Supporting Information

The influence of calcium ions on rhamnolipid and rhamnolipid / anionic surfactant adsorption and self-assembly.

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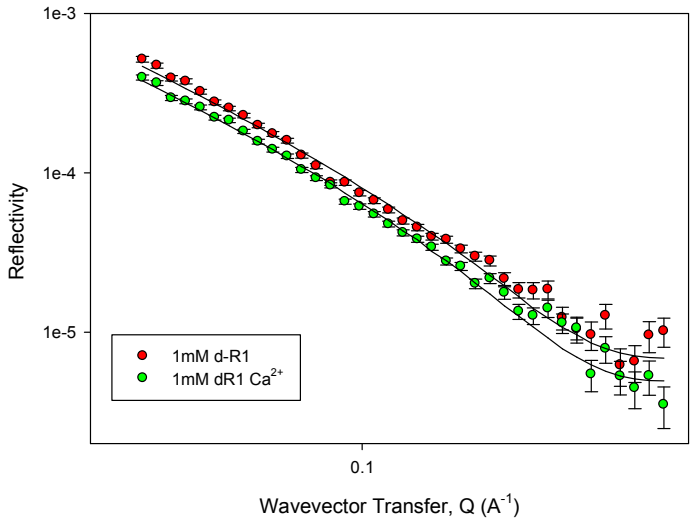
Figure 1. *Neutron Reflectivity for* ***(a)*** *d-R1 in NRW buffer (pH 9) with and without 1mM* Ca^{2+}*,* ***(b)*** *d-R2 in NRW buffer (pH 9) with and without 1mM* Ca^{2+}*.*

(a)



(b)

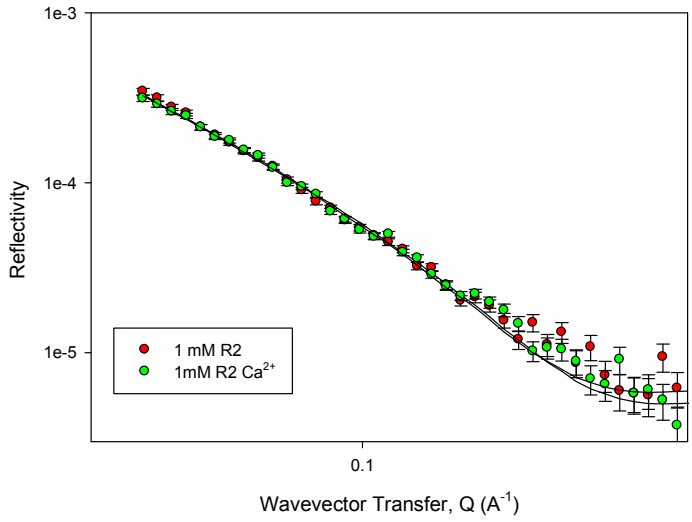


TABLE 1. *Model parameters from analysis of neutron reflectivity data for* ***(a)*** *1mM d-R1 + 1mM Ca^{2+}/NRW buffer (pH 9)* ***(b)*** *1mM d-R2 + 1mM Ca^{2+}/NRW buffer (pH 9)*

Surfactant concentration (M)	**τ (±1 Å)**	**ρ (±0.2x10^{-6} Å^{-2})**	**A (Å^2)**	**Γ (±0.1 x 10^{-10} mol cm^{-2})**
1x10^{-3} R1	22 (21)	3.5 (4.1)	63 (57) ±2	2.7 (2.9)
1x10^{-3} R2	21 (21)	3.4 (3.3)	83 (84) ±2	2.0 (2.0)

TABLE 2. *Variation in adsorbed amounts and surface composition for 1 mM R1/R2 with 1mM Ca^{2+} at pH 9 (in buffer)*

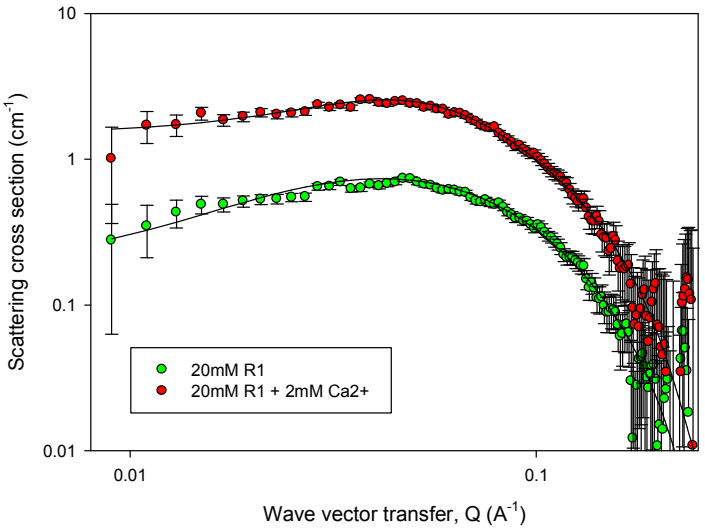
Solution composition (mole fraction R1)	**Contrast**	**τ (±1 Å)**	**ρ (±0.2x 10^{-6} Å^{-2})**	**A (Å^2)**	**Γ (±0.02x 10^{-10} mol cm^{-2})**	**Γ_{total} (±0.04x 10^{-10} mol cm^{-2})**	**Surface composition (mole fraction R1) ±0.02**
0.7	dh	21	3.13	76±2	**2.20 (2.12)**	**2.66 (2.60)**	0.83 (0.82)
	hd	23	0.75	363±10	**0.46 (0.48)**		
0.6	dh	22	2.72	83±2	**2.01 (1.95)**	**2.57 (2.51)**	0.78 (0.78)
	hd	23	0.89	295±10	**0.56 (0.56)**		
0.5	dh	21	2.51	93±4	**1.78 (1.80)**	**2.47 (2.51)**	0.72 (0.72)
	hd	22	1.18	239±10	**0.69 (0.71)**		
0.4	dh	21	2.20	107±4	**1.55 (1.55)**	**2.38 (2.39)**	0.65 (0.65)
	hd	23	1.34	200±10	**0.83 (0.84)**		
0.3	dh	26	1.60	118±4	**1.41 (1.35)**	**2.41 (2.30)**	0.59 (0.60)
	hd	22	1.66	167±4	**1.00 (0.95)**		

TABLE 3. *Variation in adsorbed amounts and surface composition for 1 mM R2/LAS with 1 mM Ca^{2+} at pH 9 (in buffer)*

Solution composition (mole fraction R2)	**Contrast**	**τ (±1 Å)**	**ρ (±0.2x 10^{-6} Å^{-2})**	**A (Å^2)**	**Γ (±0.02x 10^{-10} mol cm^{-2})**	**Γ_{total} (±0.04x 10^{-10} mol cm^{-2})**	**Surface composition (mole fraction R2) ±0.02**
0.7	dh	20	2.27	132±4	**1.25 (1.08)**	**3.04 (2.85)**	0.41 (0.38)
	hd	21	1.75	93±4	**1.79 (1.77)**		
0.6	dh	20	2.01	150±4	**1.11 (0.96)**	**3.20 (2.95)**	0.35 (0.32)
	hd	23	1.89	79±2	**2.10 (1.99)**		
0.5	dh	22	1.66	168±4	**0.99 (0.79)**	**3.21 (3.03)**	0.31 (0.26)
	hd	21	2.27	75±2	**2.22 (2.24)**		
0.4	dh	25	1.27	194±4	**0.86**	**3.40**	0.25
	hd	24	2.18	65±2	**2.54**		
0.3	dh	24	1.18	217±10	**0.76 (0.51)**	**3.52 (3.02)**	0.22 (0.17)
	hd	26	2.19	60±2	**2.76 (2.51)**		

Figure 2. *SANS data and model fits (solid lines) for* ***(a)*** *R1 with and without 2 mM Ca^{2+} at 20 mM;* ***(b)*** *R2, with 2 mM Ca^{2+} at 20, 50 and 100 mM.*

(a)



(b)

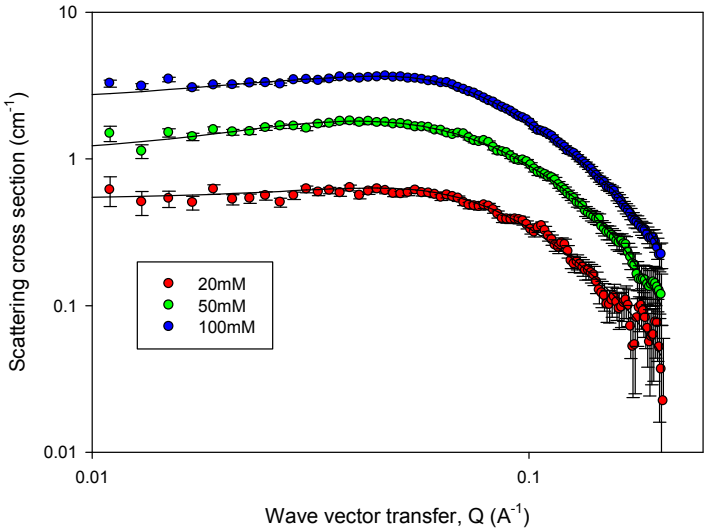


Table 4. *Key model parameters for micelle core+shell model for 20 mM R1/R2 with and without 2 mM $CaCl_2$ (13).*

Solution composition (mole fraction R2)	**Without calcium**		**2 mM $CaCl_2$**	
	Aggregation number (±2)	**Degree of ionisation (±0.02)**	**Aggregation number (±2)**	**Degree of ionisation (±0.02)**
0.6	33	0.18	28	0.16
0.5	36	0.14	33	0.12
0.4	37	0.14	38	0.11
0.2	42	0.14	48	0.08
0.1	49	0.16	56	0.06

Table 5. *Key model parameters from core+shell micelle model fits to R2/LAS mixed data in 2 mM $CaCl_2$ (values in brackets are data in absence of calcium, from reference 13).*

Surfactant concentration (mM)	Solution composition (mole fraction LAS)	ν (±3)	Z (±0.5)	δ (±0.02)	Ri (±1 Å)	Ro (±1 Å)	ext (±0.05)	ee (±0.5)
20.0	0.2	24 (37)	4(2)	0.17 (0.05)	12 (12)	15 (16)	0.85 (0.9)	2.0 (2.6)
	0.5	38 (58)	3(3)	0.08 (0.05)	12 (13)	15 (16)	0.92 (0.95)	2.4 (3.3)
	0.6	47 (63)	3(3)	0.05 (0.05)	13 (13)	16 (16)	0.95 (0.99)	2.8 (3.2)
50.0	0.2	28 (52)	8 (3)	0.3 (0.06)	10 (14)	13 (16)	0.76 (0.91)	3.2 (3.4)
	0.4	30 (63)	7 (3)	0.23 (0.05)	11 (13)	14 (16)	0.82 (0.94)	2.9 (3.7)
	0.5	37 (70)	7 (3)	0.19 (0.04)	12 (13)	14 (16)	0.86 (0.99)	2.9 (3.6)
	0.6	43 (80)	7 (5)	0.14 (0.06)	12 (13)	15 (16)	0.90 (1.0)	2.9 (3.9)
	0.8	83 (103)	5 (5)	0.06 (0.05)	14 (15)	17 (18)	1.04 (1.09)	3.6 (4.3)
100.0	0.2	120 (86)	12 (7)	0.1 (0.07)	13 (11)	16 (15)	0.8 (0.83)	8.0 (9.1)
	0.4	90 (106)	11 (8)	0.12 (0.06)	12 (12)	15 (15)	0.9 (0.9)	6.0 (8.7)
	0.5	74 (130)	10 (8)	0.14 (0.06)	12 (13)	15 (15)	0.98 (0.93)	5.0 (8.6)
	0.6	66 (151)	11 (8)	0.17 (0.05)	12 (13)	15 (15)	0.91 (0.97)	4.3 (8.1)
	0.8	99 (215)	8 (9)	0.09 (0.04)	13 (14)	15 (15)	0.98 (1.1)	5.4 (7.8)

Figure 3. *Variation in micelle aggregation number with solution composition for R1/LAS mixtures at 20 and 50 mM, in the absence of $CaCl_2$, in the micellar or predominantly micellar regions.*

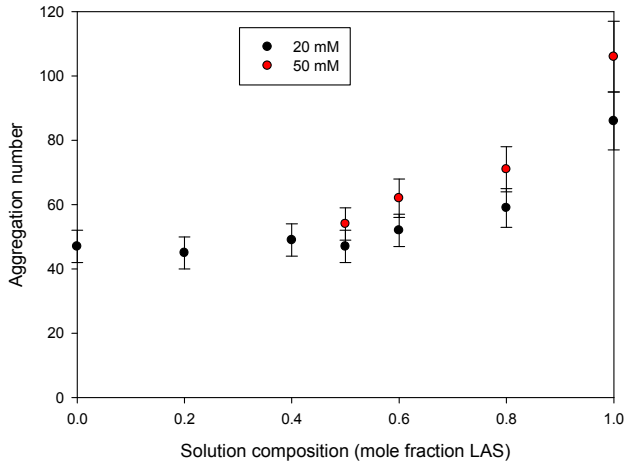


Figure 4. *SANS data for 100 mM 20/80 mole ratio R1/LAS, with and without 2 mM $CaCl_2$.*