Supplementary Material (ESI) for Green Chemistry

SUPPLEMENTARY MATERIAL

Choline Carboxylate Surfactants: Biocompatible and Highly Soluble in Water

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Soap synthesis

Dodecanoic acid (Merck, p.a.), tetradecanoic acid (Sigma, puriss.), hexadecanoic acid (Sigma, ≥ 99%) and octadecanoic acid (Fluka, puriss.) were used as received. Choline base (ChOH) was purchased from Fluka as methanolic solution (45 wt%, purum). Soaps were prepared by neutralization of the fatty acids with choline hydroxide in ethanol (Baker, p.a.). The resulting choline surfactants (ChC*m*, with *m* = 12, 14, 16, 18) were recrystallized twice from a 1:100 mixture of ethanol and diethylether (Acros Organics, p.a.). Drying for a minimum of two days yielded the choline carboxylates as shiny, white powders.

All choline salts were found to be highly hygroscopic. Therefore, surfactant solutions were prepared by weighing the appropriate amount of choline carboxylate in nitrogen atmosphere and adding Millipore water afterwards. After 12 hours of stirring at 25°C, the samples were flame sealed for subsequent temperature studies.

The potassium and tetramethylammonium (TMA) carboxylate solutions, KC*m* and TMAC*m* with *m* = 12 – 18, were synthesized correspondingly by direct equimolar neutralisation of the fatty acids with 1 N titer potassium hydroxide solution and 10 wt% tetramethylammonium hydroxide solution, respectively, both received from Merck. Samples were afterwards treated for the subsequent temperature analysis as described for the choline soaps.

All choline salts were analyzed using ^{1}H NMR ($CDCl_3$), ^{13}C NMR ($CDCl_3$) and ES-MS (electro-spray mass spectroscopy) (H_2O/AcN):

ChC12:

δH (300 MHz; CDCl3) 0.85 (3 H, t, J1,2 = 6.31 Hz, J2,3 = 7.14 Hz, Me), 1.22 (16 H, s, CH2), 1.55 (2 H, quintet, $J_{1,2}$ = 7.41 Hz, $J_{2,3}$ = 7.14 Hz, CH_2), 2.1 (2 H, t, $J_{1,2}$ = 7.68 Hz, $J_{2,3}$ = 7.96 Hz, CH_2), 3.34 (9 H, m, NMe_3), 3.7 (2 H, m, NCH_2), 4.08 (2 H, s, CH_2OH).
δ_C (300 MHz; $CDCl_3$) 14.12, 22.68, 27.17, 29.36 -30.05, 31.91, 39.22, 54.63, 55.99, 68.64, 180.31.
m/z 104 (M^+, 100%), 148 (10), 207 ($2M^+ - H^+$, 25), 199 (M^-, 100), 502.5 ($2M^- + M^+$, 17).

ChC14:

δ_H (300 MHz; $CDCl_3$) 0.86 (3 H, t, $J_{1,2}$ = 6.31 Hz, $J_{2,3}$ = 7.14 Hz, Me), 1.22 (20 H, s, CH_2), 1.56 (2 H, quintet, $J_{1,2}$ = 7.41 Hz, $J_{2,3}$ = 7.41 Hz, CH_2), 2.1 (2 H, t, $J_{1,2}$ = 7.41 Hz, $J_{2,3}$ = 7.96 Hz, CH_2), 3.35 (9 H, m, NMe_3), 3.7 (2 H, m, NCH_2), 4.09 (2 H, s, CH_2OH).
δ_C (300 MHz; $CDCl_3$) 14.12, 22.69, 27.18, 29.36 – 30.06, 31.92, 39.23, 54.66, 55.99, 68.66, 180.36.
m/z 104 (M^+, 100%), 148 (17), 227 (M^-, 100), 558.6 ($2M^- + M^+$, 3%).

ChC16:

δ_H (300 MHz; $CDCl_3$) 0.86 (3 H, t, $J_{1,2}$ = 6.31 Hz, $J_{2,3}$ = 7.14 Hz, Me), 1.22 (24 H, s, CH_2), 1.54 (2 H, quintet, $J_{1,2}$ = 7.41 Hz, $J_{2,3}$ = 7.14 Hz, CH_2), 2.1 (2 H, t, $J_{1,2}$ = 7.68 Hz, $J_{2,3}$ = 7.96 Hz, CH_2), 3.35 (9 H, m, NMe_3), 3.7 (2 H, m, NCH_2), 4.11 (2 H, s, CH_2OH).
δ_C (300 MHz; $CDCl_3$) 14.13, 22.69, 27.16, 29.36 – 30.05, 31.93, 39.18, 54.70, 56.04, 68.72, 180.38.
m/z 104 (M^+, 100%), 148 (43), 255 (M^-, 100), 512 ($2M^- + H^+$, 82), 615 ($2M^- + M^+$, 10).

ChC18:

δ_H (300 MHz; $CDCl_3$) 0.86 (3 H, t, $J_{1,2}$ = 6.59 Hz, $J_{2,3}$ = 6.86 Hz, Me), 1.24 (28 H, s, CH_2), 1.57 (2 H, quintet, $J_{1,2}$ = 7.41 Hz, $J_{2,3}$ = 7.14 Hz, CH_2), 2.1 (2 H, t, $J_{1,2}$ = 7.41 Hz, $J_{2,3}$ = 8.23 Hz, CH_2), 3.35 (9 H, m, NMe_3), 3.7 (2 H, m, NCH_2), 4.10 (2 H, s, CH_2OH).
δ_C (300 MHz; $CDCl_3$) 14.13, 22.69, 27.11, 29.36 – 30.04, 31.93, 39.07, 54.70, 56.02, 68.70, 180.32.

m/z 104 (M^+, 100%), 148 (28), 283 (M^-, 100), 568 ($2M^- + H^+$, 14), 671 ($2M^- + M^+$, 10).

Methods

The Krafft temperature T_{Kr} was determined by direct visual observation, spotting the temperature at which a 1 wt% surfactant solution turned completely clear and isotropic.[1] For this purpose, samples of ChC12, ChC14 and ChC16, all of them being clear at ambient temperature, were cooled down slowly until turbidity was discernible. Thereby, ChC12 and samples remained clear and isotropic throughout the whole temperature range investigated (-3°C to 90°C). The Krafft temperatures of ChC14 and ChC16 were confirmed by reheating the samples with a rate of about 1°C per hour. ChC18 samples were turbid at room temperature, so T_{Kr} was measured by slow heating.

The TMA carboxylate solutions were analysed in the same manner as the corresponding choline samples, the determined T_{Kr} values being approximately the same. Regarding the potassium soaps, only KC12 had to be cooled down from room temperature until precipitation occurred. All other KC*m* samples were turbid at room temperature. The values of T_{Kr} for potassium carboxylates were determined as described above by heating the samples with about 1°C per hour until a completely clear and isotropic solution was obtained.

The critical micellization concentrations (cmc) of the choline surfactants were determined by conductivity measurements. Cmc's can be obtained from the breakpoint in the plot of the conductivity versus the concentration (see Figure 1-3). Experiments were conducted at 25°C using an autobalance conductivity bridge (Konduktometer 702, Knick) equipped with a Consort SK41T electrode cell. In order to obtain specific conductivities, the cell constant was determined by measuring known conductivities of 0.01 m, 0.1 m and 1 m potassium chloride solutions at 25°C.[2] The cmc values were determined to within ±4%.

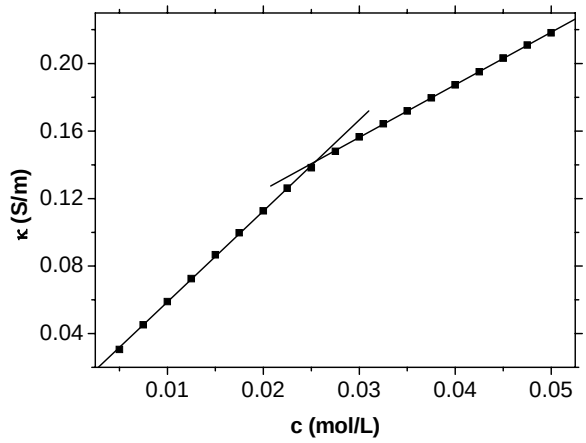

Fig. 1 Concentration-dependent plot of the specific conductivity κ of ChC12 at 25°C.

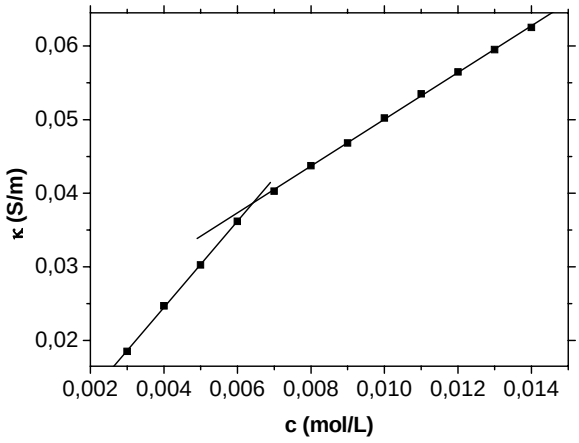

Fig. 2 Concentration-dependent plot of the specific conductivity κ of ChC14 at 25°C.

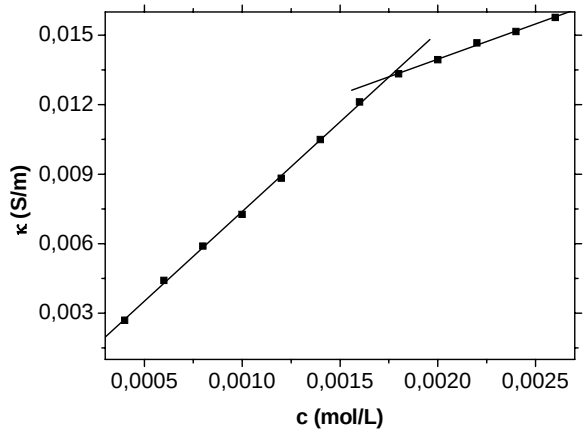

Fig. 3 Concentration-dependent plot of the specific conductivity κ of ChC16 at 25°C.

The values of the micelle ionization degree α at the cmc were calculated from the obtained conductivity data using equation 1 derived by Evans.[3]

$$1000S_2 = N^{2/3}\,\alpha^2\,(1000S_1 - \Lambda_{Ch}) + \alpha\,\Lambda_{Ch} \qquad (1)$$

In equation 1, S_1 and S_2 denote the slopes of the plot of the specific conductivity versus the concentration below and above cmc (see Table 1). Λ_{Ch} is the limiting equivalent conductivity of choline, which is 42.0 Scm^2 according to Fleming.[4] N terms the aggregation number at the cmc and was calculated according to Tanford, assuming the maximal possible aggregation number of a spherical micelle with a fully extended hydrocarbon chain.[5] However, the value of α (estimated to within ±3% and shown in Table 1) derived from equation 1 is not very sensitive to the value of N.

Table 1: Values of the Slopes of the Conductivity Plots versus the Concentration before (S_1) and after (S_2) the Cmc with the resulting α values.

surfactant	$1000S_1$ ($S \cdot cm^2$/ mol)	$1000S_2$ ($S \cdot cm^2$/ mol)	α
ChC12	53.87	31.13	0.33
ChC14	58.52	31.68	0.28
ChC16	77.37	30.44	0.18

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