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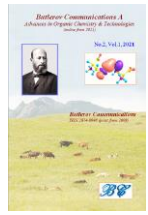

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Modeling the sorption of low-molecular compounds on the surface of copper phthalocyanine by the method of density functional theory

Andrey A. Degtyarev,*[+] **Irina V. Zarapina**, and **Alena V. Zdereva**
Department of Chemistry and Chemical Technologies. Tambov State Technical University. Soviet St., 106. Tambov, 392000. Russia. Phone: +7 (4752) 63-44-44. E-mail: ad.dycost@gmail.com; zarapina@mail.ru; azderevaa@gmail.com

*Supervising author; [+]Corresponding author

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Abstract

The work is devoted to the study of the processes of sorption of water and ethanol molecules on the surface of copper phthalocyanine from the gas and water phases.

The density functional theory (PBE, PBE0, B3LYP, LC-BLYP, ωB97x) with the L1, 6-31G**, cc-pVDZ basis sets and D3BJ, D2 corrections for dispersion interaction was used as a calculation method. The non-specific interaction with the solvent was taken into account according to the COSMO continuum model; the contribution of the specific interaction was estimated based on comparison with experimental data. The surface of copper phthalocyanine was modeled by a four-molecular cluster with crystallographic surfaces (100) and (130).

It was determined that water molecules form three types of complexes with the surface of copper phthalocyanine: with two hydrogen bonds through the nitrogen atoms of the surface (100) (-42.61 kJ/mol), one hydrogen bond through the nitrogen atom of the surface (100) (-30.71 kJ/mol) and through the copper atom on the surface (130) (-23 kJ/mol). Nonspecific interaction with a solvent reduces the energy of formation of complexes through a hydrogen bond by 20÷25 kJ/mol, and complexes through a copper atom by 10 kJ/mol. Ethanol molecules form three types of complexes with the surface of copper phthalocyanine: with a hydrogen bond through the surface nitrogen atoms (100) (-34.5÷-38 kJ/mol), a four-center hydrogen bond with the participation of nitrogen and copper atoms on the surface (130) (-30.12 kJ/mol) and through the copper atom on the surface (130) (-38.78 kJ/mol). Nonspecific interaction with the solvent decreases the energy of formation by 9-12 kJ/mol for complexes with the (100) surface, by 3 and 8.5 kJ/mol for complexes with the (130) surface. Taking into account the specific solvation leads to positive heats of ethanol sorption from an aqueous solution onto the surface of copper phthalocyanine (3.09-10.26 kJ/mol), which corresponds to the equilibrium constants of ethanol between the liquid phase and the surface of 0.016-0.287, and indicates the possibility of using ethanol as an additive hydrophilizing the surface.

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