Synthesis, Characterization and Study of Biological Activities to the Anionic Surfactants

Muhannad.Jawad.Kadhim.Al.Assadi
Chemistry Department, Education College, Basra University
Basra-Iraq

Abstract

Sodium salt of a-sulphonated fatty acid hydrazide was used as starting material to synthesis some important heterocycles as oxadiazoles to produce novel groups of anionic surfactants having a double function, antimicrobial and surface active agents. The structures of these compounds were performed by FTIR and CHN-analysis. The physical properties as (Density, pH, Concentration, Color, Viscosity and Stability to hydrolysis) were determined. The surface active agents were used in (O/W) emulsions depend on value of (HLB) [Hydrophilic-Lipophilic Balance].

Introduction

Amoning anionic surfactants containing an aromatic structure element, the most common group, are alkyl benzene sulphonates accompanied by alkyl-naphthalene sulphonates. In these compounds, hydrophilic sulphonic group is separated from long chain alkyl hydrophobic by single six member benzene or naphthalene rings. As an example, the derivatives of alkyl thiophene or alkyl pyrrole having a sulphonic or carboxylic hydrophilic group can be mentioned. Long chain (C_8 – C_{18}) 3-n-alkyl thiophene, 1-and 3-n-alkyl and 3-n-alkanoyl derivatives of pyrrole were obtained as hydrophobic intermediates for synthesis of anionic surfactants containing sulphonic or carboxylic group. In the literature, mainly in patent description, the examples of synthesis of surface active alkyl benzopyrrole and alkyl benzimidazole sulphonates have been reported [(1)].

The reaction of butyrol acetone with primary amines at high temperatures produces N-alkyl substituted pyrrolidones. However, other methods of incorporating the pyrolidone nucleus also have been investigated. Butyrolactone reacts with diamines, when the diamine is in excess, to afford N-amino alkyl pyrrolidones, which can be further condensed with fatty acid , anhydrides, acid chlorides, or esters to produce amido alkyl pyrrolidones,. When the fatty acids are in the surfactant range (C_8 – C_{16}), highly surface active compounds are formed [(2)].

A family of novel mono alkyl glycerol ether surfactants with different hydrophobic lengths (C_9 – C_{16}) and tryptophane were synthesized on a laboratory scale and their aqueous surface active properties are studied [(3, 4)].

More recently new bis-quaternary pyridinium surfactants were synthesized and characterized. The surface tension in aqueous media, cmc value, and area per molecule were determined and compared with corresponding mono quaternary-pyridinium bromides which were synthesized and studied [(5-7)]. It has been well established that various trizoles, oxazoles, benzoxazoles are biological interest [(8-11)]. This encouraged me to synthesize novel groups of anionic surfactants containg pyridazine, oxadizole, phthalazinone and thiazole derivatives from sodium salt of a

sulphonated long chain fatty acids (myristic, palmitic and stearic) hydrazide (I_{a-c}) hopping to possessing good surface properties and expected to have biological activities.

Key ward: Anionic surfactants, anionic surfactants hydrazides containing heterocyclic.

Experimental

A. Instruments

1. **FTIR-Infrared photometer (8400S) from made by (SHIMADZU) the range (4000-200 cm^{-1}) from Petrochemical Laboratories/ Basra.**
2. **Freezing point osmometer from made by (OSMOMAT 030) from College of Education/ Basra-University.**
3. **Elemental analysis (CHN) from College of Science/ Cairo University.**
4. **PH-meter from made by (WTW) from College of Science/ Basra-university [Calomel and Glass Electrodes].**
5. **Density metre kind density bottle glass.**
6. **Viscosity metre kind Viscometer by units (cent-poise).**

B. Chemicals

Fatty acid, hydrazine, chloro sulphonic acid, sodium hydroxide, chloro acetic acid, acetic anhydride, sodium acetate, ethyl alcohol, acetone, carbon tetra chloride. [Fluka, BDH and North Oil Company / Baiji].

C. Bacterial Removals (*Bacillus sublitis* (NCTC 5933), *Escherichia coli* (PC1 219), *Aspergillus's Niger* (NCTC 6571) and *Candida albicam* (NCTC 6350) were supplied from Defo Laboratories (U.S.A).

D. The using Agricultural environment [Nutrient Agar (NA) was supplied from Mast Laboratories Led. (U.K) and [Nutrient Broth (AB) and Muller-Hinton Agar (MHA) were supplied from Defo Laboratories (U.S.A).

Synthesis of fatty acid chloride

Fatty acid chloride was prepared depending on Ref. [15].

Synthesis of fatty acid hydrazides

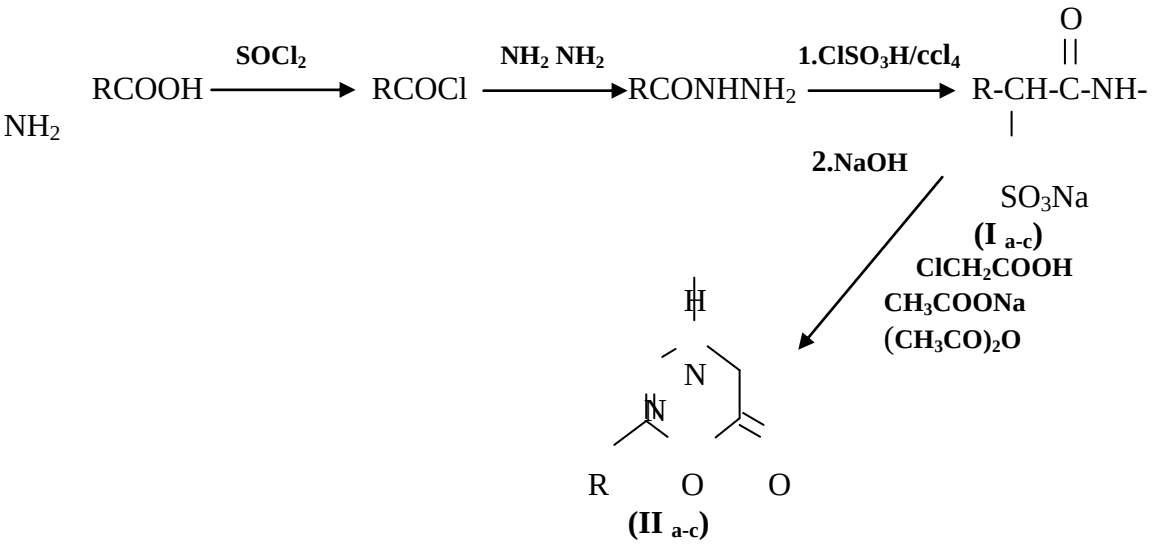
Fatty acid hydrazide was prepared from its acid chloride (0.01mol) [2.46 ml] through its reaction with hydrazine hydrate (0.01mol) [0.32 ml] in dry acetone by reflux for (2 h) then recrystalization by hot water to obtain hydrazide [12].

Synthesis of sodium salt of a-sulphonated fatty acid hydrazides (I)

A solution of fatty acid hydrazide (0.01mole) [2.5 ml] and chloro sulphonic acid (0.01mole) [1.16 ml] in carbon tetra chloride was stirring at room temperature about (2 h), then neutralized by (0.1 N) of sodium hydroxide. The solid product was separated and recrystallized by DMF to obtain the product (I_{a-c}) [12].

Synthesis of oxapyridazinone derivatives (II_{a-c})

A solution of sodium salt of a-sulphonated fatty acid hydrazides (I) (0.01 mole) and chloro acetic acid (0.01 mole) in presence of sodium acetate and acetic anhydride was refluxed for (4 h) then poured on water , a solid product was obtained. Filtration and recrystallization by [Toluene, benzene and ethanol] solvents to give oxapyridazine derivatives (II_{a-c}) [12].



R- **a.** $CH_3(CH_2)_{11}CH$- SO_3Na **b.** $CH_3(CH_2)_{13}CH$- SO_3Na **c.** $CH_3(CH_2)_{15}CH$- SO_3Na

Table (1) shows the values of melting points and recrystallization solvents to the prepared compounds.

Table (1) the melting point and type of recrystallization Solvents, Compounds (I_{a-c}), (II_{a-c})

Compound	M.P[^{0}C]	Solvent	Material State
I_a	196	Ethanol	Solid
I_b	201	methanol	Solid
I_c	216	Benzene	Solid
II_a	245	Toluene	Solid
II_b	266	Benzene	Solid
II_c	280	Ethanol	Solid

Stability to hydrolysis

A mixture of (10 mmol) surfactant and (10 ml) from (0.05N) sodium hydroxide were placed in thermostats at (40^{0}C). The time taken by sample solution to be clouded on a result of hydrolysis shows the stability surfactant to hydrolysis [14]. The time of stability surfactant was calculated and shown in Table (2).

Table (2) the physical properties of surfactants, Compounds (I_{a-c}), (II_{a-c})

Compound	M.Wt	Color	Density (g/cm^3)	Viscosity (c.p)	Conc. (mol)	PH	Stability to hydrolysis (h)
I_a	344	Yellow	1.125	1.546	34.4%	8.1	3.7
I_b	372	White Yellow	1.144	1.568	37.2%	8.3	4
I_c	400	White Yellow	1.148	1.570	40%	8.5	4.3
II_a	384	Yellow	1.234	1.645	38.4%	7.5	5.75
II_b	412	Pale Yellow	1.254	1.663	41.2%	7.8	5.81
II_c	440	Pale Yellow	1.263	1.678	44%	8	5.9

Selection of Surfactants

The selection of surfactants depends on Hydrophilic-Lipophilic Balance (HLB) which was calculated by equation (1). The prepared surfactants were used in (O/W) emulsion as shown in Table (3). This value then is an induction of the oil or water solubility of the product. The lower (HLB) number is more water- soluble the product; and in turn the higher (HLB) number is more oil- soluble the product [13].

$$HLB = 20 * \frac{\text{mole wt.EO} * \text{moles EO}}{\text{mole wt. of adduct}} \quad \ldots\ldots (1)$$

Table (3) the application of surfactants

Value of HLB	Application
0-3	Anti-foaming
4-6	(W/O) emulsifying
7-9	Wetting
8-18	(O/W) emulsifying
13-15	Detergent
10-18	Solubilizing

The (HLB) was calculated to the prepared surfactants as shown in Table (4).

Table (4) the value of HLB

Compound	Value of HLB
II_a	14
II_b	16
II_c	18

Biological activities

The prepared surfactants were test for their bactericidal activities against (*Bacillus sublitis* and *Escherichia coli*) and other their antifungal activity against (*Aspergillus's Niger* and Yeast (*Candida albicam*). The results obtained indicated that compounds

(II_{a-c}) were relativity more active as bactericide or fungicide agent as shown in Table (5).

Table (5) Biological activity of prepared surfactants, Compounds (II_{a-c})

Compound	*Bacillus sublitis*	*Escherichia coli*	*Aspergillus's Niger*	*Candida albicam*
II_a	+	-	-	+
II_b	+ +	+	+	+ +
II_c	+ +	+	+	+ + +

Procedure

The Hahn method was used in obtained on disc with diameter (6mm) from filter paper Watman (No.3). The filter paper was electrical treatment in 121^0C and (1jaw) for 15min. The prepared surfactants were used as dilute solutions and concentrations (50, 150 and 250ηg/disc). The discs were left in room temperature to dry and keep in refrigerator until using.

The Pauen and others were used in determined inhibition zone which was measured by (mm). The Muller-Hinton Agar was prepared and poured in betriedish glass. The four stander bacterial plankton were prepared and moved (4-5) pure colony of bacteria grown on Nutrient Borth and keep in 37^0C for (4-6h) until appearing turbid. The area of sterilized cotton containing the Muller-Hinton Agar was abundant in the prepared bacteria plankton in three dimensions to obtain on homogenous grow, after that the betriedishes were moved to incubation in 37^0C for (24h) and the measured biological activities through measured the inhibitor zones around all disc in mm. The prepared surfactants were activated toward the bacterial used as shown in Table (6).

Table (6) Inhibitor zones around all discs to the prepared surfactants, Compounds (II_{a-c})

	Bacillus sublitis			*Escherichia coli*			*Aspergillus's Niger*			*Candida albicam*		
Compound	50	100	150	50	100	150	50	100	150	50	100	150
II_a	-	1	1.4	3	3.5	4	1	1.5	2	1.1	2	2.5
II_b	-	1.3	2.4	4	5	7	1.5	3	3.5	1.3	2.3	3
II_c	-	1.5	2.5	4.5	6	7.5	2	3.5	4	1.6	2.7	3.4

Synthesis of the solution surfactants

A soluble of (0.1 mole) from the surfactants prepared through the present study in (100 ml) water: ethanol (70:30) to obtain a solution from II_a (38.4%), II_b (41.2%) and II_c (44%). These solutions were used for dispersing the oil spots in the Iraqi Ports Company with out any negative effect on the water environment and this was a proved by the measurements of biological activity in the laboratories of Petrochemical Company.

Table (7) shows the values of absorption bands to the prepared surfactants.

Table (7) Show the absorption bands of surfactants, Compounds (I_{a-c}), (II_{a-c})

Compound	Wave numbers(cm^{-1})								
	C-H	C-C	C-N	N-H	C-S	C=N	C=O	C-O	C=C
I_a	al.(2920-2851), b.720	1250	3175	3450	692	-	1680	-	-
I_b	al.(2921-2850), b.723	1253-1248	3178-3174	3452	695	-	1685	-	-
I_c	al.(2920-2852), b.725	1260	3180	3450	695-698	-	1687	-	-
II_a	al.(2919-2850), ar.3030, b.730	893	3065	3437	685-660	1618	1654	1465	1580
II_b	al.(2920-2851), ar.3032, b.735	899	3068	3434	665	1619	1650	1462	1575
II_c	al.(2920-2853), ar.3033, b.738	910	3070	3432	662	1619	1649	1460	1570

al-aliphatic**, ar**-aromatic**, b**- bending

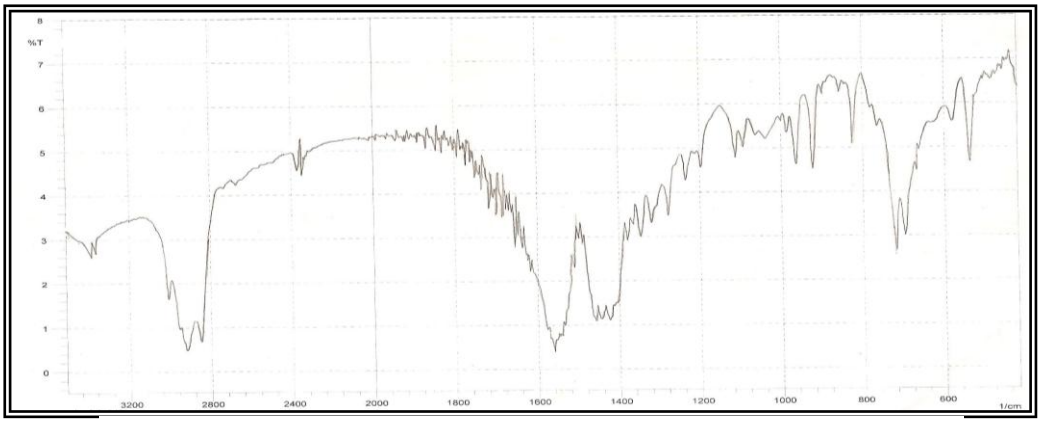


Figure (1) I.R-spectrum of (I_a) as KBr disc

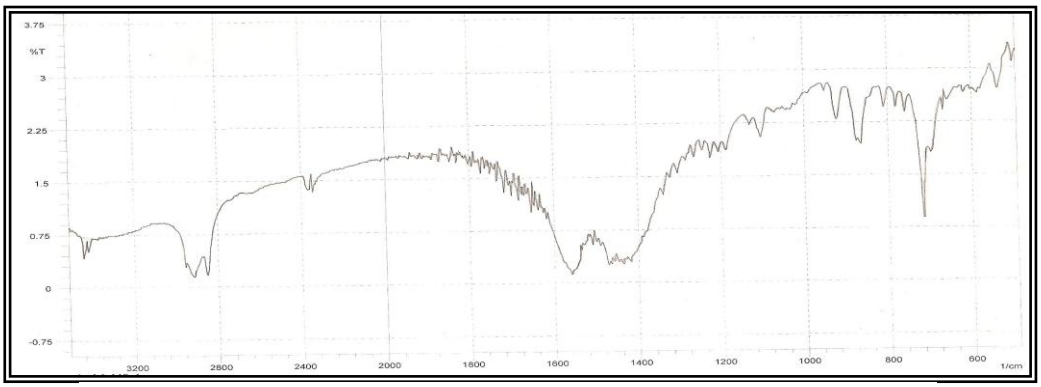


Figure (2) I.R-spectrum of (I_b) as KBr disc

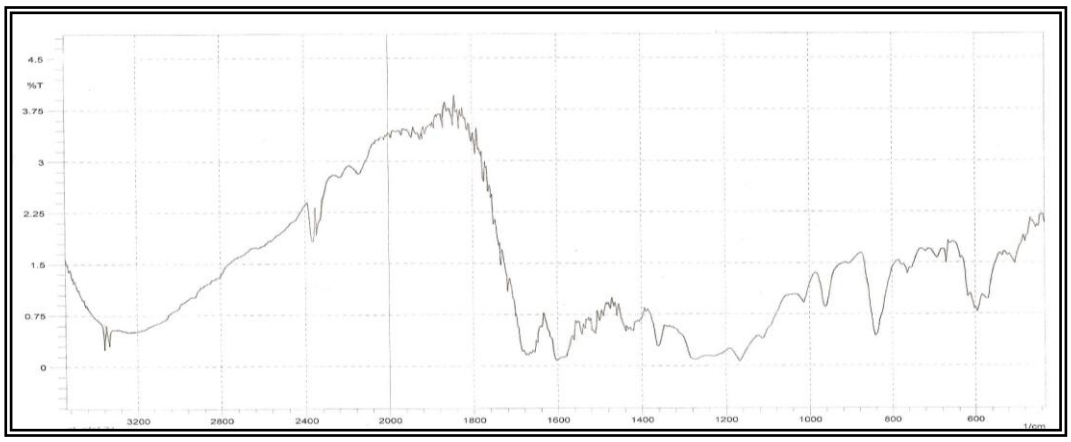


Figure (3) I.R-spectrum of (I_c) as KBr disc

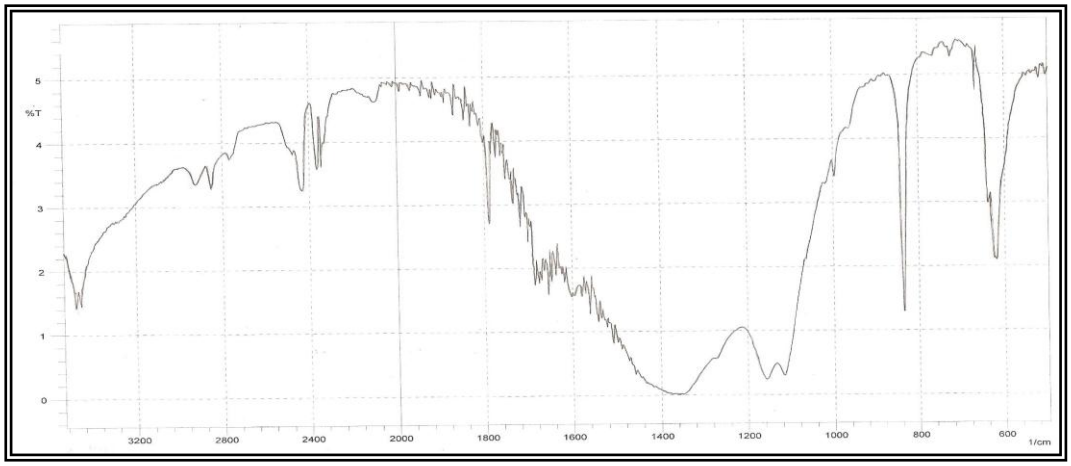


Figure (4) I.R-spectrum of (II_a) as KBr disc

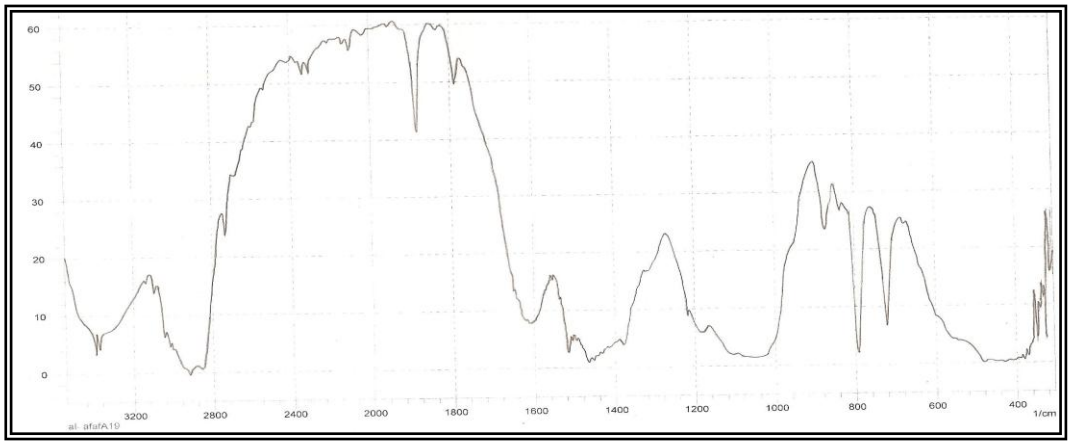


Figure (5) I.R-spectrum of (II_b) as KBr disc

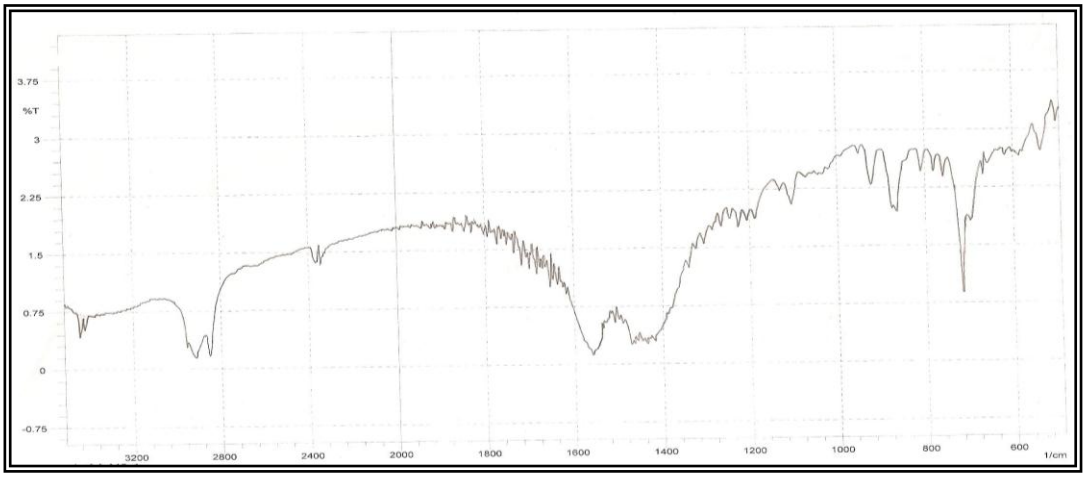


Figure (6) I.R-spectrum of (II $_c$) as KBr disc

Results and discussion

The compounds (I_{a-c}) were allowed to react with chloroacetic acid in ethyl alcohol yielded oxapyridazinone derivatives (II_{a-c}) [65%, 60% and 60%].

IR-spectra shows (N-H) at 3452-3450 cm^{-1}, (C=O) at 1680-1687 cm^{-1}, (C-N) at 3174-3180 cm^{-1}, (C-H) aliphatic at 2920-2852 cm^{-1}, 720-730 cm^{-1}, (C-C) at 1260-1248 cm^{-1} and (C-S) at 692-698 cm^{-1} for the compounds (I $_{a-c}$) as explained in Figures (1-3) and Table (7).

While, the compounds of (II $_{a-c}$) gives different bands (N-H) at 3437-3432 cm^{-1}, (C=O) at 1649-1654 cm^{-1}, (C-N) at 3070-3065 cm^{-1}, (C-H) aliphatic at 2919-2853 cm^{-1}, 738-730 cm^{-1}, (C-H) aromatic at 3030-3032 cm^{-1}, (C-S) at 685-660 cm^{-1}, (C-O) at 1460-1465 cm^{-1}, (C-C) at 910-893cm^{-1} and (C=C) at 1570-1580 cm^{-1} because of containing the aromatic structure as shown in Figures (4-6) and Table (7).

The mechanism of the surfactants is used in dispersion oil in water emulsion; the samples were taken from the Iraqi Ports Company was poured in containers and add the surfactants by spray on the surface. The activity of dispersion was studied with time to know the efficiency of Compounds (II_a, II_b, and II_c) on dispersing oil spots. It was noted that the surfactants reduced the surface tension of liquid. In addition to the effect of long chain on dispersion was studied as shown in Table (8).

Table (8) the surfactants, Compounds (II $_{a-c}$) activity with time

Compound	Time (Day)				
	1st	2nd	3rd	4th	5th
II_a	40%	60%	70%	90%	-
II_b	50%	65%	78%	92%	95%
II_c	56%	68%	80%	94%	98%

Elemental analysis (CHN) shows the practical and theoretical values in Table (9).

Table (9) the values of CHN for Compounds (II_{a-c})

Compound	Practical Value %			Theoretical Value %		
	C	H	N	C	H	N
II_a	49.16	7.24	6.84	50.03	7.53	7.25
II_b	52.12	7.62	6.37	52.44	8.01	6.71
II_c	54.18	7.88	5.73	54.52	8.44	6.34

The selection of surfactants depend on the value of (HLB) calculated by equation (1) and used in the dispersion of (o/w) emulsion as shown in Tables (3, 4).

The stability to hydrolysis of compounds was increased by increase the alkyl chain length [13]. As shown in Table (2).

Also, the biological activity and dispersion activity were increased with increase the alkyl chain length as shown in Tables (5, 8).

The physical properties (melting point, solvent, pH, color, molecular weight , viscosity, concentration and stability of hydrolysis were studied as shown in Tables (1,2).

References

1. **Janik, R. and Kucharski, S., "Synthesis and properties of new anionic surfactants containing heteroaromatic ring", 4th, P. (288-300) (2000).**
2. **Robert.B.Logine, "Pyrrolidone-based surfactants (a literature review)" – J.Am.Chem.Soc. 72 (7), P.759-771 (2003).**
3. **Bender, D. A., "Metabolic and Pharmacological suits", P. 140,179,183 (1995).**
4. **Pegiadou, S. Perez, "Synthesis, Characterization and surface properties of 1-N-L-tryptophan glycerol ether surfactants"- Journal of surfactants and detergents, 3(4), 517-525 (2000).**
5. **Pegiadou, S. Perez, "Synthesis and properties of new cationic surfactants", J.Am.Chem.Soc. 63, 1583 (1996).**
6. **Pegiadou, E., Tsatsaroni, "Synthesis and properties of new cationic surfactants", J.Am.Chem.Soc. 64, 1444 (1997).**
7. **Pegiadou, Koemtzoponlou, "Synthesis, Characterization and surface properties of new bis-quaternary pyridinium surfactants"- Journal of surfactants and detergents, 3(1), 73-76 (1993).**

8. Amin, M.S., Eissa,"Uses of quinazoline-2-[(b-propionoyl) isothio cyanate]-4-one as a building block in synthesis of some hetero cyclic compounds of expected biological activity" India-Journal of chemistry, 37B, 1153-1156 (1998).

9. Albright, J.D., Moran," Synthesis and an oxiolytic of 6-(substituted-phenyl)-1, 2, 4-triazolo (4, 3-b) pyridazines", J.Med.Chem. 24, 592 (1981).

10. Pegiadou, Koemtzoponlou, "Synthesis of some new pyrimido [1, 6-] pyrimidines", J. Hetero cyclic.Chem. 23, 335 (1986).

11. Pegiadou, Koemtzoponlou, "Pyrimidinium cationic surfactants as emulsifiers in (o/w) emulsion ", J.Surfact.Deterg. 1,499 (1998).

12. Eissa, A.M.F." Preparation and surface active properties of oxapyridazinone of fatty acid", 44, 203, 216 (1992).

13. Eissa, A.M.F. "Preparation and surface active properties of oxypropylated diol mono esters of fatty acids with an amide oxime terminal group", Grassy Aceites, 45, 306-308 (1993).

14. El.Sukkary, M.A., El.Sawy." synthetic detergents from crud rice bran oil". Hungarian Journal of Industrial Chemistry.15, 317 (1987).

15. Melvin, D.G., C.A., 46, 7, 10601c (1952).