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ORIGINAL CONTRIBUTION

New anionic gemini surfactant based on EDTA accessible by convenient synthesis

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Abstract A straightforward, broadly applicable synthetic strategy to anionic dimeric ("gemini") surfactants is demonstrated, reacting ethylenediamine tetraacetic acid (EDTA) dianhydride with fatty amines. Characteristic surfactant properties in water are examined for the model compound based on *N*-methyldodecylamine. The new dimeric surfactant exhibits a low value for the critical micellization concentration (cmc$<10^{-4}$ mM), low surface tension at the cmc, and an enhanced solubilization capacity in comparison with a monomeric reference surfactant, sodium laurate. In particular, solutions of the gemini surfactant are remarkably stable in hard water, compared to conventional carboxylate surfactants.

Keywords Gemini surfactant · Synthesis · EDTA

Introduction

The "dimerization" of two independent surfactant units results in new surfactant types, namely, the so-called "bola" amphiphiles, if dimerization occurs via the hydrophobic chain end, and the so-called "gemini" surfactants, if dimerization occurs via the hydrophilic groups [1]. The growing interest in the latter is due to their particularly appealing properties [1–4]. For instance, gemini surfactants exhibit remarkably lower critical micellization concentrations (cmc), compared to their monomeric analogues. Although anionic surfactants are of the highest practical interest, most reports on gemini surfactants deal so far with cationic ones, in particular, from the family of alkanediyl-α,ω-bis(dimethylalkylammonium bromide)s [3]. These are easy to synthesize and to purify and can be often produced in a one-pot reaction. In contrast, the synthesis of anionic surfactants is usually more complicated. Thus, only few anionic geminis with sulfonate [5–13], sulfate [6, 14–16], phosphate [16–20], and carboxylate head groups [21–30] have been reported and their properties, such as cmc, surface tension, foaming, and wetting abilities investigated. Therefore, alternative, more accessible structures would be most welcome. In this context, we designed a straightforward, mild synthetic route to a carboxylate gemini surfactant, which should allow for versatile variations, contrasting with most pathways towards the anionic geminis reported so far. Some fundamental properties of the new compound were examined.

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Experimental section

Materials

N-methyldodecylamine (97%, M_r=199.38), ethylenediaminetetraacetic acid (EDTA) dianhydride (98%, M_r=256.22), $CaCl_2$ (>97%, M_r=110.98) and *para*-xylene (>98%, M_r=106.17) were used as received from Aldrich. Sodium laurate (SL) ($C_{11}H_{23}COONa$, M_r=222.32), sodium dodecylsulfate (SDS) ($C_{12}H_{25}OSO_3Na$, M_r=288.38), and benzoylacetone ($C_{10}H_{10}O_2$, M_r=162.19) were from Fluka. Standard solution of NaOH (0.1 M aq) and hydrochloric acid (0.1 M aq) were from Merck. Solvents were analytical grade. Water used for

all experiments was purified by a Millipore Qplus water purification system (resistance 18 MΩ cm).

Synthesis of the gemini surfactant **1**: *N*-methyldodecylamine (3.20 g, 16 mmol) and EDTA anhydride (2.05 g, 8 mmol) suspended in CH_3OH (50 ml) are reacted for 22 h at 40–45 °C. The anhydride particles progressively disappear as the reaction progresses. After cooling of the sample to room temperature, the remaining particles are filtered off. The reaction mixture is evaporated to give a yellowish oil. Acetone is then added until a white solid precipitates. The precipitate is filtered off and is further purified by dissolution in $CHCl_3$ and precipitation in acetone, to yield a white powder (3.7 g, 71%). Elemental analysis results ($C_{36}H_{70}N_4O_6$, MW=654.94 g/mol): Calculated: C 66.02; N 8.55; H 10.77; Found: C 65.97; N 8.93; H 11.22; Mass Spectrometry (APCI, +) Signal at *m/z*= 655.52 [M+1]; Fourier transform-infrared (FT-IR) spectroscopy (KBr, selected bands in cm^{-1}) 2,958; 2,921; 2,852; 1,712; 1,656; 1,639; 1,373; 1,196; 893.

Finally, the intermediate product is neutralized with sodium hydroxide (1 M aq, 2 equivalents), and the obtained solution is freeze–dried to give gemini surfactant **1** in quantitative yield a colorless, hygroscopic powder. Proton nuclear magnetic resonance (^1H NMR) ($CDCl_3$, 300 MHz, δ in ppm): 0.88 (*t*, 6H, CH_3–); 1.15–1.35 (*m*, 36H, $–(CH_2)_9–$); 1.46 (*m*, 4H, $–CH_2–C–N–CO$); 2.39 (*m*, 4H, $N–CH_2–CH_2–N$); 2.86 (*s*, 6H, $CO–N–CH_3$); 2.95–3.35 (*m*, 4H+4H+4H, $C–CH_2–N–CO$, $N–CO–CH_2–N$, $N–CH_2–COO$). ^{13}C NMR ($CDCl_3$, 75 MHz, δ in ppm): 14.06 ($CH_3–$); 22.65 ($CH_3–CH_2–$); 27.09 ($N–CH_2–CH_2–CH_2–$); 28.45 ($N–CH_2–CH_2–CH_2$); 29.5–29.7 ($–(CH_2)_6–$); 31.89 ($CH_3–CH_2–CH_2–$); 33.76, 34.52 (CH_3NCH_2); 48.11, 49.11 ($N–CH_2–CH_2–N$); 52.23 (CH_3NCH_2); 55.66, 59.36 ($CH_2–CO–N$ + $CH_2–CO–O$); 170.91 (N–C=O); 177.75, 178.13 (O–C=O). Elemental analysis ($C_{36}H_{68}N_4O_6Na_2$, $2H_2O$ MW=734.96 g/mol): Calculated: C 58.83; N 7.62; H 9.87; Found: C 58.63; N 7.75; H 9.41. According to thermogravimetric analysis, about 5 wt% water is contained in the sample, which is consistent with the dihydrate form found by elemental analysis; thermal decomposition starts above 180 °C.

Methods

^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were taken with a Bruker Avance 300 apparatus. Mass spectra were recorded by a TSQ Quantum spectrometer (Thermo Finnigan). Elemental analysis was done with a model EA 1110 (CHNS-O) from CE Instruments. IR-spectra were taken from KBr pellets with a Bruker IFS FT-IR spectrometer 66/s. Ultraviolet (UV) spectra were recorded with a CARY UV-vis spectrophotometer (Varian). Thermal stability was measured with a TGA/SDTA 851 thermal gravimetric analyzer (Mettler Toledo). Aggregate sizes were measured by a temperature controlled High Performance Particle Sizer (Malvern Instruments, 633 nm laser source, optical path 10 mm). Equipment and experimental set-ups to determine Krafft temperatures, surface tension measurements (Du Noüy ring method), and solubilization studies are described elsewhere [31, 32].

Acid–base titration was performed using a 670 Titroprocessor (Metrohm). Hydrochloric acid, 0.1 M, was added progressively to the anionic dimer solution via a Metrohm 665 Dosimat, and the pH was measured with a pH electrode Metrohm 6.0233.100. Gemini **1** in its acidic form (0.1217 g, $nNH^+–CH_2–COO^-$=0.372 mmol) was first neutralized with excess NaOH (6 ml of 0.1 M NaOH, i.e., 0.6 mmol). The initial pH value of the solution with a calculated molar excess of 0.228 mmol of NaOH is 11.80. Subsequently, the solution was titrated with 0.1 M HCl.

To determine the critical micellization concentration (cmc) by solubilization of the solvatochromic probe benzoylacetone, various volumes of a starting surfactant solution (compound neutralized, pH of solutions near 7) were diluted in graduated flasks by adding precise volumes of the stock solution of the probe (0.05 g/l) and completing with milliQ water, so that the final concentration of the probe in each surfactant solution is 0.001 wt%. The evolution of the absorbance of the enol form of benzoylacteone at 315 nm with increasing surfactant concentration is followed. The onset of the increase in the absorbance trace is taken as the cmc value.

The stability of surfactants in hard water was determined by recording the turbidity of surfactant solutions upon addition of aliquots of a stock solution of aqueous $CaCl_2$ (concentration 0.5 g/l=4.5 mmol/l). The computer-assisted titration was performed in a thermostated glassware at 30 °C under stirring. The turbidity was recorded as a function of the amount of calcium chloride added to 25 ml of surfactant solution via a self-made turbidity sensor previously described [33]. Micellar solutions of SL and gemini **1** with a concentration of 2 g/l (9 and 5.7 mM of alkyl chains, respectively) were used for measurements.

For quantitative solubilization studies, 10 mg of surfactant is dissolved in 1 ml of D_2O (concentration ≫ cmc of the studied surfactants). After adding about 0.4 ml of *p*-xylene, the mixture is vigorously shaken and allowed to phase separate for 24 h. The relative amounts of surfactant and solubilized material are quantified by ^1H-NMR, by comparing the intensity of a signal characteristic for *p*-xylene (singlet at 6.81 ppm for aromatic protons, and singlet at 2.03 ppm for methyl protons) to the intensity of a characteristic signal of the surfactant: for SL, the multiplet at 1.43 ppm corresponding to the $–CH_2–CH_2–COO^-$ group was taken, for SDS the triplet at 3.90 ppm of the $–CH_2–OSO_3^-$ group, and for gemini **1**, the multiplet at 1.34 ppm of the $–CH_2–CH_2–NCO<$ group.

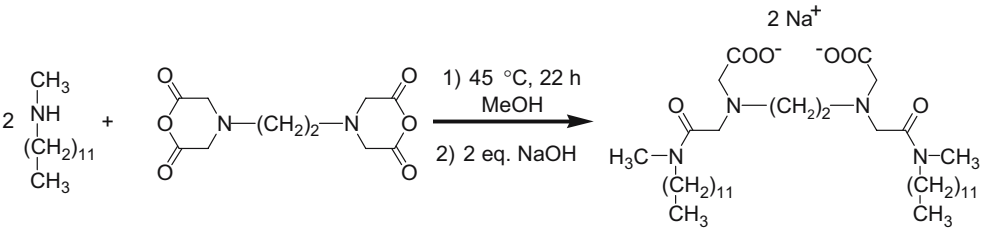

Fig. 1 Schematic synthesis of the gemini surfactant **1** from EDTA anhydride

Results and discussion

Synthesis and molecular characterization

Recently, a straightforward synthesis to anionic carboxylate gemini surfactants was reported, by adding 2 equivalents of long chain alkenyl succinic anhydride to a primary diamine, thus producing mixtures of gemini isomers [23, 24]. The striking simplicity of this approach is unfortunately counterbalanced by the product mixture obtained. We redesigned this appealing chemical approach by reacting a dianhydride with 2 equivalents of a simple secondary fatty amine to prepare a novel type of carboxylate gemini surfactant (Fig. 1), thus, avoiding the drawbacks of regioselectivity, for example. Moreover, the available choice of fatty amines is much larger than that of long alkyl chain bearing anhydrides. Also, the use of tetraacid dianhydrides exploits a different pool of commercial starting compounds, thus enlarging the versatility of the synthetic methodology. As a model case, *N*-methyldodecylamine and ethylenediaminetetraacetic acid dianhydride (EDTA-dianhydride) were used as reagents. Both are commercially available and inexpensive. This adds to the attractivity of the proposed synthetic approach. The reaction proceeds under mild conditions and is effective. Simple precipitation procedures suffice to give a clean product (Fig. 2). The secondary amine dodecylmethylamine was preferred over the analogous primary dodecylamine, as the tertiary amides formed should increase the hydrophilicity of the head group. Also, intermolecular H-bonding is avoided, which usually leads to high Krafft temperatures [34].

Acidic titration of the anionic gemini **1** was performed to determine the different species present in solution as a function of the pH (Fig. 3). The derivative of the titration curve exhibits three maxima corresponding to three equivalent points (Fig. 3). The first equivalent point (E_0) corresponds to the neutralization of the excess NaOH added before the titration to convert the surfactant from its acidic to its anionic form. The second equivalent point E_1 at pH= 8.51 corresponds to the addition of one equivalent proton to the anionic dimer. It can be assumed that the protonation of one tertiary amine occurs, as an amine is more basic than a carboxylate group. The third equivalent point E_2 at pH 4.98 is attributed to the protonation of the second amine of the spacer group. The different equilibria involved in the titration are schematized in Fig. 4. From the titration data, the protonation constants pK_{a1} and pK_{a2} are calculated as:

$$pK_a = pH + \log([base]/[acid]) \quad (1)$$

with pK_a=pH at the half equivalence.

Values for pK_{a1} and pK_{a2} were found to be 10.0 and 6.8, respectively (Fig. 3). These are much higher than the pK_a values of carboxylic acid-based surfactants (see e.g., 30), thus corroborating that the protonation takes place at the amine sites of the compounds. The surfactant precipitates in the neutral, zwitterionic form (below pH values of 5, see Fig. 3), as may have been expected. Still, the compound does not redissolve when lowering the pH further down to pH 0. Possibly, the insolubility of the new dimeric surfactant at low pH in the fully protonated, i.e., dicationic

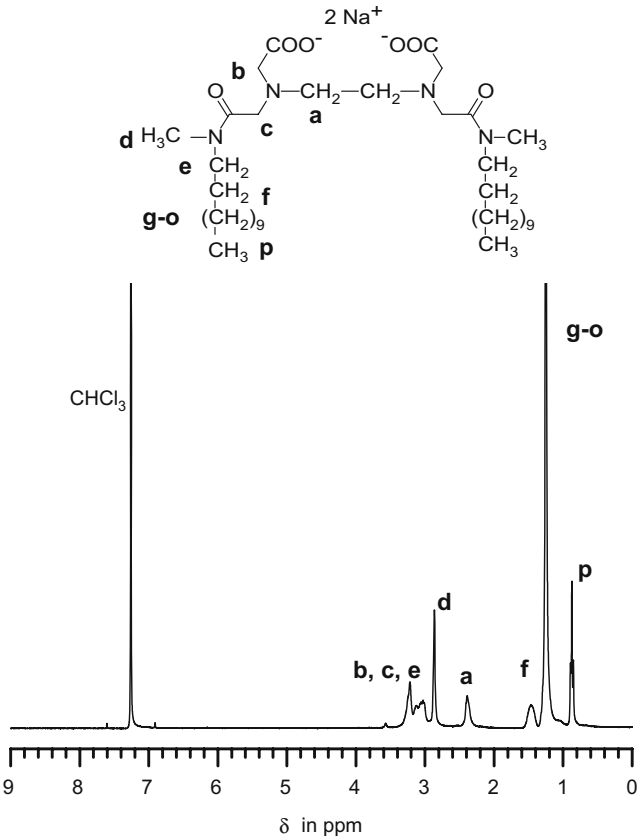

Fig. 2 ^{1}H-NMR spectrum (300 MHz) of neutralized gemini surfactant **1** in $CDCl_3$

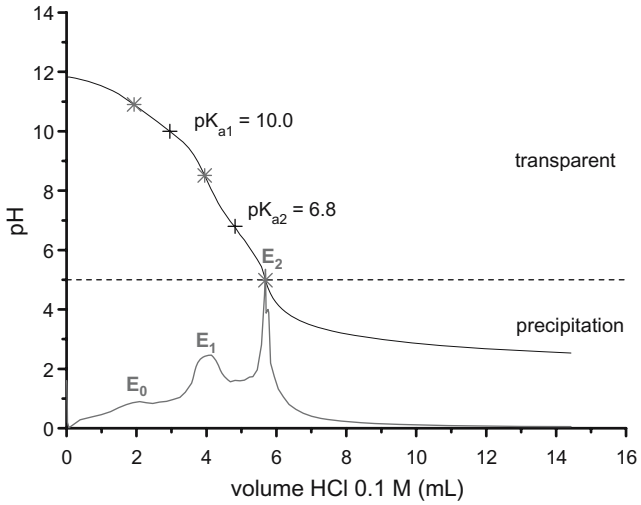

Fig. 3 Titration curve by addition of HCl (0.1 M) to surfactant **1** previously neutralized with a known excess of NaOH and its derivative giving the equivalent points (E_0–E_2). The *dotted line* indicates a visual change in the aspect of the solution (from transparent to turbid)

form is a consequence of intermolecular H-bonding, giving rise to a high Krafft temperature.

Surfactant properties

The new gemini surfactant **1** is readily soluble as sodium salt in water at ambient temperature and neutral pH. Whereas the common surfactant SL exhibits a Krafft temperature, T_{Krafft} of 21.5 °C, gemini **1** has a T_{Krafft} below 0 °C. Low Krafft temperatures have been reported for gemini surfactants occasionally before [29, 31, 32]. But in the special case of gemini **1**, the tertiary amide design is assumed to be particularly helpful.

The micellization of gemini **1** at about neutral pH was studied by probe solubilization (Table 1), exploiting the keto-enol tautomerism of benzoylacetone [35]. The tautomerism depends sensitively on the molecular environment, with two characteristic absorption bands in aqueous solution at about 250 and 315 nm for the ketone and enol form, respectively. The probe is more enolized in both polar and nonpolar organic solvents than in water [36]. Thus, the absorbance of the enol form increases sharply above the cmc, whereas the absorbance of the keto form decreases, enabling an accurate cmc determination for common nonionic and ionic surfactants [35, 37]. Figure 5 illustrates the evolution of the UV spectra of the probe with increasing concentration of gemini surfactant **1**. The presence of an isosbestic point at λ=280 nm points to an equilibrium between only two species in solution. From a certain concentration, the absorbance at 315 nm of the enol form of the probe increases, while the absorbance at 250 nm for the keto form decreases, revealing the micellization of the surfactant (Fig. 5). The plot of the absorbance at 315 nm (or the absorbance at 250 nm) vs the concentration of surfactant gives the cmc as 0.06 mmol/l (Fig. 6).

Table 1 Surface activity and micellization data of gemini surfactant **1** and reference carboxylic type surfactant "monomer" sodium laurate

Surfactant	T_{Krafft} (°C)	cmc[a] (g/l)	cmc[a] (mmol/l)	σ_{cmc}[a] (mN/m)	cmc [b] (mmol/l)
Sodium laurate	21.5	4.4[c]	20[c]	37.5[c]	
SDMA	<0[d]	23[d]	76[d]	41[d]	
1[e]	<0	0.015	0.02	31	0.06
1[f]	<0	0.020	0.03	35	

[a] Measured by tensiometry
[b] Measured by solubilization of probe benzoylacetone
[c] Measured at pH 7–8 (neutralized compound redissolved in water)
[d] Measured at pH 12 (phosphate buffer: [Na_3PO_4]=0.01 M)
[e] Measured at pH 10; value taken from Zhu et al. [39]
[f] Measured at neutral pH; value taken from Tsubone et al. [26]

The surface-active behavior of gemini **1** is illustrated in Fig. 7, and derived key parameters are summarized in Table 1. The surface tension curves present virtually no minimum, indicating the high purity of the substance [38]. The break in the surface tension vs log(concentration) curves indicates that gemini **1** forms micelles at room temperature, at pH 7–8 and pH 12, with values for the critical micellization concentration (cmc) of 0.02 and 0.03 mmol/l, respectively (Table 1). These values agree reasonably well with the one derived from the solubilization study of benzoylacetone. The cmc values are considerably lower than that of the monomeric reference carboxylate surfactants SL (20.0 mmol/l at pH 10) [15] or sodium *N*-dodecanoyl-*N*-methyl-β-alanate (SDMA) (7.6 mmol/l or 2.3 g/l at pH 10.5) [26]. This result goes along with various reports comparing monomeric and dimeric surfactants [3, 32, 39, 40]. In fact, the low cmc value of the new gemini is in

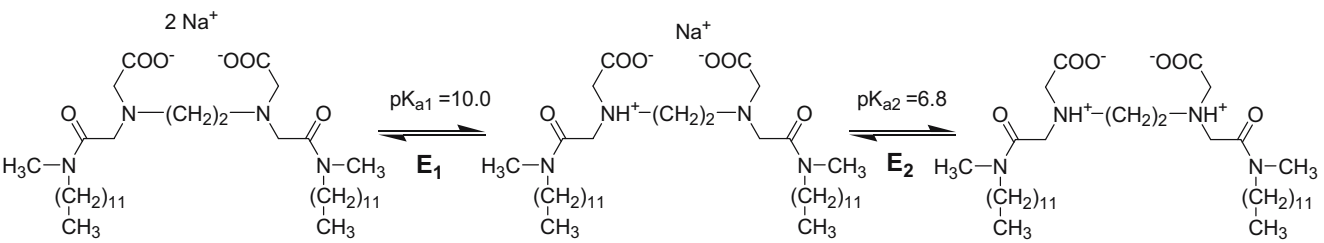

Fig. 4 Transitions occurring during the titration of gemini **1** with HCl

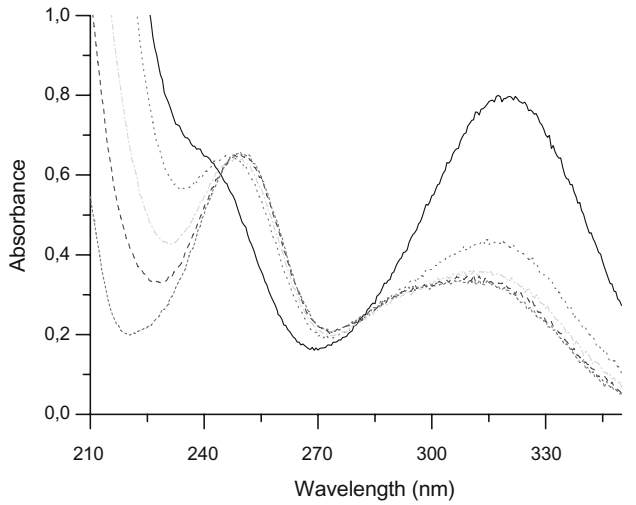

Fig. 5 UV-vis spectra of probe benzoylacetone in water after adding 0.002 g/l (*green broken line*), 0.030 g/l (*blue broken line*), 0.06 g/l (*turquoise broken line*), 0.120 g/l (*red broken line*), 0.15 g/l (*black line*) of gemini **1**

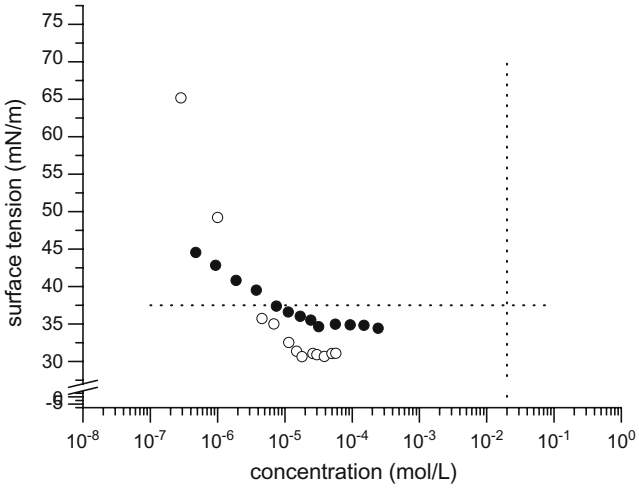

Fig. 7 Surface tension vs concentration curves of surfactant **1** at neutral pH (*dots*) and pH 12 (*filled circles*). *Vertical and horizontal dotted lines* are a guide for the eyes, positioning cmc and σ_{cmc} values of reference surfactant SL (at pH 10), respectively

the same range as those found for other carboxylate gemini surfactants with dodecyl chains. For instance, the cmc value of 1,2-bis (*N*-β-carboxypropanoyl-*N*-dodecylamino)ethane was reported as 0.01 mmol/l at pH 11–12 [25]; while the sodium salt of *N*,*N*′-ethylenebis(sodium *N*-dodecanoyl-β-alanin) has a cmc value of 0.04 mM at pH 10.5 [26], the sodium salt of *bis*(1-dodecenylsuccinamic acid) has a cmc value of 0.1 mmol/l at pH 10 [23], and the sodium salt of *N*, *N*′-didodecanoylethylenediamine-*N*,*N*′-diacetic acid has a cmc value of 0.25 mmol/$_l$ [21].

In phosphate buffer at pH 12, most molecules of dimer **1** are fully deprotonated as divalent anions. In contrast, when the neutralized compound is dissolved in pure water, the pH value obtained lies between 7 and 8. This implies that most surfactant molecules are monoprotonated in solution (as determined by acid–basic titration; see Fig. 3). Hence, a majority of the surfactant molecules possesses a zwitterionic unit and an anionic one. Nevertheless, the cmc at pH 7 is only slightly lower than at pH 12, as reported recently for another carboxylic acid type gemini surfactant [30].

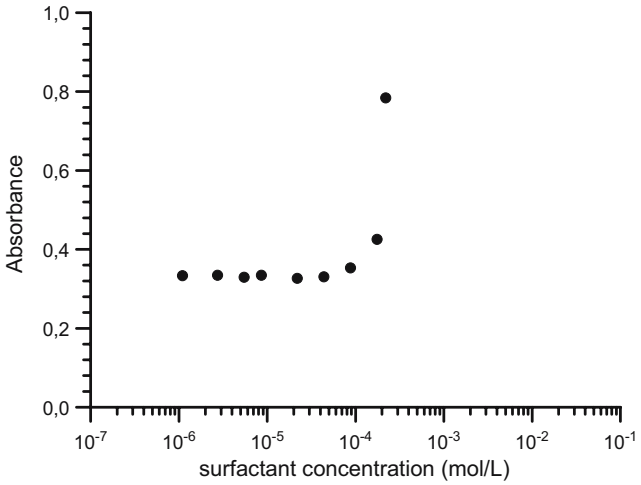

Fig. 6 Evolution of the absorbance of the enol form of benzoylacteone at 315 nm in aqueous solution with increasing concentration of surfactant **1**

Comparing the surface activity, the surface tension at the cmc (σ_{cmc}) of gemini **1** is lower than that of monomer analog SL. This is particularly true at pH values where most of both surfactant molecules are fully neutralized. Hence, the dimeric compound is quite effective in reducing the surface tension of water. Also, the σ_{cmc} value of gemini **1** increases with pH, as generally found for carboxylate based surfactants [30, 41]. Presumably, this reflects a tighter packing of the hydrophobic chains at the surface due to reduced electrostatic repulsion of the head groups, as partial protonation of the molecules produces ampholytic surfactant fragments.

When studied by a nanosizer, solutions of dimer **1**, either at pH 7–8 (neutralized product redissolved in MilliQ water) or at pH 12 (neutralized product redissolved in a phosphate buffer), showed only the presence of small aggregates, i.e., with 3 nm hydrodynamic diameter or smaller. This holds at least up to 5 wt% of surfactant in the absence of salts, suggesting the formation of spherical micelles. In agreement with this, the solutions did not reveal any marked thickening behavior. Thickening is typically observed for a special gemini structure [31], namely, quaternary ammonium bromides with very short alkyl spacer groups, due to the formation of entangled cylindrical micelles [3]. Note that the presence of vesicular aggregates was recently reported for a carboxylic acid type gemini surfactant in aqueous solution when the pH drops from 12.0 to 7.0 [30]. It is well known that monomeric surfactants based on carboxylic acid (e.g., alkali–metal alkanoates such as decanoate or oleate)

usually form micelles above the cmc at alkaline pH, but form vesicles as the pH decreases towards the pK_a [42, 43]. Apparently, such a behavior is not observed for gemini **1**, as the hydrodynamic diameters found remain always in the range of 3 nm with decreasing pH. This is presumably due to different protonation mechanisms. The tertiary amine groups of **1** are more basic than the carboxylate groups and become protonated first with decreasing pH (see above). At pH values 7–8, most of the compound is mono-protonated. Hence, one surfactant fragment possesses a zwitterionic head-group, and the other fragment bears an anionic one. This system may be compared with mixtures of zwitterionic and anionic surfactant monomers, which often form mixed micelles [44]. In contrast, the hitherto carboxylic acid based gemini surfactants are singly protonated as monovalent anions at pH 7.0 [30]. They resemble a double chain lipid structure, with hydrogen bonds between the carboxylic head-groups, which generate a polymeric type of complex stabilizing the bilayer structure.

The low cmc of **1** allows the solubilization of hydrophobic compounds already at low surfactant content. This makes this new gemini a priori attractive compared to conventional low molar-mass surfactants with higher cmc values. Using ^{1}H-NMR spectroscopy, preliminary quantitative solubilization studies with the model compound *p*-xylene were performed for concentrated surfactant solutions (10 g/l). The solubilization capacities of gemini **1** and surfactant "monomers", SL and SDS, are compared in Table 2. The capacities are expressed in number of *p*-xylene molecules solubilized per surfactant molecule and per alkyl chains, to allow significant comparisons. The solubilization capacity of the gemini surfactant is found to be higher than that of monomeric surfactants even when normalized on the numbers of alkyl chains. This finding is in agreement with the-yet limited-solubilization studies of other dimeric surfactants, which show often improved solubilization capacities [2–4, 31, 45, 46].

The properties of common anionic, in particular, of carboxylate surfactants in water are generally deteriorated by the presence of calcium and magnesium ions. Accordingly, the development of surfactants that are stable in hard water is desirable to reduce the use of softening agents while maintaining the surfactant efficiency [47]. The new gemini surfactant **1** is based on EDTA, which is a well-known chelating agent for Ca^{2+} and Mg^{2+} ions. Hence, it was interesting to test the stability of **1** in hard water. The tolerance of **1** against Ca^{2+} was evaluated by recording the turbidity, while adding $CaCl_2$ to the surfactant solution. From the corresponding turbidimetric curves (Fig. 8), it can be inferred that the new gemini is much more resistant against the addition of Ca^{2+} ions than the reference carboxylate surfactant SL. The solution of **1** remains completely clear upon addition of a large amount of $CaCl_2$ (ca 200 mg of $CaCl_2$/g of **1**), above which catastrophic precipitation is observed. Based on the maximum amount of Ca^+ ions that is tolerated in the titration curve, a calcium binding capacity of 75 mg Ca^{2+}/g of surfactant (i.e., 0.65 mol Ca^{2+}/mol head-group) can be estimated for gemini **1**. In contrast, solutions of SL become turbid already after addition of a very small amount of $CaCl_2$ (less than 1 mg of $CaCl_2$/g of SL). Turbidity increases progressively upon further addition, although no macroscopic precipitate is observed. This reflects a high number of insoluble particles, which sediment slowly on standing. Therefore, the amount of $CaCl_2$ at which the solution becomes visually white was chosen arbitrarily as upper estimation of the calcium ion tolerance. A maximum capacity of 13 mg Ca^{2+}/g of surfactant (i.e., 0.07 mol Ca^{2+}/mol head-group) was accordingly calculated for **SL**, which is much lower than the capacity found for **1**.

The high tolerance of calcium ions of the new gemini surfactant can be attributed to the EDTA building block. Possibly, the simultaneous presence of amine, amide, and carboxylate moieties in the head group permits the chelation of Ca^{2+}, while still providing sufficient hydrophilicity to maintain water solubility. We assume that **1** can

Table 2 Solubilization capacity of solutions of monomeric and gemini surfactants in D_2O for *para*-xylene, as determined by ^{1}H NMR (surfactant concentration: 1 wt%)

Surfactant	*Para*-xylene solubilized	
	Per surfactant	Per alkyl chain
SL	0.18	0.2
SDS	0.55	0.5
1	1.46	0.7

Values calculated per alkyl chain are rounding ones (one decimal).

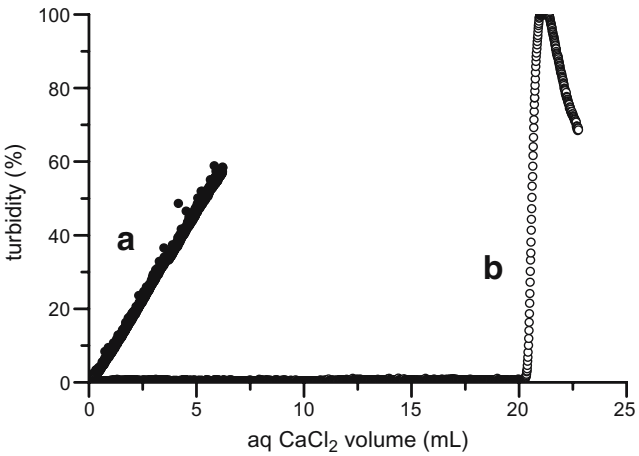

Fig. 8 Turbidimetric titration of aqueous surfactant solutions (25 ml; 2 g/l) with aqueous $CaCl_2$ (0.5 g/l) at 30 °C, pH 7. *filled circles* SL (*a*), *empty circles* gemini **1** (*b*)

chelate other kinds of metal ions, too, which could imply promising applications not only in detergents but also in other fields including metal anticorrosion, solid surface treatment, and catalysis (as amphiphilic metal complex).

Conclusions

A convenient synthesis strategy to a new type of gemini carboxylate surfactant based on EDTA is presented. Preparation is straightforward, and the purification is easy. The new surfactant has a Krafft temperature below 0 °C and a very low critical micellization concentration compared to the monomeric reference SL. This makes it attractive, e.g., for the solubilization of hydrophobic substances at low surfactant content. Moreover, the new dimer showed a higher solubilization capacity than monomeric analogs. The micellar aggregates formed, between pH 7 and 12, are small. Aqueous solutions of the new surfactant exhibit a remarkable tolerance against calcium ions. The new anionic gemini surfactant has model character, as the synthetic concept can be easily extended to other types of amines (e.g., fatty alkylamines or dialkylamines) and dianhydrides, thus, modifying easily and widely the hydrophobic tail and the spacer group, respectively, of the resulting dimeric surfactants.

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