

ABSTRACT

This research focused on the study of the ethanol-water azeotropic mixture, in order to provide information that can be used in new low-cost separation techniques. The study was carried out through the computational analysis of intermolecular interactions responsible for the stability of (ethanol)₈-water heterononamers. The starting structures were optimized with the method B3LYP/6-31+G(d); obtaining 9 stable heterononamers. After reoptimizing these structures using a larger base, the number of stable structures was reduced to 7. From the most stable and abundant heteronamer, homologous structures of (ethanol)₉, (methanol)₈-water and (methanol)₉ were designed and optimized. The measurements taken include geometrical, energetic and topological data. It was found that the cycles formed by the O-H...O interactions are fundamental for the stability of the heteronamer regardless of its nature.

OBJECTIVE

Analyzing structurally and energetically (ethanol)₈-water heterononamers and compare the results with their homologous systems: (ethanol)₉, (methanol)₈-water and (methanol)₉ using DFT calculations.

METHODOLOGY

The optimizations were made in the *Gaussian09* program as well as the construction and visualization of the structures using its *Gaussview05* visualizer. The potential energy surface was explored using the ab-initio molecular dynamics method (ADMP) and a stochastic method (Simulated Annealing) to find starting structures that were optimized with the theoretical approximation B3LYP/6-31+G(d). With subsequent reoptimization with B3LYP-D3/6-311++G(d,p). The weakest interactions (C-H...O and H...H) were revealed using the molecular graphs calculated through the topological analysis of the electronic density: AIMALL Professional according to the Quantum Theory of Atoms in Molecules.

RESULTS

Optimized geometries and geometric parameters

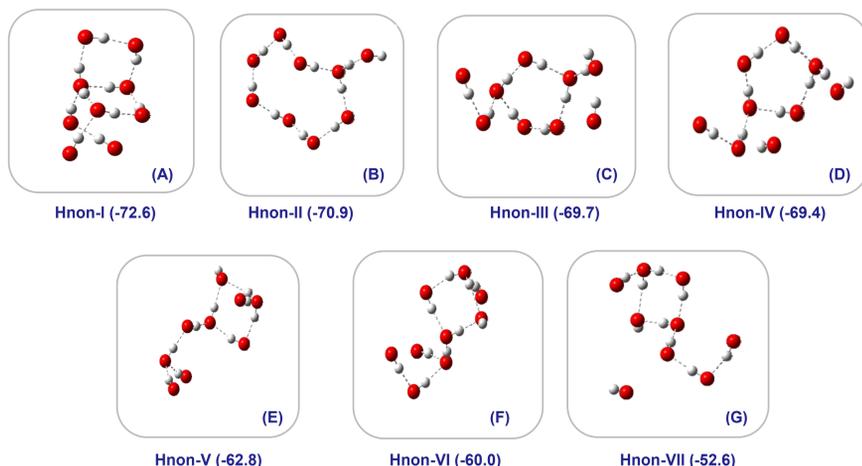


Figure 1. (Ethanol)₈-water heterononamers. Spatial arrangement among OH groups. ΔE in kcal/mol.

Comparison among dihedral angles and distances among bases.

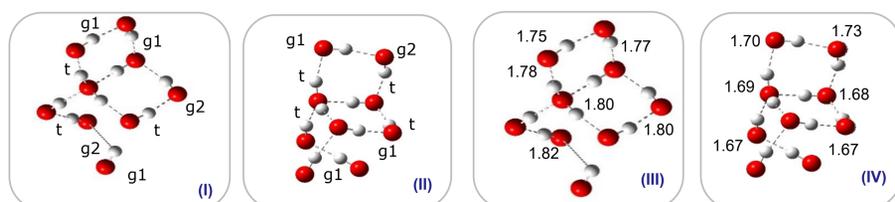


Figure 2. Dihedral angles: g_1 (60°), g_2 (-60°) and $trans$ (180°) in the Hnon-I and H...O distances of hydrogen bonds in Å. I and III: B3LYP/6-31+G(d); II and IV: B3LYP-D3/6-311++G(d,p).

RESULTS (continued)

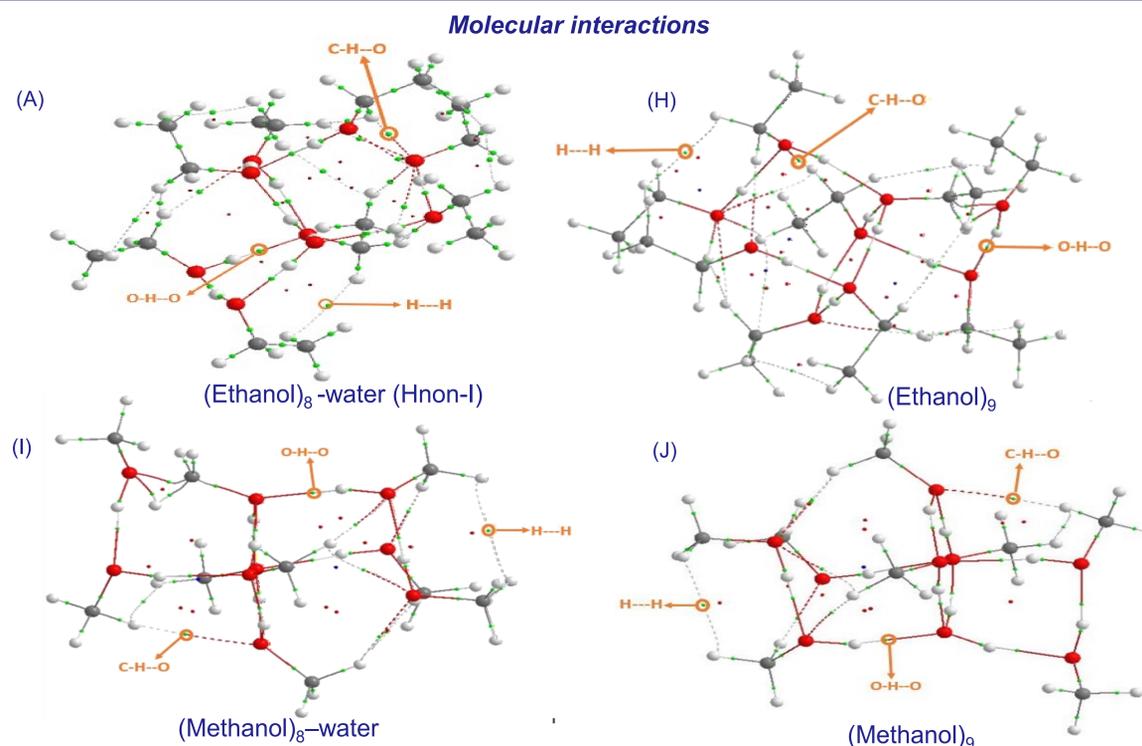


Figure 3. Molecular graphs of Hnon-I and its homologous structures.

Energetic parameters

Table 1. Thermodynamic parameters in kcal/mol (ΔS in cal/(mol*K))

Structure	ΔE	ΔH	ΔG	ΔS
A	-72.6	-81.1	1.0	-275.3
B	-70.9	-79.3	1.8	-271.9
C	-69.7	-77.4	3.2	-270.4
D	-69.4	-77.3	3.9	-272.4
E	-62.8	-70.3	11.8	-275.2
F	-60.0	-69.5	13.5	-278.1
G	-52.6	-69.9	11.3	-272.5

Structure	ΔE	ΔH	ΔG	ΔS
H	-70.3	-76.6	2.6	-267.4
I	-64.6	-80.0	6.2	-245.3
J	-63.2	-77.6	1.7	-292.2

CONCLUSIONS

- The most stable heteronamer has an isomeric population of 98% and is characterized because it contains the highest number of hydrogen bonds as well as a greater number of *trans* ethanol. It is also the only structure where water acts as a double acceptor of proton, which makes its donor character doubly favored and vice versa.
- The inclusion of correction by dispersion and a larger base affected the strengthening among the distances of the hydrogen bonds, since they decreased; maintaining the geometric arrangements of the OH groups.
- The dihedral angles vary according to the size of the base, which directly affects the energy among interactions of the clusters.

REFERENCES

- DiLabio, G et al., (2013). Extension of the B3LYP-dispersion correcting potential approach to the accurate treatment of both inter- and intra-molecular interactions. *Theoretical Chemistry Accounts* 132:1-44.
- Franzin, A et al., (2018). Revisiting simulated annealing: A component-based analysis. *Computers & Operations Research* 104:191-206.
- Kumar, P et al., (2016). Bader's Theory of Atoms in Molecules (AIM) and its Applications to Chemical Bonding. *Journal of Chemical Sciences* 128:1527-1536.

ACKNOWLEDGMENTS

Karen and Marly thank to "Universidad Jorge Tadeo Lozano" and "Pontificia Universidad Javeriana" for making the inter-institutional agreement. The authors thank to Bank of Republic's foundation to the promotion of research and also for financing the Project No. 4.217.