

Structural changes of a sodium dodecyl sulfate (SDS) micelle induced by alcohol molecules

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Abstract Coarse-grained dynamical simulations have been performed to investigate the behavior of a surfactant micelle in the presence of six different alcohols: hexanol, octanol, decanol, dodecanol, tetradecanol, and hexadecanol. The self-assembly of sodium dodecyl sulfate (SDS) is modified by the alcohol molecules into cylindrical and bilayer micelles as a function of the alcohol/SDS mass ratio. Therefore, in order to understand, from a molecular point of view, how SDS and alcohol molecules self-organize to form the new micelles, different studies were carried out. Analysis of micelle structures, density profiles, and parameters of order were conducted to characterize the shape and size of those micelles. The density profiles revealed that the alcohol molecules were located at the water–micelle interface next to the SDS molecules at low alcohol/SDS mass ratio. At high alcohol/SDS mass ratios, alcohol molecules moved to the middle of the micelle by increasing their size and by producing a structural change. Moreover, micelle structures and sizes were influenced not only by the alcohol/SDS mass ratio but also by the order of the SDS and alcohol tails. Finally, the size of the micelles and enthalpy

calculations were used as order parameters to determine a structural phase diagram of alcohol/SDS mixtures in water.

Keywords Alcohol/surfactant mixtures · Structural transitions · Coarse-grained molecular simulations · Bilayer and double bilayer structures

Introduction

It is well known that amphiphilic molecules in aqueous solution give rise to different phases such as micelles, bilayers, vesicles, etc. [1] and their structures depend on temperature, concentration, or by the presence of additives such as alcohols, polymers, surfactants, etc. In particular, it has been observed that the adsorption of alcohol molecules in biological membranes (cell membrane) influences their structure and functions. For instance, Ly et al., in an experimental study, investigated the ability of ethanol to alter mechanical and structural properties of a lipid bilayer and how short-chain alcohols (from methanol to butanol) increase the area per molecule and membrane thickness [2]. On the other hand, due to the anesthetic potency, alcohols have been used in pharmaceutical applications to study the mechanism of anesthesia. Klacsová et al. [3], in combined small-angle neutron-scattering experiments and coarse-grained simulations, studied structural parameters such as bilayer thickness and interfacial areas of vesicles with long alcohol chains (C_nOH , $n = 8 - 18$). They found that the polar region thickness of the bilayers decreases as a function of the alcohol chain length [3]. They also found, from scattering experiments, that the phase transition temperature decreases with the alcohol chain length and concentration [4]. Then, they suggested that the variations in the bilayer thickness can be due to the differences in the alcohol and lipid chain

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lengths. In another combined simulational-experimental work, Griepner et al. [5] studied the effects of 1-alkanols (up to tetradecanol) in lipid membranes. They found that the use of long alcohols reduces the area per lipid while the bilayer thickness and the order of the lipids increase. In contrast, a short alcohol, such as ethanol, increases the area per lipid and reduces the bilayer thickness [5].

Besides the experiments, theoretical works have also investigated alkanols in bilayers. Cantor, using statistical thermodynamics, studied how alkanols (from chain lengths $n = 1 - 18$) modify lateral pressure profiles in bilayers [6]. Dickey and Faller [7], using coarse-grained and atomistic simulations of dipalmitoylphosphatidylcholine (DPPC) and butanol, have shown how alcohol molecules enter the membrane and how the area per molecule increases with the alcohol concentration. Some other authors have studied the effects of butanol adsorption in distearoylphosphatidylcholine (DSPC) by mesoscopic models (such as the dissipative particle dynamics, DPD) by reproducing the experimental phase diagram [8]. On the other hand, coarse-grained models have also been used to study lipid droplets to understand biological systems. Simulations of droplets composed of different lipids, triolein, and cholesterol have shown how those last two components form a liquid phase inside the droplet core with few molecules at the lipid interface [9, 10].

It has found that SDS micelles doped with hexanol present different phases, spherical, cylindrical and bilayers micelles, which can be arranged in lamellar, sponge or vesicular geometries [11–13]. The lamellar phase is an anisotropic arrangement of parallel stacking of bilayers separated by a solvent layer [11, 14] whereas the sponge and vesicular phases are isotropic. Moreover, the sponge structure is a random array of multiply continuous connected surfaces in three dimensions, i.e., the structure can be pictured as a porous media [11, 12, 15] whereas the vesicle phase can be seen as closed aggregates.

In the present paper, we are interested in the interaction of a SDS surfactant micelle with different alcohols. The relevance of these studies is important not only from the scientific point of view (to understand the properties of lamellar surfactant phases doped with alcohol molecules) but also for the several industrial applications (detergency, oil industry, emulsification, etc.). Moreover, the present results will help us to understand better more complex systems such as surfactant/alcohol/brine mixtures in the presence of polymers. In the literature, experiments on SDS/alcohol mixtures have been conducted to study conductivity, scattering relaxation times, bending elastic modulus [13, 16] and phase diagrams [12, 17, 18]. In particular, in references [12] and [18] the phase diagrams of the SDS/*n*-hexanol/brine and SDS/decanol/water systems are shown, respectively. However, information about the phase behavior over a wide

interval of alcohol compositions and alcohol chains has not been extensively analyzed. Moreover, the structure of those mixtures has not been studied in detail. For instance, we want to know where the SDS and alcohol molecules are located in the mixture and how those molecules interact with each other to form different structures.

Therefore, in this work, we have conducted computer simulations to obtain more information, from a molecular level, about the structure of the molecules in the mixture and how different alcohol chains modify those structures. Finally, with the information obtained from the micelles structures and sizes, a phase diagram was constructed as a function of the alcohol/SDS mass ratio. Bilayer systems can be conducted using atomistic simulations if micelles sizes are not too big. However, since information about phase behavior can take relatively long time, atomistic simulations might be very long, therefore we decided to use a coarse-grained model for the present simulations.

Computational model

Simulations of SDS and alcohol mixtures were carried out with the coarse-grained (CG) model developed by Marrink et al. [19] where several atomistic sites correspond to one coarse-grained site. Compare to atomistic approaches coarse-grained models are less accurate to obtain physical properties since they do not consider the exact molecular structure of molecules and they handle differently the long-range interactions. However, structural properties are well reproduced in most of the cases. Then, the martini force field has been used for instance in lipid systems (where molecules are composed of one hydrophilic and one hydrophobic part) to study the structure of lipid micelles [9, 10]. Surfactants and alcohols are also molecules with hydrophilic and hydrophobic parts as lipids and then, parameters for those molecules have been also developed in the same martini force field. In the hexanol and octanol molecules, the mapping from atomistic to CG model was three-to-one and four-to-one, respectively, as used in previous works [3]. Similar mapping was used for the other alcohol molecules, for decanol and dodecanol was three-to-one and four-to-one, respectively, and for tetradecanol and hexadecanol was three-to-one and four-to-one, respectively, [3, 20]. In the case of three-to-one mapping, the beads had a mass of 54 amu per site, whereas for the four-to-one, the beads had a mass of 72 amu per site. In fact, those alcohol coarse-grained models have good agreement when they are compared with neutron scattering experiments of alcohol on fluid bilayers [3]. In this model, a water CG site represents four atomistic molecules. As discussed in previous papers, to avoid freezing of the CG water, antifreeze molecules were introduced in the simulations [19, 21]. The

parameters used in the simulations are given in the supplementary information (Tables 1 and 2).

For the charged sites, a shifted Coulombic potential with the same dielectric constant, $\epsilon_r = 15$, discussed in previous papers [19] was used. The large value of $\epsilon_r = 15$ was introduced in the CG model to account for the appropriate screening due to the missing electrostatic properties of water. Previous works have suggested the possibility of using a polarizable water model to overcome the situation in the same CG approach, where the dielectric constant is $\epsilon_r = 2.5$ [22]. For instance, that model has been tested in a lipid membrane system by observing differences in electrostatic properties compared with the standard model, however, the structural properties do not show significant changes [22]. Another CG model, which considers a water dipole moment, has been developed to simulate lipid membranes where explicit charges and dipoles sites are included [23]. In those simulations, the relative dielectric constant $\epsilon_r = 1.0$. In the present study, we are interested mainly in structural properties, therefore, we consider that the standard martini force field is appropriate for our simulations.

Previous simulations have reported a stable SDS micelle with 60 molecules [24, 25]. Therefore, simulations were conducted to have a single micelle of 60 SDS molecule, i.e., only one micelle structure. Simulations with 120 and 180 SDS molecules were also carried out and the formation of one micelle with a cylindrical-like shape was observed in both cases. Since both systems were in the micellar region, those structures might also be found. However, since we did not find experimental available data to compare with this structure, it was difficult to identify if it was a real structure. Therefore, the analyses were conducted for the system with the spherical micelle since it is a stable structure [24, 25]. Then, the first simulations were conducted with 60 SDS molecules in 3500 CG water molecules located in a rectangular box of dimensions 5 nm \times 5 nm \times 20 nm. It is observed that SDS molecules formed a spherical micelle with radius of gyration and micelle radius of $R_g = 1.50$ nm and $R_s \approx 1.94$ nm (obtained from $R_s = R_g \sqrt{5/3}$ [21, 26]), respectively. The micelle radius was in agreement with previous simulations (1.99 nm [27], 2.09 nm [24], 2.03 nm [21]), and experimental results (1.81 nm [28]).

As stated before, simulations were conducted to have a single micelle, i.e., only one structure was depicted in the simulations. This could be a limitation of the system if direct comparisons with actual experiments are attempted. Nevertheless, some insights about the micelle behavior and the micelle structure can be given.

With the spherical SDS micelle already formed, different alcohol molecules at several alcohol/SDS mass ratios were added randomly in the system. In order to have similar experimental conditions, all mixtures were defined in terms of mass ratio, i.e., alcohol mass divided by SDS mass. In all

the simulations, the amount of water molecules was sufficient to have a bulk phase in all the systems (see the density profile results).

In all simulations, GROMACS package version 4.5.4 was used [29]. As it mentioned above, antifreeze particles were used in 10 % by changing water site parameters, P4 to BP4 [19, 21]. The nonbonded interactions were calculated with a cut-off radius of $r_{\text{cut}} = 1.2$ nm and the LJ potential was switched from $r_{\text{shift}} = 0.9$ to r_{cut} . The electrostatic potential was shifted from $r_{\text{shift}} = 0.0$ to r_{cut} [19]. Simulations were carried out in the NPT ensemble with temperature $T = 298.15$ K and pressure $P = 1$ bar using the Nosé–Hoover thermostat and Parrinello–Rahman barostat [30] with temperature and pressure relaxation time constants of $\tau_T = 2.5$ ps and $\tau_P = 8.0$ ps, respectively. Simulations were performed with a time step of 10 fs and they were run for a total time of 2 μ s, however, for some states, simulations were run up to 4 μ s.

Results and discussion

In this section, the results for the structure and phase behavior of the SDS/alcohol/water systems were analyzed. Simulations were conducted at constant number of surfactant and water molecules whereas the number of alcohols were changing. Therefore, the relative composition of each component in the systems is different with the amount of alcohol. For instance, for simulations of the SDS/decanol/water systems, the compositions (in weight percent) were; 5.4–6.4% for SDS, 0.82–16.2% for decanol and 78.5–92.8% for water. In the literature, an experimental phase diagram of the same mixture was found [18], however, those data are given for a different region of compositions. Nevertheless, using that phase diagram and with the calculated compositions, the mixtures seemed to be in the micellar (L_1) phase. It is worthy to mention that even though the relative composition of water was changing, by the addition of the alcohol, the mixtures seem to remain in the same micellar phase.

In the literature, experiments of a SDS/hexanol/brine system (for small SDS and hexanol compositions, [11, 12]) were also found, which can be used to compare with the present results with hexanol. However, the experimental and the simulated composition regions do not exactly coincide each other. For these simulations, all compositions were very similar to those obtained with decanol (≈ 5.4 –6.4 %). In any case, the mixtures seem to be placed again in the micellar region (L_1) [11, 12].

Structure

As stated above, a spherical micelle of SDS molecules was formed at zero alcohol/SDS mass ratio and once alcohol

molecules were added, the shape of the micelle changed. For instance, the hexanol/SDS mixture formed a cylindrical shape at low alcohol/SDS mass ratios (see Fig. 1a) and a bilayer structure at higher mass ratios (see Fig. 1b). The cylinder shape was formed along the Y direction and we observed the cylinder diameter in the X-Z plane. It is worthy to mention that to the best of our knowledge, there are no reports of cylindrical micelle formation for these systems. From experiments of SDS/alcohol/water mixtures, a micellar phase (L_1) has been reported at low SDS and alcohol compositions, however, the structure of those micelles at very low compositions are not specified (spherical or cylindrical) [12, 18]. Therefore, it is not possible to affirm that the observed cylinders are actual structures or they could be unreal states due to the simulations, nevertheless those structures remained up to 4 μ s run. In fact, simulations with larger box dimensions were conducted and the cylinders were still observed. A possible justification for these structures can be given in terms of the experimental SDS phase diagram where cylindrical and planar micelles as function of the surfactant concentration have been observed [31]. Therefore, it could be that few alcohol molecules worked as co-surfactants by increasing the composition in the mixture and they help the formation of cylindrical geometries.

As a general feature, it was noted that the hexanol head groups were located next to the SDS head groups.

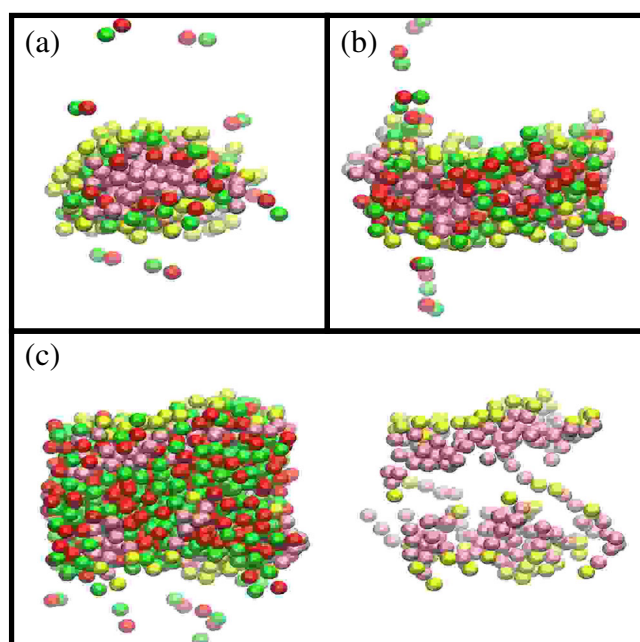


Fig. 1 Hexanol/SDS snapshots at alcohol/SDS mass ratios of **a** 0.250, **b** 1.000, and **c** 2.000. Yellow balls represent the SDS headgroups, pink balls the SDS tails, green balls the hexanol heads, and red balls the hexanol tails. Only SDS molecules are shown in the right of **c**. Water molecules are not shown for clarity of the figures

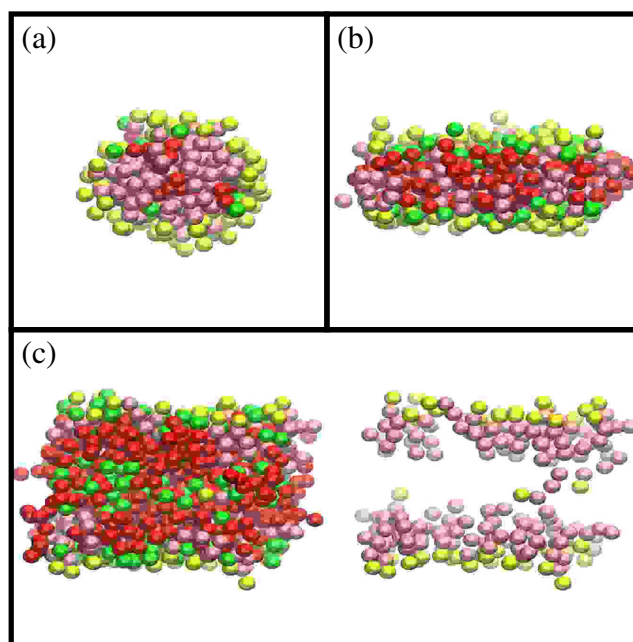


Fig. 2 Hexadecanol/SDS snapshots at alcohol/SDS mass ratios of **a** 0.375, **b** 1.000, and **c** 2.875. Notation is the same as in Fig. 1

Once the bilayer structure was formed, it remained until it was possible to distinguish a double bilayer structure (see Fig. 1c). The same structures were identified at different alcohol/SDS mass ratios when different alcohol molecules were used. In Fig. 2, snapshots of the hexadecanol/SDS mixture are shown for comparison with the hexanol/SDS mixture where it was possible to observe similar structures.

Density profiles

The structure of the surfactant/alcohol mixtures were analyzed in terms of density profiles along the z-direction, i.e., perpendicular to the interface. Typical plots are shown in Fig. 3 for the hexanol/SDS mixture. In that system, the formation of a bilayer structure from alcohol/SDS mass ratios 0.625 to 1.5 was observed, indicated by the location of the peaks in the density profiles. Figure 3 depicts two SDS headgroup peaks located at the water interface with the SDS tails inside the bilayer (Fig. 3a). The hexanol headgroups were also located at the interface next to the SDS headgroups. At higher alcohol/SDS mass ratios, not only two SDS headgroup peaks were depicted but also another small peak in the middle of the micelle. At the same time, two tail peaks were also formed (Fig. 3b at alcohol/SDS mass ratio of 2.0). Those results indicated the formation of a double bilayer, as is also indicated by the snapshots of Fig. 1c). The hexanol molecules present similar features, three headgroup peaks, and two tail group profiles. Since at those alcohol/SDS mass ratios there were more hexanol molecules than SDS molecules, the density profiles were higher for

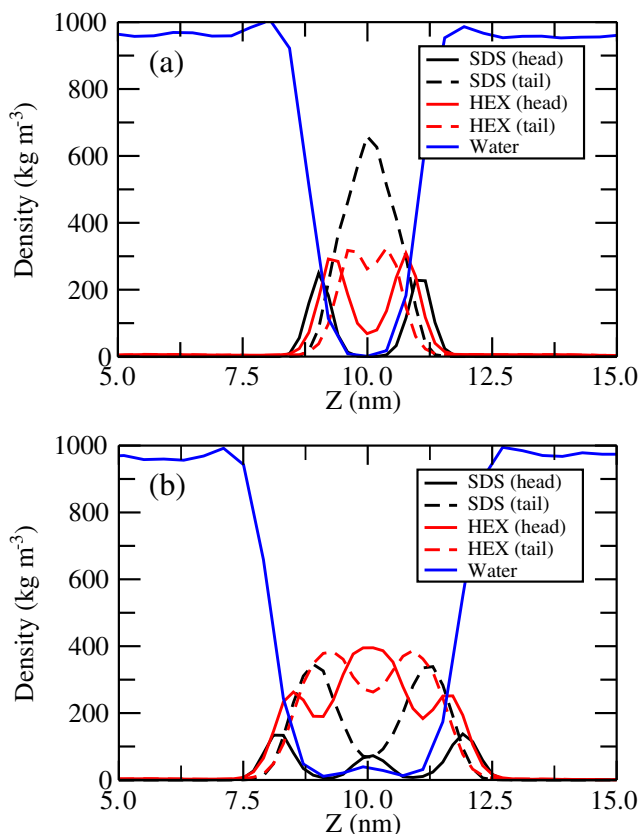


Fig. 3 Hexanol/SDS density profiles at alcohol/SDS mass ratios of **a** 0.875 and **b** 2.000. The blue solid line is for water, and the black solid lines and dashed lines are for the SDS heads and tails, respectively. The red solid lines and dashed lines are for the hexanol heads and tails, respectively

the alcohol than for the SDS. Moreover, the high alcohol headgroup peak in the middle suggested high composition of hexanol molecules inside the double bilayer.

Some experiments of a SDS/hexanol/brine system have suggested that alcohol molecules penetrate the surfactant membrane and its hexanol/SDS mass ratio determines the phase structure (lamellar or sponge) [13]. In fact, in the present simulation, alcohol molecules were observed to move inside the bilayer as the alcohol/SDS mass ratio increased and a double bilayer was formed. Then, the results are in agreement with the experimental observation, i.e., a change in the structure was depicted when alcohol molecules moved into the bilayer.

A similar behavior was observed for mixtures of SDS with long alcohols (Fig. 4). For instance, for the hexadecanol/SDS system, at a mass ratio of 0.750, a bilayer structure was formed with the SDS and hexadecanol headgroups located at the water interface and the tails inside the bilayer (Fig. 4a). At higher hexadecanol/SDS mass ratio (Fig. 4b), a double bilayer was formed, suggested by the three peaks of the SDS and hexadecanol headgroups. In this case, it was observed that the middle hexadecanol peak

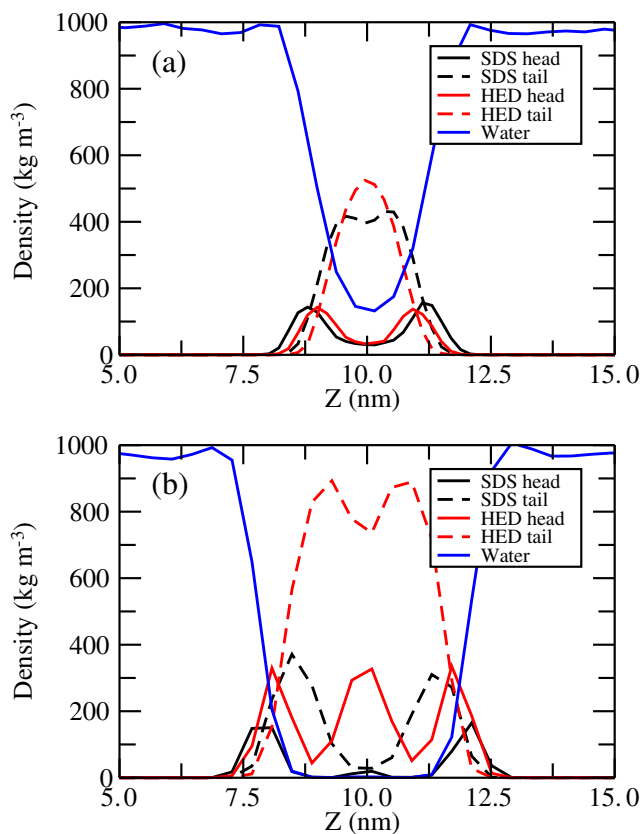


Fig. 4 Hexadecanol/SDS density profiles at alcohol/SDS mass ratios of **a** 0.750 and **c** 2.875. Notation is the same as in Fig. 3

was higher than that of the SDS. In fact, the hexadecanol tails profiles were also much higher than those of the SDS. Therefore, as for the hexanol, the results indicated that the double bilayer was mainly formed by the alcohol molecules.

Phase transitions

The structure changes of the alcohol/SDS aggregates were also analyzed by the size of the micelles. In fact, the size was used as a parameter to determine a transition in the system. In Fig. 5, the thickness, ΔZ , of the different structures were calculated as a function of the alcohol/SDS mass ratio. In the case of the cylinder structures, the size was measured as the diameter of the micelle whereas for the bilayer and the double bilayer the thickness was measured as the distance from the SDS headgroup peaks in contact with the water interface (defined in the density profiles). In Fig. 5a, the hexanol/SDS micelle size is shown. It was observed that at low alcohol/SDS mass ratios, from 0.125 to 0.5 (where the cylinder-like shape was obtained), there were no significant changes in the size of the micelles. As the alcohol/SDS mass ratio increased, the bilayer structure was formed (above alcohol/SDS mass ratio of 0.5) indicated by a small jump in the size parameter. The bilayer remained

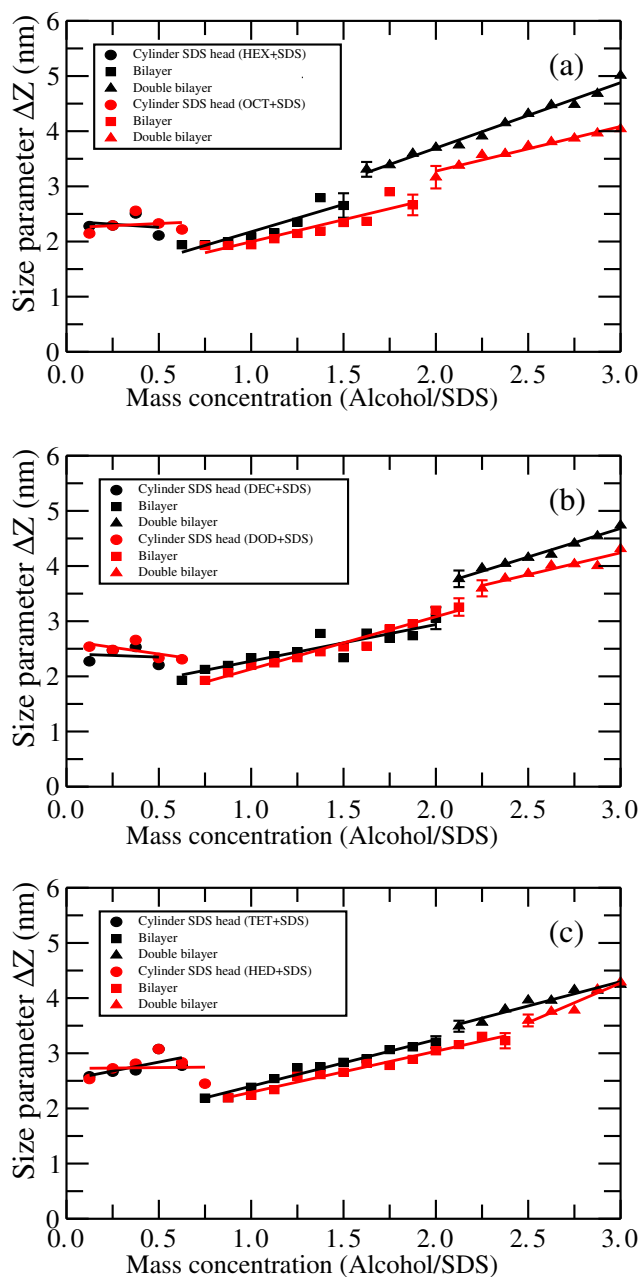


Fig. 5 Size of the micelles as a function of the alcohol/SDS mass ratio. Circles are for cylinders (*diameter*), squares are for bilayers thickness, and triangles are for double bilayers thickness. **a** hexanol/SDS (*black symbols*) and octanol/SDS (*red symbols*). **b** decanol/SDS (*black symbols*) and dodecanol/SDS (*red symbols*). **c** tetradecanol/SDS (*black symbols*) and hexadecanol/SDS (*red symbols*). The lines are the best fitting to the data and they are just given to guide the eye

up to alcohol/SDS mass ratio of 1.5 with thickness between 1.94 and 2.76 nm. The values were in agreement with those reported in real experiments of the same hexanol/SDS system where they found a bilayer thickness of 2.0 nm [13]. At an alcohol/SDS mass ratio of 1.625, the double bilayer structure was formed indicated by another jump in the size

of the micelle. In this case, the double bilayer thickness changed from 2.67 to 5.00 nm. It is worthy to note that the double bilayer thickness was not twice the size of the single bilayer thickness. Additional time, up to 4 μ s, was run for alcohol/SDS mass ratios close to the transitions and data did not change significantly.

In the same figure, the octanol/SDS mixture was also plotted (red symbols in Fig. 5a). Since octanol and hexanol had the same number of CG sites (with different masses) similar features were observed, however, the transitions (jumps in the size parameter) were located at different alcohol/SDS mass ratios. In this case, the transition from cylinder to bilayer was found around an alcohol/SDS mass ratio of 0.625 and the transition from bilayer to double bilayer around an alcohol/SDS mass ratio of 2.0. The bilayer thickness changed from 1.93 nm to 2.37 nm, in agreement with the experimental value of 2.2 nm [32]. The double bilayer thicknesses were around 4–5 nm.

In Fig. 5b, the decanol/SDS and dodecanol/SDS systems are shown. In these cases, similar features were observed, however, the bilayers were slightly thicker than those obtained for the hexanol/SDS and octanol/SDS mixtures. Moreover, the transition from bilayer to double bilayer were shifted to higher alcohol/SDS mass ratios, i.e., it was observed alcohol/SDS mass ratios around 2.0 and 2.25 for the decanol/SDS and dodecanol/SDS mixtures, respectively. The mixtures with the longest alcohols, tetradecanol and hexadecanol, are plotted in Fig. 5c. For those systems, the bilayers were even thicker than those with short alcohol chains. There, the transitions occurred at higher alcohol/SDS mass ratios, 0.75 and 2.125–2.5 for the cylinder to bilayer and bilayer to double bilayer structures, respectively.

For high alcohol compositions above 8 %, a lamellar phase is observed in the experimental phase diagram of the SDS/alcohol/water system [18]. In our simulations for higher alcohol compositions (above 9 %), where the double bilayer appeared, it could be an indication that the mixture might be in a lamellar phase (or very close to that). However, to say that the formation of a single double bilayer is a lamellar phase is not straightforward. Therefore, we can only affirm that the presence of a double bilayer is associated with a structural transition.

Order of the molecules

The structure of the molecules in the micelles was also analyzed by the order of the SDS and alcohol tails with the parameter,

$$S_{zz} = \frac{1}{2}(3 \cos^2 \theta - 1) \quad (1)$$

where θ is the angle between the vector normal to the interface and the vectors which join the nearest-neighbor atoms

along the chain. For $S_{zz} = -0.5$ the molecules present a complete order parallel to the interface and for $S_{zz} = 1.0$ the order is normal to the interface.

In Fig. 6, the order parameter ($\langle |S_{zz}| \rangle$) averaged over all tail atoms in the SDS and alcohol molecules are shown. Moreover, the ($\langle |S_{zz}| \rangle$) was calculated for each alcohol/SDS mass ratio above the cylindrical structure, i.e., for the bilayer and double bilayer micelles. For the hexanol/SDS mixture, an increment in the order parameter until it reached a maximum was observed (Fig. 6a). Then the order decreased to nearly a constant value, suggesting that the tails did not change their structure significantly. The above results indicated that, at low alcohol/SDS mass ratios, the increment in the micelle thickness was due to the increment in the SDS tails order. However, at higher alcohol/SDS mass ratios, the micelles became thicker due to the alcohol molecules located the middle of the bilayer. In fact, those alcohol molecules reduced the order of the SDS tails as seen in Fig. 6a. It was also worthy to note that the SDS tails present lower order at high alcohol/SDS mass ratios than that at low ratios and this could be the reason why the double bilayer was not twice the size of a single bilayer.

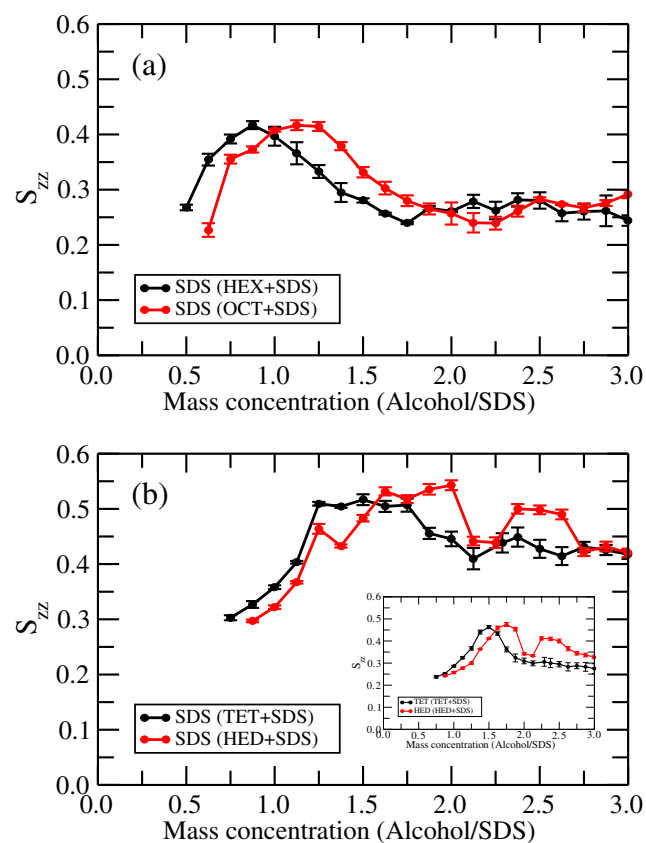


Fig. 6 Tail SDS order parameter, ($\langle |S_{zz}| \rangle$), for the systems **a** hexanol/SDS (black dots) and octanol/SDS (red dots), **b** tetradecanol/SDS (black dots), hexadecanol/SDS (red dots). The alcohol tail order parameter is also shown for the last mixture in the inset of figure b

The bilayer thickness was in agreement with the density profiles data, which indicated that hexanol molecules moved inside the bilayer at alcohol/SDS mass ratios above 1.0. For the octanol/SDS mixture, the same issues were observed, however, the maximum in the order parameter was shifted to a higher alcohol/SDS mass ratios (red data in Fig. 6a). The results suggested that alcohol molecules moved to the center of the micelle at high alcohol/SDS mass ratios.

In the case of the longest alcohols, tetradecanol and hexadecanol, we calculated the S_{zz} parameter for the SDS and alcohol tails (Fig. 6b). For the SDS tails, similar features than those for short alcohols were depicted, however, in this case, two maximums were observed for the alcohol tails (inset of Fig. 6b). The reduction of the order parameter after the first maximum was produced for the first molecules which moved inside the micelles. It was also noted that the second maximum coincided with the development of the middle alcohol peak in the double bilayer (see Fig. 4b). Moreover, for long alcohols, their tails tried to extend and to accommodate better in the micelle by producing slightly thicker double bilayers (in agreement with data of Fig. 6). Then, stretching of those alcohol molecules might produce more chain order, which could explain the second peak in the ($\langle |S_{zz}| \rangle$) order parameter.

It was not found any specific tendency in the micelle structures with the alcohol chain lengths. However, it was observed that the double bilayers' thickness slightly increased as the alcohol chains increased. Moreover, the systems with long alcohol tails present a extended bilayer region and the corresponding transitions were moved to higher mass concentration values. It was also noted that the order parameter maximum, ($\langle |S_{zz}| \rangle$), was shifted to higher mass ratios and it became higher as the alcohol tails increased.

Enthalpy

It is known that a phase transition, in systems at constant pressure, can be shown by a discontinuous jump in the enthalpy [33]. Therefore, calculations of the enthalpy changes were carried out for the present systems, $\Delta H = H - H_0$ where H is the enthalpy in each state. Since we were interested to observe structural transitions, the reference enthalpy, H_0 , was taken as the enthalpy of the last state of the previous structure, i.e., for the bilayer micelles H_0 was taken as the enthalpy of the last state of the cylindrical micelle and for the double bilayer structure H_0 was taken as the enthalpy of the last bilayer state.

The values for the hexanol/SDS and octanol/SDS are plotted in Fig. 7a. Discontinuous jumps in the same positions where the micelles thickness (size parameter in Fig. 5) changed were noted. It is observed that the enthalpy difference of the cylinder-bilayer transition was smaller than

the enthalpy difference of the bilayer-double bilayer transition. Moreover, the enthalpy difference in the transition states became larger with the alcohol chain, i.e., long alcohol chains present larger discontinuities at the transition points (Fig. 7b and c).

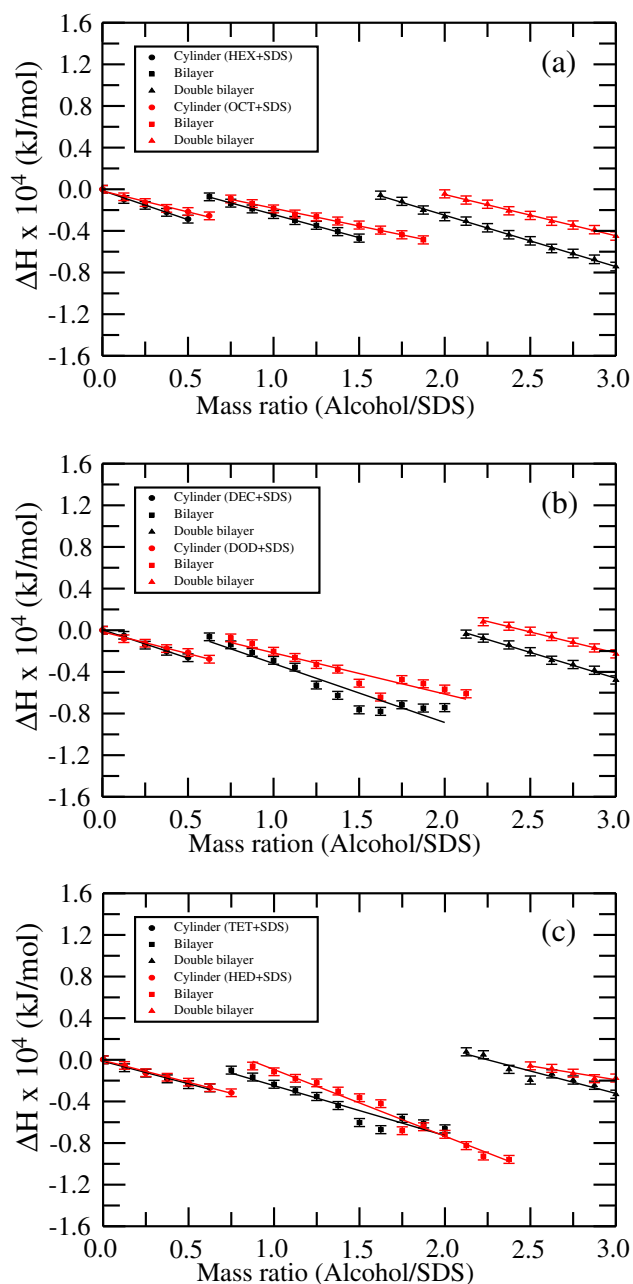


Fig. 7 Enthalpy for the alcohol/SDS systems, **a** hexanol/SDS (*black data*) and octanol/SDS (*red data*), **b** decanol/SDS (*black data*) and dodecanol/SDS (*red data*). **c** tetradecanol/SDS (*black data*) and hexadecanol/SDS (*red data*). The lines are the best fitting to the data and they are just given to guide the eye

Conclusions

Coarse-grained computer simulations were used to study the structural transition of several alcohol/SDS mixtures. The current results present relevant information about the phase behavior of these systems by showing the mechanism of how alcohol molecules are deposited in surfactant micelles to modify their structures.

As the composition of alcohol molecules increased in a SDS micelle, different structures were obtained. At low alcohol/SDS mass ratios, cylindrical micelles were formed, at intermediate alcohol/SDS mass ratios, the structures changed to bilayer micelles, and at high alcohol/SDS mass ratios, double bilayer structures were obtained. In fact, the structure sequence can be pictured as follows; the structure transition started from a SDS spherical micelle with alcohol molecules next to the micelle surface. Then, the alcohol-surfactant interactions formed a cylindrical shape. It is important to mention that more investigations should be conducted to determine if the cylindrical micelles are real structures in these ternary mixtures since they have not been explicitly reported in the experiments. As the number of alcohols increased the cylindrical structure broke to build a bilayer micelle with the alcohol molecules located at the water interface next to the SDS molecules. In those configurations, the SDS tails present large order suggesting more *trans* conformation of the chains. As the alcohol composition increased, the alcohol molecules moved to the middle of the micelle by reducing the SDS tails order and increasing the size of the micelle. Then, a double bilayer was formed. It was noted that the micelle changes were related to the insertion of alcohol molecules in the SDS structures, as suggested in the experiments of a SDS/hexanol/brine mixture [13]. Penetration of hydrophobic chains into micelle structures has also been observed in lipid droplets simulations with cholesterol and triolein molecules [9, 10]. Therefore, those results, and the ones of the present simulations, could suggest that molecules with hydrophobic tails might present similar behavior when they interact with micelles.

Finally, it is known that coarse-grained models lack microscopic details, however, they give reasonable good structural behavior to gather information on the phase behavior of complex systems. They also have the inconvenience of how to handle the electrostatic interactions (even when some corrections have done). Nevertheless, despite these limitations, the present results give us more insights into how the presence of alcohol molecules modifies SDS micelles to form different structures and how those molecules are located in the mixture.

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References

1. Gelbart WM, Ben-Shaul A, Roux D (eds) (1994) *Micelles, membranes, microemulsions and monolayers*. Springer, New York
2. Ly HV, Longo ML (2004) The influence of short-chain alcohols on interfacial tension, mechanical properties, area/molecule, and permeability of fluid lipid bilayers. *Biophys J* 87:1013–1033
3. Klacsová M, Bulacu M, Kučerka N, Uhríková D, Teixeira J, Marrink SJ, Balgavý P (2011) The effect of aliphatic alcohols on fluid bilayers in unilamellar DOPC vesicles. A small-angle neutron scattering and molecular dynamics study. *Biochem Biophys Acta* 1808:2136–2146
4. Klacsová M, Karlovská J, Uhríková D, Balgavý FSS (2014) Phase behaviour of the DOPE + DOPC + alkanol system. *Soft Matter* 10:5842–5848
5. Griepnerau B, Leis S, Schneider MF, Sikor M, Steppich D, Bockmann RA (2007) 1-Alkanols and membranes: a story of attraction. *Biochem Biophys Acta* 1768:2899–2913
6. Cantor RS (1997) The lateral pressure profile in membranes: a physical mechanism of general anesthesia. *Biochemistry* 36:2339–2344
7. Dickey AN, Faller R (2005) Investigating interactions of biomembranes and alcohols: a multiscale approach. *J Polym Sci B* 43:1025–1032
8. Kranenburg M, Smit B (2004) Simulating the effect of alcohol on the structure of a membrane. *FEBS Lett* 568: 15–18
9. Chaban VV, Khandelia H (2014) Lipid structure in triolein lipid droplets. *J Phys Chem B* 118:10335–10340
10. Chaban VV, Khandelia H (2014) Distribution of neutral lipids in the lipid droplet core. *J Phys Chem B* 118:11145–11151
11. Maugey M, Bellocq AM (2001) Effect of adsorbed and anchored polymers on membrane flexibility: a light scattering study of sponge phases. *Langmuir* 17:6740–6742
12. Alibert I, Coulon A, Bellocq AM, Gulik-Krzywicki T (1997) Dielectric study of the dilute part of a SDS/brine/alcohol system: a new sequence of phases? *Europhys Lett* 39:563–568
13. Íñiguez-Palomares R, Acuña-Campa H, Maldonado A (2011) Effect of polymer on the elasticity of surfactant membranes: a light scattering study. *Phys Rev E* 84:011604
14. Helfrich W (1994) Lyotropic lamellar phases. *J Phys Condens Mat* 6:A79–A92
15. Daicic J, Olsson U, Wennerström H, Jerke G, Schurtenberg P (1995) Thermodynamics of the L₃ (sponge) phase in the flexible surface model. *J Phys II France* 5:199–215
16. Íñiguez-Palomares R, Maldonado A (2009) Topology change by screening the electrostatic interactions in a polymer–surfactant system. *Colloid Polym Sci* 287:1475–1479
17. Vinches C, Coulon C, Roux D (1994) The symmetric–asymmetric transition of the sponge phase: I. Effect of the salinity. *J Phys II France* 4:1165–1193
18. Quist P-O, Halle B, Furó I (1991) Nuclear spin relaxation in a hexagonal lyotropic liquid crystal. *J Chem Phys* 95:6945–6961
19. Marrink SJ, Risselada HJ, Yefimov S, Tieleman DP, de Vries AH (2007) The MARTINI force field: coarse grained model for biomolecular simulations. *J Phys Chem B* 111:7812–7824
20. Marrink SJ, de Vries AH, Mark AE (2004) Coarse-grained model for semiquantitative lipid simulations. *J Phys Chem B* 108:750–760
21. Jalili S, Akhavan MA (2009) Coarse-grained molecular dynamics simulation of a sodium dodecyl sulfate micelle in aqueous solution. *Colloids and Surfaces A: Physicochem Eng Aspects* 352:99–102
22. Yesylevskyy SO, Schäfer LV, Sengupta D, Marrink SJ (2010) Polarizable water model for the coarse-grained MARTINI force field. *PLoS Comput Biol* 6:e1000810
23. Orsi M, Essex JW (2011) The ELBA force field for coarse-grain modelling of lipid membranes. *PLoS ONE* 6:28637
24. Bruce CD, Berkowitz ML, Perera L, Forbes MDE (2002) Molecular dynamics simulation of sodium dodecyl sulfate micelle in water: micellar structural characteristics and counterion distribution. *J Phys Chem B* 106:3788–3793
25. MacKeller A (1995) Molecular dynamics simulation analysis of a sodium dodecyl sulfate micelle in aqueous solution: decreased fluidity of the micelle. *J Phys Chem* 99:1846–1855
26. Bogusz S, Venable RM, Pastor RW (2000) Molecular dynamics simulations of octyl glucoside micelles: structural properties. *J Phys Chem B* 104:5462–5470
27. Wang H, Zhang H, Liu C, Yuan S (2012) Coarse-grained molecular dynamics simulation of self-assembly of polyacrylamide and sodium dodecylsulfate in aqueous solution. *J Colloid Interface Sci* 386:205–211
28. Almgren M, Swarup S (1982) Size of sodium dodecyl sulfate micelles in the presence of additives. 2. Aromatic and saturated hydrocarbons. *J Phys Chem* 86:4212–4216
29. Hess B, Kutzner C, van der Spoel D, Lindahl E (2008) GROMACS 4: algorithms for highly efficient, load-balanced, and scalable molecular simulation. *J Chem Theory Comput* 2008:435–447
30. Rossi G, Monticelli L, Puisto SR, Vattulainen I, Ala-Nissil T (2011) Coarse-graining polymers with the MARTINI force-field: polystyrene as a benchmark case. *Soft Matter* 7:698–708
31. Kekicheff P, Grabielle-Madellmont C, Ollivon M (1989) Phase diagram of sodium dodecyl sulfate–water system: 1. A calorimetric study. *J Colloid Int Sci* 131:112–132
32. Ficheux M-F, Bellocq A-M, Nallet F (2001) Elastic properties of polymer-doped dilute lamellar phases: a small-angle neutron scattering study. *Eur Phys J E* 4:315–326
33. Castellan GW (1983) *Physical Chemistry*. Addison Wesley