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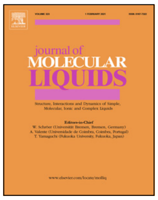

Synthesis, aggregation, and biocidal properties of N-2-hydroxypropyl piperidine based cationic surfactants

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ABSTRACT

New cationic ionic liquid surfactants (ILS) based on (C_9-C_{10}, C_{12} and C_{14}) alkyl bromides and N-2-hydroxypropyl piperidine have been synthesized. Colloidal parameters of aqueous solutions of the obtained ILSs were studied by surface tension and dynamic light scattering methods. Specific electrical conductivity was measured by the conductometric method. Depending on the alkyl chain length, critical micelle concentration (CMC), maximum adsorption (Γ_{max}), the minimum cross-sectional area of the surfactant polar group (A_{min}), adsorption efficiency (pC_{20}), surface pressure (π_{CMC}), degree of counterion binding (β), changes of the Gibbs free energy of micellization and adsorption (ΔG_{mic} and ΔG_{ad}) were studied. The ILSs antimicrobial properties were tested on various bacteria and fungi.

1. Introduction

Ionic liquids are salts consisting of organic cations and organic or inorganic anions in liquid state at temperatures below 100 °C [1]. Ionic liquids are compounds with unique physicochemical properties such as high thermal stability, low flammability, low vapor pressure, and suitable solvents for many polar and non-polar substances [2]. The unique properties mentioned above lead to the expansion of the ionic liquids application area. Ionic liquids with long alkyl chains possess amphiphilic properties and exhibit similar properties to conventional cationic surfactants [3]. Therefore, ILSs have been utilized in liquid–solid extraction [4], corrosion protection [5], synthesis of functionalized carbon nanotubes [6,7], phase-transfer catalysts [8], oil recovery industry [9], dispersants [10], green solvents [11], cosmetics, and textile industries [12]. For this reason, the analysis of the physical and colloid-chemical properties of surface-active ionic liquids in aqueous solutions is very important for the investigation of possibilities of their application in various fields. Extensive studies were carried out on the micellization abilities of ILSs based on imidazolium, morpholinium, pyrrolidinium, pyridinium, and piperidinium cations [13]. In addition to research on the synthesis and study of conventional ionic liquids, considerable works have been carried out on functionalized ionic liquids. Namely, ionic liquids functionalized with the carboxyl group exhibit the ability to dissolve large quantity metal salts [14]. Nitrile group containing ionic liquids boost electrochemical stability [15], and they are distinguished from primary ionic liquids by the extraction efficiency of amines [16]. Hydroxyl-functionalized ionic liquids have been of interest to researchers in recent years [17,18]. Hydroxyl-functionalized imidazolium-based ionic liquids have increased the dissolution of $HgCl_2$ and $LaCl_3$ salts and effective adsorption of amino acids [19,20]. In addition, by changing the length of the alkyl chain of

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Abbreviations: CMC, Critical micelle concentration; C_nHPB, N-alkyl-N-methyl-3-hydroxypiperidinium bromides; C_nHPPB, N-alkyl-N-(2-hydroxypropyl)piperidinium bromides; C_nPDB, N-alkyl-N-methyl-piperidinium bromides; CPP, Critical packing parameter; DLS, Dynamic light scattering; ILS, Ionic liquid surfactant; N, Aggregation number.

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a surfactant, it is possible to change the size of metal nanoparticles [21,22]. In functionalized imidazolium-based ionic liquids, the value of CMC is lower than imidazolium-based surfactants with the same alkyl chain [23]. Hydroxyl-functionalized pyrrolidinium ionic liquid was more effective than other ionic liquid solvents during the transesterification reaction [24]. The CMC value of 2-hydroxyethyl-functionalized ILSs with pyrrolidinium head group is two-fold smaller than that of surfactants with a similar pyrrolidinium head group. At the same time, the micellization and solubilization abilities of these surfactants are higher than those of other cyclic head group surfactants (imidazolium and morpholinium) and classical alkyltrimethylammonium bromides. Consequently, these surfactants can retain antibacterial properties at very low concentrations [25]. Mirgorodskaya et al. synthesized surfactants with the 3-hydroxypiperidinium head group and studied their aqueous solutions by various physicochemical methods. It was determined that surfactants with the 3-hydroxypiperidinium head group exhibit higher solubilization ability than the surfactants with the piperidinium head group, and their CMC value is lower [26]. Therefore, the synthesis and study of the new hydroxyl-functionalized ILSs can be a vital contribution to the area of surfactants.

The work was devoted to the synthesis of new surfactants with C_9-C_{10}, C_{12} and C_{14} alkyl chain and (2-hydroxypropyl)piperidinium head group, and their aqueous solutions were investigated by tensiometric, conductometric, and DLS methods. The surfactivity parameters of the obtained surfactants were compared to the methylpiperidinium and N-methyl-3-hydroxypiperidinium head groups. Additionally, the antimicrobial properties of the synthesized surfactants with (2-hydroxypropyl)piperidinium were investigated.

2. Experimental part

2.1. Reagents and devices

Bruker NMR spectrometer (300.13 MHz) was used for recording ^{1}H NMR spectra. 1-bromononane (Alfa Aesar GmbH & Co KG, Germany), 1-bromodecane (Alfa Aesar, England), 1-bromododecane (Alfa Aesar, England), 1-bromotetradecane (Sigma Aldrich, Japan), piperidine (99%, Alfa Aesar) and propylene oxide (98%, Alfa Aesar) of analytical grade were taken. All the spectra of the synthesized compounds were added to the supporting information (SI).

2.2. Synthesis of N-2-hydroxypropyl piperidine

N-2-hydroxypropyl piperidine was synthesized from piperidine and propylene oxide in a 1: 1 mol ratio according to the following scheme (Scheme 1):

0.1 mol of piperidine was placed in a flat-bottomed flask, and 0.12 mol of propylene oxide was added. The reaction was carried out at room temperature for 50 h in a nitrogen atmosphere by mixing with a magnetic stirrer in a solvent-free condition. Because of the exothermic reaction, the flask was initially poured into the ice bath, thus preventing a temperature elevation. Impurities were removed from the reaction product by vacuum distillation. The reaction yield was defined as 97%. The reaction product is a yellowish clear liquid. It is miscible in water, ethanol, acetone and partially soluble in hexane. The structure of the synthesized N-2-hydroxypropyl piperidine was confirmed by NMR and IR spectroscopic methods. IR ν, cm^{-1}: 3419 ν (OH), 2930, 2855 and 2796 ν (C – H), 1446 and 1373 δ (C – H), 1276 and 1211 ν (C – N), 1089 and 1045 ν (C – O). (Fig. S1). ^{1}H NMR, (300.13 MHz, D_2O), δ (ppm): 1.02 (d, 3H), 1.32–1.46 (m, 6H), 2.25–2.38 (m, 6H), 3.92 (m, 1H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 68.10, 62.09, 55.57, 27.49, 24.11, 21.06.

2.3. Synthesis of cationic ILSs based on N-2-hydroxypropyl piperidine

0.1 mol of N-2-hydroxypropyl piperidine and 30 ml of acetonitrile were placed in a flat-bottomed double-necked flask. After the proper homogenization, 0.1 mol of 1-bromononane (1-bromodecane, 1-bromododecane or 1-bromotetradecane) was added to it. The reaction was conducted in a flask equipped with a magnetic stirrer at reflux condition of acetonitrile for 30–35 h.

The scheme of obtaining ILSs can be shown as follows (Scheme 2).

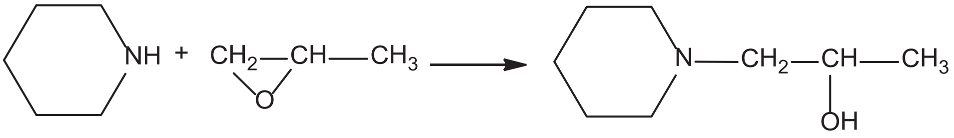
The synthesized cationic ILS was distilled in a vacuum to purify the reaction mixture. In this case, the ILSs were separated from the solvent and the unreacted 1-bromoalkane. For purification of the synthesized gemini surfactants, they were crystallized in acetone thrice. The yield of the synthesized ILSs was 94–95%. They are miscible in ethanol, acetone, ethyl acetate, and partially dissolved in water. The structure of the cationic ILSs was elucidated by NMR and IR spectroscopic methods. 1-bromododecane based ILS: IR ν, cm^{-1}: 3288, 3256 ν (OH), 2919 and 2852 ν (C – H), 1462 and 1373 δ (C – H), 1263 ν (C – N), 1081 and 1043 ν (C – O), 722 δ -(CH_2)-$_x$ (Fig. S3). ^{1}H NMR, (300.13 MHz, D_2O), δ (ppm): 0.77 (t, 3H), 1.16–1.18 (d, 3H), 1.26–1.32 (m 18H), 1.58–178 (m, 6H), 3.22–3.47 (m, 6H), 4.31 (m,1H) (Fig. S4).

2.4. Surfactivity measurement of the produced ILSs

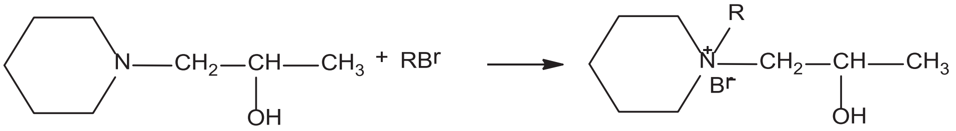
The surface tension of the synthesized ILSs was measured using Du Nouy tensiometer [27]. For this purpose, 0.00025–0.3% aqueous solutions of the cationic ILSs were prepared, and after 24 h storage, their surface tension was recorded at 298 K. All the solutions were prepared with distilled water. The surface tension of the utilized water at the border with air at 298 K was measured as 72.0 mN/m. The results with an error of the tensiometer less than ± 0.2 mN/m were used.

2.5. Specific electroconductivity measurement of the synthesized ILSs

Specific electroconductivity of the aqueous solutions of the cationic ILSs was recorded using Anion-402 conductometer. For this purpose, 0.001–0.5% aqueous solutions were prepared, and after 24 h, their specific electroconductivity was determined at 298 K [27]. Specific electroconductivity of distilled water used for the preparation of the solutions at 298 K was equal to 2.0–2.3 µS/cm. During the study, the results with an error of the conductometer less than ± 0.2 µS/cm were used.



Scheme 1. Reaction scheme of the synthesis of N-2-hydroxypropyl piperidine.



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

Scheme 2. Synthesis of cationic ILSs by the interaction of N-2-hydroxypropyl piperidine with 1-bromoalkanes.

2.6. Dynamic light scattering (DLS)

The size distribution of the aggregates formed by the cationic ILSs in water was recorded at 25 °C using the Particle Size Analyzer (HORIBA LB-550, Japan). The device uses a 650 nm laser diode with a power of 5 mW as a light source. The measurement range of the device was at the range of 1 nm – 6 μm. The concentration of the samples taken for the study was CMC and 3 × CMC. Each sample was measured at least thrice. The distribution of solvent diffusion coefficients (D) was defined by analyzing the correlation function of data scattering through the CONTIN process. The hydrodynamic diameter (D_h) of the aggregates was then obtained using the Stokes-Einstein equation $D_h = kT/3\pi\eta D$, where k is the Boltzmann constant, T is the absolute temperature, and η is the solvent viscosity at that temperature.

2.7. Antimicrobial properties of ILSs

In order to study the antimicrobial properties of ILSs, the suspensions prepared at concentrations 10^6 cells/ml (cfu/ml) from the test cultures of two Gram-positive (*Staphylococcus aureus, Bacillus anthracoides)* bacteria, three Gram-negative (*Pseudomonas aeruginosa, Escherichia coli, Klebsiella pneumoniae*) bacteria and fungi (*Candida albicans*) were evenly distributed on the surface of the appropriate nutrient media using a spatula. The 6-mm-diameter sterile discs made of filter paper were soaked in the studied cationic surfactant and/or its solutions of different concentrations and placed on the surface of the nutrient medium inoculated with microorganisms. The samples were incubated at 37 °C for one day. The effect of cationic surfactants is determined by the diameter of the sterile zone (in mm) around the disc, where no growth of microorganisms is monitored.

The diameter of the sterile zone, which is free of microbial growth, is inversely proportional to the minimum inhibitory concentration of the chemical for the microorganism and describes the degree of sensitivity.

3. Results and discussion

3.1. Surface properties of the ILSs in aqueous solutions

The surface tension values of the aqueous solutions of the cationic ILSs based on N-2-hydroxypropyl piperidine at the border with air were determined by tensiometric method. The surface tension isotherms based on the obtained results were shown in Fig. 1. As can be seen from the figure, as the concentration of all the four ILSs in water increases, the values of surface tension decrease. After reaching a certain concentration, a stabilization in the surface tension value is observed. The minimum concentration corresponding to the point of stabilization is considered as CMC. Table 1 shows the CMC values of the ILSs synthesized. The CMC values of C_9HPPB, C_{10}HPPB, C_{12}HPPB, and C_{14}HPPB ILSs are 2.80, 2.03, 1.10, and 0.58 mM, respectively. As can be seen from the table, the CMC values decrease as the alkyl chain length extends from C_9 to C_{14}. A similar pattern is observed in cationic surfactants with a different head group [28–30]. With elongation of the hydrocarbon chain, the hydrophobicity of the cationic ILSs increases; therefore their CMC values decrease. The head group of a surfactant is one of the main factors affecting micelle stability. In homologous series of single-alkyl chain surfactants differing by alkyl chains, CMC follows the Stauff-Klevens rule forecasting the logarithmic dependence of CMC on the number of carbon atoms in the alkyl group [31]:

$$\log CMC = A - Bn$$

where A and B are constants for a particular homologous series of surfactants at a specific temperature, and n is the number of carbon atoms in the hydrocarbon chain. A constant varies depending on the nature and number of hydrophilic groups. However, B is a constant, indicating the effect of each methylene group added to the alkyl chain on CMC. For non-ionic surfactants, the value of B is about 0.5, for surfactants with a paraffin-chain ionic head group, B = 0.28–0.30, and for bivalent ionic surfactants, B = 0.25 [32]. Fig. 2 shows the dependence of the logarithmic values of CMC at a concentration of mmol/L and 25 °C on the number of carbon atoms in the alkyl chain of the synthesized ILSs. The figure shows a straight line with a slope (B) of 0.1363, intercept (A) 1.3271 and a coefficient of determination of 0.9999.

Table 1 shows the surfactivity parameters of N-alkyl-N-methylpiperidinium bromide and N-alkyl-N-methyl-3-hydroxypiperidinium bromide class surfactants with alkyl chain lengths C_{12} and C_{14}. When comparing the values of CMC in Tables 1 and 2, the following sequence will be obtained: C_nPDB > C_nHPB > C_nHPPB. Thus, when the N-methylpiperidinium head group is replaced by the N-(2-hydroxypropyl) piperidinium group, the CMC value decreases. The CMC value is further reduced when the hydroxyl group in the N-methyl-3-hydroxypiperidinium head group is

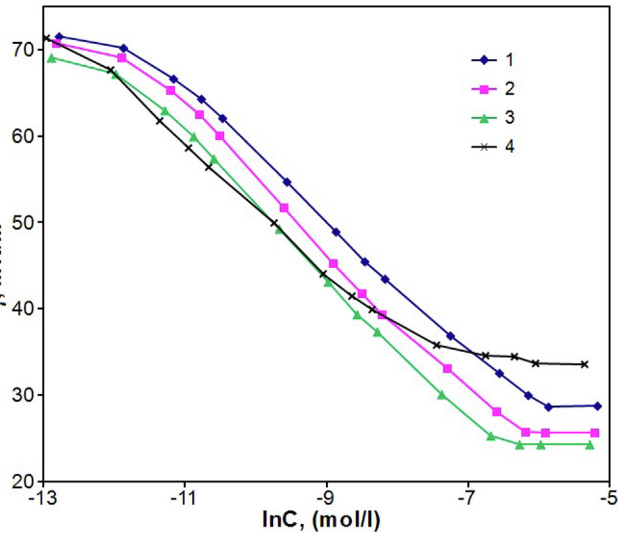


Fig. 1. Surface tension plots of C_9HPPB (1), C_{10}HPPB (2), C_{12}HPPB(3) and C_{14}HPPB(4) in aqueous solution at 25 °C versus natural logarithmic concentration of surfactants.

Table 1
Surfactivity parameters of cationic surfactants with different head groups (25 °C).

Surfactants	CMC × 10^3, mol·dm^{-3}	Γ_{max} × 10^{10}, mol·cm^{-2}	A_{min} × 10^2, nm^2	π_{CMC}, mN·m^{-1}	γ_{CMC}, mN·m^{-1}
C_{12}PDB	11.83	2.31	71.82	31.57	41.43
C_{14}PDB	3.22	2.35	70.65	31.77	41.23
C_{12}HPB	10.0	2.04	81.60	29.90	42.10
C_{14}HPB	3.0	2.37	70.10	31.60	41.40

C_nPDB – N-alkyl-N-methyl-piperidinium bromides [33]
C_nHPB – N-alkyl-N-methyl-3-hydroxypiperidinium bromides [26]

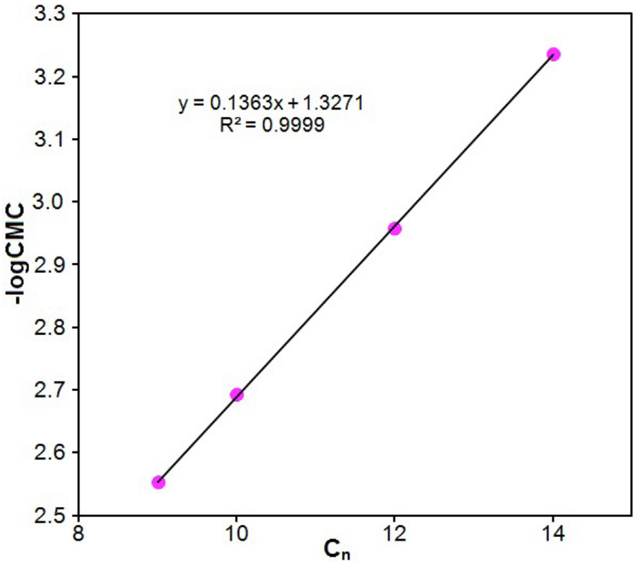


Fig. 2. Dependence of -log(CMC) for C_nHPPB on the number of carbon atoms in the alkyl chain.

replaced by the 2-hydroxypropyl group. Therefore, the CMC value is lower in C_nHPPB- type surfactants.

The value of the maximum surface excess concentration (Γ_{max}) of the synthesized ILSs was determined using Gibbs adsorption isotherm (1), and the minimum surface area occupied by the polar group was calculated using equation (2) [32]:

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

$$A_{min} = 10^{16}/N_A\Gamma_{max}$$

here R is the universal gas constant (8.314 J/mol·K), T is the absolute temperature, C is a surfactant concentration, N_A is Avogadro's number. The value of n is accepted as 2 since there is one counterion linked with each cationic head group.

Γ_{max} and A_{min} values for the synthesized ionic-liquid surfactants are given in Table 2. As shown in Table 2, in ILSs, the Γ_{max} value increases, and the A_{min} value decreases as the length of the alkyl chain increases from C_9 to C_{12}. The same pattern is observed in cationic surfactants with other head groups [28,34]. Γ_{max} and A_{min} values of surfactants with the same alkyl group are given in Tables 1 and 2. It is evident that Γ_{max} values of surfactants with N-(2-hydroxypropyl) piperidinium head group are lower, and A_{min} values are higher than for surfactants bearing the N-methylpiperidinium and N-methyl-3-hydroxypiperidinium head groups.

The surface pressure (π_{CMC}) and the adsorption efficiency (pC_{20}) are two important parameters to characterize the surface activity. These parameters were calculated using the following equations:

$$\pi_{CMC} = \gamma_0 - \gamma_{CMC} \quad (3)$$

$$pC_{20} = -\log C_{20} \quad (4)$$

where γ_0 is the surface tension of a solvent without a surfactant and γ_{CMC} is the surface tension in the presence of a surfactant at CMC [32].

C_{20} is the concentration of a surfactant used to reduce the value of surface tension at the water–air interface by 20 mN·m^{-1}. Table 2 shows the surface pressure and adsorption efficiency of the synthesized ILSs. Surface pressure values decrease in the following order: C_{12}HPPB > C_{10}HPPB > C_9HPPB > C_{14}HPPB. The values of adsorption efficiency increase with the elongation of the alkyl chain. A similar pattern is observed in other classes of cationic [26,32,33] surfactants.

The surface pressure values of the surfactants containing the N-methylpiperidinium and N-methyl-3-hydroxypiperidinium head groups given in Table 1 are lower than the corresponding values of surfactants with N-(2-hydroxypropyl) piperidinium head group.

The critical packing parameter (CPP) values of the cationic ILSs are based on the morphology of aggregates formed in an aqueous solution and calculated by the following equation:

$$CPP = \frac{V_H}{a_0 \times l_C} \quad (5)$$

V_H is the effective volume of the hydrophobic chain, a_0 is the surface area of the polar head group, and l_C is the length of the alkyl chain. At maximum concentration, a_0 can be replaced by A_{min}.

The V_H value changes relevant to the number of carbon atoms in the hydrophobic chain. V_H value should be generated by the following formula [32]:

$$V_H = 27.4 + 26.9 \times (n - 1)\text{Å}^3 \quad (6)$$

The value of l_C can be computed by the following formula depending on the length of the alkyl chain:

$$l_C \le 1.5 + 1.265 \times (n - 1)\text{Å} \quad (7)$$

Table 2
Surfactivity parameters of N-alkyl-N-(2-hydroxypropyl)piperidinium bromide class cationic ILSs (25 °C).

Surfactants	CMC × 10^3, mol·dm^{-3}	Γ_{max} × 10^{10}, mol·cm^{-2}	A_{min} × 10^2, nm^2	β	γ_{CMC}, mN·m^{-1}	pC_{20}	π_{CMC}, mN·m^{-1}	ΔG_{mic}, kJ·mol^{-1}	ΔG_{ad}, kJ·mol^{-1}
C_9HPPB	2.80	1.54	107.5	0.24	28.7	4.01	43.3	–30.29	–33.03
C_{10}HPPB	2.03	1.68	98.9	0.30	25.8	4.19	46.2	–32.90	–35.66
C_{12}HPPB	1.10	1.73	95.8	0.46	24.3	4.33	47.7	–39.17	–41.92
C_{14}HPPB	0.58	1.46	113.5	0.58	36.0	4.36	36.0	–44.90	–47.36

Table 3 shows the critical packaging parameters. As can be observed from the table, CPP values are in the range of 0 ÷ 1/3. Therefore, the micelles of these ILSs in an aqueous solution are in a spheroidal form.

The aggregation number, N, can be determined using methods such as ^{1}H NMR spectroscopic measurements and fluorescence quenching [35]. However, some authors [36,37] have determined the aggregation number by the calculation method:

$$N = \frac{4 \times \pi \times l_C^2}{A_{min}} \tag{8}$$

Table 3 shows the aggregation numbers of ionic ILSs. As seen from the table, the aggregation number in surfactants increases with an increase of the alkyl chain length.

3.2. Specific electroconductivity of ILSs

The specific electroconductivity of aqueous solutions of ILSs was determined by conductometric method at a temperature of 25 °C. Based on the obtained values, dependency graphs between the specific electrical conductivity and concentration were constructed (Figs. 3 and 4). As can be seen from the figures, the specific electroconductivity values increase as the concentration of cationic ILSs in water rises. The dependence of the specific electrical conductivity on concentration is characterized by two linear dependencies at low and large concentrations. The point of intersection of these straight lines corresponds to CMC. The ratio of the angle coefficient of a straight line (S_1) representing the dependence of the specific electrical conductivity on high concentrations to the angle coefficient (S_2) of a straight line at low concentrations is equal to the degree of dissociation of the counterion of ILSs:

$$\alpha = S_1/S_2 = 1\text{-}\beta (9)$$

where α is the degree of dissociation and β is the degree of binding of a counterion. Table 2 shows the binding rates of the counterions of the synthesized ILSs. As can be seen from the table, the value of β rises in surfactants as the length of the alkyl chain increases. This is due to a decrease in the micelle surface charge density [38]. Surfactants with longer alkyl chains form larger aggregates, especially in large structures where the surface-to-volume ratio is small. This means that the polar head groups are more densely packed and surrounded by a large number of counterions.

3.3. Size of the aggregates

The dimensions of the aggregates formed by the synthesized ILSs in an aqueous solution were defined by the DLS method (Fig. 5). As can be seen from the figures, the diameter of C_nHPPB class surfactant aggregates in an aqueous solution at critical micelle concentration is about 10–11 nm. The aggregates formed by C_9HPPB at this concentration are 11 nm in size and 10 nm in other surfactants. At a concentration three times higher than CMC, the size of the surfactant aggregates decreases with elongation of the alkyl chain. Thus, the diameter of the aggregate in C_9-HPPB was 1980 nm, in C_{10}HPPB 65 nm, in C_{12}HPPB 55 nm, and in C_{14}HPPB 9 nm. In cationic ILSs with an alkyl chain length of C_9-C_{12}, the first peak is the presence of small vesicles and the second peak is the presence of large vesicles or bilayer systems. In a surfactant with an alkyl chain length of C_{14}, the size of the aggregates does not change with the change of concentration.

Table 3
Critical packaging parameter and aggregation number of ILSs synthesized on the basis of N-2-hydroxypropyl piperidine.

Surfactants	CPP	N
C_9HMP	0.19	16
C_{10}HMP	0.21	21
C_{12}HMP	0.22	31
C_{14}HMP	0.19	36

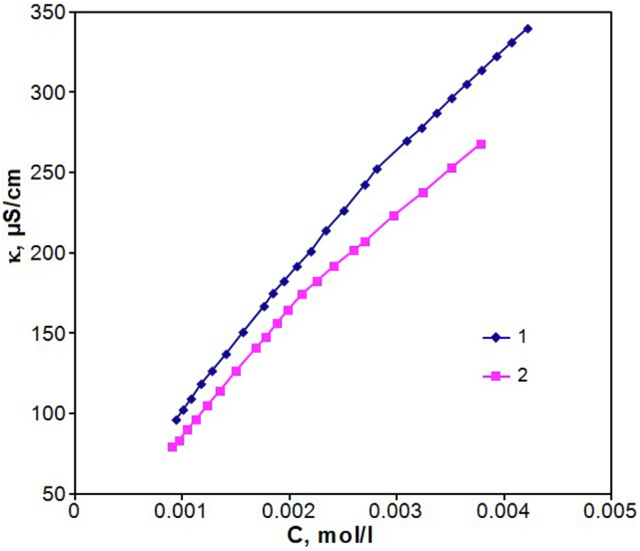


Fig. 3. Plots of specific electrical conductivity versus surfactant concentration for aqueous solutions of C_9HPPB (1) and C_{10}HPPB (2) at 25 °C.

3.4. Antimicrobial activity of the synthesized ILSs

The antimicrobial properties of the ILSs were determined on Gram-positive (*Staphylococcus aureus, Bacillus anthracoides*) bacteria, Gram-negative (*Pseudomonas aeruginosa, Escherichia coli, Klebsiella pneumoniae*) bacteria, and fungi *(Candida albicans)*. The results obtained were described in Table 4. As can be observed from the table, the antimicrobial capacity of the ILSs is high and

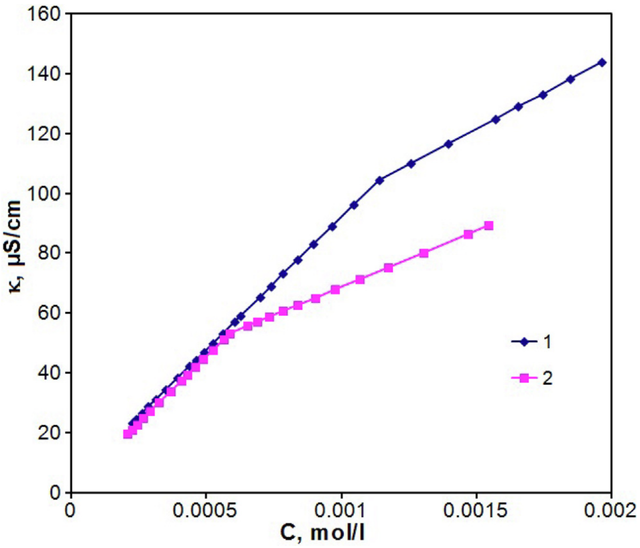


Fig. 4. Plots of specific electrical conductivity versus surfactant concentration for aqueous solutions of C_{12}HPPB (1) and C_{14}HPPB (2) at 25 °C.

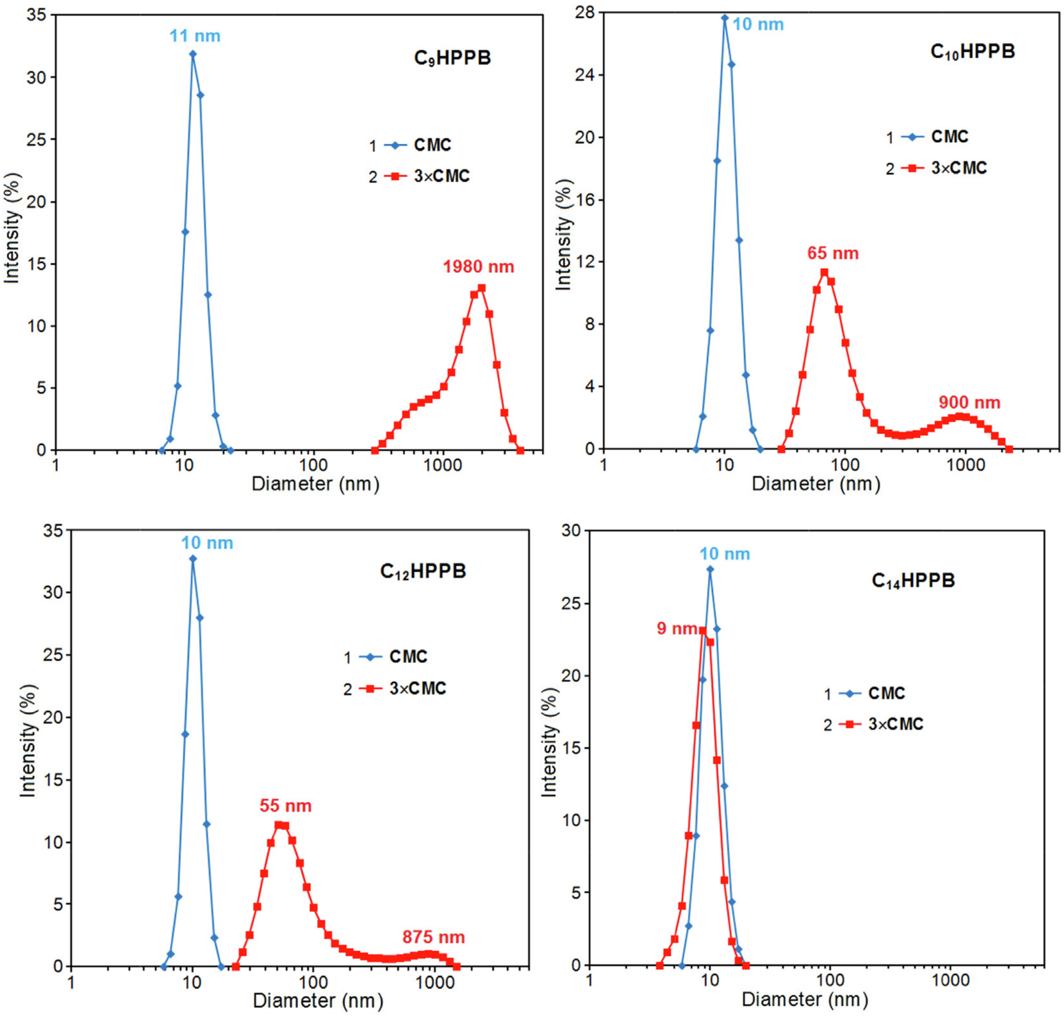


Fig. 5. The results of DLS measurements (25 °C) for the synthesized ILSs at various concentrations.

changes according to the length of the alkyl chain. The data from the table shows that the synthesized cationic surfactants have antimicrobial activity against both Gram-negative and Gram-positive bacteria.

As seen from the table C_{14}HPPB has an intense effect than the other surfactants. As can be seen from Table 2, CMC and ΔG_{ad} values decrease as the length of the alkyl chain increases. Hence, the C_nHPPB class surfactants with lower CMC and ΔG_{ad} values will have higher activity against bacteria growth. It can be said that the antibacterial activity of cationic ILSs against Gram-positive bacteria is higher. The surfactant C_{14}HPPB demonstrated the highest antibacterial properties against *Staphylococcus aureus*. As the length of the alkyl chain increases, the effect of surfactants against the development of *Candida albicans* rises. Therefore, ILSs with a longer alkyl chain ($\geq C_{14}$) can be proposed as a highly effective antimicrobial agent.

3.5. Thermodynamic parameters of the ILSs

Using CMC and β values of the cationic ILSs, the standard Gibbs energy values of micellization at a given temperature were identified based on the following formula [32]:

$$\Delta G_{mic} = (1+\beta)RT\ln X_{CMC} \tag{10}$$

where X_{CMC} is CMC in molar fraction, X_{CMC} = CMC/55.4, where CMC is in mol/L, 55.4 is generated from 1 L of water corresponding

Table 4
Antimicrobial activity of the synthesized surfactants measured by the disc-diffusion method.

Bacteria and fungi	C_9HPPB	C_{10}HPPB	C_{12}HPPB	C_{14}HPPB
	Diameter of inhibition zone (mm)			
Escherichia coli	11	15	18	24
Pseudomonas aeruginosa	7	15	20	13
Klebsiella pneumoniae	11	12	15	13
Staphylococcus aureus	18	14	24	36
Bacillus anthracoides	–	13	11	24
Candida albicans	15	16	21	23

to 55.4 mol of water at 25 °C, β - the degree of counterion binding, R is the universal gas constant, and T is standard absolute temperature (298 K).

The values of the standard Gibbs energy of adsorption process of ILSs at the water–air interface were calculated by the following formula [32]:

$$\Delta G_{ad} = (1+\beta)RT\ln X_{CMC} - 0.6023\pi_{CMC}A_{CMC} \tag{11}$$

where A_{CMC} has the unit $Å^2$ per molecule, and π_{CMC} denotes the surface pressure (in mN/m) at CMC at the border of a surfactant in an aqueous solution with air.

Table 2 shows Gibbs energy values for micellization of the synthesized ILSs in an aqueous solution and adsorption process at the water–air interface. As can be seen, the values of standard Gibbs energy for both micellization and adsorption processes are negative. Thus, in these surfactants, the processes of micelle formation and adsorption occur spontaneously. At the same time, a higher negative value of ΔG_{ad} indicates that the adsorption process takes place prior to the micellization. Figs. 6 and 7 show a dependence graph of ΔG_{mic} and ΔG_{ad} on the alkyl chain length of ILSs. As can be seen from the graph, as the length of the alkyl chain increases, the values of ΔG_{mic} and ΔG_{ad} decrease further. Elongation of the chain creates favorable conditions for micellization due to an increase in hydrophobic interactions between hydrophobic chains.

The Gibbs energy of aggregation contains contributions from the transfer of the ionic liquid segments from bulk water to the aggregates, and bears, therefore, on the relative importance of ionic liquid hydrophilic and hydrophobic moieties to its aggregation. As mentioned earlier [39], the ΔG_{mic} value consists of the head group of a surfactant (ΔG_{mic}, head group), the methylene group of the hydrophobic chain ($\Delta G^{\circ}_{mic,\ CH_2}$) and the CH_3 group at the beginning of the alkyl chain ($\Delta G^{\circ}_{mic,CH_3}$):

$$\Delta G^{\circ}_{mic} = \Delta G^{\circ}_{mic,head\ group} + \Delta G^{\circ}_{mic,CH_3} + n_{CH_2}\Delta G^{\circ}_{mic,CH_2} \tag{12}$$

Then, ΔG_{ad} can be written as follows:

$$\Delta G^{\circ}_{ad} = \Delta G^{\circ}_{ad,head\ group} + \Delta G^{\circ}_{ad,CH_3} + n_{CH_2}\Delta G^{\circ}_{ad,CH_2} \tag{13}$$

where n_{CH_2} is the number of CH_2 groups in the hydrophobic chains of C_nHPPB.

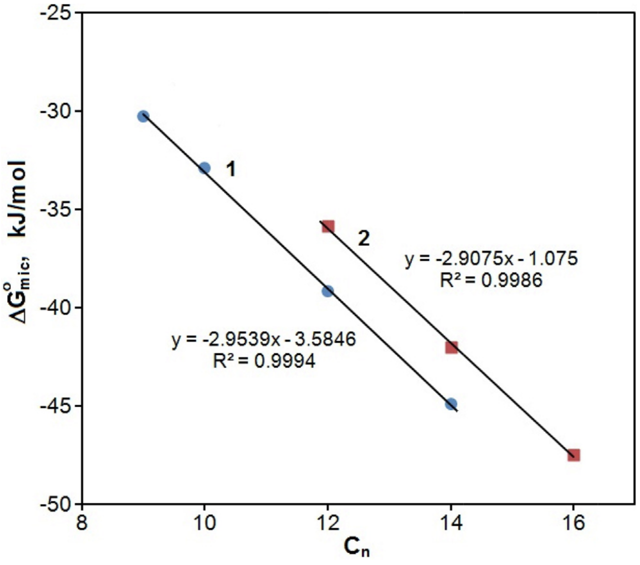


Fig. 6. Dependence of Gibbs free energy change for micellization process of C_nHPPB (1) and C_nPDB (2) on the number of carbon atoms in the alkyl chain.

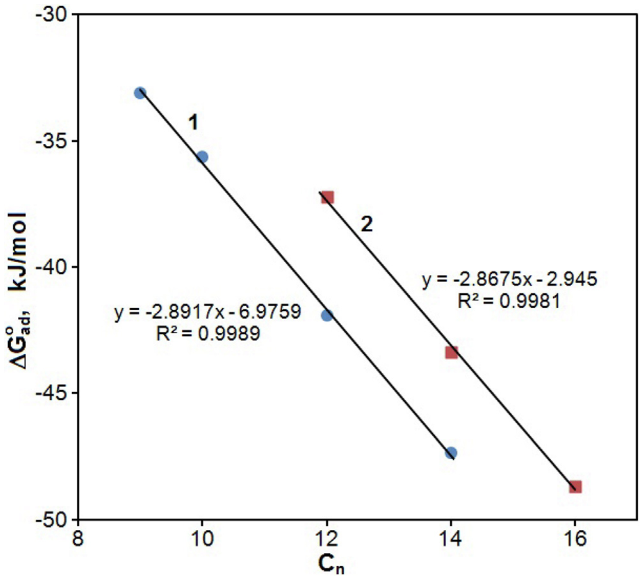


Fig. 7. Dependence of Gibbs free energy change for adsorption process of C_nHPPB (1) and C_nPDB (2) on the number of carbon atoms in the alkyl chain.

As shown in Fig. 6, ($\Delta G_{mic,\ head\ group} + \Delta G_{mic,\ CH_3}$) is equal to −6.54 kJ/mol, and for each methylene group $\Delta G_{mic,CH_2}$ is equal to −2.95 kJ/mol. For N-alkyl-N-methylpyrrolidinium bromide [40] and N-alkyl-N-methylimidazolium bromide [39] class ILSs $\Delta G_{mic,CH_2}$ is also equal to – 3.01 kJ/mol. So, the thermodynamics of the additional methylene groups shift from aqueous solution to a micelle does not depend on the cationic head group. For N-alkyl-N-methyl-piperidinium bromide, N-alkyl-N-methylmorpholinium bromide [33], N-alkyl-N-methylmorpholinium bromide, N-alkyl-N-methylpyrrolidinium bromide and N-alkyl-N-methylimidazolium bromide class ILSs ($\Delta G_{mic,\ head\ group} + \Delta G_{mic,\ CH_3}$) is equal to – 1.08, −3.50, −3.61 and – 3.7 kJ/mol, respectively. In the synthesized N-alkyl-N-(2-hydroxypropyl) piperidinium bromide class ILSs ($\Delta G_{mic,headgroup} + \Delta G_{mic,CH_3}$)value equals −3.59 kJ/mol, being smaller than for N-alkyl-N-methylpiperidinium bromide class ILSs and close to N-alkyl-N-methylpyrrolidinium bromide class ILSs. Thus, in N-alkyl-N-methylpiperidinium bromide class surfactants, the ability of the head group to form micelles improves when the methyl group attached to the nitrogen atom is replaced by the 2-hydroxypropyl group. As shown in Fig. 7, the values of $\Delta G_{ad,CH_2}$ in N-alkyl-N-methylpiperidinium bromide and N-alkyl-N-(2-hydroxypropyl) piperidinium bromide class ILSs are very close to each other. In N-alkyl-N-methylpiperidinium bromide class and N-alkyl-N-(2-hydroxypropyl) piperidinium bromide class ILSs, ($\Delta G_{ad,headgroup} + \Delta G_{ad,CH_3}$) values are equal to −2.95 kJ/mol and −6.98 kJ/mol, respectively. Thus, in ILSs, the adsorption capacity of a surfactant is further improved when the methyl group of the head group is replaced by the 2-hydroxypropyl group.

4. Conclusions

New ILSs based on N-2-hydroxypropyl piperidine and alkyl bromides (nonyl-, decyl, dodecyl, and tetradecyl) have been synthesized and characterized by spectroscopic methods (^{1}H, NMR, and IR). The micellization and adsorption properties of the ILSs were studied using surface tension and specific electroconductivity measurements. It has been found that in ILSs, the CMC, A_{min}, ΔG_{mic}, and ΔG_{ad} values decrease as the alkyl chain length increases, while the β, Γ_{max} and pC_{20} values increase. The CMC values of the synthesized ILSs were found to be significantly lower than similar ILSs with the N-methylpiperidinium and N-methyl-3-hydroxypiperidinium head groups. The antimicrobial activity of the proposed ILSs was studied as well. The surfactant with the alkyl chain length of C_{14} was shown to have higher antimicrobial properties.

CRediT authorship contribution statement

Ravan A. Rahimov: Writing – review & editing, Supervision, Methodology. **Gulnara A. Ahmadova:** Investigation, Resources, Writing – original draft. **Khuraman A. Huseynova:** Investigation, Resources, Writing – original draft. **Rustam Kh. Mammadov:** Investigation, Resources, Writing – original draft. **Nahida Z. Asadova:** Investigation, Data curation. **Yusif Abdullayev:** Writing – review & editing. **Minaver J. Ibrahimova:** Validation, Data curation. **Atash V. Gurbanov:** Validation, Formal analysis. **Fedor I. Zubkov:** Validation, Formal analysis.

Declaration of Competing Interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molliq.2021.117783.

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