Structure of the porphyrazine monolayer at the air–water interface: Computer simulation*

A. Borodin and M. Kiselev[‡]

Institute of Solution Chemistry of Russian Academy of Sciences, Akademicheskaya Str. 1, 153045, Ivanovo, Russia

Abstract: Molecular dynamics simulations of porphyrazine monolayers at the air–water interface have been carried out. All possible molecular orientations found by analysis of the π-A isotherms are reproduced by computer simulations. The existence of "guest-water" molecules has been observed in the simulation; this confirms the assumptions of experimentalists concerning this phenomenon.

INTRODUCTION

A number of studies within the past decades were focused on Langmuir–Blodgett (LB) films based on tetrapyrroles due to their potential applications in molecular electronics, optical data storage devices, gas sensors, etc. The structural characteristics of monolayers at the air–water interface provide important information about the structure of built-up LB films. These data are essential for the understanding of the structure and dynamics of highly ordered films. It is quite difficult to obtain from experiments a self-consistent picture of the structure at the molecular level. Thus, the implementation of computer simulation methods is particularly important for the study of such complex systems [1]. In the present work, all components (water, air, PzH_2 monolayer) were considered at the molecular level using molecular dynamics (MD) simulations without any restrictions on the motions of molecules. From data available for CuPz Langmuir films [2], it follows that even rarefied CuPz films are discontinuous. Molecular assemblies consisting of several molecules occur. As compression increases two different types of orientation with angles 65°–72° and 47° may occur depending on experimental conditions (initial, coverage, surface concentration, etc). These structures are assumed to be analogs of the α and β forms of the crystalline phthalocyanines, respectively. Being less stable, β monolayer occurs at lower surface concentration and lower initial coverage.

MOLECULAR STRUCTURE FROM QUANTUM CALCULATIONS

In order to estimate the molecular structure of porphyrazine, quantum calculations were performed. The density functional method with Becke's three parameter hybrid functional, the correlation functional of Lee, Yang, and Parr, and 6-31G** basis set were used [3]. These methods reproduces physical properties of organic molecules remarkably well and lead to reliable results also in the quantum chemistry of tetrapyrroles [4].

A full geometry optimization of the isolated PzH_2 molecule has been performed. The geometrical and electronic structures are in a good agreement with results obtained by Parrinello [5] and Ghosh [6] using another basis set. A charge distribution was obtained via Mulliken population analysis. The

---

‡Corresponding author

atomic charges are shown in Table 1. The different configurations of the PzH_2 dimer have been studied at the same level of theory as for isolated molecule. The minimal energy configuration, as obtained from the quantum calculations, is depicted in Fig. 1. The distance of 3.9 Å between macrocycle planes is larger than interplanar separations for porphyrins [7] and phthalocyanines [8] (3.4–3.6 Å in crystalline phase). The relative offset of two PzH_2 molecules is 2.25 Å. This value is 3–4 Å for porphyrins. Being placed on the edges, two PzH_2 molecules form a dihedral angle between surface and planes of macrocycles equal to 60°.

Table 1 Force field parameters.

| Molecule	Interacting site	Charge	ε (kJ\mol)	σ (nm)
H_2O	O	–0.82	–0.6500	0.3166
H_2O	H	0.41	0.0	0.0
PzH_2	N_{meso}	–0.54944	–0.8368	0.3296
PzH_2	$N_{,pyr}$	–0.59418	–0.8368	0.3296
PzH_2	$C_{,\alpha}$	0.50563	–0.2929	0.3564
PzH_2	$C_{,\beta}$	–0.10663	–0.2929	0.3564
PzH_2	H	0.11841	–0.0437	0.2503
PzH_2	$N_{B,pyr}$	–0.63858	–0.8368	0.3296
PzH_2	$C_{B,\alpha}$	0.47301	–0.2929	0.3564
PzH_2	$C_{B,\beta}$	–0.10012	–0.2929	0.3564
PzH_2	H_B	0.11841	–0.0437	0.2503
PzH_2	H_{pyr}	0.33872	–0.0920	0.2352
N_2	N_2	0.0	–0.5937	0.3798
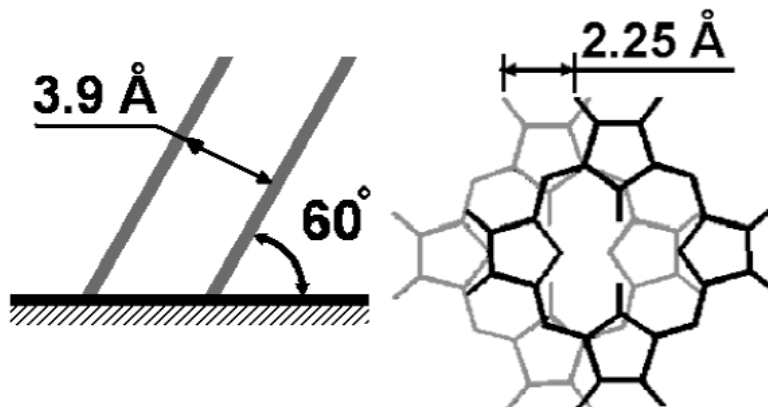
Fig. 1 Optimal configuration of the PzH_2 dimer.

MODEL AND DETAILS OF SIMULATION

The molecular dynamics simulation of the PzH_2 monolayer at the air–water interface has been carried out with 15 PzH_2, 864 water and 216 nitrogen molecules in a rectangular box. Periodic boundary conditions were applied in all three directions of space. Details of the simulation are shown in Table 2. A rigid SPC (simple point charge) model [10] for water was chosen because it reproduces many of the experimentally determined structural and dynamical properties. The Lennard–Jones parameters for the PzH_2 species were taken from the OPLS force field [11] and supplemented with the geometry and

atomic charges obtained by the quantum calculations described above. We started with a perfectly aligned PzH_2 monolayer and a previously equilibrated (at 300 K) configuration of water and nitrogen. Typical run lengths were 1.5 ns for equilibration followed by 3 ns for data collection.

Table 2 Simulation cell details.

Molecule	Number of the molecules	Layer dimensions (nm)	Phase volume (nm^3)
H_2O	864	3.7712 ∈ 3.7712 ∈ 1.8856	26.8169
PzH_2	15	3.7712 ∈ 3.7712 ∈ 0.7980	11.3491
N_2	216	3.7712 ∈ 3.7712 ∈ 7.8584	111.7618
System	1095	3.7712 ∈ 3.7712 ∈ 10.542	149.9278

RESULTS AND DISCUSSION

One of the important questions that appeared from the analysis of experimental isotherms [2] is how far the density distribution of Langmuir monolayer is from homogeneous. In order to understand this, the local density distribution, plotted out within 0.75 ns, is depicted in Fig. 2. As one can clearly see, at least for the run lengths considered, the PzH_2 monolayer is highly inhomogeneous. The formation of aggregates consisting of several molecules is observed (Fig. 3). The other important point of discussion, regarding the monolayer structure, is whether the preferred orientation of the PzH_2 molecule at the interface basically follows from the PzH_2 intermolecular interactions or whether PzH_2–water interactions play an important role. In order to analyze the orientational structure of the PzH_2 monolayer, the cosine distribution between planes of PzH_2 and the interface has been calculated; four pronounced peaks have been observed. The peak near 0° corresponds to the planar arrangement of the PzH_2 molecules on water surface. Molecules "leaning" on ones lying on the water surface give a shoulder at 23°. Structures with tilt angles of 76° and 56° are assumed to correspond to the alpha and beta crystalline phthalocyanines, respectively. On the other hand, very close orientations follow from the DFT calculations (Fig. 1). Therefore, the interactions between water and PzH_2 play a crucial role in determining the orientations of the molecules near the interface.
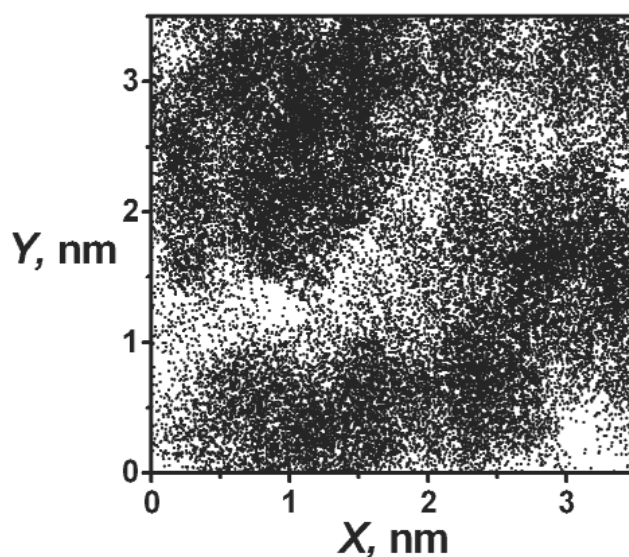

Fig. 2 Lateral density distribution of PzH_2 molecules. Symbols are plotted within 0.75 ns.
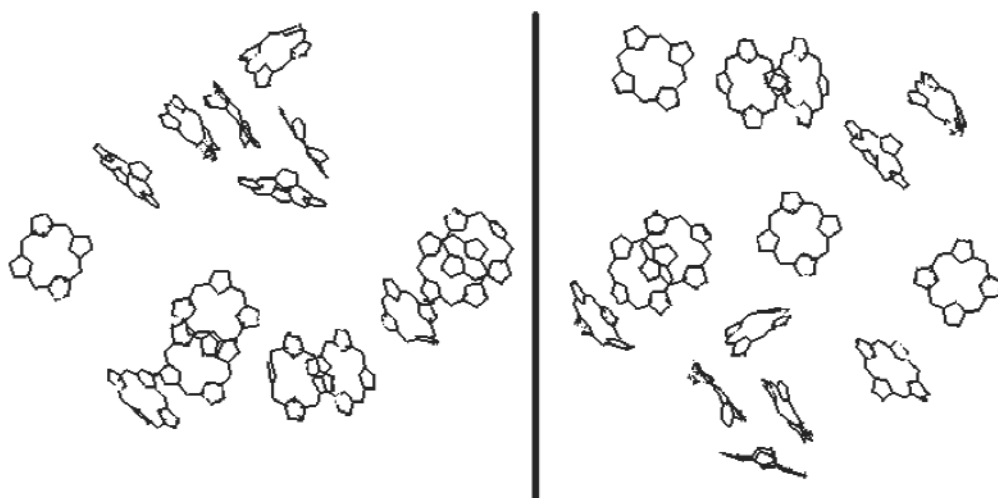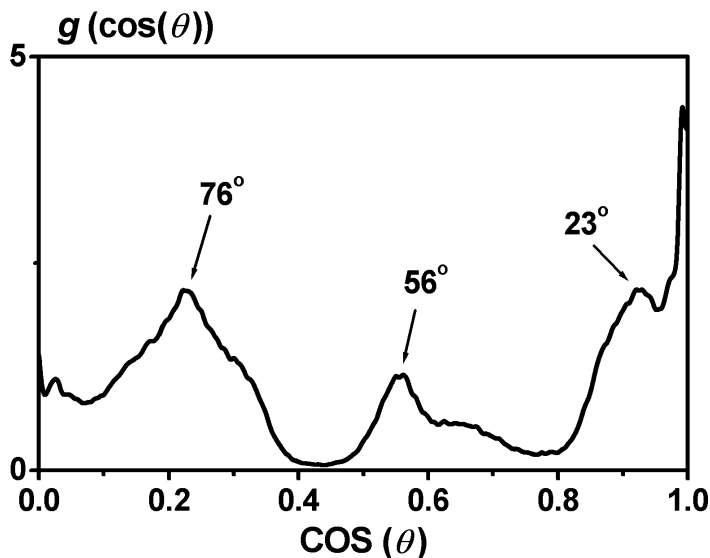
Fig. 3 PzH$_2$ monolayer snapshots.

Fig. 4 PzH$_2$ molecules tilt angles cosines distribution.

The local density distribution of water molecules across the Z-direction of the simulation box is shown in Fig. 5. The nonvanishing water density at Z > 2.13 nm (interface position) identifies the so-called "guest-water". A hypothesis about the existence of guest-water has been introduced recently [2] from the analysis of experiments. It follows from the present simulation that the number of guest-water molecules is significant. There are three peaks in the water density profiles beyond the interface. This complex behavior of the density profile is due to the different types of the orientations of the PzH$_2$ molecules. Strong variations in the water density up to 1.1 nm from the "floating layer" illustrate the layered structure of water. Near the interface, up to 0.7 nm, the water structure is quite stretched and only two prepeaks can be observed in the density profile. This is because of guest-water molecules, which effectively decrease the density of the first, second, and even third solvation shells at the interface. On the other hand, the structure induced by the interface is pronounced even at distances around 10–15 Å.

This finding contradicts the results on water–metal interfaces [11] where a pronounced structure has been observed only up to 4th solvation shell. The reason of such behavior may be found from the assumption that water molecules in the first and second layers are preferentially oriented. The average dipole moments orientations vs. distances from the interface for the first and second layers of guest-water are shown in Fig. 6. Shallow, but still pronounced preferential orientation of water molecules dipole moments is found to exist for all guest-water molecules, distributed near the first and second prepeaks of density profile. The average direction of dipole moments of water molecules placed at distances from
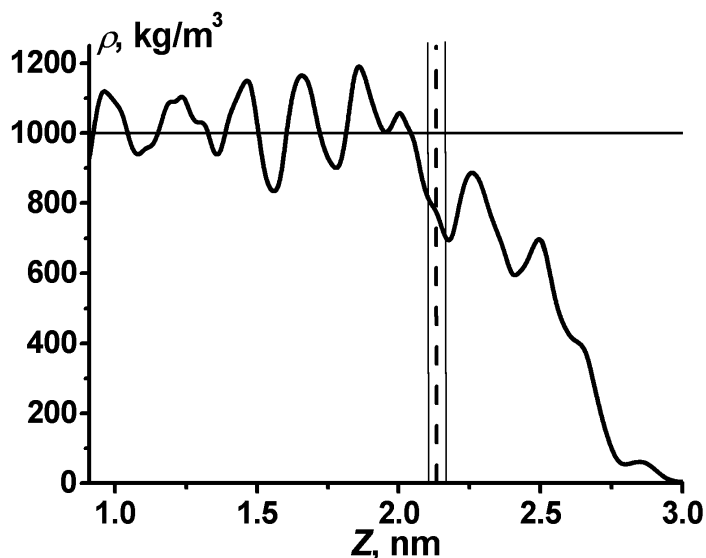

Fig. 5 Water density profile across Z direction. Dashed line is position of the interface with calculation bars (two thin solid lines).
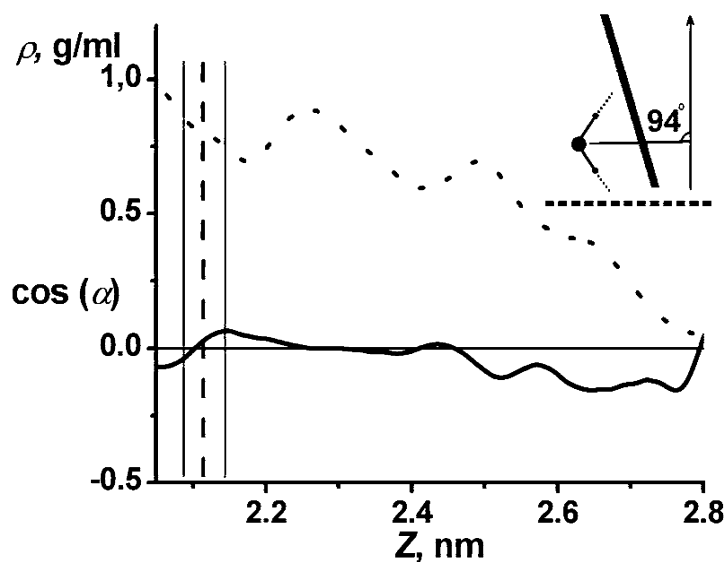

Fig. 6 Water dipoles: Z axis angle distribution across Z direction. Dashed curve: water density profile. Dashed line is position of the interface. Upright corner: guest-water orientation.

the interface corresponding to the second prepeak is found to be 94° relatively to Z-axis. The reason for this orientation is twofold. First, this orientation is preferable because of the screening from the dipole field of the first water layer below the interface. Second, as follow from recent simulations of the PzH_2 hydration [12], the water molecules form stable hydrogen bonds with PzH_2. From this point of view, one can expect the formation of hydrogen bonds by guest-water as shown in Fig. 6. On the other hand, being hydrogen-bonded with PzH_2 through first hydrogen, water molecules direct other hydrogen atom toward the water surface, attempting to realize a maximum number of hydrogen bonds. Thus, built-in water molecules prevent the formation of the PzH_2 aggregates with tilt angle of 60°, as it follows from quantum calculations (Fig. 1).

CONCLUSION

The simulation presented here demonstrates the usefulness of the computer chemistry methods in the investigation of such complex system as porphyrazine Langmuir films. Qualitative agreement with experimental data on the structure of CuPz films was obtained. The influence of the guest-water on the floating layer structure was examined. It was shown that the interaction of the PzH_2 molecules with guest-waters leads to the layered structure of the underlaying water. Thus, it is particularly important to take into consideration the water phase in theoretical investigations of Langmuir films. Simulations of the PzH_2 monolayers with different surface concentrations are in progress now. Moreover, layer-by-layer water dynamics and structure analysis is absolutely necessary for the understanding of the influence of the solvent on the structure of Langmuir films.

REFERENCES

1. F. M. Haas, R. Hilfer, K. Binder. *J. Phys. Chem.* **100**, 15290 (1996); J. Böcker, M. Schlenkrich, Ph. Bopp, J. Brickmann. *J. Phys. Chem.* **96**, 9916 (1992); S. Karaborni and S. Toxvaerd. *J. Phys. Chem.* **96**, 4965 (1992).
2. L. Valkova, N. Borovkov, M. Pisani, F. Rustichelli. *Thin Solid Films* **401**, 267 (2001).
3. A. D. Becke. *J. Chem. Phys.* **98**, 5648 (1993).
4. A. Ghosh. *Acc. Chem. Res.* **31**, 189 (1998).
5. D. Lamoen and M. Parrinello. *Chem. Phys. Lett.* **248**, 309 (1996).
6. A. Ghosh, P. G. Gassman, J. Almlof. *J. Am. Chem. Soc.* **116**, 1932 (1994).
7. C. A. Hunter and J. K. M. Sanders. *J. Am. Chem. Soc.* **112**, 5525 (1990) and references cited therein.
8. H. S. Nalwa. *Supramolecular Photosensitive and Electroactive Materials*, Academic Press, New York (2001).
9. H. J. C. Berendsen, P. M. J. Postma, A. DiNola, J. R. Haak. *J. Chem. Phys.* **81**, 3684 (1984).
10. W. L. Jorgensen and J. Tirado-Rives. *J. Am. Chem. Soc.* **110**, 1658 (1996).
11. J. Böcker, E. Spohr, K. Heinzinger. *Z. Naturforsch.* **50a**, 611 (1995).
12. A. Borodin. Bachelor thesis, Ivanovo, Russia (2000).