

Gemini surfactants: A distinct class of self-assembling molecules

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Gemini surfactant is the family of surfactant molecules possessing more than one hydrophobic tail and hydrophilic head group. These surfactants usually have better surface-active properties than corresponding conventional surfactants of equal chain length. Geminis are used as promising surfactants in industrial detergency and have shown efficiency in skin care, antibacterial property, metal-encapped porphyrane and vesicle formation, construction of high-porosity materials, etc. This review deals with synthesis, structure, critical micellar concentration, surface active properties and uses of geminis.

Definition

SURFACTANTS show interesting interfacial and bulk properties¹ and have a wide variety of uses², which are mostly met by conventional representatives. Changes in the molecular structure and type to improve upon their properties have attracted the attention of chemists³⁻⁶. This has led to the preparation of new generation surfactants such as geminis. Conventional surfactant has a single hydrophobic tail connected to an ionic or polar head group, whereas a gemini has in sequence a long hydrocarbon chain, an ionic group, a spacer, a second ionic group and another hydrocarbon tail. A schematic representation of gemini is given in Figure 1. Related surfactants with more than two tails are also known. To provide greater surface activity, chemists have been in search of newer surfactants and the preparation started with *bis*-surfactants, which were later renamed as 'gemini' surfactants. Geminis are considerably more surface-active than conventional surfactants. Menger and Littau⁷ assigned the name gemini to *bis*-surfactants with rigid spacer (i.e. benzene, stilbene). The name was then extended to other *bis* or double-tailed surfactants, irrespective of the nature of spacers.

Structure

Geminis can have unusual and exceptional structural features, one of which is illustrated in Structure 1. All

geminis possess at least two hydrophobic chains and two ionic or polar groups, and a great deal of variation exists in the nature of spacers⁸. Short or long methylene groups, rigid (stilbene), polar (polyether), and nonpolar (aliphatic, aromatic) groups may be used as spacers. The ionic group can be positive (ammonium) or negative (phosphate, sulphate, carboxylate), whereas the polar nonionics may be polyether or sugar. The great majority of geminis have symmetrical structures with two identical polar groups and two identical chains. A gemini with two C_m (m is the number of alkyl carbon atoms) tails and a C_s (s is the number of alkyl carbon atoms) spacer separating the quaternary nitrogen atoms can be represented as m - s - m . Some unsymmetrical geminis and geminis with three or more polar groups or tails have recently been reported⁹⁻¹⁴. A sugar moiety can be also present as a spacer in the molecule. Recently, a gemini-type surfactant with four ionic head groups and four hydrophobic chains has been reported¹⁵, where the tails are tetrahedrally arranged about an adamantane moiety (Structure 2). The morphology of the arrangements of gemini monomers in polar solvent may be of four different types depending on the structure of the molecule and its orientation (Figure 2). The long hydrocarbon chain tends to increase the surface activity. But increasing hydrophobicity may make the molecule insoluble, whereas increasing hydrophilicity of the head group may impart solubility in water. Hydrophilic groups in the spacer also increase the aqueous solubility. Increase in carbon number in the nonpolar chain increases both

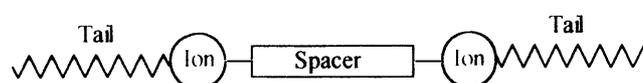
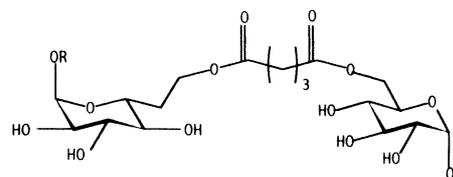


Figure 1. Schematic representation of gemini surfactant.



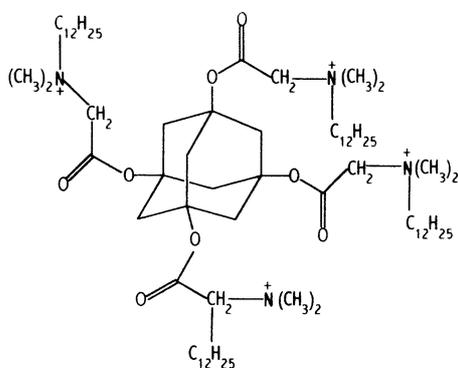
Structure 1. Novel gemini surfactant with sugar moiety.

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lipophilicity and surface activity with decrease in critical micellar concentration¹⁶.

Preparation and characterization of gemini surfactants

The surfactant Na 2-bis ethyl hexyl sulphosuccinate (Aerosol OT or AOT) is a versatile double-tailed¹⁷ surfactant (Structure 3). As an alternative to AOT some new double-chain compounds with one head and two tails (with lower critical micelle concentration (CMC) values than AOT) have been derived from glutamine and lactone¹⁸. To obtain much lower CMC values, preparation of geminis came into the picture. Two factors are important in their preparation; one is synthesis and the other is purification. Simple cationic geminis with alkyl spacers can be prepared¹⁹⁻²¹ in two ways depending on the length of the spacer (Scheme 1). The choice depends on reactivity of dibromide. Anionic geminis, mainly phospho diester with either rigid or flexible spacer^{7,13,22,23} can be prepared as shown in Scheme 2. The formation of nonionic geminis is also reported by Eastoe, Menger and others²⁴⁻²⁶. A typical nonionic gemini surfactant prepared from D-glucose is also presented²⁷ in Scheme 3. Menger has recently prepared two types of gemini surfactants with a disaccharide spacer (trehalose). One group is nonionic with



Structure 2. Gemini-type surfactant with four ionic groups and four hydrophobic groups.

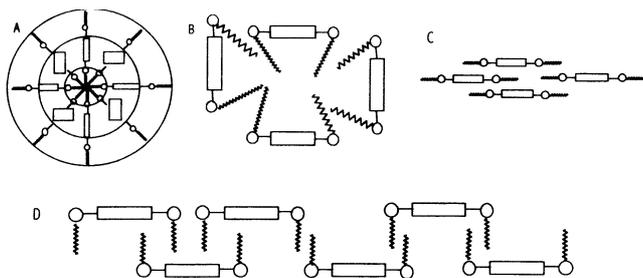


Figure 2. Possible morphology of gemini surfactants.

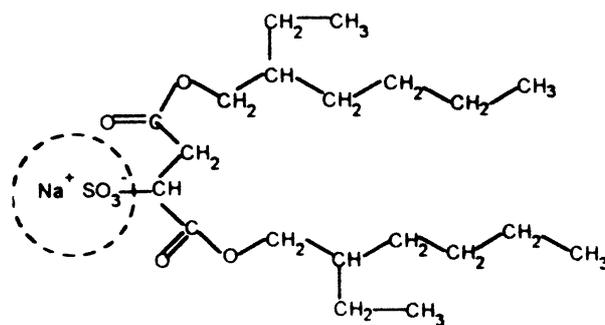
amide linkage and the other is ionic with quaternary ammonium ion^{26,28}. The purity of the gemini is critical as the surface activity can be changed in the presence of traces of impurities. The compounds are normally characterized by Nuclear Magnetic Resonance (NMR) spectroscopy (¹H, ¹³C, ³¹P), mass spectroscopy (fast atom bombardment), Fourier-transformed infrared spectroscopy (FT-IR) and elemental analysis. Synthesis and characterization of metal-capped gemini porphyrazine in the form of both *cis* and *trans* isomers have been reported²⁹⁻³¹. As an example, Ni-capped *trans* porphyrazine tetrathiolate is presented in Structure 4.

Properties of gemini surfactants

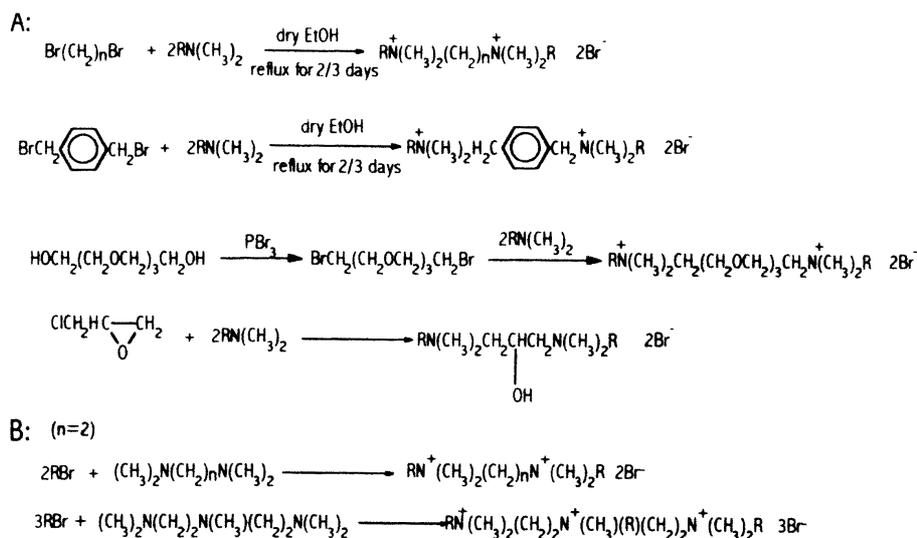
Critical micellar concentration

Critical micellar concentration (CMC) is the concentration above which monomeric surfactant molecules abruptly aggregate to form micelles. It is determined mostly by tensiometry, conductometry, goniometry, etc. Using these techniques, CMC, shape and structure of micelle, surface activity, solubilization, adsorption, wetting, phase behaviour, etc. of surfactants can be accounted for. The value of CMC decreases with increase in the hydrophobic chain length of the molecule. Hydrophobic interaction opposed by electrostatic repulsion among the ionic head groups drives the process of micellization. A list of CMC data of some geminis with some conventional surfactants determined by static surface tension method is presented in Table 1. The following conclusions can be drawn from the data in Table 1.

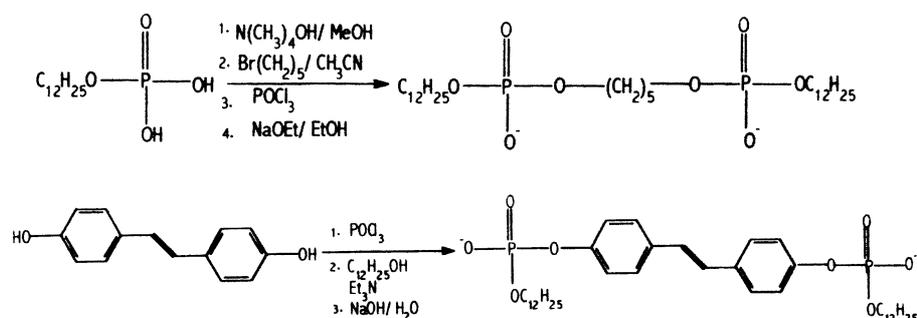
1. Geminis have remarkably low CMC values compared to the corresponding conventional surfactants of equivalent chain length.
2. CMC values are not sensitive to the polarity of short spacers (2–8 atoms).
3. A long hydrocarbon spacer of 16 methylene groups reduces the CMC almost ten-fold relative to a short spacer of 3–8 methylene groups. The long spacer contributes to the overall hydrophobicity of the gemini reducing the monomer solubility and enhancing its tendency to self-assemble.



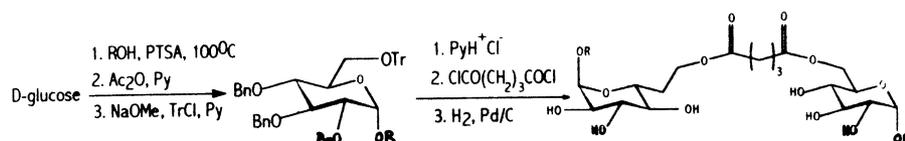
Structure 3. AOT.



Scheme 1. Synthesis of simple cationic geminis.



Scheme 2. Synthesis of simple anionic geminis.



Scheme 3. Synthesis of simple nonionic geminis.

4. Geminis are more responsive to tail length than conventional surfactants. Thus, increasing the tail length by four carbon atoms in a conventional cationic surfactant lowers the CMC 16-fold. A corresponding tail lengthening in the gemini series lowers the CMC by two orders of magnitude.

5. Anionic gemini surfactants have somewhat lower CMC values than their cationic counterparts.

Thermodynamic parameters for micellization of geminis with varying spacer length (*m-s-m*; *m* = 12) obtained by calorimetry are reported by Bai *et al.*³². They have compared the results with conventional surfactants. It is found that CMC values are in good agreement with the

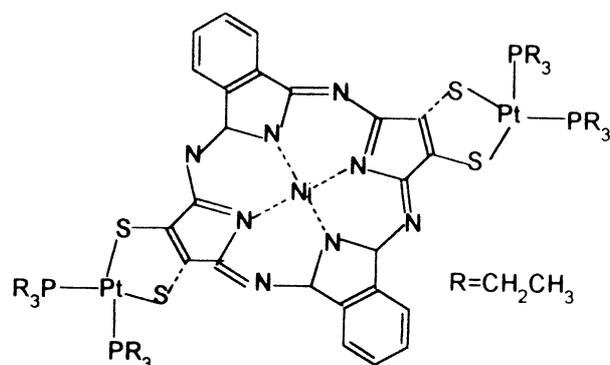
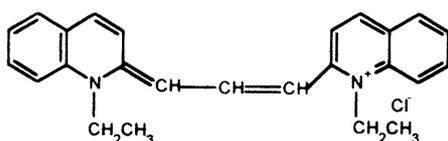
Structure 4. Ni-capped *trans* porphyrazine tetrathiolate.

Table 1. CMC values of representative conventional (1–4) and gemini surfactants¹⁵

	Surfactant	CMC/mM
1	C ₁₂ H ₂₅ N ⁺ (CH ₃) ₃ Br ⁻ (DOTAB)	16
2	C ₁₂ H ₂₅ N ⁺ (CH ₃) ₃ Cl ⁻ (DOTAC)	22
3	C ₁₆ H ₃₃ N ⁺ (CH ₃) ₃ Br ⁻ (CTAB)	1
4	C ₁₂ H ₂₅ OSO ₃ ⁻ Na ⁺ (SDS)	8
5	C ₁₂ H ₂₅ N ⁺ (CH ₃) ₂ -(CH ₂) _n -N ⁺ (CH ₃) ₂ C ₁₂ H ₂₅ 2Br ⁻ (n = 3–8)	1
6	C ₁₂ H ₂₅ N ⁺ (CH ₃) ₂ -(CH ₂) ₁₆ -N ⁺ (CH ₃) ₂ C ₁₂ H ₂₅ 2Br ⁻	0.12
7	C ₁₆ H ₃₃ N ⁺ (CH ₃) ₂ -(CH ₂) ₂ -N ⁺ (CH ₃) ₂ C ₁₆ H ₃₃ 2Br ⁻	0.003
8	C ₈ H ₁₇ N ⁺ (CH ₃) ₂ -(CH ₂) ₃ -N ⁺ (CH ₃) ₂ C ₈ H ₁₇ 2Br ⁻	55
9	C ₁₂ H ₂₅ N ⁺ (CH ₃) ₂ -(CH ₂) ₂ -O-(CH ₂) ₂ -N ⁺ (CH ₃) ₂ C ₁₂ H ₂₅ 2Cl ⁻	0.5
10	C ₁₆ H ₃₃ N ⁺ (CH ₃) ₂ -(CH ₂) ₅ -N ⁺ (CH ₃) ₂ C ₁₆ H ₃₃ 2Br ⁻	0.009
11	C ₁₆ H ₃₃ N ⁺ (CH ₃) ₂ -(CH ₂) ₂ -O-(CH ₂) ₂ -N ⁺ (CH ₃) ₂ C ₁₆ H ₃₃ 2Br ⁻	0.004
12	C ₁₆ H ₃₃ N ⁺ (CH ₃) ₂ -CH ₂ -(CH ₂ -O-CH ₂) ₃ -CH ₂ -N ⁺ (CH ₃) ₂ C ₁₆ H ₃₃ 2Br ⁻	0.02
13	C ₁₂ H ₂₅ N ⁺ (CH ₃) ₂ -CH ₂ -CH(OH)-CH ₂ -N ⁺ (CH ₃) ₂ C ₁₂ H ₂₅ 2Br ⁻	0.8
14	C ₁₂ H ₂₅ N ⁺ (CH ₃) ₂ -CH ₂ -C ₆ H ₄ -CH ₂ -N ⁺ (CH ₃) ₂ C ₁₂ H ₂₅ 2Br ⁻	0.03
15	C ₁₂ H ₂₅ N ⁺ (CH ₃) ₂ -CH ₂ -CH(OH)-CH(OH)-CH ₂ -N ⁺ (CH ₃) ₂ C ₁₂ H ₂₅ 2Br ⁻	0.7
16	C ₁₂ H ₂₅ N ⁺ (CH ₃) ₂ -CH ₂ -CH(OH)-CH ₂ -N ⁺ (CH ₃) ₂ -CH ₂ -CH(OH)-CH ₂ -N ⁺ (CH ₃) ₂ C ₁₂ H ₂₅ 3Cl ⁻	0.5
17	C ₁₂ H ₂₅ OPO ₂ ⁻ -O-(CH ₂) ₆ -OPO ₂ ⁻ -OC ₁₂ H ₂₅ 2Na ⁺	0.4
18	C ₁₀ H ₂₁ O-CH ₂ -CH(OSO ₃ ⁻)-CH ₂ -O-(CH ₂) ₂ -O-CH ₂ -CH(OSO ₃ ⁻)-CH ₂ -OC ₁₀ H ₂₁ 2Na ⁺	0.01


Structure 5. Pinacyanol chloride.

other methods employed, showing a maximum at $s = 4-6$. The enthalpies of micellization, ΔH_{mic} are all exothermic and had shown a marked minimum in magnitude at $s = 4-6$. The variation of ΔH_{mic} and ΔS_{mic} shows that the balance between enthalpic and entropic contribution to micellization process changes substantially with s . The micellization process is more spontaneous, and spontaneity decreases with increasing spacer length. The CMC also decreases with increasing spacer length. The CMC of geminis can be conveniently measured using the spectral method. Menger and Littau²² have reported the use of pinacyanol chloride (Structure 5) to investigate micellization of gemini surfactants. Corrin *et al.*³³ had used the method and started a discussion based on the pink–blue colour shift. The method is not useful unless it gives a broad range of concentration values as CMC. It is applicable to anionic surfactants as they form a charge transfer complex with the dye rather than the cationic surfactants. Geminis also follow this trend in respect of colour change and CMC evaluation. It has been found that the packing of the hydrophobic groups in the geminis at the air–water interface, when the spacer is small and hydrophilic, is closer than that found in the comparable conventional surfactants, which may be the reason for more lowering of surface tension at CMC by geminis. The higher surface activity means that lower [surfactant] may be needed to perform a function. The much lower

Table 2. Interaction parameters³⁷ for the mixed systems of geminis with decyl and dodecyl sulphonates at 298 K

System	Medium	0.1 M				
		a	b^s	b^m	X^s	X^m
C ₈ Diq-C ₁₀ SO ₃ Na	NaBr	0.40	-26	-12	0.49	0.51
C ₈ Diq-C ₁₂ SO ₃ Na	NaBr	0.50	-31	-14	0.45	0.45
C ₁₀ Diq-C ₁₀ SO ₃ Na	NaBr	0.02	-34	-14	0.48	0.50
C ₁₀ Diq-C ₁₂ SO ₃ Na	NaBr	0.50	-34	-17	0.50	0.55
C ₁₀ Diq-C ₁₂ SO ₃ Na	NaCl	0.22	-40	-19	0.44	0.48

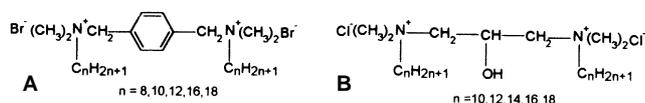
C_nDiq = (C_nNme₂CH₂CHOH)₂²⁺ 2Br⁻; **a** is the stoichiometric mole fraction of cationic surfactant; **b^s** is the interaction parameter in the mixed monolayer at the aqueous solution–air interface, and **b^m** is that in the mixed micelle. **X^s** is the mole fraction of the surfactant in the mixed monolayer and **X^m** is that in the mixed micelle.

CMC of the geminis produces less skin irritation which normally depends on concentration of surfactant monomer in solution. The tighter packing of the hydrophilic groups of gemini surfactant results in a more cohesive and stable interfacial film. The double-tailed and doubly charged geminis interact more prominently with neutral and oppositely charged surfactants. The CMC values of some mixed micellar systems with geminis are presented in Table 2 along with different interfacial and bulk parameters^{34–37}. The parameter **b** is positive and negative for antagonistic and synergistic interactions between two kinds of surfactants respectively^{38,39}. The superscripts **s** and **m** stand for parameters at the interface and micelle respectively. It is revealed from the results that the interaction between the gemini and the second surfactant is weaker in the mixed micelle compared with that at the interface. This is because of the difficulty in incorporating two hydrophobic groups of the gemini into a convex micelle. Surface activity parameters of cationic geminis prepared from arginine have been reported by Perez *et al.*⁴⁰.

Menger and Keiper¹⁵ and Rosen and Hua⁴¹ have reported the measurement of dynamic surface tension by the maximum bubble pressure method, in which N₂ gas at a known pressure is forced through a capillary into a surfactant solution to form bubbles. The surface tension (ST) values have been found to change with time⁴¹. Dynamic ST results can be described by the equation, $(g_0 - g_t)/(g_t - g_m) = (t/t^*)^n$, where g_t is the surface tension of the surfactant solution at surface age time (t), g_m is the *meso*-equilibrium tension, g_0 is the ST of the solvent, t^* is a constant with dimension of time, and n is a dimensionless constant. Plots of dynamic ST against time are divided into four stages. (a) An induction period, where there is slight change in surface tension value; (b) region of rapid surface tension decrease; (c) *meso*-equilibrium; and (d) equilibrium regions. Rosen and Song⁴² have examined two geminis (Structure 6), one with rigid hydrophobic spacer (A) and the other with flexible hydrophilic spacer (B), by the dynamic ST method. It has been found that in the induction period, the interface is two-thirds covered. The time required to reach the fast-fall region depends on the chain length. Long chains inhibit diffusion-controlled organization into interfacial films. They have concluded that (1) the dynamic absorption parameter, n , is relatively constant with concentration; (2) the geminis with rigid hydrophobic spacers have shorter induction times and slower surface tension fall rates; and (3) the geminis with flexible, hydrophilic spacers appear to have a greater tendency to aggregate than those with rigid hydrophobic spacers.

Micellar shape

Micellar shape of geminis is a complicated matter as it depends not only on surfactant structure, but also on solution conditions such as concentration, temperature and ionic strength. It affects rheological and solubilization properties. Small-angle neutron scattering indicates that the cationic surfactant 16-3-16 of *m-s-m* type in the concentration range of 2.5–10 mM and at 303 K forms a disk-like micelle. Upon heating to 318–343 K, it gets converted to a rod-like structure with length of 50 nm and radius of 2.7 nm (ref. 43). With spacers of 5-carbon chain or more, the shape of the micelle is prolate. Thus, spacer length controls the shape. Cryo-transmission electron microscopy studies on 12-*n*-12 and 16-*n*-16 have produced interesting morphologies⁴⁴. The 12-*n*-12 in the lower spacer length region (2, 3) forms giant, elongated worm-like micelles. Increasing spacer length in the range



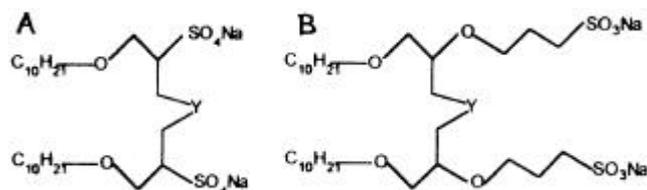
Structure 6. Gemini with (A) rigid hydrophobic spacer and (B) flexible hydrophilic spacers.

of 4-12 produces spherical micelles. Further increase in spacer length to 16 produces vesicles. The average length of the worms and hence the viscosity is affected by two opposing forces: (a) electrostatic repulsive energy among the cationic nitrogen atoms that favours scission of the worms, and (b) end cap energy that favours micelle growth by minimizing the high energy termini¹⁵.

Theoretical modelling of ionic and nonionic geminis with both hydrophobic and hydrophilic spacers using Monte Carlo simulations has been done^{45,46}. It has been found that short hydrophobic spacers give nonspherical micelles, whereas long hydrophobic spacers lead to rod-like micelles. The results also show that the bending stiffness of the hydrophobic spacer increases the CMC, which decreases for the hydrophilic spacer. Surfactants with hydrophilic spacers form spherical micelles, and the morphologies of the ionic and nonionic geminis are identical regardless of the character of the spacer. Micelle growth in the solutions of 12-2-12 conforms the model of Eriksson and Ljunggren⁴⁷ and Porte *et al.*⁴⁸. At low concentrations, the micelle is spherical but with increasing concentration, elongated micelles form and they grow both in length and number⁴⁹. Similar behaviour has been observed with nonionic surfactant C₁₂E₅ in which micellar growth is induced by temperature as well as concentration.

Surface activity

The ST of water (72 mN m⁻¹ at 25°C) is normally reduced to a value of 30–40 at the CMC of a surfactant. Surface activity has wide industrial applications. A known means of reporting the surface activity is in terms of C₂₀ values. It corresponds to the surfactant concentration that reduces the ST by 20 mN m⁻¹. It is a comparative measure of the ability of surfactants to adsorb at the air–water interface¹⁶. It is found that geminis are three orders more surface active than conventional surfactants. Surface-active properties of several anionic gemini surfactants (presented in Structure 7) are given in Table 3. It has been found that for the cationic geminis with polymethylene chain, CMC increases to a maximum when the number of polymethylene units is about 5. When the spacer between the hydrophobic groups is small or hydrophilic, the packing of the hydrophobic groups in the geminis at the aqueous solution–air inter-



Structure 7. Some anionic gemini surfactants.

Table 3. Comparative surface active properties⁶ of some anionic gemini surfactants

Compound ^a	Y	CMC/mM	$\gamma_{\text{cmc}}/\text{N m}^{-1}$	C ₂₀ /mM
A	-OCH ₂ CH ₂ O-	0.013	27.0	0.001
C ₁₂ H ₂₅ SO ₄ Na	-	8.2	39.5	3.1
B	-O-	0.033	28.0	0.008
B	-OCH ₂ CH ₂ O-	0.032	30.0	0.0065
B	-O(CH ₂ CH ₂ O) ₂ -	0.060	36.0	0.01
C ₁₂ H ₂₅ SO ₃ Na	-	9.8	39.0	4.4

^aA and B as per Structure 7.

face is closer than that found in comparable conventional surfactants. Two hydrophobic groups in a single molecule are more solvent structure-disruptive than individual chains. The higher surface activity of the geminis is useful for its applications in the industry for detergency and emulsification. The surface activity of short alkyl chain (C = 8–12) of quaternary ammonium geminis with either rigid and hydrophobic or flexible and hydrophilic spacers increases regularly with an increase in the alkyl chain length of the hydrophobic group. Geminis with a flexible hydrophilic spacer appear to aggregate more readily than those with a rigid hydrophobic one⁵⁰. The higher surface activity of geminis leads to the requirement of less raw material for synthesis and ends up with less manufacturing of by-products to be handled and less environmental impact. The tighter packing of the hydrophobic groups of the gemini surfactants compared to conventional surfactants at the interface results in a more cohesive and stable interfacial film. It indicates greater emulsion stability and greater foam stability. About 0.1% geminis may be used as emulsifying agents to make stable emulsions. Liposomes made with gemini surfactants have been found to be more stable than those made with comparable conventional surfactants.

Aggregation number

The number of surfactant monomers required to form a micelle is termed as the aggregation number (AN). It can be determined by light-scattering method, which is tedious or by small-angle neutron scattering method, which is very costly. The method of fluorescence is, therefore, widely used. In this method, the fluorescence of a probe molecule (pyrene, anthracene sulphonate, etc.) is quenched by a quencher molecule (usually cetyl pyridinium chloride) and AN is determined by following the two equations^{39,51,52}.

$$\frac{I_0}{I} = \exp\left(\frac{[Q]}{[M]}\right) \text{ and } \text{AN} = \frac{[S] - \text{CMC}}{[M]},$$

where [Q], [S] and [M] represent concentration of quencher, surfactant and micelle respectively, and I_0 and

I are the respective fluorescence emissions in the absence and presence of quencher. It has been found that AN increases with increasing concentration of surfactant. It also increases on increasing the hydrophobic chain length. For m -3- m gemini, the AN is 35 when m is 10. The value increases to 45 for $m = 12$ (ref. 53). For 16-5-16 compound the AN is 74 at 2.5 mM and increases to 138 at 50 mM (refs 20, 43). But reports on the temperature dependence of CMC and AN are rare. Such a report on 12- s -12 ($s = 2, 3, 4$) is available in the literature⁸. The CMC values increase with temperature for these three surfactants. The controlled geometry of the aggregated geminis at different surfaces (mica, graphite) and in solution is reported by Manne *et al.*⁵⁴.

Solubilization

Solubilization is an important phenomenon required in tertiary oil recovery and detergency, as both are involved with the phenomenon of homogenizing. Geminis are better solubilizers due to very low CMC values. Engberts *et al.*⁵⁵ have shown that cationic geminis are better solubilizers than conventional surfactants. This is because of the tubular shape of the aggregates. The location of a solubilized material inside the micelle depends on its structure. Saturated hydrocarbons concentrate in the micellar core. Nonpolar aromatic moieties prefer the interface. Increase in the surfactant chain length increases the solubilization power, whereas branching in the chain decreases it. For a given chain length, solubilization by micelle follows the sequence nonionic > cationic > anionic⁵⁶. Multiple interactions are supposed to take place in the core. The propensity of the gemini micelles for oil solubilization is significantly better than conventional surfactants. The 12-2-12 gemini gives [toluene]/[surfactant] ratio of 3.8 compared to 0.78 for cetyl trimethyl ammonium bromide (CTAB), most probably due to ion-dipole interaction⁵⁷. Geminis with a hydroxylated spacer (1,3-*bis*(dodecyl- N,N -dimethylammonium)-2-propanol dichloride) [given in Structure 6B with $n = 12$] have been used to separate a family of 17 ergot alkaloids by micellar electrokinetic capillary chromatography¹⁵ using 20–40 mM surfactant solution in 50 mM phosphate buffer at pH 3.0 and at 293 K. Geminis are superior to conventional surfactants in solubilizing styrene in water⁵⁸. The phase behaviour and polymerization of styrene in ternary *o/w* microemulsions with cationic gemini surfactants 12- s -12 are reported⁵⁸ with varying polymethylene spacer length $s = 2$ –12. The surfactants promote the formation of *o/w* microemulsions similar to their single-chain analogue, dodecyl trimethyl ammonium bromide (DTAB), but the solubilization properties of the m - s - m ($m = 12$) surfactants are much better. The single-phase region is strongly dependent on the spacer length; it is maximum for $s = 10$ at 298 K and $s = 12$ at 333 K. The

polymerization of monomer in microemulsion medium leads to the formation of spherical latex particles whose overall size is controlled by the monomer-to-surfactant weight ratio. A correlation between the particle size and the size of the single-phase region has been established. The optimum microemulsion formulation leading to both small particle size and high molecular weight has been found for $s = 6$ for m - s - m type surfactant series.

Gemini films

The nature of the spacer in a gemini surfactant has a say on its solubility. Water-insoluble geminis can be spread as a monolayer film on the water surface by dissolving them in a volatile organic solvent and spreading on the surface (Figure 3). In a Langmuir film balance²², the monolayer can be compressed by a movable barrier and the pressure imparted by the film can be measured. Information on the orientation and packing of the gemini surfactant on water can be obtained from the pressure–area (p - A) isotherm. It has been known that the surfactant with 18 C atom lies flat on the surface with little empty space between the molecules. A compound prepared by Karthaus and Shimomura⁵⁹ (Structure 8) has shown a steep rise at 14 nm² per molecule in the p - A isotherm. The spacer lies parallel to the surface of water, with polar groups immersed in water and tails extended outward. On irradiation at 366 nm, there is a large decrease in the surface area at constant pressure due to *trans* to *cis* isomerization of stilbene. Irradiation at 254 nm has caused a reversible change to *trans* isomer. Fluorescence microscopy has revealed a photoinduced solid to fluid transition. Sumida *et al.*⁶⁰ have reported the effect of the length of the spacer on p - A isotherm. It has been found that monolayers are tightly packed as the length of the hydrophobic tail increases. A soluble film composed of 12- n -12 has been examined both experimentally⁶¹ and theoretically⁶². The area per surfactant molecule at the air–water interface increases rapidly for short spacers, reaches a maximum for 10–12 methylene groups and decreases with very long spacers. Hairpin turns among the sufficiently long spacers impart areas that are smaller than expected¹⁵; however, spacers do not depart from the

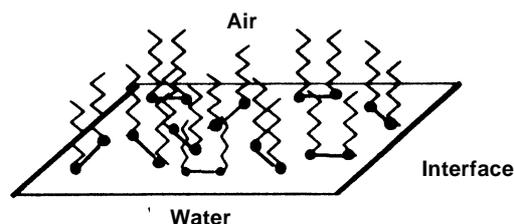


Figure 3. Monolayer film of gemini surfactant at the air–water interface. Nonpolar tails are projected outward in air and polar heads with spacers are arranged in water.

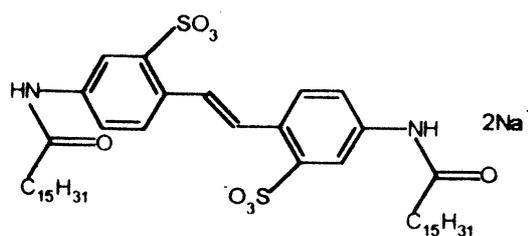
air–water interface. Explanations on the behaviour of p - A isotherm for the geminis with saccharide spacers are also given by Menger and Mbadugha²⁶. Interfacial composition at the air–water interface of gemini surfactants has been also determined by chemical trapping⁸, using an arenediazonium probe. The method is useful for evaluating the interfacial regions of cationic, anionic, nonionic and zwitterionic surfactants, as well as microemulsions (o/w and w/o) and vesicles.

Wetting and foaming properties

Weakly water-soluble surfactants in aqueous medium often increase wetting properties considerably^{16,63}. They may easily form foams. The foaming properties of gemini surfactants depend, as in conventional surfactants, upon the chain length of the hydrophobic groups, and on the length and nature of the spacer between them as well. Kim *et al.*²¹ have reported that C₁₂ cationic geminis form large amounts of foam in comparison to DTAB; in some cases even better than sodium dodecyl sulphate (SDS). Rosen and co-workers^{37,63} have found that the anionic gemini surfactants have much better soap-dispensing ability. These geminis, because of their low sensitivity to Ca²⁺ and Mg²⁺, can be used in cleaning and other industrial processes where presence of hard water makes the conventional surfactants ineffective.

Hydrotropic properties

The hydrotropic properties of surfactants stem from their ability to inhibit the formation of aggregated crystalline or liquid crystalline structures in the aqueous phase. The compounds which have large hydrophilic parts in comparison to their hydrophobic portions are good hydrotropes. The results are briefly described in Table 4 for the four types of alkylated diphenylether sulphonates (C₁₀DPE sulphonates) shown in Structure 9, where R is a linear C₁₀ alkyl chain (attached to the aromatic ring at different nonterminal carbon atoms). The data for the addition of the 2.2% of the different diphenylether sulphonates to a pasty, opaque aqueous dispersion of 23% linear alkylbenzene sulphonate (LAS) are given in Table 4. Mono-alkylated disulphonates (MADS) having the largest ratio

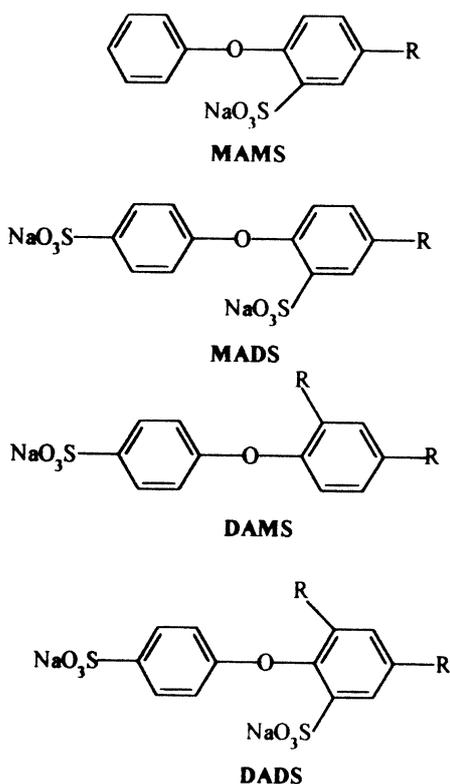


Structure 8. Photoactive gemini surfactant.

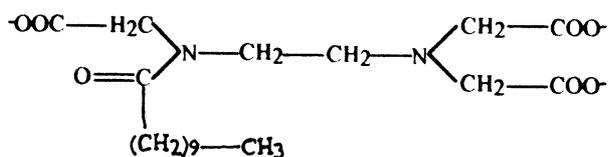
of hydrophilic to hydrophobic regions falling in this category are the best hydrotopes in the series. However, the gemini dialkylated disulphonate (DADS), with two hydrophilic groups, is a better hydrotrope than the conventional monoalkylated monosulphonate (MAMS) or the dialkylated monosulphonate (DAMS)³⁷. The *N*-acyl ethylenediamine triacetate gemini (Structure 10) can also show hydrotropic properties, even in highly alkaline medium.

Antimicrobial properties

Antimicrobial properties of geminis are important over the other conventional agents. But the effectivity of these compounds depends on the length and type of spacer and the hydrophobic counterpart. Quaternary ammonium salts are generally known as disinfectants. The common examples are hexadecyl trimethyl ammonium bromide (HTAB),



Structure 9. Four types of alkylated diphenylether sulphonates (C_{10} DPE sulphonates).



Structure 10. EDTA-like chelating gemini surfactant.

benzylododecyl dimethyl ammonium bromide (BDDAB), 2-ethoxycarbonyl pentadecyl trimethyl ammonium bromide (EPTAB), etc. A gemini, as shown in Structure 11, may display similar biosensitivity. Effects of the length of the hydrophilic tail and spacer are shown in Table 5. It is found that minimum inhibitory concentration (MIC) to inhibit visible growth after 24 h incubation at 310 K against *E. coli* is 6 μ M, when $m = 12$ and $n = 2$. The MIC for BDDAB and EPTAB is 625 and 78 μ M respectively. A detailed analysis is given by Menger and Keiper¹⁵. Di-quaternary ammonium geminis prepared from *N*-dodecyl betaine by Diz *et al.*⁶⁴ have been found to be more effective against 19 Gram-positive and Gram-negative microorganisms other than HTAB. A nonionic gemini surfactant containing dioctanoyl lysine⁶⁵ is non-irritating and non-hemolytic, and suitable for use in personal care and pharmaceutical formulations. This proves the effectiveness of geminis in medicinal chemistry. Perez *et al.*⁶⁶ have reported the synthesis and evaluation of a novel class of biocompatible gemini surfactants obtained with

Table 4. Hydrotropic properties³⁷ of C_{10} DPE surfactants (Structure 9)

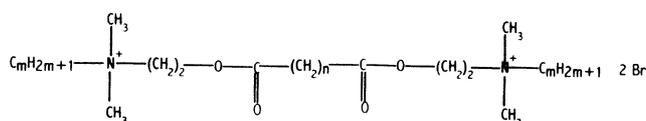
C_{10} DPE sulphonate	Appearance ^a
–	Viscous, cloudy dispersion
MADS	Clear, flowable at 288 K
DADS	Clear, viscous at 298 K, cloudy at 288 K
MAMS	Viscous, cloudy dispersion
DAMS	Viscous, cloudy dispersion

^aAppearance of 23% LAS dispersion upon addition of 2.2% C_{10} DPE sulphonate.

Table 5. MIC values for geminis against *E. coli*

Gemini ^a		
m (chain length)	n (spacer length)	MIC/ μ M
6	2	21000
12	2	6
16	2	5700
6	4	8100
12	4	25
16	4	2800
6	8	930
12	8	190
16	8	5200

^aGeneral formulation shown in Structure 11.

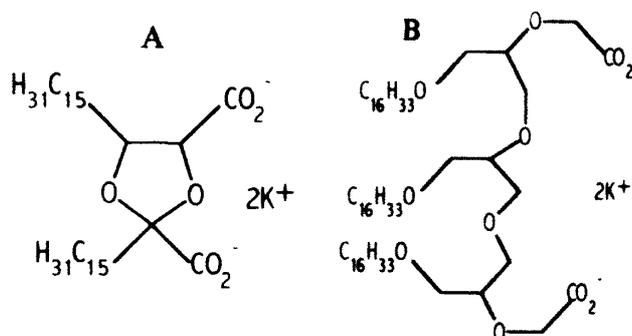


Structure 11. Antimicrobial gemini surfactant.

arginine based on chemical, biological and fundamental studies. The compounds have exhibited a broad range of antimicrobial property against 16 selected microorganisms. The Gram-negative bacteria are more resistant than the Gram-positive bacteria, which makes them in a way suitable in the biodegradability process. In contrast to the corresponding single-chain molecule, two alkyl chains in one molecule linked by a spacer chain enhance the adsorption and aggregation properties by strengthening the intra or intermolecular hydrophobic interactions.

Vesicle formation, chelation and other properties

Geminis have shown promise in the formation of vesicles, similar to lecithin, phospholipids, etc. A cyclic, double-chain, double-head gemini surfactant⁶⁷ (Structure 12A) forms vesicles when sonicated in aqueous solution above pH 9. The hydrodynamic diameter of the vesicles studied by dynamic light scattering (DLS) method is 36 nm. Sommerdijk *et al.*²⁸ have reported the preparation and properties of a diastereomeric gemini surfactant, the synthesis strategy of which is given in Scheme 4. On sonication, the surfactant molecules form unilamellar vesicles. The average radius is different for the two diastereomers, SS and RS. For SS it is 15–25 nm and for RS it is 50–100 nm. Ca^{2+} favours the fusion of SS isomer, whereas it inhibits the fusion of other diastereomers. The compounds do not immediately precipitate after Ca-binding. The fusion and fission processes have been monitored and explained. A triple-chained gemini⁶⁸ (Structure 12B) can encapsulate metal ions like ethylene diamine tetraacetate (EDTA). So the geminis may be used as chelating agents. Some gemini surfactants with modified EDTA structure may also be used as chelating agents. The *N*-acyl EDTA chelating surfactants (Structure 10) provide optimum ST reduction between pH 5 and 8. These chelating surfactants are compatible with enzymes and cationic surfactants. They are good hydrotropes even in highly alkaline condition. These products can be used as corrosion inhibitors. The products have low irritancy and low toxicity. They show lather enhancement in saline



Structure 12. Vesicle-forming gemini surfactant.

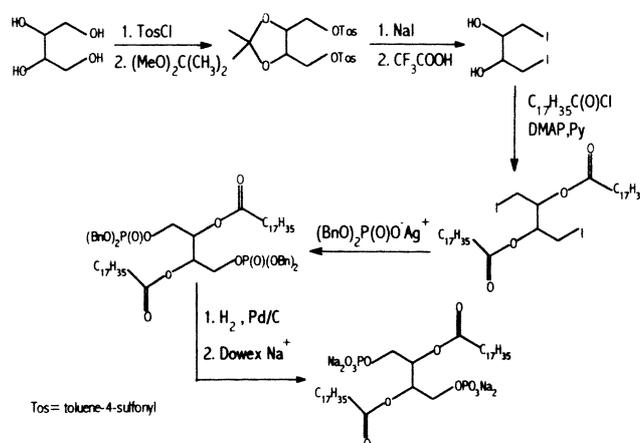
condition. These compounds are used for hard-surface cleaning, metal cleaning and degreasing, metal polishes, floatation of minerals and lubricant additives, etc.

Gelation

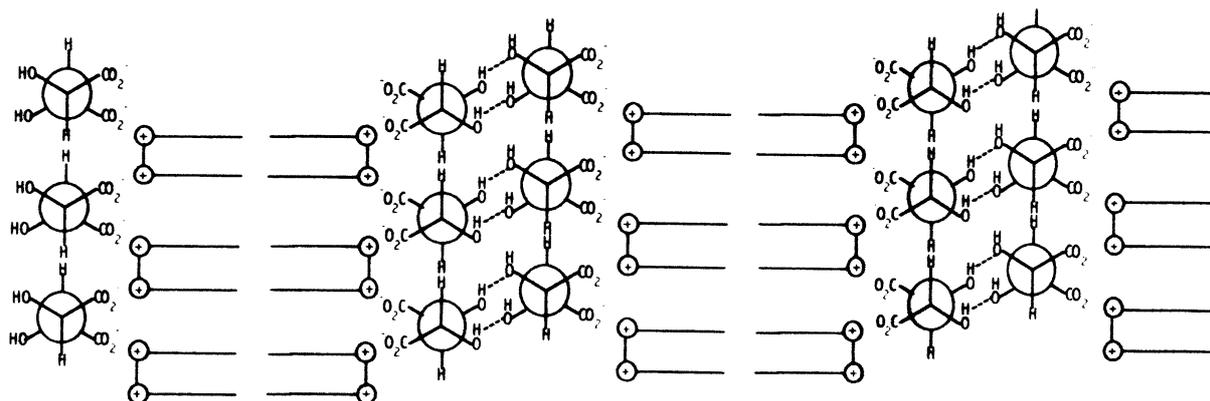
Oda and co-workers^{10,69} have studied the rheology of gemini surfactant 12-2-12. This surfactant forms a worm-like micelle at higher concentration, resulting in higher viscosity. In presence of *n*-hexanol, there is micelle to vesicle transition. The viscosity decreases at higher alcohol concentration, forming tube-like micelles. A shear-induced phase transition of cylindrical micelle has been studied⁷⁰. The aggregates are isotropic, and their size increases with shear rate up to a limiting value. Transmission electron microscopy (TEM) measurements reveal that there is a long, entangled, helical fibre when 16-2-16 geminis composed of L and D tartarate counterions form a gel in organic solvents. Oda *et al.*⁷¹ have also proposed a structure for the gel. Layer-like liquid crystalline phases of 'counterion-coupled gemini surfactants' (cocogems) are used as the medium for polymerizing acrylamide (Structure 13). The structure of the gel is controlled by the anisotropy of the surfactant and has been discussed by Antonietti *et al.*⁷². The phase behaviour and the polymerization of styrene in ternary o/w microemulsion with 12-*n*-12 are also known⁵⁸. Dreja has shown the structural parameters of the microemulsion and gel with varying spacer length for *n* = 2–12. The weight-average molecular weights of the macromolecules after polymerization have been determined in varying conditions.

Phase behaviour

Phase behaviour of mixed systems involving oil, water and surfactants is an important area of research in the field of surfactant chemistry, whose study is often tedious



Scheme 4. Structure and synthesis of diastereomeric gemini surfactant.

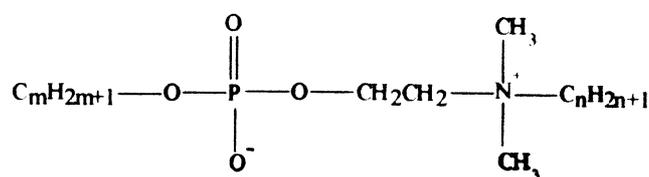


Structure 13. Proposed structure of aggregates of a gemini with tartrate counterion.

and time-consuming. The formation of liquid crystalline phase is also an important area in surface chemical research. Characteristic phases are analysed by the methods of polarized optical microscopy, calorimetry, X-ray diffraction, neutron scattering, DLS, viscometry, etc. The field has been elaborately studied. Kunieda *et al.*⁷⁴ have reported the phase behaviour of water–gemini surfactant–oil system over a wide range of compositions. It has been found that geminis may also be used to form microemulsions^{74,75}. Menger and Peresypkin¹⁴ have recently reported¹⁴ the binary structural phase diagrams for different phases of gels, micelles, polydisperse vesicles and coacervates with a zwitterionic surfactant, which is represented in Structure 14. The proposed morphology of the different structural phases reported therein¹⁴ depends on asymmetry of the two chains and on the hydrophobicity, i.e. the total number of carbon atoms in these two chains.

Concluding remarks

Gemini surfactants have good commercial utilization potential; their preparation should thus be cost-effective. As lower amount of geminis is needed for a particular performance, cost-effectiveness may not stand in the way. Costly geminis may, however, be used as additives to the conventional ones to enhance the surface-active properties. Colgate Palmolive, Dow Chemicals, Hampshire Chemical Corp., Reckitt and Colman, Rhone-Poulenc Surfactants and Specialities, Texaco Inc. and Witco Corp. have contributed a lot to the synthesis and characterization of useful geminis. Many more detergent and oil-based companies have to come forward to make newer cost-effective geminis. It will thus be a challenge for the new-generation scientists to conduct interdisciplinary chemical research by synthesizing newer compounds, characterizing them and describing their surface-active properties for effective applications. So far over 10,000 international patents on gemini surfactants have been filed



Structure 14. Zwitterionic gemini surfactant.

and investigations for newer products are in progress. The field is open to accept challenging contributions to enrich the science of physics and chemistry of interface.

It may be mentioned that in recent years attempts have been made to synthesize gemini-type surfactants having more than two heads and varied spacers, and study their physicochemical properties with a view to novel and potentially useful surface-active materials²⁰. The field of research in the area of new-generation surfactants is thus heading towards the formation of fascinating as well as demand-oriented products.

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