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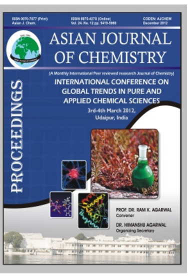

Molecular Dynamics Simulations of Micellization of Alkyl Ethoxylate†

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Micellization of the non-ionic surfactants alkyl ethoxylate (poly oxyethylene alcohols $C_{12}H_{25}(OC_2H_4)_4OH$) has been studied using atomistic explicit-solvent molecular dynamics simulations. The simulations were carried out in a wide range of surfactant concentrations (*ca.* 0.05 M-0.9 M) above the critical micelle concentration. An analysis of the number of cluster formed with time showed that all the system studied aggregated into a small number of clusters rapidly within about 200 ps and then the clusters aggregated into a spherical type micelle (in most of the cases) in about 1 ns. Various system properties are analyzed to predict trends with variation of concentration, chain lengths, *etc*. It is observed that variation of chain lengths (both polar as well as non-polar part) has a significant influence in the system properties. The implicit-solvent molecular dynamics study of the same system with dielectric constants 80 and 30 indicated that implicit-solvent model is not able to capture the phenomena of micellization properly.

Key Words: Non-ionic surfactants, Self-aggregation, Micelle formation, Implicit solvent.

INTRODUCTION

Surfactants found applications in diverse areas such as oil recovery, protein solubilization, drug delivery, electronic printing and magnetic recording, *etc.*[1]. Above their critical micellar concentration, surfactant molecules self-assemble to form multimolecular aggregates such as micelle. The structure of these aggregates influences the properties of surfactant solutions and consequently, the performance of surfactants in various applications. The process of micelle formation (or micellization) is governed by the balance of interactions of hydrophobic and hydrophilic groups with the solvent and is quite well understood[2]. However, the initial process of micellization and the manipulation of the microscopic details of micelle structure are still of current interests. The initial process of micellization occurs on a very fast time scale (nanosecond) and on a very short length scale (nanometer) making experimental investigation difficult. On the other hand, simulations can give information on surfactant micellization at molecular scale. Micellization has been studied using simulation at various levels: mean-field theories[3], bead-spring model[4], lattice and off-lattice course grained models[5]. Atomistic molecular dynamics simulations with implicit and explicit-solvent have also been reported in recent years[6].

Here, we report the atomistic molecular dynamics simulation of a class of nonionic surfactant alkyl ethoxylate (poly oxyethylene alcohols) to (a) understand the process of micellization at the molecular level, (b) study the variation of miceller properties with system parameters, such as surfactant concentration, surfactant chain length and (c) to compare the performance of implicit solvent model with that of explicit one.

EXPERIMENTAL

We simulate three alcohol ethoxylate surfactants $C_{12}E_6$, $C_{12}E_4$ and C_8E_4 [$C_nE_m = C_nH_{2n+1}(OC_2H_4)_mOH$] in five different concentration (36, 90, 216, 450 and 910 mM) well above their critical micellar concentration (ranges between 0.059-0.087 mM)[1 (a)] in explicit water. Also, the same system was simulated with implicit water at two dielectric constants 30 and 80. The surfactants considered differ from one another either by the head/tail chains. Similarly, explicit water with dielectric constant 80 was chosen to compare with the results of implicit water model.

Simulation details: The NAMD package (v2.7)[7] was used for the molecular dynamics simulations with Vega ZZ[8] as graphical interface. The surfactant structure was optimized using B3LYP/6-21G method[9] on the GAMESS[10] platform before using it to make initial configuration for simulations. These systems were then solvated in a box of TIP3P model water molecules using the automated solvation plugin of Vega ZZ. The box size was determined automatically by the software

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in accordance with the number of units present and the space occupied by them in 3-dimensions. For the two implicit solvation cases, the dielectric constants were set to 30 and 80 respectively to mimic water solvation and no water molecules were added to the system explicitly. We use NVT ensemble, the Verlet algorithm for time integration, with 1fs time step. The CHARMM22 LIPID force field[11] was used. A cutoff radius of 12 Å was used with the switching distance set at 8 Å. The distance for inclusion in pair-list was set at 12 Å. Non-bonded forces were evaluated at every other time step and full electrostatics forces at every 4 time steps. The water molecules were treated with SHAKE algorithm[12] to constrain the bond lengths and angles of water molecules. The periodic boundary conditions as well as the particle mesh ewald (PME)[13] were used with the particle mesh ewald grid spacing set to 1.0 Å. The simulated system was kept at constant temperature of 300 K using Langevin dynamics for all non-hydrogen atoms. The simulations were initialized with equilibration step to allow the system to relax for 300-500 ps followed by the production step of 1000 ps. The last 500 ps trajectories were used to calculate properties[14].

RESULTS AND DISCUSSION

The process of self aggregation and finally the micelle formation by the surfactants was observed in all the cases studied. As a representative case, we display (Fig. 1) the process of micelle formation for $C_{12}E_4$ at 0.91 M over the timescale. The aggregation takes place very rapidly and the micelle formation begins at around 500 ps and evolves into a near spherical single cluster at 800 ps. The hydrophilic polar part is observed on the outer periphery while the hydrophobic non-polar part forms the core of the micelle.

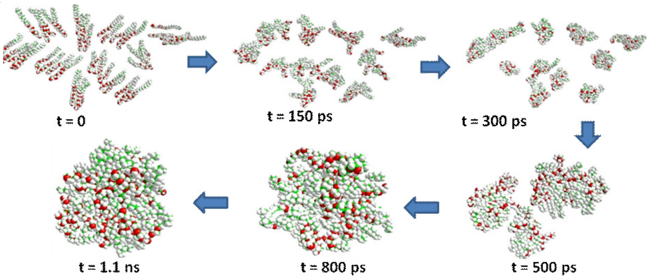

Fig. 1. Snapshots of the simulation at different stages. Water is omitted for clarity. Oxygen (red), carbon (green) and hydrogen (white)

In Fig. 2 we display the decline of total number of clusters during the simulation. An analysis of the number of clusters present in the system with time indicated that all the systems aggregate into a small number of clusters rapidly within about 200 ps after which the formed clusters come together much slower to reduce to one unit finally.

Variation of the micelle properties with surfactant concentration: For the surfactant $C_{12}E_4$, simulations were performed at five different concentrations ranging from 0.036 M to 0.91 M by varying the number of surfactant molecules. The variation of various miceller properties are plotted in Figs. 3 and 4. It is clear (Fig. 3) that with increase of surfactant concentration, the volume (V) and total surface area show an increasing trend. The polar surface area also exhibits a constant rise in value with increase in concentration. The total energy (E) of the system increases with surfacetant concentration in general, except for 90 mM. The surface diameter and the volume diameter increase (Fig. 4) rapidly till 450 mM and get almost constant beyond that while the radius of gyration first increases upto 90 mM and then decrease upto 450 mM and again increase at 910 mM. The radius of gyration at 910 mM is less than that at 36 and 90 mM, indicating storing aggregation and also penetration of water molecules inside the micelle in 36 mM case. The dipole moment (DM) increase steadily with increase of surfactant concentration.

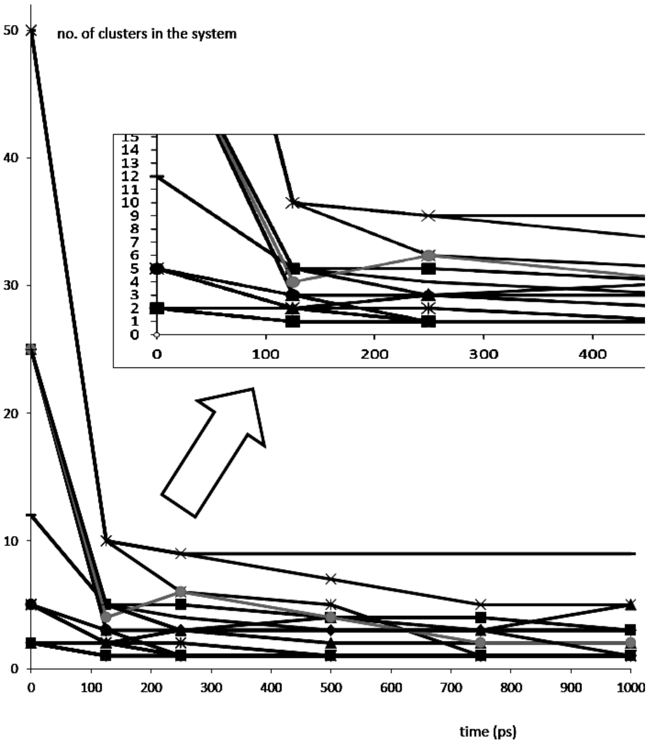

Fig. 2. Number of cluster formed during the simulation with their reduction with time

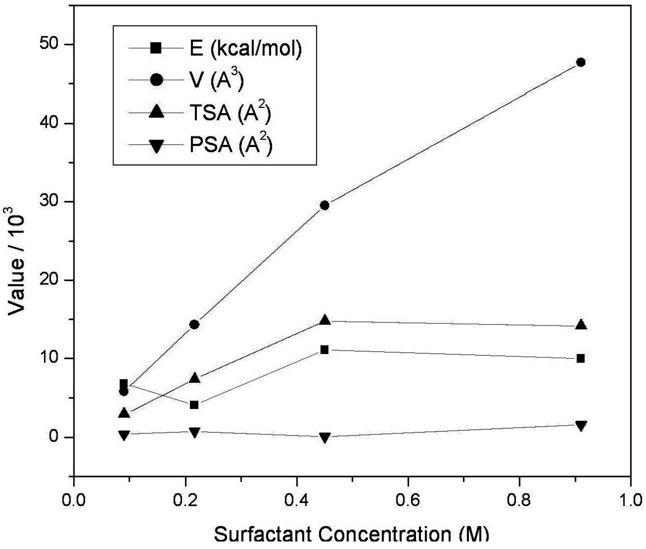

Fig. 3. Variation of miceller properties with surfactant concentration. The properties are the total energy (E), total volume (V), total surface area (TSA) and polar surface area (PSA)

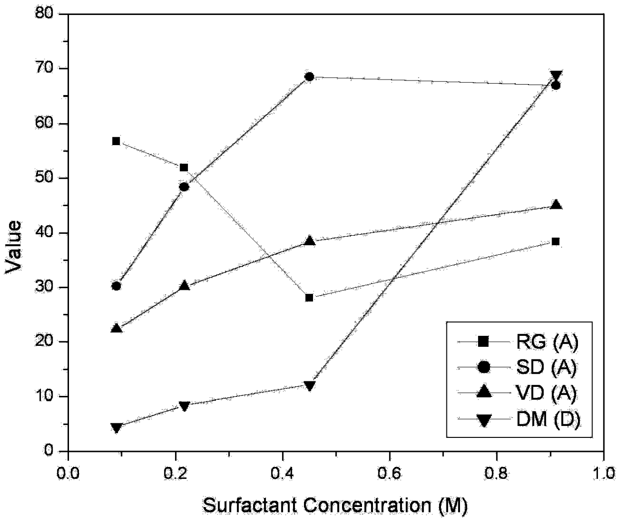

Fig. 4. Variation of miceller properties with surfactant concentration. The properties are the radius of gyration (RG), surface diameter (SD), volume diameter (VD) and dipole moment (DM)

Variation of the micelle properties with surfactant chain length: We simulate $C_{12}E_6$ and C_8E_4 systems along with $C_{12}E_4$ to analyze the effect of chain length of head/tail group on the micelle properties. The result for 0.21 mM case is displayed in Fig. 5. Increase of chain length of the surfactant in the non-polar part (C_n) leads to a reduction in all the properties calculated, while, an increase in the chain length of the polar part leads to increase in E, total surface area, total volume, radius of gyration and dipole moment and a reduction in surface diameter and dipole moment values.

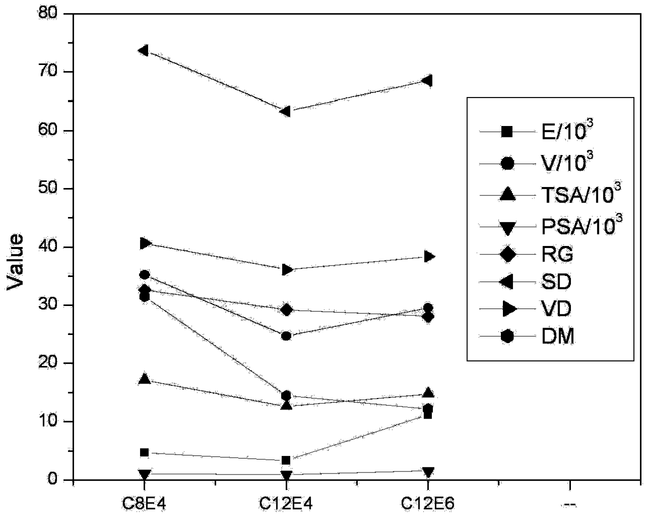

Fig. 5. Variation of miceller properties with implicit-solvent (dielectric constant 30 and 80) and explicit-solvent model. Properties are same as in Fig. 3 and Fig. 4

Variation of the micelle properties with solvent model: In order to study the effect of different solvent models on the micelle properties, we compare the results of the $C_{12}E_4$ (90 mM surfactant concentration) system (Fig. 6) for explcit solvent model (explicit) and for two cases (dielectric constants 30 and 80) of implicit solvent model (e = 30 and e = 80).

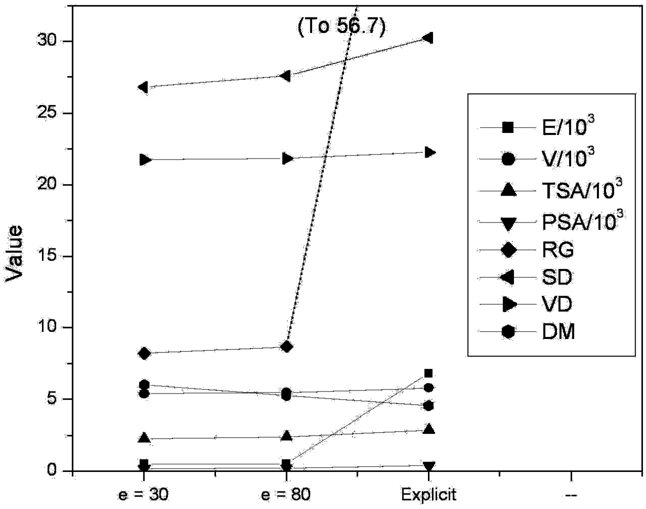

Fig. 6. Variation of micellar properties with implicit-solvent (dielectric constant 30 and 80) and explicit-solvent model. Properties are same as in Fig. 3 and Fig. 4

The total energy (E), total surface area and total volume of the system are unaffected by change in dielectric constant of the medium in the implicit-solvent but show a considerable increase on explicit solvation. The increase is most prominent in total energy. Also, as evident from Fig. 6, surface diameter and volume diameter show a slight increase on explicit solvation while being constant for implicit solvation. The values of radius of gyration increase considerably while dipole moment showed a slight decrease in value on explicit solvation. Overall, the explcit solvent model predicts the micelle properties differently than those predicted by implicit solvent model and the properties are almost insensitive with change in dielectric constants in later.

Conclusion

Micelle formation was observed in the time range *ca.* 1 ns. All system aggregate into a small number of clusters rapidly around 200 ps, after which clusters merge to one cluster slowly. The micelles formed are near-spherical and the total energy is significantly reduced on micelle formation. With increasing surfactant concentration, all the properties calculated (except radius of gyration) show increasing trends. Decrease of non-polar chain length / increase of polar chain length have similar effect on (increasing) properties; former is more effective than the later. Variation of dielectric constants of solvent in the implicit solvent model has very small effect and gives very different results than that of explicit model result. Thus, implicit solvent model is incapable to capture the initial self-aggregation process.

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