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# Molecular dynamics simulation of some cyclic compounds solubilization into the nanometric core of Cetyltrimethylammonium Bromide micelle

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## HIGHLIGHTS

- CTAB spherical micelle was studied by coarse-grained model of Molecular dynamic simulation.
- Solublization of some cyclic compounds within nanometric micelle was investigated, too.
- The results emphasize the existence of a cavity in the interior of the micelle with radius of 1.10 nm.
- Micelle size and shape alteration would take place during mounting the content of solubilizates.

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## ABSTRACT

Large-scale coarse grained molecular dynamics simulations were performed to investigate the self-assemblies of Cetyltrimethylammonium Bromide spherical micelle and the solubilization of four cyclic compounds; pyrrole, aniline, thiophene and cyclohexane within the nanometric micelle. Our results showed that solubilizates with lower polarity are located in the inner regions of micelle and materials with higher polarity are located at the outer areas of micelle and near to the surface. We observed that at low solubilizate content, these compounds are predominantly solubilized in a definite zone in the micelle and this does not significantly change micellar size and shape. With increasing of solubilizates content the location of solubilization is extended from one region to several regions into the micelle and the micelle is subjected to change in size and shape. Our findings are in good conformity with experimental results. It has also been deduced that micelle formation time is crucially bounded to solubilization stage.

## Introduction

Amphiphilic surfactants that consist of hydrophilic head and hydrophobic tail self-assemble spontaneously when are dissolved in aqueous solution above a critical micelle concentration (CMC), forming micellar structures. In micelles, hydrophobic tails shield from water in the aggregate interior, and hydrophilic heads lie near to water solvent at the aggregate surface. Therefore, the polarity of micelles increases from the central region of hydrocarbon chains of surfactants toward the micelle surface. Due to anisotropic polarity of micelles, their hydrophobic core provides a favorable environment for organic compounds that are sparingly soluble or insoluble in water. This phenomenon is called solubilization and is one of the most prominent properties of surfactants which are related to their ability of micelle formation. Solubilization in micellar solutions plays a cornerstone role in different fields such as biological, pharmaceutical, and industrial processes. Inasmuch as presence of different regions in micelles from the view point of hydrophobicity, the solubilized molecules are distributed according to their polarity in micelles. It has been concluded that constellation of parameters like the structure and nature of surfactant, the structure and nature of solubilizate and the solvent conditions determine the location of solubilizate molecules within the micelles. Upon the discussed parameters, solubilization sites are classified as: (1) at the micelle-solvent interface, on the surface of the micelle; (2) between the hydrophilic head groups; (3) between the hydrophilic groups and the first few carbon atoms of the hydrophobic groups that comprise the outer core of the micellar interior and named

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palisade layer; (4) more deeply in the palisade layer; and (5) in the inner core of the micelle that are shown in Fig. 1 [1–6].

There are many theoretical and experimental studies on the solubilization and solubilization location of hydrophobic materials such as drugs [7,8], dyes [9,10], oils [11] and other organic compounds [12–16] within the micelles. Recognizing of these solubilization sites is very essential and helps us to have a better understanding of solubilizate characteristics in micelle, to investigate reaction mechanism in micellar systems and to design the micellar systems to reach the favorite properties.

One of the most important applications of solubilization in micelles is referred to polymerization of organic compounds. Different conducting polymers such as polypyrrole, polyaniline, polythiophene and their derivatives have potential applications in various fields including electrode materials in energy storage devices like supercapacitors. Owing to importance of these polymers and their applications, in recent years, a considerable amount of experimental research has been carried out about different ways to synthesize of these materials and effective factors on their improvements [17–19]. One of these ways is chemical oxidative polymerization where various oxidants and surfactants are utilized to enhance the thermal, electrical and electrochemical properties of polymers. Formation of micelle in the reactant solution affects on the molecular and supramolecular structure of conducting polymers. Generally, the surfactants could display two major impacts on the preparation of conducting polymers including: (a) controlling of the reactant molecules distribution between the micellar and aqueous phases which alters locus and the course of polymerization and (b) adsorption of hydrophobic part of the surfactant molecules that may occur on the produced conducting polymer, so surfactant is considered as a part of the resulting material [20–24].

Four cyclic molecules; pyrrole, aniline, thiophene and cyclohexane, have been assayed as solubilizates with different polarities. This paper aim is to provide important information and insights into understanding the solubilization of these compounds within the CTAB (one of the most widely used surfactants) micelle solution from the view point of both selectivity into the different sites of micelle and their effects on size and shape control.

Since the Molecular Dynamic, MD, investigations give us complete information about dynamical and structural properties of different systems and are successful tools in complementing experimental techniques [25], in here, the study of micellar structure of CTAB with and without solubilizates have been carried out by coarse-grained (CG) Molecular Dynamic simulations with MARTINI force field [26]. We have also investigated the solubilization location of these four solubilized cyclic molecules with different amounts within the CTAB micelle.

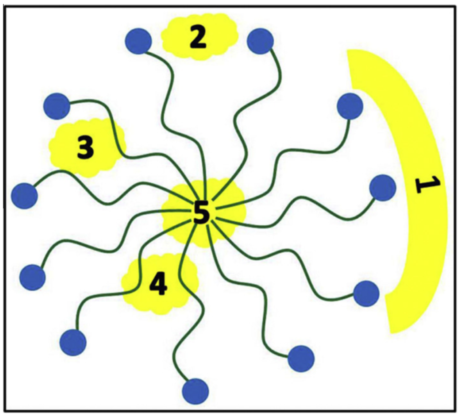

**Fig. 1.** Solubilization sites within the micelle.

## Theoretical methods

Gromacs 4.5.4 molecular dynamics package [27] was used to carry out all simulations and subsequent analyses. All systems were described by the potential parameters of the MARTINI coarse-grained (CG) force field. The MARTINI coarse-grained force field has shown accurate agreements with atomistic simulations and experimental data [28–30]. The mapping that MRATINI force field utilizes to represent molecules is a four-to-one mapping, i.e. on average four heavy atoms are represented by a single interaction center (bead). For ring structures, in order to preserve the geometry of small ring compounds, MARTINI uses a two-(or three-) to-one mapping of ring atoms onto CG beads [26]. The mapping scheme of the molecules studied in this paper is sketched in Fig. 2.

Eighty Cetyltrimethylammonium ions were used to build of CTAB micelle. This number is in consistence with the experimental [31] and theoretical [32] aggregation number of CTAB micelles which is in the range of 60–89 surfactant molecules per micelle. In the first system, the micelle was built in a cubic box by 4294 water beads. The number of water molecules was selected from previous work [33], but since the MARTINI model places four water molecules in a single CG bead, the number of water molecules in our system must be multiplied by four. Therefore the concentration of surfactant solution in our system corresponds to a 0.22 M CTAB solution, which is well above the CMC (0.9 mM). From this concentration up to approximately 0.3 M, the micelles formed in solution are spherical [34,35]. To avoid freezing of solvent, ten percent of water particles were modeled with the antifreeze CG water provided in the MARTINI force field database [26]. Eighty bromide ions (CG particles of the type Qa, with a charge of $-1$) were added to neutralize the system. In the other systems we added different amounts of additive molecules respectively: pyrrole, aniline, thiophene and cyclohexane in each system. The details of the compositions for all systems we have studied and dipole moment of solubilizates are summarized at Table 1.

The systems were subjected to energy minimization and were followed by an equilibration run of 60 ns in a NPT (constant pressure and constant temperature) ensemble to reach the correct density. The temperatures were coupled to 300 K bath using the velocity rescaling method [37], and the pressures were maintained at 1 bar by the Berendsen method [38]. A time step of 30 fs was used for integrating equations of motion with leapfrog algorithm. Periodic boundary conditions were applied in all directions, alongside with the nonbonded interactions were subjected to a cutoff of 1.2 nm has been drawn into our consideration. The *L–J* potential was shifted from 0.9 to 1.2 nm and the electrostatic potential was shifted from 0 to 1.2 nm. Then a 0.6 μs NPT simulation was carried out and Simulations were also continued till 1.2 μs to check of stability of systems.

## Results and discussion

In order to obtain information about the different regions in the micellar interior, their effects on solubilization of some cyclic compounds and effects of these compounds on micelle structure, we have carried out simulations consists of two parts: (1) the formation of CTAB micelle, investigation of its structure and comparing with previous experimental and theoretical results, (2) the studying of formation of CTAB micelle with addition pyrrole, aniline, thiophene and cyclohexane from the point of view time of simulation, distribution of solubilizates at different sites of micelle or solvent