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OBTAINING AND STUDY OF OLIGOMERIC SURFACTANT BASED ON OCTADECYLAMINE AND OXYPROPYLENE

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Abstract: *Oligomeric surfactant based on octadecylamine and propylene oxide was synthesized. The degrees of oligomerization of octadecylamine was calculated as 6.2 Structure and composition of the surfactant was confirmed by using IR and UV-spectroscopy. Surface tension values with respect to concentration were examined and respective curve was plotted. Also, main surf activity parameters like CMC, γ_{CMC}, π_{CMC}, C_{20}, pC_{20}, Γ_{max}, A_{min} were calculated. Critical micelle concentrations (CMC) and surface tensions at CMC were calculated as $1.58*10^{-4}$ mol/l and 31.92 mN/m respectively. Petrocollecting property and petrocollecting coefficients of the surfactant were studied for distilled, tap and sea water.*

Keywords: *octadecylamine, oligomer derivative, propoxylates, surfactant, petro-collecting coefficient*
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Introduction

Accidents may occur during drilling, refining or transportation of crude oil. As a result, million tons of crude oil and petro products damage the soil and water. One of the well-known methods is to use surfactants in order to clean surface of the water from thin layers of crude oil [1-6].

According to the literature, nitrogen base components have ability to create surfactants which make it possible to clean surface of water from crude oil [7-14]. For this purpose, new surfactant was synthesized based on octadecylamine and propylene oxide. Main physical-chemical properties of the new surfactants, including colloidal-chemical ones, were determined to apply them as petrocollecting agents.

Experimental Part

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

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

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

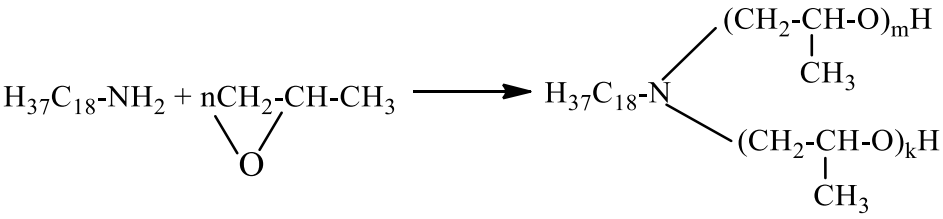
Oligomer based on octodecylamine and propylene oxide was synthesized at 140-150^{o}C for 13-14 hours in an autoclave made of stainless steel and equipped with a regulator of temperature at close conditions and constant pressure. In the given reaction, potassium hydroxide was used as a catalyst. Amount of catalyst was calculated as 3% of amount of alkylamine.

IR- spectrum was 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 KSV Sigma 702 tensiometer (Finland).

Results and Discussion

The reaction between octadecyamine and propylene oxide is illustrated as follows:



where n=m+k.

The value of propoxylation degree-n is equal 6.2. Gravitational method was used to obtain values of n.

The IR spectrum of octadecyamine propoxylate is given in Fig. 1.

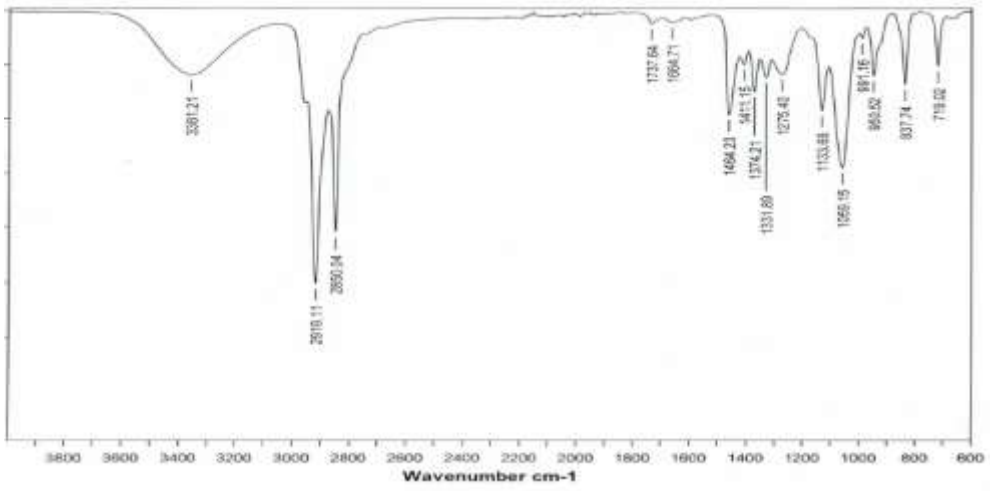


Fig.1. IR spectrum of the surfactant based on octadecylamine and propylene oxide

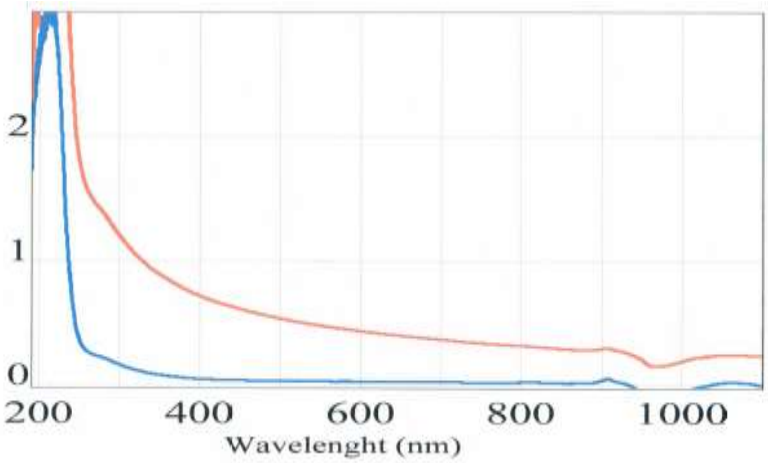


Fig.2. UV- spectrum of octadecylamine propoxylate (n = 6.2) in distilled water

According to IR- spectrum given in Fig.1, absorption bands at 3361 cm^{-1} represents OH valent vibration bands. C-H valent vibration bands of CH_3, CH_2 and CH groups are observed

at 2919-2850 cm^{-1} in the spectrum. The bands at 1464-1374 cm-1 corresponds C-H deformational vibrations, and bands 1275 cm-1 was attributed to valent vibration of C-N.

In the given spectrum band at 1059 cm^{-1} represent C-OH group. $(CH_2)_x$ "pendulum"vibrations bands exist at 719 cm^{-1} in the spectrum.

UV-spectrum of octadecylamine propoxylate in distilled water with a propoxylation degree of 6.2 is given in Fig.2. The transition n → σ * in the nitrogen atom is represented at 213 nm.

In order to study the surface activity at 21°C of synthesized octadecylamine propoxylate, aqueous solutions in different concentrations was prepared and plot was given in Fig. 3.

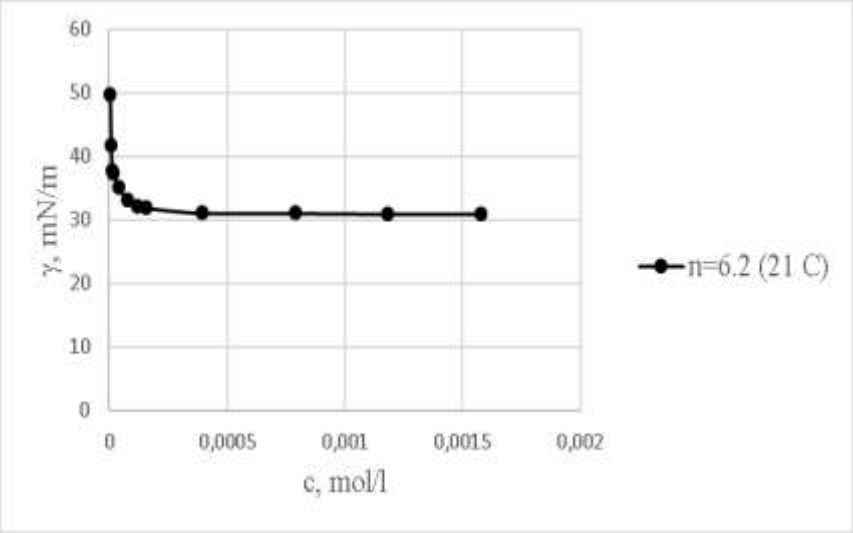


Fig.3. Surface tension at the water-air border versus concentration plot of the oligomer

Based on the plot given in Fig.3, the surface activity parameters were calculated and given in Table 1. Critical micelle concentrations (CMC) of the oligomer were revealed as 1.58* 10^{-4} mol/l and the values of π_{CMC}, Γ_{max} and A_{min} were calculated by using followin equations [5-6]:

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

where R- is universal gas constant (R=8.3145 C/mol*K) and T is absolute temperature.

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

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

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

n	CMC×10^4 (mol/l)	γ_{CMC} (mN/m)	π_{CMC} (mN/m)	Γ_{max}×10^{10} (mol/sm^2)	A_{min}×10^2 (nm^2)
6.2	1.58	31.92	40.08	0.83	193.15

Petrocollecting and dispersing properties of octadecylamine propoxylate were studied and applied to distilled, drinking and seawater as a pure form, 5% aqueous and 5% ethyl alcohol solution on Ramana crude oil. The petrocollecting result of the oligomer was given in Table 2.

Table 2. Petrocollecting coefficients of the synthesized oligomer

State of surfactant	Duration, hours	Maximum petrocollecting coefficient		
		Distilled water	Tap water	Sea water
Unthinned reagent	0.17-2	33.28	33.28	28.70
	24-30	39.06	39.06	29.44
	48-92	39.06	39.06	29.44
5% wt. aqueous solution	0.17-2	29.44	29.44	29.44
	24-92	39.06	39.06	39.06
5% wt. ethanolic solution	0.17-2	33.28	36.80	36.80
	24-92	36.80	36.80	36.80

As can be seen from Table 2, the petrocollecting coefficient during exposure in the range of 0.17-2 hours is less than the coefficient obtained after 24 hours. This is explained as being due to the aggregation state of surfactant. Thus, the substance is solid and that is the reason for late effect of surfactant on thin oil layers.

Conclusion

Surfactant based on octacedylamine and propylene oxide was synthezided at 140-150^{o}C. Surface activity property of the oligomer was studied by izoterm of surface tension versus concentration was plotted. According to the curve, the parameters such as CMC, γ_{CMC}, π_{CMC}, Γ_{max}, and A_{min} were calculated. Maximum values of petrocollecing coefficient of the oligomer in all-distilled, tap and sea water were calculated as 39.06.

References

1. Asadov Z.H., Zarbaliyeva I.A., Abilova A.Z. New surfactants based on triglycerides, (ethanol) amines and orthophosphate acid, monograph, Baku: Muallim Publ., ISBN 978-9952-435-34-4, 2020 p. 313
2. Humbatov H., Dashdiyev R., Asadov A. Et al. Chemical Reagents and Petroleum Production, Baku:Elm Publ., 2001. 448 pp.
3. Asadov Z., Zarbaliyeva I., Zargarova S. Propoxylation of Aliphatic Amines by Propylene Oxide. *Chemical Problems*. 2017, no 1, pp.44-50.
4. Sun Y., Wang C., Wang W., Yang X., Di Serio M., Zhi L. Micellar Properties for Propoxylated Surfactants in Water/Alcohol Solvent Mixtures and Their Antibacterial and Polyester Fabric Antistatic Performances. *Journal of Surfactants and Detergents*. 2016, vol. 19, no 3, pp.543-552
5. Zarbaliyeva I.A. Synthesis and properties of non-ionic surface-active substances based on heptadecanoic acid and propylene oxide. *Journal of Chemical Problems*. 2018, no 3, pp. 350-361.
6. Wang W., Li J., Yang X., Li P., Guo C., Li Q. Synthesis and properties of a branched short-alkyl polyoxyethylene ether alcohol sulfate surfactant. *Journa of Molecular Liquids*. 2015, vol. 212, pp. 418-422.
7. Yada S., Suzuki T., Hashimoto S., Yoshimura T. Adsorption dynamics of domogeneous polyoxypropylene-

polyethylene alkyl ether nonionic surfactants at the air/water interface. *Journal of Molecular Liquids.* 2018, vol. 255, pp. 208-214.
8. Casandra A., Lin Y., Tsay R., Lin S. Adsorption kinetics of the partially protonated cationic surfactant dodecylamine. *Journal of Molecular Liquids*. 2018, vol. 256, pp.312-319.
9. Mirgorodskaya A., Kushnazarova R., Lukashenko S., Voloshina A., Lenina O., Zakharova L., Sinyashin O. Carbamate-bearing surfactants: Micellization, solubilization and biological activity. *Journal of Molecular Liquids*. 2018, vol. 269, pp.203-210
10. Abo-Riya M., Tantawy A., El-Dougdoug Q. Synthesis and evaluation of novel cationic gemini surfactants based on Guava crude fat as petroleum-collecting and dispersing agents. *Journal of Molecular Liquids.* 2016, volume 221, pp.642-650.
11. Tantawy A., Mohamed H., Khalil A., Hebash K., Basyouni M. Novel bioactive imidazole-containing polymeric surfactants as petroleum-collecting and dispersing agents: Synthesis and surface-active properties. *Journal of Molecular Liquids*. 2017, volume 236, pp.376-384
12. Zargarova S.H. Synthesis and Characterization of Surfactants based on Propoxy Derıvatives of Amines and Ethylene Chlorohydrin. *Processes of Petrochemistry and Oil Refining*. 2021, vol. 22, no 1, pp. 58-65.
13. Asadov Z.H., Rahimov R.A., Allahverdiyeva L.A., Ahmadova G.A., Zarbaliyeva I.A. Obtaining and study of new flocculant for treatment of industry wastewater contaminated by petroleum. *Chemical Problems*. 2017, no. 4, pp. 412-417.
14. Zarbaliyeva I.A. Modifications of undecanoic acid with propylene oxide, orthophosphate acid and ethanolamines. *Chemical Problems*. 2017, no. 2, pp.192-200.

OKTADESİLAMİN VƏ PROPİLEN OKSİDİ ƏSASINDA OLİQOMER TƏBİƏTLİ SƏTHİ-AKTİV MADDƏNİN ALINMASI VƏ TƏDQİQİ

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*Oktadesilamin və propilen oksidi əsasında oliqomer tipli səthi aktiv maddə sintez edilmişdir. Oktadesilaminin oliqomerləşmə dərəcələri 6.2 olaraq hesablanmışdır. Səthi-aktiv maddənin quruluşu və tərkibi İQ- və UB- spektroskopiya üsulundan istifadə etməklə təsdiq edilmişdir. Qatılıqdan asılı olaraq səthi gərilmə qiymətləri tədqiq edilmiş və müvafiq izoterm əyrisi çəkilmişdir. KMQ, γ_{KMQ}, π_{KMQ}, C_{20}, pC_{20}, Γ_{maks}, A_{min} kimi əsas səthi aktivlik parametrləri hesablanmışdır. Kritik misella əmələgəlmə qatılığı (KMQ) və səthi gərilmə qiymətləri müvafiq olaraq 1,58*10-4 mol/l və 31,92 mN/m hesablanmışdır. Səthi-aktiv maddənin distillə, içməli və dəniz suyu üzərində neftyığma qabiliyyəti tədqiq edilmişdir.*

***Açar sözlər**: oktadesilamin, oliqomer törəmə, propoksilat, səthi aktiv maddə, neftyığma əmsalı*

ПОЛУЧЕНИЕ И ИССЛЕДОВАНИЕ ОЛИГОМЕРНОГО ПОВЕРХНОСТНО-АКТИВНОГО ВЕЩЕСТВА НА ОСНОВЕ ОКТАДЕЦИЛАМИНА И ОКСИПРОПИЛЕНА

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Синтезировано олигомерное поверхностно-активное вещество (ПАВ) на основе октадециламина и оксипропилена. Степень олигомеризации октадециламина составила 6.2. Структура и состав поверхностно-активного вещества подтверждены методами ИК- и УФ-спектроскопии. Определены значения поверхностного натяжения в зависимости от концентрации и построена соответствующая кривая. Вычислены основные параметры поверхностной активности, такие как ККМ, $\gamma_{ККМ}$, $\pi_{ККМ}$, C_{20}, pC_{20}, $\Gamma_{макс}$, A_{min}. Критическая концентрация мицеллообразования (ККМ) и поверхностное натяжение при ККМ были вычеслены соответственно как 1.58·10-4 моль/л и 31.92 мН/м. Исследованы нефтесобирающие свойства ПАВ на дистиллированной, пресной и морской воде.

***Ключевые слова**: октадециламин, олигомерное производное, оксипропилат, ПАВ, коэффициент нефтесобирания.*