

Supporting information for: Dioctyl sodium sulfosuccinate surfactant self-assembly dependency of solvent hydrophilicity: a modelling study

Maisa Vuorte,^{†,‡} Aapo Lokka,^{†,‡} Alberto Scacchi,^{¶,‡} and Maria Sammalkorpi^{*,†,§,‡}

[†]*Department of Chemistry and Materials Science, School of Chemical Engineering, Aalto University, P.O. Box 16100, FI-00076 Aalto, Finland*

[‡]*Academy of Finland Center of Excellence in Life-Inspired Hybrid Materials (LIBER), Aalto University, P.O. Box 16100, FI-00076 Aalto, Finland*

[¶]*Department of Applied Physics, School of Science, Aalto University, P.O. Box 11000, FI-00076 Aalto, Finland*

[§]*Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, P.O. Box 16100, FI-00076 Aalto, Finland*

E-mail: maria.sammalkorpi@aalto.fi

Supporting information

The supporting information consists of the cohesion energies and solubility parameters calculated from condensed phase and *in vacuo* simulations of octane, 2-methylheptane, sulfosuccinic acid, and water, see Table S1. Additionally, visualizations corresponding to the sensitivity analysis trajectories and a comparison of the fraction of free AOT surfactant in the original solvent variation and the sensitivity analysis systems are presented. For

details on the sensitivity analysis parameter range and examined pairings, see Table 3 of main manuscript. The presented data corresponds to the used H-S and T-S interaction parameter combinations. Finally, for one parameter set α_{1s2} , a representative aggregate size distribution is presented for evaluation of the aggregation response in this system.

DPD conservative force parameter a_{ij} estimation

To estimate the DPD conservative force repulsive parameter a_{ij} , fully atomistic simulations of each bead component and water were carried out *in vacuo* and condensed phase. The MD simulation protocol and associated parameters are described in Section 2.2 Surfactant model parametrization of the main manuscript. DPD parameters were estimated based on the Hildebrand solubility parameters δ derived from the cohesion energy E_{coh} values. The non-bonded energies of each simulated molecular dynamics (MD) system and the calculated E_{coh} and δ values have been tabulated in Table S1.

Table S1: Non-bonded energies of gas phase $E_{\text{NB,vacuum}}$ and condensed phase $E_{\text{NB,condensed}}$ octane, 2-methylheptane, sulfosuccinic acid, and water based on the atomistic detail molecular dynamics simulations. DPD parameters were derived from the calculated cohesive energies E_{coh} and Hildebrand solubility parameters δ . Energies are based on atomistic detail molecular dynamics simulations of N molecules (condensed phase) in a cubic box of $(l_{\text{box}})^3$.

Compound	N	l_{box} [nm]	$E_{\text{NB,vacuum}}$ [kJ/mol]	$E_{\text{NB,condensed}}$ [kJ/mol]	E_{coh} [kJ/mol]	δ
octane	180	3.68	16.14	-3834.20	-37.44	7.34
2-methylheptane	172	3.61	-16.12	-8894.13	-35.59	7.20
sulfosuccinic acid	122	2.94	-566.87	-83248.68	-115.49	14.85
water	2165	4.01	-180.66	-88462.22	-146.22	15.63

Sensitivity analysis of equilibrium self-assembly structures

The sensitivity of the results presented in the main manuscript to variation of the DPD interaction parameter a_{ij} was examined by varying systematically the Head–Solvent interaction parameter. Variation such as examined here can be expected to result from the diverse DPD

parametrization approaches in existing literature, see e.g. Refs. 1–6. The sensitivity analysis parameter sets are summarized in Table 3 of the main manuscript. The equilibrium assembly structures and configurations resulting from DPD self assembly simulations following the simulations protocol detailed in the main manuscript have been visualized in Figure S1.

The data shows that varying the Head–Solvent interaction parameter by 5 DPD units affects significantly the partition of AOT monomer between bulk solvent and aggregate phase at the non-polar end of the solvent spectrum, see Figure S2. This is due to the steep decrease of overall AOT solubility with increased solvent hydrophilicity, when moving from hydrocarbon-like solvents towards solvents of intermediate polarity. In reverse micelle systems (α_{1s1} and α_{1s2}), the change on Head–Solvent repulsion influences significantly the average aggregate size.

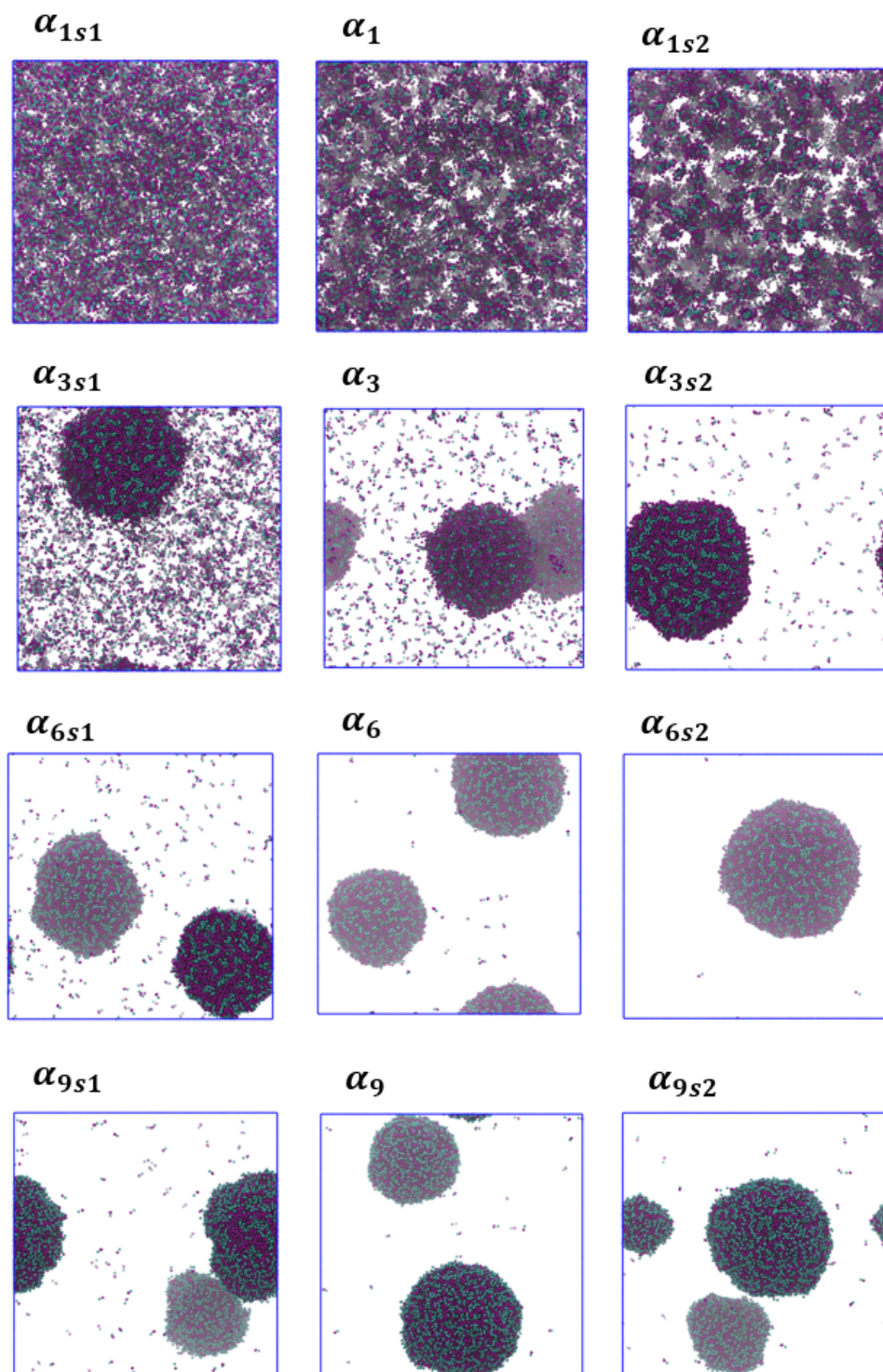


Figure S1: Simulation snapshots corresponding to the sensitivity analysis systems when scaling Head-Solvent DPD interaction parameter α_{ij} down (left column) or up (right column) from the original values (middle column). Solvent beads have been omitted in the visualization for clarity.

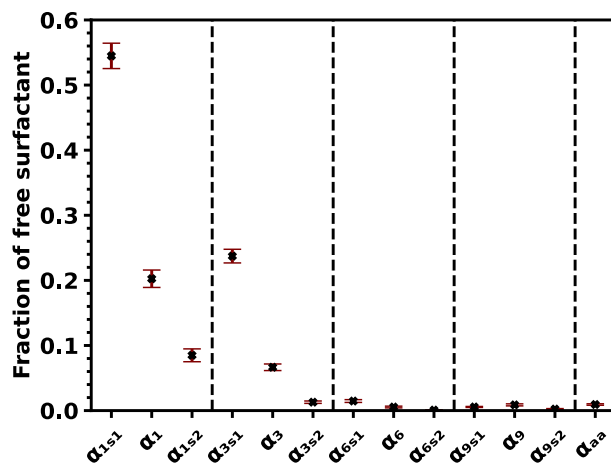


Figure S2: Fraction of free AOT surfactant monomers in the different interaction pair systems. The data shows variation resulting from the sensitivity examination in comparison to systems with the original parameter combinations.

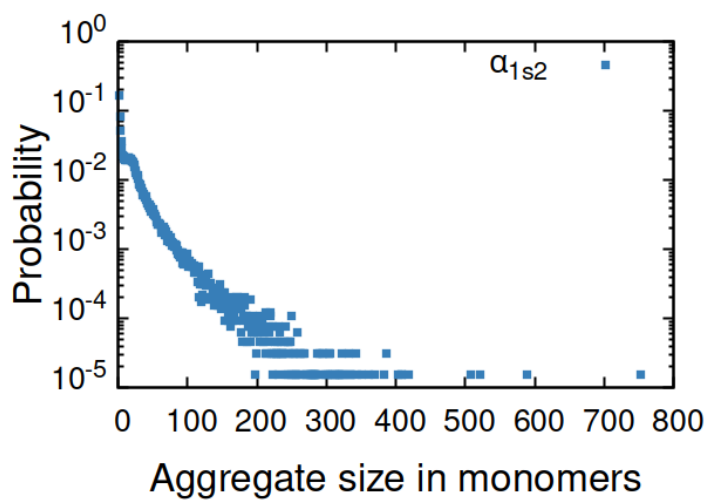


Figure S3: Aggregate size distribution as probability distribution for AOT assembly in conditions corresponding to system α_{1s2} .

References

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