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Synthesis, surface properties and oil solubilisation capacity of cationic gemini surfactants

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Abstract

The critical micelle concentration (CMC) and the surface tension at the CMC have been determined for the gemini surfactants alkanediyl-α,ω-*bis*(dimethylalkylammonium bromide) by means of dynamic surface tension measurements. For the same number of carbon atoms in the hydrophobic chain per hydrophilic head group, geminis have CMC values well below those of conventional single-chain cationic or anionic surfactants. Surface tension values at the CMC do not differ much from those observed for conventional surfactants. The propensity of gemini micelles for oil solubilisation is significantly better than that of conventional surfactants; this is true on a molar basis as well as on a weight basis. Geminis also show enhanced selectivity for aromatic compounds over paraffinic compounds. Some geminis show unusual viscoelastic behaviour at concentrations where this is not observed for conventional surfactants.

Keywords: Cationic gemini surfactants; Critical micelle concentration; Oil solubilisation capacity; Surface properties

1. Introduction

It has been known for many years that amphiphilic molecules, which consist of a hydrophilic head and a hydrophobic tail, can form a wide variety of aggregates including spherical micelles, worm-like micelles, bilayers, and reverse micelles with properties different from those of the unassembled molecules. This polymorphism forms the basis of many biochemical processes and is taken advantage of in a multitude of industrial and household applications.

A new class of amphiphilic molecules has

emerged and has attracted the attention of various industrial and academic research groups. These are the "gemini" surfactants that have two hydrophilic groups and two hydrophobic groups per molecule, separated by a spacer.

Bunton et al. [1] were the first to synthesise gemini surfactants of the *bis*(quaternary ammonium bromide) type with two C_{16} chains, separated by a spacer having lengths of two, four, or six carbon atoms. They determined the critical micelle concentrations (CMC) of these compounds by means of static surface tension and dye solubilization methods and have subsequently studied the kinetics of organic reactions in the presence of micelles formed by these gemini surfactants. Devinsky et al. [2] also synthesized *bis*(quaternary

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ammonium bromide) geminis. They studied chain lengths from 6 to 18 carbon atoms and a spacer of five carbon atoms long, and determined CMC values from surface tension and conductivity measurements. Subsequent studies of bis(quaternary ammonium bromide) geminis by Zana and co-workers [3–5] and by Zana and Talmon [6] also emphasised CMC measurements and phase behaviour. Table 1 is a guide to the current literature on the physicochemical properties of cationic gemini surfactants.

Anionic gemini surfactants bearing sulphate [7,8], sulphonate [8–11], phosphate [12], and carboxylate headgroups were prepared by Okahara and co-workers. Properties investigated included the CMC, surface tension at the air/water interface, and the foaming behaviour.

Phosphate gemini surfactants were also studied by Menger and Littau [13,14] who determined the CMC and surface tension values and probed the aggregate structure by means of dynamic light scattering. Rosen [15] then published a review on the properties of gemini and related conventional surfactants. He observed that anionic gemini surfactants, as compared to conventional surfactants having the same equivalent number of carbon

atoms per hydrophilic group, are more efficient in adsorbing at the air/water interface, in reducing the surface tension and in forming micelles. In addition, he concluded that geminis have lower Krafft temperatures and better solubilizing properties for some water-insoluble nonionic surfactants, and that they have greater potential for synergism in surface tension reduction when mixed with other surfactants. Rosen [15] also gave a qualitative interpretation of these properties in terms of the difficulty of packing two hydrophobic groups into a micelle. While this may explain why gemini surfactants are more likely than conventional surfactants to adsorb at an interface, it does not answer the question why they form micelles at such low concentrations. The question was answered in part by Zana and Talmon [6] who performed cryo-TEM studies on cationic gemini micelles. They showed that geminis with short spacers give strongly entangled worm-like micelles in water. It seems that far from having difficulties packing two hydrophobic chains into a micelle, nature has resolved the question by the evolution of worm-like micelles for geminis having short spacers. Computer simulation studies by Karaborni et al. [16], confirm that geminis form

Table 1
Literature review of gemini surfactant properties: $C_mH_{2m+1}-N^+ (CH_3)_2-(CH_2)_s-N^+ (CH_3)_2-C_mH_{2m+1}2Br^-$. [1–6]* references; [+] this work

| s | 2 | 3 | 4 | 5 | 6 | 8 | 10 | 12 | 14 | 16 |
m										
6				C[2]	C[3], TS[4]					
8				C[2]						
9				C[2]						
10	C, γ, OS[+]			C[2]						
11				C[2]						
12	C[+,3], γ[+] OS[+], PB[4,6] TS[4]	C[3,5] PB[4,6] TS[4]	C[3,5] PB[4,6] TS[4]	C[2,3] PB[4] TS[4]	C[+,3,5], γ[+] OS[+], PB[4] TS[4]	C[3,5] PB[4] TS[4]	C[+,3,5], γ[+] OS[+], PB[4] TS[4]	C[3,5] PB[4] TS[4]	C[5] PB[4]	C[3,5] PB[4] TS[4]
14	OS[+]			C[2]						
16	C[1,3], PB[4] TS[4]	C[3], PB[4] TS[4]	C[1,3], PB[4] TS[4]	C[2]	C[1,3], PB[4] TS[4]	C[3], PB[4] TS[4]				
18				C[2]						

C = Critical micelle concentration.
γ = Surface tension air/water interface.
OS = Oil solubilisation.
PB = Phase behaviour.
TS = Thermal stability.

worm-like structures that have low curvature and that their formation is preceded by the formation of semi-stable, smaller aggregates such as spheroids and cylinders that repeatedly collide and eventually merge into the equilibrium worm-like structures.

An interesting application of gemini surfactants was pointed out by Tanaka et al. [17] who observed that in micellar electrokinetic chromatography an anionic gemini surfactant gave a remarkably enhanced selectivity for substituted naphthalene and benzene derivatives and a wider migration time window than the ubiquitous sodium dodecyl sulphate. Their observation relates closely to the capability of micelles to enhance the solubility of hydrophobic compounds that are otherwise slightly soluble in water. This solubilisation in micellar solutions is of interest in many biological, pharmaceutical and industrial applications but has not been investigated in detail for gemini micelles. This paper reports on a systematic study of oil solubilisation by cationic gemini surfactants. We have chosen to work with cationic gemini surfactants as they are easier to synthesise than their anionic equivalents.

2. Experimental

2.1. Synthesis

We have synthesised a family of *bis*(quaternary ammonium bromides), the structure of which is similar to that shown in Table 1. We designate them by m–s–m, with m denoting the length of the hydrocarbon chain, and s the length of the spacer connecting the two chains. For our molecules, $m = 6$, 10, 12 and 14; $s = 2$, 6 and 10.

Chemically speaking, the formation of *bis*(quaternary ammonium bromides) involves either the coupling of two tertiary amines with a dibromoalkane or the alkylation of diamines. If primary alkyl bromides or dibromides are used as alkylating agents, the reaction is straightforward in both cases and high yields can be obtained. In general, stoichiometric amounts of diamine and alkyl bromide (or dibromide and amine) are dissolved in a solvent mixture composed of 90% nitromethane and 10% 1-butanol; the mixture is then stirred at 90°C for

24 h. After solvent stripping, the product is washed and further purified (see below). ^{13}C NMR spectroscopy was applied to determine the residual amine content (usually the reaction is quantitative with yields exceeding 95%).

Compounds with $s = 2$ were prepared from N,N,N',N'-tetramethylethylene-diamine and the corresponding alkyl bromides, since 1,2-dibromoethane is not reactive enough under standard conditions. Compounds with $s = 6$ and 10 were prepared from the respective alkyl dibromide and n-dodecyldimethylamine. All compounds from $m > 10$ onwards were observed to be excellent oil/water emulsifiers even at low concentrations; their emulsions gelified upon vigorous shaking (thixotropy, especially for $m = 12$, $s = 2$). The gel structure can be broken by the addition of 1-hexanol.

Compounds with $s = 6$ and 10 were prepared from the respective dialkyl bromide and amine. For $s = 2$, the reaction with dibromoethane was difficult and was not completed within 24 h. For further studies it is recommended that ethylenediamine be reacted with alkyl bromide. In that case HBr should be neutralised/scavenged using stoichiometric amounts of $NaHCO_3$.

2.2. Other compounds

For the purpose of comparison we have worked with two reference compounds: sodium n-dodecyl sulphate (SDS, purchased from BDH Chemicals with a stated purity of 99%), and n-hexadecyltrimethylammonium bromide (CTAB, from Merck with a stated purity of 98.5%). Both were used without further purification.

n-Hexane and toluene were p.a. chemicals from Merck with a stated purity of better than 98.5%. Both were used as-received. Deionised water was prepared using a MilliQ apparatus; the maximum electric conductance of this water was 0.6 $\mu S\ cm^{-1}$.

2.3. Surface properties

The CMC and the surface tension at the CMC (γ_{CMC}) were determined with a Sensadyne 6000 surface tensiometer using the Sugden maximum bubble pressure method; all experiments were done

at 25°C unless otherwise stated. The bubbles were blown with purified nitrogen gas from the laboratory supply line. The Sensadyne instrument was interfaced to an IBM personal computer; all data were treated with software supplied by Sensadyne.

2.4. Oil solubilisation

For the oil solubilisation experiments the solutions were prepared as follows. 3 ml of toluene or n-hexane was added to a 30 ml surfactant solution in a 100 ml glass flask. After hand shaking, the flask was put onto a Coulter mixer for 18 h at room temperature (21 °C). After the mixing period, the flask was allowed to stand at 21°C until the aqueous layer was clear again. In most cases this took at least 1 h.

Upon complete phase separation, a few microliters of the water layer were injected into a TOC Shimadzu 5000 total organic carbon analyser. Combustion of the organic carbon in the sample results in CO_2 which was detected by an infrared spectrophotometer. The carbon content is given in ppm or in mg l^{-1}. This procedure was repeated until the values were constant to within 2%. The average of the last five values is given as the total organic carbon content. The apparatus error is approximately 25 ppm. For the average surfactant solution this means an error of about 0.8%.

3. Results and discussion

Fig. 1 shows the surface tension versus log(conc) plots for geminis 10–2–10, 12–2–12, 12–6–12 and 12–10–12. From these we derived the CMC and the surface tension at the CMC. Numerical values are given in Table 2, along with the data for conventional cationic and anionic surfactants with the same number of carbon atoms per hydrophilic head group [18]. For 12–2–12, the three points at the highest concentrations were not used in drawing the surface tension versus log(conc) plot because at these concentrations 12–2–12 exhibits viscoelastic behaviour which tends to shift the CMC to a slightly higher value.

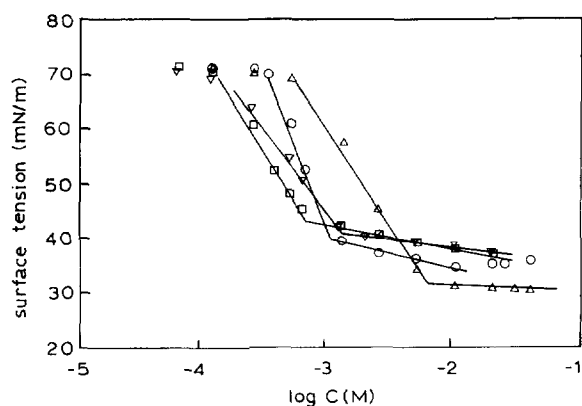No CMC was observed for compounds 6–2–6 and 14–2–14. With the latter compound we per-

Fig. 1. Variation of the surface tension with concentration of m–s–m, 2Br⁻ surfactants: 10–2–10 (△); 12–2–12 (○); 12–6–12 (▽) and 12–10–12 (□); $T=25°C$

formed additional measurements at 45 and 64°C (see Fig. 2). Although no break in these curves is apparent, 14–2–14 undoubtedly is surface active and shows a significant lowering of the surface tension. Measurements at higher concentrations were impossible due to solubility constraints.

Compound 14–2–14 also shows viscoelastic behaviour, particularly at 25°C. At 45 and 64°C, its viscoelasticity is much less pronounced. Gemini 14–2–14 is therefore an interesting compound: it does not appear to have a CMC, yet it lowers the surface tension and, as will be shown below, it is an excellent oil solubiliser.

Fig. 3 shows a plot of the surface tension of these compounds versus the number of seconds per bubble. Such a plot reveals that higher values are observed for the surface tension at higher bubble frequencies; this is more apparent for concentrations below the CMC than for those above it. Equilibrium surface tensions were estimated from plots such as shown in Fig. 3 at about three seconds per bubble. At this nitrogen flow velocity, the dynamic surface tension at concentrations above the CMC has become approximately constant; at concentrations below the CMC it is more dependent upon the bubble frequency. CMC values obtained by this technique will therefore always tend to be higher than CMC values obtained by static methods.

Comparison of the CMC values for gemini surfactants with those for conventional cationic and

Table 2
CMC, γ_{CMC}, and the Gibbs energy of micelle formation (ΔG) of cationic gemini and reference surfactants at 25°C

Surfactant	CMC[a]			γ_{CMC}[a] (mN m^{-1})	$-\Delta G$[b] (kJ mol^{-1})	Remarks
	(mmol l^{-1})		(g l^{-1})			
10–2–10		6.5	3.6	32	27	
12–2–12	1.1		0.8[c] 0.6	40	41	Viscoelastic > CMC
12–6–12	1.3	1.0[c]	1.1[d] 0.7	41	39	
12–10–12	0.7	0.6[c]	0.3[d] 0.5	43	44	
14–2–14	–[e]		–[e]	–[e]	–[e]	Viscoelastic < CMC
16–2–16		0.02	0.01		70	
$C_{10}H_{21}N^+ (CH_3)_3 Br^-$	67[f]		19	40	13	Agg. no. 39[f] @ CMC
$C_{12}H_{25}N^+ (CH_3)_3 Br^-$	15[f]		5	39	21	Agg. no. 54[f] @ CMC
$C_{14}H_{29}N^+ (CH_3)_3 Br^-$	4[f]		1	38	27	Agg. no. 72[f] @ CMC
$C_{16}H_{33}N^+ (CH_3)_3 Br^-$	1[f]		0.5	<40	34	Agg. no. 92[f] @ CMC
$C_{10}H_{21}OSO_3^-Na^+$	33[f]		9	40	17	Agg. no. 50[f] @ CMC
$C_{12}H_{25}OSO_3^-Na^+$	8[f]		2	44	24	Agg. no. 66[f] @ CMC
$C_{14}H_{29}OSO_3^-Na^+$	2[f]		0.7	40	31	
$C_{16}H_{33}OSO_3^-Na^+$	g		g	g	g	

[a] CMC and γ_{CMC} for gemini surfactants by dynamic surface tension measurements.
[b] According to Eq. (2) for gemini surfactants, and according to Eq. (4) for the others.
[c] Conductivity measurements [3].
[d] Static surface tension measurements [5].
[e] No CMC observed in our measurements.
[f] Ref [18].
[g] Krafft temperature is 31°C [18].
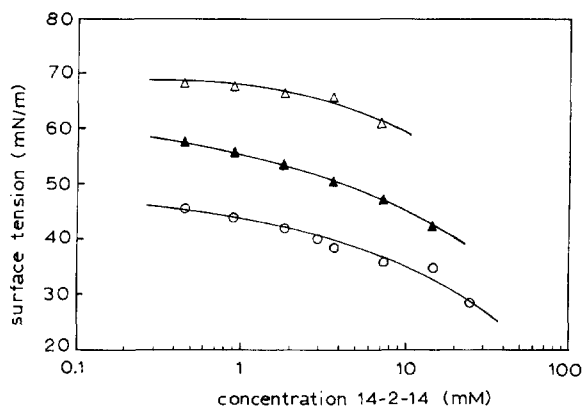
Fig. 2. Variation of the surface tension with concentration of 14–2–14 at 25°C (△); 45°C (▲) and 64°C (○)
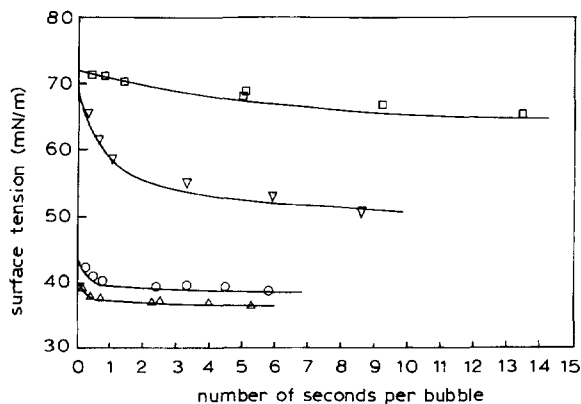
Fig. 3. Variation of surface tension with the number of seconds per bubble for four different concentrations (in mM) of 12–6–12: 0.12 (□); 0.46 (▽); 4.82 (○) and 19.3 (△); $T=25$°C

anionic surfactants in Table 2 shows the following. For the same number of carbon atoms per hydrophilic group geminis start to form micelles at lower concentrations than conventional surfactants. This is true when surfactants are compared on a molar basis but also on a weight basis (see Table 3). If one compares our cationic geminis with conven-

tional cationic alkyltrimethylammonium bromides, gemini CMC values are seen to be 10–20 times lower on a molar basis than conventional surfactant CMC values. This is remarkable, but not the two orders of magnitude quoted by Rosen [15] for anionic gemini surfactants. Note that the CMC
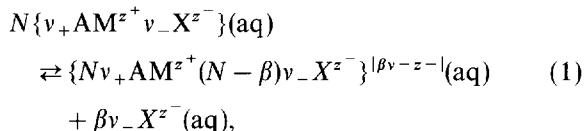
Table 3
(CMC) conventional surfactant)/(CMC gemini surfactant) for an equal number of carbon atoms in the hydrophobic chain. Conventional surfactant is either cationic or anionic.

Gemini	Conventional cationic CMC ratio		Conventional anionic CMC ratio	
	(molar)	(weight)	(molar)	(weight)
10–2–10	10	5	5	2.5
12–2–12	15	7	8	4
12–6–12	15	7	8	4
12–10–12	20	9.5	10	5
16–2–16			Anionic $< T$ (Krafft)	

values (molar basis) of our cationic geminis are 5–10 times lower than those of conventional anionic surfactants. On a weight basis, 2.5–9 times less of a gemini is needed, depending on whether the comparison is made with a conventional cationic or anionic surfactant.

According to literature data [6], 12–2–12 forms tubular micelles in aqueous solution. We also suspect that 14–2–14 forms tubular micelles on account of its viscoelastic behaviour although our dynamic surface tension measurements did not reveal any transition from monomers to aggregates. In contrast, conventional cationic and anionic surfactants with the same number of carbon atoms per hydrophilic group form small spherical or spheroidal aggregates having aggregation numbers ranging from 40 to 100 in accordance with their packing parameter values [18].

The CMC value provides a measure for the Gibbs energy of transfer (ΔG) of a surfactant from the aqueous phase to the micellized state. For the general case of an ionic salt $v_+AM^{z^+} v_-X^{z^-}$ the equation for micelle formation has the form [19]:

$$N\{v_+AM^{z^+}v_-X^{z^-}\}(aq)$$

$$\rightleftarrows \{Nv_+AM^{z^+}(N-\beta)v_-X^{z^-}\}^{|\beta v - z - |}(aq) \qquad (1)$$

$$+ \beta v_-X^{z^-}(aq),$$

where N is the aggregation number, v_+ is the number of moles of cations produced upon complete dissociation of one mole of surfactant, v_- is the number of moles of anions produced upon complete dissociation of one mole of surfactant,

z^+ is the charge number for the cation, z^- that for the anion, and β is the degree of dissociation such that $(N-\beta)$ is the number of counterions bound to each micelle. Blandamer et al. [19] have shown that if we assume ideal solution behaviour, N is larger than 30, and that the micelles have zero electric charge ($\beta=0$), ΔG^0 for micelle formation is equal to:

$$\Delta G^0 = vRT \ln(Q \cdot CMM/m^0) \qquad (2)$$

where $v = v_+ + v_-$, and Q is defined as

$$Q = (v_+)^{v+} * (v_-)^{v-}. \qquad (3)$$

CMM is the critical micellar molality, and m^0 is 1 mol kg^{-1}.

For a 1:1 surfactant such as SDS or CTAB, $v=2$ and $Q=1$ so that

$$\Delta G = 2RT \ln(CMM/m^0). \qquad (4)$$

For the gemini surfactants discussed in this paper, $v=3$, $v_+=1$ and $v_-=2$ and hence $Q=4$. Table 2 shows the Gibbs energy of micelle formation of the gemini surfactants according to Eq. (2) and that of the conventional surfactants according to Eq. (4).

The enhanced tendency of gemini surfactants to form micelles over that of single-tail surfactants is of course reflected in the much more negative values of their Gibbs energies of micelle formation. Fig. 4 shows how ΔG for gemini surfactants varies with chain length at 25°C. The slope of this plot is -6.6 kJ mol^{-1} per unit increment of m. Since this involves two CH$_2$ groups, the change in Gibbs energy upon micelle formation per CH$_2$ group
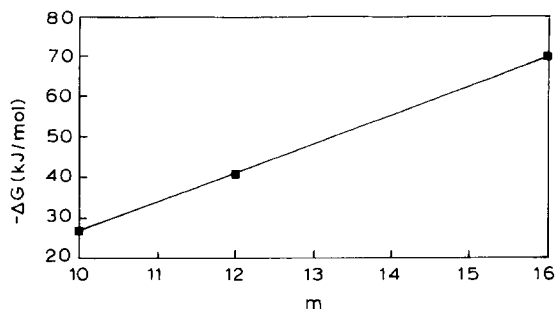

Fig. 4. Gibbs energy of micellization of m–s–m gemini surfactants with $s=2$ according to Eq. (2). CMC data for 16–2–16 taken from Zana et al. [3].

is $-3.3 \, \text{kJ} \, \text{mol}^{-1}$. This agrees nicely with $-3.3 \, \text{kJ} \, \text{mol}^{-1}$ for *n*-alkyl methyl sulphoxides [20], with $-2.8 \, \text{kJ} \, \text{mol}^{-1}$ for sodium alkylbenzene-sulfonates [21], and with $-3.5 \, \text{kJ} \, \text{mol}^{-1}$ for alkyltrimethylammonium bromides [3]. The fact that the ΔG values for micelle formation with gemini surfactants is almost exactly twice that of a corresponding conventional surfactant with the same main chain length tells us that the spacer (two CH_2 groups) does not contribute to the standard Gibbs energy of micelle formation implying that it remains within the hydration sphere of the head groups.

From Table 2 it is clear that our CMC values are higher than those obtained by Zana and co-workers [3,5], who obtained their values by electrical conductivity and static surface tension measurements. CMC values obtained by dynamic surface tension measurements always tend to be higher than those obtained by equilibrium techniques; only in the infinite time limit can a match be expected. Quite apart from this, different experimental methods will in most cases lead to different CMC values since the concentration at which micelles first become detectable depends on the experimental sensitivity; a discussion of this issue has been given elsewhere [22]. The discrepancy between CMC values for 12–10–12 (0.32 mM by electrical conductivity and 0.63–0.69 mM by surface tension methods) appears, however, to be too large to be explained solely by differences in sensitivity and may require further work.

Table 2 shows no significant difference between γ_{CMC} values determined by either method. The γ_{CMC} values of these geminis are close to the values commonly observed for conventional surfactants. Gemini 10–2–10 is an exception with a low γ_{CMC} value of 32 mN m^{-1}. The *bis*-sulphonate gemini surfactants display even lower γ_{CMC} values [8–11].

The results of the oil solubilisation experiments are shown in Table 4. The oil solubilisation is expressed in either (moles of oil)/(moles of surfactant), or in terms of the molar solubilisation ratio (MSR) which has been defined by Chaiko et al. [23] as follows:

$$MSR = \{(\text{total moles of oil in the aqueous phase}) - (\text{moles of singly dispersed oil in}$$

the aqueous phase)$\}$/$\{$(total moles of surfactant in the aqueous phase) − (moles of singly dispersed surfactant in the aqueous phase)$\}$.

Our MSR values for *n*-hexane in conventional surfactant micelles are in reasonable agreement with those from the literature [23,24]. However, our MSR value for toluene in SDS differs considerably from that obtained by Chaiko et al. [23]. As the mixture with toluene took much longer to phase separate than that containing *n*-hexane, we suspect that the rather large value obtained by Chaiko et al. [23] was caused by some of the toluene still being in the form of a macroemulsion rather than in the form of swollen micelles.

According to Table 4, the solubility of either toluene or *n*-hexane in a gemini surfactant solution increases with increasing length of the hydrocarbon chain. Gemini micelles prefer toluene over *n*-hexane; for 10–2–10 the ratio MSR(toluene)/MSR(*n*-hexane) is 5, for 12–2–12 it is 3.5. Gemini micelles may therefore be useful to separate aromatic from alkane compounds. Within the gemini 12–*s*–12 series, the capacity to solubilize oil decreases with increasing spacer length; note that this only applies for toluene as we have no data for *n*-hexane. The tol/surf ratio for 12–2–12 is at least 10 times larger than that for SDS when the comparison is made on a molar basis; on a weight basis the ratio for the gemini is 6 times larger than for the conventional surfactant. Gemini 12–2–12 also solubilises more oil than CTAB, mole for mole, or gram for gram; the difference is the more striking since CTAB has 16 carbon atoms in the hydrophobic chain. The *n*-hexane/surf ratio for 12–2–12 is three times that for SDS on a molar basis; they are about equal on a weight basis. It is, however, possible to solubilise quite large amounts of *n*-hexane with gemini 14–2–14. For this compound, the *n*-hexane/surf ratio is at least 10 times that for CTAB on a molar basis, and 7 times on a weight basis. Again, the result is even more striking as CTAB has the longer chain length of the two. We postulate that the enhanced tendency for oil solubilisation observed for gemini surfactants may be related to the tubular shape of their aggregates

Table 4
Solubility of toluene and n-hexane in in gemini and conventional surfactant solutions

Gemini or conventional surfactant	[tol]/[surf]		[n-hex]/[surf]		MSR[a] tol	MRS[a] n-hexane
	(mol/mol)	(g/g)	(mol/mol)	(g/g)		
10–2–10	1.86	0.31	0.29	0.04	3.21	0.62
12–2–12	3.84	0.60	0.99	0.14	3.50	1.03
12–6–12	2.81	0.39	c	c	2.40	c
12–10–12	2.70	0.36	c	c	2.13	c
14–2–14	b	b	2.77	0.35	b	d
$C_{12}H_{25}N^+ (CH_3)_3 Br^-$						0.40[e]
$C_{14}H_{29}N^+ (CH_3)_3 Br^-$						0.40[e]
$C_{16}H_{33}N^+ (CH_3)_3 Br^-$	0.78	0.20	0.23	0.05	0.59	0.21
$C_{12}H_{25}OSO_3^- Na^+$	0.35	0.10	0.32	0.09	0.25	0.35
					1.36[f]	0.39[f]

[a] Molar solubilization ratio (see text).
[b] Stable emulsion.
[c] Not determined.
[d] No CMC available.
[e] Ref. [24].

as evidenced by cryo-TEM and molecular dynamics studies.

4. Conclusions

(1) Cationic gemini surfactants having two hydrophilic groups and two hydrophobic groups per molecule and separated by a spacer have been synthesised and their physicochemical properties evaluated. The designation of these compounds is m–s–m, with m the length of the hydrophobic chain and s the length of the hydrophobic spacer.

(2) The critical micelle concentrations (CMC) for cationic gemini surfactants with C_{10} and C_{12} alkyl chains are significantly below those for conventional anionic and cationic surfactants. This is so not only on a molar basis but also gram for gram. The C_{12} geminis have surface tension values comparable to those observed for conventional surfactants; for the 10–2–10 gemini, the surface tension value at the CMC is well below that of a conventional surfactant.

(3) Geminis solubilise more oil inside their interior than conventional surfactants with comparable chain lengths. This is true on a molar basis and on a weight basis. The effect is most pro-nounced for geminis 12–2–12 and 14–2–14. Geminis prefer toluene over n-hexane and may possibly be used to separate aromatic from paraffinic compounds.

(4) Geminis 12–2–12 and 14–2–14 are viscoelastic at low concentrations where such behaviour is not observed for conventional surfactants.

(5) Potentially interesting applications of geminis are foreseen in the areas of solubilisation, cosolubilisation, and gellable liquid formulations.

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