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ORIGINAL CONTRIBUTIONS

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Spacer effects in dimeric cationic surfactants

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Abstract A series of dimeric cationic surfactants (gemini surfactants), which have spacer groups of varying length and flexibility, was synthesized. The series is derived from the parent compounds dodecyltrimethylammonium chloride or benzyldodecyldimethylammonium chloride. Characteristic surfactant properties of the dimeric ammonium compounds such as surface activity, micellization, viscosity effects, foaming, and solubilization, were studied with respect to the influence of the spacer group on the surfactant. For all properties, the influence of the length of the spacer group was predominant though the chemical nature of the spacer cannot be neglected.

Keywords Gemini surfactant · Spacer group · Surface tension

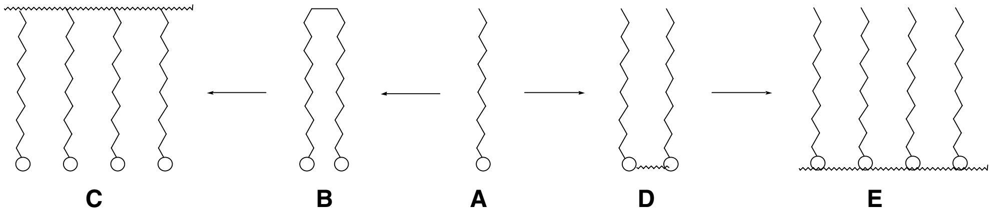
Introduction

For many decades, the search for new surfactants with new property profiles was focused on the variation of the hydrophilic–lipophilic balance (HLB). Thus, molecular variations concerned the nature of the hydrophilic head group, the general nature of the hydrophobic group (linear, branched, aliphatic, cyclic, aromatic, perfluorocarbon, silicone, etc.) and its size (homologous series) [1]. Only rather recently, has the influence of the overall surfactant shape and size been recognized as a major additional factor controlling the properties of surfactants. Polymeric surfactants made from individual surfactant monomer units, so-called “polysoaps”, have been known for nearly 50 years [2]. Still, these molecules have attracted so far only limited interest. They have been generally considered only as exotic macromolecules, much more than as surfactants. But, since the mid-1980s, Colloid Science has realized the unusual properties of defined surfactant dimers. Initially focusing in the 1980s on surfactants having two hydrophilic head groups at opposite ends of the hydrophobic group (frequently referred to as bola surfactants), the 1990s saw the uprise of the so-called “gemini” surfactants due to their particularly appealing properties [3–5]. Recently, cationic “gemini” surfactants have found additional interest, as non-viral transfecting agents [6–10].

From the molecular point of view, "bolas" are surfactant dimers coupled via the end of the hydrophobic chain, whilst "geminis" are dimers coupled via the hydrophilic head groups. Whereas, Colloid Science tends to consider "bolas" and "geminis" as two distinct groups of molecules with little in common, Polymer Science emphasizes that both are analogous intermediates between the classical monomeric surfactants and polymeric surfactants (see Fig. 1), namely the "tail-end type" and the "head-type", respectively [2]. For the latter, the nature and the length of the spacer group linking individual surfactant units together has been shown to be of primordial importance. A marked influence of the spacer group was found for "gemini" surfactants, too [3, 11–29]. But most studies on the influence of the spacer group have been focused on only one class of dimeric surfactants, the alkanediyl-α,ω-bis(dimethylalkylammonium bromide)s [5, 12, 13, 15, 19, 21, 23, 27, 30–33]. Accordingly, the variation of the spacer length has gone mostly along with a change in its hydrophobic character, thus rendering it difficult to distinguish between architectural and compositional effects on the surfactant properties.

Here, the synthesis and the surfactant behavior of a new series of dimeric "gemini" surfactants (see Fig. 2) are reported, derived from the parent compounds dodecyltrimethylammonium chloride, or benzyldodecyldimethylammonium chloride, respectively. The dodecyl chain was chosen as hydrophobic fragment because it is already sufficient to confer good surfactant properties to amphiphiles [1]. Moreover, the dodecyl chain is still short enough to expect water-soluble higher oligomeric or polymeric derivatives, as will be presented in a forthcoming report. The solubility of the dimeric cationic surfactants in water is enhanced by employing chloride counter-ions, instead of the mostly used bromide (presumably mainly because the bromides are easier to synthesize). In the few reports comparing analogous cationic dimeric surfactants with chloride and bromide as counterions, the critical micellization concentration (cmc) values of the chlorides were reported to be about twice higher than the ones of the analogous bromides [16]. Also, the analogous bromide salt of surfactants **8** has been described before [33–35], exhibiting a high Krafft-temperature of about 44 °C [33]. In our study, the spacer length was chosen to be in the range between C_3 and C_6, because the most pronounced changes in properties have been found for rather short spacer groups [3, 5]. In particular, we focused on rigid spacer groups, and compared two sets of isomeric compounds (**3**, **4**, and **6–8**, respectively) in order to keep the hydrophobicity of the spacer groups almost constant for comparisons. For comparison, the dimeric surfactant **5** [36] with a very flexible spacer group was included in the study, as reference.

Fig. 1 Scheme of the structural relationship of simple (**a**), dimeric (**b**, **d**) and polymeric (**c**, **e**) surfactants, linked via the end of the hydrophobic chain ("tail end type": **b**, **c**), or via the hydrophilic group ("head type": **d**, **e**)



Experimental

Materials

N,*N*-Dimethylaminododecane (>97%, $\rho = 0.775$ g/ml), α,α'-dichloro-*o*-xylene 98%, α,α'-dichloro-*m*-xylene (98%), α,α-dichloro-*p*-xylene (98%), and 2,3-dimethyl-2-butene (98%) were used as received from Aldrich; 3-chloro-2-chloromethyl-1-propene (96%) from Acros; 2,2'-dichloro-diethylether (puriss), *trans*-1,4-dichloro-2-butene (94%), benzyldimethyldodecylammonium chloride ($C_{21}H_{38}ClN$, $M_r = 339.99$, puriss. ≥99%), and *p*-xylene (puriss. p.a. >99%) were used as received from Fluka. Solvents were analytical grade, or were distilled prior to use. Water used for all experiments was purified by an Elgastat water purification system (resistance 18 MΩ cm).

Synthesis of 3

Two grams (0.0154 mol) of 3-chloro-2-chloromethyl-1-propene in 10 ml of acetonitrile are added dropwise under stirring to 15.0 g (0.0682 mol) of *N*,*N*-dimethylaminododecane at 105 °C, and the mixture is refluxed for 20 h. After evaporation of the solvent, the addition of 200 ml of acetone induces precipitation, yielding 7.25 g (85%) of crude, yellowish product. The crude product is purified by repeated dissolution in CH_2Cl_2 and precipitation by acetone, to give a white hygroscopic powder, apparent m.p. 61 °C.

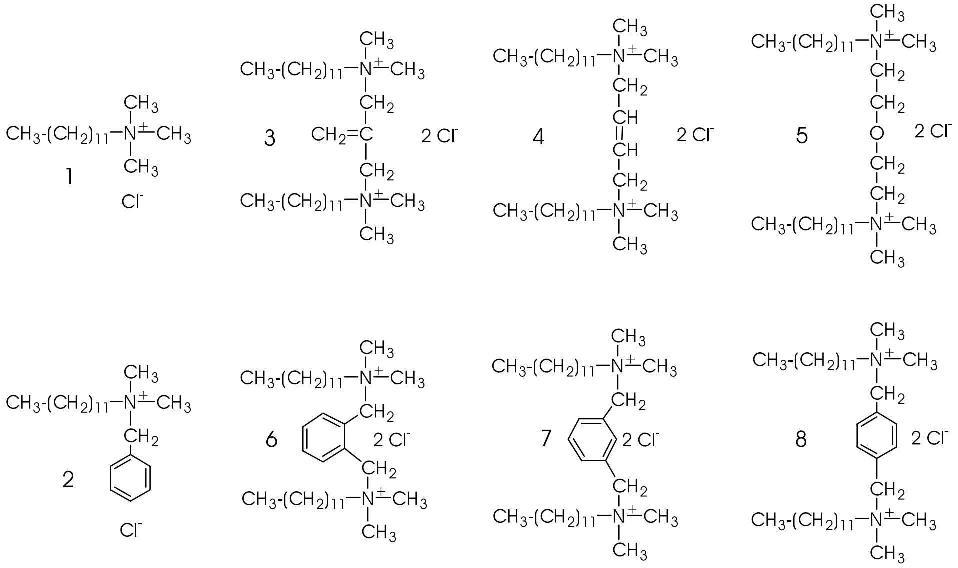


Fig. 2 Chemical structure of the surfactants studied

Elemental analysis ($C_{32}H_{68}N_2Cl_2$, $M_r = 551.81$). Calc. for dihydrate (%): C 65.38; H 12.34; N 4.77; Cl 12.06. Found (%): C 66.30; H 12.24; N 4.74; Cl 13.34.

^{1}H-NMR (200 MHz, $CDCl_3$, δ in ppm): 0.85 (t, 6H, CH_3–); 1.15–1.40 (m, 36H, –$(CH_2)_9$–) ; 1.75 (m, 4H, –CH_2–C–N^+) ; 3.28 (s, 12H, CH_3–N^+) ; 3.57 (m, 4H, –CH_2–N^+) ; 4.78 (m, 4H, =C–CH_2–N^+) ; 6.59 (m, 2H, =CH_2).

^{13}C-NMR (50 MHz, $CDCl_3$, δ in ppm): 14.0 (CH_3–); 22.6, 22.9 (CH_3– CH_2–; – CH_2–C–N^+); 26.3 (–CH_2–C–C–N^+) ; 29.29, 29.41, 29.46, 29.57 (–$(CH_2)_6$–); 31.9 (CH_3–C– CH_2–); 49.4 (CH_3–N^+); 65.0, 66.5, (– CH_2–N^+–CH_2–); 126.0 (CH_2=), 142.2 (= C<). Mass spectroscopy (FAB+): signal at = 515.5 (*m*/*z*) [M–Cl^-]$^+$.

Synthesis of 4

Six grams (0.045 mol) of *trans*-1,4-dichloro-2-butene in 50 ml of acetonitrile are added dropwise under stirring to 30.0 g (0.136 mol) of *N*,*N*-dimethyldodecylamine at 105 °C. The mixture is refluxed for 3 days, then cooled to room temperature. The precipitate is filtered off, and the filtrate concentrated. After adding 200 ml of acetone, more precipitate is formed that is filtered off. The combined precipitates are purified by repeated dissolution in ethanol and precipitation by acetone. Yield: 23.8 g (96%) of white hygroscopic powder, apparent m.p. 62 °C.

Elemental analysis ($C_{32}H_{68}N_2Cl_2$, $M_r = 551.81$). Calc. for dihydrate (%): C 65.38; H 12.34; N 4.77; Cl 12.06. Found (%): C 65.60; H 12.36; N 4.75; Cl 13.19.

^{1}H-NMR (200 MHz, $CDCl_3$, δ in ppm): 0.84 (t, 6H, CH_3–); 1.15–1.40 (m, 36H, –$(CH_2)_9$–) ; 1.71 (m, 4H, –CH_2–C–N^+) ; 3.30 (s, 12H, CH_3–N^+) ; 3.47 (m, 4H, –CH_2–N^+) ; 4.48 (m, 4H, =C–CH_2–N^+) ; 7.06 (m, 2H, –CH=).

^{13}C NMR (50 MHz, $CDCl_3$, δ in ppm): 14.0 (CH_3–); 22.6, 22.9 (CH_3– CH_2–; – CH_2–C–N^+); 26.2 (–CH_2–C–C–N^+) ; 29.22, 29.29, 29.42, 29.54 (–$(CH_2)_6$–); 31.9 (CH_3–C– CH_2–); 50.6 (CH_3–N^+); 65.0, 65.8, (– CH_2–N^+– CH_2–); 130.6 (– CH=).

Mass spectroscopy (FAB+): signal at = 515.5 (*m*/*z*) [M–Cl^-]$^+$.

Synthesis of 5

An amount of 86.03 g (0.391 mol) of *N*,*N*-dimethylaminododecane and 25.62 g (0.179 mol) of 2,2'-dichlorodiethylether in 300 ml of ethanol is refluxed for 4 days. After evaporating most of the solvent, the product is precipitated by adding 900 ml of acetone. The crude product is recovered by filtration, and crystallized thrice from acetonitrile. Yield 52.9 g (52%), white hygroscopic solid, apparent m.p. 58 °C.

Elemental analysis ($C_{32}H_{70}N_2Cl_2O$, $M_r = 569.82$). Calc. for monohydrate (%): C 65.38; H 12.34; N 4.77; Cl 12.06. Found (%): C 65.35; H 12.29; N 4.62; Cl 12.01.

^{1}H-NMR (200 MHz, $CDCl_3$, δ in ppm): 0.86 (t, 6H, CH_3–); 1.15–1.40 (m, 36H, –$(CH_2)_9$–) ; 1.69 (m, 4H, –CH_2–C–N^+) ; 3.42 (s, 12H, CH_3–N^+) ; 3.57 (m, 4H, –CH_2–N^+) ; 4.01 (m, 4H, –O–C–CH_2–N^+) ; 4.30 (m, 4H, –CH_2–O–).

^{13}C NMR (50 MHz, $CDCl_3$, δ in ppm): 14.0 (CH_3–) ; 22.6, 22.8 (CH_3– CH_2–; – CH_2–C–N^+) ; 26.3 (–CH_2–C–C–N^+) ; 29.2, 29.3, 29.4, 29.5 (–($CH_2)_6$–) ; 31.8 (CH_3–C– CH_2–) ; 51.4 (CH_3–N^+) ; 63.8, 64.5 (– CH_2–N^+– CH_2–) ; 65.7 (– CH_2–O–).

Mass spectroscopy (FAB+): signal at = 533.5 (m/z) $[M–Cl^{-}]^{+}$

Synthesis of 6

An amount of 40 ml (30.1 g, 0.141 mol) of *N*,*N*-dimethylaminododecane and 10.02 g (0.056 mol) of α,α'-dichloro-*o*-xylene in 150 ml of ethanol is refluxed for 6 days. Then, the solvent is removed in vacuo. Addition of 200 ml of diethylether gives a gel-like precipitate that is separated, washed, and dried to yield 19.2 g (57%) of crude product. Purification by repeated dissolution in acetone and precipitation by diethylether was carried out to give a white hygroscopic powder, with an apparent m.p. 51 °C.

Elemental analysis ($C_{36}H_{70}N_2Cl_2$, M_r = 601.87). Calc. for trihydrate (%): C 65.92; H 11.68; N 4.27; Cl 10.81. Found (%): C 65.77; H 11.91; N 4.15; Cl 10.55.

^{1}H-NMR (200 MHz, $CDCl_3$, δ in ppm): 0.84 (t, 6H, CH_3–); 1.15–1.40 (m, 36H, –$(CH_2)_9$–) ; 1.69 (m, 4H, –CH_2–C–N^+) ; 3.23 (s, 12H, CH_3–N^+); 3.71 (m, 4H, –CH_2–N^+); 5.45 (s, 4H, N^+–CH_2–Aryl); 7.69, 8.03 (m, 2H + 2H, CH_{aryl}).

^{13}C NMR (50 MHz, $CDCl_3$, δ in ppm): 14.0 (CH_3–) ; 22.6, 22.9 (CH_3– CH_2–; – CH_2–C–N^+) ; 26.4 (–CH_2–C–C–N^+) ; 29.27, 29.34, 29.43, 29.54, 29.64 (–($CH_2)_6$–) ; 31.8 (CH_3–C– CH_2–) ; 48.6 (CH_3–N^+) ; 64.1, (– CH_2–N^+ – CH_2–) ; 129.9 (= C_{aryl}–), 131.3, 136.3 (=CH_{aryl}–).

Mass spectroscopy (FAB+): signal at = 565.5 (m/z) $[M–Cl^{-}]^{+}$

Synthesis of 7

An amount of 40 ml (30.09 g, 0.141 mol) of *N*,*N*-dimethylaminododecane and 10.02 g (0.056 mol) of α,α'-dichloro-*m*-xylene in 150 ml of ethanol is refluxed for 4 days. Then, most of the solvent is removed in vacuo, and 200 ml of acetone are added. The precipitate formed is filtered off, and crystallized thrice from acetonitrile. Yield: 32.5 g (96%) of white hygroscopic solid, apparent m.p. 65 °C.

Elemental analysis ($C_{36}H_{70}N_2Cl_2$, M_r = 601.87). Calc. for dihydrate (%): C 67.78; H 11.69; N 4.39; Cl 11.11. Found (%): C 68.30; H 11.90; N 4.31; Cl 10.78.

^{1}H-NMR (200 MHz, $CDCl_3$, δ in ppm): 0.84 (t, 6H, CH_3–); 1.15–1.40 (m, 36H, –$(CH_2)_9$–) ; 1.78 (m, 4H, –CH_2–C–N^+) ; 3.20 (s, 12H, CH_3–N^+); 3.48 (m, 4H, –CH_2–N^+); 5.01 (s, 4H, N^+–CH_2–Aryl); 7.42 (m, 1H, CH_{aryl} in meta); 7.74 (d, 2H, CH_{aryl} in ortho); 8.45 (s, 1H, CH_{aryl} in ortho).

^{13}C NMR (50 MHz, $CDCl_3$, δ in ppm): 14.0 (CH_3–) ; 22.6, 22.8 (CH_3– CH_2–; – CH_2–C–N^+) ; 26.3 (–CH_2–C–C–N^+) ; 29.22, 29.36, 29.41, 29.50 (–($CH_2)_6$–) ; 31.8 (CH_3–C– CH_2–) ; 49.7 (CH_3–N^+) ; 64.5, 66.7 (– CH_2–N^+– CH_2–) ; 128.8 (= C_{aryl}–), 129.6, 135.0, 138.7 (=CH_{aryl}–).

Mass spectroscopy (FAB+): signal at = 565.7 (m/z) $[M–Cl^{-}]^{+}$, (FAB−): signal at = 635.5 (m/z) $[M+Cl^{-}]^{-}$.

Synthesis of 8

An amount of 75 ml (56.3 g, 0.264 mol) of *N*,*N*-dimethylaminododecane and 21.88 g (0.122 mol) of α,α'-dichloro-*p*-xylene in 300 ml of ethanol is refluxed for 4 days. Then, most of the solvent is removed in vacuo, and 200 ml of acetone is added. The precipitate formed is filtered off, and crystallized repeatedly from acetonitrile. Yield: 63.2 g (86%) of white hygroscopic solid, apparent m.p. 79/84 °C (double melting).

Elemental analysis ($C_{36}H_{70}N_2Cl_2$, M_r = 601.87). Calc. for trihydrate (%): C 65.92; H 11.68; N 4.65; Cl 10.81. Found (%): C 65.35; H 11.82; N 4.05; Cl 11.00.

^{1}H-NMR (200 MHz, $CDCl_3$, δ in ppm): 0.85 (t, 6H, CH_3–); 1.15–1.40 (m, 36H, –$(CH_2)_9$–) ; 1.85 (m, 4H, –CH_2–C–N^+) ; 3.21 (s, 12H, CH_3–N^+) ; 3.52 (m, 4H, –CH_2–N^+) ; 5.22 (s, 4H, N^+–CH_2–Aryl) ; 7.80 (s, 4H, CH_{aryl}).

^{13}C NMR (50 MHz, $CDCl_3$, δ in ppm): 14.0 (CH_3–) ; 22.5, 22.9 (CH_3– CH_2–; – CH_2–C–N^+) ; 26.4 (–CH_2–C–C–N^+) ; 29.2, 29.4, 29.5 (–($CH_2)_6$–) ; 31.8 (CH_3–C–CH_2–) ; 49.2 (CH_3–N^+) ; 64.6, 66.2 (– CH_2–N^+– CH_2–); 103.3, 133.0 (=CH_{aryl}–, =C_{aryl}–).

Mass spectroscopy (FAB+): signal at = 565.6 (m/z) $[M–Cl^{-}]^{+}$, (FAB−): signal at = 635.6 (m/z) $[M+Cl^{-}]^{-}$.

Methods

Elemental analysis was done by the University College of London. NMR spectra were taken with Gemini-200 and 300 spectrometers (Varian), and with an Avance 300 apparatus (Bruker). Infrared spectra were recorded with an FTS 135 Infrared Fourier Transform spectrometer (BioRad). Thermogravimetric experiments were performed under nitrogen with an apparatus TGA/SDTA851 (Mettler Toledo), heating rate 10 °C/min. Differential scanning calorimetry was performed on a DSC7 apparatus (Perkin Elmer), heating rate 10 °C/min. Viscometric measurements were performed at 30 °C with a semiautomatic Ubbelohde viscosimeter (Schott, Type 538 10), capillary no. 0. Particle size distributions were measured by a temperature controlled High Performance Particle Sizer (Incorporation NIBS Technology, Malvern Instruments, 633 nm laser source, optical path 10 mm). Surface tensions were measured with a du Noüy ring tensiometer (Lauda TE 1C) at room temperature (about 296 K) taking into account necessary modifications for the measurement of surfactant solutions [37, 38]. Krafft-temperatures were estimated by observing the dissolution of a small crystal of the surfactants in water by a microscope equipped with a hot stage.

For solubilization studies, 10 mg of surfactant are dissolved in 1 ml of D_2O. After adding about 0.4 ml of organic liquid, the mixture is vigorously shaken and allowed to phase separate for 24 h. The relative amounts of surfactant and solubilized material are quantified by ^{1}H-NMR, by comparing the integration of the signal at ca. 3.2 ppm (characteristic for the N^+–CH_3 group of all surfactants) to the integration of the singulet at 1.6–1.7 ppm characteristic for methyl groups in 2,3-dimethyl-2-butene, or of the singulet at about 2 ppm, respectively, characteristic for the methyl groups of *p*-xylene.

The foaming of the surfactants was studied by placing 5 ml of an aqueous solution of 5 g/l of the surfactant in a narrow glass tube. Air was gently pressed to the bottom of the tube via a metal needle and thus bubbled through the solution until a foam height of 20 cm was reached. Then the airflow was stopped, and the time taken for the foam to decay was measured.

Results and discussion

Surfactant synthesis

The dimeric surfactants **3–8** are synthesized by alkylating an excess of *N*,*N*-dimethyldodecylamine by the appropriate dichloro compound. Though chlorides are often somewhat sluggish as alkylating agents, reactions proceeded smoothly even under mild conditions as the chlorines are activated in the reagents employed towards nucleophilic substitution by their allylic, or benzylic position, respectively, or by an ether moiety in *β*-position. Synthesis of the surfactants by this strategy was thus straightforward. In agreement with the ease of alkylation, the thermal retro-alkylation is facilitated, too. The sterically somewhat congested dimers **3** and **6** decompose according to the thermogravimetric analysis already above 160 °C, whereas decomposition starts for dimers **4** and **7** at 210 °C, and for dimers **5** and **8** at about 220 °C only. Due to the thermal sensitivity, efficient and rigorous drying of the hygroscopic surfactants is difficult. Therefore, the observed thermal transition temperatures (see Experimental) probably do not reflect the values of the anhydrous compounds. The surfactants were purified by repeated crystallization until no impurities could be detected by thin layer chromatography or by NMR-spectroscopy. Still, the minimum in the surface tension versus concentration curves of the compound **6** (see Fig. 3) indicates the presence of some strongly surface-active trace impurity that could not be removed. Putatively, this may be due to a slow hydrolytic decomposition of the compound, which is sensitive to nucleophilic attack as reflected in the low thermal stability.

Krafft temperatures

All dimeric surfactants are soluble in water at ambient temperature. The Krafft-temperatures of the compounds are below 0 °C, except for **8**, the Krafft-temperature of which is slightly higher than 20 °C. Putatively, we attribute this finding to a particularly favorable molecular packing in the solid state. Nevertheless, the exchange of the bromide counterion [36] with the chloride for **8** induced a substantial increase in solubility, as observed in another case [16].

Surface tension

The surface active behavior of the reference surfactant **2** and of the surfactant dimers **3–8** is illustrated in Fig. 3, and the characteristic parameters derived therefrom are listed in Table 1. All dimeric surfactants **3–8** form micelles at room temperature, with values for the critical micelle concentration (CMC) between 1.2 and 2.2 mmol/l, i.e. the cmc values are very similar. But the CMC values of dimers **3–8** are considerably lower than the cmc values of the structurally closely related single tail surfactant “monomers” **1** and **2**, in agreement with the literature on dimeric surfactants. The marked

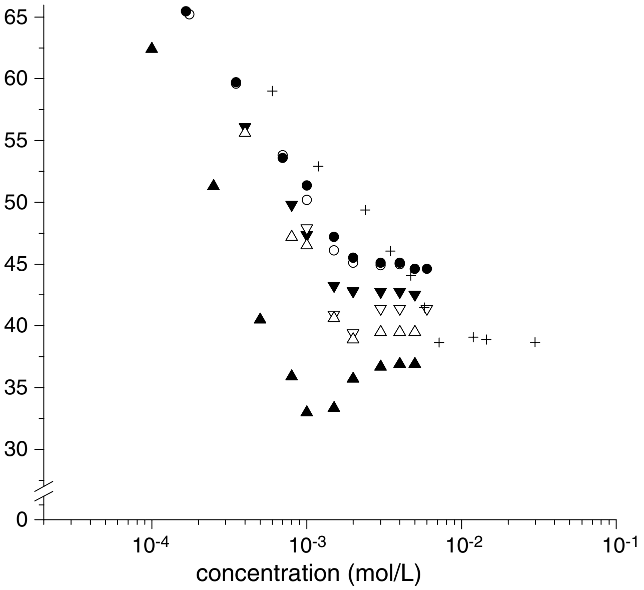


Fig. 3 Surface tension versus concentration curves of surfactants **2–8**: (*positive sign*) = **2**, (*open triangle*) = **3**, (*open inverted triangle*) = 4, (*open circle*) = **5**, (*black triangle*) = **6**, (*black inverted triangle*) = **7**, (*black circle*) = **8**

Table 1 Surface activity and micellization data of surfactants **1–8**

Compound	T_{Krafft} (°C)	CMC (mmol/l)	CMC (g/l)	σ_{cmc} (mN/m)	π_{cmc} (mN/m)
1[a]	< 0	21.5	8.2		
2	< 0	7.0	2.4	39	33.4
3	< 0	1.8	1.0	39.5	32.9
4	< 0	2.0	1.1	41.4	31.0
5	< 0	2.2	1.25	44.9	27.5
6	< 0	1.2	0.72	37	35.4
7	< 0	1.5	0.90	42.8	29.6
8	22–23	2.1	1.3	45.0	27.4

[a] Data taken from reference [39]

decrease of the cmc value when substituting one methyl group on the ammonium nitrogen in **1** [39] by a benzyl group in **2**, underlines that spacer group effects in dimeric surfactants may at least partially result from a change in the hydrophilic–hydrophobic balance of the surfactants. Note that the cmc-value determined for dimer **5** is about four times higher than the value reported previously in the literature [36], but only twice as high as the value reported for the cmc of its bromide analog [11] as would be expected [16].

Analyzing the surface tension (σ) versus concentration curves and the cmc values of the various dimeric surfactants, some differences are noticeable. The differences in the cmc value seem small, though clearly existing. Within the two series of isomeric dimeric surfactants, i.e. of such with a spacer group of identical hydrophobicity, namely butenylene and xylylene, the cmc values increase slightly with **3** < **4**, and with **6** < **7** < **8**. This means that the cmc values increase with increasing spacer length ($C_3 < C_4$, and $C_4 < C_6 < C_8$, respectively). This finding for the two rigid spacer groups coincides with a similar observation in the most-studied series of dimeric surfactants with flexible spacers, the alkanediyl-α,ω-bis(dimethylalkylammonium bromide)s, for which a maximum for the cmc is observed for the C_6-spacer [5]. Dimer **5** whose flexible spacer is roughly equivalent to an aliphatic C_5 unit, exhibits a cmc value that is slightly higher than the values for **3** and **4**. This behavior seems to fit into the general scheme, but may be fortuitous considering the different flexibility and polarity of the bisethyleneglycol spacer compared to the butenylene group. In any case, the different cmc values within the two series of isomeric compounds illustrate the importance of steric effects of the spacer for dimeric surfactants, despite a constant hydrophilic–hydrophobic balance. The effect of the spacer groups can be explained by steric constraints imposed on the self-organization of the surfactants, affecting the packing density of the alkyl chains as well as the ability to minimize hydrophobic interactions intramolecularly by an appropriate conformation of the alkyl chains [28, 39–41].

Still, the chemical nature of the spacer is not negligible, as exemplified by the comparison of dimers **4** and **6**, which both have a C_4-spacer unit between the surfactant fragments, as reported for flexible C_4-spacers before [18]. Dimer **6** exhibits the lower cmc, which can be rationalized by the more hydrophobic xylylene spacer of **6** (see discussion for the standard surfactants **1** and **2** above). In agreement, the cmc of **4** with the butenylene spacer matches well with the reported cmc of the similar dimeric ammonium chloride bearing a butinediyl spacer [16] with nearly identical hydrophobicity. Within this reasoning, the very close cmc values found for dimers **5** and **8** should be seen as accidental, with the effects of differing spacer lengths and differing polarity just compensating. Note that this observation agrees well with the recent findings for the analogous pair of **5** and **8** having the bromide counterion [28].

The similarity of the surface tension (σ) versus concentration isotherms of dimers **3–8** (see Fig. 3) indicates that their standard energy of adsorption is very similar and nearly independent of the type of the spacer. However, some noticeable differences in their surface properties are found when comparing their σ_{cmc}-values (see Table 1). The σ_{cmc}-values increase with **6** < **3** < **4** < **7** < **8** ≈ **5** from 37 to 45 mN/m. The σ_{cmc}-values of 39 mN/m of the reference monomeric surfactants **1** and **2** lie in between this range. Looking separately at the two series of isomeric dimeric surfactants, the σ_{cmc}-values increase with **3** < **4**, and with **6** < **7** < **8**. Hence as for the cmc values, the σ_{cmc}-values increase with increasing spacer length for a given polarity of the spacer. In other words, the closer the two substituents are positioned, the higher will be their surface pressure at the cmc, π_{cmc}. This suggests that the isomers have different packing densities: the para isomer cannot be packed as tightly as the corresponding ortho isomer. If this explanation is true, this tendency will be reflected in the maximum surface excess determined from the equilibrium surface tension versus concentration isotherms of the amphiphiles. Still, the comparison of the two isomeric series of surfactants—with butenylene and xylylene spacer—shows that not only the length but also the chemical nature of the spacer contributes to the extent of reduction of the surface tension. For a given spacer length, the xylylene spacer reduces the surface tension above the cmc more than the butenylene spacer (compare e.g. **4** and **6**). Once more, the different effects of their spacer groups seem to compensate for the pair **5** and **8**.

A thorough discussion of the packing density of the dimeric surfactants at the air–water interface, and of the state of adsorption, is a complex topic [40–42]. Nevertheless, we can do some reasonable approximations for evaluating the surface tension data with respect to the limiting surface area demand per molecule adsorbed. Therefore, we consider the cmc together with the corresponding σ_{cmc}-value and/or the surface pressure at the cmc, $\pi_{\mathrm{cmc}} = \sigma_{\mathrm{w}} - \sigma_{\mathrm{cmc}}$. As long as the σ_{cmc}-value is virtually constant for different concentrations above the cmc (i.e. no minimum), this indicates a rather good purity of the substances, though it does not necessarily guarantee sufficient surface-chemical purity in its strict requirement [43]. Except the substances **6** which reveals a clear minimum and **4** which shows a slight minimum in the σ_{e} versus log(concentration) isotherm, all other substances did not exhibit any noticeable minimum. In order to be able to evaluate also the two somewhat contaminated surfactants in this comparison, we used their constant σ_{cmc}-values, which are observed at concentrations well above cmc. The constant surface tension value indicates that the surface-active impurity producing the minimum was solubilized in the micelles and no longer influences the adsorbed layer.

The cmc-values of the dimeric surfactants are roughly identical, and the slopes of the σ_{e} versus c curves are very similar, too. Assuming identical degrees of dissociation, we can conclude that their surface activities do not differ much and their surface interaction is similar. Then, the Szyszkowski–Langmuir adsorption equation can be used [44]. Applying this for the concentration of critical micelle formation, cmc, results in

$$\sigma_{\mathrm{w}} - \sigma_{\mathrm{cmc}} = RT\Gamma_{\infty} \ln\left(\frac{1 + \mathrm{cmc}}{a_{\mathrm{L}}}\right), \tag{1}$$

with Γ_{∞} and a_{L} saturation adsorption and surface activity parameter, respectively. As cmc/a » 1 Eq. 1 can be simplified to

$$\sigma_{\mathrm{w}} - \sigma_{\mathrm{cmc}} = \pi_{\mathrm{cmc}} \cong RT\Gamma_{\infty} \ln\left(\frac{\mathrm{cmc}}{a_{\mathrm{L}}}\right). \tag{1a}$$

Furthermore, since $\mathrm{cmc}/a_{\mathrm{L}} \approx$ constant, it follows as a first approximation that

$$\pi_{\mathrm{cmc}} \propto \Gamma_{\infty}. \tag{2}$$

Finally, as the limiting cross-sectional area per molecule adsorbed, $A_{\min}$, is inversely proportional to the maximum surface excess, Γ_{∞}, according to

$$A_{\min} = (N_{\mathrm{L}}\Gamma_{\infty})^{-1}, \tag{3a}$$

we have

$$A_{\min} \propto \frac{1}{\pi_{\mathrm{cmc}}}. \tag{3b}$$

Consequently, the following estimation holds for the surface area requirements of these adsorbed dimeric amphiphiles **5** ≅ **8** > **7** > **4** > **3** > **6**, i.e. concerning the spacer groups we find $-\mathrm{CH_2{-}CH_2{-}O{-}CH_2{-}CH_2}-$ ≅ *p*-xylenyl– > *m*-xylenyl– > –butylene– > –isobutylene– > *o*-xylenyl–. This sequence corresponds reasonably well to the molecular geometrical requirements of these groups. Hence, in this particular case we can conclude that the surface area requirement at the cmc critically depends on the geometry of the spacer group. The longer the molecular distance between the two head groups, the larger is the surface area demand of the surfactant.

However, we wish to emphasize that an exact quantitative determination of these relationships needs to use the corresponding adsorption parameters of the surfactants. They can only be obtained by the evaluation of the whole equilibrium surface tension (σ_{e}) versus log concentration isotherm at concentrations below the cmc, and by using surface-chemically pure surfactant solutions. This is a comprehensive work that is to be treated in a future contribution.

Viscosifying effects

The association of dimeric surfactants in aqueous solutions into very large aggregates was reported in certain cases [32, 45]. The so-called giant or worm-like micelles formed caused a strong increase of the solution viscosity [46–48]. For instance, 1,2-bis(*N*,*N*′-dimethyl-*N*-dodecylammonio) ethane dibromide (12-2-12) is an excellent thickener, but the effect disappears rapidly with increasing spacer length, i.e. with increasing separation of the two hydrophobic chains [5]. As this dependence might be a function of the rigidity of the spacer, too, we looked into the viscosity behavior of aqueous solutions of surfactants **3–8**. Up to concentrations of 1 wt%, i.e. up to concentrations much above the cmc, the effects on the viscosity are equally small for **4–8** (see Fig. 4). This is

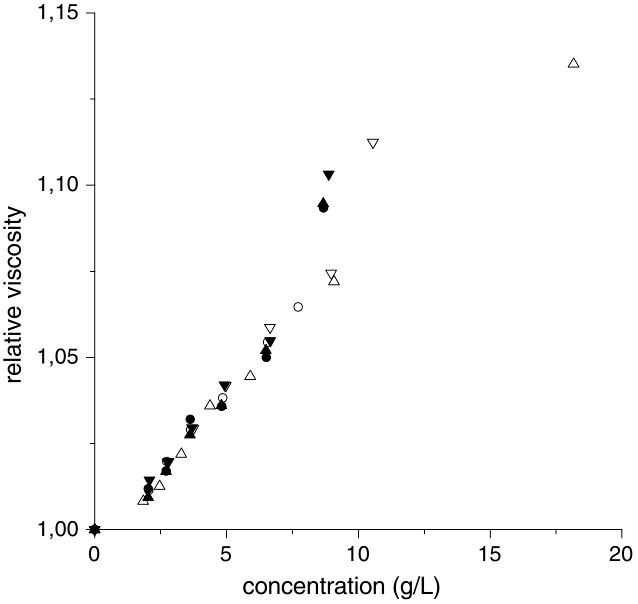


Fig. 4 Viscosifying effects of surfactants **3–8** in aqueous solution. Same symbols as in Fig. 3

also true for the compound **3** with the shortest spacer (C_3) in the series, up to concentrations of at least 3 wt%. This observation indicates the absence of large, rod-like aggregates. Our findings corroborate that the often cited remarkable ability of pure dimeric surfactants to increase the viscosity of their aqueous solutions is not a general feature of this class of surfactants, but seems mostly to be restricted to one very particular molecular structure, namely the 1,2-bis(*N*,*N*′-dimethyl-*N*-alklylammonio) ethane series, and to a lesser extent to the next homologous series, namely the 1,3-bis(*N*,*N*′-dimethyl-*N*-alklylammonio) propane series.

Table 2 ^{1}H-NMR data of surfactants **2–7** at 0.03 wt% (below the cmc, value in upper row) and 1 wt% (above the cmc, value in lower row) in D_2O

Surfactant	Chemical shift of groups (in ppm)							
	CH_3–	–$(CH_2)_9$–	–CH_2–C–N^+	CH_3–N^+	–CH_2–N^+ (chain)	N^+–CH_2– (spacer)	O–CH_2–	=CH–
2	0.78	1.21	1.70	2.94	3.25	4.41		7.46–7.48
	0.82	1.19	1.69	2.95	2.99	4.39		7.34–7.42
3	0.79	1.20	1.72	2.99	3.25	4.02		6.27
	0.80	1.23	1.77	3.08	3.32	4.10		6.34
4	0.78	1.20	1.71	3.00	3.19	3.98		6.26
	0.80	1.22	1.71	3.09	3.22	4.07		6.34
5	0.78	1.20	1.71	3.03	3.27	3.51	3.88	
	0.82	1.23	1.71	3.08	3.32	3.56	3.95	
6	0.76	1.18	1.74	2.88	3.25	[a]		7.65
	0.79	1.19	1.75	3.02	3.38	4.75		7.64–7.73
7	0.76	1.18	1.76	2.96	3.18	4.45		7.52–7.67
	0.76	1.16	1.76	3.06	3.17	4.54		7.53–7.76

[a] Signal hidden by solvent signal at 4.689 ppm

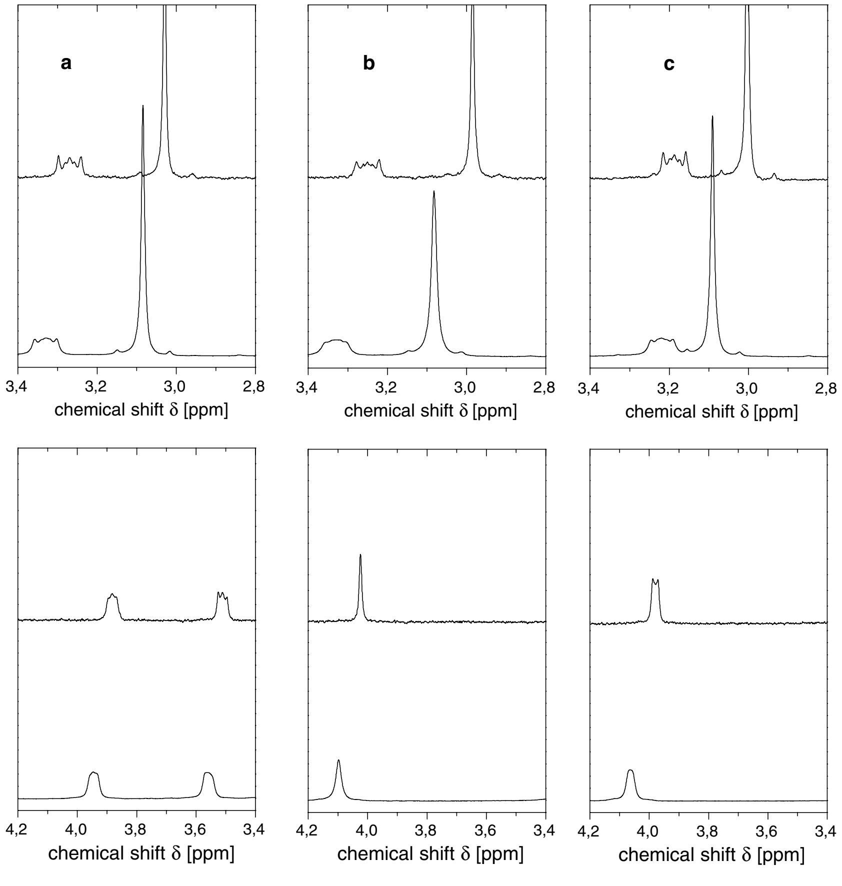


Fig. 5 Selected parts of the ^{1}H-NMR spectra of dimeric surfactants in D_2O, at 0.03 wt% (below the cmc, *upper graphs*), and at 1 wt% (above the cmc, *lower graphs*). **a** = **5**, **b** = **3**, **c** = **4**

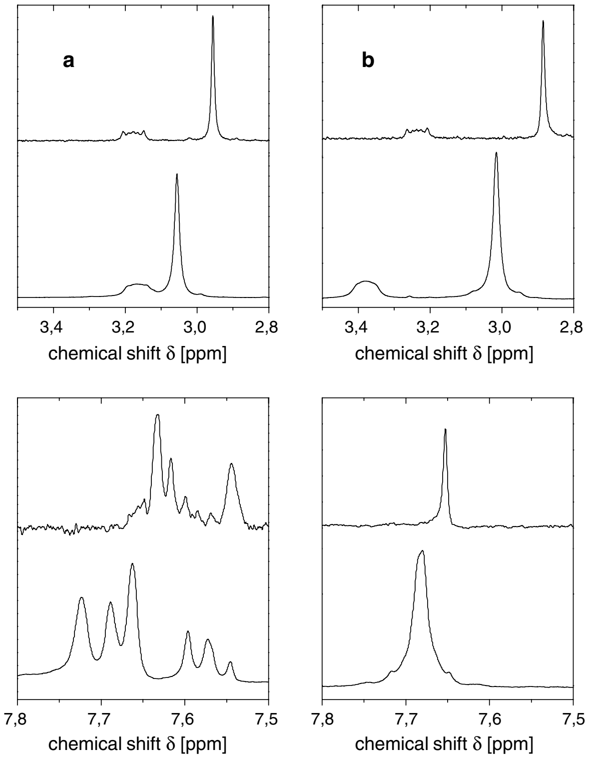


Fig. 6 Selected parts of the ^{1}H-NMR spectra of dimeric surfactants in D_2O, at 0.03 wt% (below the cmc, *upper graphs*), and 1 wt% (above the cmc, *lower graphs*). **a** = **7**, **b** = **6**

Dynamic light scattering and NMR spectroscopy

In agreement with the viscosimetric studies, dynamic light scattering of solutions of **3–8** indicated only the presence of very small structures at the lower detection limit of the apparatus, i.e. of 2 nm diameter or smaller, up to 7 wt% of surfactant. Some qualitative information on the structure of the surfactant micelles can be obtained by comparing their ^{1}H-NMR spectra in water below and above the cmc [49] (see Table 2, Figs. 5, 6). For surfactants **2–7** (dimer **8** is not soluble with 1 wt% in water at ambient temperature), only very small changes of the chemical shift are observed for the protons of the hydrophobic chains, whereas the protons in the vicinity of the hydrophilic ammonium group as well as in the spacer undergo more notable changes. For the monomeric reference **2**, these protons (including the protons of the benzyl moiety) feel a shielding upon micellization. In contrast, in the case of all dimeric surfactants **3–7**, these protons feel a deshielding upon micellization. The effect is the least pronounced for **5**, i.e. the dimer with the flexible spacer group. This observation suggests a basically different conformational change occurring in the hydrophilic portion of dimeric surfactants compared to their monomeric analogs. Interestingly, the changes in the ^{1}H-spectrum of **7** (see Fig. 6a) correspond closely to the ones reported for its octyl bromide analog upon micellization, whereas the changes in the ^{1}H-spectrum of **6** are much weaker [49]. This implies that the length of the hydrophobic alkyl chain can influence the conformation adopted by the spacer group in the micelle.

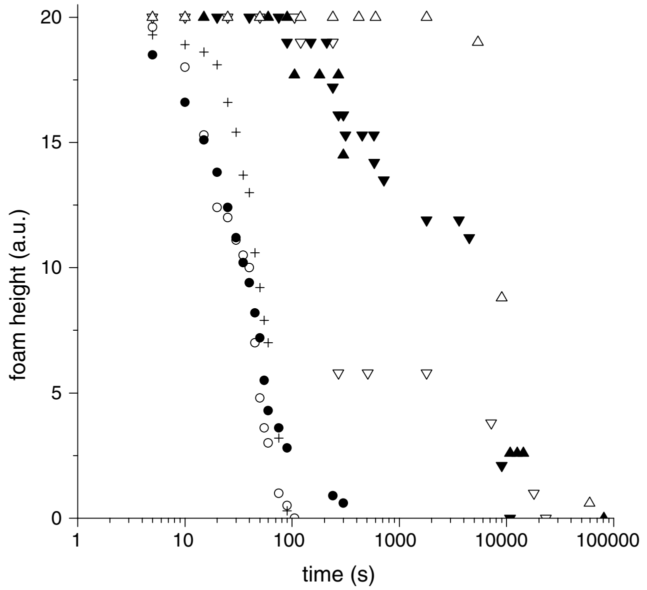


Fig. 7 Foam stability of foams made from surfactants **2–8** in aqueous solution. Same symbols as in Fig. 3

Table 3 Solubilization capacity of solutions of surfactants **2–8** in D_2O for *p*-xylene and 2,3-dimethylbut-2-ene, as determined by ^{1}H-NMR (surfactant concentration: 1 wt%)

Surfactant	*p*-Xylene solubilized		2,3-Dimethylbut-2-ene solubilized	
	Per surfactant	Per alkyl chain	Per surfactant	Per alkyl chain
2	1.0	1.0	0.70	0.70
3	1.9	0.95	1.50	0.75
4	1.3	0.65	1.20	0.60
5	1.5	0.75	0.75	0.38
6	2.4	1.20	1.60	0.80
7	1.4	0.70	0.80	0.40
8	1.5	0.75	0.85	0.43

Foaming

In order to learn about the foaming properties of the dimeric surfactants, they were subjected to a simple test: air was bubbled through aqueous solutions of a fixed concentration until a given height of foam was produced. The air stream was stopped, and the residual height of foam was recorded with time. Marked differences are found between different dimers. Judging the relative foam stability by comparing the height of residual foam after a given time, the stability increases in the series $\mathbf{2} \cong \mathbf{5} \cong \mathbf{8} < \mathbf{4} < \mathbf{6} \cong \mathbf{7} < \mathbf{3}$ (see Fig. 7). This sequence coincides with the rate of foam formation. The sequence correlates directly with the lengths of the spacer group, namely that short spacer groups favor foam formation and stability, whereas long spacers give results comparable to those obtained for classical monomeric surfactants such as reference compound **2**. The few previous reports on foaming of dimeric surfactants fit well into our findings that short spacers give rise to particularly stable foams [50], whereas long spacers do not [36]. It seems reasonable to correlate this result with the σ_{cmc}-values of the surfactants (vide supra). In fact, the general tendencies agree with each other, but in detail, more factors must influence the foaming behavior (compare e.g. surfactant pairs **3** and **6**, or **4** and **7**), as shown in the literature [51]. But differences in viscosity cannot be responsible in our case (see Fig. 4).

Solubilization tests

Solubilization of poorly water-soluble compounds is a key property of surfactants. Typically, a marked solubilization effect is observed only above the cmc [52]. Improved solubilization capacities were discussed for dimeric surfactants [53–55], but the reports on the solubilization capacity of dimeric surfactants have been scarce so far. The spacer group seems to influence the capacity, but no uniform picture has emerged yet. Whereas in some cases, an optimum length of the spacer was found at intermediate spacer lengths (C_8–C_{10}) [12, 56], two other reports revealed decreasing capacity with increasing spacer length [54, 55]. In the case of surfactants **2–8**, preliminary solubilization studies were performed with *p*-xylene and with 2,3-dimethyl-but-2-ene. As summarized in Table 3, for both solubilizates, the solubilization capacity is apparently increased with decreasing spacer length, in analogy to the reports of Dreja et al. [54] and Dam et al. [55]. The monomeric surfactant **2** performs between the extremes. Interestingly, the aromatic spacer group seems to favor the solubilization of *p*-xylene, compared to the olefin (see Table 3, compare series **3–5** with series **6–8**). Qualitatively, we observed a notable shielding of the chemical shifts of the ^{1}H signals attributed to the aliphatic chains for all surfactants, when 2,3-dimethyl-2-butene was solubilized. However, when *p*-xylene was solubilized, a similar effect was observed only for dimers **3–5**, whereas dimers **7** and **8** exhibited a notable shielding of the protons of the spacer group. Dimer **6** showed a notable shift for both the protons of the aliphatic chain as well as of the spacer group. These findings suggest a specific interaction of the aromatic spacer group with the aromatic solubilizate, favoring its dissolution.

Conclusions

A series of dimeric cationic surfactants derived from the parent compound dodecyltrimethylammonium chloride with different, mostly rigid spacer groups was prepared. The series shows a pronounced influence of the spacer on several surfactant properties, such as water solubility, CMC, reduction of the surface tension, foaming ability, and solubilization capacity. The length of the spacer group has the strongest influence on the properties, but the chemical nature of the spacer is effective, too. The study corroborates that the spacer group of dimeric surfactants (as in polymeric soaps [2]) is an additional structural variable that allows one to tune the aqueous solution behavior of surfactants.

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