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PROPOXYLATION OF ALIPHATIC AMINES BY PROPYLENE OXIDE

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Nonyl amine, octadecyl amine and aminoamide of carboxylic acid fraction of linseed oil have been propoxylated using propylene oxide and the structure and composition of obtained propoxylates confirmed by IR-spectroscopy. Tensiometric measurements made it possible to reveal high surface activity of these propoxylates. As a result of laboratory tests through the use of thin films of Ramana crude oil on the surface of distilled, fresh and sea water, a good petroleum-collecting capacity of the synthesized reagents has been determined.
Keywords: amines, propoxylation, surface activity, petroleum-collecting properties

INTRODUCTION

Surfactants are widely used in various spheres of mankind's activity [1]. Among these spheres, oil and gas industry must be mentioned first of all [2, 3]. In the world practice, mainly ethoxylates of higher alcohols and monocarboxylic acids are utilized [4]. However, over the past two decades, propoxylates of the mentioned alcohols and acids also drew great interest of specialists [2, 5, 6].

The present paper highlights propoxylation of higher aliphatic amines. An introduction of propoxy-groups into composition of alkyl amines promises obtaining of valuable surface-active compounds. A study into their physical-chemical properties is also of interest, especially for identifying new fields of application of these surfactants.

EXPERIMENTAL

Nonyl amine and octadecyl amine were products of "Alfa Aesar" firm (Great Britain).

Linseed oil was the product of "Sultanbeyli" firm (Istanbul, Turkey).

Propylene oxide (PO) was the industrial product of "Organic Synthesis" plant (Sumgayit, Azerbaijan) of 99.8% purity.

Sodium hydroxide was used as a reagent of "analytically pure" grade ("Chemapol" firm, Czech Republic).

Potassium hydroxide was taken as a reagent of "analytically pure" grade ("Chemapol" firm, Czech Republic).

Nonyl amine and octadecyl amine were propoxylated by PO at 53°C and equimolar ratio of reactants for six hours in an autoclave made of stainless steel and equipped with a controlled heating system. The unreacted amount of PO was evaporated from the final mixture at mild temperature until a constant mass obtained. By gravimetric measurements conversion of PO and average degree of propoxylation – n (the number of PO moles added to 1 mol of amine) were calculated. In both cases, the value of "n" was close to 1.0.

Propoxylated nonyl amine is a white paraffin-like soft solid. Propoxylated octadecyl amine is also a white paraffinic solid.

Diethylene triamine (DETA) was the reagent of Russia, molar mass-73.14 $q.mol^{-1}$, density-0.707 qml^{-1}, boiling point-55-56 °C, refractive index was 1.3850 (20 °C).

Surface activity of the synthesized products was studied at the air-water interface by means of "KSV Sigma 702" tensiometer (Israel) using Du Nouy ring [7]. The method

consists in measuring the maximum force necessary for detaching the ring off the liquid surface.

Specific electro-conductivity (κ) of the aqueous solutions of the obtained compounds was measured by "Anion-4120" electro-conductometer (Russian Federation).

Petroleum-collecting capacity of the synthesized surfactants was evaluated according to the well-known method [3]. Distilled, fresh and sea waters were introduced into three Petri dishes (40 ml per each dish). 1 ml of petroleum was added to the surface of water in each dish (thickness of petroleum layer makes up ~0.165 mm). The surfactant (or its 5% wt. solution in water or ethanol) was added at the amount of 0.02 g. The petroleum-collecting capacity was estimated according to a change of surface area of the petroleum which becomes collected into a spot. This area was measured by a stencil plate with accuracy ~10%. The petrocollecting activity was characterized by collecting ratio – k, which indicates how many times the surface area of the initial oil slick decreases under impact of the surfactant. Retention time of the collected oil - τ is also registered and used for characteristics of the reagent.

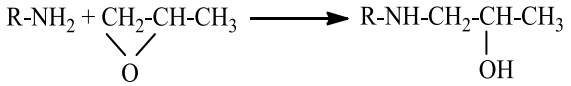
Petrodispersing capacity of the reagents was estimated as the ratio of the cleaned water surface area and surface area of the initial oil slick (in %).

Characteristics of the used fresh water: density at 20°C 0.996 g•mL^{-1}; pH 7.0-7.6; chemical composition (g-equiv / 100 g): Ca^{2+} 0.0052; Mg^{2+} 0.0023: Cl^- 0.0007; SO_4^{2-} 0.0044; HCO_3^- 0.0273; CO_3^{2-} 0.0009; total hardness 4.5 mg-equiv L^{-1}; the sea (Caspian) water: density at 20°C 1.0098 g•mL^{-1}; pH 7.7; chemical composition (mg / 1000 g): Na^+ 2650; K^+ 20: 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; SiO_2 0.5; total hardness 69.0 mg-equiv. L^{-1}.

Ramana crude oil had the following characteristics: at 20°C the density – 0.86 g•mL^{-1}; kinematic viscosity at 20°C - 0.16 cSt.

RESULTS AND THEIR DISCUSSION

The performed reactions of PO with nonyl amine and octadecyl amine may be described by the following scheme:



where R is C_9H_{19} or $C_{18}H_{37}$.

The structure and composition of the obtained alkyl aminoalcohols were identified by İR-spectroscopy method. For example, in the spectrum of octadecyl isopropylolamine there are the following absorption bands (cm^{-1}): 3329.9 ν (OH), 3274.8 ν (NH), 2957.0, 2914.3 and 2849.0 ν (CH), 1643.6, 1568.1 and 848.9 δ (N-H), 1467.7, 1380.9 and 1342.3 δ (CH), 1307.2 ν (C-N), 1157.6 and 951.2 ν (C-N), 1043.6, ν (C-O), 718.4, δ $(CH_2)_x$.

Results of tensiometric measurements of interfacial tension (σ) at the border of aqueous solutions of the obtained alkyl aminoalcohols with air as well as the determined values of specific electro-conductance of these solutions are given in Table 1.

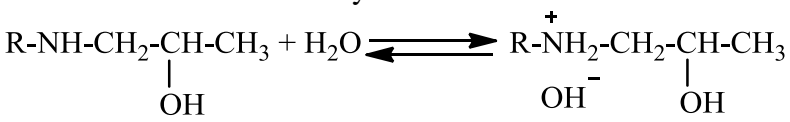
Table 1. Results of measurements of interfacial tension at the border of aqueous solutions of the synthesized alkyl aminoalcohols with air and specific electro-conductance

Concentration of aqueous solution of alkyl aminoalcohol, % wt.	Interfacial tension, mN/m	Specific electrocon-ductance, μS/cm (20°C)	Remarks
Nonyl isopropylolamine (19 °C)			Amine number – 54.75 mg HCl/g
0.010	38.97	16.3	

0.025	28.56	32.9	At the lack of surfactant σ is 72.0 mN/m
0.050	31.50	51.5	
0.100	26.51	94.5	
0.300	25.46	134.7	
0.500	23.95	220.8	
1.000	24.34	302.0	
3.000	23.93	208.6	
5.000	24.13	229.0	
7.000	24.51	171.4	
Octadecyl isopropylolamine (21 °C)			
0.01	34.69	11.6	
0.03	33.90	8.5	
0.05	33.16	8.1	
0.10	32.87	24.7	
0.30	32.54	18.7	
0.50	32.98	23.1	
1.00	33.16	11.3	
3.00	33.88	50.8	
5.00	34.51	19.7	

As is seen from the obtained tensiometric results, nonyl iso-propylolamine is more surface-active than octadecyl isopropylolamine. The first alkyl aminoalcohol lowers σ from 72.0 down to 24.1 mN/m (at concentration 5.0% wt.) whereas the second one decreases the interfacial tension down to only 32.5 mN/m (at concentration 0.3% wt.).

Electroconductometric analysis shows that aqueous solutions of nonyl isopropylolamine have markedly higher values of specific electroconductivity than those of octadecyl isopropylolamine which may be explained by presence of significantly shorter alkyl group in the first one. Manifestation of conductivity by aqueous solutions of non-charged alkyl aminoalcohols is ensured by partial hydration of amino-fragments with the charged groups as follows:



In Tables 2 and 3, the results of laboratory studies of petrocollecting capacity of the synthesized surfactants are presented.

As is seen from Table 2, nonyl isopropylolamine in unthinned state is effective in all three waters (k_{max} is 44.25 in distilled and fresh waters, 22.25- in the sea water; τ exceeds 3 days in all three cases). 5% wt. aqueous solution of this reagent demonstrates a good petrocollecting capability in fresh water (k_{max} is 18.42, τ is longer than ~ 4 days). 5% wt. ethanolic solution manifests marked petrocollecting properties in distilled (k_{max}=18.99, τ>4 days) and sea (k_{max}=20.26, τ>4 days) waters.

Table 2. Results of laboratory studies of petrocollecting capacity of nonyl isopropylolamine with regard to Ramana crude oil thin (thickness ~0.17 mm) film; room conditions

State of reagent	Distilled water		Fresh water		Sea water	
	τ, hour	k	τ, hour	K	τ, hour	k
Unthinned reagent	0.17	10.66	0.17	11.05	0.17	10.66
	21.00	11.26	21.00	11.26	21.00	11.26
	25.50	14.92	25.50	14.92	25.50	11.26
	44.50	22.25	44.50	22.25	44.50	14.92
	68.00	44.25	68.00	44.25	68.00	22.25
	72.00	44.25	72.00	44.25	72.00	22.25

5% wt. aqueous solution	0.17 20.00 23.50 43.50	4.79 1.58 1.58 1.46	0.17 20.00 23.50 43.50 67.00 71.00 94.50	18.42 14.47 14.83 14.83 16.89 17.88 15.18	0.17 20.00 23.50 43.50	1. 45 1.31 1.24 1.24
5% wt. ethanolic solution	0.17 20.00 23.50 43.50 67.00 71.00 94.50	18.99 14.14 14.47 14.14 15.99 18.42 10.86	0.17 20.00 23.50 43.50	6.39 1.67 1.73 1.67	0.17 20.00 23.50 43.50 67.00 71.00 94.50	17.37 13.51 16.43 16.88 20.26 20.26 11.69

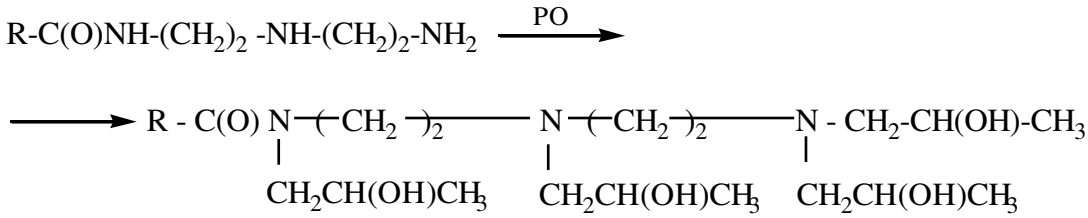
Table 3. Results of laboratory studies of petrocollecting capacity of octadecyl isopropylolamine with respect to Ramana crude oil thin (thickness ~0.17 mm) film; room conditions

State of reagent	Distilled water		Fresh water		Sea water	
	τ, hour	k	τ, hour	K	τ, hour	K
Unthinned reagent	0.17 21.00 24.50 44.50 68.00 72.00 95.50	16.43 25.33 33.77 35.76 24.32 24.32 5.06	0.17 21.00 24.50 44.50 68.00 72.00 95.50	7.99 23.38 26.43 26.43 22.51 22.51 11.05	0.17 21.00 24.50 44.50 68.00 72.00 95.50	11.52 21.51 23.38 21.51 18.42 18.42 9.35
5% wt. aqueous solution	0.17 1.50 21.00 44.50 48.50 72.00	3.25 14.47 27.83 27.83 27.83 13.15	0.17 1.50 21.00 44.50 48.50 72.00	8.35 12.52 30.14 25.84 19.04 12.47	0.17 1.50 21.00 44.50 48.50 72.00	12.25 16.25 16.25 26.79 27.83 20.67
5% wt. ethanolic solution	0.17 1.50 21.00 44.50 48.50 72.00	13.15 7.59 12.39 30.14 31.45 11.48	0.17 1.50 21.00 44.50 48.50 72.00	24.95 28.94 36.17 31.45 31.45 20.67	0.17 1.50 21.00 44.50 48.50 72.00	12.52 12.52 16.52 19.55 20.09 9.91

From Table 3 it follows that octadecyl isopropylol amine is an effective petroleum-collecting agent in all waters and in all forms of application. For example, in the sea water, when using 5% aqueous solution of this surfactant, k_{max} has the value 27.83, the retention time surpassing 3 days.

To compare results shown in Tables 2 and 3, it may be concluded that the second synthesized surfactant with a longer hydrocarbon group (C_{18}) has a higher petrocollecting capacity.

The use of PO propoxylation was also performed with DETA-based aminoamide of monocarboxylic acids fraction of linseed oil. The procedure of obtaining this amino amide is described in [8]. The scheme of the aminoamide propoxylation is as follows:



Propoxylation degree was found to be 4. The obtained product is a light-brown viscous liquid. Its structure and composition have been confirmed by IR-spectroscopy. The IR-spectrum is presented in Fig.1.

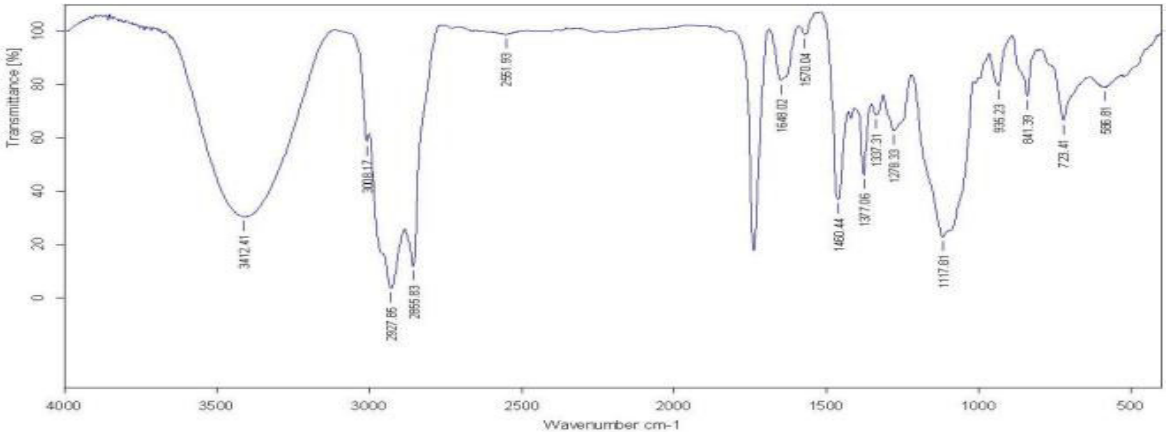


Fig. 1. IR-spectrum propoxylate (n=4) of DETA – based aminoamide of linseed oil acid fraction

In the range 3200-3600 cm^{-1} O-H and N-H bonds valent, at 2966 cm^{-1} – C-H (of double bond) valent, 2925 and 2856 cm^{-1} – C-H (of CH_3) and C-H (CH_2) valent, 1645 cm^{-1} – C=O valent, 1550 cm^{-1} – NH deformational, 1456, 1416 and 1373 cm^{-1} – C-H (of CH_3 and CH_2 groups) deformational, 1279 and 1131 cm^{-1} – C-N valent, 1050 cm^{-1} – C-O valent (of C-OH group) and 716 cm^{-1} –$(CH_2)_n$– "pendulum" vibrations bands are observed.

The results of surface tension measurements for the synthesized propoxylate at the border air-water are given in Table 4.

Table 4. Results of surface tension measurements for propoxylate (n=4) of DETA-based aminoamide of linseed oil acid fraction at the border air - water at 25°C

Concentration of the reagent, % wt						
0.0010	0.0025	0.0075	0.0100	0.0250	0.0750	0.1000
Surface tension, mN/m						
29.03	29.79	29.00	28.50	28.56	28.76	28.52

From these results it may be concluded that this propoxylate is surface-active because it lowers surface tension at the indicated border from ~ 72.0 down to 28.5 mN/m (at 0.01% wt).

The results of laboratory tests of the obtained propoxylate on petrocollecting and petrodispersing capacities are presented in Table 5.

Table 5. Results of laboratory tests of propoxylate (n=4) of aminoamide of linseed oil acid fraction on petrocollecting an petrodispersing capacities by the example of thin (thickness ~0.17 mm) films of Ramana crude oil; room conditions.

State of reagent at application	Distilled water		Fresh water		Sea water	
	τ, hour	k	τ, hour	k	τ, hour	k
Unthinned reagent	0-2.0	5.1	0-2.0	Disp. (98.7%)	0-2.0	3.7
	2.0-24.5	13.5	2.0-24.5	29.7	2.0-24.5	24.3
	25.0-169.0	30.4	25.0-169.0	30.4	25.0-169.0	30.4
	169.0-280.0	-40.5	169.0-280.0	24.3	169.0-280.0	24.3
5% wt. aqueous solution	0-2.0	4.7	0-2.0	5.1	0-2.0	60.8
	2.0-24.5	6.0	2.0-24.5	Disp. (99.7%)	2.0-24.5	40.5
	25.0-169.0	40.5	25.0-169.0	30.4	25.0-169.0	20.3
	169.0-280.0	61.0	169.0-280.0	40.5	169.0-280.0	30.4

According to the results above, the mentioned propoxylate manifests mainly petrocollecting properties. The values of collecting ratio exceed those for propoxylates of the two alkyl amines as shown above. For example, in fresh and sea waters the value of "k" reaches 40.5 and 60.9, respectively.

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ОКСИПРОПИЛИРОВАНИЕ АЛИФАТИЧЕСКИХ АМИНОВ С ПОМОЩЬЮ ОКСИДА ПРОПИЛЕНА

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Осуществлено оксипропилирование нониламина, октадециламина и аминоамида фракции карбоновых кислот льняного масла с использованием оксида пропилена. Строение и состав полученных оксипропильных производных подтверждены методом ИК-спектроскопии. Тензиометрическими измерениями обнаружена высокая поверхностная активность этих соединений. Лабораторными испытаниями на примере тонких пленок раманинской нефти на поверхности дистиллированной, пресной и морской вод установлена хорошая нефтесобирательная способность синтезированных реагентов.
Ключевые слова: *амины, оксипропилирование, поверхностная активность, нефтесобирательная способность*

ALİFATİK AMİNLƏRİN PROPİLEN OKSİDİ İLƏ OKSİPROPİLLƏŞDİRİLMƏSİ

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Nonilamin, oktadesilamin və kətan yağının karbon turşuları fraksiyasının aminoamidinin propilen oksidi ilə oksipropilləşdirilməsi həyata keçirilmişdir. Alınmış oksipropil törəmələrinin quruluşu və tərkibi İQ-spektroskopiya üsulu ilə təsdiq edilmişdir. Tenziometrik ölçmələrlə bu birləşmələrin yüksək səthi aktivliyə malik olması aşkar olunmuşdur. Ramana neftinin distillə, içməli və dəniz suyu səthindəki nazik neft təbəqələri üzərində aparılmış laboratoriya sınaqları nəticəsində həmin reagentlərin yaxşı neftyığıcılıq qabiliyyəti müəyyən edilmişdir.
Açar sözlər: *aminlər, oksipropilləşdirilmə, səthi aktivlik, neftyığma xassələri.*

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