Supporting Information (SI)

Exploration of the Presence of Bulk-like Water in

AOT Reverse Micelles and Water-in-Oil

Nanodroplets: Role of Charged Interface,

Confinement Size and Water Properties

Vrushali R. Hande and Suman Chakrabarty*

Physical and Materials Chemistry Division, CSIR-National Chemical Laboratory, Pune-411008, India

Corresponding Author

*s.chakrabarty@ncl.res.in

Table S1: The initial packing radii (in nm) supplied to the Packmol software for preparation of the initial structures of the RM systems. The radii of the outermost layer for packing the following species are shown in the increasing order: water, Na^+ ions, sulfur (S) atoms of the AOT head groups, and C₉ atoms (terminal carbon atoms of the AOT monomer). The minimum inter-atomic distance while packing these molecules has been set to 0.2nm to avoid overlap.

For example, for RM $w_0 = 20$: The water molecules have been put inside a sphere of radius 3.7nm centered at the origin. Na⁺ ions have been constrained to be at a distance of 3.75nm (just outside water sphere, but within the AOT head group layer), and the sulfur (S) atoms of polar head groups have been constrained inside the sphere of radius 3.9nm, and finally C₉ atoms (terminal carbon of tail groups) have been constrained to be outside the sphere of radius 5.0nm. The input structure of AOT monomer contains the Na⁺ ion proximally placed to the head group.

Identical protocol has been used for preparing the W/O systems, where only the water sphere has been prepared using Packmol with identical number of water molecules as the respective RM systems and solvated with isooctane subsequently.

Please note that these spherical distance constraints are used to prepare the initial structures only. No position or distance constraint has been used during the MD simulation, which would allow sufficient equilibration of the internal structure.

| System/Residue | Water (in nm) | Na ⁺ (in nm) | S (in nm) | C_9 (in nm) |
|----------------|---------------|-------------------------|-----------|---------------|
| RM $w_0 = 20$ | 3.7 | 3.75 | 3.9 | 5.0 |
| RM $w_0 = 15$ | 3.0 | 3.05 | 3.2 | 4.3 |
| RM $w_0 = 10$ | 2.1 | 2.15 | 2.3 | 3.4 |

Table S2: The ranges of error bars in calculation of radial profiles of shell-wise (a) average number density (ρ), (b) average tetrahedral order parameter (Q) and (c) average dipolar orientation of water molecules with respect to the radial vector ($\langle \cos\theta \rangle$). The block averaging method has been used to estimate the error bars for each bin of the radial profile and five blocks have been used for each segment. The error bars have been shown in Fig.S2 only for the radial density profile of the RM systems, since in all other cases the error bars are smaller than the line thickness/symbol size.

| Systems / Property | < \rho > | <q></q> | <cost< th=""></cost<> |
|--------------------|----------|--------------|-----------------------|
| RM | 0-2.25 | 0.0030-0.060 | 0.0005-0.0450 |
| W/O and Bulk water | 0-0.25 | 0.0005-0.015 | 0.0001-0.0060 |



Figure S1. Time evolution of (a) radius of gyration (R_g) and (b) anisotropy parameter defined as ratio of smallest to largest principal components of R_g for all the systems studied in this work.



Figure S2. Radial profile of shell-wise average number density with error bars only for RM systems. For all other systems and properties, the calculated error bars are smaller than the line thickness/symbol size. The ranges of error bars for all systems have been summarized in the Table S2 for all the three radial properties.



Figure S3. Radial distribution function of Na⁺ ions around S atoms of AOT surfactants in case of all three RMs, i.e. $w_0 = 20$, 15 and 10. The first strong peak at ~0.36nm indicates that the ions stick close the negatively charged interior of the RMs.