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The phenomenon of water penetration into sodium octanoate micelles studied by molecular dynamics computer simulation

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Abstract In this publication we have studied the penetration process of water molecules into the hydrophobic core of a sodium octanoate micelle. The analysis of this phenomenon was based on a molecular dynamics computer simulation. We calculated the probability to find water molecules within a specific sphere which was adjusted in the center of the micelle. It turned out that the position of the micellar mass and geometry center was not too different, so that this reference point was well characterized. Water penetration was observed within the whole aggregate but if the radius is smaller than 300 pm, polar solvent molecules are very rarely observed. The results of our computer simulations suggest that significant water diffusion into the micelle occurs at larger distances from the micellar center with a lower threshold value of about 400 pm. In addition to these calculations, we used the Connolly algorithm in order to determine the solvent accessible surfaces of different micellar equilibrium structures. We observed large dynamical fluctuations with the formation of pores and channels. These structures are occasionally filled with water molecules.

Key words Molecular dynamics simulations – micellar structure

Introduction

It is well known that aqueous solutions of amphiphilic molecules tend to form different types of aggregates. This association process occurs at the well-defined critical micelle concentration (cmc). In the highly dilute concentration regime, one observes often spherical aggregates consisting of 30–80 monomers. The formation of these particles is an energetically favorable process because direct contacts between polar solvents and unpolar paraffin chains are reduced to some extent. It is well known that in aqueous solution the polar head groups are oriented towards the water phase and the alkyl chains tend to avoid the unfavorable contact with water. The internal phase of the aggregates consists mainly of hydrophobic chains and has similar properties as the corresponding alkane liquid. The solvation of polar headgroups and the hydrophobic interactions between paraffin chains results in forming stable micelles.

As the self-assembling process is based on these hydrophilic and hydrophobic forces, the aggregates can change their size and shape continuously as a function of temperature. This parameter has an influence on dynamic properties as molecular motions. Due to these thermal shape fluctuations, parts of the hydrophobic core must be in direct contact with water molecules. It seems also possible that some solvent molecules are able to penetrate into the core of the micelle; a process which is induced by conformational changes of the hydrocarbon chains. Rotations around carbon–carbon bonds generating trans and gauche conformations can lead to pore structures which can be filled with water molecules. It is easy to show that this effect of water penetration depends on the size of the micellar particles. A large aggregation number results in a more compact structure with few possibilities of water–hydrocarbon contacts. Due to these phenomena, water penetration into micelles is a complicated process depending on various parameters.

From the experimental point of view the degree of water penetration into the hydrocarbon core of micelles has been controversialy debated. Optical rotary dispersion measurements suggested a strong presence of water inside micelles [1] whereas Wennerström and Lindman suspected these results [2, 3]. In the opinion of these authors the structure of a micelle corresponds to the classical picture as an aggregate having an apolar hydrophobic interior and a polar surface in direct contact with the solvent molecules. In agreement to this classical micellar structure small-angle neutron scattering experiments of lithium dodecyl sulfate [4] and recently published ^{1}H-NMR studies of a series of alkyltrimethylammonium micelles [5] confirmed that hydration occured only on the first methylene group directly attached to the polar head group. The hydrophobic core seemed to be completely dry. However, small-angle X-ray scattering investigations of aggregates of relatively small surfactant monomers like potassium hexanoate, sodium octanoate and sodium decanoate suggested that the micelle can be described as an open structure with a rather small anhydrous core [6].

Due to the recent advance in computer techniques, it is now possible to investigate the phenomenon of water penetration on a detailed molecular level using molecular dynamics simulations. Forcefield parameter and potential functions have been developed for the calculation of the interatomic forces which are required for an comprehensive simulation of molecular dynamics. These methods are especially useful to get more detailed informations on the molecular structure of aggregated surfactants.

Up to now, a limited number of molecular dynamics simulations concerning the structure of micellar aggregates were published [7–26]. Some of these investigations [8, 10, 11, 15, 17, 20, 23] were also used to determine the amount of water penetration into sodium octanoate micelles. Typical results of these experiments are average density profiles of solvent water molecules at different values of the micellar radius. It is interesting to note that the molecular dynamics studies revealed a considerable penetration of water molecules into the micelle. A remarkable increase of the density function was observed for a distance larger than 500–600 pm measured from the mass center of the micelle. This corresponds to the existence of a relatively broad wet interface whereas a completely dry core region would intuitively be expected. In contrast to these results, it was also claimed in Ref. [11] that water molecules can be observed in a distance of only 100 pm measured from the mass center of the micelle. However, in a recently published molecular dynamics simulation of a sodium dodecyl sulfate aggregate in aqueous solution at the cmc, significant water penetration into the micelle was not detected [21]. This result is not surprising because the investigated micelles have different aggregation numbers. It turns out that a sodium dodecyl sulfate micelle consists of 62 monomers, and a sodium octanoate micelles contains only 15 single molecules at the cmc. For a detailed analysis of water penetration, it is also essential to take into account the different volumes occupied by the polar head groups. Another parameter, influencing this process are all kinds of interactions which occur between the surfactant molecules. A micelle formed by sodium dodecyl sulfate surfactants seems to be a rather rigid and compact structure which makes water penetration unfavorable. Due to these different phenomena it is still difficult to get precise informations on the solubilization process of water molecules. This phenomenon is closely related to thermal structure fluctuations and it is, therefore, essential to analyze these processes in more details.

In a preceding paper [24] we focused our attention on the molecular structure of the hydrophobic core of a sodium octanoate micelle. Typical features like the conformation distribution of alkyl chains, the shape of the micelle and its size could be calculated and the results coincided pretty well with the experimental data. We determined an average hydrophobic cavity radius of the order of 0.59 ± 0.21 nm measured from the mass center of the micelle. At the present state it is still an open question whether water molecules can penetrate into the hydrophobic micellar core to occupy sites in the vicinity of the terminal methyl groups of the surfactants. In a second publication we have investigated the interactions of the polar head groups with solvent molecules [25]. We discussed average hydrogen bond lengths between the hydrophilic head groups and the surrounding water molecules and the average coordination number. Recently we published calculated self-diffusion constants of water around the polar head groups [26]. We observed a significant smaller mobility of those water molecules which are directly connected to the surfactant head groups by hydrogen bonds compared to those belonging to the bulk phase. In contrast to these investigations we now focus our attention on the problem of water penetration. Systematic studies of this process offer new insights into various aspects of current research and it opens interesting new technical applications.

With regard to the recently published simulations of water penetration into micelles, our molecular dynamics simulation is different from the procedures utilized by other authors. We used another type of forcefield parameters to calculate the interatomic interactions. Therefore, in a first step, it seemed to be useful to determine the water penetration in a similar way as it was done before. In contrast to the applied methods of Refs. [8, 10, 11, 15, 17, 20 23], we performed a detailed statistical analysis of frequency distributions of distances between the micellar center and water molecules. This procedure was used to calculate the probability of water penetration into different core regions of the micelle. Furthermore, we analyzed different micellar conformations which resulted in new insights and a better understanding of the mechanism of water penetration into the hydrophobic micellar core.

Method and theory

We performed a 400 ps molecular dynamics simulation of 15 sodium octanoate surfactants in aqueous solutions in the NPT ensemble at a temperature of 300 K and a pressure of 10^5 Pa. The liquid was modeled by 813 water molecules in a box using periodic boundary conditions. The SPC water model was applied and the appropriate parameters were assigned to each water atom. The potential functions and parameters which are used to calculate the different types of atomic interactions were taken from the AMBER forcefield [27–29]. The simulation model and the simulation conditions are summarized in all details in Ref. [24]. In contrast to former investigations we have selected now different cut-off radii for various types of interactions. For the long-range Coulomb charge–charge electrostatic energy we used a cut-off value of 1.5 nm whereas for the van der Waals interactions energy, a radius of only 1.0 nm was selected. This procedure ensures an increasing speed of the computer simulation.

From the molecular dynamics trajectory we investigated the structural equilibrium properties in the simulated time interval between 300–350 ps. As it can be concluded from Fig. 1, the sum of kinetic and potential energy, thus the total energy, is rather constant after a period of about 200 ps. We can, hence, conclude that this time is necessary to reach the thermodynamic equilibrium of the simulated system.

Our efforts are directed to the problem of calculating the probability to find a water molecule in a certain distance R_i. This parameter was measured in respect to the mass center of the micelle, which might be different from the geometry center. We shall now describe each water molecule which is located at this specific distance R_i with a number A_i. The probability of finding water molecules $P(A_i)$, is then given by the limiting value of the relative frequency, $h(A_i)$, (Eq. (1)). This parameter can be expressed as the number of water molecules which are located at a certain distance $n(A_i) = n_i$ divided by the total number of all water molecules which are found in the whole micellar region between 0 and R. This denominator is denoted by n_R. All these definitions are mathematically described in Eq. (1).

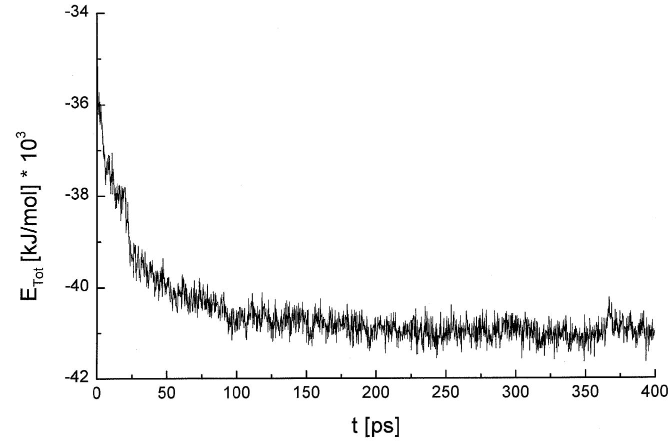


Fig. 1 Plot of the total energy as a function of the simulation time. At approximately 200 ps the total energy remains constant and the thermodynamical equilibrium is reached

$$P(A_i) = \lim_{n\to\infty} h(A_i) = \lim_{n\to\infty} \frac{n_i}{n_R} . \qquad (1)$$

This equation holds for infinite large numbers of n_R. This theoretical problem leads to the following practical procedure which was used to calculate the probability of water penetration into micelles.

During the whole molecular dynamics computer simulation the current cartesian coordinates of the surfactant and water atoms were saved and stored in a file every 200 fs. In this way we calculated 502 different micellar structures in the selected time interval between 300–350 ps. In order to evaluate the sites in the hydrophobic core of the micelle which are filled with water molecules, we analyzed every second conformation, this means 251 different structures from the trajectory. We developed a computer program to measure all distances, R_i, between the mass center ($\mathbf{r}_{cm}$) and the geometry center ($\mathbf{r}_{cg}$) of the micelle. The water distance was characterized by the positions of the oxygen atoms. This analysis was performed for a sphere radius of 1.3 nm which corresponds to the average size of the micelle. We define R_{CM} and R_{CG} as limiting values with the notation that R_{CM} is the radius measured from the mass center and R_{CG} is the radius in respect to the origin of the geometry center. The position vectors of the geometric centroids are defined in

Eqs. (2) and (3).

$$\mathbf{r}_{\mathrm{cm}} = \frac{\sum_{i=1}^{N} m_i \mathbf{r}_i}{M} , \tag{2}$$

$$\mathbf{r}_{\mathrm{cg}} = \frac{\sum_{i=1}^{N} \mathbf{r}_i}{N} . \tag{3}$$

Here $\mathbf{r}_i$ denotes the position vectors of atom i, and m_i is the atom mass of atom i in the micelle. M describes the molecular weight of the micelle. The sum includes all atoms of the micellar aggregate, N. Due to the dynamic nature of the micellar structure, $\mathbf{r}^{\mathrm{CM}}$ and $\mathbf{r}^{\mathrm{CG}}$ are different in each of the 251 conformations. Therefore, in order to get precise distance informations, separate calculations of the mass and geometry centers were required for each conformation.

The defined value of 1.3 nm for R^{CM} and R^{CG} corresponds to the average micellar radius obtained from a previously performed molecular dynamics simulation [24]. Consequently, each water molecule located in the micelle was included in the above mentioned analysis. The precise definitions of the spheres are summarized in Fig. 2.

It is easy to see that the value of n_{R} is the product of the number of the selected micellar conformations (251) and the number of water molecules located in the sphere. These values are, of course, different for each conformation due to the rapid exchange of water molecules.

Results

Statistical analysis

First, we calculated the total number of water molecules located into the two different spheres originating from the mass and geometry center. N^{CM} corresponds to a sphere with radius R^{CM} and N^{CG} is based on the analysis of a sphere with radius R^{CG}. These numbers were calculated from 26 equilibrium conformations which could be obtained from the corresponding trajectories. Typical results are summarized in Fig. 3 and from these values the average number of water molecules located in the micellar core was calculated. We obtain $N^{\mathrm{CM}} = 45.08 \pm 4.08$ and $N^{\mathrm{CG}} = 45.00 \pm 4.20$.

Similar values of N^{CM} and N^{CG} suggest that the distances are not too different for an analysis based on mass and geometry centers. It is interesting to note that the average distance between CM and CG is about 29.67 ± 3.46 pm. This points to the existence of a slight difference between the mass and geometry center. It can be concluded that about 45 water molecules are located within the micelle.

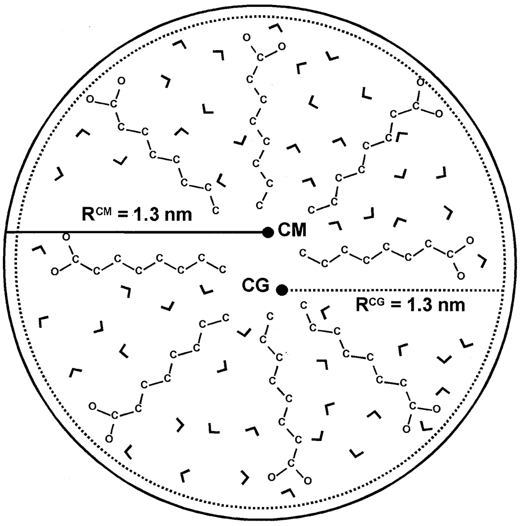


Fig. 2 Definition of the different spheres with radii R^{CM} and R^{CG}. R^{CM} is the radius of 1.3 nm measured from the mass centre of the micelle. R^{CG} is related to the geometry center of the micelle

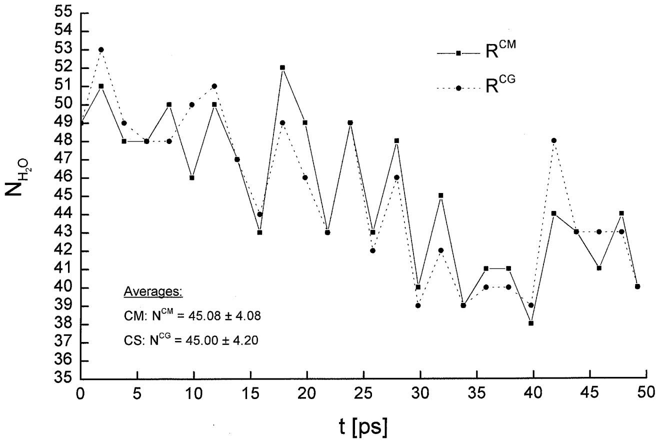


Fig. 3 Number of water molecules in the different spheres with radii R^{CM} and R^{CG} as a function of the simulation time. About 45 water molecules are located in the micellar core

The amount of total distance measurements, n_{R}, can be easily be calculated to

$$n_{\mathrm{R}} = 45 \times 251 = 11295 .$$

It is now interesting to analyze the distribution of water molecules within the micellar core. We can expect that the probability of finding water molecules near the polar head groups is different from the corresponding values near the centroids CM or CG. Figure 4 gives some informations on the calculated relative frequency distributions defined in Eq. (1).

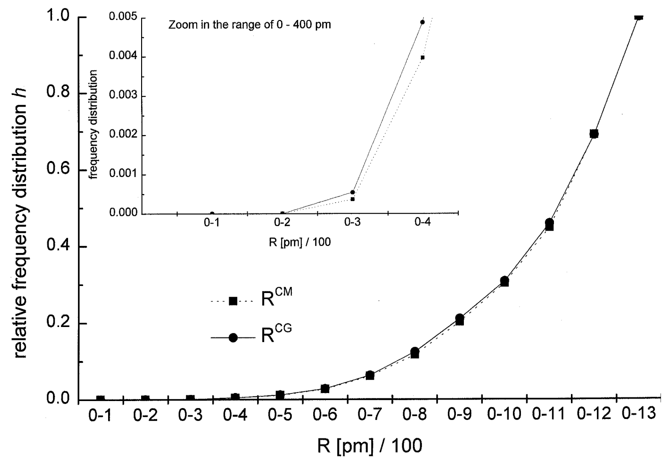


Fig. 4 The relative frequency distribution of water molecules as a function of the radius

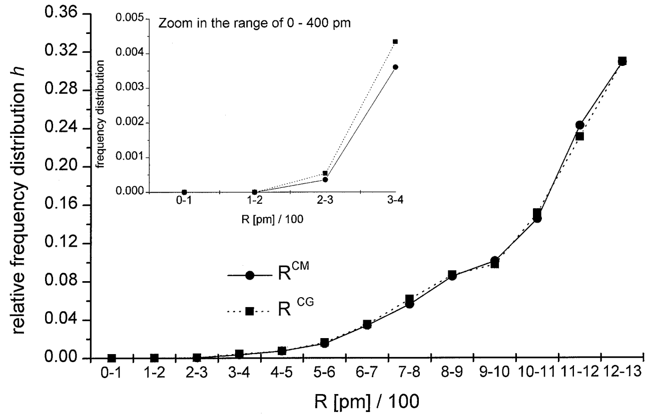


Fig. 5 The relative frequency distribution of the location of water molecules which are located in different shells as a function of the distance. All shells have a constant width of 100 pm

The diagram shows the relative frequency, h, of water locations at different distance intervals measured in respect to the mass and geometry centers, CM and CG. Of course, all water molecules are located within a sphere of 1.3 nm radius. For a distance of 1.3 nm, h is equal to one (or 100%, if a relative frequency scale is chosen). In directions towards the micellar center h decreases rapidly. It is interesting to note that in the central region only a small amount of water molecules was found. A central sphere with a radius of 0.7 nm contains less than 10% of the water molecules. From an enlarged drawing visualizing the range between 0 and 400 pm it is evident that water molecules seek to avoid the central regions of the micelle. Due to the very small h value of about 5×10^{-4} in the regime between 0–300 pm, water penetration is still possible but very rarely observed. A detailed analysis of the micellar structure revealed that at a given time interval only one water molecule is able to occupy the central region of the aggregate. During an investigated time period of 50 ps, only six water molecules entered and left the internal core regime.

The frequency of finding water molecules in a special shell of the micelle is summarized in Fig. 5. We investigated constant distance intervals with a width of 100 pm. It turns out that the largest relative frequencies are observed in the vicinity of the polar headgroups, positioned at the distance intervals between 1.1–1.2 and 1.2–1.3 nm. We calculated values of 25% and 32% for the surface of the micelle. Near the center of the aggregate, h decreases slightly. The probability of finding water molecules is less than 10% in each interval below a distance of 900 pm.

According to Eq. (1) the analysis of water penetration approaches realistic values if we assume that the number of distance evaluations, $n_R = 11\,295$ is large enough to reach equilibrium conditions. In this case h has to remain constant with varying n_R values. In order to prove this assumption, we changed n_R by counting only 125 conformations. This corresponds to a selection of every fourth conformation which was calculated in the equilibrium time interval ($n_R \approx 45 \times 125 = 5625$). In comparison to the analysis of the 251 conformation we observed no significant differences. We can, hence, conclude that already 125 conformations lead to a statistical relevant number of n_R. At such conditions, the relative frequency is equal to the probability of finding water molecules within a special region of the micelle.

Solvent accessible surfaces

In order to get a better understanding on the basic mechanisms of water penetration, it is useful to visualize all parts of the micelle that can be exposed to polar solvent molecules. Recently, Connolly developed a special computer algorithm for calculating the van der Waals surface representing all solvent accessible sites around a molecule or aggregate [30]. In this procedure a solvent molecule is replaced by a sphere which is rolled over the surfactants of the micelle calculating the van der Waals interaction energy between the solvent molecule and the different atoms of the aggregate. In Fig. 6A–F the solvent accessible surfaces of equilibrium micellar structures which were observed for different simulation times between 300–350 ps are summarized on the right-hand side of each plot. Dark areas represent regimes of possible solvent location. In order to get a better insight into the three-dimensional

Fig. 6 (A–F) Molecular structures and Connolly-surfaces of the sodium octanoate micelles calculated at different simulation times. The sites inside the dotted area are not accessible to water molecules. The colored water molecules are described as a function of their distance from the mass center of the micelle. On grounds of simplification we did not plot the sodium counterions

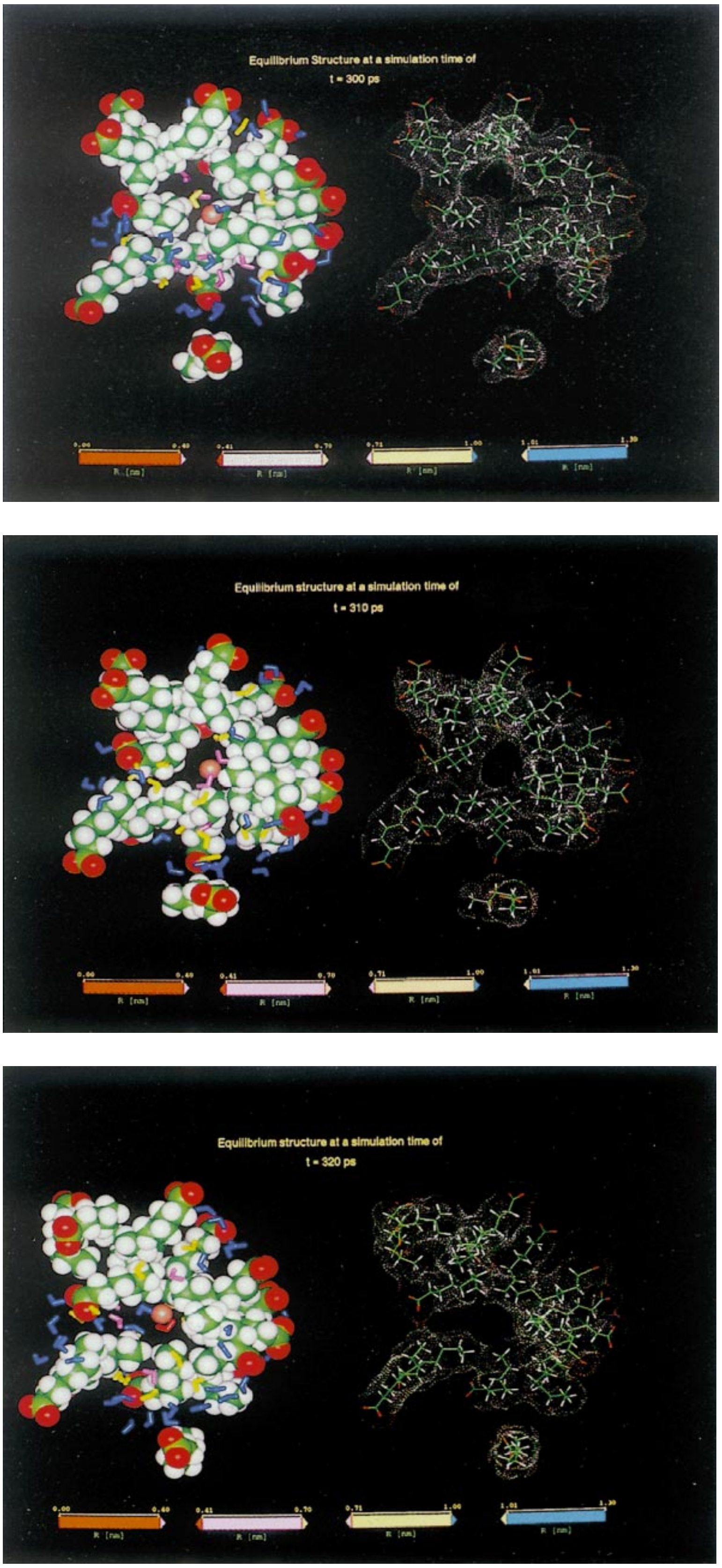
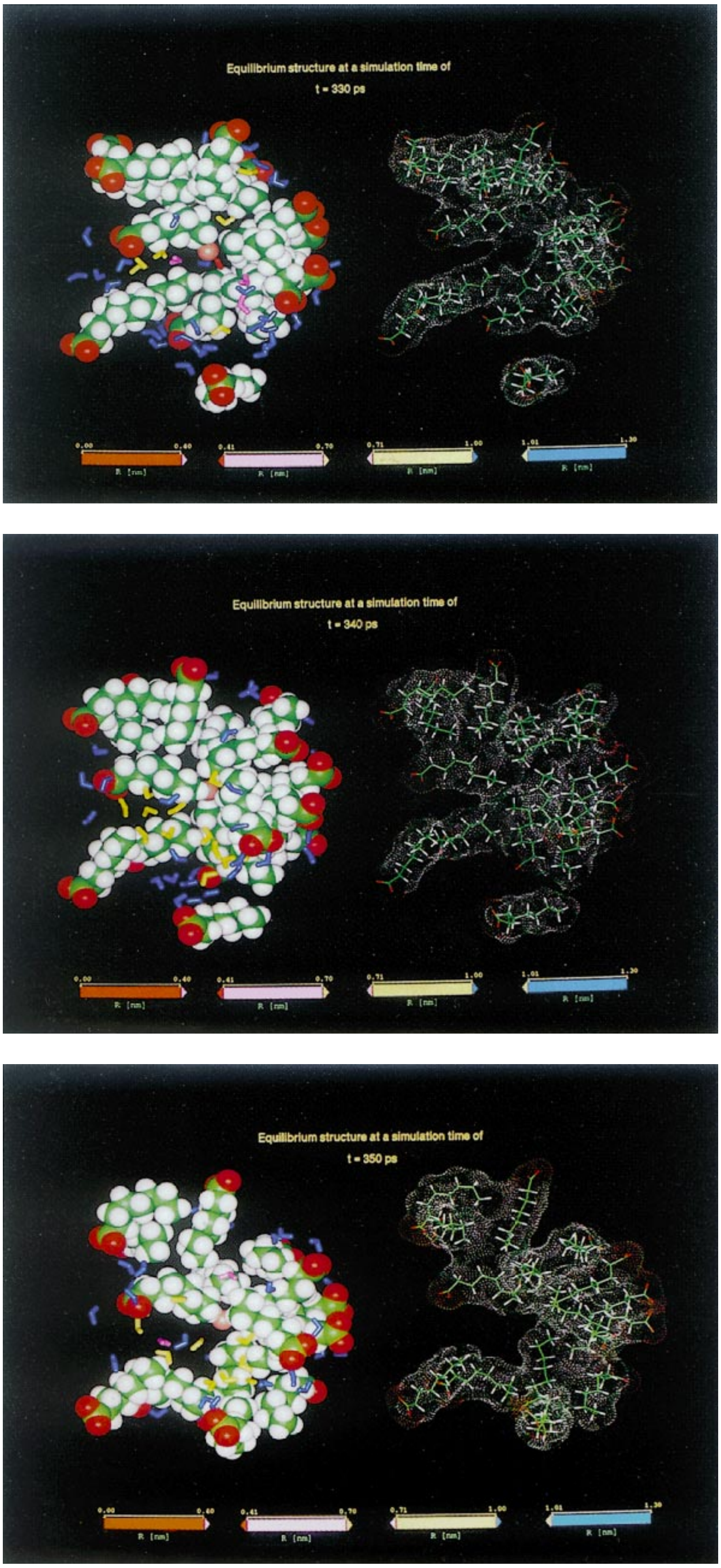


Fig. 6 (Continued)



shape of the micelle, the molecular structure is also presented on the left-hand side. These plots show the van der Waals' radii for each micellar atom. Furthermore, all water molecules within a sphere of 1.3 nm radius around the mass center of the micelle are plotted as rods in different colours. This procedure allows to characterize special distance intervals. The blue colored water molecules, for example, are all located in a shell with a distance of 1.01–1.30 nm. The brown colored sphere in the micellar core denotes the center of mass. In order to compare different micellar equilibrium structures we plotted always the same orientation in space.

At this point it should be noted that the plots of the micellar structures and solvent accessible surfaces do not represent a realistic three-dimensional picture. This can only be achieved by plotting a hologram or using other types of advanced optical techniques. A picture, projected onto the paper plane gives only a rough impression of the real micellar structure and it is difficult to interpret on grounds of the limited depth of focus. We should also keep in mind that the selected conformations are only snap-shots extracted from a movie showing the real thermal fluctuations of the micelle.

Despite all these restrictions and simplifications, it is evident from Fig. 6A–F that a pore is formed in the micellar core which can be filled with water. This structure strongly fluctuates and can change its size and shape frequently. The micellar structures at 320 and 330 ps are excellent examples for the penetration of water molecules into the vicinity of the mass center. It turns out that exactly one water molecules is located at the distance interval of 0–400 pm.

At a simulation time of 340 ps (Fig. 6E) the micellar core is more compact and the mass center is surrounded by terminal methyl groups preventing considerable water penetration. On the left-hand side only a small pore in the direction towards the mass center can be detected. In this special case water molecules were found at distances between 0.71—1.3 nm. At elevated simulation times of 350 ps we observe an opening of the small pore and some water molecules are able to penetrate closer to the mass center. We detect now two water molecules in a range between 410–700 pm. On close inspection it becomes evident that the micelle does not show a spherical shape. This problem and its explanation was extensively described in Refs. [11, 24]. It is easy to see that a separated surfactant monomer, visible in the previous structures just starts to join the micelle. This process is correlated with strong fluctuations of the equilibrium structure.

Discussion and conclusions

From molecular dynamics computer simulations we calculated the penetration of water molecules into sodium octanoate micelles. We obtained large numbers of water molecules arranged in a globular shell with a diameter of 0.9–1.3 nm which corresponds to the surface of the micelle. The internal core region between 500–900 pm contains also water but only 10% of the total amount. Some molecules can even penetrate into the vicinity of the center of the micelle, but this process rarley occurs. These results are in pretty good aggreement with other studies of molecular dynamics simulations [8, 10, 15, 17, 20, 23].

The calculation of solvent accessible surfaces and micellar structures leads to a more detailed insight into the complicated mechanism of water penetration. On grounds of the thermal motion, hollow spaces, pores and channels are continuously formed and destroyed in which occasionally some water molecules are able to penetrate. This is, of course, a dynamic process with time constants of only a few picoseconds. In contrast to the micellar systems consisting of sodium dodecyl sulfate surfactants [21], we have observed a significant amount of water penetration. As mentioned before, this process is certainly related to the aggregation number and the lengths of the paraffin chains. Keeping the experimental results in mind [2–6], a sodium dodecyl sulfate micelle has a more compact structure and packing of the paraffin chains seems to be more effective. In this case, there are only a few solvent accessible sites, and water penetration is, therefore, reduced. This situation changes, however, if micelles with small aggregation numbers like sodium octanoate micelles are considered. Due to less distinctive hydrophobic forces, the micellar core is not very stable, and these aggregates are characterized by large thermal fluctuations. It turns out that water penetration is mainly controlled by these interactions between the hydrophobic paraffin chains. To verify this statement we plan to study another surfactant micelle which is characterized by high aggregation numbers and long paraffin chains. This work is still in progress.

To summarize we may state that water penetration seems to be influenced by the compact structure of micellar aggregates. These results are in pretty good agreement with Refs. [2–6].

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