Synthesis and analysis of salts based on oleic acid and diethyletriamine

Ilhama Agalar Zarbaliyeva
Doctor of Chemical Sciences, Associate Professor, Chief Researcher
Y.H.Mammadaliyev Institute of Petrochemical Processes of Azerbaijan National Academy of Sciences
Hajar Tahir Nabiyeva
Postgraduate
Y.H.Mammadaliyev Institute of Petrochemical Processes of Azerbaijan National Academy of Sciences
Amina Nadir Alimova
Postgraduate
Y.H.Mammadaliyev Institute of Petrochemical Processes of Azerbaijan National Academy of Sciences
Ayaz Muzaffar Mammadov
Postgraduate
Y.H.Mammadaliyev Institute of Petrochemical Processes of Azerbaijan National Academy of Sciences
Nazli Afgan Rzayeva
Technologist
Y.H.Mammadaliyev Institute of Petrochemical Processes of Azerbaijan National Academy of Sciences

Abstract. The current scientific work contains detailed information on the synthesis and some properties of the products obtained from the reaction between oleic acid and diethylene triamine. The composition and structure of the reaction products were identified by NMR spectroscopy. Some physical and chemical indicators of the synthesized compounds were determined, surface-active parameters were calculated, petrocollecting and petrodispersing properties were studied. In the end, the final recommendations were given, taking into account the applied properties of the salts.

Keywords: surfactants, oleic acid, diethylenetriamine, petrodispersing, petrocollecting

Introduction

Thus, the oil layer creates an additional environment between air and water, preventing the dissolution of oxygen in the air, and the sun's rays entering the lower aquifers of the oceans and seas. The vital activity of flora and fauna within water basins, which cannot be enriched with oxygen and deprived of sunlight, is weakening. One of the most important branches of chemistry is the rapid accumulation of thin layers of oil in order to preserve the balance of nature. To do this, various surfactants are synthesized and investigated. About 10% of the demand for surfactants

1:1 $$NH_2-CH_2-CH_2-NH-CH_2-CH_2-NH_2+C_{17}H_{33}-COOH \rightarrow NH_2-CH_2-CH_2-NH-CH_2-CH_2-NH_2 \cdots HOOC-C_{17}H_{33}$$

1:2 $$NH_2-CH_2-CH_2-NH-CH_2-CH_2-NH_2+2C_{17}H_{33}-COOH \rightarrow NH_2-CH_2-CH_2-NH-CH_2-CH_2-NH_2$$

$$C_{17}H_{33}-COOH\cdots \qquad \cdots HOOC-C_{17}H_{33}$$

(more than 12 million tons) falls on nitrogen compounds. Although such substances have been known for about 50 years, they have been used more in the last 20 years due to their high efficacy surfactants. When surfactant collects oil from the water surface, the negative impact on the environment is relatively reduced [1-3].

There are different tools and techniques which specialists can employ to contain or remove oil from the environment when an oil spill occurs such as booms and skimmers [4]. However, those mechanical clean-up activities can never remove thin layer of oil remaining on the surface. Surfactants can be the very effective solution to this problem. Surfactants lower the surface and interfacial tension between two media because of their specific characteristics [5-8].

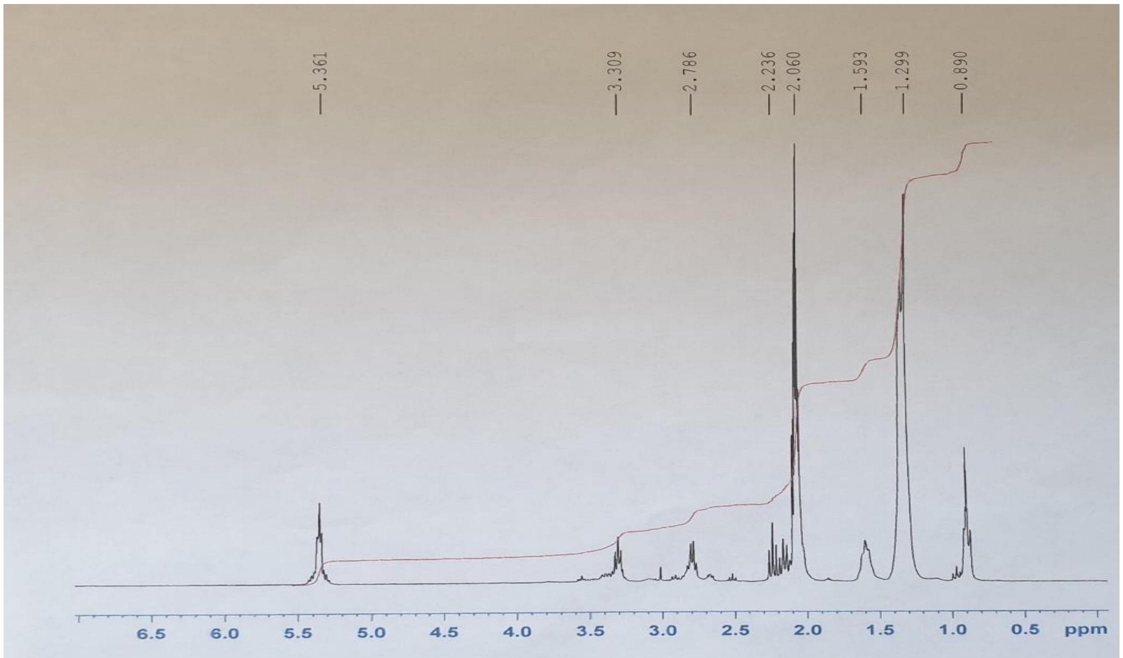
Purpose of the study: The present work is dedicated to obtainment and study of new surfactants based on oleic acid and diethylene triamine. It is aimed to analyse if obtained surfactants are applicable for clean-up activities for oil spills.

Material and methods: Relevant salts in two different proportions were synthesized as a result of a reaction based on oleic acid and diethylene triamine. The first salt was obtained from the reagents in equimolar proportions at 60-65 degrees Celsius for 9-10 hours. The other substance was the product of a 2: 1 reaction of oleic acid and diethylene triamine at a temperature of 55-60 ^{0}C. The reaction schemes are as follows:

The structure and composition of obtained salt were confirmed with NMR-spectroscopy in Figure 1,2 for ^{1}H NMR of Salt 1 and Salt 3 and Figure 3,4 for ^{13}C NMR of Salt 1 and Salt 2 respectively.

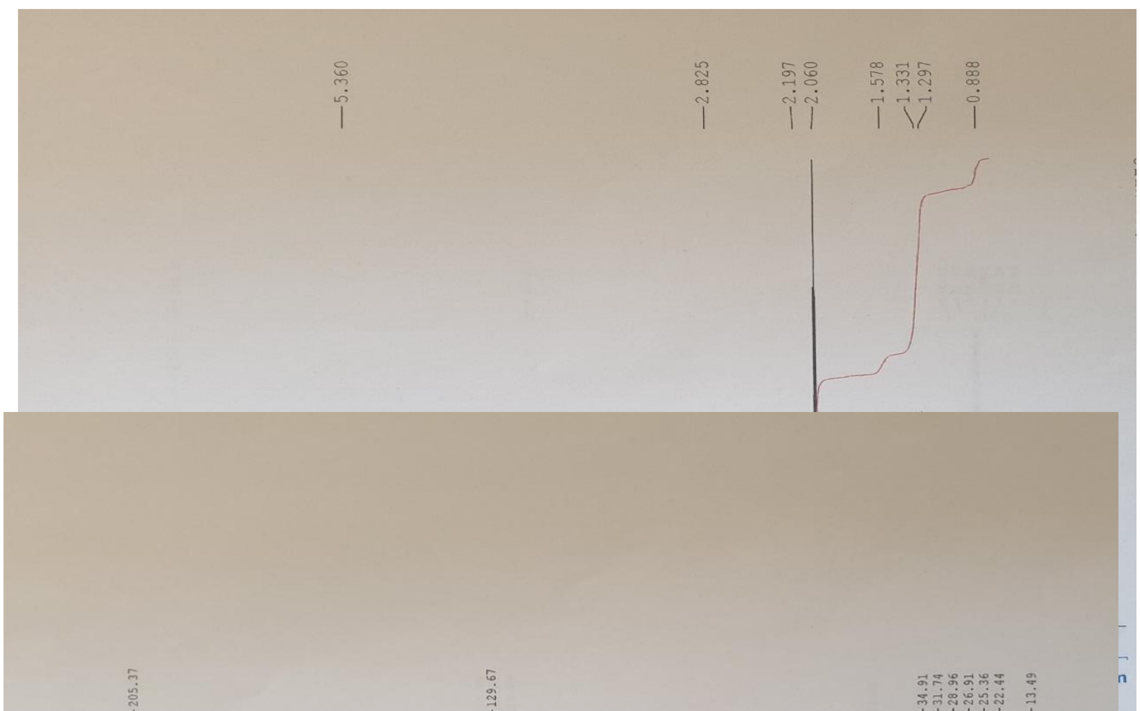
^{1}H NMR (BRUKER-Fourier 300.18 MHs, Asetone-D6, δ, ppm.): 0.88 (t., 3H, CH_3), 1.23-1.41 (m., 20H, CH_2),1.57 (m., 2H, CH_2), 2.19 (t., 2H, CH_2COO), 2.60-3.12 (m., 12H, CH_2-NH, CH_2-CH=), 5.36 (m., 2H, CH=CH)

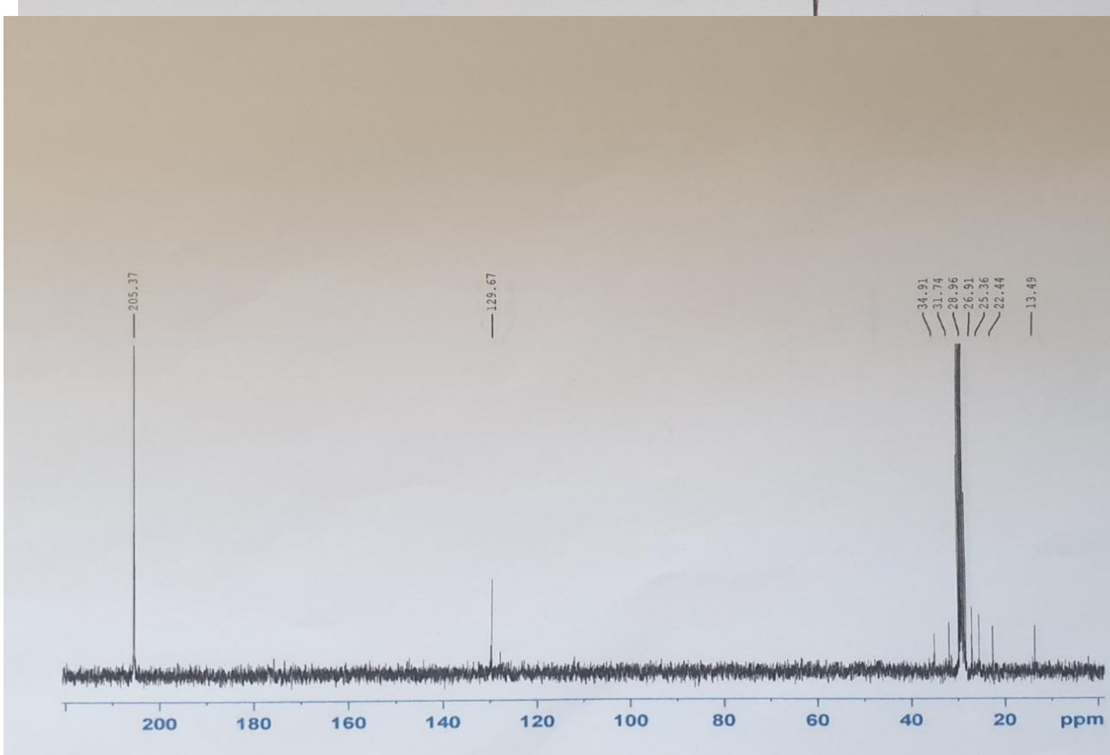
^{1}H NMR (BRUKER-Fourier 300.18 MHs, Asetone-D6, δ, ppm.): 0.89 (t., 6H, CH_3), 1.22-1.41 (m., 40H, CH_2), 1.59 (m., 4H, CH2), 2.23 (t., 4H, CH_2COO), 2.45-3.53 (m., 16H, CH_2-NH, CH_2-CH=), 5.36 (m., 4H, CH=CH)



^{3}C NMR ppm.: 13.49 (CH_3), 22.44, 25.36, 26.91, 31.74, 34.91 (CH2), 129.67 (CH=CH)

^{13}C NMR ppm.: 13.49 (CH3), 22.45, 25.10, 25.38, 26.92, 31.75, 34.49, 35.84 (CH_2), 127.89, 129.67 (C^{13}C NMR ppm.: 13.49 (CH_3), 22.45, 25.10, 25.38, 26.92, 31.75, 34.49, 35.84 (CH_2), 127.89, 129.67 (CH=CH),127.89, 129.67 (CH=CH)





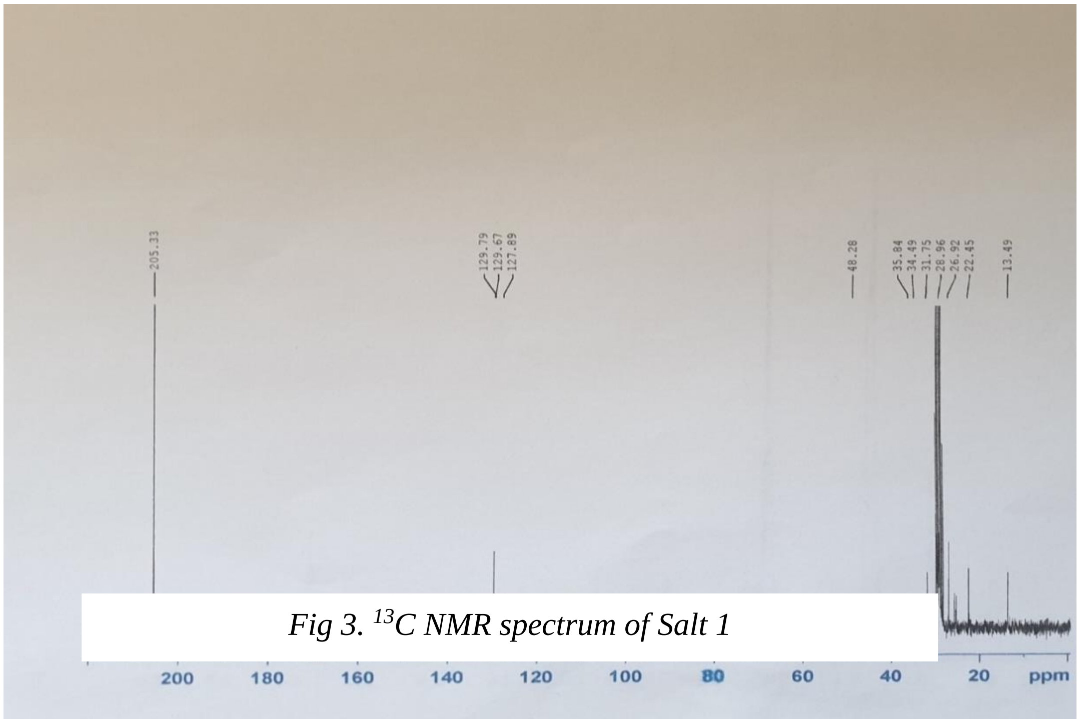


Fig 3. ^{13}C NMR spectrum of Salt 1

Fig 4. ^{13}C NMR spectrum of Salt 2

Fig 4. ^{13}C NMR spectrum of Salt 2

The melting point of the Salt1 and Salt2 are 62℃ and 58℃ respectively. Both products have good solubility in ethanol and acetone. Salt 1 is brownish, viscous liquid, while Salt 2 is lighter and more viscous substance than Salt 1. Amin number is 86 mgHCl/g for Salt1 and 45 mgHCl/g for Salt 2. Throughout various experiments surface activity parameters and specific electrical conductivity values/thermodynamic properties of the synthesized surfactants were determined and the graphs were plotted and described in Figure 5. Using the data obtained from Fig.5, surface activity parameters of the synthesized surfactants were determined using the method given in [3]

Results and discussions

Critical Micelle Concentrations (CMC) of the obtained salts were determined as 0.00194*10^{-4} and 0.00112*10^{-4}mol/l respectively. Besides that, γ_{CMC}, surface pressure (π_{CMC}), C_{20} (the concentration for decrement of γ by 20 mN/m), adsorption efficiency ($pC_{20} = -logC_{20}$), as well as CMC/C_{20} (interfacial activity) parameters of obtained surfactants were determined.

Fig 5. *Surface tension at water-air interface versus concentration of the obtained salts at 26˚C*

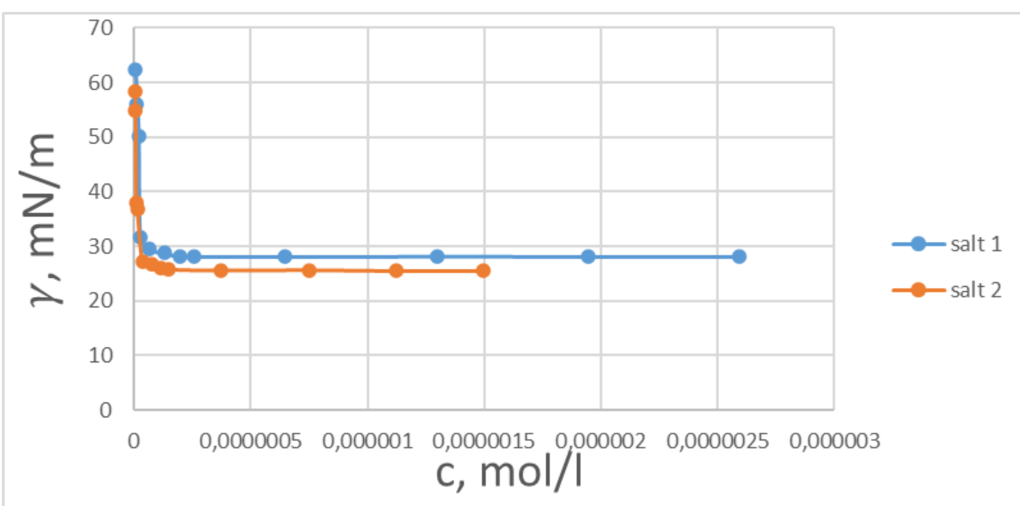
Maximum surface excess concentration (Γ_{max}) and minimum area of one surfactant molecule at water-air border (A_{min}) were calculated using the given equations

$$\Gamma_{max} = \frac{1}{n * R * T} * \lim_{c \to CMC} \frac{d\gamma}{dlnc}$$

where n is the number of dissociated ions which is 2 and 3 respectively for Salt 1 and Salt 2, R is universal gas constant (8.314 J/mol*K) and T is absolute temperature;

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

The surface activity



parameters were tabulated in Table 1.

Table 1

Surface activity parameters of the synthesized surfactants

Surfactant	CMC*10^4 (mol/L)	γ_{CMC} (mN,m)	π_{CMC} (mN,m)	C_{20}*10^4 (mol/L)	pC_{20}	CMC/ C_{20}	Γ_{max}*10^{10} (mol/cm^2)	A_{min}*10^2 (nm^2)
Salt 1	0.00194	28.17	43.87	0.000162	7.79	12	2.031	81.77
Salt 2	0.00112	25.93	45.09	0.000075	14.97	8.18	1.29	129.21

As it seems from the Table 1, salt 2 which is the gemini surfactant has a lower CMC value which is more desirable for surfactants. Besides that, the minimum area for one molecule of salt 2 surfactant is less than salt 1, which is also preferable.

Petrodispersing and petrocollecting properties of the surfactants was determined according to the known procedure described in [2]. 40 ml of water are placed in a Petri dish. 1 ml of crude oil (in this work, Pirallahi) is spread over the water (thickness of the film is ~ 0.17 mm). Then, 0.02 g of the surfactant (or its 5% wt. solution) is added to the film from the side wards. The surface area of the initial oil film and current areas of the formed oil slicks are measured at certain time intervals. The coefficient K_d - denoting the degree of the surface cleaning is calculated (in %).

Table 2

Petrodispersing and petrocollecting properties of the synthesized surfactants

<table>
<tr><th rowspan="2">Ratio</th><th rowspan="2">State of surfactant</th><th colspan="2">Sea water</th><th colspan="2">Tap water</th><th colspan="2">Distilled water</th></tr>
<tr><th>K_d</th><th>Duration- τ, hours</th><th>K_d</th><th>Duration- τ, hours</th><th>K_d</th><th>Duration- τ, hours</th></tr>
<tr><td rowspan="6">1:1</td><td rowspan="6">5 wt. % aqueous solution</td><td>86.7%</td><td>0-20</td><td>10</td><td>0-3</td><td>12.3</td><td>0-3</td></tr>
<tr><td>80.2%</td><td>20-72</td><td>15.1</td><td>3-5</td><td>74%</td><td>3-16</td></tr>
<tr><td>70%</td><td>72-216</td><td>87%</td><td>5-20</td><td>84%</td><td>16-260</td></tr>
<tr><td>68%</td><td>216-312</td><td>2.67</td><td>20-72</td><td colspan="2" rowspan="3">spilling</td></tr>
<tr><td colspan="2" rowspan="2">spilling</td><td>1.92</td><td>72-264</td></tr>
<tr><td colspan="2">spilling</td></tr>
</table>

Continuation of Table 2

<table>
<tr><td rowspan="7"></td><td rowspan="5">5 wt. % ethanolic solution</td><td>88%</td><td>0-20</td><td>90%</td><td>0-23</td><td>12.3</td><td>0-3</td></tr>
<tr><td>80%</td><td>20-72</td><td>6.4</td><td>23-51</td><td>18.02</td><td>3-5</td></tr>
<tr><td>2.04</td><td>72-240</td><td>1.96</td><td>51-243</td><td>6</td><td>5-21</td></tr>
<tr><td colspan="2" rowspan="2">drying</td><td colspan="2" rowspan="2">spilling</td><td>84%</td><td>21-145</td></tr>
<tr><td colspan="2">spilling</td></tr>
<tr><td rowspan="2">Solid</td><td>95%</td><td>0-1</td><td>11</td><td>0-1</td><td>8.5</td><td>0-19</td></tr>
<tr><td>86%</td><td>1-17</td><td>13.75</td><td>1-3</td><td colspan="2">spilling</td></tr>
</table>

		15.4	17-141	92%	3-43		
		6.41	141-237	spilling			
		spilling					
2:1	*5 wt. % aqueous solution*	94%	0-19	16.7	0-72	12.8	0-1
		88%	19-163	9	72-168	5.57	1-73
		1.5	163-513	spilling		5	73-265
		spilling				spilling	
	5 wt. % ethanolic solution	9.89	0-72	12.03	0-1	12.26	0-1
		84	72-88	89%	1-73	88%	1-217
		89	88-232	86%	73-169	dag	
		2.03	232-328				
	Solid	87%	0-168	12.03	0-1	12.26	0-1
		spilling		9.625	1-3	10.13	1-3
				11	3-19	9.625	3-19
				12.83	19-312	spilling	
				spilling			

It can be seen from the Table 3, salt 1 shows the maximum petrocollecting property in the distilled water treated with 5 wt% ethanolic solution which is 18.02, while its maximum petrodispersing factor is seen in sea water treated with solid. Observing salt 2, it can be noted that maximum petrocollecting property is seen in tap water treated with 5 wt% aqueous solution, which is 16.7%. Maximum petrodipersing factor for the mentioned salt is inspected in sea water treated with 5 wt% aqueous solution, which is 94%.

Conclusion

Analyzing the results of surface activity measurements, petrocollecting and petrodispersing properties, it can be concluded that both salts have good surface activity and are recommended for the process of cleaning thin oil layers from the water surface.

References

1. A.Bhardwaj, S. Hartland, Applications of Surfactants in Petroleum Industry. Journal of Dispersion Science and Technology, 1993, Volume 14, - Issue 1, p.87-116
2. L.L.Schramm, E.N.Stasiuk, D.G.Marongoni, Surfactants and their applications. Annual Reports Section C, August 2003, 99, p.3-48
3. Asadov Z.H., Aga-zade A.D., Zarbaliyeva I.A.,et all. Petroleum-collecting and dispersing properties of oxypropylates of individual monocarboxylic acids (C_{16}, C_{18}) and their natural fractions // Processes of petrochemistry and oil refining, 2003, N4 (15), p. 4-16
4. Z.H. Asadov, A.H. Tantawy, A.H. Azizov, I.A. Zarbaliyeva, R.A. Rahimov. *Synthesis of new complexes surfactants based on fatty acids and Study the effect of length of fatty acid chain on the petroleum and surface-active properties.*Caspian Journal of Applied Sciences Research, 2013 2(3), p. 24-34
5. H.H.Humbatov, R.A.Dashdiyev, *Liquidation of accidental petroleum spills using surfactants* Baku: Elm,1998.200 p.(in Russian)

6. Z.H.Asadov, H.T.Nabiyeva. *Synthesis and study of new surfactants based on oleic acid and diethyletriamine*. Magyar Tudományos Journal, 2020 No 39, p. 14-19
7. Bogumil E. Brycki, Iwona H. Kowalczyk, Adrianna Szulc, Olga Kaczerewska andMarta Pakiet, *Multifunctional Gemini Surfactants: Structure, Synthesis, Properties and Applications*, 2017
8. KajolBhati, DivyaBajpaiTripathy and Anjali Gupta, *Gemini ImidazoliniumSurfactants: A Versatile Class of Molecules*,2020