Electronic Supplementary Information

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Aqueous solution behaviour and solubilisation properties of octadecyl cationic gemini surfactants and their comparison with their amide gemini analogues

1. Synthesis of amine intermediate and 18-*s*-18(Et) gemini surfactants

Synthesis of *N,N*-diethyloctadecylamine, (amine C_{18}). 1-bromooctadecane (42.34 g; 127 mM) and diethylamine (110.0 g; 1500 mM) were refluxed under dry, oxygen free, nitrogen conditions for 24 h. After this time, a white solid, the side product, was filtered and discarded. The excess of diethylamine was distilled off from the filtrate, and the residue poured into 500 mL 1M NaOH solution and stirred for 30 min. The solution was extracted three times with ethyl acetate and the organic layer was dried under anhydrous magnesium sulphate and filtered. After evaporation of the ethyl acetate, the crude product in the form of a yellowish oil was distilled under vacuum. The fraction with the boiling point of 170-172°C (0.1 mbar) was collected as creamy, viscous liquid.

Synthesis of gemini surfactants 18-*s*-18(Et). Amine C_{18} (4.10 g, 12.3 mM) was poured into 30 mL of propionitrile and heated until complete dissolution (about 70 °C). Then, alkyl dibromide (6.0 mM Br-*s*-Br, with *s* = 4, 6, 8, 10) was added and the reaction mixture was refluxed for 36 h. After this time, the precipitate was filtered and recrystallised three times from the ethyl acetate/acetonitrile mixture. Surfactants were obtained as white solids in the yields shown in Table S1.

Table S1. Yields of the obtained compounds

Compound	Systematic name	Yield of compound, %
Amine C_{18}	*N,N*-diethyloctadecylamine	55.1
18-4-18(Et)	*N,N'*-dioctadecyl-*N,N,N',N'*-tetraethyl-1,4-butane diammonium dibromide	60.4
18-6-18(Et)	*N,N'*-dioctadecyl-*N,N,N',N'*-tetraethyl-1,6-hexane diammonium dibromide	59.9
18-8-18(Et)	*N,N'*-dioctadecyl-*N,N,N',N'*-tetraethyl-1,8-octane diammonium dibromide	56.3
18-10-18(Et)	*N,N'*-dioctadecyl-*N,N,N',N'*-tetraethyl-1,10-decane diammonium dibromide	61.4

2. 1H NMR data of obtained surfactants in $CDCl_3$

Table S2. 1H NMR data for the obtained compounds

Compound	Head		Tail		Spacer
	$-CH_3$	**$-CH_2$**	**$-CH_3$**	**$-CH_2$**	**$-CH_2$**
Amine C_{18}	1.03 (6 H)	2.54 (4 H)	0.88 (3 H)	1.28 (30 H) 1.45 (2 H) 2.42 (2 H)	–
18-4-18(Et)	1.42 (6 H)	3.44 (4 H)	0.88 (3 H)	1.29 (28 H) 1.34 (2 H) 1.72 (2 H) 3.22 (2 H)	3.70 (2 H) 2.21 (2 H)
18-6-18(Et)	1.37 (6H)	3.54 (4H)	0.88 (3 H)	1.29 (28 H) 1.37 (2 H) 1.66 (2 H) 3.29 (2 H)	3.48 (2 H) 1.96 (2 H) 1.62 (2 H)
18-8-18(Et)	1.36 (6H)	3.52 (4H)	0.88 (3 H)	1.29 (28 H) 1.36 (2 H) 1.67 (2 H) 3.16 (2 H)	3.30 (2 H) 2.06 (2 H) 1.48 (2 H) 1.44 (2 H)

18-10-18(Et)	1.36 (6H)	3.52 (4H)	0.88 (3 H)	1.26 (28 H) 1.32 (2 H) 1.68 (2 H) 3.29 (2 H)	3.42 (2 H) 1.76 (2 H) 1.40 (2 H) 1.32 (2 H) 1.27 (2 H)

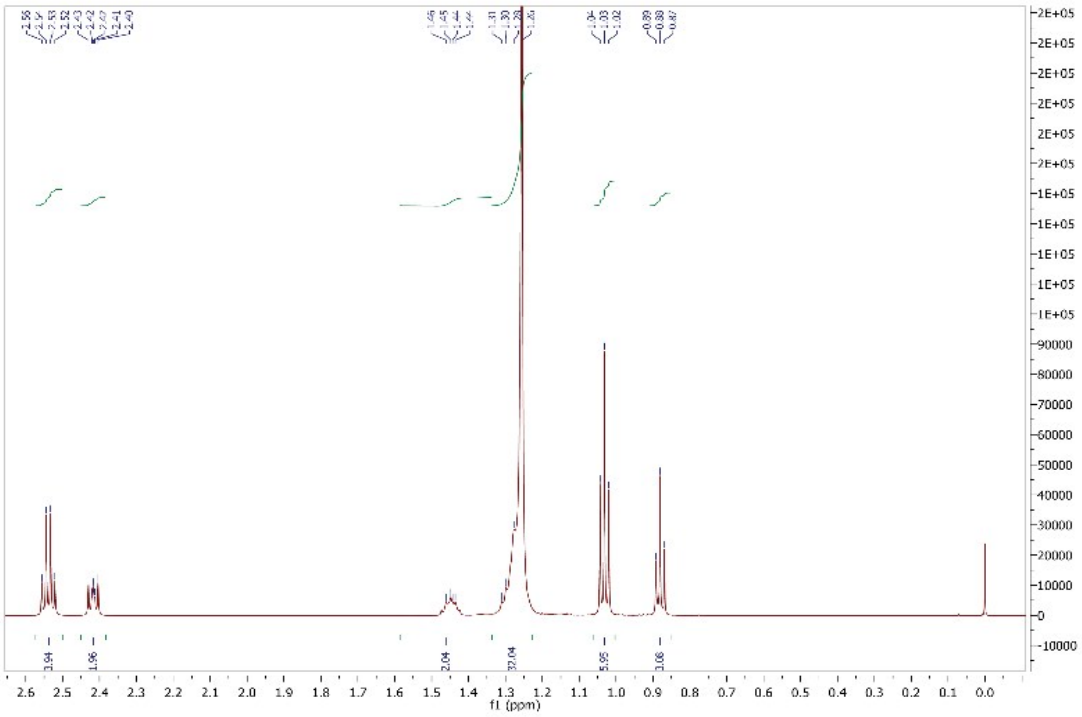


Fig. S1. 1H NMR spectrum of N,N-diethyloctadecylamine (amine C_{18}) in $CDCl_3$.

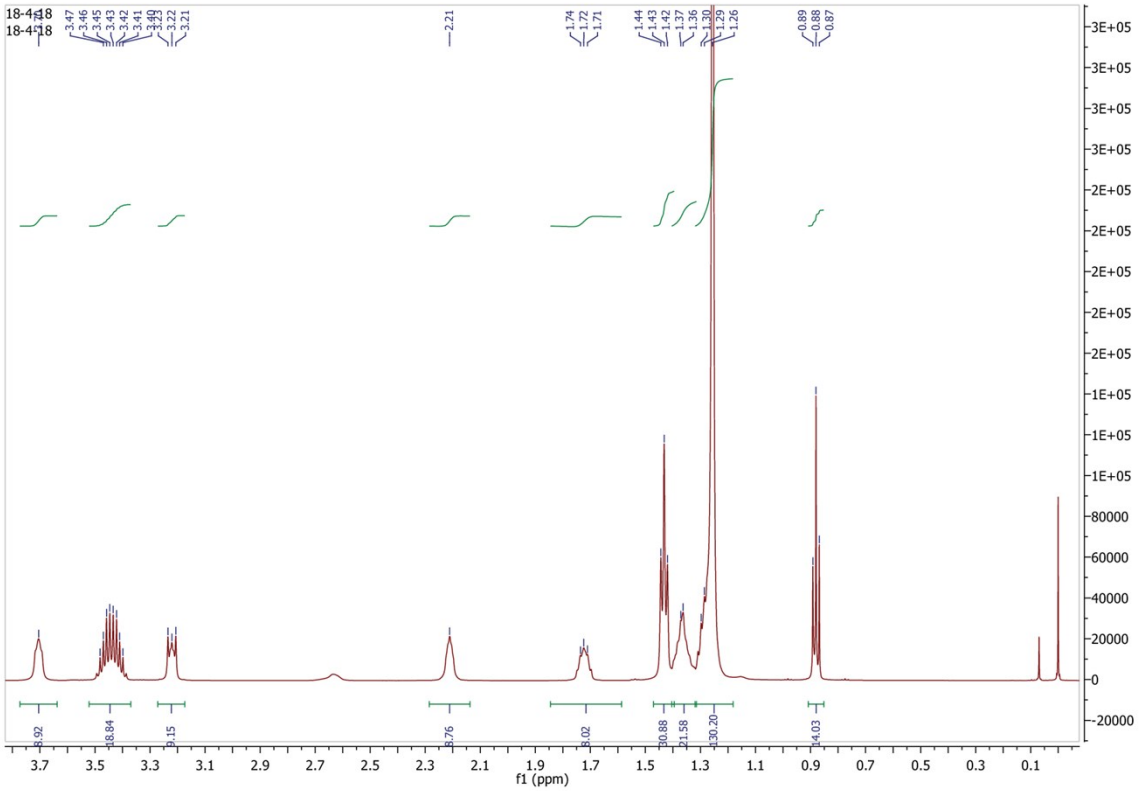


Fig. S2. 1H NMR spectrum of 18-4-18(Et) gemini surfactant in $CDCl_3$.

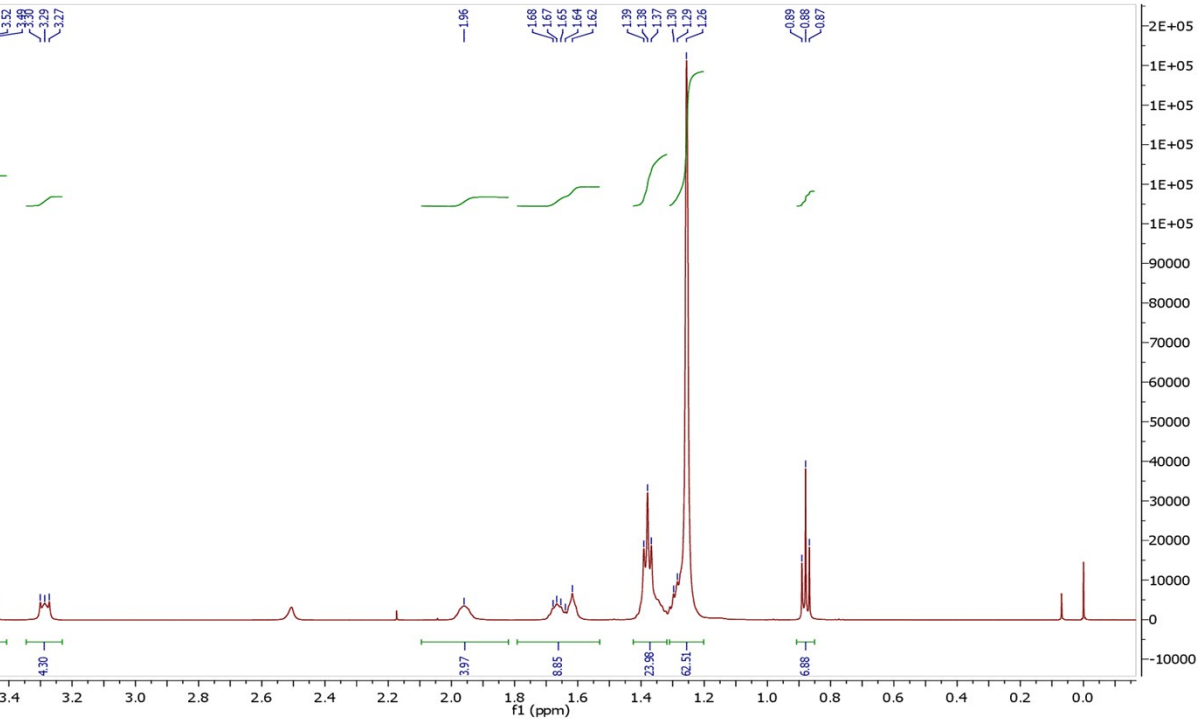


Fig. S3. 1H NMR spectrum of 18-6-18(Et) gemini surfactant in $CDCl_3$.

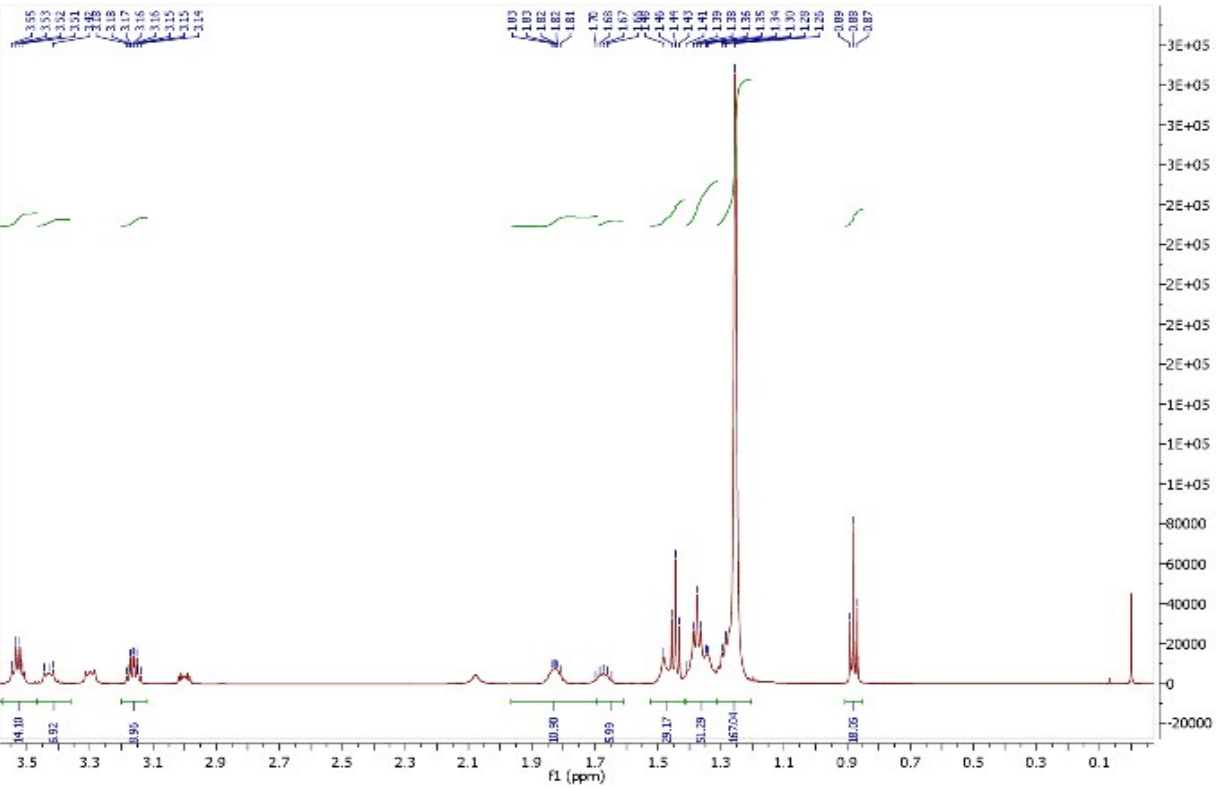


Fig.S4. 1H NMR spectrum of 18-8-18(Et) gemini surfactant in $CDCl_3$.

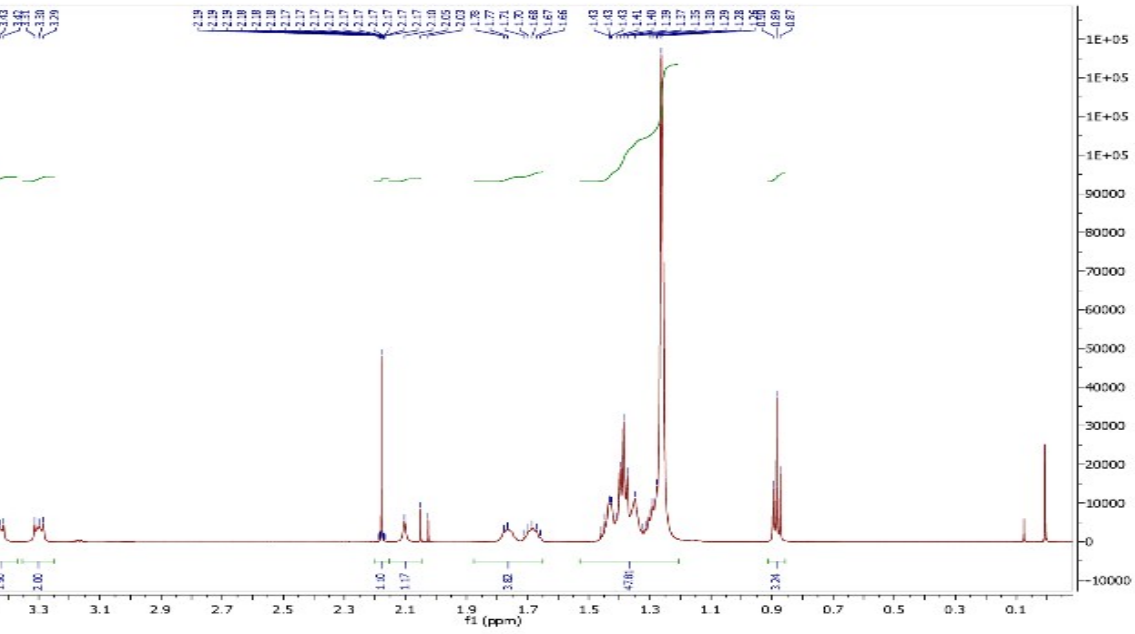


Fig. S5. 1H NMR spectrum of 18-10-18(Et) gemini surfactant in $CDCl_3$.

3. 13C NMR data, 13C NMR spectra of obtained surfactants

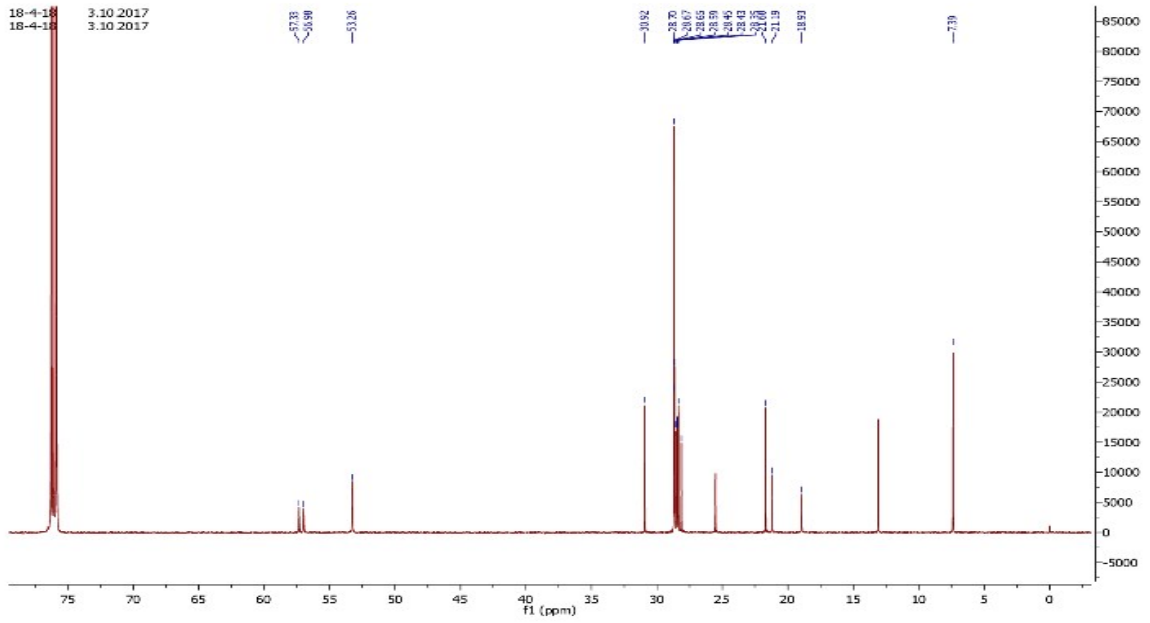
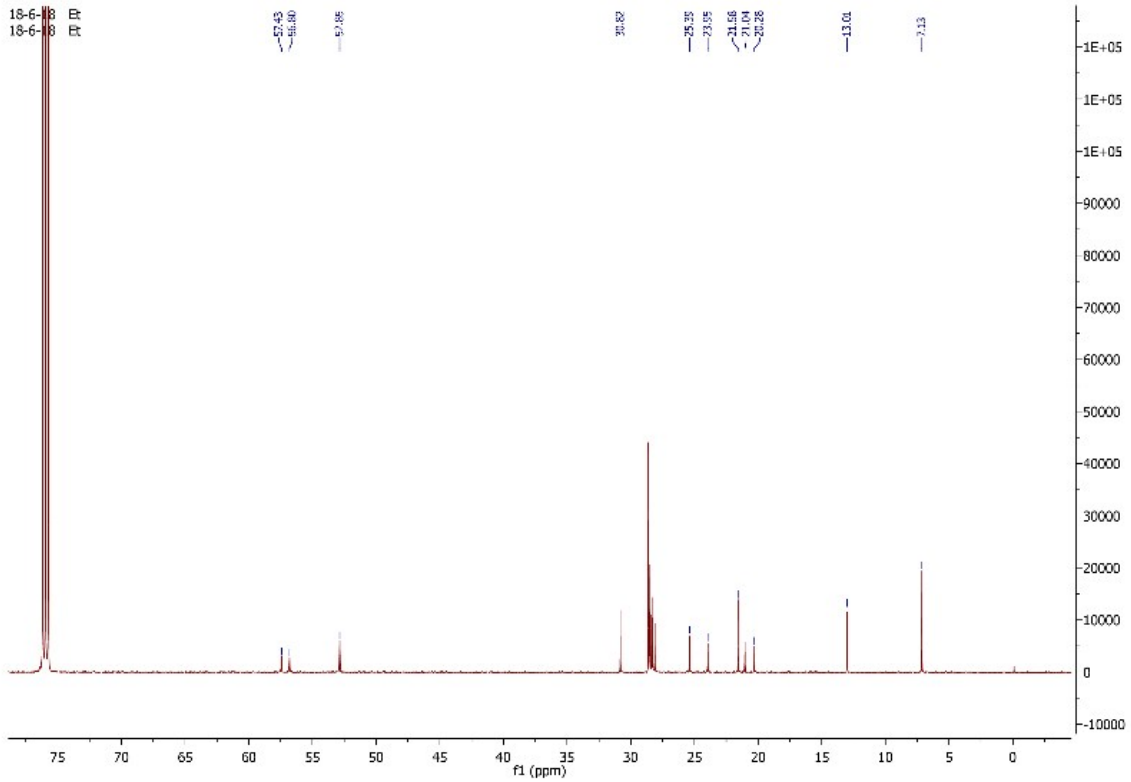
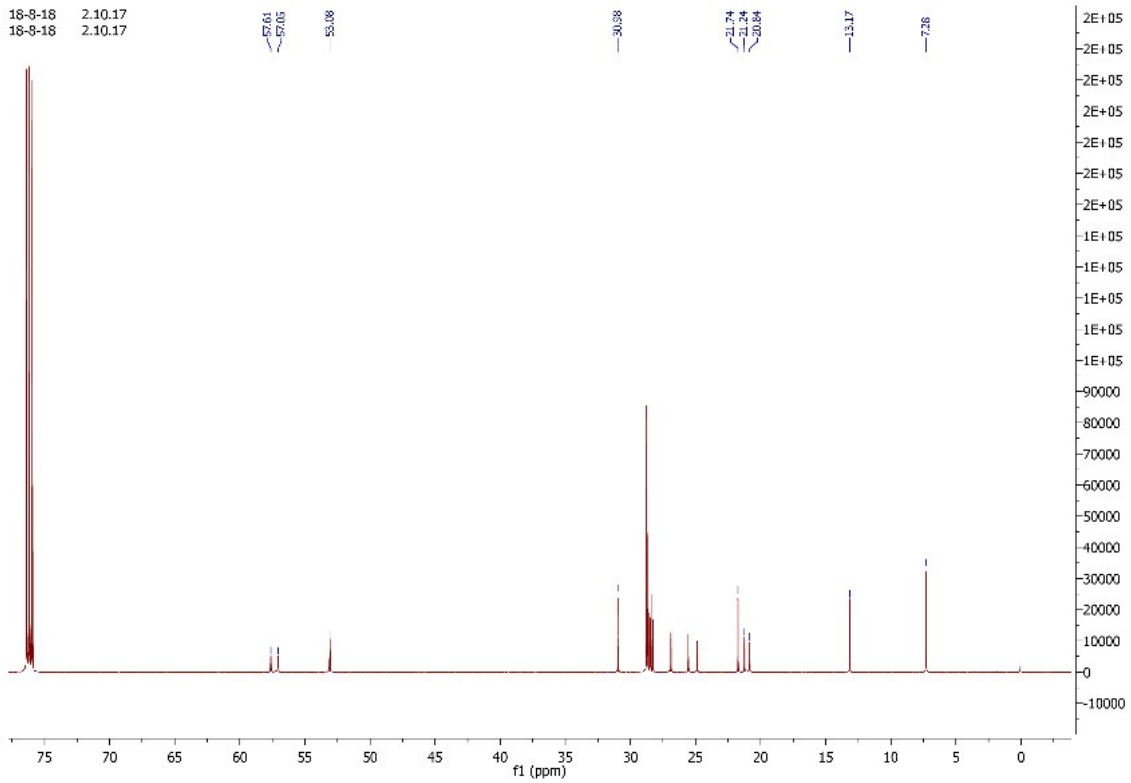


Fig. S6. 13C NMR spectrum of 18-4-18(Et) gemini surfactant in $CDCl_3$.



Fi

g. S7. 13C NMR spectrum of 18-6-18(Et) gemini surfactant in $CDCl_3$.



Fi

g. S8. 13C NMR spectrum of 18-8-18(Et) gemini surfactant in $CDCl_3$.

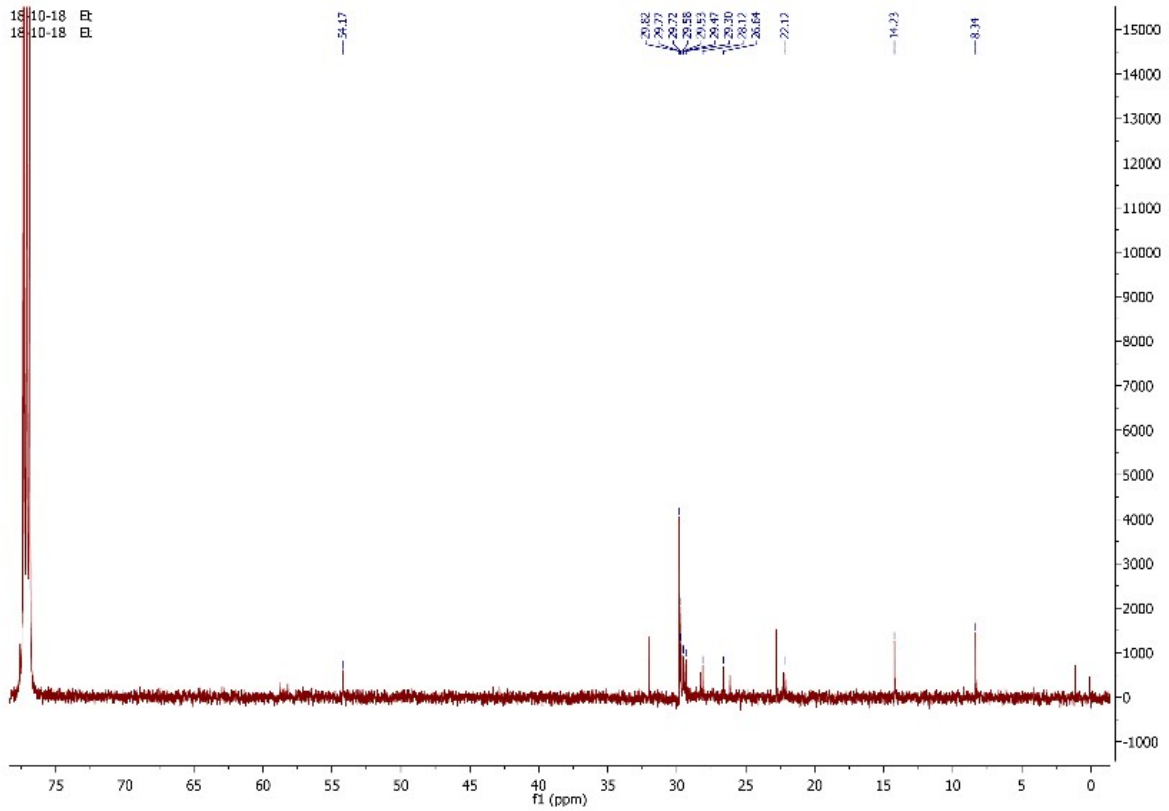


Fig. S9. 13C NMR spectrum of 18-10-18(Et) gemini surfactant in $CDCl_3$.

4. MS data

Table S3. MS data for the 18-s-18(Et) gemini surfactants

Compound	Neutral mass , Da	Ions detected by ESI MS (positive) m/z, Da
18-4-18(Et)	867.1	354.0 $[M-2Br]^{2+}$ 787.7 $[M-Br]^{+}$
18-6-18(Et)	895.2	368.1 $[M-2Br]^{2+}$ 815.7 $[M-Br]^{+}$
18-8-18(Et)	923.2	382.1 $[M-2Br]^{2+}$ 843.9 $[M-Br+H]^{+}$
18-10-18(Et)	951.3	396.1 $[M-2Br]^{2+}$ 871.9 $[M-Br]^{+}$

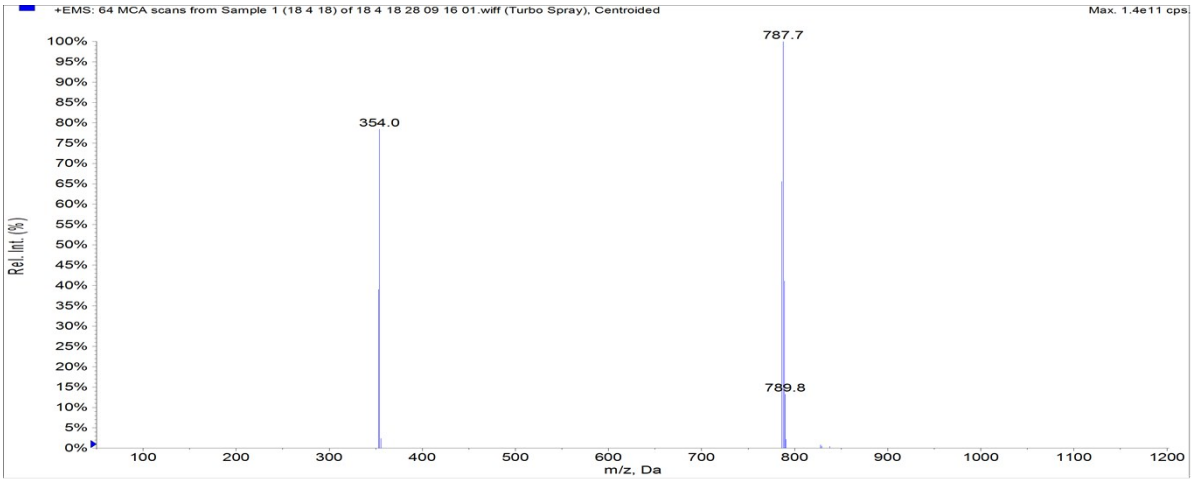


Fig. S10. MS spectrum of 18-4-18(Et) gemini surfactant.

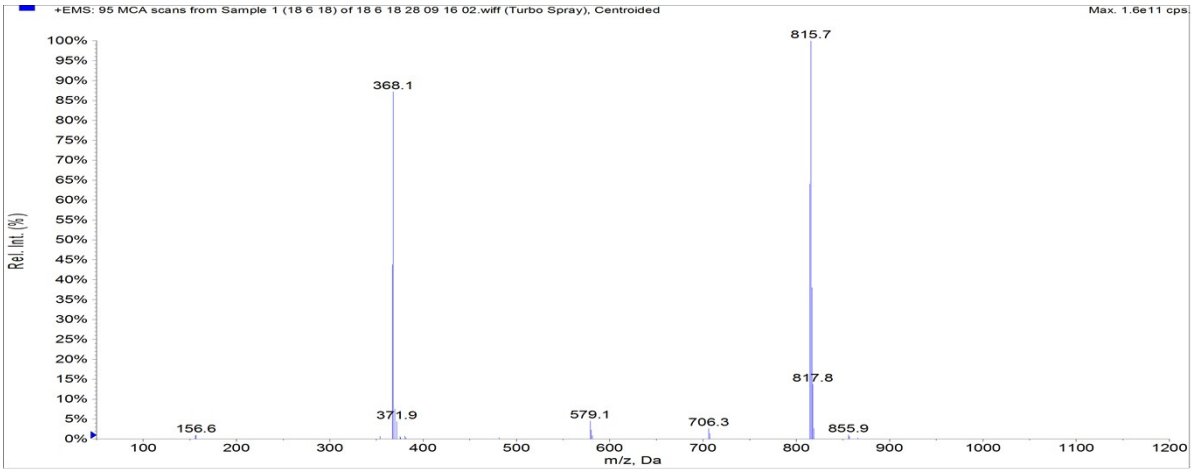


Fig. S11. MS spectrum of 18-6-18(Et) gemini surfactant.

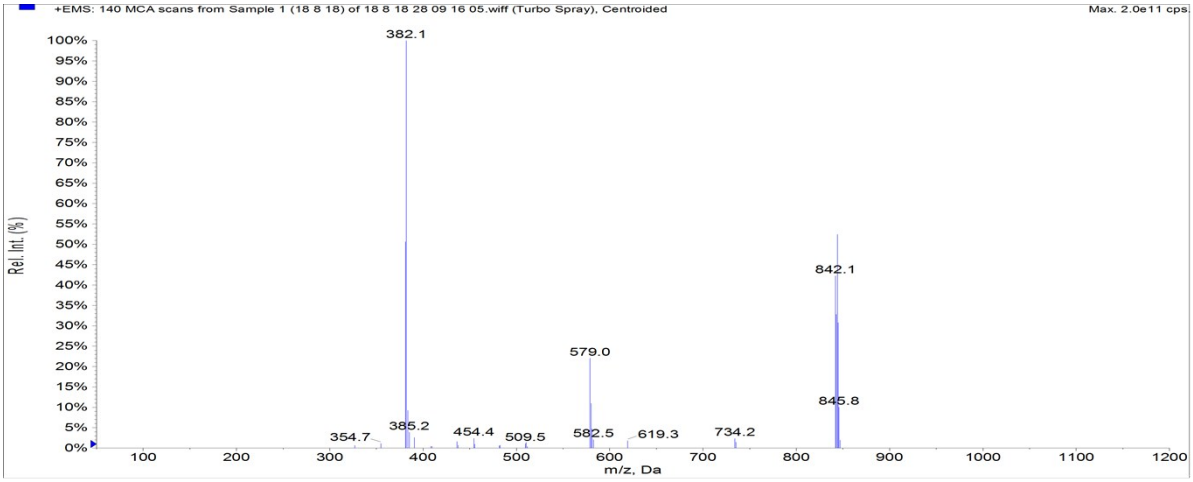


Fig. S12. MS spectrum of 18-8-18(Et) gemini surfactant.

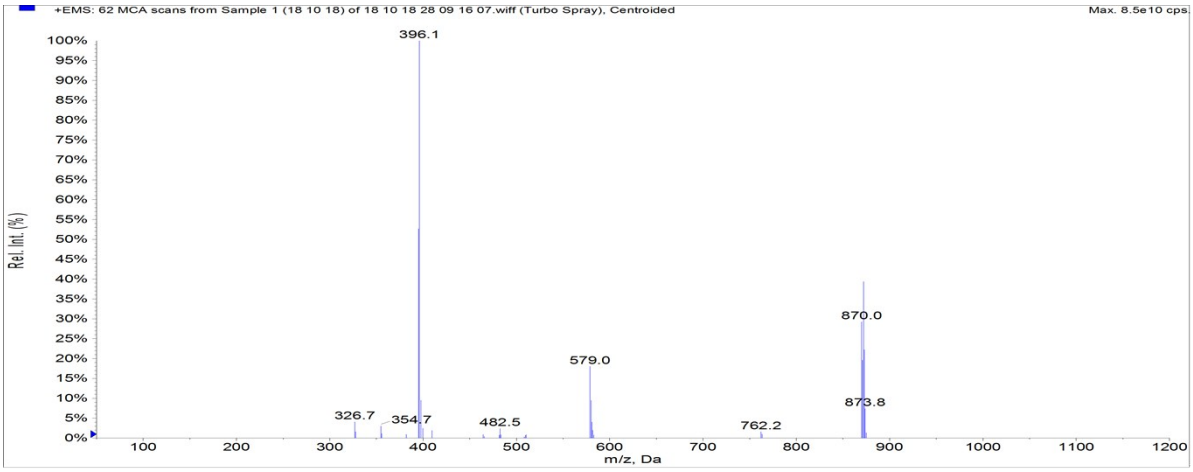


Fig. S13. MS spectrum of 18-10-18(Et) gemini surfactant.

5. Krafft temperature determination

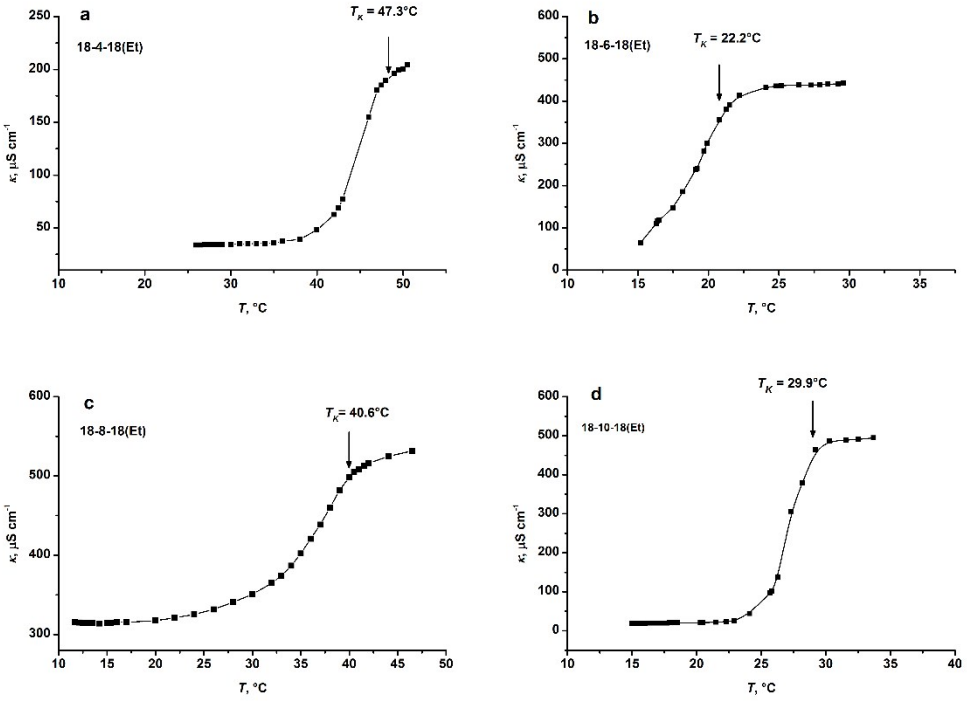


Fig. S14. Conductivity versus temperature dependence and Krafft point determination for 18-*s*-18(Et) with *s* = 4, 6, 8, 10.

6. **DLS data**

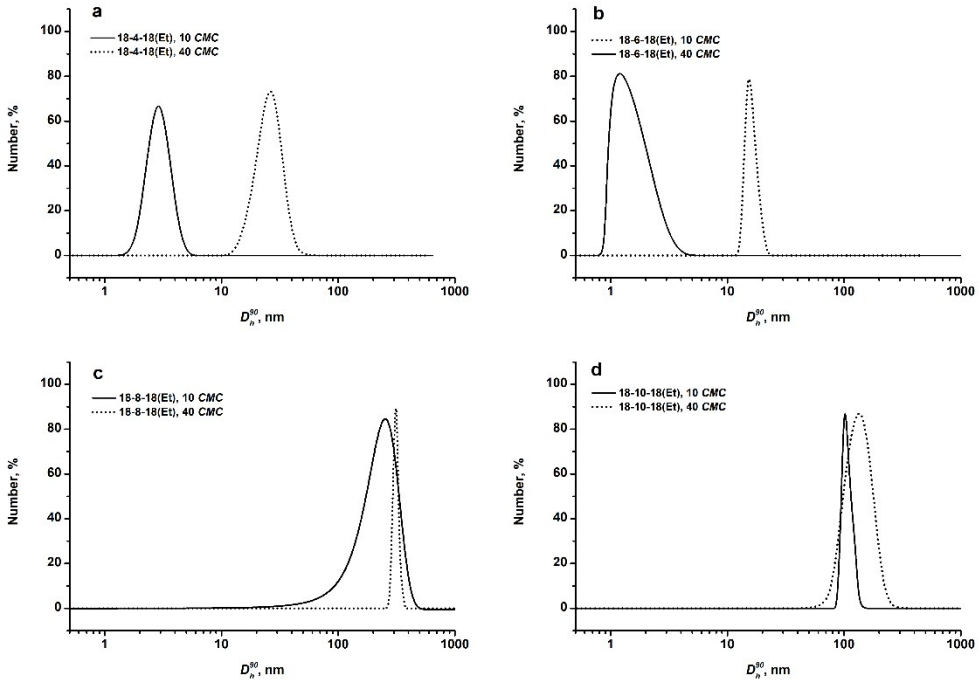


Fig. S15. Size distribution by number of aggregates formed in (a) 18-4-18(Et), (b) 18-6-18(Et), (c) 18-8-18(Et) and (d) 18-10-18(Et) solutions at 50 °C.

7. **FTIR data**

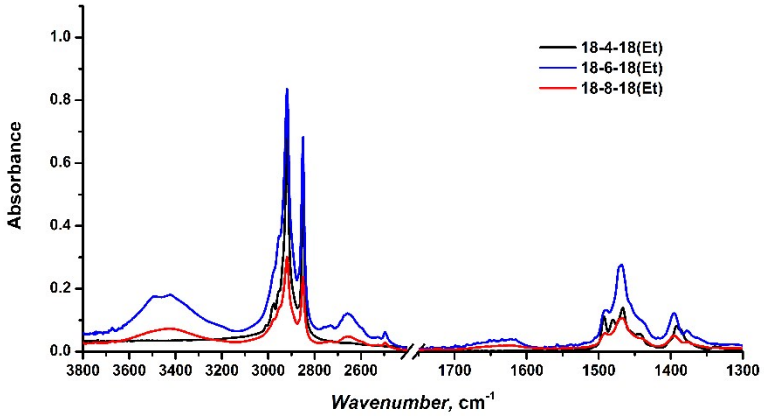


Fig. S16. FTIR spectra of dry 18-*s*-18(Et) surfactants with *s* = 4, 6, 8, 10.

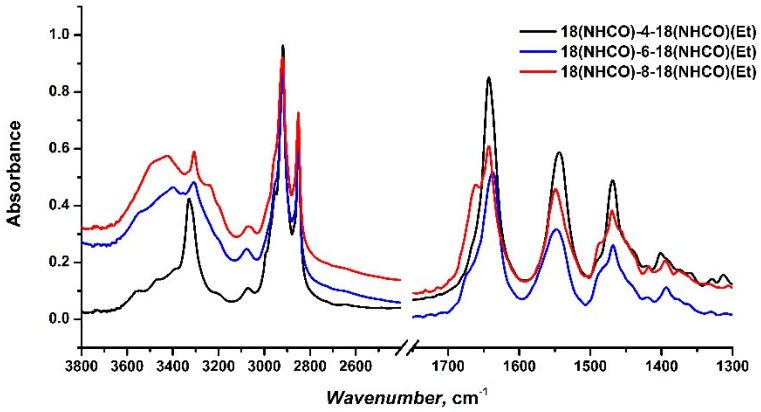


Fig. S17. FTIR spectra of dry 18(NHCO)-*s*-18(NHCO)(Et) surfactants with *s* = 4, 6, 8.

8. **Solubilization of Sudan I**

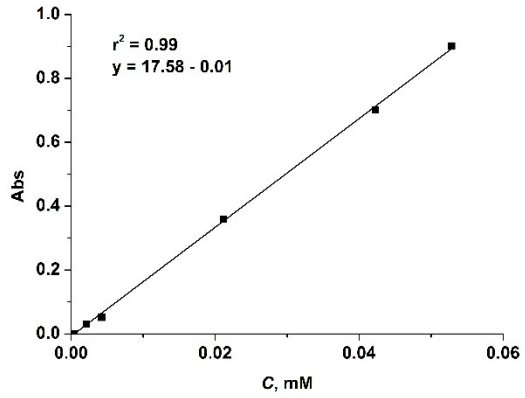


Fig. S18. Calibration curve of Sudan I in ethanol-water 1:1 solution

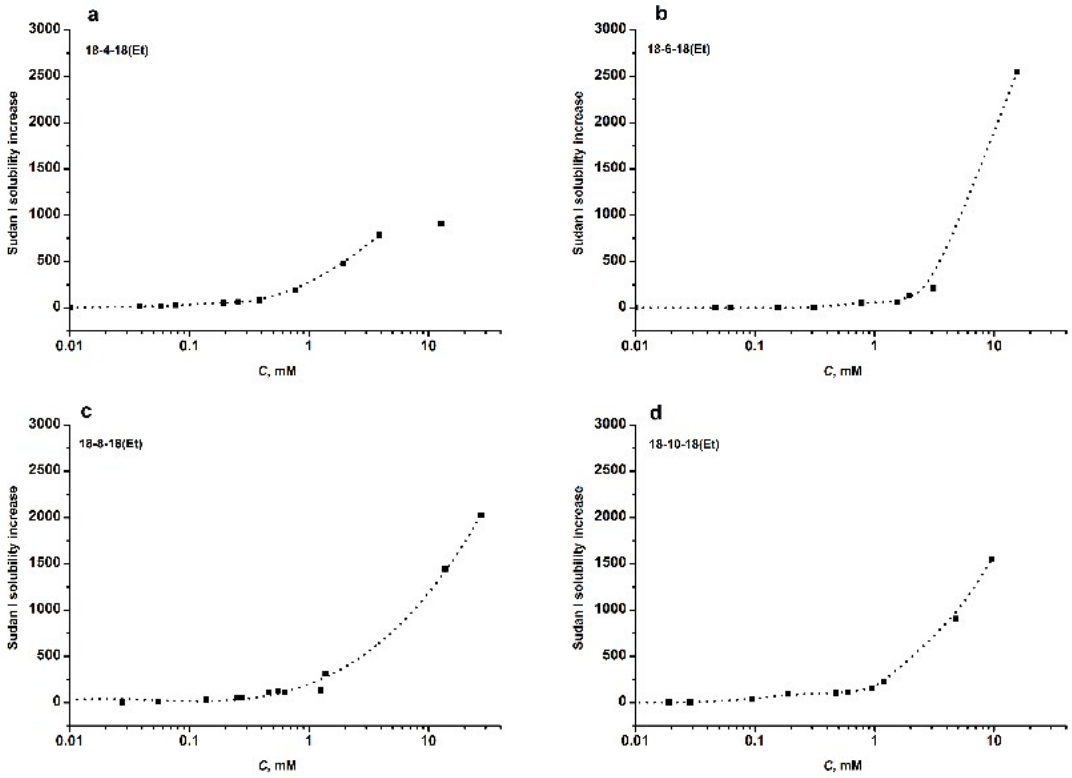


Fig. S19. Sudan I solubilisation curves in water versus surfactant concentration for 18-*s*-18(Et) gemini surfactants, where s = 4 (a), 6 (b), 8 (c), 10 (d)

9. 1H NMR study of hydrogen bond formation in 18-s-18(NHCO)

18-*s*-18(Et) cannot form hydrogen bonds. However, 18(NHCO)-*s*-18(NHCO)(Et) can and does, as evidenced by FT IR study described in the main text.

Here we supply an additional proof of the formation of hydrogen bonds by the 18(NHCO)-*s*-18(NHCO)(Et) family by 1H NMR.

We used the method described by Abraham et al (Michael H. Abraham, Raymond J. Abraham, Jonathan Byrne, Lee Grifith, J. Org. Chem. 2006, 71, 3389 – 3394, Michael H. Abraham, Raymond J. Abraham, New J. Chem. 2017, doi 10.1039/c7nj01044c). They measured the chemical shifts δ of NH protons in many compounds in CDCl3 and in DMSO. Basing upon this values they calculated the magnitude of A = 0.0065 + 0.133(δ(DMSO) – δ(CDCl3)).

Was the A value close to zero, strong hydrogen bonds were present. Did the value of A reach 0.3 – 0.4, no hydrogen bonds were concluded. The limiting values of A were derived basing upon acidity equilibria, they seem to be well justified. They have been tested on some dozens of different compounds.

For the studied geminis 18(NHCO) -s-18(NHCO)(Et), where *s* = 4 and *s* = 6, we measured (see fig. S20 as an example):

For 18(NHCO)-4-18(NHCO)(Et): δ(DMSO) = 7.99 ppm, δ(CDCl3) = 8.00 ppm; A = -0.0068

For 18(NHCO)-6-18(NHCO)(Et): δ(DMSO) = 8.00 ppm, δ(CDCl3) = 8.08 ppm; A = -0.0048

For both gemini surfactants, the measured A value was, within the experimental error, very close to zero. This indicates that hydrogen bonds engaging the NH protons are formed and is in agreement with the FT IR data.

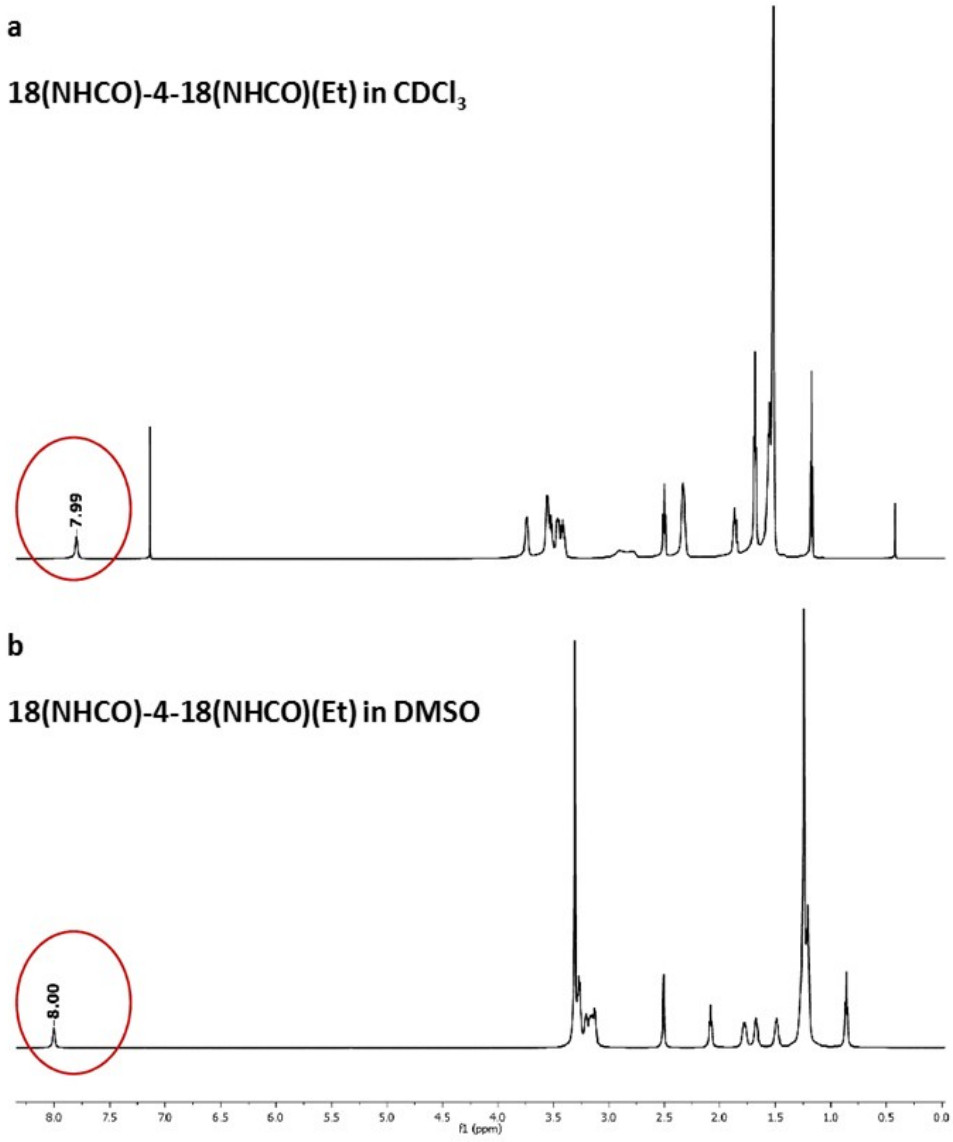


Fig. S20. 1H NMR spectra of 18(NHCO)-4-18(NHCO)(Et) in $CDCl_3$ (a) and DMSO (b). The signal from NH group forming the hydrogen bonding is highlighted.