. It should be mentioned here that analysis carried out (below) shows that different models of humics have unique protonation/deprotonation ability and coordination fashion towards metal ions. Given that, we can argue that the powerful ability of quantum chemistry to provide meaningful information about molecular structure and reactivity, including the coordination ability of so important objects to many interdisciplinary fields like the humics, cannot be consider as widely employed. The studies have rather sporadic character. We highlight in this paper,

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