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ORIGINAL ARTICLE

Synthesis and Characteristics of Dodecyl Isopropylolamine and Derived Surfactants

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Abstract Dodecyl isopropylolamine has been synthesized on the basis of dodecylamine and propylene oxide. The structure of dodecyl isopropanolamine has been determined by X-ray diffraction, elemental analysis, IR- and NMR-spectroscopic methods. Ionic surfactants have been synthesized by interaction of dodecyl isopropylolamine with various acids (HCl, HBr, acetic and propionic) and alkyl halides (methyl iodide, ethyl bromide and *n*-propyl bromide). Colloidal-chemical parameters, petroleum-collecting and petroleum dispersing capacities of the synthesized cationic surfactants have been studied.

Keywords Amine · Surfactant · Surface tension · Micellization · Adsorption · Counterion · Petroleum-collecting

Introduction

Introduction of alkoxy-groups into alkylamines leads to valuable products that are important for various applications. For example, they may be used as auxiliary agents in the textile industry and activators for pesticide formulations, thickeners for acidic reagents, and antistatic agents, improvers of detergency, lubricity and wear resistance [1, 2]. However, it should be mentioned that ionic derivatives of such alkoxy-derivatives have not been studied extensively. It is known that a rise in concentration results in formation of micelles which causes a change in surfactants properties [3, 4]. For instance, some authors [5] observed various types of self-organization and formation of different structures that are dependent on geometrical packing parameters.

Study of the solid-state structure of surfactants may be informative for clarifying hydrogen bond interactions and understanding local forces responsible for association of surfactant molecules. The intrinsic structure of solids may be studied by X-ray diffraction of single crystals. However, as obtaining single crystals is difficult, this method enables revelation of only some crystalline structure [6–10]. It is known that head-group substantially impacts properties of surfactants [11, 12]; thus, by variation of head-group structure it is possible to change the properties of surfactants. From this standpoint, the synthesis of surfactants with different head-groups based on dodecyl isopropylolamine (DIPA) is of scientific and practical interest. As the synthesized surfactant has petrocollecting and petrodispersing properties, it is possible to obtain more effective petrocollecting and petrodispersing reagents by changing a polar group structure. Creation of effective petrocollecting and petrodispersing surfactants is one of the most impactful applications for surfactants now [4, 13, 14].

In this work, single crystals of DIPA were obtained for the first time by employing a solvent-evaporation method. DIPA was then reacted with various acids and alkyl halides. The properties of the cationic surfactants were studied.

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Experimental Procedures

Reagents and Instruments

A Bruker TOP SPIN spectrometer (300.13 and 75.46 MHz) was used for recording ^{1}H-NMR and ^{13}C-NMR spectra. Chemical shift values (δ) in ppm are given downfield with regard to TMS. Ethanol-d_6 was used as a solvent. For recording IR spectra (in KBr disks), an ALPHA FT-IR (Bruker) spectrometer was used.

Propylene oxide (PO) was of 99.8 % purity, manufactured by the "Organic Synthesis" factory in Sumgayit City, Azerbaijan. Acetic acid and propionic acid had purity higher than 95 % (Sigma–Aldrich®, Germany). Hydrochloric and hydrobromic acids were used as aqueous solutions of concentration 37 and 48 %, respectively (Merck, Germany). 1-Dodecylamine of purity >98 % was provided by Alfa Aesar GmbH and Co KG (Germany). Alkyl halides were of "Chemical line" (Russian Federation) production. The purity was higher than 98 %.

Water Types Used

Three types of water were used: distilled, fresh (hardness 4.2 mg equiv/L), and sea water. Water of the Caspian sea had the following characteristics: $\rho^{20} = 1.0098$ g/mL, pH = 7.7. Its composition is as following (mg/L): Na^{+} 2650; K^{+} 90; Ca^{2+} 250; Mg^{2+} 900; NH_4^{+} 0.15; Cl^{-} 500; SO_4^{2-} 2800; NO_3^{-} 0.1; PO_4^{3-} 0.35; NO_2^{-} 0.007; SiO_2 0.5; oil products −0.005 %; dissolved oxygen 8 mg/L. Total hardness is 69.0 mg eq/L.

Surface Tension Measurements

Measurements of surface tension were performed on a DuNoüy ring KSV Sigma 702 tensiometer (Israel). The measured sample was placed in a glass cell (with a double jacket) using a water bath for thermostatting. A Pt wire ring was placed inside the sample solution and gradually pulled through the liquid–air surface. Surface tension values were reported as an average over three readings with 3 min interval between measurements. The Pt wire ring was washed with water and flamed with a Bunsen burner between measurements. The surface tension of distilled water did not deviate from 72.1 (20 °C) by more than ±0.2 mN/m.

Synthesis of DIPA

A 50-mL flat-bottom flask equipped with a magnetic stirrer, thermometer, and reflux condenser was charged with 0.1 mol dodecylamine and 0.1 mol PO. To avoid oxidation of alkyl amines the reaction was carried out in a nitrogen atmosphere. The reaction was performed with mixing at a temperature of 23–25 °C over a 120–150 h duration. During the reaction viscosity increases, color darkens and crystal formation is observed. The amine concentration becomes stabilized at the end part of the reaction, when no weight decrease is observed upon heating of the mixture. Recrystallization of the formed DIPA was performed in cold acetone. DIPA yield equaled 74 %.

IR, results were, in cm^{-1}: 3333.9 ν (OH), 3280.8 ν (NH), 2957.0, 2915.1 and 2848.2 ν (CH), 1464.6, 1371.5 and 1298.0 δ (CH), 1157.4, 954.7 and 915.3 ν (C–N), 720.0 δ $(CH_2)_x$ (Fig. S1). ^{1}H NMR (300.18 MHz, ethanol-d_6), δ (ppm): 0.92 ($\underline{CH_3}$), 1.29 (CH–$\underline{CH_3}$), 1.30–1.32 ($\underline{CH_2}$ chain), 1.5 ($\underline{CH_2}$–CH_2–NH), 2.36–2.52 ($\underline{CH_2}$–NH) 3.79–3.87 (CH_2–$\underline{CH}$) (Fig. S 2). ^{13}C NMR (75.49 MHz, ethanol-d_6), δ (ppm): 13.7 ($\underline{CH_3}$), 21.7 ($\underline{CH_3}$–CH), 22.6–31.9 (alkyl group), 49.5 (NH–$\underline{CH_2}$–CH_2), 62.7–63.7 (NH–$\underline{CH_2}$–CH), 64.2–65.3 (NH–CH_2–$\underline{CH}$) (Fig. S 3). Elemental analysis results for $C_{15}H_{33}NO$ in mass %: N, 5.75; C, 74.02; H, 13.60. Calculated: N, 5.75; C, 74.01; H, 13.66.

X-Ray Structure Determination

The crystal of DIPA ($C_{15}H_{33}NO$, Mr = 243.42) is colorless, with T_m = 44 °C, 0.03 × 0.03 × 0.30 mm, triclinic, space group P 1, at T = 100 K: a = 4.2071(16), b = 13.246(5), c = 14.621(6) Å, α = 77.326(5), β = 87.102(5), γ = 81.809(5), V = 786.7(5) Å^3, Z = 2, d_{calc} = 1.028 g/cm^3, F(000) = 276, μ = 0.062 mm^{-1}. 12162 total reflections (4532 unique reflections, R_{int} = 0.0336) were measured on a Bruker SMART APEX II CCD automated diffractometer (MoK$_\alpha$ radiation, λ = 0.71073, Å graphite monochromator, φ- and ω-scan modes, $2\theta_{max}$ = 60°). Determination of the structure was made using direct methods. Refining was performed by full-matrix least squares method using anisotropic displacement parameters for all types of atoms except hydrogen. Identification of hydrogen atoms in the amino fragments was made in Fourier difference syntheses. They were included into the refinement at fixed positions. Isotropic thermal positions were taken as [$U_{iso}(H) = 1.5U_{eq}(O)$ and $U_{iso}(H) = 1.2U_{eq}(N)$]. For the other hydrogen atoms, the coordinates were computed on the basis of geometrical considerations, then they were refined using the Riding model using thermal parameters $U_{iso}(H) = 1.5U_{eq}(C)$ for the methyl groups and $U_{iso}(H) = 1.2U_{eq}(C)$ for all the remaining groups. The final divergence factors were R_1 = 0.042 for 3561 independent reflections with $I > 2\sigma(I)$ and wR_2 = 0.123 for all independent reflections, S = 1.057. All calculations were carried out using the SHELXTL (PC version 6.12) program [15], (Table S1, S2).

Crystallographic data for DIPA have been deposited in the Cambridge Crystallographic Data Center, CCDC 874945. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Synthesis of Ionic Surfactants Based on DIPA

DIPA (0.3 mol) and hexane (10 mL) were placed in a 3-neck round-bottomed flask. This mixture was agitated till the DIPA was fully dissolved. The corresponding quantity (0.3 mol) of organic acid or alkyl halides was added to the mixture to form the respective anion and new head hydrophilic groups of DIPA. During the reaction a weak evolution of heat is observed. The final mixture underwent vacuum distillation to remove the solvent. The ammonium salts obtained dissolve in water well and their aqueous solutions possess electroconductivity. The carboxylate salts and the salt derived from methyl iodide are liquids but the rest of the salts are paste-like substances. The yield of the salts based on alkyl halides was 92–93 %. The yield of carboxylate-type salts was 97–98 %. Observation of the absorption band at 2066 cm^{-1} of IR-spectra of the synthesized salts characteristic for N^+H_2 group as well as disappearance of the bond at 1705 cm^{-1} intrinsic for COOH–group in the carboxylate-type salts and appearance, instead of it, of bonds at 1407 and 1568 cm^{-1} belonging to COO^--group evidence formation of ionic surfactants.

Determination of Petroleum-Collecting and Petroleum-Dispersing Capacities

Studies of petroleum-collecting and petroleum-dispersing capacities of the obtained surfactants have been conducted in parallel for pure-state reagents and their 5 % wt. alcoholic solutions. As an example of crude oil, Ramana petroleum (from an oil field in Absheron peninsula, Azerbaijan) was taken (at 20 °C its density was 0.86 g cm^{-3} and kinematic viscosity was 0.16 $cm^2\ s^{-1}$). To a thin film (0.15–0.16 mm thickness) of the petroleum on the water surface (in petri dishes) 0.02 g of the surfactant (or its solution) was added. Petrocollecting factor-K was computed using the relationship $K = S_o/S$, where S_o is the initial area of the petroleum slick surface at the start of the test, and S is an area of the petroleum surface accumulated in the form of thickened spot. During the observations, the spot surface area was periodically measured and for these certain time intervals (τ) the values of K were calculated. Petroleum-dispersing capacity was estimated by the degree of cleaning of contaminated water surface from petroleum $-K_D$ which was computed as a ratio of surface areas of the cleaned water and the initial area of the petroleum film.

Results and Discussion

Synthesis of DIPA

The reaction between dodecylamine and PO can be illustrated by the following reaction Scheme 1.

The obtained DIPA is a transparent solid which melts at 44 °C. It has a goad solubility in ethanol, isopropyl alcohol, acetone, benzene, hexane, and CCl_4. DIPA only partially dissolves in water (when 5 g of DIPA and 95 g of water are mixed, 10–12 % of DIPA are dissolved). The reaction between DIPA and carboxylic acids proceeds according to Scheme 2.

The obtained salts have good solubility in water, ethyl and isopropyl alcohols, acetone, hexane, benzene and CCl_4. Dodecylisopropanolammonium carboxylate salts are transparent viscous liquids.

The reaction between DIPA and alkyl halides proceeds according to Scheme 3.

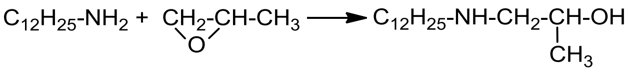
The resulting salts dissolve in such solvents as water, ethyl and isopropyl alcohols, benzene, acetone, hexane and CCl_4. Dodecylmethylisopropylolammonium iodide salt is a transparent viscous liquid whereas dodecylethylisopropylolammonium bromide and dodecylpropylisopropylolammonium bromide salts are solid substances.

Crystal Structure of DIPA

The perspective view of the structure is depicted in Fig. 1. As a result of intermolecular O–H…N and N–H…O hydrogen bonds, molecules are connected in the form of a unidimensional chain extended along the *a* axis with parallel arrangement of the alkyl chain. The geometric parameters of the hydrogen bonds are summarized in Table 1. The structure shows intermolecularly directed four-membered O–H…OH…OH… interactions which are illustrated in the packing diagram (Fig. 2).

Colloidal-Chemical Parameters of the Synthesized Ionic Surfactants

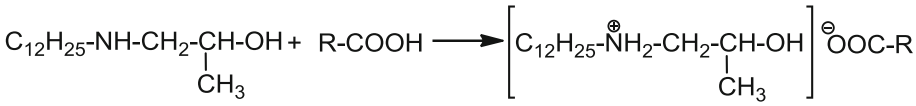
The plots of the surface tension (γ) *vs* the molar concentration on the natural logarithmic scale (lnC) for the salts at 25 °C are shown in Figs. 3, 4 and 5. Critical micelle concentration (CMC) which is defined by a sharp break and the surface tension at CMC obtained from Figs. 3, 4 and 5 are summarized in Table 2. As is seen from this table, when chloride counterion of the surfactant is replaced by



$$C_{12}H_{25}\text{-}NH_2 + \underset{O}{\underbrace{CH_2\text{-}CH}}\text{-}CH_3 \longrightarrow C_{12}H_{25}\text{-}NH\text{-}CH_2\text{-}\underset{CH_3}{\underset{|}{CH}}\text{-}OH$$

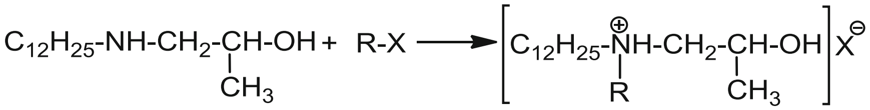
Scheme 1 Synthesis of DIPA

Scheme 2 Synthesis of dodecylisopropylolammonium carboxylate salts



$$C_{12}H_{25}\text{-NH-}CH_2\text{-}\underset{CH_3}{\underset{|}{C}}H\text{-OH} + R\text{-COOH} \longrightarrow \left[C_{12}H_{25}\text{-}\overset{\oplus}{N}H_2\text{-}CH_2\text{-}\underset{CH_3}{\underset{|}{C}}H\text{-OH}\right]\overset{\ominus}{O}OC\text{-}R$$

$R=CH_3$; C_2H_5.



$$C_{12}H_{25}\text{-NH-}CH_2\text{-}\underset{CH_3}{\underset{|}{C}}H\text{-OH} + R\text{-X} \longrightarrow \left[C_{12}H_{25}\text{-}\underset{R}{\underset{|}{\overset{\oplus}{N}}}H\text{-}CH_2\text{-}\underset{CH_3}{\underset{|}{C}}H\text{-OH}\right]X^{\ominus}$$

$R=H$; $X=Cl$. $R=H$; $X=Br$. $R=CH_3$; $X=I$. $R=C_2H_5$; $X=Br$. $R=C_3H_7$; $X=Br$.

Scheme 3 Synthesis of dodecylalkylisopropylolammonium halide salts

Fig. 1 X-ray structure of DIPA

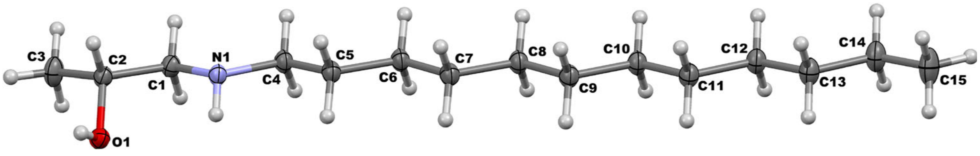
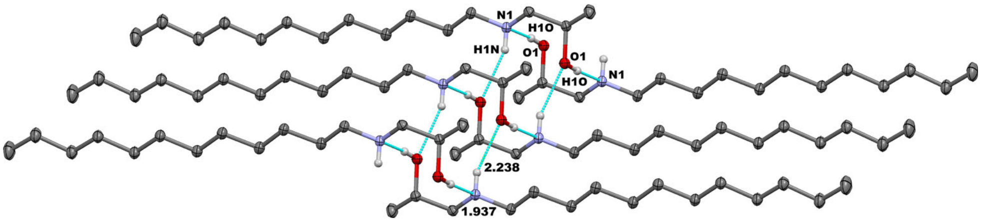


Table 1 Parameters of H–bonds (Å and deg) in the structure of DIPA

D-H…A	*d*(D*-H)	*d*(H…A*)	*d*(D…A)	<(DH…A)
O(1)–H(1O)…N(1) [$-x + 1,-y + 1,-z$]	0.851	1.94	2.779(1)	170
N(1)–H(1 N)…O(1) [$-x + 2,-y + 1,-z$]	0.863	2.24	3.059(1)	159

* *D* is the proton donor; *A* is the proton acceptor

Fig. 2 Intermolecular hydrogen bonds in DIPA



bromide-anion and acetate-ion by propionate-ion, the value of CMC decreases. CMC also diminishes when passing from methyl iodide-based salt to ethyl bromide- and propyl bromide-based salts. Similar trends are observed for gemini [ethanediylbis(dimethyltetradecylammonium)] [16], alkylpyridinium [17], cetyltrimethylammonium [18], 1-dodecylammonium [19], decyltrimethylammonium [20] and other type surfactants [21–23].

Table 2 indicates that the counterions are important for maximum values of surface excess concentration–$\Gamma_{\max}$, as well as the minimal surface area per molecule of surfactant—$A_{\min}$ at the border of aqueous solution with air.

The values of surface excess concentrations–Γ (mol/cm^2) were computed by the formula [21, 23]:

$$\Gamma = (1/\mathrm{n}RT)(-\delta\gamma/\delta\ln C) \tag{1}$$

where ($-\delta\gamma/\delta\ln C$) indicates the surface activity, *T* is the absolute temperature and *R* is the universal gas constant. It is evident that Γ is dependent on the concentration of surfactant and $\Gamma_{\max}$ is attained at CMC. The pre-factor-"*n*" shows the number of ions formed by a surfactant molecule. In the case of our salt, the value of "*n*" may be taken as 2.

The value $\Gamma_{\max}$ is necessary for computing the minimal area (symbolized by $A_{\min}$, nm$^{2)}$ of a molecule at the solution-air surface according to the equation [21, 23]:

$$A_{\min} = 10^{16}/N\Gamma_{\max} \tag{2}$$

where *N* represents Avogadro's number. The values of $\Gamma_{\max}$ and $A_{\min}$ depend on the molecular structure. As is seen from the table, upon replacing of chloride counterion by bromide or acetate anion by propionate anion the value

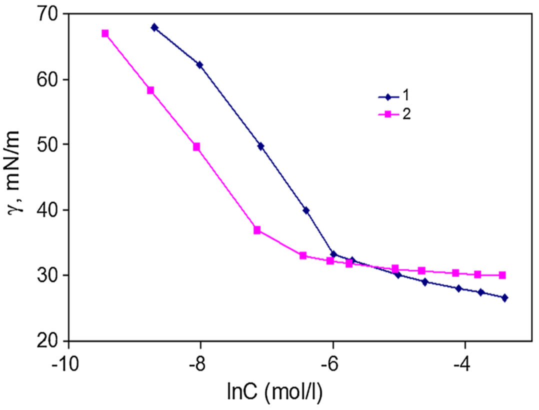


Fig. 3 Surface tension *vs* the concentration of dodecylisopropylolammonium carboxylate salts in aqueous solution (25 °C). 1-Dodecylisopropylolammonium acetate, 2-dodecylisopropylolammonium propionate

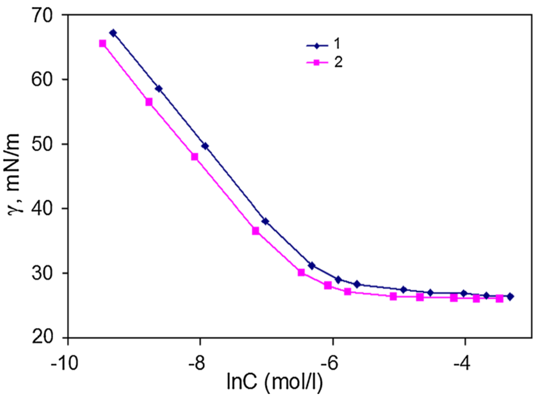


Fig. 4 Surface tension *vs* the concentration of dodecylisopropylolammonium halide salts in aqueous solution (25 °C). 1-Dodecylisopropylolammonium chloride, 2-dodecylisopropylolammonium bromide

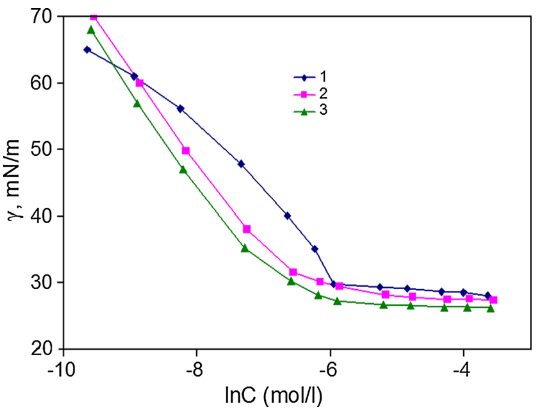


Fig. 5 Surface tension *vs* the concentration of dodecylalkylisopropylnolammonium halide salts in aqueous solution (25 °C). 1-Dodecylmethylisopropylolammonium iodide, 2-dodecylethylisopropylolammonium bromide, 3-dodecylpropylisopropylolammonium bromide

Table 2 Surface properties of the surfactants based on DIPA; 298 K temperature

Surfactants	β	γ_{CMC} (mN m^{-1})	$\Gamma_{\max} \times 10^{10}$ (mol cm^{-2})	$A_{\min} \times 10^2$ (nm^2)	CMC × 10^3, (mol dm^{-3})	pC$_{20}$	π_{CMC} (mN m^{-1})	ΔG_{mic} (kJ mol^{-1})	ΔG_{ad} (kJ mol^{-1})
Dodecylisopropylolammonium acetate	0.34	26.7	2.88	57.6	2.47	3.16	45.3	−19.93	−21.50
Dodecylisopropylolammonium propionate	0.23	30.1	2.62	63.4	1.13	3.58	41.9	−20.68	−22.28
Dodecylisopropylolammonium chloride	0.25	26.4	2.46	67.6	2.03	3.52	45.6	−19.20	−21.06
Dodecylisopropylolammonium bromide	0.28	26.1	2.41	68.8	1.66	3.65	45.9	−20.30	−22.20
Dodecylmethylisopropylolammonium iodide	0.32	28.1	2.55	65.0	2.60	3.39	43.9	−19.47	−21.18
Dodecylethylisopropylolammonium bromide	0.39	27.4	2.81	59.0	1.30	3.61	44.6	−22.89	−24.47
Dodecylpropylisopropylolammonium bromide	0.31	26.2	2.87	57.9	1.11	3.72	45.8	−22.08	−23.68

β Counterion binding degree, *CMC* critical micelle concentration, γ_{CMC} equilibrium surface tension at the CMC, Γ_{max} the maximum surface excess concentration at the aqueous solution/air interface, A_{min} the minimum area per surfactant molecule at the aqueous solution/air interface, π_{CMC} effectiveness of surface tension reduction, pC_{20} the efficiency of surface adsorption, measured as the negative logarithm of the bulk surfactant concentration C$_{20}$ required to reduce the surface tension of water by 20 mN/m, ΔG_{mic} change of standard free energy of micellization, ΔG_{ad} change of standard free energy of adsorption of $\Gamma_{\max}$ decreases, whereas $A_{\min}$ increases. In the salts based on methyl-, ethyl- and propyl halides with an elongation of alkyl chain $\Gamma_{\max}$ rises, while $A_{\min}$ diminishes, despite the fact that in the case of methyl group the counterion of the surfactant is iodine.

The effectiveness of surface tension reduction (π_{CMC}) is estimated from the equation [21, 23].

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

where γ_0 is the surface tension of water and γ_{CMC} is the surface tension of surfactant solution at CMC. The values of π_{CMC} for the obtained salts at 298 K temperature fall into the range 41.9–45.9 mN m^{-1}. When Cl^- is replaced by Br^-, π_{CMC} increases, but with replacement of the acetate anion as a counterion by a propionate anion π_{CMC} decreases. In the case of the salts derived from methyl-, ethyl- and propyl halides π_{CMC} rises with an increase in the alkyl chain length.

Further, the values of adsorption efficiency (pC_{20}), are useful in comparing the efficiency of adsorption of surfactant at the air/water interface [4]. The larger the pC_{20} value, the higher is the efficiency of surface adsorption of the surfactant and the bigger is the decrease of surface tension. pC_{20} rises when Cl^- counterion is substituted by Br^- and acetate-ion by propionate-anion and, also, if alkyl chain is elongated in the salts based on alkyl halides.

Conductimetric Measurements

Graphs showing dependence of specific electroconductivity on the surfactant concentration at 25 °C were drawn (Figs. 6, 7, 8). As can be seen, specific conductivity rises with an increase in concentration. On the basis of slopes of conductivity/concentration plots both above and below the CMC of the curve the ionization degree (α) was found [24]:

$$\alpha = S_2/S_1 \quad (4)$$

where S_1 and S_2 are slopes of the conductivity dependence at the concentrations lower and higher than CMC. The degree of counterion binding (β) was computed as [24]:

$$\beta = 1 - \alpha \quad (5)$$

The values of β are shown in Table 2. The values of CMC determined by intersection point of two straight lines differ little from those found on the base of surface tension measurements.

If Cl^--counterion in the surfactant becomes replaced by Br^-, β increases. Similar trends were shown by J Keiper and LS Romsted [25] for tetramethylammonium halides, S Manet and coauthors for ethanediylbis(dimethyltetradecylammonium) halides [16], and HN Patreck et al. for cetyltrialkylammonium halides [26]. But when acetate-anion is substituted by propionate-anion, the value of β diminishes. Similar results were obtained in [16] for ethanediylbis(dimethyltetradecylammonium) carboxylate surfactants in the range of carboxylate chain C_1–C_4. In the case of the salts based on ethyl- and propyl bromide elongation of the alkyl chain makes β lower. In cetyltrialkylammonium bromide salts [26] with elongation of alkyl group the value of β decreases too.

Thermodynamic Properties of the Synthesized Salts

In the case of these salts the change in the standard Gibbs free energy of micelle formation (ΔG_{mic}) may be computed according to Eq. 6 [27].

$$\Delta G_{\mathrm{mic}} = (2 - \alpha)\mathrm{RTlnCMC} \quad (6)$$

where R is universal gas constant, and T is the absolute temperature (298.15 K).

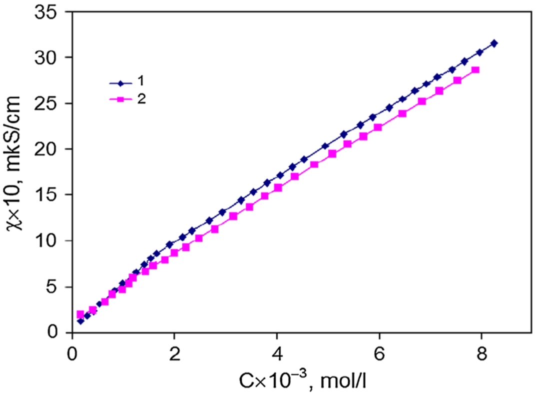


Fig. 6 The plots of electrical conductivity against concentration of dodecylisopropylolammonium carboxylate. 1-Dodecylisopropylolammonium acetate, 2-dodecylisopropylolammonium propionate. The *error* of electrical conductivity value is ±0.3 μS/cm

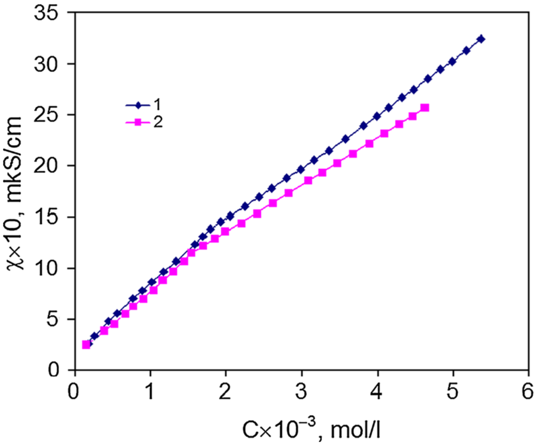


Fig. 7 The plots of electrical conductivity against concentration of dodecylisopropylolammonium halide. 1-Dodecylisopropylolammonium chloride, 2-dodecylisopropylolammonium bromide. The *error* of electrical conductivity value is ±0.3 μS/cm

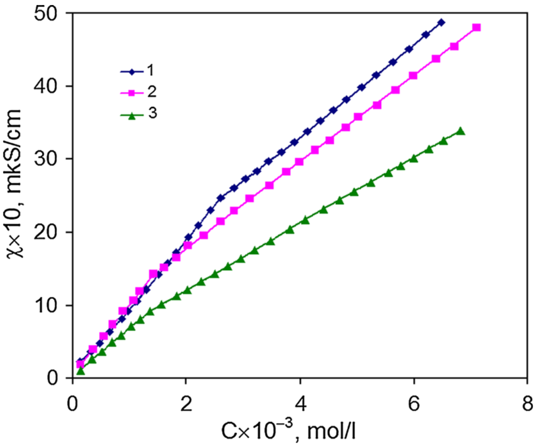


Fig. 8 The plots of electrical conductivity against concentration of dodecylalkylisopropylolammonium halide. 1-Dodecylmethylisopropylolammonium iodide, 2-dodecylethylisopropylolammonium bromide, 3-dodecylpropylisopropylolammonium bromide. The *error* of electrical conductivity value is ±0.3 μS/cm

The changes of the standard value of Gibbs free energy for adsorption process (ΔG_{ad}) for the synthesized salts were calculated by Eq. (7) [27].

$$\Delta G_{ad} = (2 - \alpha)\text{RTlnCMC} - 0.6023\pi_{CMC}A_{CMC} \quad (7)$$

here A_{CMC} has the unit $\mathring{A}^2$ per molecule, and π_{CMC} shows the surface pressure (in mN/m) at CMC.

The values of ΔG_{mic} and ΔG_{ad} are given in Table 2. It is evident that both micelle formation and adsorption are spontaneous processes as the values of ΔG_{mic} and ΔG_{ad} are negative. At the same time, ΔG_{ad} is more negative from which it may be concluded that adsorption precedes micellization.

Cationic Surfactants as Oil Slicks Collection Agents

It has been established that dodecylisopropylolammonium chloride as a 5 % aqueous solution has a higher petroleum-collecting capacity ($K_{max} = 34.4$, $\tau = 144$ h) than the other compounds in distilled water (Table 3). However, as the mineralization degree of water rises, the petrocollecting effect of the compound decreases (in the sea water $K_{max} = 20.3$, $\tau = 192$ h). This compound in undiluted form, in all three types of water, shows a petro-dispersing capability ($K_D = 86.8$–91.1 % $\tau = 192$ h). Dodecylisopropylolammonium bromide as 5 % aqueous solution is a more effective collector than the other compounds in fresh and sea waters ($K_{max} = 30.4$, $\tau = 100$ h). In distilled water "K" equals 20.3. In undiluted form the compound has a

Table 3 Petroleum-collecting and petroleum dispersing properties of ionic surfactants

State of surfactant added to petroleum film	Distilled water		Fresh water		Sea water	
	τ (h)	K (K_D)[a]	τ (h)	K (K_D)	τ (h)	K (K_D)
Dodecylisopropylolammonium acetate						
Undiluted product	0–100	95.5 %	0-100	95.5 %	0-100	95.5 %
5 % wt aqueous solution	0–25, 30–100	20.3, 86.8 %	0–100	30.4	0–100	91.3 %
Dodecylisopropylolammonium propionate						
Undiluted product	0–100	86.8 %	0–100	91.1 %	0–100	95.7 %
5 % wt aqueous solution	0–100	12.2	0–100	30.4	0–100	20.3
Dodecylisopropylolammonium chloride						
Undiluted product	0–192	86.8 %	0–192	86.8 %	0–192	91.1 %
5 % wt aqueous solution	0–144	34.4	0–192	91.1 %	0–192	20.3
Dodecylisopropylolammonium bromide						
Undiluted product	0, 1–100	20.3, 91.1 %	0, 1–100	30.4, 93.4 %	0, 1–100	30.4, 86.8 %
5 % wt aqueous solution	0–100	20.3	0–100	30.4	0–100	30.4
Dodecylmethylisopropylolammonium iodide						
Undiluted product	0–100	91.1 %	0–100	30.4	0–100	91.1 %
5 % wt aqueous solution	0–100	91.1 %	0–100	95.5 %	0–100	95.5 %
Dodecylethylisopropylolammonium bromide						
Undiluted product	0, 1–100	15.2, 86.8 %	0, 1–100	15.2, 95.5 %	0–100	98.9 %
5 % wt aqueous solution	0–100	15.2	0–100	20.3	0–100	20.3
Dodecylpropylisopropylolammonium bromide						
Undiluted product	0–100	12.3	0–100	15.2	0–100	95.5 %
5 % wt aqueous solution	0–100	14.5	0–100	16.2	0–100	91.1 %

[a] K petrocollecting factor, K_D degree of cleaning of water surface from petroleum

petrocollecting effect during the initial time but at the end petrocollecting becomes replaced by petrodispersing. Dodecylisopropylolammonium acetate and dodecylisopropylolammonium propionate as 5 % aqueous solutions possess a high petrocollecting capacity in fresh water ($K_{\max} = 30.4$, $\tau = 100$ h). In the sea water dodecylisopropylolammonium acetate 5 % aqueous solution of demonstrates petrodispersing ($K_{\mathrm{D}} = 91.3$ % $\tau = 100$ h), while 5 % aqueous solution of dodecylisopropylolammonium propionate shows petrocollecting properties ($K_{\max} = 20.3$, $\tau = 100$ h). Dodecylisopropylolammonium acetate and dodecylisopropylolammonium propionate in undiluted form mainly manifest petrodispersing capability. Among the obtained salts dodecylmethylisopropylolammonium iodide, dodecylethylisopropylolammonium bromide, dodecylpropylisopropylolammonium bromide salts and their 5 % aqueous solutions have a higher petrocollecting and petrodispersing effectiveness in distilled and fresh waters. The other reagents have a relatively low petroleum-collecting activity. As among the synthesized salts dodecylisopropylolammonium bromide in the form of 5 % wt. aqueous solution has the highest effectiveness in petrocollecting in the sea water, it may be used for removing thin petroleum films off the water surface.

Conclusion

DIPA in the form of a single crystal has been synthesized on the basis of dodecylamine and PO and has been characterized by IR- and NMR-spectroscopy. The crystal structure DIPA has been determined by X-ray diffraction techniques. Novel surfactant salts were synthesized by the interaction of DIPA with different electrophilic agents (carboxylic acids, hydrogen halides and alkyl halides). In the ammonium salts obtained, the nature of the head group and counterion largely influences colloidal-chemical parameters and their surface-active properties. In sea water, the highest petroleum-collecting capacity is exhibited by 5 % aqueous solution of dodecylisopropylolammonium bromide.

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