Molecular Dynamics Study of Micellization Thermodynamics in AOT/Hexane System

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Received June 9, 2016

Abstract—The thermodynamics of reverse micelle formation from an ionic surfactant, sodium bis(2-ethylhexyl) sulfosuccinate (Aerosol OT, AOT), in hexane is studied by molecular dynamics simulation. A change in the Gibbs free energy upon the addition of one AOT molecule to a reverse micelle is calculated as depending on aggregation number N by the thermodynamic integration method. This dependence has a minimum at $N \approx 20$ and maximum at $N \approx 35$ and predetermines the monotonically decreasing character of the standard chemical potential of AOT in a micelle with the increase of the aggregation number. The simulation results predict the formation of reverse AOT micelles with an average aggregation number of ≈ 30, which is in good agreement with experimental data.

INTRODUCTION

The study of micellar systems is of importance from both the fundamental and applied points of view. The practical significance of micelles is due to their application for the synthesis of nanoparticles with controlled sizes and shapes [1, 2], separation and refolding of proteins [3], as nanocarriers of drugs [4], etc. Therefore, it is urgent to develop a theory and models for calculating the thermodynamic characteristics of different micellar systems with the aim of predicting the equilibrium structure of micelles, critical micelle concentration, and micelle size distribution.

One of the first theories describing micelles in solutions of amphiphilic molecules was proposed by Izraelashvili [5], who, based on the general geometrical considerations, obtained an exponential dependence of the chemical potential of surfactant molecules on aggregation number. Then, many theories were proposed to describe the free energy of micelles in different colloidal systems [6–10]. The theory of micellization in aqueous solutions of surfactants was discussed in detail in a monograph by Rusanov [11]. Reverse micelles and water-in-oil emulsions occupy a special place in the micellization theory. The thermodynamic theory of water-in-oil AOT microemulsions was developed in [12], where, under the assumption that the Helfrich equation [13] is applicable to the dependence of the surface energy on the curvature of a monolayer at a water–oil interface, the chemical potential of surfactants was obtained as a function of micelle composition. In [14], the same dependence was found with allowance for the electrical double layer energy, Derjaguin "internal" disjoining pressure, and interfacial tension at the polar core boundary, which made it possible to explain the spherical shape of such micelles.

The atomistic simulation methods are also widely used to investigate micelles, because they allow one to describe realistically and completely the structural characteristics of components and the interactions in a system. One of the approaches consists in the large-scale and long-term simulation of colloidal solutions, which enables one to observe the nucleation and growth of micelles and determine their average size and shape [15, 16]. However, this approach does not clarify the features of the thermodynamic driving forces of the micellization process.

In [17–19], simulation within the framework of the mean-field theory and Monte Carlo method was employed to calculate the chemical potential of micellized nonionic surfactants. In particular, it was found that symmetric surfactants form spherical micelles, while a transition from the spherical shape to an elongated or toroidal shape with a rise in concentration was observed for asymmetric surfactants.

This work is devoted to the investigation of so-called dry reverse micelles of an ionic surfactant, sodium bis(2-ethylhexyl) sulfosuccinate (Aerosol OT, AOT), in hexane, i.e., a particular case of a well-studied experimentally AOT/water/oil micellar system, in
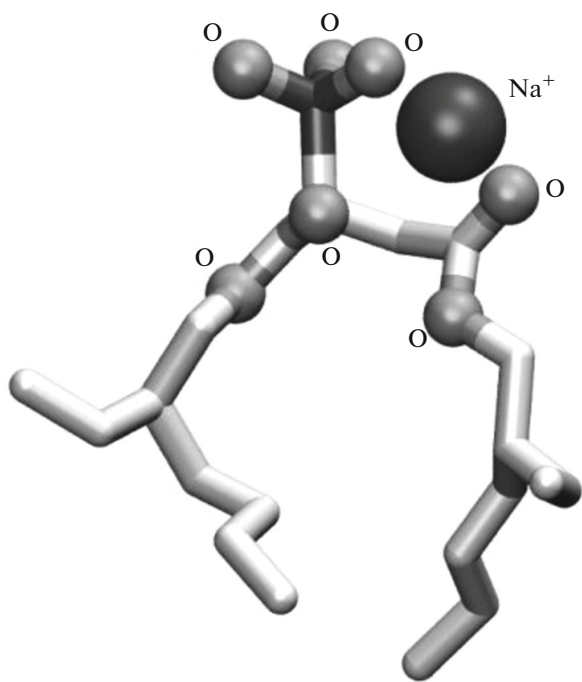
Fig. 1. Structure of an AOT molecule in vacuum at a random moment of MD simulation. Hydrogen atoms are not presented to improve readability.

which spherical reverse micelles can be obtained in a wide range of sizes (2−20 nm) [20−22]. Thermodynamic integration method combined with the molecular dynamics (MD) simulation is used to calculate the free energy of the addition of one AOT molecule to a micelle as depending on the aggregation number.

SIMULATION DETAILS

MD simulation was performed using the DL_POLY Classic software [23] with MVS-100K and MVS-10P supercomputers (Joint Supercomputer Center of the Russian Academy of Sciences). A cubic cell with periodic boundary conditions containing one micelle in hexane was used for the calculations. Micelle size was varied in the range of $N = 1−45$, where N is the number of OAT molecules in the micelle (aggregation number). The cell size was from 9 to 10 nm depending on micelle size.

To construct the starting computational configuration, a spherical cavity with a required size was cut in hexane, and a preformed micelle, which represented a spherically symmetric structure composed of N AOT molecules with nonpolar moieties facing the solvent, was placed into it. The system was equilibrated by a 5-ns calculation in an NPT-ensemble at $T = 300$ K and $P = 1$ atm. The temperature and pressure were maintained by the Nose−Hoover algorithm. The time step was 1 fs.

The CHARMM27 all-atom force field was used for AOT molecules [24]. The atom charges were taken from [25]. A visualization of the AOT molecule structure obtained in vacuum with the use of this force field is presented in Fig. 1. Hexane molecules were simulated in the monoatomic approximation as Lennard-Jones particles [26].

Since the simulated system was inhomogeneous and had the form of a polar micelle in a nonpolar solvent, when calculating the electrostatic interaction, all pair Coulomb interatomic interactions inside the micelle were taken into account (a cutoff radius a fortiori larger than the micelle characteristic size was introduced). The van der Waals interaction was calculated using a cutoff radius of 1.5 nm. To implicitly take into account the electronic polarization of atoms, the interatomic electrostatic interactions were corrected with respect to the factor $1/\varepsilon_\infty$ [27, 28], where ε_∞ is the optical dielectric permittivity, which weakly depends on the nature of a medium and is ≈ 2.

A change in the Gibbs free energy upon the addition of an AOT molecule to the micelle was calculated by the thermodynamic integration method. According to this method, the concept of mixed Hamiltonian $H(\lambda)$ is introduced, the application of which enables one to transfer a system from the state described by the $H(0)$ Hamiltonian to the state described by the $H(1)$ Hamiltonian by varying parameter λ from 0 to 1. In our case, a virtual process is implemented to transfer an AOT molecule from the state of noninteraction with other molecules of AOT and hexane (AOT in "vacuum") to the state of completely switched-on interaction. It may be shown that the change in the free energy in this process is equal to [29]

$$\Delta G = \int_0^1 \left\langle \frac{\partial H(\lambda)}{\partial \lambda} \right\rangle_{NPT,\lambda} d\lambda,$$

where $\left\langle \dfrac{\partial H(\lambda)}{\partial \lambda} \right\rangle_{NPT,\lambda}$ is a value obtained by averaging in the NPT-ensemble at a specific value of the λ parameter. The trajectory duration at each λ parameter was 0.2 ns.

For convenience, we, in this work, considered the inverse process of switching off the interaction of an arbitrary AOT molecule in a micelle with the rest of the system. For this purpose, the charges of atoms in an isolated molecule and corresponding intermolecular van der Waals interactions were multiplied by λ. Part of the Hamiltonian describing the interaction of the isolated molecule with the rest of the system was written as

$$H'^{(\lambda)} = \sum 4(\lambda \varepsilon_{ij})\left(\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^6\right) + \sum \frac{(\lambda q_i) q_j}{r_{ij}}.$$

Thus, the change in the λ parameter from 1 to 0 leads to "switching off" of the electrostatic and van der Waals interactions. However, the atomic charges of a molecule transferred this way into "vacuum" were found to be switched off; the intramolecular interaction and, hence, the desired free energy appeared to be distorted. Therefore, another procedure was realized, in which a quasi-static process of charge switching-on was performed for a single AOT molecule in the cell. The process free energy, which was also calculated by the thermodynamic integration, was used to correct the desired Gibbs free energy of AOT molecule addition to the micelle. To decrease the statistical error, the free energy was calculated for several AOT molecules randomly chosen in the micelle (for example, at $N \geq 27$, the calculations were performed for nine molecules). The obtained values were averaged.

RESULTS AND DISCUSSION

Figure 2a shows the dependence of Gibbs free energy increment ΔG_N^0, resulting from the addition of one AOT molecule to a micelle with a size of $N-1$ on the aggregation number, i.e., the free energy of the following reaction:

$$\text{micelle}_{N-1} + 1\text{AOT} \xrightarrow{\Delta G_N^0} \text{micelle}_N.$$
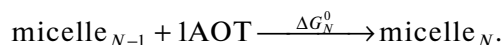
The points in Fig. 2a were obtained by thermodynamic integration, while the solid line shows their approximation by a smooth curve. It can be seen that, at small aggregation numbers, the ΔG_N^0 function decreases. There is a minimum at $N \approx 20$, which is followed by a maximum at $N \approx 35$. At larger N values, ΔG_N^0 seems to converge to a constant value. A hyperbola was used for the analytical approximation; the maximum at $N \approx 35$ was approximated by a Gaussian curve. A qualitatively similar dependence found in [30] for normal micelles of sodium dodecyl sulfate molecules in water seems to indicate a common character of the ΔG_N^0 dependence for different micellar systems.

It is of importance that ΔG_N^0 is not the chemical potential of surfactant molecules. Let μ_N^0 be the AOT chemical potential in a micelle with aggregation number N under the conditions corresponding to the simulation. We shall take these conditions as standard and the μ_N^0 potential to be the standard chemical potential. Then, the standard free energy of the micelle is equal to $N\mu_N^0$, and, for the change in the free energy due to the addition of one AOT molecule, the following formula can be written:

$$\Delta G_N^0 = N\mu_N^0 - (N-1)\mu_{N-1}^0.$$

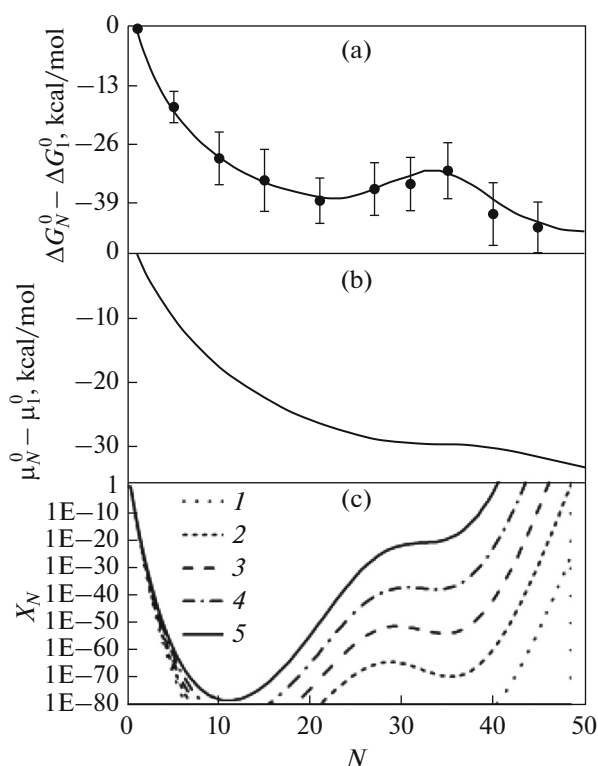This formula yields the following relation for the standard chemical potential of surfactant molecules:

Fig. 2. (a) The change in free energy upon the addition of an AOT molecule to a micelle, (b) the standard chemical potential of AOT in a micelle, and (c) micelle size distribution as depending on N aggregation number at different monomer concentrations: $X_1 = (1)\ X_1^0$, (2) $5X_1^0$, (3) $10X_1^0$, (4) $30X_1^0$, and (5) $100X_1^0$.

$$\mu_N^0 = \frac{\sum_{i=1}^{N} \Delta G_i^0}{N}.$$

The dependence of the chemical potential on N is given in Fig. 2b. The μ_N^0 function decreases monotonically and has an inflection point at $N \approx 30$, which reflects the nonmonotonic behavior of ΔG_N^0.

The equilibrium concentration of micelles with aggregation number N was calculated using the following standard relation [5]:

$$X_N = \left(X_1 \exp\left(-\frac{\mu_N^0 - \mu_1^0}{kT} \right) \right)^N, \quad (1)$$

where X_1 is the concentration of nonaggregated free monomers in the system. The X_1 value in Eq. (1) is a free parameter, variations in which enable one to observe changes in the micelle size distribution. Figure 2c illustrates micelle size distributions (nor-
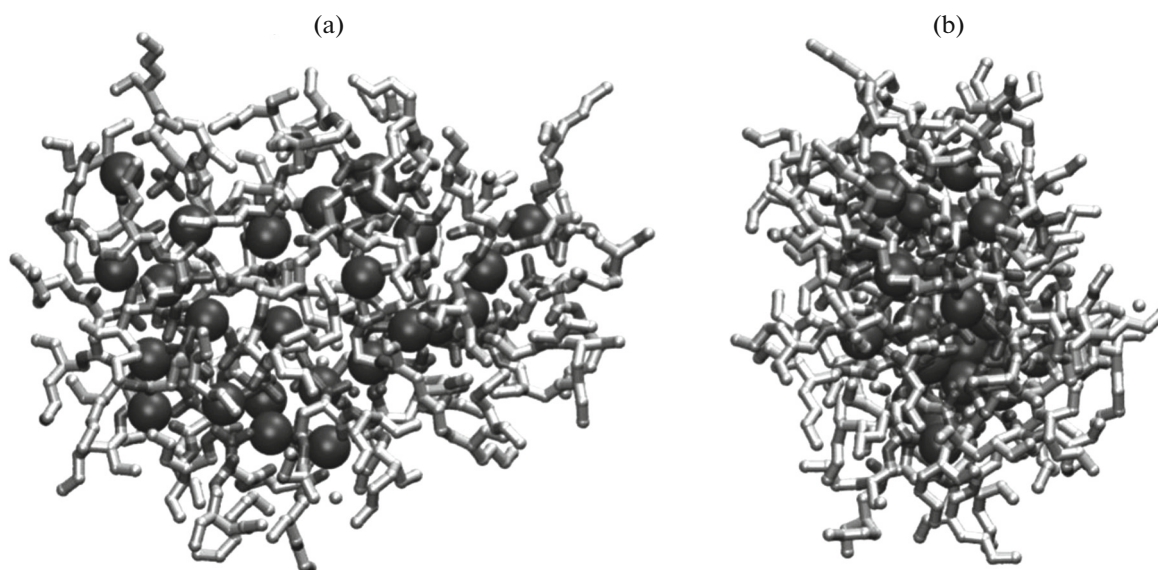
Fig. 3. Visualization of micelle ($N = 30$): (a) orientation providing maximum cross-sectional area and (b) side view.

malized with respect to the free monomer concentration) at different values of X_1. At rather small concentrations X_1^0, a maximum is observed at $N = 1$, with this maximum rapidly deceasing to 0. That is, surfactant molecules are not aggregated, but rather are distributed in hexane as monomers. As the monomer concentration in the system increases, a maximum arises at $N \approx 30$, thereby indicating micellization. Micelle concentration in the system increases with monomer concentration. The experimental values of the average aggregation numbers of dry micelles in the AOT/oil system fluctuate in a range of 20−30 [31−33]. Thus, it may be stated that there is a good agreement with the experiment. The visualization of the micelle structure corresponding to the distribution maximum at $N \approx 30$ is illustrated in Fig. 3. The micelle shape differs from a spherical one and resembles a flattened spheroid.

The distribution in Fig. 2c predicts the aggregation (separation of an AOT phase) at large N values as well, thus being in conflict with the experiment. This effect can be explained by the imperfection of the widely used force fields, thereby setting the problem of the individual optimization of AOT−AOT and AOT−hexane interactions for calculating the thermodynamic characteristics of the reverse micelles in the AOT/hexane system.

CONCLUSIONS

MD simulation was performed for AOT reverse micelles in hexane, with the micelles containing 1−45 monomers. For AOT, the all-atom force field with an implicit account of the electronic polarization was used, while hexane molecules were simulated in the monoatomic approximation. Within the framework of the MD simulation, the thermodynamic integration was realized to calculate the change in the Gibbs free energy due to the addition of an AOT molecule to a micelle as depending on aggregation number N. This value decreases at low aggregation numbers; at $N \approx 20$, a minimum arises followed by a maximum at $N \approx 35$. The calculation of the standard chemical potential for monomers in a micelle as depending on N predicts the formation of micelles with size $N \approx 30$, which is in good agreement with the experimental data. The micelles have the shape of a flattened spheroid. The simulation data predict incorrectly the separation of an AOT phase and do not enable one to reproduce the critical micelle concentration. This fact requires the development of a special version of the force field for the calculation of the thermodynamic characteristics of AOT reverse micelles in hexane.

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Translated by K. Aleksanyan