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Geometric, Energetic and Topological Analysis of (Ethanol)$_9$-Water Heterodecamers

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Abstract : The purification of bio-ethanol through distillation methods is an unresolved issue at the biofuel industry because of the ethanol-water azeotrope formation, which increases the steps of the purification process and subsequently increases the production costs. Therefore, understanding the mixture nature at the molecular level could provide new insights for improving the current methods and/or designing new and more efficient purification methods. For that reason, the present study focuses on the evaluation and analysis of (ethanol)$_9$-water heterodecamers, as the systems with the minimum molecular proportion that represents the azeotropic concentration (96 %m/m in ethanol). The computational modelling was carried out with B3LYP-D3/6-311++G(d,p) in Gaussian 09. Initial explorations of the potential energy surface were done through two methods: annealing simulated runs and molecular dynamics trajectories besides intuitive structures obtained from smaller (ethanol)n-water heteroclusters, n = 7, 8 and 9. The energetic order of the seven stable heterodecamers determines the most stable heterodecamer (Hdec-1) as a structure forming a bicyclic geometry with the O-H---O hydrogen bonds (HBs) where the water is a double proton donor molecule. Hdec-1 combines 1 water molecule and the same quantity of every ethanol conformer; this is, 3 trans, 3 gauche 1 and 3 gauche 2; its abundance is 89%, its decamerization energy is -80.4 kcal/mol, i.e. 13 kcal/mol most stable than the less stable heterodecamer. Besides, a way to understand why methanol does not form an azeotropic mixture with water, analogous systems ((ethanol)10, (methanol)10, and (methanol)9-water)) were optimized. Topologic analysis of the electron density reveals that Hec-1 forms 33 weak interactions in total: 11 O-H---O, 8 C-H---O, 2 C-H---C hydrogen bonds and 12 H---H interactions. The strength and abundance of the most unconventional interactions (H---H, C-H---O and C-H---O) seem to explain the preference of the ethanol for forming heteroclusters instead of clusters. Besides, O-H---O HBs present a significant covalent character according to topologic parameters as the Laplacian of electron density and the relationship between potential and kinetic energy densities evaluated at the bond critical points; obtaining negatives values and values between 1 and 2, for those two topological parameters, respectively.

Keywords : ADMP, DFT, ethanol-water azeotrope, Grimme dispersion correction, simulated annealing, weak interactions
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