

Colloid chemical applications of computer simulation methods

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PhD thesis summary

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1. Introduction and purpose of the study

Computer simulation has become an essential tool in the fields of chemistry and condensed matter physics in the past decades. Studying the atomic motions and interactions by computer simulation enables us to explain and interpret experimental findings. Simulations provide deeper insight into atomic processes. Due to the increasing computational capacity, a great number of chemical and physical properties have become predictable. In particular, such predictions in case of novel materials have great importance in nanotechnology and pharmaceutical research.

In case of colloid systems the computational approach can be even more useful. Colloid systems are usually difficult to study experimentally, because their physical properties are very sensitive to external conditions such as temperature, composition or contaminants. In most cases only indirect measurements can be performed. The interpretation of experiments often relies on assumptions and models, thus computer simulations provide important details that enable us to explain the results and extend our knowledge of colloid systems.

During my PhD, I studied two different kinds of colloidal systems. We used molecular dynamic simulations to study the properties of several liquid/vapour and liquid/liquid interfaces as well as the aggregational properties of a group of amphiphilic molecules, the bile acids.

The main aim of our work on fluid/fluid interfaces was to develop a method capable of determining the truly interfacial molecules in computer simulations. This method enables us to study surface properties in detail, moreover, the roughness of surfaces can also be studied. We applied our new method to study the liquid/vapour interface of water, water-methanol and water-acetonitrile mixtures and the liquid/liquid interface the water/carbon-tetrachloride system. We calculated the distribution of surface molecules along the surface normal axis, the ratio and distribution of the different components in the surface layer of the mixtures, as well as the dynamical, orientational and hydrogen-bonding properties of the surface molecules.

Bile acids are among the most important biological surfactants, they act as

emulsifiers of lipids and fat-soluble compounds in the living cell. Due to their unusual shape and special structure, the properties of the bile acids differ from that of the common aliphatic surfactants: they have a stepwise aggregation process, and their micelle-size distribution is wider¹. Bile acids have been in the focus of research for several decades, but the different aggregation models developed on the basis of experimental results are contradictory and the role of different interactions in the micelle formation has not been clarified. During our work, we studied the aqueous solutions of two bile acid salts, sodium cholate and sodium deoxycholate at three different concentrations. We studied the role of hydrophobic and hydrogen-bonding interactions in the aggregation process, the structural and morphological properties of the micelles and the relative orientation of the bile ions within the aggregates. Finally, we also studied the properties of the counterion and we calculated the degree of counterion binding.

2. Results

The most relevant results presented in the thesis can be summarised as the following.

2.1. Study of vapour/liquid and liquid/liquid interfaces

1. The basis of our new method ITIM (Identifying the Truly Interfacial Molecules) is the detection of the interfacial molecules by scanning the surface with test spheres. The test spheres determine the covering sheet of the surface and the molecules touching a test sphere are identified as interfacial ones.
2. By determining the covering sheet of the surface, its roughness can also be characterised. We demonstrated two ways of performing this: calculating (i) the two dimensional distribution of the normal distance of the surface

¹D. M. Small *The Physical Chemistry of Cholic Acids. In Chemistry; The Bile Acids* Vol. 1 (Plenum Press: New York, 1971)

points as a function of their lateral distance, and (ii) the projection of this function, i.e. the distribution of the average normal distance as a function of the lateral distance. The main properties of this function characterise the surface roughness with an amplitude and a frequency like parameter.

Study of the liquid vapour interface of water and the liquid/liquid interface of the water/carbon-tetrachloride systems

3. The density distribution of the surface molecules along the surface normal axis can be characterised by a Gaussian function, indicating that these molecules are symmetrically distributed around the macroscopic plane of the surface.
4. Besides what was found in previous studies ^{2,3}, we identified a new preferred orientational alignment of water molecules that are at the valleys of the molecularly rough surface. Considering all the preferred orientational alignments, we concluded that the orientation of the molecules strongly depend on the local curvature of the surface, in order to maximise the number of possible hydrogen bonds among the surface water molecules. We did not find any orientational preference in the second layer beyond the surface.
5. In the surface layer, water molecules form percolating hydrogen-bonded clusters, in which the majority of the molecules are involved. However, we found that this strong percolation weakens in deeper layers beyond the surface.
6. We found the properties of the liquid/liquid interface of the water/carbon-tetrachloride system very similar to that of the liquid/vapour interface of water, thus we concluded that the apolar phase has only weak influence on the properties of surface water molecules.

²J. Chem. Phys. **117**, 2271 (2002)

³Phys. Chem. Chem. Phys. **6**, 1874 (2004)

7. The study of dynamical properties showed that carbon-tetrachloride molecules remain in the surface layer for longer than water molecules. Both type of molecules has shorter average residence time in the second layer beyond the surface than in the surface layer.

The study of the liquid/vapour interface of water-methanol mixtures

8. The calculation of the composition of the surface layer showed that the ratio of methanol molecules is larger in the surface region than in the bulk. However, the methanol content of the second layer does not differ from that of the bulk phase. The roughness of the surface increases with the methanol concentration.
9. The preferred orientational alignments of the water molecules do not differ from the ones found at the liquid/vapour interface of neat water, but at the tip of the molecularly rough surface water molecules with perpendicular alignment disappear, as their hydrogen-bonding role is substituted by methanol molecules. The orientation of methanol molecules does not change with the concentration, the methyl group points straight to the vapour phase.
10. The surface residence time of both components shrinks with larger methanol concentration. The average residence time of methanol molecules are always larger than that of the water in the surface layer, while these values are the same for both components in a reference layer in the bulk phase, suggesting that the two species have different affinity to the surface. The presence of methanol molecules at the surface is favourable because of their hydrophobic property, while the hydrogen-bonding possibilities are better in the bulk phase for the water molecules.
11. The distribution of molecules is inhomogeneous in the surface layer, methanol molecules preferably stay at the tips of the molecularly rough surface, while water molecules prefer to stay in the wells. The two dimensional Voronoi analyses of the surface molecules showed that the component present in smaller concentration forms aggregates.

The study of the liquid/vapour interface of water-acetonitrile mixtures

12. The concentration of the acetonitrile molecules is larger in the surface layer than in the bulk phase, and their adsorption is stronger than in case of methanol. The composition of the second layer differs from that of the bulk phase, the ratio of the acetonitrile molecules is larger. The roughness of the surface increases with increasing concentration.
13. The preferred orientational alignment of the acetonitrile molecules is determined by dipole-dipole interactions, the molecules are aligned such that their dipole vectors point to the opposite direction. The orientational preferences of the water molecules differ from the systems studied previously. Due to the fact that the water content of the surface layer is low, and the acetonitrile molecules can only act as acceptors in hydrogen-bonding, the orientation of the water molecules is also determined by dipole-dipole interactions. A weak orientational preference can be observed also in the second layer of molecules.
14. The residence time of the water molecules is an order of magnitude smaller than for acetonitrile molecules, and the average residence time shrinks with increasing concentration for both compounds.
15. We found that the distribution of molecules is inhomogeneous in the surface layer, the component present in smaller concentration forms aggregates.

2.2. Study of the aqueous solution of bile acid salts

Aggregational properties, the structure of micelles

16. We observed the stepwise aggregation in case of the solution of both studied bile acid salts: although the size distribution of the hydrophobically and hydrogen-bonded clusters does not change significantly with the concentration, at higher bile ion content these micelles bound to each other forming much larger aggregates.

17. At smaller concentration the deoxycholate ions prefer to form hydrophobically bound micelles, the probability of finding a hydrogen-bonded cluster is small. Nevertheless, even at higher concentrations the number of hydrogen bonds is small, those are enough to connect the primary micelles together. In contrary, in cholate systems the hydrogen-bonded clusters are already present at smaller concentrations. We found that the average size of secondary clusters is larger in case of cholate ions.
18. By studying the dynamical properties, we concluded that the average lifetime of cholate micelles is longer than that of the deoxycholate ones. In average, a cholate ion is bound to a micelle for 2–3 ns, while this value is only 1 ns for deoxycholate ions. The lifetime of monomers is smaller in the cholate systems. The average lifetime increases with increasing concentration in case of both ions.
19. The relative orientation of the bile ions within the micelle showed that the hydrophobic pairs are either parallel to each other or tilted by 60° depending on whether they form a dimer or a trimer. They prefer to form head-to-head or head-to-tail pairs, thus their carboxylic groups point to the same or opposite directions. In the hydrogen-bonded pairs, the bile ions turn to each other with their hydrophilic sides, the planes of the steroid rings are parallel. In order to maximise the number of hydrogen bonds, the cholate ions prefer to stay in head-to-tail alignment and they get tilted in higher concentrations. Because of the lack of one OH group in the deoxycholate ion, the parallel alignment is not favoured in these systems.
20. The morphological study of the micelles showed that the structure of the secondary micelles varies in a wide range: as well as spherical micelles, both oblate and prolate shaped aggregates can be observed.

Counterion binding

21. The distribution of Na^+ counterions around the micelles showed that the counterions stay within two preferred distances from the aggregates, the contact bound ions are closer than 3.1 \AA , while the solvent separated ones are further, at 5.4 \AA .
22. Our results showed that the counterions are bound for longer time to the cholate ions than to the deoxycholate ones, and the lifetime of bonding increases with increasing concentration.
23. We found that the counterion binding increases with increasing concentration, and at smaller concentration it is larger for the cholate system, while at 300 mM it is larger for the deoxycholate. There is almost an order of magnitude difference between the obtained values of counterion binding, depending upon whether the solvent separated counterions are excluded from the analysis or not. These results show a good agreement with different experimental findings^{4,5}, indicating that the different experimental techniques do not necessarily measure the solvent separated counterions as bound ones. This explains the big differences between different experimental counterion binding results.

3. Papers published in the subject of the thesis

1. A new method for determining the interfacial molecules and characterizing the surface roughness in computer simulations. Application to the liquid-vapor interface of water Pártay LB, Hantal G, Jedlovsky P, Vincze Á, Horvai G *J. Comp. Chem.* **29**, 945 (2008).
2. Properties of free surface of water–methanol mixtures. Analysis of the truly interfacial molecular layer in computer simulation Pártay LB, Jedlovsky P,

⁴Biochim. Biophys. Acta **189**, 1580 (2002)

⁵J. Phys. Chem. **97**, 10186 (1993)

- Vincze Á, Horvai G *J. Phys. Chem. B* **112**, 5428 (2008).
3. Molecular level structure of the liquid/liquid interface. Molecular dynamics simulation and ITIM analysis of the water-CCl₄ system
Pártay LB, Horvai G, Jedlovszky P *Phys. Chem. Chem. Phys.* **10**, 4754 (2008).
 4. Structure of the liquid-vapor interface of water-acetonitrile mixtures as seen from molecular dynamics simulations and ITIM analysis Pártay LB, Jedlovszky P, Horvai G *submitted*
 5. Molecular aggregates in aqueous solutions of bile acid salts. Molecular dynamic simulation study Pártay LB, Jedlovszky P, Segá M *J. Phys. Chem. B* **111** 9886 (2007).
 6. Morphology of Bile Salt Micelles, as Studied by Computer Simulation Methods Pártay LB, Segá M, Jedlovszky P *Langmuir* **23** 12322 (2007).
 7. Counterion binding in the aqueous solutions of bile acid salts, as studied by computer simulation methods Pártay LB, Segá M, Jedlovszky P *Langmuir* **24**, 10729 (2008).

Papers published during the PhD, but not included in the thesis

8. Determination of the adsorption isotherm of methanol on the surface of ice. An experimental and grand canonical Monte Carlo simulation study Jedlovszky P, Pártay L, Hoang PNM, Picaud S, von Hessberg P, Crowley JN *J. Am. Chem. Soc.* **128** 15300 (2006).
9. Counterion and surface density dependence of the adsorption layer of ionic surfactants at the vapor-aqueous solution interface: A computer simulation study Hantal G, Pártay LB, Varga I, Jedlovszky P, Gilányi T *J. Phys. Chem. B* **111** 1769 (2007).

10. Formation of mesoscopic water networks in aqueous systems Pártay LB, Jedlovszky P, Brovchenko I, Oleinikova A *Phys. Chem. Chem. Phys.* **9** 1341 (2007).
11. Percolation transition in supercritical water: A Monte Carlo simulation study Pártay LB, Jedlovszky P, Brovchenko I, Oleinikova A *J. Phys. Chem. B* **111** 7603 (2007).
12. Free-energy profile of small solute molecules at the free surfaces of water and ice, as determined by cavity insertion widom calculations Pártay LB, Jedlovszky P, Hoang PNM, Picaud S, Mezei M *J. Phys. Chem. C* **111** 9407 (2007).
13. Structure of coexisting liquid phases of supercooled water: Analogy with ice Jedlovszky P, Pártay LB, Bartók AP, Garberoglio G, Vallauri R *J. Chem. Phys.* **126** 241103 (2007).
14. Behavior of molecular oxygen at the liquid–liquid interface: A molecular dynamics simulation study Vincze Á, Jedlovszky P, Pártay LB, Horvai G *Chem. Phys. Lett.* **457**, 78 (2008).
15. Structural and thermodynamic properties of different phases of supercooled liquid water Jedlovszky P, Pártay LB, Bartók AP, Garberoglio G, Vallauri R *J. Chem. Phys.* **128**, 244503 (2008).