REPUBLIC OF AZERBAIJAN

On the rights of the manuscript

ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

SYNTESIS AND INVESTIGATION OF SURFACTANTS ON THE BASIS OF HIGH ALIPHATIC AMINES CONTAINING HYDROXYL GROUP AND ALKYL HALIDES

Speciality: 2314.01 – Petrochemistry

Field of science: Chemistry

Applicant: **Seyid Zeynab Fatdakh Hashimzade**

Baku – 2021

The work was performed at the laboratory "Surface-active reagents and preparations" of the Institute of Petrochemical Processes named by acad. Y.H. Mammadaliyev of National Academy of Sciences of Azerbaijan

Scientific supervisor: -Doctor of chemical sciences, associate professor
Ravan Abdullatif Rahimov

Official opponents: -Doctor of chemical sciences, professor
Qasım Zulfali Huseynov
-Doctor of chemical sciences, professor
Sevinj Abdulhamid Mammadkhanova
-Doctor of philosophy on chemistry, associate professor
Nazila Feyruz Sadiyeva

Dissertation council ED 1.16 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating at Institute of Petrochemical Processes of the National Academy of Sciences of Azerbaijan

Chairman of the Dissertation Council: Doctor of chemical sciences, academician
Vagif Majid Farzaliyev

Scientific Secretary of the Dissertation Council: Doctor of chemical sciences, associate professor
Lala Mahammad Afandiyeva

Chairman of the Scientific Seminar: Doctor of chemical sciences, associate professor
Fuzuli Akbar Nasirov

GENERAL DESCRIPTION OF THE WORK

The current state of the problem and its relevance. Recently, the field of application of surfactants is expanding. Since the properties of surfactants depend on the nature of hydrophilic and hydrophobic groups, it is possible to change their properties in a purposeful way by changing their structure[1-2]. While conventional surfactants have one hydrophilic and one hydrophobic group, gemini surfactants have two hydrophilic and two hydrophobic groups, and they are connected to each other by a functional group. Such surfactants are called gemini surfactants in the world literature.

Gemini surfactants have superior properties compared to mono-alkyl chain surfactants. Such that, they have a lower critical micelle concentration (CMC) than the corresponding mono-alkyl chain surfactants; are more effective in reducing water surface tension than the corresponding monomer surfactants; and aqueous solutions of some short-chain gemini surfactants have high viscosity properties even at low concentrations, low Krafft point (or temperature, better solubility), foam-forming and emulsion-forming ability.

Some gemini surfactants have the same production cost as conventional single-chain surfactants, which allows them to be widely used in industry and agriculture. The literature mainly emphasizes the biological importance of gemini surfactants. Some of them are suitable for skin contact due to their antimicrobial and low critical micelle-formation properties and are environmentally safe. In this regard, the presented dissertation is devoted to a topical issue - the effective synthesis and study of a novel class of surfactants containing isopropylol groups in the hydrophilic part.

---

[1] Asadov, Z.H. Surface activity, adsorption, and micellization parameters of ammonium surfactants containing a hydroxyethyl and hydroxypropyl head group / Z.H. Asadov, G.A. Ahmadova, R.A. Rahimov // Journal of Chemical and Engineering Data, -2017. Vol. 62(10), - p. 3297-3305.[2] Asadov, Z.H. Synthesis and Characteristics of Dodecyl Isopropylolamine and Derived Surfactants / Z.H. Asadov, R.A. Rahimov, G.A. Ahmadova // Journal of Surfactant and Detergent, -2016. Vol. 19, -p. 145-153

The object and the subject of the research. The main object of research is the synthesis of cationic gemini surfactants from the interaction of amino alcohol obtained from oxypropylation of ethylenediamine (EDA) with propylene oxide (PO) and from the interaction of amino alcohols obtained from oxypropylation of alkylamines with dibromoalkanes. The subject of the research is the study of petrocollection, petrodispersion, bactericidal and antimicrobial properties of gemini cationic surfactants, which differ in the number of alkyl chains, spacers and isopropylol groups in the hydrophilic part.

The purpose and objectives of the research. Synthesis of gemini cationic surfactants with different lengths of alkyl chains, different lengths of spacer chains, containing mono- and diisopropylol fragments in the polar group, based on haloalkanes (C_7-C_{10}, C_{12}, C_{14}), aliphatic diamines (EDA and hexamethylenediamine (HMDA)) and PO, as well as dihaloalkanes (dibromoethane, dibromopropane, dibromobutane, dibromopentane), aliphatic amines (C_8, C_9, C_{12}, C_{16}, C_{18}) and PO; determination of their colloid-chemical parameters and determination of more effective petrocollecting and antimicrobial surfactants by studying their structure-property dependences based on the structure of surfactants.

Investigation methods. In the research work, synthesis of novel gemini surfactants in the laboratory, their analysis by conductometric and tensiometric methods, confirmation of their structure by infrared (IR) and nuclear-magnetic resonance (NMR) spectroscopy, measurement of the diameter of aggregates by the method of dynamic light scattering (DLS), bactericidal activity against sulfate-reducing bacteria (SRB), antimicrobial properties by disk diffusion test, oil accumulation and oil dispersion properties were studied.

The main provisions submitted to the defence:

– Relevant gemini cationic surfactants were synthesized by reactions of diamines, which contain hydroxyl groups and are obtained by the interaction of EDA and HMDA with PO in ratios of 1:2 and 1:4 moles, with nonyl-, dodecyl- and tetradecyl bromide; the surface activity and specific electrical conductivity of their aqueous solutions at different

(10°C, 20°C, 30°C and 40°C) temperatures at the water-air boundary were studied and their colloid-chemical parameters (critical micelle concentration (CMC), critical premicelle concentration (CPC), maximum adsorption (Γ_{max}), the minimum surface area occupied by the polar group (A_{min}), adsorption efficiency (pC_{20}), surface pressure (π)) were calculated;

– Gemini surfactants were synthesized based on the reaction of isopropylolalkylamines, obtained by the interaction of octylamine (OA), nonylamine (NA), dodecylamine (DDA), hexadecylamine (HDA) and octadecylamine (ODA) with PO in ratios of 1:1 and 1:2 moles, with dibromopentane. Specific electrical conductivity values of gemini surfactants, surface activity indicators of their aqueous solutions at water-air boundary and diameter of aggregates by DLS method were determined;

– Based on the reaction of amines, which contain hydroxyl groups and are obtained by the interaction of DDA and PO in ratios of 1:1 and 1:2 moles, with 1,2-dibromoethane, 1,3-dibromopropane, 1,4-dibromobutane and 1,5-dibromopentane, gemini cationic surfactants with different lengths of the spacer chain were synthesized; the dependence of colloidal chemical parameters, which were calculated on the basis of surface activity and specific electrical conductivity of aqueous solutions of surfactants, on the length of the spacer chain was determined;

– Novel cationic gemini surfactants were synthesized by the reaction of diamines, which contain hydroxyl groups and are obtained by the interaction of EDA with PO in the ratios of 1:2 and 1:4 moles, with heptyl-, octyl-, nonyl- and decyliodide; and the surface activities of surfactants were determined;

– Petroleum-collecting, petroleum-dispersing and bactericidal properties of synthesized gemini surfactants were revealed.

Scientific novelty of the investigation. Here for the first time:

– Gemini cationic surfactants were synthesized by the interaction of alkyl bromides (C_9, C_{12}, C_{14}) and alkyl iodides (C_7–C_{10}) with oxypropylated EDA;

– Gemini surfactants were synthesized by the interaction of dibromopentane with isopropylol and diisopropylolalkylamines (C_8, C_9, C_{12}, C_{16}, C_{18});
– Gemini cationic surfactants were synthesized by the interaction of dibromoalkanes (dibromoethane, dibromopropane, dibromobutane, dibromopentane) with dodecylisopropyl and dodecyldiisopropylamine;
– Relevant amino alcohols were obtained by oxypropylation of HMDA with PO;
– Gemini surfactants were synthesized from the interaction of amino alcohols obtained on the basis of HMDA with alkyl bromides (C_9, C_{12}, C_{14}).

Theoretical and practical value of the work. The synthesis and study of gemini cationic surfactants are more important than mono-alkyl surfactants. Gemini surfactants are widely used in the detergent and cleaning reagents industry, food industry, medicine, cosmetology, corrosion protection of metals, catalysis and mainly in the oil industry, waste treatment and other fields. The synthesized gemini surfactants have antimicrobial properties against various bacteria (*Staphylococcus aureus* (gram-positive), *Pseudomonas aeruginosa* (gram-negative), *Escherichia coli* (gram-negative)) and a fungus (*Candida albicans*). At the same time, they can be used as antimicrobials and petroleum-collecting, as they have the ability to remove thin layer of oil on the surface of the water. It is possible to further improve the properties of surfactants by changing the length of their hydrophilic group and the nature of their hydrophobic group.

Personal presence of the author. The results mentioned in the dissertation were obtained by the author. Problem statement, experiments and tests, analysis, systematization and generalization of results were carried out with the participation of the author.

Approbation and application of the work. The results of the dissertation work were reported and discussed at the following conferences: II International Scientific Conference of Young Researchers dedicated to the 95th anniversary of National Leader Heydar Aliyev, Baku, 2018; Republic Scientific and Technical

Conference of Students and Young Researchers on “Youth and Scientific Innovations”, dedicated to the 95th anniversary of the National Leader of the Azerbaijani people, Heydar Aliyev, Baku, 2018; International Scientific-Practical Conference dedicated to the 110th anniversary of Academician Vahab Aliyev, Baku, 2018; "Chemistry, chemical technology and ecology: science, production, education" Materials of the international scientific-practical conference and the school of young scientists, Makhacqala, 2018; I International Science and Technology Conference, Baku, 2018; III International Scientific Conference of Young Researchers dedicated to the 96th anniversary of the National Leader of the Azerbaijani people Heydar Aliyev, Baku, 2019; The International Scientific Conference “Actual Problems of Modern Chemistry,” dedicated to the 90th anniversary of the Academician Y.H.Mammadaliyev, Institute of Petrochemical Processes, Baku, 2019; 1st-İnternational Conference on Noncovalent İnteractions, Lissabon, 2019; Scientific Conference on the “Actual Problems of Modern Natural Sciences”, Ganja, 2020.

22 scientific works on the topic of the dissertation have been published. 8 of them are articles and have been published in the Journal of Chemical & Engineering data (USA), Colloids and Surfaces A: Physicochemical and Engineering Aspects (Elsevier, Netherlands), Journal of Molecular Liquids (Elsevier, Netherlands), Ecological Chemistry (Russia), Journal of Baku Engineering University (Baku), Young Researcher (Baku) and Journal of Surfactants and Detergents (USA).

Name of the organization where the dissertation work was performed. The dissertation work was carried out in the “Surfactants and preparations” laboratory of the “Monomers, oligomers and catalysis” department of the Institute of Petrochemical Processes of the Azerbaijan National Academy of Sciences.

The total volume of the dissertation with volumes of separate structural units of the dissertation indicated.

The dissertation consists of 182 pages; an introduction, 5 chapters, results, and 172 references. The dissertation includes 35 tables and 89 figures. The structure of the dissertation; the table of contents consists of 2113 characters, introduction 9609 characters, first chapter 31538 characters, second chapter 14885 characters, third chapter 71766 characters, fourth chapter 16859 characters, fifth chapter 10561 characters, results 4109 characters, and list of abbreviations 1134 characters. The dissertation has a total of 160461 characters (excluding the spaces, figures, tables, and graphs in the text, appendices and bibliography).

First chapter contains a large body of literature on the production of anionic monomer and dimer surfactants of dihydroxysulfate-betaine type, cationic with carbonate group in the spacer, based on imidazole 1,4-dibromobutane.

Second chapter provides information on the main physical and chemical properties of the primary substances used in the research and the methods used.

Third chapter provides information on the synthesis of gemini surfactants with different lengths of alkyl chains and containing mono-2-hydroxypropyl or di-2-hydroxypropyl group in the hydrophilic part, and the determination of their colloidal chemical parameters.

Fourth chapter examines the effect of the length of the spacer chain on the electrical conductivity and surface tension properties of the synthesized gemini surfactants, as well as on their petroleum-collecting, bactericidal and antimicrobial properties, and the results are noted.

Fifth chapter V studies the synthesis of novel gemini surfactants based on alkyl iodides, their physical and chemical characteristics and provides general information.

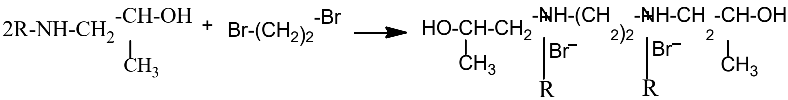
THE MAIN CONTENT OF THE WORK

Synthesis and study of gemini surfactants on the basis of ethylenediamine, alkylamine, propylene oxide and alkyl bromides

To synthesize gemini surfactants with C_2 spacer, two different synthesis pathways were followed. In the first case, C_8–C_{16} alkylamines were initially oxypropylated with PO at ratios of 1:1 and

1:2, and secondary and tertiary C_8–C_{16} alkylamines containing 2-hydroxypropyl group were obtained. $C_nC_2C_n$[iso-Pr(OH)] and $C_nC_2C_n$[iso-Pr(OH)]$_2$ class surfactants were then synthesized by the interaction of the obtained secondary and tertiary amines with dibromoethane. However, in the reaction with 1,2-dibromoethane, the yield of the obtained surfactant turned out to be 20–40%. The second way is to first oxypropylate diamine in ratios of 1:2 and 1:4 moles with PO and to obtain gemini surfactants through quaternization reaction of obtained functionalized diamines with C_9–C_{14} alkyl bromides. The yield of gemini surfactants obtained in this way was relatively high (96-97%). Therefore, the synthesis of the gemini surfactants with a spacer s=2 according to the reactions given in Schemes 1 and 2 is more convenient. General information about the synthesis method is given in more detail below.

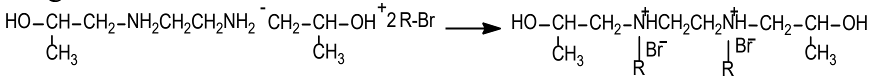
For the synthesis of gemini surfactants through the first method, alkylisopropylolamine was synthesized at an initial stage by taking alkylamines and propylene oxide in a ratio of 1:1 at room temperature. In the second stage, the reaction of synthesis of alkylisopropylolamine with dibromoethane was carried out in a flask equipped with a magnetic stirrer at a temperature of 75-85 °C for 24 hours and gemini surfactants were synthesized. The general scheme of the reaction is as follows:



R= C_8H_{17}; C_9H_{19}; $C_{12}H_{25}$; $C_{14}H_{29}$ **$C_nC_2C_n$[iso-Pr(OH)]**

The structure of synthesized $C_nC_2C_n$[iso-Pr(OH)] class surfactants was identified by IR-, NMR- and UV-spectroscopy.

The reaction of amino alcohol obtained from the interaction of EDA and PO in a ratio of 1:2 mol with nonyl-, decyl- and tetradecyl bromide was carried out at a temperature of 65-75 °C for 18-20 hours. The general scheme of the reaction is as follows:



R= C_9H_{19}; $C_{12}H_{25}$; $C_{14}H_{29}$ **$C_nC_2C_n$[iso-Pr(OH)]**

The structures of the obtained gemini cationic surfactants were confirmed by IR- and NMR-spectroscopy.

Using a tensiometer, it was determined that the synthesized gemini cationic surfactants have a high surface activity at the water-air boundary at different temperatures (10, 20, 30, 40°C) and graphs were constructed based on the values obtained (Figure 1). It was found that as the temperature increased, the values of CMC and surface tension decreased, and the values of electrical conductivity increased. The concentration requiring a reduction in surface tension of water to 20 mN/m at the water-air boundary of surfactants is denoted as C_{20} (logarithmic value of concentration). Its negative logarithmic value is expressed as pC_{20} (adsorption efficiency). Studies have shown that the value of pC_{20} decreases as the temperature increases, and the value of pC_{20} increases as the length of the alkyl chain increases. Therefore, the elongation of the alkyl chain increases the tendency of surfactants to adsorb at the water-air boundary.

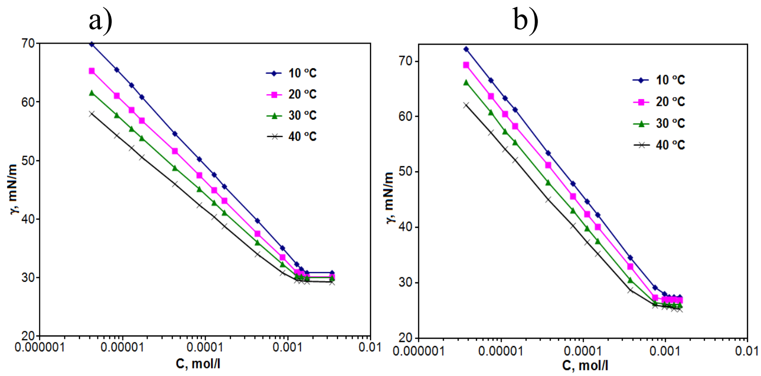


Figure 1. Surface tension isotherms of $C_9C_2C_9$[iso-Pr(OH)] (a) and $C_{12}C_2C_{12}$[iso-Pr(OH)] (b) at different temperatures.

Based on the given graphs, colloid-chemical parameters of surfactant were calculated and the obtained results are given in Table 1. As can be seen from Table 1, the CMC value of the surfactant $C_{14}C_2C_{14}$[iso-Pr(OH)] is lower than that of other surfactants. For synthesized gemini surfactants, the value of A_{min} decreases as the length of the alkyl chain increases from C_9 to C_{12}, but the value of A_{min}

begins to increase during the transition from C_{12} to C_{14}. As the length of the alkyl chain of surfactants increases from C_9 to C_{14}, the surface pressure value first increases and then decreases. The value of surface pressure (π_{CMC}) is higher in gemini surfactants with an alkyl chain length n=12 than in other surfactants.

Table 1.

Colloid-chemical parameters of $C_nC_2C_n$[izo-Pr(OH)] class surfactants

Surfactants	T, K	β	CMC×10^3, mol/l	Γ_{max}×10^{10}, mol/cm^2	A_{min}, Å^2	π, mN/m	pC_{20}	γ_{CMC}, mN/m	ΔG_{mic}, kJ/mol	ΔG_{ad}, kJ/mol
$C_9C_2C_9$[iso-Pr(OH)]	283	0.55	1.69	0.94	177.4	43.4	4.19	30.9	-51.38	-56.01
	293	0.53	1.44	0.82	201.7	42.7	4.40	30.1	-52.98	-58.17
	303	0.51	1.26	0.73	226.7	41.2	4.62	30.0	-54.40	-60.03
	313	0.48	1.05	0.66	250.5	40.1	4.88	29.4	-55.27	-61.32
$C_{12}C_2C_{12}$[iso-Pr(OH)]	283	0.52	0.91	1.16	142.9	46.3	4.35	28.0	-52.88	-56.86
	293	0.50	0.74	1.08	153.5	45.8	4.47	27.0	-54.68	-58.92
	303	0.46	0.62	1.02	162.5	45.0	4.64	26.2	-55.14	-59.55
	313	0.43	0.55	0.93	177.8	43.7	4.82	25.8	-55.76	-60.44
$C_{14}C_2C_{14}$[iso-Pr(OH)]	283	0.49	0.82	1.01	165.2	43.3	4.34	31.0	-51.81	-56.12
	293	0.44	0.65	0.92	180.6	42.1	4.54	30.7	-51.99	-56.57
	303	0.40	0.53	0.85	194.8	41.5	4.74	29.7	-52.41	-57.27
	313	0.36	0.45	0.79	210.6	40.7	4.97	28.8	-52.46	-57.62

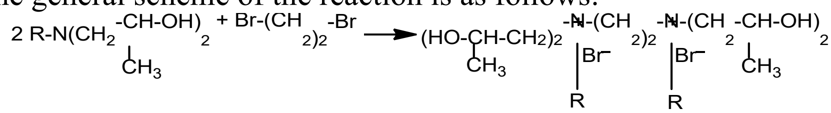
As the length of the alkyl chain of the gemini surfactants increases from C_9 to C_{12}, the ΔG_{mic} value is lowered. But when the alkyl chain is elongated from C_{12} to C_{14}, the value of ΔG_{mic} rises.

The antibacterial properties of the obtained gemini cationic surfactants were applied against SRB by water dilution method. The gemini surfactant $C_9C_2C_9$[iso-Pr(OH)] completely stopped the development of SRB at low concentrations (15 mg/l). Although the gemini surfactant $C_{12}C_2C_{12}$[iso-Pr(OH)] did not fully affect the development of SRB at a concentration of 15 mg/l, it was highly effective at 75 mg/l. The gemini surfactant $C_{14}C_2C_{14}$[iso-Pr(OH)] had a relatively weak effect at low concentrations but was able to completely stop the development of SRB at 150 mg/l. According to the results, it can be stated that the antibacterial properties of the synthesized gemini surfactants against SRB are weakened by the elongation of the alkyl chain. The highest antibacterial effect among the obtained gemini surfactants was observed with the surfactant $C_9C_2C_9$[iso-Pr(OH)].

The petrocollecting and dispersing properties of the gemini surfactants with structures of $C_9C_2C_9$[iso-Pr(OH)], $C_{12}C_2C_{12}$[iso-Pr(OH)] and $C_{14}C_2C_{14}$ [iso-Pr(OH)] have been studied in the laboratory. Such that, the analysis was conducted on three different water surfaces using Pirallahi (a port town of Baku, Azerbaijan) oil with a thickness of 0.17 mm. The efficiency of the synthesized SAM is estimated by petroleum-collecting coefficient (K) indicating reduction of petroleum layer surface area, K_D (%) – indicating purification degree of water surface from petroleum under reagent effect and shelf life – τ. In order to study the properties of oil accumulation and oil dispersion of gemini surfactants, their undiluted forms and 5% aqueous solutions were used to study the petroleum-collecting and petroleum-dispersing properties in undiluted form and in 5% aqueous solutions. The obtained surfactants showed high petrocollecting properties. Maximum oil accumulation factor is 30.4; recovery time is 98 hours.

Synthesis and study of surfactants based on the interaction of N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine with dibromoethane and alkyl bromides

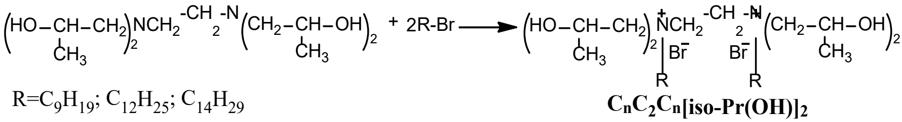
In order to synthesize the gemini cationic surfactant $C_8C_2C_8$[iso-Pr(OH)]$_2$, at the first stage, synthesis of alkylamine and PO in a ratio of 1:2 moles was carried out at room temperature. In the second stage, the reaction of octyldiisopropylamine with dibromoethane was carried out at a temperature of 90°C for 32 hours. The general scheme of the reaction is as follows:



R= C_8H_{17}; C_9H_{19}; $C_{12}H_{25}$; $C_{14}H_{29}$

$C_nC_2C_n$[iso-Pr(OH)]$_2$

The obtained surfactant is a brown substance, well soluble in ethyl alcohol and acetone, partially soluble in water. The reaction of amino alcohol obtained from the 1:4 mole interaction of EDA and PO with nonyl-, decyl- and tetradecyl bromide was carried out at a temperature of 75-85°C for 20-25 hours and novel gemini surfactants were synthesized. The general scheme of the reaction is as follows:



To determine the surface activity of these substances, their aqueous solutions were prepared and measured with a tensiometer. The electrical conductivity values were determined by conductometric method (Figure 2). Based on the obtained values, graphs were constructed and the calculated colloidal chemical parameters are shown in Table 2.

Table 2.

Colloid-chemical parameters of $C_{12}C_2C_{12}$[iso-Pr(OH)]$_2$ və $C_{14}C_2C_{14}$[iso-Pr(OH)]$_2$ surfactants (25°C)

Gemini surfactants	β	$\Gamma_{max}\times10^{10}$, mol/cm^2	A_{min}, Å^2	CMC×10^4, mol/l	ΔG_{mic}, kJ/mol	π, mN/m	ΔG_{ad}, kJ/mol
$C_{12}C_2C_{12}$[iso-Pr(OH)]$_2$	0,42	0,85	194,6	3,16	-27,52	38,9	-32,08
$C_{14}C_2C_{14}$[iso-Pr(OH)]$_2$	0,38	0,84	197,4	3,00	-26,44	36,7	-30,80

As can be seen from Table 2, the surfactant with an alkyl chain length n=14 has a higher surface activity. CMC values of $C_{12}C_2C_{12}$[iso-Pr(OH)]$_2$ and $C_{14}C_2C_{14}$[iso-Pr(OH)]$_2$ class surfactants are 3.16×10^{-4} mol/l and 3.00×10^{-4} mol/l.

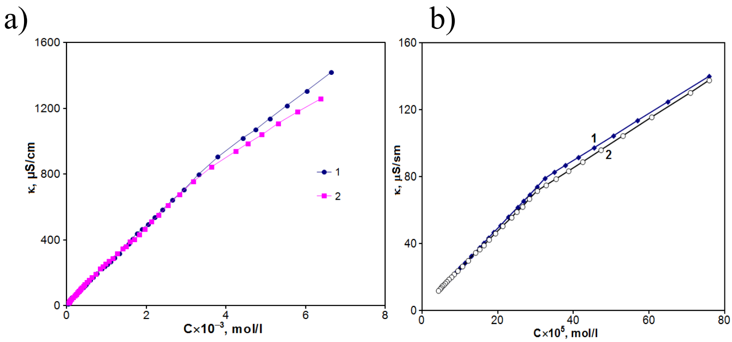


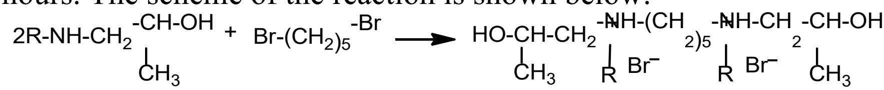
Figure 2. Concentration dependence of specific electrical conductivities of the gemini surfactants $C_8C_2C_8$[iso-Pr(OH)]$_2$ (1 a),

$C_9C_2C_9$[iso-Pr(OH)]$_2$ (2 a) and $C_{12}C_2C_{12}$[iso-Pr(OH)]$_2$ (1 b), $C_{14}C_2C_{14}$[iso-Pr(OH)] (2 b) (25°C).

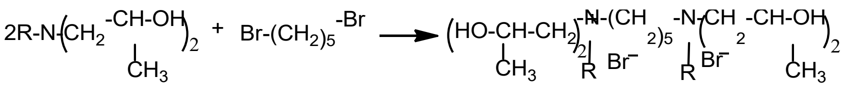
The petrocollecting and dispersing properties of the synthesized gemini surfactants were studied in the example of Pirallahi oil. Dodecyl-bromide-based surfactant showed high oil dispersion properties in seawater (K_D=94.2%), while tetradecyl-bromide-based surfactant showed high oil petrocollecting properties in seawater (K_{max}=30.4; τ=72 hours). The $C_{12}C_2C_{12}$[iso-Pr(OH)]$_2$-structured gemini surfactant has been found to have antibacterial properties against SRB. Such that, it had a bactericidal effect of 79.5% at a concentration of 50 mg/l and 94.8% at 150 mg/l.

Synthesis and properties of gemini surfactants based on alkylamines (C_8, C_9, C_{12}, C_{16}) and dibromopentane

Mono- and di-2-hydroxypropylalkylamines were obtained from the interaction of OA, NA, DA, HDA and ODA with PO in the ratio of 1:1 and 1:2 moles. The obtained mono-2-hydroxypropylalkylamine (or -2-hydroxypropylalkylamine) was reacted with 1,5-dibromopentane at a temperature of 75°C for 18-20 hours. The scheme of the reaction is shown below:



$C_nC_5C_n$[iso-Pr(OH)]



$C_nC_5C_n$[iso-Pr(OH)]$_2$

R=C_8H_{17}; C_9H_{19}; $C_{12}H_{25}$; $C_{16}H_{33}$; $C_{18}H_{33}$

The synthesized surfactants are brown, single-phase viscous liquids, soluble in ethyl acetate, ethanol, isopropanol and water, but insoluble in isooctane. Their surface tension values and electrical conductivity properties were determined, corresponding graphs were constructed based on the obtained values, and colloidal chemical parameters were calculated (Table 3). The concentration where the surface tension value starts to stabilize is taken as CMC. As is evident from the table 3, the CPC and CMC values for the gemini surfactants of $C_nC_5C_n$[isoPr(OH)]$_2$ group are lower than those for $C_nC_5C_n$[iso-Pr(OH)] group surfactants. In the case of both group surfactants, the CPC and CMC values decrease as the alkyl chain is elongated. The pC_{20} value increases with elongating the alkyl chain length in both group surfactants. This index for the $C_nC_5C_n$[izo-Pr(OH)]$_2$ gemini surfactants is higher than that of gemini surfactants of other classes. The π_{CMC} value of the $C_nC_5C_n$[izo-Pr(OH)]$_2$ type gemini surfactants augments with an elongation of the alkyl chain from C_8 up to C_{12}, then, it remains constant. In the case of $C_nC_5C_n$[izo-Pr(OH)] gemini surfactants, the π_{CMC} value is the highest for the chain length C_9.

For the synthesized gemini surfactants the values of specific electroconductivity of their aqueous solutions were determined.

Table 3.

Colloid-chemical parameters of synthesized gemini surfactants (25 °C)

Surfactants	$CPC^a\times10^4$ mol·dm^{-3}	$CMC^b\times10^4$ mol·dm^{-3}	$CMC^c\times10^4$ mol·dm^{-3}	$\Gamma_{max}\times10^{10}$, mol·cm^{-2}		$A_{min}\times10^2$, nm^2		pC_{20}	γ_{CMC}, mN·m^{-1}	π_{CMC}, mN·m^{-1}
				n=2	n=3	n=2	n=3			
$C_8C_5C_8$[iso-Pr(OH)]	158.0	330.0	340.0	2.27	1.51	73.2	109.8	2.54	29.9	42.1
$C_9C_5C_9$[iso-Pr(OH)]	79.0	245.0	252.9	2.16	1.44	77.0	115.4	3.04	25.7	46.3
$C_{12}C_5C_{12}$[iso-Pr(OH)]	3.49	13.95	14.35	2.07	1.38	80.2	120.3	4.02	30.7	41.3
$C_{16}C_5C_{16}$[iso-Pr(OH)]	0.30	0.90	0.88	2.84	1.89	58.5	87.7	5.02	30.0	42.0
$C_8C_5C_8$[iso-Pr(OH)]$_2$	10.68	27.70	28.54	2.03	1.36	81.6	122.5	3.79	29.0	43.0
$C_9C_5C_9$[iso-Pr(OH)]$_2$	6.677	22.70	24.04	1.98	1.32	83.7	125.5	4.04	28.0	44.0
$C_{12}C_5C_{12}$[iso-Pr(OH)]$_2$	0.890	6.60	7.20	1.97	1.32	84.2	126.3	4.90	27.9	44.1
$C_{16}C_5C_{16}$[iso-Pr(OH)]$_2$	0.265	0.79	0.85	3.18	2.12	52.3	78.4	5.05	27.9	44.1

b The CMC is determined by surface tension method.

c The CMC is determined by electroconductivity method.

It was determined that, for the the $C_8C_5C_8$[iso-Pr(OH)]$_2$ surfactant, value of specific electroconductivity is higher than those other surfactants.

Values of β and thermodynamic parameters of the synthesized gemini surfactants were calculated (Table 4).

Table 4.

Values of β and thermodynamic parameters of the synthesized gemini surfactants

Surfactants	β	ΔG_{agg}, kJ·mol^{-1}	ΔG_{mic}, kJ·mol^{-1}	ΔG_{ad}, kJ·mol^{-1}
$C_8C_5C_8$[iso-Pr(OH)]	0.537	-42.80	-39.02	-41.80
$C_9C_5C_9$[iso-Pr(OH)]	0.518	-45.53	-39.82	-43.04
$C_{12}C_5C_{12}$[iso-Pr(OH)]	0.462	-57.94	-51.34	-54.33
$C_{16}C_5C_{16}$[iso-Pr(OH)]	0.426	-67.07	-62.02	-64.24
$C_8C_5C_8$[iso-Pr(OH)]$_2$	0.585	-59.23	-54.10	-57.28
$C_9C_5C_9$[iso-Pr(OH)]$_2$	0.573	-61.08	-54.57	-57.90
$C_{12}C_5C_{12}$[iso-Pr(OH)]$_2$	0.549	-70.21	-59.79	-63.15
$C_{16}C_5C_{16}$[iso-Pr(OH)]$_2$	0.527	-74.93	-69.36	-71.44

As is noticed from the table 4, in the case of both $C_nC_5C_n$[iso-Pr(OH)] and $C_nC_5C_n$[iso-Pr(OH)]$_2$ gemini surfactants, the β value decreases as the alkyl chain lengthens. The β value for $C_nC_5C_n$[iso-Pr(OH)]$_2$ gemini surfactants is larger than that of $C_nC_5C_n$[iso-Pr(OH)] group surfactants. ΔG_{agg} and ΔG_{mic} values diminish as the as the length of the alkyl chain value increases. Overall, for the $C_nC_5C_n$[iso-Pr(OH)]$_2$ gemini surfactants, ΔG_{aq}, ΔG_{mis} and ΔG_{ad} values are lower.

In Table 5, the results of antimicrobial properties studies regarding the synthesized gemini surfactants are described. It was observed that the synthesized gemini surfactants exhibited higher antibacterial properties against Gram-positive bacteria than the Gram-negative. The synthesized surfactants of gemini structure demonstrate a weak antimicrobial activity with regard to P.aeruginosa bacterium. It may be noted that the gemini surfactants with C_{12} alkyl chain possess a more pronounced antimicrobial activity than the other synthesized surfactants.$C_{12}C_5C_{12}$[iso-Pr(OH)] gemini surfactant shows a more effective action against E.coli bacterium and Candida albicans fungus. Partial weakening of the antimicrobial properties when passing from

C_{12} to C_{16} is related to a diffusion of surfactant molecules in the medium.

Table 5.

Antimicrobial properties of gemini surfactants studied by disk-diffusion method

Surfactants	Diameter of inhibition zone (mm)				
	Concent., mg/ml	*S.aureus*	*E.coli*	*P. aeruginosa*	*C.albicans*
$C_8C_5C_8$[iso-Pr(OH)]	8	-	18	13	8
	4	-	11	8	8
	2	11	-	-	-
$C_9C_5C_9$[iso-Pr(OH)]	8	30	14	9	12
	4	9	10	8	-
	2	-	-	-	-
$C_{12}C_5C_{12}$[iso-Pr(OH)]	8	36	21	11	44
	4	29	18	-	37
	2	21	9	-	26
$C_{16}C_5C_{16}$[iso-Pr(OH)]	8	40	19	10	20
	4	15	-	-	12
	2	14	-	-	9
$C_8C_5C_8$[iso-Pr(OH)]$_2$	8	35	13	-	25
	4	29	11	-	17
	2	18	8	-	10
$C_9C_5C_9$[iso-Pr(OH)]$_2$	8	31	18	12	20
	4	21	7	-	11
	2	16	-	-	-
$C_{12}C_5C_{12}$[iso-Pr(OH)]$_2$	8	41	15	10	32
	4	25	8	8	29
	2	22	8	-	15
$C_{16}C_5C_{16}$[iso-Pr(OH)]$_2$	8	28	19	-	21
	4	19	-	-	11
	2	18	-	-	10

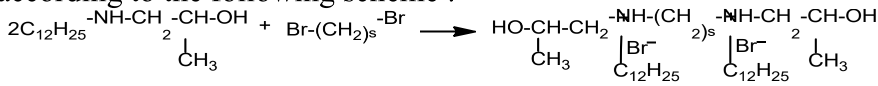
So, an elongation of the alkyl chain and an increase of the number of 2-hydroxypropyl groups cause a decrease in CMC and their antimicrobial activity should have been increased.

Experiments have shown that in both $C_nC_5C_n$[iso-Pr(OH)] and $C_nC_5C_n$[iso-Pr(OH)]$_2$ class surfactants, the petrocollecting ability increases with increasing alkyl chain length. In the first hours, the $C_nC_5C_n$[iso-Pr(OH)]$_2$ gemini surfactants are mainly petrodispersing in hard waters, while $C_nC_5C_n$[iso-Pr(OH)] gemini surfactants demonstrate petrocollecting capacity (K_D=94.1%; K_{max}=30.4; τ=120 hours).

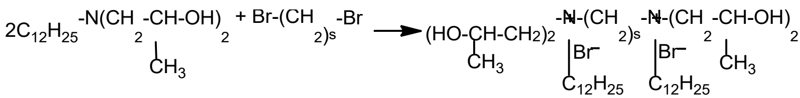
Synthesis of gemini cationic surfactants, the lengths of the spacer chain of which are two, three, four, five and six

It is also possible to change the properties of gemini surfactants by changing the length and nature of the space chain. For synthesis of the gemini surfactants with the spacer chain length C_2, C_3, C_4 and C_5, at the first stage, dodecylamine was propoxylated with PO at molar ratios 1:1 and 1:2.

In the second stage, the synthesized mono- and di-(2-hydroxypropyl)dodecylamines were reacted with 1,3-dibromopropane (1,2-dibromoethane, 1,4-dibromobutane and 1,5-dibromopentane) according to the following scheme :



$C_{12}C_sC_{12}$[iso-Pr(OH)]



$C_{12}C_sC_{12}$[iso-Pr(OH)]$_2$

For the synthesized gemini surfactants C_{12}-C_s-C_{12}[iso-Pr(OH)] and C_{12}-C_s-C_{12}[iso-Pr(OH)]$_2$, surface tension values at the border with air were determined and the values of specific electroconductivity was studied. In accordance with the obtained values, isotherms were built (Figure 3).

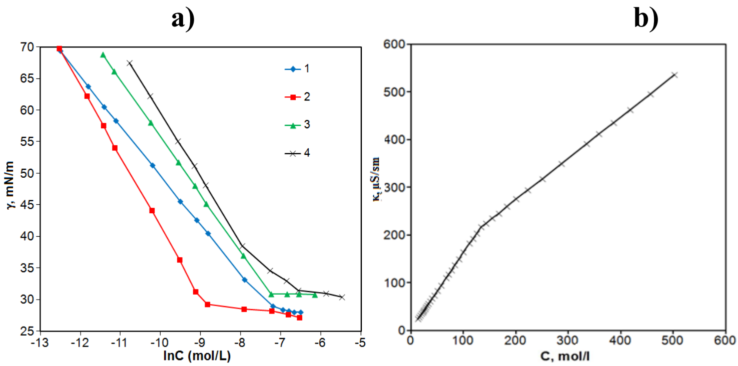


Figure 3. Surface tension isotherms of C_{12}-C_s-C_{12}[iso-Pr(OH)] at different concentrations. 1. s=2; 2. s=3; 3. s=4; 4. s=5 (a); Concentration dependence of specific electroconductivity of the gemini surfactant C_{12}-C_5-C_{12}[iso-Pr(OH)]

The surface activity parameters of the synthesized gemini surfactants are presented in Table 6.

As is evident from the table, in the case of the gemini surfactants of the C_{12}-C_s-C_{12}[iso-Pr(OH)] class, with lengthening the spacer chain from C_2 to C_3, the CMC value diminishes, but with an elongation from C_3 to C_5, the CMC rises.

Table 6.

Surface activity parameters of the synthesized gemini surfactants (25°C)

Surfactants	$CMC^b \times 10^4$, $mol \cdot dm^{-3}$	$CMC^c \times 10^4$, $mol \cdot dm^{-3}$	π_{CMC}, $mN \cdot m^{-1}$	β	ΔG_{mic}, $kJ \cdot mol^{-1}$	ΔG_{ad}, $kJ \cdot mol^{-1}$
C_{12}-C_2-C_{12}[iso-Pr(OH)]	6.66	6.67	43,4	0,480	-55.01	-59.14
C_{12}-C_3-C_{12}[iso-Pr(OH)]	1.45	1.49	42,7	0,474	-62.03	-64.88
C_{12}-C_4-C_{12}[iso-Pr(OH)]	7.11	7.32	41,1	0,469	-54.08	-58.36
C_{12}-C_5-C_{12}[iso-Pr(OH)]	13.95	14.35	40,5	0,462	-50.48	-53.47
C_{12}-C_6-C_{12}[iso-Pr(OH)]	4.43	4.61	36.0	0,409	-52.86	-55.41
C_{12}-C_2-C_{12}[iso-Pr(OH)]$_2$	3.16	3.25	38,9	0,420	-55.04	-59.60
C_{12}-C_3-C_{12}[iso-Pr(OH)]$_2$	3.10	3.19	43,2	0,406	-54.29	-57.68
C_{12}-C_4-C_{12}[iso-Pr(OH)]$_2$	3.05	3.14	43,5	0,386	-53.17	-56.88
C_{12}-C_5-C_{12}[iso-Pr(OH)]$_2$	6.60	7.20	44,1	0,549	-58.93	-62.29
C_{12}-C_6-C_{12}[iso-Pr(OH)]$_2$	3.54	3.47	39,3	0,284	-46.47	-53.31

Regarding the C_{12}-C_s-C_{12}[iso-Pr(OH)]$_2$ class gemini surfactants, as the spacer chain length increases from C_2 to C_4, the CMC decreases but, at s=5, its value starts to augment.

In Table 7, the results of the study of antimicrobial properties of the synthesized gemini surfactants against SRB are set. Compared to Gram-positive bacteria, Gram-negative bacteria are more resistant to antimicrobial surfactants.

Table 7.

Results of study of antibacterial effect of the synthesized gemini surfactants against SRB

Gemini surfactants	Concentration of gemini surfactants, mg/l The number of bacteria at the initial stage, 10^8		
	15	75	150
	The number of bacteria remaining in 1 g water		
C_{12}-C_2-C_{12}[iso-Pr(OH)]	10^3	0	0
C_{12}-C_3-C_{12}[iso-Pr(OH)]	10^4	10^3	10^1
C_{12}-C_4-C_{12}[iso-Pr(OH)]	10^2	10^1	10^1
C_{12}-C_5-C_{12}[iso-Pr(OH)]	10^5	10^4	10^2

C_{12}-C_2-C_{12}[iso-Pr(OH)]$_2$	10^4	10^3	10^2
C_{12}-C_3-C_{12}[iso-Pr(OH)]$_2$	10^5	10^4	10^1
C_{12}-C_4-C_{12}[iso-Pr(OH)]$_2$	10^4	10^2	10^1
C_{12}-C_5-C_{12}[iso-Pr(OH)]$_2$	10^2	10^1	10^1

As is seen from table, at a concentration of 150 mg/l, surfactants significantly reduced the growth of SRB. C_{12}-C_2-C_{12}[iso-Pr(OH)] class gemini surfactant can completely stop the SRB growth at a 75 and 150 mg/l concentrations.$C_{12}C_2C_{12}$[izo-Pr(OH)] and $C_{12}C_4C_{12}$[izo-Pr(OH)] gemini surfactants demonstrate a higher effect as compared with the other surfactants. $C_{12}C_sC_{12}$[izo-Pr(OH)]$_2$ class gemini surfactants, $C_{12}C_4C_{12}$[izo-Pr(OH)]$_2$ and $C_{12}C_5C_{12}$[izo-Pr(OH)]$_2$ gemini surfactants have a stronger antibacterial effect.

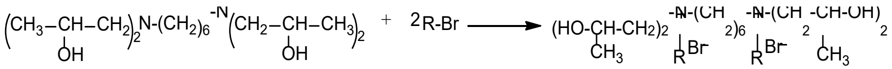
In addition, antibacterial properties of the synthesized gemini surfactants are determined. C_{12}-C_5-C_{12}[iso-Pr(OH)] and C_{12}-C_5-C_{12}[iso-Pr(OH)]$_2$ surfactants exhibit more effective antimicrobial properties against S. aureus bacterium, C_{12}-C_5-C_{12}[iso-Pr(OH)] and C_{12}-C_2-C_{12}[iso-Pr(OH)] surfactants - against E. coli bacterium, C_{12}-C_2-C_{12}[iso-Pr(OH)] and C_{12}-C_3-C_{12}[iso-Pr(OH)] surfactants – against P. aeruginosa bacterium, C_{12}-C_5-C_{12}[iso-Pr(OH)] and C_{12}-C_5-C_{12}[iso-Pr(OH)]$_2$ surfactants – against C. albicans fungus. In comparison with Gram-positive bacteria, Gram-negative bacteria are usually more stable against antimicrobial means.

In the example of Pirallahi oil, the petrocollecting and dispersing properties of the synthesized gemini cationic surfactants have been studied in distilled, drinking and sea water. Based on the results of the study, it was determined that, among the surfactants of C_{12}-C_s-C_{12}[iso-Pr(OH)] structure, the surfactant with a spacer chain length s=2 exhibits high petroleum-collection (K_{max}=40.5) in seawater. Such that, the surfactants with spacer chain lengths s=2-3 exhibited only petroleum-collecting properties on all three types of water surfaces. The surfactant with a spacer chain length s=4 showed high petroleum-dispersion ability (K_D=94.1%). Among the C_{12}-C_s-C_{12}[iso-Pr(OH)]$_2$ class gemini surfactants, the one with a spacer chain length s=2 has a higher petroleum-collecting property (K_{max}=30.4). The surfactant with a spacer chain length s=4 showed mainly petroleum-dispersion properties.

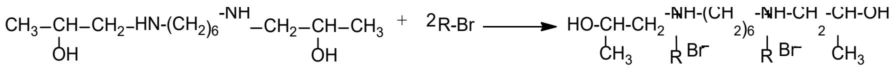
Synthesis and study of gemini surfactants synthesized on the basis of alkyl bromides (C_9, C_{10}, C_{12}, C_{14}) and oxypropyl derivatives of HMDA

In the initial stage, amino alcohols obtained by the interaction of HMDA and PO in ratios of 1:2 and 1:4 mol were treated with nonyl-, decyl-, dodecyl- and tetradecyl bromide. The reaction was conducted at 95°C for 24-26 hours.

The reactions were performed according to the following scheme:



$C_nC_6C_n$[iso-Pr(OH)]$_2$



$C_nC_6C_n$[iso-Pr(OH)]

R=C_9H_{19}; $C_{10}H_{21}$; $C_{12}H_{25}$; $C_{14}H_{29}$.

$C_nC_6C_n$[iso-Pr(OH)] class gemini surfactants are solids, while $C_nC_6C_n$[iso-Pr(OH)]$_2$ class gemini surfactants are viscous liquids. The surface tension values of these surfactants were determined and graphs were constructed based on the obtained values (Figure 4).

As can be seen from the graphs, the surface tension values of $C_nC_6C_n$[iso-Pr(OH)]$_2$ structural surfactants were lower than those of $C_nC_6C_n$[iso-Pr(OH)] structural ones. This result is explained by the number of hydroxyl groups in the composition.

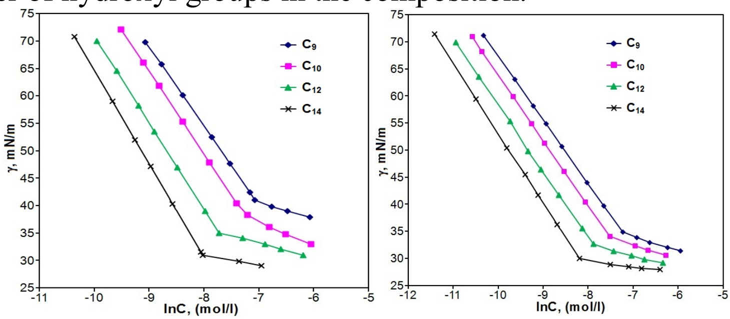


Figure 4. Concentration dependence of surface tension at the water-air boundary for substances with structures $C_nC_6C_n$[iso-Pr(OH)] and $C_nC_6C_n$[iso-Pr(OH)]$_2$ (25°C).

Surface tension and CMC values of tetradecyl bromide based surfactants are lower than those of other surfactants. This is explained by the length of the spacer chain. The calculated colloid-chemical parameters for gemini cationic surfactants synthesized on the basis of N,N'-bis(2-hidroxypropil)hexametilenediamine (N,N,N',N'-tetrakis(2-hidroxypropil)hexametilenediamine) and nonyl-, decyl-, dodecyl- and tetradecyl bromide are given in Table 7. As shown on the table, the value of Γ_{maks} increases and the value of Amin decreases as the length of the hydrocarbon chain increases from C_9 to C_{14} in both classes of gemini cationic surfactants. In $C_nC_6C_n$[iso-Pr(OH)] and $C_nC_6C_n$[iso-Pr(OH)]$_2$ gemini cationic surfactants, the value of Γ_{max} diminishes and the value of A_{min} rises

with increasing hydrocarbon chain. The analogy between the values of Γ_{max} of the $C_nC_6C_n$[iso-Pr(OH)]-type and $C_nC_6C_n$[iso-Pr(OH)]$_2$-type gemini cationic surfactants showed that as the length of the spacer chain increases, the hydrophobicity in the gemini cationic surfactants enhances, causing them to pack more tightly at the water–air boundary. Thus, since the hydrophobicity of $C_nC_6C_n$[iso-Pr(OH)] gemini cationic surfactants is greater than that of $C_nC_6C_n$[iso-Pr(OH)]$_2$ gemini cationic surfactants, their Γmax values are relatively small. The value of pC_{20} rises with increasing hydrocarbon chain length in both classes of surfactants (Table 8).

Table 8.

Colloid-chemical parameters of surfactants with structures of alkyl bromides, N,N'-bis(2-hidroxypropil)hexametilenediamine and (N,N,N',N'-tetrakis(2-hidroxypropil)hexametilenediamine).

Surfactants	$CMC^b \times 10^4$, $mol \cdot dm^{-3}$	$CMC^c \times 10^4$, $mol \cdot dm^{-3}$	$\Gamma_{max} \times 10^{10}$, $mol \cdot cm^{-2}$		$A_{min} \times 10^2$, nm^2		pC_{20}	γ_{CMC}, $mN \cdot m^{-1}$	π_{CMC}, $mN \cdot m^{-1}$
			n=2	n=3	n=2	n=3			
$C_9C_6C_9$[iso-Pr(OH)]	8.50	8.78	2.93	1,95	56.7	85,0	2.54	42.2	29.8
$C_{10}C_6C_{10}$[iso-Pr(OH)]	5.99	6.14	3.05	2,03	54.4	81,6	3.04	38.0	34.0
$C_{12}C_6C_{12}$[iso-Pr(OH)]	4.43	4.61	3.20	2,14	51.8	77,8	4.02	36.0	36.0
$C_{14}C_6C_{14}$[iso-Pr(OH)]	3.27	3.24	3.43	2,29	48.4	72,6	5.02	35.5	36.5
$C_9C_6C_9$[iso-Pr(OH)]$_2$	6.18	6.25	2.36	1,57	70.4	105,6	3.78	34.9	37,1

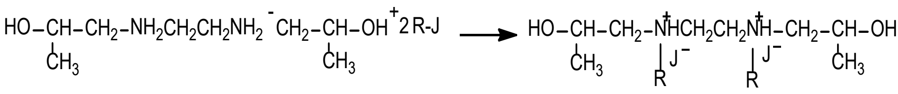
$C_{10}C_6C_{10}$[iso-Pr(OH)]$_2$	5.60	5.86	2.43	1,62	68.3	102,4	3.92	34.1	37.9
$C_{12}C_6C_{12}$[iso-Pr(OH)]$_2$	3.54	3.47	2.48	1,65	67.0	100,5	4.13	32.7	39.3
$C_{14}C_6C_{14}$[iso-Pr(OH)]$_2$	2.65	2.66	2.59	1,73	64.0	96,0	4.31	30.0	42.0

As the alkyl chain length increases from C_9 to C_{14} in the gemini surfactants of both classes, the value of π_{CMC} increases. The $C_nC_6C_n$[iso-Pr(OH)]$_2$ class gemini surfactants have higher values of π_{CMC} and pC_{20} than those of the $C_nC_6C_n$[iso-Pr(OH)] class gemini surfactants.

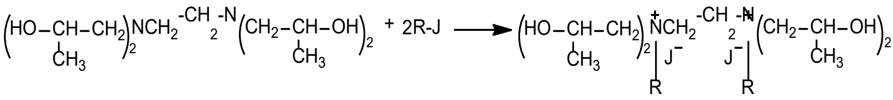
Antibacterial properties of the synthesized gemini surfactants were studied and determined that, $C_{14}C_6C_{14}$[iso-Pr(OH)] and $C_{14}C_6C_{14}$[iso-Pr(OH)]$_2$ surfactants, are more effective against S. aureus bacteria. The $C_{14}C_6C_{14}$[iso-Pr(OH)]$_2$ surfactant is effective against the E.coli bacterium, and $C_{14}C_6C_{14}$[iso-Pr(OH)] and $C_{14}C_6C_{14}$[iso-Pr(OH)]$_2$ surfactants with long alkyl chains have more effective antifungal properties against the C. albicans fungus. Gemini cationic surfactants have relatively weak antibacterial properties against the bacterium P. aeruginosa. Due to the length of the hydrocarbon chain, it is observed that the C_{14} chain gemini cationic surfactants possess more antimicrobial properties than other surfactants. Thus, as the value of CMC decreases, the biocidal properties of the synthesized gemini cationic surfactants increase.

Synthesis and study of gemini surfactants synthesized on the basis of alkyl iodides (C_7-C_{10}) and oxypropyl derivatives of PO

Novel gemini surfactants, the opposite ion of which is iodine, have been synthesized on the basis of N,N'-bis(2-hydroxypropyl)ethylenediamine, N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine and alkyl iodides (heptyl-, octyl-, nonyl- and decyl iodide). The synthesis was conducted based on a quaternization reaction of amino alcohols with heptyl iodide (or octyl iodide, nonyl iodide, decyl iodide) in a ratio of 1:2 moles at a temperature of 70-72°C for 7-14 hours. The general scheme of the reaction is as follows:



$C_nC_2C_n$[iso-Pr(OH)]J



$C_nC_2C_n$[iso-Pr(OH)]$_2$J

R=C_7H_{15}, C_8H_{17}, C_9H_{19}, $C_{10}H_{21}$.

The obtained cationic gemini surfactants are well soluble in ethanol, acetone, and ethyl acetate, and partially soluble in water. The surface activity of aqueous solutions of gemini surfactants was determined and surface tension isotherms were plotted. As can be seen from Table 7, in surfactants of $C_nC_2C_n$[iso-Pr(OH)]J structure, the value of surface tension decreases as the length of the alkyl chain increases. The CMC value of decyl-iodide-based surfactant is lower than that of other surfactants.

The properties of petrocollecting and dispersing properties were studied in laboratory medium with undiluted and 5% solutions of the obtained cationic gemini surfactants with an opposite ion of iodide. When comparing the petrocollection ability and surface tension values of the gemini surfactants with the same alkyl chain length and an opposite ion of bromide or iodide, it was found that the petrocollection ability of the surfactant with an opposite ion of bromide was higher than that of the surfactant with an opposite ion of iodide. On the other hand, when comparing the values of surface tension, it was observed that the surface activities of the surfactants with the opposite ion of bromide were lower.

RESULT

1. Reactions of diamines, which contain hydroxyl groups and are obtained by the interaction of EDA and PO in the ratios of 1:2 and 1:4 moles, with nonyl-, dodecyl- and tetradecyl bromide were carried out and the corresponding cationic gemini surfactants were obtained. The surface activity and specific electrical conductivity of their aqueous

solutions at the water-air boundary (at the temperatures of 10°C÷40°C) were measured, the size of the aggregates was determined by DLS method and colloidal chemical parameters (CMC, Γ_{max}, A_{min}, pC_{20}, π) of the surfactants were calculated. Thermodynamic parameters (ΔG, ΔH, ΔS) of micellization and adsorption processes were determined. The obtained gemini surfactants reduced the value of surface tension at the water-air boundary from 72.0 to 25.8 mN/m [4, 7, 12, 20].

2. Gemini surfactants were obtained based on the reaction of isopropylolalkylamines, which were produced by the interaction of OA, NA, DDA, HDA and ODA with PO in ratios of 1:1 and 1:2 moles, with dibromopentane. The diameters of the aggregates of the synthesized gemini surfactants, their special electrical conductivity and surface activities at the water-air boundary were determined and it was observed that the surface tension value decreased from 72.0 to 25.7 mN/m [5, 13].

3. Novel cationic gemini surfactants were synthesized by the interaction of diamines, which contain hydroxyl groups and are obtained by the interaction of HMDA and PO in the ratios of 1:2 and 1:4 moles, with nonyl-, decyl-, dodecyl- and tetradecyl bromides. The values of specific electrical conductivity and surface tension of aqueous solutions of these surfactants were determined and the corresponding colloidal-chemical parameters were calculated. The diameters of the aggregates were determined by the DLS method [10, 22].

4. Based on the reaction of amines, which contain a hydroxyl group obtained by the interaction of DDA and PO in molar ratios 1:1 and 1:2, with 1,2-dibromoethane, 1,3-dibromopropane, 1,4-dibromobutane and 1,5-dibromopentane, gemini surfactants with various lengths of spacer chain were synthesized. The dependence of colloidal-chemical parameters calculated of these surfactants on the length of the spacer chain was determined. In the gemini surfactants of both classes, the value of CMC decreases at first with the elongation of the spacer chain, and then with the decrease in the value of β, the value of CMC increases. Elongation of the spacer chain causes a decrease in surface

pressure in C_{12}-s-C_{12}[iso-Pr(OH)] class surfactants and an increase in C_{12}-s-C_{12}[iso-Pr(OH)]$_2$ class surfactants. The C_{12}-s-C_{12}[iso-Pr(OH)]$_2$ class gemini surfactants are more prone to premicellar aggregation than other surfactants. As the spacer chain lengthens, the formation of premicellar aggregates increases. In the C_{12}-C_s-C_{12}[iso-Pr(OH)]$_2$ class gemini surfactants, the concentration dependence of the diameters of the aggregates is weakened by the elongation of the spacer chain [11, 17, 19, 21].

5. Novel cationic gemini surfactants were obtained by the interaction of diamines, that contain hydroxyl groups and are produced by the reaction of EDA with PO in mole ratios of 1:2 and 1:4, with heptyl-, octyl-, nonyl- and decyl iodide. Surface activities, specific electrical conductivities and colloidal-chemical parameters of these surfactants were determined [3, 6, 8, 9, 18].

6. The oil accumulation and oil dispersion abilities of synthesized gemini surfactants were investigated on a thin layer of petroleum (0.17 mm) spread over various (distilled, drinking and marine) types of water surfaces. It was found that, in seawater, 5% aqueous solutions of the surfactants $C_9C_2C_9$[iso-Pr(OH)]$_2$ (K_{max} ~ 40.5; τ = 112 hours) and $C_{12}C_4C_{12}$[iso-Pr(OH)] (K_D ~ 94.1%; τ = 120 hours) demonstrate the highest petrocollection capacity. In gemini surfactants, the petrocollection ability increases as the length of the alkyl chain increases and it decreases as the number of isopropylol groups in the hydrophilic part increases. The length of the spacer chain, on the other hand, does not sharply affect the petrocollection ability [1, 2].

7. The antimicrobial properties of the synthesized gemini surfactants have been studied in various bacteria (*S. aureus*, *E. coli* and *P. aeruginosa*) and a fungus (*C. albicans*). It was determined that an 8 mg/l solution of gemini surfactants with spacer chain lengths s=5 and 6 and an alkyl chain length n=12 has more effective antimicrobial properties against *Staphylococcus aureus* and *Candida albicans*. In gemini surfactants, the antimicrobial activity increases as the length of the alkyl chain increases and it decreases as the number of isopropylol groups in the hydrophilic part increases. The length of the spacer chain does not significantly affect the antimicrobial activity. Surfactants also

have high antibacterial properties against SRB. Such that, the solutions of surfactant $C_9C_2C_9$[iso-Pr(OH)] with concentrations of 15.75 and 150 mg/l stop the development of SRB by 99% [14-16].

MAIN CONTENT OF THE DISSERTATION PUBLISHED IN THE SCIENTIFIC PAPERS:

1. Rahimov, R.A., Asadov, Z.H., Hashimzada, S.Z.F. Synthesis and properties of gemini surfactants based on N,N'-bis(2-hydroxypropyl)ethylenediamine and nonyl halogenides // II International Scientific Conference of Young Researchers dedicated to the 95th anniversary of National Leader Heydar Aliyev, -Baku: April 27-28, -2018, -pp.210-211.
2. Hashimzada, S.Z.F. Synthesis and properties of novel gemini surfactants based on alkyl bromides (C_{12}, C_{14}), ethylenediamine and propylene oxide / S.Z.F.Hashimzada, R.A.Rahimov, Z.H.Asadov // Journal of Baku Engineering University Chemistry and Biology, -2018. Vol. 2, № 2, -pp. 85-91.
3. Rahimov, R.A., Hashimzada, S.Z.F., Asadov, Z.H. Synthesis and oil accumulation properties of novel gemini surfactants based on ethylenediamine, propylene oxide, heptyl- and octyl iodide // Republic Scientific and Technical Conference of Students and Young Researchers on “Youth and Scientific Innovations”, dedicated to the 95th anniversary of the National Leader of the Azerbaijani People, Heydar Aliyev, -Baku: May 3-5, -2018, -pp.367-368.
4. Rahimov, R.A., Hashimzada, S.Z.F., Asadov, Z.H., Mammadbeyli, E.H., Aghamaliyeva, D.B., Ayyubova, S.K. Synthesis and properties of novel dialkyl gemini surfactants on the basis of ethylenediamine, propylene oxide and alkyl bromides. // International Scientific Conference “Actual Problems of Modern Natural and Economic Sciences” dedicated to the 95th anniversary of National Leader Heydar Aliyev, -Ganja: May 04-05, -2018, -pp.300-302.
5. Rahimov, R.A., Hashimzada, S.Z.F., Asadov, Z.H., Ahmadova, G.A. New dimeric surfactants of oil-accumulating activities based on aliphatic amines, propylene oxide and 1,5-dibromopentane // International Scientific-Practical Conference dedicated to the 110th

anniversary of Academician Vahab Aliyev, -Baku: October 9-10, -2018, -pp.138.
6. Rahimov, R.A., Hashimzada, S.Z.F., Asadov, Z.H., Ahmadova, G.A., Huseynova, S.M. New dimeric surfactants based on N,N`-bis(2-hydroxypropyl)ethylenediamine and alkyl iodides for the localization of thin oil layers on the water surface // "Chemistry, chemical technology and ecology: science, production, education." Materials of the International Scientific and Practical Conference and Schools of Young Scientists, -Makhachkala: October 18-19, -2018, -pp.227.
7. Asadov, Z.H., Rahimov, R.A., Hashimzada S.Z.F. Obtaining gemini surfactants of different hydrophilic groups on the basis of dodecyl bromide, tetradecyl bromide and oxypropylated ethylenediamine // I International Conference on Science and Technology, -Baku: November 29-30, -2018, -pp.23-25.
8. Rahimov, R.A., Hashimzada, S.Z.F. Synthesis and properties of gemini surfactants based on ethylenediamine and alkyl iodides // III International Scientific Conference of Young Researchers dedicated to the 96th anniversary of National Leader of the Azerbaijani People, Heydar Aliyev, -Baku: April 29-30, -2019, -pp.532-533.
9. Rahimov, R.A., Hashimzade, S.Z.F. Obtaining and properties of gemini surfactants on the basis of N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine and alkyl iodides // Goals and Prospects of the International Scientific and Practical Conference "The role of engineering in the innovative development of Azerbaijan", -Baku: November 29-30, -2019, -pp.45-46.
10. Khasıyev, H.G., Rahimov, R.A., Hashimzade, S.Z.F. Synthesis and properties of new gemini surfactants based on hexamethylenediamine, propylene oxide and alkyl bromides // Goals and Prospects of the International Scientific and Practical Conference "The role of engineering in the innovative development of Azerbaijan", -Baku: November 29-30, -2019, - pp.27-28.
11. Asadov, Z.H., Ahmadova, G.A., Rahimov, R.A., Hashimzade, S.Z.F. Formation of Premicellar Aggregates in the Surfactants Containing 2-hydroxypropyl Fragment in Head Group // 1st-İnternational Conference on Noncovalent İnteractions. -Lisbon:

September 2-6, -2019, - P 66.
12. Asadov, Z.H. Micellization and Adsorption properties of New Cationic Gemini Surfactants Having Hydroxyisopropyl Group / Z.H.Asadov, G.A.Ahmadova, R.A.Rahimov, S.Z.F.Hashimzade, E.H.Ismayilov, N.Z.Asadova, S.A.Suleymanova, F.I.Zubkov, A.M.Mammadov, D.B.Agamaliyeva // Journal of Chemical & Engineering Data, -Niderland: - 2019. Vol. 64, -pp.952−962.
13. Asadov, Z.H. Surface properties and premicellar aggregation behavior of cationic gemini surfactants with mono- and di-(2-hydroxypropyl)ammonium head groups / Z.H.Asadov, G.A.Ahmadova, R.A.Rahimov, S.Z.F.Hashimzade, Sh.M.Nasibova, E.H.Ismayilov, S.A.Suleymanova, S.A.Muradova, N.Z.Asadova, F.I.Zubkov // Colloids and Surfaces A: Physicochemical and Engineering Aspects, -2019. Vol. 575, -pp.212–221.
14. Rahimov, R.A., Hashimzada, S.Z.F., Asadov, Z.H., Ahmadova, G.A. Effect of the length of the hydrocarbon radical on the petrocollecting ability of dimeric surfactants derived from amino alcohols and dibromopentane // The International Scientific Conference “Actual Problems of Modern Chemistry” Dedicated to the 90th Anniversary of the Academician Y.H. Mammadaliyev, Institute of Petrochemical Processes, -Baku: October 2-4, -2019, -pp.426.
15. Rahimov, R.A., Hashimzada, S.Z.F., Asadov, Z.H. Obtaining and properties of gemini surfactants on the basis of N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine and nonyl halogenides. // The International Scientific Conference “Actual Problems of Modern Chemistry” Dedicated to the 90th Anniversary of the Academician Y.H. Mammadaliyev, Institute of Petrochemical Processes, -Baku: October 2-4, -2019, -pp.419.
16. Rahimov, R.A., Hashimzada, S.Z.F., Asadov, Z.H., Ahmadova, G.A. Obtaining and investigating the properties of new gemini-type surfactants based on higher aliphatic amines, propylene oxide and dibromopentane // The International Scientific Conference “Actual Problems of Modern Chemistry” Dedicated to the 90th Anniversary of the Academician Y.H. Mammadaliyev, Institute of Petrochemical Processes, -Baku: October 2-4, -2019, -pp.429.

17. Hashimzada, S.Z.F. Obtaining and characteristics of tri-and tetramethylenedibromide-based gemini-type surfactants // Journal of Baku Engineering University - Chemistry and Biology, -2019. Vol. 3, № 1, -pp.71-77.

18. Rahimov, R.A. Synthesis and properties of a new dimeric surfactants based on N,N'-bis(2-hydroxypropyl)-ethylenediamine and alkyl iodides for cleaning the water surface from thin oil films / R.A. Rahimov, Z.H. Asadov, S.Z.F. Hashimzada, G.A. Ahmadova // Journal of Environmental Chemistry, -2019, Vol. 28, № 3, -pp.147-153.

19. Hashimzada, S.Z.F., Huseynova, S.M., Rustamova, I.V. Obtaining and characteristics of new gemini-type surfactants based on 1,3-dibromopropane and 1,5-dibromopentane. // International Scientific Conference on "Actual Problems of Modern Natural and Economic Sciences", -Ganja, - November 12-15, -2020, -pp.225-227.

20. Hashimzada, S.Z.F. Obtaining and investigation of gemini-type surfactants based on mono-(2-hydroxypropyl)dodecylamine. // -Baku: Young Researchers, -2020. Vol. VI, № 2, -pp.23-29.

21. Asadov, Z.H. Aggregation and antimicrobial properties of gemini surfactants with mono- and di-(2-hydroxypropyl) ammonium head-groups: Effect of the spacer length and computational studies / Z.H.Asadov, G.A.Ahmadova, R.A.Rahimov, S.Z.F.Hashimzade, Yusif Abdullayev, E.H.Ismayilov, S.A.Suleymanova, N.Z.Asadova, F.I.Zubkov // Journal of Molecular Liquids, -2020. Vol. 302, article 112579.

22. Rahimov, R.A. Surface and biocidal properties of gemini cationic surfactants based on propoxylated 1,6-diaminohexane and alkyl bromides / R.A.Rahimov, G.A.Ahmadova, S.Z.F. Hashimzade, E.Imanov, N.K.Karimova, F.I.Zubkov // Surfactants and Detergents, -2021. Vol.24. -pp.433-444.

The defense will be held on the 23rd of December 2021 at 10:00 AM at the meeting of the Dissertation council ED 1.16 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating at Institute of Petrochemical Processes of the National Academy of Sciences of Azerbaijan

Address: AZ 1025, Baku, Khojaly ave., 30

Dissertation is accessible at the library of the Institute of Petrochemical Processes named after acad. Y.H. Mammadaliyev of National Academy of Sciences of Azerbaijan

Electronic versions of dissertation and its abstract are available on the official website of the www.nkpi.az

Abstract was sent to the required addresses on 19th November 2021

Signed for print: 18.11.2021
Paper format: 60x90 1/16
Volume: 37940
Number of hard copies: 20