



Molecular dynamics simulations of liquid crystalline phases of dodecyltrimethylammonium chloride



Vitaly Kocherbitov

Biomedical Science, Faculty of Health and Society, Malmö University, SE-20506 Malmö, Sweden

ARTICLE INFO

Article history:

Received 14 October 2014

Received in revised form 8 May 2015

Accepted 2 June 2015

Keywords:

Surfactants

Liquid crystalline phases

Hexagonal phase

Bicontinuous cubic phase

MD simulations

ABSTRACT

Molecular dynamics simulations of four different phases of a cationic surfactant dodecyltrimethylammonium chloride (DTAC) are presented. It is shown that when the topology of the initial configuration matches that of the equilibrium structure, the required equilibration times of MD simulations are only few nanoseconds. The methods of building initial configurations for simulations of the hexagonal and Ia3d bicontinuous cubic phases are described. The simulation results show that locally, the hydrophilic part of the hexagonal phase has a flat bilayer structure. Analysis of radial distribution functions shows that the properties of the hydrophilic layers of the phases are dominated by ion–ion and ion–water interactions. The dynamic properties of the system are dependent on the curvature of the aggregates, and calculated diffusion coefficients are in agreement with experimental NMR data.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Phase studies of surfactants and lipids are time, material and work consuming. A large amount of material is required to cover a two- or three-dimensional phase diagram space. Equilibration of each sample at specific conditions takes days or weeks; synchrotron radiation is often required to resolve structures of liquid crystalline phases. Due to rapid development of simulation methods, computer modeling will soon be an alternative approach for the determination of phase diagrams. There are, however some challenges that have to be overcome before this approach will be used in practice. The system size required for simulation has to be rather large, and simulation times have to be long. Coarse grained simulations [1,2] can be of help in solving this problem, but they have their obvious limitations; detailed information about simulated structures can only be obtained in full-atomic simulations.

Two different approaches can be used for computer simulations of phase behavior. In the unbiased approach, the initial configuration of the system should not be built according to the structural information on the expected phase. The simulated molecules are expected to obtain required configuration spontaneously during equilibration process. The unbiased approach has however two limitations. Firstly, equilibration times for experimental surfactant and lipid studies can be up to several weeks, while simulation times on modern computers are most often limited to tens or hundreds of nanoseconds. In other words, the discrepancy between required and available times is 12 orders of magnitude.

Secondly, surfactants and lipids often form 3D structures, for example liquid crystalline cubic structures. In order to simulate such structure, one needs a configuration containing a certain number of molecules that matches the number of molecules in the unit cell. This is impossible without using experimental information on phase structures; purely unbiased approach is thus not realistic unless the simulation box is much larger than the unit cell.

In a biased approach, initial configuration should be built taking into account expected equilibrium configuration of the system. In that case, equilibration process is expected to take much shorter time. Several expected structures can be simulated and the equilibrium structure should be selected based on the lowest Gibbs energy criterion. This approach is not yet developed for surfactant and lipid phase studies. To the best of our knowledge so far only reversed phases of monoolein were simulated [3,4] while no simulations of direct non-lamellar phases of surfactants are reported in literature.

Dodecyltrimethylammonium chloride (DTAC, DoTAC, C₁₂TAC) is one of the most industrially important surfactants. It is used as emulsifier, pigment disperser [5], hair conditioning agent, antimicrobial agent [6], collector surfactant in froth flotation [7], antistatic agent and as a surface active compound in other applications. The phase behavior of DTAC is relatively well studied. Already in 1969 Balmбра et al. [8] presented the DTAC–water phase diagram that is often referred to in current publications. The phase diagram shows the presence of four liquid crystalline phases: lamellar, hexagonal and two cubic phases as well as solid crystalline phases. Later, Kang et al. [9] claimed presence of intermediate phases between the hexagonal and the concentrated cubic phase in this system. Moreover, Paccamiccio et al. [10] studied the effects of pressure on the phase behavior of DTAC–water system.

E-mail address: vitaly.kocherbitov@mah.se.

In this work, molecular dynamics simulations of four different phases of DTAC (lamellar, hexagonal, bicontinuous cubic and liquid micellar) are presented. Structure and dynamics of liquid crystalline phases possessing different curvatures are discussed.

2. Methods

The molecular dynamics simulations were performed using GROMACS [11] software package, version 4.5.4 on resources provided by the Swedish National Infrastructure for Computing (SNIC) at LUNARC center for scientific and technical computing in Lund.

The force field used was based on GROMOS96 53a6 force field [12] with few modifications. In particular, Lennard–Jones parameters united CH₂ and CH₃ groups were taken from Berger et al. [13]. The alkane dihedrals were modeled using Ryckaert–Bellemans potential [14]. The length of N–C bond was set to 0.150 nm according to crystallographic data on a hexadecyltrimethylammonium surfactant [15]. SPC model of water was used. The charges on the N atom and four neighboring carbon atoms were set to +0.2.

LINCS algorithm was used to constrain bond lengths, cut-off for van der Waals interactions was 1.2 nm, long range electrostatics was treated using PME approach, and temperature was 300 K with time constant of 0.1 ps. Periodic boundary conditions in all directions were used in all simulations, isotropic or semi-isotropic pressure coupling was applied depending on a type of the phase (see below). In all simulations, initial configurations were constructed as described below, and then energy minimizations were performed, followed by short equilibration runs (typically about 1 ns). After that, production runs of 100 ns were performed (60 ns for the cubic phase). For calculations of thermodynamic properties, first 10 ns of each run were excluded.

The snapshots were created using RasMol [16], the density maps were computed using GROMACS software package and then visualized in MATLAB (The MathWorks, Inc.).

2.1. Initial configurations

Four different phases of DTAC–water system were simulated; the water contents and the number of molecules in simulation boxes in each phase are shown in Table 1. To set up the initial configuration of the lamellar phase, a bilayer of 200 surfactant molecules with interdigitated chains and 320 water molecules was formed. In simulations of the lamellar phase semiisotropic pressure coupling was applied using Berendsen barostat with pressures 1.0 bar and time constants 10 ps in both dimensions. To set up the initial configuration of the liquid micellar phase, 40 surfactant molecules arranged in parallel were placed in a simulation box and then hydrated with 1200 water molecules. Isotropic pressure coupling (1.0 bar) with time constant 10 ps was applied using Berendsen barostat in simulations of the liquid micellar phase. To set up initial configurations of the hexagonal and especially of the cubic phase is a less trivial task and it is discussed below in details.

2.1.1. Hexagonal phase

Firstly, a configuration consisting of one DTAC molecule and six water molecules placed close to the headgroup was generated. Secondly, nine such configurations were created by rotation of the initial complex by 40 degrees around a point close to the last carbon atom of the tail. The

nine configurations were merged into one, thus a disc consisting of nine hydrated surfactant molecules was created. Then ten such discs formed a cylinder and finally two parallel cylinders were placed in a simulation box. The distance between the cylinders was 3.3 nm and the simulation box size was 3.3 × 5.715768 × 9.0 nm. The y to x ratio of the simulation box size was equal to the square root of three in order to ensure that simulation box shape was consistent with the geometry of hexagonal phase. This type of simulation box comprises two unit cells (and two cylinders), which can be useful for monitoring internal stability of the phase, for example possible redistribution of the material between two cylinders.

Semiisotropic pressure coupling was applied using Berendsen barostat with pressures 1.0 bar and time constants of 10 ps in both dimensions.

2.1.2. The 1a3d cubic phase

Unlike other phases considered in this work, the cubic phase is periodically structured in all three dimensions, which implies that a certain unit cell size corresponds to a certain number of molecules. Therefore in order to simulate a cubic phase one must select the correct number of molecules based on experimental structural data, for example X-ray scattering data. The unit cell size of cubic 1a3d phase of DTAC is about 7.9 nm at 17 wt.% of water [10] and 25 °C. This corresponds to three water molecules per surfactant, and the molecular mass M_c of such complex is 317.9 g/mol. The number of molecules N per unit cell is then given by the following formula:

$$N = \frac{N_a V d_c}{M_c} \quad (1)$$

where N_a is the Avogadro's number, V – unit cell volume, d_c – density. The number of DTAC molecules calculated from Eq. (1) is about 854 and this number was used in simulations.

Bicontinuous cubic phases can be described using minimal surfaces, i.e., surfaces with zero mean curvature [17]. In particular, cubic 1a3d phase can be approximated with a gyroid surface [18].

$$\begin{aligned} \sin(\pi(x+y)) + \sin(\pi(x-y)) + \sin(\pi(x+z)) + \sin(\pi(z-x)) \\ + \sin(\pi(y+z)) + \sin(\pi(y-z)) = 0 \end{aligned} \quad (2)$$

For a normal cubic phase this equation describes the position of the water layer. The whole phase can be considered as this surface is decorated with a water–surfactant complex. To generate initial conformation of the cubic phase, a cubic grid in the x, y, z range 0–2 was built and parameter t the value of the left side of the expression (2) was calculated for each point of the grid. Only 427 points which had absolute t values lower than a certain threshold (for the present geometry it was 0.189) were selected for further evaluation. Then for each point a normal to the surface was calculated by differentiating the left part of the Eq. (2) with respect to x, y and z . Finally the grid was scaled to match the size of the unit cell, 427 DTAC–water complexes were placed at each point and aligned along the normal vectors and 427 other DTAC–water complexes were placed and aligned opposite to normal vectors. To maintain the cubic shape of the simulation box, isotropic pressure coupling (1 bar) was applied using Berendsen barostat.

The procedure described above can be generalized for other types of normal cubic and non-cubic phases if an equation describing the position of the water layer is known. For reverse (inverted) cubic phases the procedure will include decoration of the surface by surfactant or lipid molecules with hydrophobic tails pointing towards the surface.

3. Results and discussion

When simulating large systems with complex geometries, it is important to make sure that the system has come to equilibrium, which can be verified through monitoring stability of energy of the system.

Table 1

Number of molecules, water contents and obtained densities of the simulated phases. Dimensions of simulation cells for periodic structures are also shown.

Phase	Lam	1a3d	Hex	Mic	Water
DTAC:H ₂ O	200:320	854:2562	180:1080	40:1200	0:1728
$x_{w, wt\%}$	9.85	17.00	29.06	67.19	100
Density, kg/m ³	896	912	928	959	977
d, nm	2.86	7.907	3.705 × 6.417		

Download English Version:

<https://daneshyari.com/en/article/5410735>

Download Persian Version:

<https://daneshyari.com/article/5410735>

[Daneshyari.com](https://daneshyari.com)