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

Supporting Information: Short-chain branched sulfosuccinate as missing link between surfactants and hydrotropes

Simon Stemplinger,[*,†,‡] Jeremy Causse,[†] Sylvain Prévost,[¶] Stéphane Pellet-Rostaing,[†] Thomas Zemb,[†] and Dominik Horinek[*,‡]

†*ICSM, CEA, CNRS, Univ Montpellier, ENSCM, Marcoule, France*

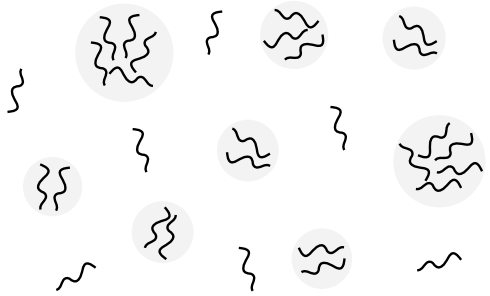
‡*Institut für Physikalische und Theoretische Chemie, Universität Regensburg, Regensburg, Germany*

¶*Institut Laue-Langevin, Grenoble, France*

E-mail: simon.stemplinger@ur.de; dominik.horinek@ur.de

Classification of aggregation and aggregate properties

Aggregation



N_{agg}	1	2	3	4	5	Σ
N	7	5	1	0	2	15
N'	7	10	3	0	10	30
P	$^{7}/_{15}$	$^{5}/_{15}$	$^{1}/_{15}$	$^{0}/_{15}$	$^{2}/_{15}$	1
P'	$^{7}/_{30}$	$^{10}/_{30}$	$^{3}/_{30}$	$^{0}/_{30}$	$^{10}/_{30}$	1

Figure S1 & Table S1: Illustration of monomers forming aggregates of various sizes and tabulated values of the number of aggregates N and the total number of monomers N' in aggregates of given size N_{agg}, as well as the respective probabilities P and P'.

Figure and Table S1 illustrate the key quantities number of aggregates N and number of monomers N', as well as their probabilities, in dependency of the aggregation number N_{agg}. In the main text, the probability P' is used, see Fig. 3 and 4.

For the practical calculation of the aggregates, a custom script was used. Initially, the cutoff radius is defined by finding the first minimum in the radial distribution function of the tertiary C atoms in the hydrophobic chain, *i.e.* 0.8 nm, see Figure S2. Two chains are considered interacting if their tertiary C atoms have a distance smaller than this cutoff. One chain can interact with multiple other chains and a molecule can simultaneously form interactions with both its chains. The aggregation size is then computed as the number of monomers interacting directly or indirectly with other monomers.

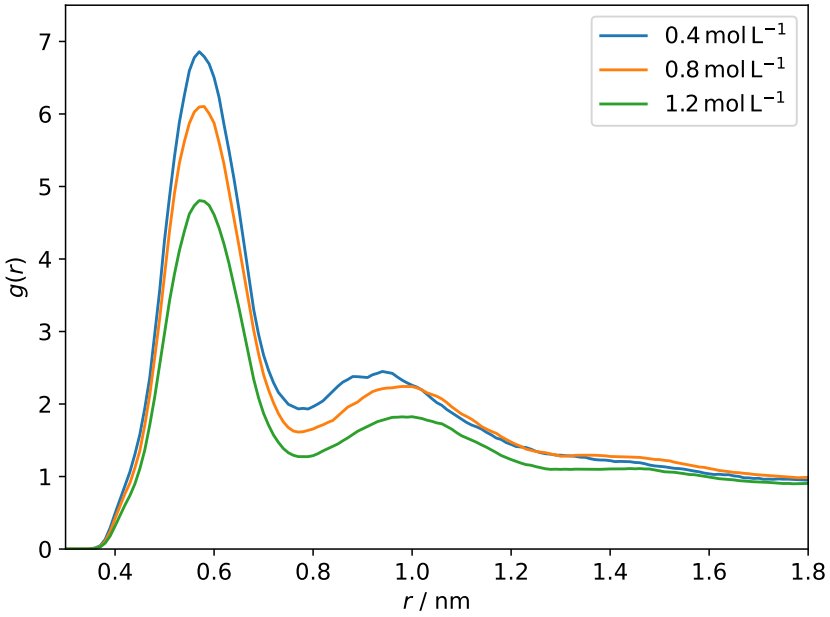


Figure S2: Radial distribution function of the tertiary carbon atoms of the AOT3 molecule. For all concentrations a first minimum is visible at 0.8 nm.

Hydration

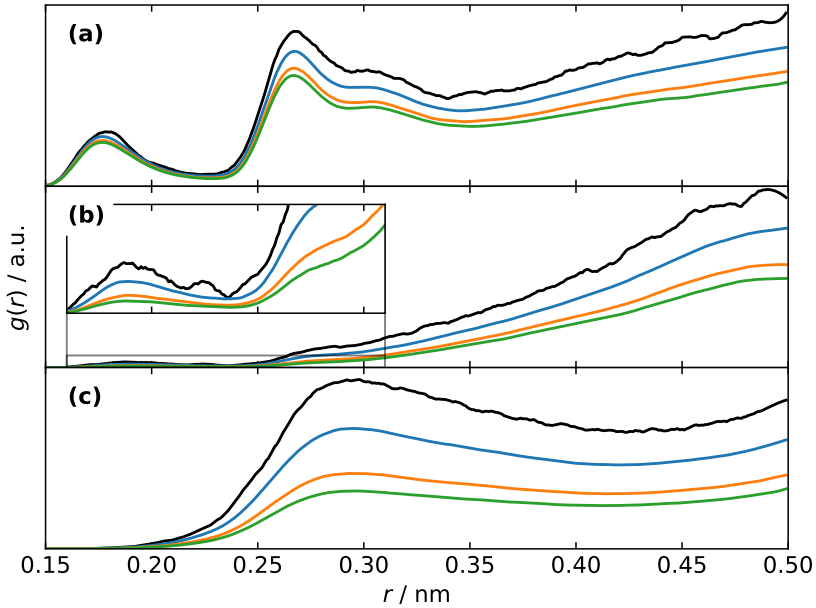


Figure S3: Radial distribution function of water molecules around the three segments of the AOT3 for the concentrations 0.4 mol L^{-1} (blue), 0.8 mol L^{-1} (orange), 1.2 mol L^{-1} (green), as well as one monomer (black). (a), (b) and (c) are the head group, the linker and the tail, respectively.

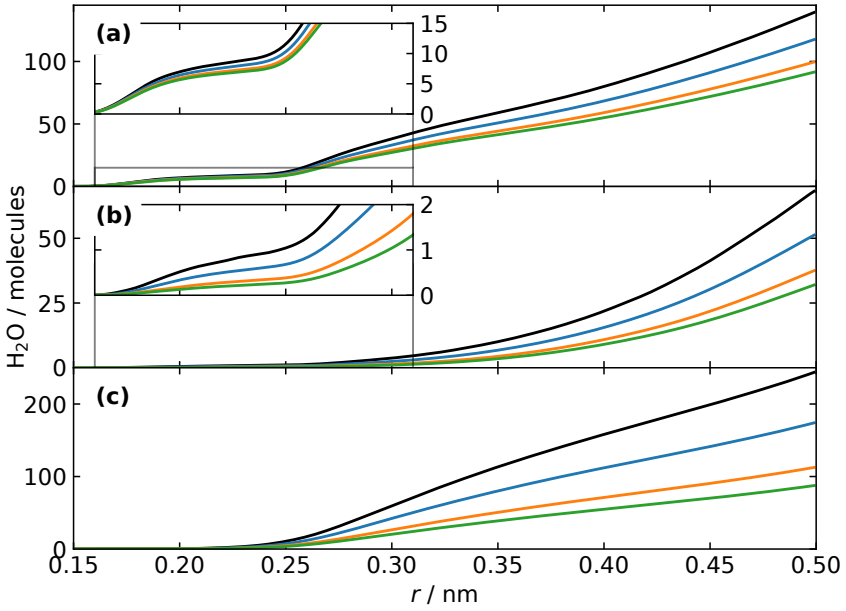


Figure S4: Number of water molecules around the three segments of the AOT3 for the concentrations 0.4 mol L^{-1} (blue), 0.8 mol L^{-1} (orange), 1.2 mol L^{-1} (green), as well as one monomer (black). (a), (b) and (c) are the head group, the linker and the tail, respectively.

The radial distribution functions (RDFs) of water around the three segments of the AOT3 molecule and their integrals were computed, see Figures S3 and S4. For each segment the radius of the first minimum and the corresponding coordination number are determined, see Table S2. Practically, the gromacs command `gmx rdf` was used with the `-surf` option set to `mol` and the `-cn` option to calculate the cumulative RDFs.

Table S2: Hydration of the three AOT3 segments head group (HG), linker and tail for different concentrations in absolute and relative numbers.

		monomer	0.4 mol L^{-1}		0.8 mol L^{-1}		1.2 mol L^{-1}	
	r_{min}	abs.	abs.	rel.	abs.	rel.	abs.	rel.
HG	0.23	8.77	8.00	0.91	7.31	0.83	6.97	0.79
linker	0.24	0.91	0.60	0.66	0.34	0.37	0.24	0.27
tail	0.42	173.65	123.09	0.71	78.43	0.45	60.52	0.35

Solvent accessible surface area

The solvent accessible surface area is calculated with the gromacs `gmx sasa` functionality. The command only allows the calculation of the total area as a function of time or the averaged area of a single monomer for the total time. As we were interested in the area of a single monomer as a function of time, a script was used to call the `gmx sasa` command with the `-or` option (to calculate the monomer area) for single trajectory frames from 500 to 1000 ns in steps of 5 ns. This was done for the whole AOT3 molecule and only the head group (as defined in the main document), then the calculated areas from all steps were combined and the histogram was computed.

Scattering

The computed SAXS spectra were calculated with the gromacs command `gmx saxs`. The last 500 ns of the trajectory were used with a time step of 10 ns.

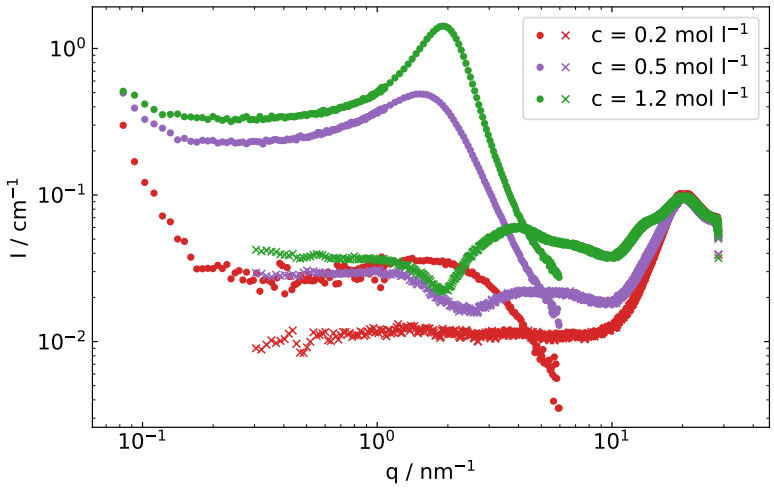
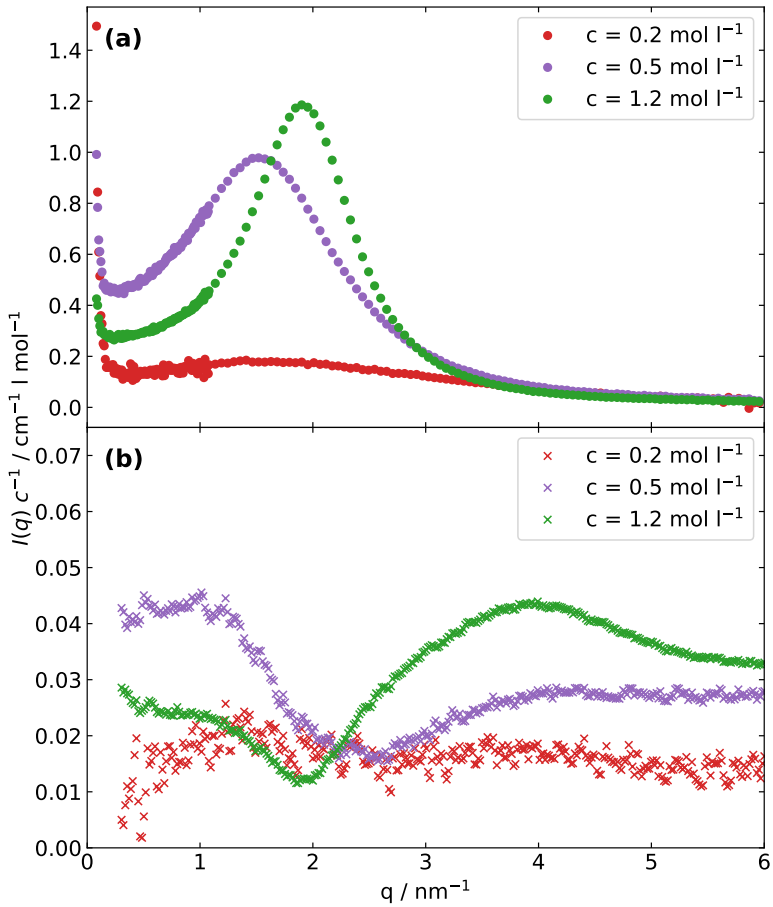


Figure S5: Scattering intensities for small angle neutron scattering (points) and small angle x-ray scattering (crosses) experiments on a log-log scale.



The neutron scattering is completely different from the x-ray pattern. The ionic head groups are no more dominant, and the interference term is much more visible. The broad bump cannot be fitted directly by any structure and form factor combination only because of the presence of an aggregate-monomer crossed term as already noticed by Nave and Eastoe in the case of two hexyl chains attached to the sulfosuccinate.[S1]

In the direction of more structured solution like LC a missing link with conventional surfactants forming micelles was described by Eastoe et al.:[S2] this was obtained by drafting aromatic chains instead of branched hydrocarbon chain and obtaining a still effective surfactant with strong mesogenic power. LC are dominant in this case in low concentrations.

General synthesis of AOT derivates

General synthesis of maleate derivatives

In a 500 mL flask, maleic acid, alcohol and H_2SO_4 98 % were stirred under reflux in toluene (100 mL) for 16 h. The water produced during the reaction was gradually removed from the mixture by Dean-Stark. The mixture was then cooled at room temperature and concentrated to dryness under vacuum. The residue was diluted in ethyl acetate (100 mL) and washed with a saturated aqueous Na_2CO_3 (2 x 150 mL) and a saturated aqueous $NaHCO_3$ (2 x 150 mL). Organic phase was then dried over sodium sulfate, filtered and concentrated under vacuum affording maleate derivatives after distillation.

bis(2-ethylbutyl) maleate 1

From maleic acid (21.19 g, 0.18 mol), 2-ethylbutanol (37.3 g, 0.36 mol) and H_2SO_4 98 % (0.93 mL, 0.018 mol), distillation (134 °C, 0.06 mbar) gave pure 1 as a colorless oil (47.24 g, 91 %).

bis(2-methylbutyl) maleate 2

From maleic acid (21.19 g, 0.18 mol), 2-ethylbutanol (37.3 g, 0.36 mol) and H_2SO_4 98 % (0.93 mL, 0.018 mol), distillation (134 °C, 0.06 mbar) gave pure 2 as a colorless oil (47.24 g, 91 %).

Diisobutyl maleate 3

From maleic acid (20.74 g, 0.18 mol), 2-methylpropan-1-ol (26.47 g, 0.36 mol) and H_2SO_4 98 % (0.91 mL, 0.02 mol), distillation (100 °C, 0.2 mbar) gave pure 3 as a colorless oil (38.72 g, 95 %).

General synthesis of AOT derivatives

To a solution of the corresponding maleate in EtOH (100 mL) was added $NaHSO_3$ in distilled water (100 mL). The mixture was then heated at 100 °C for 16 h under Ar. After cooling at room temperature, the mixture was dried under vacuum affording a white powder which was washed with ketone in a Soxhlet to remove the excess of $NaHSO_3$. Ketone was then evaporated under vacuum to give the corresponding AOT as a white powder

Sodium 1,4-bis(2-ethylbutoxy)-1,4-dioxobutane-2-sulfonate (AOT1)

From bis(2-ethylbutyl) maleate (20 g, 0.07 mol) with $NaHSO_3$ (14.7 g, 0.14 mol). **AOT1** is purified as a white powder (25.48 g, 93%).

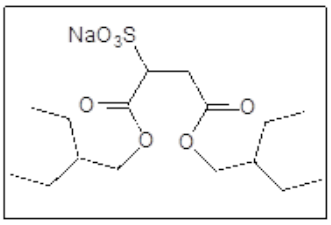


Figure S6: Structure AOT1.

^{1}H NMR (400 MHz, D_2O, 298K): δ 0.89-093 (m, 12H, (CH_3CH$_2$)$_2$CHCH$_2$O), 1.33-1.44 (m, 8H, (CH$_3$CH_2)$_2$CHCH$_2$O), 1.48-1.61 (m, 2H, (CH$_3$)$_2$CHCH$_2$O), 3,09 (dd, 1H, ABX spin system, ROOC-CH(SO$_3^-$)-CH_2-COOR, ^2J (AB) = 17.4 Hz, ^3J (BX)= 3.9 Hz), 3.19 (dd, 1H, ABX spin system, ROOC-CH(SO$_3^-$)-CH_2-COOR, ^2J (AB) = 17.4 Hz, ^3J (AX)= 11.5 Hz), 4.02 (dd, 1H, ABX spin system, OCH_2CH(CH$_3$)$_2$, ^2J (AB) = 10.9 Hz, ^3J (BX)= 5.8 Hz), 4.07 (dd, 1H, ABX spin system, OCH_2CH(CH$_3$)$_2$, ^2J (AB) = 10.9 Hz, ^3J (AX)= 5.9 Hz), 4.10-4.20 (m, 3H, OCH_2CH(CH$_2$CH$_3$)$_2$ and ROOC-CH(SO$_3^-$)-CH$_2$-COOR) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, D_2O, 298K): δ 10.47, 10.49 and 10,61 (3s, OCH$_2$CH(CH$_2$CH_3)$_2$), 22.81,22.82, 22.86 and 22.90 (4s, OCH$_2$CH(CH_2CH$_3$)$_2$), 33.36 (s, ROOC-CH(SO$_3^-$)-CH_2-COOR), 39.92 and 39.95 (2s, OCH$_2$CH(CH$_3$)$_2$), 61.93 (s, ROOC-CH(SO$_3^-$)-CH$_2$-COOR), 67.30 and 68.13 (2s, OCH_2CH(CH$_3$)$_2$, 168.69 and 171.86 (2s, C(O)OR) ppm. HRMS (ESI-MS) calcd for

$C_{16}H_{29}O_7S$ $[M]^-$ 365.1639, found 365.1639.

Sodium 1,4-bis(2-methylbutoxy)-1,4-dioxobutane-2-sulfonate (AOT2)

From bis(2-methylbutyl) maleate (20 g, 0.08 mol) with $NaHSO_3$ (16.3 g, 0.16 mol). **AOT2** is purified as a white powder (20.79 g, 82%).

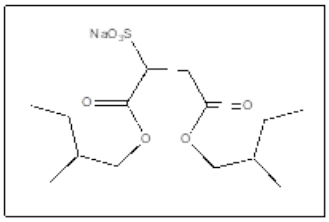


Figure S7: Structure AOT2.

^{1}H NMR (400 MHz, D_2O, 298K): δ 0.90-0.97 (m, 12H, (CH_3CH_2)(CH_3)$CHCH_2O$), 1.15-1.29 (m, 2H, (CH_3CH_2)(CH_3)$CHCH_2O$), 1.39-1.53 (m, 2H, (CH_3CH_2)(CH_3)$CHCH_2O$), 1.67-1.84 (m, 2H, (CH_3)(CH_2CH_3)$CHCH_2O$), 3.12 (dd, 1H, ABX spin system, ROOC-CH(SO_3^-)-CH_2-COOR, ^2J (AB) = 17.3 Hz, ^3J (BX)= 4.1 Hz), 3.21 (dd, 1H, ABX spin system, ROOC-CH(SO_3^-)-CH_2-COOR, ^2J (AB) = 17.3 Hz, ^3J (AX)= 11.5 Hz), 3.91-4.15 (m, 4H, OCH_2CH(CH_3)(CH_2CH_3)), 4.23 (dd, 1H, ABX spin system, ROOC-CH(SO_3^-)-CH_2-COOR, ^3J(AX) = 11.3 Hz, ^3J(BX) = 4.1 Hz) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, D_2O, 298K): δ 10.67, 10.71 and 10,76 (3s, OCH_2CH(CH_3)(CH_2CH_3)), 15.70 and 10.77 (2s, OCH_2CH(CH_3)(CH_2CH_3)), 25.45, 25.50, 25.53 and 22.56 (4s, OCH_2CH(CH_3)(CH_2CH_3)), 33.41 (s, ROOC-CH(SO_3^-)-CH_2-COOR), 33.66 and 33.71 (2s, OCH_2CH(CH_3)(CH_2CH_3)), 61.91 (s, ROOC-CH(SO_3^-)-CH_2-COOR), 70.15 and 70.93 (2s, OCH_2CH$(CH_3)_2$, 168.84 and 172.07 (2s, C(O)OR) ppm. HRMS (ESI-) calcd for $C_{14}H_{25}O_7S$ $[M]^-$ 337.1326, found 337.1323.

Sodium 1,4-diisobutoxy-1,4-dioxobutane-2-sulfonate (AOT3)

$NaHSO_3$ (18.8g, 0.18 mol). **AOT3** is purified as a white powder (28.55g, 95%).

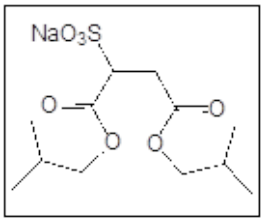


Figure S8: Structure AOT3.

^{1}H NMR (400 MHz, D_2O, 298K): δ 0.94 (d, 6H, $(CH_3)_2CHCH_2O$, ^{3}J = 6.8 Hz), 0.96 (d, 6H, $(CH_3)_2CHCH_2O$, ^{3}J = 6.8 Hz), 1.90-2.06 (m, 2H, $(CH_3)_2CHCH_2O$), 3,13 (dd, 1H, ABX spin system, ROOC-CH(SO_3^-)-CH_2-COOR, ^{2}J (AB) = 17.3 Hz, ^{3}J (BX)= 4.4 Hz), 3.23 (dd, 1H, ABX spin system, ROOC-CH(SO_3^-)-CH_2-COOR, ^{2}J (AB) = 17.3 Hz, ^{3}J (AX)= 11.1 Hz), 3.95 (d, 2H, $OCH_2CH(CH_3)_2$, ^{3}J = 6.5 Hz), 4.02 (dd, 1H, ABX spin system, $OCH_2CH(CH_3)_2$, ^{2}J (AB) = 10.5 Hz, ^{3}J (BX)= 6.4 Hz), 4.07 (dd, 1H, ABX spin system, $OCH_2CH(CH_3)_2$, ^{2}J (AB) = 10.5 Hz, ^{3}J (AX)= 6.6 Hz), 4.30 (dd, 1H, ABX spin system, ROOC-$CH(SO_3^-)$-CH_2-COOR, ^{3}J(AX) = 11.1 Hz, ^{3}J(BX) = 4.4 Hz) ppm. $^{13}C\{^{1}H\}$ NMR (100.6 MHz, D_2O, 298K): δ 18.19 (s, $OCH_2CH(CH_3)_2$), 27.14-27.21 (2s, $OCH_2CH(CH_3)_2$), 33.42 (s, ROOC-CH(SO_3^-)-CH_2-COOR), 61.90 (s, ROOC-$CH(SO_3^-)$-CH_2-COOR), 72.17 and 72.83 (2s, $OCH_2CH(CH_3)_2$), 169.18 and 172.64 (2s, C(O)OR) ppm. HRMS (ESI^-) calcd for $C_{12}H_{21}O_7S$ $[M]^-$ 309.1013, found 309.1013.

References

(S1) Nave, S.; Eastoe, J.; Penfold, J. What is so special about Aerosol-OT? 1. Aqueous systems. *Langmuir* **2000**, *16*, 8733–8740.

(S2) Nave, S.; Paul, A.; Eastoe, J.; Pitt, A. R.; Heenan, R. K. What is so special about Aerosol-OT? Part IV. Phenyl-tipped surfactants. *Langmuir* **2005**, *21*, 10021–10027.