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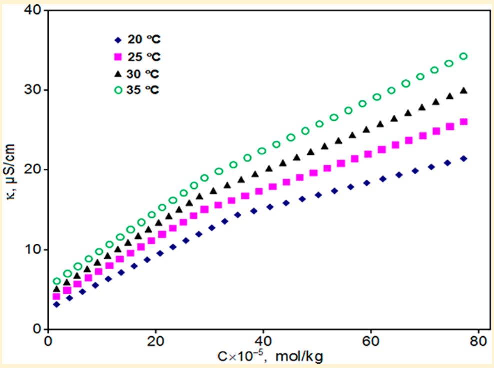
Surface Activity, Adsorption, and Micellization Parameters of Ammonium Surfactants Containing a Hydroxyethyl and Hydroxyisopropyl Head Group

Ziyafaddin H. Asadov,[†] Gulnara A. Ahmadova,[†] Ravan A. Rahimov,[*,†,§] Aygul Z. Abilova,[†] Iqrar G. Nazarov,[‡] and Fedor I. Zubkov[§]

[†]Institute of Petrochemical Processes of Azerbaijan National Academy of Sciences, Hojaly ave. 30, AZ 1025, Baku, Azerbaijan
[‡]Lomonosov Moscow State University, Baku Branch, B. Vahabzade str., 14, AZ 1143, Baku, Azerbaijan
[§]Organic Chemistry Department, RUDN University, 6 Miklukho-Maklaya str., Moscow 117198, Russian Federation

Ⓢ *Supporting Information*



ABSTRACT: On the basis of measurements of conductivity and surface activity, adsorption and micellization parameters such as critical micellization concentration (CMC), adsorption efficiency, effectiveness of surface tension reduction, and a degree of counterion dissociation (α) for four new ammonium surfactants, octyl-*N*-(2-hydroxyethyl)-*N*-(2-hydroxypropyl) ammonium chloride, nonyl-*N*-(2-hydroxyethyl)-*N*-(2-hydroxypropyl) ammonium chloride, dodecyl-*N*-(2-hydroxyethyl)-*N*-(2-hydroxypropyl) ammonium chloride, and hexadecyl-*N*-(2-hydroxyethyl)-*N*-(2-hydroxypropyl) ammonium chloride in aqueous solutions have been determined. The values of CMC determined by two different methods are compared, and they show reasonable agreement. Using the results of electroconductometric and tensiometric measurements, enthalpy (ΔH), the Gibbs free energy (ΔG), and entropy (ΔS) for processes of adsorption and micellization have been computed. The influence of the length of the alkyl chain in the synthesized salts on surface activity and thermodynamic parameters has been clarified. The petrocollecting capacity of the obtained surfactants has been studied on the surface of waters having various mineralization degrees. It has been revealed that the surfactant containing C_{12} chain is the most effective petrocollecting reagent among the synthesized salts.

1. INTRODUCTION

Surfactants always attract significant attention because of their various spheres of applications such as oil industry, medicine, biological systems, and many others. The amphiphilicity of surfactant molecules may bring about the formation of micelles in water systems, hydrophilic head-groups being localized at the surface and hydrophobic fragments being screened from water. The critical micellization concentration (CMC), at which micelles start to form, is one of the most important parameters of surface activity and micellization of surfactants.[1] In the case of surfactants of ionic structure, at concentrations lower than CMC, the species are only ions. After micellization, however, counterions become to be attracted to micelle core, and a very small part may be regarded as free ions that is reflected in another index—a degree of dissociation counterions (α). As is known, the nature of headgroup and dimensions of alkyl group considerably influence such physicochemical parameters of surfactants as CMC, α, and the number of aggregation for micelles.[2−5] Furthermore, the difference in the dimensions of head-groups in two similar surfactants may cause different micellization behaviors.[6−8] Micellization is markedly affected by such factors as solvent nature, temperature, ionic strength, pH, pressure, and presence of cosolvents.[9−11] In particular, the formation of micelles is strongly affected by temperature because hydrophobic and headgroup interactions significantly change with temperature variation. Respective investigations on the dependence of CMC from temperature have been carried out to get some knowledge on these interactions. The enthalpy and entropy of micellization are considerably contributed by the release of structurized water near separate hydrocarbon chains during the formation of micelles.[12]

The presence of the hydroxyl group in the hydrophilic part of surfactants influences some of their properties. Thus, their CMC is lower than that of surfactants of similar structures.[13] The surfactants containing the hydroxyl group have a good water-solubility and also possess high antibacterial and antifungal properties.[14] In the literature, there is a lot of data mainly on surfactants containing a hydroxyethyl group.[15−17] However, the information on the surfactants having hydroxyisopropyl group is very little.[18,19] From this standpoint, obtaining and studying the surfactants containing both

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Table 1. Specification of Chemical Samples

chemical name	source	initial mass fraction purity	CAS no.	purification method	final mole fraction purity	analysis method
1-octyl amine	Alfa Aesar GmbH & Co KG	>99%	111-86-4	none		
1-nonyl amine	Merck KGaA	>98%	112-20-9	none		
1-dodecyl amine	Alfa Aesar GmbH & Co KG	>98%	124-22-1	none		
1-hexadecyl amine	Alfa Aesar GmbH & Co KG	>90%	143-27-1	none		
propylene oxide	"Organic Synthesis" factory	>99%	75-56-9	none		
2-chloroethanol	Sigma-Aldrich	>99%	107-07-3	none		
octyl-*n*-(2-hydroxyethyl)-*n*-(2-hydroxypropyl) ammonium chloride	synthesis			recrystallization	>95%	NMR[a], IR[b]
nonyl-*N*-(2-hydroxyethyl)-*N*-(2-hydroxypropyl) ammonium chloride	synthesis			recrystallization	>96%	NMR, IR
dodecyl-*N*-(2-hydroxyethyl-*N*-(2-hydroxypropyl) ammonium chloride	synthesis			recrystallization	>97%	NMR, IR
hexadecyl-*N*-(2-hydroxyethyl)-*N*-(2-hydroxypropyl) ammonium chloride	synthesis			recrystallization	>92%	NMR, IR

[a] Nuclear magnetic resonance. [b] Infrared spectroscopy.

hydroxyethyl and hydroxypropyl fragments are of a big scientific and practical importance.

In this work, we report on the synthesis of a novel series of ammonium salts, containing hydroxyethyl and hydroxypropyl groups, from alkylamines (AA), 2-chloroethanol, and propylene oxide (PO). Colloidal-chemical parameters of the synthesized ammonium salts have been determined; thermodynamic parameters of their micelle formation and adsorption processes have been calculated, and their capacities to remove thin petroleum films from water surface have been estimated.

2. EXPERIMENTAL PROCEDURES

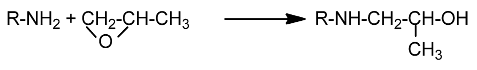
2.1. Reagents and Instrumentation. Spectra of ^{1}H NMR and ^{13}C NMR were registered using Bruker TOP SPIN spectrometer 300.13 and 75.46 MHz) with chemical shifts (δ in ppm) downfield from TMS using such solvents as $CDCl_3$. IR spectra were recorded by ALPHA FT-IR spectrometer (Bruker) using NaCl disks. PO was used as a product of "Organic Synthesis" factory (Sumgayit, Azerbaijan). As AA, 1-octyl amine (Alfa Aesar, Great Britain), 1-nonyl amine (Merck KGaA, Germany), 1-dodecyl amine (Alfa Aesar GmbH & Co KG, Germany), and 1-hexadecyl amine (Alfa Aesar GmbH & Co KG, Germany) of analytical grade were taken. The used 2-chloroethanol (Sigma-Aldrich) was also a reagent of analytical grade. The chemicals as well as their purities and suppliers are listed in Table 1.

2.2. Method of Alkyl Isopropylolamine Synthesis. Alkyl isopropylolamines were obtained according to the scheme of the reaction of AA with PO at 1:1 molar ratio (Scheme 1):

To synthesize alkyl isopropylolamines, 0.1 mol of AA and 0.1 mol of PO are entered into a flask. To avoid AA oxidation, the reaction is performed in the atmosphere of nitrogen.[20]

2.3. Synthesis of Cationic Surfactants Based on Alkyl Isopropylolamines. Alkyl isopropylolamine (0.03 mol) and hexane (20 mL) were introduced into a three-neck flask with a round-bottom. The mixture was stirred until alkyl isopropylolamine was completely solved. The necessary amount (0.035 mol) of 2-chloroethanol was introduced into the mixture for the formation of the chloride counterion and a new hydroxyethyl headgroup in the hydrophilic part of alkyl isopropylolamine. The reaction system was heated with reflux for 20 h.

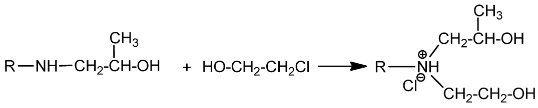
Scheme 1. Reaction Scheme of the Synthesis of Alkyl Isopropylolamines on the Basis of AA and PO



R=C_8H_{17} (A_1); C_9H_{19} (A_2); $C_{12}H_{25}$ (A_3); $C_{16}H_{33}$ (A_4)

The reaction of alkyl isopropylolamines with 2-chloroethanol occurs according to Scheme 2:

Scheme 2. Synthesis of Ammonium-Type Surfactants by the Interaction of Alkyl Isopropylolamines with 2-Chloroethanol



R=C_8H_{17} (B_1); C_9H_{19} (B_2); $C_{12}H_{25}$ (B_3); $C_{16}H_{33}$ (B_4)

The final mixture was subjected to distillation in vacuum to remove hexane and unused 2-chloroethanol. The formed salts of ammonium type are well-soluble in water, and their water solutions exhibit a high electroconductivity. The synthesized salts were recrystallized three times from acetone to obtain pure products. Their yields were equal to 92–93%. The purity of the synthesized compounds is determined according to NMR and IR spectra. These products are well-soluble in ethanol, ethyl acetate, chloroform, and partially soluble in water and dimethyl sulfoxide. The spectra of B_1–B_4 are shown in Figures S1–S12 (Supporting Information).

2.4. Surface Tension Measurements. The surface activity of the cationic surfactants synthesized on the basis of AA was measured on a DuNouy ring KSV Sigma 702 tensiometer. Preparations of aqueous solutions of the surfactants and measurements were conducted in accordance with the known procedure.[20] In these measurements, the surface tension of demineralized water equaled 72.0 mN/m (25 °C). The uncertainty did not exceed ±0.1 mN/m.

2.5. Evaluation of Petroleum-Collecting Properties. The petrocollecting capacity of the cationic surfactants synthesized on the base of AA was determined on the surface of three waters of different mineralization degrees. With this purpose, both unthinned surfactant and its 5% wt aqueous solution were applied. At the tests, Pirallahy crude oil of Absheron peninsula (from the oil field near Baku, Azerbaijan) was used, its density being 0.9244 g/cm^3 at 20 °C and kinematic viscosity equaling 1.05 cm^2/s at 30 °C. The studies were carried out according to the known procedure.[20]

2.6. Electroconductometric Measurements. Measurements of specific electroconductivity (κ) of the prepared surfactant solutions were carried out by "ANION 4120" conductometer (Russia). The range of electroconductometric measurements is 10^{-4} S/m to 10 S/m, the temperature ranging at 0–100 °C and relative error not exceeding ±2%.

Portions of 30–40 mL of solutions of surfactant are prepared at the concentration range 0.001–5%. These solutions are thermostated in a water bath (±0.1 °C). The solutions are stirred before measurements. During measurements no gas bubbles must be seen in the solution, and the level of the solution must exceed the top of the electrodes. The electrode is held in the solution for 3–5 min, and the value of κ is read. After each measurement, the electrode is rinsed with distilled water and then dried. The value of κ for distilled water must be in the 2.0–2.5 μS/cm interval.

3. RESULTS AND DISCUSSION

3.1. Surface Properties. *3.1.1. Critical Micelle Concentration (CMC).* CMC values of the obtained cationic surfactants have been found graphically from dependence of the surface tension (γ) of their aqueous solutions from their bulk concentrations (in mol/kg solvent) at 20, 25, 30, and 35 °C temperatures as shown in Figures 1–4 (or Supporting Information, Tables S1–S4). According to the data in Table 2, the CMC values of the synthesized cationic surfactants diminish when elongating the hydrophobic chain. Lowering the CMC with a temperature rise is caused by a diminished hydration of hydrophilic group that contributes to micelle formation. A temperature elevation also brings about a destruction of water aggregate near hydrophobic fragment that hinders micellization (a rise of CMC). Hence, the resulting sum of these two opposite tendencies determines a change in CMC within a certain temperature interval.[6] In the headgroup of dodecyltrialkylammonium bromide-type surfactants, an increase of alkyl group volume in the series methyl < ethyl < propyl < butyl causes a decrease in CMC. In the case of the surfactants containing methyl- and ethyl fragments in the headgroup, with an increase of temperature, the values of CMC

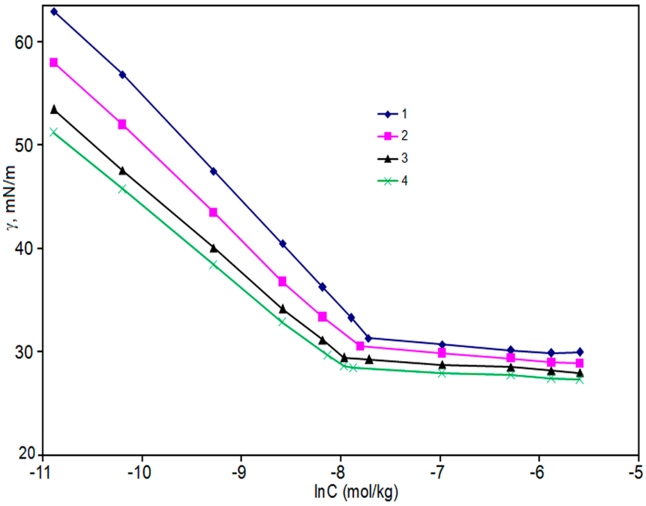


Figure 1. Surface tension vs concentration plot of B_1 salt at different temperatures. Temperature, °C: 1. 20; 2. 25; 3. 30; 4. 35.

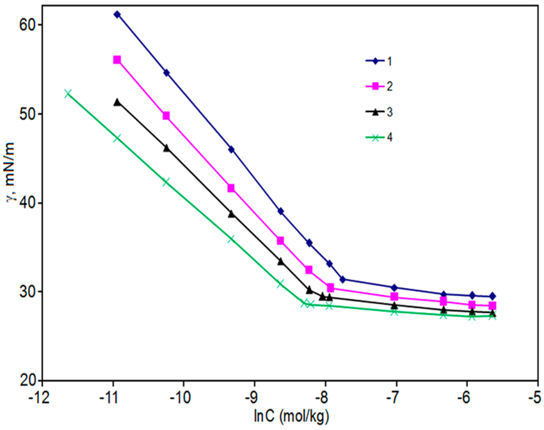


Figure 2. Surface tension vs concentration plot of B_2 salt at different temperatures. Temperature, °C: 1. 20; 2. 25; 3. 30; 4. 35.

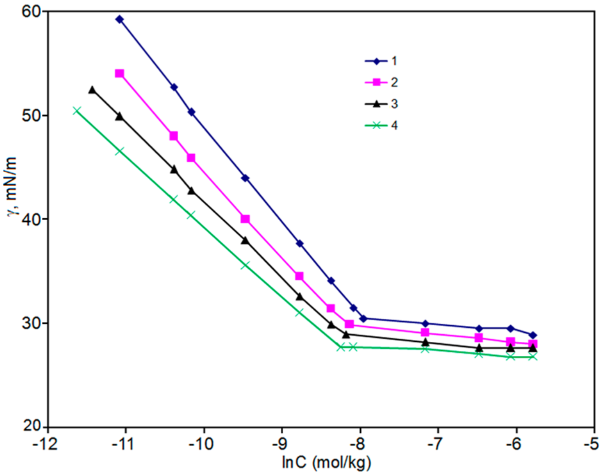


Figure 3. Surface tension vs concentration plot of B_3 salt at different temperatures. Temperature, °C: 1. 20; 2. 25; 3. 30; 4. 35.

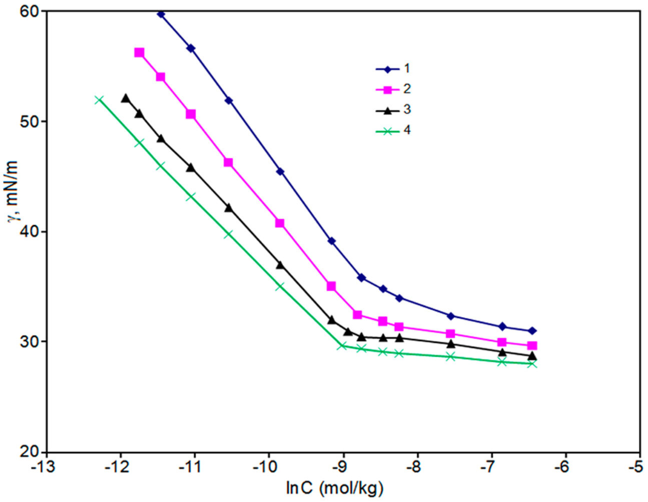


Figure 4. Surface tension vs concentration plot of B_4 salt at different temperatures. Temperature, °C: 1. 20; 2. 25; 3. 30; 4. 35.

Table 2. Surface Activity Parameters (Temperature T; Critical Micelle Concentration CMC; γ_{CMC} Equilibrium Surface Tension at the CMC; Effectiveness π_{CMC}; Efficiency pC_{20}; Maximum Surface Excess Γ_{max}; Minimum Surface Area A_{min}; Degree of Counterion Binding to Micelles β) of the Synthesized Ammonium Salts at 20, 25, 30, and 35 °C[a]

surfactant	t (°C)	β	$\Gamma_{max} \times 10^{10}$ (mol/cm^2)	A_{min} (Å^2)	CMC × 10^4 (mol/kg)	π (mN/m)	γ_{CMC} (mN/m)	pC_{20}
B_1	20	0.29	2.10	79.1	4.43	42.7	30.1	4.26
	25	0.27	1.84	90.3	4.09	43.0	29.0	4.39
	30	0.26	1.63	101.6	3.91	42.2	29.0	4.61
	35	0.24	1.54	108.2	3.47	43.0	27.4	4.68
B_2	20	0.41	1.93	86.1	4.26	43.2	29.6	4.36
	25	0.37	1.78	93.4	3.63	43.5	28.5	4.56
	30	0.34	1.55	107.2	3.22	43.4	27.8	4.75
	35	0.29	1.37	121.1	2.48	43.1	27.3	4.95
B_3	20	0.47	1.89	87.7	3.52	43.3	29.5	4.52
	25	0.42	1.69	98.5	2.94	43.8	28.2	4.71
	30	0.40	1.47	113.0	2.80	43.6	27.6	4.88
	35	0.38	1.32	126.1	2.61	43.5	26.9	5.05
B_4	20	0.57	1.85	89.6	1.56	41.8	31.0	4.62
	25	0.55	1.65	100.6	1.52	42.0	30.0	4.86
	30	0.51	1.43	116.0	1.30	42.1	29.1	5.12
	35	0.49	1.32	126.2	1.21	43.5	26.9	5.24

[a] The standard uncertainties u are $u(t) = 0.01$ °C and $u(p) = 10$ kPa. The combined expanded uncertainties U_c are $U_c(\beta) = 0.005$, $U_c(\Gamma_{max}) = 0.01$ mol/cm^2, $U_c(A_{min}) = 0.5$ Å^2, $U_c(\mathrm{CMC}) = 10^{-6}$ mol/kg, $U_c(\pi) = 0.1$ mN/m, $U_c(\gamma) = 0.1$ mN/m, and $U_c(pC_{20}) = 0.02$ (0.95 level of confidence).

increase, but in the surfactants having propyl- and butyl fragments, CMC decreases.[21,22] In dodecylalkylisopropylolammonium bromide-type surfactants, with an elongation of alkyl chain in the headgroup in the direction methyl < ethyl < propyl, CMC is lowered.[20] Burczyk and Wilk have established that, in cetyldimethylethylolammonium bromide, on replacing the ethylol group by isopropylol fragment CMC decreases from 8.7×10^{-4} down to 8.3×10^{-4} mol/kg.[23] According to ref 24, the CMC of dodecyldiethylolammonium chloride at 25 °C is 3.56×10^{-2} mol/kg. When the ethylol group in the headgroup of this salt is substituted by isopropylol fragment (B_3), CMC diminishes down to 3.04×10^{-4} mol/kg. Jordan et al.[25] introduced the methylol group (CH_2OH) into the headgroup of cationic surfactants of two series containing different alkyl groups. By comparing their CMC values, it was concluded that the introduction of methylol group decreases the CMC. From the above-said it may be stated that, with an elongation of alkyl and alkylol chains in the headgroup as well as with the replacement of alkyl group by alkylol fragment, CMC of cationics decreases.

3.1.2. Efficiency (pC_{20}). A concentration necessary for a decrease in surface tension of water itself by 20 mN/m (C_{20}) is called surfactant efficiency (pC_{20}). It is calculated as the negative logarithm of C_{20}. pC_{20} values of the synthesized cationic surfactants were computed and set in Table 2. From these values, it was deduced that elongation of the alkyl chain and a rise in temperature lead to the efficiency increase; that is, a shift of pC_{20} to lower concentrations is observed. A rise in the number of $-CH_2-$ groups in the hydrocarbon group increases hydrophobic interactions of water that decreases the surface tension. It results in a rise in both effectiveness and the efficiency (a shift to smaller concentrations).[26] The volume and nature of the headgroup of surfactants exert an impact on the value of pC_{20}. Thus, when comparing pC_{20} values for cetyldimethylethylolammonium bromide and cetyldimethylisopropylolammonium bromide salts, it becomes evident that the replacement of ethylol fragment in the headgroup by the isopropylol fragment brings about a rise in pC_{20} value from 3.52 to 3.72.[23] A similar regularity may be seen when comparing the appropriate values for dodecyldiethylolammonium chloride and B_3 salts.

3.1.3. Effectiveness (π_{CMC}). Effectiveness is measured as the difference between the surface tension of pure water (γ_0) and the surface tension of surfactant aqueous solution (γ) at the CMC: $\pi_{CMC} = \gamma_0 - \gamma_{CMC}$. From Table 2 it is seen that B_3 salt at 25 °C has the highest effectiveness (43.8 mN/m). π_{CMC} for dodecyldiethylolammonium chloride equals 31.0 mN/m.[24] In the case of cetyldimethylethylolammonium bromide and cetyldimethylisopropylolammonium bromide salts, the values of π_{CMC} are respectively 35.2 and 35.4 mN/m.[23] Therefore, when the ethylol group in the hydrophilic part of surfactant is replaced by isopropylol group, the magnitude of π_{CMC} increases.

3.1.4. Maximum Surface Excess (Γ_{max}). The maximum surface excess (Γ_{max}) is an amount of surfactant molecules at a unit interface area. It depends mainly on the dimension of hydrocarbon fragment and temperature. The Γ_{max} values have been computed through Gibbs equation knowing surface tension:[27]

$$\Gamma_{max} = -\frac{1}{nRT} \lim C \to C_{CMC} \frac{d\gamma}{d \ln C} \tag{1}$$

where ($d\gamma/d \ln C$) is the surface activity at absolute temperature T, R being the gas constant. From the data in Table 2, it is noticed that an increase in temperature and length of hydrophobic chain of the mentioned cationic surfactants shifts Γ_{max} to lower concentrations. An increase in temperature causes a rise in the surface area for each molecule, probably, because of strengthened thermal movement that leads to deteriorated packing of the adsorbed molecules of surfactant with the following lowering in Γ_{max}. The nature of the headgroup substantially impacts the value of Γ_{max}. Thus, with an elongation of alkyl moiety in the headgroup of dodecylalkylammonium bromide-type surfactants, Γ_{max} diminishes.[22] A similar tendency is observed when the ethylol group is replaced by the isopropylol fragment. For instance, in the case of cetyldimethylethylolammonium bromide, Γ_{max} is 3.14 μmol/m^2, whereas for cetyldimethylisopropylolammonium bromide[23]

Γ_{max} equals 2.06 μmol/m^2. The value of Γ_{max} for dodecyldiethylolammonium chloride[24] is 2.48 μmol/m^2, but for B_3 surfactant, this parameter is equal to 1.69 μmol/m^2.

3.1.5. Minimum Surface Area (A_{min}). This parameter regards a mean area (measured in Å^2) per surfactant molecule at the border between phases. The lower the angle between surfactant molecule and the interface, the higher the values of A_{min}. So, this angle is extremely important for A_{min}.[23,27] Its values being calculated by the Gibbs adsorption equation are given in Table 2:

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

As is seen from the table, A_{min} rises by the elongation of the hydrocarbon group and elevating temperature due to diminished values of Γ_{max}. This is an unexpected result since, as is known, the minimum area per a molecule of common surfactant of ionic type at the water surface is lowered by elongating a hydrocarbon group. The reason consists in competition between hydrophobic interaction of hydrocarbon groups and repulsion between polar fragments of headgroup as a result of electrostatic forces as well as hydration energy.[28] In Table 2, A_{min} increases with the elongation of hydrocarbon chain for all of the obtained surfactants. This fact is in accordance with the results described in ref 29. An increase in A_{min} is also caused by increasing temperature which leads to a more thermal motion resulting in poorer packing.[30] It is known that the volume and nature of a headgroup of surfactant are among main factors influencing the value of A_{min}. In ammonium-type cationic surfactants, with an elongation of alkyl- and alkylol groups bonded to N atom, the value of A_{min} increases. But, as the number of ethylol fragments linked to N atom rises, the value of A_{min} diminishes. Its reason is the creation of hydrogen bonds among OH groups.

3.2. Specific Electroconductivity Measurements. The results of electroconductivity measurements of B_1−B_4 surfactants at different temperatures (20, 25, 30, 35 °C) are shown in Figure 5−8 (or Supporting Information, Tables S5−S8), where the experimental values of κ are plotted as a function of surfactant concentration. It may be seen that there are two linear parts in the typical curves and the steep change of the slope is assigned to the CMC of the surfactants (Table 2). The values of CMC obtained by electroconductometric and

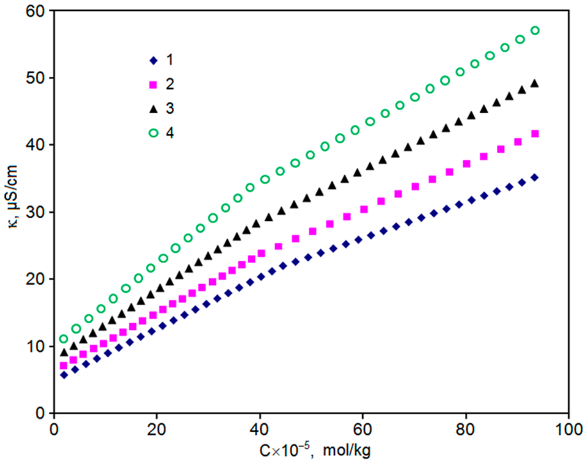


Figure 5. Dependence of specific electrical conductivity from the concentration of B_1 salt at different temperatures. Temperature, °C: 1. 20; 2. 25; 3. 30; 4. 35.

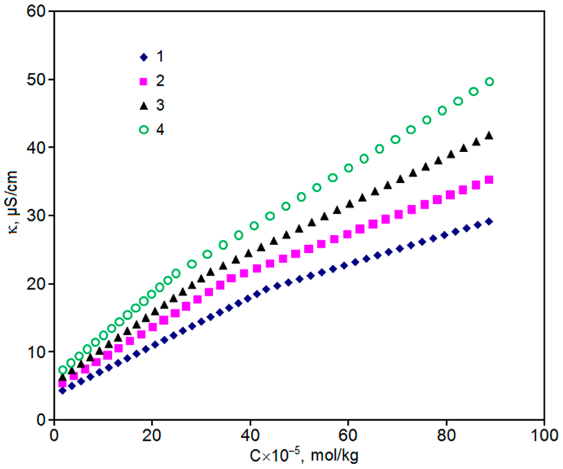


Figure 6. Dependence of specific electrical conductivity from the concentration of B_2 salt at different temperatures. Temperature, °C: 1. 20; 2. 25; 3. 30; 4. 35.

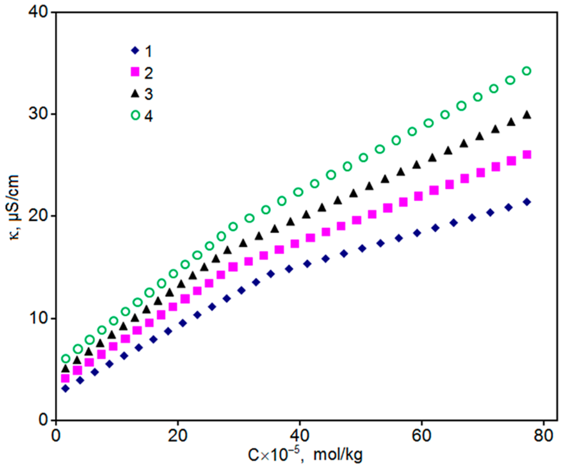


Figure 7. Dependence of specific electrical conductivity from the concentration of B_3 salt at different temperatures. Temperature, °C: 1. 20; 2. 25; 3. 30; 4. 35.

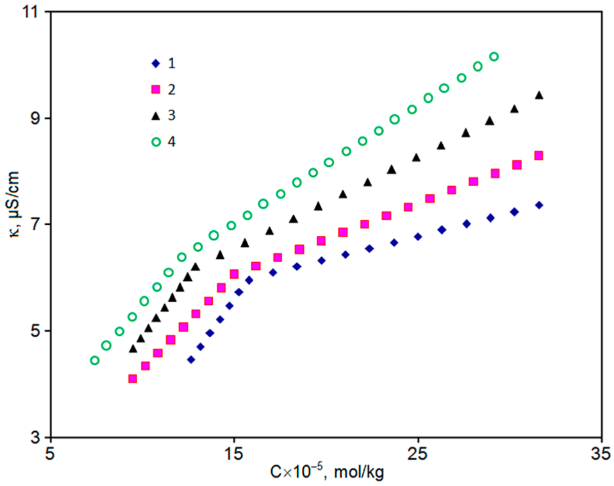


Figure 8. Dependence of specific electrical conductivity from the concentration of B_4 salt at different temperatures. Temperature, °C: 1. 20; 2. 25; 3. 30; 4. 35.

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Table 3. Thermodynamic Parameters of Micellization (Free Energy of Micellization ΔG_{mic}; Entropy of Micellization ΔS_{mic} and Enthalpy of Micellization ΔH_{mic}) and Adsorption (Free Energy of Adsorption ΔG_{ads}; Entropy of Adsorption ΔS_{ads} and Enthalpy of Adsorption ΔH_{ads}) of the Synthesized Ammonium Salts at 20, 25, 30, and 35 °C[a]

surfactant	t (°C)	ΔG_{mic} (kJ/mol)	ΔG_{ad} (kJ/mol)	ΔS_{mic} (J/mol K)	ΔH_{mic} (kJ/mol)	ΔS_{ad} (J/mol K)	ΔH_{ad} (kJ/mol)
B_1	20	−24.27	−26.30				
	25	−24.55	−26.89	56.5	−7.7	117.2	8.1
	30	−24.91	−27.49	71.6	−3.2	118.6	8.4
	35	−25.29	−28.10	77.6	−1.4	123.2	9.9
B_2	20	−26.66	−28.90				
	25	−26.89	−29.33	45.8	−13.2	87.2	−3.3
	30	−27.14	−29.95	51.4	−11.6	122.7	7.2
	35	−27.42	−30.57	56.2	−10.1	124.2	7.7
B_3	20	−28.48	−30.76				
	25	−28.60	−31.21	26.9	−20.6	89.2	−4.6
	30	−28.85	−31.82	48.5	−14.2	121.9	5.1
	35	−29.16	−32.46	61.1	−10.3	128.4	7.1
B_4	20	−33.52	−35.78				
	25	−33.76	−36.31	47.5	−19.6	105.1	−5.0
	30	−34.04	−36.98	55.1	−17.4	138.5	5.0
	35	−34.41	−37.72	75.4	−11.2	144.3	6.7

[a] The standard uncertainties u are $u(t) = 0.01$ °C and $u(p) = 10$ kPa. The combined expanded uncertainties U_c are $U_c(\Delta G) = 0.03$ kJ/mol, $U_c(\Delta H) = 0.1$ kJ/mol, and $U_c(\Delta S) = 0.2$ J/(mol K) (0.95 level of confidence).

tensiometric methods are sufficiently close to each other. Lowering in conductivity values above the CMC is caused by the binding of the counterions to the micelle. A degree of counterion binding—β or a degree of ionization—α interrelated as $\alpha = 1 - \beta$ may be evaluated according to the slope of the curve below and above the CMC. According to Frahm et al.,[31] the contribution of the separate surfactant molecules and micelles to electroconductivity is less than the contribution of the counterions. Thus, a degree of ionization of the micelle in the Frahm's model is $\alpha = S_2/S_1$ where S_1 and S_2 are the slopes of the electroconductivity curve respectively below and higher the CMC.[12,32]

A rise in temperature intensifies the movement of species that lowers the number of counterions within the micelles. So, the dissociation degree rises with a temperature increase. It is evident that the value of α is lowered with an elongation of the alkyl chain. This effect is ascribed to lowering in the density of surface charge within micelles. Surfactants with a longer hydrocarbon group promote the micellization where the ratio surface:volume is lower. This points to tighter packing of headgroups and their binding by a larger part of counterions. In addition, the value of α increases a little with an increase in the number of hydroxyethyl fragments in the headgroups. This is also attributed to the lowering in the density of charge in the micelle surface because the volume of headgroup in the surfactant augments.[8]

In dodecyltrialkylammonium bromide-type surfactants, the value of β is lowered as the alkyl group bonded to N atom in the headgroup is elongated in the series methyl < ethyl < propyl < butyl and temperature is raised.[6] With an increase in the number of the ethylol groups linked to N atom in the headgroup or when the OH group is introduced to the headgroup, the lowering of the β value is noticed.[25,33]

3.3. Thermodynamics of Micellization and Interfacial Adsorption. Such important thermodynamic parameters of micellization and adsorption of the synthesized cationic surfactants as Gibbs free energy (ΔG), entropy (ΔS), and enthalpy (ΔH) changes were computed using Gibbs equation and the method of Rosen et al.:[34]

$$\Delta G_{mic} = (2 - \alpha)RT \ln \mathrm{CMC} \tag{3}$$

$$\Delta G_{ad} = (2 - \alpha)RT \ln \mathrm{CMC} - 0.6023\pi_{\mathrm{CMC}}A_{\mathrm{CMC}} \tag{4}$$

$$-\Delta S = (\delta \Delta G/\delta T) \tag{5}$$

$$\Delta H = \Delta G + T\Delta S \tag{6}$$

The respective results presented in Table 3 show that the ΔG_{mic} values of the obtained cationic surfactants are always negative. The negativity of these values indicates that the micellization process is of spontaneous character for all of the indicated surfactants in the solutions at CMC. The spontaneity of the process is ascribed to the repulsion between hydrophobic groups and polar-type solvent.[35] Hence, the elongation of the hydrophobic chain strengthens a tendency of these molecules toward micelle formation, which results in increased negativity of the values of ΔG_{mic}. That is clearly noticed from the ΔG_{mic} values of B_1–B_4 surfactants (Table 3). The values of ΔG_{ad} for these surfactants are much more negative than those for micellization. Hence, it may be concluded that, for the obtained surfactants, the adsorption at the interfaces is more preferable than micellization.

All of the values calculated for ΔS_{mic} are positive, which indicates that the micellar form is of less order than the free surfactant. Entropy is the main driving force for micellization, which is initiated by a highly regular structure of the water around the hydrophobic chains of surfactants.[36] With an increase of temperature the contribution of entropy to micellization diminishes, because at higher temperatures water molecules around hydrophobic chains of the surfactant molecule acquire some randomness, that is, the destruction of iceberg structure occurs.[8] Thus, micellization is characterized by dominant entropy contribution at low temperatures, whereas both the entropy and enthalpy contributions are prevalent at high temperatures.[37] The ΔS_{ads} values are positive and a little larger than the ΔS_{mic} values. This reflects a larger freedom of motion of hydrocarbon moiety at the air–water interface.[30,38]

ΔH_{mic} values are negative for B_1–B_4, evidencing that the micelle formation process is exothermic in the studied

Table 4. Petroleum-Collecting Properties of Cationic Surfactants[a]

	distilled water		fresh water		sea water	
surfactant	*t* (h)	*K*	*t* (h)	*K*	*t* (h)	*K*
			Undiluted Product			
B_1	0	80.0	0	76.0	0	56.3
	347–376	44.3	23	44.3	23	49.0
	624	22.3	143–624	22.3	143–376	33.8
					624	23.3
B_2	0	44.7	0	43.4	0	69.1
	347–376	29.8	3	40.5	624	63.3
	624	19.9	143–624	19.9		
B_3	0	60.8	0–3	17.9	0	38.0
	3	76.0	23–143	15.2	3	40.5
	23	95.0	347–624	16.0	376	23.1
	347–376	45.0			624	18.7
	624	33.8				
B_4	0	15.2	0	15.2	0	23.4
	23	30.4	347–624	16.0	376	20.4
	624	40.5			624	16.5
			5% wt Aqueous Solution			
B_1	0	38.0	0	35.6	0	18.7
	23	42.2	23	43.4	23	32.3
	72–75	30.4	75	37.1	72	23.4
	312–506	22.8	312–506	30.4	312–506	15.2
	624	15.2	624	21.7	624	13.5
B_2	0	40.5	0	40.5	0	18.7
	23	50.7	3	46.8	72	43.4
	72	15.2	23–75	50.7	75	44.7
	75–624	12.4	312–624	40.5	312–624	30.4
B_3	0	23.1	0	46.8	0	23.3
	3	38.0	3	58.5	23	41.1
	23	101.3	75	66.1	506	47.8
	312–360	45.5	312–624	60.8	624	50.7
	624	15.2				
B_4	0	12.4	0	30.4	0	20.4
	75–360	20.3	75	46.8	312	40.5
	624	24.3	312–624	40.5	624	43.4

[a] The standard uncertainties u are $u(t)$ = 4 °C and $u(p)$ = 20 kPa. The combined expanded uncertainty U_c is $U_c(K)$ = 0.2 (0.95 level of confidence).

temperature range. As is known, the enthalpy change of micellization in water solution is basically a result of hydrophobic and electrostatic interactions.[39,40] When micelle formation occurs in water solution, the hydrocarbon fragments of B_1–B_4 molecules tend to transfer from water phase to the bulk of micelle, and the hydrating water molecules are simultaneously detached from the hydrocarbon chain; this process is exothermic.[41] Electrostatic interactions may be considered from two positions. The first of them is the repulsion of headgroups and counterions, which has exothermal character. The second is the attraction between headgroup and counterion, the process being endothermal.[42,43] In the considered case, repulsion between B_1–B_4 cations is more intensive as compared with attraction. Therefore, the character of electrostatic interactions is also exothermal.

Micelle formation by surfactant molecules may be described by two processes:[44] (a) release of water molecules from the hydrocarbon group ($\Delta H_{mic} > 0$, $\Delta S_{mic} > 0$); (b) aggregation of the hydrocarbon moieties with generation of micelles ($\Delta H_{mic} < 0$, $\Delta S_{mic} < 0$). Evidently, ΔG_{mic} values depend on the comparative magnitude of enthalpy and entropy in two processes occurring in the system.[45]

In the case of the synthesized cationics, ΔS_{mic} is always positive, whereas ΔH_{mic} is always negative. As temperature rises, both parameters are increased (Table 3).

3.4. Petroleum-Collecting Properties of the Synthesized Ammonium Salts.

The results of the studies of petrocollecting properties of the obtained cationic surfactants are given in Table 4. It is obvious from the table that B_3 salt has the highest value of petrocollecting coefficient both in unthinned state and as 5% aqueous solution (K is respectively 95.0 and 101.3 in distilled water). For the salts B_1 and B_2 in distilled water, this coefficient respectively equals 80.0 and 44.7 in the case of unthinned reagent and 42.2 and 50.7 for 5% aqueous solution. In fresh water, when unthinned surfactant is applied, with an elongation of the alkyl chain in the series $B_1 > B_2 > B_3 > B_4$, the value of K decreases (for B_1 K_{max} = 76.0). In the case of 5% aqueous solution, with an increase of the length of the hydrocarbon chain up to C_{12}, the value of K rises, but then it is relatively lowered. In fresh water, for 5% aqueous solution of B_3 salt, K_{max} is equal to 66.1. In the seawater, as unthinned reagent, B_2 salt is more effective (K_{max} = 69.1), but as 5% aqueous solution, the B_3 salt is more noticeable (K_{max} = 50.7). In the seawater medium, for the case of applying 5%

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aqueous solution, with an elongation of the alkyl chain up to C_{12} (B_3), the value of K increases but, then, decreases.

An analysis of these results demonstrates that the B_3 salt having the C_{12} alkyl chain displays more effectiveness as a petrocollecting agent, and its 5% aqueous solution may be recommended for removing thin petroleum films off the surface of hard waters.

4. CONCLUSION

Ammonium-type salts containing one hydroxyethyl- and one hydroxyisopropyl groups have been synthesized on the basis of C_8, C_9, C_{12}, C_{16} AA, PO, and 2-chloroethanol. Colloidal-chemical parameters of these cationic surfactants have been determined using the results of the applied tensiometric and electroconductometric methods. An impact of the alkyl chain length on the mentioned parameters has been elucidated. As in similar ammonium-based surfactants containing the hydroxyethyl headgroup, in the synthesized surfactants, the Gibbs free energy change diminishes with an increase in hydrocarbon group length. Thermodynamic parameters indicate that adsorption and micellization processes are of spontaneous nature, and the obtained cationics tend initially to be adsorbed at surface, then, to undergo micellization. In the seawater, the highest petroleum-collecting capacity is displayed by B_3 in the form of 5% wt aqueous solution. The time of this salt effect is longer than 25 days.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jced.7b00347.

> IR, ^{1}H NMR, and ^{13}C NMR spectra of B_3 (Figures S1–S3); dependence of surface tension from natural logarithm of molality for B_1–B_4 at different temperatures (Tables S1–S4); dependence of specific electrical conductivity from concentration of B_1–B_4 salts at different temperatures (Tables S5–S8) (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*Tel.: +99450 545 20 48. Fax: +99412 490 24 76. E-mail: revan_chem@mail.ru.

ORCID

Ravan A. Rahimov: 0000-0001-5619-4041

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Notes

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