CHEMICAL SCIENCES

SYNTHESIS AND STUDY OF SURFACE-ACTIVE SALTS OBTAINED FROM THE REACTION OF 1,2-DIAMINOETHANE WITH CIS-9-OCTADECANOIC ACID AND TETRADECANOIC ACID

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Abstract

In this research work comparative analysis of four different surfactants has been given. The identification of these products has been made by IR- and UV- spectroscopy. The physical and chemical properties of the formed surfactants including interfacial tension and specific electroconductivities have been determined. From these measurements, the maximum surface excess concentration and the minimum area of the molecule at the water /air interface, the surface pressure, the standard thermodynamic parameters of adsorbtion and micellization have been calculated. Moreover, petrocollecting and petrodispersing properties of these substances have been measured and maximum values of petrocollecting coefficients have been determined. Some correlations between these parameters of the synthesized surfactants and their ability to collect thin petroleum films from the water surface have been obtained.

Keywords: tetradecanoic acid, Cis-9-octadecanoic acid; 1,2-Diaminoethane; surfactant; petrocollecting, petrodispersing, electroconductivity, micellization

Introduction

The expanding request to crude oil and item of its refining comes about in environmental problems and dis-balance [1, p 87-116]. Large spills like these are frequently the result of pipeline breaks, oil ship sinkings, or poor drilling techniques. Lean oil layers on the surface of the water gotten to be one of such biological issues which may happen amid transportation of rough oil and its refining items [2, p 3-48]. Surfactants frame a special course of chemical compounds. Surfactants have physical properties such emphasizing their ability to profoundly change surface and interfacial properties and to self-associate and solubilize themselves in micelles [7, p 9]. These properties give opportunity to apply surfactants in wettability adjustment, detergency, and the uprooting of liquid phases through permeable media [6, p 1189-1196]. These in turn lead to a tremendous cluster of practical application ranges which are outlined in terms of mineral and petroleum processing, biological frameworks, wellbeing and individual care items and nourishments [3, p 11-21; 4, p 3-7; 5, p 24-34]. It is known that recently the application of surfactants to high technology, such as printing, magnetic recording, electronics, biotechnology, as well as microelectronics, has become widespread. Surfactants are consumed in large quantities every day in the world. Thus, the demand for high-performance surfactants is constantly increasing, as a reduction in the amount of surfactants used can help reduce the load on the natural treatment system. Therefore, new surfactants have been successfully designed and developed [8, p 200; 9, p 199; 10, p 621-630; 11, p 444].

Experimental part

Cis-9-octadecanoic acid was a product of Moscow's ''ComponentReactant'' Joint Stock Company (Russia) with ≥ 98% purity. Tetradecanoic acid is a fatty acid found in nutmeg, palm oil, coconut oil, butter fat, and spermacetin, the oil from the sperm whale. It has a variety of uses in the beauty industry, including as a: Fragrance Ingredient; Opacifying Agent; Surfactant; Cleansing Agent; and Emulsifier. 1,2 ethane diamine was used as received from chemical suppliers (Aldrich), molar mass is 60.1 g mol^{-1},colourless liquid, ichthyal (fishy) or ammonia calodor, density is 899 mg mL^{-1},boiling point is 117-119 ℃and refractive index is 1.4565.

In our research work 1,2-Diaminoethaneentered the reaction with tetradecanoic acid and Cis-9-octadecanoic acid at different ratios. Two salts in different composition were synthesized and learnt comparatively. The first salt was a product of reaction between tetradecanoic acid and 1,2 ethane diamine at equimolar ratios. The reaction was carried out at 70-80℃ and equimolar proportion of components. The ultimate item was yellowish strong, like solidified greasy oil. The duration of the reaction was 9-10 hours.

The other salt which was the product of the reaction between 1,2 ethane diamine and cis-9-octadecanoic acid at equimolar ratio was carried out at 55-60˚C during 9-10 hours at equimolar ratio. The final product at equimolar ratio was brownish and viscous oily product.

The reaction salts were synthesized using the same acid and amine at 2:1 ratio of acids to amine. The reaction continued 9-10 hours at 65-70˚C, 2:1 ratio of cis-9-octadecanoic acid and ethylene diamine, while the second reaction was carried out at 2:1 ratio of cis-9-octadecanoic acid and 1,2-Diaminoethaneand the reaction continued 9-10 hours at 50-55 ˚C. The final products were yellowish solid, like frozen fatty oil and dark-red for the first and second product respectively.

Surface tension and conductivity measurements

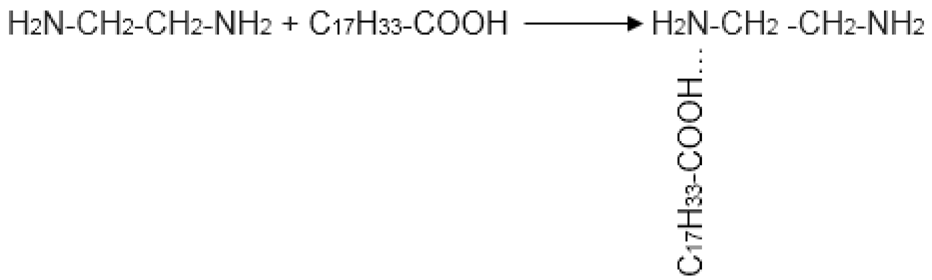
Surface tension of aqueous solutions of obtained surfactants were recorded with Du Nouy ring KSV Sigma 702 tensiometer equipped with Pt ring (AttensionBiolin Scientific, Finland). Surface tension of the double distilled water used for preparing solutions was 71.5 mN/m at 25 °C. γ CMC values of surfactant was determined based on these measurements.

Electrolytic conductivity of aqueous solutions of surfactants were measured with VWR® pHenomenal® CO 3000 L benchtop conductivity meter (Germany). All the measured values were referenced to 25 °C and were accurate to ±1 %. Conductivity of the double distilled water used for the experiment was lying in the interval 2-2.8 μS/cm. CMC values of surfactants were determined from the plots of conductivity vs. molar concentration [4, p 3-7; 5, p 24-34; 6, p 1189-1196].

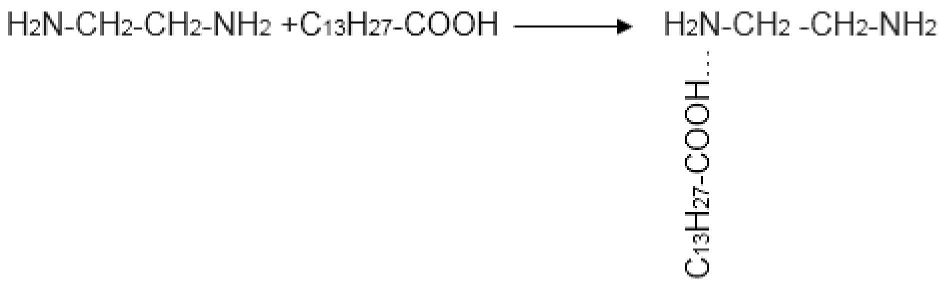
Petrodispersing property of the surfactants was determined according to the known procedure described in [8, p 200]. 40 ml of water are placed in a Petri dish. 1 ml of crude oil (in this work, of “Azeri Light” trade mark) is spread over the water (thickness of the film is ~ 0.17 mm). Then, 0.02 g of the surfactant (or its 5% wt. solution) is added to the film from the sidewards. 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 %).

Result and discussion:

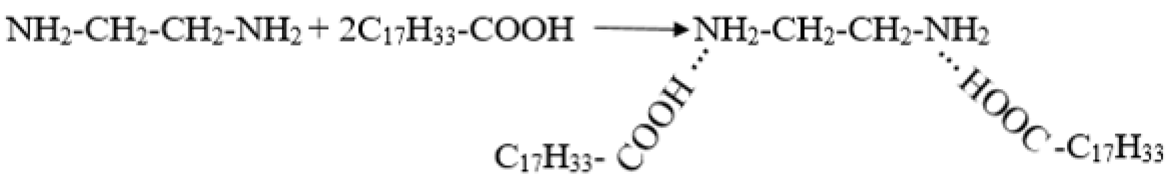
The schemes of the reactions are shown below.



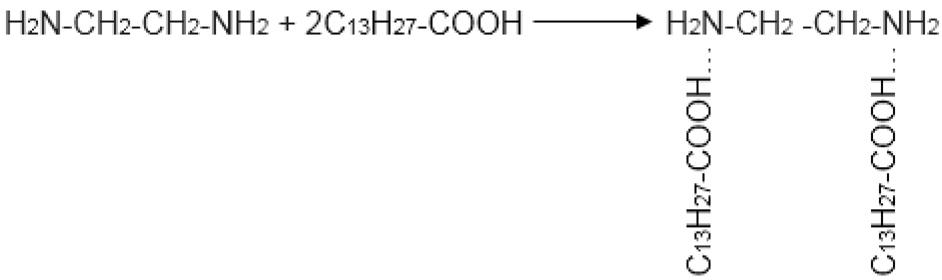
Salt 1



Salt 2



Salt 3



Salt 4

The structure and composition of the synthesized salts were confirmed by IR spectroscopy.

Results of FTIR data. The chemical structure of cis-9-octadecanoic acid and tetradecanoic acid complexes with 1,2 ethane diamine were identified by FT-IR spectroscopy as showed in Figure 1-4. The FT-IR absorption spectra for 4 salts showed an absorption band at the 1547.4-1551.4 cm-1 region characteristic for δ COO-stretches. This proves formation of the target complexes.

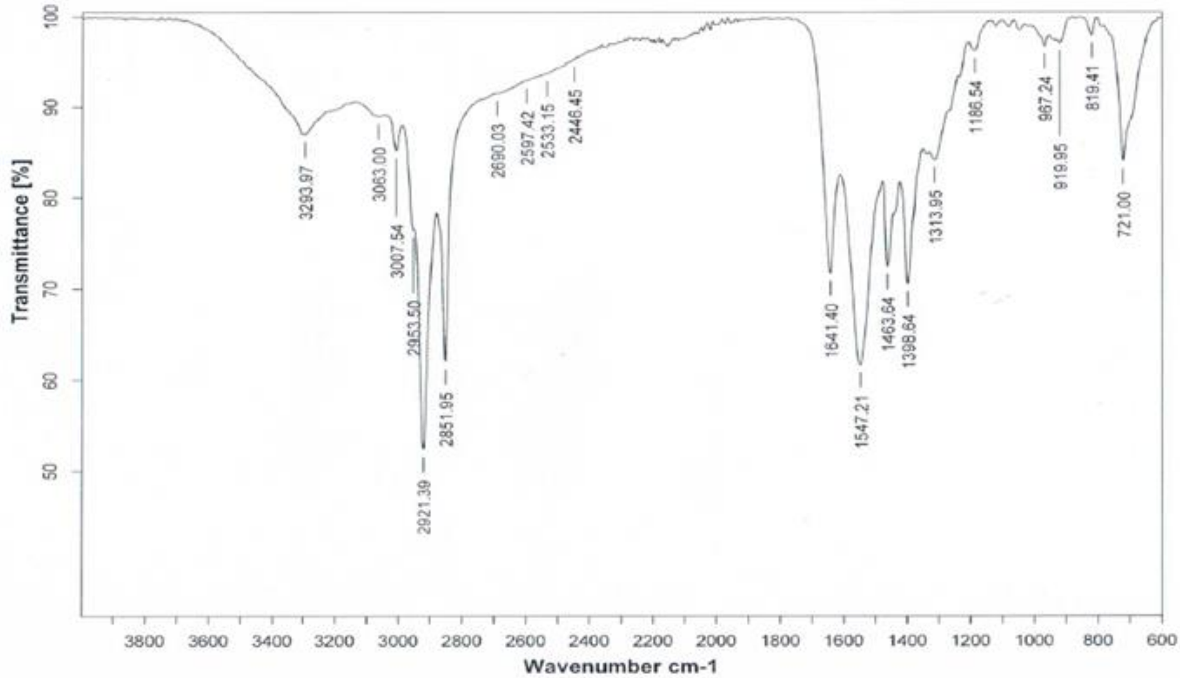


Figure 1. Cis-9-octadecanoic acid and 1,2 ethane diamine 1:1 (Salt 1)

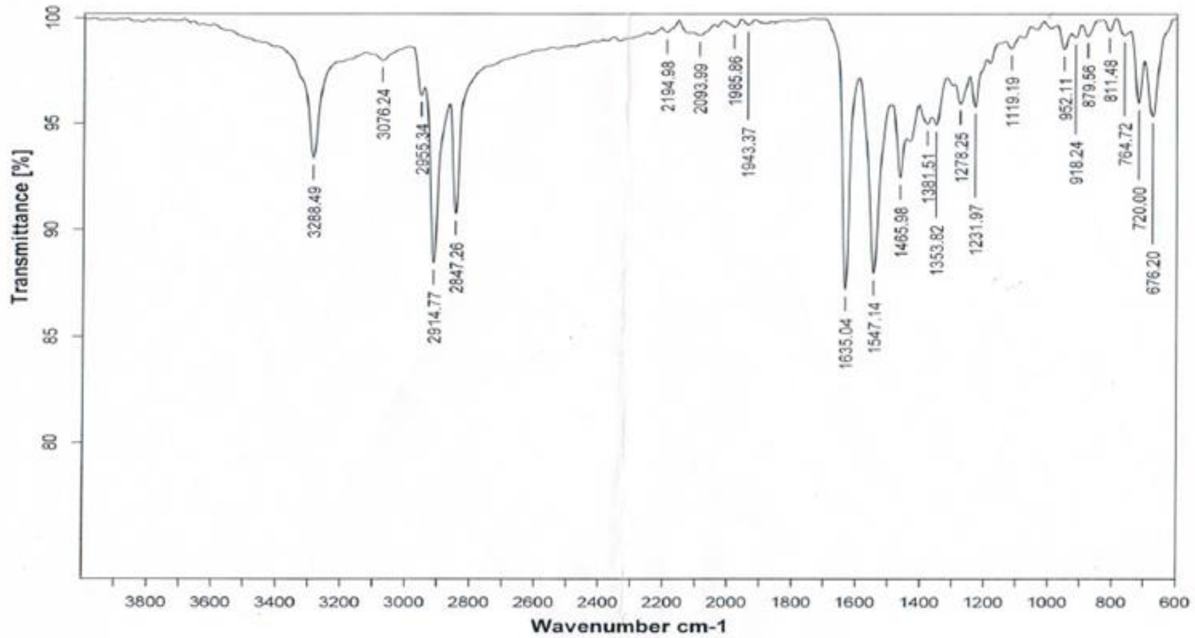


Figure 2. Tetradecanoic acid and 1,2 ethane diamine 1:1 (Salt 2)

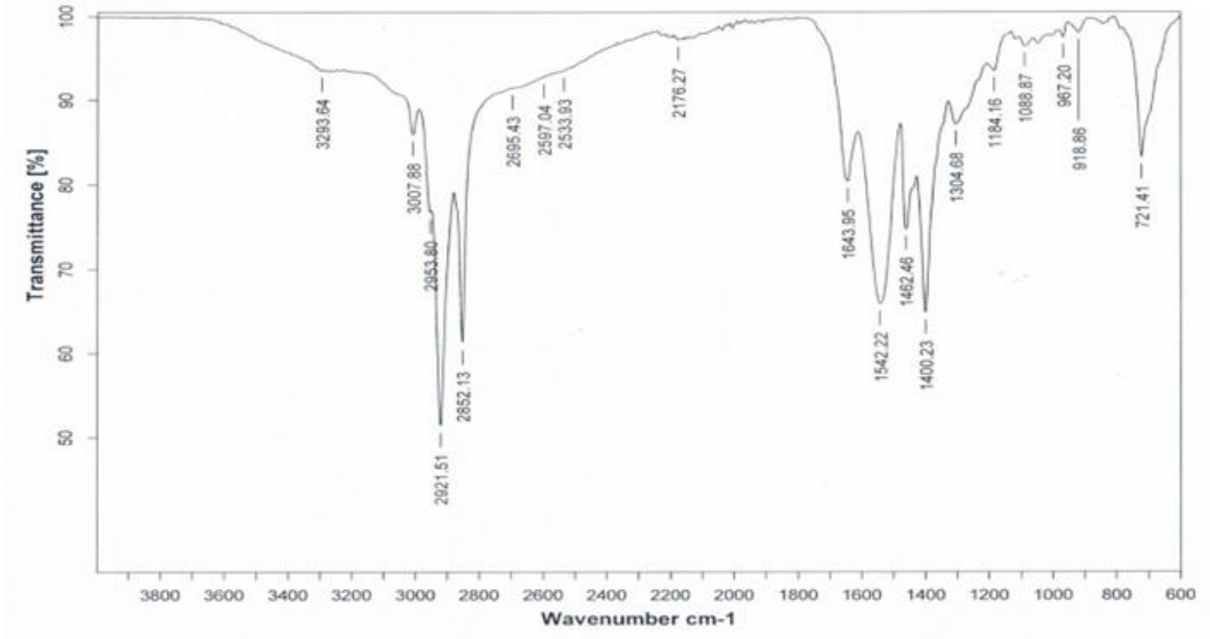


Figure 3. Cis-9-octadecanoic acid and 1,2 ethane diamine 1:2 (Salt 3)

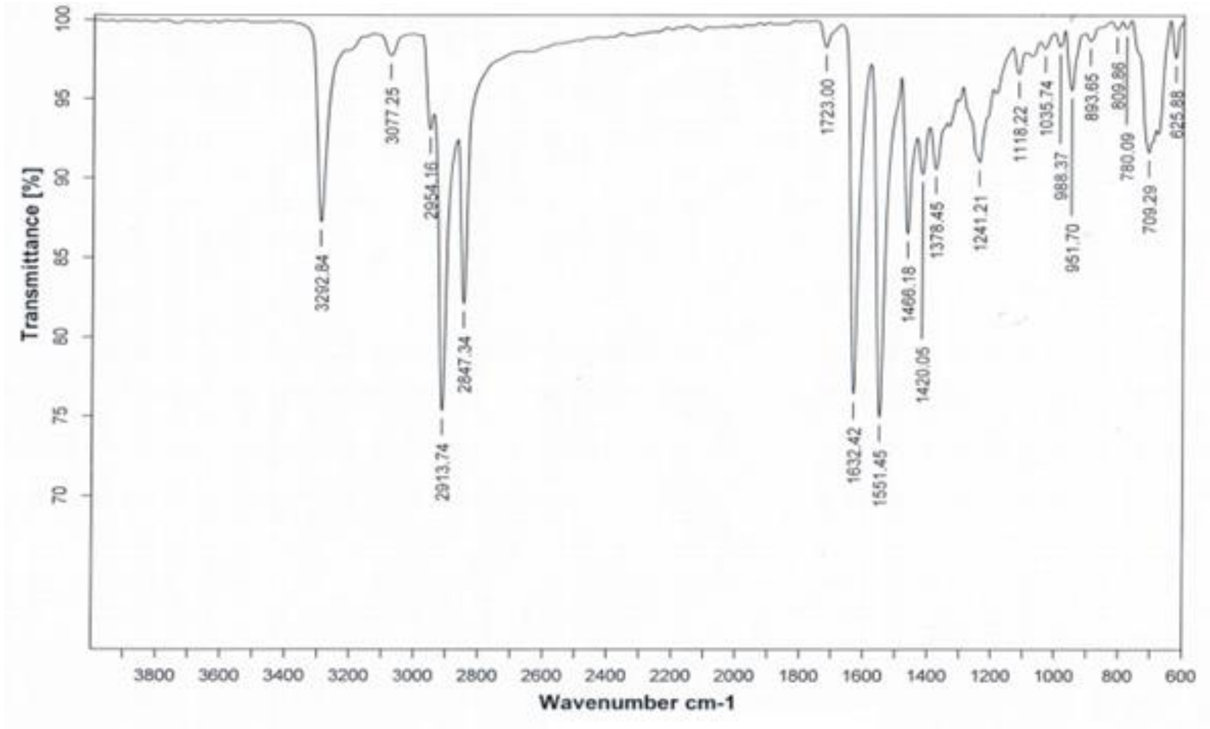


Figure 4. Tetradecanoic acid and 1,2 ethane diamine 1:2 (Salt 4)

In Figure 5-8, UV spectra of the obtained salts were given.

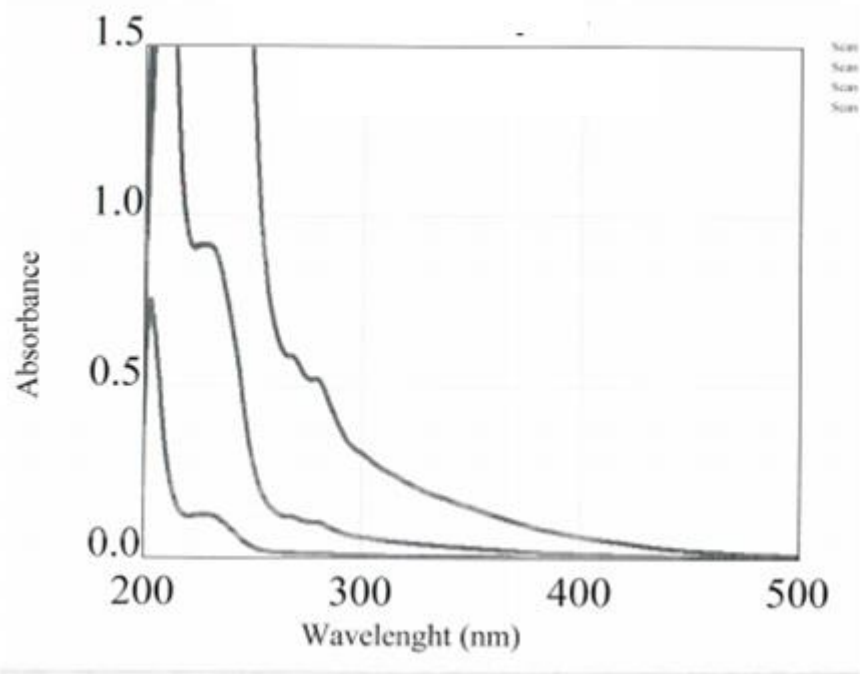


Figure 5. UV spectrum of Salt 1

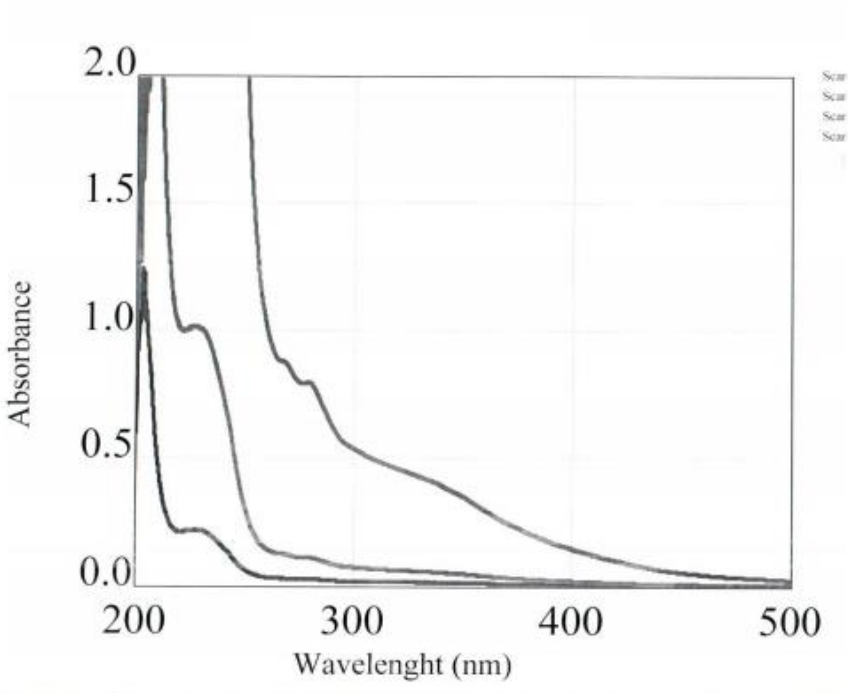


Figure 6. UV spectrum of Salt 2

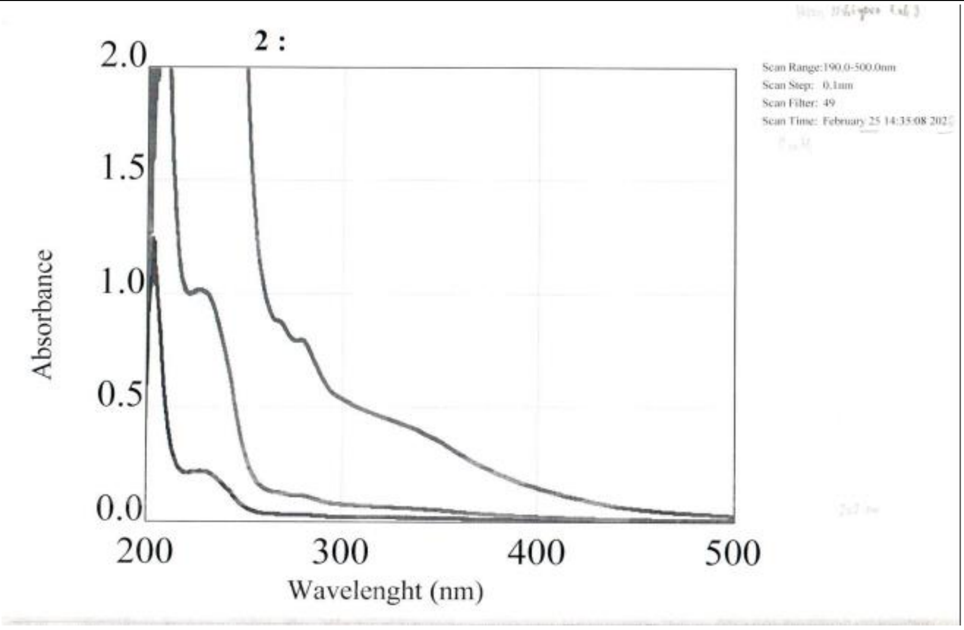


Figure 7. UV spectrum of Salt 3

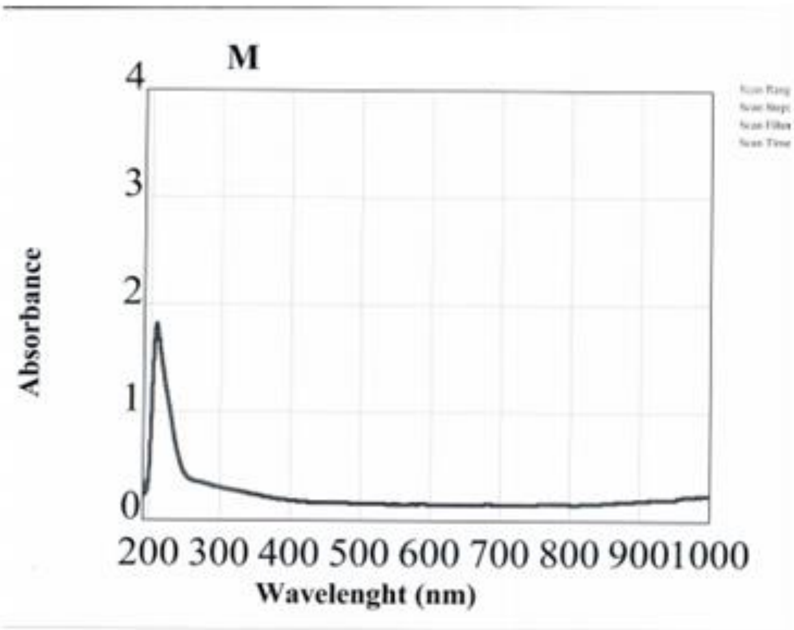


Figure 8. UV spectrum of Salt 4

The melting points of Salt 1 and Salt 2 are 57℃ and 75℃, while it is 52℃, and 67℃for Salt 3 and Salt 4. As is seen from the melting point of the final products we can conclude that because of the double bond in the second salt it has lower melting point. Increasing the amount of acid even enhances the decreasing melting point.

The surface activity parameters were measured using Tensiometer in air-water border. The surface tension of the obtained salts depending on different concentrations have been measured and from the graph in Fig. 9, CMC (critical micella concentration) which the point where the change in the surface tension is negligible. Using the data obtained from Fig. 9, surface activity parameters of the synthesized surfactants were determined and shown in Table 1.CMC of the obtained salts were determined, 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. 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;

$$A_{min} = \frac{1}{N_A * \Gamma_{max}}$$

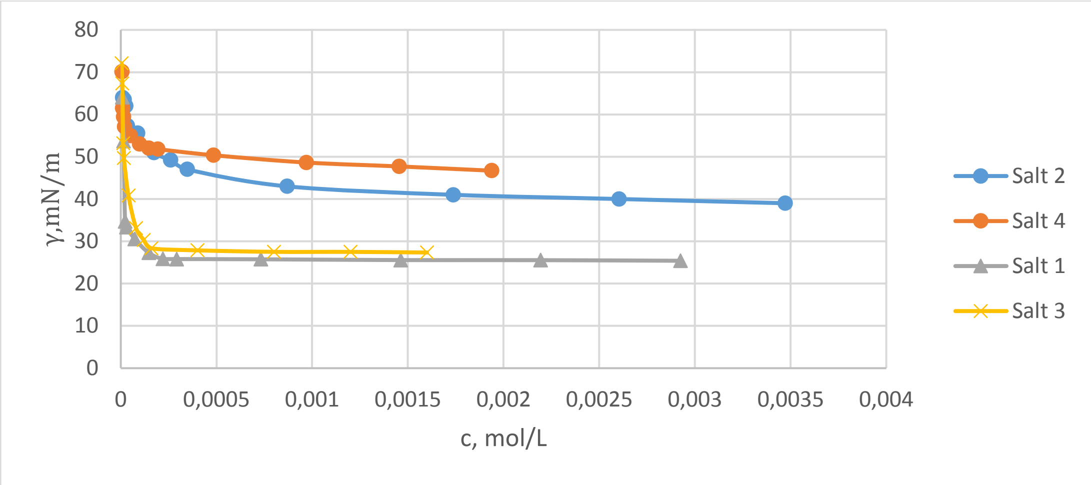


Figure 9. Surface tension at water-air interface versus concentration of the obtained salts

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	2.19	25.84	46.54	1.09	4.96	20.04	2.1	47.6
Salt 2	3.47	47	24	0.0002	3.76	2	0.95	175.32
Salt 3	1.60	28.37	44.01	1.96	4.70	8.18	1.65	60.6
Salt 4	1.45	52	19	0.0003	3.46	0.42	0.73	227.48

As it seems from the table above the salts obtained using cis-9-octadecanoic acid are more surface active than the surfactants synthesized from tetradecanoic acid. From the above table we can see that minimum CCM value and maximum area for one molecule on surfactant is observed in Salt 4. In more detailed, the best surface activity is observed in the salt 1, which is the product of the reaction between cis-9-octadecanoic acid and 1,2-Diaminoethaneat equimolar ratio.

Electroconductivity values of the different concentrated solution of the synthesized salts have been measured and the graph of the conductivity versus concentration has been plotted in Figure 10. Considering the plots some thermodynamic parameters of the electroconductivity have been calculated and given in Table 2.

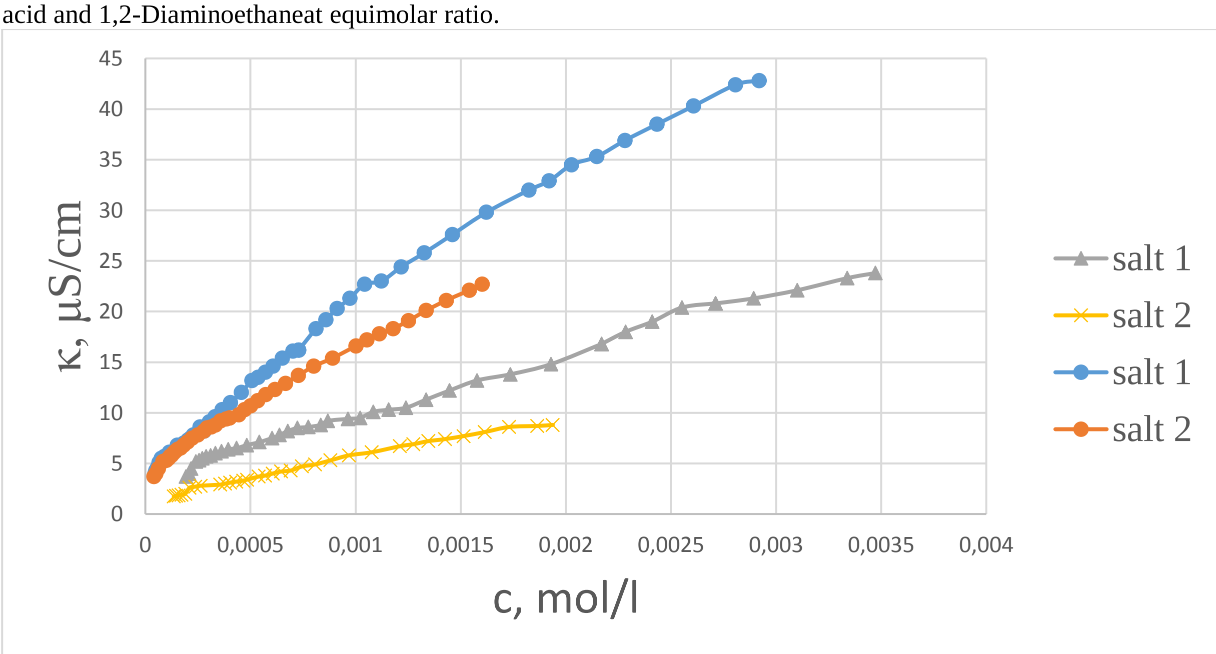


Figure 10. Electroconductivity of the synthesized salts.

Table 2

Electroconductivity parameteres

Surfactant	α	B	ΔG_{mic}, kJ/mol	ΔG_{ad}, kJ/mol
Salt 1	0.72	0.28	-26.72	-28.05
Salt 2	0.37	0.63	-31.6	-34.13
Salt 3	0.51	0.49	-32.25	-33.87
Salt 4	0.89	0.11	-23.99	-26.59

As for both salts Gibbs free energy of micellization (ΔG_{mic}) and Gibbs free energy of adsorption (ΔG_{ad}) is negative, both micelle formation and adsorption of surfactants in air-water border is spontaneous. In each case (ΔG_{ad}) is more negative than (ΔG_{mic}) and it is explained as the preference of adsorption of surfactants than micelle formation. Refering to datas given in the Table 3 we can note that the micelle formation for all salts is less spontaneous than adsorption of surfactants.

One of the most important properties for surfactants are petrodispersing or petrocollecting characteristics depending on chemical composition of them.

The petrodispersing property of the salts was examined applying the salts in solid state, 5% wt. aqueous solution and 5% wt. ethanolic solution on the film of "Azeri Light" Crude Oil on the surface of waters with different salinity which are Caspian Sea water, tap water and distilled water. Firstly, 40 ml of water in different salinity is added to Petri dishes, crude oil with 1 mm thickness is added on the water surface. After 30-60 minutes, water is treated with different solution with 0,02 g. K and Kd coefficients are calculated. K is a petrocollecting coefficient and it is the decreasement of the oil surface, while Kd isa petrodispersing coefficient and meaning is the percentage of clean water surface to compared to maximum clean water surface.

Table 3

The results of study of petrocollecting and petrodispersing property of the synthesized salts

Ratio	State of surfactant	Sea water		Tap water		Distilled water	
		K_d	Duration-τ, hours	K_d	Duration-τ, hours	K_d	Duration-τ, hours
Cis-9-octadecanoic: 1,2-Diaminoethane 1:1	*5 wt. % aqueous solution*	95%	0-27	86%	0-27	9,6	0-2
		98,5%	27-51	95%	27-123	86%	2-3
		spilling		spilling		90%	3-27
						94,8	27-123
						spilling	
	5 wt. % ethanolic solution	95%	0-27	87%	0-27	12.82	0-2
		98,5%	27-51	95,71%	27-123	95%	2-27
		drying		drying 86%		97,14%	27-123
						Spilling	
	Solid	93%	0-2	93%	0-2	90%	0-2
		95%	2-27	95%	2-27	95%	2-27
		97,14	27-123	97,14	27-123	94,28%	27-123
		spilling		spilling		Spilling	
Tetradecanoic: 1,2-Diaminoethane 1:1	*5 wt. % aqueous solution*	6,4	0-1	8,54	0-1	21,37	0-144
		8	1-2	10,12	1-144	Drying	
		9	2-144	drying			
		drying					
	5 wt. % ethanolic solution	25,64	0-144	25,6	0-144	29,59	0-144
		drying		drying		Drying	
	Solid	10,99	0-144	19,2	0-144	10,1	0-144
		spilling		spilling		Spilling	
Cis-9-octadecanoic :1,2-Diaminoethane 2:1	*5 wt. % aqueous solution*	95%	0-50	88%	0-2	88%	0-2
		86%	50-74	93%	2-50	92%	2-178
		84%	74-178	90%	50-74	Spilling	
		spilling		84%	74-178		
				spilling			
	5 wt. % ethanolic solution Solid	95%	0-50	88%	0-2	6,6	0-2
		87%	50-178	93%	2-50	93	2-178
		spilling		86%	50-74	spilling	
				40%	74-178		
				spilling			

	Solid	95	0-2	93	0-2	88	0-2
		93	2-50	95	2-50	95	2-178
		90	50-74	84	50-74	spilling	
		88	74-178	60	74-178		
		spilling		spilling			
Tetradecanoic: 1,2-Diaminoethane 2:1	*5 wt. % aqueous solution*	1	0-1	1	0-1	1	0-1
		1,36	1-4	1,36	1-4	1,96	1-28
		2,77	4-28	3	4-28	3	28-52
		34	28-76	34	28-76	7,24	52-76
		10,99	76-100	19	76-100	19	76-100
		spilling		drying 7,63		drying 19	
	5 wt. % ethanolic solution	90%	0-4	21,37	0-1	25,64	0-28
		10,99	4-28	21	1-28	34	28-52
		13,77	28-52	34	28-76	19	52-76
		13	52-76	19	76-100	15	76-100
		10,99	76-100	drying 85%		drying 15	
		spilling					
	Solid	1	0-1	1	0-1	1	0-1
		3	1-4	1,36	1-4	1,36	1-4
		12,25	4-28	3,78	4-28	2,77	4-28
		9,6	28-100	12,25	28-100	8,5	28-52
		spilling		drying 5,54		15	52-100
						drying 15	

As it seems from the table above products obtained from tetradecanoic acid shows petrocollecing while is petrodispersing for the salts synthesized from cis-9-octadecanoic acid. This can be explained by differences in Gibbs free energy of micellization (ΔG_{mic}) and Gibbs free energy of adsorption (ΔG_{ad}).

By examining the values in the Table 1 we can conclude that the Salt 1 exhibits the best petrocollecting property in sea water when treating with aqueous and ethanolic solution, while the Salt 2 shows its best property in distilled water treating with aqueous and ethanolic dispersion. Similar to the Salt 1, Salt 3 also shows good property in sea water but treated with ethanolic solution and solid form. Finally, Salt 4 gives very good results both in sea water and tap water treating with aqueous solutions. When we compare the Salt 2 and Salt 3 it is obvious that Salt 3 is better petrocollector than Salt 1. How it is for cis-9-octadecanoic acid? As it seems there is no striking differences between Salt 1 and Salt 4. Both give higher Kd coefficients. As the main aim of using surfactants in petroleum industry is cleaning the water surface from oil spills in sea water, we can recommend the Salt 2 as a good petrocollector and Salt 3 and Salt 4 as a good petrodispersant for cleaning water surface from petroleum slicks.

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. R.Nagy, R.Kothenez, Surfactants and their investigation for Petroleum Industrial Applications. International Journal of Petroleum and Petrochemical Engineering, 2015, Vol1, Issue 3, p.11-21
4. Z.H.Asadov, S.H.Zargarova, I.A.Zarbaliyeva, et al. Synthesis and study of surface-active salts based on propoxy derivatives of hexadecylamine and monocarboxylic aliphatic acids. Norwegian Journal of development of the International Science 2019,No 27, p.3-7
5. 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
6. K. E. Greber. Synthesis and Surface Activity of Cationic Amino Acid-Based Surfactants in Aqueous Solution. Journal of Surfactants and Detergents, 2017, volume 20, pages1189–1196 (2017)
7. Z.H. Asadov, S.M. Huseynova, G.A.Ahmadova, R.A.Rahimov. et al. Synthesis, colloidal-chemical and petroleum collecting properties of new counterion coupled gemini surfactants based on hexadecylbis(2- hydroxypropyl)amine and dicarboxylic acids. Journal of Dispersion Science and Technology. 9 p. Published online 07 August 2019: DOI:10.1080/01932691.2019.1650755

8. H.H.Humbatov, R.A.Dashdiyev, Liquidation of accidental petroleum spills using surfactants Baku: Elm,1998.200 p.(in Russian)

9. Asadov Z. H., Tantawy A. H.,Zarbaliyeva I.A. et al. Synthesis of New Surface-Active Ammonium-Type Complexes Based on Palmitic Acid for Removing Thin Petroleum Films from Water Surface/ The 1st Conference on Science Diplomacy and Developments in Chemistry, 2012 Alexandria, Egypt. p.199.

10. Asadov Z.H., Tantawy A.H.,Zarbaliyeva I.A. et al. Petroleum-Collecting and Dispersing Complexes Based on oleic acid and Nitrogenous Compounds As Surface-Active Agents for Removing Thin Petroleum Films from Water Surface // Journal of Oleo Science, 2012, V. 61,11, p. 621-630.

11. Rosen M.J. Surfactants and Interfacial Phenomena, 3rd Edn.NewYork:JohnWiley and Sons, Inc. 2004,444 pp.