Research Communication

Molecular Dynamics Study of Water Dynamics around the Surfactant Monolayer Adsorbed at the Air/Water Interface

Abstract : A constant volume and temperature (NVT) molecular dynamics (MD) simulation has been carried out to investigate the properties of a monolayer of monododecyl diethylene glycol ($C_{12}E_2$) surfactant adsorbed at the air/water interface at a surface coverage corresponding to that at its critical micelle concentration (34 $Å^2$/molecule). The study shows that the surfactant monolayer strongly influences the translational and rotational mobility of interfacial water molecules. A drastic change in the dipolar reorientational motion of water molecules in the aqueous layer is observed with a small variation of distance from the surfactant headgroups.

Keywords: Molecular Dynamics, NVT, Monolayer

The structure of surfactants in bulk solution and at interfaces is of great importance in industrial processes, such as detergency, oil recovery, paints, food chemistry, purification, lubrication, and so forth[1]. Much successful work has been done to understand the structure of surfactant aggregates in solutions, but at interfaces, systematic studies of the adsorbed films are still lacking.

In this work the detail dynamics of water around the $C_{12}E_2$ surfactant monolayer adsorbed at the air/water interface is studied. Only recently, neutron reflectivity study has been successfully used to study the structural characteristics of C_mE_n layers adsorbed at the air/liquid interfaces[2-7].Neutron experiments have the potential to provide accurate information on density profiles of the surfactant at interface. Thomas and co-workers[2-7] studied in detail the adsorption of a series of monododecyl ether surfactants, $C_{12}E_n$, at the air/water interface by varying the number of oxyethylene headgroups between n=1 to n=12.

The time scale associated with the adsorption of surfactants leading to the formation of the monolayer or the exchange of monomers between the monolayer and those in the bulk solution are in the range of micro to millisecond, and therefore are beyond the scope of current generation molecular dynamics (MD) simulations. However,

it is possible to study the microscopic properties of a monolayer formed at the interface within a reasonably computer time. This approach has been employed recently in some simulation studies[8-14].

$C_{12}E_2$ has not been extensively investigated by simulation techniques. Only recently, an MD simulation of $C_{12}E_2$ bilayer[15] and monolayer[16] by Bandyopadhyay et al. and a $C_{12}E_2$ reverse micelle by Allen et al.[17] has been reported. These studies provided microscopic level properties of $C_{12}E_2$ aggregates in solution, particularly the structural properties of $C_{12}E_2$ surfactants.

In this work, the detail dynamics of water around the $C_{12}E_2$ surfactant monolayer adsorbed at the air/water interface is reported. The setup of the simulation system and a brief description of the methodologies employed, discussed in the next section. The results obtained from the investigations are presented and discussed in the following section.

System Setup and Simulation Details : The initial configuration of the constant temperature and volume (NVT) simulation system was set up by arranging a uniform monolayer of 64 surfactants with the hydroxyl group on an appropriate 8×8 square lattice in the xy plane with the hydrocarbon chains extending perpendicular to the lattice plane in all trans configuration. The lattice constants were chosen to give the surface area per molecule of 34 $Å^2$, corresponding to the experimentally observed value for adsorption at the air/water interface at the cmc[2]. Then two such Langmuir type monolayers were placed, with their headgroups solvated, in the xy plane of a roughly 30 Å thick slab of water molecules. A 30 Å thick layer of water should be large enough to give a distinct region of bulk solution in the middle of the simulation cell. The overall system contained 128 surfactants and 2127 water molecules. The dimension of the simulation box in the x and y direction was 46 Å, while the z dimension was kept large at 100 Å. This is done to minimize the interactions between the periodic replicas in the z direction.

The simulations utilized the Nosé-Hoover chain thermostat extended system method[18] as implemented in the PINY-MD computational package[19]. A recently

developed reversible multiple time step algorithm[18] allowed us to employ a 4-fs MD time step. This was achived using a three-stage force decomposition into intramolecular forces (torsion/bend-bond), short-range intermolecular forces (a 7.0 Å RESPA cutoff distance), and long-range intermolecular forces. Electrostatic interactions were calculated by using the particle mesh Ewald method[20]. The minimum image convention[21] was employed to calculate the Lennard-Jones interactions and the real-space part of the Ewald sum using a spherical truncation of 7 and 10 Å respectively. The intermolecular potential model was based on pair wise additive site-site electrostatic and Lennard-Jones contributions. The rigid three-site SPC/E model[22] was employed for water. The CH_3 and CH_2 groups of the surfactants were treated as united atoms. The potential parameters for the alkane chain groups were taken from the work of Martin and Siepmann,[23] while the oxyethylene groups were modeled using the OPLS parameters [24,25]. The surfactant chains were made flexible by including bond stretching, bending, and torsion interactions.

Results and Discussion : The dynamics of water near the interface is likely to play a crucial role in determining the behavior of surfactant aggregates. In this section the detail of the translational and reorientational motions of water molecules present near the interface is studied.

The translational dynamics of interfacial water was measured by calculating the mean square displacements (MSD) of water molecules at different distances from the surfactant headgroups at the interface. To be specific, three hydration layers or regions have been defined. Water molecules that are within a distance of 4 Å from the OH group oxygen atoms of the surfactant headgroups form region-1. This essentially corresponds to the first hydration layer with respect to the OH group oxygen atoms of the surfactants. Region-2 comprises of water molecules within 4-7 Å from the OH group oxygen atoms, while those beyond 7 Å are considered to be in Region-3. The distances are measured with respect to both the monolayers by tagging the water molecules at different time origins. The plots are displayed in (Figure 1). For comparison; We have also displayed the same for pure bulk water, which is obtained from a MD simulation of bulk SPC /E water at room temperature.

It is evident from the figure that the translational mobility of the water molecules in Region-1 is significantly restricted. However, the mobility of water increases as the distance from the surfactant headgroups is increased. It can be seen that within a short distance of 7 Å from the surfactant headgroups (Region-3), the mobility of the water molecules approaches that of pure bulk water. Such
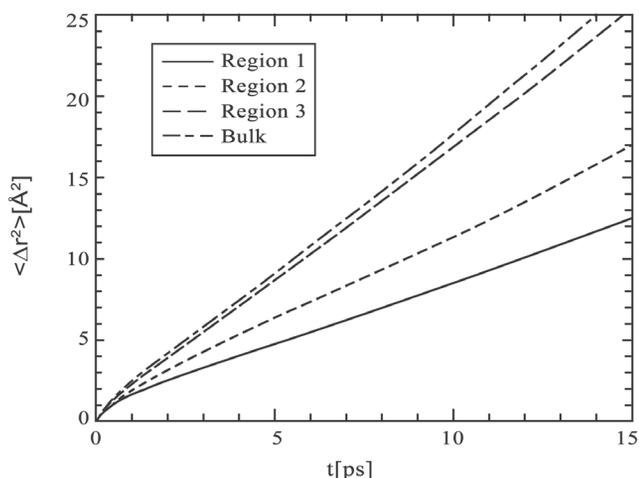

Figure1: Mean square displacement (MSD) of the water molecules in different regions of the aqueous layer. Region-1 comprises of water molecules that are within 4 Å from the OH group oxygen atoms, those that are within 4-7 Å form Region-2, while those that are beyond 7 Å are said to be Region-3. The MSD of the water molecules in pure bulk SPC/E water is also shown for comparison.

restricted mobility of water near the interface of organized molecular assemblies has been studied recently[26-28].This might arise because of the strong interaction between the hydrophilic oxyethylene headgroups of the surfactants and the surrounding water molecules. One can calculate the translational diffusion coefficients (D) from the slope of the MSD vs time curve, using the well known Einstein's relation[29],

$$D = \lim_{\Delta t \to \infty} \frac{\left\langle \left| r_i(t) - r_i(0) \right|^2 \right\rangle}{2d\,\Delta t} = \lim_{\Delta t \to \infty} \frac{\left\langle \Delta r_i^2(t) \right\rangle}{2d\,\Delta t} \qquad (1)$$

where d is the dimensionality of the system, $r_i(t)$ and $r_i(0)$ are coordinates of the oxygen atom of the i-th water molecule at time t, and at time t=0 respectively, and the averaging is over both the time origins and the water molecules. Using this relation, the diffusion coefficients of water molecules in the three regions have been calculated from a linear fit to the corresponding mean square displacements, which are listed in (Table 1).

TABLE1: Diffusion Coefficients (D) of the Water Molecules in Different Regions as obtained from their Mean Square Displacements. The Value for Bulk Water is also listed for comparison

Region	$D(10^{-5}\ cm^2\ sec^{-1})$
Region-1(0-4 Å)	1.22
Region -2 (4-7 Å)	1.69
Region-4 (› 7 Å)	2.69
Bulk water (SPC/E)	2.84

The data shows that the water molecules in Region-1 and 2 are much less mobile than those in region-3 and pure bulk water. In fact, the Region-3 water molecules are almost twice faster than the Region-1 water molecules. Similar approach to calculate the diffusion coefficients of interfacial water molecules from MD studies has been reported earlier[28]. It may be noted at this point that the absolute values of the calculated diffusion coefficients may not be very authentic for these systems. This is because the surfactant monolayers provide a heterogeneous anisotropic environment for the water molecules that is not strictly three dimensional [30, 31]. However, the main focus here is to compare the relative diffusion of water in different hydration layers or regions close to the interface, rather than measuring the absolute diffusion coefficient values.

It is expected that the rotational motions of the interfacial water molecules will also be affected by the surfactants. The rotational motion of water can be investigated by measuring the reorientational dynamics of its electrical dipole μ, defined as the vector connecting the oxygen atom of the water molecule to the center of the line connecting the two hydrogen atoms. The time evolution of μ can be estimated by measuring the dipole-dipole time correlation function (TCF), defined as

$$C_\mu(t) = \frac{\left\langle \mu_i(t+\tau) \cdot \mu_i(t) \right\rangle}{\left\langle \mu_i(\tau) \cdot \mu_i(\tau) \right\rangle} \tag{2}$$

Where, μ(t) is the unit dipole moment vector of the i-th water molecule at a time t and the angular brackets denote averaging over the tagged water molecules and over
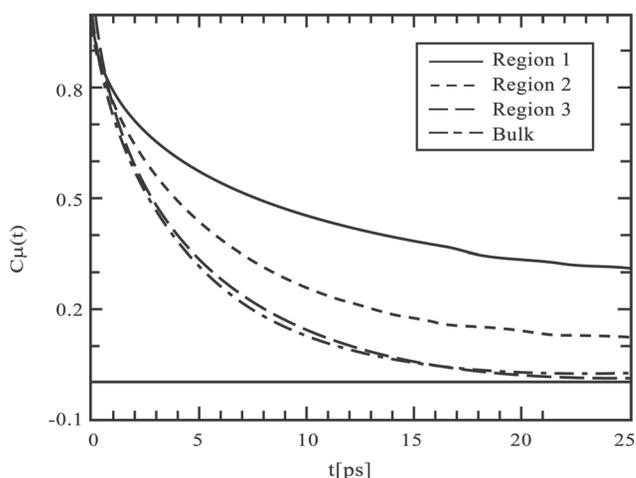

Figure 2: Reorientational time correlation function (TCF) of the water dipoles, $C_i(t)$, for the water molecules in three regions of aqueous layer. The definitions of the regions are same as in Figure 1. The TCF for pure bulk SPC/E water is also shown for comparison.

initial times τ. The correlation functions are calculated by averaging over the water molecules in the three regions as defined before which are shown in (Figure 2). For comparison, the corresponding decay curve for pure bulk SPC/E water is also displayed.

It is clear from the figure that the relaxation curves decay nonexponentially, and for water close to the surfactants (Region 1&2)they do not decay to zero. This shows that the presence of the surfactants significantly restricts the reorientational motion of water. However, similar to the translational mobility, the reorientational motion of the water molecules too approaches that of pure bulk water within a short distance of ~7 Å (Region 3). To obtain a quantitative estimation of the time scales associated with the reorientational motion of the water molecules from the dipolar correlation functions, We have fitted the functions with multiexponentials. It is a common practice to use multiexponentials, as one can then directly obtain time constants associated with different motions[26]. These time constants can be assigned two different relaxation processes of the system. Here I have used a sum of three exponentials for each of the three TCFs, and the parameters for best fit are listed in (Table 2).The average reorientational time constant values clearly indicate that the rotational motion of water close to the surfactant headgroups (Region 1) is severely restricted. This arises due to strong interaction between the polar oxyethylene

TABLE 2: Multiexponential Fitting Parameters for the Dipolar Time Correlation Function of Water Molecules in Different Regions. <τμ> is the Average Time Constant. Corresponding Parameters for Bulk Water are also listed for Comparison

Region	Time Constant (ps)	Amplitude (%)	<τμ> (ps)
Region-1(0-4 Å)	0.26	15.4	27.46
	5.24	36.7	
	53.23	47.9	
Region -2 (4-7 Å)	0.25	14.5	20.72
	5.83	71.7	
	119.6	13.8	
Region-4 (› 7 Å)	0.14	11.5	4.75
	2.24	12.8	
	5.87	75.7	
Bulk water(SPC/E)	0.22	13.8	4.73
	4.68	80.6	
	16.63	5.6	

headgroups of the surfactants and the water molecules which are bound to the interface. It may be noted that the ô value for water in Region 3 approaches that for pure bulk water and is about six times smaller than that for water in the first hydration layer (Region 1).Thus it was observed a drastic changes in the dynamics of water molecules with a slight variation of distance from the surfactant headgroups of the adsorbed monolayer.

Conclusion : In this article we have presented results obtained from an atomistic MD simulation of the monolayers of nonionic surfactant $C_{12}E_2$ adsorbed at the air/water interface. The simulation has   been performed at a surface coverage of 34 $Å^2$ /molecule, which corresponds to the surface coverage of the surfactant at the cmc. The dynamics of the interfacial water molecules is also investigated in detail. Both translational and reorientational motions of the water molecules have been found to be restricted near the interface. Most importantly, a drastic increase in the mobility of the water molecules with increasing distance from the surfactant headgroups has been noticed. It is found that the average reorientational relaxation time of water in different regions of the aqueous layer can be highly sensitive to the distance from the surfactant headgroups.

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1. R. G. Laughlin, The Aqueous Phase Behavior of Surfactants, Academic Press; New York, 1994

2. J. R. Lu, Z. X. Li, T. J. Su, R. K. Thomas, *J. Penfold*; Langmuir, **9**, 2408 (1993)

3. J.R. Lu, Z. X. Li, R. K. Thomas, E. J. Staples, I. Tucker, J. Penfold; *J. Phys. Chem.* **97**, 8012 (1993)

4. J.R. Lu, Z. X. Li, R. K. Thomas, E. J. Staples, L. Thompson, I. Tucker, J. Penfold; *J. Phys. Chem.* **98**, 6559 (1994)

5. J. R. Lu, T. J. Su, Z. X. Li, R. K. Thomas, E. J. Staples, I. Tucker, J. Penfold; *J. Phys. Chem.* B. **101**, 10322 (1997)

6. J. Penfold, E. J. Staples, I. Tucker, R. K. Thomas; *J. Colloid Interface Sci,* **201**, 223 (1998)

7. J. R. Lu, Z. X. Li, R. K. Thomas, B. P. Binks, D. Crichton, P. D. I. Fletcher, J. R. McNab, J. Penfold; *J. Phys. Chem.* B. **102**, 5785 (1998)

8. S. Bandyopadhyay, J. C. Shelly, M. Tarek, P. B. Moore, M. L. Klein; *J. Phys. Chem.* B **102** 6318 (1998)

9. S. Bandyopadhyay, M. Tarek, M. L. Lynch, M. L. Klein; *Langmuir,* **16**, 942 (2000)

10. W. X. Shi, H. X. Guo; J. Phys. Chem. B. **114**, 6365 (2010)

11. M. Szori, D. J. Tobias, M. Roeselova; *J. Phys. Chem.* B. **113**, 4161 (2009)

12. X. Tang, K. J. Huston, R. G. Larson; *J. Phys. Chem.* B. **118**, 12907 (2014)

13. W. X. Shi, H. X. Guo; *J. Phys. Chem.* B. **114**, 6365 (2010)

14. X. He, O. Guvench, A. D. MacKerell, Jr., M. L. Klein, *J. Phys. Chem.* B. **114**, 9787 (2010)

15. S. Bandyopadhyay, J. Chanda; *Langmuir* **19**, 10443 (2003)

16. S. Bandyopadhyay, J. Chanda; *J. Chem. Theor. Comput.* **1**, 963 (2005)

17. R. Allen, S. Bandyopadhyay, M. L. Klein; *Langmuir,* **16**, 10547 (2000)

18. G. J. Martyna, M. E. Tuckerman, D. J. Tobias, M. L. Klein; *Mol. Phys,* **87**, 1117 (1996)

19. M. E. Tuckerman, D. A. Yarne, S. O. Samuelson, A. L. Hughs, G. J. Martyna; *Comput. Phys. Commun.* **128**, 333 (2000)

20. T. Darden, D. York, L. Pederson; *J. Chem. Phys.* **98**, 10089 (1993)

21. M. P. Allen, D. J. Tildesely, Computer Simulation of Liquids, Clarendon: Oxford, 1987

22. H. J. C. Berendsen, J. R. Grigeria, T. P. Straatsma; *J. Phys. Chem.* **91**, 6269 (1987)

23. M. G. Martin, J. I. Siepmann; *J. Phys. Chem.* B. **102**, 2569 (1998)

24. W. L. Jorgensen. *J. Phys. Chem.* **90**, 1276 (1986)

25. J. M. Briggs, T. Matsui, W. L. Jorgensen, *J. Comput. Chem.* **11**, 958 (1990)

26. S. Balasubramanian, B. Bagchi. *J. Phys. Chem.* B **106**, 3668 (2002)

27. S. Balasubramanian, S. Pal, B. Bagchi. *Phys. Rev. Lett.* **89**, 115505 (2002)

28. J. Faeder, B. M. Ladyani. *J. Phys. Chem.* B. **104**, 1033 (2000)

29. M. P. Allen, D. J. Tildesely. Computer Simulation of Liquids; Clarendon, Oxford, (1987)

30. P. Liu, E. Harder, B. J. Berne. *J. Phys. Chem.* B. **108**, 6595 (2004)

31. M. Christensen, B. J. Pedersen. *J. Chem. Phys.* **119**, 5171 (2003)