

A new class of bolaforms bearing sulfobetaine and cationic heads: Synthesis and aggregation properties

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Abstract: We describe here a convenient route to a new family of bolaforms bearing sulfobetaine and cationic heads, which could be scaled up for industrial applications. Their aggregation modes were studied by measurement of surface tension and by dynamic light scattering and transmission electronic microscopy methods. Grafting a hydrophobic chain onto the cationic head modifies both the surface properties and aggregation. Compared to conventional bolaforms, the relationship between the length of the spacer and the side-chain and the resultant hydrophobic interactions are at the origin of these novel properties. Various models of these molecular associations were proposed.

Key words: dissymmetric bolaform, sulfobetaine, cationic amphiphile, aggregation.

Résumé : Nous décrivons une nouvelle famille de bolaformes comportant une tête sulfobétaine et une tête cationique. Les synthèses proposées sont aisément transposables à l'échelle industrielle. Le mode d'agrégation de ces bolaformes a été étudié par diverses techniques: tensiométrie, diffusion de la lumière et microscopie électronique à transmission. Il en résulte que le greffage d'une chaîne hydrophobe sur la tête cationique modifie les propriétés de surface et d'agrégation comparativement aux conventionnels bolaformes. Une relation entre la longueur de l'espaceur et celle de la chaîne carbonée additive est mise en évidence en fonction des interactions hydrophobes propres à la structure chimique de ces nouveaux bolaformes. Différents modèles d'association moléculaire sont dès lors proposés.

Mots clés : bolaforme dissymétrique, sulfobétaine, amphiphile cationique, agrégation.

Introduction

There is growing interest in the properties of difunctional surfactants such as bolaforms. Surfactants of this category, characterized by two hydrophilic heads linked by a hydrophobic chain, are attractive models for biological membranes (1–3) and can display various properties (4, 5). The potential applications suggested by these properties have led to a renewed interest in bolaforms by the industrial community (6, 7). However, from an academic standpoint, the molecular self-association of these molecules still leaves various questions unanswered. To further our understanding of these systems, it therefore appears necessary to make available a large range of these compounds with varied chemical structures. But the synthesis of bolaforms with non-identical head-groups presents certain technical difficulties, which explains the rather limited number of studies reported to date. Recently, we proposed a simple, efficient, and industrially realistic route to obtain bolaforms either with two betaine heads (carboxybetaine and (or) sulfobetaine) (8) or with at least one sulfobetaine head (9) (Fig. 1). These molecules have also shown interesting

surfactant properties that depend on the structure of the polar head as well as on the length of the spacer that links them (10).

Pursuing this line of research, the reaction scheme we developed was used to graft a second long hydrophobic chain onto one of the nitrogen atoms. This generated original compounds **1** with a structure intermediate between that of conventional bolaforms and of gemini surfactants (Fig. 2). Longer than the rather rigid C6 spacer but shorter than the very flexible C16 spacer, the dodecyl spacer appeared to be the most suitable for our research aims. Owing to the molecular organisation properties of these novel compounds, we were able to study the influence of chain–chain interactions in relation with the different structures of the polar heads. It is in this perspective that we report a new extended range of hybrid molecules **1** and the study of their aggregation properties.

Results and discussion

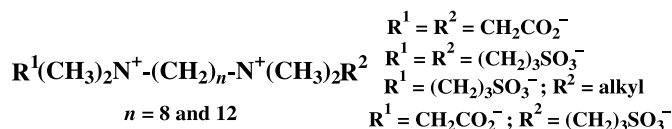
Synthesis

The synthetic approach used is based on previous studies (9) into the preparation of sulfobetaine bolaforms. From the monosulfobetaine intermediate **3**, formation of a quaternary nitrogen by reaction with dodecyl bromide led quantitatively to the required bolaforms **1** (Scheme 1). Table 1 reports the various bolaforms **1** synthesized.

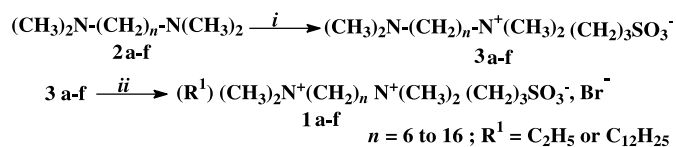
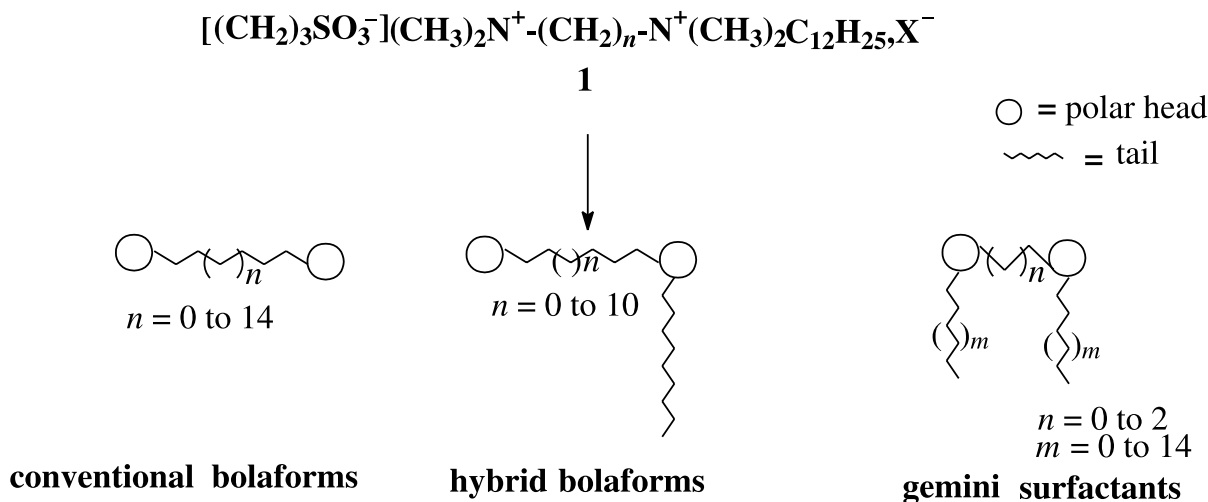
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Fig. 1. Various structures of the betaine bolaforms.

Scheme 1. Synthesis of the hybrid bolaforms **1**; (i) 1,3-propane sultone, acetone, 15–20°C; (ii) R¹X, methanol, reflux.

**Fig. 2.** Structure of the hybrid bolaforms **1**.

Surface properties

The surfactant properties of these hybrid bolaforms **1** were studied by measuring interfacial tension in water and calculating the surface property parameters using the Gibbs' equation (11). The data are illustrated in Fig. 3 and listed in Table 2.

All compounds tested led to a marked reduction in interfacial tension at the air–water interface (29–36 mN·m⁻¹). In the interfacial tension vs. concentration plots, we noted that the values of the critical micellar concentration (cmc) (2.4–8.2 mmol⁻¹) were strongly decreased in comparison with those of conventional bolaforms, which is promising for industrial applications. This was attributed to increased hydrophobicity on addition of the second alkyl chain (comparison between **1a**, **1c**, **1e**, and **1f**) and is in agreement with the values reported in the literature. However, an “anomaly” was observed with compound **1e** ($n = 16$), as shown in the curve of Fig. 3 where the linear decrease in the value of the cmc vs. increasing spacer length shows that the cmc of **1e** ($n = 16$; cmc = 3.1 mmol⁻¹) is greater than that of **1d** ($n = 12$; cmc = 2.4 mmol⁻¹).

This result is difficult to explain, but it can be proposed that differences in chain–chain interactions are responsible. This hypothesis is supported by the analysis of the curve in Fig. 4, which reveals differences in the conformations of the various bolaforms at the air–water interface. Compounds **1a**, **1b**, and **1c** present total areas for the polar heads of 280, 275, and 284 Å², respectively, which is much greater than the sum of the head areas taken individually (135 Å²). This suggests that a “straight” conformation is taken up by the bolaforms, leaving the hydrophobic side chain as far from the interface as possible (Fig. 5a). This arrangement could

be favoured because the chain (C12) is longer than the spacer (C6–C10). This hypothesis is supported by data from the literature, which attribute strong rigidity to bolaforms with a spacer of 10 carbon atoms or fewer (12, 13). A spacer with 12 carbons is known to make the molecule take up a looped (“wicket-like”) conformation, bringing about a total polar surface area equivalent to the sum of the areas of the two polar heads. This is what was observed for compound **1d** ($n = 12$, total area 188 Å² (Fig. 4)), as illustrated by Fig. 5b. Moreover, it should be noted that this value is close to the total polar head area (167 Å²) found for a similar compound **1f** ($n = 12$) in which the side-chain only has two carbon atoms ($\text{R} = \text{C}_2\text{H}_5$).

Taking into account the margins of error inherent in the measurements, it could also be proposed that the slightly higher value for the total area of bolaform **1d** with respect to **1f** indicates the beginnings of chain–chain interactions, impeding the flexibility of the spacer and not allowing complete folding (Fig. 5b). But there is once more a spread-out conformation for bolaform **1e** ($n = 16$, total area 254 Å²), as illustrated in Fig. 5c. However, the chain–chain interactions (side-chain shorter than the spacer) reduce the flexibility of the spacer, making these structures act similarly to bicatener bolaforms. Overall, from these results, it appears that the term of critical aggregation concentration (cac) would be more appropriate for this type of compound.

Dynamic light scattering

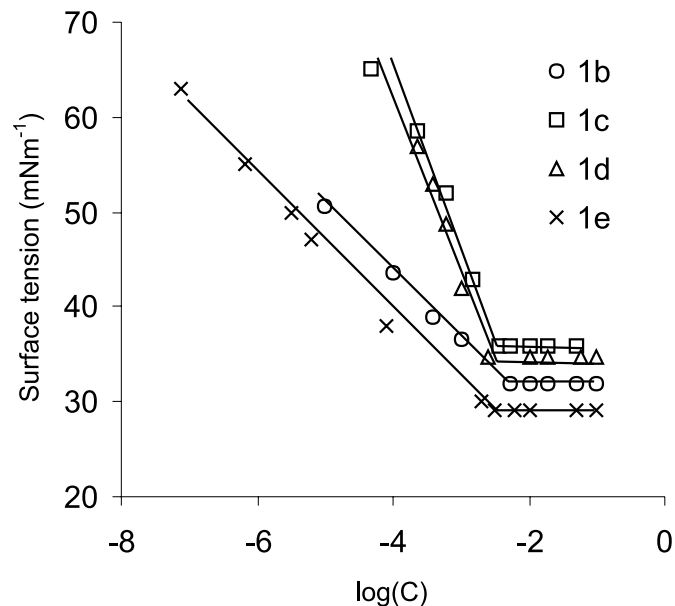
With the exception of compound **1e** ($n = 16$), none of the bolaforms synthesized here underwent spontaneous molecular aggregation without sonication. After 15 min sonication all the bolaforms generated various objects. Typical results,

Table 1. Yield of the synthesized hybrid bolaforms **1**.

<i>n</i>	Compound 2		Compound 3		R ¹	Compound 1	
	No.	Yield (%)	No.	Yield (%)		No.	Yield (%)
6	2a	98	3a	98	C ₁₂ H ₂₅	1a	90
8	2b	98	3b	96	C ₁₂ H ₂₅	1b	87
10	2c	92	3c	97	C ₁₂ H ₂₅	1c	92
12	2d	98	3d	95	C ₁₂ H ₂₅	1d	85
16	2e	75	3e	75	C ₁₂ H ₂₅	1e	85
12					C ₂ H ₅	1f	90

Table 2. Surface parameters of the hybrid bolaforms **1** at 25°C in water.

Compound No.	<i>n</i>	γ^a (mN·m ⁻¹)	cmc ^b (mM)	Γ^c (mol·m ⁻²)	A ^d (Å ²)	Light scattering	
						\emptyset (nm)	%
1a	6	35	8.2	5.7×10^{-7}	280	—	—
1b	8	32	5	6.02×10^{-7}	275	286	80
1c	10	36	3.6	5.85×10^{-7}	284	399	15
1d	12	35	2.4	8.83×10^{-7}	188	281	56
1e	16	29	3.1	6.53×10^{-7}	254	180	30
1f	12	33	70	10×10^{-7}	167	—	—

^a γ = surface tension.^bcmc = critical micellar concentration.^c Γ = superficial excess.^dA = total area of the polar heads.**Fig. 3.** Plots of the surface tension vs. log[bolaform] at 25°C in water.

from an average of 10–15 trials for each determination of the diameter, are reported in Table 2. In general, for 10 carbons or more, the distribution of the objects was found to follow a dispersion with a fairly low percentage. The diameter of the objects, which was closely linked to the spacer length, decreased as the number of carbon atoms increased. However, for 8 carbons, polydispersion occurred, but the size of the main objects remained close to that obtained for molecules with spacers 10 or more carbons long.

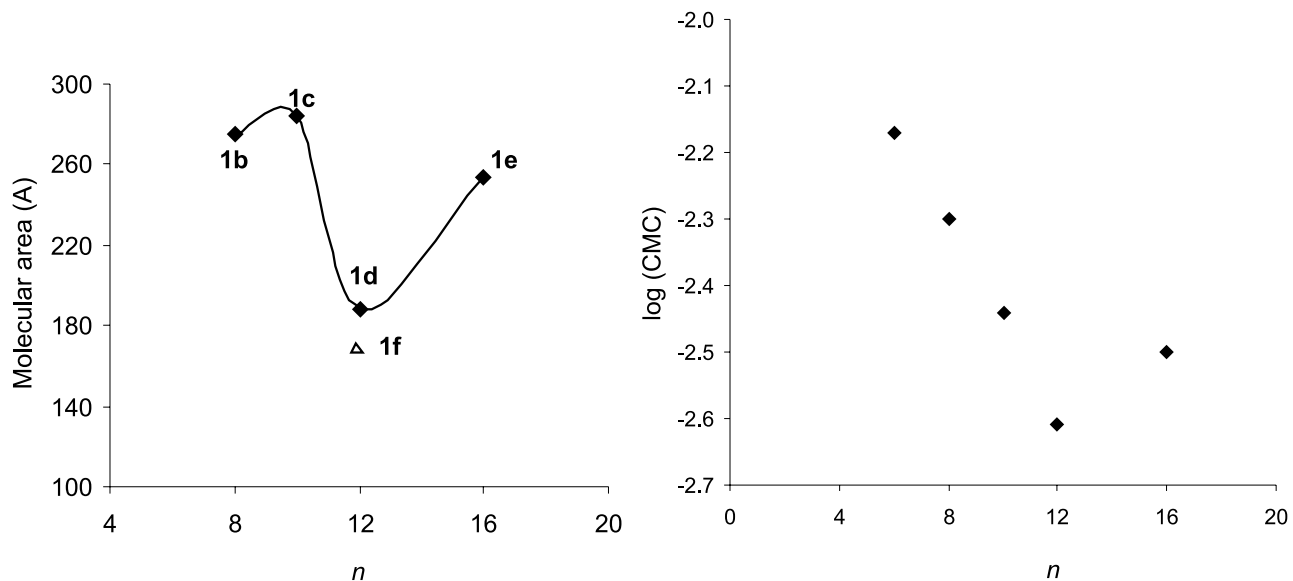
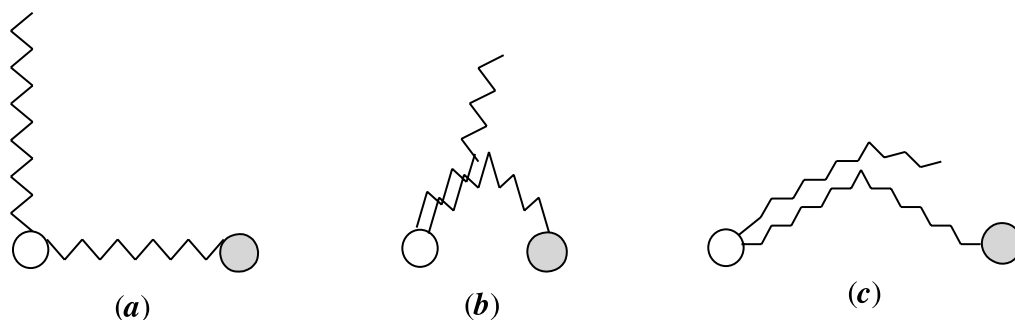
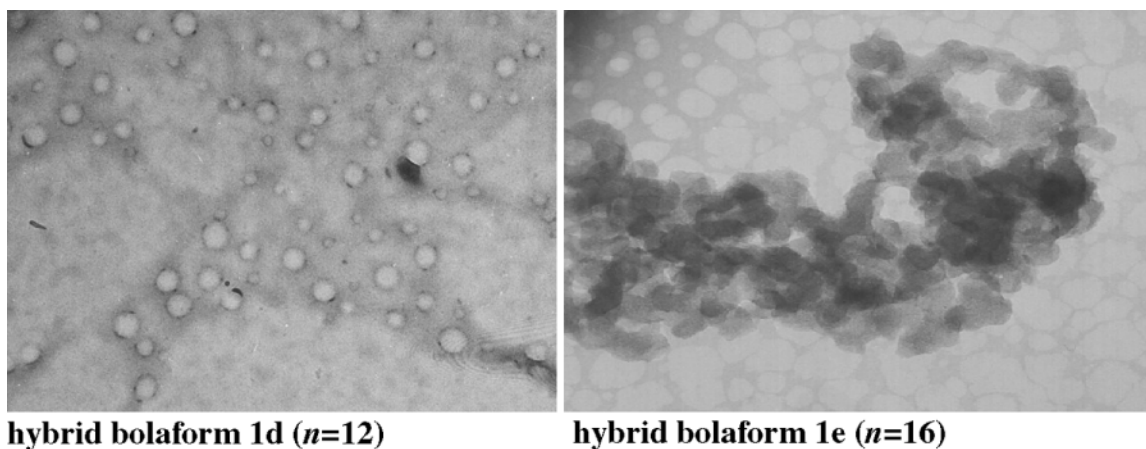
Transmission electronic microscopy (TEM)

The sonicated aqueous solutions prepared for TEM observation remained optically translucent for several weeks. As mentioned, without sonication only compound **1e** spontaneously formed aggregates. This self-organisation was not modified by sonication. This result illustrates the influence of spacer length (only parameter modified) and thus the role played by variations in the hydrophobic interactions allowed by the structure of the hybrid molecules studied here. The analogy with 2-chain bolaforms is again possible in that the latter are known to spontaneously form vesicles when the spacer is over 8 carbons long (14). It should however be noted that whereas sonication gave rise to vesicles for compounds with from C10 to C16 spacers (examples **1d** and **1e** given in Fig. 6), no aggregates were found for compound **1a** ($n = 6$). These results call for comments.

Based on previous results and on the “straight” molecular organisation that bicatener bolaforms tend to adopt (15), we propose that compound **1e** ($n = 16$) is organised in a monolayer. However, the possibility for the spacer in compound **1d** ($n = 12$) to fold suggests bilayer aggregation similar to that proposed for cationic (16) and gemini (17, 18) bolaforms. These types of molecular association present an interesting advantage, owing to the difficulties of the synthesis of the bicatener and gemini bolaforms with two different heads.

Conclusion

During this study, we have shown that the synthesis route we recently proposed for bolaforms with sulphobetain heads can be easily generalized to obtain high yields of cationic sulphobetain hybrid bolaforms. Grafting a hydrophobic

Fig. 4. Molecular area and cmc values in function of the length of the spacer of the hybrid bolaforms **1**.**Fig. 5.** Schematic proposition for the conformation of the hybrid bolaforms **1**.**Fig. 6.** Representative micrographs of aggregates by TEM method obtained from sonicated solutions (5×10^{-3} M) of **1d** (1 cm = 660 nm) and **1e** (1 cm = 350 nm).

chain onto the cationic head modifies both the surface properties and aggregation in aqueous medium. Compared to conventional bolaforms, the relationship between the length of the spacer and of the side-chain and the resulting hydrophobic interactions are at the origin of these novel proper-

ties. Favouring a given molecular association can therefore be envisaged by modulating these interactions by adjusting the chemical structure of the two chains. Access to new molecules should be possible using the reaction scheme proposed here. Work along these lines is in progress.

Experimental

General

Reagents were of commercial quality and were used without purification. Anhydrous acetone and methanol were of extra dry quality (Acros Organics France). IR spectra (ν , cm^{-1}) were recorded on a PerkinElmer 683 spectrophotometer. ^1H and ^{13}C NMR spectra (δ , ppm; J , hertz) were obtained on Bruker AC 80 or Bruker AC 200 instruments.

Aggregation mode

Parameters of the surface-active properties were calculated using Gibbs' equation (11) with the data obtained from measurements carried out on a Prolabo n°3 tensiometer using the stirrup detachment method. The size of aggregates was determined by light scattering using a Malvern Zetasizer 3000 instrument. An EM-301 Philips transmission electron microscope was used for TEM studies. Vesicles were prepared by sonication (Sonics instrument: 600 W) at 110 W for 15–20 min. Dust was removed by centrifugation (3000 rpm for 10 min) and filtration through a millipore 0.45 μ filter. One drop of the above dispersion was placed onto a carbon-coated grid (400 mesh). Filter paper was employed to wick away the excess water. One drop of 2% uranyl acetate solution was added.

It was then kept under mechanical vacuum for approximately 1 h. Micrographs were then recorded.

Typical procedure for the synthesis of compounds 2

A solution of dimethylamine (33% of ethanol) (3×10^{-2} mol) and dibromoalkane (10^{-2} mol) were added with sodium carbonate (2×10^{-2} mol) into 60 mL of ethanol and 15 mL of water. The reaction mixture was refluxed and stirred for 24 h. Then the resulting compound was isolated by evaporation of the solvent under reduced pressure. The crude product, washed with 10 mL of water, was extracted with EtO_2 . The organic phase was dried on anhydrous Na_2SO_4 and evaporated in vacuo. The crude oil was purified by distillation.

1,6 Bis (N,N-dimethylamino)hexane, 2a

Yield: 98%. Colourless oil, bp = 68°C at 1 mmHg (1 mmHg = 133.322 Pa). ^1H NMR (200 MHz, CDCl_3) δ : 1.10 (m, 8H, $(\text{CH}_2)_4$), 1.92 (s, 12H, $2 \times \text{N}(\text{CH}_3)_2$), 2.31 (t, $J = 6.4$, 4H, $2 \times \text{NCH}_2$). ^{13}C NMR (200 MHz, CDCl_3) δ : 27.23–28.30 ($(\text{CH}_2)_4$), 45.20 (NCH₃), 59.66 (NCH₂). Anal. calcd. (%) for $\text{C}_{10}\text{H}_{24}\text{N}_2$ (172.30): C 69.70, H 14.04, N 16.25; found: C 69.82, H 14.24, N 16.02.

1,8 Bis (N,N-dimethylamino)octane, 2b

Yield: 98%. Colourless oil, bp = 60°C at 0.06 mmHg. ^1H NMR (200 MHz, CDCl_3) δ : 1.12 (m, 12H, $(\text{CH}_2)_6$), 1.92 (s, 12H, $2 \times \text{N}(\text{CH}_3)_2$); 2.31 (t, $J = 6.5$, 4H, $2 \times \text{NCH}_2$). ^{13}C NMR (200 MHz, CDCl_3) δ : 27.23–28.30 ($(\text{CH}_2)_6$), 45.20 (NCH₃), 59.66 (NCH₂). Anal. calcd. (%) for $\text{C}_{12}\text{H}_{28}\text{N}_2$ (200.37): C 71.86, H 13.97, N 13.97; found: C 71.66, H 14.15, N 14.13.

1,10 Bis (N,N-dimethylamino)decane, 2c

Yield: 92%. Colourless oil, bp = 62°C at 0.05 mmHg. ^1H NMR (200 MHz, CDCl_3) δ : 1.09 (m, 12H, $(\text{CH}_2)_6$), 1.24 (m, 4H, $2 \times \text{CH}_2\text{-C-N}$), 1.92 (s, 12H, $2 \times \text{N}(\text{CH}_3)_2$), 2.03 (t, $J =$

6.3, 4H, $2 \times \text{CH}_2\text{N}$). ^{13}C NMR (200 MHz, CDCl_3) δ : 27.4–28.51 ($(\text{CH}_2)_8$), 45.42 (NCH₃), 59.87 (NCH₂). Anal. calcd. (%) for $\text{C}_{14}\text{H}_{32}\text{N}_2$ (228.40): C 73.61, H 14.12, N 12.26; found: C 74.08, H 13.96, N 12.62.

1,12 Bis (N,N-dimethylamino)dodecane, 2d

Yield: 98%. Colourless oil, bp = 80–82°C at 0.05 mmHg. ^1H NMR (200 MHz, CDCl_3) δ : 1.12 (m, 20H, $(\text{CH}_2)_{10}$), 1.91 (s, 12H, $2 \times \text{N}(\text{CH}_3)_2$), 2.12 (t, $J = 6.3$, 4H, $2 \times \text{NCH}_2$). ^{13}C NMR (200 MHz, CDCl_3) δ : 27.43–28.53 ($(\text{CH}_2)_{10}$), 45.42 (NCH₃), 59.87 (NCH₂). Anal. calcd. (%) for $\text{C}_{16}\text{H}_{36}\text{N}_2$ (256.47): C 74.86, H 14.03, N 10.92; found: C 74.73, H 13.90, N 11.62.

1,16 Bis (N,N-dimethylamino)hexadecane, 2e

Yield: 75%. Colourless oil, decomposition during the distillation. ^1H NMR (200 MHz, CDCl_3) δ : 1.19 (m, 24H, $(\text{CH}_2)_{12}$), 1.23 (m, 4H, $2 \times \text{CH}_2\text{CN}$), 2.16 (s, 12H, $2 \times \text{N}(\text{CH}_3)_2$), 2.25 (t, $J = 6.4$, 4H, $2 \times \text{NCH}_2$). ^{13}C NMR (200 MHz, CDCl_3) δ : 27.43–28.53 ($(\text{CH}_2)_{14}$), 45.42 (NCH₃), 59.87 (NCH₂). Anal. calcd. (%) for $\text{C}_{20}\text{H}_{44}\text{N}_2$ (312.56): C 76.85, H 14.19, N 8.96; found: C 76.73, H 13.92, N 8.62.

Typical procedure for the synthesis of compounds 3

Sulfobetaine **3** was prepared by the addition of α,ω -bis(*N,N*-dimethylamino) alkane **2** (10^{-2} mol) to a stirred solution of 1,3-propane sultone (7×10^{-3} mol) in 50 mL of anhydrous acetone. The reaction mixture was stirred at room temperature for 3 h, cooled, and filtered. The amphiphilic product was purified by recrystallization from methanol-ether (1:9) and dried in vacuo over phosphorus pentoxide.

1-(N,N-Dimethylammonio,N-propyl-1-sulfonate)-8-(N',N'-dimethylamino) octane, 3b

Yield: 96%. White powder, mp = 198–200°C. IR (KBr) ν : 1480 (C-N⁺), 1040 (S = O). ^1H NMR (80 MHz, D_2O) δ : 1.25 (m, 12H, $(\text{CH}_2)_6$), 1.99–2.18 (m, 10H, NCH₂, $\text{N}(\text{CH}_3)_2$, $\text{CH}_2\text{-C-SO}_3^-$), 2.72–3.21 (m, 12H, N⁺(CH₃)₂, N⁺CH₂, CH_2SO_3^-). ^{13}C NMR (200 MHz, D_2O) δ : 20.73–31.66 ($(\text{CH}_2)_6$), 46.52 (NCH₃), 49.81 ($\text{CH}_2\text{-C-SO}_3^-$), 53.16 (N⁺CH₃), 61.43 (NCH₂), 64.54 (N⁺CH₂), 66.71 (CH_2SO_3^-). Anal. calcd. (%) for $\text{C}_{15}\text{H}_{34}\text{N}_2\text{SO}_3$ (322.5): C 55.86, H 10.63, N 8.69, S 9.94; found: C 55.50, H 10.46, N 8.46, S 9.62.

1-(N,N-Dimethylammonio,N-propyl-1-sulfonate)-10-(N',N'-dimethylamino) decane, 3c

Yield: 97%. White powder, mp = 218°C. IR (KBr) ν : 1480 (C-N⁺), 1040 (S = O). ^1H NMR (80 MHz, D_2O) δ : 1.27 (m, 16H, $(\text{CH}_2)_8$), 1.82–2.16 (m, 8H, NCH_2 , $\text{N}(\text{CH}_3)_2$), 2.33 (t, $J = 6.6$, 2H, NCH₂), 2.65 (t, $J = 8.1$, 2H, CH_2SO_3^-), 3 (s, 6H, $\text{N}(\text{CH}_3)_2$). ^{13}C NMR (200 MHz, D_2O) δ : 20.72–31.65 ($(\text{CH}_2)_{10}$), 46.52 (NCH₃), 49.84 ($\text{CH}_2\text{-C-SO}_3^-$), 53.16 (N⁺CH₃), 61.44 (NCH₂), 64.52 (N⁺CH₂), 66.71 (CH_2SO_3^-). Anal. calcd. (%) for $\text{C}_{17}\text{H}_{38}\text{N}_2\text{SO}_3$ (350): C 58.09, H 10.52, N 4.7, S 5.34; found: C 57.80, H 10.57, N 4.3, S 5.27.

1-(N,N-Dimethylammonio,N-propyl-1-sulfonate)-12-(N',N'-dimethylamino) dodecane, 3d

Yield: 95%. White powder, mp = 230°C. IR (KBr) ν : 1480 (C-N⁺), 1040 (S = O). ^1H NMR (80 MHz, D_2O) δ : 1.22 (m, 20H, $(\text{CH}_2)_{10}$), 1.91–2.15 (m, 10H, NCH₂, $\text{N}(\text{CH}_3)_2$,

$\text{CH}_2\text{-C-SO}_3^-$), 2.91–3.25 (m, 12H, $\text{N}^+(\text{CH}_3)_2$, N^+CH_2 , $\text{CH}_2\text{-CH}_2\text{SO}_3^-$). ^{13}C NMR (200 MHz, D_2O) δ : 20.75–31.65 ($(\text{CH}_2)_{10}$), 46.52 (NCH_3), 49.84 ($\text{CH}_2\text{-C-SO}_3^-$), 53.16 (N^+CH_3), 61.44 (NCH_2), 64.52 (N^+CH_2), 66.72 (CH_2SO_3^-). Anal. calcd. (%) for $\text{C}_{19}\text{H}_{42}\text{N}_2\text{SO}_3$ (378.6): C 60.27, H 11.18, N 7.40, S 8.47; found: C 59.93, H 11.02, N 7.07, S 8.54.

1-(N,N-Dimethylammonio,N-propyl-1-sulfonate)-12-(N',N'-dimethylamino) hexadecane, 3e

Yield: 75%. White powder, mp = 238°C. IR (KBr) v: 1480 (C-N⁺), 1040 (S = 0). ^1H NMR (80 MHz, D_2O) δ : 1.22 (m, 28H, $(\text{CH}_2)_{14}$), 1.72 (m, 2H, NCCCH_2), 2.13–2.55 (m, 8H, $\text{N}(\text{CH}_3)_2$, NCH_2), 2.84 (m, 2H, $\text{CH}_2\text{-CSO}_3^-$), 3.18 (m, 8H, $\text{N}^+(\text{CH}_3)_2$, N^+CH_2), 3.45 (t, $J = 7.9$, 2H, SO_3CH_2). ^{13}C NMR (200 MHz, D_2O) δ : 19.51–29.6 ($(\text{CH}_2)_{14}$), 45.54 (NCH_3), 47.63 ($\text{CH}_2\text{-C-SO}_3^-$), 50.61 (N^+CH_3), 60.40 (N^+CH_2), 63.52 (N^+CH_2), 63.42 (N^+CH_2), 64.54 (CH_2SO_3^-). Anal. calcd. (%) for $\text{C}_{23}\text{H}_{50}\text{N}_2\text{SO}_3$ (434.4): C 63.59, H 11.52, N 6.44, S 7.37; found: C 62.93, H 11.22, N 7.01, S 7.54.

Typical procedure for the synthesis of compounds 1

A mixture of sulfobetaine **3** (10^{-2} mol) and of haloalkane (1.2×10^{-2} mol) in 50 mL of absolute MeOH was heated at reflux for 4 h. After removing the solvent in vacuo, the residual oil was precipitated by trituration with anhydrous ether. After filtration, the solid was washed by 3×20 mL of anhydrous ether and dried in vacuo over phosphorus pentoxide.

1-(N,N-Dimethylammonio,N-propyl-1-sulfonate)-8-(N',N'-dimethyl,N'-dodecylammonium bromide) octane, 1b

Yield: 87%. White powder, mp = 120°C. IR (KBr) v: 1480 (C-N⁺), 1040 (S = 0). ^1H NMR (80 MHz, D_2O) δ : 0.85 (t, $J = 7.3$, 3H, $\text{CH}_3\text{-C}_{11}$), 1.26 (m, 32H, $(\text{CH}_2)_{10}$, $(\text{CH}_2)_6$), 2.09 (m, 2H, $\text{CH}_2\text{-C-SO}_3^-$), 2.64–3.33 (m, 22H, $2 \times \text{N}(\text{CH}_3)_2$, $4 \times \text{NCH}_2$, CH_2SO_3^-). ^{13}C NMR (200 MHz, D_2O) δ : 16.61 (C- CH_3), 20.75–34.61 ($(\text{CH}_2)_6$, $(\text{CH}_2)_{10}$), 49.90 ($\text{CH}_2\text{-C-SO}_3^-$), 53.51 and 54.45 (NCH_3), 64.46 and 66.32 (NCH_2), 66.69 (CH_2SO_3^-), 69.35 (N^+CH_2). Anal. calcd. (%) for $\text{C}_{27}\text{H}_{59}\text{N}_2\text{SO}_3\text{Br}$ (574.77): C 56.61, H 10.38, N 4.89, S 5.59; found: C 56.95, H 10.95, N 4.80, S 6.00.

1-(N,N-Dimethylammonio,N-propyl-1-sulfonate)-10-(N',N'-dimethyl,N'-dodecylammonium bromide) decane, 1c

Yield: 92%. White powder, mp = 115°C. IR (KBr) v: 1480 (C-N⁺), 1040 (S = 0). ^1H NMR (80 MHz, D_2O) δ : 0.85 (t, $J = 7.1$, 3H, $\text{CH}_3\text{-C}$), 1.23 (m, 36H, $(\text{CH}_2)_{10}$, $(\text{CH}_2)_8$), 1.72–2.15 (m, 10H, CH_2CN , $\text{CH}_2\text{-C-SO}_3^-$), 2.84–3.05 (m, 12H, $2 \times \text{N}(\text{CH}_3)_2$), 3.35 (m, 2H, CH_2SO_3^-). ^{13}C NMR (200 MHz, D_2O) δ : 16.63 (C- CH_3), 20.75–34.59 ($(\text{CH}_2)_8$, $(\text{CH}_2)_{10}$), 49.96 ($\text{CH}_2\text{-C-SO}_3^-$), 53.25 and 53.63 (NCH_3), 64.33 and 66.96 (NCH_2), 66.48 (CH_2SO_3^-), 69.76 (N^+CH_2). Anal. calcd. (%) for $\text{C}_{29}\text{H}_{63}\text{N}_2\text{SO}_3\text{Br}$ (599.86): C 57.96, H 10.57, N 4.66, S 5.33; found: C 58.79, H 10.05, N 4.42, S 5.55.

1-(N,N-Dimethylammonio,N-propyl-1-sulfonate)-12-(N',N'-dimethyl,N'-dodecylammonium bromide) dodecane, 1d

Yield: 85%. White powder, mp = 105°C. IR (KBr) v: 1480 (C-N⁺), 1040 (S = 0). ^1H NMR (80 MHz, D_2O) δ : 0.85 (t, $J = 7.2$, 3H, $\text{CH}_3\text{-C}_{11}$), 1.27 (m, 40H, $2 \times (\text{CH}_2)_{10}$), 2.09 (m, 2H, $\text{CH}_2\text{-C-SO}_3^-$), 3.07–3.33 (m, 22H, $2 \times \text{N}(\text{CH}_3)_2$, $4 \times \text{NCH}_2$, CH_2SO_3^-). ^{13}C NMR (200 MHz, D_2O) δ : 16.61

(C- CH_3), 20.63–34.40 ($(\text{CH}_2)_{10}$), 49.90 ($\text{CH}_2\text{-C-SO}_3^-$), 53.52 and 54.36 (NCH_3), 64.21 and 66.06 (NCH_2), 66.34 (CH_2SO_3^-). Anal. calcd. (%) for $\text{C}_{31}\text{H}_{67}\text{N}_2\text{SO}_3\text{Br}$ (627.87): C 59.20, H 10.74, N 4.45, S 5.09; found: C 59.79, H 10.35, N 4.42, S 5.55.

1-(N,N-Dimethylammonio,N-propyl-1-sulfonate)-16-(N',N'-dimethyl,N'-dodecylammonium bromide) hexadecane, 1e

Yield: 85%. White powder, mp = 135°C. IR (KBr) v: 1485 (C-N⁺), 1040 (S = 0). ^1H NMR (80 MHz, D_2O) δ : 0.87 (t, $J = 7.3$, 3H, CH_3), 1.24–1.35 (m, 48H, $(\text{CH}_2)_{14}$, $(\text{CH}_2)_{10}$), 2.13 (m, 2H, $\text{CH}_2\text{-C-S}$), 2.91–3.13 (m, 14H, $2 \times \text{N}(\text{CH}_3)_2$, CH_2SO_3^-), 3.35 (m, 8H, $4 \times \text{N}^+\text{CH}_2$). ^{13}C NMR (200 MHz, D_2O) δ : 18.13 (CH_3), 21.10–35.12 ($(\text{CH}_2)_{14}$, $(\text{CH}_2)_{10}$), 48.98 ($\text{CH}_2\text{-C-S}$), 50.40 and 52.2 (NCH_3), 60.62, 64.75, and 65.81 (N^+CH_2), 66.75 (CH_2S). Anal. calcd. (%) for $\text{C}_{35}\text{H}_{75}\text{N}_2\text{SO}_3\text{Br}$ (683.98): C 61.36, H 11.03, N 4.09, S 4.68; found: C 61.82, H 10.35, N 4.98, S 4.35.

1-(N,N-Dimethylammonio,N-propyl-1-sulfonate)-12-(N',N'-dimethyl,N'-ethylammonium bromide) dodecane, 1f

Yield: 90%. White powder, mp = 125°C. ^1H NMR (80 MHz, D_2O) δ : 1.13 (t, $J = 7.2$, 3H, CH_3), 1.34 (m, 16H, $(\text{CH}_2)_8$), 2.25 (m, 2H, $\text{CH}_2\text{-C-SO}_3^-$), 2.94–3.25 (m, 14H, $2 \times \text{N}(\text{CH}_3)_2$, CH_2SO_3^-), 3.31 (m, 8H, $4 \times \text{NCH}_2$), 3.52 (t, $J = 7.2$, 2H, $\text{NCH}_2\text{-C-C-S}$). ^{13}C NMR (200 MHz, D_2O) δ : 10.03 (CH_3), 20.73–31.12 ($(\text{CH}_2)_8$), 49.81 ($\text{CH}_2\text{-C-S}$), 52.43 (NCH_3), 53.21 ($\text{CH}_3\text{N-S}$), 62.0, 64.48, and 65.75 (NCH_2), 66.6 (CH_2S). Anal. calcd. (%) for $\text{C}_{21}\text{H}_{47}\text{N}_2\text{SO}_3\text{Br}$ (487.62): C 49.88, H 9.77, N 5.54, S 4.08; found: C 50.12, H 10.02, N 5.38, S 4.32.

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