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ORIGINAL ARTICLE

Synthesis, Surface Active and Thermodynamic Parameters of Novel Quaternary Ammonium Salts

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Abstract Reactions of octanol, nonanol, decanol, and dodecanol with epichlorohydrin were carried out in the presence of sodium hydroxide as a catalyst. The synthesized non-ionic surfactants were modified with triethanolamine. Surface activity at the water-air interface and electrical conductivity of the resulting surfactants at 10, 20, 30 and 40 °C were determined and thermodynamic parameters of micellization and adsorption were calculated. It was established that the synthesized quaternary ammonium salts have the ability to localize thin crude oil films on the water surface formed due to spill.

Keywords Cationic surfactant · Micellization · Adsorption · Oil spill

Abbreviations

TEA	Triethanolamine
C_8ETEA	TEA salt of chloroxypropyl ether of octanol
C_9ETEA	TEA salt of chloroxypropyl ether of nonanol
C_{10}ETEA	TEA salt of chloroxypropyl ether of decanol
C_{12}ETEA	TEA salt of chloroxypropyl ether of dodecanol

Introduction

Various cationic (including gemini-type) surfactants synthesized on the basis of epichlorohydrin (ECH) possess antimicrobial [1–5], biological activity [6], foaming [7], wetting [5], antielectrostatic [8] and other useful properties. These surfactants find application in the oil industry, for example, in enhanced oil recovery [9]. In addition to being highly surface active, chloropropoxylate surfactants have the ability to collect and disperse thin films on the water surface [10, 11]. The authors [11] synthesized chloropropoxylates of the higher alcohols and investigated their surface-active properties. They have indicated that these ethers are capable of removing thin crude oil slicks off the surface of water of various mineralization degrees. To decrease toxicity of these covalent-chlorine-containing reagents and to improve their water solubility they may be reacted with nitrogenous bases, transforming covalent chlorine to non-hazardous ionic ones. Indian researchers [12] obtained highly surface-active agents by quaternization of chloropropoxylates of C_{10}–C_{15} higher alcohols, synthesized at an equimolar ratio of the initial reactants, with phe-gly dipeptide.

In this submitted article, chloropropoxylates of C_8–C_{10} and C_{12} higher alcohols were modified by triethanolamine, obtaining new surfactants. The surface-active and thermodynamic parameters of these cationic surfactants were determined.

Experimental Procedures

Reagents and Instruments

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker TOP SPIN 300.13 and 75.46 MHz spectrometer with chemical shift values (δ) in ppm downfield from TMS using D_2O and CCl_4 as solvents. IR spectra were recorded on an FT-IR, Spectrum BX model spectrometer using KBr disks.

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ECH is a product of the Organic Synthesis Factory (Sumgayit, Azerbaijan) with 99.97–99.98 % purity. NaOH is a product of Merck (Germany, ≥99 % purity). Triethanolamine is of analytical grade (Merck, Germany, ≥98 % purity).

Surface-Tension Measurements

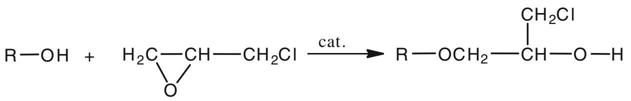
All the surface tension measurements were carried out using deionized water to make the solutions. The solutions kept at the desired temperature (in the dark) were measured 45 s after transfer to the thermostated measuring dishes. The actual temperature within the dishes was controlled prior to and after the measurement by means of a thermocouple. Deviations from the desired temperature were ±0.2 °C at temperatures below 30 °C and ±0.5 °C above it. The surface tension as a function of concentration was measured at 10, 20, 30, and 40 °C using a drop volume Traube stalagmometer (Russian Federation). For mixed solutions, particularly at low surfactant concentrations, the approach to equilibrium took several hours. The reproducibility (including long equilibration times and/or contamination effects) was ±1 %.

Electrical Conductivity Measurements

Electrical conductivity measurements were performed for different concentrations of quaternary ammonium salts solutions in the temperature range 10–40 °C, using a conductivity meter OK-102/1 (Budapest) type conductometer. The solutions were continuously stirred and thermostated at ±1 °C. The measured conductivity was plotted as a function of the surfactant concentration, and the critical micelle concentration (CMC) was taken at the intersection of the two linear parts of the conductivity curve by the least-squares method.

Water Types Studied

In the experiments four kinds of water were taken: (1) Distilled water. (2) Fresh water. (3) Caspian sea water having the following physico-chemical characteristics and composition: $\rho^{20} = 1.0098$ g/mL, pH = 7.7. The contents of ions and other species (mg/L): Na^+-2,650; K^+-90; Ca^{2+}-250; Mg^{2+}-900; NH_4^+-0.15; Cl^--500; SO_4^{2-}-2,800; NO_3^--0.1; PO_4^{3-}-0.35; NO_2^--0.007; SiO_2-0.5; petroleum products −0.005 %; dissolved oxygen-8 mg/L, total hardness-69.0 mg-equiv/L. 4. The layer water from Surakhany oil field (near Baku) of such physico- chemical characteristics: $\rho^{20} = 1.040$ g/mL, pH = 7.1. Chemical composition (mg/L): Ca^{2+}-2,280; Mg^{2+}-690; SO_4^{2-}-2,640; Cl^--49,900; iodine (bound)-1,860; naphthenic acids-6.6; petroleum-28.0; dissolved oxygen-6.0; suspended substances-360.0; dry residue-81.26; alkalinity-16.0 mg-eq/L, total hardness-60.0 mg-equiv/L.



Scheme 1 Synthesis of C_8–C_{10}, C_{12} alcohol ethers—nonionic surfactants

Synthesis of C_8–C_{10}, C_{12} Alcohol Ethers and Their Salts with TEA

C_8–C_{10} and C_{12} alcohols were chloropropoxylated with epichlorohydrin (Scheme 1) as follows. 0.1 mol of alcohol was added to 0.001 mol of NaOH and stirred for 1 h at room temperature. Then 0.1 mol of epichlorohydrin was added and the reaction was carried out in a stainless steel autoclave at 140–160 °C. The reaction was conducted within 10–12 h.

The scheme of the reaction for obtaining the quaternary ammonium salts of the alcohol ether is shown below (Scheme 2). To 0.1 mol of alcohol ester, 0.1 mol of TEA was added and their interaction was conducted for 12 h at 50–55 °C. The product obtained was washed with hexane and then dried. The synthesized quaternary ammonium salts are highly viscous liquids or solid substances.

The salt based on C_8 alcohol ether and TEA (C_8ETEA): yield 68 %, yellow-brown in color, soluble in water and partially soluble in ethanol and insoluble in carbon tetrachloride, hexane, benzene, acetone and isopropanol.

IR, cm^{-1}: 3,268.5 γ (OH), 3,021.5, 2,928.1 and 2,884.2 γ (CH), 2,329.5 γ (N^+H), 1,646.0 δ (NH), 1,453.7 and 1,374.4 δ (CH), 1,248.2 γ (C–N), 1,042.4 γ (C–O).

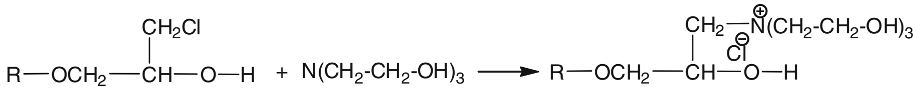
The salt based on C_9 alcohol ether and TEA (C_9ETEA): yield 71 %, brown in color, soluble in water, ethanol and insoluble in carbon tetrachloride, hexane, benzene, acetone and isopropanol.

IR, cm^{-1}: 3,341.9 γ (OH), 2,923.9 and 2,854.4 γ (CH), 2,356.9 γ (N^+H), 1,646.0 δ (NH), 1,461.9 and 1,377.1 δ (CH), 1,250.9 γ (C–N), 1,069.8 γ (C–O). ^1H NMR (300.15 MHz, D_2O), 0.79 (3H, CH_3), 1.20–1.30 $(CH_2)_x$, 3.4 (2H, N–CH_2), 3.7 (2H, O–CH_2), 3.8 (H, O–CH), 3.9 (2H, CH_2–OH), 4.9 (1H, OH). ^{13}C {^1H} NMR (75.15 MHz, D_2O and CCl_4). 14.0 (CH_3), 22.6–31.9 $(\mathbf{CH_2})_x$, 61.5 (N–$\mathbf{CH_2}$–CH), 63.5 (N–$\mathbf{CH_2}$), 65.8 ($\mathbf{CH_2}$–OH), 70.2 (**CH**–O), 72.3 (O–$\mathbf{CH_2}$), 74.3 (O–CH_2–**CH**–O).

The salt based on C_{10} alcohol ether and TEA (C_{10}ETEA): yield 72 %, brown in color, soluble in water, ethanol and partially soluble in acetone and insoluble in carbon tetrachloride, hexane, benzene and isopropanol.

IR, cm^{-1}: 3,305.0 γ (OH), 2,923.0 and 2,856.8 γ (CH), 2,362.5 γ (N^+H), 1,648.8 δ (NH), 1,455.4 and 1,374.4 δ

Scheme 2 Interaction between C_8–C_{10}, C_{12} alcohol esters and TEA



$$R{-}OCH_2{-}\underset{}{\overset{CH_2Cl}{CH}}{-}O{-}H + N(CH_2\text{-}CH_2\text{-}OH)_3 \longrightarrow R{-}OCH_2{-}\overset{CH_2-\overset{\oplus}{N}(CH_2\text{-}CH_2\text{-}OH)_3\ \overset{\ominus}{Cl}}{CH}{-}O{-}H$$

(CH), 1,283.8 γ (C–N), 1,034.1 γ (C–O). ^{1}H NMR (300.15 MHz, D_2O), 0.85 (3H, CH_3), 1.24–1.26 $(CH_2)_x$, 3.5 (2H, N–CH_2), 3.64 (2H, O–CH_2), 3.94 (2H, $\mathbf{CH_2}$–OH), 4.20 (1H, **CH**–OH), 4.9 (1H, OH). ^{13}C {^{1}H} NMR (75.15 MHz, D_2O and CCl_4). 14.1 (CH_3), 22.7–31.9 $(\mathbf{CH_2})_x$, 63.5–65.8 ($\mathbf{CH_2}$–$\mathbf{CH_2}$–OH, $\mathbf{CH_2}$–N), 72.1 (O–$\mathbf{CH_2}$).

The salt based on C_{12} alcohol ether and TEA (C_{12}ETEA): yield 76 %, dark-brown in color, soluble in water and partially soluble in ethanol, acetone and insoluble in carbon tetrachloride, hexane, benzene and isopropanol.

IR, cm^{-1}: 3,292.0 γ (OH), 2,922.0 and 2,856.8 γ (CH), 2,362.5 γ (N^+H), 1,646.0 δ (NH), 1,454.9 and 1,374.4 δ (CH), 1,248.2 γ (C–N), 1,045.1 γ (C–O).

Study of Petroleum-Collecting and Petroleum-Dispersing Capacities

Investigations of petroleum-collecting and dispersing ability of chloropropoxylates of higher alcohols and their salts with TEA were carried out on the example of Ramany crude oil films (density and kinematic viscosity at 20 °C are respectively 0.86 g cm^{-3} and 0.16 cm^2 s^{-1}; Absheron peninsula, Azerbaijan) crude oil (thickness of the film 0.165 mm) and four types of water: distilled, fresh, Caspian sea and Surakhany layer. In these experiments, a film was formed by 1 mL of crude oil on the surface of 40 mL water and then 0.02 g of the tested reagents were introduced. The chloropropoxylates and their salt were used as 5 wt% aqueous solutions.

Petroleum-collecting and dispersing ability was estimated by the coefficient of collection-K (the ratio of the initial area of petroleum film surface and the surface area of the petroleum spot formed under the action of the reagent) within the time (τ, hour) of observation in the experiment.

Results and Discussion

Critical Micelle Concentration

The critical micelle concentrations (CMC) of the investigated quaternary ammonium salts at 10, 20, 30, and 40 °C were determined by plotting the surface tension (γ) versus lnC where C is a concentration (Figs. 1, 2, 3, 4). The CMC was determined from intersection points in the (γ) versus the logarithm of concentration curves. The CMC values shown in Table 1 were found to decrease with the number of methylene groups (CH_2) in the alkyl side chains gradually increased from nonyl chain up to dodecyl chain.

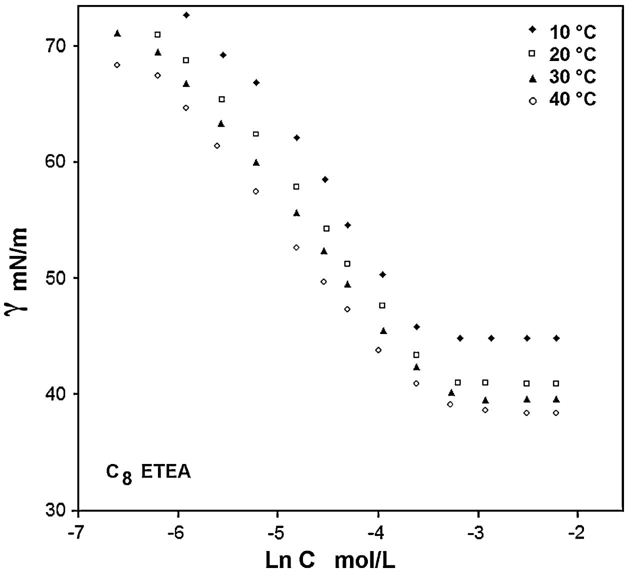


Fig. 1 Surface tension versus ln of concentration of C_8ETEA in aqueous solution at 10, 20, 30 and 40 °C

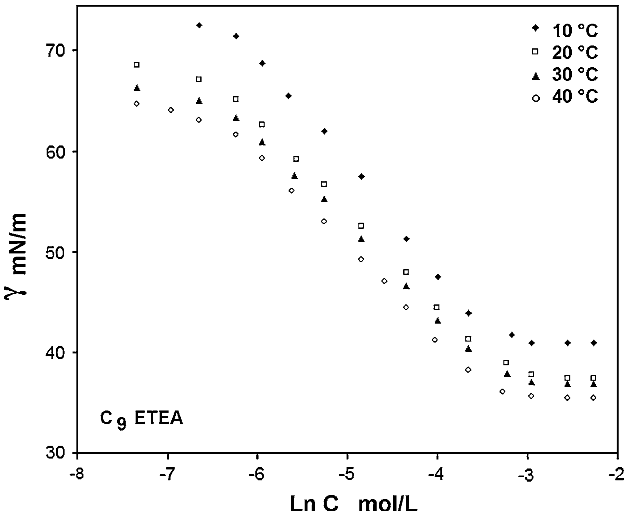


Fig. 2 Surface tension versus ln of concentration of C_9ETEA in aqueous solution at 10, 20, 30 and 40 °C

From Table 1 it can be seen that for each of the studied surfactants there was a gradual decrease in the surface tension with increasing concentration of the solution up to a certain level above which a nearly constant value was obtained. Such constant values of surface tension (at 20 °C) were found to be 41.0, 37.7, 35.5 and 33.2 mN m^{-1} for the surfactants containing C_8, C_9, C_{10} and C_{12} hydrocarbon chain, respectively.

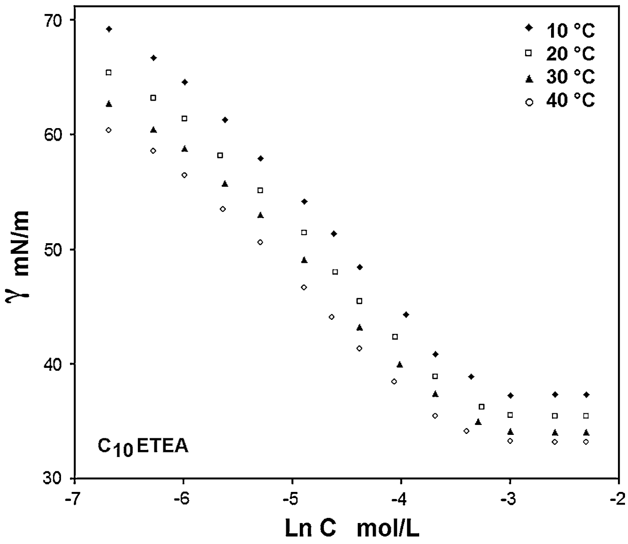


Fig. 3 Surface tension versus ln of concentration of C_{10}ETEA in aqueous solution at 10, 20, 30 and 40 °C

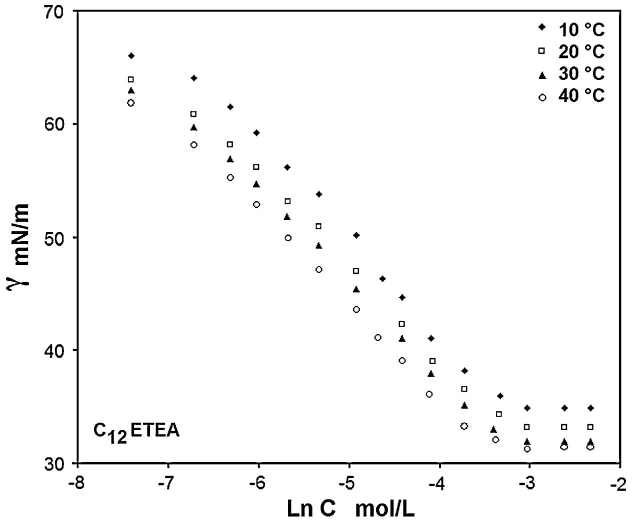


Fig. 4 Surface tension versus ln of concentration of C_{12}ETEA in aqueous solution at 10, 20, 30 and 40 °C

Conductometer Measurements

Typical plots of conductivity χ versus concentration for the quaternary ammonium salts were graphed at various temperatures (10–40 °C). Conductivity increases with increasing temperature and concentration of surfactant. The ionization degree-α was calculated from the slopes of the two linear parts of the conductivity curves according to the relationship [13]:

$$\alpha = \frac{S_2}{S_1} \tag{1}$$

where S_1 and S_2 are slopes of the respective dependence $\chi = f$ (concentration of surfactant) below and above the CMC. The values for counterion binding degree-β were calculated according to the relationship (2) [13]:

$$\beta = 1 - \alpha = 1 - \frac{S_2}{S_1} \tag{2}$$

Figure 5 shows the plot of electric conductivity versus concentration of C_{12}ETEA solution at various temperatures. As is evident from this figure, the graph consists of two straight lines. Their intersection point corresponds to the CMC. Its value differs slightly from the one determined by surface-tension measurements. In the same way the conductivity versus concentration plots were obtained for C_8ETEA, C_9ETEA and C_{10}ETEA salts and on their basis the values of counterion binding degree were calculated (Table 1).

Effectiveness (π_{CMC}) and Efficiency (pC_{20})

The difference between surface tension of quaternary ammonium salts solution at their CMC (γ_{CMC}) and that of pure water (γ_0) is defined as the effectiveness (π_{CMC}), and expressed as

$$\pi_{CMC} = \gamma_0 - \gamma_{CMC} \tag{3}$$

For the synthesized salts the effectiveness values ranged between 30.2 and 39.9 mN m^{-1}. The increase in hydrophobic chain length had a positive effect on π_{CMC} values.

The efficiency (pC_{20}) is the negative of the logarithm of concentration of the surfactant solution, which lowers the surface tension 20 units. A more efficient surfactant produces a greater depression of the surface tension at CMC. The quaternary ammonium salts obtained had a good surface activity. Table 1 shows, in general, the decrease in surface tension values at the CMC in homologous series. The same behavior was also observed in the efficiency values, pC_{20} (Table 1). Increasing the number of methylene groups (–CH_2–) along the hydrophobic chains increased the hydrophobicity of the molecules, hence hydrophobe interactions became enhanced which decreased the surface tension. Elevating the temperature increased the efficiency (pC_{20}) of the synthesized quaternary ammonium salts.

Minimum Interfacial Area/Molecule and Maximum Interfacial Excess Concentration

Table 1 indicates that the number of hydrophilic groups plays an important role in determining the maximum surface excess concentration (Γ_{max}) and the area occupied per molecule (A_{min}) at the aqueous solution-air interface.

Surface excess concentrations (Γ) in mol dm^{-3} were calculated from the relationship:

$$\Gamma = (1/nRT)(-\delta\gamma/\delta \ln C) \tag{4}$$

Table 1 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 quaternary ammonium salts at 10, 20, 30 and 40 °C

Reagent	T (°C)	β	$\Gamma_{max} \times 10^{10}$ (mol/cm^2)	A_{min} (Å^2)	CMC $\times 10^2$ (mol/L)	π (mN/m)	γ_{CMC} (mN/m)	pC_{20}
C_8ETEA	10	0.78	2.33	71.2	4.24	30.2	44.0	4.30
	20	0.75	2.22	74.8	4.08	31.8	41.0	4.40
	30	0.72	2.09	79.3	3.99	31.5	39.5	4.47
	40	0.69	1.92	86.5	3.84	31.4	38.2	4.51
C_9ETEA	10	0.83	2.21	75.0	4.12	34.1	40.1	4.60
	20	0.79	1.91	86.9	3.99	35.1	37.7	4.69
	30	0.74	1.74	95.5	3.74	34.2	37.0	4.76
	40	0.70	1.61	103.3	3.50	34.0	35.6	4.81
C_{10}ETEA	10	0.86	2.14	77.6	3.88	37.7	36.5	4.91
	20	0.81	1.98	84.0	3.69	37.3	35.5	4.97
	30	0.77	1.78	93.5	3.48	37.1	34.1	5.03
	40	0.73	1.46	113.5	3.34	36.2	33.4	5.09
C_{12}ETEA	10	0.92	2.50	66.4	3.72	39.9	34.3	5.52
	20	0.88	1.99	83.2	3.62	39.6	33.2	5.56
	30	0.85	1.63	101.7	3.54	39.2	32.0	5.58
	40	0.81	1.53	108.8	3.32	38.1	31.5	5.62

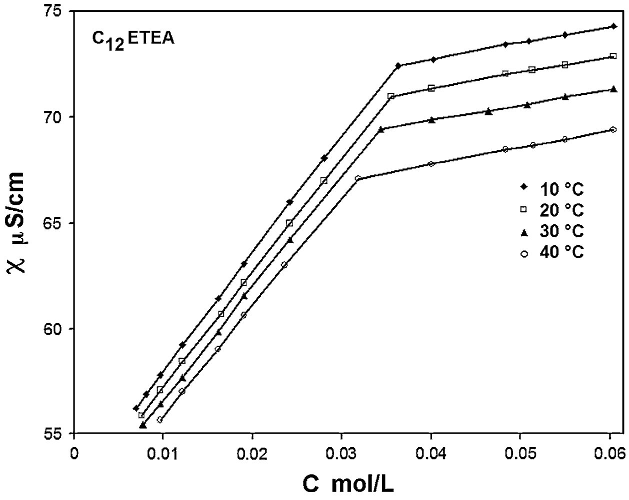


Fig. 5 The plots of electrical conductivity, χ, against concentration of C_{12}ETEA at different temperatures. The error of electrical conductivity value was ±0.3 μS/cm

where ($-\delta\gamma/\delta$lnC) is the surface activity (slope of γ vs lnC plots at constant absolute temperature, T) and $R = 8.314$ J mol^{-1} K^{-1}. As is seen, a value of Γ depends on surfactant concentration, but Γ_{max} has a certain value at CMC. The Gibbs pre-factor 'n' in the equation represents the number of particles per surfactant molecule whose surface concentration changes with change in the bulk concentration of the surfactant. For monovalent ionic surfactant, $n = 2$.

The Γ_{max} values were used to calculate the minimum area (A_{min}, in nm^2) of a molecule, at the aqueous solution/air interface using the relationship:

$$A_{min} = 10^{16}/N\Gamma_{max} \tag{5}$$

where N is Avogadro number (6.023×10^{23}). The maximum surface excess, Γ_{max}, and the area per molecule, A_{min}, varied with the molecule structure, showing a larger area per molecule with increasing alkyl chain length which indicates that the molecules were less tightly packed at the air/water interface for the flexible, longer alkyl chain surfactants [14].

Thermodynamic Parameters of Micellization

The thermodynamic parameters of micellization expressed by standard free energies ΔG_{mic}, enthalpies ΔH_{mic} and entropies ΔS_{mic} of micellization for the investigated surfactants were calculated from the equations [15]

$$\Delta G_{mic} = (2 - \alpha)\mathrm{RT}\ln \mathrm{CMC} \tag{6}$$

and

$$-\Delta S_{mic} = (\delta \Delta G_{mic}/\delta T) \tag{7}$$

and by using the values of ΔG_{mic} at 10, 20, 30, and 40 °C, ΔH_{mic} values were calculated as

$$\Delta H_{mic} = \Delta G_{mic} + T\Delta S_{mic} \tag{8}$$

Analyzing the thermodynamic parameters of micellization listed in Table 2 we may conclude that micellization process

Table 2 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 quaternary ammonium salts at 10, 20, 30 and 40 °C

Reagent	T (°C)	ΔG_{mic} (kC/mol)	ΔG_{ad} (kC/mol)	ΔS_{mic} (kC/mol K)	ΔH_{mic} (kC/mol)	ΔS_{ad} (kC/mol K)	ΔH_{ad} (kC/mol)
C_8ETEA	10	−13.2	−14.5	0.0360	−3.05	0.0470	−1.25
	20	−13.6	−15.1				
	30	−13.9	−15.5				
	40	−14.3	−15.9				
C_9ETEA	10	−13.7	−15.3	0.0366	−3.34	0.0552	0.32
	20	−14.0	−15.9				
	30	−14.4	−16.4				
	40	−14.8	−16.9				
C_{10}ETEA	10	−14.2	−16.0	0.0368	−3.79	0.0602	1.12
	20	−14.6	−16.4				
	30	−14.9	−17.1				
	40	−15.3	−17.8				
C_{12}ETEA	10	−14.9	−16.5	0.0388	−3.86	0.0700	3.32
	20	−15.2	−17.2				
	30	−15.6	−18.0				
	40	−16.0	−18.5				

is spontaneous ($\Delta G_{mic} < 0$). Also, a decrease in the standard free energy becomes larger with increasing hydrophobic chain length. This is due to the hydrophobic chains and their repulsion by water molecules which is the motivating factor in micelle formation. In spite of the formation of hydrogen bonds and the attraction of head groups by water molecules, the alkyl chain-water molecules repulsion enforces the surfactant molecules to pass into a less energetic state which is the micelle form to reduce the mentioned repulsion.

Thermodynamic Parameters of Adsorption

The ΔG_{ad} values were calculated by using the relationship [15]

$$\Delta G_{ad} = (2 - \alpha)\mathrm{RTl}n\mathrm{CMC} - 0.6023\pi_{\mathrm{CMC}}A_{\mathrm{CMC}} \qquad (9)$$

The ΔH_{ad} and ΔS_{ad} were obtained from the relationships corresponding to Eqs. (7) and (8).

The ΔS_{ad} values were all positive and slightly greater than the ΔS_{mic} values for the same surfactants. This may reflect the greater freedom of motion of the hydrocarbon chains at the planar air/aqueous solution interface compared to that in the relatively cramped interior beneath the convex surface of the micelle.

Table 2 shows the variation of adsorption parameters of the synthesized quaternary ammonium salts at different temperatures. The standard free energy change of adsorption (ΔG_{ads}) was found to be more negative than that for the micellization process (ΔG_{mic}), which refers to the higher tendency of these quaternary ammonium salts to adsorption at the air–water interface rather than micellization. The preference of adsorption is governed by the thermodynamic stability of the molecules at the air–water interface. The free energy change of adsorption per methylene group for the quaternary ammonium salts was found to be 0.7–0.8 kC.

Table 3 Petroleum-collecting and petroleum dispersing properties of quaternary ammonium salts against Ramany crude oil films

Surfactants	Distilled water		Fresh water		Sea water		Surakhany layer water	
	τ, h	K	τ, h	K	τ, h	K	τ, h	K
5 wt% solution								
C_8ETEA	102	12.2	102	15.2	102	Disp.	102	Disp.
C_9ETEA	165	12.3	165	15.3	165	Disp.	165	Disp.
C_{10}ETEA	165	Disp.	165	24.3	165	Disp.	165	Disp.
C_{12}ETEA	165	Disp.	165	Disp.	165	Disp.	165	Disp.

K maximum values of petroleum collecting coefficient; τ fixed time intervals

The Prepared Quaternary Ammonium Salts as Oil Slicks-Collecting and Dispersing Agent

The petroleum-collecting and petroleum-dispersing properties of the synthesized quaternary ammonium salts were studied with regard to Ramany crude oil films on the surface of distilled, fresh, sea and Surakhany layer waters (Table 3). It was established that 5 % aqueous solutions of $C_{8\text{-}12}$ETEA salts possess petroleum-dispersing and properties in the sea and Surakhany layer waters. In the distilled water 5 % aqueous solution of C_8ETEA had the value $K = 12.2$ (at $\tau = 102$ h) and for the same solution of C_9ETEA K was equal to 12.3 (at $\tau = 165$ h). 5 % aqueous solution of C_{10}ETEA and C_{12}ETEA exhibit petroleum-dispersing properties. In the fresh water for 5 % aqueous solutions of C_8ETEA, C_9ETEA and C_{10}ETEA the values of K were respectively 15.2 (at $\tau = 102$ h), 15.3 (at $\tau = 165$ h) and 24.3 (at $\tau = 165$ h). Therefore, with elongation of the alkyl chain in the synthesized salts their petroleum-collecting capacity was improved. A 5 % aqueous solution of C_{12}ETEA possesses petroleum-dispersing properties in the fresh water.

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References

1. Chlebicki J, Wegrzynska J, Maliszewska I, Oswiecimska M (2005) Preparation, surface-active properties, and antimicrobial activities of bis-quaternary ammonium salts from amines and epichlorohydrin. J Surfactant Deterg 8:227–232
2. Badr EE, Kandeel EM, El-Sadek BM (2010) Novel gemini cationic surfactants based on *N*,*N*-dimethyl fatty hydrazide and 1,3-dibromopropane: synthesis, evaluation of surface and antimicrobial properties. J Oleo Sci 59:647–652
3. Shukla D, Tyagi VK (2006) Cationic gemini surfactants: a review. J Oleo Sci 55:381–390
4. Hongqi L, Chaochao Y, Rui C, Juan L, Jinxing L (2012) Novel ionic liquid-type Gemini surfactants: synthesis, surface property and antimicrobial activity. Colloids Surf A 395:116–124
5. Wegrzynska J, Chlebicki J, Maliszewska I (2007) Preparation, surface-active properties and antimicrobial activities of bis(ester quaternary ammonium) salts. J Surfactants Deterg 10:109–116
6. Mohamed AS, Mohamed MZ (2010) Preparation of novel cationic surfactants from epichlorohydrin: their surface properties and biological activities. J Surfactant Deterg 13:159–163
7. Kim T-S, Kida T, Nakatsuji Y, Ikeda I (1996) Preparation and properties of multiple ammonium salts quaternized by epichlorohydrin. Langmuir 26:6304–6308
8. Wegrzynska J, Chlebicki J (2006) Preparation, surface-active and antielectrostatic properties of multiple quaternary ammonium salts. J Surfact Deterg 9:221–226
9. Hoskin DH (1985) Low cost, brine tolerant sulfonate and sulfate surfactants having 1,3-dihydrocarboxy-2-propyl hydrophobic tails. US Patent 4,515,701
10. Asadov ZH, Ahmadova GA, Rahimov RA (2010) Colloidal-chemical parameters and petroleum-collecting properties of chloropropoxylate surfactants based on epichlorohydrin and carboxylic acids fractions of animal origin. Mater Res Innov 14:327–331
11. Asadov ZH, Ahmadova GA (2003) Synthesis of nonionic surfactants based on higher saturated aliphatic linear alcohols (C7–C15) and epichlorohydrin. Azerb Chem J 4:112–117
12. Kushwaha SSS, Katiyar A (2008) Synthesis, characterization and surface-active properties of surfactants having dipeptidyl linkage as hydrophilic group. Indian J Chem 47A:1818–1822
13. Alehyen S, Bensajjay F, Achouri MEl, Perez L, Pinazo A, Infante MR (2010) Preparation of a new oligomeric surfactant: N,N,N′,N″,N″–pentamethyl diethyleneamine–N,N″-di-[tetradecylammonium bromide] and the study of its thermodynamic properties. J Surfactant Deterg 13:339–348
14. Mohamed AS, Mohamed MZ, Ismail DA (2004) Alanine-based surfactants: synthesis and some surface properties. J Surfactant Deterg 7:415–419
15. Rosen MJ (2004) Surfactants and interfacial phenomena, 3rd edn. Wiley, New York

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