

## Supporting Information for

‘The impact of multivalent counterions,  $Al^{3+}$ , on the surface adsorption and self-assembly of the anionic surfactant alkyloxyethylene sulfate and anionic / nonionic surfactant mixtures’

**Table S1.** Micelle model parameters for 20 mM SLES /  $C_{12}E_{12}$  in  $AlCl_3$  / NaCl and  $CaCl_2$  / NaCl.

(a) 95/5 mole ratio SLES /  $C_{12}E_{12}$  in  $CaCl_2$  / NaCl.

$CaCl_2$ / NaCl conc(mM)	Aggregation number, $\nu$	Charge, $z$ ( $\pm 1$ )	$R_1$ ( $\pm 1$ Å)	$R_2$ ( $\pm 1$ Å)	ee ( $\pm 0.1$ )	ext ( $\pm 0.05$ )
4.8 / 57.6	148 $\pm$ 7	4	20	24	1.6	1.2
9.6 / 42	138	4	20	24	1.4	1.2
12 / 36	169	2	20	24	1.8	1.2
14.4 / 28.8	176	2	20	24	1.8	1.2
19.2 / 14.4	186 $\pm$ 10	0	20	24	1.9	1.2
24 / 0.0	255	0	20	24	2.7 $\pm$ 0.2	1.2

(b) 90/10 mole ratio SLES /  $C_{12}E_{12}$  in  $CaCl_2$  / NaCl.

$CaCl_2$ / NaCl conc(mM)	Aggregation number, $\nu$	Charge, $z$ ( $\pm 1$ )	$R_1$ ( $\pm 1$ Å)	$R_2$ ( $\pm 1$ Å)	ee ( $\pm 0.1$ )	ext ( $\pm 0.05$ )
4.8 / 57.6	136 $\pm$ 7	4	19	24	1.6	1.1
9.6 / 42	109	5	19	24	1.3	1.1
12 / 36	153	4	19	24	1.8	1.1
14.4 / 28.8	161	4	19	24	1.7	1.1
19.2 / 14.4	171 $\pm$ 10	2	19	24	1.8	1.1
24 / 0.0	179	1	19	24	1.9	1.1

(c) 95/5 mole ratio SLES /  $C_{12}E_{12}$  in  $AlCl_3$  / NaCl.

$AlCl_3$ / NaCl conc(mM)	Aggregation number, $\nu$	Charge, $z$ ( $\pm 1$ )	$R_1$ ( $\pm 1$ Å)	$R_2$ ( $\pm 1$ Å)	ee ( $\pm 0.1$ )	ext ( $\pm 0.05$ )
0.0 / 72	125 $\pm$ 7	4	19	23	1.5	1.1
2.4 / 57.6	150	4	19	23	1.7	1.1
4.8 / 43.2	193 $\pm$ 10	0	19	23	2.2 $\pm$ 0.2	1.1
6.0 / 36	286 $\pm$ 20	0	19	23	3.6 $\pm$ 0.2	1.1
7.2 / 28.8	418 $\pm$ 30	0	19	23	5.3 $\pm$ 5	1.1

(d) 90/10 mole ratio SLES / C<sub>12</sub>E<sub>12</sub> in AlCl<sub>3</sub> / NaCl.

AlCl <sub>3</sub> / NaCl conc(mM)	Aggregation number, v	Charge, z (±1)	R <sub>1</sub> (±1 Å)	R <sub>2</sub> (±1 Å)	ee (±0.1)	ext (±0.05)
0.0 / 72	116±7	4	19	24	1.6	1.2
2.4 / 57.6	140	4	19	24	1.6	1.2
4.8 / 43.2	171±10	2	19	24	2.0	1.2
6.0 / 36	223	0	19	24	2.5±0.2	1.2
7.2 / 28.8	337±20	0	19	24	3.7±0.2	1.2
9.6 / 14.4	570±30	0	19	24	6.3±0.5	1.2
12.0 / 0.0	734±50	0	19	24	8.3±1	1.2

(e) 80/20 mole ratio SLES / C<sub>12</sub>E<sub>12</sub> in AlCl<sub>3</sub> / NaCl

AlCl <sub>3</sub> / NaCl conc(mM)	Aggregation number, v	Charge, z (±1)	R <sub>1</sub> (±1 Å)	R <sub>2</sub> (±1 Å)	ee (±0.1)	ext (±0.05)
0.0 / 72	108±7	4	18	24	1.5	1.1
2.4 / 57.6	132	4	18	24	1.6	1.1
4.8 / 43.2	152	3	18	24	1.9	1.1
6.0 / 36	161±10	2	18	24	1.9	1.1
7.2 / 28.8	178	0	18	24	2.2±0.2	1.1
9.6 / 14.4	210	0	18	24	2.6±0.2	1.1
12.0 / 0.0	261	0	18	24	3.3±0.2	1.1

**Table S2.** Micelle model parameters for 5 mM SLES / C<sub>12</sub>E<sub>12</sub> in AlCl<sub>3</sub> / NaCl

SLES / C <sub>12</sub> E <sub>12</sub> composition (mole % SLES)	AlCl <sub>3</sub> / NaCl conc(mM)	Aggregation number, $\nu$	Charge, $z$ ( $\pm 1$ )	R <sub>1</sub> ( $\pm 1$ Å)	R <sub>2</sub> ( $\pm 1$ Å)	ee ( $\pm 0.1$ )	ext ( $\pm 0.05$ )
100/0	0 / 15	103 $\pm$ 7	3	17	20	1.7	1.0
	0.6 / 12	134	1	18	22	1.7	1.1
	1.2 / 9	193 $\pm$ 10	0	20	24	2.0	1.2
	1.5 / 7.5	282	0	19	23	3.3	1.1
93.5 / 6.5	0 / 15	105 $\pm$ 7	1	17	21	1.7	1.0
	1.8 / 6	531 $\pm$ 30	0	18	22	7.0	1.1
95/5	0 / 15	106 $\pm$ 7	5	17	21	1.6	1.0
	1.8 / 6	548 $\pm$ 30	0	18	22	6.9	1.1
90/10	0/15	95 $\pm$ 7	4	17	21	1.5	1.0
	0.6/12	113	1	17	21	1.9	1.0
	1.2/9	159 $\pm$ 10	1	18	23	2.0	1.1
	1.8/6	284 $\pm$ 20	1	18	23	3.6	1.1

**Table S3.** SLES adsorption, monolayer model parameters.

SLES concentration (M)	d ( $\pm 1$ Å)	$\rho$ ( $\pm 0.1 \times 10^{-6} \text{ Å}^{-2}$ )	A ( $\text{Å}^2$ )	$\Gamma$ ( $\pm 0.1 \times 10^{-10} \text{ mol cm}^{-2}$ )
3.1x10 <sup>-6</sup>	-	-	-	-
1.25x10 <sup>-5</sup>	32	0.3	212 $\pm$ 10	0.8
4x10 <sup>-5</sup>	21	1.8	80 $\pm$ 4	2.0
5x10 <sup>-5</sup>	19	1.9	80 $\pm$ 4	2.0
2x10 <sup>-4</sup>	23	2.8	45 $\pm$ 2	3.7
2.5x10 <sup>-4</sup>	23	2.5	51	3.3
4x10 <sup>-4</sup>	22	3.2	41	4.0
8x10 <sup>-4</sup>	23	3.3	38	4.4
5x10 <sup>-3</sup>	22	3.2	41	4.0

**Table S4.** 5 mM SLES adsorption for different isotopic combinations, in 10 mM CaCl<sub>2</sub>, monolayer model parameters.

<b>Isotopic composition</b>	<b>d (±1Å)</b>	<b>ρ (± 0.1 x10<sup>-6</sup> Å<sup>-2</sup>)</b>	<b>A (±2Å<sup>2</sup>)</b>	<b>Γ (±0.1x10<sup>-10</sup> mol cm<sup>-2</sup>)</b>
d-SLES	24	3.4	36	4.6
50/50 d, h-SLES	25	1.8	33	5.0

**Table S5.** 5 mM SLES / C<sub>12</sub>E<sub>12</sub> in AlCl<sub>3</sub> / NaCl, surface layer model parameters.

SLES / C <sub>12</sub> E <sub>12</sub> composition (mole ratio)	AlCl <sub>3</sub> / NaCl conc(mM)	d <sub>1</sub> (±1Å)	ρ <sub>1</sub> (± 0.1 ×10 <sup>-6</sup> Å <sup>-2</sup> )	d <sub>2</sub> (±1Å)	ρ <sub>2</sub> (± 0.1 ×10 <sup>-6</sup> Å <sup>-2</sup> )	d <sub>3</sub> (±1Å)	ρ <sub>3</sub> (± 0.1 ×10 <sup>-6</sup> Å <sup>-2</sup> )
95/5	1.8/5.0	27	2.5	-	-	-	-
95/5	2.1/3.25	24	2.7	-	-	-	-
SLES / C <sub>12</sub> E <sub>12</sub> composition (mole ratio)	AlCl <sub>3</sub> / NaCl conc(mM)	d <sub>1</sub> (±0.2Å)	ρ <sub>1</sub> (± 0.1 ×10 <sup>-6</sup> Å <sup>-2</sup> )	d <sub>2</sub> (±0.2Å)	ρ <sub>2</sub> (± 0.1 ×10 <sup>-6</sup> Å <sup>-2</sup> )	N	ΔQ
95/5	2.4/2.5	25.2	3.1	25.2	1.7	40	0.05
SLES / C <sub>12</sub> E <sub>12</sub> composition (mole ratio)	AlCl <sub>3</sub> / NaCl conc(mM)	d <sub>1</sub> (±1Å)	ρ <sub>1</sub> (± 0.1 ×10 <sup>-6</sup> Å <sup>-2</sup> )	d <sub>2</sub> (±1Å)	ρ <sub>2</sub> (± 0.1 ×10 <sup>-6</sup> Å <sup>-2</sup> )	d <sub>3</sub> (±1Å)	ρ <sub>3</sub> (± 0.1 ×10 <sup>-6</sup> Å <sup>-2</sup> )
93.5/6.5	2.4/2.5	24	2.7	-	-	-	-
	2.7/1.25	25	2.4	-	-	-	-
92/8	2.4/2.5	24	2.7	-	-	-	-
90/10	0.0/15	26	2.2	-	-	-	-
	1.8/5	27	2.5	-	-	-	-
	2.4/2.5	22	2.7	-	-	-	-
	2.7/1.25	25	2.4	-	-	-	-
	3.0/0.0	24	3.1	-	-	-	-

**Table S6.** 1mM SLES / C<sub>12</sub>E<sub>12</sub> / AlCl<sub>3</sub> / NaCl

<b>SLES / C<sub>12</sub>E<sub>12</sub> composition (mole ratio)</b>	<b>AlCl<sub>3</sub> / NaCl conc(mM)</b>	<b>d<sub>1</sub> (±1Å)</b>	<b>ρ<sub>1</sub> (± 0.1 ×10<sup>-6</sup> Å<sup>-2</sup>)</b>	<b>d<sub>2</sub> (±1Å)</b>	<b>ρ<sub>2</sub> (± 0.1 ×10<sup>-6</sup> Å<sup>-2</sup>)</b>	<b>d<sub>3</sub> (±1Å)</b>	<b>ρ<sub>3</sub> (± 0.1 ×10<sup>-6</sup> Å<sup>-2</sup>)</b>
90/10	0.12/2.4	19	3.1	-	-	-	-
90/10	0.24/1.8	19	3.2	17	1.2	25	3.1
90/10	0.3/1.5	24	3.2	17	1.3	20	3.3
90/10	0.35/1.2	18	3.8	17	1.0	25	2.5
90/10	0.48/0.6	18	3.8	17	1.0	25	2.5
<b>SLES / C<sub>12</sub>E<sub>12</sub> composition (mole ratio)</b>	<b>AlCl<sub>3</sub> / NaCl conc(mM)</b>	<b>d<sub>1</sub> (±0.2Å)</b>	<b>ρ<sub>1</sub> (± 0.1 ×10<sup>-6</sup> Å<sup>-2</sup>)</b>	<b>d<sub>2</sub> (±0.2Å)</b>	<b>ρ<sub>2</sub> (± 0.1 ×10<sup>-6</sup> Å<sup>-2</sup>)</b>	<b>N</b>	<b>ΔQ</b>
90/10	0.6/0.0	21.4	3.5	21.8	1.4	3	0.1