Molecular dynamics simulations of branched polyethyleneimine in water-in-heptanol micelles stabilized by zwitterionic surfactants

Armen H. Poghosyan [a,*], Levon H. Arsenyan [b], Lilit A. Antonyan [a], Aram A. Shahinyan [a], Joachim Koetz [c]

[a] International Scientific-Educational Center of National Academy of Sciences, M. Baghramyan Ave. 24d, 0019 Yerevan, Armenia
[b] The Institute of Applied Problem of Physics of National Academy of Armenia, Hr. Nersessian str. 25, 0014 Yerevan, Armenia
[c] Institut für Chemie, Universität Potsdam, Karl-Liebknecht-Straße 24-25, Haus 25, 14476 Potsdam, Germany

HIGHLIGHTS

- Molecular dynamics simulation of branched polymer in inverse micelle is performed.
- The simulation in the microemulsion droplet shows shrinking of polymer.
- The inverse micelle has predominantly spherical shape.

GRAPHICAL ABSTRACT
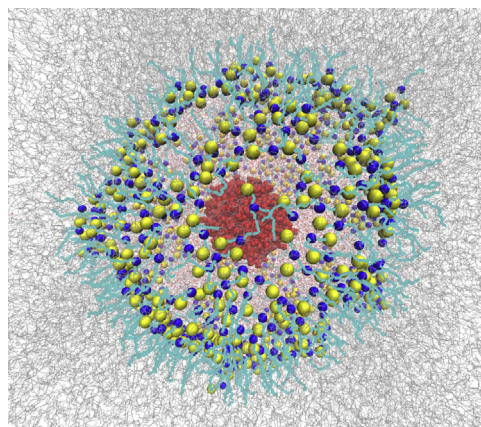
50ns of production run

ABSTRACT

We have performed a 50 ns molecular dynamics simulation of a hyperbranched polymer, i.e. polyethyleneimine (PEI), inside inverse micelles formed with zwitterionic surfactants 3-(N,N-dimethyl-dodecylammoniio)-propansulfonate (SB) in heptanol. The runs were performed using the GROMACS simulation package. During simulation time the PEI molecule undergoes a conformational deformation and compaction. The radius of gyration of the PEI molecule finally located in the center of the water droplet is decreased from 3 nm to 1.7 nm. The unusual shrinking of the PEI molecule inside the micelle explains the extraordinary template effect of these microemulsions by making cadmium sulfide or gold clusters.

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1. Introduction

Microemulsions are already well known for a long period, after the first paper published by Schulman in 1943 [1]. Nowadays, microemulsions (μE) are defined as spontaneously formed, self assembled mixtures of two non-mixable liquids, e.g. oil and water,

in presence of surface active species, i.e. surfactants [2]. However, the most important factor for the formation of microemulsions is the spontaneous curvature of the surfactant film (H_0) in comparison to the curvature of the droplets (H), defined as the reciprocal droplet radius [3]. When H equals H_0, the conditions for a spontaneous μE formation are fulfilled. Hereby, one can differ between oil-in-water (o/w) and water-in-oil (w/o) microemulsions. Noteworthy, when H and H_0 are zero, a bicontinuous, sponge-like μE is formed.

In the last years the class of microemulsions is expanded by using ionic liquids as one mixing component [4–6]. In dependence on the type of anion of the ionic liquid used different effects can be observed. For example anions with a long carbon tail, this means surfactant-like anions, can be well incorporated into the surfactant film, resulting in the formation of a so called "palisade layer" [7]. Recently, we were able to show, that microemulsions can be formed also by combining two ionic liquids with one oil component [8,9].

Another interesting approach is to modify the spontaneous curvature of the surfactant film by incorporating additional components, e.g. polymers. Different groups were able to show that water soluble polymers can be incorporated into w/o microemulsions without phase separation [10–12]. However, in dependence on the molar mass of the polymer a clustering of individual microemulsion droplets is assumed by using a long chain polymer with a radius of gyration larger than the diameter of the microemulsion droplets [13]. Our approach based on the incorporation of polyelectrolytes (PEL), this means water soluble polymers with anionic or cationic functional groups, into microemulsions with ionic surfactants [14,15]. Surprisingly oppositely charged polyelectrolytes as well as polyampholytes [16] can be incorporated into the w/o droplets up to higher polymer concentrations. These PEL-modified microemulsions show special properties and can be used as a template for the formation of nanoparticles [17–20]. Especially in presence of polyampholytes a surfactant film tuning becomes possible by varying the pH [21,22]. The idea hereby is to stabilize on the one hand the surfactant film (templating effect) and on the other hand the finally produced nanoparticles. Our investigations have shown that the polyelectrolyte inside the microemulsion droplets can directly control the nanoparticle size and therefore the optical properties of the quantum dots formed [23]. Additional investigations have shown that microemulsions consisting of water and heptanol (as oil component) in presence of surfactants with sulfobetaine (SB) head groups, show the best results for redispersing ultrafine CdS or Au quantum dots in presence of the hyper-branched polyethyleneimine (PEI) [24].

However, for a more detailed discussion and mechanistical interpretation of the obtained results model simulations are very important. Recently, we were able to show by MD simulations, that a linear polycation, i.e. poly(diallyldimethylammonium chloride) (PDADMAC), located inside of the w/o microemulsion droplets nearby the SDS surfactant head-groups [25] can stabilize the surfactant film. Similar effects were already observed in lamellar liquid crystalline systems by incorporating PDADMAC [26]. By means of MD simulations we were able to localize the polymer in the water layer between the surfactant double-layer.

Taking this knowledge into account the aim of the given research is to use the MD simulation approach to localize the hyper-branched PEI inside of water-in-heptanol microemulsion droplets stabilized by SB-surfactants for a better understanding of the extraordinary effect of branched PEI solubilized in microemulsion droplets as a template phase for the nanoparticle formation.

2. Simulation and construction details

The zwitterionic 3-(N,N-dimethyl-dodecylammonio)-propanesulfonate (SB-12) and heptanol molecules coordinate files and correspondingly the force fields were taken from ATB Server [27]. A spherical patch of $R = 58$ Å radius was created consisting of 630 SB-12 molecules and 25,784 water molecules inside. The SB-12 reverse micelle was constructed using our own *tcl* code, by evenly locating the SB-12 headgroups on the surface of water droplets with the radius of $R = 58$ Å in full agreement with experimental data given in [20]. Note that for secondary alkane sulfonate the surface area per headgroup was found to be ~0.6 nm^2 [28]. A hyperbranched poly(ethylenimine) (PEI) with a molar mass of 25.000 g/mol and a primary:secondary:tertiary amino group ratio 25%:50%:25% was created using GROMACS tools, where 10% of PEI amino groups are protonated. It is well established that ~10–20% of PEI amino groups are protonated at physiological pH (~7.4) [29], meanwhile different values of the protonation state of PEI are also reported in the literature [30–33]. After a short minimization, the molecule of PEI was inserted into water droplet. An adequate number of CL ions were added to a simulation box in order to preserve neutrality. A short MD run of 1 ns was first performed at higher temperature keeping water droplet and PEI molecules fixed, to further randomize the hydrocarbon chain configurations. Then, the SB-12/PEI/water system was inserted into a large periodic box of well equilibrated 1-heptanol. After a minimization of 5000 steps we have done 200 ps run at constant volume, where we keep SB-12 head group, water and polymer frozen, meanwhile hydrocarbon tails were randomized at 500 K. Further, the temperature turned slowly down to room temperature. The production run at $T = 300$ K and $P = 1$ atm was performed over 50 ns. The runs were performed using the GROMACS simulation package [34] with GROMOS96 53a6 force field.

The SPC model [35] for water molecules was used and the covalent bonds were kept fixed at their equilibrium distances with LINCS constrain algorithm [36]. The temperature was maintained using V-rescale algorithm with the time constant of 0.1 ps, while the isotropic pressure was controlled using Berendsen algorithm [37]. The PME [38] was used for long-range electrostatic interactions, meanwhile the van der Waals interactions were cut at 1.4 nm. The equations of motion are integrated using leapfrog Verlet integrator [39] with a time step of 2 fs. The cutoff distance for the short-range neighbor list was set to 1 nm, and the short-range neighbor list was updated every 5th timestep. Three dimensional periodic boundary conditions were applied and the coordinates and velocities were saved every 20 ps. The visualization of the molecular configurations was produced with VMD software package [40].

The simulations were carried out parallel on Linux cluster and partially on Hungarian supercomputer at Hungarian National Academy.[1] The final structures and force field protocols are available in the supplementary part.

3. Results and discussion

Before starting the discussion of calculated parameters, first we provide the snapshots of the system resulted from molecular dynamics simulation, which is illustrated in Fig. 1. One can see two configurations, it is obvious that the polymer undergoes a conformational change and finally is located in the center of water droplet.

To reveal whether the system is reached equilibrium, we inspect the root mean square deviation (RMSD) of system components relative to their initial structure. Based on presented curves (see Supplementary materials – Fig. S1), we argue that the convergence and stability of a simulation in terms of structure is reached, as it is commonly known that the RMSD is used as a convergence indicator of the structure toward equilibrium [41].