RESEARCH PAPER

Synthesis and surface activity properties of new gemini surfactants with hydroxyl group and piperazine ring

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Abstract

The reaction of 1,4-bis(2-hydroxypropyl)piperazine with alkyl bromides produced cationic gemini surfactants at a 1:2 molar ratio. Tensiometric, conductometric, and dynamic light scattering techniques were employed to measure the surface activity, specific electrical conductivity, and aggregate size of the obtained gemini surfactants, respectively. The critical micelle concentration, polar group cross-sectional area, maximum adsorption, surface pressure, degree of counterion association, and Gibbs free energy variations during micelle formation and adsorption processes were computed based on the obtained data. It was established how the length of the hydrophobic group in gemini surfactants affected their colloid-chemical characteristics. The antibacterial properties of these compounds were evaluated using the disk-diffusion method against various Gram-positive and Gram-negative bacteria, as well as fungi. Researchers also investigated the C_{12} chain gemini surfactant's capacity to prevent corrosion of mild steel in a CO_2-saturated NaCl solution.

Keywords: Adsorption, Antibacterial, Micelles, Gemini surfactant, Surface tension

1. Introduction

The monomer structure of most surfactants consists of two: *hydrophilic and hydrophobic* groups. A large number of surfactants have been created by structural modification, which, compared to monomeric surfactants, have better qualities and functions.[1–3] Innovative form of these Gemini surfactants has received recent interest. Structurally, they are related to monomeric surfactant spacers. Gemini surfactants have critical micelle concentration (CMC) values that are 10 or 100 times fewer than their related traditional surfactants.[4] They work best when it comes to reducing water surface tension. Gemini surfactants have a major impact on solubilization procedures,[5] analytical separations,[6] enhanced oil recovery,[7] nanotechnology,[8] biotechnology,[9] and catalysis[10] and adsorption.[11] Y. Wang et al.[12] made brand new gemini surfactant by synthesis based on piperazine, epichlorohydrin and dimethylalkylamines. The structure of the synthesized gemini surfactants was verified using spectroscopic techniques, and their properties were analyzed through surface tension, specific electrical conductivity and

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steady-state fluorescence methods. Studies have demonstrated that these gemini surfactants exhibit a reduced CMC compared to other surfactants lacking a hydroxy group in the spacer, owing to the formation of hydroxy hydrogen bonds within the spacer. F.M.Abdelhafiz et al.[13] synthesized oligomeric surfactants based on piperazine. These oligomeric surfactants have higher capabilities than mono chain surfactants. They have a high antibacterial effect. Sh. Zhong et al.[14] synthesized a new gemini surfactant based on 1,4-dibenzylpiperizine and bromododecane. The optimal synthesis conditions of this gemini surfactant have been determined. Compared with the known mono-chain C_{12}TAB and gemini surfactant C_{12}-O-C_{12}, the synthesized gemini surfactant exhibits higher surface activity and effective antibacterial properties. C_8 chain nitrated benzene head group gemini surfactant also has effective antibacterial properties.[15] M. Nessim et al.[16] synthesized gemini surfactants based on 1,4-dimethylpiperizine and n-alkyl bromides. The CMC levels of synthesized gemini surfactants are smaller compared to mono-chain surfactants. A Japanese study[17] synthesized quaternary ammonium salt-based gemini surfactants with C_{12} alkyl chains and varying spacer groups, then compared their colloid-chemical parameters. It was established that the gemini surfactant containing a 1,4-dimethylpiperazine fragment in its spacer exhibited higher surface activity than the other gemini surfactants. According to the literature, it is known that surfactants with a hydroxy group head group have a higher effect than other surfactants.[18] Thus, the synthesis of piperazine-based surfactants with a hydroxy group and the investigation of their antibacterial properties hold both scientific and practical significance.

The presented article focuses on the synthesis of novel gemini surfactants derived from 1,4-bis(2-hydroxypropyl)piperazine and alkyl bromides, as well as the investigation of their surface activity, antibacterial, and anticorrosion properties.

2. Experimental section

2.1. Reagents

Piperazine (>99 % purity) and dodecyl bromide (98 % purity) were obtained from Alfa Aesar, Shore Road, Heysham. Propylene oxide (99.9 % purity) was sourced as a reactive product from Alfa Aesar, a Johnson Matthey Company. Heptyl bromide, octyl bromide, nonyl bromide and tetradecyl bromide (each with 98 % purity) were purchased from Alfa Aesar GmbH & Co KG.

2.2. Instruments

NMR spectra of ^{1}H and ^{13}C were noted on a Bruker Avance II+ 300 spectrometer (Ultra Shield™ Magnet) at an operating frequency of 300.13 MHz and 75.46 MHz dimethyl sulfoxide-d_6 was used as solvent. Spectrum BX model FT-IR spectrometer using KBr disks recorded IR spectra. Spectral data confirm the structure of the obtained substances. Using an LB-550 Particle Size Analyzer (HORIBA Scientific, Japan), the size distribution of aggregates generated in aqueous solutions of gemini surfactants was ascertained by DLS.

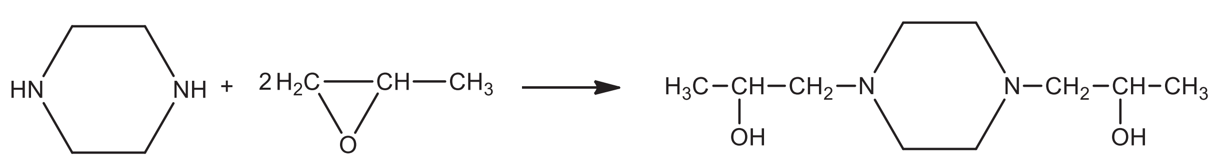
2.3. Synthesis of 1,4-bis(2-hydroxypropyl)piperazine

The synthesis was carried out using the propoxylation reaction of piperazine in 1:2 ratio. In a flask which is provided with a magnetic stirrer, supplemented propylene oxide to 0.1 mol of piperazine was 0.2 mol.[19] Carrying out of these syntheses was at room temperature in a methanol solvent under a nitrogen atmosphere. Heating the product at a moderate temperature (~45-50 °C) till forming mass of constant mixture leads to extracting unreacted propylene oxide and methanol from the reaction mixture. The software conversion was determined gravimetrically and was 95−96 %. The reaction scheme for the propoxylation of piperazine can be depicted as follows (see Scheme 1).

The resulting product is pasty, light yellow in color, and there is no smell of the original products. The degree of purity of the substance was determined by the method of thin layer chromatography. The degree of purity of the substance is 97 %.

2.4. Synthesis of cationic gemini surfactants

Six novel cationic gemini surfactants were synthesized based on 1,4-bis(2-hydroxypropyl)piperazine and various alkyl bromides. The synthetic



Scheme 1. Synthesis of 1,4-bis(2-hydroxypropyl)piperazine.

procedure involved slowly adding the corresponding n-alkyl bromides (0.06 mol) to a heated solution of 1,4-bis(2-hydroxypropyl)piperazine (0.03 mol). The reaction mixture was then refluxed for 18–20 h with continuous stirring. After the reaction, methyl cyanide was removed using a rotary evaporator, yielding a white-yellow substance. The crude products were extracted with diethyl ether and subsequently recrystallized from an acetone/ethyl acetate mixture. The reaction can be represented schematically as follows (see Scheme 2).

The yields of the synthesized gemini surfactants are as follows: C_7PiC_7 85 %, C_8PiC_8 85 %, C_9PiC_9 83 %, $C_{10}PiC_{10}$ 81 %, $C_{12}PiC_{12}$ 79 %, $C_{14}PiC_{14}$ 77 %. Gemini surfactants are brown solids, able to be dissolved easily in ethanol, acetone, isopropanol, heptane, chloroform, partly soluble in kerosene, CCl_4 and water. IR and ^1H NMR spectra were identifier of the structures of the synthesized gemini surfactants (see Figs. S1–S12 in Supplementary Material (https://ejp.researchcommons.org/cgi/viewcontent.cgi?filename=0&article=1081&context=journal&type=additional&preview_mode=1)). The degree of purity of surface-active substances was determined by the NMR spectroscopy method. It has been determined that the degree of purity of the substances is higher than 95 %.

2.5. Method of determination of surface tension

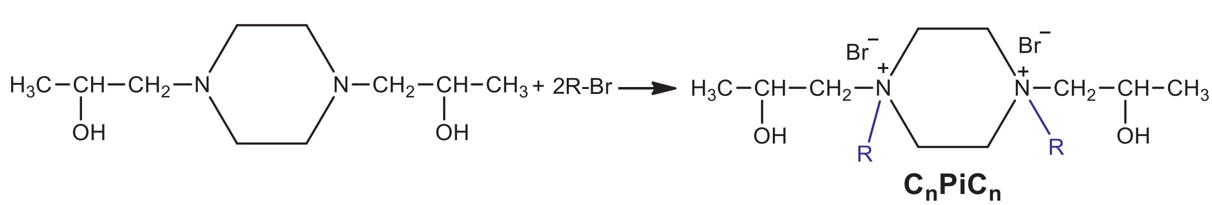
A KSV Sigma 702 tensiometer was used to measure surface tension. Using a water bath, the sample under measurement was maintained at a constant temperature inside a glass cell with two jackets. A cleaned 20 mL beaker containing 10 mL of the broth-free sample was set up on the tensiometer platform. To ascertain the value of surface tension (mN/m), wire ring of a platinum (or Pt/Ir) was dipped inside of the mixture and then gradually drawn via the liquid–air contact. For each sample, calculation of the surface tension values apparently was implemented as the mean of three readings, separated by 3 min. The platinum wire ring was flamed using a Bunsen burner and cleaned with water after each dimension. Prior to measurement 72.1 ± 0.2 mN/m was confirmed range for the deionized water surface tension.

2.6. Method of determination of specific electrical conductivity

An ANION 4120 conductometer was used to measure the surfactant solutions under study's specific electroconductivity. The temperature range for electroconductometric measurements is 0–100 °C, the relative error is less than ±2 %, and the measurement interval is 10^{-4}–10 S m^{-1}. The sample's solutions are made in thirty to 40 mL at a concentration range of 0.001–5%. Thermostating of solutions is implemented by water bath (0.1 °C). Dimensions are performed after agitating the liquids. The solution should be above highest point of electrodes and free of any gas bubbles when taking measurements. Measurement of the specific electroconductivity value is accomplished after submerging of electrodes in the solution for three to 5 min. The electrode cleaning by distilled water and drying processes are realized for following each measurement. The specific electroconductivity of distilled water needs to be between 1.2 and 1.8 μS cm^{-1}.

2.7. Test of antimicrobial properties

Laboratory strains of *Staphylococcus aureus, Bacillus anthracoides* gram-positive bacteriums, *Pseudomonas aeruginosa, Escherichia coli, Klebsiella pneumonia* gram-negative bacterias and *Candida albicans* fungi were taken to study the antimicrobial properties of gemini surfactants obtained by the disk-diffusion method. The indicated bacteria were cultured on meat-peptone agar, and the yeast fungus was cultured on Sabouraud's medium. For this method, suspensions were prepared from 24-h cultures of microorganisms, with a concentration of 10^8 microbial cells per 1 ml of suspension. Each prepared suspension of microorganisms was evenly distributed over the corresponding nutrient medium surface with the help of tampons. After that, each gemini surfactant, as well as their solutions, were soaked on sterile paper discs with a diameter of 6 mm and spread on the surface of nutrient media inoculated with microorganisms. 37 °C heated thermostat used for keeping prepared



R=C_7H_{15} (**C_7PiC_7**), C_8H_{17} (**C_8PiC_8**), C_9H_{19} (**C_9PiC_9**), $C_{10}H_{21}$ (**$C_{10}PiC_{10}$**), $C_{12}H_{25}$ (**$C_{12}PiC_{12}$**), $C_{14}H_{29}$ (**$C_{14}PiC_{14}$**).

Scheme 2. Synthesis of cationic gemini surfactants.

samples during 24 h and dimension were accomplished.

2.8. Test procedure for petroleum-collecting and petroleum-dispersing

Collection petroleum slicks property of the synthesized gemini cationic surfactants has been investigated using crude oil which taken from the oil field of Ramana located on the Absheron (Azerbaijan). On the distilled water surface and water of Caspian Sea (privately) in Petri plates, a little thickness coating (0.15–0.16 mm) of the petroleum was added together with the surfactant solution (0.02 g). $K=S_1/S$ is the formula for computing petroleum-collecting coefficient value (K), where S_1 represents the area of the initial petroleum film's surface and S represents accumulated petroleum's surface area (in a thicker spot). Measurements of the petroleum spot surface area and K value determination are done at predetermined intervals (τ) starting from the moment the surfactant is applied. "τ" characterizes the length of time the oil slick remains localized.

2.9. Study of the inhibitory properties of $C_{12}PiC_{12}$ gemini surfactant

Using one of the most modern devices, ACM GILL AC, the potential of the synthesized $C_{12}PiC_{12}$ surfactant to defend against corrosion was investigated. The device is made up of an HP Pavilion personal computer (CPU and display), a Potentiostat/Galvanostat model ACM GILL AC (UK), one 1000 ml glass piece, electrodes, a CO_2 tank, and installations that control the amount of CO_2 fed. Investigations of corrosion were implemented on electrodes made of steel C1018. Steel composition C 1018: 98.81–99.26 % Fe, 0.14–0.20 % C, 0.60–0.90 % Mn, 0.04 % P and 0.05 % S. In the experiments working and comparative electrode was a cylindrical electrode which is made of mild steel C1018 with an area of 7.9 cm^2. The Core Running software was used to transmit obtaining result by the potentiostat every 15 min. During the tests, property of corrosion potential of the studied electrode in the environment without an inhibitor and with an inhibitor stabilizes to the free potential throughout 60 min afterwards placing the electrodes in the environment. Electrochemical measurements were carried out continuously for 15–20 h at a temperature of 50 °C and 0.9 bar pressure in a medium containing a 1 % solution of NaCl in water saturated with carbon dioxide. The influence of the compound $C_{12}PiC_{12}$ as an inhibitor of the corrosion process in the electrode was investigated. The inhibitory properties of gemini surfactant were studied at various concentrations. The inhibitory protective effect of $C_{12}PiC_{12}$ was determined by the rate of corrosion appropriate to the 17th time of the experiment used item is steel C1018 electrode.

3. Results and discussion

3.1. Surface properties of gemini surfactants

The surface activity properties of the synthesized gemini surfactant aqueous solutions are determined at the air-water interface. According to the surface tension dimension, the isotherm of surface tension was constructed in coordinates γ-lnC (Figs. 1–2).

From these figures it is obvious that with increasing concentrations of surfactants, the value of surface tension decreases and then, when a certain concentration is reached, the surface tension tends to a stable value and stabilizes. On the graph, surfactant transition is corresponded by the break point abscissa from the molecularly dispersed state to micelles. This process occurs when the CMC is reached, which corresponds to the thermodynamic equilibrium of micelles with unassociated surfactant molecules. Determining the CMC allows one to draw conclusions about the structure of the solution and the shape of the micelles. The CMC was evaluated by the point corresponding to the break in the isotherm (γ_{CMC}). Gemini surfactants CMC values are given in Table 1. As evident from the above data, the CMC values ware evaluated for surfactants C_nPiC_n by the tensiometric and conductometric methods vary, respectively, in the range of

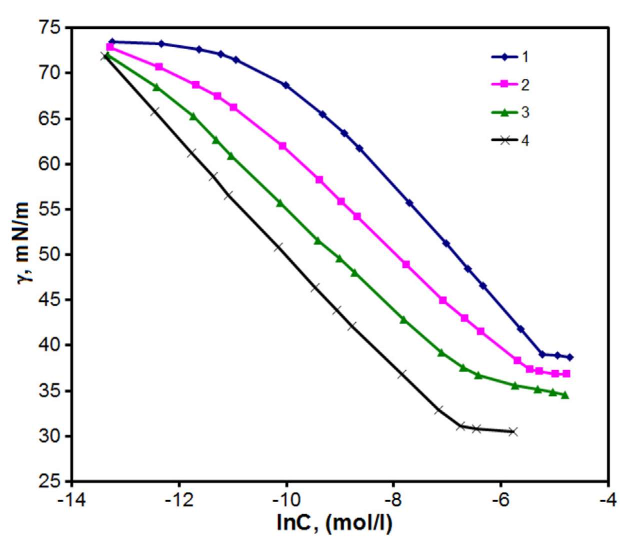


Fig. 1. Surface tension versus-ln conc. of C_nPiC_n at 25 °C (1- C_7PiC_7, 2- C_8PiC_8, 3- C_9PiC_9, 4- $C_{10}PiC_{10}$).

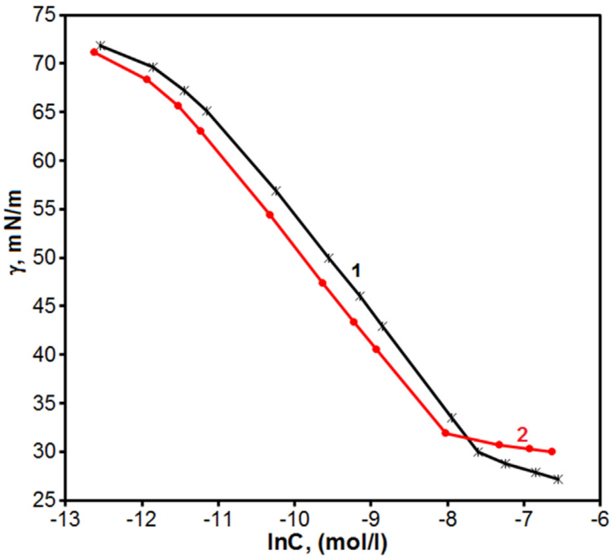


Fig. 2. Surface tension versus-ln conc. of C_nPiC_n at 25 °C (1- $C_{12}PiC_{12}$, 2- $C_{14}PiC_{14}$).

0.32–5.35 mM and 0.33–5.58 mM. As length of the alkyl chain radical of the alkyl bromide growths from C_7PiC_7 to $C_{14}PiC_{14}$, the CMC decreases. 1,4-dialkyl-1,4-dimethyl-l-piperazine-1,4-diium bromide[16] class surfactants with a methyl fragment instead of a 2-hydroxypropyl fragment within the head groups, while the C_{12} alkyl chain surfactant CMC value is 2 mM, and the CMC value of the surfactant with the same chain length that we have synthesized is 0.5 mM. In contrast those with C_{14} indicates that CMC of 1,4-ditetradecyl-1,4-dimethyl-l-piperazine-1,4-diium bromide is smaller than that of our synthesized surfactant. It is apparent from the Table 1, measured CMC of mono-chain surfactants accompanied by N-(2-hydroxypropyl)piperidinium[20] head group is higher than the gemini surfactants we have synthesized. The comparison of CMCs for similarly structured 1,4-dialkyl-1-(2-hydroxypropyl)-4-ethyl piperazine-1,4-diium bromide[21] type gemini surfactants reveals that the CMC values of the synthesized symmetrically structured gemini surfactants are smaller. This observation is attributed to two primary factors: the larger spatial volume occupied by the isopropylol group compared to the ethyl group, and the formation of an ordered structure facilitated by intermolecular hydrogen bonding between the isopropylol groups.

The calculation of the adsorption property of gemini surfactants is accomplished by the Gibbs equation at the solution-air interface,[22] substituting into it the dγ/dlnC value determined by the graphical method:

$$\Gamma = -\frac{1}{nRT}\cdot\frac{d\gamma}{d\ln C}$$

Where universal gas constant is referred by R and unit is $J\cdot mol^{-1}\cdot K^{-1}$, dγ/dlnC refers slope angle of the dependence of γ on lnC at the case of constant temperature -T, characterizes the surface activity. The top point of value that adsorption can reach (Γ_{max}) corresponds to the dense packing of adsorbed molecules in a monolayer. Using the values of Γ_{max}, you can determine the size of the molecules of the adsorbed substance.

The following formula was used to calculate the minimum cross-sectional areas in the synthesized gemini surfactants polar group:[22]

$$A_{min} = \frac{1}{\Gamma_{max}\cdot N_A}$$

where N_A refers Avogadro's number ($6.023\cdot 10^{23}$).

Table 1 shows the Γ_{max} and A_{min} values of the synthesized gemini-surfactants. T is apparent from the table, the value of Γ_{max} decreases as the alkyl chain length changes between C_7–C_9, while the value of A_{min} increases. Lengthening of alkyl groups from C_9 to C_{14}, contributes increasing of Γ_{max}, decreasing of A_{min}. In 1,4-dialkyl-1,4-dimethyl-piperazine-1,4-diium bromide class gemini surfactants,[16] the length of the alkyl chain from C_{12} to C_{16}

Table 1. Surface parameters of cationic gemini surfactants.

Surfactants	β	CMC[a] × 10^3, $mol\cdot dm^{-3}$	CMC[b] × 10^3, $mol\cdot dm^{-3}$	Γ_{max} × 10^{10}, $mol\cdot cm^{-2}$		A_{min} × 10^2, nm^2		pC_{20}	γ_{CMC}, $mN\cdot m^{-1}$	π_{CMC}, $mN\cdot m^{-1}$	ΔG_{mic}, $kJ\cdot mol^{-1}$	ΔG_{ad}, $kJ\cdot mol^{-1}$
				n = 2	n = 3	n = 2	n = 3					
C_7PiC_7	0.36	5.35	5.58	1.294	0.863	128.2	192.4	3.30	39.0	33.0	−39.4	−42.8
C_8PiC_8	0.35	4.25	4.26	1.130	0.753	147.0	220.4	3.61	37.3	34.7	−39.9	−43.8
C_9PiC_9	0.31	1.62	1.63	1.121	0.748	148.1	222.1	4.13	36.7	35.3	−41.9	−45.9
$C_{10}PiC_{10}$	0.29	1.16	1.14	1.408	0.939	117.9	176.8	4.54	31.1	40.9	−42.2	−46.0
$C_{12}PiC_{12}$	0.27	0.50	0.51	1.928	1.285	86.1	129.2	4.32	30.0	42.0	−44.3	−47.4
$C_{14}PiC_{14}$	0.25	0.32	0.33	1.978	1.319	83.9	125.9	4.38	31.9	40.1	−44.7	−47.6

[a] The surface tension method is used for determining the CMC.
[b] The electroconductivity method is used to determine the CMC.

contribute an increase in the value of Γ_{max}, and a decrease in the value of A_{min}. In mono-chain N-(2-hydroxypropyl) piperidinium head group surfactants,[20] increasing of alkyl chain length from C_9 to C_{12} leads to increasing the value of Γ_{max}, and decreases when it is extended from C_{12} to C_{14}.

Following formula indicates calculation of pC_{20} value, which defines the cost-effectiveness of surfactant use and characterizes the concentration as surface tension property of surfactant solutions declines by 20 mN/m:[22]

$$pC_{20} = -\lg C(-\Delta\gamma = 20)$$

The higher the pC_{20} value, this surfactant is adsorbed more effectively on the surface and reduces surface tension more efficiently at low concentrations. Following formula was used to calculate the efficiency of reducing surface tension (π_{CMC}) of new synthesized gemini surfactants in watery solutions at the water-air interface:[22]

$$\pi_{CMC} = \gamma_0 - \gamma_{CMC}$$

where γ_{CMC} refers surface tension of the solution with CMC, surface tension is referred by γ_0 in the absence of a surfactant.

In Table 1 two properties the adsorption efficiency (pC_{20}) and the effectiveness of surface tension reduction (π_{CMC}) are listed according to synthesized gemini surfactants. It is apparent from the table, as the length of the alkyl chain increases, the adsorption efficiency value increases, while increase is occurred in the effectiveness of surface tension reduction with the length of the chain from C_7 to C_{12}, and after C_{12}, a decrease is observed.

3.2. Investigation of the specific electrical conductivity of gemini surfactants

The conductometric method was used for determination of property of the specific electrical conductivity of watery solutions of various concentrations of synthesized gemini surfactants. On the basis of receiving values, the following constructed graphs was about change in specific electrical conductivity depending on the concentration (Figs. 3–5). It is obvious from the graphs, as the concentration increases, the values of the specific electrical conductivity increase. In this linear dependence, observed breaking point of the graph was noticed. The concentration appropriate to the break point of the straight line is equal to the CMC. The surfactant dissociation degree (α) counterion was calculated on the basis of the ratio of the angle coefficient (S_2) of the straight line at concentrations higher than CMC to the angle coefficient (S_1) of the straight line at concentrations lower than CMC:[22]

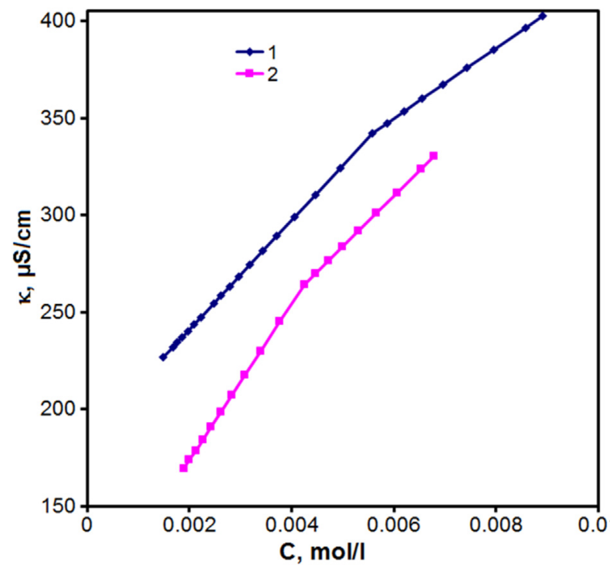


Fig. 3. Specific electrical conductivity versus concentration of C_7PiC_7 (1) and C_8PiC_8 (2) in aqueous solution at 25 °C.

$$\beta = 1 - \alpha = S_2/S_1$$

where β refers the binding degree of the counter ion.

The degrees of counterion binding of gemini surfactants are shown in Table 1. As able to be seen from Table 1, in gemini surfactants lengthening of the alkyl chain leads to decreases the value of β. As can be seen from the table, the degree of counterion

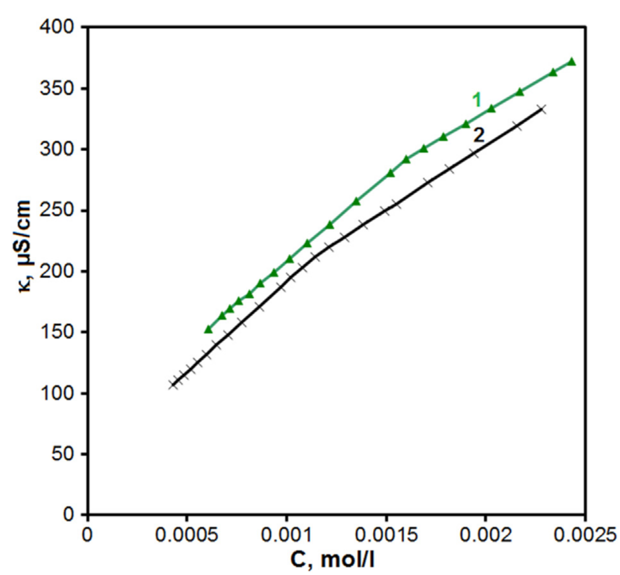


Fig. 4. Specific electrical conductivity versus concentration of C_9PiC_9 (1) and $C_{10}PiC_{10}$ (2) in aqueous solution at 25 °C.

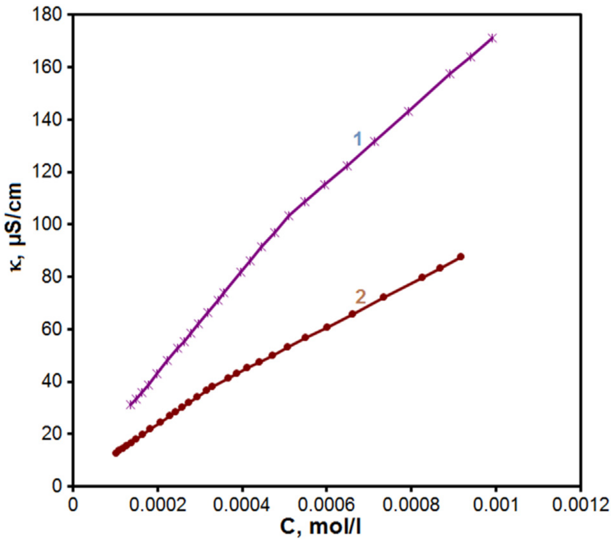


Fig. 5. Specific electrical conductivity versus concentration of $C_{12}PiC_{12}$ (1) and $C_{14}PiC_{14}$ (2) in aqueous solution at 25 °C.

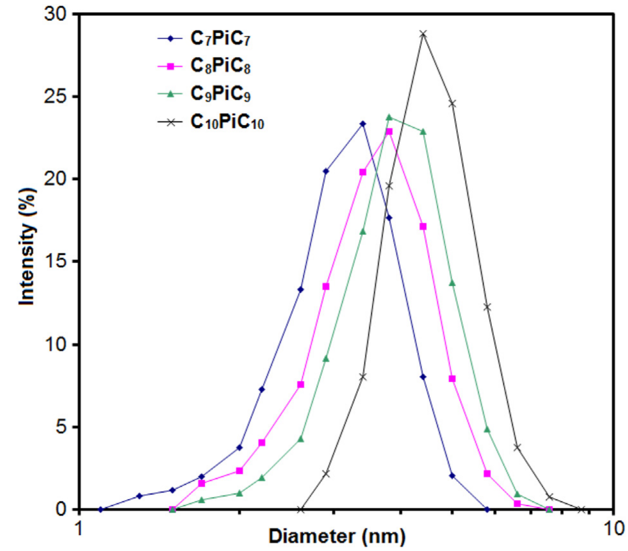


Fig. 6. Size distribution diagram of aggregates formed by gemini surfactants in aqueous solution.

binding for the synthesized gemini surfactants is higher than that observed for gemini surfactants of the similar 1,4-dialkyl-1-(2-hydroxypropyl)-4-ethyl piperazine-1,4-diium bromide type.[21] The likely reason for this in the synthesized gemini surfactants is the presence of two hydroxyl groups per headgroup. These hydroxyl groups can participate in significant hydrogen bonding with the bromide counterions and modify the local electrostatic environment around the charged centers, leading to stronger counterion association.

3.3. Size of gemini surfactants aggregates in aqueous solution

Fig. 6 illustrates the size scale diagram of cationic gemini surfactants aggregates synthesized on the basis of C_7-C_{10} alkyl bromides in aqueous solution at CMC concentrations. It is apparent from the picture, the size of aggregates formed by the synthesized gemini surfactants in watery solution at CMC is less than 10 nm. Aggregate sizes increase from 3.4-nm to 4.4-nm as alkyl chain length increases from C_7 to C_{10} in gemini surfactants. In formed gemini surfactants with chain length C_{12}–C_{14} in water the size of aggregates at CMC concentrations also fall within that interval.

3.4. Gibbs free energy changes of micellar formation and adsorption processes

Following formula indicates calculation Gibbs free energy change (ΔG_{mic}) of micellization for cationic gemini surfactants:[22]

$$\Delta G_{mic} = RT(0.5+\beta) ln\, X_{CMC} - 0.5RTln2$$

where CMC unit is mol/L, β is the counterion binding degree, and 1 L of water gives 55.5, which is equivalent to water 55.5 mol at 298 K.

Following equation is used to calculate Gibbs free energy change in adsorption process (ΔG_{ad}) at the water-air interface:[22]

$$\Delta G_{ad} = \Delta G_{mic} - 0.6023\, \pi_{CMC} A_{CMC}$$

Table 1 provides data about the values of ΔG_{mic} and ΔG_{ad} in the gemini surfactants. It is observed that conventional Gibbs free energies have negative values for both the adsorption and micelle production processes. It indicates that micellization and adsorption processes happen spontaneously when these gemini surfactants are present. Conversely, higher negative values of ΔG°_{mic} indicate that micelle production comes before the adsorption process. In Table 1 ΔG°_{mic} and ΔG°_{ad} values show that when the alkyl chain lengthens, they decrease. This chain's lengthening promotes micelle formation and hydrophobic contact between the alkyl chains. The Gibbs free energy values for both micelle formation and adsorption processes are smaller than those of similarly structured 1,4-dialkyl-1-(2-hydroxypropyl)-4-ethyl piperazine-1,4-diium bromide-type gemini surfactants.[21] Consequently, replacing the ethyl group in the hydrophilic part with an isopropyl group facilitates both adsorption and micelle formation processes.

3.5. Anticorrosion properties of $C_{12}PiC_{12}$ gemini surfactant

As evidenced in the literature,[23,24] the corrosion inhibitory effect of surfactants generally increases with longer alkyl chain lengths. Consequently, the corrosion inhibitory abilities of the synthesized gemini surfactants with longer alkyl chains were investigated. However, due to its poor solubility in saltwater, the $C_{14}PiC_{14}$ gemini surfactant could not be tested for its corrosion inhibitory properties. Therefore, only the $C_{12}PiC_{12}$ gemini surfactant underwent corrosion inhibition testing. The inhibitory effect of the $C_{12}PiC_{12}$ gemini surfactant was determined by measuring the rate of metal corrosion in a CO_2 environment. Fig. 7 illustrates the variations in corrosion rate for the inhibitors under investigation at various concentrations.

The following formulas have been used to compute the surface coating (θ) and inhibition efficiency (η%):[25]

$$\eta\ \% = \frac{CR_0 - CR_i}{CR_0} \times 100$$

$$\theta = 1 - \frac{CR_i}{CR_o}$$

where CR_0 − corrosion rate without an inhibitor and in the participating of inhibitor corrosion rate is CR_i. As follows from the presented figures, in the presence of inhibitors, the corrosion rate is sharply decreased. Increasing of inhibitor concentration leads to decreasing of corrosion rate and the top percentage of inhibition efficiency is 98.2 % at 50 ppm after 17 h action. This tendency may arise from the fact that surface coating and adsorption increase with concentration, there by shielding a surface from the aggressive medium's action.[26,27] The corrosion rate values, efficiency of inhibition, and coating of the metal surface have all been calculated at 50 °C in various concentration participating or absence. Data demonstrating the inhibitor concentration dependence on corrosion rate, inhibition efficiency, and surface coating. As the reagent concentration increases, the corrosion rate (CR_i) decreases and the inhibition efficiency (η%) and surface coating (θ) increase. This indicates that molecules adsorption on the surface of metal, which prevents the mild steel samples from decaying, can be thought of as the inhibitor braking action against mild steel corrosion. The evaluation of surface coverage rates (θ) in CO_2-which is used to saturate 1% NaCl solution at changing inhibitor doses has been conducted and using dimensions are linear polarization resistance corrosion rates. A number of adsorption isotherms, for instance the Frumkin, Temkin, Freundlich, and Langmuir isotherms, were tried to match θ values to standard isotherms.[25] To date, nevertheless, the gemini surfactant studied and adsorbed on a mild steel surface gave the best fit when the Langmuir isotherm was assumed.[28] This indicates that since the Langmuir model describes monolayer adsorption, the adsorption of gemini surfactant on the metal surface in

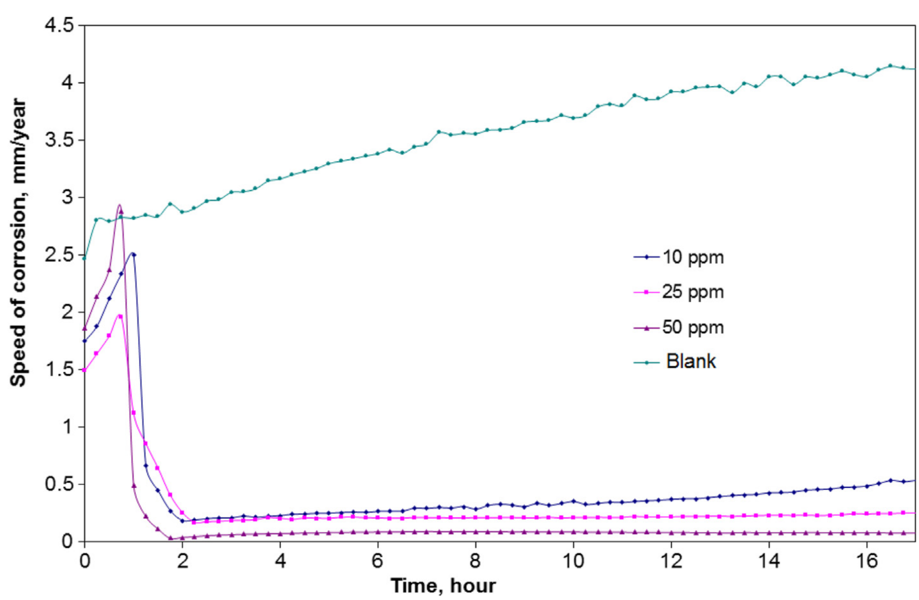


Fig. 7. Graph of the corrosion rate versus time of an electrode made of C1018 steel in 1 % NaCl solutions was saturated by CO_2 in the participation of $C_{12}PiC_{12}$.

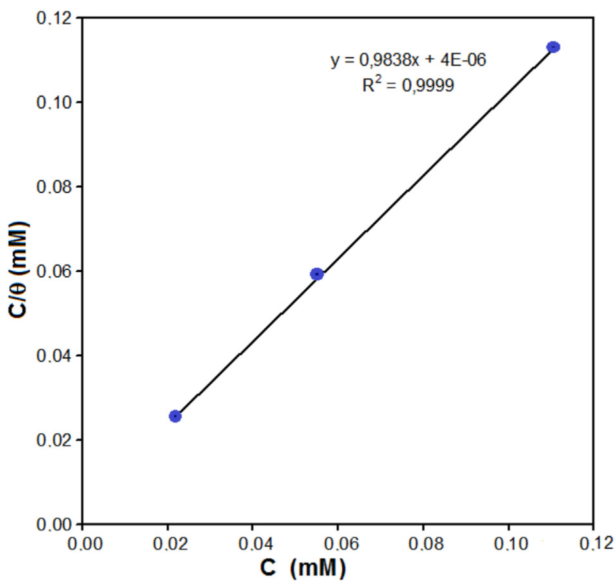


Fig. 8. Langmuir adsorption isotherm fitting of mild steel corrosion rate data in CO_2 saturated brine with different $C_{12}PiC_{12}$ concentrations at 50 °C.

CO_2-saturated fluid is most likely monolayer adsorption. The following equations[28] describe the Langmuir adsorption isotherm:

$$\frac{C_{inh}}{\theta} = C_{inh} + \frac{1}{K_{ads}}$$

the inhibitor concentration is referred as C_{inh}, surface covered as θ and K_{ads} refers adsorption coefficient which is measured from the plots and is connected to the adsorption standard free energy, ΔG^0_{ads} by:[25]

$$\Delta G^0_{ads} = -RTln(55.5K_{ads})$$

By measuring the corrosion quantity of linear polarization resistance in CO_2-saturated brine, the surface coverage (θ) was calculated at various inhibitor doses. The dependence of C_{inh}/θ on C_{inh} of the gemini surfactant studied is displayed in Fig. 8, and the plot of the inhibitor is linear, with a R^2 – correlation coefficient of 0.9999. This shows that the Langmuir adsorption isotherm is followed by the inhibitor's adsorption on the surface of mild steel in the studied conditions. Table 2 displays the computed values for K_{ads} and ΔG^0_{ads}.

On the mild steel surface the adsorption process of the inhibitor is spontaneously occurred, as indicated by the negative values of ΔG^0_{ads}. The general consensus is that ΔG^0_{ads} values up to -20 kJ mol^{-1} are considered physisorption, where through the electrostatic interaction between the charged metal and the charged molecules is acted inhibition. Values around -40 kJ mol^{-1} or smaller are considered chemisorption, where the inhibition acts through charge sharing or a transfer from the inhibitor molecules to the metal surface to form a covalent bond.[29,30] Table 2 makes it evident that our measurement's ΔG^0_{ads} value is -44.17 kJ mol^{-1}. These findings suggest that, at the temperature under study, typical chemisorption is the adsorption mechanism of gemini surfactant on mild steel in CO_2 saturated brine. Chemisorption of gemini surfactant molecules can occur due to the formation of bonds between the electron pair present in N and O atoms of the inhibitor and the d orbitals of iron atoms.

3.5. Antimicrobial properties

Cationic surfactants, including gemini surfactants, exhibit antimicrobial activity mainly by targeting the negatively charged elements of microbial cell membranes.[31] Their interaction with these membrane components results in membrane disruption, increased permeability, leakage of internal cellular contents, and eventually, cell death. The antimicrobial effectiveness is influenced by the length of the alkyl chain, with an optimal chain length providing the best activity. This optimal length allows the hydrophobic tail to efficiently penetrate and destabilize the microbial lipid bilayer without becoming overly hydrophobic, which could reduce solubility or promote aggregation, thus hindering its action. Disk diffusion method investigated the antimicrobial properties of the synthesized gemini cationic surfactants. The receiving consequences are shown in Table 3. As it is apparent from the Table 3, $C_{14}PiC_{14}$ gemini surfactant has a better effect against *Candida albicans* fungus and *Staphylococcus aureus*

Table 2. The mild steel electrode corrosion characteristics in CO_2 saturated brine, both in the presence and absence of $C_{12}PiC_{12}$ surfactant concentrations at 50 °C.

Inhibitor	Conc, ppm	Corrosion rate, mm/year	Inhibition efficiency, η, %	Degree of surface coverage, θ	Adsorption coefficient, K_{ads}	Gibbs energy, ΔG^0_{ads} kJ mol^{-1}
Without inhibitor	–	4.13	–	–		–
$C_{12}PiC_{12}$	10	0.54	86.92	0.8692	25.08	−44.17
	25	0.25	93.95	0.9395		
	50	0.074	98.21	0.9821		

Table 3. Results of investigation of antimicrobial properties of C_nPiC_n gemini surfactants.

Microbes	C_7PiC_7	C_8PiC_8	C_9PiC_9	$C_{10}PiC_{10}$	$C_{12}PiC_{12}$	$C_{14}PiC_{14}$
Candida albicans	10	13	16	0.9	13	19
Staphylococcus aureus	21	22	24	15	14	26
Escherichia coli	14	11	0.9	0.9	0.8	0.9
Pseudomonas aeruginosa	0.8	0.8	0.8	0.8	10	12
Klebsiella pneumoniae	13	0.8	10	10	0.9	11
Bacillus anthracoides	15	15	19	18	0.9	0.8

and *Pseudomonas aeruginosa* bacteria. Short alkyl chain (C_7PiC_7 and C_8PiC_8) gemini surfactants can negatively affect the development of *Escherichia coli* bacteria, and C_7-C_{10} chain gemini surfactants can affect *Bacillus anthracoides* bacteria. C_9PiC_9 gemini surfactant is more active than them. C_7PiC_7 gemini surfactant against *Klebsiella pneumoniae* bacteria is partially superior to other substances. The observed patterns-such as the broad-spectrum activity of $C_{14}PiC_{14}$, the increased effect of shorter chains on *Escherichia coli*, and the peak activity of C_9PiC_9 against *Bacillus anthracoides* -align with the well-established principle that the antimicrobial efficacy of cationic surfactants is closely tied to the interplay between electrostatic attraction from the positively charged head group and hydrophobic interactions from the alkyl chains with microbial membranes.

3.6. Effect of gemini surfactants on oil slick

The consequence of laboratory investigation of petroleum-collecting and dispersing ability are given in Table 4. The studies were implemented on the sample of a thin oil film (thickness ~0.165 mm) on the surface of waters with differing mineralization degree. Gemini surfactants were used in the form of 5 % aqueous solutions. As can be seen from the Table 4, gemini surfactants C_7PiC_7 and C_8PiC_8, obtained on the basis of heptyl bromide and octyl bromide, do not have a petroleum-collecting effect. This is possibly due to the short hydrocarbon chain.

Table 4. Petroleum collecting and petroleum dispersing properties of C_nPiC_n surfactants.

Surfactants	Sea water		Distilled water	
	τ, hour	K (K_D,%)	τ, hour	K (K_D,%)
C_7PiC_7	0–120	Not valid	0–120	Not valid
C_8PiC_8	0–120	Not valid	0–48	Not valid
C_9PiC_9	0	79.9 %	0	3.7
	1	3.1	1	3.1
	4	Spilled	4	Spilled
$C_{10}PiC_{10}$	0–120	91.1 %	0–48	5.9
			49–120	3.6
$C_{12}PiC_{12}$	0–120	87.3 %	0–120	87.3 %
$C_{14}PiC_{14}$	0	2.2	0	4.8
	1	6.9	1	19.4
	4–120	95.6 %	4–120	95.6 %

Starting with nonyl bromide-based gemini surfactants, a petroleum-collecting and petroleum-dispersing effect is observed, which rises with the alkyl chain elongation. Thus, the maximum petroleum-dispersing efficiency in Sea and distilled water (K_D = 95.6 %) is demonstrated by $C_{14}PiC_{14}$ gemini surfactant based on tetradecyl bromide. The alkyl chain length dictates the surfactant's hydrophobicity, its CMC, and its efficiency in adsorbing at the oil-water interface, all of which directly impact its effectiveness in collecting and dispersing petroleum.

Conclusions

Novel cationic gemini surfactants were synthesized using 1,4-bis(2-hydroxypropyl)piperazine and (C_7-C_{14}) alkyl bromides. The surface activity properties of these substances were determined by measuring surface tension and specific electrical conductivity. A decrease in both the CMC and the β parameter was observed with an increase in the alkyl chain length of the gemini surfactants. This trend led to an enhancement in their antibacterial and petroleum-collecting properties. Based on DLS measurements, it was determined that these gemini surfactants form aggregates with diameters smaller than 10 nm in water. An increase in the alkyl chain length of the gemini surfactants from C_7 to C_{10} resulted in an insignificant increase in aggregate diameter. Due to its solubility in brine and lower CMC, the synthesized gemini surfactant derived from dodecyl bromide was investigated for its inhibitory effectiveness against mild steel corrosion in a CO_2-saturated brine environment. It was established that this surfactant is effective even at low concentrations. At a concentration of 100 ppm, the corrosion inhibition efficiency reached 98.2 %.

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Ethics information

No human participants or animals were involved in this study; ethical approval was not required.

Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

R.A. Rahimov: Supervision, Writing – review & editing. **G.A. Ahmadova**: Resources, Writing – original draft. **Kh.A. Mammadova**: Resources, Writing – review & editing. **K.Sh. Tagiyeva**: Resources, Writing – original draft. **F.M. Vekilova**: Investigation. **S.A. Muradova**: Data Curation. **U.J. Yolchuyeva**: Investigation, Data curation, Methodology. **A.V. Gurbanov**: Formal analysis. **N.I. Mursalov**: Methodology, Writing – review & editing. **F.I. Zubkov**: Formal analysis.

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