MULTIFUNCTIONAL SURFACTANTS

Surface-active compounds, i.e. surfactants, constitute one of the major groups of chemical compounds which is of fundamental importance to household chemistry, mining, petrochemical and pharmaceutical industries, the high-tech sector, molecular biology and nanomedicine. [1,2]. The massive use of surfactants, which exceeds 10 million tonnes a year on a global scale, and is forecast to reach 25 million tonnes in 2020, poses a serious threat to the natural environment [3]. [Fig.1]

Therefore, intensive research is being carried out with a view to developing new, more effective surface-active compounds whose properties would meet the principles of sustainable development and which would substantially reduce the amount of the surfactants currently in use. Surface-active compounds are classified into four basic types, i.e. anionic, cationic, non-ionic and amphoteric surfactants, of which the cationic surface-active compounds, in particular the quaternary alkylammonium salts (QAC- Quaternary Ammonium Compounds), play the most important role. This is largely due to the ability of cationic surfactants to form morphologically varied structures in aqueous solutions, which exhibit strong emulsification and dispersion properties, as well as high antimicrobial activity against fungus, bacteria, algae and viruses. As is the case with natural surfactants in biological systems, synthetic surfactants display much higher activity in binary mixtures, especially in those where the difference in charges between surfactants is the biggest. Hence, the synergism of action reaches its maximum in the mixtures of cationic and anionic surfactants, however the effect is also visible in the binary mixtures of

Fig. 1. The use of surfactants across different industry sectors [3].

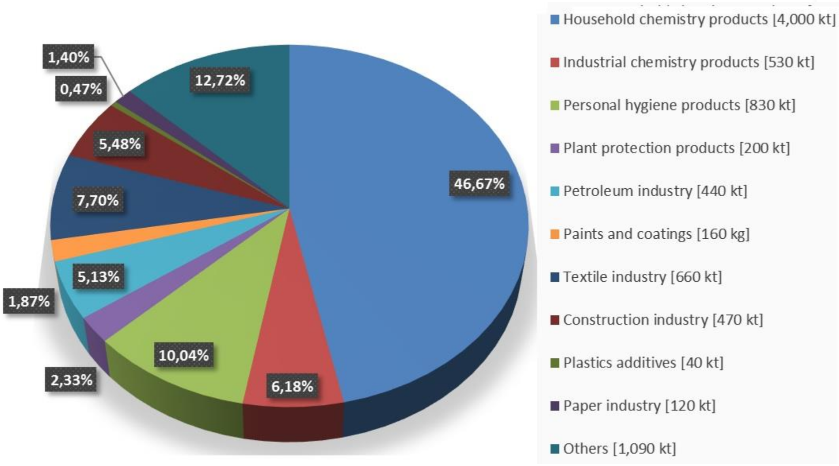
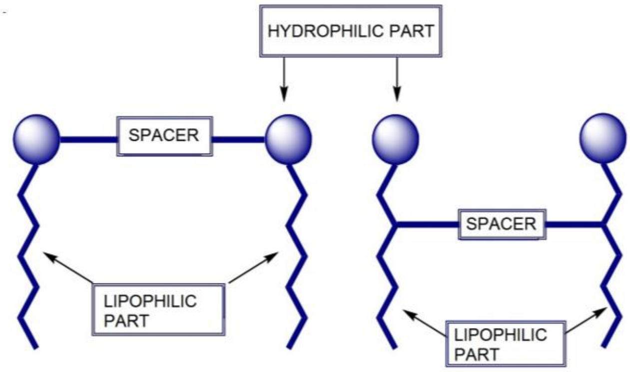


Fig. 2. Structure of gemini surfactants.



cationic/non-ionic surfactants, or cationic/cationic surfactants.

The synergistic action of cationic and anionic surface active agents is exemplified by the binary equimolar mixture of sodium dodecyl sulphate (SDS) and dodecyltrimethylammonium bromide (DTAB). Pure sodium dodecyl sulphate (SDS) at a concentration of 4.5 M reduces the surface tension to 50mN/m, whereas in an equimolar mixture of the anionic SDS and cationic DTAB, the same value of surface tension is achieved at a five hundred- fold lower concentration, i.e. 9×10^{-3} M [4].

Dimeric quaternary alkylammonium salts, known as gemini surfactants, have gained particular importance over the recent years. The compounds can be treated as combinations of monomeric alkylammonium salts with identical, or different structures (Fig. 2).

The spacers which link monomeric surfactants at their polar heads, or their immediate vicinity, may be flexible, rigid or semi-rigid, hydrophobic, or hydrophilic (Fig. 3).

The nomenclature for unsubstituted gemini surfactants is often used in the simplified form [m-s-m] which denotes the length of the hydrophobic chain, and the number of methylene groups in the spacer.

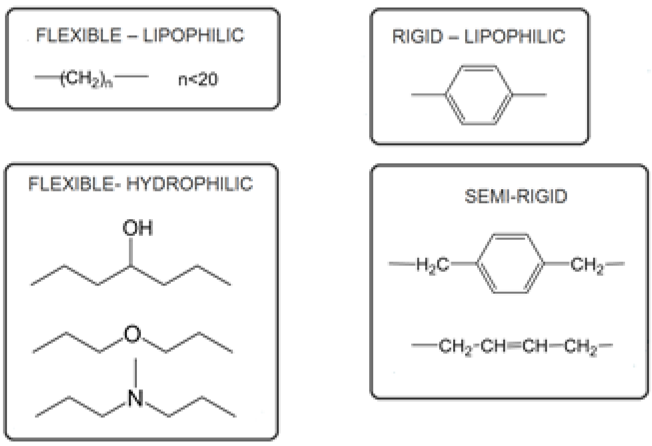
Thus, the simplified notation for the gemini surfactant polymethylene -α,ω-bis (N-alkyl-N,N-dimethylammonium) dibromide is [m-s-m] (Fig.4].

Surface-active properties of gemini surfactants, expressed e.g. in terms of the surface tension (γ), or the critical micelle concentration (cmc), as well as their antimicrobial effects expressed in terms of the Minimal Inhibitory Concentration (MIC), are by two or three orders of magnitude better than those of their monomeric analogues. The unique properties of gemini surfactants result directly from the structure of the aggregates formed in aqueous solutions. Monomeric surfactants in water form micelles whose size, morphology and degree of aggregation depend primarily on the length of the hydrophobic chain. The structure of the spacer in gemini surfactants is an additional factor determining the degree of aggregation and the size of micelles. For identical lengths of the hydrophobic chain in a monomeric and dimeric surfactant, the number of molecules forming micelles in the dimeric system will always be smaller due to the predetermined spacing between the hydrophilic parts of the surfactant.

Surface and interfacial activity

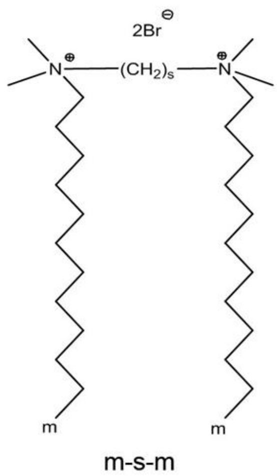
The ability to modify the structure of dimeric alkylammonium salts (gemini surfactants) opens up nearly endless possibilities for developing a compound intended for specific applications (Fig. 6). Change in the lengths of the hydrophobic chains, introduction of heteroatoms, such as nitrogen, sulphur, oxygen or phosphorous into the spacer, introduction of rigid, or semi-rigid π-electron systems, or introduction of hydroxyethyl or glucityl groups enables the creation of a surfactant with the desired HLB, cmc and MIC values, suitable dispersion characteristics, and strong corrosion inhibition properties. The diversification of the hydrophilic and lipophilic (HLB) properties of surfactants, which allows them to be used as emulsifiers, detergents or solubilisations, is an outcome of the introduction of hydroxyl groups, or hydrophilic substitutes, and the optimisation of hydrophobic groupings.

Fig. 3. Structure of spacers in gemini surfactants.



This results in achieving the suitable HLB value, as well as minimising the cmc value. This is well illustrated by comparing the dodecyl-trimethylammonium bromide (DTAB), a model monomeric alkylammonium salt showing a cmc value of 15.1 mM, with a 16-2-16 gemini surfactant containing 16 carbon atoms in the hydrophobic chain and two methylene groups in the spacer, showing a cmc value of 0.021mM, i.e. over seven hundred times lower than that of the monomeric compound [5]. Similar changes occur as a result of the decrease in the C_{20} value, i.e. the surfactant concentration, which produces a 20mN/m reduction in the surface tension of the solution. For the DTAB, the above value corresponds to 5.25 mM, whereas for the [16-2-16], it drops to $2.6x10^{-4}$, i.e. by over thirty thousand times [5]. The introduction of hydroxyethyl groups into the structure of a gemini surfactant produces changes in both the HLB and cmc values. In a 12-4-12 gemini surfactant, the substitution of methyl groups with hydroxyethyl groups leads to a substantial increase in hydrophilicity, i.e. an increase in the HLB value.

Fig. 4. Nomenclature of gemini surfactants



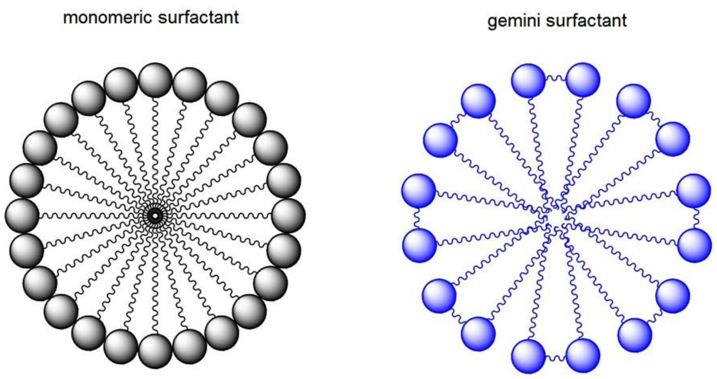
Polymethylene -α,ω-bis (N-alkyl-N,N-dimethylammonium) dibromide

Simultaneously, the cmc value is reduced by nearly 160 times [6]. The excellent emulsification, dispersion and solubilisation properties of gemini surfactants provide the basis for their application in molecular biology (gene transfection, DNA intercalation), nanomedicine (drug encapsulation, microbicidal nanogels), and nanotechnology (electro-optical systems, holography). The ability to create three-dimensional supermolecular systems, such as hybrid micelles/ liquid crystals/polymer matrices has found application e.g. in high-resolution monitors (Fig. 7) [7].

Antimicrobial activity

Quaternary ammonium salts contain a positively charged nitrogen atom, as a result of which they are capable of being adsorbed on negatively charged surfaces. As the cell walls in the majority of microorganisms are negatively charged, the ammonium salts present in the solution are strongly adsorbed on the cell surface through electric interaction. Hydrocarbon chains of alkylammonium salts are adsorbed on the cell wall and penetrate through the lipid layer of the micro-organism, causing damage to the layer and an efflux of low molecular intracellular components, which leads to the death of the microbial cell.

Fig. 5. Structure of micelles

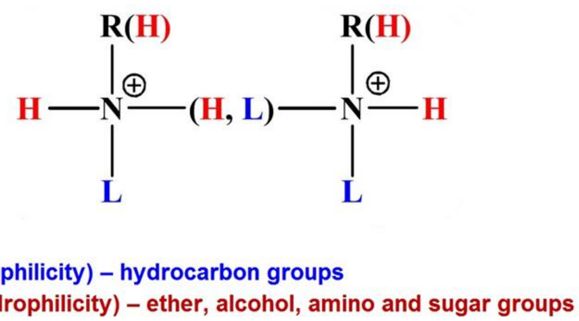


The kinetics and dynamics of the biocidal action of alkylammonium salts is determined during the phase of adsorption on the negatively charged cell wall. Therefore, the greater number of positive charges is present in a microbicidal molecule, the higher the effectiveness of the process. The antimicrobial activity of alkylammonium salts is largely dependent on their hydrophilic-lipophilic balance (HLB) as expressed by the equation:

$$\text{Log}1/\text{MIC} = a + b\log P + C[\log P]^2$$

where P is the octanol-water partition coefficient which describes the HLB of a molecule. The antimicrobial activity depends on the alkyl chain length, and, consequently, on the value of logP [8,9]. Compounds containing C10-C12 alkyl chains are active against yeast and fungi, while Gram-negative micro-organisms are more susceptible to the action of highly lipophilic compounds, which is due to the higher lipophilicity of their cell membranes that cannot be easily penetrated by hydrophilic compounds. Gemini surfactants meet all of the assumptions above, i.e. they contain two positively charged nitrogen atoms that facilitate adsorption on the cell wall, their hydrophobic chains have a suitable length, and they are characterised by an optimal HLB value.

Fig. 6. Modifications of the hydrophilic-lipophilic balance (HLB) in gemini surfactants.



As a result, gemini surfactants exhibit high antimicrobial effectiveness at extremely low concentrations. Examples of MIC values for a 12-4-12 gemini surfactant are: 1.5µg/mL for *Staphylococcus aureus*, and 50µg/mL for *Escherichia coli.* [10]

The extremely low biostatic and biocidal concentrations of gemini surfactants allows them to be used as inhibitors in the biodeterioration process of technical materials, without causing discolouration, or other damage to soft materials, such as paper, wood, or leather. Both the functional concentrations and the safety of use of gemini surfactants are of vital importance to sustainable development.

Anticorrosive activity

The strong affinity of gemini surfactants to surfaces, especially the negatively charged ones, makes them effective corrosion inhibitors.

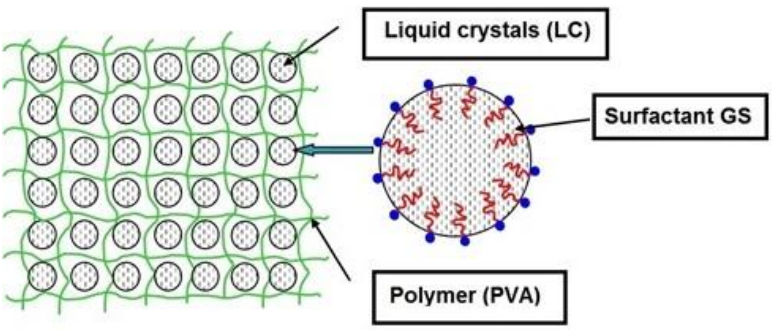
Corrosion is a physicochemical process causing the desintegration of metal surfaces, which results in economic losses of up to 5% GDP. The process affects both the ferrous and non-ferrous metal surfaces across a variety of industries, especially in the steel, petrochemical, energy, maritime and construction industries.

One of the methods of preventing corrosion is the use of organic corrosion inhibitors. The corrosion inhibition mechanism involves the adsorption of the inhibitor on the metal surface, displacement of water molecules, and formation of a protective film [12-14].

Quaternary alkylammonium salts that have an additional heteroatom with a lone pair of electrons (nitrogen, oxygen, sulphur), or a group containing π electrons, are highly effective corrosion inhibitors, which is a result of their better adsorption on metal surfaces.

In addition to the electron-related factors, the formation of a protective film is largely determined by the molecular surface area of the inhibitor, i.e. the ability to cover the largest possible area of the protected metal. A comparison of monomeric alkylammonium salts with gemini surfactants demonstrates that a gemini surfactant achieves similar corrosion inhibition effects (~90%) at a five-fold lower concentration than its monomeric analogue, which is directly linked to the larger surface area of a gemini surfactant molecule compared to its monomeric analogue [15]. For the same type of m-s-m gemini surfactant, compounds containing 16 carbon atoms in the hydrocarbon chain displayed higher effectiveness (98%) compared to compounds containing 12 carbon atoms in the alkyl chain, which showed 93% effectiveness [15].

Fig. 7. Dispersion of liquid crystals in a polymer matrix (PVA) using gemini surfactants.



Diiodide N, N' – didodecyl- N,N,N',N',N''– pentamethyl-1 4 7- triaza heptane

4-penthyl-4'-cyanobiphenyl

The high corrosion inhibition efficiency of gemini surfactants, combined with their strong antimicrobial properties, opens up rich possibilities for the application of those compounds as inhibitors of biocorrosion processes which are mainly brought about by the sulphate reducing bacteria (SRB), the primary cause of the corrosion of metal tanks in refinery industry [16].

Gemini surfactants are a modern group of multifunctional surfactants which exhibit very good surface-active, interfacial, antimicrobial and anti-corrosive properties. The use of molecular modelling and advanced synthesis methods allows the design of gemini surfactants that are effective at low concentrations and meet the requirements of strictly defined applications, which is critical for the processes of sustainable development.

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