Synthesis of surfactants from furfural derived 2[5*H*]-furanone and fatty amines

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Furfural was oxidized to 2[5*H*]-furanone **2** using hydrogen peroxide. Furanone **2** was transformed with two equivalents of fatty amines. A condensation and a Michael reaction occurred. Ethyl bromoacetate **5** or methyl acrylate **6** were then added to the secondary amine function. Saponification of the ester function leads to amphoteric surfactants **8a**,**b**,**c** and **10a**,**b**,**c** possessing two n-alkyl chains as hydrophobic part. The resulting products can also be considered as Gemini surfactants or twin-tail amphoteric surfactants. Biodegradation studies have been performed on these compounds and the surfactant properties of **8a** have been determined in detail.

Introduction

Furfural obtained from pentose containing biomass is a valuable synthon for fine chemistry. Currently, about 280 000 tons per year[1] are produced mainly by cyclodehydration of pentoses.[2,3,4] Many transformations of furfural into intermediates for chemical industry have been reported with the aim to replace fossil based resources.[3] Various oxidation products are used in production of fine chemicals. For instance, 2*H*-pyran-3[6*H*]-one derivatives obtained from oxidation of furfuryl alcohols are easily transformed into a large variety of compounds possessing biological activities.[5] We are particularly interested in furanones or α,β-unsaturated butyrolactones. For example, 2[5*H*]-furanone is easily available in one step by oxidation of furfural using hydrogen peroxide.[6] Photooxygenation is another efficient oxidation method which leads to hydroxy or alkoxy furanones.[2,7] These compounds have less frequently been applied as intermediates to organic synthesis. Recently, we have used such compounds in combination with tertiary amines for the synthesis of surfactants.[8]

In this article, we describe a synthesis and the biodegradation of amphoteric surfactants obtained from 2[5*H*]-furanone and primary fatty amines[9] as a second renewable material also obtained from biomass. It should be pointed out that these compounds are also easily obtained on industrial scale directly from esters such as triglycerides or the corresponding methyl esters.[10] The physico-chemical properties of one of these compounds are reported. Since the surfactants possess two hydrophobic moieties on two amino groups, they can also be considered as Gemini surfactants[11,12] or amphoteric twin-tail surfactants.[13,14]

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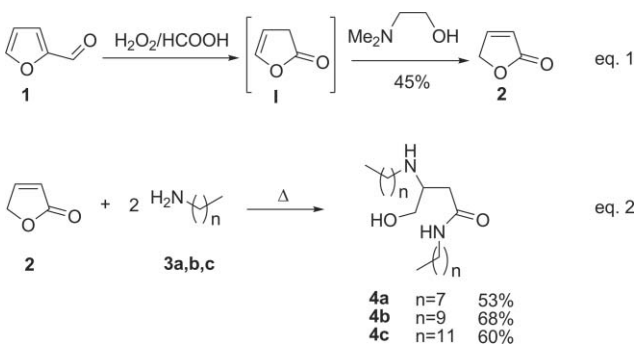
Results and discussion

We started our investigations with the oxidation of furfural **1** with hydrogen peroxide and formic acid which gives in moderate yield (45%) 2[5*H*]-furanone **2** (Scheme 1, equation 1).[6] The presence of *N*,*N*-dimethylethanolamine is necessary to catalyse the isomerization of 2[3*H*]-furanone **I** which is generated at first.[15] The furanone **2** was then transformed with two equivalents of fatty amines (equation 2). One equivalent was condensed leading to an amide function while a second one was added via a Michael reaction to the electron deficient double bond. The products have been obtained in moderate to good yields.

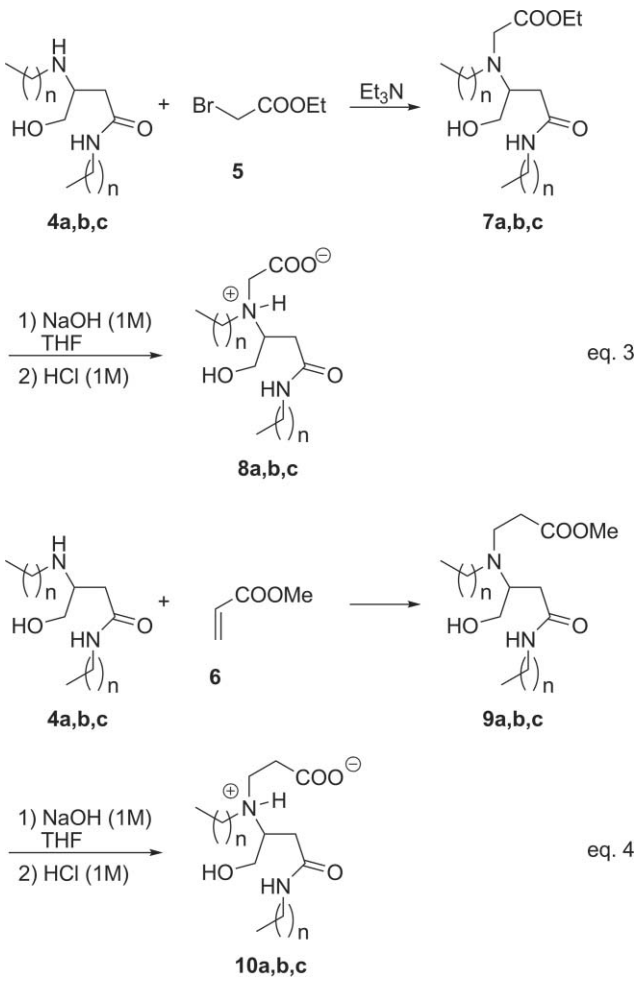


Scheme 1 Synthesis of 2[5*H*]-furanone **2** and transformation with two equivalents of fatty amines.

In order to establish an amphoteric hydrophilic moiety,[16] ethyl bromoacetate **5** or methyl acrylate **6** were added to the secondary amine function in **4a**,**b**,**c** (Scheme 2, Table 1).[17] Without purification, the resulting adducts **7a**,**b**,**c** (equation 3) and **9a**,**b**,**c** (equation 4) have been transformed into amphoteric surfactants **8a**,**b**,**c** and **10a**,**b**,**c** respectively. Saponification of compounds **7a**,**b**,**c** and **9a**,**b**,**c** was performed by addition of NaOH to a solution of these compounds in THF–water and heating of the resulting mixture. After extraction with ethyl acetate, neutralization with hydrochloric acid and lyophilization, samples containing NaCl were obtained in good yields.

Table 1 Synthesis of amphoteric surfactants from compounds **4a**,**b**,**c** (Scheme 2)

Entry	Substrates	n	Surfactants from the addition of **5**	Yield (%)	Surfactants from the addition of **6**	Yield (%)
1	**4a**	7	**8a**	81	**10a**	93
2	**4b**	9	**8b**	99	**10b**	96
3	**4c**	11	**8c**	95	**10c**	76



Scheme 2 Synthesis of amphoteric surfactants from compounds **4a**,**b**,**c** by addition of ethyl bromoacetate **5** and methyl acrylate **6** to the secondary amine function (Table 1).

These amphoteric compounds possess two n-alkyl chains as hydrophobic moieties. Such compounds are also called "Gemini Surfactants".[11,12,18] Generally, they possess remarkable surfactant properties such as particularly low critical micellization concentrations (CMC). Gemini surfactants are usually composed of two hydrophilic and two hydrophobic parts.[11] Amphoteric Gemini surfactants of this type have also been described.[18,19,20] They possess at least two hydrophilic betaine and two hydrophobic parts. Recently, zwitterionic Gemini surfactants have been reported in which one positive and one negative charge constitute the hydrophilic moiety.[21] Similar compounds are also named twin-tail surfactants.[14] In our case, the hydrophilic moieties are mainly constituted of one betaine form of a glycine part in **8a**,**b**,**c** or a β-amino acid in **10a**,**b**,**c**.

Table 2 Biodegradation after 28 days according to OECD Test guideline 301 F[24]

Entry	Surfactants	n	Biodegradation after 28 d (%)
1	**8a**	7	47 (± 3)
2	**8b**	9	22 (± 8)
3	**8c**	11	12 (± 3.5)
4	**10a**	7	40 (± 2)
5	**10b**	9	29 (± 10.5)
6	**10c**	11	32.5 (± 9)

Additional hydrophilicity is induced by a primary alcohol function. Similar surfactants possessing only one n-alkyl chain as hydrophobic moiety, have been synthesized by addition of chloroacetate[22] or acrylic acid[23] to a corresponding secondary amine.

Biodegradability of the surfactants

Biodegradation of surfactants is an important parameter of sustainability. We were particularly concerned with this study since ammonium based surfactants are often bactericide and thus biodegradation is slow. The biodegradation of our surfactants was determined according to the OECD Test guideline 301 F[24] which is particularly demanding. This test uses a manometric respirometer to follow the consumption of oxygen during 28 days in a closed flask containing 30 to 60 mg l^{-1} of test substance and inoculums coming from a sewage plant. The percentage of biodegradation is obtained by dividing the resulting biological oxygen demand (BOD) by the theoretical oxygen demand (ThOD) of the test substance. Three replicates have been carried out for each surfactant. The results of biodegradation after 28 days are given in Table 2.

Significant effects of biodegradation were observed in the cases of **8a**, **10a** and **10c** (Fig. 1, compare entries 1, 4 and 6 in Table 2). In all cases, degradation starts immediately and no induction period is detected. After 28 days, the biodegradation is well advanced in the cases of **8a** and **10a** and almost reaches its maximum. In the case of **10c**, the process is slower. According to the E.U. directive (Commission Regulation (EC) No 907/2006 of 20 June 2006),[25] surfactants are considered as biodegradable when degradation reaches 60% after 28 d. Therefore, our compounds should be considered as potentially biodegradable.

Physicochemical characteristics of surfactant 8a

Due to its relatively good biodegradation and its high solubility in water, the surfactant properties of the homologue **8a** were studied in detail. The following investigations were performed on this surfactant: Zeta potential measurement, the equilibrium surface tension with the determination of CMC, and the head group area at the air–water interface and the dynamic surface tension reduction behaviour.

Zeta potential measurement. The amphoteric properties of the surfactant **8a** were determined by the measurement of the electrophoretic mobility dependence on the pH of a diluted solution. Under acidic conditions, the amino groups are ionised and the cationic behaviour is detected. At a high pH value, the carboxylic part is ionised and a more anionic surfactant results. Between these extreme pH values, the molecule passed by a

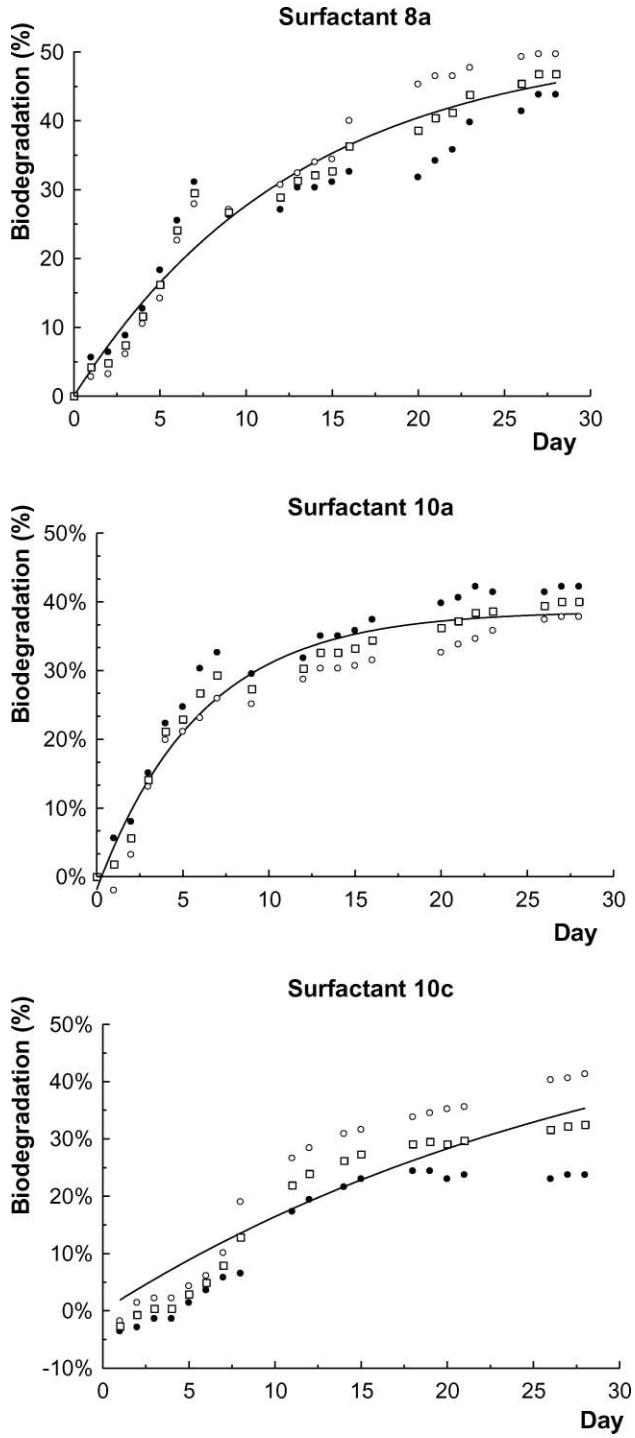


Fig. 1 Biodegradation of surfactants **8a**, **10a** and **10c** using OECD Test guideline 301 F.[24]

neutral state and a isoelectric point can be determined. For the amphoteric compound **8a**, the isoelectric point was detected at pH 3.94 (Fig. 2).

Micelle formation. The surfactant concentration at which micellization begins is known as the critical micelle concentration (CMC). This value is one of the most important properties of surfactant solutions, because the micelle formation affects both the surface or interfacial tension reduction and

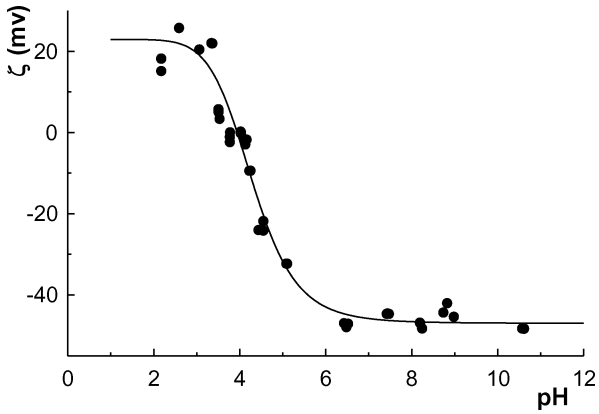


Fig. 2 Zeta potential measurements of compound **8a**.

the properties of the surfactants such as the solubilisation and detergency. The CMC was detected by the break of the curve of the surface tension measured with the Wilhelmy plate method[26] and depending on the concentration of surfactant in solution.

The efficiency of a surfactant in reducing the surface tension γ is measured by the C_{20} value, the surfactant concentration needed to reduce the surface tension by 20 mN m^{-1}.[27] The efficiency, is also measured by the surface tension at the CMC. The Gibbs equation (eqn (5)) shows the relationship between the surface excess (Γ in mol m^{-2}) and the slope of the plot of the surface tension (γ in Nm^{-1}) *versus* the logarithm of the surfactant concentration.

$$\Gamma = -\frac{1}{2\mathbf{RT}}\left(\frac{d\gamma}{d\ln C}\right)_T \quad (5)$$

The measurement was performed at pH 10 at which the ionic dissociation was considered and the coefficient 2 was introduced in eqn (5). The reciprocal of this value gives the area of surface occupied by a mole of adsorbed molecules. Division by Avogadro's number converts this value into the area per molecule at the interface A.

The results for compound **8a** obtained from the Fig. 3 are listed in Table 3. These results are compared with those obtained for compound **11** (Fig. 4) which we have previously obtained *via* photochemically induced radical addition of *N*-octylpyrrolidine to the furanone **2**.[8] The latter compound also possesses an amphoteric head group but only one hydrophobic n-alkyl group with the same number of carbon atoms. The presence of a second n-alkyl group (Gemini effect) tremendously diminishes the CMC and the C_{20}.

The CMC value of **8a** is also significantly lower than the corresponding value for a anionic surfactant with a single hydrophobic chain and a carboxylate, sulfate or sulfonate head group (for instance $C_8H_{17}SO_4^-Na^+$ has a CMC of 140 mM) or even those that contain two alkyl chains (for instance $C_8H_{17}CH(C_6H_{13})CH_2SO_4^-Na^+$ has a CMC of 2.3 mM).[27] This low CMC value is in accordance with those for other Gemini surfactants.[11] The surface tension at the CMC is below 30 mN m^{-1} and with this value, we will expect a relatively good wetting properties. The head group area value of 34 $Å^2$ was calculated with the Gibbs equation. This low value indicates that the Gemini surfactant molecules are arranged closed to

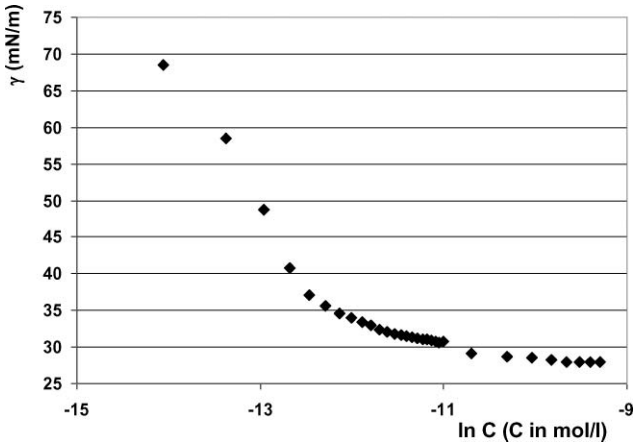


Fig. 3 Surface tension (γ) as a function of ln$C$.

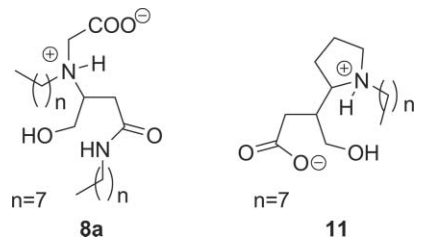


Fig. 4 Amphoteric surfactants possessing two (**8a**) or one (**11**)[8] octyl substituent(s).

Table 3 Calculated parameters from equilibrium surface tension (pH 10, $T = 25$ °C) (compare Fig. 3 and 4)

Surfactant	n	CMC/10^{-6} mol l^{-1}	C_{20}/10^{-6} mol l^{-1}	γ CMC/ mN m^{-1}	A/Å^2
8a	7	5.8	2.0	29.0	34.0
11	7	11 090	123.4	29.5	153.3

each other in the air–water interface. Due to the high pH of 10, this observation is remarkable.

Dynamic surface reduction. The dynamic surface tension plays an important role for the determination of the global performance of surfactant.[27] The dynamic surface tension $\gamma(t)$ was performed with a maximum bubble pressure tensiometer at 0.1% and a pH fixed at 10.[28] A typical decay curve is given for surfactant **8a** (Fig. 5). The measured data fit well with a Rosen-Hua equation (eqn (6)) where $\gamma(t)$ is the surface tension of the surfactant solution at time t, γ_m the *meso*-equilibrium surface (where $\gamma(t)$ shows only a small change with time), γ_0 is the surface tension of the pure solvent (water).[29] n and t^* are calculated from the plot. t^* is the time required for $\gamma(t)$ to reach a value half-way between γ_0 and γ_m and is related to the surfactant concentration. n is a constant related to the molecular structure of the surfactant. In an empirical manner,[27] an increase in n, indicates an increase in the hydrophobicity.

$$\gamma(t) = \gamma_m + \frac{\gamma_0 - \gamma_m}{1 - \left(\frac{t}{t^*}\right)^n} \quad (6)$$

Table 4 Dynamic characteristics of surfactant **8a** for a 0.1% w/w solution at pH 10 and $T = 25$ °C

	γ_m/mN m^{-1}	n	t^*/ms	V_{max} /mN m^{-1} s^{-1}	D/10^{12} m^2 s^{-1}
8a	29	0.6	128	50.9	146.0

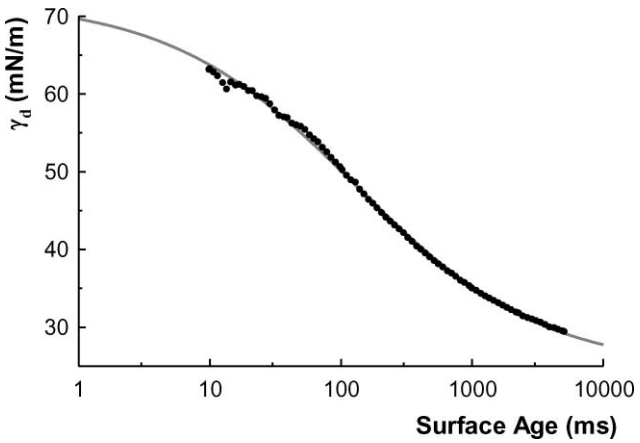


Fig. 5 Evolution of surface tension over time, 0.1% w/w, pH 10, $T = 25$ °C. The continuous line corresponds to the Rosen-Hua equation.

The derivative of the Rosen-Hua equation gives the new parameter V_{max} expressed in N ms^{-1} and as the expression of the speed of surface tension decline (eqn (7)).[30]

$$-\left(\frac{d\gamma_t}{dt}\right)_{max} = V_{max} = \frac{n(\gamma_0 - \gamma_m)}{4t^*} \quad (7)$$

The diffusion coefficient was determined according to the Joos Rilaerts equation (eqn (8))[31] where R is the universal gas constant, T the absolute temperature, C the surfactant concentration, D_s is the diffusion coefficient. The results are resumed in Table 4.

$$\gamma(t) = \gamma_0 - 2R \cdot T \cdot C = \left(\frac{D_S t}{\pi}\right)^{0.5} \quad (8)$$

Conclusions

We have synthesized amphoteric surfactants possessing two n-alkyl chains as hydrophobic parts. These compounds can also be considered as Gemini surfactants or twin-tail amphoteric surfactants. The synthesis starts with the oxidation of furfural which is associated to renewable feedstock for chemical industry since it is obtained from pentose containing biomass. The resulting furanone is transformed with two equivalents of fatty amines also obtained from biomass. A betaine moiety is then generated starting with the addition of ethyl bromoacetate or methyl acrylate to a secondary amine function. The compounds are potentially biodegradable. The surfactant properties of one compound (**8a**) were determined. A particularly low CMC was detected and the low surface tension should induce good wetting properties.

For application to the industrial scale and to enhance attractiveness in the context of green chemistry, the synthesis can be optimized as follows. The oxidation of furfural should be improved. The generation of the betaine function must

be facilitated. Thus an additional carboxylic function can be introduced by a Michael addition of the amine function of **4a**,**b**,**c** to acrylic acid. This transformation diminishes the formation of salts. Biodegradation as well as surfactant parameters can be improved by modification of the alkyl side chains.

Experimental

General

NMR spectra were recorded with a Bruker AC 250 (250 MHz for ^{1}H and 62 MHz for ^{13}C). Chemical shifts are given in ppm relatively to TMS using residual solvent signals as secondary references. IR spectra were recorded on a Nicolet AVATAR 320 FT-IR. MS and HRMS were obtained on a hybrid tandem quadrupole/time-of-flight (Q-TOF) instrument, equipped with a pneumatically assisted electrospray (Z-spray) ion source (Micromass, Manchester, UK) operated in positive mode (EV = 30 V, 80 °C, flow of injection 5 ml min^{-1}). Atom absorption spectroscopy was carried out with a Variant Liberty 2 (ICPAES). Preparative chromatography was carried out with silica gel 60 Å from SDS. TLC was carried out with Kieselgel 60F_{254} plates form Merck. 2[5*H*]-furanone **2** has been synthesized as previously described.[6]

Condensation and addition of fatty amines with 2[5H]-furanone 2. Compound 4a

A solution of octylamine **3a** (15 g, 0.11 mol) and 2[5*H*]-furanone **2** (4.41 g, 0.052 mol) in dry acetonitrile (100 ml) was heated at 80 °C for 12 h. After evaporation of the solvent, the residual white solid (**4a**) was treated with ethyl acetate, then dried. Yield: 9.6 g (53%), mp: 78-80 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.62 (s, broaden), 3.50-1.99 (m, 35H), 0.65 (t, J = 5.6 Hz, 6H). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 172.18, 62.79, 56.66, 46.81, 39.34, 37.60, 31.89 (2x), 30.48, 29.61 (2x), 29.31 (3x), 27.50, 27.15, 22.71 (2x), 14.14 (2x). IR (KBr): ν = 3290, 3091, 2919, 1635, 1540, 1465 cm^{-1}. TOFMSES$^+$ [M+H$^+$]=343.3317. Elemental analysis: calcd (%) for $C_{20}H_{42}N_2O_2$ (342.32): C 70.12, H 12.36, N 8.18; found: C 69.94, H 12.52, N 8.23.

Compound 4b

A solution of decylamine **3b** (15 g, 95.3 mmol) and 2[5*H*]-furanone **2** (2.0 g, 23.8 mmol) in dry acetonitrile (100 ml) was heated under reflux for 24 h. After evaporation of the solvent, the residual white solid (**4b**) was treated with ethyl acetate, then dried. Yield: 6.5 g (68%), mp: 87-88 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.86 (s, broaden), 4.0-2.0 (m, 13H), 1.95-1.00 (m, 30H), 0.91 (t, J = 6.8 Hz, 6H). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 172.40, 63.13, 56.96, 47.15, 39.71, 39.72, 38.00, 32.3 (2x), 30.77, 30.02 (2x), 29.76 (3x), 27.84, 27.51, 23.09 (2x), 14.53 (2x). IR (KBr): ν = 3300, 2921, 1636, 1545, 1469 cm^{-1} TOFMSES$^+$ [M+H$^+$]=399.4, [2M+H$^+$]=797.0. Elemental analysis: calcd (%) for $C_{24}H_{50}N_2O_2$ (398.39): C 72.31, H 12.64, N 7.03; found: C 71.44, H 12.60, N 6.90.

Compound 4c

A solution of dodecylamine **3c** (30 g, 162 mmol) and 2[5*H*]-furanone **2** (3.39 g, 40.4 mmol) in dry acetonitrile (100 ml) was heated under reflux for 24 h. After evaporation of the solvent, the residual white solid (**4c**) was treated with ethyl acetate, then dried. Yield: 11.0 g (60%), mp: 86-88 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.65 (s, broaden), 4.0-2.0 (m, 11H), 1.80-1.00 (m, 40H), 0.90 (t, J = 6.4 Hz, 6H). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 172.31, 63.82, 57.12, 47.13 (2x), 39.77, 37.64, 32.33 (2x), 30.40, 30.11 (6x), 30.07, 29.98, 29.91, 29.78, 27.77, 27.51, 23.10 (2x), 14.53 (2x). IR (KBr): ν = 3299, 3099, 2919, 2849, 1636, 1542, 1467 cm^{-1} TOFMSES$^+$ [M+H$^+$]=455.36. Elemental analysis: calcd (%) for $C_{28}H_{58}N_2O_2$ (454.45): C 73.95, H 12.85, N 6.16; found: C 73.72, H 12.85, N 5.89.

Addition of ethyl bromoacetate 5 and synthesis of amphoteric surfactants. Compound 8a

Compound **4a** (3 g, 8.8 mmol), triethylamine (12.2 ml, 88 mmol) and ethyl bromoacetate **5** (14.6 g, 88 mmol) were successively added to ethanol (18 ml). The resulting mixture was heated under reflux for 4 h. Water (12 ml) was then added. After phase separation, the aqueous phase was extracted three times with ethyl acetate. The combined organic phases were dried with $MgSO_4$. After evaporation of the solvent the residue **7a** (3 g) was treated with NaOH (0.47 g, 11.8 mmol) in a mixture of water (2 ml) and THF (2 ml) at 80 °C for 4 h. After phase separation, the aqueous phase was extracted three times with ethyl acetate and then neutralized with HCl (1M). The mixture was diluted with ethanol and the liquid phase was concentrated to yield a white powder. Yield: 3.27 g (81%). ^{1}H NMR (250 MHz, D_2O): δ = 2.14-2.00 (m, 11H), 1.6 (m, 2H), 1.20 (m, 24H), 0.7 (t, J = 6.7 Hz, 6H). ^{13}C NMR (62 MHz, D_2O): δ = 177.42, 171.37, 62.74, 59.09, 54.38, 47.99, 39.94, 32.97 (2x), 31.46 (2x), 28.58 (3x), 26.04 (2x), 25.00 (2x), 22.45 (2x), 13.88 (2x). IR (KBr): ν = 3248, 2941, 1652, 1557, 1231 cm^{-1} TOFMSES$^+$ [M+H$^+$]=401.3, [M+Na$^+$]=423.3, [M+2Na$^+$-H]=423.3. Elemental analysis: calcd (%) for $C_{22}H_{44}N_2O_4$.NaCl (458.04): C 57.56, H 9.66, N 6.10, Na 5.01; found: C 50.37, H 8.58, N 4.96 Na 8.36. The value for Na was determined by atomic absorption spectroscopy.

Compound 8b

Compound **4b** (3 g, 7.53 mmol), triethylamine (7.6 g, 10 mmol) and ethyl bromoacetate **5** (12.6 g, 75 mmol) were successively added to ethanol (10 ml). The resulting mixture was heated under reflux for 4 h. Water (12 ml) was then added. After phase separation, the aqueous phase was extracted three times with ethyl acetate. The combined organic phases were dried with $MgSO_4$. After evaporation of the solvent the residue **7b** (3.6 g) was treated with NaOH (0.45 g, 11.3 mmol) in a mixture of water (1.5 ml) and THF (7 ml) at 80 °C for 4 h. After phase separation, the aqueous phase was extracted three times with ethyl acetate and then neutralized with HCl (1M). The mixture was diluted with ethanol and the liquid phase was concentrated to yield a white powder. Yield: 3.83 g (99%). ^{1}H NMR (250 MHz, DMSO-d_6): δ = 8.54 (s, 1H), 2.0-4.3 (m, 13H), 1.43 (m, 32H), 1.05 (t, J = 6.7 Hz, 6H). ^{13}C NMR (62 MHz, DMSO-d_6): δ = 173.97, 171.03, 60.80, 54.96, 53.86, 52.02, 34.19, 31.70 (2x), 29.13, 27.92 (2x), 26.90 (2x), 22.49 (2x), 14.45, 14.32. IR (KBr): ν = 3397, 2924, 2951, 1653, 1634, 1112 cm^{-1} TOFMSES$^+$ [M+H$^+$]=457.4, [M+Na$^+$]=479.3, [M+2Na$^+$-H]=501.3.

Elemental analysis: calcd (%) for $C_{26}H_{52}N_2O_4$.NaCl (514.35): C 60.62, H 10.17, N 5.44, Na 4.46; found: C 54.59, H 9.26, N 4.78 Na 7.37. The value for Na was determined by atomic absorption spectroscopy.

Compound 8c

Compound **4c** (3 g, 6.6 mmol), triethylamine (9 ml, 10 mmol) and ethyl bromoacetate **5** (11.0 g, 66 mmol) were successively added to ethanol (10 ml). The resulting mixture was heated under reflux for 4 h. Water (12 ml) was then added. After phase separation, the aqueous phase was extracted three times with ethyl acetate. The combined organic phases were dried with $MgSO_4$. After evaporation of the solvent the residue **7c** (3.4 g) was treated with NaOH (0.37 g, 9.3 mmol) in a mixture of water (1.0 ml) and THF (6 ml) at 80 °C for 4 h. After phase separation, the aqueous phase was extracted three times with ethyl acetate and then neutralized with HCl (1M). The mixture was diluted with ethanol and the liquid phase was concentrated to yield a white powder. Yield: 3.36 g (95%). ^{1}H NMR (250 MHz, DMSO-d_6): δ = 8.39 (s, 1H), 1.85-4.00 (m, 13H), 1.23 (m, 20H), 1.43 (m, 16H), 1.05 (t, J = 6.7 Hz, 6H). ^{13}C NMR (62 MHz, DMSO-d_6): δ = 171.92, 169.17, 61.20, 59.15, 59.06, 58.43, 50.64, 31.80, 29.76, 27.54 (2x), 27.51 (3x), 27.48 (3x), 27.33, 27.18, 24.97, 24.84 (3x), 20.56, 19.68 (3x), 12.41, 12.40. IR (KBr): ν = 3194, 2920, 2951, 1652, 1631, 1112 cm^{-1} TOFMSES$^+$ [M+H$^+$]=513.4, [M+Na$^+$]=535.4. Elemental analysis: calcd (%) for $C_{30}H_{60}N_2O_4$.NaCl (570.41): C 63.08, H 10.59, N 4.90, Na 4.02; found: C 56.05, H 9.40, N 4.21 Na 13.15. The value for Na was determined by atomic absorption spectroscopy.

Addition of methyl acrylate 6 and synthesis of amphoteric surfactants. Compound 10a

A solution of compound **4a** (1.75 g, 5.11 mmol) and methyl acrylate **6** (4.4 ml, 51 mmol) in methanol (5 ml) was heated under reflux for 12 h. After evaporation, the residue (**9a**) was treated with NaOH (0.31 g, 7.7 mmol) in a mixture of water (2.0 ml) and THF (7 ml) at 80 °C for 4 h. After evaporation, the residue was picked up with a mixture of ethyl acetate (10 ml) and water (6 ml). The phases were separated and the water phase was extracted three times with ethyl acetate. The water phase was then neutralized with HCl (1M). After lyophilization, an amorphous solid was obtained. Yield: 2.21 g (93%). ^{1}H NMR (250 MHz, D_2O): δ = 1.4-4.0 (m, 13H), 1.23 (m, 24H), 0.85 (t, J = 6.7 Hz, 6H). ^{13}C NMR (62 MHz, DMSO-d_6): δ = 177.11, 177.07, 61.36, 58.95, 50.83, 48.6, 47.69, 32.38, 32.26, 32.03, 30.91, 29.60, 29.50, 29.06, 28.98 (2x), 26.5, 25.46, 22.88, 22.72 (2x), 14.09 (2x). IR (KBr): ν = 3560, 2925, 1699, 1652, 1112 cm^{-1} TOFMSES$^+$ [M+H$^+$]=415.35. Elemental analysis: calcd (%) for $C_{23}H_{46}N_2O_4$.NaCl (472.30): C 58.39, H 9.80, N 5.92, Na 4.86; found: C 45.56, H 8.09, N 5.01, Na 10.03. The value for Na was determined by atomic absorption spectroscopy.

Compound 10b

A solution of compound **4b** (2 g, 5.0 mmol) and methyl acrylate **6** (4.3 g, 50 mmol) in methanol (5 ml) was heated under reflux for 12 h. After evaporation, the residue **9b** (2.4 g) was treated with NaOH (0.3 g, 7.5 mmol) in a mixture of water (2.0 ml) and THF (7 ml) at 80 °C for 12 h. After evaporation, the residue was picked up with a mixture of ethyl acetate (10 ml) and water (6 ml). The phases were separated and the water phase was extracted three times with ethyl acetate. The water phase was then neutralized with HCl (1M). After lyophilization, an amorphous solid was obtained. Yield: 2.25 g (96%). ^{1}H NMR (250 MHz, D_2O): δ = 1.4-4.0 (m, 13H), 1.2 (m, 32H), 0.75 (t, J = 6.7 Hz, 6H). ^{13}C NMR (62 MHz, D_2O): δ = 177.69, 176.86, 61.36, 59.06, 50.99, 48.63, 47.57, 44.68, 39.74, 32.95, 32.93 (2x), 32.70, 32.50, 30.26, 30.10 (2x), 30.02 (2x), 29.84, 28.59, 27.75, 27.14, 26.36, 25.94, 23.15 (2x), 14.28 (2x). IR (KBr): ν = 3399, 2957, 2924, 1694, 1399 cm^{-1} TOFMSES$^+$ [M+H$^+$]=471.4. Elemental analysis: calcd (%) for $C_{27}H_{54}N_2O_4$.NaCl (528.37): C 61.28, H 10.29, N 5.29, Na 4.34; found: C 49.65, H 8.95, N 4.16, Na 9.06. The value for Na was determined by atomic absorption spectroscopy.

Compound 10c

A solution of compound **4c** (2.2 g, 4.8 mmol) and methyl acrylate **6** (4.1 g, 48 mmol) in methanol (5 ml) was heated under reflux for 12 h. After evaporation, the residue **9c** (2.6 g) was treated with NaOH (0.29 g, 7.1 mmol) in a mixture of water (1.0 ml) and THF (5 ml) at 80 °C for 12 h. After evaporation, the residue was picked up with a mixture of ethyl acetate (10 ml) and water (6 ml). The phases were separated and the water phase was extracted three times with ethyl acetate. The water phase was then neutralized with HCl (1M). After lyophilization, an amorphous solid was obtained. Yield: 2.11 g (76%). ^{1}H NMR (250 MHz, DMSO-d_6): δ = 8.65 (s, 1H), 1.30-4.50 (m, 15H), 1.16 (m, 40H), 0.77 (t, J = 6.5 Hz, 6H). ^{13}C NMR (62 MHz, DMSO-d_6): δ = 173.45, 172.42, 59.87, 59.09, 58.26, 57.63, 48.78, 45.81, 30.97, 33.60, 30.67 (3x), 28.41 (4x), 28.09 (3x), 26.51, 25.93, 25.88, 25.82, 21.46 (2x), 21.38 (3x), 13.31 (2x). IR (KBr): ν = 3398, 2956, 2924, 2853, 1691, 1405, 1115 cm^{-1} TOFMSES$^+$ [M+H$^+$]=527.4, [M+Na$^+$]=549.0. Elemental analysis: calcd (%) for $C_{31}H_{62}N_2O_4$.NaCl (584.43): C 63.62, H 10.68, N 4.79, Na 3.93; found: C 54.49, H 9.14, N 3.72, Na 8.0. The value for Na was determined by atomic absorption spectroscopy.

Physicochemical characterization

Solution preparation and materials. Surfactants were used after drying at 30 °C under vacuum during 12 h. All solutions were prepared using water that was completely deionized (Millipore) and filtered (0.22 μm). Hydrochloric acid, 0.1 N in solution was supplied by VWR (France) and sodium hydroxide (0.1 N) by Labosi (France)

Zeta potential and determination of the isoelectric point (iep). The Zeta potentials were measured with Zeta Compact instrument (CAD, France) by determination of electrophoretic mobility on the diluted solution in ionic strength buffer solution (NaCl 50 mM) at different pH. One the electrophoretic mobility was measured, the zeta potential value was calculated using the Smoluchowski equation. Three to five replicate were performed for each pH. All measurements were performed at room temperature (22±2 °C). The plot of zeta potential against pH was been well described by a four parameters logistic model (eqn (9)) where A_1 and A_2 denote the upper and lower asymptote at

zero and infinite pH. a and b denote the characteristic of the linear part of the S-sharpe curve. The iep points were determined for the pH where the zeta potential is equal to zero after non-linear regression by fitting the curve by the least squares method with the freeware software Kyplot (Koichi Yoshioka, 1997-2001).

$$Y = A_1 + \frac{A_1 - A_2}{1 + \exp(-2 \times (a + b\log(X))} \quad (9)$$

Surface tension, CMC and area/molecule. The plot of the surface tension against Ln*C* for surfactant were obtained from freshly prepared solutions and by the universally Wilhelmy plate method with a automatic tensiometer (KRUSS K100, Germany) at 25±0.5 °C.

Dynamic surface tension measurement. The dynamic surface tension of a fresh solution was determined with the maximum bubble pressure method and the BP2 tensiometer (KRUSS, Germany). In a bubble pressure tensiometer gas bubbles were produced in the sample liquid at an exactly defined bubble generation rate. The gas bubbles enter the liquid through a capillary whose radius is known. During this process the pressure passes through a maximum whose value was recorded by the instrument. The following relationship (eqn (10)) exists between the maximum pressure P_{max}, the hydro-static pressure in the capillary P_0, the inner radius r of the capillary and the surface tension γ:

$$\gamma = \frac{(P_{\max} - P_0).r}{2} \quad (10)$$

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Notes and references

1 A. S. Mamman, J.-M. Lee, Y.-C. Kim, I. T. Hwang, N.-J. Park, Y. K. Hwang, J.-S. Chang and J.-S. Hwang, *Biofuels, Bioprod. Biorefin.*, 2008, **2**, 438–454.
2 K. J. Zeitsch, *The chemistry and technology of furfural and its many by-products*, Elsevier, Amsterdam, 2000.
3 B. Kamm, M. Kamm, M. Schmidt, T. Hirth and M. Schulze, *Biorefineries–Industrial Processes and Products, Vol. 2* (B. Kamm, P. R. Gruber and M. Kamm, ed.) Wiley-VCH, Weinheim, 2006, pp. 97-149.
4 J. N. Chheda, G. W. Huber and J. A. Dumesic, *Angew. Chem., Int. Ed.*, 2007, **46**, 7164–7183.
5 E. A. Couladouros and A. T. Strongilos, *Angew. Chem., Int. Ed.*, 2002, **41**, 3677–3680.
6 J. H. Näsman, A. T. Johnson and J. D. White, *Org. Synthesis*, 1989, **68**, 162–174.
7 G. O. Schenck, *Justus Liebigs Ann. Chem.*, 1953, **584**, 156–176; G. Bolz and W.-W. Wiersdorff, (BASF) German Offen. 2111119, 1972; P. Esser, B. Pohlmann and H.-D. Scharf, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2009–2023; S. Marinković, C. Brulé, N. Hoffmann, E. Prost, J.-M. Nuzillard and V. Bulach, *J. Org. Chem.*, 2004, **69**, 1646–1651.
8 A. Gassama, C. Ernenwein and N. Hoffmann, *ChemSusChem*, 2009, **2**, 1130–1137.
9 J. Barrault and Y. Pouilloux, *Catal. Today*, 1997, **37**, 137–153For more recent reports on the synthesis of these compounds see: D. J. Ostgard, R. Olindo, M. Berweiler, S. Röder and T. Tacke, *Catal. Today*, 2007, **121**, 106–114; C. Buch, R. Jackstell, D. Bühring and M. Beller, *Chem. Ing. Tech.*, 2007, **79**, 434–441 and references cited therein.
10 J. Barrault, M. Seffen, C. Forquy and R. Brouard, *Stud. Surf. Sci. Catal.*, 1988, **41**, 361–369; H. Baumann, M. Bühler, H. Fochem, F. Hirsinger, H. Zoebelein and J. Falbe, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 41–62; A. Biswas, B. K. Sharma, J. L. Willett, S. Z. Erhan and H. N. Cheng, *Energy Environ. Sci.*, 2008, **1**, 639–644.
11 F. M. Menger and J. S. Keiper, *Angew. Chem., Int. Ed.*, 2000, **39**, 1906–1920.
12 L. Wattebled and A. Laschewsky, *Colloid Polym. Sci.*, 2007, **285**, 1387–1393; M. In and R. Zana, *J. Dispersion Sci. Technol.*, 2005, **26**, 421–427; M. J. Rosen and D. J. Tracy, *J. Surfactants Deterg.*, 1998, **1**, 547–554.
13 S. Bhattacharya and J. Haldar, *Colloids Surf., A*, 2002, **205**, 119–126; Z. Chen, Y. Feng, D. Zhou, P. Zhu and D. Wu, *Cent. Eur. J. Chem.*, 2008, **6**, 477–481.
14 M. S. Bakshi, K. Singh and J. Singh, *J. Colloid Interface Sci.*, 2006, **297**, 284–291.
15 J.-A. H. Näsman and G. Pensar, *Synthesis*, 1985, 786–788; L. A. Badovskaya, V. M. Latashko, V. V. Poskonin, E. P. Grunskaya, Z. I. Tyukhteneva, S. G. Rudakova, S. A. Pestunova and A. V. Sarkisyan, *Chem. Heterocycl. Compd.*, 2002, **38**, 1040–1048.
16 R. G. Laughlin, *Langmuir*, 1991, **7**, 842–847; G. Uphues, *Fett/Lipid*, 1998, **100**, 490–497; D. T. Floyd, C. Schunicht and B. Gruening, *Handbook of Applied Surface and Colloid Chemistry, Vol. 1* (K. Holmberg, D. O. Shah and M. J. Schwuger, ed.), J. Wiley & Sons, Chichester, 2002, pp 349-372; P. G. Nilsson, W. F. Pacynko and G. J. T. Tiddy, *Curr. Opin. Colloid Interface Sci.*, 2004, **9**, 117–123; R. Otterson, *Chemistry and Technology of Surfactans* (R. J. Farn, Ed.), Blackwell Publishing, Oxford, 2006, pp 170-185.
17 For this transformation and from the point of view of sustainable chemistry the use of acrylates or acrylic acid rather than bromoacetate is preferable.
18 G. S. Gabriel, R. Gabriel, M. S. Dahanayake and J.-P. Derian, (Rhodia Inc.) US Patent 6,358,914 B1, 2002.
19 K. Kwetkat, (Hüls AG) World Patent, WO 973189, 1997.
20 D. J. Tracy, R. Li and J. Yang, (Rhodia Inc.) World Patent, WO 9847859, 1998.
21 V. Seredyuk, E. Alami, M. Nydén, K. Holmberg, A. V. Peresypkin and F. M. Menger, *Langmuir*, 2001, **17**, 5160–5165.
22 H. I. Leidreiter, B. Grüning and D. Käseborn, *Int. J. Cosmet. Sci.*, 1997, **19**, 239–253; H. I. Leidreiter, B. Grüning and D. Käseborn, *SÖFW-Journal*, 2000, **126**, 2–10.
23 A. Behler, M. Biermann, K. Hill, H.-C. Raths, M.-E. Saint Victor and G. Uphues, *Surfactant Science Series*, 2001, **100**, 1–44(Reactions and Synthesis in Surfactant Systems).
24 OECD Test Guideline 301F, 1992, http://www.oecd.org/dataoecd/17/16/1948209.pdf.
25 *Official Journal of the European Union* Vol 49, 21 June 2006, L168.
26 P. C. Hiemenz and R. Rajagopalan, *Principles of Colloid and Surface Chemistry* (3rd Ed.), Marcel Dekker, New York, 1997.
27 M. J. Rosen, *Surfactants and Interfacial Phenomena* (3rd Ed.), John Wiley & Sons, Chichester, 2004.
28 R. Miller, V. B. Fainerman, K. H. Schano, A. Hofmann and W. Heyer, *Tenside Surf. Det.*, 1997, **34**, 357–363.
29 X. Y. Hua and M. J. Rosen, *J. Colloid Interface Sci.*, 1988, **124**, 652–659.
30 M. J. Rosen, X. Y. Hua and Z. H. Zhyu, *Surfactants in Solution*, 1991, **11**, 315–327.
31 P. Joos and E. Rillaerts, *J. Colloid Interface Sci.*, 1981, **79**, 96–100.

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