## Supporting information for "Mechanisms of Neutral and Anionic Surfactant Sorption to Solid-Phase Microextraction Fibers"

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**Figure S1.** Percentage of alkyl sulfate concentrations in water versus estimated area of unexposed glass surface in 20-mL glass vials (total volume ranged from 20 to 24.5 mL). Open symbols are from direct sampling of the water phase (V=0.5 ml) and closed symbols are from liquid-liquid extraction with 50/50 methanol/water of vials (including glass, vial cap, and water). No salts were added to the water phase.



**Figure S2.** Recoveries of alkyl sulfates extracted by liquid-liquid extraction from ultrapure water (with 0.77 mM NaN<sub>3</sub>), phosphate buffered medium (with 5 mM NaH<sub>2</sub>PO<sub>4</sub>/ Na<sub>2</sub>HPO<sub>4</sub> and 0.77 mM NaN<sub>3</sub> at pH 7), and Dutch Standard Water (with 1.36 mM CaCl<sub>2</sub>.2H2O, 0.73 mM MgSO<sub>4</sub>.7H<sub>2</sub>O, 1.19 mM NaHCO<sub>3</sub>, 0.20 mM KHCO<sub>3</sub>, and 0.77 mM NaN<sub>3</sub>). Standard errors of triplicate measurements are shown.



**Figure S3.** Sequential desorption of alkyl sulfates from 35  $\mu$ m polyacrylate SPME fibers (length 4 cm) with 90/10 methanol/water without and with 5 mM of ammonium acetate (NH<sub>4</sub>Ac). Prior to desorption, fibers were equilibrated with water containing 1 mM sodium azide for 7 days. The total concentration in the fiber is the sum of amounts from individual fibers extracted twice for 20 minutes and subsequently extracted overnight with methanol/water. Standard errors of triplicate measurements are shown.



**Figure S4.** Concentrations of alcohol ethoxylates ( $C_xEO_y$ ) in 35 µm polyacrylate fibers versus time. The data were fitted with a one-compartment model assuming first-order kinetics. Depletion of the water phase was taken into account. The medium was buffered with 5 mM sodium phosphate at pH 7 and contained 1 mM sodium azide. Aqueous concentrations ranged from 130 to 670 µg/L.



**Figure S5.** Concentrations of alkyl carboxylates ( $C_xCO_2$ ) in 35 µm polyacrylate fibers versus time. The data were fitted with a one-compartment model assuming first-order kinetics and taking depletion of the water phase into account. The medium was buffered with 5 mM sodium phosphate at pH 7 and contained 1 mM sodium azide. Aqueous concentrations ranged from 80 ( $C_{14}CO_2$ ) to 1700 ( $C_{11}CO_2$ ) µg/L.



**Figure S6.** Concentrations of alkyl sulfates ( $C_xSO_4$ ) and alkyl sulfonates ( $C_xSO_3$ ) in 35 µm polyacrylate fibers versus time. The data were fitted with a one-compartment model assuming first-order kinetics. A replicates test showed a poor fit for  $C_{15}SO_3$  and all alkyl sulfates (indicated by dashed lines). The medium was buffered with 5 mM sodium phosphate at pH 7 and contained 1 mM sodium azide. Aqueous concentrations ranged from 80 to 160 µg/L.



**Figure S7.** Logarithmic uptake ( $k_1 \pm SE$ ) and elimination ( $k_2 \pm SE$ ) rate constants versus logarithmic fiber-water partition ( $K_{\text{fiber}} \pm SE$ ) or distribution ( $D_{\text{fiber}} \pm SE$ ) coefficients (35 µm polyacrylate fibers were used) for alcohol ethoxylates ( $C_x EO_y$ ) and alkyl carboxylates ( $C_x CO_2$ ).



**Figure S8.** Fiber-water sorption isotherms of dodecyl sulfate ( $C_{12}SO_4$ ) measured with 35  $\mu$ m polyacrylate fibers at different pH values and different ionic strengths. The medium was buffered with 5 mM sodium phosphate at pH 7 and contained 1 mM sodium azide. Additional sodium chloride was added to increase ionic strength.



**Figure S9.** Fiber-water sorption isotherms of alkyl sulfates ( $C_{13}SO_4$ ,  $C_{15}SO_4$ ,  $C_{16}SO_4$ , and  $C_{17}SO_4$ ; Figure A) and alkyl sulfonates ( $C_{14}SO_3$ ,  $C_{15}SO_3$ ,  $C_{16}SO_3$ ; Figure B) measured with 35 µm polyacrylate fibers at pH 6.9. The medium was buffered with 5 mM sodium phosphate at pH 7 and contained 1 mM sodium azide.



**Figure S10.** Fiber-water sorption isotherms of dodecyl sulfate ( $C_{12}SO_4$ ) measured with two types of 7  $\mu$ m polyacrylate fibers – purchased in May 2001 (old) and January 2012 (new) – and 35  $\mu$ m polyacrylate fibers (new; purchased January 2012) at pH 8.1. The medium contained 10 mM calcium chloride and 1 mM sodium azide.



**Figure S11.** Surface area normalized fiber-water sorption isotherms of dodecyl sulfate ( $C_{12}SO_4$ ) measured with two types of 7  $\mu$ m polyacrylate fibers – purchased in May 2001 (old) and January 2012 (new) – and 35  $\mu$ m polyacrylate fibers (new; purchased January 2012) at pH 8.1. The medium contained 10 mM calcium chloride and 1 mM sodium azide.



**Figure S12.** Surface area normalized fiber-water sorption isotherms of dodecyl sulfate ( $C_{12}SO_4$ ) measured with 35  $\mu$ m polyacrylate fibers at pH 6.88. The medium was buffered with 5 mM sodium phosphate at pH 7 and contained 1 mM sodium azide.



**Figure S13.** Predicted versus experimental 35  $\mu$ m polyacrylate fiber-water partition/ distribution coefficients for alcohol ethoxylates (C<sub>x</sub>EO<sub>y</sub>) and alkyl carboxylates (C<sub>x</sub>CO<sub>2</sub>).

Compound	Q <sub>1</sub> mass	Q₃ mass	DP (V)	FP (V)	CE (V)	IS (V)	TEM (°C)
Alcohol ethoxylates							
C <sub>10</sub> EO <sub>4</sub>	352.5	89.0	35	240	31	1500	250
C <sub>12</sub> EO <sub>4</sub>	380.5	89.0	30	240	30	1500	250
C <sub>12</sub> EO <sub>5</sub>	424.4	89.0	45	240	22	1500	250
C <sub>12</sub> EO <sub>6</sub>	468.6	89.0	40	240	35	1500	250
C <sub>12</sub> EO <sub>7</sub>	512.7	89.0	50	240	45	1500	250
C <sub>12</sub> EO <sub>8</sub>	556.5	89.0	55	240	43	1500	250
C <sub>13</sub> EO <sub>4</sub>	394.5	89.0	45	240	33	1500	250
C <sub>13</sub> EO <sub>8</sub>	570.7	89.0	40	240	48	1500	250
C <sub>14</sub> EO <sub>4</sub>	408.7	89.0	38	240	33	1500	250
C <sub>14</sub> EO <sub>8</sub>	584.5	89.0	55	240	30	1500	250
C <sub>16</sub> EO <sub>8</sub>	612.5	89.0	49	240	50	1500	250
Alkyl carboxylates							
C <sub>11</sub> CO <sub>2</sub>	199.2	199.2	-55	-350	-11	-4500	400
C <sub>13</sub> CO <sub>2</sub>	227.3	227.3	-55	-350	-12	-4500	400
C <sub>14</sub> CO <sub>2</sub>	241.3	241.3	-55	-350	-13	-4500	400
Alkyl sulfonates							
C <sub>11</sub> SO <sub>3</sub>	235.3	80.1	-65	-350	-43	-4500	400
C <sub>13</sub> SO <sub>3</sub>	263.4	80.1	-65	-350	-47	-4500	400
C <sub>14</sub> SO <sub>3</sub>	277.5	80.1	-70	-350	-55	-4500	400
C <sub>15</sub> SO <sub>3</sub>	291.5	80.1	-70	-350	-55	-4500	400
C <sub>16</sub> SO <sub>3</sub>	305.8	80.1	-70	-350	-60	-4500	400
C <sub>18</sub> SO <sub>3</sub>	333.9	80.1	-75	-350	-65	-4500	400
Alkyl sulfates							
C <sub>11</sub> SO <sub>4</sub>	251.2	97.0	-57	-400	-35	-4500	400
C <sub>12</sub> SO <sub>4</sub>	265.2	97.0	-60	-400	-37	-4500	400
C <sub>13</sub> SO <sub>4</sub>	279.2	97.0	-55	-400	-40	-4500	400
C <sub>15</sub> SO <sub>4</sub>	307.2	97.0	-65	-400	-40	-4500	400
$C_{16}SO_4$	321.2	97.0	-65	-400	-45	-4500	400
C <sub>17</sub> SO <sub>4</sub>	335.9	97.0	-70	-400	-50	-4500	400
C <sub>18</sub> SO <sub>4</sub>	349.8	97.0	-70	-400	-50	-4500	400

Table S1. Mass spectrometer setting for all analyzed surfactants.<sup>a</sup>

<sup>a</sup> DP = declustering potential; FP = focusing potential; CE = collision energy; IS = ion source voltage; TEM = temperature of ion source

Compound	log K <sub>fiber</sub> or log D <sub>fiber</sub> ±SE	log k <sub>1</sub> ±SE	log k <sub>2</sub> ±SE	t <sub>95%</sub> (h)	Fiber (%)	Recovery (%)
Alcohol ethoxylates						
C <sub>10</sub> EO <sub>4</sub>	2.36±0.03	$1.48\pm0.02$	-0.88±0.02	23	0.57±0.01	107±3
C <sub>12</sub> EO <sub>4</sub>	3.39±0.03	2.49±0.02	-0.91±0.02	24	6.28±0.23	66±3
C <sub>12</sub> EO <sub>5</sub>	3.09±0.02	2.08±0.02	-1.01±0.02	30	2.84±0.09	74±5
C <sub>12</sub> EO <sub>6</sub>	2.81±0.03	1.75±0.02	-1.06±0.02	34	1.53±0.02	98±3
C <sub>12</sub> EO <sub>7</sub>	2.57±0.03	1.45±0.02	-1.12±0.02	39	0.86±0.02	84±2
C <sub>12</sub> EO <sub>8</sub>	2.22±0.05	$1.16\pm0.03$	-1.05±0.04	34	$0.40 \pm 0.01$	98±3
C <sub>13</sub> EO <sub>4</sub>	3.78±0.03	2.62±0.02	-1.16±0.02	43	16.23±0.53	100±3
C <sub>13</sub> EO <sub>8</sub>	2.76±0.03	1.55±0.02	-1.20±0.02	48	$1.49 \pm 0.05$	102±3
C <sub>14</sub> EO <sub>8</sub>	3.33±0.03	2.18±0.02	-1.16±0.03	43	4.69±0.31	98±3
C <sub>16</sub> EO <sub>8</sub>	4.14±0.04	2.61±0.03	-1.53±0.03	101	24.84±1.18	89±9
Alkyl carboxylates						
C <sub>11</sub> CO <sub>2</sub>	2.40±0.03	1.85±0.04	-0.55±0.04	11	1.24±0.04	102±6
C <sub>13</sub> CO <sub>2</sub>	3.48±0.04	2.54±0.04	-0.95±0.04	26	13.71±0.78	105±4
C <sub>14</sub> CO <sub>2</sub>	4.02±0.06	2.76±0.04	-1.28±0.05	57	40.36±2.03	103±6

**Table S2.** Logarithmic values of 35  $\mu$ m polyacrylate fiber-water partition coefficients (log  $K_{\text{fiber}}$ ), uptake (log  $k_1$ ) and elimination (log  $k_2$ ) rate constants, 95% equilibration times ( $t_{95\%} = \ln(0.05)/-k_2$ ), depletion by the fiber, and recoveries for alcohol ethoxylates ( $C_x EO_y$ ) and alkyl carboxylates ( $C_x CO_2$ ).

**Table S3.** Effect of pH and medium composition on sorption isotherm parameters for 35  $\mu$ m polyacrylate-coated fibers and dodecyl sulfate (C<sub>12</sub>SO<sub>4</sub>).<sup>a</sup>

рН	Medium	log <i>K</i> <sub>F</sub> ±SE	<i>N</i> ±SE	R <sup>2</sup>	Recovery±SD
8.10	10 mM Ca <sup>2+</sup>	-1.30±0.03	0.48±0.01	0.9935	92±6
6.88	$8 \text{ mM Na}^+$	-1.76±0.13	0.38±0.03	0.9536	112±10
6.84	469 mM Na $^{+}$	-0.67±0.07	0.51±0.02	0.9841	80±7
6.08	$8 \text{ mM Na}^+$	-2.13±0.07	0.25±0.02	0.9419	95±12
5.09	$8 \text{ mM Na}^+$	-2.52±0.04	0.11±0.01	0.9106	94±11
4.34	$8 \text{ mM Na}^+$	-2.48±0.01	0.09±0.00	0.9827	92±12
4.06	469 mM Na <sup>+</sup>	-1.56±0.05	0.25±0.01	0.9682	78±11
3.19	$8 \text{ mM Na}^+$	-1.73±0.05	0.20±0.01	0.9522	96±9

<sup>a</sup> log  $K_F$  is the Freundlich sorption coefficient in (mol/L<sub>polyacrylate</sub>)/(mol/L)<sup>N</sup>, N is the non-linearity exponent, and R<sup>2</sup> is the correlation coefficient. All treatments contained 1 mM sodium azide. With the exception of the calcium chloride treatment (10 mM Ca<sup>2+</sup>), all treatments were buffered to the desired pH with a phosphate or acetate buffer. Higher concentrations of sodium were obtained by addition of sodium chloride to the medium.

**Table S4.** Effect of different chain lengths on sorption isotherm parameters for alkyl sulfates  $(C_xSO_4)/$  alkyl sulfonates  $(C_xSO_3)$  and 35 µm polyacrylate-coated fibers.<sup>a</sup>

any surbitates (C <sub>x</sub> 503) and 55 µm polyaci yiate-coated fibers.						
Compound	рН	log K <sub>F</sub> ±SE	<b>N</b> ±SE	R <sup>2</sup>	<b>Recovery</b> ±SD	
C <sub>13</sub> SO <sub>4</sub>	6.93	-0.98±0.10	0.46±0.02	0.9748	100±4	
C <sub>15</sub> SO <sub>4</sub>	6.93	-1.28±0.09	0.33±0.02	0.9622	106±4	
C <sub>16</sub> SO <sub>4</sub>	6.93	-1.37±0.10	0.29±0.02	0.9468	105±4	
C <sub>17</sub> SO <sub>4</sub>	6.93	-0.47±0.18	0.41±0.03	0.9253	114±20	
C <sub>14</sub> SO <sub>3</sub>	6.96	-1.04±0.22	0.51±0.04	0.9075	100±3	
C <sub>15</sub> SO <sub>3</sub>	6.96	-0.60±0.29	0.54±0.05	0.8750	101±8	
$C_{16}SO_3$	6.96	0.36±0.27	0.65±0.04	0.9326	96±5	

<sup>a</sup> log  $K_F$  is the Freundlich sorption coefficient in (mol/L<sub>polyacrylate</sub>)/(mol/L)<sup>N</sup>, N is the non-linearity exponent, and R<sup>2</sup> is the correlation coefficient. All treatments contained 1 mM sodium azide. All treatments were buffered to the desired pH with a phosphate buffer.