Electronic Supplementary Material (ESI) for Green Chemistry.

# Electronic Supplementary Information

## A New Strategy to Dissolve Long-Chain Surfactants in Water at Low Temperatures

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## S1. Experimental Section

### S1.1 Chemicals

Sodium octadecyl sulfate (NaS18, Alfa Aesar, >98 %, LOT: 10176541), stearic acid (C18, ≥98.5 %, Sigma), choline chloride (ChCl, Sigma, >98 %) and Sudan Black B (Sigma) were used as received. Sodium hydroxide solution (NaOH) was purchased from Merck (TitriPur). Choline hydroxide (ChOH) was provided as ~46.5 wt% solution in water by TAMINCO. $ChEO_n$ (n = 1-3) was synthesized at BASF as described in Section S1.2 and obtained as chloride salts in aqueous solutions. Biskin® was purchased as pure vegetable fat in the supermarket.

The main component of each $ChEO_nCl$ stock solution was determined by mass spectroscopy, while its concentration (as moles of quaternary ammonium ions in $ChEO_nCl$ per gram of stock solution) was determined by $^1$H-NMR experiments using an internal standard. Solid contents and $ChEO_nCl$ concentrations of the different samples are summarised in Table S1.

| Substance | c [mol/g solution] | wt% $ChEO_nCl$ | wt% total |
|---|---|---|---|
| **$ChEO_1Cl$** | 0.00204 | 37.5 | 40.0 |
| **$ChEO_2Cl$** | 0.00152 | 34.6 | 40.0 |
| **$ChEO_3Cl$** | 0.00119 | 32.3 | 39.0 |

**Table S1:** Concentrations of $ChEO_nCl$ (in mol per gram stock solution and wt%) and total solid contents determined for the different aqueous stock solutions of $ChEO_nCl$ used in this work.

Comparing the amount of total solid content to the weight fraction of $ChEO_nCl$ shows that the solutions were not completely pure. The main impurities in the products were the corresponding non-methylated (and thus uncharged) amines (i.e. DMAEE, (DMAEE)$EO_1$) and (DMAEE)$EO_2$) in the case of $ChEO_1Cl$, $ChEO_2Cl$ and $ChEO_3Cl$, respectively; cf. Section S1.2 for molecular structures of the amines and corresponding quaternised choline derivatives). The content of residual methylchloride (used for quaternisation) was found to be <0.02 % in all products. In the following experiments and discussions, the potential influence of any of these impurities on the solubility and other physicochemical properties of alkyl sulfate and alkyl carboxylate surfactants with $ChEO_n^+$ counterions was neglected.

$ChEO_nOH$ stock solutions were obtained from $ChEO_nCl$ by ion exchange using the strong basic ion exchanger III (hydroxide form) from Merck. The resin was first rinsed with 2 M NaOH to ensure complete loading and afterwards with Millipore water until the effluent had a pH around 7. Then, a 0.1 M $ChEO_nCl$ solution was slowly passed through the column at ambient temperature. The amount of used $ChEO_nCl$ was around 25 % of the maximum exchange capacity. Near-complete exchange of $Cl^-$ against $OH^-$ was verified by adding 1 M silver nitrate ($AgNO_3$) to samples of the $ChEO_nOH$ solution after acidification with nitric acid. It should be noted that this ion exchange procedure has most likely not removed the non-methylated amine impurities mentioned above, as these compounds will not interact strongly with the resin due to their lack of cationic charge.

## S1.2 $ChEO_n$ Synthesis

Figure S1 shows the general reaction schemes for the synthesis of the different choline alkoxylates.

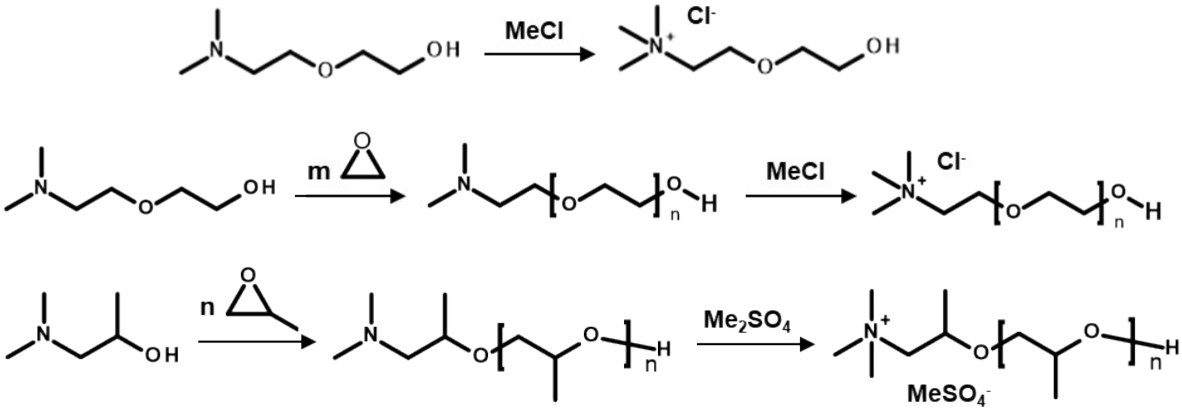

**Figure S1:** Reaction schemes for the synthesis of $ChEO_1Cl$ (top) and $ChEO_nCl$ (middle, with n = 2 or 3 and n = m + 1) from 2-[2-(dimethylamino)ethoxy]-ethanol (DMAEE), and $MeChPO_nMeSO_4$ from 1-(dimethylamino)-2-propanol (bottom, with $n_{average} \approx 5$).

The chloride salt of choline carrying one EO unit ($ChEO_1Cl$) was obtained by quaternisation of 2-[2-(dimethylamino)ethoxy]-ethanol (DMAEE) by reaction with methylchloride (MeCl). For products with higher degrees of ethoxylation ($ChEO_nCl$), DMAEE was first reacted with ethylene oxide to yield a mixture of (uncharged) compounds with different numbers of EO units (i.e. $(DMAEE)EO_n$, with m = 0-2). This mixture was characterized by NMR spectroscopy and subsequently separated into individual fractions by distillation. Finally, the fractions with m = 1 and 2 were quaternised to obtain $ChEO_2Cl$ and $ChEO_3Cl$. Propoxylates of methylcholine were prepared by reaction of 1-(dimethylamino)-2-propanol with propylene oxide, followed by quaternisation with dimethylsulfate ($Me_2SO_4$) without prior separation of adducts with different degrees of propoxylation. The obtained product thus was a mixture of methylcholine carrying different numbers of PO unit, with an average n of ca. 5. Detailed synthesis procedures and analytical data for the different products ($^1$H-NMR, $^{13}$C-NMR and ES-MS) are described below.

### S1.2.1 ChEO$_1$Cl

2-[2-(Dimethylamino)ethoxy]-ethanol (DMAEE) (347.3 g, 2.6 mol) and 700 g water were placed into a 1.4 L autoclave under nitrogen atmosphere. Then, methylchloride (126.2 g, 2.5 mol) was added at 85 °C over a period of 40 min, reaching a maximum pressure of 5 bar. To complete the reaction, the mixture was aged for 4 h at 85 °C at a pressure of 4 bar. Finally, the temperature was decreased to 25 °C and ChEO$_1$Cl (442.9 g) was obtained as aqueous solution.

*ChEO$_1$Cl:*

**$^1$H-NMR** (400 MHz, $D_2O$, 25 °C, TMS): δ = 3.18 (s, 9H; -N(C**H$_3$**)$_3$), 3.59 (m, 2H, -O-C**H$_2$**), 3.63 (t, 2H, -O-C**H$_2$**-OH), 3.72 (m, 2H, -O-C**H$_2$**), 3.96 (dq, 2H, -N-C**H$_2$**CH$_2$).

**$^{13}$C-NMR** (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 53.93 (N(**C**H$_3$)$_3$), 60.37 (**C**H$_2$OH), 64.36 (N(CH$_3$)$_3$**C**H$_2$), 65.36 (N(CH$_3$)$_3$CH$_2$**C**H$_2$), 71.76 (**C**H$_2$CH$_2$OH).

**ES-MS (Agilent):** m/z (+p): 148.13 [M$^+$].

### S1.2.2 ChEO$_n$Cl

2-[2-(Dimethylamino)ethoxy]-ethanol (DMAEE) (554.5 g, 4.2 mol) was placed into a 5 L autoclave. After purging with nitrogen, the pressure was adjusted to 1 bar and the mixture was homogenised at 120 °C for 1 h. Then, ethylene oxide (550.6 g, 12.5 mol) was added at 120 °C over a period of 30 min, reaching a maximum pressure of 5 bar. To complete the reaction, the mixture was aged for 1 h at 120 °C at a pressure of 5 bar. Finally, the temperature was decreased to 40 °C and volatile compounds were removed in vacuum at 80 °C. This gave a raw product of uncharged adducts (i.e. (DMAEE)EO$_m$) carrying different numbers of ethylene oxide units in a certain distribution (1087.2 g).

*(DMAEE)EO$_m$:*

**$^1$H-NMR** (400 MHz, $D_2O$, 25 °C, TMS): δ = 3.19 (s, 9H; -N(C**H$_3$**)$_3$), 3.60 (m, 2H, -O-C**H$_2$**), 3.63 (t, 2H, -O-C**H$_2$**-OH), 3.72 (m, 14H, -O-C**H$_2$**), 3.99 (dq, 2H, -N-C**H$_2$**CH$_2$).

**$^{13}$C-NMR** (300 MHz, $D_2O$, 25 °C, TMS): δ = 53.93 (N(**C**H$_3$)$_3$), 60.39 (**C**H$_2$OH), 64.35 (N(CH$_3$)$_3$**C**H$_2$), 65.32 (N(CH$_3$)$_3$CH$_2$**C**H$_2$), 69.50-69.68 (O**C**H$_2$**C**H$_2$O), 71.72 (**C**H$_2$CH$_2$OH).

In order to separate the compounds with different degrees of ethoxylation, the raw product was fractionated by vacuum distillation at 0.001 mbar and a maximum temperature of 175 °C, yielding three fractions that were subsequently analyzed by $^1$H-NMR spectroscopy.

*Fraction 1 ((DMAEE)EO$_0$):* **$^1$H-NMR** (400 MHz, $D_2O$, 25 °C, TMS): δ = 2.27 (s, 6H; -N(C$\mathbf{H_3}$)$_\mathbf{2}$), 2.52 (m, 2H, -O-C$\mathbf{H_2}$), 3.65 (t, 4H, -O-C$\mathbf{H_2}$), 3.73 (dq, 2H, -N-C$\mathbf{H_2}$CH$_2$).

*Fraction 2 ((DMAEE)EO$_1$):* **$^1$H-NMR** (400 MHz, $D_2O$, 25 °C, TMS): δ = 2.27 (s, 6H; -N(C$\mathbf{H_3}$)$_\mathbf{2}$), 2.52 (m, 2H, -O-C$\mathbf{H_2}$), 3.65 (t, 8H, -O-C$\mathbf{H_2}$), 3.73 (dq, 2H, -N-C$\mathbf{H_2}$CH$_2$).

*Fraction 3 ((DMAEE)EO$_2$):* **$^1$H-NMR** (400 MHz, $D_2O$, 25 °C, TMS): δ = 2.27 (s, 6H; -N(C$\mathbf{H_3}$)$_\mathbf{2}$), 2.52 (m, 2H, -O-C$\mathbf{H_2}$), 3.65 (t, 12H, -O-C$\mathbf{H_2}$), 3.73 (dq, 2H, -N-C$\mathbf{H_2}$CH$_2$).

Fractions 2 and 3 (i.e. the DMAEE adducts carrying additional EO units) were quaternised as described below to obtain ChEO$_2$Cl and ChEO$_3$Cl.

Fraction 2 (278.3 g, 1.6 mol) and 489.5 g water were placed into a 1.4 L autoclave under nitrogen atmosphere. Then, methylchloride (75.7 g, 1.5 mol) was added at 85 °C over a period of 40 min, reaching a maximum pressure of 5 bar. To complete the reaction, the mixture was aged for 4 h at 85 °C at a pressure of 4 bar. Finally, the temperature was decreased to 25 °C and ChEO$_2$Cl (258.2 g) was obtained as aqueous solution.

*ChEO$_2$Cl:* **$^1$H-NMR** (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 3.19 (s, 9H; -N(C$\mathbf{H_3}$)$_\mathbf{3}$), 3.62 (m, 2H, -O-C$\mathbf{H_2}$), 3.66 (t, 2H, -O-C$\mathbf{H_2}$-OH), 3.74 (m, 6H, -O-C$\mathbf{H_2}$), 4.08 (dq, 2H, -N-C$\mathbf{H_2}$CH$_2$).

**$^{13}$C-NMR** (300 MHz, $D_2O$, 25 °C, TMS): δ = 53.93 (N($\mathbf{C}$H$_3$)$_3$), 60.37 ($\mathbf{C}$H$_2$OH), 64.35 (N(CH$_3$)$_3$$\mathbf{C}$H$_2$), 65.32 (N(CH$_3$)$_3$CH$_2$$\mathbf{C}$H$_2$), 69.42-69.65 (O$\mathbf{C}$H$_2$$\mathbf{C}$H$_2$O), 71.71 ($\mathbf{C}$H$_2$CH$_2$OH).

**ES-MS (Agilent):** m/z (+p): 192.16 [M$^+$].

Fraction 3 (283.5 g, 1.28 mol) and 489.5 g water were placed into a 1.4 L autoclave under nitrogen atmosphere. Then, methylchloride (61.44 g, 1.21 mol) was added at 85 °C over a period of 40 min, reaching a maximum pressure of 5 bar. To complete the reaction, the mixture was aged for 4 h at 85 °C at a pressure of 4 bar. Finally, the temperature was decreased to 25 °C and ChEO$_3$Cl (302.48 g) was obtained as aqueous solution.

*ChEO$_3$Cl:* **$^1$H-NMR** (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 3.19 (s, 9H; -N(C$\mathbf{H_3}$)$_\mathbf{3}$), 3.62 (m, 2H, -O-C$\mathbf{H_2}$), 3.66 (t, 2H, -O-C$\mathbf{H_2}$-OH), 3.74 (m, 10H, -O-C$\mathbf{H_2}$), 4.08 (dq, 2H, -N-C$\mathbf{H_2}$CH$_2$).

**$^{13}$C-NMR** (300 MHz, $D_2O$, 25 °C, TMS): δ C= 53.93 (N(**C**$H_3$)$_3$), 60.37 (**C**$H_2$OH), 64.35 (N($CH_3$)$_3$**C**$H_2$), 65.32 (N($CH_3$)$_3$$CH_2$**C**$H_2$), 69.42-69.65 (O**C**$H_2$**C**$H_2$O), 71.71 (**C**$H_2$$CH_2$OH).

**ES-MS (Agilent):** m/z (+p): 236.32 [$M^+$].

### S1.2.3 MeChPO$_5$MeSO$_4$

1-(Dimethylamino)-2-propanol (206 g, 2.0 mol) and 1.6 g potassium tert-butoxide (0.014 mol, 0.7 mol%) were placed into a 2 L autoclave. After purging with nitrogen, the pressure was adjusted to 2 bar and the mixture was heated to 130 °C. Then, propylene oxide (581.0 g, 10.0 mol) was added at 130 °C over a period of six hours. To complete the reaction, the mixture was aged for 6 h at 130 °C at a pressure of 5 bar. Finally, the temperature was decreased to 80 °C and volatile compounds were removed in vacuum at 80 °C. This gave a raw product (785 g) of adducts carrying different numbers of propylene oxide units in a certain distribution; on average, five propylene oxide units were added.

200 g of the obtained product (0.51 mol) was placed in a round bottom flask under inert gas atmosphere and heated to 75 °C. Subsequently, 64.1 g dimethylsulfate (0.51 mol) were added over a period of one hour. Then the reaction mixture was kept at 75 °C for two hours of post-reaction time. Finally, the pH was adjusted to 8.6 using 50 % sodium hydroxide solution. The solid content of the product was determined to be 94 %.

*MeChPO$_5$MeSO$_4$:* **$^1$H-NMR** (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.32-0.86 (m, 18H, -O-CH-C**$H_3$**), 3.27 (s, 9H, -N(C**$H_3$**)$_3$), 3.79-3.38 (m, 12H; -O-C**$H_2$**,-O-C**H**-$CH_3$), 4.23-3.69 (m, 5 H, CH2-C**H**-CH3-).

## S1.3 Preparation of Alkyl Sulfate Surfactant Solutions

ChS18 was prepared by ion exchange according to a procedure described elsewhere.[S1] A strong acidic ion exchanger (Merck, Type I) was first rinsed with 1 M HCl (Merck) and afterwards with Millipore water until the effluent had a pH around 7. The ion exchange resin was loaded with a 1 M aqueous ChCl solution (the used amount of choline was about 8 times the maximum exchange capacity). To ensure complete loading, the column was treated with 100 mL of 5 wt% ChOH solution in a final step. Afterwards, the loaded column was heated above the Krafft point of NaS18 (65 °C) and a 0.025 M solution of NaS18 was slowly passed over the ion exchanger. The amount of used surfactant was about 25% of the maximum exchange capacity. After removal of most water by freeze-drying, the solid surfactant was further dried at 0.01 bar in a desiccator for 1-2 weeks and was finally obtained as a white powder. ChEO$_n$S18 surfactants were prepared in the same way, with the only difference that the ion exchanger was loaded with a ChEO$_n$OH solution at around 3 times the maximum capacity of the ion exchanger (note that this procedure has likely removed most of the non-methylated impurities described in Section S1.1, due to their arguably much lower affinitiy to interact with the ion exchange resin). The surfactants were obtained as white and slightly sticky solids.

The purity of the products was checked by $^1$H-NMR and $^{13}$C-NMR in $CDCl_3$ using a Bruker Advance 300 spectrometer at 300 MHz and tetramethylsilane as internal standard, as well as electro-spray mass spectroscopy (ES-MS), which was carried out on an Agilent Q-TOF 6540 UHD instrument. The analytical results are given below.

*ChS18:*

**$^1$H-NMR** (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.87 (t, 3H; $CH_2C\mathbf{H_3}$), 1.25 (m, 30H; $C\mathbf{H_2}C\mathbf{H_2}CH_3$), 1.64 (quin, 2H; $C\mathbf{H_2}CH_2SO_4^-$), 3.31 (s, 9H; $N(C\mathbf{H_3})_3$), 3.65 (t, 2H; $N(CH_3)_3C\mathbf{H_2}$), 3.99 (t, 2H; $C\mathbf{H_2}SO_4^-$), 4.08 (m, 2H; $C\mathbf{H_2}OH$).

**$^{13}$C-NMR** (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.16 ($CH_2\mathbf{C}H_3$), 22.72 ($\mathbf{C}H_2CH_3$), 25.84 ($\mathbf{C}H_2CH_2CH_3$), 29.41-29.75 ($\mathbf{C}H_2CH_2$), 31.95 ($\mathbf{C}H_2CH_2SO_4^-$), 54.48 ($N(\mathbf{C}H_3)_3$), 56.44 ($\mathbf{C}H_2OH$), 67.91 ($\mathbf{C}H_2SO_4^-$), 68.56 ($N(CH_3)_3\mathbf{C}H_2$).

**ES-MS (Agilent):** m/z (+p): 104.11 [$M^+$], 148.13, 192.16; (p-): 349.24 [$M^-$], 699.49 [$(2M^- + H^+)$].

*$ChEO_2S18$:*

**$^1$H-NMR** (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.87 (t, 3H; $CH_2C\mathbf{H_3}$), 1.25 (m, 30H; $C\mathbf{H_2}C\mathbf{H_2}CH_3$), 1.65 (quin, 2H; $C\mathbf{H_2}CH_2SO_4^-$), 3.33 (s, 9H; $N(C\mathbf{H_3})_3$), 3.58-3.75 (m, 10H; $N(CH_3)_3C\mathbf{H_2}$, $C\mathbf{H_2}OH$ and $C\mathbf{H_2}C\mathbf{H_2}OC\mathbf{H_2}$), 4.00 (m, 4H; $C\mathbf{H_2}SO_4^-$ and $N(CH_3)_3CH_2C\mathbf{H_2}$).

**$^{13}$C-NMR** (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.16 ($CH_2\mathbf{C}H_3$), 22.72 ($\mathbf{C}H_2CH_3$), 25.87 ($\mathbf{C}H_2CH_2CH_3$), 29.39-29.74 ($\mathbf{C}H_2CH_2$), 31.95 ($\mathbf{C}H_2CH_2SO_4^-$), 54.50 ($N(\mathbf{C}H_3)_3$), 61.43 ($\mathbf{C}H_2OH$), 65.29 ($N(CH_3)_3\mathbf{C}H_2$), 65.81 ($N(CH_3)_3CH_2\mathbf{C}H_2$), 68.23 ($\mathbf{C}H_2SO_4^-$), 70.27-70.32 ($O\mathbf{C}H_2\mathbf{C}H_2O$), 72.38 ($\mathbf{C}H_2CH_2OH$).

**ES-MS (Agilent):** m/z (+p): 192.16 [$M^+$]; (p-): 349.24 [$M^-$].

*$ChEO_3S18$:*

**$^1$H-NMR** (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.87 (t, 3H; $CH_2C\mathbf{H_3}$), 1.24 (m, 30H; $C\mathbf{H_2}C\mathbf{H_2}CH_3$), 1.65 (quin, 2H; $C\mathbf{H_2}CH_2SO_4^-$), 3.34 (s, 9H; $N(C\mathbf{H_3})_3$), 3.56-3.76 (m, 14H; $N(CH_3)_3C\mathbf{H_2}$, $C\mathbf{H_2}OH$ and $C\mathbf{H_2}C\mathbf{H_2}OC\mathbf{H_2}$), 4.00 (m, 4H; $C\mathbf{H_2}SO_4^-$ and $N(CH_3)_3CH_2C\mathbf{H_2}$).

**$^{13}$C-NMR** (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.16 ($CH_2\mathbf{C}H_3$), 22.72 ($\mathbf{C}H_2CH_3$), 25.87 ($\mathbf{C}H_2CH_2CH_3$), 29.39-29.74 ($\mathbf{C}H_2CH_2$), 31.95 ($\mathbf{C}H_2CH_2SO_4^-$), 54.50 ($N(\mathbf{C}H_3)_3$), 61.37 ($\mathbf{C}H_2OH$), 65.19 ($N(CH_3)_3\mathbf{C}H_2$), 65.73 ($N(CH_3)_3CH_2\mathbf{C}H_2$), 68.20 ($\mathbf{C}H_2SO_4^-$), 69.97-70.49 ($O\mathbf{C}H_2\mathbf{C}H_2O$), 72.39 ($\mathbf{C}H_2CH_2OH$).

**ES-MS (Agilent):** m/z (+p): 236.19 [$M^+$]; (p-): 349.24 [$M^-$].

Mixtures of NaS18 and ChCl or $ChEO_nCl$ (for $T_{Kr}$ measurements as a function of added choline salts) were prepared by combining corresponding stock solutions at the desired ratios and heating until a clear and homogeneous solution was obtained, which then was frozen at -20 °C overnight and used for analysis on the next day.

## S1.4 Preparation of Alkyl Carboxylate Surfactant Solutions

Aqueous solutions of carboxylate surfactants with different counterions (i.e. NaC18, ChC18, $ChEO_2C18$ and $ChEO_3C18$) were prepared by mixing defined amounts of stearic acid, stock solution of base (NaOH, ChOH or $ChEO_nOH$) and water in a vial. In the case of $ChEO_nOH$, the actual active matter (as given in Table S1) was taken into account; however, non-methylated amines (described as impurities in Section S1.1) were likely still present in solution after the neutralisation reaction. The mixtures were heated until a clear and homogeneous solution was obtained. Then, the samples were frozen at -20 °C overnight and used for analysis on the next day.

## S1.5 Determination of Krafft Temperatures

Krafft points of aqueous solutions containing S18 surfactant were obtained by turbidity measurements with a custom-designed automated setup that was equipped with a computer-controlled thermostat, a light-emitting diode (LED) and a light-dependent resistor (LDR). Turbidity was detected by recording the transmission of light through the samples while increasing the temperature at a constant rate. All measurements were carried out at a surfactant concentration of 1 wt% and a heating rate of 1.5 °C/h, at least in duplicate determinations. $T_{Kr}$ was taken as the average temperature (with typical maximum standard deviations of ± 1 °C) where the transmission reached its maximum value on an absolute level. To validate the obtained results, 1 wt% solutions of NaS12, NaS16 and NaS18 were regularly measured as references with known Krafft points. Values determined for $T_{Kr}$ of these sodium alkyl sulfate surfactants were in very good agreement (typically ± 0.5 °C) with the literature.[S1] For aqueous solutions containing C18 surfactant, Krafft temperatures were determined by heating in a water bath at a rate of around 0.2 °C/min, at least in three independent experiments. The samples were visually inspected during the measurement and $T_{Kr}$ was taken as the average temperature (with typical maximum standard deviations of ± 2 °C), above which the surfactant solution was optically as clear as water.

## S1.6 Surface Tension Measurements

Surface tensions (γ) of the surfactant solutions were determined on a Krüss tensiometer (model K100 MK2) using the Du Noüy method with a platinum-iridium ring. The instrument was equipped with a dosing system (Metrohm Liquino 711), allowing for the surface tension to be measured automatically as a function of the surfactant concentration. The temperature was monitored and kept constant at (25 ± 0.5) and (40 ± 0.5) °C, respectively. The obtained data were corrected according to the procedure developed by Harkins and Jordan.[S2] The resulting concentration-dependent surface tension curves are shown in Figure S2. Each γ = f(lnc) profile was measured at least in duplicate, giving the shown average values with maximum relative standard deviations of individual surface tension data points as low as <1 %.

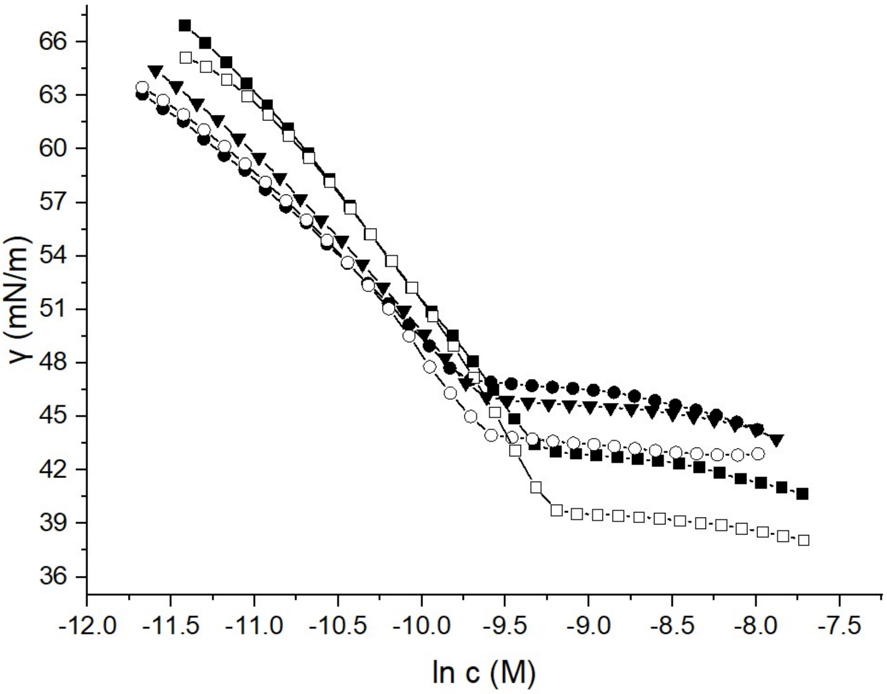

**Figure S2:** Plots of the surface tension (mean value of at least two independent determinations with relative deviations of <1 %) as a function of concentration for S18 surfactants. (■) ChS18 at 25 °C, (□) ChS18 at 40 °C, (▼) $ChEO_2S18$ at 25 °C, (●) $ChEO_3S18$ at 25 °C, (○) $ChEO_3S18$ at 40 °C.

The cmc was determined from the intersection of fits to the two linear parts of the curve, while the surface excess concentration (Γ) was derived from the slope of the γ = f(lnc) plot at concentrations lower than the cmc according to:[S3]

$$\Gamma = -\frac{d\gamma}{2RTd\ln c}$$

From Γ, the area per molecule (A) at the surface is can be obtained via the following equation (where N is Avogadro's number):[S3]

$$A = \frac{10^{16}}{\Gamma N}$$

## S1.7 Laundry Detergency Tests

Washing tests were performed with a custom-built apparatus as shown in Figure S3, in which 15 sample vessels consisting of stainless steel are rotated at 40 rpm in a tempered water bath. Each vessel has a volume of 100 mL and was filled with 50 mL of the washing formulation to be investigated. Five stainless steel balls were added to the solution in each vessel to account for the mechanical forces present in the drum of a washing machine filled with clothes. Finally, one stripe of 2 x 8 $cm^2$ of soiled fabric (ca. 0.27 g) was put into each vessel (approximate mass ratio of soiled fabric to washing formulation ≈ 1:185) and washed for 30 min at a temperature of 25 °C.

**Figure S3:** Photographs of the custom-designed washing apparatus used for detergency tests.

The used cotton textile was purchased from swissatest and soiled by dipping (for several seconds) into a solution of Biskin® grease in chloroform (1:5 w/w), which was coloured with 0.5 wt% Sudan Black B. The stained rags were dried overnight at ambient conditions and characterised with respect to optical remission using a colourimeter (Elrepho SE 071 from Lorentzen & Wettre). After the washing process, the cotton stripes were again dried overnight and analysed with the colourimeter on the next day. On each stripe, ten different positions were measured. The resulting average values are given as the difference (ΔE) in optical remission before and after the washing process, calculated as follows:

$$\Delta E = \sqrt{L^2 + a^2 + b^2}$$

where a, b and L are the coordinates of a colour system, with a and b characterising the colourfulness and L representing the brightness. The higher the ΔE value, the larger is the difference in colour (which mainly comes from the used dye) and, assuming that dye and grease are removed in equal amounts, the better the detergency performance of the studied surfactant solution. To confirm the colourimetric results by an independent method, the masses of the unsoiled, soiled and washed cotton strips were also determined (with higher mass removal upon washing indicating better detergency).

### S1.8 Cytotoxicity and Biodegradability Tests

The cytotoxicity of the newly synthesised counterions was determined by a PrestoBlue assay using human skin keratinocytes (HaCaT cells). The viability of the cells was determined by fluorescence measurements. To that end, the cells were seeded in 96-well plates and each well was incubated for 24 h with 100 µL of the solution to be investigated (test compounds solubilised in a phosphate-buffered saline (PBS) at different concentrations). Untreated cells were used as negative control. After incubation, the sample solutions were removed and 100 µL of the PrestoBlue dyeing solution (1:10 PrestoBlue in PBS buffer containing 1 g/L glucose) were added to each well, followed by incubation for another hour. The sample fluorescence was then detected by a microplate reader from Tecan with an excitation wavelength of 532 nm and an emission wavelength of 600 nm. In this way, cell viabilities were determined at different concentrations of the test compounds (ChCl, $ChEO_1Cl$ and $ChEO_3Cl$) in three independent experiments, giving the average values shown in Figure 5a of the main text with typical standard deviations of <5 %.

Biodegradability was studied according to the OECD 301 F standard. Biodegradation of a substance was calculated from the ratio of the real biological and the theoretical oxygen consumption, which reflects the amount of oxygen required for complete oxidation of the compound, as calculated from its molecular structure. The real biological oxygen consumption was measured by a respirometer in triplicate determinations for each sample, which were averaged to obtain the mean values shown in Figure 5b of the main text. The observed maximum standard deviation was about 5 %. The samples were tested at a concentration of 0.1 wt%. Experiments were performed at 21 °C for 28 days in a medium specified by the OECD guidelines.

# S2. Supplementary Data and Discussions

## S2.1 Solubility Behaviour of Octadecyl Sulfate Surfactants

The Krafft point of surfactants is defined as the temperature at which the monomer solubility equals the cmc. Thus, the surfactant will dissolve well in water at temperatures $\geq T_{Kr}$ and will be poorly soluble at $T < T_{Kr}$. This strong temperature dependence and abrupt change in solubility is referred to as the “Krafft phenomenon”.[S4,S5] Usually, the Krafft point is determined by the interplay of two opposing thermodynamic factors: the free energy of the surfactant in a micellar solution and the corresponding value in the solid crystalline state. While the former seems to vary only slightly as a function of surfactant chain lengths and/or counterions, the energetics of the crystalline state can show drastic differences.[S6] For concentrations above the cmc of the surfactant, $T_{Kr}$ values usually increase only slightly over a broad concentration range. For simple alkali and alkaline-earth alkyl sulfates in aqueous solutions, this was proven by measuring temperature-dependent solubility curves.[S7-S9] In such systems, the amount of surfactant exceeding the solubility limit precipitates as hydrated crystals.[S4,S5] According to a common convention, the Krafft point is often taken as the clearing temperature of a 1 wt% aqueous surfactant solution.[S5]

During the work with NaS18, ChS18 and $ChEO_nS18$, it became obvious that only NaS18 behaves as it would be expected from the considerations made above. This is illustrated by the turbidity curves for aqueous 1 wt% solutions of these surfactants shown in Figure S4. Taking the maximum transmittance (corresponding to an optically clear solution) as the Krafft temperature yields $T_{Kr}$ values of 58 °C for NaS18, 49 °C for ChS18 and 35 °C for $ChEO_3S18$ (indicated by fine arrows in Figure S4). Indeed, the value for NaS18 is in perfect agreement with literature values.[S10] However, the actual difference in the macroscopic solubility behaviour for S18 with Ch and $ChEO_n$ counterions (as clearly observed in photographs of the solutions at 25 °C, see Figure 2 in the main text) is underrepresented in this case and only becomes fully evident when analysing the detailed evolution of turbidity as a function of temperature: the transmittance of the NaS18 sample is very low up to a few degrees before the maximum is reached and the subsequent steep increase towards optical clearness occurs within a few degrees, again in line with data reported in the literature.[S7-S10] By contrast, the temperature-dependent profile recorded for ChS18 exhibits a considerable increase in transmittance already soon after melting of the sample (at ca. 2 °C, indicated by the bold arrow in Figure S4), followed by a plateau of more or less constant transmittance up to ca. 25 °C. Subsequently, a second slow increase is observed up to ca. 50 °C, where the maximum is reached. In the case of $ChEO_3S18$, this behaviour is even more pronounced, with a rapid increase in transmittance directly after melting to a plateau along which only minor changes occur up to the absolute maximum at ca. 35 °C and beyond. This suggests that 1 wt% $ChEO_3S18$ solutions are more or less completely transparent soon after melting and do not turn significantly turbid upon heating, which is in good agreement with visual observations. The slight turbidity remaining after initial clearing (as well as the streaks observed for the 1 wt% solution of $ChEO_3S18$ at 25 °C, cf. Figure 2 in the main text) could also be caused by impurities, given that the synthesised $ChEO_n$ salts were not purified further before use (cf. Table S1). Transmittance curves measured in the same way for 1 wt% solutions of $ChEO_2S18$ were found to be nearly identical to the profile shown for ChEO$_3$S18 in Figure S4, with a $T_{Kr}$ value of 43 °C (as determined from maximum of the curve).

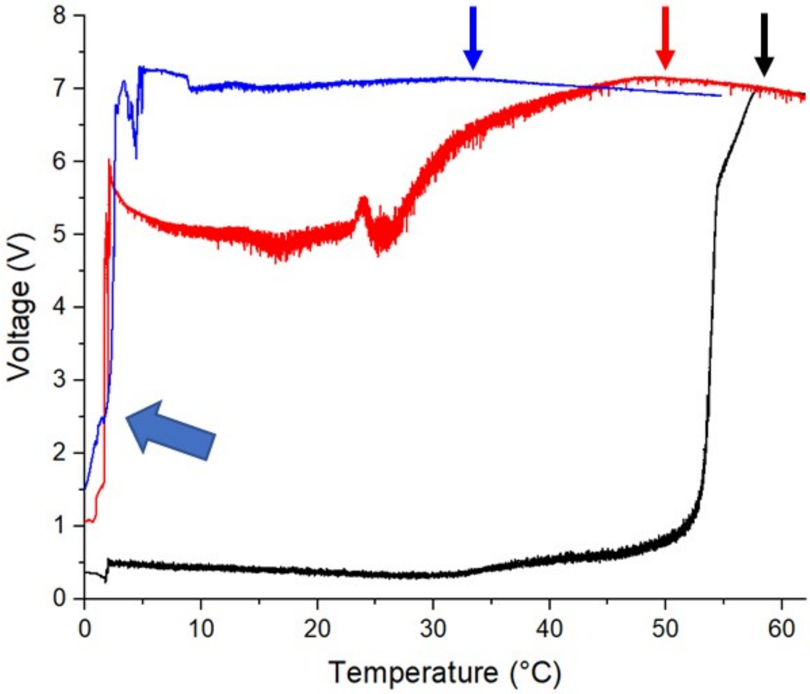

**Figure S4:** Comparison of the temperature-dependent optical transmission (given as detector voltage) of 1 wt% aqueous solutions of NaS18 (black), ChS18 (red) and ChEO$_3$S18 (blue), as determined by a custom-built apparatus. Fine arrows indicate the respective absolute maxima in transmittance, while the bold arrow highlights the initial increase after melting for ChS18 and ChEO$_3$S18.

The second slow increase in optical transmittance observed for ChS18 between ca. 30 and 50 °C is quite uncommon for anionic surfactants like alkyl sulfates. A possible explanation for this behaviour could be the formation of a liquid-crystalline phase at concentrations significantly higher than the cmc, potentially triggered by strong interactions between the headgroup of the surfactant and the choline counterion. In an extreme case, the ethanol moiety of choline could penetrate the micelle corona and act as a kind of co-surfactant. Indeed, alcohols used as co-surfactants are well-known to promote the formation of various liquid crystalline phases at low surfactant concentrations in aqueous solutions.[S11] In this regard, the Krafft point of a 1 wt% solution of ChS18 can be described as the temperature, at which the liquid-crystalline phase has completely vanished and only micelles are present. If the octadecyl chains exist in a fluid-like state within these liquid crystals, the transition from hydrated crystals to micellar aggregates must occur below room temperature, as otherwise it would not be possible to dissolve 0.02 wt% ChS18 (which is far above the cmc) in water at ambient conditions. This complicates the definition of Krafft points in these systems and shows that further studies are needed to understand the phase behaviour of (alkoxylated) choline alkyl sulfate surfactants.

## S2.2 Solubility Behaviour of Octadecyl Carboxylate Surfactants

The Krafft temperatures reported for $ChEO_2C18$ (25 °C) and $ChEO_3C18$ (29 °C) indicate that the number of EO units in the counterion do not strongly influence the solubility behaviour of alkyl carboxylate surfactants. However, the lack of significant differences and the slightly higher $T_{Kr}$ value found for $ChEO_3C18$ might also be related to the presence of a small amount of weak amine bases (5-10 mol%) in the $ChEO_3OH$ stock solution, as suggested by acid/base titration curves acquired for this sample (data not shown). This would mean that stoichiometric addition of $ChEO_3OH$ to solutions of stearic acid in practice leads to 90-95 % neutralization with the strong $ChEO_3OH$ base, while the remaining 5-10 % of fatty acid reacts with the weaker amine bases. This would result in certain fractions of protonated acid in the system which, as discussed below, could explain the observed increase in the Krafft temperature. In turn, no signs of weak amine bases were found by acid/base titrations on the stock solutions of $ChEO_2OH$.

The marked differences found for the solubility behaviour of NaC18 and $ChC18/ChEO_nC18$ in aqueous media can be rationalised based on the structure of the distinct counterions as well as the hydrolysis reaction of fatty acids in water. The latter can be written as follows:

$$Z^- + H_2O \rightleftarrows HZ + OH^-$$

where $Z^-$ represents the alkanoate anion and HZ the protonated fatty acid. It is well known that protonated fatty acid molecules and alkanoate ions can form acid-soap complexes and crystals of various stoichiometry according to[S12,S13]

$$nHZ + mZ^- + mM^+ \rightleftarrows M_mH_nZ_{m+n}$$

where $M^+$ is the counterion of the alkanoate anion. Both uncharged species, i.e. the fatty acid and the acid-soap complexes, are significantly less water-soluble than the charged alkanoate anion.[S12] Due to the weak acidity of the carboxylate group, the composition of dilute soap solutions is heavily dependent on the pH, which is determined by the molar ratio of base to C18. Accordingly, it was found that the addition of excess NaOH can considerably simplify the phase behaviour of NaC14 solutions in water at 25 °C,[S12] as the higher pH prevents the formation of protonated fatty acid and acid-soap complexes. Therefore, only neutral soap (NaC14) precipitates as soon as its solubility limit is reached with increasing concentration.

For the longer chains studied in the present work, the solubility of the sodium salts (NaC18) is likely to be considerably lower than that of NaC14 (ca. 6 mM at 25 °C)[S12]. This explains why a 1 wt% sample of NaC18 in water ($c \approx 33$ mM) turns into a solid white mass due to the large amount of neutral soap precipitate. Moreover, excess of base has no significant effect on the solubility of NaC18, since the higher pH will only prevent the formation of protonated fatty acid and acid-soap crystals, but the scarcely soluble neutral sodium soap can still be formed.

For mixtures of stearic acid with (ethoxylated) choline counterions, the situation changes drastically, as shown by the data reported in the main text. This can be explained by the bulky structures of the organic ions, which inhibit the formation of neutral sodium soaps at 25 °C by increasing the free energy of their solid crystalline state. Direct evidence supporting this notion is provided by the fact that an excess of $ChEO_n$ base is able to depress the Krafft point of ChC18 to values near or even below 0 °C (cf. Figure 3 in the main text). At the high pH caused by the excess of base, protonated fatty acid and acid-soap crystals are largely absent and the solution can be regarded as a simple binary system of ionic surfactant and water. Consequently, the same arguments can be put forward to explain the heavily increased solubility of ChC18/$ChEO_nC18$ as in the case of the corresponding alkyl sulfates (see Section S2.1), which per se do not show any significant pH dependency in terms of solubility and crystallisation. In other words, the complex speciation of fatty acids and their adducts with counterions and alkanoates does not have to be taken into account when it comes to solubility, which is mainly determined by the interaction between the charged alkanoate micelles and their counterions at sufficiently high pH.

Finally, the difference between the efficiency of ethoxylated choline derivatives and choline itself in decreasing the Krafft point of fatty acid solutions remains to be discussed. Indeed, the fact that the Krafft temperature of ChC18 is far above 0 °C could be related to the formation of liquid-crystalline phases, as conjectured in the case of alkyl sulfates (see Section S2.1). This notion is supported by the observation that directly after melting (at ca. 1 °C), all ChC18 solutions were highly viscous and similar to ChS18 solutions in terms of appearance at room temperature. Precipitates formed in solutions at lower pH (i.e. at lower ratios of ChOH/$ChEO_nOH$ to C18) can likely be attributed to the crystallisation of fatty acid or acid-soap complexes, enabled by the presence of certain amounts of hydrolysed soap under these conditions. Possibly, even more complex lamellar phases could be formed, i.e. bilayers in a rigid gel state, as reported for 1 wt% solutions of ChC14 in water at ChOH/C14 ratios lower than 1.[S14] For any of these presumed structures, the solubility temperature is expected to be lower for $ChEO_n$ as compared to choline itself, due to the more bulky and flexible character of the ethoxylated counterions, which i) renders the formation of acid-soap crystals or rigid lamellar phases less favourable compared to the micellar state, and ii) may allow for a larger fraction of protonated fatty acid to be solubilised in the micellar aggregates.

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