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Molecular dynamics study of stability and disintegration of long rod-like micelles: Dodecyltrimethylammonium chloride in solutions of hydroxybenzoates[☆]

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ABSTRACT

Recently it was found out that different positions of the hydroxylic group on hydroxybenzoate anions (HB) crucially affect the thermodynamics of the self-organization of the cationic surfactant dodecyltrimethylammonium chloride (DTAC) and also the structure of resulting aggregates. In our previous work, the properties of stable long cylindrical DTAC micelles in the presence of NaHB at 1:1 DTAC/NaHB molar ratio in aqueous solutions were investigated by atomistic molecular dynamics simulations. In the present work, we first study the decay of cylindrical DTAC micelles in water without added salt and then extend our research to systems with low NaHB concentrations (DTAC/NaHB molar ratios of 4:1 and 2:1) in order to approach the real experimental conditions more closely. The geometry and structural properties of DTAC micelles in water are investigated, and also the decomposition of long cylindrical micelles and the solvent accessible surface area of micelles is discussed. We observe that the initial DTAC micelle without NaHB quickly disintegrates into smaller stable spherical micelles. At the 2:1 DTAC/NaHB molar ratio we find all initial DTAC micelles to remain stable; however, their geometry deviates significantly from initial cylindrical one. Furthermore, it is observed that *o*-HB induces a more ordered internal structure of the micelle, and is more strongly oriented than the other two isomers, which agrees well with the experiments and observations reported in our previous work. When the NaHB concentration is decreased to 4:1 DTAC/NaHB molar ratio, an initial DTAC micelle disintegrates forming smaller aggregates of spherical or elongated shapes regardless of the nature of the HB isomer present. The microscopic structure of the resultant micelles is very similar to the structure observed at higher NaHB concentration, however, the effect of HB ions is smaller. It was also observed that the micelle remains stable longer in the presence of *o*-HB than in the presence of the other two isomers.

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1. Introduction

Some surfactant micelles undergo shape transition after the addition of a sufficient amount of an electrolyte. Usually, initially spherical micelles transform themselves into rod-like, thread-like or worm-like aggregates. This effect has been observed for nonionic, anionic and cationic surfactants; however, it is the most pronounced in the case of the latter, especially in the presence of counterions containing an aromatic ring [7–13]. The reason for the sphere-to-rod transition in

cationic micelles with aromatic counterions has been experimentally investigated for cetyltrimethylammonium bromide (CTAB) [14–16] and dodecyltrimethylammonium bromide (DTAB) [17] and attributed to the specific ion hydration in the interfacial region [15]. Several computational studies were also conducted [18, 19] suggesting the shape transition occurs due to reduced micelle-water interfacial tension.

While it is not surprising that the concentration and the nature of the added salt influence the self-assembly, it is more intriguing that also the change in the substitution pattern of the benzene ring can have a dramatic effect [11, 12, 20]. The thermodynamics and structural consequences of this behavior have been recently investigated for the micellization of dodecyltrimethylammonium chloride (DTAC) in the presence of sodium 2-hydroxybenzoate (*o*-HB), 3-hydroxybenzoate (*m*-HB) and 4-hydroxybenzoate (*p*-HB) [21, 22]. The *para* isomer was found to have the smallest effect on the micellisation of DTAC. It decreases the critical micelle concentration (cmc)

[☆] This work has been dedicated to Prof. Vojko Vlady on the occasion of his 70th birthday. V. Vlady has contributed substantially to the theory and simulations of aqueous solutions of electrolytes; here we wish to cite just a few of his contributions that are related to this work [1–6].

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from 22 mM in pure water to 9.7 mM, and it is incorporated only weakly into the DTAC micelles, whereas the *meta* and *ortho* isomers have stronger influence. The *meta* isomer lowers the cmc to 4.5 mM, and the *ortho* isomer to 0.9 mM. In the presence of *o*-HB, which is also called salicylate, the enthalpy of micellization is the lowest, and, at sufficiently high salt concentration, thread-like micelles appear, seemingly due to the expulsion of water from the micelle interior and the simultaneous insertion of salicylate molecules in the vicinity of the polar head of the surfactant. In our recent paper [23] we conducted atomistic molecular dynamics simulations of infinitely long cylindrical DTAC micelles in the presence of all three isomers of NaHB at a DTAC/NaHB molar ratio of 1:1. We observed that *o*-HB interacts most strongly with the DTAC micelle, penetrates more deeply into the micellar core and induces a more ordered arrangement of surfactant headgroups and denser packing of unimers than the other two isomers. Furthermore, it exhibits stronger preferential orientation with respect to surfactant molecules and main micellar axis and has also a pronounced second preferential orientation, which is due to the hydrogen bonding between *o*-HB molecules. On that basis we speculated that the *ortho* isomer may form a “bridge” between two smaller DTAC micelles, which could lead to their fusion.

In the present work we extend our previous research, where the DTAC/NaHB molar ratio was 1, and approach the real experimental conditions more closely. Here the systems with lower NaHB concentrations (2:1 and 4:1 DTAC/NaHB molar ratios) and an aqueous solution of DTAC in the absence of NaHB were treated. In this way we qualitatively investigate the dependence of the strength of the HB effect on micellar stability, and at the same time we can prove that our previous findings about microscopic structure of the micelles were not only a consequence of a too high HB concentration.

The next section contains a brief description of the simulation protocol and types of system studied. The main results section discusses the simulations of an infinitely long (under periodic boundary conditions) DTAC micelle in pure water and the same DTAC micelles in the presence of NaHB at two different DTAC/NaHB molar ratios. The mesoscopic structure of the studied micelles is described in terms of shape and size, and their nanoscopic structure is described through radial distribution functions and distribution of angles between certain vectors. In addition, the time evolution of micellar microscopic structure in terms of coordination numbers is discussed. Finally, the solvent accessible surface area and its distribution among different parts of DTAC and HB molecules is calculated and discussed for systems with different DTAC/NaHB molar ratios. In the final section we summarize the findings of our research.

2. Force field and simulation parameters

Force field parameters and system preparation were identical to the procedures explained in detail in our previous work [23]. Molecular dynamics (MD) simulations were performed with the LAMMPS simulation package (9. April 2014) [24, 25]. The GROMOS96 53a5 force field [26] was used for all the interactions except for the -C-C-C- torsions in hydrocarbon chains, where the Ryckaert-Bellemans torsion potential [27] was used. Partial charges were taken from our previous work [23, 28] and the particle-particle particle-mesh (PPPM) solver included in the LAMMPS package [29] was used to handle long-range electrostatic interactions. An accuracy parameter of 10^{-5} and a real space cutoff of 10 Å were used. The same cutoff distance was used for Lennard-Jones interactions. Two water models, the SPC [30] and the SPC/E [31] model, were used to solvate all species. The only difference between them are partial atomic charges: -0.82 for the O and 0.41 for the H atoms in the SPC model and -0.8472 for the O and 0.4238 for the H atoms in the SPC/E model. The water geometry was constrained with the SHAKE algorithm [32].

We studied systems with an infinitely long DTAC micelle in pure water or in hydroxybenzoate solutions. The periodic rectangular simulation box was initially 7.5 nm long in the *x* and *y* dimensions and 10 nm long in the *z* dimension. The infinitely long micelle spans the entire simulation box along the *z* direction; it consists of 180 DTAC unimers and was initially placed in the center of the *xy* plane of the simulation cell. The positive charges of DTAC molecules were compensated by an equal number of chloride ions, those of the hydroxybenzoates by an equivalent number of sodium ions. Solutions with DTAC/NaHB molar ratios of 1:1 (see also Ref. [23]), 1:2 and 1:4 were studied in addition to the system without NaHB, which corresponds to 180, 90, 45 and 0 NaHB ion pairs, respectively. Details about systems with equal amounts of DTAC and NaHB, which are compared with the systems studied in this research, are given in our previous work [23]. In addition, we tested the effect of ionic strength by adding enough NaCl ions to the systems with 45 HB anions so that we reached the same ionic strength as for the system with 180 HB anions. The number of added water molecules was calculated as following:

$$N_{\text{water}} = 15000 - (N_{\text{Cl}^-} - 180) - N_{\text{Na}^+} - N_{\text{HB}^-}, \quad (1)$$

where *N* means the number of molecules or ions in the subscript. After equilibration, the DTAC concentration was approximately 0.54 M, which is well above the critical micelle concentration (22 mM) in water [21]. Further details of the initial assembly of the micelles and their subsequent equilibration are given in our previous publication [23]. Composition and particle numbers of investigated NaHB systems are summarized in Table 1.

Production runs were performed at constant temperature ($T = 298.15$ K) and pressure ($P = 1$ atm) with time step of 2 fs. Temperature and pressure control was achieved with the Nosé-Hoover [33] thermostat and Nosé-Hoover barostat [34]. A semi-isotropic pressure coupling scheme was applied. In order to allow the length of the cylindrical micelle to equilibrate (under periodic boundary conditions) independently from the pressure in the cell, the pressure tensor element along the axis of the cylindrical micelles was decoupled from the remaining two elements. Thus, the *z* dimension of the simulation box was rescaled independently of the *x* and *y* dimensions. Simulations in SPC/E water were run for longer times than those in SPC water (see Table 1), because the dynamics is generally somewhat slower in SPC/E water due to its twofold lower self-diffusion coefficient in comparison to that of SPC water. The final length of the *z* dimension of the box depends on the system studied. In the 2:1 DTAC/NaHB molar ratio case, where the micelles did not disintegrate the average length of the *z* dimension changed from the initial 10 nm to roughly 8.5 nm in the *ortho*, 9.5 nm in the *meta* and 11 nm in the *para* case. In the case when the initial micelle disintegrates the average *z* dimension of the box was roughly 13 nm.

3. Results and discussion

In the following section we will compare the results of simulations of long cylindrical micelles at different concentrations of sodium hydroxybenzoates for molar ratios between HB anions and DTAC molecules of 0:1 (in pure SPC water) to 1:1. Except for the pure water system, for which only the SPC water model was used, simulations were performed both in SPC and in SPC/E water; it was observed that the results obtained for SPC water are similar to those obtained for SPC/E water. Thus, for most properties only the results for the SPC water model are presented and discussed in this section. Relevant results for the SPC/E water model are given in SI.

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