RESULTS AND DISCUSSION

3/1- Preparation of surfactants and their physico-chemical properties:

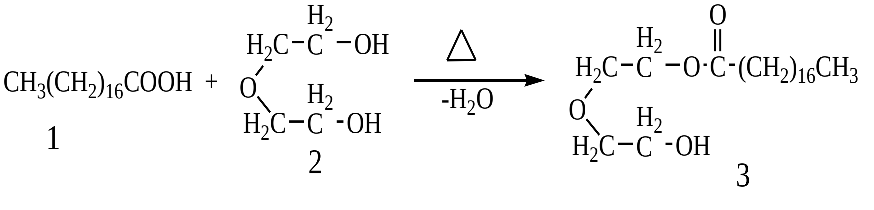
3/1/1- Preparation and identification of non-ionic surfactants:

3/1/1/a- preparation of non-ionic surfactants

The reaction of organic acids and alcohols to give the corresponding esters that were used as surfactants for the preparation of pesticides. So that three long chain fatty acids stearic, lauric, and oleic were treated with glycerol as trihydroxy alcohol and diethylene glycol as dihydroxy alcohol (mono fatty acid esters).

3/1/1/a/1-The reaction of stearic acid and diethylene glycol.

Stearic acid (1) reacted with diethylene glycol (2) to afford diethylene glycol mono stearate (3).



The structure of compound (3) was confirmed according to the following spectral data:

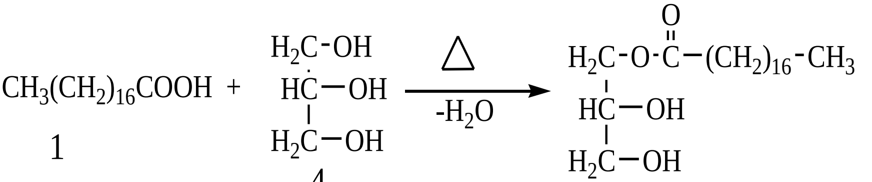
i) The infrared spectrum of this compound showed well defined bands for υ_{OH} at 3408cm^{-1}, υ_{CH} aliphatic at 2919cm^{-1}, $\upsilon_{C=O}$ at 1703cm^{-1} and υ_{C-O-C} at 1066cm^{-1} as shown in fig (1).

ii) The mass spectrum displayed the correct molecular ion peak at m/z= 372 with 22.8 relative abundance corresponding to molecular formula $C_{22}H_{44}O_4$.The mass spectrum also showed fragments of m/z value followed by percentages of relative abundance as following:

373(M^++1, 5.21), 372(M^+, 22.8), 344(18.54), 284(100), 256(32.35), 185(19.92), 129(42.79) and 83(49.17) as shown in fig (2).

1/1/a/2- The reaction of stearic acid with glycerol.

Stearic acid (1) reacted with glycerol (4) to afford glycerol mono stearate (5).



1 4 5

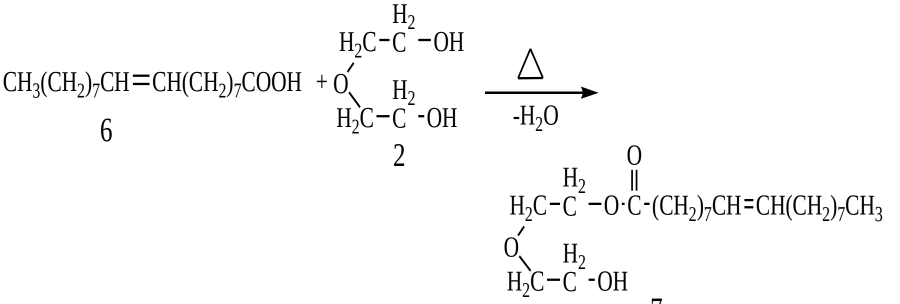
The structure of compound (5) was confirmed according to the following spectral data:

i) IR spectrum of this compound showed the following absorption bands for υ_{OH} at 3419cm^{-1} ,υ_{CH} aliphatic at 2919cm^{-1}, $\upsilon_{C=O}$ at 1704cm^{-1} and υ_{C-O-C} at 1045cm^{-1} as shown in fig (3).

ii) The mass spectrum displayed the correct molecular ion peak at m/z= 358 with 48.08 relative an abundance corresponding to molecular formula $C_{21}H_{42}O_4$. The mass spectrum of this compound also showed fragments of m/z value followed by percentages of relative abundance as follows: 359(M^++1, 10.7), 358(M^+, 48.08), 330(73.4), 284(57.8), 267(24.0), 256(18.66), 154(14.7), 134(46.3) and 79(100.0) as shown in fig (4).

1/1/a/3- The reaction of oleic acid (unsaturated long chain fatty acid) with diethylene glycol.

Oleic acid (6) was reacting with diethylene glycol (2) to afford diethylene glycol mono oleate (7)



6, 2, 7

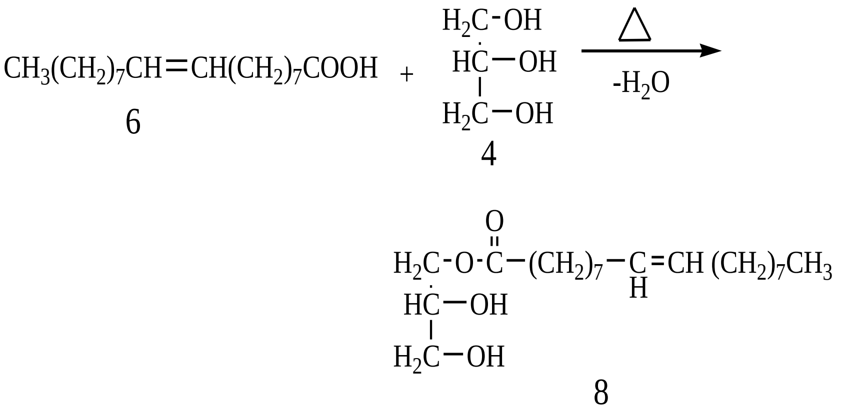
The structure of compound (7) was confirmed according to the following spectral evidence:

i) IR spectrum of this compound showed will defined bands for υ_{OH} at 3394cm^{-1}, υ_{CH} aliphatic at 2931cm^{-1}, $\upsilon_{C=O}$ at 1645cm^{-1} and υ_{C-O-C} at 1062cm^{-1} as shown in fig (5).

ii) The mass spectrum of this compound showed the correct molecular ion peak at m/z= 370 with 4.55 relative abundance corresponding to molecular formula $C_{22}H_{42}O_4$. The mass spectrum of this compound also showed fragments of m/z value followed by percentages of relative abundance as follows: 372(M^++2, 0.52), 371(M^++1, 2.93), 370(M^+, 4.55), 264(23.42), 223(1.85), 207(2.32), 169(4.14), 152(8.41), 111(25.24) and 95(100.0) as shown in fig (6).

1/1/a/4- The reaction of oleic acid and glycerol.

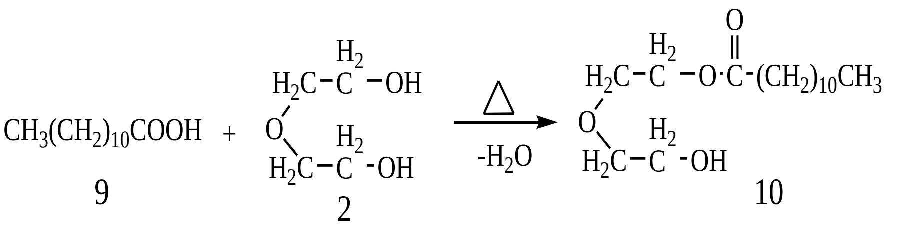
Oleic acid (6) reacted with glycerol (4) afforded glycerol mono oleate (8).



The structure of compound (8) was identified as before so that the IR spectrum showed well defined bands for υ_{OH} at $3388 cm^{-1}$, υ_{CH} aliphatic at $2938 cm^{-1}$, $\upsilon_{C=O}$ at $1643 cm^{-1}$ and $\upsilon_{C\text{-}O\text{-}C}$ at $1042 cm^{-1}$ as shown in fig (7).

1/1/a/5- The reaction of lauric acid and diethylene glycol to afford diethylene glycol mono laurate.

Lauric acid (9) was reacting with diethylene glycol (2) to give diethylene glycol mono laurate (10).

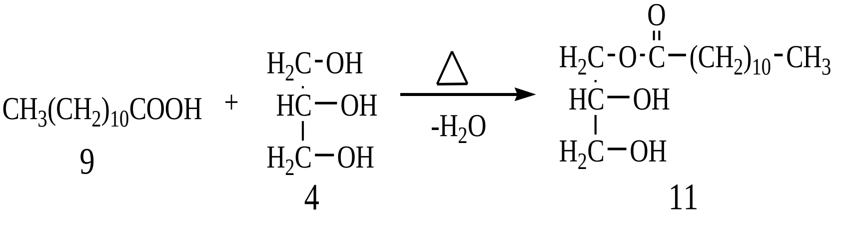


i) IR spectrum of this compound showed well defined as bands for the following functional groups: υ_{OH} at $3426 cm^{-1}$, υ_{CH} aliphatic at $2926 cm^{-1}$, $\upsilon_{C=O}$ at $1726 cm^{-1}$ and $\upsilon_{C\text{-}O\text{-}C}$ at $1068 cm^{-1}$ as shown in fig (8).

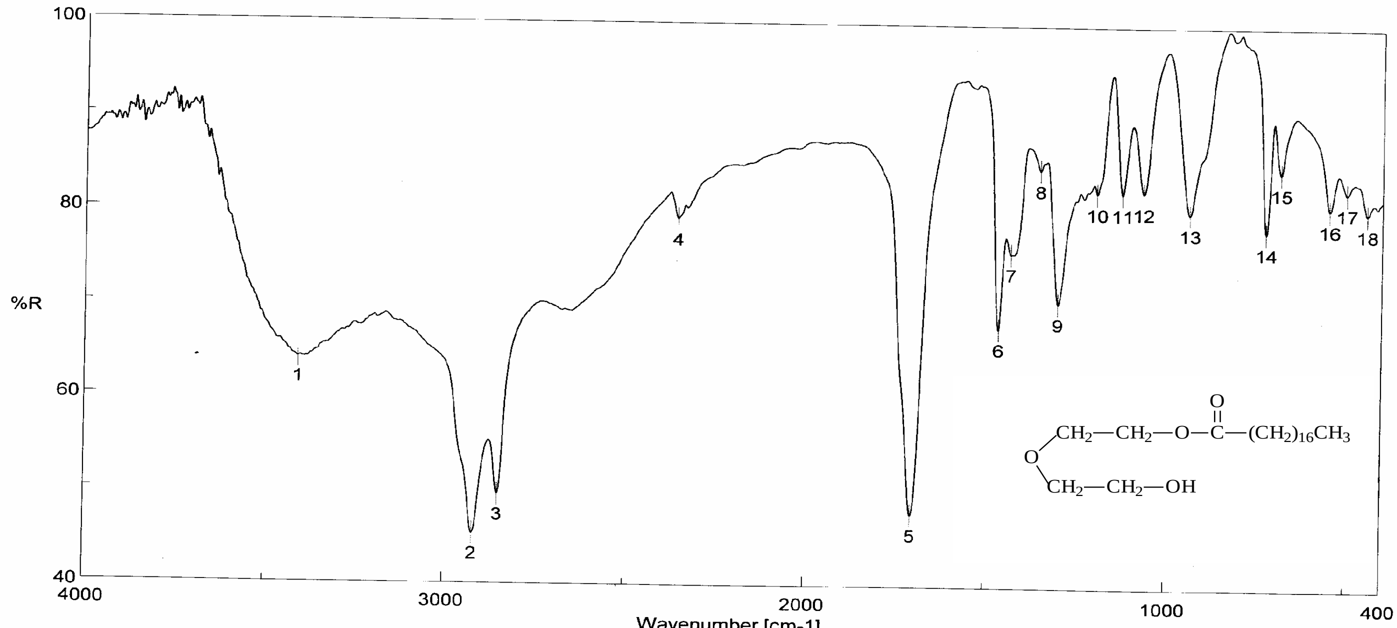
ii) The mass spectrum of this compound showed the correct molecular ion peak at m/z= 288 with 0.78 relative abundance corresponding to molecular formula $C_{16}H_{32}O_4$. The mass spectrum of this compound also showed fragments of m/z value followed by percentages of relative abundance as follows: 290(M^++2, 2.39), 289(M^++1, 10.74), 288(M^+, 0.78), 227(100.0),183(43.11), 155(10.05), 112(5.49) and 99(32.62), 78(26.15) as shown in fig (9).

1.1.a.6. The reaction of lauric acid and glycerol to afford glycerol mono laurate.

Lauric acid (9) was reacting with glycerol (4) to give glycerol mono laurate.



The structure of compound (11) was confirmed by IR spectrum showed the following functional groups: υ_{OH} at 3417cm^{-1}, υ_{CH} aliphatic at 2922cm^{-1}, $\upsilon_{C=O}$ at 1728cm^{-1} and $\upsilon_{C\text{-}O\text{-}C}$ at 1049cm^{-1} as shown in fig (10).



[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3408.57	64.0353	2	2919.7	45.3002	3	2851.24	49.4603	4	2357.55	79.0871
5	1703.8	47.636	6	1464.67	67.6772	7	1431.89	75.7149	8	1352.82	84.6012
9	1301.72	70.4554	10	1195.65	82.1926	11	1125.26	82.1403	12	1066.44	82.2728
13	937.235	80.0927	14	724.139	78.2042	15	683.642	84.523	16	547.685	80.7253
17	500.437	82.4593	18	442.583	80.2528						

Fig (1-3) Infra-red Spectrum of fatty acid ester 3

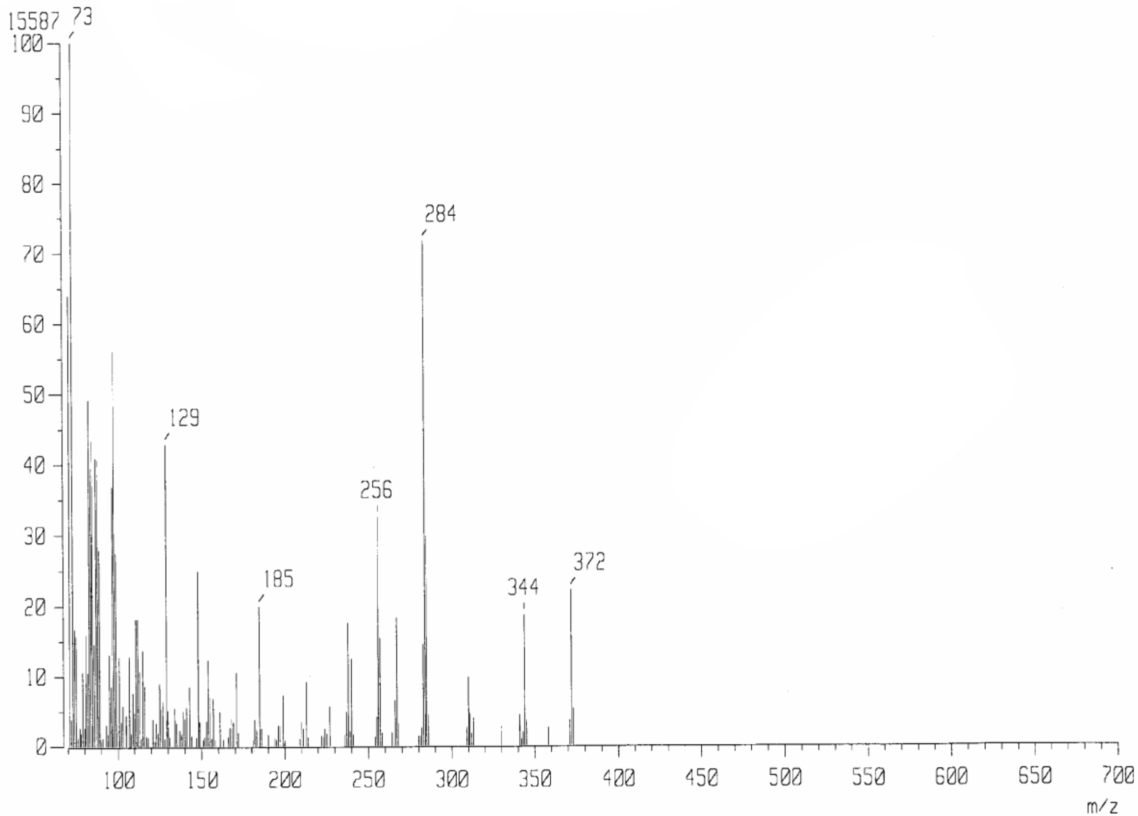
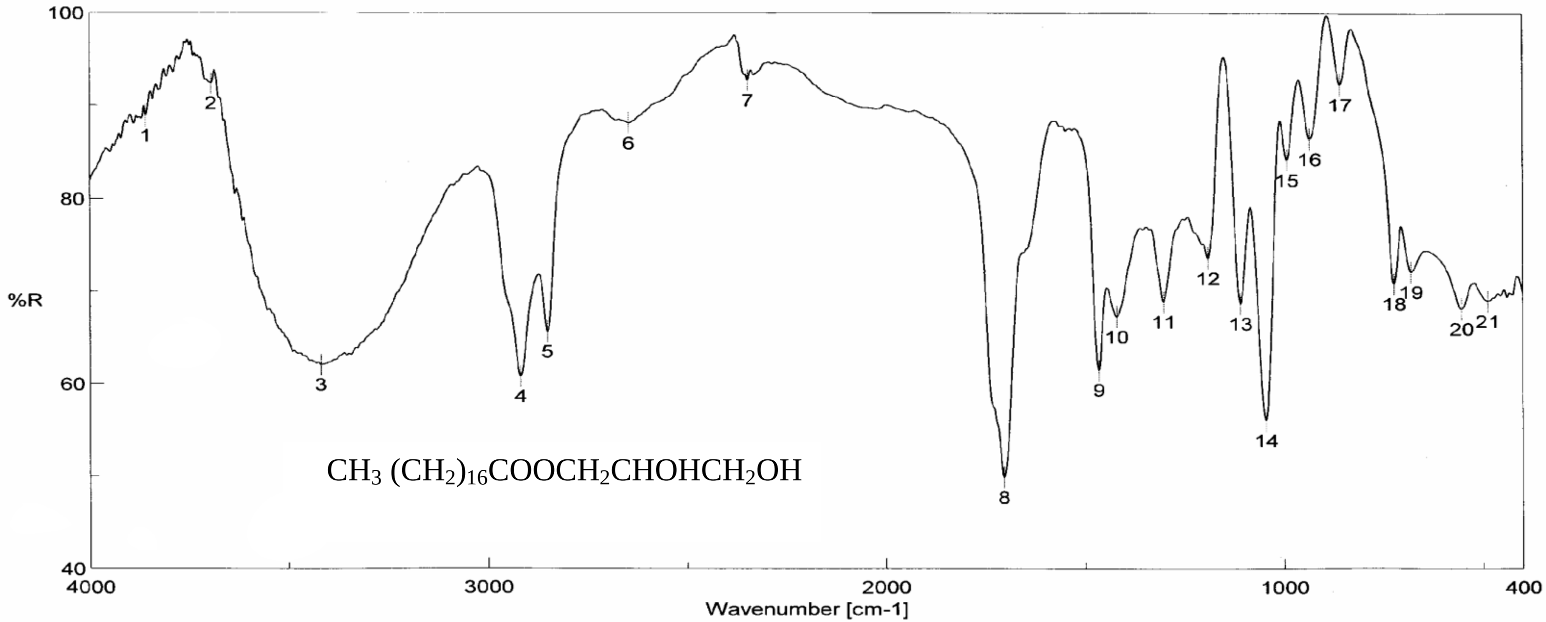


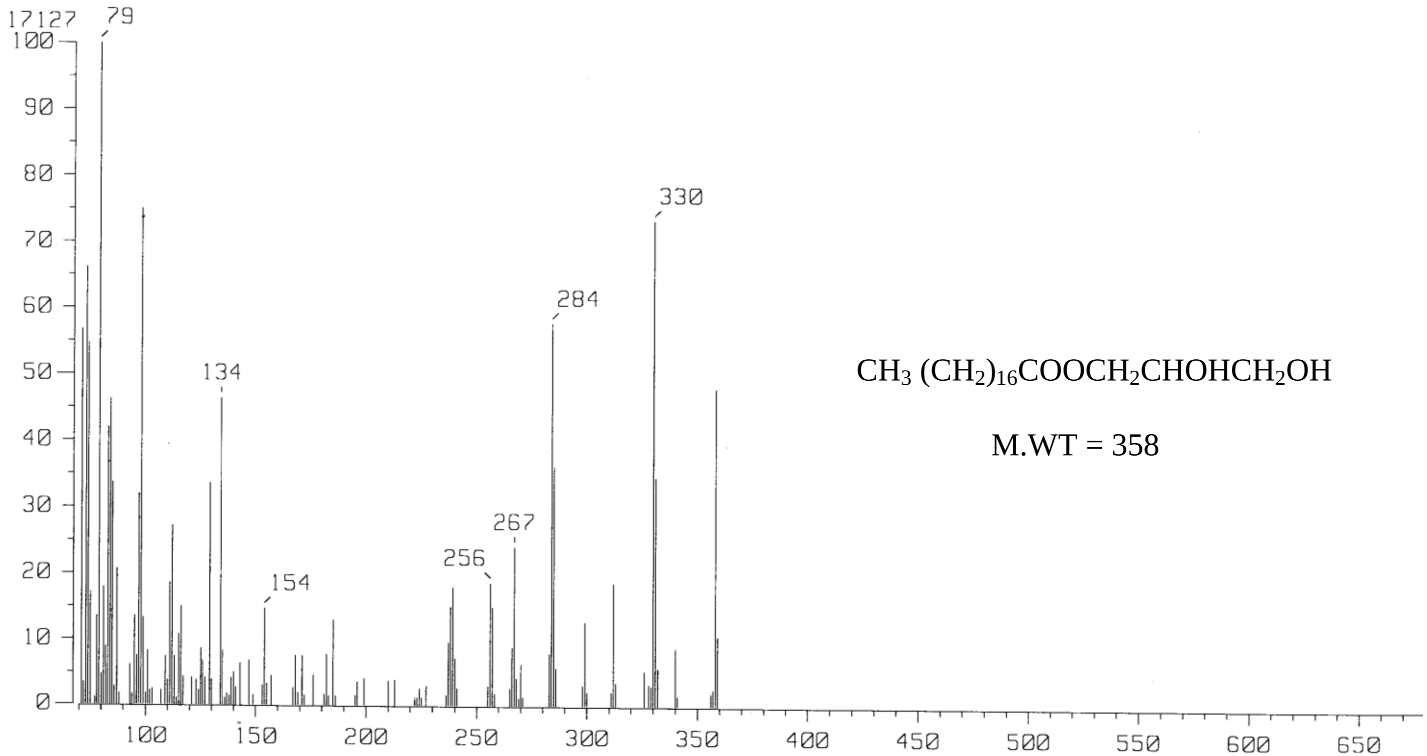
Fig (2-3) Mass Spectrum of fatty acid ester 3



[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3858.86	88.8795	2	3694.94	92.3959	3	3419.17	62.057	4	2919.7	60.8315
5	2852.2	65.6764	6	2645.86	88.0538	7	2345.98	92.6692	8	1704.76	49.8237
9	1465.63	61.5009	10	1421.28	67.2998	11	1302.68	68.8938	12	1190.83	73.5851
13	1108.87	68.697	14	1045.23	55.9859	15	991.232	84.1416	16	933.378	86.3867
17	856.239	92.2263	18	722.211	70.8623	19	679.785	72.1306	20	552.506	68.1607
21	486.938	68.9961									

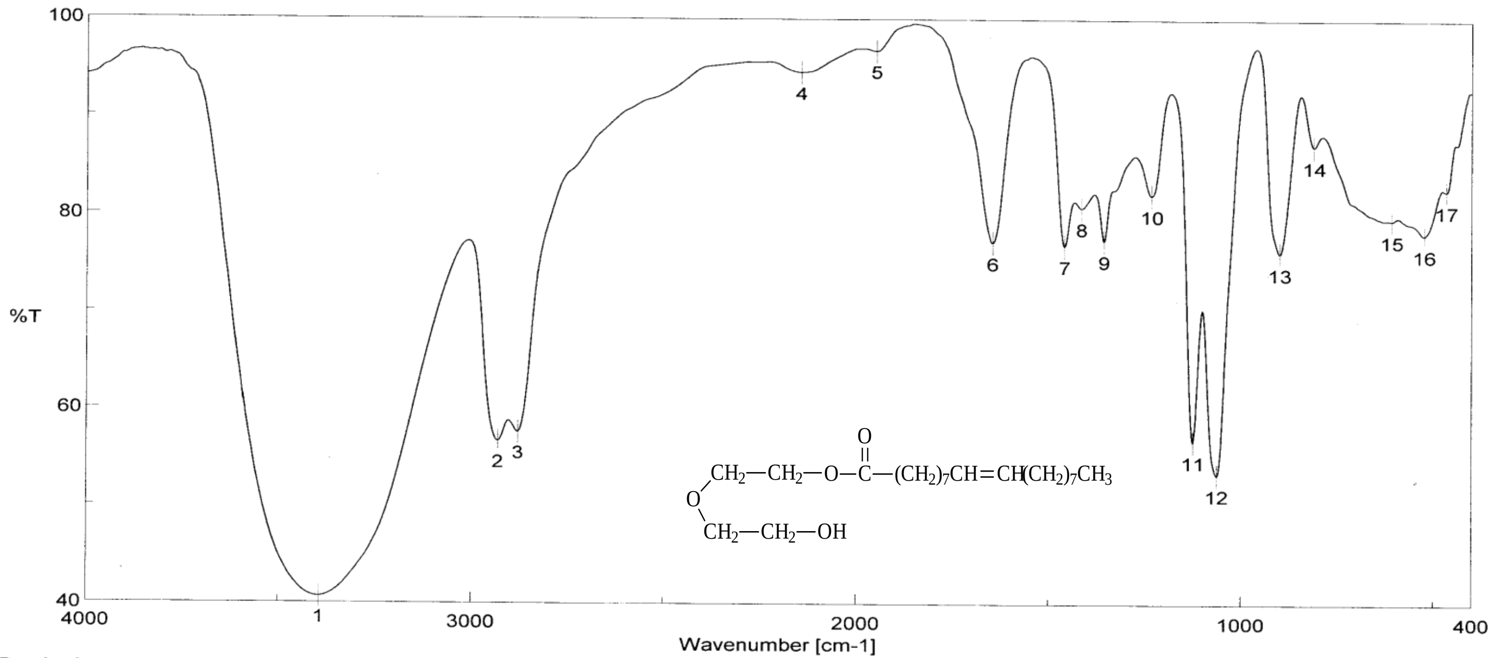
Fig (3-3) Infra-red Spectrum of fatty acid ester 5



$CH_3\ (CH_2)_{16}COOCH_2CHOHCH_2OH$

M.WT = 358

Fig (4-3) Mass Spectrum of fatty acid ester 5



[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3394.1	40.662	2	2931.27	56.6085	3	2879.2	57.5551	4	2143.49	94.4795
5	1948.72	96.6998	6	1645.95	77.117	7	1458.89	76.7836	8	1414.53	80.658
9	1355.71	77.3319	10	1232.29	81.9641	11	1124.3	56.6777	12	1062.59	53.2678
13	900.594	76.0874	14	811.885	87.0006	15	609.396	79.4781	16	524.543	78.0126
17	466.689	82.5147									

Fig (5-3) Infra-red Spectrum of fatty acid ester 7

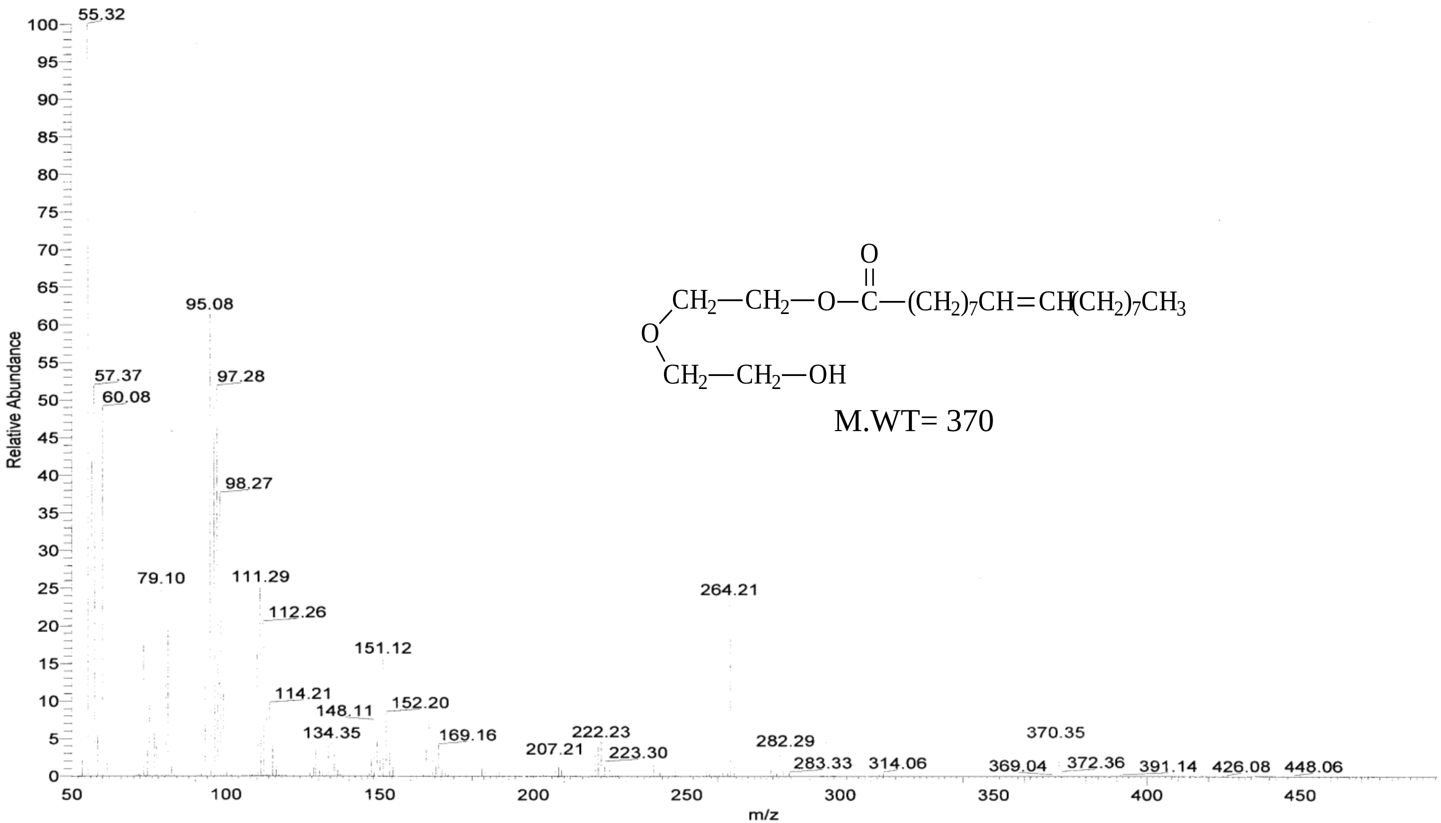
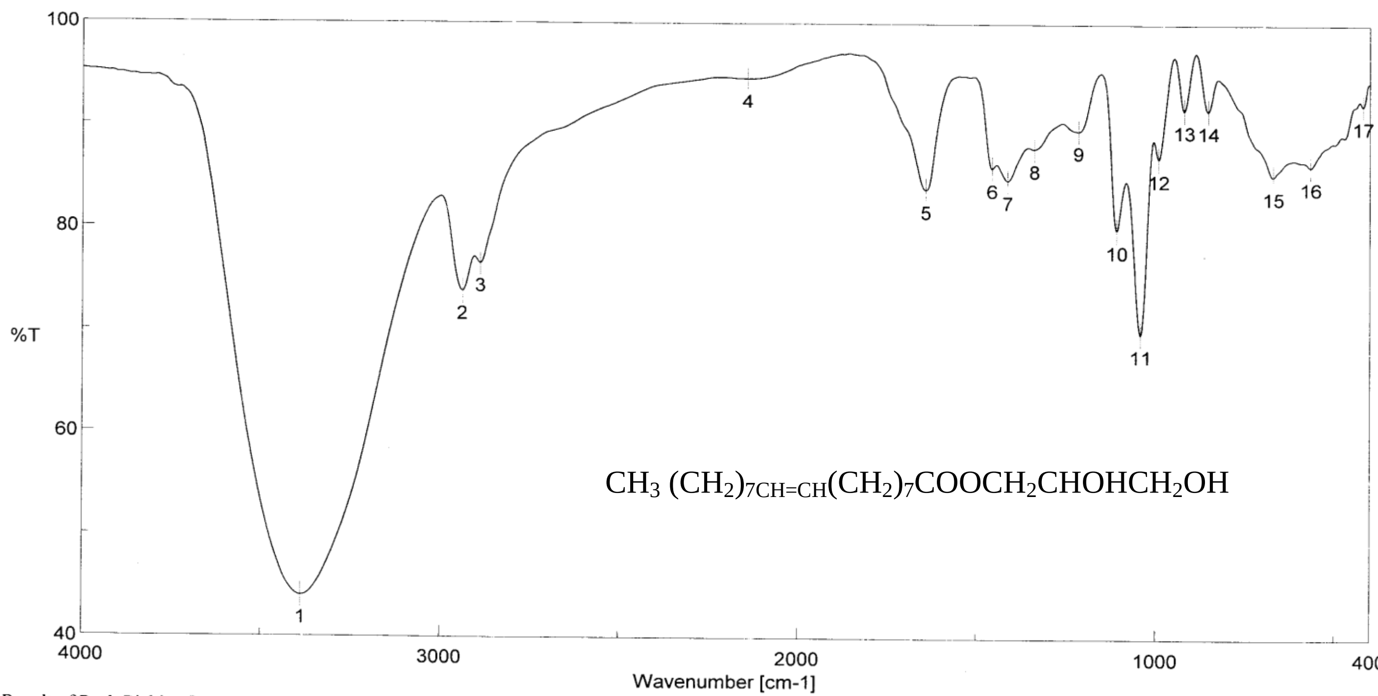


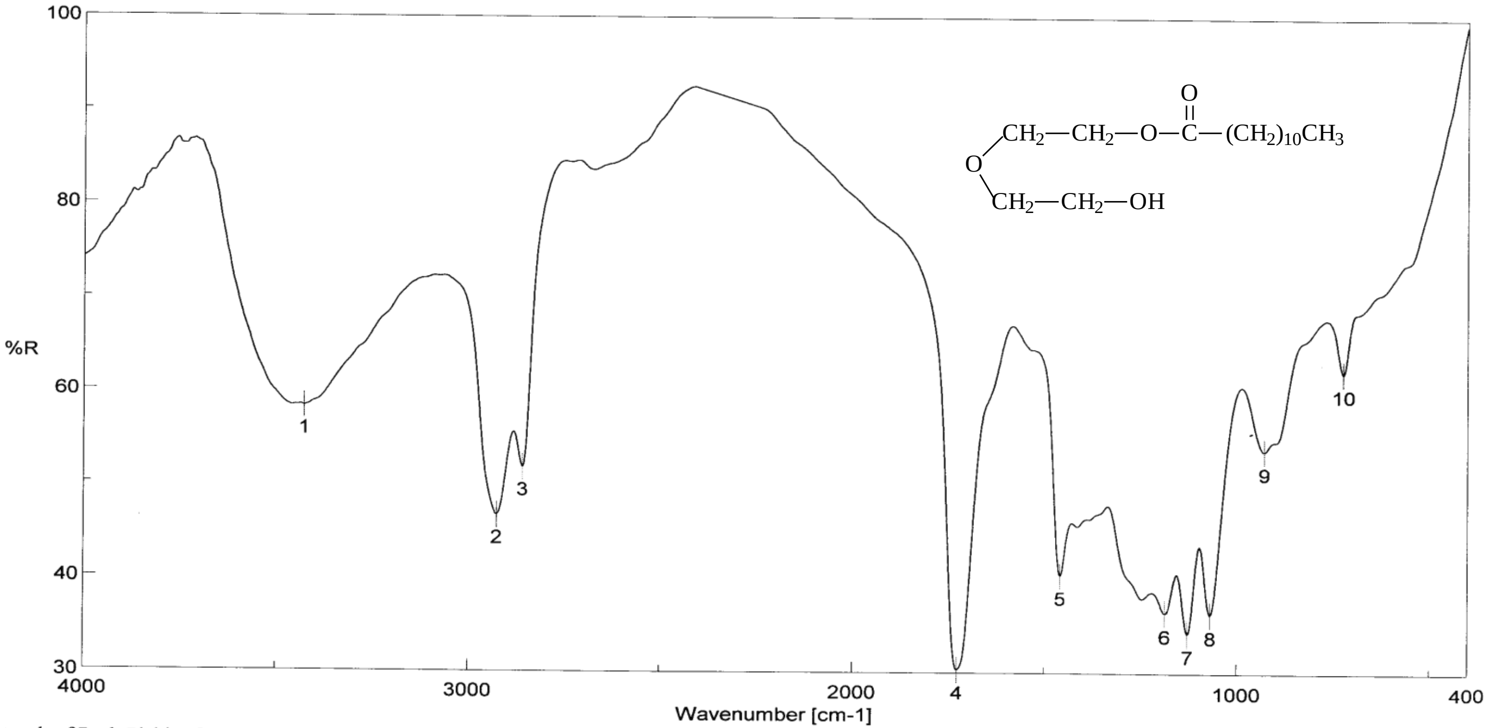
Fig (6-3) Mass Spectrum of fatty acid ester 7



[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3388.32	43.9789	2	2938.02	73.7729	3	2887.88	76.4654	4	2141.56	94.5221
5	1643.05	83.7365	6	1456.96	85.8298	7	1413.57	84.6714	8	1339.32	87.7283
9	1216.86	89.4996	10	1108.87	79.8601	11	1042.34	69.7555	12	992.196	86.7851
13	921.807	91.5491	14	854.311	91.5031	15	672.071	85.1204	16	566.969	86.0863
17	419.442	92.0411									

Fig (7-3) Infra-red Spectrum of fatty acid ester 8



esult of Peak Picking]

.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
	3426.89	58.2411	2	2926.45	46.5815	3	2859.92	51.7123	4	1726.94	30.3447
	1458.89	40.3377	6	1186.01	36.366	7	1127.19	34.2269	8	1068.37	36.2294
	929.521	53.6419	10	724.139	62.0403						

Fig (8-3) Infra-red Spectrum of compound

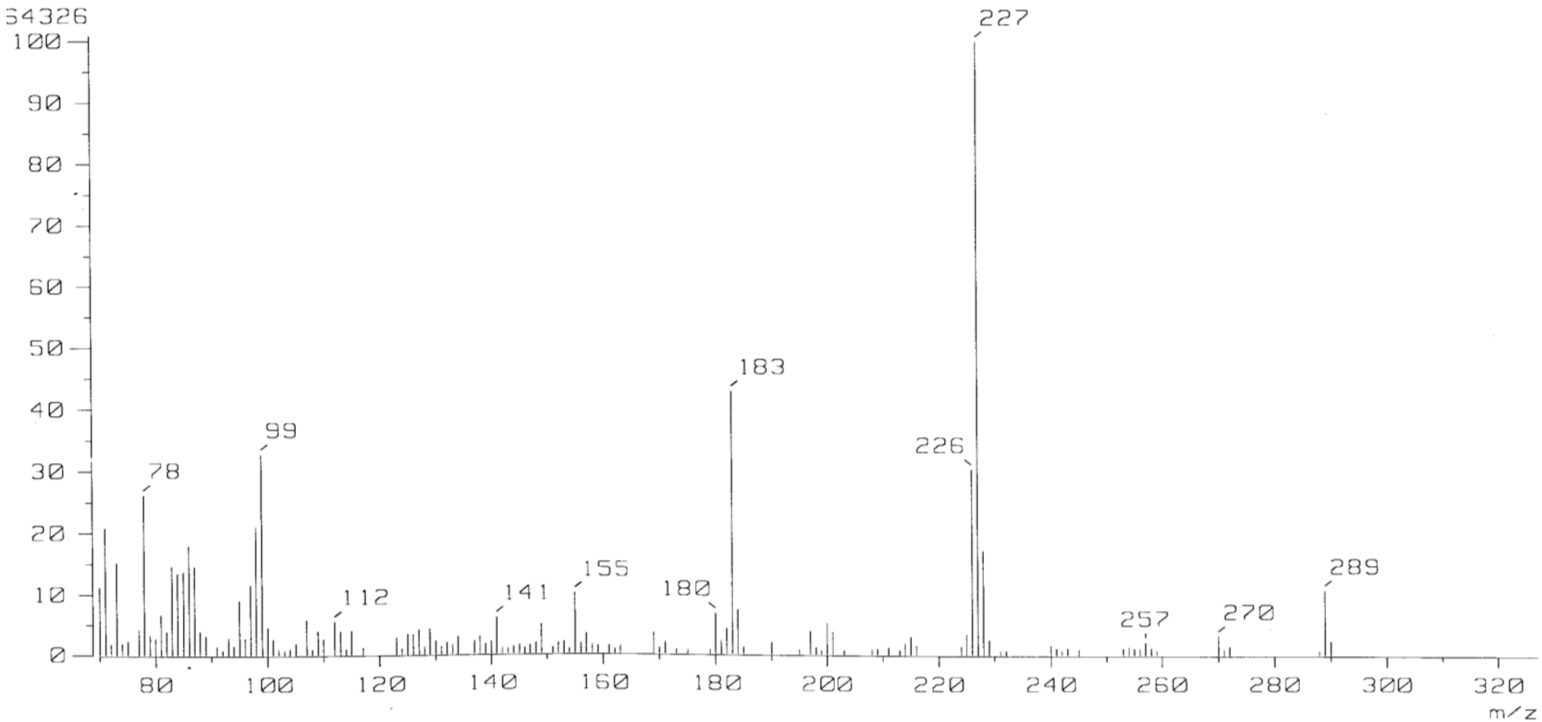
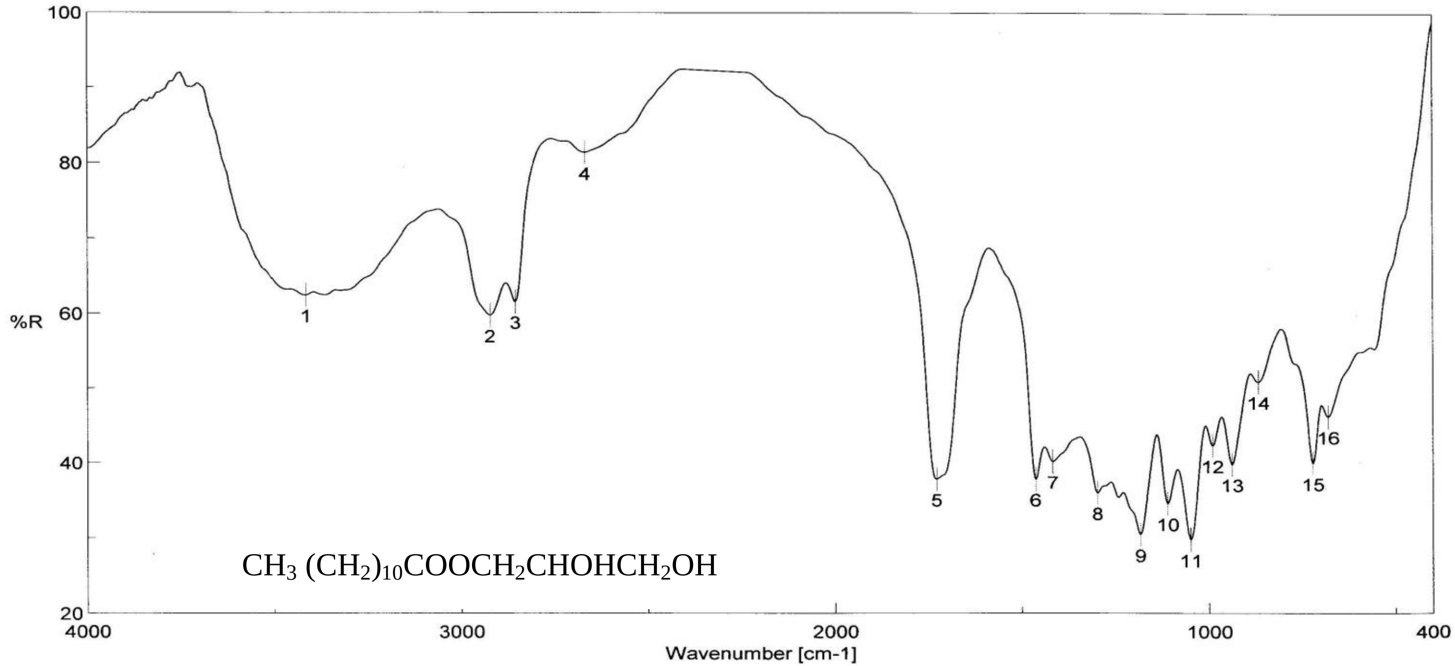


Fig (9-3) Mass Spectrum of fatty acid ester 10



[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3417.24	62.4339	2	2922.59	59.7715	3	2856.06	61.5694	4	2668.03	81.3751
5	1728.87	37.8379	6	1462.74	37.8253	7	1417.42	40.1882	8	1297.86	35.9762
9	1183.11	30.4121	10	1110.8	34.5419	11	1049.09	29.7653	12	991.232	42.273
13	939.163	39.7649	14	868.774	50.8412	15	722.211	39.8891	16	680.749	46.1533

Fig (10-3) Infra-red Spectrum of fatty acid ester 11

1.1.b- preparation of anionic surfactants:

The same idea was applied to the reaction of the three long chain fatty acids with sodium hydroxide to give the corresponding salt, which were considered as surfactants that constitute an important class for manufacturing pesticides.

$$RCOOH + NaOH \xrightarrow[-H_2O]{\Delta} RCOONa$$

12a, $R = (CH_2)_{16}CH_3$ **13a-c**

b, $R = (CH_2)_7CH{=}CH(CH_2)_7CH_3$

c, $R = (CH_2)_{10}CH_3$

3/1/2- Determination of physico-chemical properties of surfactants:

3/1/2/1- Solubility and hydrophilic lipophilic balance (HLB)

The most important requirement in formulating pesticide is the solubility of surfactants in solvent. Data in table (1-3) show that, all prepared nonionic surfactants were insoluble in water but they show different solubility in xylene and acetone. The maximum solubility values in xylene and acetone occurred in case of diethylene glycol mono oleate 83.33, 55.55, respectively while the minimum value occurred in case of, glycerol mono stearate and the recorded data were 3.125 and 2.85, respectively. **Zaazo *et al.*, (1966)** demonstrated that local aromatic solvents such as xylene had higher solvency than aliphatic solvents. The all prepared anionic surfactants were insoluble in xylene and acetone but they soluble in water except sodium stearate partially soluble by heat.

On the other hand, results in table (1-3) indicated that, all prepared nonionic surfactants have 1-3 HLB which have no dispersibility in water. Also, the results showed that, the sodium oleate and sodium laurate have the highest HLB value (15-18) which could be considered it as solubilizers because they are complete soluble in water.

3/1/2/2- Free acidity or alkalinity

Data presented in table (2-3) indicated that, all tested non ionic surfactants (esters) have weakly acidic nature, so it is suitable in case of pesticides which have slightly acidic nature or neutral to avoid chemical reaction. While the anionic surfactants have the basic nature.

Table (1-3): The solubility and HLB of the prepared surfactants.

Surfactants	HLB	Solubility in water %(wt. /v.)	Solubility in acetone %(wt./v.)	Solubility in xylene %(wt./.v.)
Glycerol mono laurate	1-3	insoluble	31.25	55.55
Glycerol mono stearate	1-3	insoluble	2.85	3.125
Glycerol mono oleate	1-3	insoluble	7.69	12.5
Diethylene glycol mono laurate	1-3	insoluble	41.66	71.42
Diethylene glycol mono stearate	1-3	insoluble	4	5
Diethylene glycol mono oleate	1-3	insoluble	55.55	83.33
Sodium laurate	15-18	soluble	insoluble	insoluble
Sodium stearate	4-6	Partially Soluble by heat	insoluble	insoluble
Sodium oleate	15-18	soluble	insoluble	insoluble

Table (2-3): The free acidity or alkalinity of prepared surfactants.

Surfactants	Free acidity % as H_2SO_4	Free alkalinity % as NaOH
Glycerol mono laurate	0.245	-
Glycerol mono stearate	0.0196	-
Glycerol mono oleate	0.1127	-
Diethylene glycol mono laurate	0.1862	-
Diethylene glycol mono stearate	0.0294	-
Diethylene glycol mono oleate	0.0392	-
Sodium laurate	-	1.24
Sodium stearate	-	2.63
Sodium oleate	-	0.64

3/1/2/3- Critical micelle concentration (CMC)

The result in table (3-3) showed that, the surface tension of water decreased by adding surfactants and the concentration of surfactants at which no more decrease in surface tension could be obtained is called CMC. The data in table (3-3) showed that, the CMC value of sodium oleate has the maximum value followed by sodium laurate and sodium stearate. The recorded values were 0.8, 0.6 and 0.4 % (wt. /v.), respectively. Whereas, the double bond in sodium oleate increase the CMC value these results are in agreement with those of **Rosen, (2004)** who postulated a carbon-carbon double bond are present in the compounds increases the CMC compared to the corresponding saturated compounds.

Table (3-3): The critical micelle concentration (CMC) of the soluble anionic surfactants.

Surfactants	Surface tension (dyne/cm)	CMC % (wt./v.)
Sodium laurate	22.8	0.6
Sodium stearate	45.3	0.4
Sodium oleate	27.36	0.8

3/2- Using of the prepared surfactants as additives for improving the physico-chemical properties and insecticidal efficiency of candidate insecticides:

3/2/1- Physical compatibility between surfactants and insecticides for:

3/2/1/a- Direct mixed mixtures

The successful emulsifiable concentrate formulation depends on passing the emulsion stability test in soft and hard water where no oil separation occurred and precipitation or cream separation should not exceed than 2 ml at the rate of 5%. All prepared non ionic surfactants with pesticides (selecron and decis) failed in emulsions stability test at different concentrations formed precipitation and cream separation increased than 2ml.

Data in tables (4, 5, and 6-3) showed that, the emulsion stability of tested pesticides alone and mixed with prepared nonionic surfactants at different concentrations. Data present in table (4-3) show that, the fatty acid ester of diethylene glycol and glycerol with sumi alpha were more stable and successfully passed in emulsion stability at concentration 2% and 3% in hard and soft water except glycerol mono laurate. While the all fatty acid esters with sumi-alpha failed in emulsion stability test at concentration 5%.

Results present in table (5-3) indicated, all fatty acids esters with kendo were more stable in emulsion stability at concentration 1% and 2% in hard and soft water except glycerol mono laurate and glycerol mono oleate at concentration 2% in hard water. Also the table showed that, all prepared non-ionic surfactants failed in emulsion stability at concentration 3% and 5% in hard water gives cream separation increased than 2ml.

Data in table (6-3) showed that, all prepared fatty acids esters of glycerol with match successfully passed in emulsion stability test at concentration 0.5% in hard and soft water. While, fatty acids esters of diethylene glycol failed in hard water. Also data showed that, all prepared non ionic surfactants failed in emulsion stability test at concentration (1%, 2%, 3% and 5%) in hard water.

Table (4-3): The emulsion stability of sumi-alpha alone and mixed with prepared non-ionic surfactants at different concentrations.

Treatment	% Surfactant concentration in insecticides	Emulsion stability (ml.cream.sep)	
		HW	SW
sumi- alpha	0.0	2	1
sumi- alpha + GML	5%	10	8
	3%	7	5.5
	2%	6	4
sumi- alpha + GMO	5%	7	5
	3%	2	1
	2%	0.0	0.0
sumi- alpha + GMS	5%	7	4
	3%	2	1
	2%	0.0	0.0
sumi- alpha +DEGML	5%	3	1
	3%	2	1
	2%	0.0	0.0
sumi- alpha +DEGMO	5%	3	1
	3%	2	1
	2%	0.0	0.0
sumi- alpha +DEGMS	5%	3	3
	3%	2	2
	2%	0.0	0.0

S.W = Soft water

H.W = Hard water

Table (5-3): The emulsion stability of kendo alone and mixed with prepared non ionic surfactants at different concentrations.

Treatment	% Surfactant concentration in insecticides	Emulsion stability (ml.cream.sep)	
		HW	SW
kendo	0.0	0.0	0.0
kendo +GML	5%	6	4
	3%	5	3
	2%	4	2
	1%	0.0	0.0
kendo +GMO	5%	5	4
	3%	4.5	2
	2%	3	1
	1%	0.0	0.0
kendo +GMS	5%	4	2
	3%	2.5	1
	2%	1	0.5
	1%	0.0	0.0
kendo +DEGML	5%	3	1.5
	3%	2.5	1
	2%	1	0.0
	1%	0.0	0.0
kendo +DEGMO	5%	3	2
	3%	2.5	2
	2%	0.0	0.0
	1%	0.0	0.0
kendo +DEGMS	5%	3	2
	3%	2.5	1
	2%	0.0	0.0
	1%	0.0	0.0

S.W = Soft water

H.W = Hard water

Table (6-3): The emulsion stability of match alone and mixed with prepared non-ionic surfactants at different concentrations.

Treatment	% Surfactant concentration in insecticides	Emulsion stability (ml.cream.sep)	
		HW	SW
match	0.0	0.0	0.0
match + GML	5%	12	10
	3%	6	5
	2%	5	2
	1%	2.5	1
	0.5%	0.0	0.0
match + GMO	5%	12	10
	3%	6	4
	2%	4	2
	1	2.5	1
	0.5%	0.0	0.0
match + GMS	5%	13	10
	3%	6.5	5
	2%	4	2
	1%	3	1
	0.5%	0.0	0.0
match + DEGML	5%	12	10
	3%	5	4
	2%	3	3
	1%	3	2.5
	0.5%	2.5	2
match + DEGMO	5%	10	9
	3%	6	6
	2%	3	3
	1%	3	1.5
	0.5%	3	1
match + DEGMS	5%	10	8
	3%	5	4
	2%	3.5	3
	1%	3.5	2
	0.5%	2.5	2

The following tests were carried out only for (insecticides-surfactants) mixtures which passed successfully in emulsion test in table 4, 5 and 6-3. Which are free acidity or alkalinity, cold test and accelerate storage that carried out according world specifications.

Results in table (7-3) indicated that all mixtures of sumi-alpha and surfactants passed successfully through all tests according to world specifications for emulsifiable concentrate which are the cream separation should not exceed than 2ml. When the EC added at the rate 5%, it should not show any solid or oily separation when it cooled at 0.0°C (cold test), its free acidity or alkalinity should not exceed than 0.3%. All prepared non-ionic surfactants with sumi-alpha successfully passed in emulsion stability test after heat storage test except glycerol mono oleate and glycerol mono stearate.

Results in table (7-3) indicated that the free acidity of all prepared non-ionic surfactants with sumi-alpha before storage increased compared with pesticide alone. The diethylene glycol mono stearate gave the highest value of free acidity followed by diethylene glycol mono laurate, diethylene glycol mono oleate and glycerol mono stearate. While after heat storage the free acidity of pesticide alone decreased compared to pesticide before storage. The free acidity of all prepared non-ionic surfactants with sumi-alpha after heat storage increased than pesticide alone. The values were fall between 0.0392- 0.225.

Data in table (8-3) showed that, the all prepared non ionic surfactants with kendo were stable and successfully passed in emulsion stability test. Also results indicated that, all treatments were passed in cold stability test. While, all prepared non ionic surfactants with kendo failed in emulsion stability after heat storage test, they formed oil separation and cream separation. The free acidity of all prepared nonionic surfactants with kendo before storage increased compared with pesticide alone. Also, the free acidity of pesticides alone and mixed with tested surfactants after heat storage test increased than before storage. The values were fall between 0.0882 - 0.1372.

Table (7-3): Physical compatibility between sumi-alpha and the prepared nonionic surfactants at 2%.

Treatment	Emulsion stability (ml. cream. sep)		Free acidity % as H_2SO_4 after preparation	Cold test	Accelerate storage		
					Emulsion stability (ml. cream. sep)		Free acidity % as H_2SO_4 after heat storage
	HW	SW			HW	SW	
Sumi-alpha	2	1	0.0882	passed	2	1	0.0392
Sumi-alpha+ DEGMO	0.0	0.0	0.1862	passed	0.5	0.0	0.0784
Sumi-alpha + DEGML	0.0	0.0	0.196	passed	0.0	0.0	0.225
Sumi-alpha + DEGMS	0.0	0.0	0.2156	passed	0.0	0.0	0.2156
Sumi-alpha + GMO	0.0	0.0	0.0882	passed	3	1	0.1176
Sumi-alpha + GMS	0.0	0.0	0.1274	passed	4	2	0.147

Table (8-3): physical compatibility between kendo and prepared nonionic surfactants at 2%.

Treatment	Emulsion stability (ml. cream. sep)		Free acidity % as H_2SO_4 after preparation	Cold test	Accelerate storage		
					Emulsion stability (ml. cream. sep)		Free acidity % as H_2SO_4 after heat storage
	HW	SW			HW	SW	
kendo	0.0	0.0	0.0343	passed	0.0	0.0	0.0882
Kendo+ DEGML	1	0.0	0.147	passed	2-2°o	2	0.245
kendo+ DEGMO	0.0	0.0	0.0686	passed	1-2°o	1	0.1274
Kendo+ DEGMS	0.0	0.0	0.0882	passed	2-2°o	2	0.1274
kendo+ GMS	1	0.5	0.0882	passed	3	1	0.1372

O: oil separation

Results in table (9-3) indicated that, all prepared non-ionic surfactants with kendo were more stable and successfully passed in emulsion stability test before and after heat storage. Results indicated that, all treatments were passed in cold stability test. The free acidity before storage slightly increased compared to pesticide alone. The glycerol mono laurate gave the maximum value and the recorded value was 0.107. The free acidity after heat storage increased compared to pesticide alone and the records range fall between 0.0882- 0.1372.

Results in table (10-3) indicated that, all esters of glycerol with match were successfully passed in emulsion stability test before storage test. While, all esters failed in emulsion stability test after heat storage gave cream separation increased than 2ml. The data showed that, all esters of glycerol with match were passed in cold stability test. The free acidity before storage increased of all tested surfactants with match compared to pesticide alone. While after heat storage, the free acidity of prepared non-ionic surfactants with match decreased compared to pesticide alone. But the glycerol mono stearate gave slightly increase of free acidity compared to match alone.

Table (9-3): physical compatibility between kendo and the prepared nonionic surfactants at 1%.

Treatment	Emulsion stability (ml. cream. sep)		Free acidity % as H_2SO_4 after preparation	Cold test	Accelerate storage		
					Emulsion stability (ml. cream. sep)		Free acidity % as H_2SO_4 after heat storage
	HW	SW			HW	SW	
kendo	0.0	0.0	0.0343	passed	0.0	0.0	0.0882
Kendo+ DEGMO	0.0	0.0	0.049	passed	0.0	0.0	0.1274
kendo+ DEGML	0.0	0.0	0.098	passed	0.0	0.0	0.1274
Kendo+ DEGMS	0.0	0.0	0.0686	passed	0.0	0.0	0.147
kendo+ GMO	0.0	0.0	0.0588	passed	0.5	0.0	0.1176
Kendo+ GML	0.0	0.0	0.107	passed	1	0.0	0.1372
Kendo+ GMS	0.0	0.0	0.049	passed	0.5	0.0	0.1372

Table (10-3): physical compatibility between match and the prepared nonionic surfactants at 0.5%.

Treatment	Emulsion stability (ml. cream. sep)		Free acidity % as H_2SO_4 after preparation	Cold test	Accelerate storage		
					Emulsion stability (ml. cream. sep)		Free acidity % as H_2SO_4 after heat storage
	HW	SW			HW	SW	
Match	0.0	0.0	0.6076	passed	0.0	0.0	0.784
Match+ GML	0.0	0.0	1.078	passed	6	5.5	0.780
Match+ GMS	0.0	0.0	0.637	passed	8	7	0.833
Match+ GMO	0.0	0.0	1.0584	passed	7	5	0.735

3/2/1/b- Tank- mixed mixtures

This method was carried out in case of surfactants solubilized or gave emulsion when mixed with water.

Data recorded in table (11-3) indicated that, the spray solutions of all tested pesticides alone and mixed with tested anionic surfactants passed successfully in emulsion stability test in all types of water.

Table (11-3): The emulsion stability of tank mix anionic surfactants and mixed with tested pesticides at 0.5%.

Treatment	Emulsion stability (ml.cr.sep)	
	HW	SW
kendo	0.0	0.0
Kendo+ sodium oleate	0.0	0.0
Kendo+ sodium laurate	0.0	0.0
Sumi-alpha	0.5	0.1
Sumi-alpha+ sodium oleate	0.0	0.0
Sumi-alpha+ sodium laurate	0.0	0.0
Match	0.0	0.0
Match+ sodium oleate	0.0	0.0
Match+ sodium laurate	0.0	0.0
Silicron	0.0	0.0
Silicron+ sodium oleate	Traces	Traces
Silicron+ sodium oleate	Traces	Traces
Decies	0.0	0.0
Decies+ sodium oleate	2	1
Decies+ sodium oleate	0.5	0.1

3/2/2- Physico-chemical properties of spray solution of pesticides alone and its mixture with additives at field dilution rate.

3/2/2/ a- In case of direct mixing:

Data in table (12-3) demonstrated that, the physical properties of spray solution of tested pesticide alone and its mixture with surfactants at 2%. The sumi- alpha solutions in different types of water with and without tested surfactants succeeded in emulsion stability test and there is no oily separation or creamy layer. The all tested surfactants decrease pH values of spray solution of sumi- alpha, whereas diethylene glycol mono stearate gave maximum decrease in pH value in case of H.W. (5.70), also the same indication was recorded with diethylene glycol mono laurate in case of S.W. (5.60). Decrease in pH values of insecticidal spray solution would lead to increase attraction between spray solution and treated plant and increase its deposit and penetration in the tested surface then will increase the insecticidal efficiency **(Tawfik and EL- Sisi, 1987, Molin and Hirase, 2004).**

For viscosity test all tested surfactants increased the viscosity of sumi- alpha in H.W. and S.W. whereas diethylene glycol mono stearate gave the highest increase of viscosity in H.W. and S.W., the recorded values were 11.95 and 11.21 mpoise, respectively. **Richardson, (1974)** stated that, increasing viscosity of spray solution cause reduction drift and increasing the retention sticking and insecticidal efficiency.

The all prepared nonionic surfactants decreased surface tension values of sumi- alpha. Diethylene glycol mono stearate gave the highest decrease value in surface tension with H.W. and S.W. (35.07 and 33.36 dyne/cm, respectively). Decrease of surface tension of pesticide spray solution give a prediction of increasing wettability and spreading on the treated surface then increasing pesticidal efficiency **(Osipow, 1964)**.

On the other hand, all prepared tested surfactants caused decrease in conductivity in case of H.W. but slightly increase in case of S.W.

Data in table (13-3) determined the physical properties of spray solution of kendo alone and its mixture with surfactants at 1%.The spray solution of kendo alone and mixed with prepared non-ionic surfactants were stable in emulsion stability in hard and soft water. The all tested surfactants decrease pH values of spray solution of kendo. Whereas glycerol mono laurate gave the highest increase of pH in H.W. and S.W., the recorded values were 5.90 and 5.57, respectively. All surfactants decreased surface tension with hard and soft water, whereas diethylene glycol mono stearate gave highest decreased in surface tension, followed by glycerol mono stearate. This decreased in surface tension give a prediction that they will increasing wettability and spreading on the treated surface then increasing pesticidal efficiency (**Furmidge, 1962**). All surfactants increased viscosity of spray solution in H.W and S.W except glycerol mono oleate in soft water. diethylene glycol mono stearate and diethylene glycol mono laurate gave highest increasing in viscosity followed by glycerol mono laurate, diethylene glycol mono oleate and glycerol mono stearate. The increase of the viscocity of the spray solution reduced the drift and increased the retention of spray solution on the surface of plant (**Bode *et al*., 1976**). Also, all prepared tested surfactants caused increased in conductivity, whereas glycerol mono stearate gave the highest increased in conductivity with H.W. and slightly increase in case of S.W. while glycerol mono laurate caused decrease the conductivity in case of S.W. The elevation of the electrical conductivity of spray solution, it possible lead to deionizaton of pesticide formulation and consequence increase its deposit and penetration through the surface of tested plant. Consequently, the pesticidal efficiency of these formulations was increased **(El-Attal *et al*., 1984)**.

Table (12-3): Physico-chemical properties of spray solution of Sumi-alpha alone and its mixture with additives at 2%.

physicochemical properties	Emulsion stability (ml. cream. sep)		pH		Conductivity (μ mhos)		Surface tension (dyne/cm)		Viscosity (mpoise)	
	HW	SW	HW	SW	HW	SW	HW	SW	HW	SW
Sumi - alpha	0.5	0.1	6.08	6.10	885	168.7	39.08	36.97	10.73	10.56
Sumi -alpha + DEGMS	0.0	0.0	5.70	5.82	872	170.7	35.07	33.36	11.95	11.21
Sumi -alpha + DEGML	0.0	0.0	5.78	5.60	867	169.7	36	35.07	10.97	10.73
Sumi -alpha + DEGMO	0.1	0.0	5.73	5.97	871	167.7	36.97	34.2	11.21	10.73

Table (13-3): Physico-chemical properties of spray solution of kendo alone and its mixture with additives at 1%.

physicochemical properties	Emulsion stability (ml. cream. sep)		pH		Conductivity (μ mhos)		Surface tension (dyne/cm)		Viscosity (mpoise)	
	HW	SW	HW	SW	HW	SW	HW	SW	HW	SW
kendo	0.0	0.0	6.18	6.26	864	182.9	35.07	34.2	10.24	10
Kendo+ DEGMS	0.0	0.0	6.07	5.96	884	185.3	31.8	30.4	10.97	10.73
Kendo+ DEGML	0.0	0.0	6.05	5.72	871	183	33.3	31.81	10.89	10.73
Kendo+ DEGMO	0.0	0.0	6.15	5.78	865	184.5	34.2	33.36	10.73	10.65
Kendo+ GMS	0.1	0.0	5.98	5.70	908	183.7	32.57	31.81	10.73	10.24
Kendo+ GML	0.5	0.0	5.90	5.57	898	182	34.2	33.36	10.89	10.24
Kendo+ GMO	0.1	0.0	6.04	5.99	907	186	33.36	32.57	10.73	10

3/2/2/ b- In case of tank mixing:

Data recorded in table (14-3) indicated that the conductivity increased after addition tested surfactants to pesticide solutions**.** Sodium laurate gave the maximum increase in case of hard water solution which increased from 885 to 1700 μ mhos in case of sumi-alpha and increased from 864 to 1600 μ mhos in case of Kendo.

Also sod.laurate caused increasing the pH of pesticide solutions. The pH values increased in soft water more than hard water, the recorded results were 8.02 and 8 for sumi-alpha and kendo, respectively

The results presented in table (14-3) illustrated that the tested surfactants caused decreasing in surface tension of pesticide solutions for all types of water. The sodium laurate surfactant more affected on tested pesticides solutions than sodium oleate. The highest depression occurred in sumi-alpha solutions from 39.08 to 23.18 dyne/cm in case of hard water solution.

For viscosity test, data in table (14-3) showed that the viscosity of the pesticide solutions increased after adding prepared surfactant. The sodium laurate more affected on tested pesticides spray solution than sodium oleate. Whereas sodium laurate gave the highest increase of viscosity in case of kendo and sumi-alpha in hard water solution and the recorded data were 10.75 and 11.21 mpoise, respectively. While the sodium oleate gave the lowest increase of viscosity of kendo and sumi-alpha in case of soft water and the recorded data were and from 10.16 and 10.62 m poise respectively.

Data in table (15-3) demonstrated the physicochemical properties of spray solutions of match, silicron and decies alone and there mixtures with anionic surfactants at 0.5%. The results recorded in table (14-3) indicated that, the sodium laurate gave decreasing in the surface tension with all spray solutions of tested pesticides in hard and soft water. While the sodium oleate increasing the surface tension except sodium oleate with pesticide decies. Sodium laurate gave the maximum decreasing in the surface tension with decies followed by match and silicron in case of hard water. The recorded data were 25.81, 24.42 and 26.30 dyne/cm, respectively. On the other hand the conductivity of pesticides solution increased by adding prepared surfactants, the sodium laurate caused maximum increase in the conductivity of Match solutions followed by Silicron and Decies. The recorded results were 1200, 1300 and 1200μ mhos, respectively in case of S.W solution.

Also, sod.laurate caused increasing the viscosity of pesticides solutions. The highest effect occurred in decies followed by silicron and Match in case of hard water solution, the recorded results were 11.95, 11.77 and 11.21 m poise, respectively. The all tested anionic surfactants increased pH in hard and soft water.

Table (14-3): Physico-chemical properties of spray solutions of kendo and sumi-alpha alone and with tank mixed anionic surfactants at 0.5%.

Treatment	pH		Conductivity (µ mhos)		Surface tension (dyne/cm)		Viscosity (mpoise)	
	HW	SW	HW	SW	HW	SW	HW	SW
Kendo	6.18	6.26	864	182.9	35.07	34.2	10.24	10
Kendo+ Sod.oleate	6.25	7.44	1400	1000	30.4	28.5	10.70	10.16
Kendo+ sod.laurate	7.85	8	1600	1200	23.58	22.42	10.75	10.24
Sumi-alpha	6.08	6.10	885	168.7	39.08	36.97	10.73	10.56
Sumi-alpha+ Sod.oleate	6.31	7.53	1420	990	32.57	29.73	11.05	10.62
Sumi-alpha+ sod.laurate	7.85	8.02	1700	1100	23.18	21.71	11.21	10.73

Table (15-3): Physico-chemical properties of spray solutions of match, silicron and decies alone and with tank mixed anionic surfactants at 0.5%.

Treatment	pH		Conductivity (µ mhos)		Surface tension (dyne/cm)		Viscosity (mpoise)	
	HW	SW	HW	SW	HW	SW	HW	SW
Match	4.83	4.56	877	189	34.2	32.57	10.24	9.75
Match +Sod.oleate	6	7.31	1420	980	36	31.09	10.73	10.24
Match+Sod.laurate	7.65	7.92	1600	1200	26.30	24.87	11.21	10.73
Silicron	3.03	3.29	939	213	30.4	29.7	11.75	11.21
Silicron +Sod.oleate	6.26	7.52	1420	1000	31.81	33.7	10.73	10.24
Silicron +Sod.laurate	7.77	7.95	1600	1300	24.42	23.18	11.70	10.73
Decies	6.29	5.56	913	230	39.08	36.08	10.73	10.24
Decies +Sod.oleate	6.19	7.52	1410	980	34.2	32.57	11.21	10.73
Decies +Sod.laurate	7.78	7.99	1600	1200	25.81	24.42	11.70	11.21

3/2/3- Effect of surfactants as adjuvants on the pesticidal efficiency of some insecticides against cotton leafworm:-

2/3/ a- In case of direct mixing:

Data present in table (16-3) show that, the initial toxic effect as mortality percentages was 100% for all treatments (sumi-alpha alone at complete and 75% of field rate and sumi-alpha + tested surfactants at 75% field rate). According to the mean residual effect, all tested surfactants increased the residual toxicity of sumi alpha at 75% rate against cotton leafworm larvae as compared with sumi alpha alone at 75% rate. Whereas, DEGMS was the most effective surfactant and the recorded mean residual effect more than sumi alpha at complete rate depending on the general mean of mortalities. All tested surfactants increased the insecticidal effect of sumi alpha at 75% rate, the descending order of treatments was sumi alpha + DEGMS, sumi-alpha + DEGML, sumi-alpha + DEGMO, the respective % mortalities were 51.998, 48.66and 46.66. So the most effective surfactant was selected for another field experiment. The experiment was carried out by decreasing the dose of sumi-alpha to 62.5% and mix with the most effective surfactant (diethylene glycol mono stearate). Results in table (16a-3) show that, the addition of diethylene glycol mono stearate increase slightly the initial larval mortality than 62.5% of complete rate but the average residual and general effects were decreased than pesticide alone at complete and 62.5% of complete rate.

It could be concluded that mixture of sumi-alpha with DEGMS and DEGML at 75% of complete rate could be use for controlling cotton leafworms since they gave already the same insecticidal effect of sumi-alpha with complete rate.

Table (16-3): Toxicity of sumi-alpha alone and with direct mixture prepared nonionic surfactants against 4th instars larvae of cotton leafworm.

Treatment	Rate of application	Initial toxic effect %(mortalities)	Residual toxic effect %mortalities after indicated days				Mean residual effect %(mortalities)	General effect % (mortalities)
			3	6	9	12		
Sumi-alpha	1F	100	70	46.66	33.33	6.66	39.1625	51.33
Sumi-alpha	F*	100	60	36.66	23.33	3.33	30.83	44.664
Sumi-alpha + DEGMS	F*	100	70	53.33	30	6.66	39.9975	51.998
Sumi-alpha + DEGMO	F*	100	60	43.33	26.66	3.33	33.33	46.664
Sumi-alpha + DEGML	F*	100	63.33	46.66	30	3.33	35.83	48.664

F: complete rate **F*: 75% of complete rate**

Table (16a-3) Toxicity of sumi-alpha alone and with direct mixture prepared nonionic surfactants against 4^{th} instars larvae of cotton leafworm.

Treatment	Rate of application	Initial toxic effect % (mortalities)	Residual toxic effect %mortalities after indicated days				Mean residual effect %(mortalities)	General effect% (mortalities)
			3	6	9	12		
Sumi-alpha	**62.5F**	**92**	**57**	**29.33**	**12.66**	**3.33**	**25.58**	**38.862**
Sumi-alpha + DEGMS	**62.5F**	**92.5**	**57**	**28.66**	**11.33**	**2.66**	**24.9125**	**38.462**

Results present in table (17-3) show that, all tested surfactants improved the insecticidal efficiency of kendo at 75% of field rate against 4^{th}cotton leafworm larvae. The results revealed that GMS caused the maximum mean residual effect (34.16%) than the other tested surfactants depending on the general mean effect of mortality. The glycerol mono stearate and diethylene glycol mono stearate increased insecticidal efficiency of kendo at 75% rate of complete rate and achieve mortality percentage near to complete rate, the recorded data were 45.998%, 44.664% respectively. Therefore, the most effective surfactants were selected for another field experiment by decreasing the dose of kendo to 62.5% and mix it with the most effective surfactants (GMS and DEGMS). Results in table (17a-3) indicated that, the diethylene glycol mono stearate slightly increased the mean residual and general effect of mortality than pesticide alone at 62.5% of complete rate. While glycerol mono stearate decrease them.

Table (17): Toxicity of kendo alone and with direct mixture additives against 4th instars larvae of cotton leafworm.

Treatment	Rate of application	Initial toxic effect % (mortalities)	Residual toxic effect %mortalities after indicated days				Mean residual effect %(mortalities)	General effect% (mortalities)
			3	6	9	12		
kendo	1F	100	63.33	33.33	23.33	6.66	31.6625	45.33
Kendo	F*	86.66	50	26.66	16.66	3.33	24.1625	36.662
Kendo + DEGMS	F*	93.33	60	40	23.33	6.66	32.4975	44.664
Kendo + DEGMO	F*	90	53.33	26.66	10	10	24.9975	37.998
Kendo + DEGML	F*	93.33	53.33	36.66	16.66	0.0	26.6625	39.996
Kendo + GMS	F*	93.33	63.33	43.33	23.33	6.66	34.1625	45.998
Kendo + GMO	F*	90	50	30	10	0.0	22.5	36
Kendo + GML	F*	90	53.33	40	13.33	3.33	27.4975	39.98

F: complete rate
F*: 75% of complete rate

Table (17a-3): Toxicity of kendo alone and with direct mixture additives against 4th instars larvae of cotton leafworm.

Treatment	Rate of application	Initial toxic effect % (mortalities)	Residual toxic effect %mortalities after indicated days				Mean residual effect %(mortalities)	General effect% (mortalities)
			3	6	9	12		
Kendo	62.5F	77.33	41.66	22.33	10.66	3	19.4125	30.996
Kendo + DEGMS	62.5F	77.66	42.33	22.33	10.33	3	19.4975	31.13
Kendo + GMS	62.5F	77.33	42	22	9.66	2.66	19.08	30.73

2/3/b- In case of tank mixing:

Result in table (18-3) showed that, sodium oleate and sodium laurate increase insecticidal action of kendo at 75% of the recommended field rate of the application and give 93.3% and 96.6% initial larval mortality respectively. The sodium laurate gave the highest increase of mean residual effect compared with that of kendo at complete and 75% of the recommended field rate, the recorded result was 34.995%. So we carried another field experiment by decreasing the dose of kendo to 62.5%. The Result in table (18a-3) indicated that, addition of sodium laurate and sodium oleate slightly increased the initial larval mortality than tested pesticide at 62.5% of complete rate**.** Also, the mean residual and general effects were slightly increased than kendo alone at 62.5% of complete rate.

Results presented in table (19-3) showed that, all additives improved insecticidal action of sumi-alpha at 75% of recommended field rate, they gave 100% initial toxic effect as pesticide alone at complete and 75% field rate of application. The sodium oleate and sodium laurate gaves the maximum mean residual effect than pesticide alone at complete and 75% of field rate of application. The results were 49.99 and 44.98, respectively. Therefore, another experiment was carried out to decrease the dose of pesticide. Data in table (19a-3) indicated that, sodium laurate increased pesticidal efficiency of sumi- alpha at 62.5% of field rate than sodium oleate. Concerning the residual toxic effect, the tested surfactants gave lower values of mean residual effects than pesticide alone at 62.5% of complete rate.

Results in tables (20-3) showed that, the addition of prepared anionic surfactants improved pesticidal efficiency of selecron, match and decies at 75% of field rate against 4^{th} instars larvae of cotton leafworm. Data present in table (20-3) indicated that, sodium laurate gave the highest increasing in initial toxic effect with selecron, decies and match at 75% of field rate, the recorded data were 100, 84.66and 98.33, respectively. Also, sodium laurate cause maximum increase in mean residual and general effect of mortality with the tested pesticides at 75% of field rate.

Table (18): Toxicity of kendo alone and with tank mix additives against 4th instars larvae of cotton leafworm.

Treatment	Rate of application	Initial toxic effect % (mortalities)	Residual toxic effect %mortalities after indicated days				Mean residual effect %(mortalities)	General effect% (mortalities)
			3	6	9	12		
kendo	1F	100	63.33	33.33	23.33	6.66	31.6625	45.33
kendo	F*	86.66	50	26.66	16.66	3.33	24.1625	36.662
Kendo + Sod.Oleate	F*+0.5%	93.33	63.33	40	16.66	6.66	31.6625	43.996
Kendo + Sod.Laurate	F*+0.5%	96.66	66.66	46.66	20	6.66	34.995	47.328

Table (18a): Toxicity of kendo alone and with tank mix additives against 4th instars larvae of cotton leafworm.

Treatment	Rate of application	Initial toxic effect % (mortalities)	Residual toxic effect %mortalities after indicated days				Mean residual effect %(mortalities)	General effect% (mortalities)
			3	6	9	12		
kendo	62.5F	77.33	42	22.33	10.66	3	19.49	31.06
Kendo + Sod.oleate	62.5F+0.5%	78.66	42	22.33	10.33	2.66	19.33	31.196
Kendo + Sod.Laurate	62.5F+0.5%	79	42.33	23.66	11	3.33	20.08	31.864

Table (19-3) Toxicity of sumi-alpha alone and with tank mix additives against 4th instars larvae of cotton leafworm.

Treatment	Rate of application	Initial toxic effect % (mortalities)	Residual toxic effect %mortalities after indicated days				Mean residual effect %(mortalities)	General effect% (mortalities)
			3	6	9	12		
Sumi-alpha	1F	100	70	46.66	33.33	6.66	39.1625	51.33
Sumi-alpha	F*	100	60	36.66	23.33	3.33	30.83	44.664
Sumi-alpha + Sod.Oleate	F*+ 0.5%	100	83.33	66.66	43.33	6.66	49.995	59.996
Sumi-alpha + Sod.Laurate	F*+ 0.5%	100	76.6	60	40	3.33	44.9825	55.986

Table (19a-3): Toxicity of sumi-alpha alone and with tank mix additives against 4th instars larvae of cotton leafworm.

Treatment	Rate of application	Initial toxic effect % (mortalities)	Residual toxic effect %mortalities after indicated days				Mean residual effect %(mortalities)	General effect% (mortalities)
			3	6	9	12		
Sumi-alpha	62.5F	92	57	29.33	12.66	3.33	25.85	38.864
Sumi-alpha + Sod. Oleate	62.5F+0.5%	92	56.55	28.33	10.33	3.33	24.6625	38.13
Sumi-alpha + Sod.Laurate	62.5F+0.5%	93.3	57.33	29	11.66	3.66	25.4125	38.99

Table (20): Toxicity of (selecron, decies and match) alone and with tank mixed anionic surfactants against 4th instars larvae of cotton leafworm.

Treatment	Rate of application	Initial toxic effect % (mortalities)	Residual toxic effect %mortalities after indicated days				Mean residual effect %(mortalities)	General effect% (mortalities)
			3	6	9	12		
selecron	1F	100	68.66	40.66	32.33	8.33	37.495	49.996
selecron	F*	100	55.33	37.66	25.33	5.33	30.9125	44.73
Selecron + Sod.Oleate	F*+0.5%	98.33	51.66	37	22.66	4.66	28.995	42.862
Selecron + Sod.Laurate	F*+0.5%	100	62.66	38.33	24.33	6	32.83	46. 264
Decies	1F	100	5866	29.66	12.33	4.66	26.3275	41.062
Decies	F*	81.33	41	17.33	10.66	3	18.1625	30.796
Decies + Sod. Oleate	F*+0.5%	82.66	47	18	11.66	3	19.915	32.464
Decies + Sod.Laurate	F*+0.5%	84.66	49.33	19.33	12	3.33	20.997	33.73
Match	1F	100	61.33	32.66	19.33	5.33	29.6625	43.73
Match	F*	94.66	50.66	27.66	14.33	3.66	24.0775	38.194
Match + Sod.Oleate	F*+0.5%	94	47.33	26.33	14	3.33	22.7475	36.998
Match + Sod.Laurate	F*+0.5%	98.33	56.33	28.66	14.33	3.66	25.745	40.262

Field experiment was carried out to study the effect of prepared surfactants on the efficiency of tested pesticides against cotton leafworm. The prepared surfactants increased the efficiency of tested insecticides for control cotton leafworm. Whereas, the addition of prepared surfactants to the tested pesticides changes the physico-chemical properties of tested insecticidal spray solutions. These changes lead to increase field performance and insecticidal efficiency then decreasing the recommended field application to 75% of complete rate in case of:

1- Direct mixtures of diethylene glycol mono stearate and glycerol mono srearate with all tested pesticides.

2- Tank mixtures of sodium laurate and sodium oleate with all tested pesticides.

These effects may be due to:-

The increasing of viscosity of tested insecticidal spray solutions would increase spray droplet size, which reduce the movement of the spray mixture from the target plants. These data agree with the result obtained by **McMullan, (2000) and Spanoghe *et al*., (2007).**

The lower surface tension of spray solution might increases the number of smaller uniformly deposited droplets, whereas better spreading on the leaf surface might also increase qualitative deposition, then increase the insecticidal efficiency **(Gaskin *et al*., 2005).** Also the decrease of surface tension leads to decrease the contact angle between the droplets and the epicuticular wax layer for better droplet contact and increase droplet spreading properties, which results in improved quantity and quality of deposition of the spray target surfaces. These effects agree with **Ryckaert *et al*., (2007).**

Also, the decreasing of pH value of insecticide spray solutions lead to increase attraction between spray solution and treated plant leaves surface then lead to increase insecticidal efficiency **(Green and Hale 2005).**

The increase of electrical conductivity of spray solution would lead to deionization of pesticides and increase its deposit and penetrate in the treated plant surfaces, then increase with the pesticidal efficiency **El- Attal *et al*., (1984).**

The surfactants also enhance retention, uptake, and penetration of tested insecticides **(Kudsk *et al*., 2007)** and to increase the spread of spray droplet on target leaf surface.

3/3- Using of prepared non-ionic surfactants as emulsifiers for reworking one of the physically deteriorated pesticide vapathion 57% EC :

The previous tests indicated that the one pesticide vapathion failed to give successful emulsion there for effort should be directed towards reworking the one pesticide.

Improving emulsion stability which done using the prepared non-ionic surfactants as emulsifiers, the first step in this work is determination the solubility of prepared surfactants at different concentration in deteriorated pesticides was done then the emulsion stability test was determined at rate 5% for insecticides alone and for it the solublized mixtures with surfactants. The other physico-chemical properties were determined for successful mixture in emulsion stability according to world specifications.

3/3/1- Using of the prepared surfactants for improving emulsion stability and other physico-chemical properties:

3/3/1/a- The Solubility of nonionic surfactants in pesticide:

Data in table (21-3) showed that, all prepared non ionic surfactants were soluble at concentration 5% in vapathion except glycerol mono stearate and diethylene glycol mono stearate which were soluble at concentration 3%.

3/3/1/b- Emulsion stability of pesticide alone and mixed with prepared non-ionic surfactants.

Data in table (22-3) showed that, the pesticide vapathion alone failed in emulsion stability at rate 5% in hard water since it gave precipitation increased than 2ml. Also, all prepared nonionic surfactants mixed with pesticide vapathion failed in improving emulsion stability at concentration 0.5% and 1% as they gave precipitation increased than 2ml in hard water.

While all treatments successfully passed in emulsion stability in hard and soft water at concentration 2%. After that the cream precipitations increased by increasing the concentrations of surfactants so stopping the concentration at 2%.

3/3/1/c- physico-chemical properties for vapathion 57% EC alone and mixed with the prepared nonionic surfactants.

Results in table (23-3) showed that, mixtures of vapathion with all prepared non ionic surfactants (esters) passed successfully through the emulsion stability test before storage in both hard and soft water compared with pesticide alone which is failed in emulsion stability test. Also, all mixtures passed successfully through the emulsion stability test after heat storage in both hard and soft water except of glycerol mono oleate, diethylene glycol mono oleate and diethylene glycol mono stearate. The results show that, all treatments passed through cold test. For free acidity or alkalinity, all surfactants increased free acidity of pesticide vapathion before storage. The glycerol mono laurate gave highest value of free acidity while glycerol mono stearate gave the lowest value. Also, after heat storage the free acidity of prepared nonionic surfactants with pesticides increased compared with pesticide alone except glycerol mono laurate and diethylene glycol mono oleate.

Table (21-3): The solubility of prepared non ionic surfactants in pesticides

surfactants	Concentration % (wt. /v.)	Vapathion
Glycerol mono laurate	5	Soluble
Glycerol mono stearate	5 3	insoluble soluble
Glycerol mono oleate	5	Soluble
Diethylene glycol mono laurate	5	Soluble
Diethylene glycol mono stearate	5 3	insoluble soluble
Diethylene glycol mono oleate	5	Soluble

Table (22-3): Emulsion stability of vapathion alone and its direct mixture with prepared nonionic surfactants at different concentrations.

Treatment	Concentration of surfactants % (wt. /v.)	Emulsion stability (ml.cream.sep)	
		HW	SW
Vapathion	0.0	3P	Traces
Vapathion + GML	0.5%	3.5p	Traces
	1%	3p	Traces
	2%	2p	Traces
	2.5%	2.5p	1P
Vapathion + GMO	0.5%	3.5p	Traces
	1%	2.5	Traces
	2%	2p	Traces
	2.5%	3p	1p
Vapathion + GMS	0.5%	3p	Traces
	1%	2.5p	Traces
	2%	2p	1p
	2.5%	3p	1p
Vapathion + DEGML	0.5%	4.5p	Traces
	1%	3p	Traces
	2%	1p	0.0
	2.5%	2.5p	Traces
Vapathion + DEGMO	0.5%	4.5	Traces
	1%	3.5p	Traces
	2%	1p	Traces
	2.5%	3p	1p
Vapathion + DEGMS	0.5%	3.5p	Traces
	1%	3p	Traces
	2%	2p	1p
	2.5%	2.5p	1p

Table (23): physico-chemical properties of vapathion alone and mixed with the prepared nonionic surfactants at 2%.

Treatment	Emulsion stability (ml. cream. sep)		Free acidity % as H_2SO_4 after preparation	Cold test	Accelerated storage		
					Emulsion stability (ml. cream. sep)		Free acidity % as H_2SO_4 after heat storage
	HW	SW			HW	SW	
Vapathion	3P	Traces	4.9	passed	3p	Traces	5.39
Vapathion + GML	2p	Traces	7.84	passed	2p	1p	4.41
Vapathion + GMO	2p	Traces	5.88	passed	3p	2p	6.37
Vapathion + GMS	2p	1p	5.782	passed	2p	1p	5.88
Vapathion + DEGML	1p	0.0	7.35	passed	2p	2p	6.37
Vapathion + DEGMO	1p	Traces	6.37	passed	2.5p	2p	4.9
Vapathion + DEGMS	2p	1p	6.86	passed	3p	1p	6.37

3/3/2- Physico-chemical properties of spray solution of pesticide alone and its mixture with emulsifiers:

Data in table (24-3) demonstrate the important role of surfactants to improvement the physico-chemical properties of spray solution of pesticides. Result in this table showed that, all prepared nonionic surfactants with pesticide vapathion passed successfully in emulsion stability in hard and soft water. All prepared nonionic surfactants decrease surface tension values whereas diethylene glycol mono laurate gave highest decrease in surface tension in H.W. and S.W. (29.73 and 29.11 dyne/cm, respectively). On the other hand, all prepared tested surfactants caused decreased in conductivity in case of H.W. and S.W. Also, all prepared nonionic surfactants decreased pH in hard and soft water. For viscosity test all tested surfactants increased the viscosity of vapathion in H.W. and S.W. whereas, diethylene glycol mono laurate gave the highest increase of viscosity in H.W. and S.W. followed by glycerol mono laurate and glycerol mono stearate.

3/3/3- Effect of surfactants as emulsifiers on the pesticidal efficiency of vapathion 57% EC against cotton leafworm.

Results in table (25-3) showed that, the spray solution of vapathion alone and with surfactants at complete field rate gave 100% initial larval mortality. All tested surfactants with vapathion at complete field rate increase average residual effect than pesticide alone at complete field rate. Whereas DEGML gave the highest increase in average residual effect. Data present in table (25-3) explained that, the all tested prepared nonionic surfactants successful in the improvement pesticidal efficiency of vapathion against 4^{th} instars larvae of cotton leafworm.

Table (24-3): physico-chemical properties of spray solution of vapathion alone and its mixture with additives at 2%.

Physico-chemical properties	Vapathion		Vapathion + GML		Vapathion + GMS		Vapathion + DEGML	
	HW	SW	HW	SW	HW	SW	HW	SW
Emulsion Stability (ml. cream. sep)	1p	0.5p	0.5p	Traces	0.5p	Traces	Traces	Traces
pH	2.67	2.50	2.49	2.45	2.62	2.50	2.36	2.35
Conductivity (μ mhos)	875	397	854	370	833	336	865	377
Surface tension (dyne/cm)	32.57	30.4	30.32	29.73	30.4	29.15	29.73	29.11
Viscosity (mpoise)	10.24	10	10.73	10.35	10.26	10.07	10.76	10.43

Table (25-3): Toxicity of vapathion alone and its direct mix with emulsifiers against 4th instars larvae of cotton leafworm.

Treatment	Rate of application	Initial toxic effect % (mortalities)	Residual toxic effect %mortalities after indicated days				Mean residual effect% (mortalities)	General effect % (mortalities)
			3	6	9	12		
vapathion	1F	100	73.33	60	31.66	6.33	42.83	54.26
vapathion + GML	1F	100	85.66	77.33	53.33	21.66	59.495	67.596
vapathion + DEGML	1F	100	87	79.66	59.33	32.33	64.58	71.664
vapathion + GMS	1F	100	76.66	64.33	48.66	17.33	51.745	61.396

F: complete rate