ANALYSING THE EFFECT OF THE AMINE GROUP ON THE PROPERTIES OF THE GEMINI SURFACTANTS

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Abstract:

A comparative examination of two distinct surfactants has been provided in this research paper. Using IR and UV spectroscopy, the structure and composition of the surfactants have been identified. The produced surfactants' physical and chemical characteristics, such as interfacial tension and certain electrical conductivities have been identified. From these observations, the surface pressure, the typical thermodynamic parameters of adsorption and micellization, as well as the maximum surface excess concentration and the minimum area of the molecule at the water/air interface, have all been computed. Additionally, these compounds' petrodispersing and petrocollecting properties have been examined, and their maximum petrocollecting coefficient values have been established.

Key words: surfactant, lauric acid, ethylenediamine, diethylenetriamine, petrocollecting, petrodispersing

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1.Introduction:

The growing demand for crude oil and its refined products causes environmental difficulties and an unbalance [1]. These kinds of large spills are typically caused by pipeline breakage, oil ship sinkings, or subpar drilling methods. One of these biological concerns that may arise during the transportation of crude oil and its refining components has been identified as lean oil layers on the water's surface [2]. Oil spilled at water resources threatens marineorganisms, whole ecosystems, and economic resources in the immediate vicinity, such as fisheries, aquaculture, recreation, andtourism. Due to the fact that water have more density than most sorts of oil, it sprawls out over the surface of water and hydrocarbons whose molecular weight is low, are vaporizing and diminishing the level of spillage while contaminating the air. Adequate response to any oil spill to minimize damage is therefore of great importance. The ever-developing and advanced technologies, namely, physical, chemical, thermal or in-situ burning andbioremediationshould be used to treat and recover fast, efficiently oil spills and oil slicks [3].A unique group of chemical substances is framed by surfactants. Physical characteristics of surfactants emphasize their capacity to significantly alter surface and interfacial properties, as well as their capacity to associate with one another and dissolve in micelles [8]. Due to these characteristics, surfactants can be used to uproot liquid phases from porous mediums, modify their wettability, and perform detergency [7]. These in turn give rise to a massive collection of practical application fields that are described in terms of biological structures, health and personal care products, mineral and petroleum processing, and food [4-6]. It is generally known that surfactants are now frequently used in high technology fields like microelectronics, magnetic recording, printing, electronics, and biotechnology. Every day, enormous amounts of surfactants are consumed worldwide. As a result, there is a growing need for high-performance surfactants because using fewer of them can lighten the load on the natural treatment system. As a result, researchers have effectively engineered and created novel surfactants [9–11].

2. Experimental details.

Diethylamine (DEtA) is a product produced in the Russian Federation. It is a transparent liquid with a molar mass of73.14 g.mol-1 and an ammonia smell. Its density is 0.707 gml-1, its boiling point is 55-56 °C, and its refractive index is 1.3850.

Ethylenediamine (EDA) is a product of Aldrich. It is a colorless liquid with a molar mass of 60.1 gmol-1. Ammonia is odorous. Its density is 0.899 gml-1, its boiling point is 117-119 °C, and its refractive index is 1.4565.

Lauric acid produced as a white crystalline powder, has a slight odor of bay oil with a molar mass of 200 g/mol. Its density is 0.883 g/ml. Melting point is 44.2 ℃ and boiling point is 298.9 ℃.

Two salts have been synthesized using the lauric acid and ethylenediamine and diethylenetriamine. The first Gemini surfactant which is the product of the reaction between lauric acid and ethylenediamine defined as Salt 1 and the other which is also Gemini surfactant obtained from lauric acid with diethlenetriamine defined as Salt 2.

2.1. Surface tension and conductivity measurements.

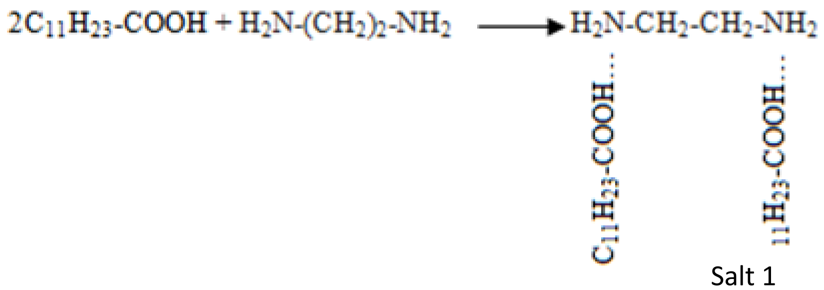
Surface tension of the obtained surfactants' aqueous solutions has been measured using a Du Nouy ring KSV Sigma 702 tensiometer with a Pt ring (AttensionBiolin Scientific, Finland). At 25 °C, the surface tension of the double-distilled water used to make solutions was 71.5 mN/m. These measurements have been used to calculate the CMC values of the surfactant.

Utilizing a tabletop conductivity meter called the VWR® pHenomenal® CO 3000 L, electrolytic conductivity of surfactant aqueous solutions has been determined (Germany). All measurements had a reference temperature of 25 °C and were accurate to within 1%. The double-distilled water used for the experiment had a conductivity in the range of 2-2.8 S/cm. Plots of conductivity vs. molar concentration have been used to calculate the CMC values of surfactants [5-7].

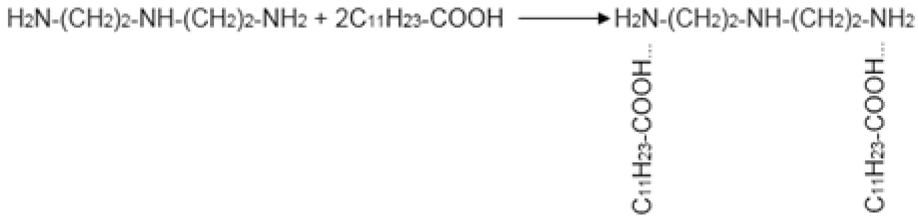
The surfactants' ability to disperse oil was assessed using the established method described in [9]. An empty Petri dish is filled with 40 cc of water. In this work, 1 ml of crude oil bearing the “Pirrallahi” is applied to the water, with a film thickness of approximately 0.17 mm. The surfactant (or its 5% wt. solution) is then added to the film from the side at a rate of 0.02 g. At specific time intervals, the initial oil film's surface area and the current extent of the oil slicks that have formed are measured. Calculation of the coefficient Kd, which represents the degree of surface cleaning (in%)

3. Result and discussion:

The schemes of the reactions are shown below.



Salt 1



Salt 2

The structure and the composition of the obtained salts have been confirmed by IR and UV spectroscopy, which are given in Fig 1-4.

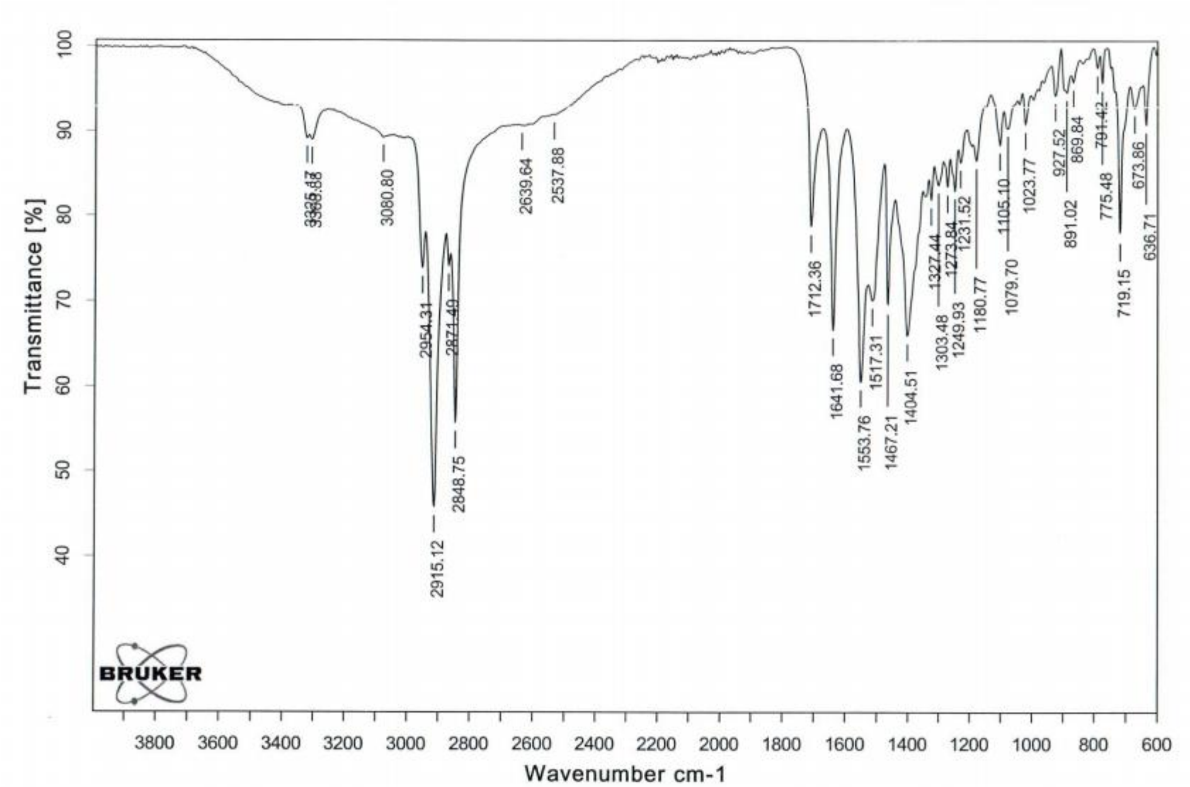


Fig 1. IR spectrum of Salt 1

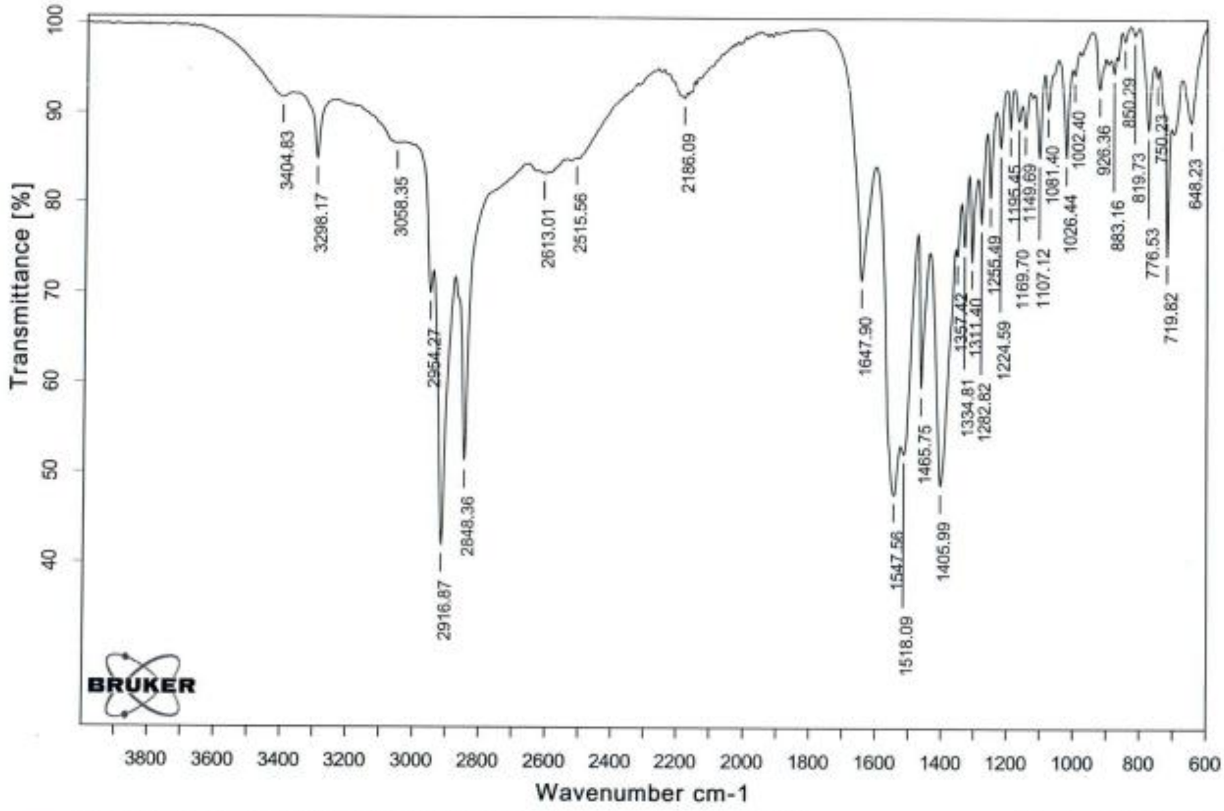


Fig 2. IR spectrum of Salt 2

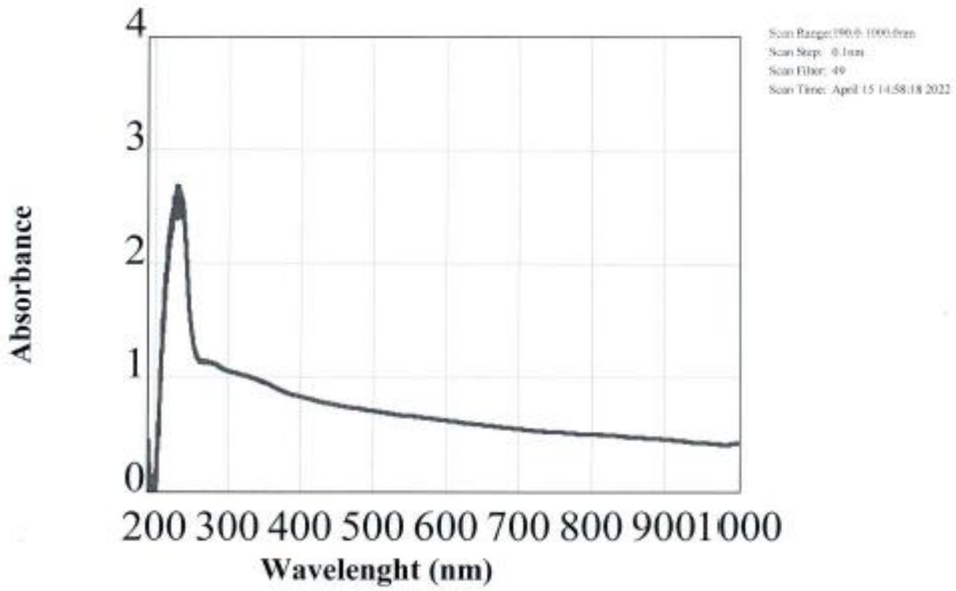


Fig 3. UV spectrum of Salt 1

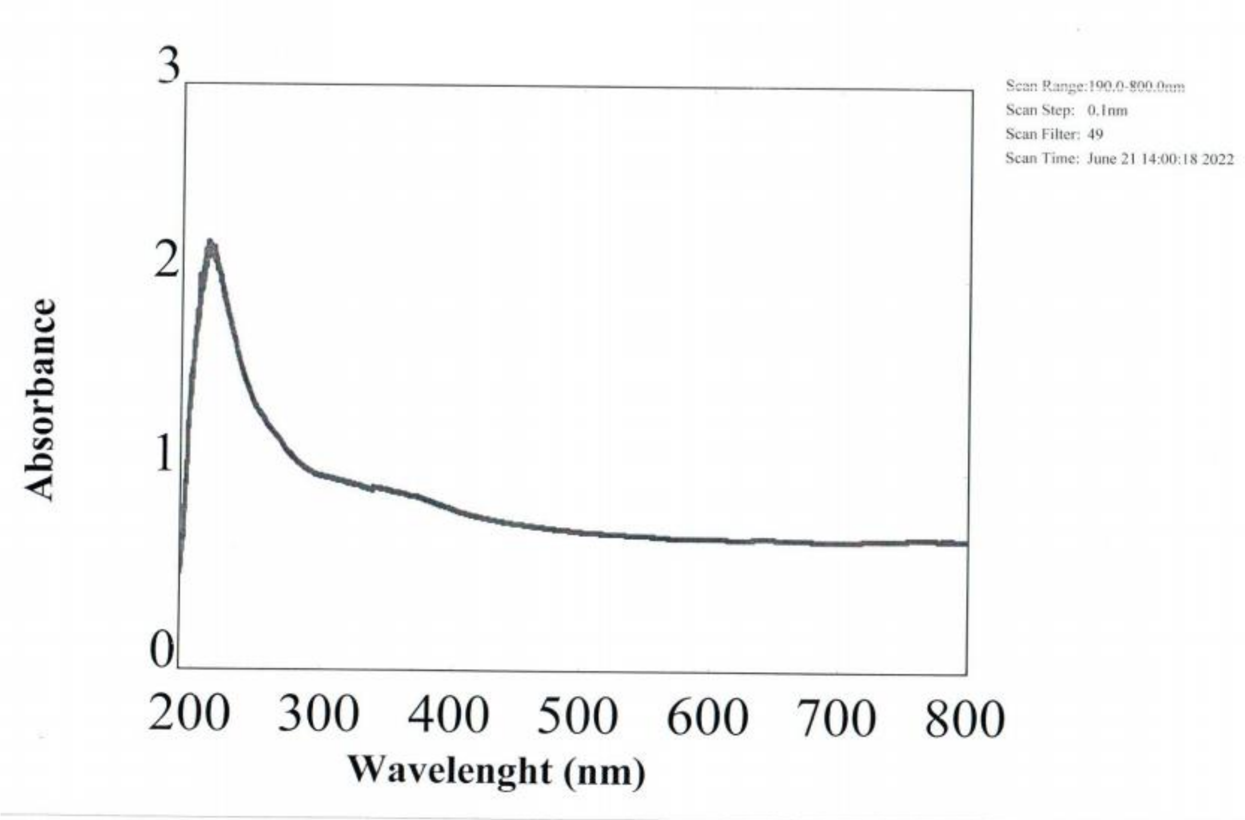


Fig 4. UV spectrum of Salt 2

The amine and acid number of the salts were measured. Acid number is 47 and 48 respectively, besides that, HLB (hydrophilic-lipophilic balance) value which is 18.6 and 30.2 respectively. When HLB value is 0, it is called hydrophobic, when its value is 40, it is called as hydrophilic. Referring to the HLB values it can be concluded that Salt 2 shows hydrophilic property more than Salt 1.

Surface tensions of the obtained salts were measured using Tensiometer and the dependence of the surface tension on concentration is shown in Fig 5.

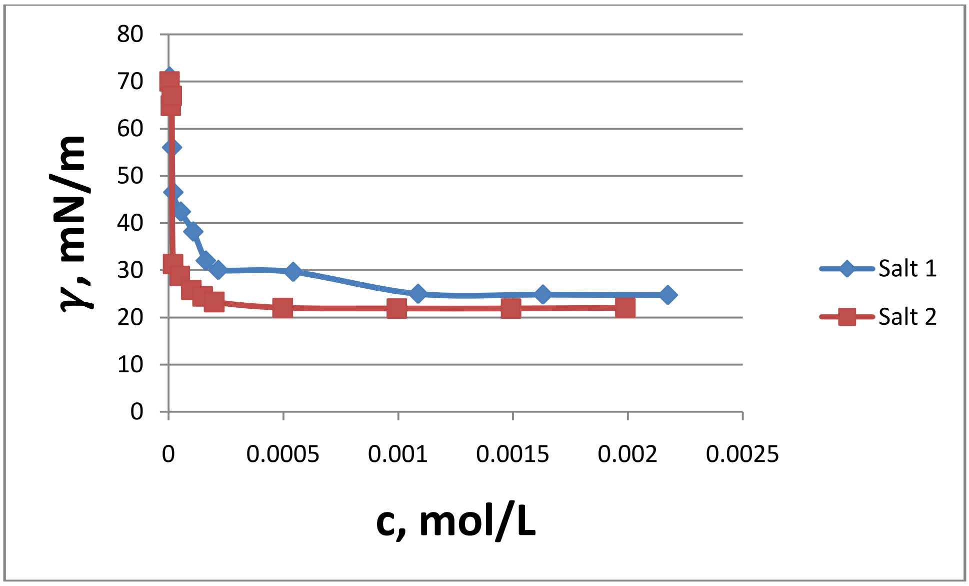


Fig 5. Surface tension versus concentration

From the graph given above, CCM which is the minimum concentration of the surfactant in order to form micelle. Besides that other surface activity parameters were calculated and shown in Table 1.

Table 1

Surface activity properties

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 (22℃)	2.17	30	41.37	0.19	4.7	11.4	1.51	109.78
Salt 2 (22℃)	1.99	23.24	49.14	0.16	4.79	12.3	1.72	96.30

Referring to the table above it can be seen that Salt 2 decrease the surface tension between air-water border more than Salt 2. Addition to that, Salt 2 forms micelle in a lower concentration. Another important parameter which is π_{CMC} , which is called surface pressure and shows the effect of petrocollecting and petrodispersing. The higher value of it, means better cleaning agent. Besides that Salt 2 has lower value for A_{min}, which means the minimum surface area for one molecule of surfactant.

Electrical conductivity of the same solutions used in surface tension measurement was measured by electrical conductivity meter and shown in Figure 6.

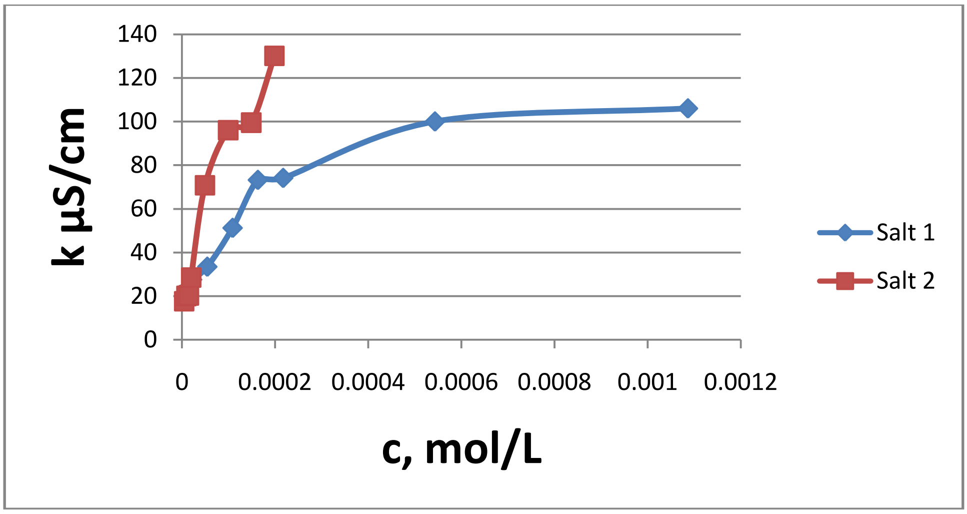


Fig 6. Electrical conductivity versus concentration

From the graph above α, which is the ratio of the slopes after and before CMC point was found. Following that Gibbs free energy of micelle and adsorption were calculated and results were described in Table 2.

Table 2

Thermodynamic properties of the electrical conductivity

Surfactant	α	β	ΔG_{mic}, kJ/mol	ΔG_{ad}, kJ/mol
Salt 1	0.9	0.1	-22.77	-25.48
Salt 2	0.55	0.45	-30.17	-33.00

As it can be seen from the Table 2, adsorption of the molecules is more spontaneous than the micelle formation. Addition to that, for Salt 2, these processes are even more spontaneous than Salt 1.

In the Table 3, petrocollecting and petrodispersing properties of the synthesized surfactants were given.

Table 3

Petrocollecting and petrodispersing properties

Ratio	State of surfactant	Sea water		Tap water		Distilled water	
		K_d, K	Duration-τ, hours	K_dK	Duration-τ, hours	K_d K	Duration-τ, hours
Salt 1	*5 wt. % aqueous solution*	2.12	0-1	1.8	0-1	10	0-1
		1.67	1-25	1.67	1-25	3	1-25
		87%	25-49	1.56	25-49	1.68	25-49
		12%	49-169	1.56	49-169	1.68	73-265
		12% drying		84% dry		70% dry	
	5 wt. % ethanolic solution	5	0-1	5	0-1	19.15	0-1
		1	1-25	1.95	1-25	3	1-217
		9	25-49	1.56	25-49	1.36	
		9	49-169	1.56	49-169	1.36	
		9 dry		70%		1.36 dry	
	Solid	50%	0-1	3	0-1	24.4	0-1
		9.07	1-25	4.79	1-25	97%	1-25
		13	25-49	12.8	25-49	97.3%	25-49
		13	49-169	12.8	49-169	97.3%	49-169
		spilling		spilling		83% drying	
Salt 2	*5 wt. % aqueous solution*	16,7	0-24	25,5	0-24	98,7%	0-24
		15,32	24-48	97,3%	24-48	98%	24-48
		19,2	48-240	19	48-240	95,5%	48-240
		70% drying		90% drying		90% dry	
	5 wt. % ethanolic solution	25,5	0-24	19,15	0-24	21,3	0-24
		97%	24-48	96,4%	24-48	21,3	24-48
		21,33	48-240	15,36	48-240	15,36	48-240
		Drying 80%		Drying 80%		Drying 88%	
	Solid	92,20%	0-24	19,15	0-24	24,4	0-24
		97,3%	24-48	97,4%	24-48	97,6%	24-48
		55,2%	48-240	55,2%	48-240	94,24%	48-240
		spilling		spilling		Dry 85%	

From the Table 3,. The maximum petrocollecting coefficient for the Salt 1 is 24.4, although this parameter is 25.5 for the Salt 2, this property is higher for all points.We can observe the higher K and K_d coefficient for the Salt 2. It is important to note that Salt 1 represents its best results only in distilled water treated with solid phase. However, Salt 2 displays similar results in all cases. Generally both surfactants show good petrodispersing and petrocollecting property in distilled water treated with solid.

4. Conclusion

Referring to the measured physical-chemical properties we can summarize that Salt 2 shows better surface activity properties which is seen as lower CMC and γ_{CMC}surface tension. Besides that, Salt 2 has higher tendency to form micelle and adsorption. Better results of the Salt 2 are not ended with the properties mentioned above. It is also repeated in petrocollecting and petrodispersing properties. All these results allow us to state that increasing the number of the nitrogen atoms improves the physical-chemical properties of the surfactant. It can also be explained with increasing hydrophilic property of the surfactant from Salt 1 to Salt 2.

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