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 (CH₃(CH₂)₁₁OSO₃⁻Na⁺) while cetyltrimethylammonium bromide (C₁₆H₃₃(CH₃)₃N⁺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,
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 (methylenechains); 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-