

THESES of

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**ADSORPTION LAYERS OF SURFACTANTS FORMED AT LIQUID/GAS
INTERFACES: A COMPUTER SIMULATION STUDY**

PhD dissertation

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INTRODUCTION AND AIMS

Surfactants are amphipatic molecules having distinguished nonpolar and polar molecular parts within a molecule. This structure explains that surfactants tend to accumulate on surfaces at very low bulk phase concentration, thus, they can decrease surface tension of the bulk liquid phase. This highly advantageous property is widely utilized by the chemical industry.

The molecular arrangement of surfactants at the free water surface is well-known: their polar parts are heading the polar bulk phase, while their nonpolar hydrocarbon chains turn against air due to hydrophobic interactions. Very little is known, however, about the details of this kind of arrangement on the atomistic length scale. In other words, how atoms or atomic groups of the polar headgroup are arranged in aqueous medium and what is the conformation of the alkyl chains at the interface.

The experimental investigation of the interface layer on microscopic length scale has become feasible only for a couple of decades and only a few published studies focus on the structural analysis of adsorption layer formed by surfactants at water/air interfaces. In addition to surface sensitive experimental methods and theoretical approaches, rapidly developing simulation methods have exceptional prospects in this field. In computational simulation, the real system is substituted by a model system set up by the user. The properties of the model system can be defined exactly, without the need for applying any approximations. It also means that computational simulation enables us to validate theoretical approximations, nevertheless, only congruent experimental results can confirm the suitability of the applied model system.

In my doctoral work, the so-called molecular dynamics computational simulation method was used to determine the structure of the adsorption layers formed by a number of structurally different surfactants at the water/air interface at atomistic resolution. The compositional variation of the interface was systematically investigated with regard to the dependence of i) the structure of the headgroup (i.e., cationic, anionic, non-ionic), ii) the length of the alkyl chain ($5 \leq C_n \leq 12$, where n is the number of carbon atoms in the chain), and iii) the surface density.

The second aim of my work was to carry out a partial validation of the principles of two adsorption models, namely the Langmuir and Volmer models that both assume

monomolecular adsorption layers, and have originally been developed for the description of adsorption occurring at solid/gas interfaces. It was tested whether the surfactant molecules in the adsorption layer formed in our systems are bound to localized adsorption sites according to the Langmuir model, or, according to the Volmer model, they are bound to mobile adsorption sites. In other words, the extent of lateral diffusion along with the mechanism of diffusion of the studied surfactant molecules was also investigated.

METHODS

SIMULATIONS: deterministic *molecular dynamics* computational simulation method was applied to unravel the structure and determine the dynamic properties of the interface layer.

ANALYSIS: The ITIM (Identification of Truly Interfacial Molecules) method, developed by our research group in 2008, was applied to determine the atoms and atomic groups consisted in the interface layer as well as in the deeper molecular layers reside underneath the interface layer.

SCIENTIFIC NOVELTIES

Scientific results of my doctoral research can be summarized as follows:

1. It was established that in the case of ionic surfactants the distribution of the counterions in the bulk phase is influenced by the surface density. As the surface density increases, the energy contribution resulting from the attractive interaction between headgroups and counterions becomes dominant with respect to the entropy term in the free energy of solvation.
2. It was shown that the alkyl chain conformation of surfactant molecules at the interface is not influenced by the structure of the headgroup; it depends only on the length of the hydrocarbon chain and on the surface density.
3. The roughness of the surface layer formed by surfactants with various structures was studied and it was established that the headgroup atoms of ionic surfactants substantially increase the roughness of the surface as compared to the functional group of alcohols.

4. Investigating the immersion depth of surfactants it was established that the surface arrangement of ionic surfactants differs from the arrangement experienced in the case of alcohols. While the headgroups of alcohol molecules immerse only into the top layer of the aqueous phase, the headgroups of ionic surfactant molecules penetrate into deeper layers. The thermodynamic driving force of this behavior is the intention of the ionic headgroups to be fully surrounded by water neighbors. This immersion of ionic headgroup pulls also several carbon atoms of the hydrocarbon tail into the aqueous environment.
5. It was established that among the two theories originally developed for the description of solid/gas adsorption, where the Langmuir model assumes localized, whilst the Volmer model assumes mobile adsorption sites, our results support the validity of the Volmer model.
6. It was shown that the lateral dynamics of the surfactant molecules is also influenced by the surface density, the structure of the headgroup and the length of the alkyl chain. Nevertheless, the characteristic diffusion time, a typical quantity characterizing diffusion, was in the same order of magnitude in every simulated system as the value determined for the three-dimensional diffusion of water in the bulk phase.
7. Based on the mean residence time of water molecules in the first hydration shell of the surfactant headgroups and as a result of the studies relating to binding energy values between first shell and bulk phase water molecules as well as between non-first shell surface and bulk phase water molecules it was established that the lateral diffusion of surfactants is permitted and, moreover, this movement is done independently from the first hydration shell water molecules.

FURTHER RESEARCH PERSPECTIVES

This research may be continued following two separate directions. Based on simulation data, in cooperation with Marcello Sega, a professor of the University of Rome „Tor Vergata” and the University of Vienna, the collective dynamics of surfactants at the interface can be determined. On the other hand, small modifications in the equilibrium configurations of the already simulated systems enable us to perform simulation studies on an interesting group of surfactants, and

thus provide the opportunity to model the behavior of the so-called cationic surfactants at the water/air interface.

PUBLICATIONS

Related publications in peer-reviewed journals:

1. Nóra Abrankó-Rideg, George Horvai, Pál Jedlovsky

„Structure of the Adsorption Layer of Various Ionic and Non-Ionic Surfactants at the Free Water Surface, as Seen from Computer Simulation and ITIM Analysis”

Journal of Molecular Liquids, 2014, in press Impact factor: 1,684 (2012)

2. Nóra Abrankó-Rideg, Mária Darvas, George Horvai, Pál Jedlovsky

„Immersion Depth of Surfactants at the Free Water Surface. A Computer Simulation and ITIM Analysis Study”

J. Phys. Chem. B, 2013, 117 (29), pp 8733–8746. Impact factor: 3,607 (2012)

3. Nóra A. Rideg, Mária Darvas, Imre Varga, Pál Jedlovsky

„Lateral Dynamics of Surfactants at the Free Water Surface. A Computer Simulation Study”

Langmuir 28 (42) (2012), pp 14944–14953 Impact factor: 4,187 (2012)

Miscellaneous poster presentations

1. Nóra Rideg and Imre Varga

„Fluorescent Silica Nanoparticles: Effect of Synthesis Conditions on the Dye Incorporation into the Silica Particles”

Euro Nano Forum (2011), Budapest

2. Rideg Nóra, Varga Imre

„A reakciókörülmények hatása a fluoreszcens szilika nanorészecskék tulajdonságaira”

MKE 1. Nemzeti Konferencia, (2011), Sopron

3. N. Rideg, T. Gilányi, I. Varga

„Optimization of the Fluorescent Dye Incorporation into Silica Nanoparticles”

XIVth International Symposium on Fluorescence Spectrometry – Recent advances of luminescence techniques in research and modern technology; (2010), Prague, p.:147.