Modeling of the interaction of porphyrin molecules in a nonpolar solvent

V N Mironyuk\textsuperscript{1,5}, A J R Al-Hassani\textsuperscript{2}, A J K Al-Alwani\textsuperscript{1}, N N Begletsova\textsuperscript{1}, M V Gavrikov\textsuperscript{1}, A S Kolesnikova\textsuperscript{1,3}, M V Pozharov\textsuperscript{4} and E G Glukhovskoy\textsuperscript{1}

\textsuperscript{1} Education and Research Institute of Nanostructures and Biosystems, Saratov State University, Saratov, 410012, Russia
\textsuperscript{2} The Iraqi Ministry of Education, 8CH9+9F Baghdad, Iraq
\textsuperscript{3} Bogoliubov Laboratory of Theoretical Physics, Joint Institute for Nuclear Research, Dubna, Moscow Oblast, 141980, Russia
\textsuperscript{4} Institute of Chemistry, Saratov State University, Saratov, 410012, Russia
\textsuperscript{5} E-mail: bestblogger@yandex.ru

Abstract. The article presents the data of a theoretical molecular dynamics study of the interaction between a pair of porphyrin molecules, i.e. symmetrically substituted 5,10,15,20-tetra-(4-n-methyloxyphenyl) porphyrin (P) and asymmetrically substituted 5-(4-hydroxyphenyl)-10,15,20-tris-(4-n-methyloxyphenyl) porphyrin (P-OH). We studied three systems, each of which consisted of a pair of porphyrin molecules (P || P, P-OH ↑↑ P-OH and P-OH ↑↓ P-OH) and chloroform molecules as a non-polar solvent. The effect of substitution, different orientations of asymmetrically substituted molecules and temperature on the geometry and energy of the system was investigated. It was shown that all three systems show signs of a true solution with chloroform as a solvent; the distance between asymmetrically substituted P-OH molecules was less than in the case of two P molecules. This may serve as an indirect evidence that the molecules are not prone to aggregation in the presence of chloroform.

1. Introduction and motivation

An important point in the Langmuir-Blodgett technology is the formation of highly organized floating monomolecular layers on the water surface. This process can be seriously disrupted by uncontrolled aggregation of molecules that make up a monolayer. Moreover, such aggregation can occur at the initial stage of preparing a solution for LB technology. In the case of simple surfactant molecules, this problem is not very common. They dissolve quite well in highly volatile solvents such as chloroform, i.e. form true solutions. Such solutions easily and evenly spread out over the water surface between barriers over the entire area of the Langmuir bath, and, after the solvent evaporates, the surfactant molecules are separated by distances commensurate with the sizes of the molecules themselves.

The task of obtaining a true monolayer becomes more complicated when the surface is comprised of molecules with a complex structure and uneven charge distribution or induction of dipoles. Such molecules include derivatives of porphyrin, phthalocyanine, proteins, etc. Some authors often conclude that it is impossible to obtain a true monolayer for such substances [1]. Nevertheless, this problem can be solved by varying the required conditions, i.e. introducing additional spacer substances into the composition of the monolayer substrate (MS), adding nanoparticles, changing the ratio of surfactants and quantum dots, and using various physical fields and radiation [2-4].
One of the most powerful technological factors is temperature. It has a significant impact on the state of multicomponent systems such as "water-air-monomolayer". So, when the water temperature changes from 0 to 100 °C, its surface tension of water will change from 75 to 59 mN/m. In the absolute majority of cases, water is used in the LB bath to form MS. Therefore, the temperature during the formation of MS in the LB bath is the most important technological factor [5-7].

The aim of this work is theoretical study of the effect of temperature on various aspects of interaction between molecules of porphyrin derivatives with different substitutions and orientations of asymmetrically substituted molecules surrounded by solvent (chloroform) molecules.

2. Object of research

The objects of the study are molecules of porphyrin derivatives with symmetric substitution – 5,10,15,20-tetra (4-n-methyloxyphenyl) porphyrin (P) – and with asymmetric substitution -5- (4-hydroxyphenyl) -10,15,20- tris (4-n-methyloxyphenyl) porphyrin (P-OH). Their structural formulas are shown in figure 1.

![Structural formula of: (a) symmetric 5,10,15,20-tetra (4-n-methyloxyphenyl)porphyrin (P), (b) asymmetric 5- (4-hydroxyphenyl) -10,15,20-tris (4-n-methyloxyphenyl) porphyrin(P-OH).](image)

Three model systems were investigated. Each (of them) consisted of a pair of identical porphyrin molecules and chloroform molecules. System I contained two molecules of symmetrically substituted porphyrins (P || P); system II contained two molecules with asymmetric substitution with central macrocycles aligned in parallel, so that their dipole moments were oriented in one direction (P-OH ↑↑ P-OH); system III consisted of two molecules with asymmetric substitution with a parallel arrangement of central macrocycles, however, their dipole moments were counter-oriented (P-OH ↑↓ P-OH). System I included 292 chloroform molecules, systems II and III - 244 chloroform molecules each.

Due to the fact that the porphyrin molecule has a dipole moment, the interaction of two electric dipoles with dipole moments $\mu_1$ and $\mu_2$ located at a distance $r$ from each other and oriented relative to each other, produces energy $w$. According to [8] this energy of the «charge-dipole» interaction can be written as:

$$w(r, \theta_1, \theta_2, \varphi) = -\frac{\mu_1 \mu_2}{4\pi \varepsilon_0 \varepsilon r^3} [2\cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \varphi]$$

(1)

where $\varepsilon_0$ is the dielectric permeability of space, $\varepsilon$ is the dielectric permeability of molecules, $\varphi$ is the angle made by two oppositely charged dipoles, while $\theta_1$ and $\theta_2$ are the angles formed by two with respect to the line connecting their centers. From the same equation, it follows that the maximum attraction will be observed when the dipoles are lined up along a single line connecting the centers of mass of the dipoles, and the energy will be determined as:

$$w(r, 0, 0, \varphi) = -\frac{2\mu_1 \mu_2}{4\pi \varepsilon_0 \varepsilon r^3}$$

(2)

If the dipoles are located parallel to each other and perpendicular to the line connecting their centers of mass, then the energy of their interaction $w(r, 90^\circ, 90^\circ, 180^\circ)$ at the same distance $r$ will be two times less than in the first case.
In the first variant of the arrangement of such molecules (when $\theta_1 = 0, \theta_2 = 0$), the distances between them are too great for the interaction to be effective. The molecules selected for the calculation have a large extension in the plane of the macrocycle. In the first variant of the arrangement of such molecules (when $\theta_1 = 90, \theta_2 = 90$).

3. Research method
The search for the equilibrium state of the systems under study was carried out by the method of molecular mechanics MM+ with the calculation algorithm of Polak - Reiber. In all cases, the simulation began with the same position of the porphyrin molecules: the planes of the macrocycles of the molecules were parallel to each other and located at a distance of 1.55 nm from each other. For this, all three systems were constructed from a single initial model with a pair of symmetrically substituted porphyrin molecules (system I). To create systems II and III, -OH groups were introduced into the molecules P (initial system I) as the replacement of the aliphatic chains in the required fragments so as to obtain asymmetrically substituted molecules with the desired mutual orientation of the dipole moments - parallel (system II) and antiparallel (system III), as shown in Figure 2. This made it possible to keep the same initial positions of the central macrocycles in all molecular systems. The distance between the centers of mass of the central porphyrin macrocycle of two molecules was associated with the distances between the molecules and was subsequently used for analysis.

![Figure 2](image.png)

**Figure 2.** Systems of pairs of molecules of porphyrin derivatives in chloroform: (a) symmetrically substituted (P || P), (b) asymmetrically substituted with parallel orientation (P-OH ↑↑ P-OH), (c) asymmetrically substituted with antiparallel orientation (P-OH ↑↓ P-OH). Chloroform molecules are shown in green.

To calculate the geometry of molecular systems, a thermostat was used, in which the temperature was set to 293; 313; 333; 354 K. The temperature was set using a thermostat. Each state of the systems after reaching the preset temperature was optimized with the search for an energy minimum.

4. Results and discussion
The molecule of symmetrically substituted 5,10,15,20-tetra (4-n-methyloxyphenyl) porphyrin in vacuum at a temperature of 0 K is practically non-polar and has a dipole moment close to 0 in the case of a symmetric arrangement of aliphatic chains, when they and the macrocycle lie in the same plane.
Figure 3 shows asymmetric 5-(4-hydroxyphenyl)-10,15,20-tris(4-n-methyloxyphenyl) porphyrin (P-OH) optimized by MM+ at 293 K. It can be seen that at this temperature the P-OH has a dipole moment of $\mu_{P-OH} = 1.17$ D. The direction of the vector of the dipole moment is shown in Figure 3 as a segment with the signs «+» and «−» at its ends.

![Figure 3. Asymmetric 5-(4-hydroxyphenyl)-10,15,20-tris(4-n-methyloxyphenyl) porphyrin (P-OH) optimized by MM+ at 293K.](image)

Figure 4 demonstrates the temperature dependence of the distance between the centers of mass of molecules and the total energy of the system. As can be seen, at relatively low temperatures (293 and 313 K), the difference in distances is not significant – about 1 Å. Moreover, the intermolecular distance in system I is less than that for system III. There are two possible reasons for this behavior. First, the allotted time might not have been enough for the molecules to find a deeper local energy minimum. On the other hand, the value of the temperature, and, consequently, the intensity of the internal displacements of individual fragments of molecules, might not be sufficient for the system to arrive at a deeper energy minimum. This is also evidenced by the higher energy values at low temperatures for all systems. This is especially evident for system I: its transition from a temperature of 293 to 313 K is accompanied by a noticeable decrease in the total energy by 60 kcal/mol. For systems II and III $\Delta w_I = w_I(293) - w_I(313) = 60$ this decrease was less pronounced, but also took place: $\Delta w_{II} = 5 \Delta w_{II} = 15$.

At higher temperatures, the behavior of systems becomes more logical and expected. It is likely that at such temperatures, the system moving more intensively manages to find a deeper energy minimum in a shorter time.

The difference in the strength of molecular interaction systems II and III are less significant as compared with the system I. Nevertheless, it can be noted here that the distances between molecules with oppositely oriented dipole moments are slightly smaller (and, accordingly, the interaction is greater) than for molecules with dipole vectors directed in one direction.

5. Conclusion

The effect of temperature on the features of the interaction of molecules of porphyrin derivatives surrounded by chloroform molecules as a solvent has been studied. Numerical experiment at temperatures 293; 313; 333; 354 K revealed a non-monotonic effect of temperature on the intermolecular distance.

The total energy of the system with a parallel arrangement of porphyrin molecules (P-OH ↑↑ P-OH) was higher than in the case of an antiparallel arrangement (P-OH ↑↓ P-OH).

The results obtained show that the molecules of symmetrically and asymmetrically substituted porphyrin form a true solution with chloroform. The presence of a weak intermolecular interaction is not critical and does not lead to the formation of aggregates.
Figure 4. Dependence of the distance between the centers of mass of porphyrin molecules (a), and the total energy of the system (b) on temperature.

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