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Multifunctional Gemini Surfactants: Structure, Synthesis, Properties and Applications

Bogumil E. Brycki, Iwona H. Kowalczyk,
Adrianna Szulc, Olga Kaczerewska and Marta Pakiet

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Abstract

Gemini cationic surfactants are compounds which are composed of two hydrophilic head groups and two hydrophobic tails linked by a spacer at the head groups or closed to them. The spacer can be either hydrophobic or hydrophilic. It can be rigid or flexible. The neutral charge of the molecule is retained by the presence of organic or inorganic counterions. Critical micelle concentrations (CMCs), surface tension (γ) and minimal inhibitory concentration (MIC) are dozen times lower than corresponding parameters of monomeric surfactants. The unique properties of gemini surfactants with a wide range of hydrophilic-lipophilic balance (HLB) make them a very useful, innovative material in detergents, cosmetics, personal care products, additives for paints and coatings, biocides, material science, organic synthesis, pharmacy, textiles, enhanced oil recovery, nanotechnology, petroleum and many other branches of life. A large number of papers concerning gemini surfactants have been published so far. This review presents a synthetic look at current work devoted to structure, synthesis and applications of gemini surfactants.

Keywords: gemini surfactant, surface activity, antimicrobial activity, corrosion inhibitors, smart materials

1. Introduction

Everything in the world involves chemistry and chemicals. Chemistry is essential for our life and our existence in the material world. Without chemistry there would literally be nothing. The diversity of life and material forms is based on versatility of chemical compounds and interactions between them. Therefore, the better we know chemistry, the better we know our world. From among of over 120 millions of currently known organic and inorganic

compounds [1], some of them have a very special meaning to facilitate our life. One of the very important and it seems to be irreplaceable groups of chemicals are surfactants.

The surfactant molecules contain at least two moieties, hydrophobic and hydrophilic one. Hydrophobic moiety is usually a straight or branched hydrocarbon or fluorocarbon chain with 8–18 carbon atoms, whereas hydrophilic moiety is a polar or ionic group. The balance between hydrophobic and hydrophilic parts, hydrophilic-lipophilic balance (HLB), is responsible for special properties of these amphiphilic compounds in solutions such as adsorption on the surfaces and interfaces and formation of self-assembly aggregates. The driving force for amphiphiles' adsorption is the lowering of the free energy of the phase boundary that provides to lowering the surface and interface tension.

This fundamental feature of amphiphiles is a base of their very wide practical applications. Surfactants are used in almost every field of our activities. They find application in detergents [2], in personal care products [3], as additives for paints and coatings [4], as dye-stuffs [5, 6], as biocides [7–10], in material science [2], in organic synthesis [11, 12], in pharmacy [5, 13], in textiles and leather [2, 14, 15], in agrochemicals [16], in fibres [17–19], in plastics [20], in food processing [21, 22], in petroleum industry for enhanced and tertiary oil recovery [23–25], in environmental protection (*oil slick dispersant*) [26, 27] and in explosives [28]. Surfactants are also used to replace traditional solvents, giving lower risk and reduced environmental impacts [29]. Surfactants can also play a key role in the development of technologies such as nano- and smart materials [30].

Currently, the global surfactant market has been segmented into anionic, cationic, non-ionic and amphoteric [31]. Anionic surfactants, like alkylbenzene sulfonates, α -olefin sulfonates, sulphates and ether sulphates, carboxylates, isethionates, taurates and phosphate surfactants held around 50% share of the global surfactant market. These surfactants are largely used in industrial and institutional cleaners and detergents. Cationic surfactants, like quaternary alkylammonium salts, exhibit mainly softening, antistatic, soil-repellent, antibacterial and corrosion inhibitory effects, whereas non-ionic surfactants, that is, alcohol ethoxylates, are suitable for cleaning purposes, as they are not sensitive to water hardness. Amphoteric (zwitterionic) surfactants, mainly derivatives of trimethyl glycine, are pH sensitive and have excellent dermatological properties. Besides, of these four main groups, there are also special surfactants, that is, fluorocarbon and silicone surfactants, sugar-based surfactants derived from mono- and polysaccharides, biosurfactants and polymeric surfactants. A very special group of surfactants are naturally occurring in living organisms' amphipathic molecules, *phospholipids*, like phosphatidylcholine (lecithin) (**Figure 1**), phosphatidylserine, phosphatidylethanolamine (cephalin), phosphatidylinositol and sphingomyelin, with the main applications in drug delivery systems [32].

The global surfactant market has been exceeded 15 million tons [31] and is expected to reach a valuation of US\$28.8 billion by 2023, increasing at a 4.20% compound annual growth rate (CAGR) upon its 2014 value of close to US\$20.3 billion [33].

An increasing use of surfactants is mainly driven by higher demand for personal care products, detergents, cleaners and industrial—anticorrosion and biocidal—products. This, in turn, is expected to lead to the introduction of innovative, more effective, surfactant-based products in

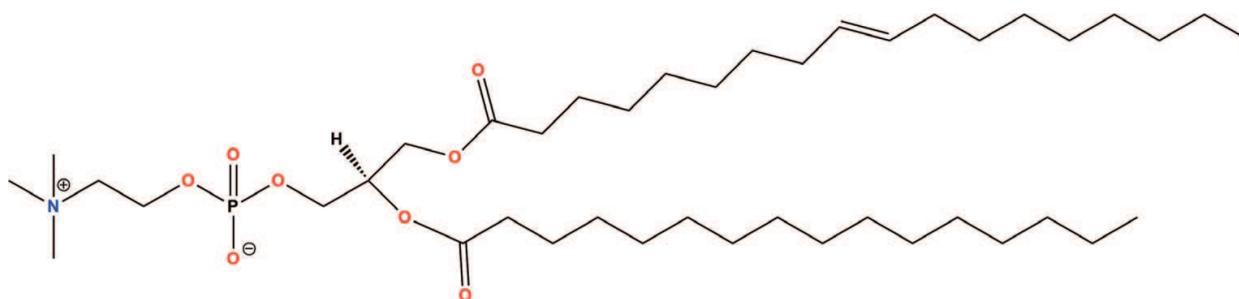


Figure 1. Structure of lecithin.

the near future. The higher efficacy of surfactants is directly related to lower CMC and surface tension as well as the efficient emulgation and solubilization effects. Such profile of innovative surfactants is accomplished to a high extent by gemini surfactants [34–36]. These compounds contain two hydrophilic head groups and two hydrophobic tails linked by a spacer at the head groups or closed to them. The structure of linker and its affinity to solvents can vary in a wide range. The gemini alkylammonium salts show unique surface and interfacial properties in aqueous solution. Critical micelle concentrations (CMCs) of gemini surfactants are usually much lower, up to hundred times, than CMCs of corresponding monomeric surfactants. The effectiveness of dimeric surfactants in lowering the surface tension is also much better than their monomeric analogues. The values of C_{20} , that is, surfactant concentration at which the surface tension (γ) is lowered by 20 mN/m, are dozen times smaller for gemini surfactants than monomeric surfactants. Moreover, gemini surfactants can form in solution many morphological structures, like spherical, ellipsoidal, rod shape and worm-like micelles as well as vesicles and helical or tubular forms. These unusual properties of gemini surfactants are ground of their applications as emulsifiers, dispersants, coating agents and corrosion inhibitors. Dimeric quaternary ammonium salts are also the excellent microbiocides. The antimicrobial activity (minimal inhibitory concentration - MIC) of quaternary ammonium salts strongly depends on their hydrophilic-lipophilic balance (HLB) and the length of the spacer. The longer the spacer, the better the antimicrobial activity. It is because gemini surfactants with longer spacers are more flexible and easily connect with the negative-charged surface of bacteria or fungi.

To better understand the fascinating physicochemical and biological properties of gemini surfactants and their wide potent applications, we present a review of synthesis, structure, properties and applications of these compounds.

2. Structure

Gemini surfactants contain two hydrophilic head groups and two hydrophobic tails linked by a spacer at the head groups or closed to them. When both hydrophobic parts are the same and hydrophilic groups are identical, then gemini surfactant forms symmetric structure (**Figures 2–4**) [37].

In contrast to symmetric dimeric surfactants are *heterogemins* with two different, or the same, polar head groups and two different, or the same, hydrophobic groups (**Figures 5 and 6**) [38].

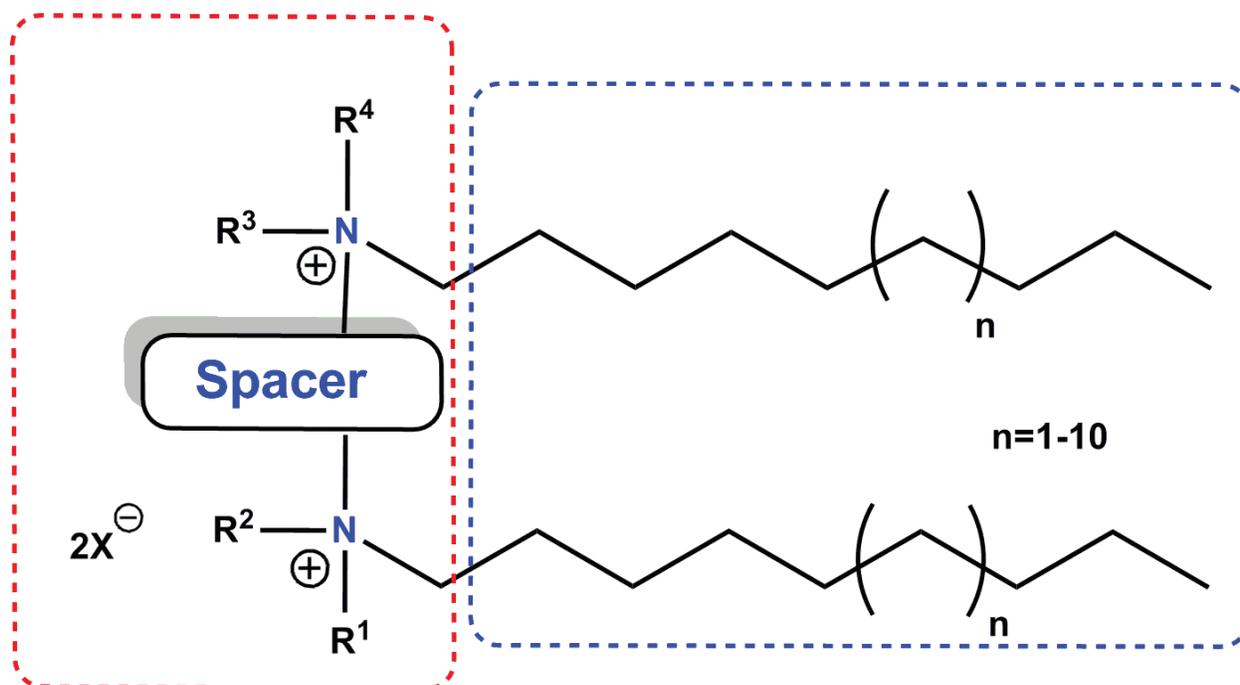


Figure 2. Structure of gemini surfactant with spacer at head groups.

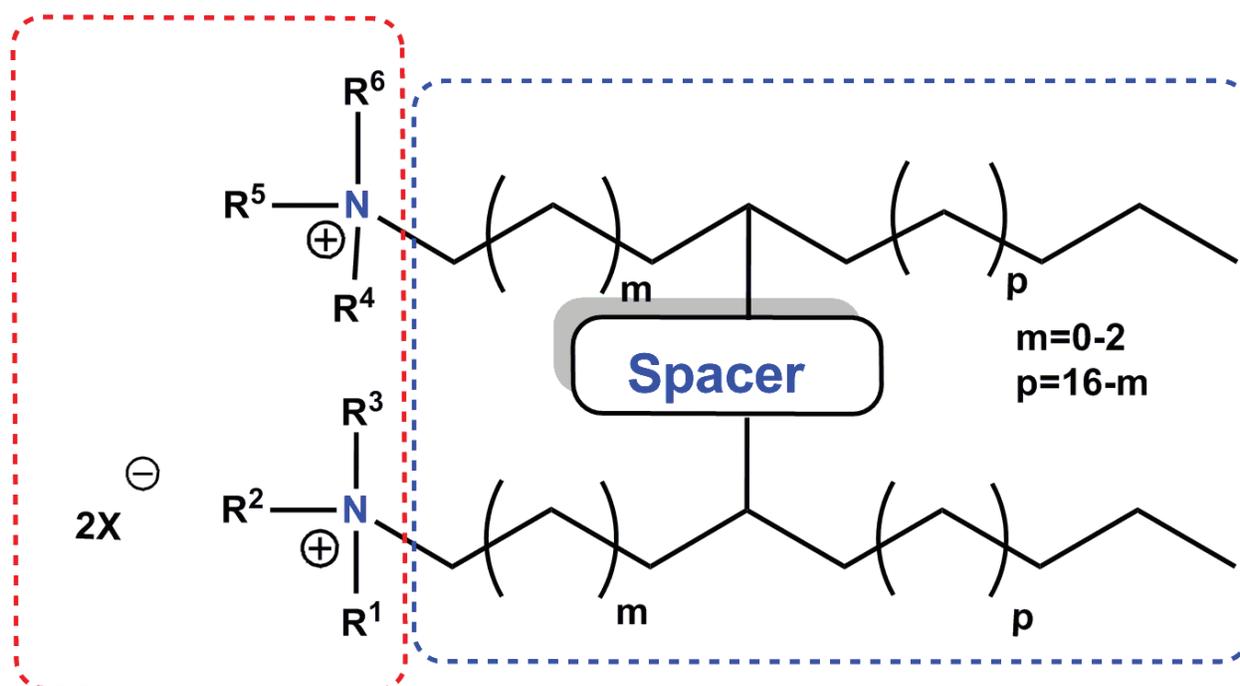


Figure 3. Structure of gemini surfactant with spacer in hydrophobic part.

The substituents in gemini surfactants are responsible to high extent for behaviour of these compounds in solution and their possible applications. Some examples of a large group of substituents, both hydrophobic and hydrophilic, are shown in Figure 7.

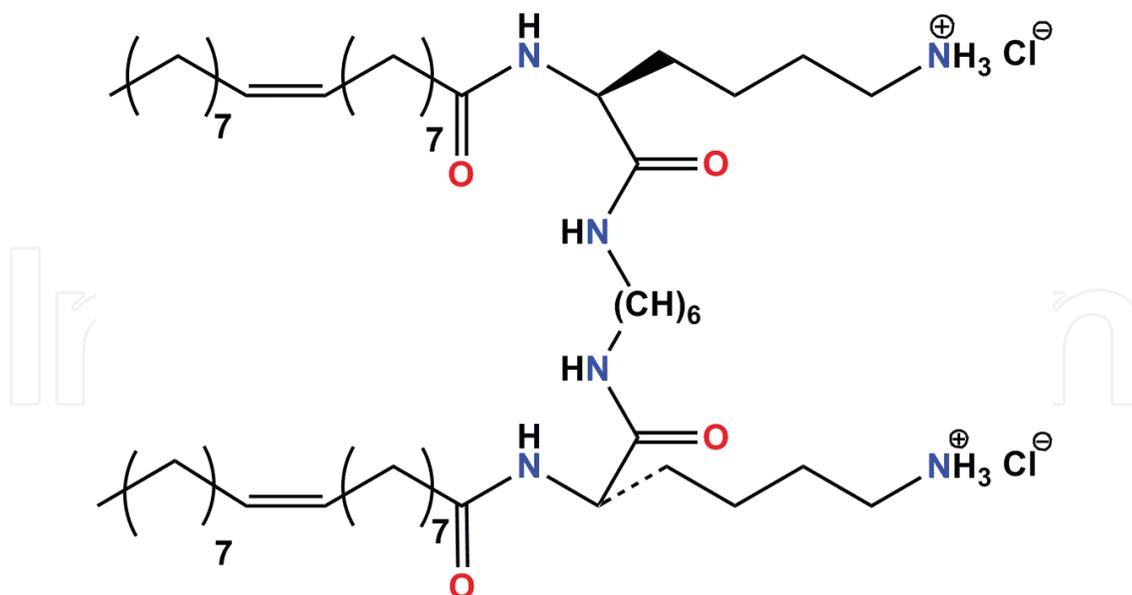


Figure 4. Bolaform of gemini surfactant and lysine-based gemini surfactant.

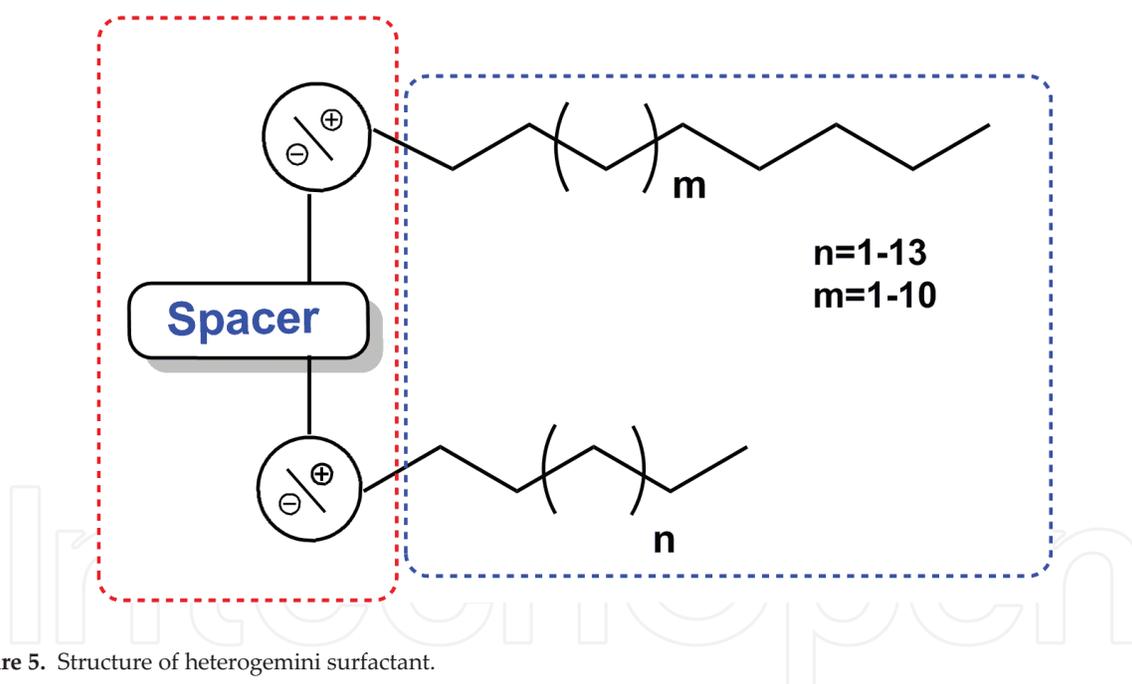


Figure 5. Structure of heterogemini surfactant.

Quaternary nitrogen atom usually exists in acyclic forms; however, there are many geminis with nitrogen involved in saturated and unsaturated rings (Figure 8).

Compounds with nitrogen involved in annulene unsaturated ring have a very special character because a ring plays to some extent a role of spacer (Figure 9) [39].

The spacer can be either rigid or flexible with tendency to hydrophobicity or hydrophilicity (Figure 10). It is a very important part of gemini surfactant which regulates the adsorption on the surfaces and interfaces and formation of self-assembly aggregates.

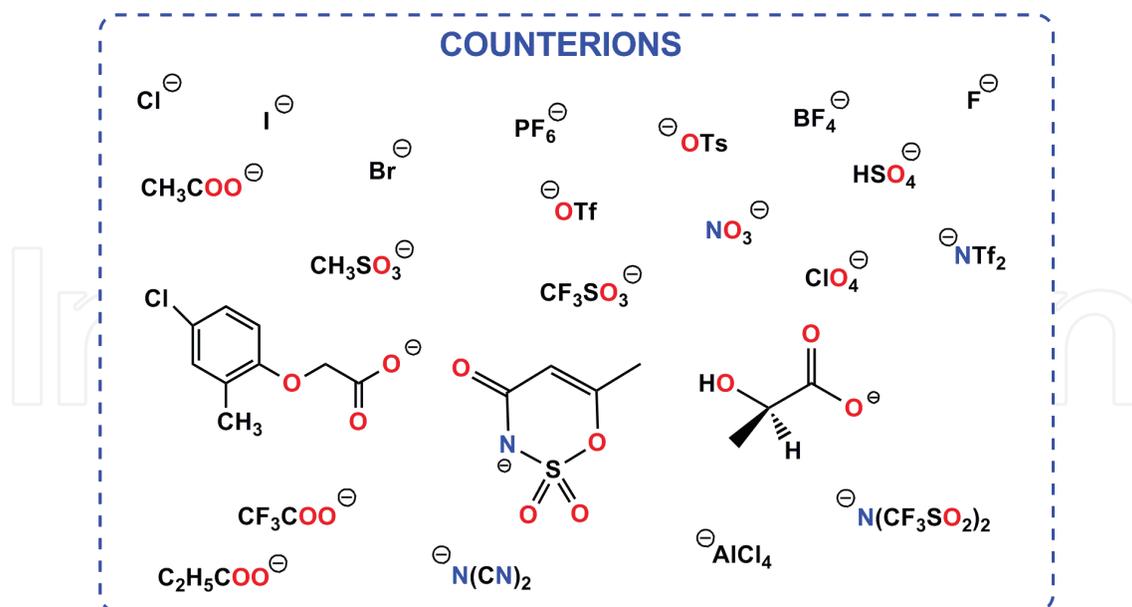


Figure 11. Organic and inorganic counterions in gemini surfactants.

3. Synthesis

The study of bisquaternary ammonium surfactants—gemini surfactants—has been commenced by Bunton and collaborators in 1974 [45]. They described the synthetic approach and kinetic of these nucleophilic reactions. Some years later Devinsky et al. synthesized a great variety of bisquaternary ammonium surfactants and investigated their surface activity and micellization [46]. A unique self-assembly behaviour of gemini surfactants in comparison to their monomeric analogues has been perceived by Zana [47] and Esumi et al. [48]. The first anionic dimeric salts with two sulphate groups and two alkyl chains have been synthesized by Okahra in 1990 [49]. Currently there are three main routes to obtain symmetric gemini surfactants, that is, (1) reaction of long-chain tertiary amines with dihalogenated substrates such as organic dibromides or dichlorides, (2) reaction of *N,N,N',N'*-tetramethylpolymethylene diamines with alkyl halides and (3) reaction of long-chain tertiary amines with a haloalkylene oxide substrate, commonly epichlorohydrin (Figure 12).

The yield of the synthesis of the symmetrical gemini surfactants mainly depends on reactivity of dihalogenoalkanes and polarity and protic character of solvent [50–52]. The best results are achieved in aprotic and polar solvents. Some of these reactions can also be carried out without solvent in mild conditions with very high yields [53].

Cationic gemini surfactants with ester bond as a spacer can be synthesized by the method given by Liao [54] and Gao (Figure 13) [55].

The gemini ester quats (ethylene-bis-alanine-*n*-alkylesterquats bromides) TMEAL-*n* (Br) and (1,3-propylene-bis-alanine-*n*-alkylesterquats bromides) TMPAL-*n* (Br) were synthesized in two steps. In the first step, intermediates—alkyl 2-bromopropionates with 6, 8, 10, 12 and 14 carbon atoms in their alkyl chain—were obtained by acylation of the appropriate alkanols with 2-bromo-

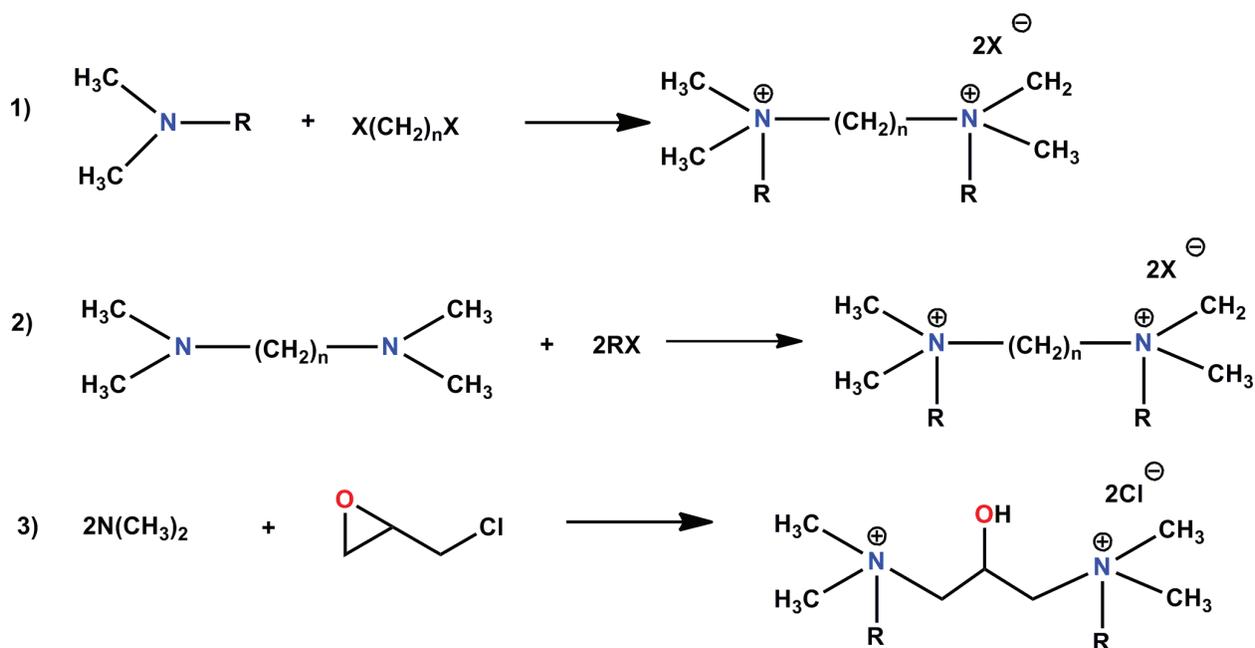


Figure 12. The general routes to prepare symmetric gemini surfactants.

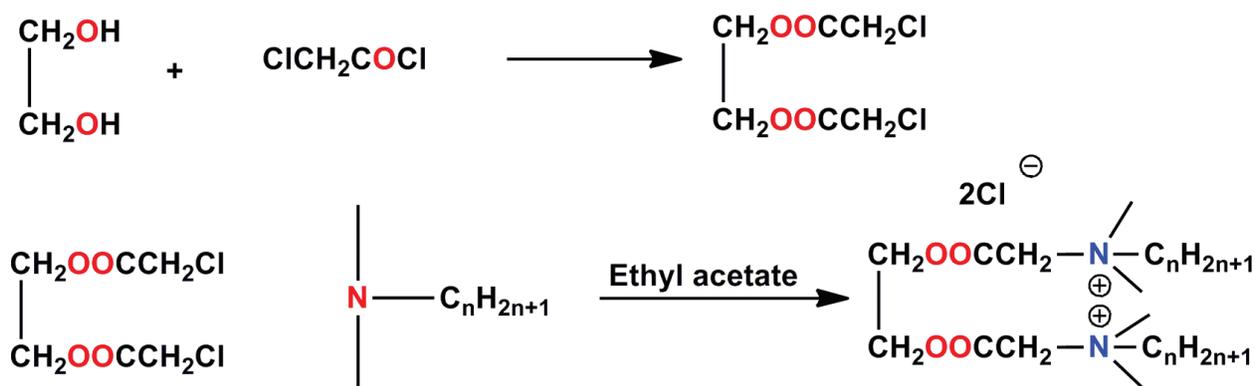


Figure 13. The synthesis method for preparing ester derivatives of gemini surfactants.

propanoyl bromide. In the second step, the alkyl 2-bromopropionates were reacted with *N,N,N',N'*-tetramethyl-ethylene diamine (for TMEAL-*n* synthesis) or *N,N,N',N'*-tetramethyl-propylene diamine (for TMPAL-*n* synthesis). Bis-quaternization was performed in the acetonitrile solution (Figure 14) [56].

Most of the amino acid-based gemini surfactants synthesized so far are *N*-alkylamides and ester derivatives of the amino acids (*N*-alkanoyl derivatives, *N*-alkylamides and *O*-alkyl esters). These compounds are prepared by condensation reactions at either the amino or the carboxyl group of the amino acid [57].

Cationic serine-based gemini surfactants were obtained by the reductive amination of glutaraldehyde with the *O*-protected amino acid. To avoid the cyclization reaction, the dialdehyde substrates must contain very short or very long alkyl substituent. Another possibility is to prepare *N*-alkyl derivatives before introduction of the linker [58].

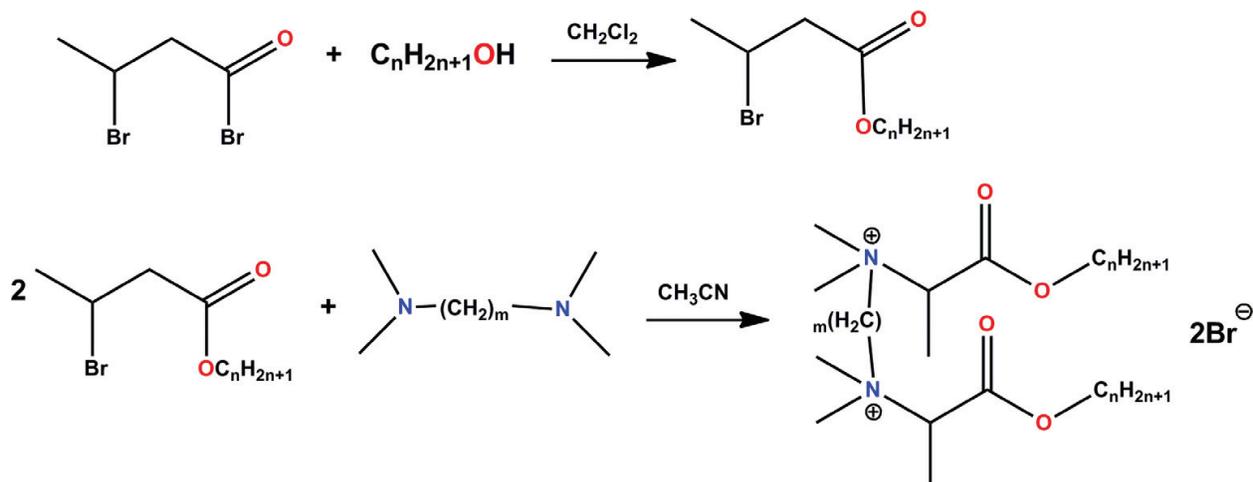


Figure 14. Bis-quaternization ester derivatives of gemini surfactant.

Most studies on the synthesis and biological evaluation of the amino acid gemini surfactants address arginine derivatives [59]. A few reports on lysine-, glycine- and cystine-based gemini surfactants have also been published [60–63].

Sugar-based gemini surfactant (polymethylene- α,ω -bis(*N,N*-dialkyl-*N*-deoxy-*D*-glucitolammonium iodides)) was synthesized in multistep reactions, by a condensation of *D*-glucose with diamine, followed by reduction of *D*-glucopyranosyle ring with sodium borohydride and a reductive alkylation with aliphatic aldehydes, containing from 6 to 12 carbon atoms, in the presence of sodium cyanoborohydride as a selective reducing agent. Quaternization of nitrogen atoms by aliphatic *n*-iodides was the last step of the reaction procedure [64].

Zwitterionic gemini surfactants contain positive and negative atoms inside one molecule [64]. The synthesis of zwitterionic geminis is quite complicated; therefore only a few reports appeared so far. The work of Peresykin and Menger [65] concerns a preparation of zwitterionic gemini surfactant with phosphodiester as a negatively charged group and a positively charged quaternary ammonium salt separated by two pairs of methylene groups [$C_x-PO_4^--(CH_2)_2-N^+(CH_3)_2-C_y$, where $x + y = 22$]. Yoshimura et al. [66, 67] synthesized sulfobetaine-type zwitterionic gemini surfactants and heterogemini zwitterionic surfactants containing ammonium and carboxylate head groups. Xie et al. [68] offered a simple method for synthesizing alkylbetaine zwitterionic gemini surfactants based on 1,2-bis[*N*-methyl-*N*-carboxymethyl-alkylammonium] ethane (C_nAb , where *n* represents a hydrocarbon chain with a length of 8, 10, 12 or 14) that were synthesized by alkylation of *N,N*-dimethylethylenediamine with an alkyl bromide, followed by reaction with sodium 2-bromoacetate.

Quagliotto et al. [69] synthesized a series of pyridinium cationic gemini surfactants by quaternization of the 2,2'-(*R,\omega*-alkanediyl)bispyridines with *N*-alkylating agents. Limei Zhou et al. [70] synthesized novel gemini pyridinium surfactants by using 1,4-dibromobutane and *R*-alkyl pyridine.

Gemini surfactants with a non-Hückel diaza[12]annulene core were synthesized by treating *N*-(2,4-dinitrophenyl) pyridinium chloride with long-chain amines (Figure 15) [71, 72].

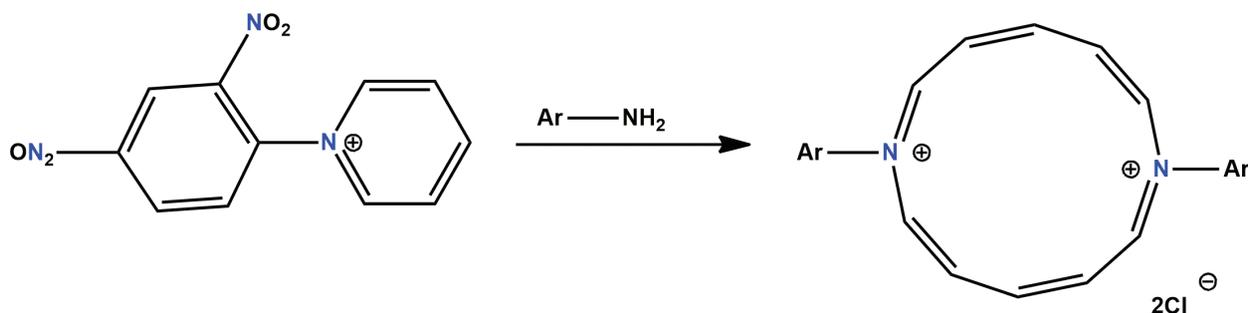


Figure 15. Synthesis of annulene derivatives.

Dissymmetric gemini surfactants contain two nonidentical polar head groups and two different (or identical) lengths of alkyl tails according to Alami and Holmberg [73]. The first heterogemini surfactants containing quaternary ammonium and carboxylate head groups and two dodecyl or tetradecyl tails have been obtained by Jaeger et al. [74]. Some other dissymmetric gemini cationic surfactants with hydroxyl group in the spacer and different long carboxylic acid dimethylethylamine esters as cationic parts [75].

Surface activity of heterogemini strongly depends on degree of the asymmetry. For pyrene-based dissymmetric gemini surfactants synthesized in five-step reactions (Figure 16) [76], the Krafft temperatures increase with the increase of the alkyl chain length. Similarly, CMC values are much lower than those of their symmetrical counterparts.

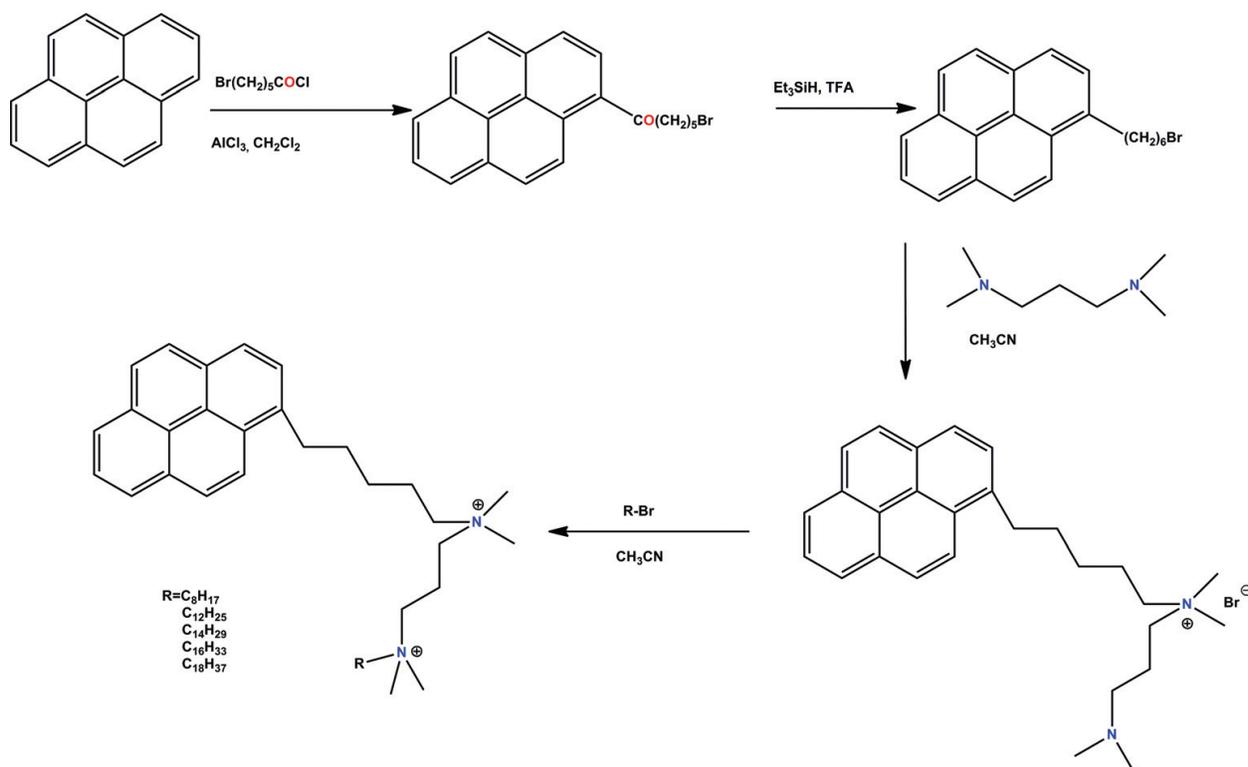


Figure 16. Preparation of dissymmetric gemini surfactant.

Gemini surfactants can be also prepared in microwave-assisted organic syntheses. The usefulness of 5.8-GHz microwaves is demonstrated by the solvent-free synthesis of 2-allylphenol through a Claisen rearrangement process and by the synthesis of the C₁₂-C₂-C₁₂ [77].

4. Analytical methods

A large number of analytical methods can be applied to study gemini surfactants and their structure, surface behaviour and interaction with polymers and other materials.

To determine structures of gemini surfactants, the standard spectroscopic methods, nuclear magnetic resonance (NMR) spectroscopy (¹H, ¹³C and ³¹P), mass spectrometry (fast atom bombardment) and Fourier-transformed infrared spectroscopy (FT-IR) are mostly used.

For cationic gemini surfactants, ¹H NMR chemical shift values (δ/ppm) are generally higher for head group protons because of the proximity of the positive charge on the nitrogen atom. In turn, protons of hydrocarbon chain at highly hydrophobic section of the surfactant residue in the core portion of micelle are highly shielded; hence ¹H NMR peaks are observed in lower ppm regions [78].

The variation of the chemical shifts due to the hydrophobicity can be used as a method to study of the aggregation process. For example, the correlation between ¹H NMR shifts and ([gemini]/CMC)⁻¹ for the terminal methyl group of the chains suggests the presence of transient proximity between the methyl group and the annulene ring system. Diffusion coefficients from pulsed gradient spin-echo (PGSE) NMR experiments reveal that the annulene gemini micelles are similar in size and shape to those of simple monomeric surfactants [71].

The very interesting results have also been observed for ¹H NMR study of two series of quaternary ammonium gemini surfactants 12-s-12 and 14-s-14 at concentrations below their CMC in aqueous solutions. The analysis of self-diffusion coefficients, changes in chemical shift, line width and line shapes indicates the premicellization of these two series of geminis below their CMC values [79]. NMR technique has been also applied to study of the binding isotherms of the surfactants to the polymers [79–82]. McLachlan and Marangoni have investigated the interactions between poly(styrenesulfonate) (PSS), dodecyltrimethylammonium bromide (DTAB) and cationic gemini surfactants (12-s-12) [80]. For the gemini cationic surfactants, the NMR chemical shifts indicate that the manner in which the gemini surfactants self-assemble with the polymer is dependent on the spacer length of the surfactant. The ¹H chemical differences indicate that the manner in which the DTAB and the long-spacer gemini surfactants interact with the PSS is fundamentally similar, whereas the short-spacer gemini surfactants have a different ¹H chemical shift difference pattern for the spacer and chain protons; this may indicate subtle differences in the nature of the binding of these cationic surfactants to the polyanions.

The unusual self-assembly behaviour of gemini surfactants possesses challenging puzzles to theoretical investigations [83]. In view of the above, the cationic gemini surfactant designated as 16-E2-16 (ethane-1,2-diyl bis(*N,N*-dimethyl-*N*-hexadecylammoniumacetoxo)-dichloride)

was obtained and investigated as a corrosion inhibitor for mild steel (MS) in 1 M HCl solution by refined analytical methods and weight loss measurements. Moreover, the inhibition effect of the investigated compound was analysed by DFT method [84].

Cationic gemini surfactants of the m-2-m type have been investigated with luminescence probing and neutron scattering [85]. Dynamic light scattering (DLS) shows that the surfactant interacts with the polymer at low concentrations and 12-2-12 mixed systems grow to large aggregates with surfactant concentration. It is also confirmed that the longer the hydrocarbon chain length of surfactant, the stronger the interactions.

The molecular composition of each G12-s and G18:1-s gemini surfactant was determined by quadrupole time-of-flight mass spectrometry analysis (QqToF-MS). The fragmentation pattern of the investigated compounds was done by QqToF-MS=MS and showed that the geminis share fragmentation patterns that are specific to their respective gemini surfactant families. At present, a study of some gemini surfactant families are directed to identify for each gemini surfactant two or three product ions with unique m/z values which can be utilized in multiple-reaction monitoring and analysis of biological samples [86].

The combined MS and DFT methods can be very useful for studying competitive S_N2 and E2 reactions in the gas phase. The $M2+X^-$ pairs formed from hexadecyldiyl-R, ω -bis(dimethylalkylammonium) surfactants are stable in the ion trap of spectrometer, which is consistent with DFT computations of the bolaform analogues. It shows that $M2+X^-$ pairs are extremely stable in the gas phase [87].

The self-aggregation behaviour of gemini surfactant 12-2-12 (ethanediyl-1,2-bis(dimethyldodecylammonium bromide)) in water was investigated by dielectric relaxation spectroscopy (DRS) over a frequency range from 40 Hz to 110 MHz [88]. A defined, widely distributed dielectric relaxation was observed in the 107–108 Hz frequency range for all micelle suspensions; the relaxation mechanism was recognized as the interfacial polarization between the micelles and solution medium.

Currently, the most common method for quantitative determination of surfactants is high-performance liquid chromatography (HPLC) [89, 90] and GC-MS method [91].

Many HPLC methods for the determination of quaternary alkylammonium compounds have been reported. Wee and Kennedy reported a normal phase method for the determination of cationic surfactants without separation of the homologous series in environment samples [92]. One of the methods which can differentiate and quantitate the homolog mixture is high-performance capillary electrophoresis (HPCE) that separates compounds in an electric field according to their charge and size [93, 94].

One of the simplest methods of determining the amount of surfactants in the sample is titration. The first method is turbidimetric titration. In this method cationic surfactants are titrated with anionic surfactants. The next method is a two-phase colorimetric titration. Two-phase titration was first described by Epton in 1947 [95]. Soon it became a commonly used method. This method was developed as a standard method and published as ASTM, BSI and DIN standards [96–99].

Another method is potentiometric titration in the aqueous phase. The potential of a solution containing surfactants is measured as a function of added titrant. The potential of the sample is measured by means of electrode-sensitive surfactants [100].

5. Surface properties

One of the fundamental properties of surfactants is their tendency to adsorb at interfaces. It affects surface tension reduction because of their dual chemical nature [35, 101, 102]. The surface tension (γ) of pure water is 72 mN/m [103]. The ability to reduce it by surfactants depends on the replacement of molecules of solvent at the interface by molecules of surfactants. Mechanism of action of cationic gemini surfactants based on the adsorption of hydrophilic groups (positively charged nitrogen atoms) onto a polar phase and hydrophobic groups in a nonpolar phase. These phenomena are characterized by an efficiency factor pC_{20} which is a concentration of surfactants when the tension is reduced by 20 mN/m [101]. Gemini surfactants are better at lowering the surface tension than their monomeric analogues. The value of pC_{20} for DTAB is 2.3 ($C_{20} = 5.25$ mM) whilst for 12-2-12 is 3.78 (0.16 mM) [53, 104]. Higher pC_{20} means lowering surface tension by 20 mN/m at lower concentrations. Usually the value of surface tension is given at CMC (γ_{CMC}) which is a critical micelle concentration [105]. It is the concentration when monomeric molecules of surfactants abruptly assemble into aggregates called micelles [106] and they are in the balance. Critical micelle concentration can be estimated using different methods: conductivity measurements, surface tension measurements, UV-absorption spectroscopy, fluorescence spectroscopy, dynamic light scattering or dye solubilization [106]. Conductometry and tensiometry are the most popular and the easiest methods [35]. There are several factors affecting the value of CMC such as structure of surfactant (hydrophilic group, hydrophobic group and spacer) and temperature.

Gemini surfactants exhibit lower CMC values than conventional QAC which is connected with the number of hydrophilic groups. Monomeric quaternary ammonium salts have higher critical micelle concentrations than dimeric one [107, 108]. The relation between number of positively charged nitrogen atoms and the CMC is presented in **Figure 17** [109].

Lower CMC values for dimeric and oligomeric surfactants are connected with their packing into a micelle. Monomeric salts need more molecules to form micelles than dimeric. It is showed in **Figure 18**.

The structure of the hydrophobic groups has also a big impact on the CMC. Its value decreases as the carbon atom numbers increase [110]. The value is halved after addition of one methylene group to a straight hydrophobic chain [101]. The relationship between CMC and the length of the hydrocarbon tail, for compounds of m-s-m type, is shown in **Figure 19** [111].

Elongating the hydrocarbon chain makes the molecule more hydrophobic. The greater the hydrophobicity of the surfactant, the greater tendency to form micelles [112].

CMC can be also controlled by the type and the length of the spacer. At first, CMC gradually increases as the spacer becomes longer, up to four carbon atoms, and then for longer spacers, CMC again decreases [113]. The relationship between CMC and the length of the spacer for

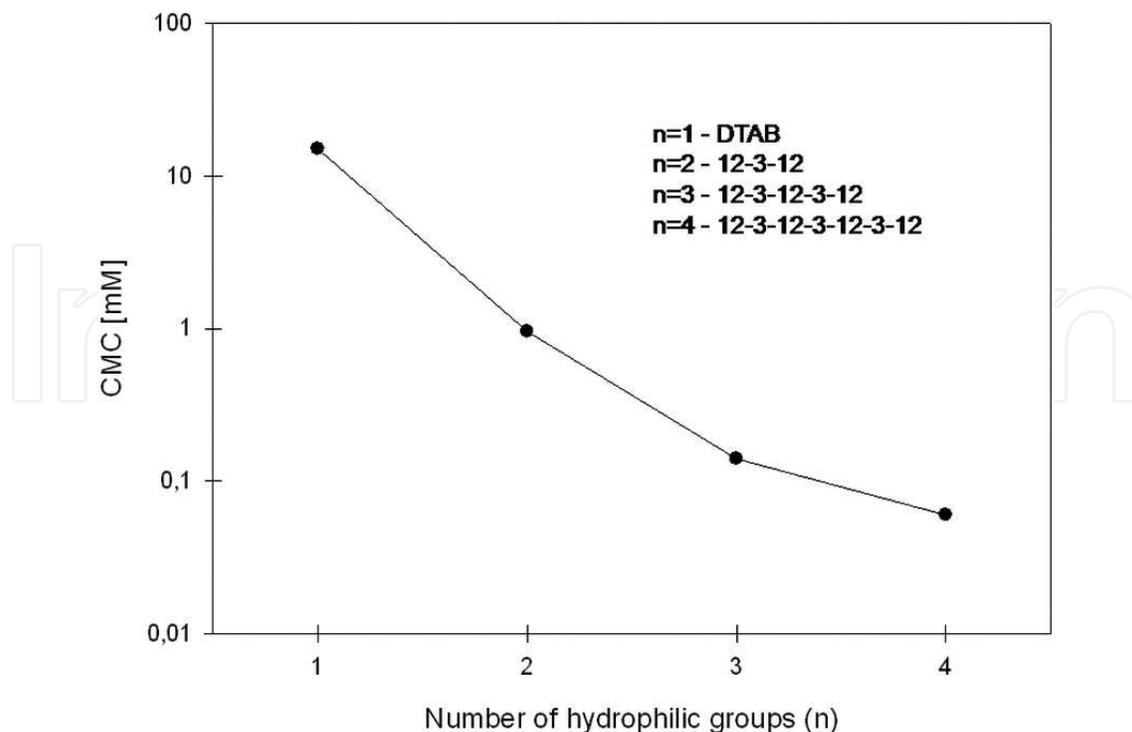


Figure 17. The correlation between number of hydrophilic groups and critical micelle concentration.

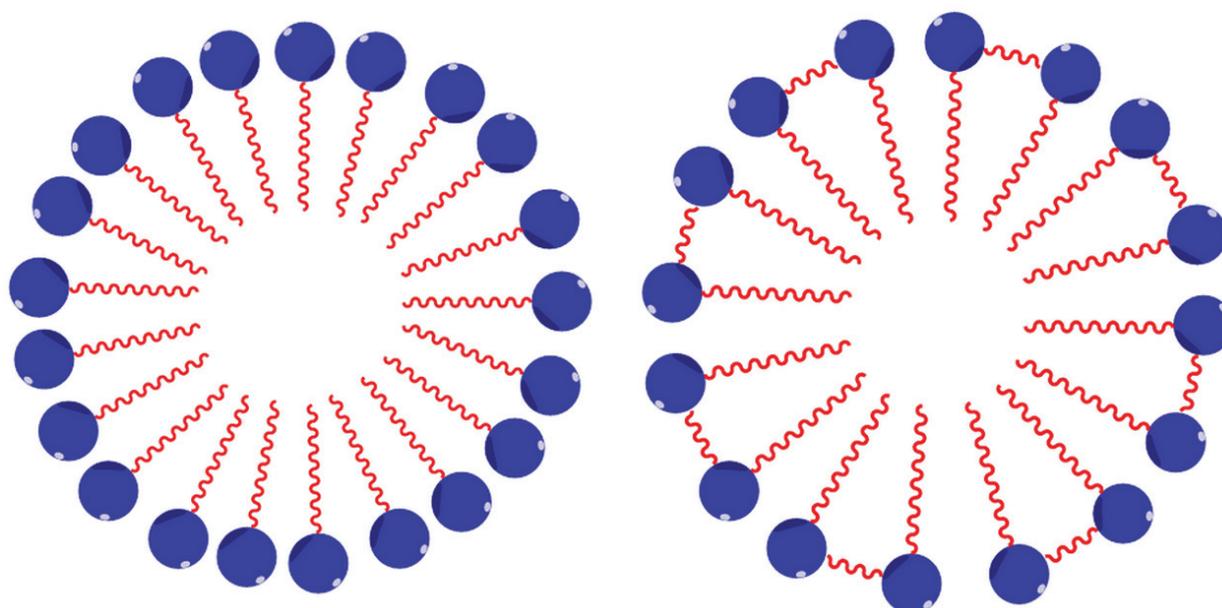


Figure 18. Micelles made of monomeric and dimeric surfactants.

geminis of type 12-s-12 (s—number of carbon atoms in the spacer) surfactants is presented in **Figure 20** [111]. This effect is due to the hydrophobicity of the spacer. The short spacers are fully extended on the air-water interface, whereas long spacers are much more hydrophobic and flexible; therefore they begin to fold into the air.

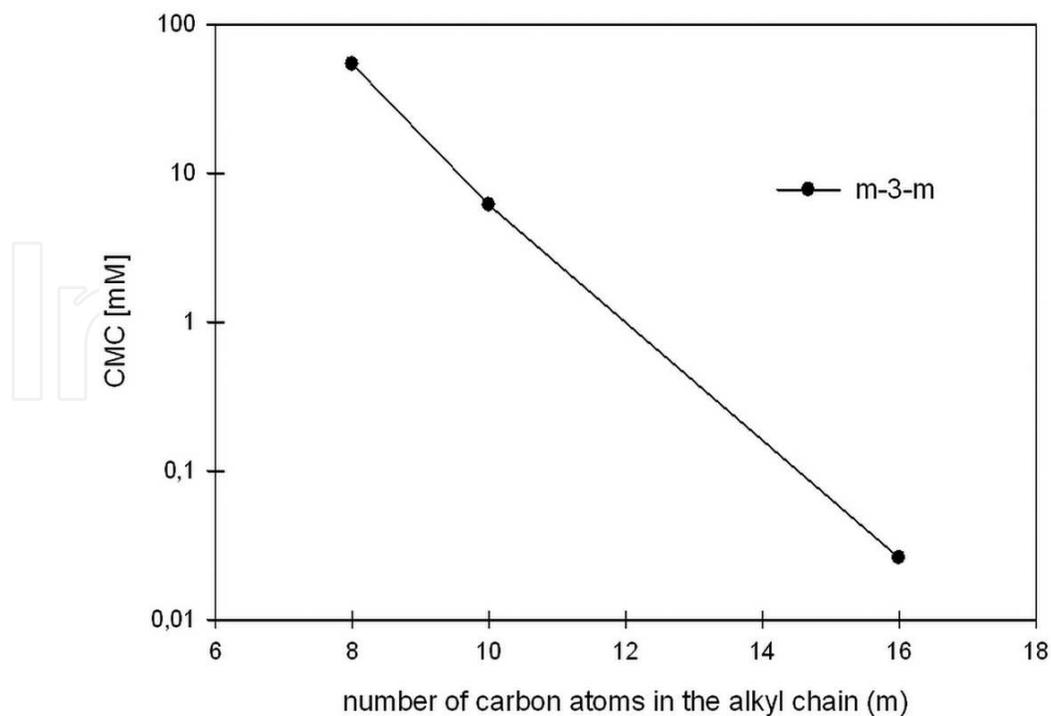


Figure 19. The relationship between the number of carbon atoms in the hydrophobic chain and the CMC values.

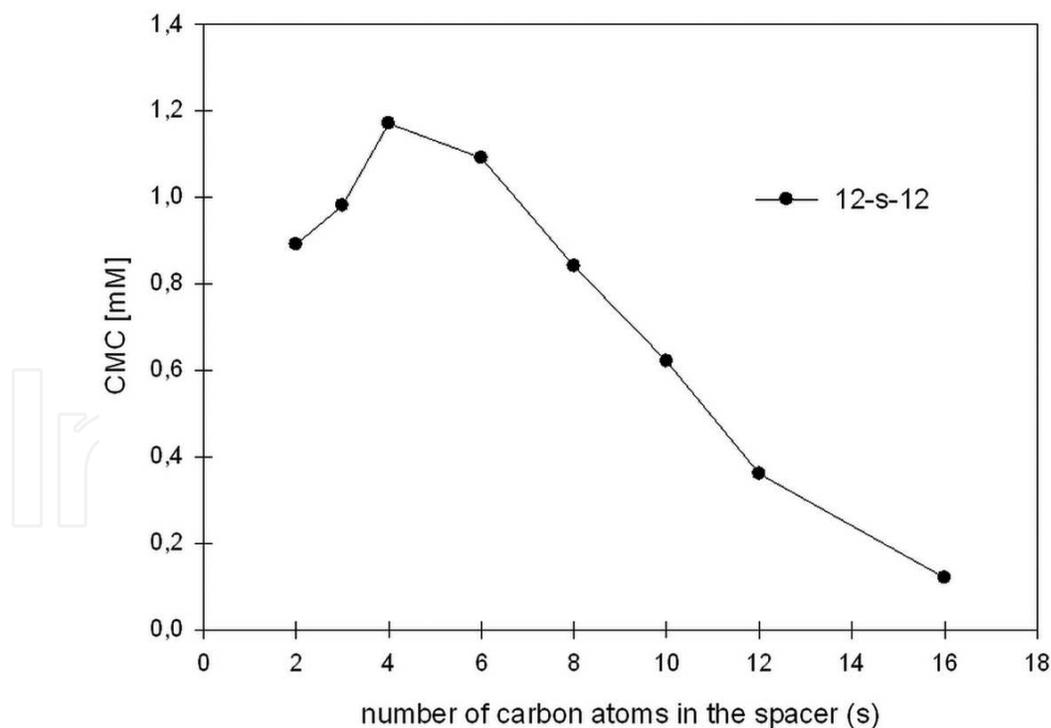


Figure 20. Relationship between the number of carbon atom in the spacer(s) and the CMC value.

The introduction of a polar group like oxygen to the spacer causes an increase of CMC. For gemini surfactant 12-5-12, the CMC value is 1.03 mM [34] and increases to 1.35 mM with spacer containing oxygen atom [114]. The multiplication of oxygen units in the spacers

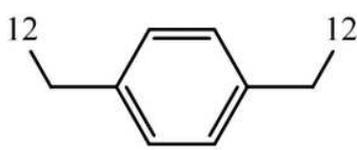
$12\text{---CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{---}12$	0.98 mM
	1.52 mM
$16\text{---CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{---}16$	0.042 mM
$16\text{---CH}_2\text{C}\equiv\text{CCH}_2\text{---}16$	0.048 mM
$12\text{---CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{---}12$	0.99 mM
$12\text{---CH}_2\text{CH}=\text{CHCH}_2\text{---}12$	2.0 mM

Table 1. CMC values for gemini surfactants with a rigid spacer and their analogues with a flexible one.

exerts a similar effect, that is, an increase of the CMC value. For gemini surfactant 16- $\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2$ -16, CMC is 0.004 mM, whilst for compound with triple oxygen units, that is, 16- $\text{CH}_2(\text{CH}_2\text{OCH}_2)_3\text{CH}_2$ -16, CMC value increases to 0.02 mM [115]. The presence of rigid spacers (unsaturated bond and benzene ring) also shifts the CMC to higher values. Some examples of CMC are presented in **Table 1** [103, 114, 116–118].

The structure of the head groups, not only the number of them, affects aggregation behaviour [118, 119]. The exchange of methyl groups at charged nitrogen atom to ethyl ones in 12-4-12 decreases the CMC value from 0.99 to 0.59 mM [120]. The relationship between critical micelle concentration and the type of groups linked to quaternary nitrogen atom is presented in **Figure 21**.

In contrast to the influence of hydrophilicity of the spacer on CMC, the increase of the hydrophilicity of the substituent significantly decreases CMC values. An example is shown in **Figure 22**.

The exchange of one methyl group to hydroxyethyl group at nitrogen atom in 12-4-12 reduces CMC value 10 times, whereas the exchange of both methyl groups to hydroxyethyl substituents lowers CMC almost 1000 times in comparison to the starting compound [121, 122].

Temperature is also a factor which affects the aggregation behaviour. An increase of temperature in the beginning causes the decrease of CMC to minimum around 25°C, and then with further increase of temperature, CMC becomes higher [101]. These effects are directly related to hydration and dehydration of alkyl chain that are sensitive to temperature. The correlation between temperature and CMC values for 12-4-12 is presented in **Figure 23** [105].

The shape of micelles may differ in a wide range, which mainly depends on the structure of surfactants. The most popular methods to estimate the shape of aggregates are dynamic light scattering, small-angle neutron scattering and NMR self-diffusion coefficients [101, 118, 123, 124].

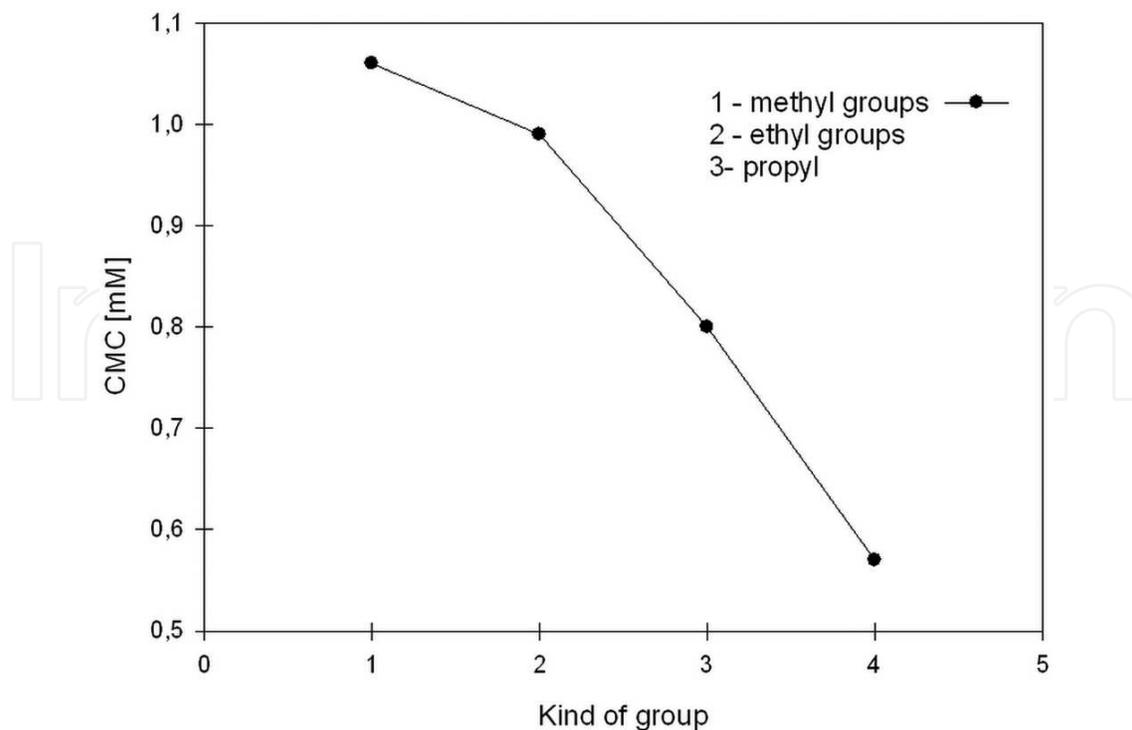


Figure 21. The relationship between CMC values and the kind of group in the hydrophilic part of the surfactant.

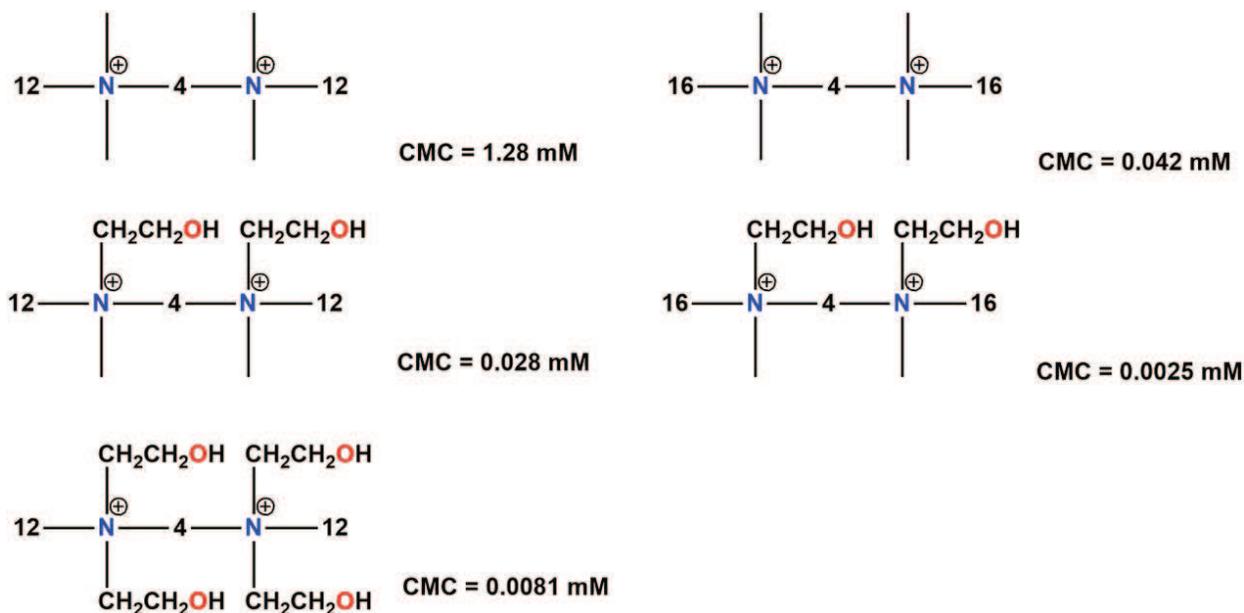


Figure 22. The CMC value for gemini surfactants modified by adding ethoxyl groups.

It was noticed that gemini surfactants with short spacers usually form cylindrical micelles, the one with medium spacers form spherical micelles and those compounds with long spacers form mainly vesicles [111]. However, gemini surfactant 12-2-12 has been shown to form spherical shape micelles [113]. The assessment of the micelle shape is somewhat difficult because it depends not only on the structure of surfactant. The significant influences on geometry and

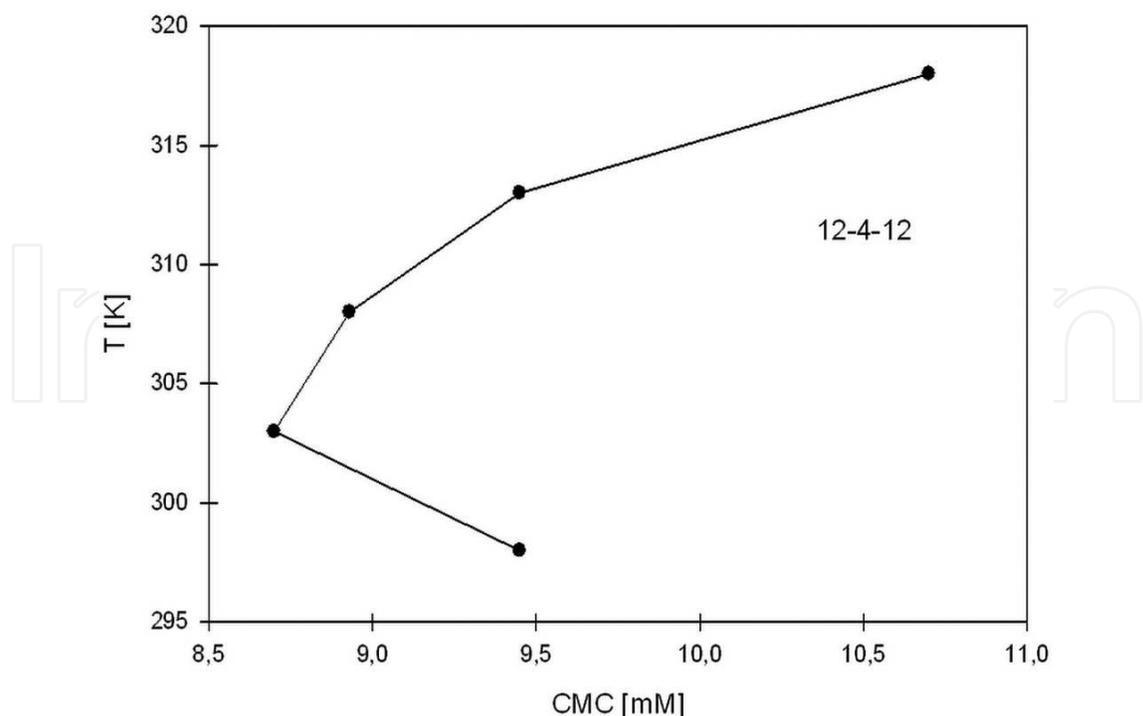


Figure 23. Relationship between temperature and CMC of 12-4-12.

structure of micelles are temperature, concentration, solution condition and ionic strength [115]. Geometrical construction of the surfactant aggregates can be determined by calculating critical packing parameter (P) [120]:

$$P = V_{\text{hydrophobic}} / (a_0 * l_0) \quad (1)$$

where $V_{\text{hydrophobic}}$ is the volume of hydrophobic chain (for gemini surfactants $V_{\text{hydrophobic}} = 2V$) and l_0 is the length of hydrophobic chain (for gemini $l_0 = 2l$). They are estimated by using Tanford's expression:

$$V = (27.4 + 26.9m) * 10^{-3} [\text{nm}^3] \quad (2)$$

$$l_0 = (0.15 + 0.1265m) [\text{nm}] \quad (3)$$

where m is the carbon atom number of a single hydrophobic chain and a_0 is the average packing area of the hydrophilic head group by a single surfactant molecule, usually for gemini surfactants $a_0 = 2$ [120]. $0 < P < 1/3$ indicates spherical micelles, $1/3 < P < 1/2$ —cylindrical, $1/2 < P < 1$ —vesicles or lamellar and $P > 1$ —inverse micelles in nonpolar media [101, 120]. Unfortunately, very often calculated shape varies from those estimated based on experimental methods. Transmission electron microscopy (TEM) is very often used to attain a direct visualization of micelles. Using a precise bar, measuring the size of micelles is possible [120].

Other aggregation parameters can be calculated from surface tension measurements. One of the most important is the aggregation number (N_A) which is the number of surfactant

monomers obligatory for micelle formation [106]. The bigger the gemini surfactant (longer alkyl chains, longer spacer, etc.), the lower the N_A [108, 123]. It is in a good agreement with the relationship between the structure of surfactant and its CMC value. π_{CMC} is an effectiveness defined as a difference between surface tension of a pure water and the surface tension of a solution of the surfactant at the CMC. This value can be used to compare surfactants within one series. The lowest value of π_{CMC} belongs to the lowest surface-active analogue [112, 125]. The amounts of surfactant molecules adsorbed at the surface Γ_{max} are estimated from the slopes of straight lines in the plot of surface tension vs. logarithmic concentration drawn in the concentration region below the CMC according to Gibbs adsorption isotherm:

$$\Gamma_{\text{max}} = 1/3 \times 2.303nRT(d\gamma/d \log C) \quad (4)$$

The number of ionic species (n) at the interface varies with the surfactant concentration in the solution [125]. The minimum surface area per molecule (A_{min}) can be calculated from the equation:

$$A_{\text{min}} = 1/N \Gamma_{\text{max}} \quad (5)$$

where N is an Avogadro number [124]. A_{min} increases with increasing the length of the spacer and the length of the hydrophobic chains [105, 111].

Free Gibbs energy of micellization (ΔG_{mic}) gives information about the nature of the aggregation process. The energy for gemini surfactants is calculated from an equation proposed by Zana [126]:

$$\Delta G^{\circ}_{\text{mic}} = 2RT(1/2 + \beta) \ln \text{CMC} - RT \ln 2 \quad (6)$$

B is the counterion binding parameter which gives the average number of counterions per surfactant ion in the micelle and can be estimated from the ratio of the slopes of conductometry measurements (conductivity vs. concentration) [127]. Negative values of ΔG_{mic} indicate that the process of micellization is spontaneous. ΔG_{mic} increases in the negative direction by increasing hydrophobic character [128]. **Figure 24** presents the relationship between the length of the spacer and ΔG_{mic} [113]. $S = 0$ represents a monomeric cationic surfactant, DTAB. It is noticed that ΔG_{mic} for gemini surfactant is much lower than for DTAB which means that forming micelles by dimeric salts is more favourable.

Using values of ΔG_{mic} at different temperatures, other thermodynamic parameters can be calculated: entropy (ΔS_{mic}), enthalpy (ΔH_{mic}) of micellization and free energy of adsorption (ΔG_{ads}) by following equations:

$$\Delta S_{\text{mic}} = -d(\Delta G_{\text{mic}}/\Delta T) \quad (7)$$

$$\Delta H_{\text{mic}} = \Delta G_{\text{mic}} + T\Delta S_{\text{mic}} \quad (8)$$

$$\Delta G_{\text{ads}} = \Delta G_{\text{mic}} - 6.023 \times 10^{-2} * \Pi_{\text{CMC}} * A_{\text{min}} \quad (9)$$

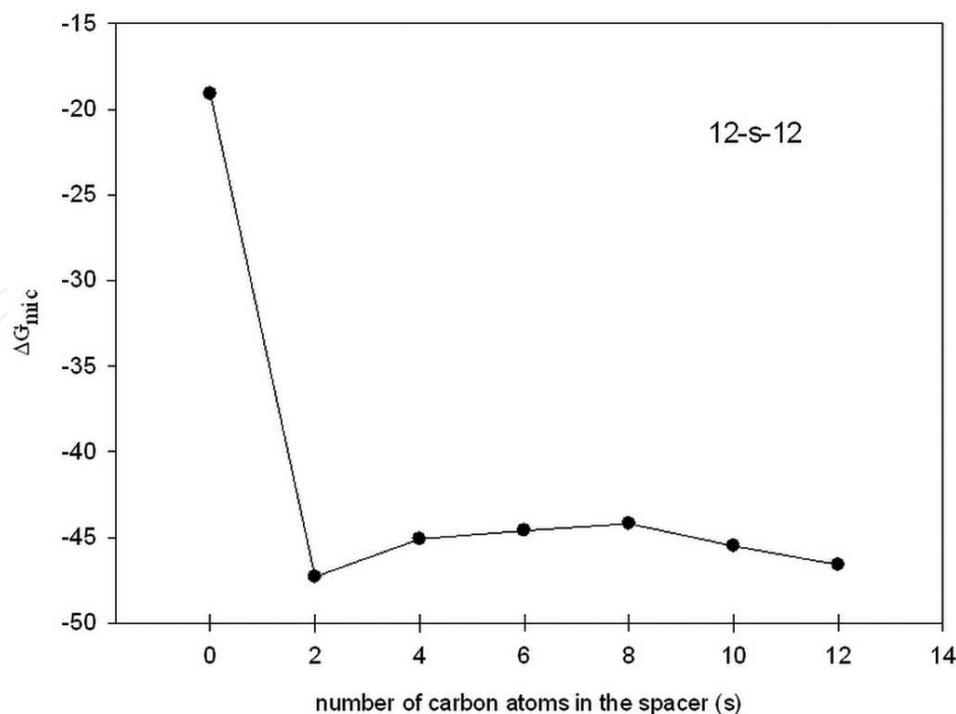


Figure 24. The relationship between the Gibbs free energy of micellization and the number of carbon atom is in the spacer(s).

Positive value of entropy indicates that the process of micellization is favoured. $\Delta H_{mic} < 0$ indicates an exothermic process whereas $\Delta H_{mic} > 0$ an endothermic. A negative value of ΔG_{ads} means that process of adsorption is spontaneous and usually increases by increasing temperature and the length of hydrophobic chain [106, 112, 113, 120, 128]. Moreover, if the value is more negative than ΔG_{mic} , the molecules of surfactants tend to adsorb at the air-water interface until complete surface coverage and afterwards micelles are formed [128].

6. Biological activity

6.1. Antimicrobial activity

Microorganisms are essential for a large number of metabolic and biotechnology processes. However, they are also responsible for diseases and demises as well as biodeterioration of technical materials like wood, paper, textiles, paints, stonework and steel. To reduce this considerable risk, the chemical compounds with biocidal activity—microbiocides—have been usually used. Microbiocides include some phenols and their derivatives, organic and inorganic halogen compounds, oxidizing substances, quaternary ammonium compounds, alcohols, aldehydes and organic and inorganic acids [9, 64, 129–132]. The most important group of microbiocides is quaternary ammonium compounds (QAC) because of their wide spectrum of biocidal activity, the safety of applications and low costs. Quaternary ammonium salts belong to lytic membrane-active microbiocides [133–135].

Mechanism of their biocidal activity begins with adsorption of quaternary ammonium cation on negatively charged cell surface. Subsequently long hydrocarbon chains can diffuse through the bilayer of the cell, which increases the hydrophobicity of the bacterial cell membrane and provokes disruption of the cytoplasmatic membrane. Damage of the membrane results in the release of potassium ions and other low molecular weight cytoplasmatic constituents, finally leading to the death of the microorganism cell [136–138]. Biocidal activity of the microbiocide is usually performed with minimum inhibitory concentration (MIC), that is, minimal concentration of compound which inhibits the growth of microorganism. MIC are affected by several factors like concentration of microbiocide, time of the contact, pH, temperature, the presence of organic matter or other compounds. Moreover MIC strongly depends on the nature, numbers, location and condition of the microorganism [139].

MIC could be determined by the broth or agar dilution method [140, 141] and expressed in the concentration units. Antimicrobial activity can be also expressed as a zone of inhibition by diffusion method. This method has many limitations, which mainly depend on diffusion ability of microbiocide. According to Klančnik, there are no straight correlations between these two methods [142].

The biocidal activity of gemini surfactants depends on the type of microorganisms. Gram-positive bacteria are more sensitive than the Gram-negative bacteria to ammonium microbiocide. This is due to morphology of the cell membranes. Gram-positive bacteria cell membranes are composed of peptidoglycan layers, which could be easily penetrated by surfactant, whereas Gram-negative cell membranes are mainly composed of lipopolysaccharides and proteins that restrict the entrance of microbiocides [137]. In general, the sensitivity of the microorganisms to gemini alkylammonium microbiocide decreases in the order: Gram-positive bacteria > fungi > Gram-negative bacteria [143]. Biocidal activity also depends on the strain of the microorganism. The environmental strains are more resistant than laboratory strains [144].

Structure of the microbiocide is the most important factor affecting antimicrobial activity. Gemini alkylammonium salts are much better microbiocides than their monomeric analogues. MIC values of geminis are usually 17–70 folds lower than MIC of single analogue QAC. For example, MICs against *Staphylococcus aureus* are 0.0036 [μM] for gemini [12-6-12] and 0.252 [μM] for dodecyltrimethylammonium bromide (DTAB) [144]. This is due to the fact that gemini surfactants possess not only double positive-charged nitrogen atoms but also two long lipophilic substituents. The adsorption on the microorganism cell wall and subsequent penetration of the bilayer is more efficient [138]. It could be said that antimicrobial activity increased with numbers of quaternary ammonium cations in the molecule, but Paniak et al. showed that number of charged nitrogens was not key determinant of bioactivity of ammonium surfactants [145].

Conventional gemini alkylammonium salts could be modified by the change of number of carbon atoms in the substituent or in the spacer. Compounds, which have 10–14 carbon atoms in the substituent, are more active against bacteria than others (**Figure 25**) [146]. The shorter substituents are too short to effectively penetrate the membrane. In turn the long substituents have a tendency to coil upwards losing the ability to penetrate a cell wall. This is consistent

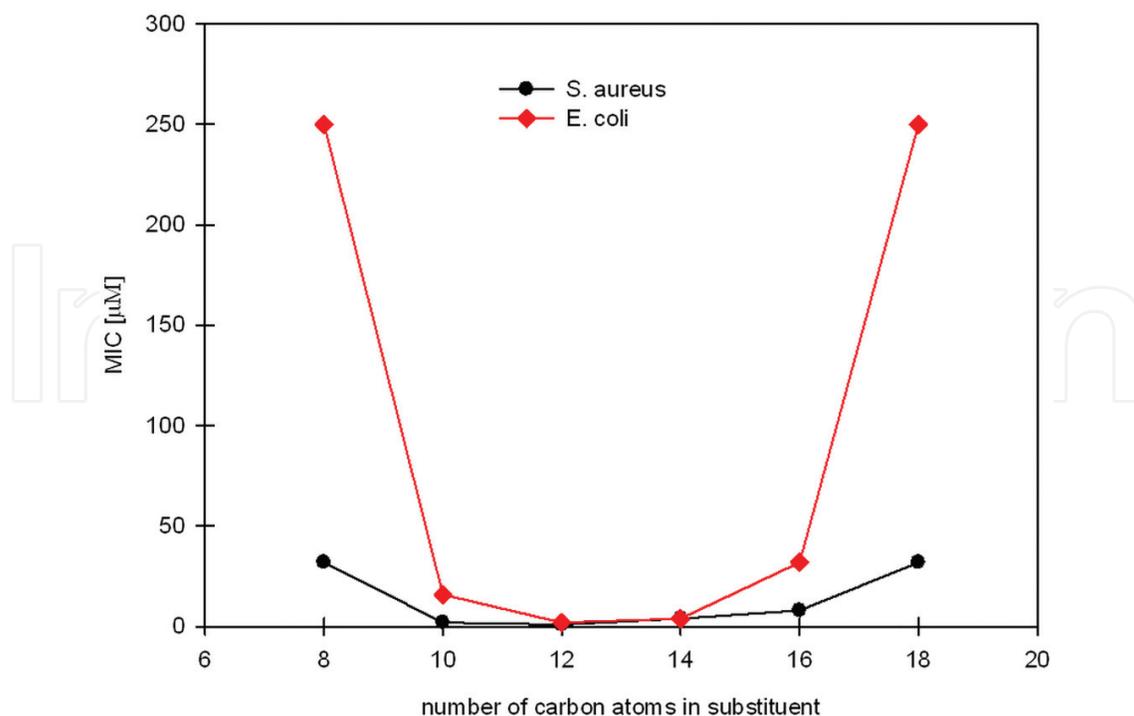


Figure 25. The relationship between MIC against *S. aureus* and *Escherichia coli* and a number of carbon atoms in the substituents in ethylene-1,2-bis(*N,N*-dimethyl-*N*-alkylammonium bromides).

with the parabolic relationship of MIC vs. the length of the substituent for monomeric QAC [129, 138].

The antimicrobial activity depends not only on the length of the substituent but also is dependent on the length of spacer [76, 137, 143, 147, 148]. In general, the longer the spacer, the better the antimicrobial activity (**Figure 26**) [77]. The longer spacers allow to better adjust of geminis to cell surface.

Tatsumi et al. compared antimicrobial activity of gemini surfactants with flexible and rigid spacers. In the case of surfactants with fourth carbon atom in the spacer, more effective are compounds with unsaturated bond in the linker [149]. Another possibility of stiffening of spacer is to introduce a ring. Martín et al. showed that the nature of the ring (aromatic or saturated) does not influence the antimicrobial activity of gemini surfactants [150].

The antimicrobial activity of gemini alkylammonium salts strongly depends on their hydrophilic-lipophilic balance (HLB), according to the equation $\log 1/\text{MIC} = a + b \log P + C[\log P]^2$, where P is octanol-water coefficient, which characterizes HLB of the molecule [138, 151, 152].

Antimicrobial activity of geminis with hydrophilic spacers modified by ester groups [148, 153–155], ether groups [156], amide groups [157, 158], amine group [145], phosphoryl group [159] and their antimicrobial has been frequently studied. It is important to note that there is no simple relationship between different types of hydrophilic groups in the spacer and antimicrobial activity of gemini surfactants. For the same type of the hydrophilic spacer, antimicrobial activity of geminis depends on the length of the alkyl substituent [145, 154].

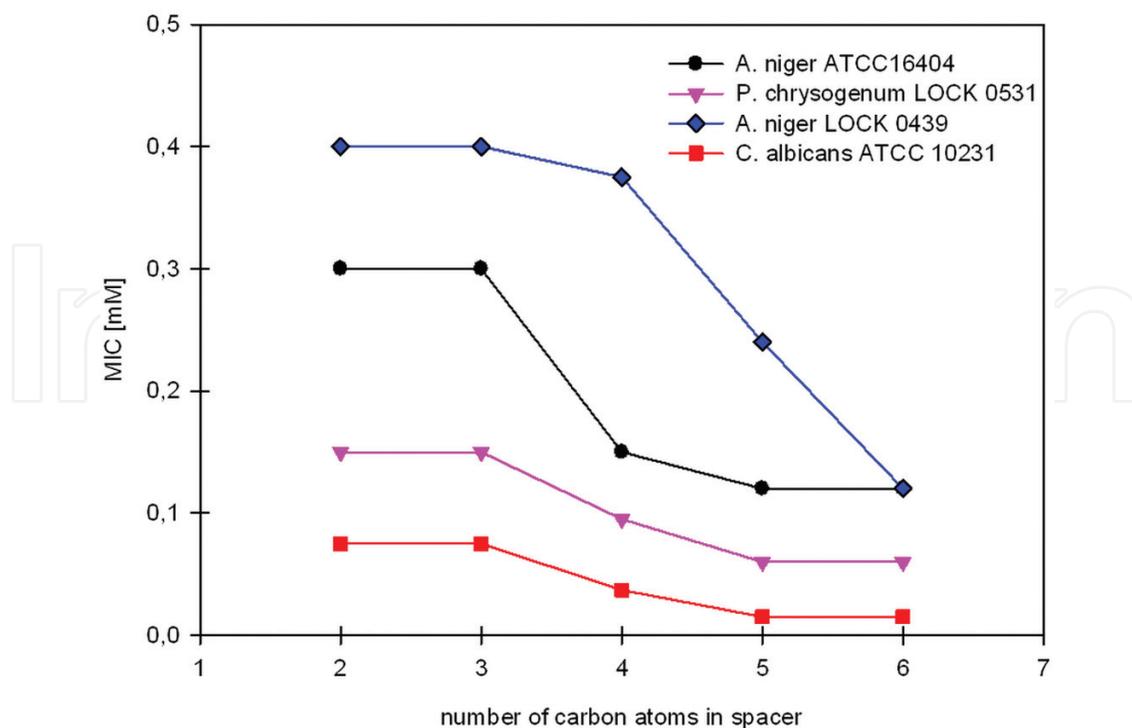


Figure 26. The relationship between MIC and a number of carbon atoms in spacer of polimethylene- α,ω -bis(*N,N*-dimethyl-*N*-dodecylammonium bromides).

Gemini surfactants with higher HLB could be also obtained by introduction ester groups [160–162], amide group [163–165] or hydroxyl group [166, 167] to alkyl chain. These compounds possess usually better antifungal activity than corresponding classical gemini surfactant.

In general, the increase of hydrophilicity causes the better antimicrobial efficacy of gemini surfactants [164, 168–170].

Gemini alkylammoniums with two hydroxyethyl groups, [12-4-12] diethanol (DEA) show higher antimicrobial activity than monohydroxyethyl derivative [12-4-12] monoethanol (MEA). The latter one in turn is better than compounds without hydroxyl groups [12-4-12]. The same trend is observed for monomeric analogues with two hydroxyethyl groups DTAB-DEA, one DTAB-MEA and one DTAB (**Figure 27**) [170].

6.2. Biodegradability

The susceptibility of gemini surfactants to biodegradation is the objects of many tests. The alteration of chemical structure of a substance changing its properties is defined as primary biodegradation, whereas mineralization to carbon dioxide, mineral salts and biomass is an ultimate biodegradation [171]. Surfactants are called to be easily biodegradable if at least 60% biodegradation occurred during 28 days [171, 172].

Martin et al. studied biodegradation of gemini surfactants with phenyl or cyclohexyl ring in the spacer. Whereas monomeric analogues are biodegradable (especially one with phenyl ring), gemini surfactants show no biodegradability [150]. Due to excellent antimicrobial activity,

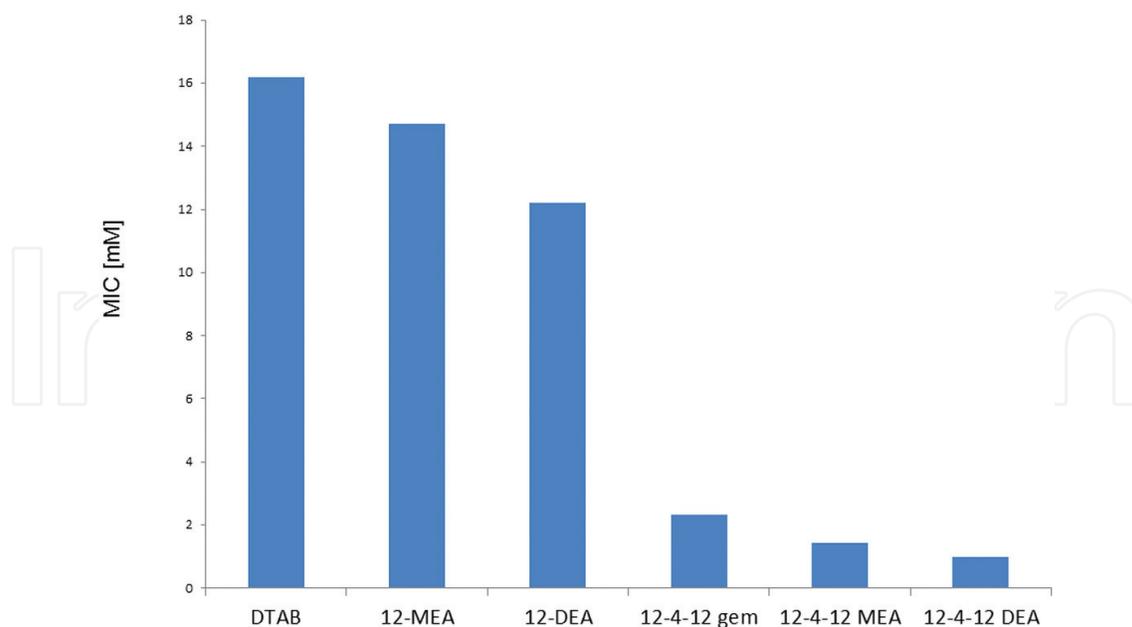


Figure 27. Antimicrobial activity of hydroxylated surfactants against *Bacillus subtilis* (MEA monoethanol, DEA diethanol).

gemini alkylammonium surfactants are considered as hard (or no) biodegradable. The high biological activity of cationic gemini surfactants might have a negative impact on their biodegradation. Modification of spacer to increase hydrophilicity of the surfactant molecule does not significantly change biodegradability of geminis [171]. Gemini surfactants with sugar substituents, like gemini alkyldeoxy-D-glucitolammonium salts, show a susceptibility to biodegradation in the range 20–32%. The degree of biodegradability depends on the length of the alkyl chain. The longer the hydrocarbon substituent or spacer, the lower the biodegradability [172]. Amino acid-based gemini surfactants are biodegradable to even 60%; however, their single analogues degrade rapidly [173]. Modification of the structure (spacer or substituent) with easily hydrolysed groups can significantly affect biodegradability. The widely described easily biodegradable gemini surfactants are that with ester bonds [125, 148, 174–177] (Table 2) [176, 178].

Another possibility to enhance the biodegradability of cationic surfactants is the use of immobilized consortium of microorganisms in Ca-alginate beads. This way allows the biodegradation of QAC up to 100% [179]. This method was applied to monomeric cationic surfactants; however, it is very possible that this would work also for gemini surfactants.

The crucial points to biodegrade chemical compounds, not only cationic surfactants, are the concerted activity of two or more groups of bacteria to fulfil enzymatic capabilities [181]. Moreover, there are no simple relationships between biocidal activity of gemini surfactants and their biodegradability.

6.3. Hemolycity

Gemini alkylammonium surfactants possess amphiphilic character and can interact with various surface, also with the membrane of erythrocytes. Łuczyński et al. report that the

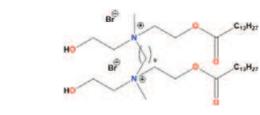
Compound		Biodegradation (%)	Reference
	s = 2	80	[179]
	s = 6	75	
	s = 12	71	
	n = 12	59.85	[177]
	n = 14	51.65	
	n = 16	52.19	

Table 2. Biodegradability of gemini surfactants with ester bond in the substituent or in the spacer.

hydrocarbon chains of the gemini surfactants penetrate the hydrophobic lipid bilayer of the erythrocyte membrane, which causes weakness of the interaction between the lipid molecules, leading to lysis of the cell [56]. The haemolytic activity of the surfactants is usually expressed as HC_{50} , that is, concentration that induces the haemolysis of 50% of the total number of erythrocytes [164], and it depends strongly on structure of surfactants. Koziróg et al. notice that gemini [12-6-12] did not exhibit haemolytic activity at MIC against *Candida albicans*, whilst monomeric surfactant DTAB at the same MIC caused a slight haemolysis of erythrocyte [144]. Similar conclusions have been described for geminis with ester group in the spacer [153, 180] and for amino acid-based gemini surfactants [181]. Łuczyński et al. have shown that haemolytic activity depends on the alkyl chain length, whilst compounds with 10 and 12 carbon atoms exhibit the highest haemolytic activity (the lowest HC_{50}) (**Figure 28**). Surfactants with shorter alkyl chain induce haemolysis only at very high concentration. Also single-chain analogue shows haemolytic activity comparable with gemini with the same length of the alkyl chain [56].

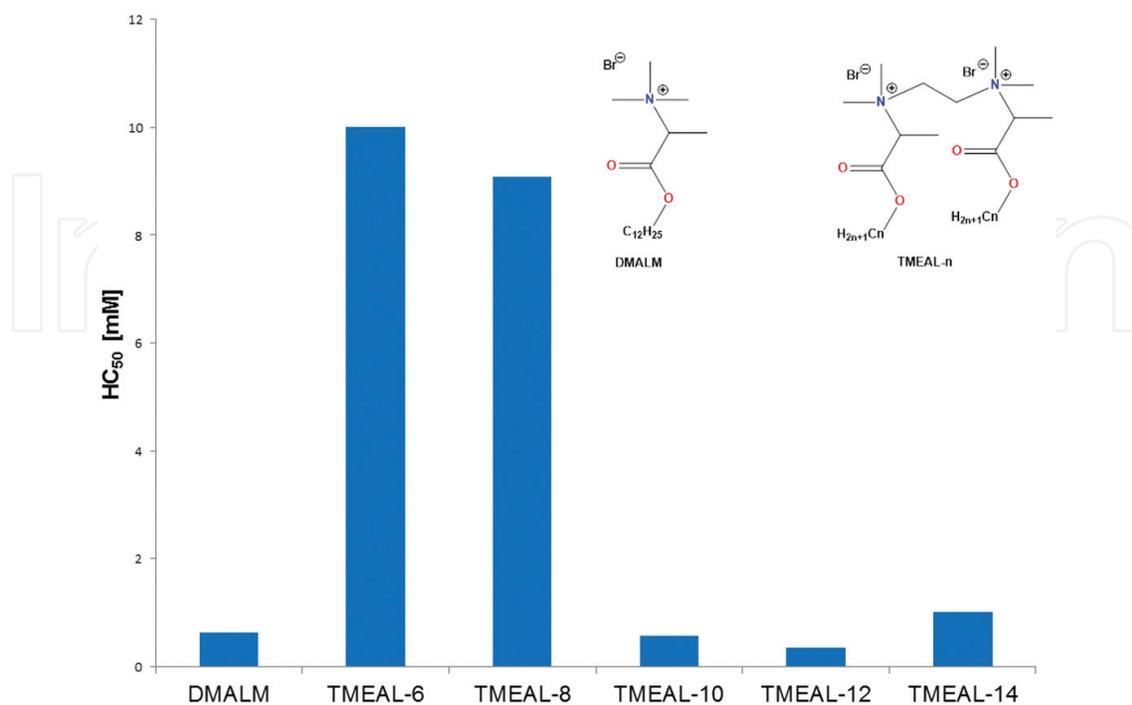


Figure 28. Comparison of HC_{50} of gemini surfactant (TMEAL-n) and its monomer analogue (DMALM).

Zhou has shown that HC_{50} of geminis is the highest for decyl, dodecyl and tetradecyl substituents that correspond to their high antimicrobial activity [182].

Hoque et al. studied haemolytic activity of amide-based gemini surfactants with different lengths of spacer. He found that the increase of the spacer length causes the increase of haemolysis (Figure 29) [164]. It is a result of an increasing hydrophobicity of gemini surfactants investigated. The similar results have been described for amino acid-based gemini surfactants; haemolytic power is higher for the compounds with more hydrophobic content, that is, with longer spacer and alkyl chain lengths [173, 181].

6.4. Cytotoxicity

Gemini alkylammonium surfactants are tested as nonviral gene vectors, so their cytotoxicity has to be studied. It is usually specified by the IC_{50} value i.e. the concentration of the compound (in μM) that attenuates the living cell survival to 50% [183]. IC_{50} depends on the structure of surfactants. For gemini surfactant with fixed length of spacer, cytotoxicity decreases as the length of alkyl chain increases (Figure 30). Moreover, for gemini surfactant with fixed length of alkyl substituent, IC_{50} decreases as number of methylene groups in spacer increases from 2 to 8 and then increases as number of methylene groups in spacer increases up to 12. These changes are very similar to those observed for MIC values. IC_{50} values show that monomeric surfactants are more cytotoxic than gemini ones, for example, IC_{50} of CTAB are 10.3 and 8.0 μM towards C6 and HEK293 cells, whilst IC_{50} of 16-4-16 are 3.5 and 4.1 μM , respectively [137]. Cytotoxicity also depends on the structure of head groups. Chauhan et al. find that pyridinium-gemini surfactant possesses lower cytotoxicity towards BV2 and C6 glioma cells than conventional gemini surfactants [14-2-14] [183].

Due to the structure of gemini alkylammonium surfactants and their ability to penetrate biological membranes, they can be potentially used as skin permeation enhancers. Almeida et al. studied cytotoxicity towards NCTC 2544 cell line, a human skin keratinocyte cell line of several dicationic gemini surfactants, and compared with a commercial single-tail surfactant

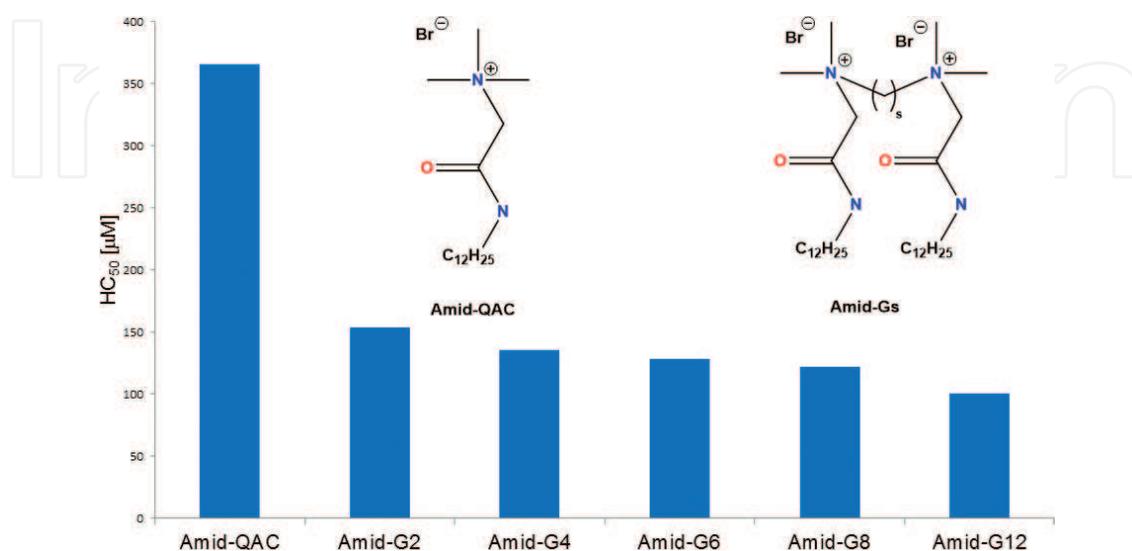


Figure 29. Comparison of HC_{50} of gemini surfactant (AMID-Gs) and its monomer analogue Amid-QAC.

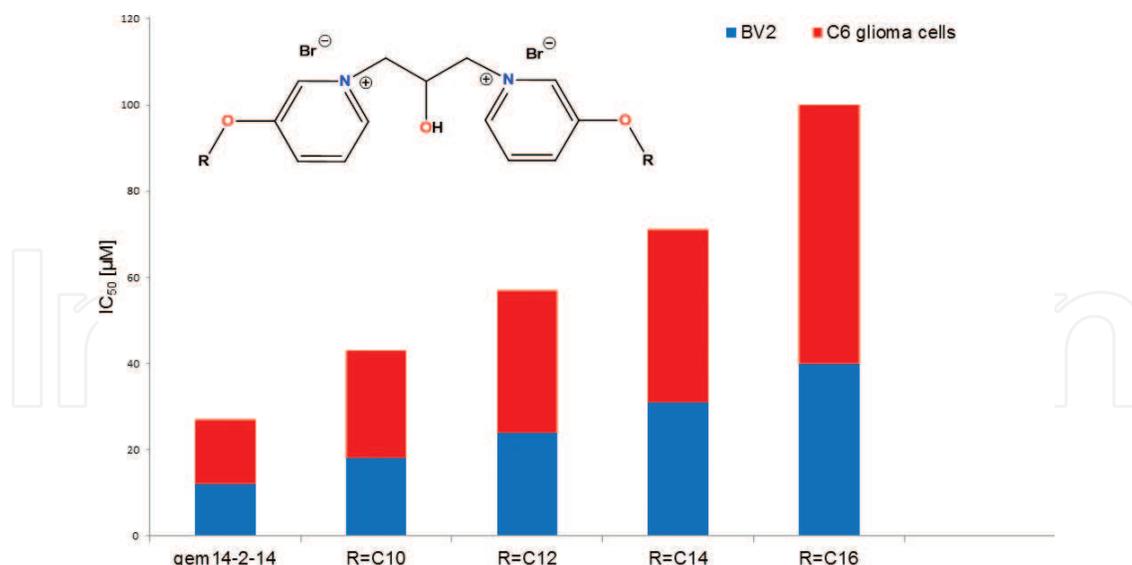


Figure 30. Cytotoxicity of gemini surfactants against BV2 and C6 glioma cells [185].

(DTAB) [184]. For the lower concentrations tested (up to 10 mM), none of gemini surfactant reveals a significant cytotoxicity upon the cellular line. However, over 25-mM toxicity is observed for some of them. Because gemini surfactants are more effective in disrupting the membrane than the single-tail counterpart, it means that a low amount of gemini, below threshold toxicity, may be needed to achieve the same effect of a significantly higher amount of DTAB. Silva et al. have shown that gemini surfactants are promising candidates, directed at permeation enhancing of hydrophilic drugs. They possess similar cytotoxic profiles and are even a little more effective than Azone (the most effective permeation enhancer for ketoprofen) [185].

6.5. Aquatic toxicity

The increasing use of gemini alkylammonium surfactants entails the need to define their biological profile, especially toxicity to aquatic organisms. For this purpose selected model organisms highly sensitive to pollution are used. Usually determined parameter is IC₅₀ i.e. concentration of surfactants to immobilize 50% of organisms. Garcia et al. studied aquatic toxicity to *Daphnia magna* of several gemini surfactants with dodecyl substituent and different spacers (**Figure 31**) (dodecyltrimethylammonium bromide, DTAB; 1,6-hexamethylene-bis(*N*-dodecyl-*N,N*-dimethylammonium) dibromide, 12-6-12; 3-oxa-1,5-pentamethylene-bis(*N*-dodecyl-*N,N*-dimethylammonium) dichloride, 12-O-12; 3-azamethyl-1,5-bis(*N*-dodecyl-*N,N*-dimethylammonium) dibromide, 3N-12; 1,4-bis-[*N*-(1-dodecyl)-*N,N*-dimethylammoniummethyl]benzene dibromide, QSB2-12; and 1,6-hexamethylene-bis(*N*-dodecyl-*N*-hydroxyethyl-*N*-methylammonium) dibromide, G6-MOH-12). They find that aquatic toxicity decreases with increasing the hydrophilicity of the surfactant molecule. The structure of the spacer, rigid (benzene ring) or flexible (alkyl chain), has no significant effect on the acute toxicity to *D. magna*. Comparing the acute toxicity of gemini surfactants with that of monomeric surfactants DTAB (IC₅₀ = 0.35 mg/l), dimeric surfactants are less toxic than monomeric surfactants [171]. Similar results were observed for amino acid-based

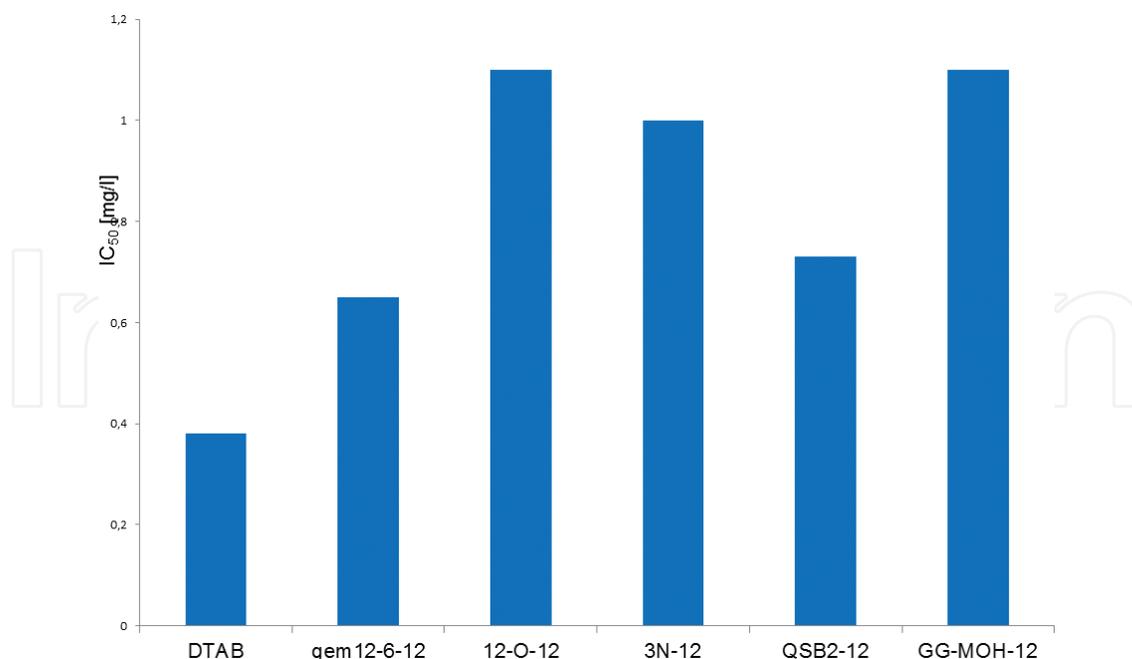


Figure 31. Aquatic toxicity to *D. magna* of DTAB and gemini surfactant with hydrophilicity of the surfactant molecule.

gemini surfactants [173]. These compounds are less toxic to freshwater *D. magna* and seawater *Photobacterium phosphoreum* than conventional monomeric ammonium salts [181].

7. Anticorrosion activity

Corrosion is a process of deterioration (degradation) of materials' properties due to the interactions between a surface and an environment [186], which leads to changes in the material properties because of a disintegration of the structure of the material. The process destroys surfaces of the metals (iron, aluminium and copper) but also non-metallic materials (concrete, wood, glass and paper) [187, 188]. Usually a term "corrosion" is booked for the deterioration of metals, and according to a definition given by the American Section of the International Association for Testing Materials (ASTM), it is the chemical or electrochemical reaction between a material, usually a metal, and its environment that produces a deterioration of the material and its properties [189]. The problem of corrosion affects many areas of industries, oil and gas [190], electronic [191], food, paint, coating [192], marine, chemical [193], automotive and in daily life [176], by destroying metallic equipment, pipelines, vessels, storage tanks [190], heaters and electrical power lines [191] and leading to scale results in reduced heat transfer, loss of production capacity and energy loss [194]. Corrosion is induced by acids that are extensively used in industry [195]. Organic acids are used for preparation of chemicals, drugs, fibers and other processes [196], whereas mineral acids (HCL, H₂S, H₂SO₄ or H₃PO₄) are used for cleaning, acidification and pickling [190, 197]. Corrosion is a costly and dangerous process, which plays an important role in the field of economic and safety [194, 195]. The damages caused by corrosion can be estimated using different methods. The most popular are gravimetric (weight loss measurements) and electrochemical (potentiometry and electrochemical

impedance spectroscopy) [198]. The rarer methods include spectroscopic (UV-VIS) [84], volumetric (amount of released hydrogen), analytical (assay of metal ions) or radiography (using radiation) [186, 188, 199, 200]. The morphology of destroyed metal surface is analysed using microscopes: scanning electron microscope (SEM) or atomic force microscope (AFM) [199].

In order to reduce the corrosion of metallic materials, several methods have been applied: electrochemical protection (anodic and cathodic), coatings (metallic and non-metallic) and corrosion inhibitors [187, 201–205]. Among them, the use of organic corrosion inhibitors, especially cationic gemini surfactants, is the most efficient and practical method [192], particularly to control acid-induced corrosion [84]. Corrosion inhibitors are chemical substances which, when added, in a small amount, to the corrosive environment, significantly decreases the corrosion rate of metals [194]. The general mechanism of action of organic corrosion inhibitors is based on adsorption of molecules of inhibitor onto a metal surface by displacing water molecules and forming a protective film [191, 206]. The adsorption process can be physical (electrostatic interaction), chemical (donor-acceptor interaction) or mixed [200]. The process is influenced by the molecular structure of inhibitor (functional groups, aromaticity and electron density at donor atoms), surface charge of metal and type of electrolyte. Compounds with heteroatoms (N, O, S, P) [84] and π groups (multiple bonds, benzene ring) [207] have been found to be more efficient due to donation of a lone pair of electrons to a free orbital of the metal making them stronger adsorbed [190]. The order of corrosion inhibition is the reverse order of the electronegativity of the heteroatoms [208]:



It was noticed that in acid environment, heteroatoms are protonated which favours the physical adsorption and has increased the interest of quaternary ammonium salts (QAS) as corrosion inhibitors [128]. Cationic gemini surfactants are more efficient than monomeric QAS. It is related with lower values of CMC which is a key from the point of view of corrosion. Cationic surfactants reach the highest inhibition efficiency around CMC [200]. The corrosion rate (CR) of steel in 0.5 M HCl with addition of monomeric quaternary ammonium salts tetradecyl trimethyl ammonium bromide (TTAB) is higher than for dimeric analogue (1,4-butan-bis(tetradecyl dimethyl ammonium bromide) (14-4-14) [192] (**Figure 32**).

Two positively charged nitrogen atoms are better adsorbed onto the metal surface due to electrostatic interactions between cations and the negatively charged surface of metal which provides better protection [186, 209, 210]. The size and molecular weight of organic inhibitors have an impact on the effectiveness of action as corrosion inhibitors [209]. Increasing the length of the aliphatic chains increases the inhibition efficiency [192, 200, 211, 212]. The relationship of m-6-m surfactants (C = 1 mM) is presented in **Figure 33** [200].

Another important factor is the length of the spacer. Surfactants with longer hydrocarbon spacer are more effective corrosion inhibitors [176, 199, 213–215]. As an example, inhibition efficiency for gemini surfactants $(\text{C}_{12}\text{H}_{25})_3\text{N}^+(\text{CH}_2)_n\text{N}^+(\text{C}_{12}\text{H}_{25})_3$ (C = 5 mM) is presented in **Figure 34** [215].

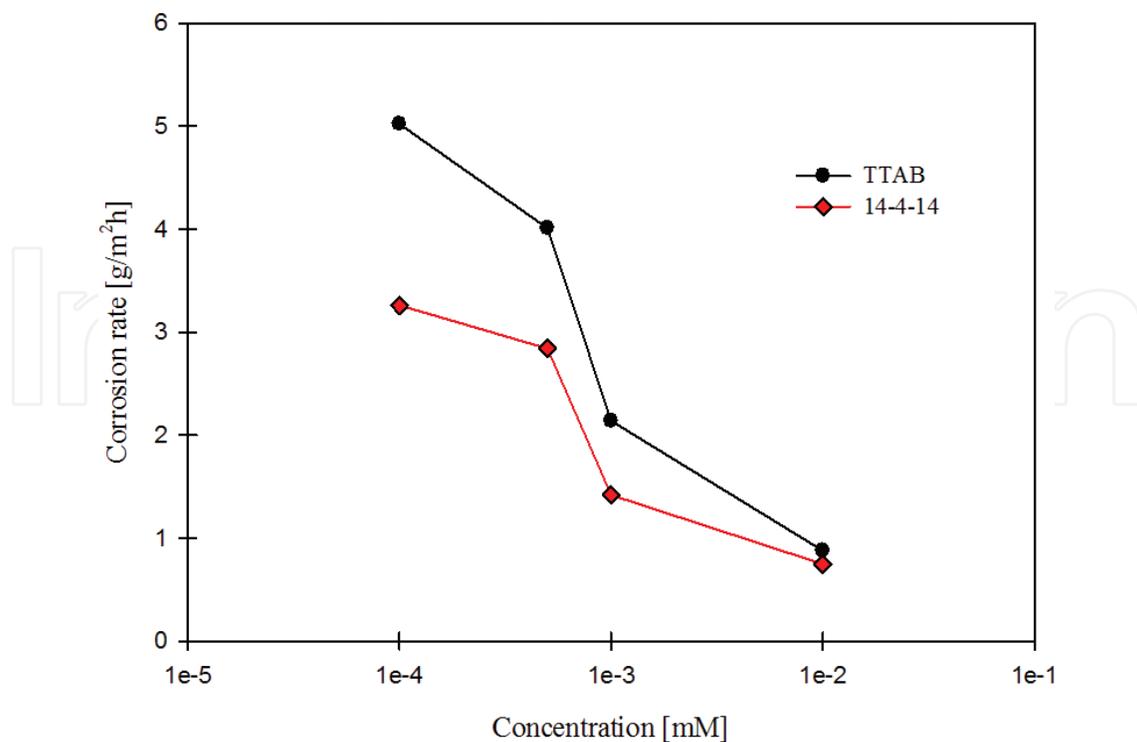


Figure 32. Corrosion rate of steel in acid in the presence of monomeric and dimeric quaternary ammonium salts.

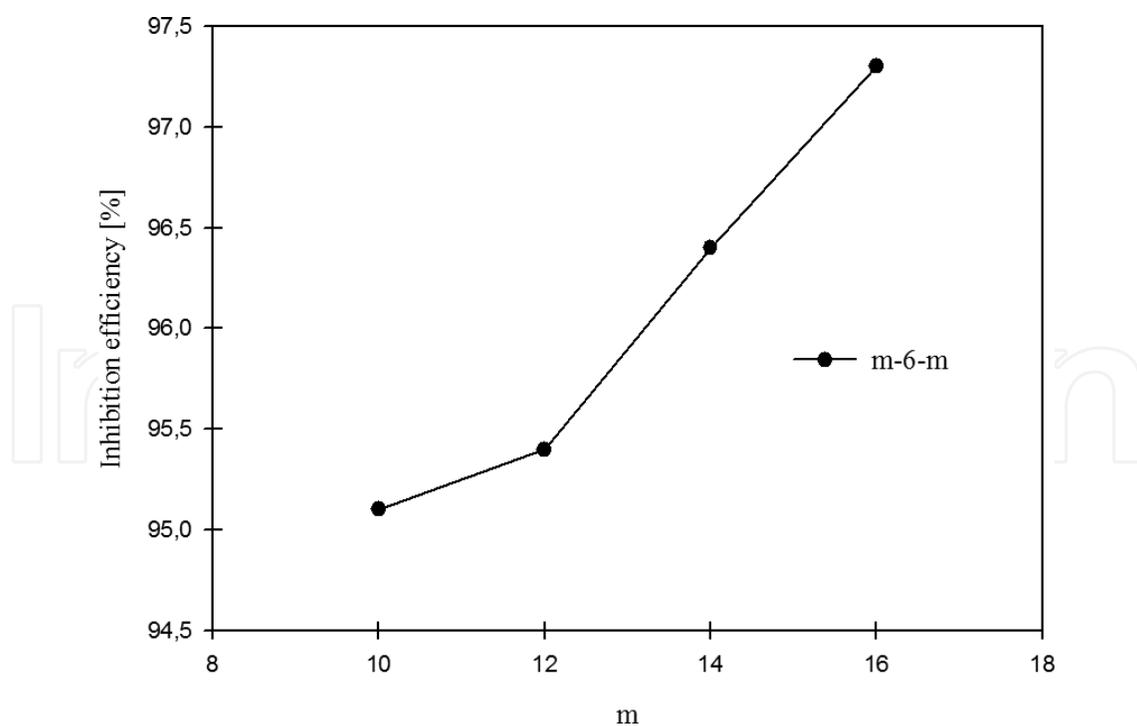


Figure 33. The relationship between the length of the alkyl chains (m) and inhibition efficiency of aluminium in hydrochloric acid.

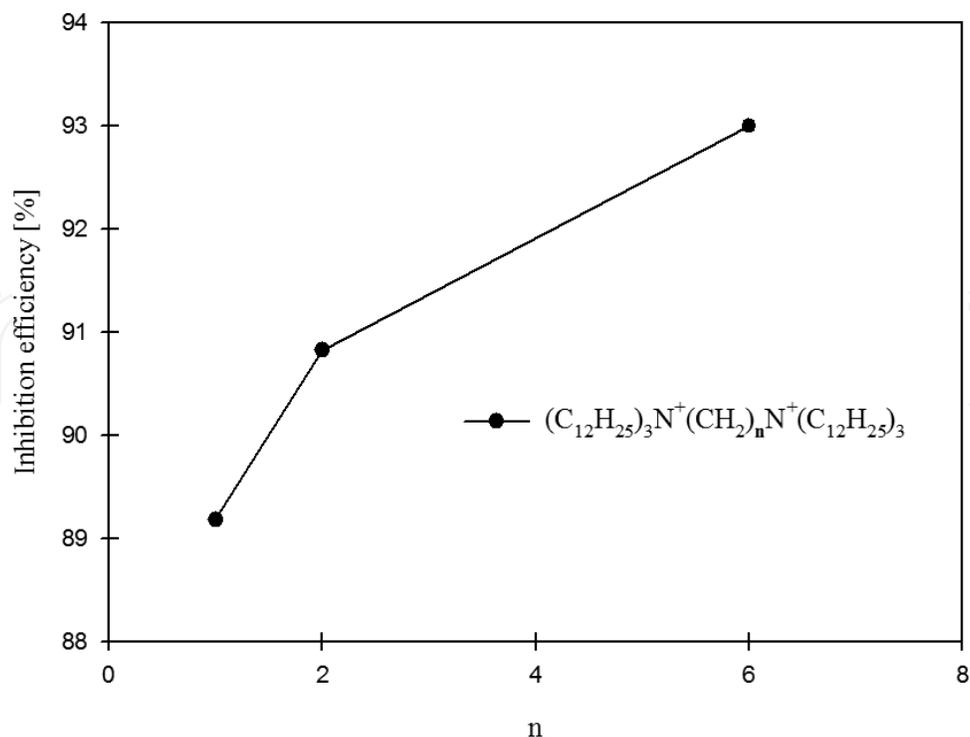


Figure 34. Inhibition efficiency of inhibition corrosion of carbon steel in 1 M HCl.

Inhibition efficiency is related to corrosion-resistance properties of the metals. The adsorption of gemini surfactant molecules changes it by increasing the values of resistance of the metal which makes the material more resistant to corrosion [198]. **Figure 35** presents the values of resistance of $(C_{12}H_{25})_3N^+(CH_2)_nN^+(C_{12}H_{25})_3$ and a value of blank sample, after immersion in acid without addition of inhibitors [215].

Introducing heteroatoms into a molecule promotes the inhibition behaviour. Due to lone electron pairs, which can additionally interact with free metal orbitals, the adsorption is stronger and inhibition efficiency higher. Exchanging ethyl groups to ethoxyl groups in gemini surfactants with rigid spacer (**Figure 36**) increases the efficiency from 91.64 to 95.63% ($C = 10$ mM, carbon steel, 1 M HCl) [210].

The standard energy of adsorption (ΔG_{ads}^0) gives information about the type of adsorption. Values up to -20 kJ/mol are related to the electrostatic interaction (physical adsorption), whereas more negative than -40 kJ/mol indicate chemisorption takes place. Negative values of ΔG_{ads}^0 mean that the process of adsorption is spontaneous [209]. The energy of adsorption first decreases with increasing the length of the spacer and after reaching maximum starts decreasing which is related to the free energy of micellization (the same relation) [113]. Increasing the length of the alkyl chain increases the values of the ΔG_{ads}^0 [199, 200]. The standard enthalpy of adsorption (ΔH_{ads}^0) provides valuable information about the mechanism of the corrosion inhibition. Chemisorption is attributed to an endothermic process ($\Delta H_{ads}^0 > 0$), whilst exothermic adsorption is represented by values lower than 0 [186] and is related to physical or mixed adsorption [215]. Another thermodynamic parameter which gives information of the adsorption process is entropy (ΔS_{ads}^0). Positive values are attributed to the increase of

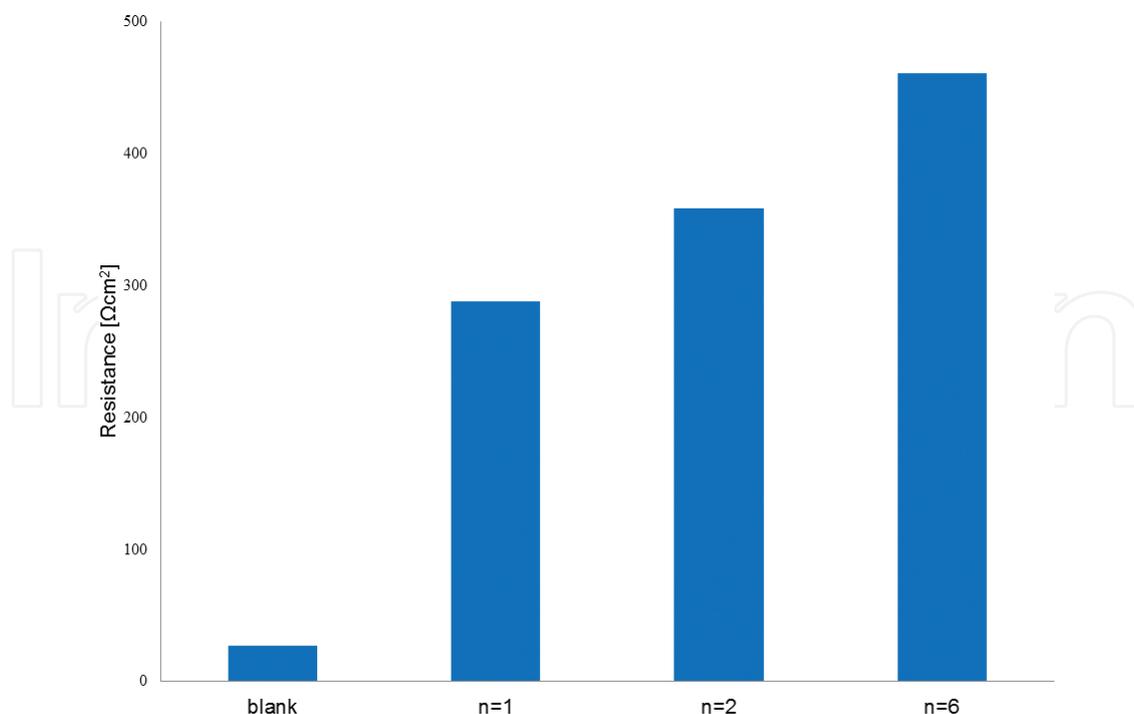


Figure 35. The values of resistance for $(C_{12}H_{25})_3N^+(CH_2)_nN^+(C_{12}H_{25})_3$.

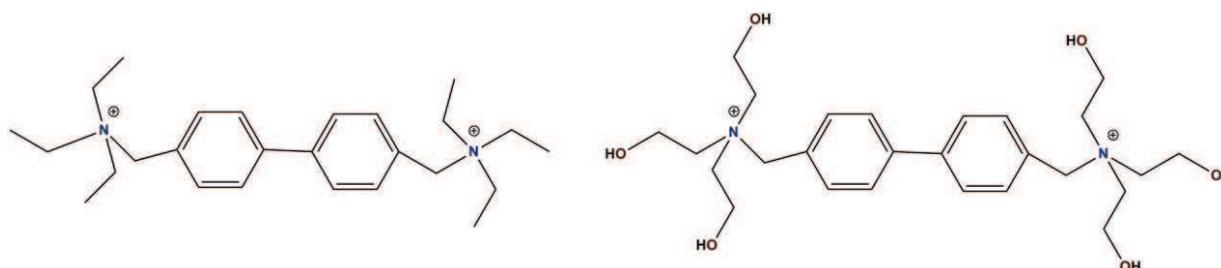


Figure 36. The structures of gemini surfactants with rigid spacer.

disorder due to the dissolution of metal and the adsorption of only one molecule of inhibitor by desorption of more water molecules [195].

Gemini surfactants which are used as commercial agents are not used alone. Special formulations are prepared based on synergistic effect. Thanks to that, the level of protection is higher, and very often due to synergism effect, less amount of surfactant is needed to protect the metal surface [193, 216–219]. The biggest consumption of corrosion inhibitors based on cationic gemini surfactants belongs to petrochemical industry. Using the special formulations leads to decreasing corrosion rate and protection against deterioration during long time. Some formulations are already used in industries. Some of gemini surfactants are already patented as multifunctional corrosion inhibitors of ferrous metals that transported or stored crude oil and liquid fuels by the presence of acidic pollutants, sulphur compounds and water and equipment and pipes used in cooling systems that use water with a high concentration of divalent ions such as calcium and magnesium, which are the main cause of producing pitting corrosion in this environment [220] and also for inhibiting corrosion and biofouling of metallic surfaces in

contact with corrosive fluids in gas- and oil-field applications [221]. All of them contain heteroatoms and π groups and exhibit good inhibition efficiency (more than 90%).

8. Special applications

The unique physicochemical and biological properties of gemini surfactants designate them to many applications in industry and pharmaceutical and biomedical branch where the safety profile of products must be optimized.

8.1. Nanoscience and nanotechnology

8.1.1. Gene therapy and bioimaging

Gemini alkylammonium surfactants are applied to introducing genes into cells, due to their ability to interact with DNA [222–224]. This interaction must be strong enough to overcome the biologic membrane barrier and weak enough to release DNA in the right place in the cell. The gemini surfactant is shown to bind and compact DNA efficiently and form a “lipoplex”. The lipoplex can penetrate the outer membranes of many cell types, to appear in the cytoplasm encapsulated within endosomes. Escape from the endosome may be controlled by changes in the aggregation behaviour of the lipoplex as the pH decreases. DNA may be released from the lipoplex before entry into the nucleus, where the new gene can be expressed with high efficiency. Some gemini surfactants with sugar substituent, peptide moiety [225, 226] or cholesterol-based diquaternary ammonium gemini surfactant [227] were tested as a gene transfection vectors. It was recently shown that hydroxyethylated gemini surfactants [228], fluorinated bispyridinium gemini surfactants [229] and geminis derived from cysteine [230, 231] can be also used for this application.

Bioimaging is a very useful technique in the cancer diagnosis where the stable fluorescent marker is necessary. It has been recently shown that geminis like 12-2-12 and 12-6-12 are good stabilizers for model genetic material constructed from DNA and polysaccharide-based chitosan on nanoemulsion core containing IR-780 indocyanine as fluorescent marker [232].

8.1.2. Drug nanocarriers

Gemini surfactants can very easily change their morphological structures upon pH, temperature and salts [233–239].

The reversible transition from micelles to other structures, especially to vesicles by changing pH, is very useful for drug delivery. Li et al. showed that gemini amino acid surfactants, where pH is the key driving force to control the aggregation behaviours, can be applied to build colloidal systems for delivering hydrophobic drugs or nutrition [240].

Similarly, Ref. [241] showed that geminis with morpholinium moieties exhibit high solubilization capacity towards a thymolphthalein as well as indomethacin, an inflammatory drug, exceeding that of reference amphiphiles.

8.1.3. Nanoparticles

Nanoparticles (NPs) have a lot of applications in medicine, physics, optics and electronics. The size and morphology of nanoparticles determine to high extent their properties and applications. These parameters can be mainly regulated by surfactants which act as soft templates or nanocontainers. The preparation of gold, silver and gold-silver alloy nanoparticles by seed-mediated method using gemini surfactant has been described by Tiwari et al. [242]. The obtained NPs were stable and were characterized by UV-vis, XPS, TEM, energy dispersive spectroscopy (EDS) and zeta potential techniques. The orientation of gemini surfactant molecules on the metal NPs has been determined by twisted intramolecular charge transfer (TICT).

A very interesting synthetic approach was developed by Wang et al. [243] for creating versatile hollow Au nanostructures. The reduction of Au(III) by ascorbic acid with the use of hexamethylene-1,6-bis(*N*-dodecyl-*N,N*-dimethylammonium bromide) (C12C6C12Br₂) as a template agent leads to vesicle, capsule-like and tube-like aggregates which act as soft templates for hollow Au nanostructures upon further reduction of Au(I) to Au(0) by NaBH₄. Gemini surfactant plays a crucial role in formation of the final structure. The electrostatic repulsion between head groups of gemini surfactant is greatly weakened as Au(III) is converted to Au(I), which is in favour of the construction of vesicle, capsule-like and tube-like aggregates. This method allows to prepare nanostructures of gold potentially useful for many applications.

The industrial scale production of monodispersed gold nanorods (AuNRs) has been described by Xu et al. [244]. By using gemini surfactants, the cost of the synthesis of high-quality AuNRs can be reduced by 90%. Moreover, varying the concentration of the surfactant, the shape of AuNRs can be tailored from straight nanorods to “dog bones”.

A special group of nanoparticles, quantum dots (QDs) [245], like lead telluride [246] hydrophobic quantum dots CdSe/ZnS [247] with strictly defined size and morphology are usually prepared with auxiliary of gemini surfactants.

8.1.4. Supramolecular solvents

Supramolecular solvents (SUPRAS) are nanostructured liquids made up of surfactant aggregates synthesized through a self-assembly process. This kind of solvent is mainly assigned to microextraction methods. Feizi et al. [248] applied a new gemini-based SUPRAS for the determination of methylparaben (MP), ethylparaben (EP) and propylparaben (PP) in cosmetics, beverages and water samples on the basis of peccation and Van der Waals interactions into the SUPRAS. The gemini-based SUPRAS followed by HPLC-UV has been found to have excellent detection sensitivity with a limit of detection (LOD, S/N = 3) of 0.5 mg/L for EP and PP and 0.7 mg/L for MP.

8.1.5. Interactions with proteins

Interactions between proteins and gemini surfactants derived from amino acids have also been investigated. This type of studies can help to understand the action of surfactants as denaturants

and solubilizing agents for proteins that is important in medical and cosmetic branch. Gemini surfactants from glutamic acid exhibit different interactions with haemoglobin than their corresponding single-chain homolog. The gemini surfactants showed lower denaturing ability to haemoglobin, probably due to their bigger size, and the denaturation degree decreased when the spacer length increased. It was also observed that when the gemini surfactants content are low, the secondary structure of haemoglobin can be stabilized [249]. Takeda et al. reported the protective effect of gemini surfactants on thermal denaturation of BSA. The gemini surfactant studied by these authors consists of two glutamic acids as polar heads and a lysine as spacer. For this gemini surfactant, the protection of the recovery of the helicity of BSA appeared at lower concentration comparing to SDS due to the higher hydrophobicity of these compounds [250].

8.2. Technology

8.2.1. Solubilization

Gemini surfactants are very good solubilization agents [251]. Polycyclic aromatic hydrocarbons (PAHs) like anthracene, naphthalene, fluorene or pyrene [252, 253], which are organic pollutants, can be easily removed from water solution by the use of gemini surfactants. It significantly reduces the risk to the environment caused by these compounds [254]. Gemini surfactants are better for solubilization of PAH than their monomeric analogues. After mixing them together, values of molar solubilization ratio (MSR) are higher (**Table 3**) [252].

Gemini surfactants are also efficient as solubilization agents of organic dyes (Quinizar, Sudan I, orange OT) which are used to colour textiles, waxes or oils [6, 255, 256]. Cationic surfactants promote the adsorption of solubilized dye to the surface, especially textile fiber surface which carries a negative charge [255].

Solubilization power of gemini surfactants increases with the elongation of the alkyl chain length [255, 257, 258] and elongation of the spacer length [257, 259] which is related to a larger size of micelles.

8.2.2. Dispersion

Another potential application of gemini surfactants due to their ability to form micelles is the capacity to disperse insoluble in water particles and form stable colloids. Carbon nanotubes (CNT) have unique electrical, optical and mechanical properties, and due to that, they are used as medical sensors, electronics and compatible materials [260]. However, because of strong Van der Waals interactions, the bundles are insoluble in water and common organic solvents

	CMC (mM)	MSR
16-6-16	0.001	0.2110
CTAB	0.776	0.1236
16-6-16 + CTAB	0.0015	0.371

Table 3. Molar solubilization of naphthalene of gemini surfactant, cationic surfactant and gemini-conventional mixtures.

which limit their potential applications [261, 262]. Cationic surfactants are widely used to disperse CNT in water even at low concentration giving stable solutions for long time [263]. Gold nanoparticles, because of their properties [264, 265], also have various potential applications in different areas, but to make them useful, forming stable nanofluids is required. It can be reached by using gemini surfactants as a stabilizer to prepare stable gold/oil nanofluids [264]. It has also been shown that gemini surfactants can effectively disperse hydrogels to form supramolecular, three-dimensional micellar-hybridized network [266–268]. The formation of a spatial network of well-dispersed molecules is very significant for biomedical and optoelectronic applications.

8.2.3. Enhanced oil recovery

Traditional oil extraction methods produce depleted reservoirs that contain about 20–40% of trapped oil [269]. The remaining oil is trapped in porous media, due to the viscous, surface and interfacial forces, which results in poor displacement efficiency [270]. The implementation of advanced methods or their combinations to enable the recovery of residual oil is called enhanced oil recovery (EOR). Some techniques can be distinguished: thermal steam flooding (for heavy and extra heavy crude oil) [271], miscible gas flooding (for light, concentrated and volatile oil reservoirs) and chemical flooding (for medium or light reservoirs) [269]. Chemical flooding is one of the successful methods, especially the use of surfactants [272]. They are added into the flooding solution and improve the properties of reservoir fluids, to make them more conducive to extraction [273]. Tuning the capillary forces of the trapped oil and to achieve a complete miscibility, interfacial tension has to be reduced to the

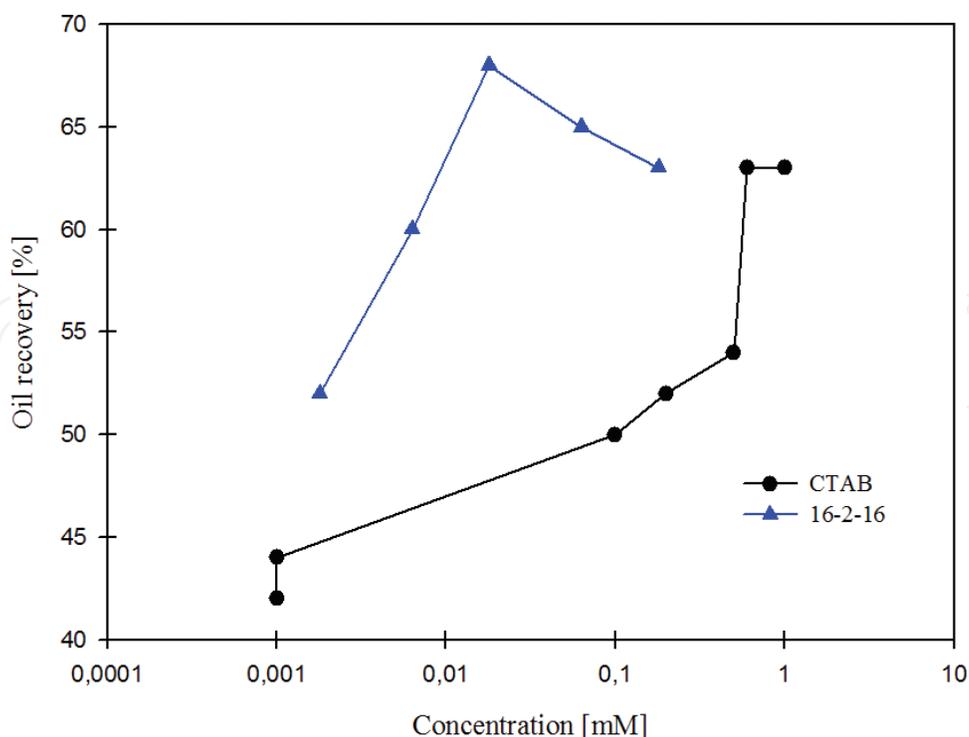


Figure 37. Mimic oil recovery of CTAB and 16-2-16 aqueous solutions.

lowest possible value [274]. Due to their excellent surface-active properties, cationic gemini surfactants are great at lowering surface tension and changing the wettability [273]. Solutions of cationic surfactants, both monomeric (CTAB) and dimeric (16-2-16), were tested as mimic flooding solution (oil, n-dodecane; porous material, silica gel powder). It was noticed that the best results were achieved around CMC values, for CTAB 1 mM and for [16-2-16] 0.018 mM [273].

The highest oil recovery of 16-2-16 (68%) was reached at 0.018 mM whereas for CTAB (63%) at 0.6 mM (**Figure 37**) [273]. The tested gemini surfactant allows to achieve similar percent of oil recovery at lower concentration which makes the process more efficient [272, 275].

Author details

Bogumil E. Brycki*, Iwona H. Kowalczyk, Adrianna Szulc, Olga Kaczerewska and Marta Pakiet

*Address all correspondence to: brycki@amu.edu.pl

Faculty of Chemistry, Laboratory of Microbiocides Chemistry, Adam Mickiewicz University, Poznan, Poland

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