

Supporting information for:

**Unraveling the Differential Aggregation of Anionic and Nonionic
Monorhamnolipids at Air-water and Oil-water Interfaces: A Classical
Molecular Dynamics Simulation Study**

Elango Munusamy,[‡] Charles M. Luft,[‡] Jeanne E. Pemberton,[‡] and Steven D.

Schwartz^{‡,*}

[‡]Department of Chemistry and Biochemistry, University of Arizona, Tucson, AZ 85721, United

States

*Email: sschwartz@email.arizona.edu.

Phone: 520-621-6363

Figure S1. Total energy of the system as a function of simulation time for nonionic Rha-C10-C10 at air-water interface.

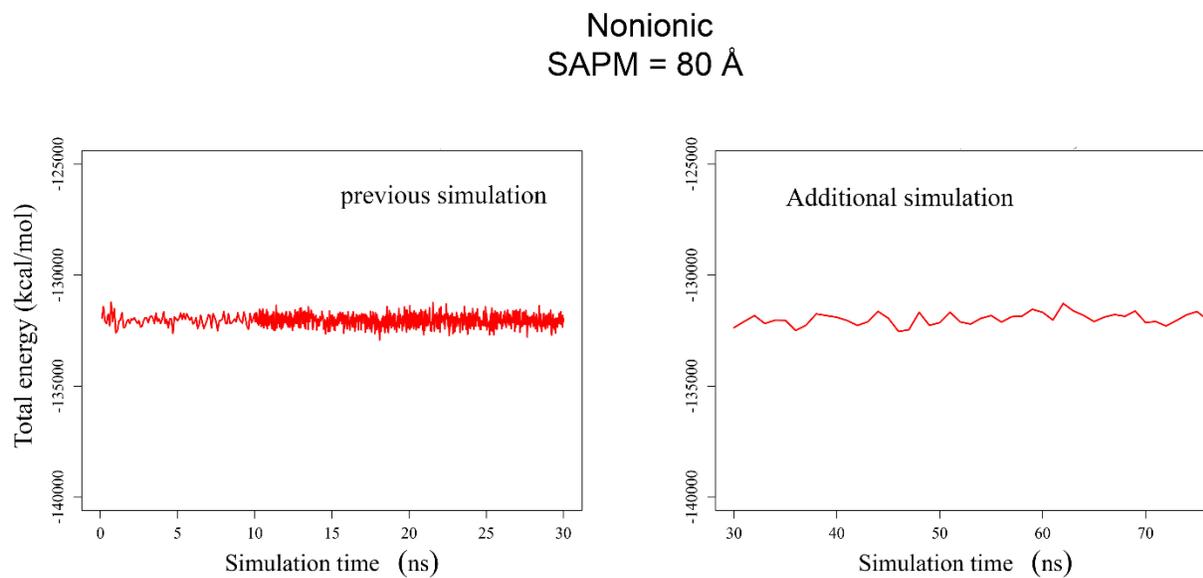


Figure S2. Total energy of the system as a function of simulation time for anionic Rha-C10-C10 at air-water interface.

Anionic
SAPM = 80 Å

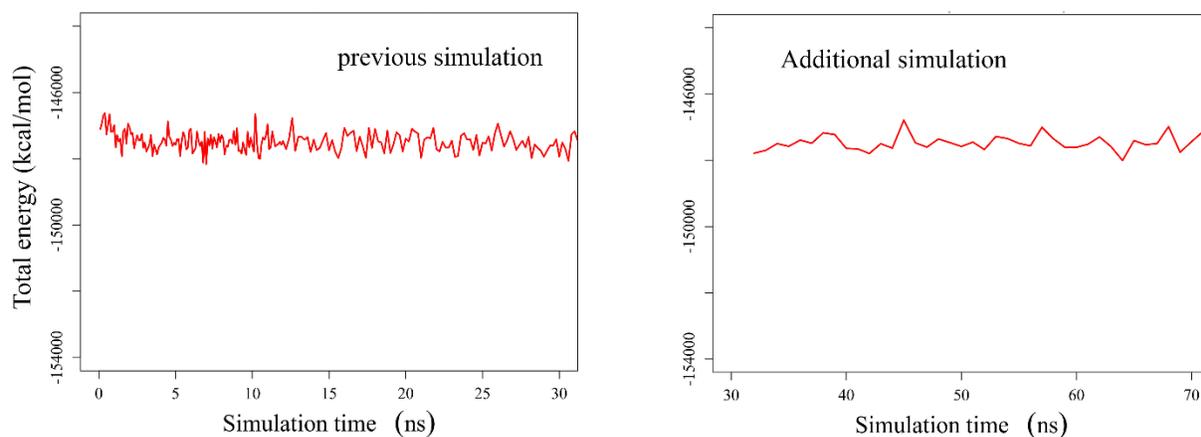


Figure S3. Average decay time of the hydrogen bonds for air-water and oil-water interfaces [1-3]. It is clear from these plots that the hydrogen bonds present in anionic Rha-C10-C10 monolayers at air-water as well as oil-water interface decays slower than nonionic. This in turn supports the hydrogen bond occupancy results presented in the main article.

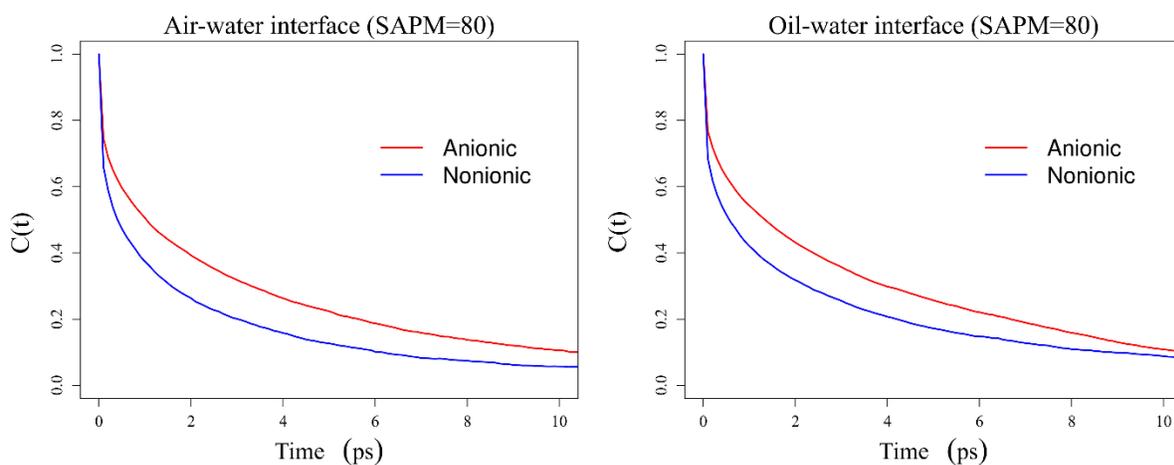


Figure S4. Average length of the two alkyl chains. It is clear that in majority of the cases the alkyl chains are close to the equilibrium bond length of a 7 carbon n-alkyl chain ~ 7.6 Å. There is no significant difference between the anionic and nonionic Rha-C10-C10 monolayers.

Equilibrium length of a 7 carbon alkyl chain

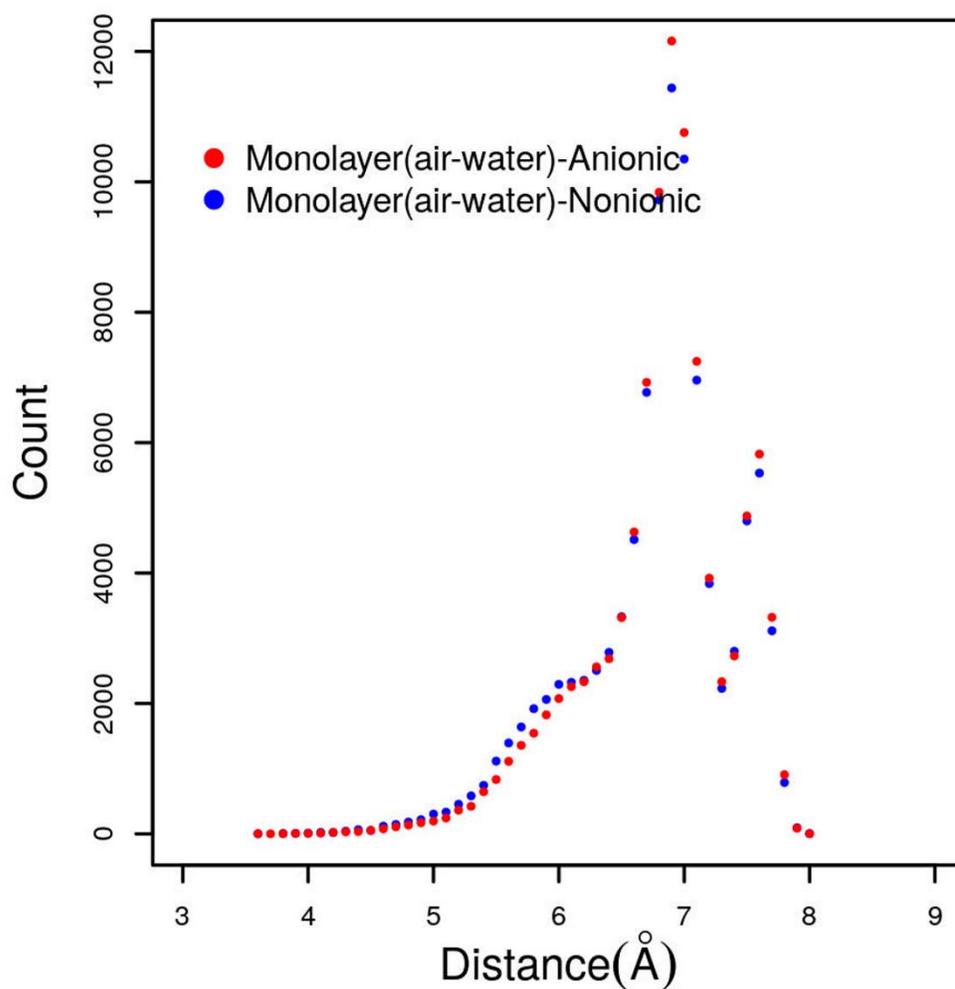


Figure S5. C-C pair distance between the two alkyl chains for nonionic and anionic Rha-C10-C10 at the air-water interface. Every pair of C...C distance has two major peaks. Farther pair of C...C has wide distribution while the closest pair of C...C has sharp distribution indicating that flexible movements of the alkyl chain. Overall there is a mixture of parallel and unparallel

orientation of the two alkyl chains in the molecules. The notable difference between anionic and nonionic Rha-C10-C10 is the density of the peaks. All the C...C pairs exhibit relatively stronger peaks near 5 Å for nonionic compared to anionic. This indicates that the density of alkyl chains are aligned parallel is more in nonionic than nonionic. This analysis complements the head group conformation analysis presented in the main text.

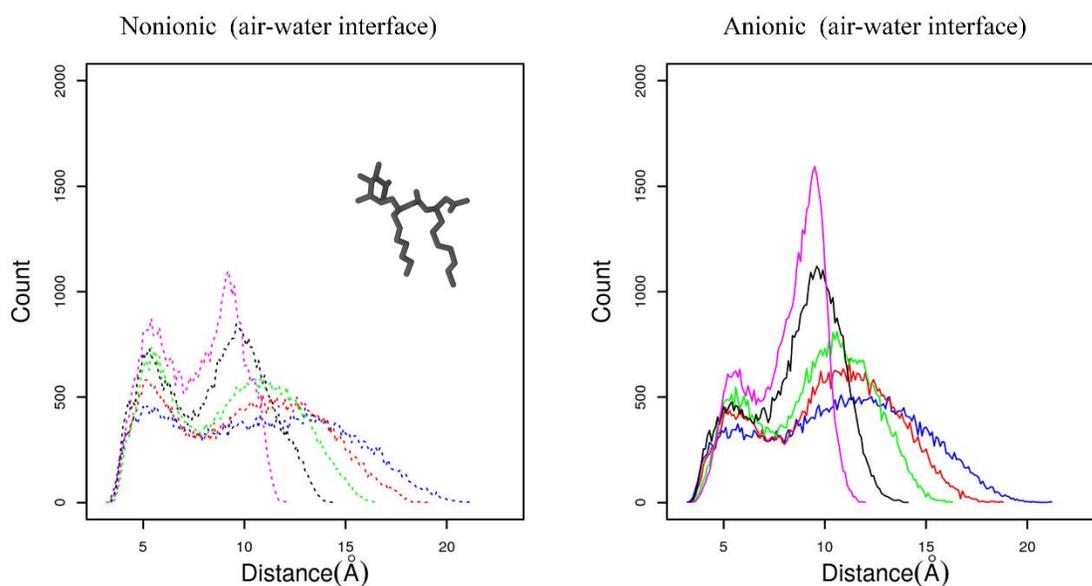


Figure S6. Relationship between number of hydrogen bonds per surfactant and interfacial formation energy per surfactant for anionic and nonionic Rha-C10-C10 at the air-water interface.

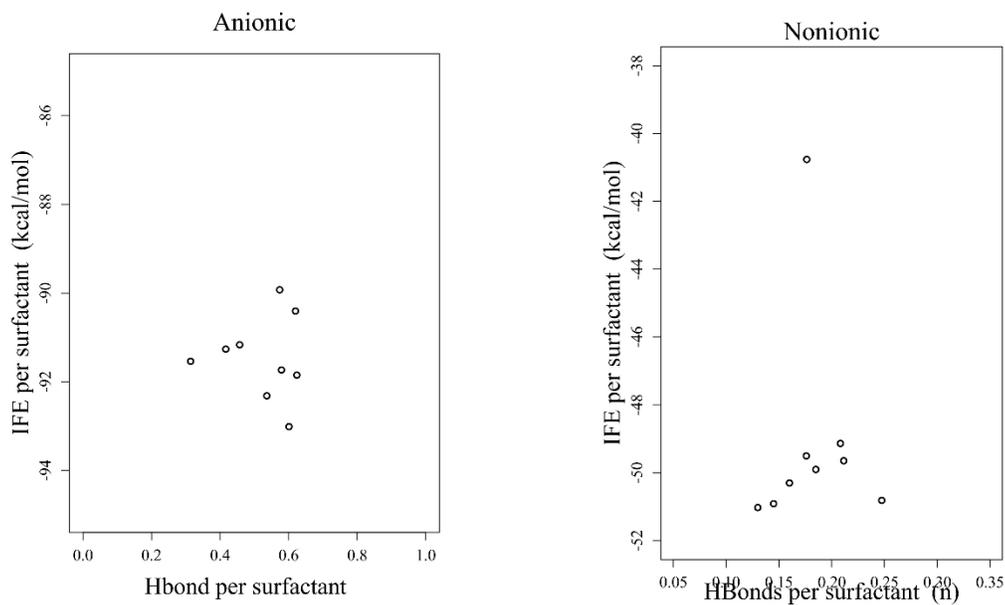


Figure S7. Intermolecular radial pair distribution function, $g(r)$ for anionic Rha-C10-C10 at the air water interface. The distribution for rhamnase group and carboxylic group are given separately. It is evident from the plots that carboxylic groups have stronger peaks and interact

with the counterions more strongly compared to the rhamnose group.

Intermolecular radial pair distribution function

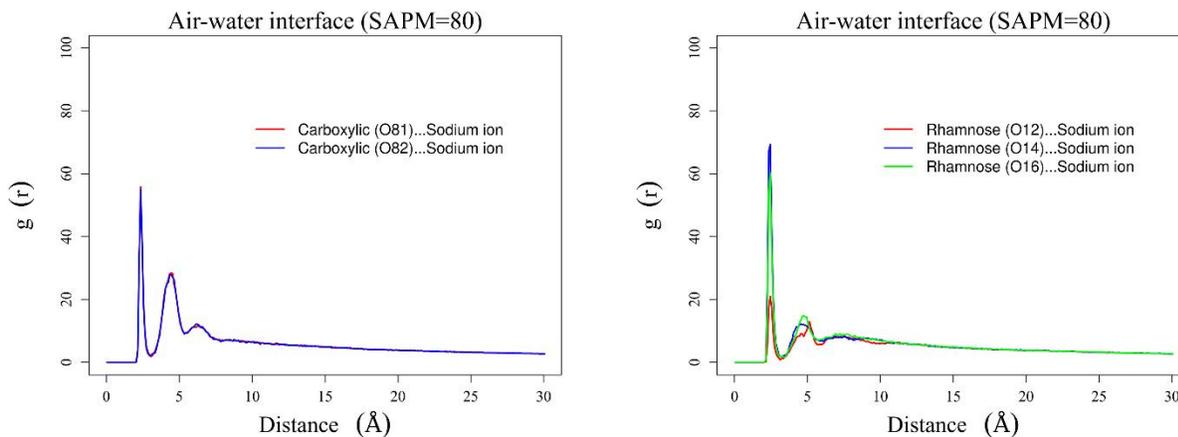
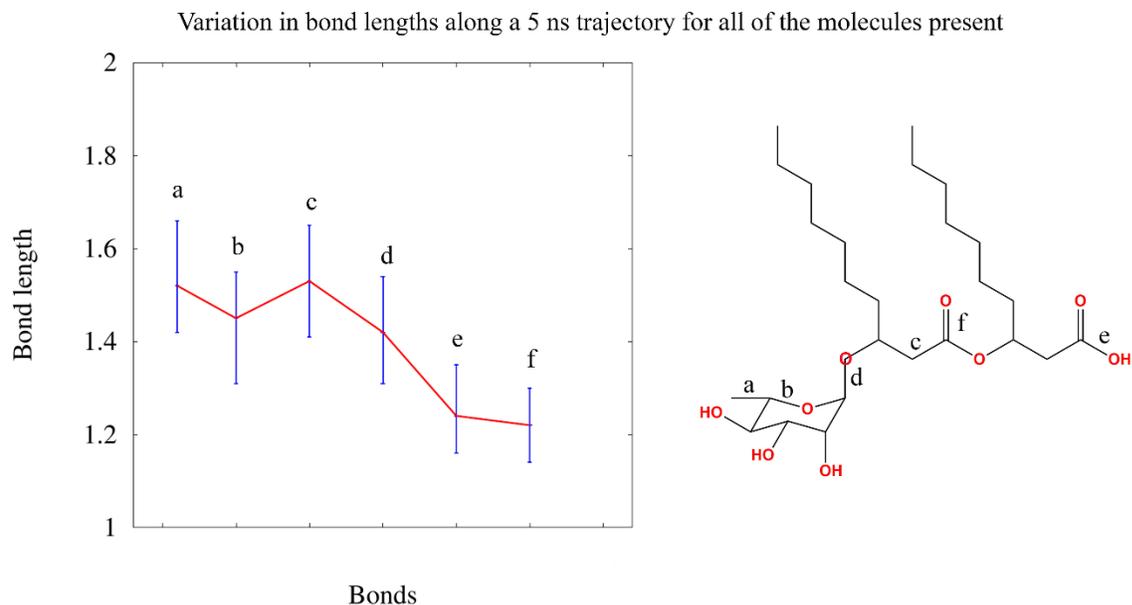


Figure S8. Variation in the representative bond lengths (\AA) along the trajectory for 5ns of simulation. The blue line is the error bar and red line is the equilibrium bond lengths. It is clear from the figure that the average deviation from equilibrium bond distance is minimal.



REFERENCES

- (1) Spoel, D. V. D; Maaren, P. J .V; Larsson, P; Timneanu, D. Thermodynamics of hydrogen bonding in hydrophilic and hydrophobic Media. *J. Phys. Chem. B*, **2006**, *110*, 4393–4398.
- (2) Martiniano, H. F. M. C; Galamba, N. Insights on hydrogen-bond lifetimes in liquid and supercooled water. *J. Phys. Chem. B*, **2013**, *117*, 16188–16195.
- (3) Gowers, R. J; Carbone, P. A multiscale approach to model hydrogen bonding: The case of polyamide. *J. Chem. Phys.*, **2015**, *142*, 224907(10).