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ORIGINAL CONTRIBUTION

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Molecular orientation of monododecyl pentaethylene glycol at water/air and water/oil interfaces. A molecular dynamics computer simulation study

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Abstract With a molecular dynamics computer simulation we investigated the dynamic properties of a monododecyl pentaethylene glycol ($C_{12}E_5$) molecule adsorbed at air/water and oil/water interfaces. In these simulations we investigated the molecular orientation of the surfactant molecules in detail. At the air/water interface the maximum of the C_{12} chain tilt angle distribution measured with respect to the water surface is about 50°. This result is in fairly good agreement with neutron reflection experiments of monododecyl glycol ethers at the air/water interface. At the oil/water interface no significant changes were detected in the molecular orientation. We found that at equilibrium oil molecules penetrate into the hydrophobic monododecyl layer, this was also found by neutron reflection studies of the interactions between $C_{12}E_5$ and dodecane. The observed oil penetration results in an increase in the surface area per surfactant molecule.

Key words Molecular dynamics simulation · Nonionic surfactants · Interfaces

Introduction

Monomolecular films are two-dimensional layers of amphiphilic molecules spread on the water surface. These monolayers are widely used in technical applications, such as in emulsions and detergents. Consequently, molecules assembled at the air/water (AW) and water/oil interfaces as well as Langmuir–Blodgett films which consist of surfactants aggregated on solid surfaces are subjects of great interest.

In the case of the AW interface the structure of monomolecular films and the understanding of the phase behaviour are often based on the characteristics of the Π/A isotherm, where Π is the surface pressure and A is the area per surfactant molecule at the interface. Insoluble surfactants show transitions from the gas phase via a liquid expanded to a liquid condensed phase if the surface pressure is increased. The gas phase corresponds to the situation when the surfactant concentration is very low and the surfactants are widely distributed at the interface. At high surface pressures the surfactants are densely packed and a solid phase appears. Film collapse results from further increasing the surface pressure. Conversely, water-soluble surfactants move into the water phase with increasing surface pressure.

Because the monomolecular film is composed of a two-dimensional layer of surfactants, this aggregate can be characterized by parameters on a molecular dimension. The forming of different phases can be well described by the orientation of the hydrophobic alkyl chains, which is called the tilt angle. At infinite dilution of the surfactants at the interface it can be assumed that the molecules lie almost flat on the surface with a small tilt angle with respect to the water surface. With inreasing film compression to the liquid expanded and liquid condensed phases the molecular area of the surfactants becomes smaller and the tilt angle increases.

In order to investigate the molecular structure of surfactant monolayers experimental methods such as fluorescence microscopy, small-angle X-ray scattering and neutron diffraction were developed. With Brewster-

angle-microscopy techniques the domain structures in surfactant monolayers at the AW interface can be visualized [1]. Recently neutron reflection experiments of tri-, penta-, hexa- and octaethylene glycol monododecylether adsorbed at the AW interface were published [2–5]. New insights into the molecular structures of these glycol ether surfactants, such as chain orientation, were obtained. These investigations revealed that at a surfactant concentration in the range of the critical micellization concentration (cmc) the hydrophobic alkyl chains are tilted by about 50° with respect to the water surface. In the regime of small concentrations the molecules were found to lie almost flat on the water surface [2].

Due to the rapid development of computer performance in the last few years it has been possible to apply the molecular dynamics simulation method to problems of surfactant monolayers at the AW interface [6–31]. Besides model surfactants representing fatty acids, the simulated monolayers consisted of sodium dodecyl sulfate [23] hexadecyltrimethylammonium chloride/bromide [24, 25], phenol and *p*-*n*-pentylphenol, *N*,*N*′-diethyl-*p*-nitroaniline [26, 27, 29] and 1-hexanol/water mixtures [28].

Recently, we investigated the orientation of glycol and hydrophobic alkyl chains of monododecyl pentaethylene glycol ($C_{12}E_5$) on the water surface by performing molecular dynamics simulations [32]. In this work we used 25 surfactant molecules adsorbed at the water surface with a surface concentration of 0.55 nm^2/molecule. From these studies we concluded an average tilt angle of the dodecyl chains of about 47° measured with respect to the water surface. This average orientation angle agrees very well with experimental data [2–5]. In contrast to the nonpolar parts of the surfactant molecules the water-soluble glycol chains were aligned almost perpendicularly to the water surface with a tilt angle of approximately 79°. Within the time scale of our simulation the surfactant molecules were firmly attached at the surface with rather stiff glycol ether chains. The alkyl and glycol chain ends showed striking flexibility.

In addition to our previous simulation the present work contains important new results. In this paper we focus our attention on the molecular structure of $C_{12}E_5$ at the octane/water (OW) interface. Octane molecules were used to build an appropriate model for the oil phase. Recently Lu et al. [5] investigated the structure of $C_{12}E_5$ on the water surface with and without added dodecane. The authors found that the C_{12} chain changes to an almost perpendicular orientation to the surface upon incorporation of dodecane into the $C_{12}E_5$ layer.

In this work the influence on the tilt angle of the C_{12} chains was investigated in detail. The computer simulation provides new insights into two-dimensional monolayers at the water/oil interface.

Methods and theory

In order to calculate the intra- and interatomic interactions in the molecular dynamics simulation we used classical mechanics approximations. The potential functions and parameters assigned to each atom of the surfactant and octane molecules were taken from the AMBER forcefield [33–35]. The simple SPC point charge parameter set [36] was used for the calculation of the inter- and intramolecular energy functions of the water molecules. The temperature was held constant at 298 K by direct scaling of atomic velocities at subsequent simulation time steps.

In the simulation of surfactants at the AW interface the number of molecules was composed of 36 surfactant and 1575 water molecules arranged in a cubic box with periodic boundary conditions. The dimensions of the simulation box were $L_x = L_y = 4.44$ nm and $L_z = 8.0$ nm. In the coordinate system the *z*-axis was directed perpendicular to the surface. Intramolecular bond length constraints in combination with the RATTLE algorithm [37] were applied for the simulation of the surfactant molecules. Except for the bond lengths constraints, all possible changes in bond angles and dihedral angles in the surfactant molecules were allowed during the simulation run.

The intermolecular van der Waals interactions and electrostatic forces were truncated using a minimum image model with an energy cutoff of 1 nm for both types of interaction. According to the conventions in the AMBER forcefield, the nonbonded 1–4 interactions were scaled by 0.5. With the charge group approximation applied in the simulation we ensured that no artificial dipole splits disturbed the calculation of the nonbonded electrostatic energy. The inital water density was 1 g/cm^3. The surface area occupied by a surfactant molecule corresponded to 0.55 nm^2/molecule. $C_{12}E_5$ dissolves well in water with the effect that at the cmc interactions between surfactant molecules adsorbed at the surface and dissolved monomers in the bulk phase become dominant. In order to avoid these complications we simulated the system somewhat below the cmc, where A is 0.50 $\pm$ 0.03 nm^2/molecule [4].

After an initial minimization of the total potential energy, random velocities, according to a Gaussian distribution and a temperature of 298 K, were assigned to each atom. In order to integrate the Newtonian equations of motion for all atoms, we used the Verlet velocity integrator [38] with an integration time step of 2 fs. During a 500-ps simulation we allowed the system to equilibrate. An additional 500-ps molecular dynamics simulation was performed for the final data collection run. Finally, structure data were obtained from averaging the atomic Cartesian coordinates collected in this 500-ps simulation.

The OW system consisted of 36 $C_{12}E_5$ surfactants, 1392 water molecules and 143 octane molecules. The difference to the AW simulation was the application of no bond length constraints. Consequently, the simulation time step in the Verlet velocity integrator scheme was reduced to 1 fs. The total simulation time was 1071 ps with a data collection period in the range 811–1071 ps. The OW simulation was performed at a constant pressure of 10^5 Pa and a constant temperature of 298 K.

We performed the molecular dynamics calculations on an IBM SP2 parallel computer with eight processors. The trajectory data were calculated using the DISCOVER [39] molecular dynamics program.

Results and discussion

For further discussion of the simulation results the numbering of the carbon and oxygen atoms in the surfactant molecule is given in Fig. 1.

The evaluation of the tilt angle of the C_{12} chain at the AW and OW interfaces requires an appropriate defini-

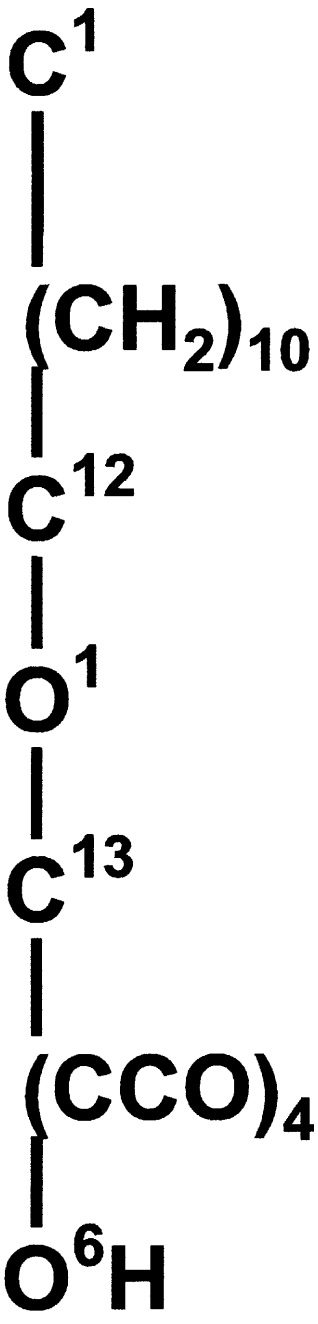

Fig. 1 Numbering of carbon and oxygen atoms in the monododecyl pentaethylene glycol ($C_{12}E_5$) surfactant molecule

tion of the water surface. For the AW and OW systems the average concentration profiles of specified atoms in the z-direction of the simulation box, $\langle c_z \rangle$, are summarized in Figs. 2 and 3.

$\langle c_z \rangle$ was calculated using Eq. (1).

$$\langle c_z \rangle = \frac{\Delta N_i}{N_A V_{Box}} \quad . \tag{1}$$

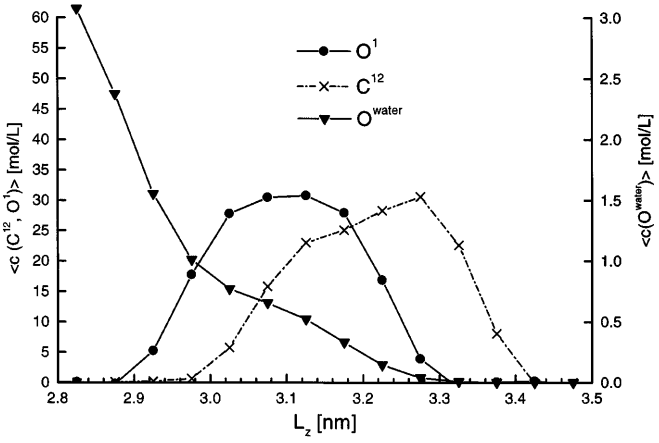

Fig. 2 Average concentration profiles of O^1, C^{12} and O^{water} atoms in the z-direction of the simulation box representing the water surface normal

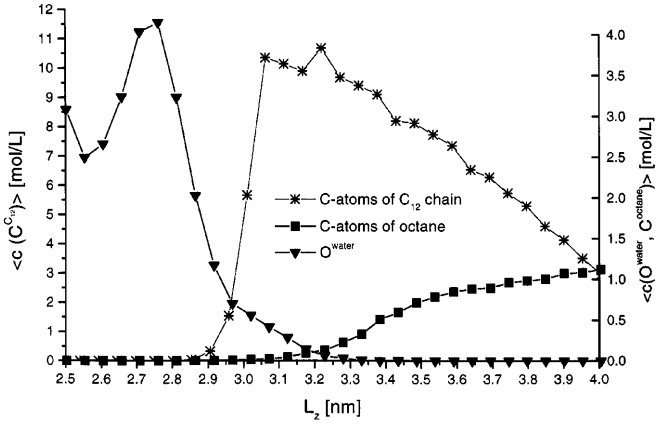

Fig. 3 Average concentration profiles of O^{water}, carbon atoms of the C_{12} chain and carbon atoms of octane molecules in the z-direction of the simulation box representing the water surface normal

ΔN_i is the amount of a specific atom, i, located in a small volume interval, $\Delta V = \Delta L_z \times L_y \times L_x$ ($\Delta L_z = 50$ pm). N_A is Avogadro's constant and V_{Box} is the total volume of the simulation box.

From Fig. 2 it is evident that the average water oxygen concentration decreases to zero at about 3.3 nm. Schweighofer et al. [23] have proposed the construction of the interface plane where the water density reaches a value of half the water bulk density. Following this suggestion we define the water surface by a plane lying between 2.9 and 3.3 nm constructed by the best fit of all water oxygen atom positions in this range. The water surface was recalculated with every stored configuration in the trajectory since the number of water molecules as well as their positions changed with every simulation time step. During the simulation the total water density changes slightly to 0.926 g/cm^3 and remains stable

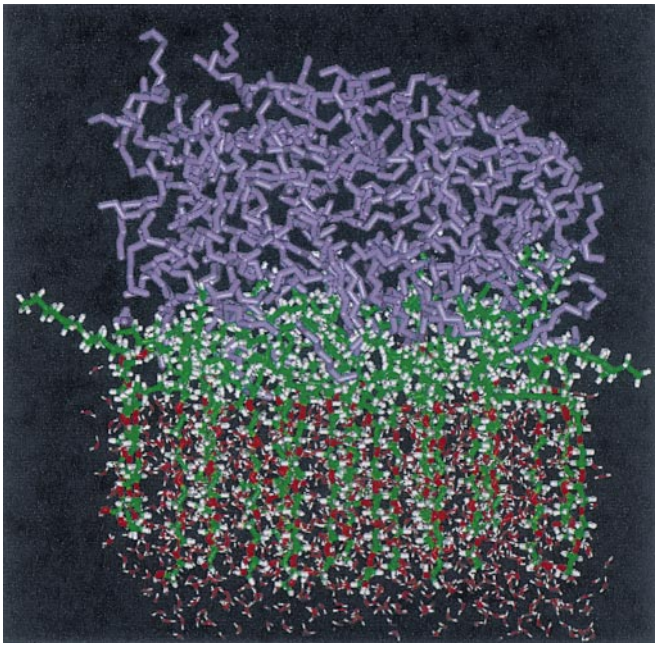

Fig. 4 A representative molecular structure of $C_{12}E_5$ surfactant molecules adsorbed on the oil/water (OW) interface. The atomic Cartesian coordinates were extracted from the trajectory at a simulation time of 900 ps

during the simulation. The C^{12} carbon atoms as well as the O^1 atoms participate in the water surface since these atoms tend to be concentrated in the interface region.

The average concentration profiles of the carbon atoms of the C_{12} chain, the carbon atoms of octane molecules and the oxygen water atoms are plotted in Fig. 3. The essential result is that the C_{12} and octane concentrations coincide from 3.0 nm. This effect leads to the conclusion that octane molecules penetrate into the C_{12} layer. Furthermore, the octane and water phases are in contact.

This penetration phenomenon can be directly observed from a picture of the molecular structure extracted from the trajectory of the OW system at the simulation time of 900 ps (Fig. 4).

The molecular orientation of the hydrophobic C_{12} alkyl chain was determined by evaluation of the average tilt angles, $\langle\varphi\rangle$, of the C_{12} chains. The tilt angles were calculated from angles between appropriate vectors and the water surface. The tilt angle definition is obvious in Fig. 5.

A distance vector was constructed between the C^{12} and C^1 carbon atoms. The tilt angle distribution is presented in Fig. 6.

From a comparison of the AW and OW simulations, it seems that no significant difference appears between the molecular orientation of the hydrophobic C_{12} chain at the AW and OW interfaces. This result is contrary to the results of experimental investigations of the interaction of $C_{12}E_5$ and dodecane. Neutron reflection measurements suggest a more upright arrangement of the C_{12} chains if dodecane penetrates into the C_{12} layer [5]. It has to be remarked that the difference between our result and the neutron reflection experiment can be explained by the fact that the simulation of the OW system was performed under constant pressure, whereas the AW system was simulated with constant volume. The result is an increase in the average surface coverage to $\langle A\rangle = 57.58 \pm 0.23$ for the OW system. In order to get a reliable comparison of the C_{12} tilt angle between the OW and AW systems the AW simulation with constant volume using the same average A value is required; this work is still in progress. However, in the AW system the maximum tilt angle of about 50° is in very good agreement with the experimentally measured

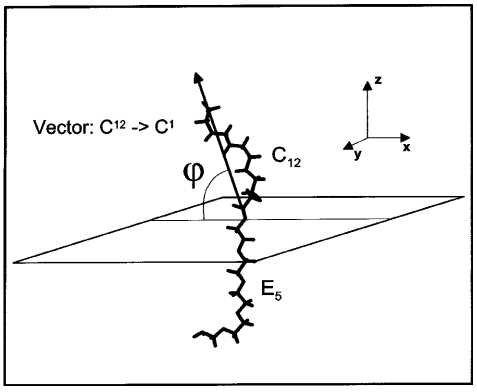

Fig. 5 Definition of the tilt angle of the hydrophobic C_{12} chain

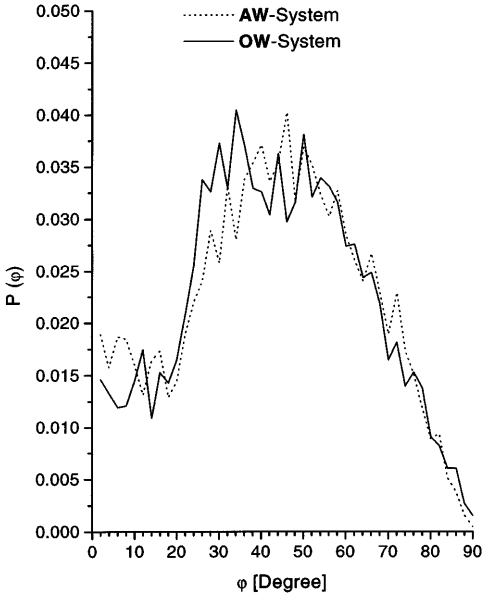

Fig. 6 Normalized tilt angle distributions calculated from the air/water (AW) and OW simulation

tilt angle values of the $C_{12}E_m$ series ($m < 6$) [5]. Furthmore, the penetration of octane in the direction of the water surface has been confirmed by experimental observations using dodecane as the oil phase [5].

Conclusion

The molecular orientation of the hydrophobic C_{12} chain of 36 $C_{12}E_5$ molecules adsorbed at the AW and OW interfaces has been studied with a molecular dynamics computer simulation. We have found that the maximum of the average tilt angle at the AW interface is approximately 50°. This result is in fairly good agreement with neutron reflection experiments of $C_{12}E_m$ ($m \leq 6$) surfactants at the AW interface. At the OW interface no significant changes were detected in the molecular orientation of the C_{12} chain. Furthermore, we concluded from average atomic concentration profiles that octane molecules penetrated into the hydrophobic C_{12} layer. This result is in accordance with neutron reflection studies of $C_{12}E_5$ and dodecane, where an increase in the surface area per surfactant molecule due to the penetration of oil molecules into the hydrophobic surfactant layer was detected.

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