Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPORTING INFORMATION

Structural organization of surfactant aggregates in vacuo. A molecular dynamics and well-tempered metadynamics study

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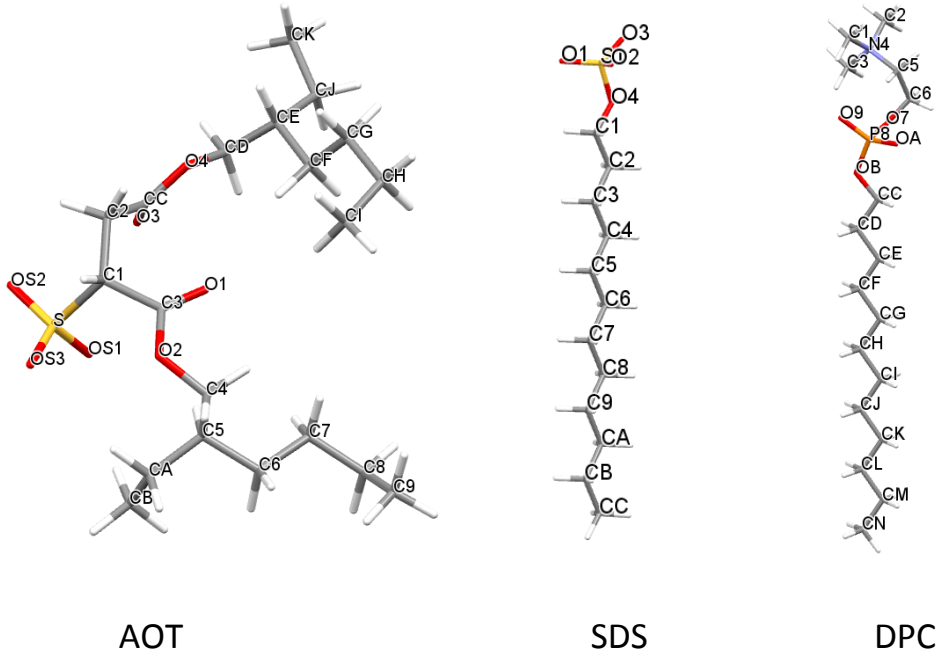
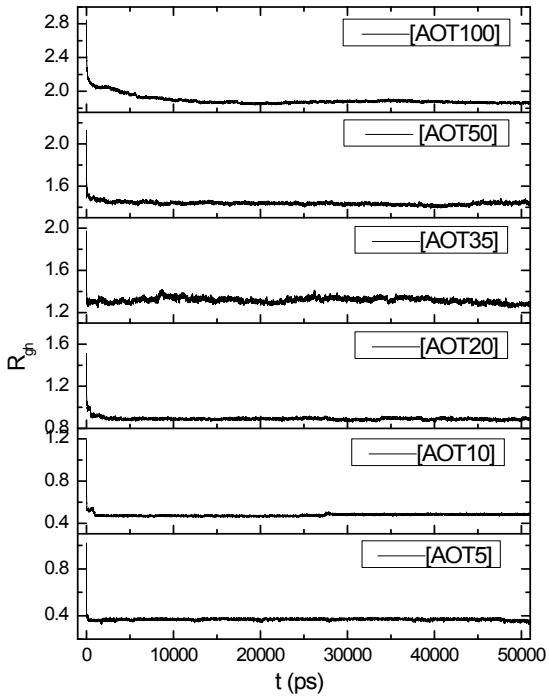


Figure 1-SI Molecular structures and atomic labels of surfactants.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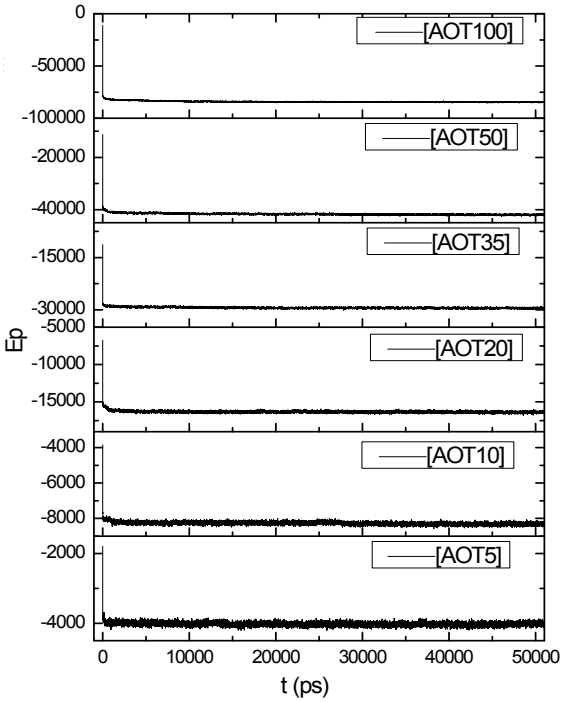
[AOT5]
R_{gh}
t (ps)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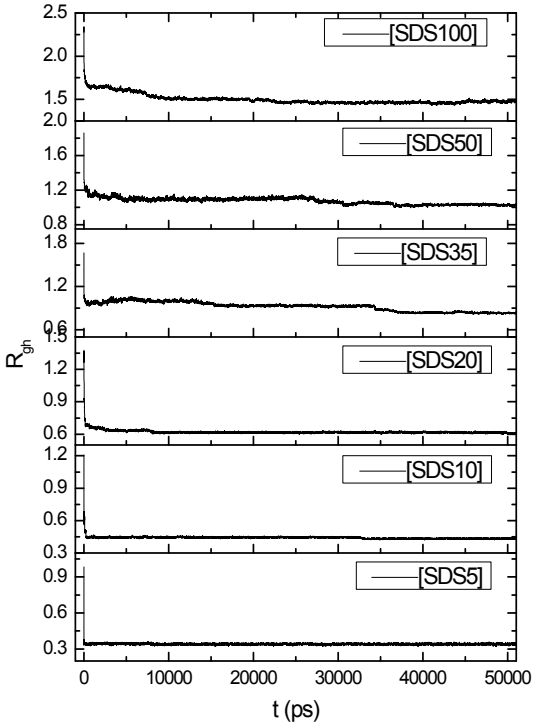
Ep
t (ps)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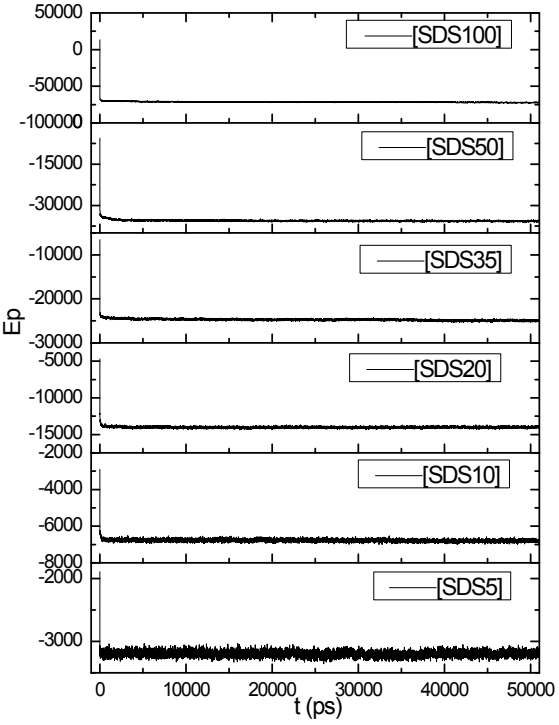
R_{gh}
t (ps)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Ep
t (ps)

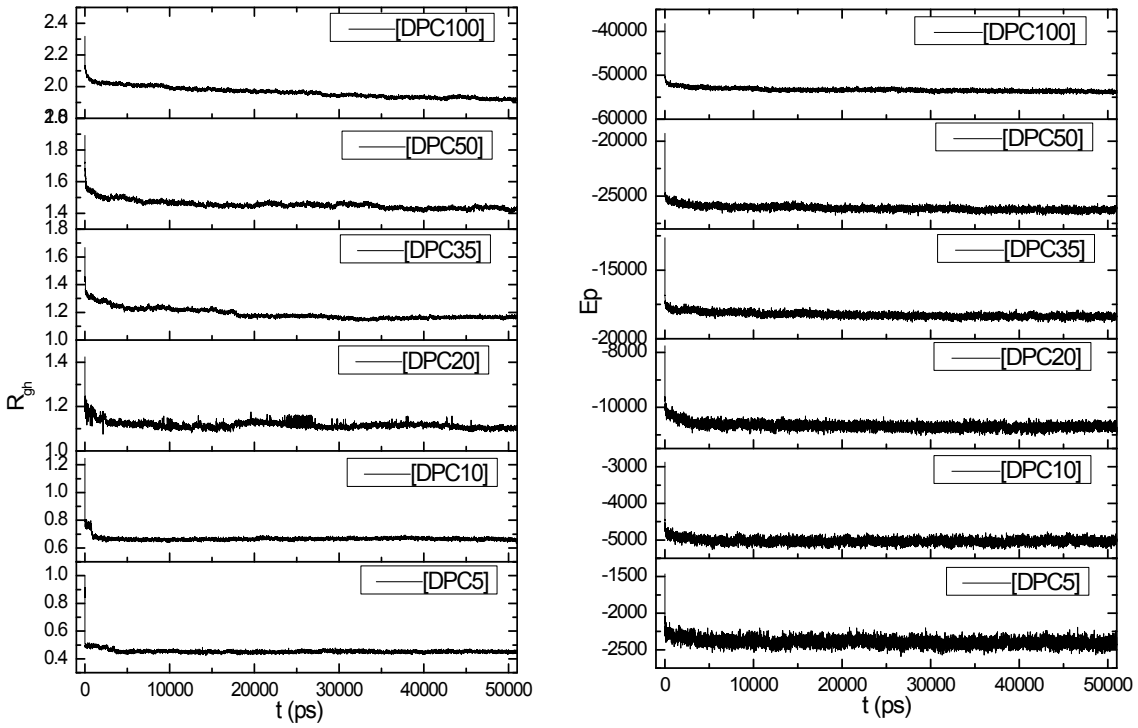

Figure 2-SI Gyration radius R_{gh} of the pivot atoms of the surfactant head group (S for AOT and SDS, and P for DPC, left panel) and aggregate potential energy (Ep) as a function of the simulation time.

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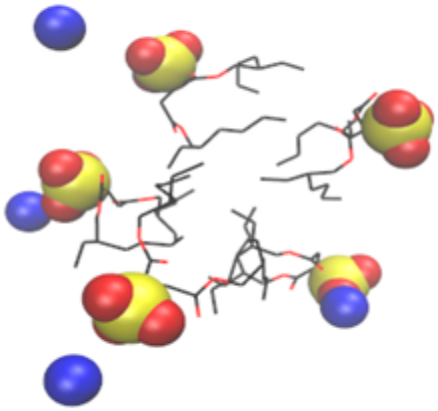

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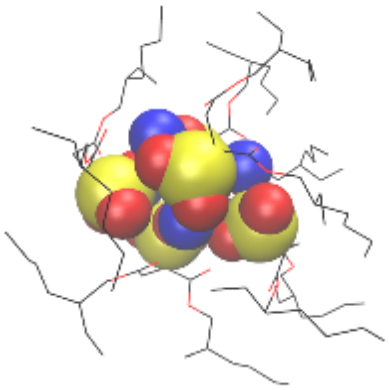

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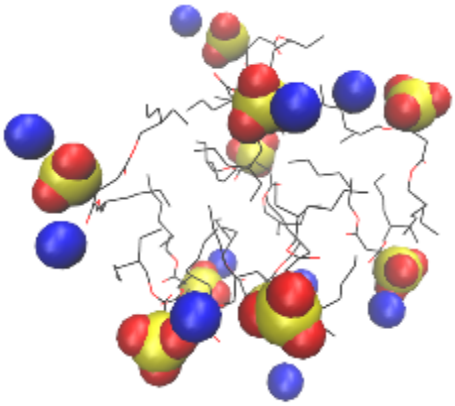

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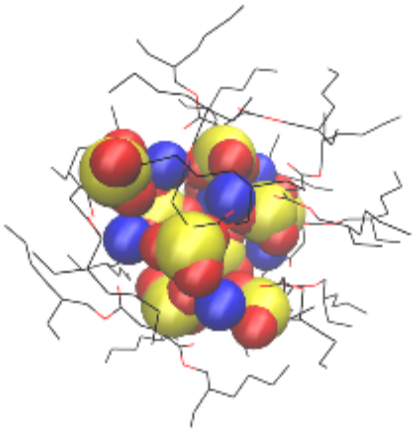

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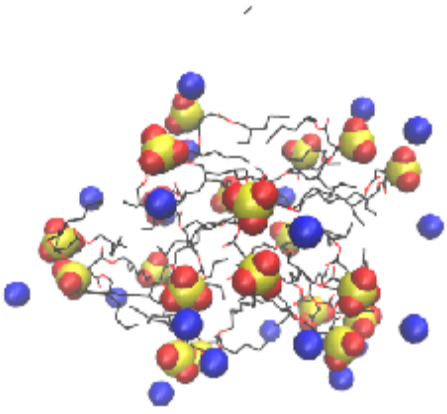

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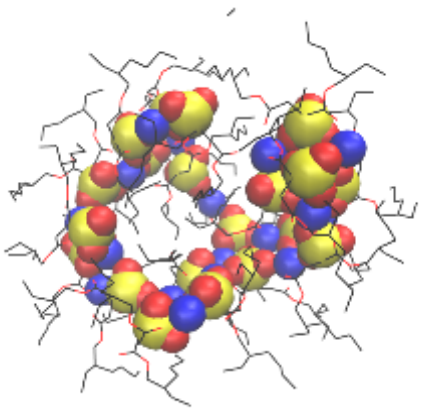

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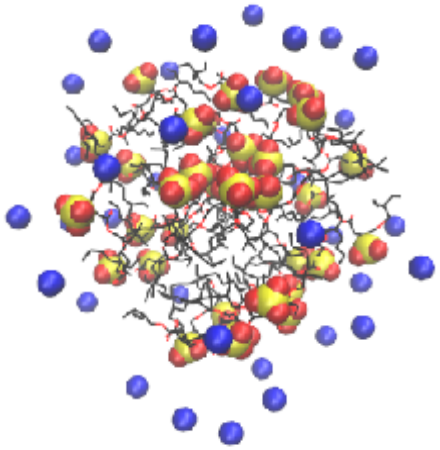

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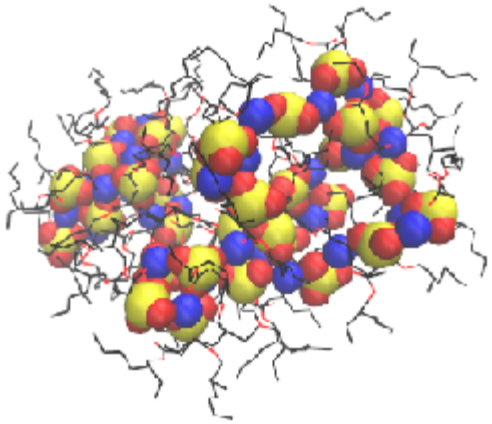

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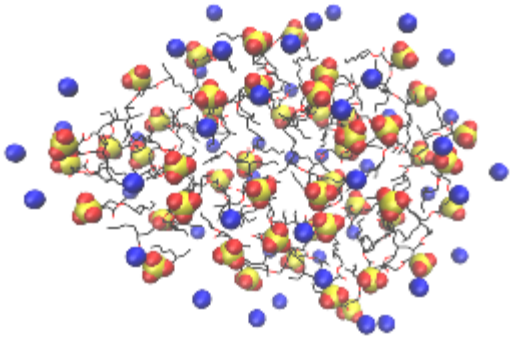

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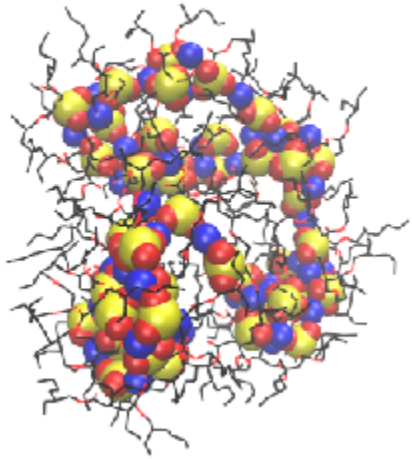

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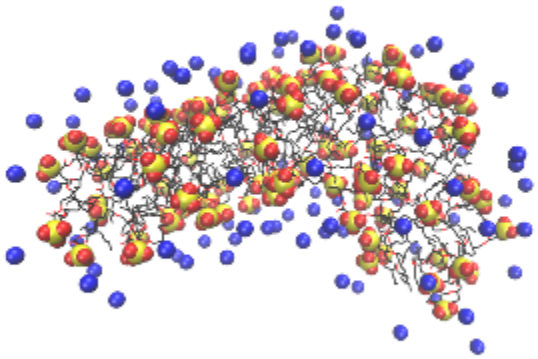

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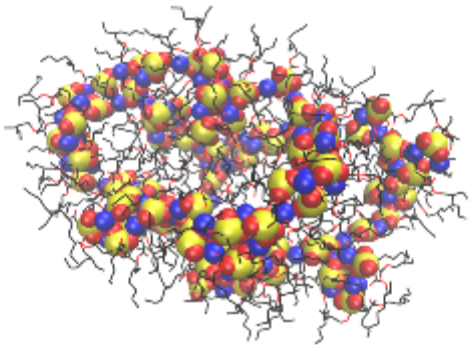

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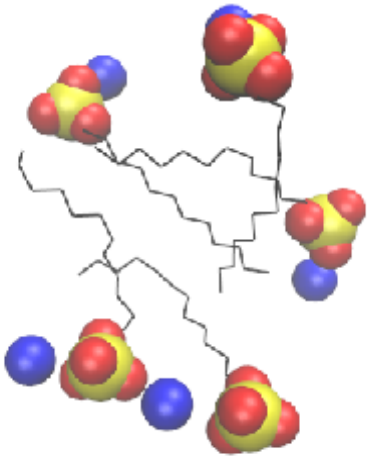

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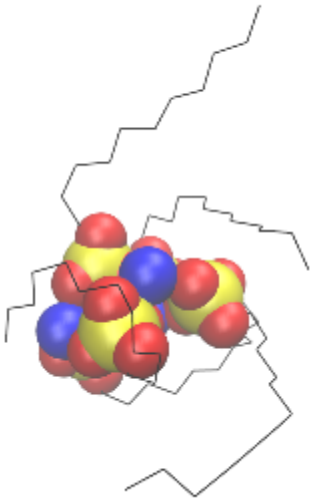

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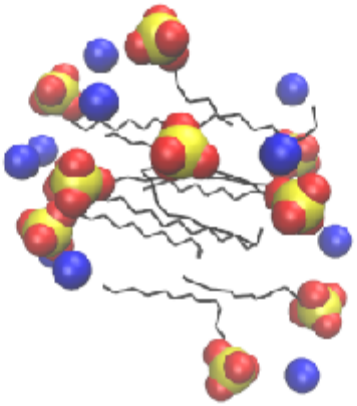

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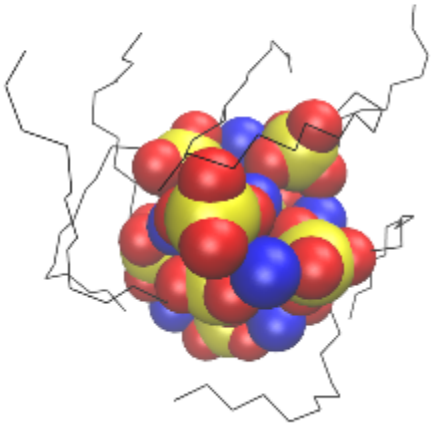

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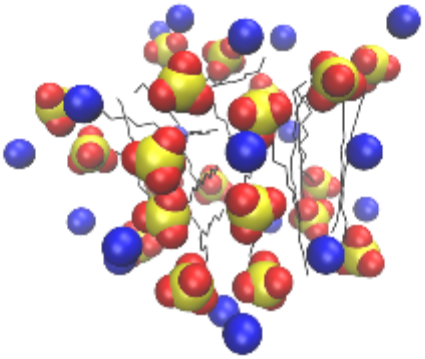

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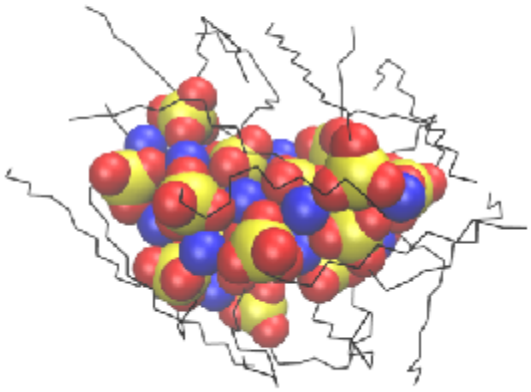

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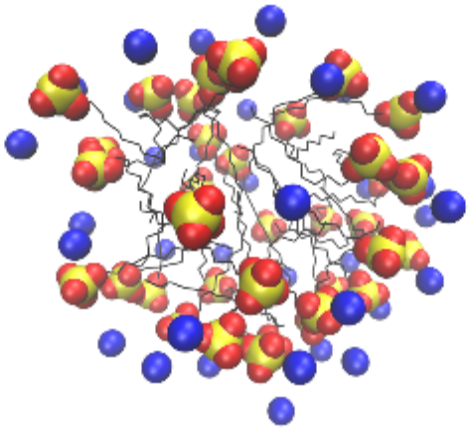

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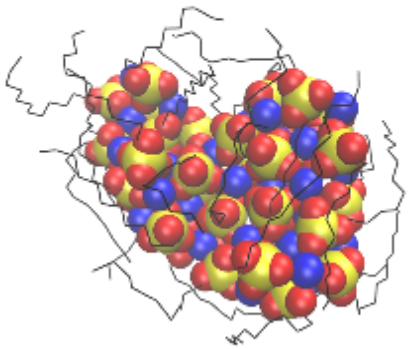

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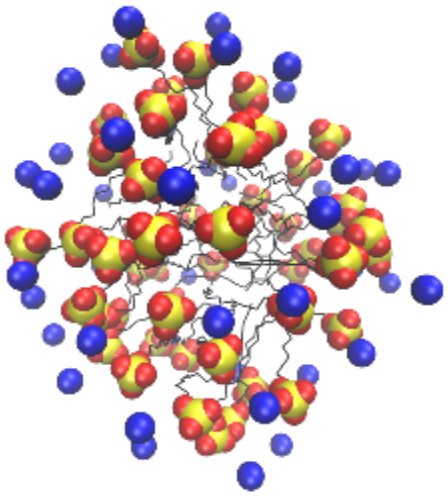

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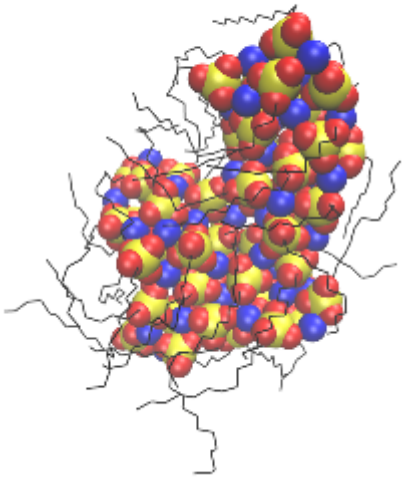

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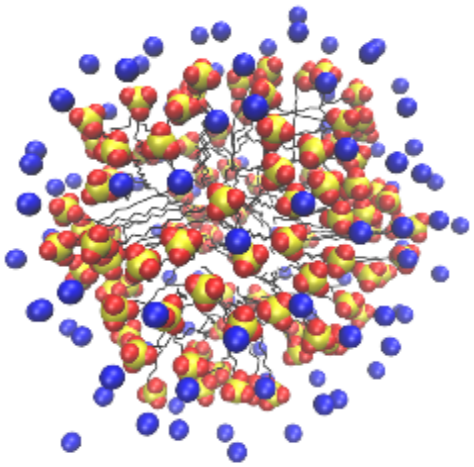

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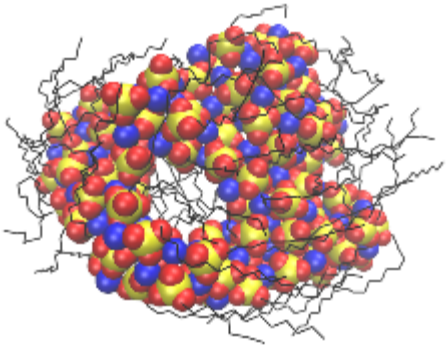

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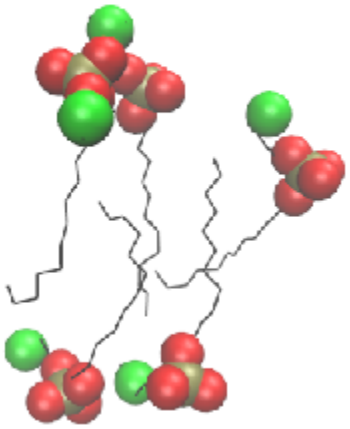

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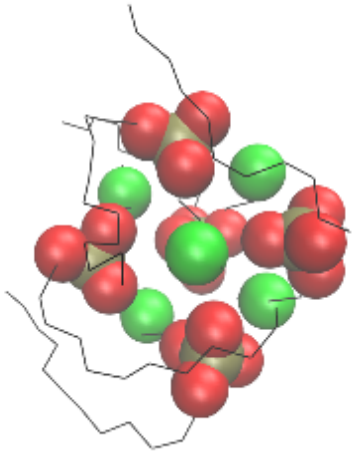

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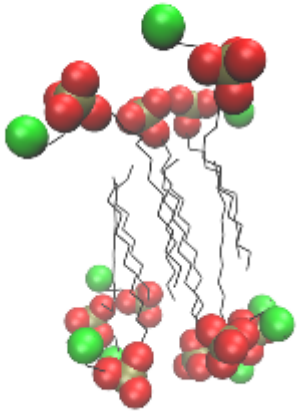

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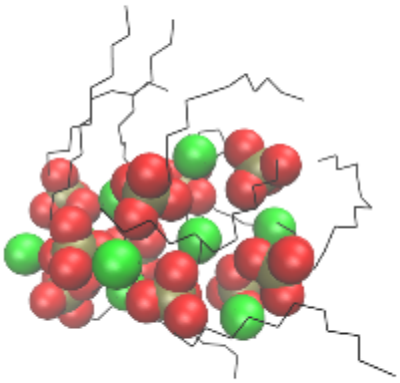

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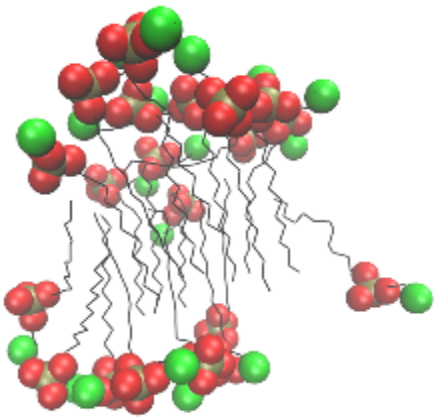

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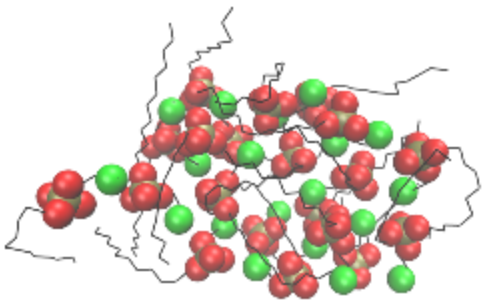

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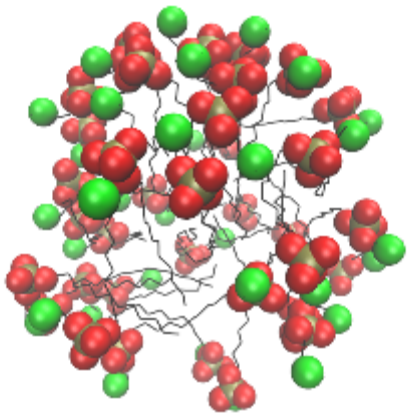

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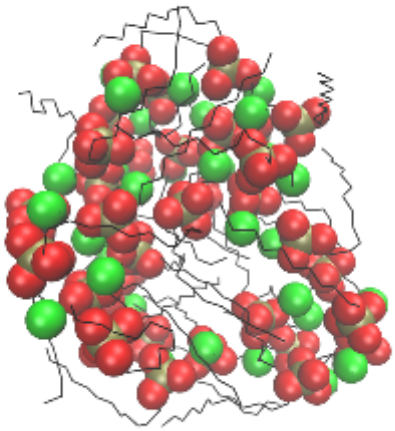

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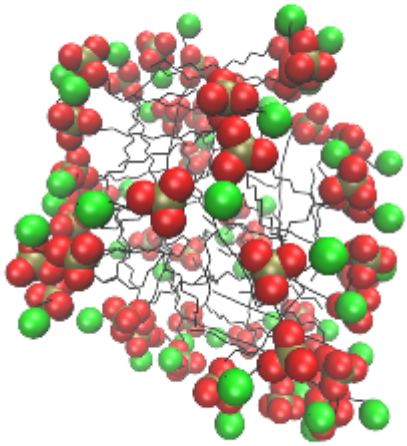

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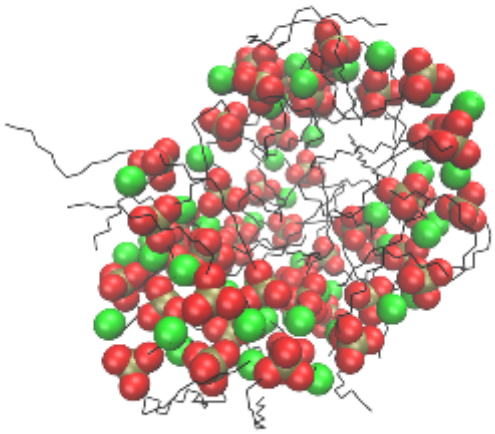

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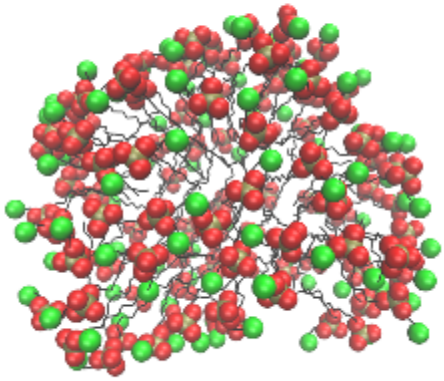

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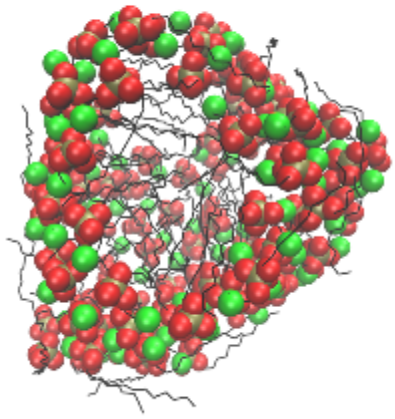

Figure 3-SI Snapshots of surfactant aggregates at the start (t=0ns), and at the end (t=50ns) of MD simulations in vacuo. Sodium ions (blue), sulfur (yellow), oxygen (red), phosphor (tan) and nitrogen (green) atoms of the SO3- and PO4- polar heads are displayed in a space-filling mode to evidence their location, whereas alkyl chains are displayed as black lines. Hydrogen atoms are not shown, to avoid crowding.

Table 1-SI Values of widths of the Gaussians whose sommation builds up the bias potentials used in the well-tempered metadynamics simulations for the examined aggregation numbers Nag; σ_t and σ_h represent the Gaussian width for the bias applied to the gyration radius R_{gh} of the pivot atoms of the surfactant head group (S for AOT and SDS, and P for DPC) and to the gyration radius R_{gt} of the terminal aliphatic carbon atoms, respectively.

N_{ag}		5	10	20	35	50	100
AOT	σ_t	0.015	0.007	0.008	0.006	0.01	0.004
	σ_h	0.003	0.002	0.005	0.004	0.006	0.003
SDS	σ_t	0.03	0.02	0.01	0.008	0.015	0.006
	σ_h	0.002	0.001	0.001	0.002	0.003	0.004
DPC	σ_t	0.03	0.02	0.015	0.008	0.015	0.005
	σ_h	0.002	0.003	0.004	0.002	0.003	0.002

Table 2-SI . Values of aggregate volume ratios V_{ext}/V_{tot} and V_{int}/V_{tot} (see text) for the final configurations of 50 ns of MD simulations in vacuo (MD) and for representative configurations corresponding to the minimum of the free energy surface (min (FES)).

AOT	MD	MD	min (FES)	min (FES)
N	Vext/Vtot	Vint/Vtot	Vext/Vtot	Vint/Vtot
5	0.91	0.01	0.92	0.01
10	0.89	0.03	0.89	0.03
20	0.81	0.12	0.85	0.07
35	0.77	0.16	0.81	0.11
50	0.75	0.17	0.77	0.16
100	0.64	0.28	0.66	0.27

SDS	MD	MD	min (FES)	min (FES)
N_{ag}	Vext/Vtot	Vint/Vtot	Vext/Vtot	Vint/Vtot
5	0.84	0.04	0.82	0.05
10	0.83	0.04	0.84	0.04
20	0.80	0.06	0.83	0.05
35	0.80	0.07	0.80	0.06
50	0.77	0.09	0.79	0.07
100	0.70	0.16	0.69	0.17

DPC	MD	MD	min (FES)	min (FES)
N	Vext/Vtot	Vint/Vtot	Vext/Vtot	Vint/Vtot
5	0.76	0.10	0.76	0.11
10	0.72	0.14	0.73	0.13
20	0.67	0.20	0.71	0.17
35	0.57	0.29	0.61	0.25
50	0.50	0.36	0.55	0.30
100	0.38	0.48	0.40	0.45