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Study of the trialkylamines adsorption on the surface of copper phthalocyanine using density functional theory methods

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Abstract: The potential use of straight-chain trialkylamines to modify the oleophilic-hydrophilic properties of the surface of copper phthalocyanine was explored. Molecular modeling methods utilizing density functional theory were employed to investigate the characteristics of the adsorption process of trialkylamines with alkyl chain lengths of $n = 1 \div 8$. The change in Gibbs free energy for the adsorption of the studied surfactants from the aqueous phase onto the surfaces (001), $(20\bar{1})$ containing the metal atom was calculated. It was determined that adsorption of trialkylamines from the aqueous phase does not occur on the non-polar surfaces (001) and $(20\bar{1})$, with ΔG values ranging from 18 to 41 kJ·mol^{-1}. For adsorption onto surfaces containing a metal atom, negative Gibbs free energy values are observed for tripentylamine and longer-chain trialkylamines (assuming complete loss of rotational and translational degrees of freedom) or for all except triethylamine (with partial retention of rotational degrees of freedom). However, for trialkylamines such as trihexylamine and longer, steric hindrances will be observed during adsorption onto surfaces with a metal atom. For all the examined trialkylamines, lower Gibbs free energy values for adsorption on surfaces with a metal atom were noted compared to non-polar surfaces, indicating selective adsorption of these surfactants on the surface of copper phthalocyanine. The study results indicate that tripentylamine exhibits the best characteristics for the oleophilization of the surface of copper phthalocyanine.

Keywords: copper phthalocyanine; surface oleophilization; surfactants; density functional theory; crystallographic surface; trialkylamines; adsorption; Gibbs free energy.

Исследование адсорбции триалкиламинов на поверхности фталоцианина меди методами теории функционала плотности

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Аннотация: Рассмотрены возможности применения триалкиламинов неразветвленного строения для изменения олеофильно-гидрофильных свойств поверхности фталоцианина меди. Методами молекулярного моделирования с использованием теории функционала плотности исследованы характеристики процесса адсорбции триалкиламинов с длиной алкильной цепи $n = 1…8$. Рассчитано изменение свободной энергии Гиббса для адсорбции исследуемых поверхностно-активных веществ из водной фазы на поверхностях (001), $(20\bar{1})$ и содержащей атом металла.

Определено, что на неполярные поверхности (001) и $(20\bar{1})$ адсорбция триалкиламинов из водной фазы не происходит ($\Delta G = 18…41$ кДж/моль). Для адсорбции на поверхность, содержащую атом металла, отрицательные значения энергии Гиббса наблюдаются для трипентиламина и выше (при условии полной потери вращательных и поступательных степеней свободы) или для всех, кроме триэтиламина (при частичном сохранении вращательных

степеней свободы). Однако для тригексиламина и выше при адсорбции на поверхность с атомом металла будут наблюдаться стерические затруднения. Для всех рассмотренных триалкиламинов наблюдаются более низкие значение энергии Гиббса для адсорбции на поверхность с атомом металла, чем на неполярные поверхности, что говорит об избирательной адсорбции данных поверхностно-активных веществ на поверхность фталоцианина меди. По результатам исследования выявлено, что наилучшими характеристиками для олеофилизации поверхности фталоцианина меди обладает трипентиламин.

Ключевые слова: фталоцианин меди; олеофилизация поверхности; поверхностно-активные вещества; теория функционала плотности; кристаллографическая поверхность; триалкиламины; адсорбция; энергия Гиббса.

1. Introduction

For organic pigments, one of the most important characteristics is the hydrophilic-oleophilic properties of the particle surfaces. These properties affect parameters such as the size and strength of agglomerates and aggregates, as well as the dispersibility and stability of pigment particles in the binder.

The surface properties can be modified using additive agents, with various surfactants being the most common. These surfactants adsorb onto the surface and alter its characteristics [1]. A frequent goal is to enhance the oleophilicity of the pigment surface to achieve dispersion in alkyd binders. This enhancement is useful for both stabilizing dispersions and for energy-efficient methods of producing pigmented alkyd materials, such as in the flushing process. The flushing process not only helps avoid one of the most costly stages of pigment production—drying—but also allows for the production of higher-quality pigmented materials. This is because undesirable processes like recrystallization, crystal growth, crystal agglomeration, and surface amorphization (the Bailby effect) do not occur during this process [2]. For the flushing process, the optimal surfactant concentration is considered to be one that forms a chemisorbed monolayer on the pigment surface [2]. It is also important for the surfactant adsorption to occur in the aqueous phase, as this significantly facilitates the transfer of crystals from the aqueous phase to the oil phase.

To impart oleophilic properties to a highly hydrophilic surface, such as those of inorganic pigments and fillers (titanium white, lead chromate, etc.), cationic surfactants are typically used, as they possess basic properties while the surface is acidic. For copper phthalocyanine (the Pigment Blue 15, CuPc), the surfactants that enhance the oleophilic properties of the surface are trialkylamines, which can chemisorb on surfaces containing copper atoms. However, the proposed mechanism of their interaction with the surface is not acid-base but rather involves the overlap of the *d*-orbitals of the copper atom and the nitrogen atom [3, 4].

Copper phthalocyanine molecules are well known to adsorb onto various metals [5–7], metal oxides [8], silicon oxide [9], as well as graphite surfaces [10]. However, the adsorption of any substances on copper phthalocyanine itself has been studied relatively little. It is known that it can absorb ammonia [8] and alcohols [9] from the gas phase, but the mechanisms of these processes have not been thoroughly investigated.

This study investigates the geometric and thermodynamic characteristics of the adsorption process of trialkylamines with straight-chain alkyl groups on various surfaces of copper phthalocyanine. The goal is to determine the adsorption mechanisms and the potential use of these substances as oleophilizers in an aqueous environment, which could facilitate the transfer of pigment particles from the aqueous phase to the alkyd phase during the flushing process.

2. Materials and Methods

To determine the mechanism and characteristics of the adsorption process, molecular modeling methods were employed. Among the two possible approaches, periodic slab and cluster methods, the latter was chosen due to its greater flexibility in terms of calculation methods and software.

Unbranched trialkylamines with the same number of atoms in each alkyl group and a general formula of $(CH_3–(CH_2)_n–)_3N$ were used as model surfactants, where *n* varies from 0 (trimethylamine) to 7 (trioctylamine).

There are many crystalline modifications of copper phthalocyanine (α, β, γ, ϵ, η) [11–14]; however, we focus on the β modification, as it has the most practical applications as a pigment. This form has a monoclinic crystal lattice (space group P1c1) with parameters: $a = 19.407$ Å, $b = 4.79$ Å, $c = 14.628$ Å, $\beta = 120.93°$ [11]. A schematic representation of the crystallographic planes for this modification is shown in Fig. 1.
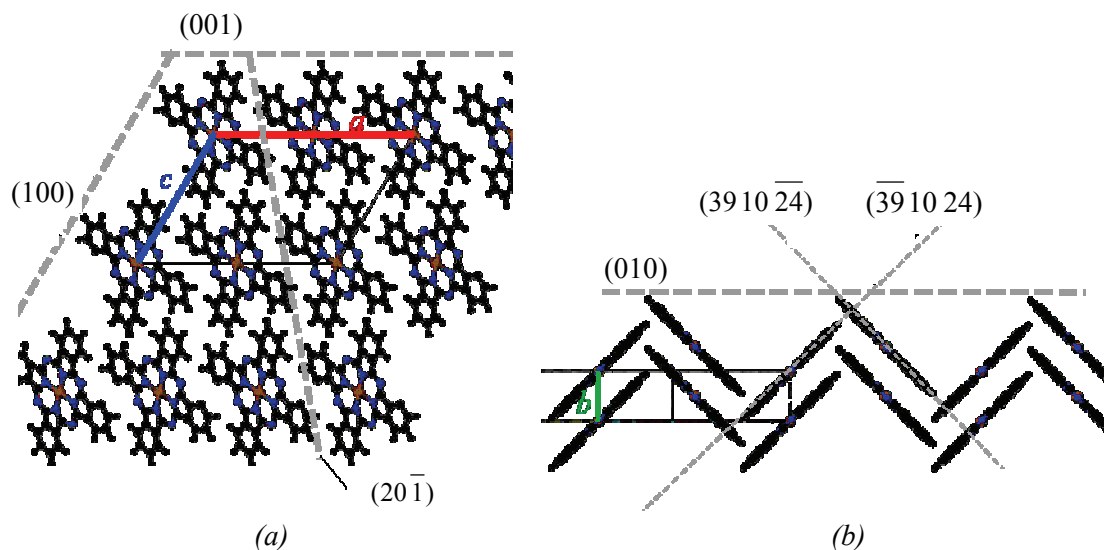
Fig. 1. Direction of crystallographic planes in the β-copper phthalocyanine

The packing of molecules in the crystal of the β modification occurs in vertical "stacks," which are arranged in a "zigzag" pattern with respect to each other (Fig. 1*b*). In this structure, three types of surfaces are most likely along the "stacks" (Fig. 1*a*). However, studies using powder X-ray diffraction show a nearly complete absence of the (100) surface in the β modification crystal [14].

The vectors [*hkl*] perpendicular to the molecular plane are given as [–3.91, 1, 2.38] and [3.91, 1, –2.38] (calculated by approximating the coordinates of the atoms in a system corresponding to the crystallographic axes). The nearest integer indices for surfaces parallel to the molecules will thus be $(\overline{39}\,10\,24)$ and $(39\,10\,\overline{24})$ (Fig. 1*b*). Surfaces with such large index values are unlikely to be encountered in a real crystal; however, it can be assumed that the copper atoms are situated on the pseudo-(010) surface, which is not a pure crystallographic plane but, at the nanoscale, consists of alternating planes (Fig. 1*b*), similar to how the (110) surface of γ-alumina actually represents alternating (111) planes [15].

Thus, it is necessary to consider the adsorption of trialkylamines on the surfaces (001), $(20\overline{1})$, and parallel to the molecular plane. To do this, we will use the clusters presented in Fig. 2.

For modeling sorption on the molecular plane and surface $(20\overline{1})$, a single "stack" is sufficient (Fig. 2*a* and Fig. 2*b*). When interacting with surface (001), the sorbate molecules (except for the smallest ones) will inevitably interact with the neighboring "stack" (Fig. 2*c*), which is why a larger cluster was selected.
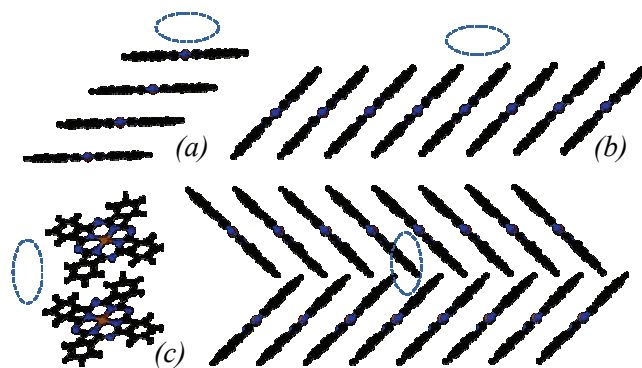

Fig. 2. Scheme of clusters for modeling sorption: *a* – per metal atom (4 molecules CuPc), *b* – per surface $(20\overline{1})$ (8 molecules CuPc), *c* – per surface (001) (16 molecules CuPc), the expected position of the sorbate molecule is shown

The method used to determine the geometric and thermodynamic characteristics of the sorption process was density functional theory (DFT), which has proven to be effective in studying sorption processes [16–19]. This approach has a relatively low computational cost, allowing for the modeling of molecular complexes that include several hundred atoms.

The optimization of the geometry of the sorbate-sorbent complexes was performed at the following levels of theory:

− XTB2 [20] – a fast method that provides a good estimate of the non-covalent dispersion interactions between the sorbate and the sorbent;

− r²SCAN-3c [21] – a composite method that includes a meta-GGA functional, a triple-ζ basis set, and two types of corrections: for dispersion interaction and for basis set superposition error (BSSE).

As a control, for some structures, single-point energy calculations were carried out at a higher level of theory: ωB97x-D4/def2-SVPD – a spatially separated hybrid functional ωB97x [22] with the Grimme D4 dispersion correction [23, 24] and a double-ζ basis set from the Karlsruhe family, including diffuse functions [25, 26]. Since this method does not include built-in corrections for BSSE, they were calculated manually following the methodology [27].

Since the modification of particle surfaces in an aqueous suspension is assumed, continuous models were used to simulate the effect of the solvent: ALPB [28] for XTB, SMD [29] for r²SCAN-3c, and ωB97x-D4/def2-SVP.

Despite the use of relatively inexpensive modeling methods, the calculation of eight- and sixteen-molecule clusters is quite labor-intensive. To reduce computational costs, a hybrid method called ONIOM [30] was applied, which allows different parts of the molecular system to be modeled at different levels. In our case, a two-layer model was used, where the first (high-level) layer consisted of the sorbent molecule and the two closest sorbate molecules.

All calculations were performed using the ORCA 5.0 software package [31].

The following designations will be used for the methods:

– QMMM1: r²SCAN-3c – first layer, XTB2 – second layer;

– QMMM2: ωB97x-D4/def2-SVPD – first layer, XTB2 – second layer.

When calculating thermodynamic parameters, we assume that no new chemical bonds are formed during sorption, and therefore the vibrational-rotational energy levels change only slightly, allowing us to accept the change in enthalpy as equal to the difference in electronic energy. The change in the entropic component will occur due to the loss of translational and rotational degrees of freedom for the sorbate molecule. The translational degrees of freedom are completely lost, but there is still some probability of rotation of the sorbate molecule when interacting with the cluster in Fig. 2, as the surface on which sorption occurs is devoid of irregularities, allowing for rotation about an axis perpendicular to the surface. This rotation will become increasingly constrained as the length of the alkyl chain increases (due to dispersion interactions with the surface and steric hindrance from neighboring "stacks") and will cease for sufficiently large sorbate molecules.

Rotational entropy changes little when transitioning from the gas phase to solution [32], so

for its determination, the values of gas-phase entropy provided by the ORCA program can be used. The translational entropy for the liquid phase differs significantly from that of the gas phase; its calculation was performed using the methodology based on the free volume occupied by the dissolved substance in the solvent [32]:

$$V_{\text{free}} = \left(\sqrt[3]{V_{\text{cav}}} - \sqrt[3]{V_{\text{mol}}}\right)^3 ; \qquad (1)$$

$$S_{\text{trans}} = R \ln\left(\frac{V_{\text{free}}}{\Lambda^3}\right) + \frac{5}{3} R , \qquad (2)$$

where $\Lambda = h / \sqrt{2\pi m k_B T}$, h is Planck's constant, k_B is Boltzmann's constant, m is the mass of the molecule, T is absolute temperature, V_{mol}, V_{cav} are the molecular volume and cavitation volume, respectively.

The volume of the molecule and the cavitation volume are calculated using the same methodology, treating them as cavities from which the solvent will be displaced [33]; the difference lies in the values of atomic radii. The Bader atomic radii [34] are used for the molecular volume, while radii based on the use of a surface of constant electronic density (isodensity surface) [35] are used for calculating the cavitation volume. Volumes were calculated in ORCA using the vdw_gaussian scheme [36].

Thus, the change in Gibbs free energy during the adsorption of a surfactant molecule on the surface of copper phthalocyanine will be calculated based on the following dependencies:

– in the case of complete loss of rotational degrees of freedom

$$\Delta G_{\text{ads}} = \Delta E_{\text{ads}} - T\left(-S_{\text{trans}} - S_{\text{rot}}\right) = \Delta E_{\text{ads}} + T S_{\text{tr}} ; \quad (3)$$

– in the case of partial loss of rotational degrees of freedom

$$\Delta G_{\text{ads}} = \Delta E_{\text{ads}} - T\left(-S_{\text{trans}} - 2/3 S_{\text{rot}}\right) = \Delta E_{\text{ads}} + T S_{\text{t2/3r}} , \qquad (4)$$

where ΔE_{ads} is the change in electronic energy upon the formation of the sorbate-sorbent complex.

3. Results and Discussion

As a result of the conformational analysis at the level of theory ωB97x-D4/def2-SVPD, it was found that in the aqueous phase, the most stable conformers of trialkylamines are the molecules with the arrangement of alkyl groups relative to the nitrogen atom, as shown in Fig. 3.
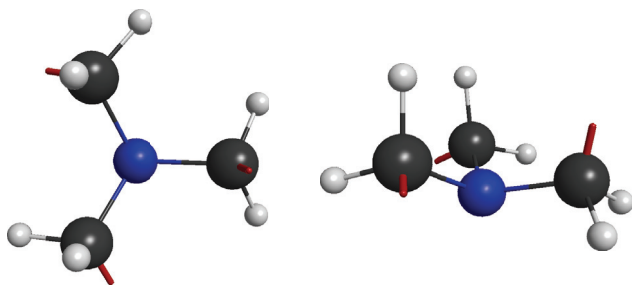
Fig. 3. Scheme of the arrangement of alkyl groups relative to the nitrogen atom for the most low-energy conformation of linear trialkylamines

In this arrangement, the average C–N–C angle is 110.7° (for triethylamine), which is close to its value in the solid phase (112.6°) [37]. For the other trialkylamines, the angles range from 108.6° to 110.8°, indicating an absence of steric strain, which is characteristic of branched trialkylamines [38]. With the exception of trimethylamine, all trialkylamines have C_1 symmetry, while trimethylamine exhibits C_3 symmetry; however, based on experimental data, it can be said that the transition between different types of symmetry occurs quite easily [37].

The scheme of the interaction of trialkylamines with the active center containing a copper atom is presented in Fig. 4.
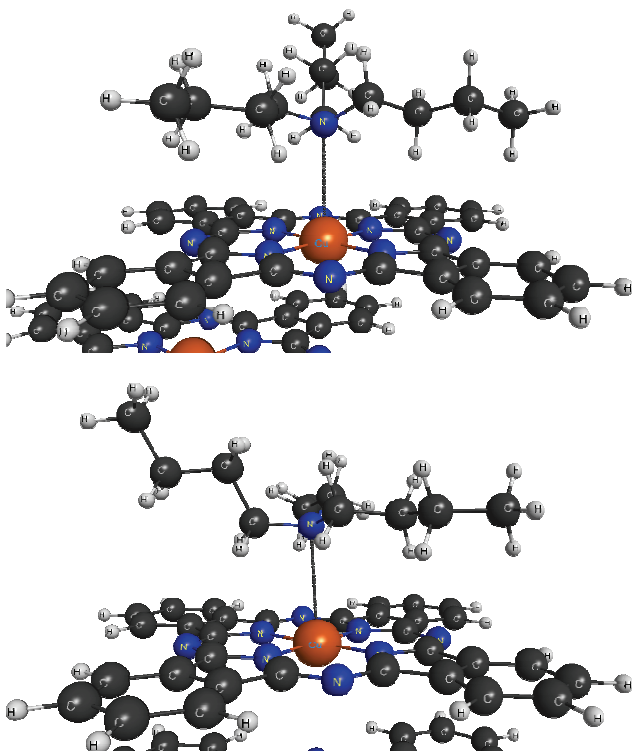

Fig. 4. Scheme of sorbate-sorbent interaction on a surface containing a metal atom using the example of tributylamine
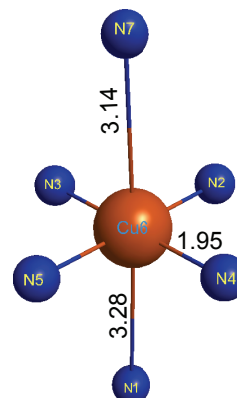

Fig. 5. Six-coordinated copper atom in a tributylamine complex with a surface, distances in angstroms

According to the scheme (Fig. 4), the sorption occurs in such a way that the nitrogen atom of the trialkylamine, which has a lone pair of electrons, is positioned near the copper atom. The copper atom has a six-coordinate structure, where four nitrogen atoms from the phthalocyanine molecule containing that atom (1.95 Å), the nitrogen atom of a neighboring phthalocyanine molecule (3.28 Å), and the nitrogen atom of the trialkylamine (3.14 Å) act as ligands (Fig. 5).

The structure of the complexes with the other trialkylamines is similar to the provided complex with tributylamine. The mechanism of ammonia adsorption on the surface of copper phthalocyanine through the metal atom was proposed in reference [8]. Trialkylamines, if their nitrogen atom is available for interaction, should behave similarly.

The distances between the surface copper atom and the nitrogen atom of the trialkylamines are presented in Table 1.

The tributylamine molecule is the largest that can fully fit on a single copper phthalocyanine molecule. The tripentylamine molecule slightly extends beyond the edges of the "pack", but does not contact neighboring molecules. For larger molecules, steric hindrances may occur during sorption on this surface (Fig. 6).

Table 1. Geometric parameters of trialkylamine sorption on the surface of copper phthalocyanine

Alkyl chain length	Cu–N length, Å
1	2.70
2	3.12
3	3.24
4	3.14
5	3.13
6	3.13
7	3.13
8	3.13

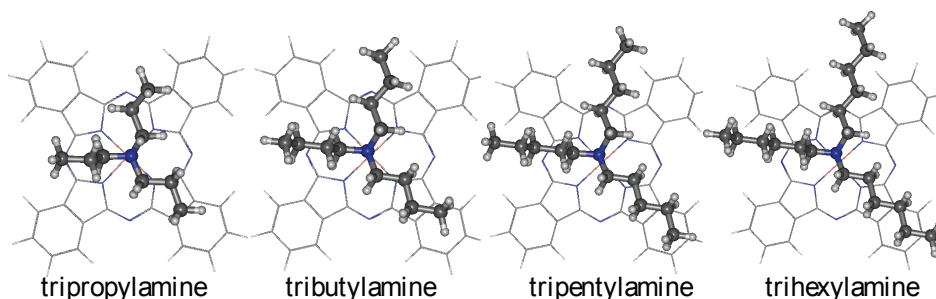tripropylamine   tributylamine   tripentylamine   trihexylamine

Fig. 6. Top view of some trialkylamine complexes with the copper phthalocyanine surface
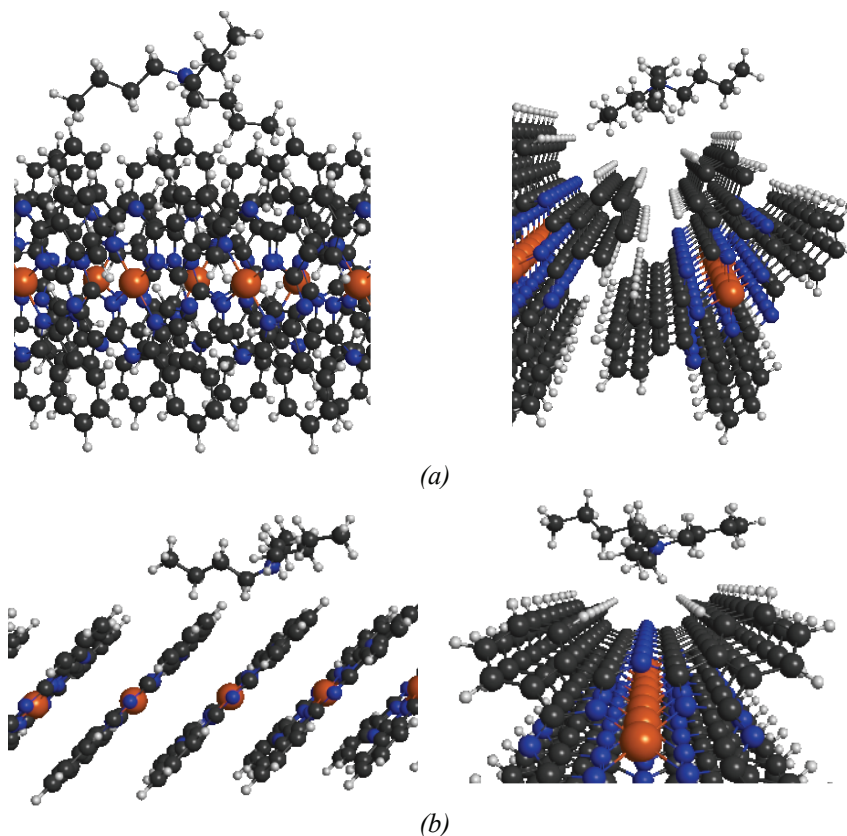

(a)

(b)

Fig. 7. Complexes of tributylamine with the surface of $(20\overline{1})$ (*a*) and (001) (*b*) copper phthalocyanine

When sorbing on surfaces (001) and $(20\overline{1})$, the only polar atoms with which the trialkylamine molecule can interact are the nitrogen atoms. However, due to steric hindrances, the strength of the nitrogen-nitrogen interaction is too low, and the main contribution to the sorption energy will come from the dispersion interactions between the nonpolar parts of the sorbate and the sorbent. The structure of the trialkylamine complexes with surfaces (001) and $(20\overline{1})$ is shown in Fig. 7.

The formation energies for the presented trialkylamine complexes with the surface of copper phthalocyanine are shown in Figs. 8–10.

As can be seen from the graphs in Fig. 8, the XTB2 method yields significantly overestimated values of sorption energy on metal atom surfaces.

Methods QMMM1 and QMMM2 provide nearly identical values when including BSSE (Basis Set Superposition Error) corrections. Without BSSE consideration, the calculation error in energy is quite significant, as expected with such a small basis set. For other surfaces, calculations were conducted using only QMMM1 and XTB2 methods, with the energy values obtained by these methods differing less significantly compared to the metal atom surface. Overall, sorption energy on non-polar surfaces (001) and $(20\overline{1})$ is substantially lower than on metal atom surfaces. Surface (001) is slightly more favorable than $(20\overline{1})$.

Gibbs sorption energies calculated using dependencies (3), (4) with electronic energies computed by the QMMM1 method are presented in Fig. 11.
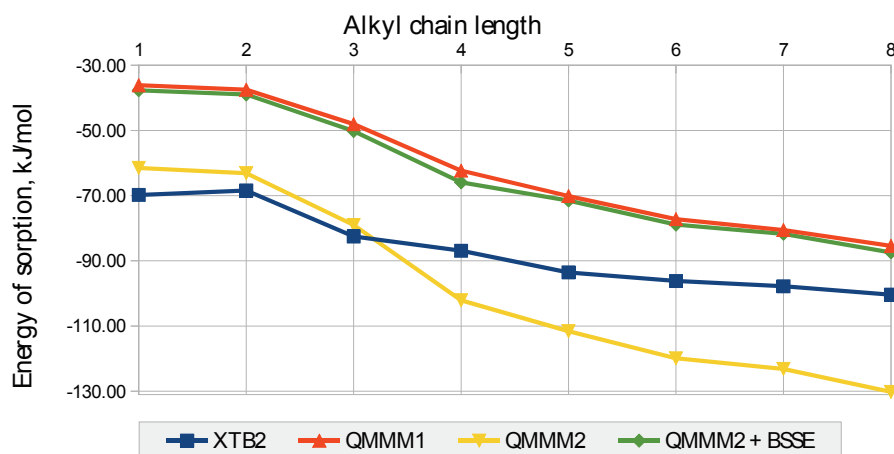
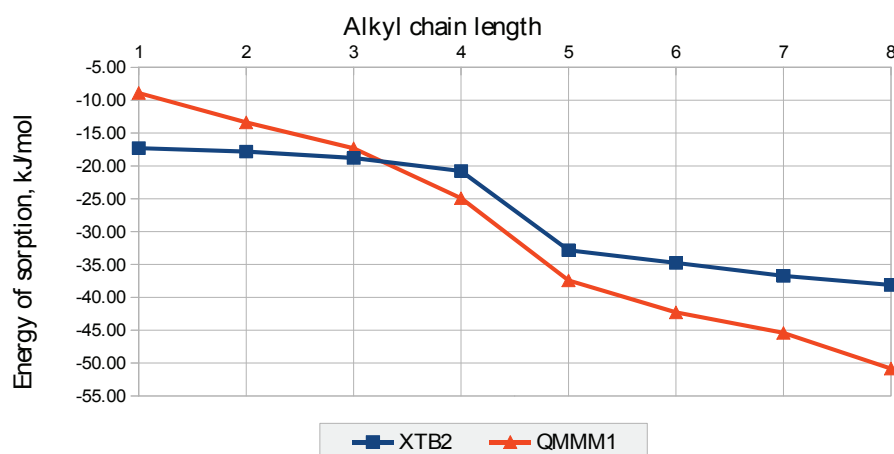**Fig. 8.** Sorption energy of trialkylamines on the surface of copper phthalocyanine containing a metal atom

Fig. 9. Sorption energy of trialkylamines on the surface of $(20\bar{1})$ copper phthalocyanine
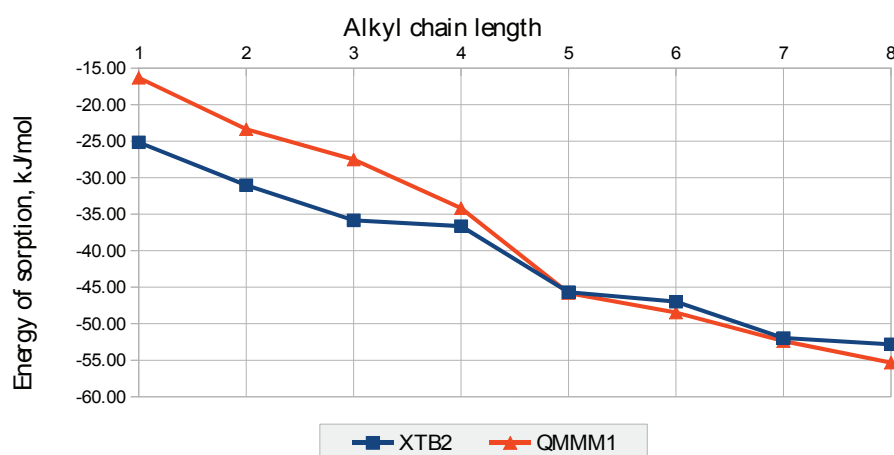

Fig. 10. Sorption energy of trialkylamines on the surface of (001) copper phthalocyanine

Based on the Gibbs energy values, it can be concluded that sorption of trialkylamines from the aqueous phase will not occur on surfaces (001) and $(20\bar{1})$ (minimum ΔG value = 18.13 kJ·mol^{-1}, corresponding to an equilibrium constant ≈ 0.0007).

The graph (Fig. 11) shows two regions for these surfaces: up to tributylamine with $\Delta G \approx 40$ kJ·mol^{-1} for surface $(20\bar{1})$ and ≈ 30 kJ·mol^{-1} for surface (001), after which the free energy decreases by approximately 10 kJ·mol^{-1}.
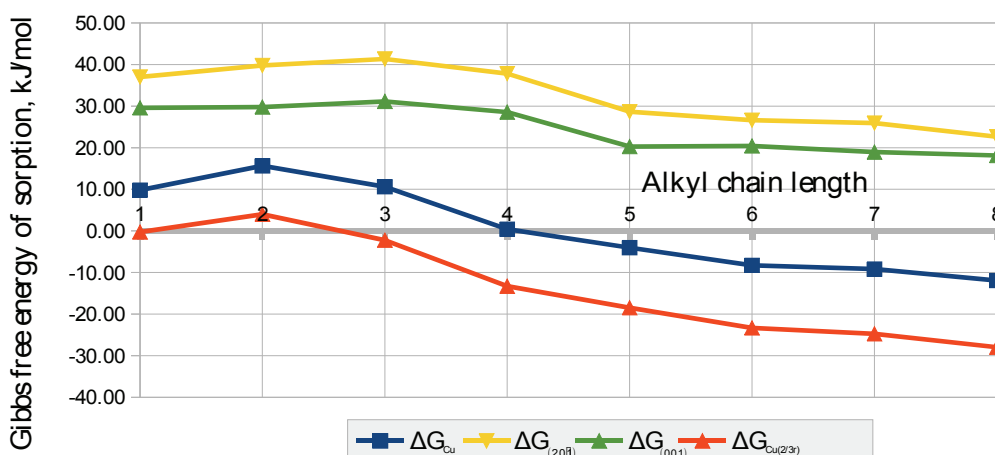
Fig. 11. Gibbs free energy of sorption of trialkylamines on various surfaces
of copper phthalocyanine, calculated by the QMMM1 method

This is explained by the fact that small molecules are rigid and dispersion forces cannot deform them sufficiently to maximize interaction area with the surface. For molecules with alkyl chains longer than 5, deformation of the alkyl groups becomes advantageous, ensuring maximum interaction area between non-polar segments of the sorbate and sorbent.

Sorption of trialkylamines on the surface containing a metal atom is feasible (Fig. 11). Clearly negative values of Gibbs free energy (both with full and partial loss of rotational degrees of freedom) are observed starting from tripentylamine. However, steric hindrances may occur starting from trihexylamine and higher, which increase the energy of the sorbate-sorbent complex and make such processes less favorable. The poorest sorption characteristics are exhibited by triethylamine. Trimethylamine and tripropylamine can sorb on this surface with partial retention of rotational degrees of freedom. Tributylamine sorbs on this surface with complete loss of rotational degrees of freedom ($\Delta G = 0.4$ kJ·mol^{-1}) and well with partial retention of rotational degrees of freedom ($\Delta G = -13.32$ kJ·mol^{-1}).

4. Conclusion

In this study, molecular modeling methods using density functional theory were used to evaluate the adsorption characteristics of trialkylamines with alkyl chain length $n = 1 \div 8$. It was found that the best trialkylamine with an unbranched alkyl group for rendering the polar surface of copper phthalocyanine oleophilic is tripentylamine. Tributylamine and trihexylamine can also be used for this purpose, albeit with lower efficiency. The effectiveness of trialkylamines with longer alkyl groups remains

questionable due to steric hindrances during adsorption on the polar surface. Thus, it is established that all trialkylamines only sorb on surfaces containing copper atoms, indicating selective adsorption of these surfactants on surfaces requiring oleophilization.

6. Conflict of interest

The authors declare no conflict of interests.

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