

Gemini (dimeric) Surfactants

The Two-Faced Molecules

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A gemini surfactant (GS) consists of two conventional surfactant molecules chemically bonded together by a spacer. The two terminal hydrocarbon tails can be short or long; the two polar head groups can be cationic, anionic or nonionic; the spacer can be short or long, flexible or rigid. The GS need not be symmetrically disposed about the center of the spacer. GS can self-assemble at much lower concentrations and are superior in surface activity as compared to conventional surfactants. GS are very attractive for catalysis and adsorption applications, new synthetic vectors for gene transfection, analytical separations, solubilization processes, nanoscale technology, biotechnology, enhanced oil recovery and as paint additives.

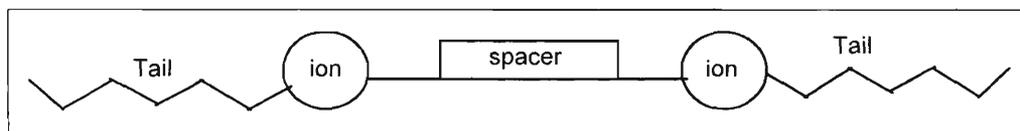
Introduction

Conventional surfactant molecules (single chained amphiphile) are composed of a long hydrophobic hydrocarbon tail with an ionic or polar hydrophilic head. An example of an anionic surfactant is sodium dodecyl sulphate ($\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^- \text{Na}^+$) while cetyltrimethylammonium bromide ($\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{N}^+ \text{Br}^-$) is a cationic surfactant. In contrast, gemini surfactant (the name *gemini* was coined by Menger [1]) is an amphiphile made up of two hydrocarbon tails and two ionic groups linked by a 'spacer' in the sequence: hydrocarbon tail / ionic group / spacer / ionic group / hydrocarbon tail (Figure 1). The spacer can be attached directly to the identical ionic groups (Figure 2A), each of which is in turn bonded to an identical hydrocarbon tail; alternatively,

Keywords

Gemini, surfactants, micelle.

Figure 1. Schematic representation of the gemini surfactant structure.



the two identical amphiphiles are joined midway (Figure 2B).

Structure

Some structural features of GS are given below:

(i) All GS have at least two hydrophobic chains and two ionic or polar groups. (ii) Spacer length can be short (2 methylene groups) or long (12 methylene groups); rigid (stilbene) or flexible (methylene chains); and polar (polyether) or non-polar (aliphatic, aromatic). (iii) The polar group

can be positive (ammonium), negative (phosphate, sulphate, carboxylate, sulphonate), or nonionic (polyether, sugar). (iv) Symmetrical and nonsymmetrical GS are known (see[2]), that is, these may or may not have two identical polar groups and two identical chains. (v) GS with three or more polar groups or chains are also known. Some representative examples [2] of GS structures (1-8) are given in Figure 3.

Synthesis

A brief summary of the methods for the synthesis ([1],[2]) of representative GS is given in Schemes 1-3.

Properties

(i) The addition of effective surfactant lowers the surface tension of water until critical micelle concentration (CMC) is reached. The CMC represents the point where individual surfactant molecules spontaneously aggregate into complex structures, including micelles, bilayer and vesicles. The type of aggregate formed is dependent on surfactant structure, temperature, ionic strength and pH. The models of GS are essentially extensions of monomeric surfactant self-assembly theories. The binding of surfactant molecules in pairs by spacer chains introduces new constraints affecting molecular arrangements in micelles.

Unlike conventional surfactants, which form spherical aggregates (Figure 4A), the aggregates of GS molecules involve expo-

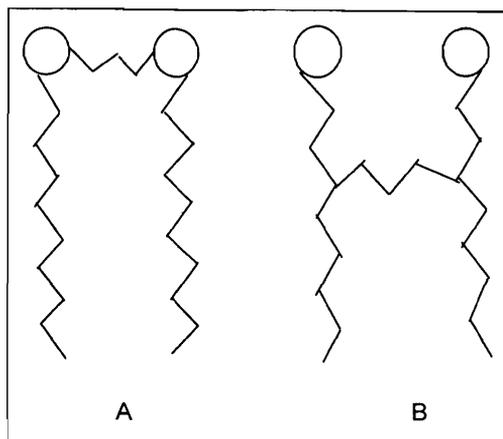


Figure 2. Two types of gemini surfactants.

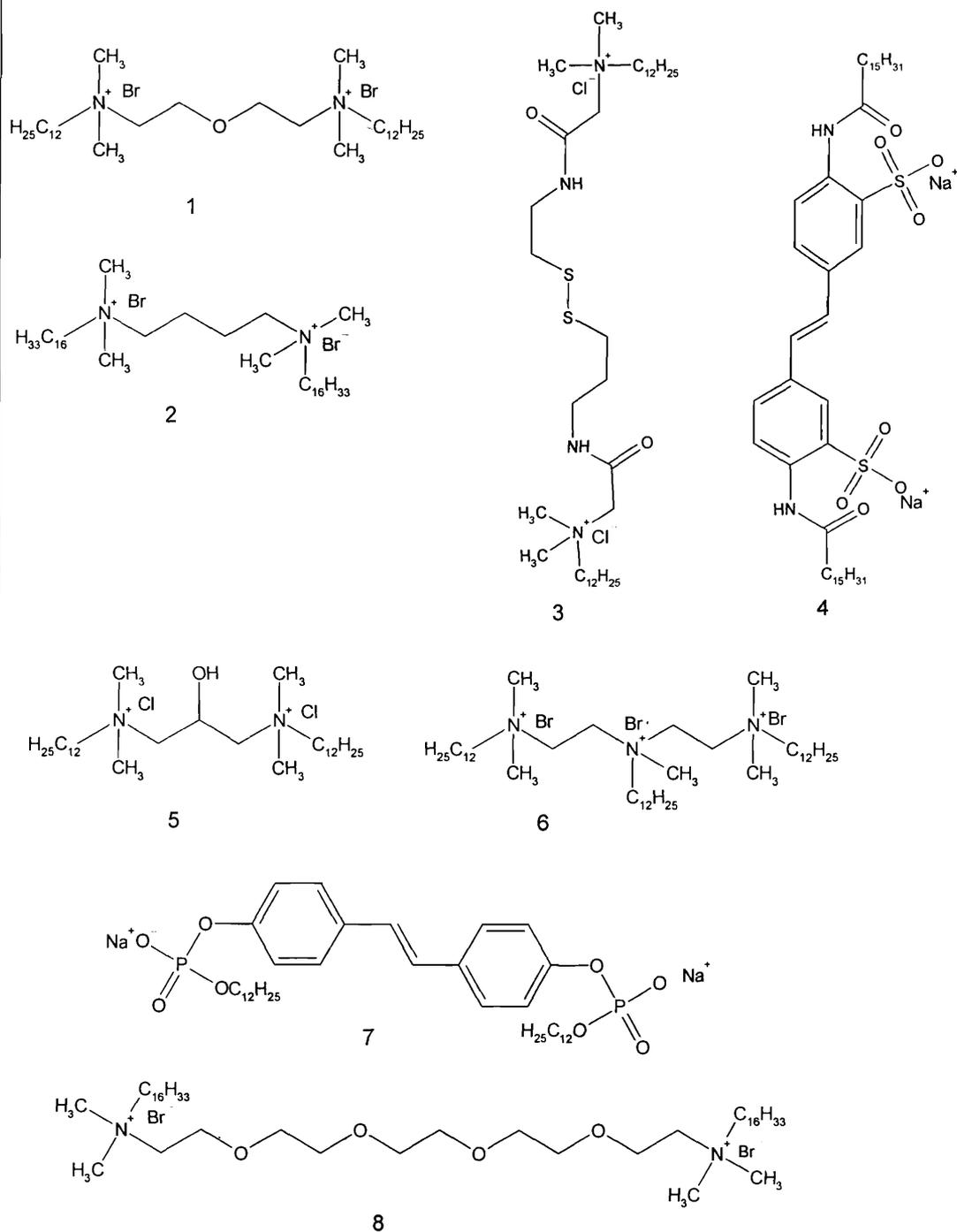


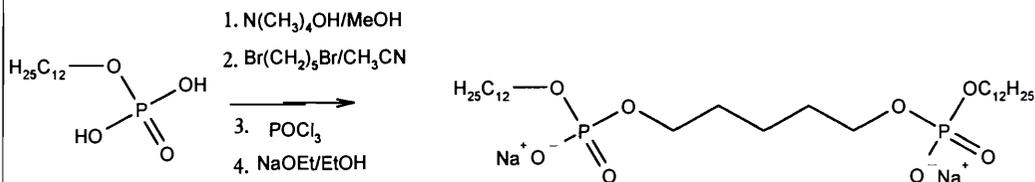
Figure 3. Some representative GS (Structures 1-8).

Method A

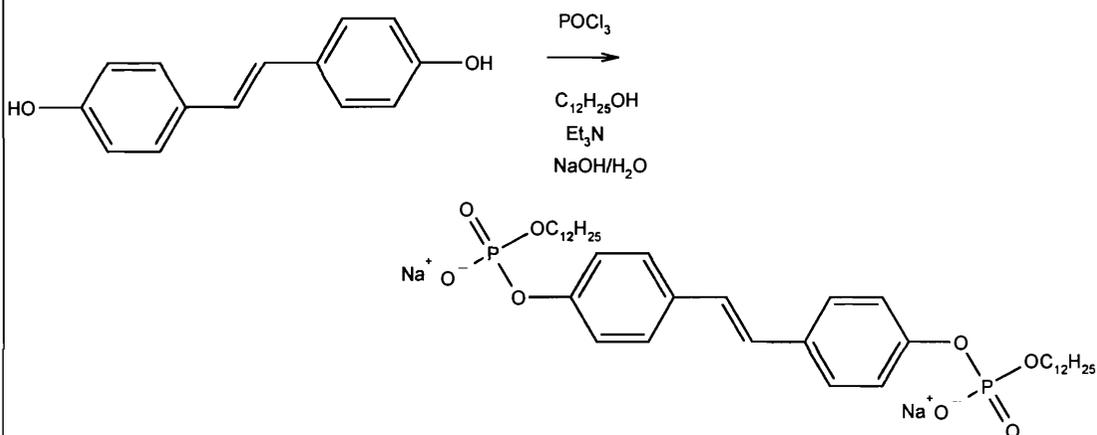
R = a long chain

**Method B**

Scheme 1. Synthesis of simple cationic GS.



Scheme 2. Synthesis of anionic GS with flexible spacer.



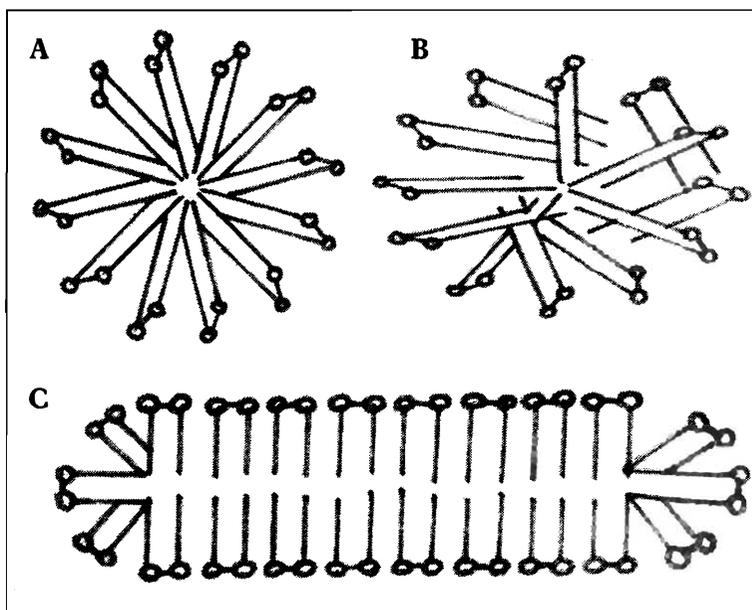
Scheme 3. Synthesis of anionic GS with rigid spacer.

Figure 4. Diagram of a section of

A: spherical micelle;

B: thread-like entangled micelle;

C: rod-like micelle.



sure of hydrocarbon moieties to water. GS with short hydrophobic spacer form thread-like micelles (*Figure 4B*) and those with long spacer form rod-like micelles (*Figure 4C*), in particular when the spacer length is comparable to the tail length. In case of GS, the distribution of head groups on the surface becomes inhomogeneous as linked head groups have a mutual distance different from that of unlinked ones. The spacer gives the surfactant molecule an inplane orientation, i.e., the combined head groups made of two monomeric heads and spacer is very anisotropic.

GS with short spacer experience the increased intermolecular repulsion between head groups, thereby forming thread-like micelles even at low concentration. On the other hand, in case of long spacer GS, the spacer shields the head group's repulsion and favors micelle formation that is continuous along a single dimension (cylindrical rods). The micellar sphere-to-rod transition is induced due to decrease in repulsion between head groups in case of ionic surfactants.

(ii) GS have low CMC values compared with corresponding conventional surfactants of equivalent chain length. For ex-



ample, the CMC for GS $[(C_{12}H_{25}N^+(CH_3)_2(CH_2)_nN^+(CH_3)_2C_{12}H_{25}\cdot 2Br^-]$, $n = 3-8$) is 1 mM compared to a CMC of 16 mM for simple surfactant $[C_{12}H_{25}N^+(CH_3)_3Br^-]$. A long hydrocarbon spacer of 16 CH_2 groups $(C_{12}H_{25}N^+(CH_3)_2(CH_2)_{16}N^+(CH_3)_2C_{12}H_{25}\cdot 2Br^-)$ lowers the CMC almost tenfold compared to a short spacer of 3-8 CH_2 groups $[(C_{12}H_{25}N^+(CH_3)_2(CH_2)_nN^+(CH_3)_2C_{12}H_{25}\cdot 2Br^-]$, $n = 3-8$].

Anionic GS $[C_{12}H_{25}OPO_2^-O-(CH_2)_6-O-PO_2OC_{12}H_{25}\cdot 2Na^+]$ have lower CMC than their cationic counterparts $[(C_{12}H_{25}N^+(CH_3)_2(CH_2)_nN^+(CH_3)_2C_{12}H_{25}\cdot 2Br^-]$, $n = 3-8$]. Some GS can assemble at a concentration hundred times lower than that needed for their conventional relatives. The increase in bending stiffness of hydrophobic spacer increases the CMC whereas the reverse is true in case of hydrophilic spacer.

The micellization behaviour of GS is qualitatively different from that of conventional ones. The lower CMC can be directly attributed to the increase in the number of hydrocarbon groups in the molecule. The CMC of GS is a non-monotonous function of the number of spacer hydrocarbon groups, with a maximum value around 4-6 polymethylene groups. Furthermore, in case of ionic GS, the spacer reduces the intermolecular repulsion between head groups. This leads to micelle formation at low CMC values in GS.

(iii) GS are generally superior over a conventional surfactant in terms of surface activity. This is due to the distortion of water by hydrophobic groups. In GS, two hydrophobic groups in a single molecule are more disruptive than individual chains in conventional surfactants. This in turn promotes the migration of a micelle to the air/water interface. Moreover, GS can be used in small quantities as compared to conventional surfactants.

(iv) A shorthand notation for cationic GS with two C_{12} tails and a C_3 spacer separating the quaternary nitrogen atoms is 12-3-12. For example, GS (12-n-12, $n = 4, 6, 8, 10, 12$) are superior to conventional single tailed surfactants in solubilizing styrene in water.



Suggested Reading

- [1] F M Menger and C A J Littau, *J. Am. Chem. Soc.*, Vol. 113, p.1451, 1991; Vol. 115, p.10083, 1993.
- [2] F M Menger and J S Keiper, *Angew. Chem. Int. Ed.*, Vol. 39, p.1906, 2000.
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- [5] A J Kirby, P Camilleri, J B F N Engberts, M C Feiters, R J M Nolte, O Soderman, M Bergsma, P C Bell, M L Fielden, C L Garcia-Rodriguez, P Guedat, A Kremer, C McGregor, C Perrin, G Ronsin, and M C P van Eijk, *Angew. Chem. Int. Ed.*, Vol. 42, p.1448, 2003.

(v) GS show bioactivity as disinfectants. For example, the GS ($C_{12}H_{25}N^+(CH_3)_2(CH_2)_2OOC(CH_2)_2COO(CH_2)_2N^+(CH_3)_2C_{12}H_{25}\cdot 2Br^-$) is one or two orders of magnitude more potent than the conventional single-chained disinfectants, i.e., amphiphilic quaternary ammonium salts, such as benzyldodecyltrimethylammonium bromide and 2-ethoxycarbonylpentadecyltrimethylammonium bromide.

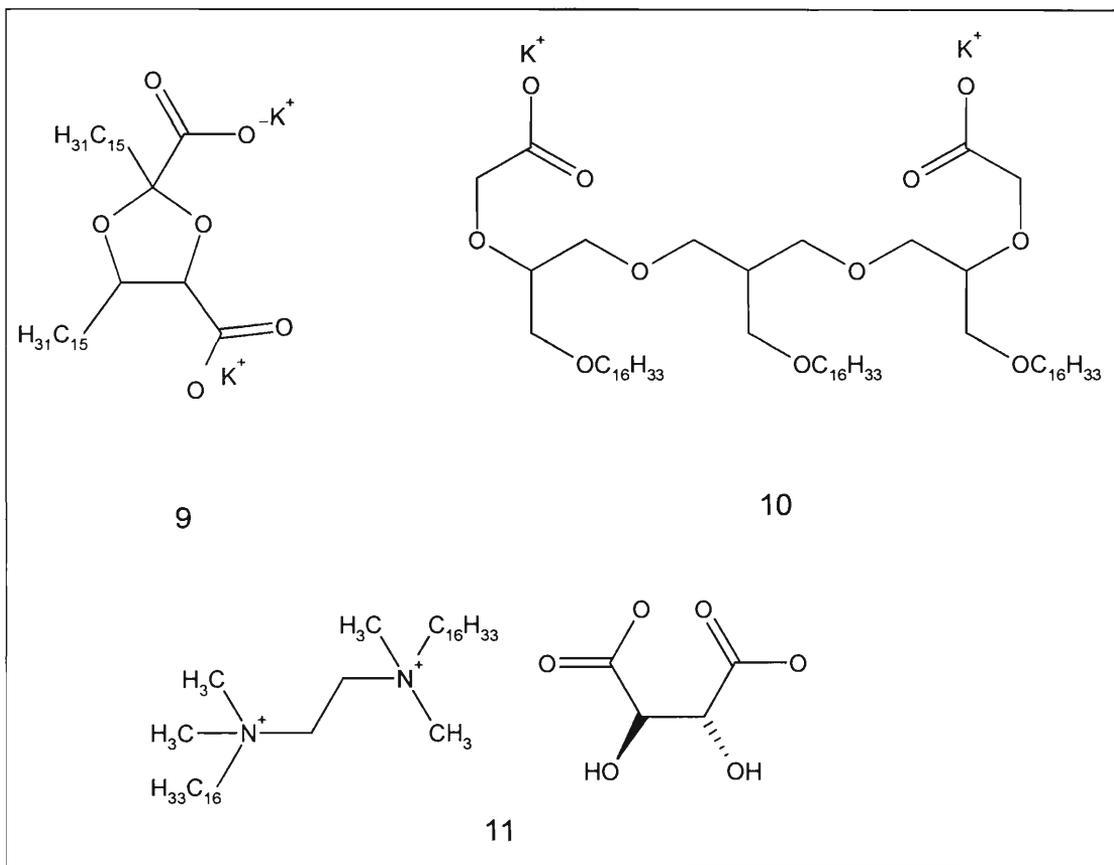
(vi) GS have been used in the synthesis of new mesoporous zeolites for catalysis and adsorption applications [3] and two types of such materials (hexagonal MCM-41 and the cubic MCM-48) have gained widespread interest. MCM-48 materials can be prepared with a surface area of 1650 m²/g and a very narrow pore size distribution (pore diameter 28 Å). Cationic GS, for example, abbreviated as 16-12-16 and 18-12-18 promote the synthesis of good quality MCM-48 with high surface area and narrow pore-size distribution.

GS with the formula $C_nH_{2n+1}N^+(CH_3)_2(CH_2)_sN^+(CH_3)_2C_mH_{2m+1}\cdot 2Br^-$ abbreviated as GS n-s-m, can be used to create a very wide range of materials [4]. Changing the chain length (n, m) will change the pore size diameter while change in spacer size(s) influences the way by which surfactants agglomerate into micelles. In other words, it determines whether MCM-41, MCM-48 or other (lamellar) structure is created. The use of a GS in the synthesis of MCM-48 reduces the overall production costs and thus has a bright future in material technology.

(vii) Double chain, double head group GS (9) and triple chain GS (10) form stable vesicles (*Figure 5*). A very small quantity (10 mM) of GS composed of 16-2-16 with L- and D-tartrate find applications in gelating organic solvents like dichloromethane, chloroform and toluene. Even one molecule of a GS (structure 11, *Figure 5*) entraps about 1200 molecules of chloroform.

(viii) Liposomes formed from cationic lipids, in combination with a neutral lipid such as 1,2-dioleoyl-sn-glycero-3-phosphatidylethanolamine have been used extensively for the delivery of





DNA into mammalian cells in culture. Successful gene therapy, that is, the replacement or addition of a gene commonly employs viruses as gene transfer 'vectors' and the procedures are complicated and expensive. In contrast, GS are new synthetic vectors for gene transfection (i.e. introduction of DNA into the cell nucleus) *in vitro* [5].

(ix). GS are also finding their way into skin care formulations, antipollution protocols, analytical separations, nanoscale technology, biotechnology, enhanced oil recovery and as paint additives [4].

Figure 5. Structures of GS 9-11.

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