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Abstract: A study of the structural features of reverse micelles of Na AOT (sodium bis(2-ethylhexyl) sulfosuccinate) molecules in cyclohexane with an aqueous core was carried out using the molecular dynamics method. Reverse AOT micelles are formed in three-component systems containing a non-polar solvent, water and AOT molecules at certain concentration ratios, expressed as w = [H2O]/[AOT]. A strong hydrogen bond between water molecules and AOT was found at w=6. For the first time, a sharp decrease in hydrogen bonding between water molecules and AOT for w =7 was shown, caused by a difference in the packing of AOT molecules and the collective dynamics of water molecules in the micelle core. The calculated results are in good agreement with experimental data of other authors. It is shown that along with the methods of vibrational spectroscopy and dynamic light scattering, the molecular dynamics method is also informative for determining the structural characteristics of supramolecular structures and analysing the collective dynamics of water molecules.

Keywords: molecular dynamics method, reverse micelles, hydrogen bonding

Introduction

The formation of reverse AOT micelles with an aqueous nano-core [1] is of particular interest, as these systems are medium for the growth of nanoparticles of various nature [2, 3], organic molecules [4-6], biomolecules [7], and metal nanoparticles [8, 9]. Information on the stability of reverse micelle solutions, the shape of reverse micelles, their size distribution, the properties of water in the core of reverse micelles is obtained using small angle X-ray [9] and neutron scattering [10], nuclear magnetic resonance [6], infrared spectroscopy [3, 6, 11], UV-vis spectroscopy [4], Raman spectroscopy, dielectric spectroscopy [c], methods of dynamic [13] and static light scattering [14], ultrafiltration [15], conductivity [16] and density measurements [17-19] as well as other physical methods. The difficulty of obtaining information on the structure of reverse micelles at the detailed molecular level is that, unlike other complex organic structures, reverse micelles are self-assembled exclusively in solutions, which does not allow for their X-ray analysis or the use of high-resolution microscopy [20]. Therefore, molecular dynamics is one of the main methods of studying supramolecular systems with a large number of degrees of freedom.

The aim of this work is the molecular dynamics investigation of self-organization of reverse micelles of AOT molecules in the cyclohexane+water system, the study of structural properties and types of interaction depending on the variation of parameter w.

Method of molecular dynamics

The self-organization of reverse AOT micelles with a change in the molar ratio of water and surfactant (w = [H2O]/[AOT −]) (Fig. 1) was studied using the GROMACS (Groningen Machine for Chemical Simulations) software package [21], version 5.0.2. To describe water, the SPC/E (Extended Single Point Charge) interaction potential was used [22], which was successfully applied in our previous studies [23-31]. Systems were chosen in such way that the number of AOT and cyclohexane molecules were constant, and the number of water molecules corresponded to the concentration range w=0.25÷11 presented in Table 1. For cyclohexane and AOT (Fig.1), the all-atom force field potential CHARMM27 [32] was chosen, as it describes well the formation of reverse micelles in other solutions [33] and clusters [34]. A cubic cell with periodic boundary conditions and a cut off radius of 1.2 nm were applied. Other parameters and detail procedure of NPT ensemble are presented in [24]. The equilibrium systems were prepared for 30 ns with a time step of 2fs (Fig. 2). Only the last 5 ns of the runs were used for data analysis. For the velocity autocorrelation function, the equilibrium system was rerun for the next 15 ps.

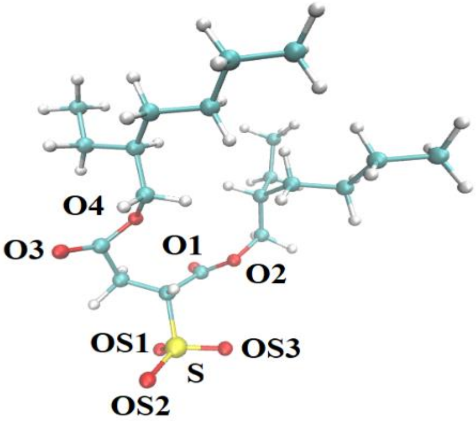

Figure 1. Chemical structure AOT.

Table 1. Number of molecules in the system as a function of water concentration.

W	Number of molecules		
	cyclohexane	water	AOT
0	1000	0	95
0.25	1000	24	95
0.5	1000	47	95
1.0	1000	95	95
2.0	1000	189	95
3.0	1000	284	95
4.0	1000	379	95
5.0	1000	473	95
6.0	1000	568	95
7.0	1000	662	95
8.0	1000	757	95
9.0	1000	852	95
10.0	1000	946	95
11.0	1000	1041	95

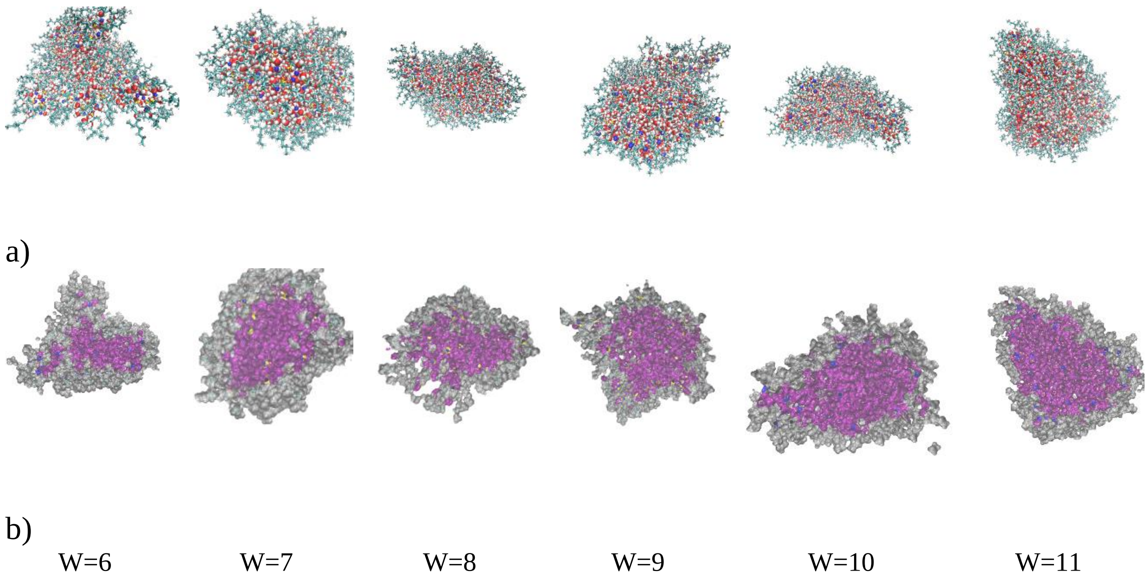

Figure 2. Formed micelles in water concentration range w=6÷11**.**

Results and discussion

The number of hydrogen bonds is presented in Figure 3. It can be seen that the number of two types of interactions, namely, between SO_3^- anion group and water, and between water molecules for w=1 and w=2 is comparable, while starting from w=3, there is a predominance of interactions between water molecules at a ratio of 2.5:1.

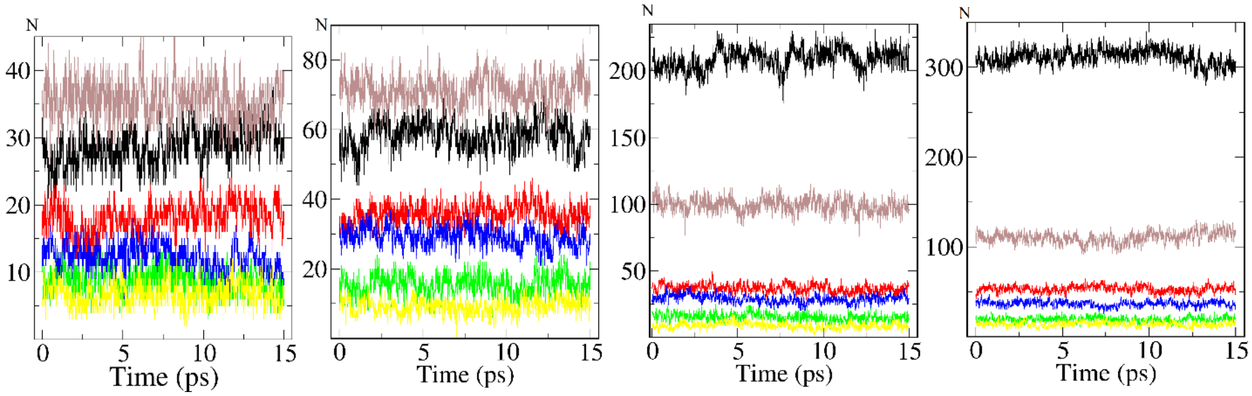

Figure 3. Number of hydrogen bonds in the system as a function of water concentration, shown from left to right: w=1, w=2, w=3, w=4. Different types of hydrogen bonds are presented: between water molecules and: molecules calculated as the centre of mass of molecules (black); hydrophilic part of SO_3^- (brown); O1 atom of AOT molecule (red); O2 atom of AOT molecule (green); O3 atom of AOT molecule (green); O4 atom of AOT molecule (yellow).

Figure 4 shows that the number of hydrogen bonds formed between the surfactant's anionic group SO_3^- and water for w=6 and w=7 is the same, but there is a sharp increase in the number of interactions between water molecules, affecting the structure of the water framework, the core, and the packing of surfactant molecules in the micellar structure. This sharp increase in the number of interactions between water molecules in the water framework indicates a change in the nature of interactions and the dynamics of the molecules. The number of interactions between O1, O2, O3, O4 and water for w = 5, w = 6 is the same and a marked decrease occurs for w = 7, and a sharp increase in interactions between O1 and O3 and water molecules is observed for w = 8 and higher at a ratio of 5:1.

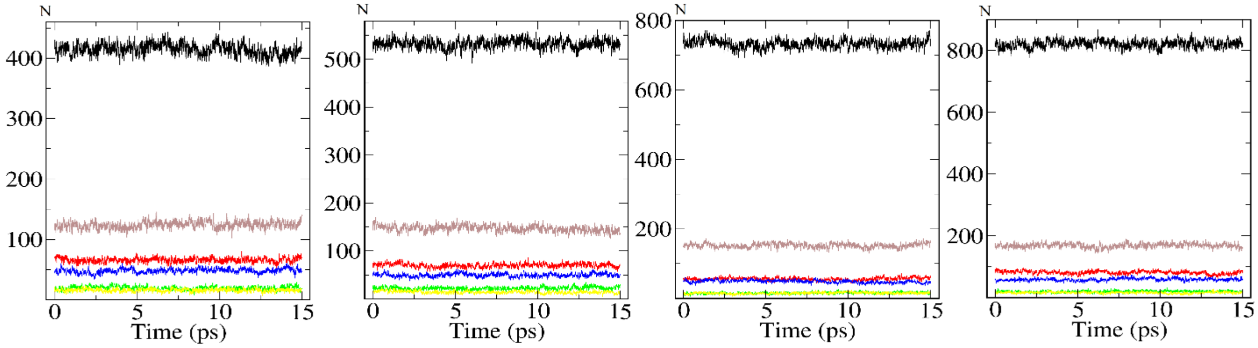

Figure 4. Number of hydrogen bonds in the system as a function of water concentration, shown from left to right: w=5, w=6, w=7, w=8. The types of hydrogen bond are shown in Figure 2.

Analysing the number of hydrogen bonds, we can conclude that at low concentrations of up to w=2.0, the number of hydrogen bonds between water molecules and the hydrophilic group of AOT is predominant (brown). At a concentration of 3.0, the nature of interactions changes dramatically, there is an increase in hydrogen bonds between water molecules. At concentrations of 6.0-7.0, the number of bonds between the hydrophilic group of AOT and water molecules remains almost unchanged, however, the ratio of the number of hydrogen bonds between water-water and water-AOT types of interactions is the highest for w=7 and is equal to 5:1.

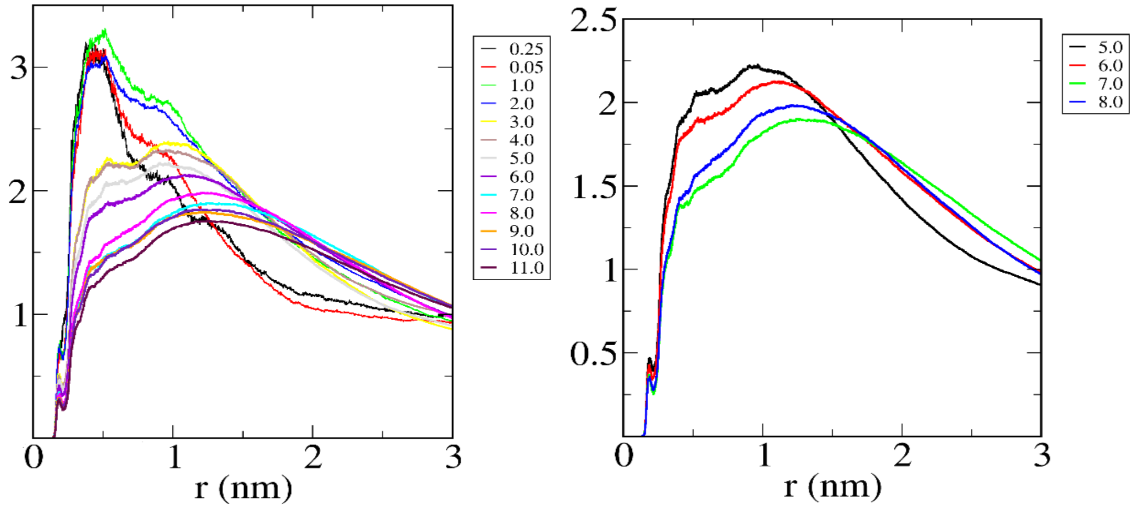

Figure 5. Radial distribution function between water molecules and AOT (calculated as the centre of mass of molecules).

It can be seen (Fig.5) that for the range of low concentrations w=0.25÷2, the molecules of two types of water and AOT, interacting with each other, are located at 0.5 nm and 1.2 nm. The intensity of the first maximum is higher compared to the second one, indicating that water molecules are predominantly located near AOT molecule. The nature of the interaction between water molecules and AOT presented in Figure 5 on the left demonstrates that a sharp change is observed when the concentration goes from 2.0 to 3.0. In the range w=3÷6, a decrease in the intensity of the first peak and its complete disappearance for w=7÷11 is observed. There is a noticeable shift of the second maximum for w=7÷11 towards long-wave interactions, which characterizes the type of interaction between the micellar system and its aqueous core. The intensity of interaction peak for w =7.0 (figure on the right) decreases sharply and a shift occurs, characterizing an increase of distance and a decrease of degree of bonding between molecules caused by repacking of surfactant molecules in the micellar structure.

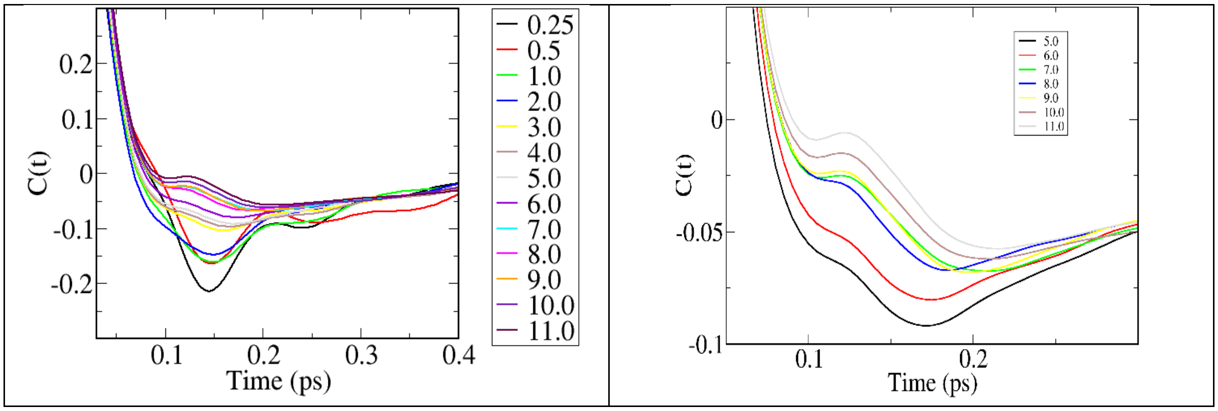

Figure 6: Autocorrelation velocity function for the water oxygen atom.

Figure 6 shows the autocorrelation velocity function for water oxygen atom. A noticeable difference in the behaviour of oxygen atom is observed in the region of low water concentrations w=0.25÷2. At low concentrations, the first global minimum appears at approximately 0.15 picoseconds and a small maximum corresponds to 0.2 picoseconds, associated with the slowing down of oxygen atom. At w=3÷6, a blurring of the first maximum occurs, which characterises the formation of a stable water core in the reverse micelles. Based on the results of static and dynamic light scattering [35], at w=4.5, the micelles are still too small to exhibit a pronounced anisotropic structure, although at w = 6.3, the micelles behave as elongated ellipsoids. For large concentrations w = 7÷11, the first minimum is observed at about 0.1 picosecond and the maximum at about 0.12. The deviation is observed at w = 7. In [36], based on the data on the change in microemulsion density with increasing w, it was concluded that there is a significant interaction of water with polar groups of AOT leading to structural changes in micelles (transition from spherical to cylindrical shape). From the above mentioned, we can conclude that a strong interaction between surfactant molecules and water occurs in micelles, leading to a changing of water dynamics and the shape of the micelle.

Conclusion

The study of structural characteristics of reverse micelles in cyclohexane solution with an aqueous core has been carried out using the method of molecular dynamics. In micelles, there is a strong interaction between surfactant molecules and water, which leads to water molecules rearrangement and changes in the micelle shape. It was shown that during the transition from w =5.6 to w =7, a difference in the packing of surfactant molecules and the water core is observed, which is related to the dynamics of water molecules. The calculation of hydrogen bonds in the system, radial distribution function between surfactant molecules and water, as well as autocorrelation velocity function for water oxygen atom showed a deviation for w=7. This deviation is related to the minimum interaction of surfactant molecules with water and compensation of Coulomb and Van der Waals forces, as well as dielectric susceptibility of water observed in similar systems [15, 19].

The results based on data analyses reveal that at w = 6, a strong hydrogen bond appears between the hydrophilic group of AOT and water, and at w = 7, the strength of hydrogen bond changes drastically, indicating that the micelle changes its shape. This fact is also confirmed by other authors [14, 35]. Thus, there is a significant increase in the interaction of water with polar groups of AOT, leading to structural changes in micelles. With a further increase w, the content of aqueous pseudophase and the interaction of polar groups of surfactant molecules with water molecules determine the size of nanoparticles obtained in micelles.

Acknowledgments

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