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Synthesis and study of surface-active salts based on propoxy derivatives of octylamine, hexadecylamine and hydrochloric acid

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ABSTRACT

Salts of the oligomeric propoxy derivatives of octylamine and hexadecylamine with hydrochloric acid were synthesized. Structure and composition of the salts were confirmed by using IR spectroscopy. Surface tension and electroconductivity properties of the oligomers were examined and corresponding main parameters of the salts were calculated. Moreover, petrocollecting properties of these salts were determined and maximum values of petrocollecting coefficients were calculated.

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I. Introduction

It is well known that demand for crude oil and petrochemical product and usage of them increase from year to year. Such increase of demand to crude oil and products of its refining results in ecological instability and disbalance. In order to improve ecological balance of the nature, surfactants are used in industry including oil production and refining [1,2]. Thin oil layers on the surface of the water become one of such ecological problems which may occur during transportation of crude oil and its refining products.

According to the literature, higher aliphatic amines may be used for synthesis of surface-active compounds [3-8]. Beside surface activity, such components are able to decrease surface area of thin pertoleum layers several times on the surface of water [3-5]. In a given study, surfactants are obtained from octylamine, hexadecylamine, propylene oxide and hydrochloric acids. Main physical-chemical properties of the new surfactants including colloidal-chemical ones were determined in order to apply them as petrocollecting agents.

II. Experimental

Octylamine was a product of "Alfa Aesar GmbH & Co KG" firm (Germany) of purity > 98%.

Hexadecylamine was a product of "Alfa Aesar GmbH & Co KG" firm (Germany) of purity > 98%.

Propylene oxide was a product "Organic Synthesis" factory (Sumgayit, Azerbaijan) of 99.97-99.98% purity.

Hydrochloric acid was "analytically pure" grade product of "Uralximinvest" (Russia) of >37% purity.

Potassium hydroxide was used as "analytically pure" product of "Chemapol" firm (Czech Republic).

Oligomers based on octylamine, hexadecylamine and propylene oxide were synthesized at 140-150°C for 13-14 hours in an autoclave made of stainless steel and equipped with a regulator of temperature. In the given reaction, potassium hydroxide was used as a catalyst. In the second

step, propoxy derivatives of the octylamine and hexadecylamine reacted with hydrochoric acid at 25°C for 5-6 hours in order to obtain salts.

All salts are liquids of yellow-brown color.

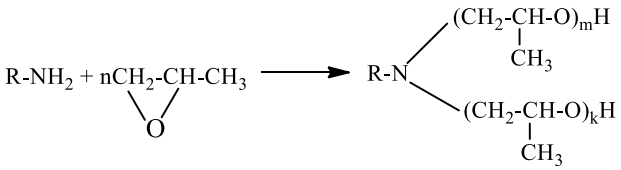
IR spectra were recorded by using an ALPHA FT-IR spectrometer (Bruker, USA) using KBr tablets.

Surface tension (γ) values were measured by Du Nouy ring method using a KSV Sigma 702 tensiometer (Finland).

Specific electroconductivity (κ) values were determined by "Anion-4120" electroconductometer (Russia).

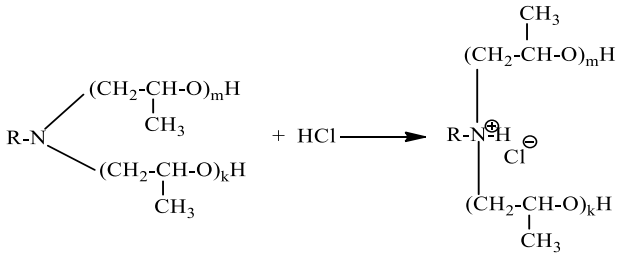
III. Resuls and Their Discussion

The reaction between alkylamine (octylamine or hexadecylamine) and propylene oxide is illustrated as following:



where R is octyl or hexadecyl group, n=m+k. Values of n are equal to 2.74 for octylamine propoxy derivative and 10.02 for hexadecylamine propoxy derivative.

In the second step, propoxy derivatives of the octylamine and hexadecylamine were reacted with hydrochloric acid as following:



Structure and composition of the final products were analyzed by using IR spectroscopy. The IR-spectra are given in Figure 1.

By examining IR spectra, it was deduced that absorption bands at 3345.25 cm^{-1} in the first spectrum, 3354.50cm^{-1} in the second spectrum represent O-H valent vibration bands. C-H valent vibration bands of C-H bonds in CH_3, CH_2 and CH groups are observed at 2957.29-2856.33cm^{-1} in the first spectrum, at 2968.20-2853.33cm^{-1} in the second spectrum. N-H deformational vibrations bands exist at 1645.85cm^{-1} in the 1st and 1638.58 cm^{-1} in the 2nd spectra. C-H deformational vibration bands are at 1458.87-1377.38 cm^{-1} and 1458.06-1374.87cm^{-1}, respectively in the first and second spectra. C-N valence vibration bands are at 1293.08cm^{-1} (1st spectrum) and 1290.55cm^{-1} (2nd spectrum). C-O valent vibrations band of C-OH group can be defined at 1078.90 cm^{-1} in Salt 1 spectrum and 1089.96cm^{-1} in Salt 2 spectrum. $(CH_2)_x$ "pendulum"vibrations bands exist at 722.44 cm^{-1} in the first spectrum and 720.62 cm^{-1} in the second spectrum.

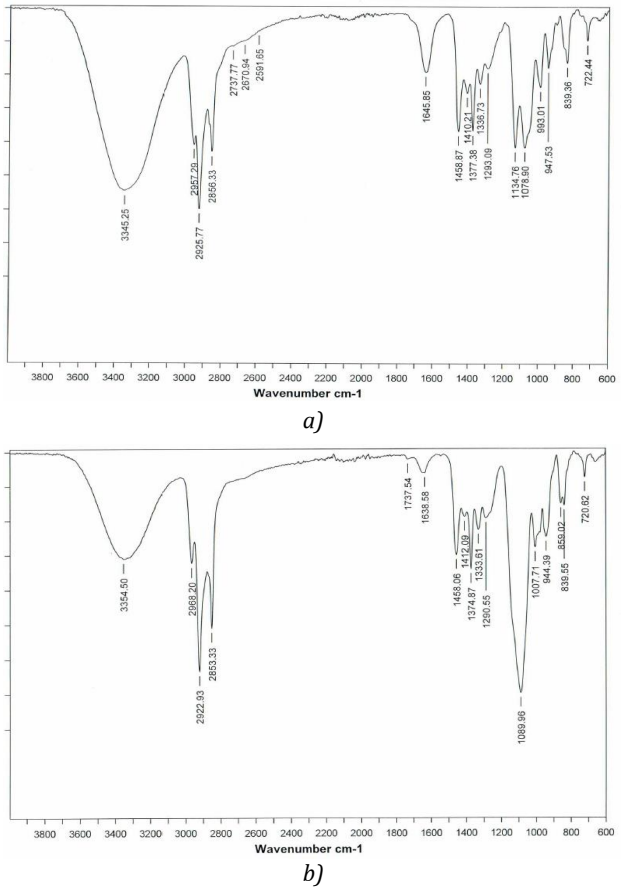


Fig 1. IR spectra of the synthesized hydrochloride salts of a) octylamine propoxy derivative (n=2.74) and b) hexadecylamine propoxy derivative (n=10.02)

Surface tension data of hydrochloride salts of alkyamine propoxy derivatives were determined at temperatures 20°C. γ versus concentration (c) plots of the components are given in Figure 2.

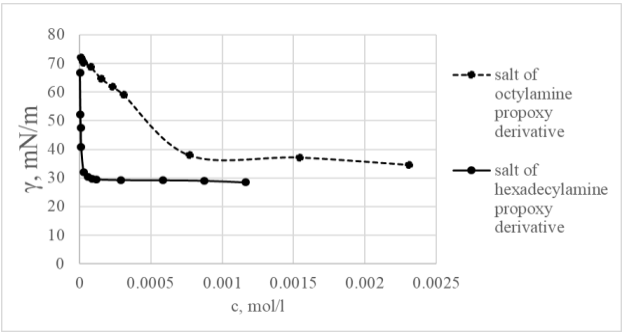


Fig 2. Surface tension at the water-air border versus concentration plots of the salts

Bu using these plots of the salts, characteristic parameters of the surface activity can be determined. Critical micelle concentrations (CMC), γ_{CMC}, surface pressure (π_{CMC}), C_{20} (the concentration

for reduction of γ by 20 mN/m), adsorption efficiency ($pC_{20}=-logC_{20}$) as well as CMC/C_{20} values of the all salts were determined according to [9] and given in Table 1.

Maximum surface excess concentration - Γ_{max} values were calculated from the following equation:

$$\Gamma_{max} = -\frac{1}{n * R * T} * \lim_{c \to c_{CMC}} \frac{d\,\gamma}{d\,lnc}$$

where R is universal gas constant (R=8.3145 C/mol*K) and T is absolute temperature. The value of n was taken as 2 because 2 ions are formed by dissociation of the salts.

The minimum value of the area for one surfactant molecule of the salts at the water-air border (A_{min}) were determined by the given equation

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

and tabulated in Table 1.

Table 1. Surface activity parameters of the synthesized surface-active salts

Surfactant	CMC×10^4 (mol/L)	γ_{CMC} (mN/m)	π_{CMC} (mN/m)	$C_{20}\times10^5$ (mol/L)	pC_{20}	$\Gamma_{max}\times10^{10}$ (mol/cm^2)	$A_{min}\times10^2$ (nm^2)
Hydrochloride salt of octaylamine propoxy derivatite	7.70	37.95	34.05	46.30	3.33	1.19	139.28
Hydrochloride salt of hexadecylamine propoxy derivatite	0.87	29.74	42.26	0.58	5.23	2.11	78.81

Specific electrical conductivity dependence on concentration was studied for hydrochloride salt of octylamine propoxy derivative at 21.8°C and hexadecylamine propoxy derivative at 26.4°C. Isotherms of the specific electrical conductivity were plotted and given in Figure 3:

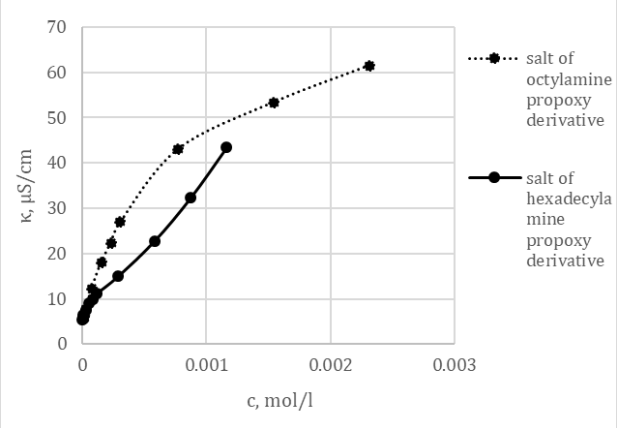


Fig 3. Specific electrical conductivity versus concentration plots of the hydrochloride salts of alkylamines (C_8 and C_{16}) propoxy derivatives

Table 2. Specific electrical conductivity parameters and thermodynamic parameters of micellization and adsorption of the hydrochloride salts of alkylamines (C_8 and C_{16}) propoxy derivatives.

Surfactant	α	β	ΔG_{mic}, kJ/mol	ΔG_{ad}, kJ/mol
Salt of octylamine propoxy derivative	0.24	0.76	-31.27	-34.13
Salt of hexadecylamine propoxy derivative	0.59	0.41	-32.67	-34.68

Slopes of the straight line before (S_1) and after (S_2) CMC value of each salt were determined. Such thermodynamic properties as Gibbs free energy of micellization (ΔG_{mic}) and Gibbs free energy of adsorption (ΔG_{ad}) values were calculated according to the following equations:

$$\Delta G_{mic} = (2-\alpha) \times R \times T \times \ln(CMC)$$

$$\Delta G_{ad} = (2-\alpha) \times R \times T \times \ln(CMC) - 0.6023 \times \pi_{CMC} \times A_{CMC}$$

where A_{CMC} is surface area of the one surfactant molecule at the interface in terms of Å^2.

As is seen, the ΔG_{ad} values are more negative than the ΔG_{mic} values which points out to preference of the adsorption of the surfactants rather than the micelle formation.

In order to identify petrocollecting property of the surface-active salts, unthinned reagents, 5% wt. aqueous and ethanolic solutions of the salts were separately added to the water with thin petroleum layer. Thin layer (~0.17 mm) of Pirallahi) petroleum was formed on the surface of 40 ml distilled, tap and sea (the Caspian) water in Petri dishes. For each salt, maximum duration of the petrocollecting action and petrocollecting coefficient-K at room temperature were determined and given in Table 3. The value of "K" is derived as the ratio of the area of the surface of initial petroleum film and the area of the surface of the petroleum spot formed under the action of the salts.

As becomes evident from the obtained data, both of the salts have petrocollecting property. Experimental durations (τ) can be considered as the same for both situations and ended with drying of the waters in Petri dishes. For the used waters, petroleum collecting coefficients are between 22 and 29. It can be deduced that, alkyl radicals in the considered alkylamine propoxy derivatives are not dominant factors for petrocolllecting coeffients.

Table 3. Maximum duration of petrocollecting action and petrocollecting coefficients of the synthesized hydrochloride salts of alkylamines (C_8 and C_{16}) propoxy derivatives

Salt	State of surfactant	Duration, hours-τ	K		
			Distilled water	Tap water	Sea water
Hydrochlorid salt of octylamine propoxy derivative (n=2.74)	Unthinned reagent	0.17-6	29.44	29.44	29.44
		25-72	22.08	22.08	22.08
		115	22.08, drying	22.08, drying	22.08, drying
	5% wt. aqueous solution	0.17-6	36.80	33.97	33.97
		25-72	29.44	29.44	29.44
		115	29.44, drying	29.44, drying	29.44, drying
	5% wt. ethanolic solution	0.17-6	33.28	33.97	33.97
		25-29	25.00	25.00	29.44
		48-72	21.97	21.97	22.08
		115	21.97, drying	21.97, drying	22.08, drying
Hydrochlorid salt of hexadecylamine propoxy derivative (n=10.02)	Unthinned reagent	0.17-4	29.44	29.44	22.08
		25-30	22.08	19.00	19.00
		74-79	22.08	14.72	14.72
		122	22.08, drying	9.63, drying	9.63, drying
	5% wt. aqueous solution	0.17-4	29.44	29.44	22.08
		25-30	19.00	17.66	19.00
		74-79	19.00	12.62	12.62
		122	19.00, drying	12.62, drying	12.62, drying
	5% wt. ethanolic solution	0.17-4	29.44	29.44	29.44
		25-79	29.44	22.08	22.08
		122	29.44, drying	22.08, drying	22.08, drying

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