Exploration of the molecular interaction of a humic acid model with the water by means of Molecular Dynamics Simulations

Jesús Roa[1,*], José G. Parra[1], Arnaldo Armado[2]

[1]Universidad de Carabobo, Facultad Experimental de Ciencias y Tecnología, Dpto. De Química, Lab. De Química Computacional, Bárbula-Venezuela.
[2]Universidad de Carabobo, Facultad Experimental de Ciencias y Tecnología, Dpto. De Química, Lab. De Investigaciones Bioquímicas, Suelos y Ambiente (LIBSA), Bárbula-Venezuela.
jesussroa@gmail.com,jgparra2@uc.edu.ve,armadoa@uc.edu.ve

Abstract

In this work, the molecular interaction of molecular structures generated from a humic acid model called TNB with water was explored with MD simulations to explore the affinity and behavior of these species in the aqueous medium. TNB model was described with the all-atom GROMOS53A6 force field. The bonding and non-bonding parameters were obtained of the GROMACS-2019.2 software package. The evaluation was realized for the functional groups $-NH_2$ and -COOH present in this molecular model. The spatial conformations of TNB molecule change considerably when evaluating the effect of pH on intermolecular interactions in aqueous solution. Molecular dynamics calculations showed that the acid sites of the TNB humic acid model to assess molecular interaction have low affinity for water. Results are consistent with the experimental behavior of humic acids in an aqueous solution.

Introduction

Humic acids are one of the main components of humic substances, which are the main constituents of humus, which forms the organic matter of the soil (see Figure 1). Due to its acid-base behavior, humic acids are extracted with highly alkaline solutions to $pH > 10$; in solutions between $pH > 3$ and $pH < 5$ they remain dissolved in solution, and precipitate in acid solutions to $pH < 3$. Studies with molecular dynamics simulations using structural models of humic acids, have allowed to have an idea of the molecular interaction and acid-base behavior of these compounds.
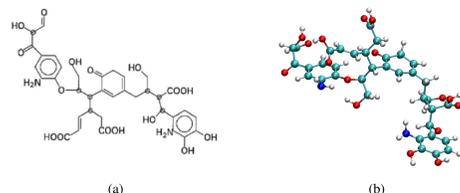
Figure 1: (a) Molecular structure of TNB model. (b) A representation of the initial configuration of TNB model.

At the molecular level, Molecular Dynamics (MD) simulations have been used to determine the molecular interaction between humic acid models and the aqueous medium in order to establish the affinity of these species with the aqueous medium. This preliminary study has been realized with classic force fields. In this sense, we have explored the molecular interaction of a humic acid model called TNB with the water in an aqueous solution by means of MD simulations using the NVT ensemble and GROMOS53A6 and SPC force fields to understand the behavior of this molecule in the aqueous medium. For this, An conformational analysis of the TNB model n water and the Radial Distribution Function between functional groups present in the TNB model with the water were evaluated from MD simulations.

Simulations details

A total of 3 systems were prepared to different structures of TNB model in aqueous solution (see Figure 1b). Systems were prepared with a molecule of TNB model inside a simulation box with water (see Figure 2b). The dimensions of the simulation cells were $60 \times 60 \times 60 \text{Å}^3$, respectively. Periodic boundary conditions were employed in xyz dimensions.
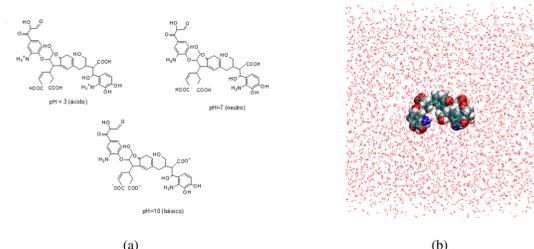
Figure 2: (a) Different molecular structures of TNB model as a function of the pH. (b) A representation of the initial configuration of TNB model in water.

TNB model was described with the all-atom GROMOS53A6 force field. The bonding and non-bonding parameters were obtained of the GROMACS-2019.2 software package. The atomic charges were determined using the GAMESS-US software package at the B3LYP/6-31G+(d) level and the CHELPG method. Charge groups were modified considering the functional groups present in the molecule. Water molecules were described with the SPC force field. In all systems, the steepest descent method was used to remove strain between molecules. MD simulations at 300 K in the NVT ensemble were carried out to equilibrate the systems. The equilibration of these systems were realized during 20 ns. Here, MD simulations were performed by 20 ns with a time step of 1 fs.
Temperature was controlled with the v-rescale thermostat method, respectively. The vdW interactions were determined with a cutoff distance between 1.25 nm and 1.30 nm. Particle Mesh Ewald method (PME) was used for the long-range electrostatic interactions. Trajectories were stored each 5.0 ps during the process of simulation.

Results and Discussion

From MD simulations in the NVT ensemble, we have found a folding of the TNB model in all systems. The intermolecular interactions between humic acid and water were carried out using the radial distribution function (RDF) and the root mean square deviation (RMSD), with which the affinity of the TNB molecule with water was evaluated at the different pH values. Also, molecular interaction between the functional groups of TNB with water were explored with the GROMACS software.
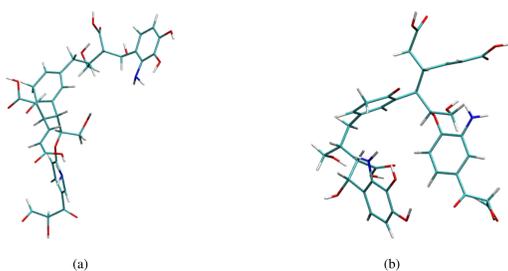
Figure 3: Stable conformations of TNB model obtained in water using molecular dynamics simulations. (a) Extended TNB molecule and (b) Folded TNB molecule.
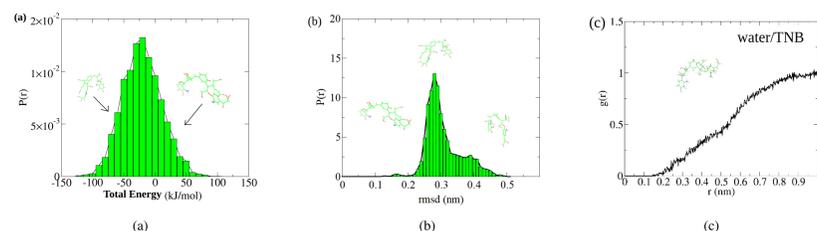
Figure 4: Gaussian distribution curves for the total energy of TNB model extracted from the water box and the TNB/water system. (a) Total energy of TNB extracted from the water box. (b) Total energy of system with water (c) RDF of the molecular interaction between TNB model and water molecules

The spatial conformations that appear in greater proportion in the system correspond to the extended conformation, which has the highest probability distribution, and its total energy ranges between -50 kJ/mol and 0 kJ/mol according to the potential energy model used in this study (see Figure 4(a)). Similarly, it is observed that the folded conformation presents the lowest potential energy (around -100 kJ/mol), which indicates that this conformation corresponds to the most stable in the aqueous medium. The folded structure of the TNB model has a larger probability distribution (see Figure 4(b). It is possible that the hydrophobic groups avoid being in contact with water and are protected from water using a conformation where the polar functional groups interact with the solvent medium. According to the RDF of the TNB molecule with water shown in Figure 4(c), this TNB model is not soluble in water.
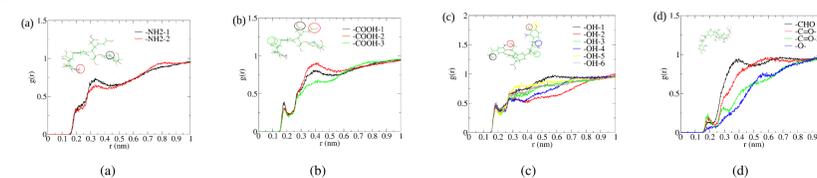
Figure 5: RDF of functional groups for intermolecular interactions in water of the TNB model. (a) amino groups, (b) carboxyl groups, (c) hydroxyl groups, and (d) aldehyde, ketone, and ether groups.

In Figure 5(a), the amino group ($-NH_2$) has no affinity for water at short distances with an undefined interaction peaks at a distance of 0.4 nm. In Figure 5(b), the $-COOH$ functional groups they contain show a first solvation layer, which present low intensity peaks located around 0.2 nm. This indicates a low intermolecular interaction with the water. Similarly, the hydroxyl groups ($-OH$) show a very slight solvation around a distance of 0.2 nm producing a low intensity peak (see Figure 5(c)).
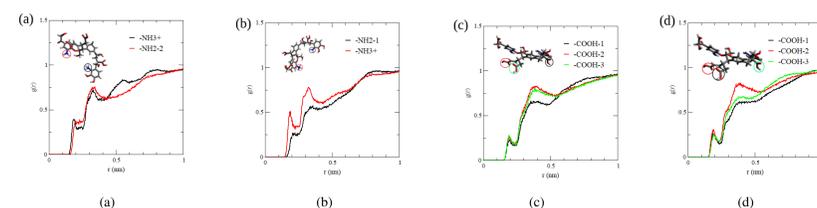
Figure 6: RDF of the $-NH_2$ and $-COOH$ functional groups of TNB model for intermolecular interactions in water at acidic pH. (a) $-NH_3^+$ bonded with the two hydroxi groups, (b) $-NH_3^+$ linked to the ether group, (c) $-COOH$ functional groups with $-NH_3^+$ bonded with two hydroxy groups, and (d) $-COOH$ functional groups with $-NH_3^+$ linked to ether group.

In Figure 6(a) and 6(b), RDFs of the $-NH_3^+$ groups shows peaks with a certain intensity that indicate more affinity with water. The $-NH_3^+$ group linked to the ether group has a higher interaction with water. In the $-COOH$ groups, water molecules form two solvation shells located at a distance of 0.18 nm and 0.23 nm. The intensity of these interaction peaks for the $-COOH$ group are higher when the second $-NH_2$ group is solvated (see Figures 6(c) and 6(d)).
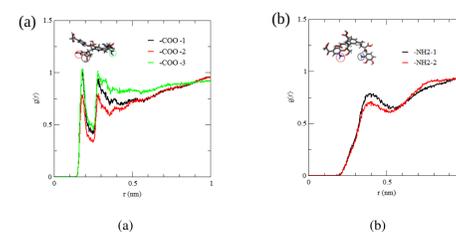
Figure 7: RDF of the $-COO^-$ and $-NH_2$ functional groups of TNB model for intermolecular interactions in water at $pH > 10$. (a) $-COO^-$ groups and (b) $-NH_2$ groups.

In Figure 7(a), RDFs of $-COO^-$ groups indicates that these groups have a strong interaction by the solvent medium producing two solvation layers located at 0.18 nm and 0.25 nm. In Figure 7(b), RDFs of $-NH_2$ groups presents a very weak interaction with water, observing a single solvation layer around of these groups.

Conclusions

In this work, according to the results obtained, they are in accordance with the study of the experimental field that the authors propose. For example, in the part of the study of the functional groups of the structural model of humic acid TNB, it reflects that the molecule is not soluble in water and experimentally, humic acids are insoluble in aqueous medium. However, it would be necessary to experiment with other structural models of humic acids using aqueous solutions in the presence of ions to know for sure what is happening.

References

1. Orsi, M. (2014). Molecular dynamics simulation of humic substances. Chemical and Biological Technologies in Agriculture, 1(1), 1-14.
2. D. van der Spoel, E. Lindahl, B. Hess, G. Groenhof, A. E. Mark, H.J.C. Berendsen, Gromacs: fast, flexible and free, J. Comp. Chem. 26 (2005) 1701-1719.
3. Ai, Y., Zhao, C., Sun, L., Wang, X., and Liang, L. (2020). Coagulation mechanisms of humic acid in metal ions solution under different pH conditions: A molecular dynamics simulation. Science of the Total Environment, 702, 135072.

Acknowledgements