J Surfact Deterg (2021) **24:** 433–444
DOI 10.1002/jsde.12506

ORIGINAL ARTICLE

Surface and Biocidal Properties of Gemini Cationic Surfactants Based on Propoxylated 1,6-Diaminohexane and Alkyl Bromides

Ravan A. Rahimov[1,2] · Gulnara A. Ahmadova[2] · Seyid-Zeynab F. Hashimzade[2] · Elmar Imanov[3] · Hajibala G. Khasiyev[1] · Nazani K. Karimova[1] · Fedor I. Zubkov[4]

Received: 17 October 2020 / Accepted: 8 March 2021

Abstract Two new classes of gemini cationic surfactants—hexanediyl-1,6-bis[(isopropylol) alkylammonium] dibromide {in the abbreviation form: $C_nC_6C_n$[iPr-OH] and $C_nC_6C_n$[iPr-OH]$_2$; alkyl: C_nH_{2n+1} with n = 9, 10, 12 and 14}—have been synthesized by interaction of alkyl bromides with N,N′-di-(isopropylol)-1,6-diaminohexane and N,N,N′,N′-tetra-(isopropylol)-1,6-diaminohexane. The surface tension, electrical conductivity, and dynamic light scattering (DLS) techniques were used to investigate the aggregation properties of the gemini cationic surfactants in aqueous solution. The formation of critical aggregates at two concentrations in an aqueous solution from obtained gemini cationic surfactants were determined *via* the tensiometric method. Thus, these gemini cationic surfactants start to form aggregates at concentrations well below their critical micelle concentrations (CMC). The surface properties and the binding degree (β) of the opposite ion were tested against the length of the surfactant hydrocarbon chain and the number of the isopropylol groups in the head group. By applying the DLS technique, it was explored that how the number of isopropylol groups in gemini cationic surfactants with $C_{12}H_{25}$ chain affects the sizes of micelles at concentrations greater than CMC. It was discovered that the obtained gemini cationic surfactants have a biocidal character.

Keywords Surface tension · Gemini cationic surfactant · Biocidal properties · Micellization · Adsorption

J Surfact Deterg (2021) **24:** 433–444.

Introduction

The gemini surfactants have a higher ability to change the properties compared to the conventional surfactants (Kuperkar et al., 2012; Shaheen et al., 2020). Thus, while changing the properties of conventional surfactants by changing the length of the alkyl chain and the nature of the polar group, properties of gemini surfactants can also be controlled by the nature and the length of the chain. Because of the two hydrophilic and two hydrophobic groups of gemini surfactants, they possess some advantages over conventional simple surfactants (Mahdavian et al., 2011; Verma and Ghosh, 2011). The critical micelle concentration (CMC) value of gemini surfactants was found to be lower than conventional surfactants, which resulted in the elevation of surface activity, wetting and foaming properties (Wang et al., 2014). The gemini surfactants and thus solubilization ability (Liu et al., 2020) was also observed higher than conventional surfactants. In

Supporting information Additional supporting information may be found online in the Supporting Information section at the end of the article.

✉ Ravan A. Rahimov
revan_chem@mail.ru; rarahimov@beu.edu.az

[1] Department of Chemical Engineering, Baku Engineering University, Hasan Aliyev Str. 120, Baku, Absheron, AZ 0101, Azerbaijan

[2] Institute of Petrochemical Processes of Azerbaijan National Academy of Sciences, Hojaly Ave. 30, Baku, AZ 1025, Azerbaijan

[3] Department of Chemistry and Biology, Baku Engineering University, Hasan Aliyev Str. 120, Baku, Absheron, AZ 0101, Azerbaijan

[4] Organic Chemistry Department, Faculty of Science, Peoples' Friendship University of Russia (RUDN University), 6 Miklukho-Maklaya St., Moscow, 117198, Russian Federation

consequence, the possibilities of application of gemini surfactants become even more significant. Gemini surfactants are widely applied in the detergent and cleaning agents industry (Huang et al., 2020), in the food industry (Kralova and Sjöblom, 2009), in medicine (Azum et al., 2020; Pavlov et al., 2020), in cosmetology (Mondal et al., 2020), in corrosion inhibition of metals (Hu et al., 2020; Shaban et al., 2020), in catalysis (Mirgorodskaya et al., 2018), and other places (Gabdrakhmanov et al., 2020). The properties of surfactants can be adjusted by changing the length of the hydrophilic group and the nature of the hydrophobic group. Over the last few years, the investigations on the acquisition and research of cationic gemini surfactants containing a hydroxyethyl group have gained significant attention. (Sun et al., 2019). The existence of -OH group in both the spacer and the hydrophilic part causes a decrease in the CMC value of the surfactant. Replacement of the methyl groups with ethylol groups in gemini bis(dodecyldimethylammonium bromide), which contains four methylene groups in the spacer causes a sharp decline in the CMC value of the surfactant; in contrast, the value of the opposite ion binding degree rises (Borse and Devi, 2004). The comparison of surface activity indicators in alkanedyl-α,ω-bis(hydroxyethylmethylhexadecyl ammonium bromide) class gemini cationic surfactants with the length of the spacer chain length(s) = 4, 6, 8, and 10 with gemini surfactants of the dimethylammonium head group with similar structure shows that their CMC value is further reduced when the methyl group in the hydrophilic part of the surfactant is replaced by the hydroxyethyl group (Borse et al., 2005). In this class of surfactants, the length of the spacer chain and the polarity of the main group have a significant effect on the ability of surfactants to form self-aggregation. Increasing the number of hydroxyethyl groups in the hydrophilic part of gemini cationic surfactants has a positive effect on its antimicrobial properties (Sharma et al., 2005), and hence toxicity is reduced (Teresa et al., 2016). In our previous studies, the results of the study of the synthesis and surface activity properties of gemini cationic surfactants with isopropylol groups and spacer chain lengths = 2, 3, 4, and 5 in the hydrophilic part were given (Asadov et al., 2020). However, despite the fact that gemini surfactants containing a hydroxyethyl group with a spacer chain length = 6 are common for studies (Huang et al., 2008), there is no information in the literature on gemini surfactants with a isopropylol group attached to an N atom in the hydrophilic fragment.

The present article deals with the synthesis of new gemini cationic surfactants C_nC_6Cn[iPr-OH] and $C_nC_6C_n$[iPr-OH]$_2$ classes based on the alkyl bromides and N,N′-di-(isopropylol)-1,6-diaminohexane and N,N,N′,N′-tetra-(isopropylol)-1,6-diaminohexane, as well as the study of the properties of aqueous solutions of surfactants was carried out by tensiometric, conductometric, and dynamic light scattering (DLS) methods.

Experimental

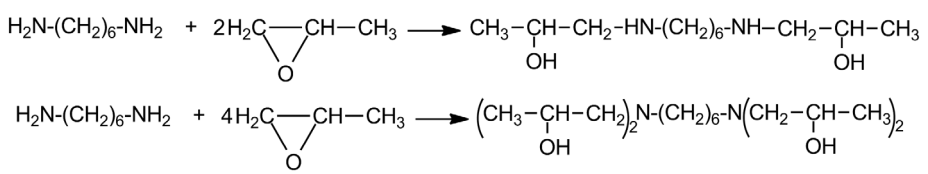
Instruments and Materials

The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker TOP SPIN spectrometer: the ^{1}H NMR spectrum at 300 MHz, and the ^{13}C NMR spectrum at 75.46 MHz. Deuterium oxide (D_2O) was taken as the solvent, tetramethylsilane was taken as the standard, and the chemical shifts were given on the δ (δ in ppm) scale. IR spectra were registered using an ALPHA FT-IR spectrometer (Bruker, Germany) using KBr disks. Propylene oxide (PO) was used as a product (99.97–99.98% purity) of the "Organic Synthesis" factory (Sumgayit, Azerbaijan). 1,6-Diaminohexane (purity > 98%, Alfa Aesar, Germany), 1-bromononane (purity > 99%; Alfa Aesar, Germany), 1-bromodecane (purity > 98%; Sigma-Aldrich, Israel), 1-bromododecane (purity > 98%; Alfa Aesar, England), and 1-bromotetradecane (purity > 98%; Alfa Aesar, Germany).

Synthesis of N,N′-Di-(Isopropylol)-1,6-Diaminohexane and N,N,N′,N′-Tetra-(Isopropylol)-1,6-Diaminohexane

The reaction of the 1,6-diaminohexane and PO, respectively, at 1:2 and 1:4 M ratios results in the formation of N,N′-di-(isopropylol)-1,6-diaminohexane and N,N,N′,N′-tetra-(isopropylol)-1,6-diaminohexane (Scheme 1).

To synthesize N,N,N′,N′-tetra-(isopropylol)-1,6-diaminohexane, 0.45 mol of PO was added in a flask to 0.1 mol of



Scheme 1 Reaction scheme of the synthesis of N,N′-di-(isopropylol)-1,6-diaminohexane and N,N,N′,N′-tetra-(isopropylol)-1,6-diaminohexane

1,6-diaminohexane. The reaction was carried out in a nitrogen atmosphere at room temperature for 2 weeks (Hasanov et al., 2020a, b).

Synthesis of Cationic Gemini Surfactants

Samples of 0.1 mol of N,N′-di-(isopropylol)-1,6-diaminohexane (or N,N,N′,N′-tetra-(isopropylol)-1,6-diaminohexane) and 0.2 mol of 1-bromononane (or respective amount of 1-bromodecane, 1-bromododecane, and 1-bromotetradecane) were refluxed with 100 mL of dry acetone at 95 °C for 24–26 h. The purification of the acquired raw white solid was carried out by washing with a hexane/ethyl acetate mixture. After that, should be obtained reaction product was exposed to further purification *via* recrystallization from an acetone/methanol mixture four to five times; then, ammonium salt was dried out in a desiccator for 15–18 h. In a yield of 88–94%, a white yellowish solid product was obtained. $C_nC_6C_n$[iPr-OH] class gemini surfactants are solids, and $C_nC_6C_n$[iPr-OH]$_2$ class gemini surfactants are viscous liquids. The structures of the synthesized surfactants were confirmed by IR and NMR spectra. The IR and ^{1}H NMR spectra of $C_{12}C_6C_{12}$[iso-Pr(OH)]$_2$ are given in Figs 1 and 2. IR spectrum ν, cm^{-1}: 3318 ν (OH), 2922 and 2854 ν (CH), 1459 and 1375 δ (CH), 1135 ν (C–N), 1086 and 1000 ν (C–O), 724 δ –(CH_2)–$_x$. ^{1}H NMR (300.13 MHz, D_2O), δ (ppm): 0.78–0.80 (C$\underline{H}_3$), 1.06–1.07 (CH-C$\underline{H}_3$), 1.20 (CH_2 chain), 1.71 (C$\underline{H}_2$-CH$_2$-N$^+$H), 3.22 (N$^+$H-C$\underline{H}_2$-CH$_2$) 3.91 (N$^+$H-C$\underline{H}_2$-CH-OH), 4.13 (N$^+$H-CH$_2$-C$\underline{H}$-OH). The IR and NMR spectra of $C_{12}C_6C_{12}$[iso-Pr(OH)] are given in Figs S1 and S2. The reactions were performed according to Scheme 2.

Determination of the Synthesized Gemini Surfactants Surface Activity and Electrical Conductivity

The surface tension values of the synthesized gemini cationic surfactants were defined using a Du Nouy tensiometer (Asadov et al., 2018); 0.00025–4.0% of aqueous solutions of gemini surfactants were prepared, and their surface tension was calculated at 298 K after 24 h of storage. Deionized water was used in the preparation of the surfactant solutions. At the boundary with air at 298 K, the surface tension of deionized water was 72 mN m^{-1}. During the study, relevant graphs were plotted using experiment results in which the tensiometer error was lower than ±0.15 mN m^{-1}.

The specific electrical conductivity of aqueous solutions of obtained gemini cationic surfactants was defined by ANION-402 techniques (Asadov et al., 2018). For the study, 0.001–4.0% of aqueous solutions were first prepared, and after 48 h, the specific electrical conductivity values of the prepared solutions were evaluated at 298 K.

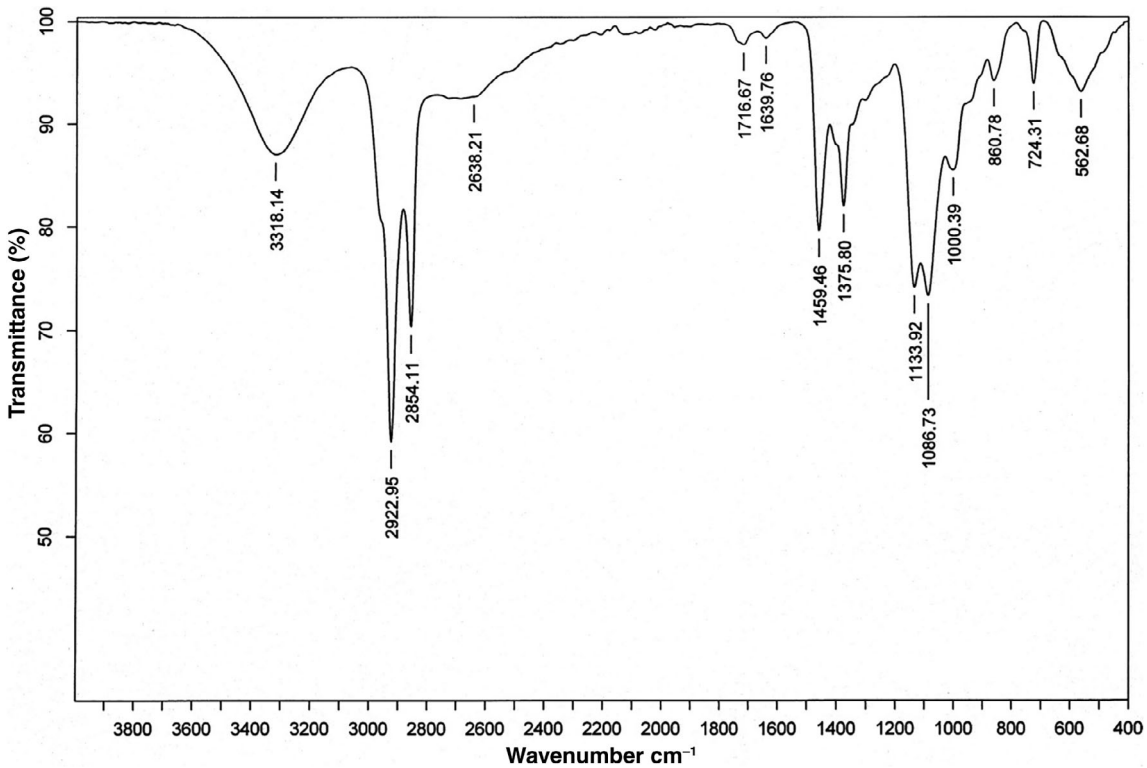


Fig 1 IR spectrum of $C_{12}C_6C_{12}$[iso-Pr(OH)]$_2$

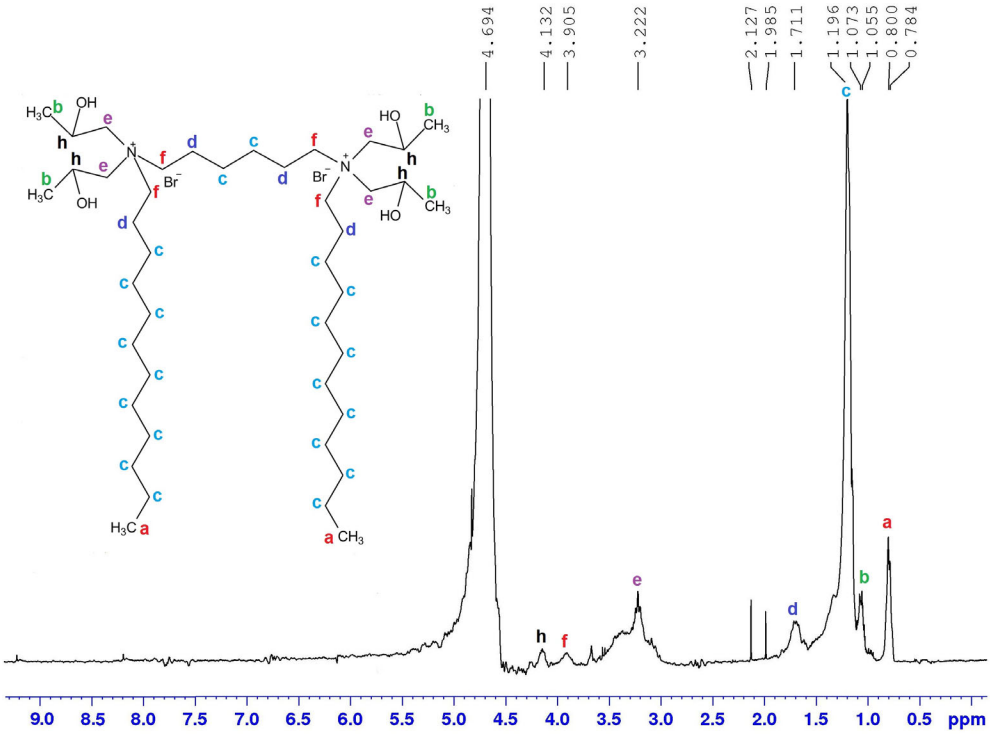
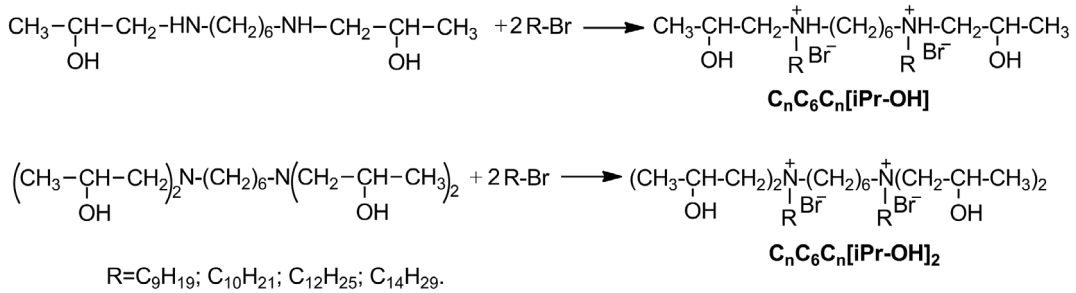


Fig 2 ^{1}H NMR spectrum of $C_{12}C_6C_{12}$[iso-Pr(OH)]$_2$



Scheme 2 Reaction scheme of the synthesis of gemini cationic surfactants

The specific electrical conductivity of double-distilled water taken in the preparation of solutions at 298 K was 1.5–2.4 μS cm^{-1}. During the tests, relevant graphs were plotted using the conductometer results with an error of ±0.3 μS·cm^{-1}.

Determination of the Size of Micellar Aggregates

The size distribution of micellar aggregates formed in an aqueous solution of obtained $C_{12}C_6C_{12}$[iPr-OH] and $C_{12}C_6C_{12}$[iPr-OH]$_2$ gemini cationic surfactants was determined using a particle size analyzer instrument (HORIBA LB-550; Japan) at 298.15 K. The 650 nm laser diode of power 5 mW was used as a light source. The measurement scale was from 1 nm to 6 μm. The sample concentration was 0.12% and 0.3%. Every sample has been weighed at least three times. Diffusion coefficients (D) distribution of the solutes was obtained by analyzing the correlation function of scattering data *via* the CONTIN process. Then, the apparent equivalent hydrodynamic diameter (Dh) was defined using the Stokes–Einstein equation (Frizzo et al., 2016) Dh = kT/3πηD, where T is the absolute temperature, k Boltzmann constant, and η viscosity of the solvent.

Biocidal Properties of Gemini Cationic Surfactants

Two gram-negative (*Escherichia coli* and *Pseudomonas aeruginosa*) bacteria and one gram-positive (*Staphylococcus aureus*) bacterium and fungus (*Candida albicans*) laboratory strains were taken to study the biocidal properties of the

obtained gemini cationic surfactants (Shaban et al., 2016). These bacteria were cultured in fleshy peptone agar, but the yeast in *Sabouraud*. The biocidal activity of gemini cationic surfactants was investigated by disk diffusion. In this method, suspensions were prepared from daily cultures of microorganisms, with 1 billion microbial cells ml^{-1}. Each prepared suspension of the microorganism was evenly distributed through tampons on the surface of the appropriate nutrient media. Each gemini surfactant and their one, two, and four times diluted solutions were then impregnated into sterile paper disks with a diameter of 6 mm, and the microorganisms were arranged on the surface of inoculated nutrient media. Measurements were made after the prepared samples were stored at 37 ° C for 24 h. The biocidal properties were evaluated by measuring the diameter of the inhibition zone (mm). Triplicates were maintained, and the procedure on inhibition was repeated three times. The measurements had been taken in three different fixed directions for each replicate. In addition, sterile water has been used as a negative control.

Result and Discussion

Surface Properties of Gemini Cationic Surfactants

The surface tension values (γ) of the aqueous solutions of both classes of obtained gemini cationic surfactants at the boundary with air were measured, and surface tension *versus* concentration were established (Figs 3 and 4). As shown in the graphics, the values of surface tension decrease sharply as the concentration of gemini cationic surfactants rises. The values of surface tension do not change after a certain concentration, *i.e.*, stability is observed. The concentration at which stabilization begins is taken as the CMC value (Table 1). As can be seen from the table, CMC values for $C_nC_6C_n$[iPr-OH]$_2$ class gemini cationic surfactants are lower than for $C_nC_6C_n$[iPr-OH] class gemini cationic surfactants. In both classes of gemini cationic surfactants, the CMC values diminish as the hydrocarbon chain length increases.

As shown on Table 2, the CMC value for $C_nC_6C_n$(Me) [hexanediyl-1,6-bis(dimethylalkylammonium dibromide)] class gemini surfactants equals to $(6.0–9.1) \times 10^{-3}$ M when n = 10 (Junior et al., 2007), $(1.03–1.08) \times 10^{-3}$ M if n = 12 (Brycki et al., 2016), and $(0.12–0.22) \times 10^{-3}$ M when n = 14 (Mirgorodskaya et al., 2014). On the other side, the CMC value for $C_nC_6C_n$(Et) [hexanediyl-1,6-bis(diethylalkylammonium dibromide)] class gemini surfactants equals to $(5.38–7.33) \times 10^{-3}$ M when n = 10, $(0.63–0.97) \times 10^{-3}$ M when n = 12, and $(0.143–0.175) \times 10^{-3}$ M if n = 14 (Zhang et al., 2011). A comparison of these values of $C_nC_6C_n$[iPr-OH] and $C_nC_6C_n$[iPr-OH]$_2$ (Tables 1 and 2) shows that the CMC value of $C_{14}C_6C_{14}$(Et) class gemini surfactants is smaller than the CMC value of gemini surfactants of $C_{14}C_6C_{14}$[iPr-OH] and $C_{14}C_6C_{14}$[iPr-OH]$_2$. In other cases, $C_nC_6C_n$[iPr-OH] and $C_nC_6C_n$[iPr-OH]$_2$ gemini surfactants CMC values are lower than those of other surfactants with the same alkyl chain. Huang et al. (2008) noted that the value of CMC in hexanediyl-bis[di(ethylol) laurylammonium]dibromide-$C_{12}C_6C_{12}(EtOH)_2$ cationic gemini surfactant is equal to $(0.53–0.68) \times 10^{-3}$ M. The surfactant with an identical length of the alkyl chain $C_{12}C_6C_{12}$[iPr-OH]$_2$, which holds isopropylol group, has

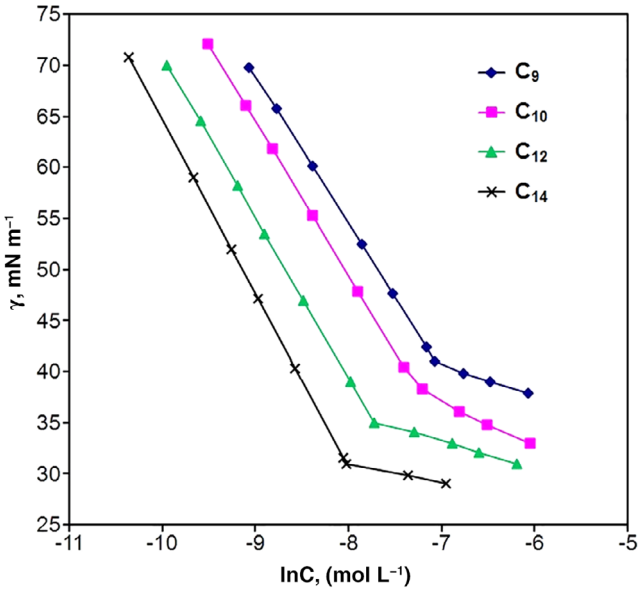


Fig 3 Natural logarithmic plots of surface tension against the concentration of $C_nC_6C_n$[iPr-OH] at 25.0 °C

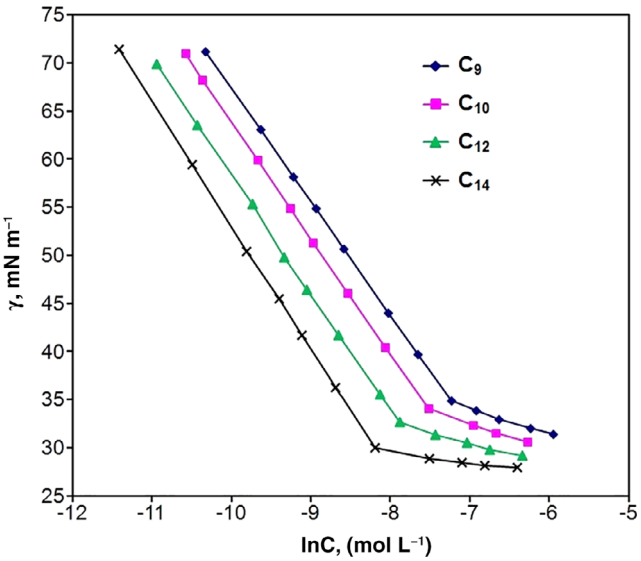


Fig 4 Natural logarithmic plots of surface tension against the concentration of $C_nC_6C_n$[iPr-OH]$_2$ at 25.0 °C

Table 1 Surface parameters of synthesized gemini cationic surfactants 298 K[a]

Surfactants	β	CMC[b] × 10^4, mol dm^{-3}	CMC[c] × 10^4, mol dm^{-3}	Γ_{max} × 10^{10}, mol cm^{-2}		A_{min} × 10^2, nm^2		pC_{20}	γ_{CMC}, mN m^{-1}	π_{CMC}, mN m^{-1}
				n = 2	n = 3	n = 2	n = 3			
$C_9C_6C_9$[iPr-OH]	0.170	8.50	8.78	2.93	1.95	56.7	85.0	3.40	42.2	29.8
$C_{10}C_6C_{10}$[iPr-OH]	0.207	5.99	6.14	3.05	2.03	54.4	81.6	3.55	38.0	34.0
$C_{12}C_6C_{12}$[iPr-OH]	0.409	4.43	4.61	3.20	2.14	51.8	77.8	3.83	36.0	36.0
$C_{14}C_6C_{14}$[iPr-OH]	0.546	3.27	3.24	3.43	2.29	48.4	72.6	4.02	35.5	36.5
$C_9C_6C_9$[iPr-OH]$_2$	0.149	6.18	6.25	2.36	1.57	70.4	105.6	3.78	34.9	37.1
$C_{10}C_6C_{10}$[iPr-OH]$_2$	0.191	5.60	5.86	2.43	1.62	68.3	102.4	3.92	34.1	37.9
$C_{12}C_6C_{12}$[iPr-OH]$_2$	0.284	3.54	3.47	2.48	1.65	67.0	100.5	4.13	32.7	39.3
$C_{14}C_6C_{14}$[iPr-OH]$_2$	0.324	2.65	2.66	2.59	1.73	64.0	96.0	4.31	30.0	42.0

[a]The standard uncertainties (u) are u(T) = 0.1 K and u(p) = 20 kPa. The combined expanded uncertainties (U_c) are $U_c(\beta)$ = 0.005, $U_c(\Gamma_{max})$ = 0.01 mol cm^{-2}, $U_c(A_{min})$ = 0.005 nm^2, U_c(CMC) =10^{-6} mol dm^{-3}, $U_c(\gamma)$ = 0.1 mN m^{-1}, $U_c(\pi)$ = 0.1 mN m^{-1}, and $U_c(pC_{20})$ = 0.003 (0.68 level of confidence).

[b]The CMC is measured by the surface tension method.

[c]The CMC is measured by the electrical conductivity method.

the CMC value as 3.54×10^{-4} M. Comparisons show that when the ethylol group in the C_{12} alkyl chain of cationic gemini surfactants is replaced with the isopropylol group, a decrease in the CMC value is observed. A similar regularity is observed in conventional cationic surfactants (Hafidi et al., 2019; Hafidi and ElAchouri, 2019).

The values of surface-chemical parameters of the acquired gemini cationic surfactants—maximum surface excess (Γ_{max}), the minimum cross-sectional area of the polar group of the surfactant (A_{min}), efficiency (pC_{20}), surface pressure (π_{CMC})—were computed using the given below equations:

$$\Gamma_{max} = -\frac{1}{nRT}\lim_{C\to C_{CMC}}\frac{d\gamma}{dlnC} \quad (1)$$

$$A_{min} = 10^{16}/N_A\Gamma_{max} \quad (2)$$

$$pC_{20} \cong -\log_{10}C_{(-\Delta\gamma=20)} \quad (3)$$

$$\pi_{CMC} = \gamma_0 - \gamma_{CMC} \quad (4)$$

where T is the absolute temperature, R is the universal gas constant at which the experiment is performed, N_A is the Avogadro constant, γ_0-SAM is the value of the surface tension at the water/air boundary, and γ_{CMC} is the value of the surface tension at the critical micelle formation concentration. "n" alters with the number of entities adsorbed at the boundary between the two phases. It is difficult for a gemini cationic surfactant to assign the magnitude of "n" directly. However, even if the value used for "n" influences the computed values of Γ_{max} and A_{min}, it does not affect alteration of the values of Γ_{max} and A_{min} by the carbon number in hydrocarbon chain. Thus, the value of "n" was taken as 2 and 3 in our study (Li et al., 2015). The calculated colloid-chemical parameters for gemini cationic surfactants were given in Table 1. As shown on the table, the value of Γ_{max} increases and the value of A_{min} decreases as

Table 2 CMC values of n-6-n–type gemini surfactants with different head groups, obtained from conductivity measurements (25 °C)

Gemini surfactants	CMC, 10^{-3} M (at 25 °C)	References
$C_{10}C_6C_{10}$(Me)	9.1	Junior et al. (2007)
$C_{12}C_6C_{12}$(Me)	1.1	Junior et al. (2007)
	1.055	Brycki et al. (2016)
$C_{14}C_6C_{14}$(Me)	0.18	Wagay et al. (2020)
	0.22[a]	Mirgorodskaya et al. (2014)
$C_{10}C_6C_{10}$(Et)	7.37	Zhang et al. (2011)
$C_{12}C_6C_{12}$(Et)	1.04	Zhang et al. (2011)
$C_{14}C_6C_{14}$(Et)	0.164	Zhang et al. (2011)
$C_{12}C_6C_{12}$(Me)(EtOH)	1.05 (at 35 °C)	Garcia et al. (2017)
$C_{12}C_6C_{12}(EtOH)_2$	0.68	Huang et al. (2008)

[a]The CMC is measured by the surface tension method.

the length of the hydrocarbon chain increases from C_9 to C_{14} in both classes of gemini cationic surfactants. In $C_nC_6C_n$[iPr-OH] and $C_nC_6C_n$[iPr-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 $C_nC_6C_n$[iPr-OH]-type and $C_nC_6C_n$[iPr-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 $C_nC_6C_n$[iPr-OH] gemini cationic surfactants is greater than that of $C_nC_6C_n$[iPr-OH]$_2$ gemini cationic surfactants, their Γ_{max} values are relatively small.

The value of pC_{20} rises with increasing hydrocarbon chain length in both classes of surfactants (Table 1).

The value of π_{CMC} increases as the length of the hydrocarbon chain in both class gemini cationic surfactants rises from C_9 to C_{14}. The value of π_{CMC} in $C_nC_6C_n$[iPr-OH]$_2$ class gemini cationic surfactants is higher than $C_nC_6C_n$[iPr-OH] class gemini cationic surfactants.

With the help of the DLS method, the dimensions of the aggregates formed by $C_{12}C_6C_{12}$[iPr-OH] and $C_{12}C_6C_{12}$[iPr-OH]$_2$ gemini cationic surfactants in the aqueous medium were determined. The distribution diagram of the dimensions determined at two different concentrations is given in Figs 5 and 6. The concentration of the surfactant was prepared close to CMC and three times higher. As shown in Fig. 5, $C_{12}C_6C_{12}$[iPr-OH] forms aggregates with a diameter of 76 nm in aqueous solution with a concentration of 0.1% gemini surfactant. When the concentration is increased by about three times, the size of the aggregates increases, and aggregates with a diameter of 115 nm are formed.

In $C_{12}C_6C_{12}$[iPr-OH]$_2$ gemini cationic surfactant, the micellar aggregates have a diameter of 11 nm in a 0.1% concentration and 87 nm in a 0.3% solution (Fig. 6). It can be concluded that when the number of isopropylol groups in the hydrophilic part of surfactant is high, the size of the aggregates in their solid solutions increases.

Specific and Molar Electrical Conductivities

The values of specific electrical conductivity of water solutions of obtained $C_nC_6C_n$[iPr-OH] and $C_nC_6C_n$[iPr-OH]$_2$ gemini cationic surfactants were defined, K *versus* C, and molar electrical conductivity $\Lambda = (K - K_0)/C$ (K_0 is the specific electrical conductivity of pure water) *versus* $C^{0.5}$ graphs were constructed (Figs 7 and S3–S9).

The degree of binding of the counterion (β) was calculated based on the concentration-dependent curves of the specific electrical conductivity of the synthesized gemini surfactants:

$$\beta = 1 - \alpha = 1 - S_2/S_1 \quad (5)$$

where α is the dissociation degree of the counterion of the gemini cationic surfactants, S_1 is the ratio of dκ/dC to the concentration of CMC, and S_2 is the ratio of dκ/dC after the concentration of CMC (Figs 7 and S3–S9). The binding degrees of the counterion of gemini surfactants are given in Table 1. It is being seen in the table, the value of β rises as the length of the hydrocarbon chain increases in both $C_nC_6C_n$[iPr-OH], and $C_nC_6C_n$[iPr-OH]$_2$ class gemini cationic surfactants. When the length of the hydrocarbon chain

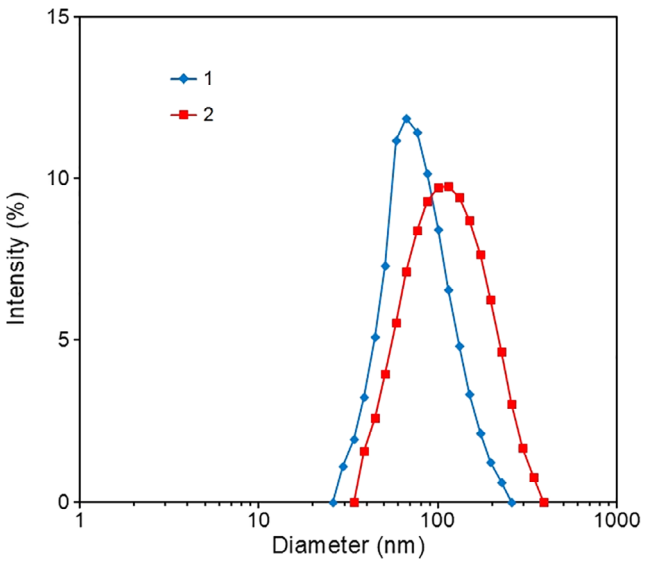


Fig 5 Size distributions of aggregates formed by $C_{12}C_6C_{12}$[iPr-OH] at different concentrations. Concentration, wt%: 0.10 and 0.30

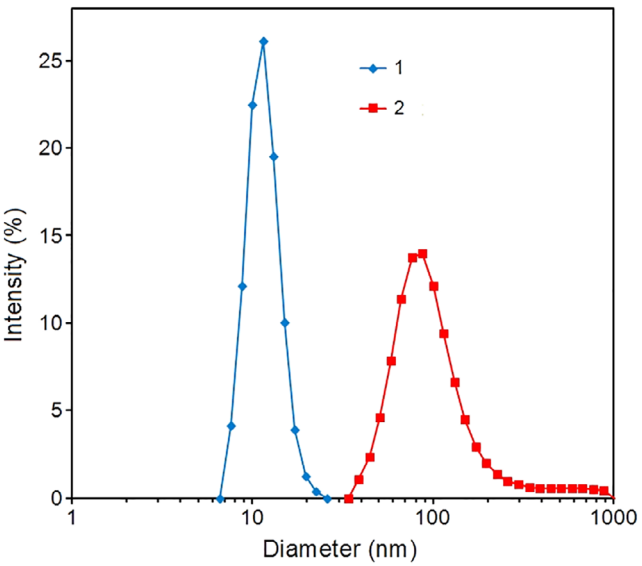


Fig 6 Size distributions of aggregates formed by $C_{12}C_6C_{12}$[iPr-OH]$_2$ at different concentrations. Concentration, wt%: 0.10 and 0.30

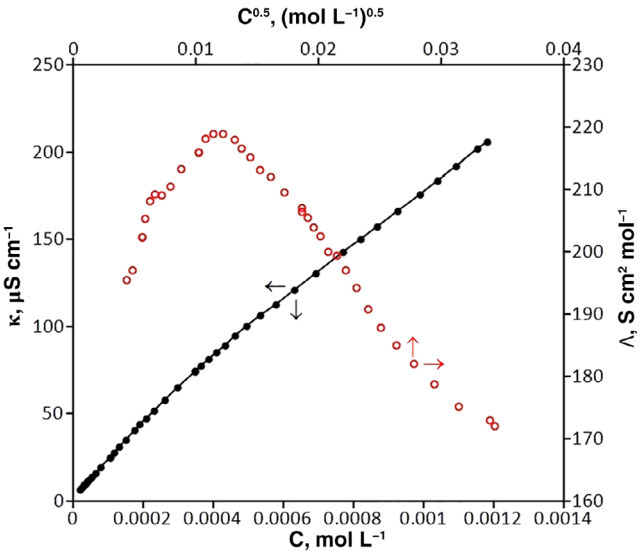


Fig 7 Plot of the specific conductivity **κ** *versus* concentration **C** and of the molar conductivity **Λ** *versus* $\mathbf{C^{0.5}}$ for gemini cationic surfactant $C_{12}C_6C_{12}$[iPr-OH]$_2$ at 25 °C

increases from C_9 to C_{14}, the value of β in $C_nC_6C_n$[iPr-OH] gemini cationic surfactants increases more than in $C_nC_6C_n$[iPr-OH]$_2$ gemini cationic surfactants.

Zana (2002) noted that the formation of premicellar aggregates occurs for the water solutions of alkanediyl-α,ω-bis(alkyl dimethylammonium) dibromide-type (abbreviated as $C_nC_sC_n$(Me)) gemini cationic surfactants with $n \geq 14$ and $s \geq 8$. He determined the formation of premicellar aggregates in these cationic surfactants based on the maxima derived from the dependency curves of Λ *versus* $C^{0.5}$ for the investigated surfactants. Similar cases have been observed in other classes of surfactants with different head groups and shorter spacer chains. Li et al. (2015) commented on the presence of premicellar aggregates in surfactants with an hydrocarbon chain length of 16 in butane-α,δ-bis-(dipropyl alkylammonium) dibromide-type ($C_nC_4C_n$(Pr)) surfactants with a propyl head group. Meanwhile, it was determined that for alkanediyl-α,ω-bis[di(2-hydroxyethyl)dodecylammonium] dibromide-type (abbreviated as C_{12}-C_s-C_{12}(OH)$_2$, with s = 4, 6, 8 and 10) gemini surfactants, dimers are formed in small concentrations due to intermolecular hydrogen bonds between OH groups in the hydrophilic part by various physicochemical ways and dimers are converted into aggregates with increasing concentration, which confirmed the formation of premicellar aggregates in such surfactants. It can be concluded that in surfactants with alkyl (CH_3, C_2H_5 and C_3H_7) groups in the main fragment, premicellar aggregates are observed for surfactants with hydrocarbon chain length ≥ 14 and spacer length ≥ 8 (Liu et al., 2017). However, for gemini cationic surfactants with OH groups in the head part, the formation of premicellar aggregates is observed even when the length of the hydrocarbon chain and spacer is small. The maximum obtained from the curves Λ with $C^{0.5}$ given in Figs 7 and S3–S9 shows that in both synthesized classes of gemini cationic surfactants, premicellar aggregates are formed when the chain length exceeds $C_{12}H_{25}$.

Critical Packing Parameter

Based on the formula proposed by Israelchvil et al. (1976), the critical packing parameter (P) of the obtained gemini cationic surfactants was calculated (Table 3):

$$P = \frac{V_{hydrophobic}}{a_0 \cdot l_0} \quad (6)$$

here, a_0 is the average surface area (mm) captured by the hydrophilic fragment of head group of the surfactants molecule, $V_{hidrophobic}$ is the volume captured by hydrocarbon chain (mm^3), and l_0 is the length of the hydrocarbon chain (mm). For the obtained gemini cationic surfactants, $a_0 = A_{min}$ (n = 3) and $V_{hidrophobic} = 2 \cdot V$ were taken. V and l_0 were estimated using the equations given by Tanford (1972):

$$V = (27.4 + 26.9n) \times 10^{-12}\ mm^3 \quad (7)$$

$$l_0 = (150 + 126.5n) \times 10^{-6} mm \quad (8)$$

Table 3 Values of packing parameter and standard Gibbs free energy changes of micellar formation and adsorption processes of gemini cationic surfactants

Surfactants	l_0, nm	V, nm^3	*P*	ΔG_{mic}, $kJ \cdot mol^{-1}$	ΔG_{ad}, $kJ \cdot mol^{-1}$
$C_9C_6C_9$[iPr-OH]	1.289	0.2695	0.49	−36.80	−39.19
$C_{10}C_6C_{10}$[iPr-OH]	1.415	0.2964	0.51	−40.06	−42.59
$C_{12}C_6C_{12}$[iPr-OH]	1.668	0.3502	0.54	−52.86	−55.41
$C_{14}C_6C_{14}$[iPr-OH]	1.921	0.4040	0.58	−62.41	−64.86
$C_9C_6C_9$[iPr-OH]$_2$	1.289	0.2695	0.40	−36.67	−39.89
$C_{10}C_6C_{10}$[iPr-OH]$_2$	1.415	0.2964	0.41	−39.38	−42.58
$C_{12}C_6C_{12}$[iPr-OH]$_2$	1.668	0.3502	0.42	−46.47	−49.70
$C_{14}C_6C_{14}$[iPr-OH]$_2$	1.921	0.4040	0.44	−50.02	−53.31

Table 4 Biocidal properties of gemini cationic surfactants investigated by the disk diffusion method

Surfactants	Diameter of inhibition zone (mm)				
	Concent. (mg mL^{-1})	*S. aureus*	*E. coli*	*P. aeruginosa*	*C. albicans*
$C_9C_6C_9$[iPr-OH]	8	12	19	14	10
	4	8	13	9	9
	2	—	7	—	—
$C_{10}C_6C_{10}$[iPr-OH]	8	22	15	10	14
	4	12	10	8	9
	2	8	7	—	—
$C_{12}C_6C_{12}$[iPr-OH]	8	37	22	13	46
	4	29	18	9	38
	2	20	9	7	25
$C_{14}C_6C_{14}$[iPr-OH]	8	40	22	16	22
	4	22	14	8	13
	2	16	7	—	10
$C_9C_6C_9$[iPr-OH]$_2$	8	10	12	10	14
	4	7	8	—	10
	2	—	—	—	—
$C_{10}C_6C_{10}$[iPr-OH]$_2$	8	21	18	14	18
	4	12	8	9	11
	2	7	—	—	—
$C_{12}C_6C_{12}$[iPr-OH]$_2$	8	28	22	12	21
	4	19	11	9	11
	2	18	7	—	10
$C_{14}C_6C_{14}$[iPr-OH]$_2$	8	39	25	14	32
	4	32	21	10	29
	2	22	12	7	15

where n is the number of C atoms in the hydrocarbon chain in the surfactant molecule.

As seen from Table 3, as the value of P in the $C_nC_6C_n$[iPr-OH]$_2$ gemini cationic surfactant equals to number in the range $0.33 < P < 0.5$, it indicates that these surfactants are cylindrical micelles in the aquatic environment, in $C_nC_6C_n$[iPr-OH] gemini cationic surfactant, if the value is in the range of $0.5 < P < 1$, so it forms bilayer aggregates in the aquatic environment (Kumar et al., 2018).

Standard Gibbs Free Energy of Adsorption and Micellization Processes of Gemini Cationic Surfactants

The change in the value of the standard Gibbs free energy of the adsorption process at the aqueous solutions - air boundary of the synthesized gemini cationic surfactants was calculated by the following formula (Rosen and Kunjappu, 2012):

$$\Delta G_{mic} = RT(0.5+\beta)\ln X_{CMC} - 0.5RT\ln 2 \quad (9)$$

where T is the absolute temperature (K); R is the universal gas constant (8.314C/mol·K); X_{CMC} is the CMC in molar fraction and X_{CMC} = CMC/55.4, CMC (mol L^{-1}), 55.4 generates from 1 L of pure water corresponding to 55.4 mol of water at 298 K; and β is the degree of binding of the opposite ion. Table 3 shows the change in the values of the Gibbs free energies of the micelle aggregation process of gemini cationic surfactants. As can be seen from the table, for both $C_nC_6C_n$[iPr-OH] and $C_nC_6C_n$[iPr-OH]$_2$ class gemini cationic surfactants, the values of ΔG_{mic} decrease as the value of n rises. These values are lower for $C_nC_6C_n$[iPr-OH] class gemini cationic surfactants than for $C_nC_6C_n$[iPr-OH]$_2$ class surfactants. Therefore, as the number of isopropylol fragments in the main group of this type of gemini cationic surfactants decreases, their tendency to micelle formation increases. A similar situation occurs with gemini surfactants of the 2-hydroxyethyl group (Borse and Devi, 2004).

The change in the value of the standard Gibbs free energy of the adsorption process at the aqueous solutions - air boundary of the synthesized gemini cationic surfactants is calculated by the following formula (Rosen and Kunjappu, 2012):

$$\Delta G_{ad} = \Delta G_{mic} - 0.6023\,\pi_{CMC}A_{CMC} \quad (10)$$

The change in the value of the standard Gibbs free energy of the adsorption process at the aqueous solutions—air boundary of gemini cationic surfactants is shown in Table 3. As can be seen from the table, the value of Gibbs free energy diminishes sharply as the length of the hydrocarbon chain rises in the gemini surfactants. In C_9–C_{10} alkyl chain gemini cationic surfactants, the value of ΔG_{ad} is similar in both classes of gemini cationic surfactants. However, as the chain length $(CH_2)_n$ rises, the value of ΔG_{ad} decreases further for $C_nC_6C_n$[iPr-OH] class gemini cationic surfactants and gets lower values than for $C_nC_6C_n$[iPr-OH]$_2$ class. A comparison of the values of ΔG_{mic} and ΔG_{ad} shows that the adsorption process is more spontaneous than the micelle formation process.

Biocidal Properties of Gemini Cationic Surfactants

It is known that the biocidal properties of surfactants change depending on the length of the hydrocarbon chain. The biocidal properties of surfactants enhance with the increasing length of the hydrocarbon chain (Birnie et al., 2000). It has been shown that in some cases, the biocidal properties of surfactants depend on the value of the CMC in addition to the length of the alkyl chain, as their CMC values decrease as the length of the alkyl chain increases. Consequently, as the value of CMC diminishes in surfactants, their biocidal properties increase.

Table 4 shows the results of the study of the biocidal properties of synthesized gemini surfactants. As can be seen from the table, $C_{14}C_6C_{14}$[iPr-OH] and $C_{14}C_6C_{14}$[iPr-OH]$_2$ surfactants, which have a longer alkyl chain length, are more effective against *S. aureus* bacteria. The $C_{14}C_6C_{14}$[iPr-OH]$_2$ surfactant is effective against the *E.coli* bacterium, and $C_{14}C_6C_{14}$[iPr-OH] and $C_{14}C_6C_{14}$[iPr-OH]$_2$ surfactants with long alkyl chains have more effective antifungal properties against the *C. albicans* fungus. The effect of $C_{14}C_6C_{14}$[iPr-OH] gemini cationic surfactant compared to this fungus is higher. Gemini cationic surfactants have relatively weak antibacterial properties against the bacterium *P. aeruginosa*, the most effective of which is the $C_{14}C_6C_{14}$[iPr-OH]$_2$ surfactant. 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.

Conclusion

Two new classes of gemini cationic surfactants based on alkyl bromides, N,N′-di-(isopropylol)-1,6-diaminohexane and N,N,N′,N′-tetra-(isopropylol)-1,6-diaminohexane, have been synthesized. The ability of gemini cationic surfactants to form micelles was determined by tensiometric and conductometric methods. Some surface activity parameters were calculated according to surface tension and specific electrical conductivity isotherms. It was determined that in both classes of gemini cationic surfactants, as the length of the hydrocarbon chain in the hydrophobic part rises, the critical micelle formation concentration (CMC), the minimum cross-sectional area of the polar group of the surfactant (A_{min}), and the standard Gibbs free energy variation of the micelle formation and adsorption processes decrease (ΔG_{mic} and ΔG_{ad}); however, maximum adsorption (Γ_{max}), binding degree (β), surface pressure (π_{CMC}), and adsorption efficiency (pC_{20}) increases. Using the DLS method, it was determined that the diameters of the aggregates of $C_{12}C_6C_{12}$[iPr-OH] and $C_{12}C_6C_{12}$[iPr-OH]$_2$ gemini cationic surfactants vary depending on the concentration of surfactants. The biocidal activities of obtained gemini cationic surfactants depend less on the number of isopropylol groups and more on the length of the hydrocarbon chain. C_{14} chain surfactants have more effective biocidal properties.

Acknowledgements Funding for this research was provided by the Ministry of Education and Science of the Russian Federation (award no. 075-03-2020-223 (FSSF-2020-0017)). (Fedor I. Zubkov determined the degree of purity and analyzed the spectroscopic results of the obtained surfactants). The authors thank the Institute of Petrochemical Processes of the National Academy of Sciences of Azerbaijan for supporting this.

Conflict of Interest The authors declare that they have no conflict of interest.

References

Asadov, Z. H., Ahmadova, G. A., Rahimov, R. A., Abilova, A. Z., Zargarova, S. H., & Zubkov, F. I. (2018) Synthesis and properties of quaternary ammonium surfactants based on alkylamine, propylene oxide, and 2-chloroethanol. *Journal of Surfactants and Detergents*, **21**:247–254. https://doi.org/10.1002/jsde.12008

Asadov, Z. H., Ahmadova, G. A., Rahimov, R. A., Hashimzade, S.-Z. F., Abdullayev, Y., Ismailov, E. H., … Autschbach, J. (2020) Aggregation and antimicrobial properties of gemini surfactants with mono- and di-(2-hydroxypropyl)ammonium head-groups: Effect of the spacer length and computational studies. *Journal of Molecular Liquids*, **302**:112579. https://doi.org/10.1016/j.molliq.2020.112579

Azum, N., Rub, M. A., Azim, Y., & Asiri, A. M. (2020) Micellar and spectroscopic studies of amphiphilic drug with nonionic surfactant in the presence of ionic liquids. *Journal of Molecular Liquids*, **315**:13732. https://doi.org/10.1016/j.molliq.2020.113732

Birnie, C. R., Malamud, D., & Schnaare, R. L. (2000) Antimicrobial evaluation of *N*-alkyl betaines and *N*-alkyl-*N*, *N*-dimethylamine oxides with variations in chain length. *Antimicrobial Agents and Chemotherapy*, **44**:2514–2517. https://doi.org/10.1128/aac.44.9.2514-2517.2000

Borse, M., Sharma, V., Aswal, V. K., Goyal, P. S., & Devi, S. (2005) Effect of head group polarity and spacer chain length on the aggregation properties of gemini surfactants in an aquatic environment. *Journal of Colloid and Interface Science*, **284**:282–288. https://doi.org/10.1016/j.jcis.2004.10.008

Borse, M. S., & Devi, S. (2004) Dependence of aggregation behavior and physicochemical properties of bis-cationic surfactants on the polarity of surfactant head group. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **245**:1–8. https://doi.org/10.1016/j.colsurfa.2004.06.019

Brycki, B., Drgas, M., Bielawska, M., Zdziennicka, A., & Jańczuk, B. (2016) Synthesis, spectroscopic studies, aggregation and surface behavior of hexamethylene-1,6-bis(N,N-dimethyl-N-dodecylammonium bromide). *Journal of Molecular Liquids*, **221**:1086–1096. https://doi.org/10.1016/j.molliq.2016.06.075

Frizzo, C. P., Bender, C. R., Salbego, P. R. S., Black, G., Villetti, M. A., & Martins, M. A. P. (2016) Thermodynamic properties of the aggregation behavior of a dicationic ionic liquid determined by different methods. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **494**:1–8. https://doi.org/10.1016/j.colsurfa.2016.01.015

Gabdrakhmanov, D. R., Vasilieva, E. A., Voronin, M. A., Kuznetsova, D. A., Valeeva, F. G., Mirgorodskaya, A. B., … Zakharova, L. Y. (2020) Soft nanocontainers based on hydroxyethylated geminis: Role of spacer in self-assembling, solubilization, and complexation with oligonucleotide. *The Journal of Physical Chemistry C*, **124**:2178–2192. https://doi.org/10.1021/acs.jpcc.9b10079

Garcia, M. T., Kaczerewska, O., Ribosa, I., Brycki, B., Materna, P., & Drgas, M. (2017) Hydrophilicity and flexibility of the spacer as critical parameters on the aggregation behavior of long alkyl chain cationic gemini surfactants in aqueous solution. *Journal of Molecular Liquids*, **230**:453–460. https://doi.org/10.1016/j.molliq.2017.01.053

Hafidi, Z., & ElAchouri, M. (2019) The effect of polar head and chain length on the physicochemical properties of micellization and adsorption of amino alcohol-based surfactants. *Journal of Surfactants and Detergents*, **22**:663–672. https://doi.org/10.1002/jsde.12241

Hafidi, Z., Yakkou, L., Guouguaou, F.-E., Amghar, S., & Achouri, M. E. (2019) Aminoalcohol-based surfactants (N-(hydroxyalkyl)-N,N-dimethyl N-alkylammonium bromide): Evaluation of antibacterial activity and molecular docking studies against dehydrosqualene synthase enzyme (CrtM). *Journal of Dispersion Science and Technology*, **42**:514–525. https://doi.org/10.1080/01932691.2019.1700134

Hasanov, E. E., Rahimov, R. A., Abdullayev, Y., Asadov, Z. H., Ahmadova, G. A., Isayeva, A. M., … Autschbach, J. (2020a) New class of cocogem surfactants based on 1,6-diaminohexane, propylene oxide, and long chain carboxylic acids: Theory and application. *Journal of Industrial and Engineering Chemistry*, **86**:123–135. https://doi.org/10.1016/j.jiec.2020.02.019

Hasanov, E. E., Rahimov, R. A., Abdullayev, Y., Asadov, Z. H., Ahmadova, G. A., Isayeva, A. M., … Autschbach, J. (2020b) Counterion-coupled gemini surfactants based on propoxylated 1,6-diaminohexane and fatty acids: Theory and application. *Journal of Molecular Liquids*, **318**:114050. https://doi.org/10.1016/j.molliq.2020.114050

Hu, S., Fu, D., Chen, H., Liu, H., & Xu, B. (2020) Surface activities, antibacterial activity and corrosion inhibition properties of gemini quaternary ammonium surfactants with amido group and carboxylic Counterions. *Journal of Oleo Science*, **69**:703–710. https://doi.org/10.5650/jos.ess19339

Huang, X., Han, Y., Wang, Y., Cao, M., & Wang, Y. (2008) Aggregation properties of cationic gemini surfactants with dihydroxyethylamino headgroups in aqueous solution. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **325**:26–32. https://doi.org/10.1016/j.colsurfa.2008.04.028

Huang, Z., Zhang, S., Zhang, F., Wang, H., Zhou, J., Yu, X., … Fu, W. (2020) Evaluation of a novel morpholine-typed gemini surfactant as the collector for the reverse flotation separation of halite from carnallite ore. *Journal of Molecular Liquids*, **313**:113506. https://doi.org/10.1016/j.molliq.2020.113506

Israelchvil, J. N., Mitchell, D. J., & Ninham, B. W. (1976) Theory of self-assembly of hydrocarbon amphiphiles into micelles and bilayers. *Journal of the Chemical Society*, **72**:1525–1568. https://doi.org/10.1039/F29767201525

Junior, P. B. S., Tiera, V. A. O., & Tiera, M. J. (2007) A fluorescence probe study of gemini surfactants in aqueous solution: A comparison between n-2-n and n-6-n series of the alkanediyl-a,w-bis (dimethylalkylammonium bromides). *Eclética Química*, **32**:47–54. https://doi.org/10.1590/S0100-46702007000200008

Kralova, I., & Sjöblom, J. (2009) Surfactants used in food industry: A review. *Journal of Dispersion Science and Technology*, **30**:1363–1383. https://doi.org/10.1080/01932690902735561

Kumar, D., Azum, N., Rub, M. A., & Asiri, A. M. (2018) Aggregation behavior of sodium salt of ibuprofen with conventional and gemini surfactant. *Journal of Molecular Liquids*, **262**:86–96. https://doi.org/10.1016/j.molliq.2018.04.053

Kuperkar, K., Modi, J., & Patel, K. (2012) Surface-active properties and antimicrobial study of conventional cationic and synthesized symmetrical gemini surfactants. *Journal of Surfactants and Detergents*, **15**:107–115. https://doi.org/10.1007/s11743-011-1269-0

Li, B., Zhang, Q., Xia, Y., & Gao, Z. (2015) Surface properties and aggregation behavior of cationic gemini surfactants with dipropylammonium head-groups. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **470**:211–217. https://doi.org/10.1016/j.colsurfa.2015.02.005

Liu, D., Yang, X., Liu, P., Mao, T., Shang, X., & Wang, L. (2020) Synthesis and characterization of gemini ester surfactant and its application in efficient fabric softening. *Journal of Molecular Liquids*, **299**:112236. https://doi.org/10.1016/j.molliq.2019.112236

Liu, Z., Ge, Y., Zhang, Q., Gao, X., Cai, X., Chen, M., & Yu, X. (2017) Adsorption and micellization of gemini surfactants with diethylammonium headgroups: Effect of the spacer rigidity. *Journal of Surfactants and Detergents*, **20**:765–775. https://doi.org/10.1007/s11743-017-1964-6

Mahdavian, M., Tehrani-Bagha, A. R., & Holmberg, K. (2011) Comparison of a cationic gemini surfactant and the corresponding monomeric surfactant for corrosion protection of mild steel in hydrochloric acid. *Journal of Surfactants and Detergents*, **14**:605–613. https://doi.org/10.1007/s11743-011-1252-9

Mirgorodskaya, A. B., Karpichev, Y., Zakharova, L. Y., Yackevich, E. I., Kapitanov, I. V., Lukashenko, S. S., … Konovalov, A. I. (2014) Aggregation behavior and interface properties of mixed surfactant systems gemini 14-s-14/CTABr. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **457**:425–432. https://doi.org/10.1016/j.colsurfa.2014.06.026

Mirgorodskaya, A. B., Valeeva, F. G., Lukashenko, S. S., Kushnazarova, R. A., Prokop'eva, T. M., Zubareva, T. M., … Zakharova, L. Y. (2018) Dicationic hydroxylic surfactants: Aggregation behavior, guest-host interaction and catalytic effect. *Journal of Molecular Liquids*, **250**:229–235. https://doi.org/10.1016/j.molliq.2017.11.175

Mondal, S., Banerjee, A., & Das, B. (2020) Spectroscopic and interfacial investigation on the interaction of hemoglobin with conventional and ionic liquid surfactants. *Journal of Molecular Liquids*, **301**:112450. https://doi.org/10.1016/j.molliq.2020.112450

Pavlov, R. V., Gaynanova, G. A., Kuznetsova, D. A., Vasileva, L. A., Zueva, I. V., Sapunova, A. S., … Sinyashin, O. G. (2020) Biomedical potentialities of cationic geminis as modulating agents of liposome in drug delivery across biological barriers and cellular uptake.

International Journal of Pharmaceutics, **119640**:587. https://doi.org/10.1016/j.ijpharm.2020.119640

Rosen, M. J., & Kunjappu, J. T. (2012) *Surfactants and interfacial phenomena* (4th ed.). Hoboken, NJ: John Wiley & Sons.

Shaban, S. M., Aiad, I., & Ismail, A. R. (2016) Surface parameters and biological activity of *N*-(3-(dimethyl benzyl ammonio) propyl) alkanamide chloride cationic surfactants. *Journal of Surfactants and Detergents*, **19**:501–510. https://doi.org/10.1007/s11743-016-1795-x

Shaban, S. M., Elsamad, S. A., Tawfik, S. M., Abdel-Rahman, A. A.-H., & Aiad, I. (2020) Studying surface and thermodynamic behavior of a new multi-hydroxyl gemini cationic surfactant and investigating their performance as corrosion inhibitor and biocide. *Journal of Molecular Liquids*, **316**:113881. https://doi.org/10.1016/j.molliq.2020.113881

Shaheen, A., Mir, A. W., Arif, R., & Wani, A. L. (2020) Synthesis, micellization behaviour and cytotoxic properties of imidazolium-based gemini surfactants. *Colloid and Interface Science Communications*, **36**:100257. https://doi.org/10.1016/j.colcom.2020.100257

Sharma, V., Borse, M., Devi, S., Dave, K., Pohnerkar, J., & Prajapati, A. (2005) Oil solubilization capacity, liquid crystalline properties, and antibacterial activity of alkanolamine-based novel cationic surfactants. *Journal of Dispersion Science and Technology*, **26**:421–427. https://doi.org/10.1081/DIS-200054563

Sun, Y., Han, F., Zhou, Y., & Xu, B. (2019) Synthesis and properties of quaternary ammonium gemini surfactants with hydroxyethyl at head groups. *Journal of Surfactants and Detergents*, **22**:675–681. https://doi.org/10.1002/jsde.12277

Tanford, C. (1972) Micelle shape and size. *The Journal of Physical Chemistry*, **76**:3020–3024. https://doi.org/10.1021/j100665a018

Teresa, G. M., Olga, K., Isabel, R., Bogumił, B., Paulina, M., & Małgorzata, D. (2016) Biodegradability and aquatic toxicity of quaternary ammonium-based gemini surfactants: Effect of the spacer on their ecological properties. *Chemosphere*, **154**:155–160. https://doi.org/10.1016/j.chemosphere.2016.03.109

Verma, S. K., & Ghosh, K. K. (2011) Micellar and surface properties of some monomeric surfactants and a gemini cationic surfactant. *Journal of Surfactants and Detergents*, **14**:347–352. https://doi.org/10.1007/s11743-010-1237-0

Wagay, T. A., Shergujri, M. A., & Askari, H. (2020) Mixed micellization behavior of benzyldimethylhexadecylammonium chloride with gemini surfactants and their applications in the synthesis of silver nanoparticles. *Journal of Dispersion Science and Technology*. https://doi.org/10.1080/01932691.2019.1710186

Wang, L., Qin, H., Ding, L., Huo, S., Deng, Q., Zhao, B., … Yan, T. (2014) Preparation of a novel class of cationic gemini imidazolium surfactants containing amide groups as the spacer: Their surface properties and antimicrobial activity. *Journal of Surfactants and Detergents*, **17**:1099–1106. https://doi.org/10.1007/s11743-014-1614-1

Zana, R. (2002) Alkanediyl-α, ω-bis(dimethylalkylammonium bromide) surfactants. 10. Behavior in aqueous solution at concentration below the critical micellization concentration: An electrical conductivity study. *Journal of Colloid and Interface Science*, **246**:182–190. https://doi.org/10.1006/jcis.2001.7921

Zhang, Q., Gao, Z., Xu, F., & Zou, X. (2011) Adsorption and corrosion inhibitive properties of gemini surfactants in the series of hexanediyl-1,6-bis-(diethyl alkyl ammonium bromide) on aluminium in hydrochloric acid solution. *Colloids and Surfaces A: Physicochemical and Engineering Aspects.*, **380**:191–200. https://doi.org/10.1016/j.colsurfa.2011.02.035