Supporting Information

Self-Assembled Surfactants on Patterned Surfaces: Confinement and Cooperative Effects on Aggregates Morphology

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S-1. Surfactants spring constant

In this study each surfactant consists of one bead for the head, and two beads for the tail. The three beads are connected by harmonic springs. The harmonic spring force (F_{ij}^{S}) is described as:

$$F_{ij}^{S} = k_S(r_{ij} - r_0)\hat{\mathbf{r}}_{ij} \quad , \qquad \text{(S1)}$$

where r_{ij} is the relative displacement of beads i and j, $\hat{\mathbf{r}}_{ij}$ is the corresponding unit vector, k_S is the spring constant, and r_0 is the equilibrium bond length.

Because the Van der Waals end-to-end length of one SDS molecule (L_s) is of 20.8 Å,[1] r_0 is set equal to 10.4 Å. We used the approach of Denham et al.,[2] who simulated non-ionic surfactants in water using DPD and suggested how to determine the optimal k_S. Based on this protocol, k_S should be set to the lowest value that is able to maintain the average bond distance to r_0.

A bulk simulation with surfactant concentration of 44.24 mM (370 surfactant molecules) was conducted in a 21×21×42 r_c^3 rectangular box, for up to ~ 0.31 μs. Three simulations were conducted varying k_S from 4 (as suggested by Kuo et al.[3]) to 100 and 200 k_BT/r_c^2. The average equilibrium bond length ($\overline{r_0}$) and its standard deviation (SD) for all surfactant bonds (740 bonds) were calculated and the data are summarized in Table S1. Our analysis indicates that when k_S = 100 k_BT/r_c^2 the bond length converges to r_0 with standard deviation of 1.2%.

Table S1. *The average bond length ($\overline{r_0}$) and standard deviation (SD) as a function of spring constant (k_S) = 4, 100, and 200 k_BT/r_c^2.*

k_S (k_BT/r_c^2)	$\overline{r_0}$ (Å)	SD (%)
4	12.73	16.5
100	10.23	1.2
200	10.18	1.5

S-2. Simulated systems

In Tables S2-S6 we summarize the composition for all systems simulated for the present study.

Table S2. *Systems simulated for bulk studies.*

Number of surfactants (molecules)	Surfactant concentration (mM)
19	2.27
28	3.35
37	4.42
46	5.50
56	6.70
65	7.77
74	8.85
83	9.93
93	11.12
102	12.20
111	13.27
130	15.55
148	17.70
167	19.97
185	22.12
370	44.24
556	66.49
741	88.61
926	110.73
1111	132.85
1297	155.09
1482	177.22
1667	199.34
1852	221.46
2778	332.19
3704	442.92

Table S3. *Systems simulated for surfactant adsorption on a homogeneous hydrophobic surface.*

Number of surfactants (molecules)	Initial surfactant concentration (mM)	Number of surfactants adsorbed on the surface (molecules)	Surfactant surface coverage (nm^2/surfactant headgroup)	Surfactant concentration in the bulk obtained from non-adsorbed surfactants (mM)
926	110.73	926	0.39	0.00
945	113.00	945	0.39	0.00
963	115.15	963	0.38	0.00
982	117.43	982	0.37	0.00
1000	119.58	1000	0.36	0.00
1019	121.85	1019	0.36	0.00
1037	124.00	1037	0.35	0.00
1056	126.28	1056	0.34	0.00
1074	128.43	1074	0.34	0.00
1093	130.70	1093	0.33	0.00
1111	132.85	1111	0.33	0.00
1130	135.12	1130	0.32	0.00
1148	137.28	1100	0.33	5.74
1167	139.55	1110	0.33	6.82
1185	141.70	1120	0.33	7.77
1204	143.97	1124	0.32	9.57
1222	146.13	1125	0.32	11.60
1241	148.40	1100	0.33	16.86
1259	150.55	1100	0.33	19.01
1278	152.82	1112	0.33	19.85
1297	155.09	1074	0.34	26.67
1482	177.22	1099	0.33	45.80
1667	199.34	1085	0.34	69.59
1852	221.46	1090	0.33	91.12

Table S4. *Systems simulated for surfactant adsorption on a homogeneous hydrophilic surface.*

Number of surfactants (molecules)	Initial surfactant concentration (mM)	Number of surfactants adsorbed on the surface (molecules)	Surfactant surface coverage (nm^2/surfactant headgroup)	Surfactant concentration in the bulk obtained from non-adsorbed surfactants (mM)
926	110.73	0	0	110.73
1852	221.46	0	0	221.46

Table S5. *Systems simulated for surfactant adsorption on one hydrophobic stripe.*

Stripe width, L			Initial surfactant concentration (mM)	Simulation progress			Surfactant concentration in the bulk at equilibrium (mM)
(r_c)	(Å)	(L_s)		Number of surfactants adsorbed on the stripe (molecules)	Surfactant concentration in the bulk (mM)	Number of surfactants added into (+) the system (molecules)	
0.35	3.18	0.15	21.52	1	21.40	N/A	21.40
			44.24	0	44.24	N/A	44.24
			110.73	1	110.61	N/A	110.61
0.70	6.36	0.31	28.70	45	23.32	N/A	23.32
			44.24	40	39.46	N/A	39.46
			110.73	41	105.83	N/A	105.83
1.05	9.54	0.46	28.70	48	22.96	N/A	22.96
			44.24	49	38.38	N/A	38.38
			110.73	45	105.35	N/A	105.35
1.40	12.72	0.61	44.24	189	21.64	0	21.64
1.75	15.90	0.76	44.24	185	22.12	0	22.12
2.10	19.08	0.92	44.24	195	20.93	0	20.93
2.45	22.26	1.07	44.24	190	21.52	0	21.52
			110.73	192	87.77	N/A	87.77
2.80	25.44	1.22	44.24	197	20.69	0	20.69
3.15	28.62	1.38	44.24	199	20.45	0	20.45
3.50	31.80	1.53	44.24	235	16.14	+ 55	22.72
			110.73	236	82.51	N/A	82.51
3.85	34.98	1.68	44.24	260	13.15	+ 70	21.52
			110.73	260	79.64	N/A	79.64
4.20	38.16	1.83	44.24	261	13.03	+ 70	21.40
			110.73	258	79.88	N/A	79.88
4.55	41.34	1.99	44.24	276	11.24	+ 100	23.20
			110.73	280	77.25	N/A	77.25
4.90	44.52	2.14	44.24	287	9.93	+ 100	21.88
			110.74	290	76.05	N/A	76.05

Table S6. *Systems simulated for surfactant adsorption on two hydrophobic stripes.*

Stripe width, L (L_s)	Separation distance, D (L_s)	Initial surfactant concentration (mM)	Simulation progress			Surfactant concentration in the bulk at equilibrium (mM)
			Number of surfactants adsorbed on the stripes (molecules)	Surfactant concentration in the bulk (mM)	Number of surfactants added into (+) the system (molecules)	
0.46	0.15	44.24	210	19.13	+ 20	21.52
		110.73	208	85.86	N/A	85.86
	0.46	44.24	265	12.56	+ 80	22.12
		110.73	266	78.92	N/A	78.92
	0.76	44.24	370	0.00	+ 180	21.52
	1.07	44.24	370	0.00	+ 180	21.52
	1.38	44.24	370	32.17	+ 100	20.21
	1.68	44.24	94	33.00	+ 100	21.05
1.07	0.15	44.24	349	2.51	+ 160	21.64
		110.73	353	68.52	N/A	68.52
	0.46	44.24	357	1.55	+ 160	20.69
		110.73	354	68.40	N/A	68.40
1.68	0.15	44.24	370 [a]	0.00	+ 400	23.20
		110.73	576	41.85	N/A	41.85
	0.46	44.24	370 [b]	0.00	+ 400	22.72
		110.73	577	41.73	N/A	41.73

[a,b] In order to maintain constant concentration in the bulk, some surfactants were added into the systems. We obtained the total number of surfactants adsorbed on two stripes of 576, and 580 molecules, respectively.

References

1. H. Zhao and K. L. Nagy, *J. Colloid Interface Sci.*, 2004, **274**, 613-624.
2. N. Denham, M. C. Holmes and A. V. Zvelindovsky, *J. Phys. Chem. B* 2011, **115**, 1385-1393.
3. M. Y. Kuo, H. C. Yang, C. Y. Hua, C. L. Chen, S. Z. Mao, F. Deng, H. H. Wang and Y. R. Du, *ChemPhysChem*, 2004, **5**, 575-580.