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Photochemical Key Steps in the Synthesis of Surfactants from Furfural-Derived Intermediates

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Furfural is oxidized to 2[5*H*]-furanone by using hydrogen peroxide or to 5-hydroxy-2[5*H*]-furanone by using photo-oxygenation. An amine function is introduced by photochemically induced radical addition of tertiairy amines, some of which carry an *n*-alkyl side chain as hydrophobic moiety. These amines are produced from fatty aldehydes and cyclic secondary amines. The resulting adducts are transformed into amphoteric surfactants possessing an ammonium and a carboxylate function. Amphoteric (pK_N and isoelectric point) and surfactant properties such as the critical micelle concentration and the adsorption efficiency are determined.

Introduction

Furfural obtained from pentose-containing biomass is a valuable synthon for fine chemistry. Currently, about 280000 tonnes are produced per year,[1] mainly by cyclodehydration of pentoses.[2–4] Many transformations into intermediates for the chemical industry have been reported with the aim to replace fossil-based resources.[3] In the context of furfural chemistry, we are particularly interested in photochemical reactions. Transformations at the electronically excited state are significantly different from transformations at the ground state of the same molecule,[5] and therefore considerably enrich the methodology of organic chemistry.[6]

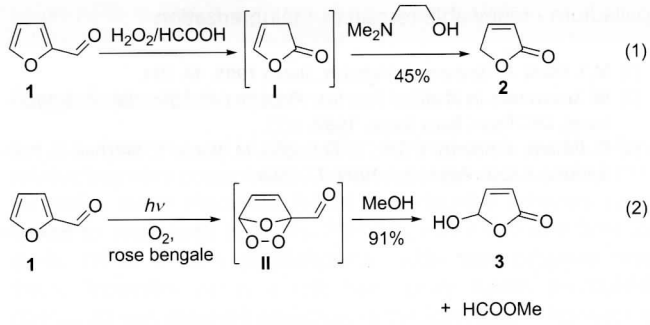
Herein, we report the application of two photochemical reactions to the synthesis of surfactants: (1) photo-oxygenation of furfural, leading to 5-hydroxy-2[5*H*]-furanones;[2,7] and (2) photochemically induced radial addition of tertiary amines to the furanones, using conditions which we have previously developed.[8,9] By the oxidation of furfural to furanones, a latent carboxylic acid is generated. A basic group is introduced by addition of an amine. In this way, surfactants are obtained that possess an amphoteric structure as hydrophilic moiety.[10] Long linear alkyl chains are used as hydrophobic part.

Surfactant properties such as surface tension reduction, micellization (determination of the critical micelle concentration (CMC)) or adsorption at the liquid/gas interface have been chracterized. The amphoteric characteristics were determined by measurements of the pK_N and the isoelectric points (IEP).

Results and Discussion

Synthesis of nitrogen-containing γ-lactone derivatives and amphoteric surfactants

We started our investigations with the oxidation of furfural **1** by hydrogen peroxide and formic acid, which leads to 2[5*H*]-furanone **2** with moderate yields (45%) [Scheme 1, Equation (1)].[11] The presence of *N,N*-dimethylethanolamine is necessary to catalyze the isomerization of 2[3*H*]-furanone **I**, which is generated at first.[12] Photo-oxygenation is a much more efficient method to oxidize furfural **1**. Thus, 5-hydroxy-2[5*H*]-furanone **3** was obtained in high yields (>90%) [Scheme 1, Equation (2)].[2,7] This transformation belongs to the most efficient oxidation methods for furfural. It can be carried out with UV and visible light.[13] The reaction starts with the generation of singlet oxygen using photochemical sensitization. Because of the low excitation energy of oxygen, 22.5 kcal mol^{-1} (1 kcal = 4.184 kJ), dyes absorbing in the visible range of light are used as sensitizers.[14] An *endo*-peroxide **II** intermediate is generated. Reaction with methanol, used as solvent, leads to **3** and methyl formiate.[15] It is important to note that the temperature



Scheme 1. Oxidation of furfural (1) by hydrogen peroxide and formic acid, and (2) by photo-oxygenation.

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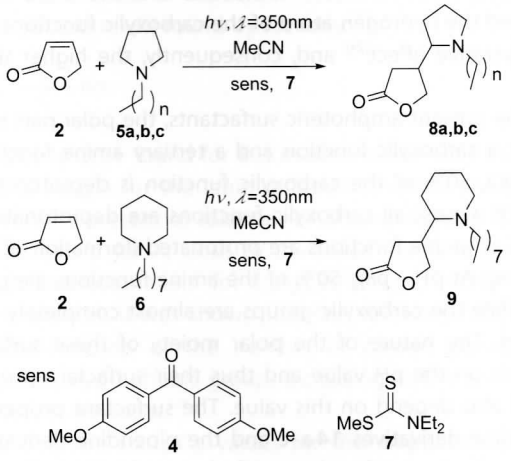
during the reaction and workup must be kept below 35 °C. Otherwise, **3** is partially transformed into 5-methyloxy-2[5*H*]-furanone, which hinders the isolation of **3** by crystallization.[7,16] We have efficiently performed this transformation by applying the classical procedure using UV light and rose bengale as sensitizer.[17]

Tertiary amines carrying long alkyl chains were chosen as the hydrophobic moieties of the surfactants. These compounds have been synthesized using reductive amination from the secondary amines pyrrolidine and piperidine and fatty aldehydes.[18,19] By using photochemically induced radical addition, tertiary amines not further functionalized have been added to furanone **2** to generate a carboxylic function in the conceived amphoteric ionic surfactants (Scheme 2).[10] Recently, we have developed an efficient method to perform this transformation.



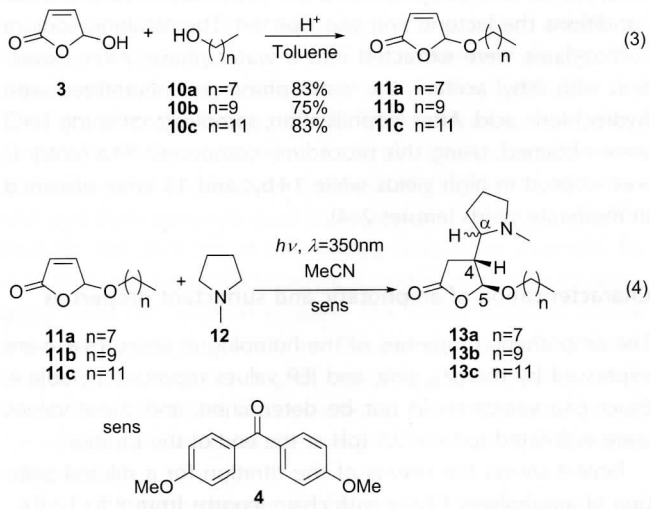
Scheme 2. Photochemically induced radical addition of tertiary amines possessing a long *n*-alkyl side chain to furanone **2** (Table 1).

The favorable results have been obtained because electron-donor-substituted aromatic ketones such as 4,4′-dimethoxybenzophenone **4** were used as sensitizers.[20] In contrast to conventional sensitizers, such as benzophenone, only catalytic amounts of these compounds were needed to induce the photochemical electron transfer reaction. In this manner, the transformation occurs under homogeneous photocatalysis. Using inorganic semiconductors such as TiO_2 or ZnS, the transformations were also carried out with heterogeneous photocatalysis.[21] In the present study, we have transformed tertiary amines **5a–c** and **6** with furanone **2** in the presence of 4,4′-dimethoxybenzophenone **4** as sensitizer in catalytic amounts, thus using homogeneous photocatalysis. Amines were added in excess to the reaction mixture. However, using these standard reaction conditions we did not observe a significant transformation. Cyclic tertiary amines possessing a long alkyl substituent revealed to be less reactive than corresponding pyrrolidine or piperidine derivatives with smaller *n*-alkyl groups.[20] We found that in such cases of less reactive amines, the presence of thiocarbonyl compounds such as the thiocarbamate **7** considerably accelerate the conversion.[9,22] Under these modified reaction conditions, the tertiary amines **5a–c** and **6** were successfully transformed into the corresponding adducts **8a–c** and **9** (Scheme 2, Table 1). It should be noted that the pyrrolidine derivatives **5a–c** (entries 1–3) are more reactive than the corresponding piperidine compound **6** (entry 4), which results in a much longer irradiation time for the latter transformation. The ratio of diastereomers is slightly increased when the *n*-alkyl side chain is prolonged from *n*-octyl (**8a** and **9**, entries 1 and 4) to *n*-dodecyl (**8c**, entry 3).

Table 1. Addition of tertiary amines **5a–c** and **6** to furanone **2** (Scheme 2).

Entry	Aminolactone	*n*	Irradiation time [h]	Yield [%]	Diastereomer ratio
1	**8a**	7	6	58	60:40
2	**8b**	9	6.5	60	70:30
3	**8c**	11	7	66	80:20
4	**9**	7	18	57	60:40

An attempt was made to attach the hydrophobic long-chain alkyl substituent to the furanone moiety. 5-Hydroxy-2[5*H*]-furanone **3** was transformed with the fatty alcohols **10a–c** into the corresponding acetals **11a–c** [Scheme 3, Equation (3)].[23] Once again, the amine function was introduced by photochemically induced radical addition of a cyclic tertiary amine (**12**) [Equation (4)]. Due to the high reactivity of *N*-methylpyrrolidine **12**,[20,22] no thiocarbamate **7** was needed. The conversion is significantly faster than that one of cyclic amines **5a–c** and **6** possessing long *n*-alkyl chains. Nevertheless, yields remained rather modest. The radical addition occurred stereospecifically *anti* with respect to the alkoxy substituent (relative configuration at centers 4 and 5).[17] The configuration in the α position of the nitrogen atom of the resulting aminolactones **13a,b,c** was not completely controlled. Therefore, two diastereomers were obtained (compare[20,21] and Table 2). This stereoselectivity was somewhat improved by the longest *n*-alkyl chain in **11c**



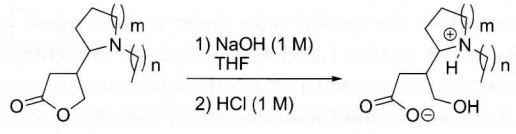
Scheme 3. Synthesis of alkoxyfuranones from **3** and fatty alcohols **10a–c** [Equation (3)] and photochemically induced radical addition of *N*-methylpyrrolidine **12** to these furanones (Equation (4), Table 2).

Table 2. Photochemically induced radical addition of *N*-methylpyrrolidine **12** to alkoxyfuranones **11a–c** [Scheme 3, Equation (4)].

Entry	Aminolactone	*n*	Irradiation time [h]	Yield [%]	Diastereomer ratio
1	**13a**	7	20	16	65:35
2	**13b**	9	20	26	65:35
3	**13c**	11	11	20	75:25

(Scheme 3, Equation (4), Table 2, entry 3). No significant surfactant properties were detected for these compounds. Therefore, their synthesis was not optimized.

Amphoteric surfactants were obtained by basic treatment followed by neutralization of aminolactones **8a–c** and **9** (Scheme 4, Table 3). The basic treatment was performed with



8a,b,c 9 **14a,b,c 15**

Scheme 4. Saponification of aminolactones **8a–c** and **9** leading to amphoteric surfactants **14a–c** and **15** (Table 3).

Table 3. Saponification of aminolactones **8a–c** and **9** leading to amphoteric surfactans **14a–c** and **15** (Scheme 4).

Entry	Ampholyte	*n*	*m*	Yield [%]
1	**14a**	7	1	87
2	**14b**	9	1	53
3	**14c**	11	1	53
4	**15**	7	2	52

solutions of the compounds in THF and NaOH. Under these conditions the lactone ring was opened. The resulting sodium carboxylates were extracted into a water phase. After extraction with ethyl acetate, the water phase was neutralized with hydrochloric acid. After lyophilization, samples containing NaCl were obtained. Using this procedure, compound **14a** (entry 1) was isolated in high yields while **14b,c** and **15** were obtained in moderate yields (entries 2–4).

Characterization of amphoteric and surfactant properties

The ampotheric properties of the homologue series **14a–c** are expressed by the pK_N, p*K*a, and IEP values reported in Table 4. Exact p*K*a values could not be determined, and these values were estimated to be <2.5 (pH at the end of the titration).

Table 4 shows the results of the titration for a diluted solution of ampholytes **14a–c** with chain lengths from 8 to 12 (i.e., $n=7$ to $n=11$) carbons. The IEP values were determined by electrophoteric mobility measurements at different pH values. Ampholyte **14c**, with a hydrophobic tail of 12 carbon atoms,

Table 4. Amphoteric properties of compounds **14a–c** ($m=1$) (Scheme 4).

Entry	Ampholyte	*n*	pK_N	IEP	p*K*a
1	**14a**	7	9.00	2.99	<2.5
2	**14b**	9	9.66	4.12	<2.5
3	**14c**	11	10.10	4.26	<2.5

had the highest pK_N value ($pK_N=10.10$) and highest IEP (IEP = 4.26), followed closely by the C10 homologue **14b** and then the C8 ampholyte **14a**. These effects are not surprising and have already been described in the context of p*K*a values of fatty acid salt solutions.[24] It was shown that the chain length of the fatty acid affects their p*K*a. As the chain length increases, the van der Waals interactions between the chains of adjacent molecules increase, bringing these molecules closer to each other. The closer the molecules are, the more strongly screened the hydrogen atom of the carboxylic functions are by a cooperative effect[24] and, consequently, the higher the p*K*a is.

In the present amphoteric surfactants, the polar part is localized at a carboxylic function and a tertiary amine function. At pH = p*K*a, 50% of the carboxylic function is deprotonated. At pH = IEP, almost all carboxylic functions are deprotonated and almost all amine functions are protonated (formation of betain function). At $pH=pK_N$, 50% of the amine functions are protonated while the carboxylic groups are almost completely deprotonated. The nature of the polar moiety of these surfactants depends on the pH value and thus their surfactant properties should also depend on this value. The surfactant properties of pyrrolidine derivatives **14a–c** and the piperidine derivative **15** have been measured and quantified at pH 10 (Table 5).

Table 5. Surfactant properties of amphotheric compounds **14a–c** and **15** (Scheme 4) at pH 10.

Entry	Ampholyte	*n*	*m*	CMC [mM]	pC_{20} [mM]	γCMC [mN m^{-1}]	*A* [Å]
1	**14a**	7	1	11.09	0.909	29.5	153.3
2	**14b**	9	1	4.04	1.799	31.9	68.8
3	**14c**	11	1	0.611	1.917	30.0	73.5
4	**15**	7	2	5.25	0.970	32.0	113.1

The surfactant concentration at which micellization starts 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 the properties of the surfactants such as the solubilization and detergency. The CMC was detected by the break of the curve of the surface tension with the concentration of surfactant in solution, measured by the Wilhelmy plate method.[25]

The efficiency of a surfactant in reducing surface tension is measured by the pC_{20} value, the negative log of the surfactant concentration necessary to reduce the surface tension by

20 mN m^{-1}.[26] The effectiveness also is measured by the surface tension at the CMC. The Gibbs equation [Equation (5)] shows the relationship between the surface excess (Γ in mol m^{-2}) and the slope of the plot of surface tension (γ in Nm^{-1}) versus the logarithm of the concentration of surfactant. The ionic dissociation is considered.

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

The reciprocal of this value gives the area of surface occupied by a mole of adsorbed molecules. Division by Avogadro's number convert this into the aera per molecule at the interface, *A*.

The ampholytes **14a–c** represent homologous straight-chain surfactants and follow the empirical equation between the CMC and the number of the carbon atoms *n* in the hydrophobic chain [Equation (6)] found by Klevens:[27]

$$\log CMC = A - Bn \quad (6)$$

The value of 0.31 found for *B* is in accordance with the general rule ($B = \log 2$) for the ionic surfactant (here at pH 10, the anionic form is present in solution for all ampholytes). A value of 3.6 was found for *A*, close to the value found for another amphoteric surfactant (3.1 for $C_nH_{2n+1}N^+(CH_3)_2CH_2COO^-$).[26] In the same manner, it was shown that the efficiency factor pC_{20} is a linear function of the number of carbon atoms in a straight-chain hydrophobic group, increasing as the number of carbon atoms increases.[26]

Figure 1 shows the pC_{20} values for the ampholytes **14a–c** depending on the numbers of carbon of the hydrophobic chain. At pH 10, the linearity was not perfectly demonstrated due to the specific value of pK_N for each surfactant, and the not strictly similar polar heads.

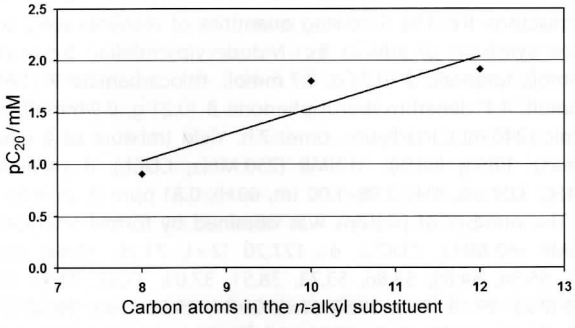


Figure 1. Effect of the hydrophobic chain length on the adsorption efficiency of compounds **14a–c** at the air/solution interface (pH 10, 25 °C).

Nevertheless the increase of the length of the hydrophobic group induced an increase of efficiency and a lowering of CMC values. The area per molecule for the homologous ampholytes **14a–c** decreases with increasing length of the carbon chain. The area value of the C8 surfactant **14a** is twice as high as the values for the C10 (**14b**) or C12 (**14c**) chain lengths owing to the potential adsorption of the part of the hydrophobic moiety at the interface. Ampholytes **14a** and **15** have the same hydrophobic chain length, but in the case of the former the amine function is integrated in a five-membered ring ($m = 1$) while for the latter the amine is placed in a six-membered ring ($m = 2$) (Scheme 4, Table 5). This modification induces a lower CMC, a higher efficiency (pC_{20}), but a lower effectiveness (surface tension at the CMC). At pH 10, the amine group is in neutral form and the ring (pyrrolidine and piperidine) seems to contribute to the hydrophobic part. The polarity of the surfactant is mainly localized at the carboxylate function.

CMC values for compounds **14a–c** were also determinated at pH = IEP (Table 6). At these pH values the CMC was significantly lower when compared to the CMC values measured at pH 10. The biggest difference was observed for compound **14b** (entry 2). The change in the conformation of the surfactant from the anionic form at $pH = pK_N$ to the neutral form at pH = IEP caused a decrease in polarity by a neutralization of these charges. This overall polarity decrease diminished the affinity for water and therefore lowered the CMC.

Table 6. CMC values of pyrrolidine compounds **14a–c** (Scheme 4).

Entry	Ampholyte	*n*	IEP	CMC [mM] pH 10	pH = IEP
1	**14a**	7	2.99	11.09	1.99
2	**14b**	9	4.12	4.04	0.21
3	**14c**	11	4.26	0.611	0.194

Conclusions

We have described a versatile method for the preparation of a new class of amphoteric surfactants. Starting from furfural obtained by dehydration of pentose-containing biomass, amporeric surfactants are obtained in only three steps. The synthesis starts with the oxidation of furfural leading to furanones. Tertiary amines obtained from fatty aldehydes are then added to these α,β-unsaturated lactones using photochemically induced radical addition. Saponification of the resulting saturated lactones leads to the final products. These reactions have been chosen on the basis of green chemistry requirements. However, for industrial applications the yield of the furfural oxidation with hydrogen peroxide must be increased. The thiocarbamate used for the addition of the amines should, for example, be used as a solid-supported reagent in order to facilitate its separation from the reaction mixture. The amine addition occurs under photocatalytic conditions. The transformation can therefore be performed with higher substrate concentrations. Thus the amount of solvent can be reduced. Further optimization of theses steps, in particular the radical addition of amines, is envisaged.

The surfactant properties of the amphoteric compounds are pH dependent. Interesting values have been detected at pH 10, where the anionic form is present. The adsorption of surfactants possessing homologous *n*-alkyl chains as hydro-

phobic part was studied. An influence of the ring size of the cyclic amine moiety was also detected.

Experimental Section

General: NMR spectra were recoded with a Bruker AC 250 (250 MHz for ^{1}H NMR and 62 MHz for ^{13}C NMR measurements). Chemical shifts are given in ppm relative to the residual solvent signal. 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 measurements were carried out with a Variant Liberty 2 (ICPAES). UV irradiation was performed with Rayonet reactors (Southern New England Ultraviolet Company, Branford, Connecticut) at $\lambda = 350$ nm. The reaction mixtures were irradiated in Pyrex tubes ($\varnothing = 1.6$ cm). Preparative chromatography was carried out with silica gel 60 A from SDS. TLC was carried out with Kieselgel 60 F254 plates from Merck. 2[5*H*]-Furanone **2**[11] and 5-hydroxy-2[5*H*]-furanone **3**[17] were synthesized as previously described.

Synthesis of tertiary amines

Pyrrolidine (13.65 g, 0.19 mol) was added to THF (250 mL) in a 2 L flask. *n*-Octanal (20 mL, 0.13 mol) and *p*-toluenesulfonic acid monhydrate (22 g, 0.13 mol) were added. Under vigorous stirring $NaBH_4$ (4.84 g, 0.13 mol) was added carefully in small portions. After this addition, stirring was continued for 6 h. A saturated solution of $NaHCO_3$ was added carefully. After separation of the phases, the aqueous phase was extracted three times with ethyl acetate. The residue was added to hydrochloric acid. The resulting mixture was extracted with ethyl acetate. By addition of NaOH, the mixture became basic and the *N*-octylpyrrolidine **5a** was extracted. The organic phase was dried with $MgSO_4$. After filtration and evaporation, **5a** was obtained in sufficient purity for further transformations.[28,29] Yield: 14.1 g (60%). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.30$ (m, 6H), 1.70–1.20 (m, 16H), 0.80 ppm (t, $J = 6.3$ Hz, 3H); ^{13}C NMR (62 MHz, $CDCl_3$): $\delta = 57.09$, 54.58 (2×), 32.21, 29.95, 29.63, 29.46, 28.13, 23.73 (2x), 23.03, 14.46 ppm; IR (film): $\nu = 2985$, 2860, 1466 cm^{-1}.

N-Decylpyrrolidine **5b**[19] was obtained from the same transformation of decanal (20 mL, 0.1 mol) and pyrrolidine (9.68 g, 0.17 mol). Yield: 12.63 g (66%). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.36$ (m, 6H), 1.66–1.16 (m, 20H), 0.77 ppm (t, $J = 6.3$ Hz, 3H); ^{13}C NMR (62 MHz, $CDCl_3$): $\delta = 56.75$, 54.23 (2×), 31.92, 29.63 (3×), 29.36, 29.18, 27.77, 23.36, 22.68, 14.46 ppm; IR (film): $\nu = 2925$, 2854, 1465 cm^{-1}.

N-Dodecylpyrrolidine **5c**[25] was obtained from the same transformation of dodecanal (30 mL, 0.14 mol) and pyrrolidine (14.52 g, 0.20 mol). Yield: 21.49 g (66%). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.36$ (m, 6H), 1.68–1.10(m, 24H), 0.76 ppm (t, $J = 6.5$ Hz, 3H); ^{13}C NMR (62 MHz, $CDCl_3$): $\delta = 57.09$, 54.68 (2×), 32.27, 30.00 (4×), 29.72, 29.53, 28.12, 23.70 (3×), 23.03, 14.41 ppm; IR (film): $\nu = 2925$, 2853, 1468 cm^{-1}.

N-Octylpiperidine **6**[30] was obtained from the same transformation of octanal with piperidine (20 mL, 0.13 mol) and piperidine (16.35 g, 0.20 mol). Yield: 16.89 g (67%). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.30$ (m, 6H), 1.70–1.00 (m, 18H), 0.72 (t, $J = 6.5$ Hz, 3H) ppm; ^{13}C NMR (62 MHz, $CDCl_3$): $\delta = 59.77$, 54.71 (2×), 31.90, 29.64, 29.33, 27.84, 27.04 (2×), 26.04, 24.57, 22.71, 14.05 ppm; IR (film): $\nu = 2931$, 2854, 1468 cm^{-1}.

Photochemically induced radical addition of tertiairy amines to 2[5H]-furanone 2

Aminolactone **8a**: *N*-Octylpyrrolidine **5a** (9.34 g, 50 mmol), furanone **2** (2 g, 25 mmol), thiocarbamate **7** (4.86 g, 75 mmol), and 4,4′-dimethoxybenzophenone **8** (0.61 g, 2.5 mmol) were added to anhydrous acetonitrile (500 mL). The resulting solution was purged with argon for about 20 min and then filled in Pyrex tubes and irradiated for 6 h. After evaporation of the solvent, the residue was subjected to flash chromatography (eluent: ethyl acetate/petroleum ether/methanol 60:35:0.5). Yield (mixture of 2 diastereomers): 3.48 g (58%). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 4.30$–3.70 (m, 4H), 3.06 (m, 4H), 2.90–1.00 (m, 44H), 0.81 ppm (t, $J = 7.0$ Hz, 3H). The number of protons was obtained by formal integration. ^{13}C NMR (62 MHz, $CDCl_3$): $\delta = 177.95$ (2×), 71.85, 70.85, 66.17, 66.06, 56.02, 55.50, 54.50, 54.36, 39.26, 37.72, 32.51 (2×), 32.27 (2×), 32.28, 30.95, 29.96 (2x), 29.72 (2x), 29.29, 29.22, 27.87, 27.64, 26.91 (2×), 23.48, 23.32, 23.08, 14.52 (2×) ppm; IR (film): $\nu = 3416$, 2926, 1778 cm^{-1}; TOFMSES$^+$ [M+H$^+$] = 268.12; Elemental analysis: calcd (%) for $C_{16}H_{29}NO_2$ (267.22): C 71.87, H 10.93, N 5.24; found: C 70.90, H 10.47, N 5.18.

Aminolactone **8b**: The following quantities of reagents were used for the synthesis of adduct **8b**: *N*-decylpyrrolidine **5b** (4 g, 19 mmol), furanone **2** (0.79 g, 9.4 mmol), thiocarbamate **7** (1.84 g, 28 mmol), 4,4′-dimethoxybenzophenone **8** (0.23 g, 0.95 mmol), acetonitrile (250 mL). Irradiation time: 6.5 h. Yield (mixture of 2 diastereomers): 1.68 g (60%). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 4.40$–3.70 (m, 4H), 3.0 (m, 4H), 2.80–1.00 (m, 52H), 0.80 (t, $J = 6.4$ Hz, 6H) ppm. The number of protons was obtained by formal integration. ^{13}C NMR (62 MHz, $CDCl_3$): $\delta = 177.95$ (2×), 71.81, 70.26, 66.14 (2×), 55.96, 53.86, 53.73, 54.32, 39.21, 37.66, 32.27, 32.29 (2×), 30.90 (2×), 30.04 (4×), 29.99 (4×), 29.72 (2×), 29.24 (2×), 27.84 (2×), 27.59 (2×), 26.87, 23.44, 23.07, 14.51 (2×) ppm; IR (film): $\nu = 2924$, 2854, 1779, 1466 cm^{-1}; TOFMSES$^+$ [M+H$^+$] = 296.17; Elemental analysis: calcd (%) for $C_{18}H_{33}NO_2$ (295.17): C 73.17, H 11.26, N 4.74; found: C 72.96, H 11.12, N 5.03.

Aminolactone **8c**: The following quantities of reagents were used for the synthesis of adduct **8c**: *N*-dodecylpyrrolidine **5c** (4.14 g, 17 mmol), furanone **2** (0.73 g, 8.7 mmol), thiocarbamate **7** (1.68 g, 27 mmol), 4,4′-dimethoxybenzophenone **8** (0.21 g, 0.9 mmol), acetonitrile (240 mL). Irradiation time: 7 h. Yield (mixture of 2 diastereomers): 1.85 g (66%). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 4.54$–4.00 (m, 4H), 3.07 (m, 4H), 2.98–1.00 (m, 60H), 0.81 ppm (t, $J = 6.35$ Hz, 6H). The number of protons was obtained by formal integration. ^{13}C NMR (62 MHz, $CDCl_3$): $\delta = 177.20$ (2×), 71.20, 69.64, 65.69, 65.61, 55.34, 54.85, 53.86, 53.73, 38.51, 37.03, 31.92, 31.78 (2×), 30.33 (2×), 29.54 (4×), 29.52 (4×), 29.44, 29.35 (2×), 29.30 (2×), 29.23, 28.57, 28.52 (2×), 27.28, 27.05 (2×), 26.34, 26.35, 22.86, 22.71, 13.98 (2×) ppm; IR (film): $\nu = 2921$, 2849, 1771, 1467 cm^{-1}; TOFMSES$^+$ [M+H$^+$] = 324.3, [2M + H$^+$] = 647.6; Elemental analysis: calcd (%) for $C_{20}H_{37}NO_2$ (323.51): C 74.25, H 11.53, N 4.33; found: C 74.53, H 11.53, N 4.53.

Aminolactone **9**: The following quantities of reagents were used for the synthesis of adduct **9**: *N*-octylpyrrolidine **6** (4.68 g, 24 mmol), furanone **2** (1.00 g, 12 mmol), thiocarbamate **7** (2.31 g, 36 mmol), 4,4′-dimethoxybenzophenone **8** (0.29 g, 1 mmol), acetonitrile (500 mL), Irradiation time: 18 h. Yield (mixture of 2 diastereomers): 1.90 g (57%). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 4.60$–3.90 (m,

4H), 3.20–1.00 (m, 52H), 0.85 ppm (t, J=6.2 Hz, 6H). The number of H were obtained by formal integration. ^{13}C NMR (62 MHz, $CDCl_3$): δ=174.88, 175.75, 72.33, 70.52, 62.45, 66.10, 52.36, 51.02, 50.85, 49.88, 36,02, 35,85, 32.53 (2×), 32.23 (2×), 32.74, 29.95, 29.71 (2×), 27.87, 27.80, 27.45 (2×), 26.55 (2×), 24.27, 23.79, 23.58, 23.28, 23.04, 22.99, 22.14, 14.48 (2×) ppm; IR (film): ν=2985, 2875, 1770, 1468 cm^{-1}. TOFMSES$^+$ [M+H$^+$]=282.02; Elemental analysis: calcd (%) for $C_{17}H_{31}NO_2$ (281.21): C 72.59, H 11.03, N 4.97; found: C 72.60, H 10.96, N 4.98.

Synthesis of 2-alkoxy-2[5*H*]-furanones

Alkoxyfuranone **11a**: A solution of 5-hydroxy-2[5*H*]-furanone **3** (15 g, 0.15 mol), 1-octanol (19.6 g, 0.15 mol), and *p*-toluenesulfonic acid (0.26 g, 1.5 mmol) in toluene (60 mL) was heated under reflux in a Dean–Stark apparatus for about 1 h. After evaporation of the solvent, the residue was distilled in high vacuum. Yield: 26.6 g (83%). bp: 130 °C (0.05 mbar); ^{1}H NMR (250 MHz, $CDCl_3$): δ=7.20 (m, 1H), 6.18 (m, 1H), 5.89 (m, 1H), 4.00–3.90 (m, 2H), 1.70–1.00 (m, 14H,), 0.84 ppm (t, J=6.54, 3H); ^{13}C NMR (62 MHz, $CDCl_3$): δ= 173.26, 150.93, 125.30, 103.86, 71.03, 32.15, 29.83, 29.65, 29.56, 26.24, 23.01, 14.46 ppm; IR (film): ν=2927, 2857, 1794, 1763, 1138 cm^{-1}; TOFMSES$^+$ [M+Na$^+$]=235.07; Elemental analysis: calcd (%) for $C_{12}H_{20}O_3$ (212.14): C 67.89, H 9.50; found: C 67.69, H 9.54.

Alkoxyfuranone **11b**: The following quantities of reagents were used for the synthesis of alkoxyfuranone **11b**: 5-Hydroxy-2[5*H*]-furanone **3** (15 g, 0.15 mol), 1-decanol (23.9 g, 0.15 mol), *p*-toluenesulfonic acid (0.26 g, 1.5 mmol), toluene (60 mL). Yield: 27.0 g (75%). bp: 130 °C (0.05 mbar); ^{1}H NMR (250 MHz, $CDCl_3$): δ=7.30 (dd, J= 1.15/4.55 Hz, 1H), 6.20 (d, J=4.8 Hz, 1H), 5.90 (d, J=1.2 Hz, 1H), 3.80 (m, 2H), 2.00–1.10 (m, 16H), 0.90 ppm (t, J=6.2 Hz, 3H); ^{13}C NMR (62 MHz, $CDCl_3$): δ=172.60, 151.05, 124.99, 103.99, 70.71, 32.18, 29.84, 29.78 (2x), 29.62, 26.16, 22.95, 14.35. IR (film): ν= 2925, 2855, 1794, 1763, 1138 cm^{-1}. TOFMSES$^+$ [M+Na$^+$]=263.10. Elemental analysis: calcd (%) for $C_{14}H_{24}O_3$ (240.17): C 67.89, H 9.50; found: C 67.69, H 9.54.

Alkoxyfuranone **11c**: The following quantities of reagents were used for the synthesis of alkoxyfuranone **11c**: 5-Hydroxy-2[5*H*]-furanone **3** (15 g, 0.15 mol), 1-dodecanol (27.7 g, 0.15 mol), *p*-toluenesulfonic acid (0.26 g, 1.5 mmol), toluene (60 mL). Yield: 33.5 g (83%). bp: 130–140 °C (0.05 mbar); ^{1}H NMR (250 MHz, $CDCl_3$): δ= 7.30 (dd, J=1.2/4.6 Hz, 1H), 6.10 (d, J=4.8 Hz, 1H), 5.89 (d, J= 1.2 Hz, 1H), 3.68 (m, 2H), 2.00–1.10 (m, 20H), 0.90 ppm (t, J=6.53, 3H); ^{13}C NMR (62 MHz, $CDCl_3$): δ=172.13, 150.44, 124.35, 103.15, 70.06, 31.63, 29.37 (3x), 29.20 (2x), 29.07 (2x), 25.58, 22.37, 13.74 ppm; IR (film): ν=2919, 2850, 1795, 1761, 1130 cm^{-1}; TOFMSES$^+$ [M+Na$^+$]=291.12; Elemental analysis: calcd (%) for $C_{14}H_{24}O_3$ (268.20): C 71.60, H 10.52; found: C 71.66, H 10.68.

Photochemically induced radical addition of *N*-methylpyrrolidine 12 to 2-alkoxy-2[5*H*]-furanones 11a–c

Aminolactone **13a**: *N*-Methylpyrrolidine **12** (11.2 g, 132 mmol), 2-octyloxy-2[5*H*]-furanones **11a** (7 g, 33 mmol), and 4,4′-dimethoxybenzophenone **8** (0.80 g, 3.3 mmol) were added to anhydrous acetonitrile (400 mL). The resulting solution was purged with argon for about 20 min and then filled in Pyrex tubes and irradiated for 20 min. After evaporation of the solvent, the residue was subjected to flash chromatography (eluent: ethyl acetate/petroleum ether/methanol 60:30:1). Yield (mixture of 2 diastereomers): 1.56 g (16%).^{1}H NMR (250 MHz, $CDCl_3$): δ=5.50 (2s, 2H), 4.00–3.40 (m, 4H), 3.10–2.00 (m, 26H), 1.90–1.00 (m, 30H), 0.90 ppm (t, J= 7.0 Hz, 6H). The number of protons was obtained by formal integration. ^{13}C NMR (62 MHz, $CDCl_3$): δ=177.06, 176.88, 107.15, 106.27, 70.25, 70.15, 66.91, 65.90, 57.59, 57.20, 43.31, 42.97, 41.16, 40.95, 32.16 (2x), 31.62, 29.77 (2×), 29.66 (2×), 29.57, 29.22, 27.22, 26.52 (2×), 26.31 (2×), 23.01 (2×), 22.81, 22.60, 14.47 (2×) ppm; IR (film): ν=2927, 2855, 2782, 1787, 1116 cm^{-1}; TOFMSES$^+$ [M+H$^+$]= 298.17; Elemental analysis: calcd (%) for $C_{17}H_{31}NO_3$ (297.23): C 68.65, H 10.51, N 4.71; found: C 68.65, H 10.27, N 4.36.

Aminolactone **13b**: The following quantities of reagents were used for the synthesis of adduct **13b**: *N*-Methylpyrrolidine **12** (10 g, 117 mmol), 2-decyloxy-2[5*H*]-furanone **11b** (7 g, 29 mmol), 4,4′-dimethoxybenzophenone **8** (0.70 g, 2.9 mmol), anhydrous acetonitrile (400 mL). Yield (mixture of 2 diastereomers): 2.48 g (26%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=5.50–5.00 (2 s, 2H), 4.00–2.10 (m, 28H), 2.10–1.00 (m, 36H), 0.90 ppm (t, J=7.8 Hz, 6H). The number of protons was obtained by formal integration. ^{13}C NMR (62 MHz, $CDCl_3$): δ=176.61, 176.47, 108.37, 107.49, 71.48, 71.38, 68.19, 67.15, 58.73, 58.85, 44.47, 44.19, 42.30, 42.04, 33.49 (2×), 32.92, 31.15 (3×), 30.99 (3×), 30.92 (3×), 30.49, 28.44, 27.73 (2×), 27.54 (2×), 24.27 (2×), 23.93, 23.76, 15.70 (2×) ppm. IR (film): ν=2925, 2854, 2782, 1788, 1115 cm^{-1}; TOFMSES$^+$ [M+H$^+$]=326.18; Elemental analysis: calcd (%) for $C_{19}H_{35}NO_3$ (325.26): C 70.11, H 10.84, N 4.30; found: C 69.93, H 10.73, N 4.09.

Aminolactone **13c**: The following quantities of reagents were used for the synthesis of adduct **13c**: *N*-Methylpyrrolidine **12** (12.7 g, 149 mmol), 2-dodecyloxy-2[5*H*]-furanone **11c** (10 g, 37 mmol), 4,4′-dimethoxybenzophenone **8** (0.90 g, 3.7 mmol), anhydrous acetonitrile (500 mL). Yield (mixture of 2 diastereomers): 2.65 g (20%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=5.60–5.00 (2s, 2H), 4.50–2.00 (m, 22H), 1.90–1.00 (m, 48H), 0.90 ppm (t, J=6.7 Hz, 6H). The number of protons was obtained by formal integration. ^{13}C NMR (62 MHz, $CDCl_3$): δ=176.86 (2×), 107.10, 106.24, 70.31, 70.20, 67.00, 65.98, 57.49, 57.10, 43.23, 42.92, 41.08, 40.81, 33.19 (3×), 31.72, 30.02 (4×), 29.72 (4×), 29.31 (4×), 28.95, 27.25, 26.52, 26.32 (2×), 23.06 (3×), 22.71, 22.56, 14.49 (2×) ppm. IR (film): ν=2924, 2853, 1788, 1733, 1466, 1115 cm^{-1}; TOFMSES$^+$ [M+H$^+$]=354.29; Elemental analysis: calcd (%) for $C_{21}H_{39}NO_3$ (353.29): C 71.34, H 11.12, N 3.96; found: C 69.65, H 10.73, N 3.02.

Synthesis of amphoteric surfactants

Compound **14a**: NaOH (1 M, 7.8 mL) was added to a solution of aminolactone **8a** (2.1 g, 7.8 mmol) in THF (7.9 mL). The resulting mixture was heated under reflux for 12 h. Cooled to room temperature, the mixture was extracted three times with ethyl acetate (3× 10 mL). The aqueous solution was then neutralized with hydrochloric acid and finally concentrated with a lyophilizer. Yield 2.35 g (87%). ^{1}H NMR (250 MHz, D_2O): δ=3.60–2.70 (m, 8H), 2.50–1.00 (m, 48H), 0.74 ppm (t, J=6.5 Hz, 6H) The number of protons was obtained by formal integration. ^{13}C NMR (62 MHz, D_2O): δ=180.85, 180.16, 70.64, 68.93, 63.60, 62.28, 55.18, 54.81, 53.92, 53.39, 37.85, 37.66, 37.55, 37.22, 35.16, 31.90 (2×), 29.17, 26.60, 26.22, 26.07, 25.46, 24.85, 23.96 (2x), 23.77, 22.98, 22.78, 22.60, 14.17 (2×) ppm; IR (KBr): ν=3404, 2956, 2928, 1581, 1405, 1076 cm^{-1}; TOFMSES$^+$ [M+H$^+$]=286.2, [M+Na$^+$]=309.2; Elemental analysis: calcd (%) for $C_{16}H_{31}NO_3$·NaCl (343.38): C 55.94, H 9.03, N 4.08, Na 6.69; found: C 48.87, H 8.09, N 3.44 Na 8.53. The value for Na was determined by atomic absorption spectroscopy.

Compound **14b**: The following quantities of reagents were used for the synthesis of amphoteric adduct **14b**: NaOH (1 M, 18.5 mL) was added to a solution of aminolactone **8b** (5.4 g, 18.4 mmol) in THF (18.5 mL). Yield: 3.75 g (55%). ^{1}H NMR (250 MHz, D_2O): δ=

3.80–2.60 (m, 8H), 2.50–1.00 (m, 56H), 0.74 ppm (t, J=6.5 Hz, 6H) The number of protons was obtained by formal integration. ^{13}C NMR (62 MHz, D_2O): δ=181.39, 180.60, 68.27, 67.85, 64.28, 62.77, 55.92, 54.46 (2×), 53.92, 53.18, 39.68, 37.95, 36.22, 35.73, 31.82 (3×), 29.66 (3×), 29.16 (2×), 28.33, 27.41, 27.13, 26.39 (2×), 23.92 (4×), 23.14 (2×), 22.49, 13.70 (2×) ppm. IR (KBr): ν=3384, 2925, 2854, 1574, 1407, 1033 cm^{-1}; TOFMSES$^+$ [M+H$^+$]=314.3, [M+Na$^+$]=336.3; Elemental analysis: calcd (%) for $C_{18}H_{35}NO_3$·NaCl (371.22): C 58.18, H 9.43, N 3.74, Na 6.18; found: C 56.54, H 8.95, N 3.56 Na 9.26. The value for Na was determined by atomic absorption spectroscopy.

Compound **14c**: The following quantities of reagents were used for the synthesis of amphoteric adduct **14c**: NaOH (1 M, 6.12 mL) was added to a solution of aminolactone **8c** (1.97 g, 6.08 mmol) in THF (6.2 mL). Yield: 1.30 g ppm (53%). ^{1}H NMR (250 MHz, D_2O): δ=3.50–1.10(m, 16H), 1.10–0.6 (m, 56H),0.57 ppm (t, J=6.5 Hz, 6H) The number of protons was obtained by formal integration. ^{13}C NMR (62 MHz, D_2O): δ=179.35, 178.87, 67.50, 67.05, 62.34, 61.17, 53.84, 53.14, 51.94, 51.75, 37.36, 36.41, 34.61, 34.28, 30.57 (3×), 28.55 (4×), 28.47 (3×), 28.22, 28.10 (3×), 26.52, 25.71, 25.34, 24.31, 22.80, 21.71, 21.65, 21.21, 12.49, 12.38 ppm; IR (KBr): ν= 3423, 2956, 2925, 1579, 1401, 1075 cm^{-1}; TOFMSES$^+$ [M+H$^+$]= 342.3, [M+Na$^+$]=364.3; Elemental analysis: calcd (%) for $C_{20}H_{39}NO_3$·NaCl (399.25): C 60.08, H 9.76, N 3.50, Na 5.75; found: C 67.13, H 9.33, N 3.29 Na 7.8. The value for Na was determined by atomic absorption spectroscopy.

Compound **15**: The following quantities of reagents were used for the synthesis of amphoteric adduct **15**: NaOH (1 M, 6.63 mL) was added to a solution of aminolactone **9** (1.85 g, 6.58 mmol) in THF (6.6 mL). Yield: 1.23 g (52%). ^{1}H NMR (250 MHz, D_2O): δ=4.00–2.80 (m, 8H), 2.79–1.00 m, 52H), 0.70 ppm (t, J=6.3 Hz, 6H) The number of protons was obtained by formal integration. ^{13}C NMR (62 MHz, D_2O): δ=180.53, 180.19, 70.80, 70.68, 65.80, 61.68, 53.46 (2×), 52.48 (2×), 37.66 (2×), 36.53 (2×), 35.89, 35.24, 31.69 (2×), 28.89 (4×), 29.48 (2×), 23.75 (2×), 23.30, 22.58 (4×), 22.09, 14.01 (2×) ppm. IR (KBr): ν=3423, 2957, 2924, 1580, 1404, 1076 cm^{-1}; TOFMSES$^+$ [M+H$^+$]=300.3, [M+Na$^+$]=322.3; Elemental analysis: calcd (%) for $C_{17}H_{33}NO_3$·NaCl (357.20): C 57.10, H 9.23, N 3.91, Na 6.42; found: C 36.69, H 7.26, N 2.10 Na 11.2. 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).

Determination of pK_N: The pK_N values were determined by titration at 23±2 °C with 0.1 N hydrochloric acid using a WTW inolab 720 pH meter. The pK_N was calculated as the pH of the solution at half the neutralization volume (the inflection of the inverse S-shape curve).

Zeta potential and determination of IEP: The zeta potentials were measured by using a 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 values. Once the electrophoretic mobility was measured, the zeta potential value was calculated using the Smoluchowski equation [Equation (7)]. Three to five replicate measurements were performed at each pH value. All measurements were performed at room temperature (22±2 °C). The plot of zeta potential against pH was well described by a four-parameters logistic model:

$$Y = A_1 + \frac{A_1 - A_2}{1 + \exp(-2x(a + b\log(X)))} \quad (7)$$

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 IEPs were determined for the pH where the zeta potential was equal to zero after nonlinear regression by fitting the curve by the least squares method with the freeware software Kyplot (Koichi Yoshioka, 1997–2001).

Surface tension, CMC, and area per molecule: The plots of the surface tension against ln$C$ for the surfactants were obtained from freshly prepared solutions and by the Wilhelmy plate method with a automatic tensiometer (KRUSS K100, Germany) at 25±0.5 °C.

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