RESULTS AND
[illegible]

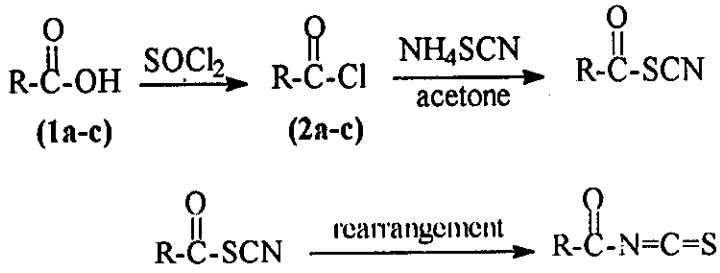
PART (I)

Nonionic surfactants containing heterocyclic moiety from fatty acid isothiocyanate

Various heterocyclic compounds like triazolines, thiazoles, oxazolidines, benzoxazoles, thiazolidines, oxadiazines and triazine are reported to be biologically activity [203-206]. This encourage us to synthesis a novel groups of nonionic surfactnats containing heterocycles as triazole, oxazole, benzoxazole and thiazole derivatives from low cost long chain fatty acids (myristic, palmitic and stearic) isothiocyanate treated with different nucleophiles as phenyl hydrazine, glycine, anthranilic acid (nitrogen nucleophile), o-aminophenol (oxygen nucleophile) and thioglycollic acid (sulphur nucleophile) to produce a novel groups of nonionic surfactants having a double function, antimicrobial and surface active agents by the reaction of these compounds with different moles of propylene oxide (3,5 and 7).

Synthesis of fatty acid isothiocyanate.

Long chain of fatty acids (myristic, palmitic and stearic) isothiocyanate **(3a-c)** are prepared from its acid chloride **(2a-c)** (these were prepared from the corresponding straight chain myristic, palmitic and stearic acids **(1a-c)** and thionyl chloride according to Gautier[207]) the reaction of these acid chloride with ammonium thiocyanate in dry acetone [208-212]. The produced thiocyanate rearranges spontaneously to the isothiocyanate **(3a-c)** as the following



(1a-c) (2a-c) (3a-c)

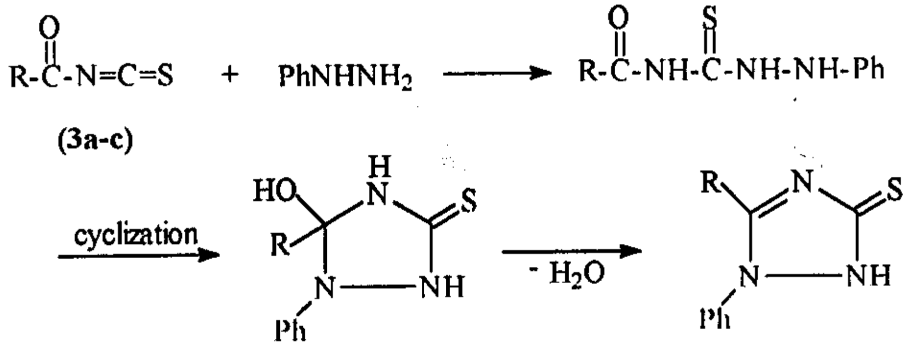
R,a = $C_{13}H_{27}$, R,b = $C_{15}H_{31}$, R,c = $C_{17}H_{35}$

The isothiocyanate **(3a-c)** were prepared insitu during the reaction to prevent its decomposition.

Synthesis of heterocyclic compounds from fatty acid isothiocyanate

1-Synthesis of 1,2,4-triazolinyl-5-thione derivatives via the reaction of isothiocyanate (3a-c) with phenyl hydrazine

When the solution of isothiocyanate **(3a-c)** in acetone (prepared in situ) was treated with phenyl hydrazine, a compound with low melting point was separated. The reaction takes place via the addition of phenyl hydrazine to isothiocyanate **(3a-c)** to give intermediate which undergoes cyclization followed by dehydration to give 3-alkyl-2-phenyl-1,2,4-triazolinyl-5-thione **(4a-c)**.



(3a-c) (4a-c)

R,a = $C_{13}H_{27}$, R,b = $C_{15}H_{31}$, R,c = $C_{17}H_{35}$

IR spectrum of **(4c)** shows bands in cm^{-1} for νNH at 3229, νC=N at 1600, νC=S at 1390 and νCH's of alkyl chain in region (2920-2850) and the characteristic band of triazole ring[213] in region (1520-1450-1410). (*cf.* fig.1). ^{1}HNMR spectrum of **(4b)** was assigned as the following δ 's at 0.8 (t, 3H, terminal CH_3), 1.1-1.3 (m, 28H, CH_2 in alkyl chain), (7.0-7.3) (m, 5H, ArH) and 7.8 (s, 1H, NH) which disappeared by addition of D_2O. (*cf.* fig.24). Mass spectrum of **(4c)** shows (M^{+}-1) at (414,3.6 %) and base peak at m/z = 57, 100 %. (*cf.* fig.40. chart 1).

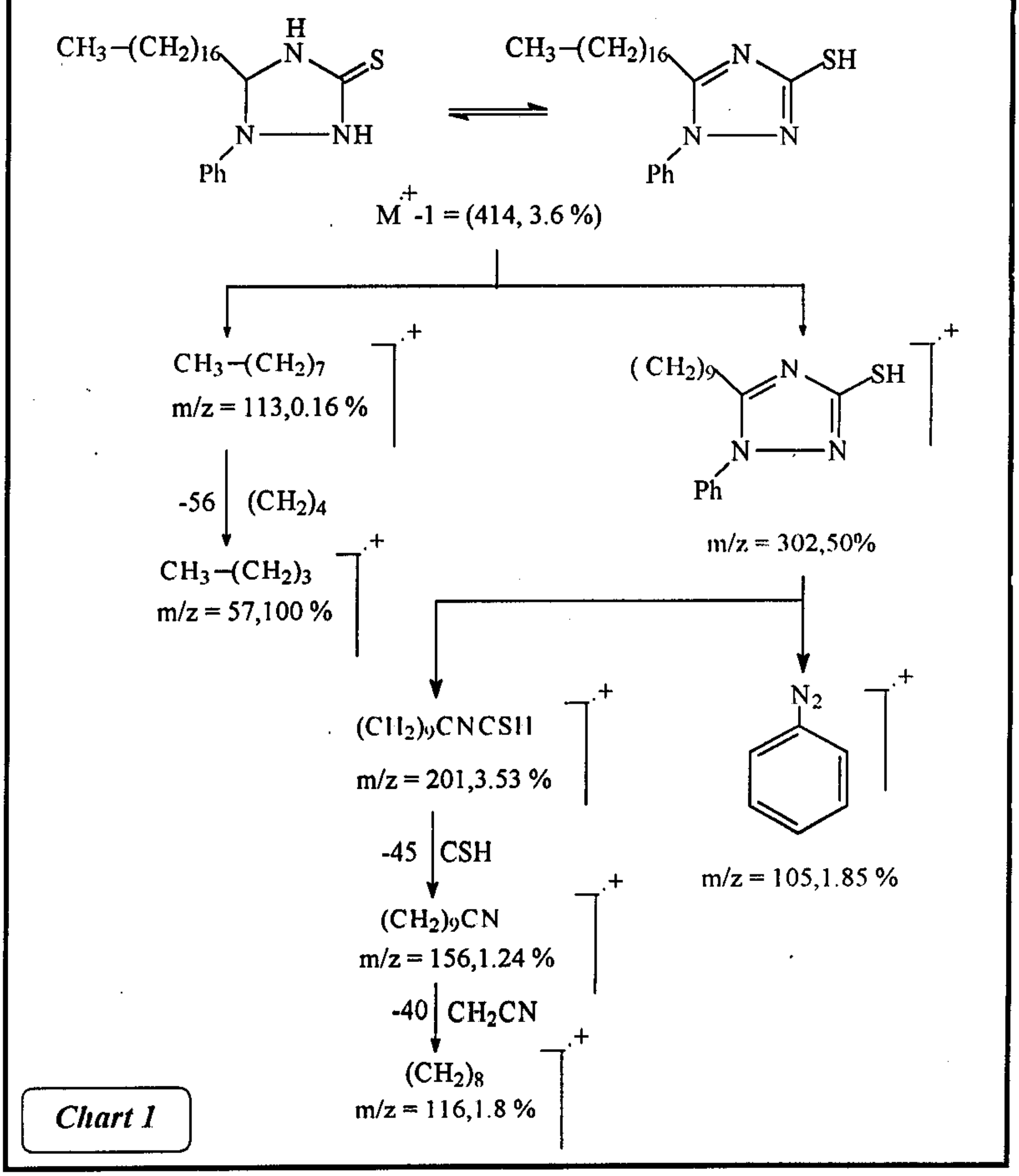
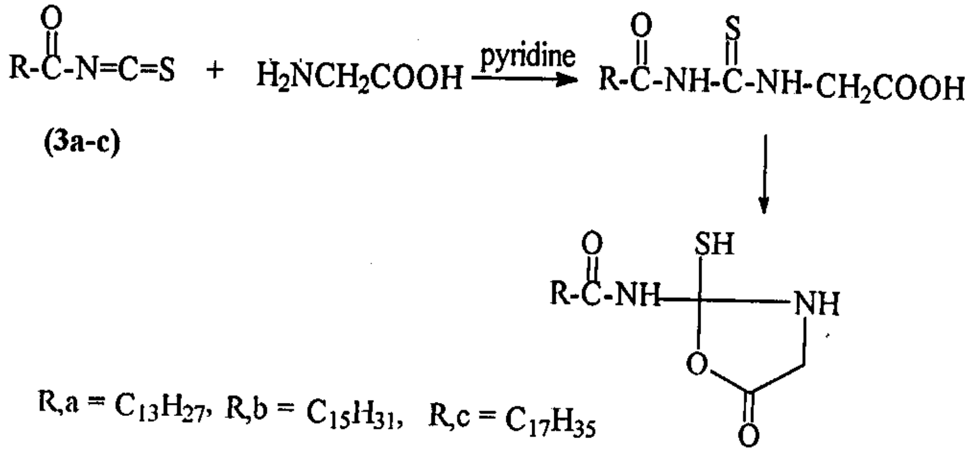


Chart 1

2-Synthesis of 1,3-oxazolidine derivatives via the reaction of isothiocyanate (3a-c) with glycine.

Glycine reacts with isothiocyanate **(3a-c)** in the presence of pyridine as a base to produce thiourea derivatives which cycliczed to 2-amidoalkyl-2-thiol-1,3-oxazolidin-5-one **(5a-c)**.



(3a-c)

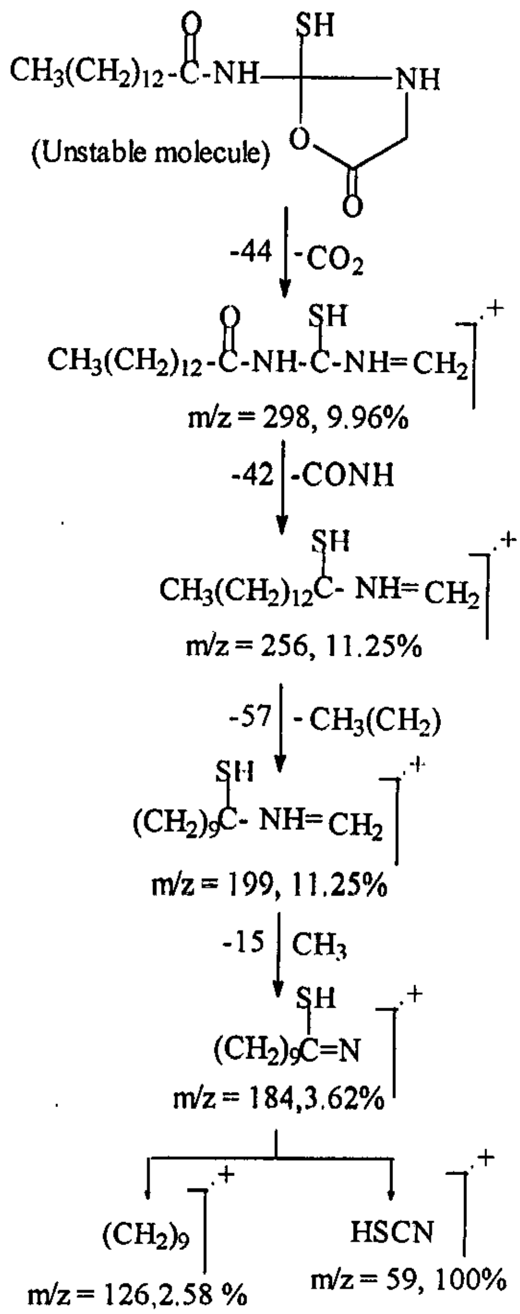
R,a = $C_{13}H_{27}$, R,b = $C_{15}H_{31}$, R,c = $C_{17}H_{35}$

(5a-c)

IR spectrum of **(5a)** which shows the following bands in cm^{-1} for $\nu NH^{'s}$ at 3392, 3188, νSH at 2049, $\nu C{=}O^{'s}$ at 1780 for cyclic amide and 1643 for aliphatic amide, and $\nu CH^{'s}$ of alkyl chain in region (2920-2850). (*cf.* fig.2).

^1H NMR spectrum of **(5b)** shows signals at δ = 0.8 (t, 3H, terminal CH_3), 1,2-1,3 (m, 28H, CH_2 in chain), 5.4 (broad s, 1H, SH) and 5.8 (broad s, 1H, NH).(*cf.* fig.25).

Mass spectrum of **(5a)** shows no molecular ion peak but shows ion peak m/z = 298, 9.9 % corresponding to M^+- CO_2, and the base peak m/z = 59, 100 % corresponding to HSCN gruop. (*cf.* fig.41.chart 2).

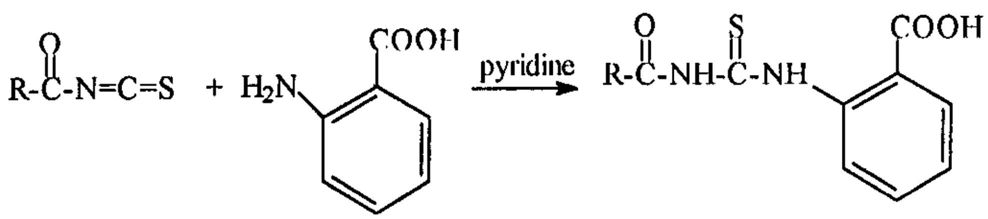


SH
$CH_3(CH_2)_{12}$-C-NH
NH
O
(Unstable molecule)
O
O
-44
- CO_2
O
SH
$CH_3(CH_2)_{12}$-C-NH-C-NH=CH_2
m/z = 298, 9.96%
-42
-CONH
SH
$CH_3(CH_2)_{12}$C- NH=CH_2
m/z = 256, 11.25%
-57
- $CH_3(CH_2)$
SH
$(CH_2)_9$C- NH=CH_2
m/z = 199, 11.25%
-15
CH_3
SH
$(CH_2)_9$C=N
m/z = 184,3.62%
$(CH_2)_9$
m/z = 126,2.58 %
HSCN
m/z = 59, 100%

Chart 2

3-Synthesis of quinazoline-2-thione -4-one derivatives via the reaction of isothiocyanate (3a-c) with anthranilic acid followed by cyclization.

Addition of anthranilic acid to isothiocyanate **(3a-c)** leads to formation of N-(O-carboxyphenyl)-N'-(alkanoyl) thiourea **(6a-c)**.



(3a-c) **(6a-c)**

R,a = $C_{13}H_{27}$, R,b = $C_{15}H_{31}$, R,c = $C_{17}H_{35}$

IR spectrum of **(6a)** exhibits νOH of acid and νNH's in region (3500-3300), νC=O of acid at 1700 and νC=O of amide at 1640, νC=S at 1340 and CH's of alkyl chain in region (2920-2850) cm^{-1} (*cf.* fig.3).

^{1}HNMR spectrum of **(6c)** shows δ' at 0.8 (t, 3H, terminal CH_3), (1.2-1.5) (m, 32H, CH_2 of alkyl chain), (6.5-7.2) (m, 4H, ArH), (8.8) (s, 1H, NH), 9.3 (s, 1H, SH) and 9.7 (s, 1H, OH). (*cf.* fig. 26).

Mass spectrum of **(6a)** shows ion peak (M^+ +1) at (407, 3.14 %) and base peak at m/z = 306, 100 %. (*cf.* fig.42).

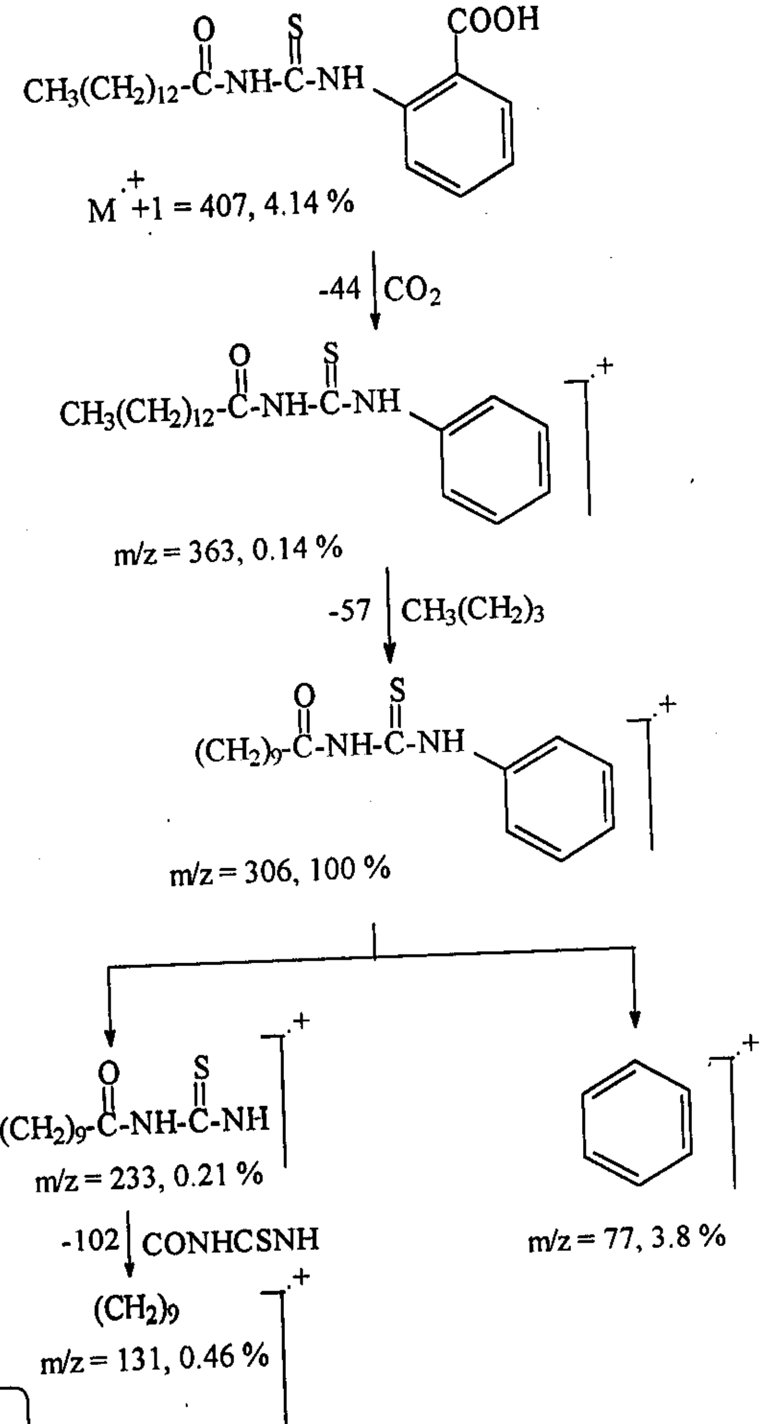
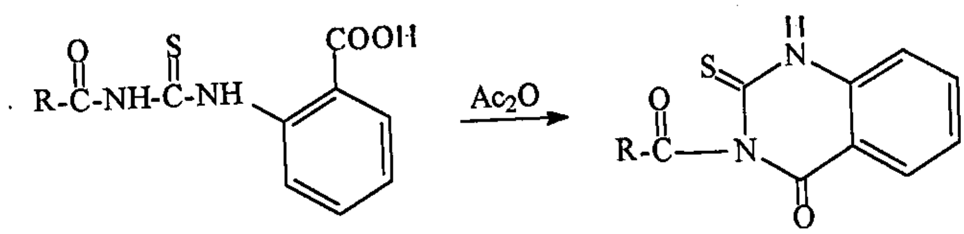

COOH
CH3(CH2)12-C-NH-C-NH
M+1 = 407, 4.14 %
-44 CO2
CH3(CH2)12-C-NH-C-NH
m/z = 363, 0.14 %
-57 CH3(CH2)3
(CH2)9-C-NH-C-NH
m/z = 306, 100 %
(CH2)9-C-NH-C-NH
m/z = 233, 0.21 %
-102 CONHCSNH
(CH2)9
m/z = 131, 0.46 %
m/z = 77, 3.8 %

Chart 3

Cylcization of thiourea derivatives **(6a-c)** with acetic anhydride afforded 3-alkanoyl-1,3-quinazoline-2-thione -4-one **(7a-c)**.



(6a-c) **(7a-c)**

R,a = $C_{13}H_{27}$, R,b = $C_{15}H_{31}$, R,c = $C_{17}H_{35}$

IR spectrum of **(7c)** which shows νNH at 3340, νC=S at 1367, νC=O's at 1766 and 1689, νCH's of alkyl chain in region (2920-2850) cm^{-1}, beside the characteristic bands (210) of quinazoline nuclei at (1630-1620), (1580-1570) and (1515-1480) cm^{-1}.

Mass spectrum of **(7a)** shows a molecular ion peak at M^+ = 388, 4.12 % which fragment to two ion peaks one corresponding to quinazoline nucleus at m/z = 179, 1.85 % and the other to the aliphatic part at m/z = 209.87%. The base peak at m/z = 87, 100 % (*cf.* fig. 43, chart 4).

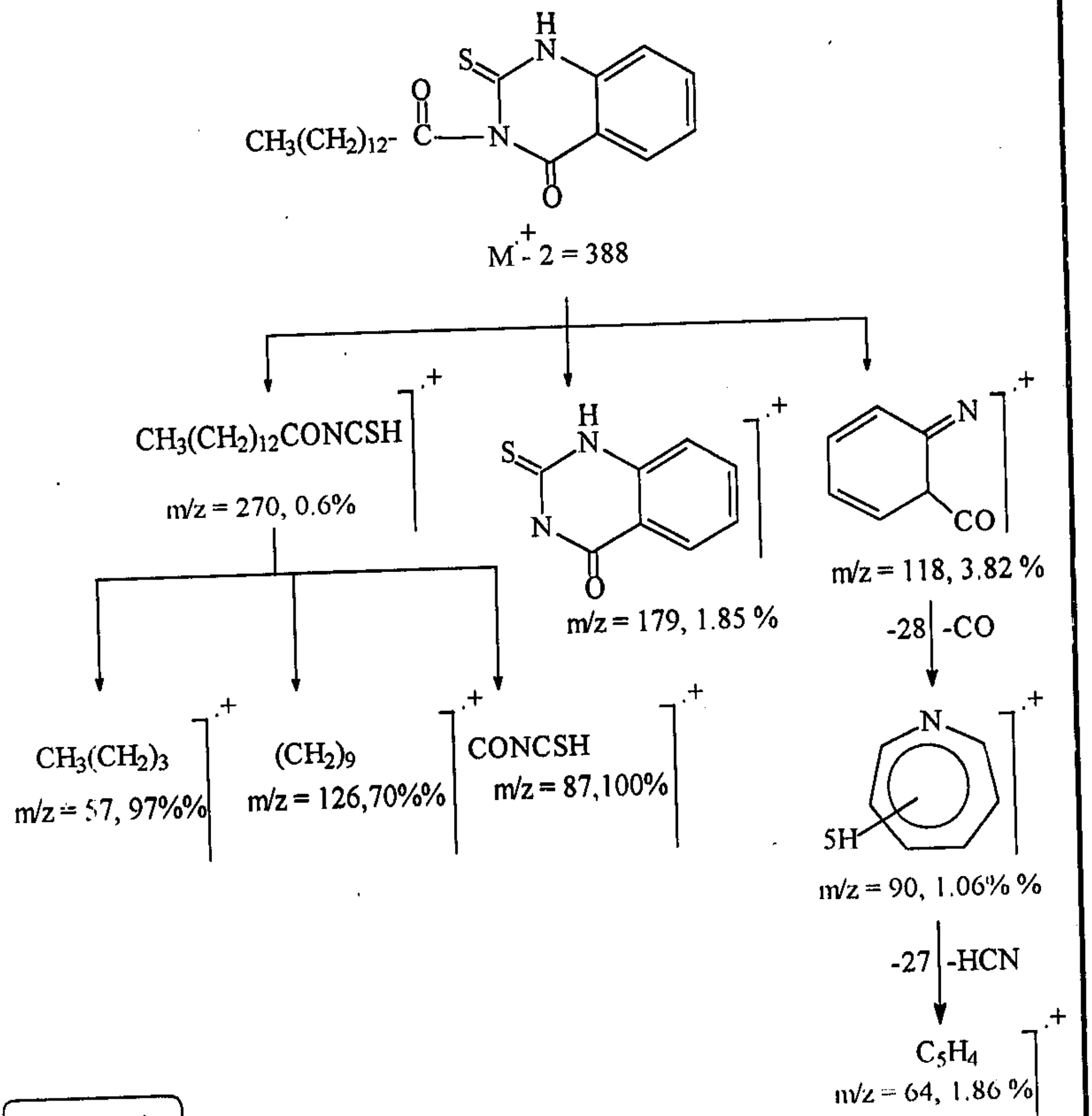
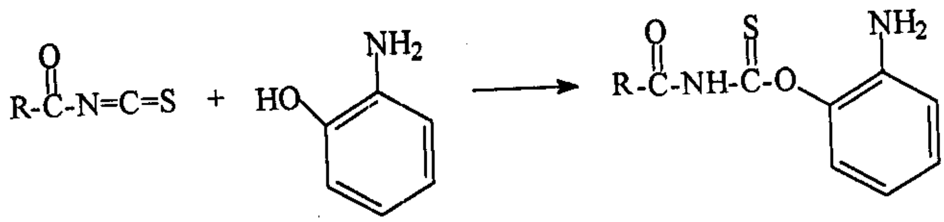

CH3(CH2)12-
$M^{.+}$ - 2 = 388
CH3(CH2)12CONCSH
m/z = 270, 0.6%
m/z = 179, 1.85 %
CO
m/z = 118, 3.82 %
-28 -CO
CH3(CH2)3
m/z = 57, 97%%
(CH2)9
m/z = 126,70%%
CONCSH
m/z = 87,100%
5H
m/z = 90, 1.06% %
-27 -HCN
C5H4
m/z = 64, 1.86 %

Chart 4

4-Synthesis of 1,3-benzoxazole derivatives via the reaction of o-Aminophenol with isothiocyanate (3a-c) followed by Cyclization.

The isothiocyanate **(3a-c)** were attacked by the oxygen-atom of o-aminophenol to form the thiocarbamate derivatives **(8a-c)**.



(3a-c) **(8a-c)**

R,a = $C_{13}H_{27}$, R,b = $C_{15}H_{31}$, R,c = $C_{17}H_{35}$

IR spectrum of **(8a)** shows, νNH's in region (3338,3170), νC=O at 1694, νC=S at 1235, νC-O-C at 1100 and νCH's of alkyl chain in region (2920- 2850) cm^{-1}. (*cf.* fig.4).

^{1}HNMR spectrum of **(8c)** which shows signals at δ (0.9) (t, 3H, terminal CH_3), 1.2-1.5 (m, 32H, CH_2 of alkyl chain), (6.9-7.3) (m, 4H, ArH) and signals at 8.0, 8.5 and 9.3 (s, 3H, NH). (*cf.* fig. 27).

Mass spectrum of **(8a)** shows a molecular ion peak at M^+ = 378, 4.1% and base peak at m/z = 59, 100 % corresponding to NHCS group. (*cf.* fig. 44.chart 5)

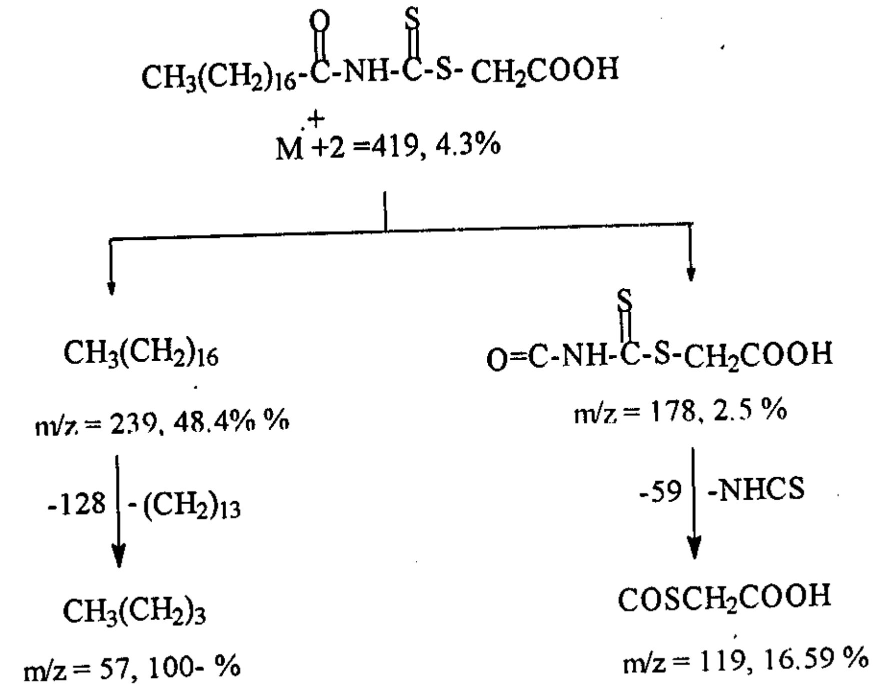
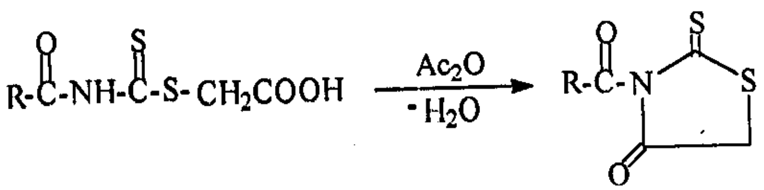


Chart 6

When the adduct (**10a-c**) were cyclized by acetic anhydride, the 3-alkanoyl-1,3-thiazolidine-2-thione-4-one (**11a-c**) were produced.



(10a-c) **(11a-c)**

R, a = $C_{12}H_{27}$, b = $C_{15}H_{31}$, c = $C_{17}H_{35}$

IR spectraum of (**11a**) shows νC=S at 1299, νC=O's centered at 1693 and νCH's of alkyl chain in region (2920-2850) cm^{-1} (*cf.* fig. 6).

Preparation of nonionic surfactants from the synthesized heterocyclic products

The terms of nonionic surfactants refers chiefly to polyoxy-propylene derivatives, they are usually prepared by the addition of different moles (n) of propylene oxide ($n \cong 3$, 5 and 7) to synthesized products which contain one or more active hydrogen atoms to yield polypropenoxylation products. This reaction is one of the principal processes used to introduce hydrophilic functional groups into an hydrophobic organic moiety.

Nonionic surfactants find diverse applications, both in industry and in the home. Their moderate foaming and good detergency are employed in a variety of ways in leather industry. It is used to accelerate soaking, and liming is improved by the addition of wetting agents [215]. Also nonionic surfactants are used extensively because of their good detergency, easy rinsing and low foaming in cleaning of milk and beer bottles.

The structures of the synthesized nonionic surfactants were confirmed via IR and ^{1}HNMR spectra e.g.

IR spectrum of (4a) after the addition of propylene oxide, showed, two broad bands at 1132 cm^{-1} and 923 cm^{-1} characteristic for νC-O-C ether linkage of polypropenoxy chain, beside the original bands of the compound. (*cf.*fig. 8).

^{1}HNMR spectrum of (4a) after the addition of propylene oxide, showed, the protons of propenoxy group were assigned as a broad multiple signals in the region (3.2-3.7) ppm, beside the other protons of the compound. (*cf.*fig. 28)

Surface active properties of nonionic surfactants

The surface active and related properties, including, surface and interfacial tension, cloud point, wetting, emulsification properties, foaming and CMC were investigated systematically in order to evaluate the possible application of these products in the different industrial fields.

1- Surface and interfacial tension.

The surface and interfacial tension of the prepared nonionic surfactants are recorded in (Table 2). It is evident that, the surfactants with heterocyclic moiety recorded lower values than those prepared from saturated fatty acids, which might be attributed to increasing the hydrophilicity of the molecules as found by [102]. On the other hand, the surface activity is improved by introducing heterocyclic nucleus in the molecules. In generally, these value increases as the mass of hydrophilic groups increase within the range under study and as the alkyl chain length increase as found by [50].

2- Cloud point.

The most efficient use of nonionic surfactants in aqueous systems is by understanding a property called cloud point, which is the temperature at which the aqueous solution of the prepared nonionic surfactants shows turbidity on heating. The cloud points of the synthesized surfactant are shown in (Table 2). The results indicate that the values of cloud point increase by increasing the number of propylene oxide units as found by[57] and decreases by the presence of aromatic ring as found by [216]. So compounds (5a-c) and (10a-c) showed high cloud points.

3- Wetting time.

Nonionic surfactants are among the most powerful wetting agents. All the synthesized surfactants are efficient wetting agents (Table 2). It was reported that nonionic with a low propylene oxide content have been found to be the most efficient wetting promoter, and increased as the alkyl chain length increased as found by [217].

4- Emulsifying properties.

Studies are still being carried out on the utilization of surfactant in emulsion formulation, which is of immense importance to technological development. The data in (Table 2) show that greater emulsifying properties were obtained with derivatives containing propylene oxide units incorporated into their structure, where the emulsifying properties increase with decreasing number of propylene oxide units and increase with increasing of alkyl chain as found by [82]. It is very interest noted that the emulsion stability of the prepared compounds is lower than the corresponding propenoxylated fatty acid which not containing the heterocyclic moiety as found by [50], these results, might lead to the application of the surfactants of choice in pesticide and cosmetic formulation.

5- Foam power.

Low foaming power is the characteristic property of nonionic surfactants, which permits some recent applications for these in dyeing auxiliary textile industry. It was reported that; nonionic surfactants have low foam, on the other hand, the foam height of the prepared surfactants increases with increasing propylene oxide unit per molecule of surfactant and the efficiency of surfactants as a foamer increases with increasing alkyl chain length as found by [218].

6- Critical micelle concentration CMC.

The critical micelle concentration (CMC) of the synthesized surfactants was determined by the surface tension method. The data reflect that, the values of CMC increase with increasing number of propylene oxide unit adducts; it decreases with increasing the number of carbon atom in alkyl chain as found by [132] as shown in (Table 2).

Biodegradability.

Biodegradation die-away test in river water gave good or excellent results (Table 3). The results of biodegradation reflect that; the biodegradability decreases with increasing the number of propylene oxide units; or the number of methylene groups in the alkyl chain as found by[219]. This leads to the conclusion that a longer propylene oxide chain makes the diffusion of the molecule through the cell membrane and thus also the degradation, more difficult.

Biological activity.

Nonionic surfactants which contain heterocyclic moiety afforded a double function as surface-active agents and antimicrobial activities [102]. So, all the prepared surfactants were tested for their antibacterial activities against the test organisms as represented Gram +ve and –ve bacteria (Bacillus cereus, Bacillus circulans and Antifungal activity against, Aspergillus niger and penicillum notatum respectively), are given in (Table 4), the data show that, the presence of heterocyclic moiety in the prepared nonionic surfactant molecule revealed an increase in the biological activity. It is therefore clear that these surfactants were effective and inhibited the growth of all tested microorganisms.

Table (1): Physical properties of prepared compounds before addition of propylene oxide

No.	M.F.	M.wt	Solvent	Yield %	Color	Analysis data calc./Found %			
						C	*H*	*N*	*S*
4a	$C_{21}H_{33}N_3S$	359	Benz.	62	Yellow	70.19 70.35	9.19 9.35	11.69 11.87	8.92 9.91
4b	$C_{23}H_{37}N_3S$	387	EtOH	65	Yellow	71.31 71.56	9.56 9.82	10.85 11.04	8.26 8.42
4c	$C_{25}H_{41}N_3S$	415	Tol.	68	Yellow	72.27 72.66	9.87 10.11	10.12 10.37	7.72 7.92
5a	$C_{17}H_{32}N_2O_3S$	344	EtOH	55	Pale Yellow	59.31 60.06	9.33 9.55	8.14 8.35	9.31 9.42
5b	$C_{19}H_{36}N_2O_3S$	372	MeOH	58	Pale Yellow	61.29 61.67	9.67 9.83	7.52 7.82	8.65 8.71
5c	$C_{21}H_{40}N_2O_3S$	400	Benz.	52	Pale Yellow	63.08 63.41	10.06 10.22	7.01 7.25	8.00 8.11
6a	$C_{22}H_{34}N_2O_3S$	406	AcOH	65	Yellow	65.12 65.30	8.32 8.62	6.89 7.03	7.88 8.09
6b	$C_{24}H_{38}N_2O_3S$	434	EtOH	62	Yellow	66.35 66.70	8.75 8.95	6.45 6.73	7.37 7.87
6c	$C_{26}H_{42}N_2O_3S$	462	EtOH	68	Yellow	67.53 67.81	9.09 9.29	6.01 6.22	6.92 7.10
7a	$C_{22}H_{32}N_2O_2S$	388	AcOH	60	Brown	68.04 68.24	8.24 8.42	7.21 7.52	8.24 8.48
7b	$C_{24}H_{36}N_2O_2S$	416	AcOH	63	Brown	69.23 69.41	8.65 8.83	6.73 6.91	7.69 7.95
7c	$C_{26}H_{40}N_2O_2S$	444	AcOH	65	Brown	70.27 70.45	9.00 9.41	6.31 6.52	7.21 7.31
8a	$C_{21}H_{34}N_2O_2S$	378	Tol.	70	Red brown	66.66 67.12	8.99 9.22	7.42 7.66	8.46 8.82
8b	$C_{23}H_{38}N_2O_2S$	406	Benz.	73	Red brown	67.98 68.20	9.35 9.65	6.89 7.08	7.88 8.03
8c	$C_{25}H_{42}N_2O_2S$	434	Zyl.	75	Red brown	69.12 69.43	9.67 9.88	6.45 6.73	7.37 7.50

Table (1): Cont.

No.	M.F	M.wt	Solvent	Yeild %	Color	Analysis data calc./Found %			
						C	*H*	*N*	*S*
9a	$C_{21}H_{32}N_2O_2$	344	Benz.	60	Yellow	73.25 73.61	9.34 9.73	8.13 8.34	
9b	$C_{23}H_{36}N_2O_2$	372	Benz.	55	Yellow	74.19 74.70	9.67 9.83	7.52 7.82	
9c	$C_{25}H_{40}N_2O_2$	400	Tol.	58	Yellow	75.0 75.41	10.0 10.33	7.04 7.24	
10a	$C_{17}H_{31}NO_3S_2$	361	MeOH	70	Pale yellow	56.5 56.91	8.58 8.83	3.87 4.12	17.72 17.85
10b	$C_{19}H_{35}NO_3S_2$	389	MeOH	73	Pale yellow	58.61 59.03	8.99 9.32	3.59 3.73	16.45 16.85
10c	$C_{21}H_{39}NO_3S_2$	417	EtOH	76	Pale yellow	60.43 60.91	9.35 9.76	3.35 3.56	15.34 15.77
11a	$C_{17}H_{29}NO_2S_2$	343	EtOH	55	Brown	59.47 59.71	8.45 8.73	4.08 4.12	18.65 18.88
11b	$C_{19}H_{33}NO_2S_2$	371	Benz.	58	Red brown	61.45 61.68	8.89 9.12	3.77 3.93	17.25 17.55
11c	$C_{21}H_{37}NO_2S_2$	399	MeOH	60	Red brown	63.15 63.41	9.27 9.46	3.5 3.86	16.04 16.32
12a	$C_{21}H_{34}N_2OS$	362	Benz.	65	Gray	69.61 70.35	9.39 9.52	7.73 7.92	8.82 8.97
12b	$C_{23}H_{38}N_2OS$	390	EtOH	67	Gray	70.76 71.1	9.74 9.92	7.17 7.31	8.21 8.32
12c	$C_{25}H_{42}N_2OS$	418	EtOH	70	Gray	71.77 72.11	10.04 10.24	6.69 6.88	7.65 7.89

Table (2): Surface properties of nonionic surfactants.

Comp.	n	Surface Tension (dyne/cm) 0.1 %	Interfacial tension (dyne/cm) 0.1 %	Cloud Point °C 1 %	Wetting time (sec.) 0.1 %	Emulsion stability (min.)	Foam height (mm) 1 %	Cmcx10^{-3} mole/l
4a	3	31	8.0	57	48	70	No foam	4.3
	5	33	9.5	70	30	72	109	4.7
	7	35	10.5	78	23	63	122	4.9
4b	3	32	8.5	55	52	80	No foam	3.8
	5	35	10.0	68	33	73	112	4.2
	7	38	11.5	77	25	64	125	4.5
4c	3	33	8.5	54	55	83	90	3.4
	5	37	11.0	66	36	75	118	3.7
	7	39	13.0	75	27	65	130	3.9
5a	3	31	9.0	79	42	111	144	4.6
	5	33	11.5	95	29	87	164	4.8
	7	37	13.0	> 100	21	82	191	5.1
5b	3	33	9.5	73	44	115	145	4.4
	5	35	12.0	87	35	91	170	4.6
	7	37	14.5	98	21	86	195	4.9
5c	3	35	10.0	71	49	120	150	4.2
	5	36	13.0	82	37	95	181	4.5
	7	38	13.5	95	24	89	200	4.7
6a	3	31	9.5	80	41	120	126	3.4
	5	33	10.0	98	35	93	151	3.7
	7	34	11.5	> 100	24	74	195	3.9
6b	3	32	10.0	75	46	125	133	3.0
	5	35	11.0	86	38	96	162	3.3
	7	37	12.5	99	29	76	198	3.6
6c	3	33	10.5	63	51	130	142	2.9
	5	37	12.0	75	41	98	168	3.1
	7	39	13.5	96	32	77	200	3.4
7a	3	30	8.0	66	47	115	No foam	4.0
	5	31	10.5	71	36	93	105	4.3
	7	34	12.0	95	20	73	123	4.7
7b	3	31	8.5	58	49	118	97	3.8
	5	33	11.0	66	38	95	115	4.2
	7	37	12.5	93	26	76	145	4.5
7c	3	32	9.0	55	53	120	117	3.6
	5	36	11.5	61	41	92	136	3.9
	7	39	14.0	81	29	80	150	4.3

n = number of moles of propylene oxide

Table (3): Biodegradability of the Prepared Surfactants.

No.	n	1st day	2nd day	3rd day	4th day	5th day	6th day	7th day
4a	3	59	68	79	84	92	-	-
	5	57	65	74	80	88	96	-
	7	56	61	72	79	85	92	-
4b	3	52	67	76	83	93	-	-
	5	47	63	73	76	86	92	-
	7	45	59	69	74	83	89	96
4c	3	50	62	70	82	93	-	-
	5	45	58	68	75	87	94	-
	7	41	53	66	72	81	86	92
5a	3	63	68	77	83	92	-	-
	5	52	65	76	82	88	97	-
	7	43	57	71	79	85	94	-
5b	3	57	64	73	81	92	97	-
	5	47	59	72	79	87	94	-
	7	40	55	69	78	83	89	96
5c	3	53	62	70	97	86	92	-
	5	47	56	69	72	83	88	-
	7	43	51	76	70	79	83	94
6a	3	53	66	75	85	95	-	-
	5	49	62	72	80	86	96	-
	7	47	59	69	77	83	93	-
6b	3	50	63	71	81	93	-	-
	5	48	59	69	77	80	91	-
	7	45	57	67	74	78	88	96
6c	3	48	60	68	78	89	-	-
	5	45	56	66	73	76	88	-
	7	41	51	64	70	73	85	92
7a	3	53	61	74	83	94	-	-
	5	51	60	67	78	91	-	-
	7	49	57	62	76	88	96	-
7b	3	49	59	70	74	83	-	-
	5	48	52	63	75	87	97	-
	7	45	50	62	74	83	93	-
7c	3	49	55	62	79	87	90	-
	5	46	51	59	67	78	88	-
	7	40	48	57	63	72	85	93

Table (3): Cont.

No.	n	1st day	2nd day	3rd day	4th day	5th day	6th day	7th day
8a	3	53	58	66	80	82	93	-
	5	50	56	63	71	79	86	-
	7	49	54	59	68	65	79	90
8b	3	51	56	63	77	84	95	-
	5	48	54	59	67	79	92	-
	7	45	52	57	63	75	89	-
8c	3	49	54	60	77	80	93	-
	5	48	59	57	65	76	90	-
	7	43	49	54	61	73	86	93
9a	3	55	63	73	82	78	92	-
	5	52	59	70	75	82	88	-
	7	49	54	69	73	79	83	95
9b	3	55	62	71	79	85	93	-
	5	49	57	69	73	83	90	-
	7	47	52	64	71	79	87	92
9c	3	51	60	69	77	84	91	-
	5	48	54	67	70	81	89	-
	7	44	49	65	68	77	85	92
10a	3	57	66	79	89	96	-	-
	5	55	63	73	86	95	-	-
	7	52	59	71	79	88	96	-
10b	3	55	65	77	86	95	-	-
	5	52	58	69	83	91	-	-
	7	49	83	65	74	80	90	-
10c	3	54	63	73	84	95	-	-
	5	48	55	67	79	92	-	-
	7	45	50	61	72	84	93	-
12a	3	55	67	75	85	95	-	-
	5	52	59	71	82	92	-	-
	7	50	56	61	75	88	93	-
12b	3	53	64	72	83	95	-	-
	5	49	57	67	78	87	95	-
	7	47	52	56	71	81	91	-
12c	3	50	62	68	79	92	-	-
	5	47	55	63	72	80	93	-
	7	43	49	45	65	77	91	-

Table (4): Antimicrobial activity of nonionic surfactants.

Compd.	Bacteria		Fungi	
	Bacillus cercus	*Bacillus circulans*	*Aspergillus's niger*	*Penicillum notation*
4a	-	+	+	+
4b	-	+	++	+
4c	+	+	+	++
5a	-	+	+	+
5b	-	+	++	++
5c	+	+	+	++
6a	+	+	++	+
6b	-	-	+	+
6c	-	-	+	+
7a	-	+	+	++
7b	-	-	+	+
7c	-	-	+	+
8a	-	+	+	++
8b	+	-	+	+
8c	+	-	+	+
9a	-	+	-	++
9b	-	+	+	++
9c	+	-	+	+
10a	+	+	+	++
10b	-	+	++	+
10c	+	+	+	++
11a	+	+	+	++
11b	+	+	++	+++
11c	+	-	+	++
12a	-	+	+	+
12b	-	-	+	+
12c	-	-	+	++

(+++) Very strong inhibition, (++) strong inhibition, (+) moderate inhibition.

PART (2)

Nonionic surface active agents containing heterocyclic moiety from fatty acid hydrazide

The hydrazide of long chain fatty acid (myristic, palmitic and stearic) was used as commercial starting material to synthesis some important heterocycles as pyrazoles, thiazoles, oxadiazoles, benzoxazoles, pyridazine and which utilized to prepare a novel groups of nonionic surface active agents having a double function with antimicrobial and surface active properties.

Synthesis of fatty acid hydrazides.

Fatty acid hydrazide **(13a-c)** was prepared from its acid chloride **(2a-c)** through its reaction with hydrazine hydrate

$$\underset{\textbf{(2a-c)}}{R\text{-}\overset{\overset{O}{\|}}{C}\text{-}Cl} \quad + \quad NH_2NH_2 \xrightarrow{\text{acetone}} \underset{\textbf{(13a-c)}}{R\text{-}\overset{\overset{O}{\|}}{C}\text{-}NH\text{-}NH_2}$$

$$R,\ a = C_{13}H_{27},\quad b = C_{15}H_{31},\quad c = C_{17}H_{35}$$

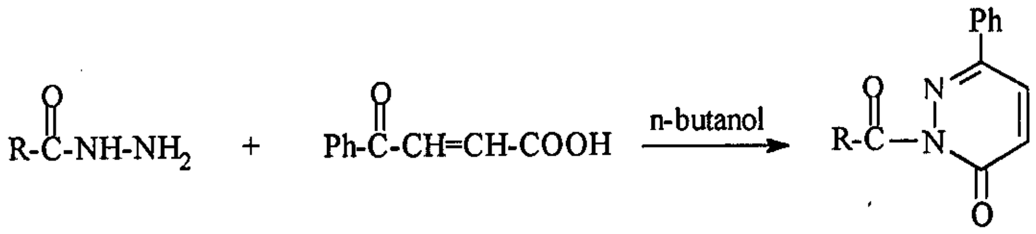
IR spectrum of **(13a)** shows the following bands in cm^{-1}, band's at 3422, 3330 and 3190 for νNH's, strong band at 2359 for the linear structure of the molecule, band at 1691 for νC=O of amide and (2920-2850) for νCH's of alkyl chain (*cf.* fig. 9).

Synthesis of heterocyclic compounds from fatty acid hydrazides.

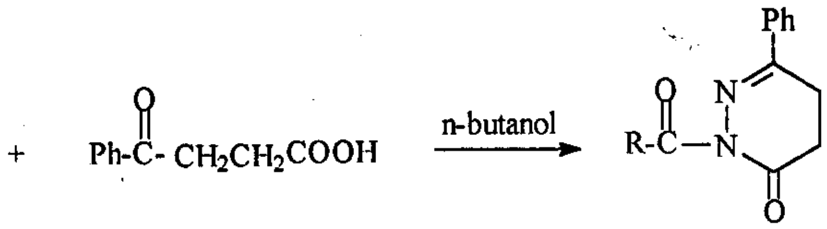
1- Synthesis of pyridazine derivatives via:

a-Reaction of fatty acid hydrazide (13a-c) with β-benzoyl acrylic acid and/or β-benzoyl propionic acid

When a solution of fatty acid hydrazide **(13a-c)** in n-butanol was treated with β-benzoyl acrylic acid and / or β-benzoyl propionic acid produced 2-alkanoyl-6-phenyl-pyridazine-3-one **(14a-c)** and/or 2-alkanoyl-6-phenyl-4,5-dihydro pyridazine-3-one **(15a-c)**.



(13a-c) **(14a-c)**



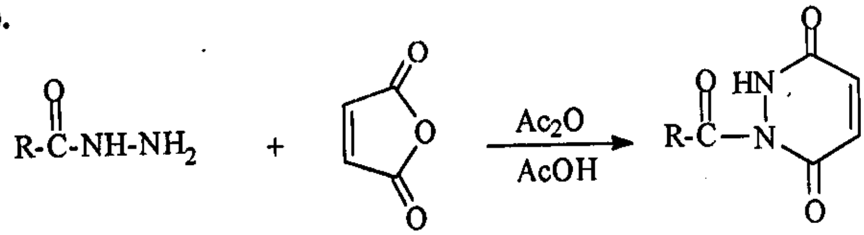
(15a-c)

R , a = $C_{13}H_{27}$, b = $C_{15}H_{31}$, c = $C_{17}H_{35}$

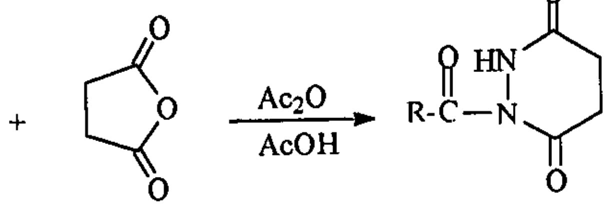
IR spectrum of **(14a)** exhibits, νC=O's at 1701, 1625, νC=N at 1588, νCH's of alkyl chain in region (2920-2850) and the characteristic band [220] of pyridazine ring in region (1560-1490) cm^{-1} (*cf.* fig.10).

b-Reaction of fatty acid hydrazide (13a-c) with maleic anhydride and/or succinic anhydride.

Fatty acid hydrazide **(13a-c)** reacts with maleic anhydride and/or succinic anhydride in acetic anhydride to give 2-alkanoyl-pyridazine-3, 6-dione **(16a-c)** and/or 2-alkanoyl-4,5-dihydro-pyridazine-3,6-dione **(17a-c).**



(13a-c) **(16a-c)**



(17a-c)

R, a = $C_{13}H_{27}$, b = $C_{15}H_{31}$, c = $C_{17}H_{35}$

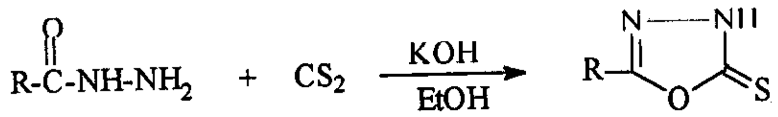
IR spectrum of **(17c)** exhibits, νNH at 3339, νC=O's at 1703 and 1594, νCH olefinic at 1525 and νCH's aliphatic in region (2920-2850) cm^{-1} (*cf.*fig. 11).

^1H NMR spectrum of **(16c)** shows signals, δ 0.9 for (t, 3H, terminal CH_3), δ 1.3 (s, 32H, CH_2 of alkyl chain), δ 6.1 (s, 1H, CH olefinic), δ 9.5 (s, 1H, NH) which disappeared by addition of D_2O (*cf.* fig. 29).

Mass spectrum of **(17c)** shows molecular ion peak at M^+-2 = 378, 0.6 % and show ion peat at m/z = 113, 3.67% corresponding to dihydro-pyridazine dione nucleus.

2-Synthesis of oxadiazole derivatives via the reaction of fatty acid hydrazide (13a-c) with carbon disulphide.

Carbon disulphide reacts with fatty acid hydrazide (**13a-c**) using potassium hydroxide as catalyst in ethyl alcohol to produce 5-alkyl-2-thion-1,3,4-oxadiazole (**18a-c**).



(13a-c) **(18a-c)**

R, a = $C_{13}H_{27}$, b = $C_{15}H_{31}$, c = $C_{17}H_{35}$

IR spectrum of (**18c**) exhibits, νNH at 3228, νC=N at 1598, νC=S at 1414 and νCH's aliphatic in region (2920-2850) and the characteristic bands [220] of oxadiazole ring in region (1190-1150, 1030-1000 and 890-825) cm^{-1}. (*cf.* fig.12).

Mass spectrum of (**18c**) shows molecular ion peak at $M^{+}+1 = 341$, 3.6% which fragmented to ions one corresponding to the side chain of alkyl at 239, 1.8% and the other corresponding to oxadiazole nucleus at m/z = 101,14.0 % (*cf.* fig. 47, Chart 8).

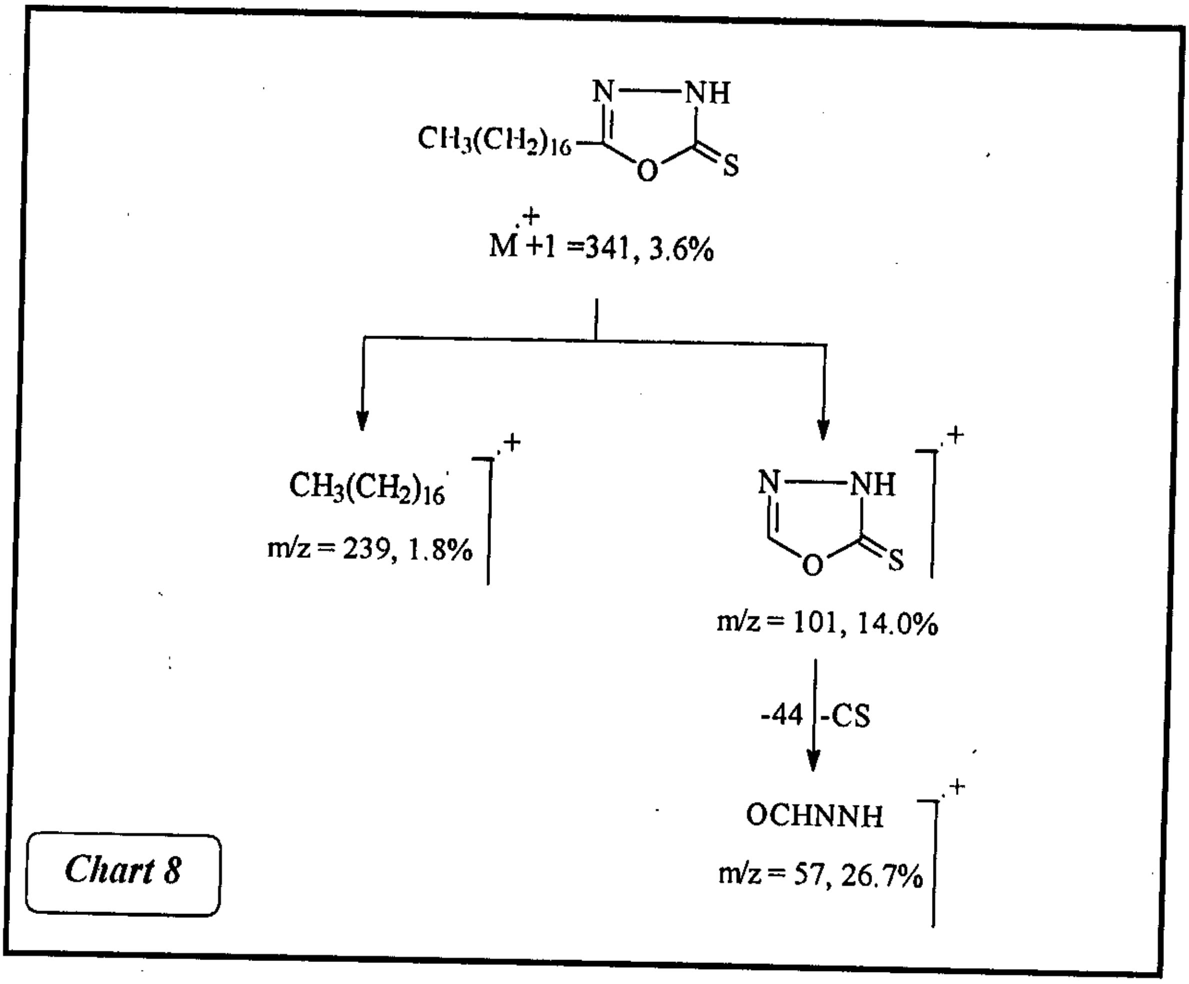
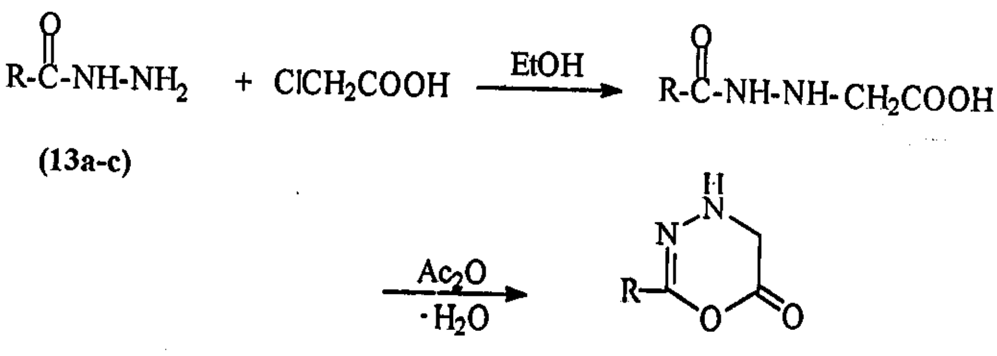


Chart 8

3- *Synthesis of oxadiazine derivatives via the reaction of fatty acid hydrazide (13a-c) with chloroacetic acid.*

Addition of chloroacetic acid to fatty acid hydrazide **(13a-c)** in dry ethyl alcohol gives intermediate which undergoes cyclization followed by dehydration to give 2-alkyl-1,3,4-oxadiazine-6-one **(19a-c)**.



(19a-c)

R, a = $C_{13}H_{27}$, b = $C_{15}H_{31}$, c = $C_{17}H_{35}$

IR spectrum of **(19b)** shows band for νNH at 3437, νC=N at 1598, νC=O at 1654, νC-O of cyclic ether at 1105 and νCH's aliphatic in region (2920-2850) cm^{-1}.

^{1}HNMR spectrum of **(19c)** shows signals at δ 0.9 (t, 3H, terminal CH_3), δ 1.2-1.6 (m, 32H, CH_2 of alkyl chain), δ 4.3 (s, 1H, NH) which disappeared by addition D_2O. (*cf.* fig.30).

Mass spectrum of **(19a)** show ion peak at $M^+ + 2 = 284$, 2.7 % and ion peak at m/z = 99, 7.3 % corresponding of oxapyridazine nucleus beside the base peak at m/z = 57, 100 % (cf. fig. 48, Chart 9).

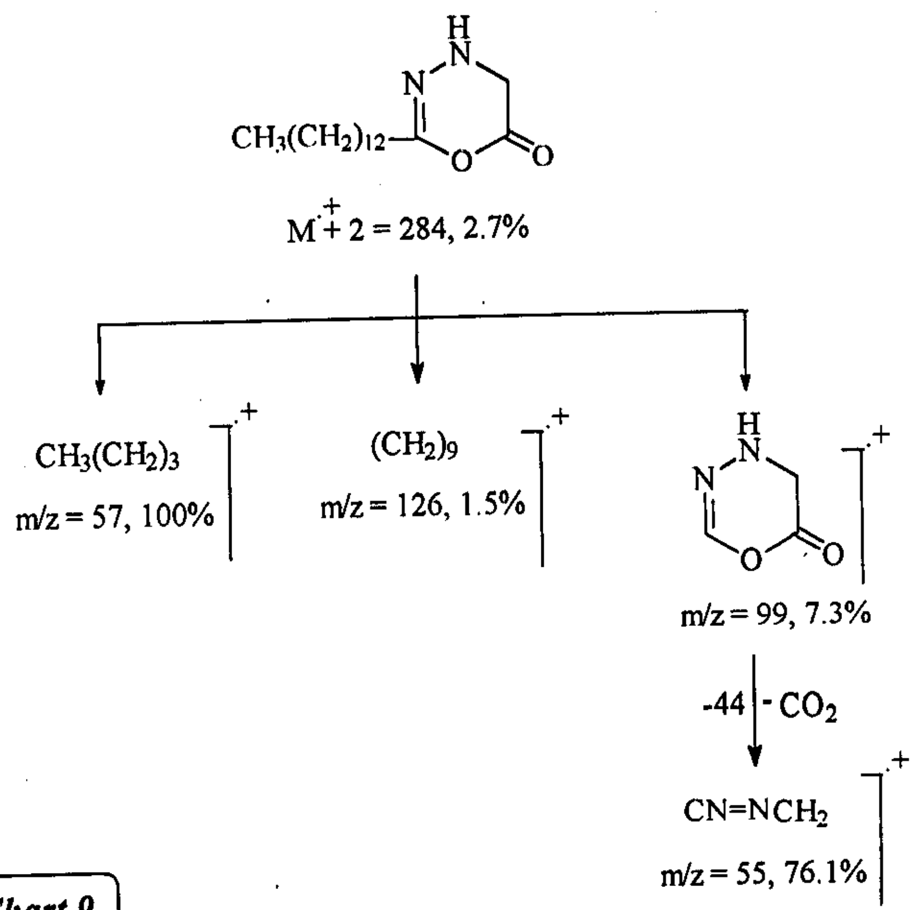
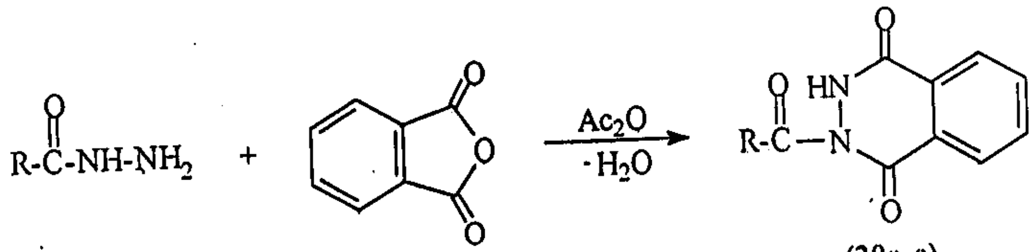


Chart 9

4- *Synthesis of phthalazine derivatives via the reaction of fatty acid hydrazide (13a-c) with phthalic anhydride.*

The reaction of fatty acid hydrazides **(13a-c)** with phthalic anhydride in acetic anhydride leads to the formation of 2-alkanoyl-phthalazine-1,4-dione **(20a-c)**.



(20a-c)

(13a-c)

R, a = $C_{13}H_{27}$, b = $C_{15}H_{31}$, c = $C_{17}H_{35}$

IR spectrum of **(20c)** shows, νNH at 3404, νC=O's at 1703, 1656 and 1597, and the characteristic band of phthalazine nucleus at 1543 cm^{-1} due to ring vibration (*cf.* fig. 13).

Mass spectrum of **(20c)** show molecular ion peak at $M^+ + 2 = 430$, 7.25% and show ion peak at m/z = 161, 72.1 % corresponding of phthalazine nucleus. (cf. fig. 49, Chart 10).

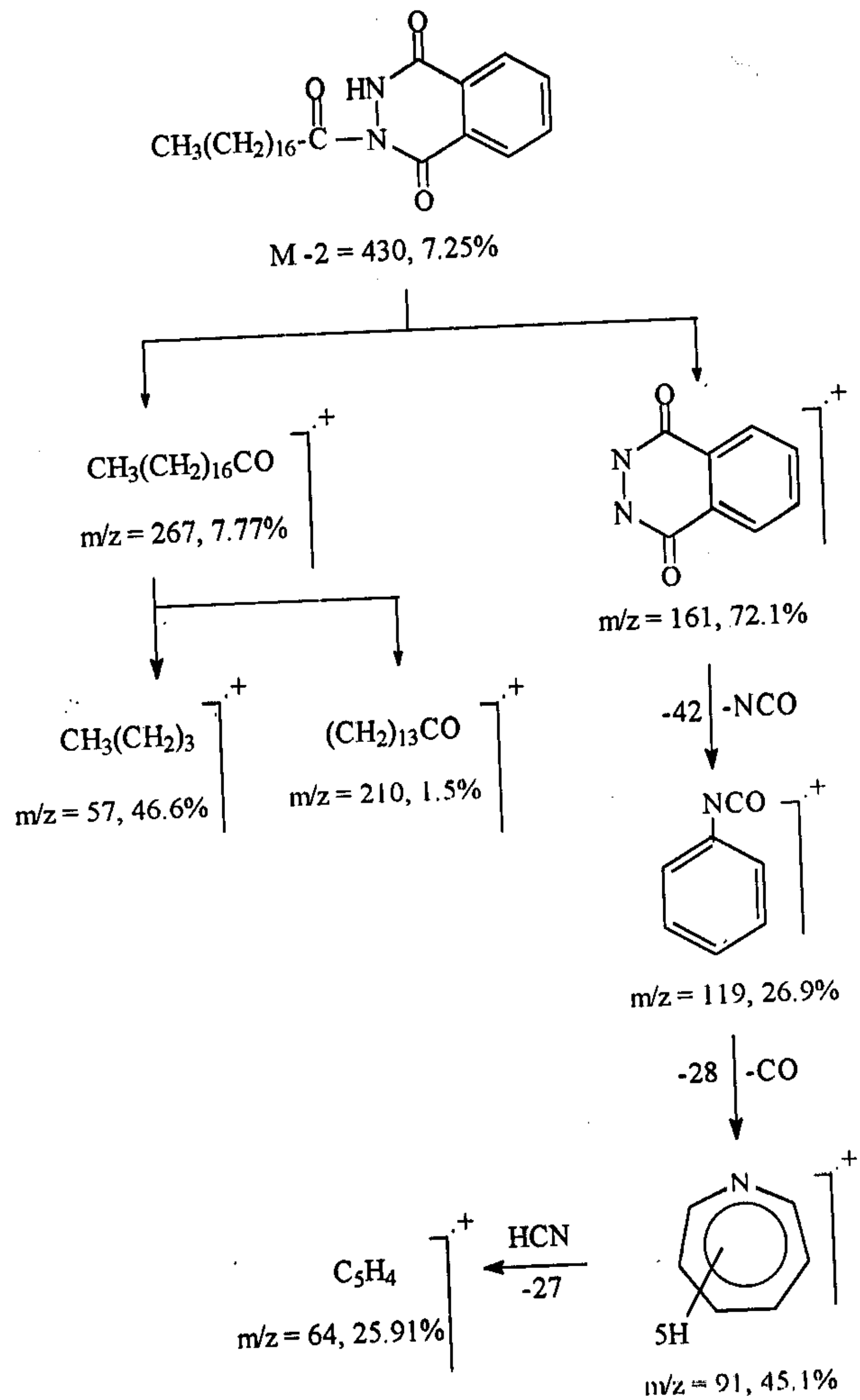
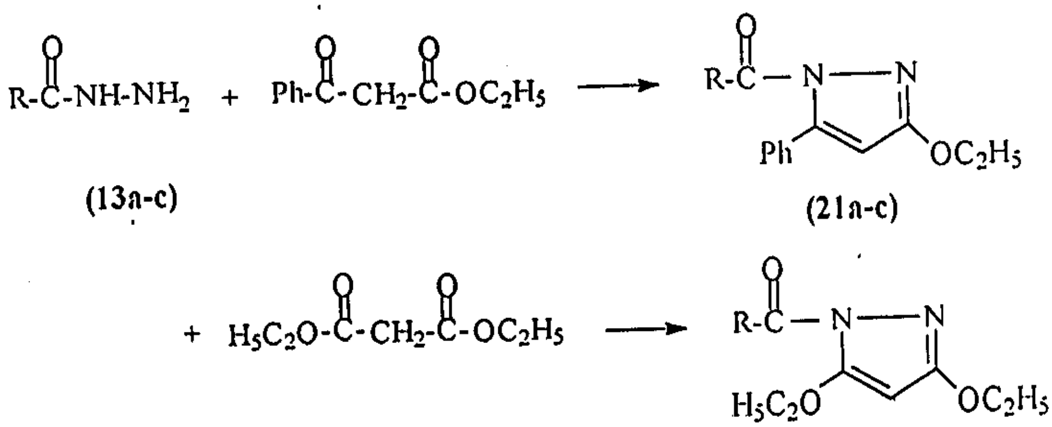

O
HN
O
CH3(CH2)16-C —N
O
M -2 = 430, 7.25%
CH3(CH2)16CO
m/z = 267, 7.77%
O
N
N
O
m/z = 161, 72.1%
CH3(CH2)3
m/z = 57, 46.6%
(CH2)13CO
m/z = 210, 1.5%
-42
-NCO
NCO
m/z = 119, 26.9%
-28
-CO
N
5H
m/z = 91, 45.1%
HCN
-27
C5H4
m/z = 64, 25.91%

Chart 10

5- *Synthesis of pyrazole derivatives via the reaction of fatty acid hydrazide with ethyl benzoyl acetate and / or diethyl malonate.*

Fatty acid hydrazide **(13a-c)** reacts with ethylbenzoylacetate and/or diethylmalonate to give 1-N-alkanoyl-3-ethoxy-5-phenyl-pyrazole **(21a-c)** and/or 1-N-alkanoyl-3,5-diethoxypyrazole **(22a-c)**.



(13a-c) **(21a-c)** **(22a-c)**

R, a = $C_{13}H_{27}$, b = $C_{15}H_{31}$, c = $C_{17}H_{35}$

IR spectrum **(21a)** exhibits, νC=N at 1593 and νC=O at 1703, νCH aliphatic in region (2920-2850) and νCH aromatic at 3020 and the characteristic band [220] of pyrazole ring at (1465) cm^{-1} (*cf.*Fig.14).

^{1}HNMR spectrum of **(22a)** shows signals at δ 0.85 (t, 3H, terminal CH_3), δ1.3 (s, 24H, CH_2 of alkyl chain), δ 2.1 (s, 2H, CH cyclic), δ7.3 (s, 5H, ArH) and δ 2.3 (m, 3H, CH_2CH_3) (*cf.* fig.31).

6- Synthesis of thiazole derivatives via the reaction of fatty acid hydrazide (13a-c) with benzaldehyde.

The reaction of fatty acid hydrazide **(13a-c)** with benzaldehyde in acetic acid give N-alkanoyl-benzal hydrazone **(23a-c)** (Schiff base).

$$R\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}NH\text{-}NH_2 \quad + \quad PhCHO \xrightarrow{EtOH} R\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}NH\text{-}N{=}CH\text{-}Ph$$

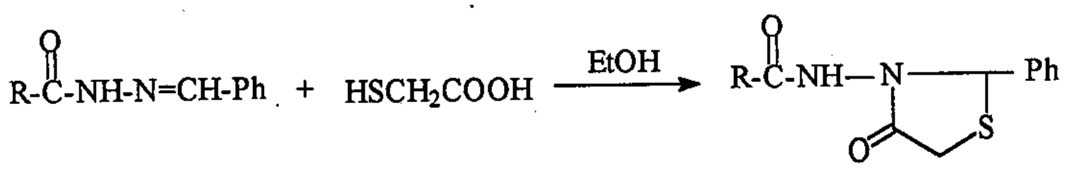
(13a-c) **(23a-c)**

R, a = $C_{13}H_{27}$, b = $C_{15}H_{31}$, c = $C_{17}H_{35}$

IR spectrum of **(23a)** exhibits, νNH at 3228, strong band at 2360 for the linear structure of the compound νC=O of amide at 1662 and νC=N at 1598 cm^{-1} (*cf.* fig.15).

^{1}HNMR spectrum of **(23c)** shows signals at δ 0.9 (t, 3H, terminal CH_3), δ 1.3 (s, 32H, CH_2 of alkyl chain), δ 1.9 (s, 1H, N=CH), δ 7.3-7.7 (m, 4H, ArH) and δ 3.7 (s, 1H, NH proton) disappeared by addition of D_2O (*cf.* fig. 32).

When the Schiff base derivatives **(23a-c)** were treated with thioglycollic acid in dry benzene leads to the formation of 3-N-amidoalkyl-2-phenyl-1,3-thiazole-4-one **(24a-c)**.



(23a-c) **(24a-c)**

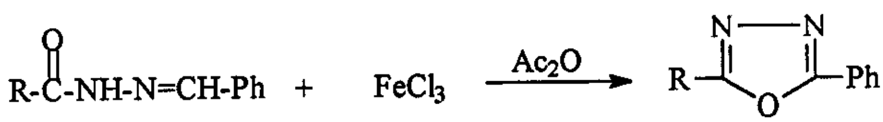
R, a = $C_{13}H_{27}$, b = $C_{15}H_{31}$, c = $C_{17}H_{35}$

IR spectrum of **(24c)** which shows, νNH at 3204, νC=O's at 1690, 1648, νCH of aromatic at 3099 and νCH's of alkyl chain in region (2920-2850) cm^{-1} (*cf.* fig. 16).

^{1}HNMR spectrum of **(24c)** shows signals at δ 0.9 (t, 3H, terminal CH_3), δ 1.2 (s, 32H, CH_2 of alkyl chain), δ 1.7 (s, 2H, S-CH_2), δ 2.6 (s, H, CH-Ph), δ 7.3-7.9 (m, 5H, ArH), δ 8.7 (s, 1H, NH proton) which disappeared by addition of D_2O (*cf.* fig. 33).

7-Synthesis of oxadiazole derivatives via the reaction of Schiff base derivative (23a-c) with ferric chloride.

When the Schiff base adducts **(23a-c)** were treated by ferric chloride in acetic acid lead to formation of 2-alkyl-5-phenyl-1,3,4-oxadiazole **(25a-c)**.



(23a-c) **(25a-c)**

R, a = $C_{13}H_{27}$, b = $C_{15}H_{31}$, c = $C_{17}H_{35}$

IR spectrum of **(25c)** exhibits, νC= N's at 1599 and 1549, νC-O-C at 1100, νCH aliphatic at 2920-2850, νCH aromatic at 3047 and the characteristic [220] band of heterocyclic ring in region (1040-1030) cm^{-1} (*cf.* fig. 17).

^{1}HNMR spectrum of **(25b)** shows signals at δ 0.9 (t, 3H, terminal CH_3), δ 1.2 (s, 28H, CH_2 of alkyl chain), δ 7.3 (s, 5H, ArH) (*cf.* fig. 34).

Preparation of nonionic surfactants from the synthesized heterocyclic compounds.

Nonionic surfactants are prepared by the addition of different moles of propylene oxide (n = 3, 5 and 7) to the synthesized heterocyclic derivatives to yield polypropenoxylation products.

The structures of the synthesized nonionic surfactants were confirmed via IR and ^1H NMR spectra

IR spectrum of **(20a)** after the addition of propylene oxide showed, two broad bands at 1100 and 950 cm^{-1} corresponding for νC-O-C ether linkage of poly propenoxy chain, beside the original bands of the compound.

^1HNMR spectrum of **(23a)** after the addition, showed the protons of propenoxy group are assigned as broad multiple signals in the region (3.2-3.7), beside the other protons of the compound.

Surface active properties of nonionic surfactants.

The surface active and related properties, including surface and interfacial tension, cloud point, foaming power, wetting time, and emulsification properties were investigated to evaluate the possible application of these products in the different industrial fields.

1- Surface and interfacial tension:

In comparing surfactants or emulsifiers by surface or interfacial tension measurements, two factors, efficiency and effectiveness need to be considered. Ross[221] suggests that a good measure of efficiency is the amount of a surfactant required to reduce the tension by 20-dyne/ cm and the minimum tension obtainable with the surfactant measured its effectiveness. The values of surface and interfacial tension of the synthesized products increased by increasing the number of propenoxy group as found by [50] per molecule of products as shown in (Table 6).

2- Cloud point:

All the synthesized products have high cloud points, which gave the good performance in hot water. Generally, the cloud point increases with increasing the number of propenoxy group per hydrophobic molecule as found by [51] as show in (Table 6).

3- Wetting time:

All the products show decreasing in wetting time, where good wetting time are recorded with a low propylene oxide content as found by [102] as shown in (Table 6).

4- Foaming power:

In general, the nonionic surfactants form unstable foam. It was reported that the foaming height of the prepared surfactants increases with increasing of propylene oxide unit per molecule of surfactant as found by [57] as shown in (Table 6).

5- Emulsifying properties:

Emulsion stability was measured using standard procedures. From the data recorded in (Table 6) the emulsifying properties increase with decreasing number of propylene oxide units and increase with increasing of alkyl chain as found by [82].

6- Critical Micelle Concentration (CMC):

The (CMC) values of aqueous solutions of the synthesized surfactants were determined from the concentration dependence of surface tension values at 25 °C. The critical micelle concentration (CMC) was determined and listed in (Table 7). The value of (CMC) increases with increasing the number of propenoxy groups and it decreases with increasing the alkyl chain length as found by [132]

Biodegradability.

Biodegradation die-away test in ordinary river water gave satisfactory results (Table 7), where, the biodegradation was expressed by measurement of the surface tension with time (day). The rate of degradation of these compounds depends on the size of molecule; bulky molecule diffuses through the cell membrane and its degradation is more difficult, this means that these compounds with lower moles of propylene oxide are more degradable than that which contains higher moles of propylene oxide as found by [51]. In general, the products have high rate of degradation ranging about 95% degradation during around 5 days.

Biological activity.

The surfactant products were screened for antibacterial activity against Bacillus cercus, Bacillus circulans and antifungal activity against Aspergillus clavatus and pencillium notatum. All the tested compounds showed antimicrobial activity against tested microorganisms, the results of the antimicrobial activity are shown in (Table 8).

Table (5): Physical properties of prepared compounds before addition of propylene oxide.

No.	M.F.	M.wt	Solvent	Yield %	Color	Analysis data calc./ Found %			
						C	*H*	*N*	*S*
13a	$C_{14}H_{30}N_2O$	242	Benz.	75	White	69.42 69.76	12.39 12.52	11.57 11.65	
13b	$C_{16}H_{34}N_2O$	270	Tol.	72	White	71.11 71.31	12.59 12.75	10.37 10.53	
13c	$C_{18}H_{38}N_2O$	298	Benz.	70	White yellow	72.4 72.63	12.75 12.88	9.39 9.52	
14a	$C_{24}H_{34}N_2O_2$	382	EtOH	65	yellow	75.39 75.58	8.91 9.21	7.33 7.53	
14b	$C_{26}H_{38}N_2O_2$	410	MeOH	63	Pale yellow	76.09 76.18	9.26 9.42	6.82 6.93	
14c	$C_{28}H_{42}N_2O_2$	438	EtOH	68	Red yellow	76.71 76.9	9.58 9.62	6.39 6.57	
15a	$C_{24}H_{36}N_2O_2$	384	Tol.	57	Yellow	75.00 75.12	9.37 9.51	7.29 7.52	
15b	$C_{26}H_{40}N_2O_2$	412	Benz.	60	Pale yellow	75.72 75.87	9.71 9.86	6.79 6.82	
15c	$C_{28}H_{44}N_2O_2$	440	MeOH	65	Brown	76.36 76.54	10.01 10.11	6.36 6.53	
16a	$C_{18}H_{30}N_2O_3$	322	Tol.	73	yellow	67.08 67.13	9.31 9.45	8.69 8.83	
16b	$C_{20}H_{34}N_2O_3$	350	Benz.	68	Red yellow	68.57 68.67	9.71 9.81	8.00 8.15	
16c	$C_{22}H_{38}N_2O_3$	378	AcOH	70	Red yellow	69.84 69.97	10.05 10.11	7.40 7.53	
17a	$C_{18}H_{32}N_2O_3$	324	EtOH	62	yellow	66.60 66.83	9.83 9.87	8.65 8.72	
17b	$C_{20}H_{36}N_2O_3$	352	AcOH	65	Pale yellow	68.18 75.3	10.22 10.35	7.95 8.11	
17c	$C_{22}H_{40}N_2O_3$	380	AcOH	68	Red yellow	69.47 69.71	10.52 10.92	7.36 7.53	

Table (5): Cont.

No.	M.F.	M.wt	Solvent	Yield %	Color	Analysis data calc./Found %			
						C	*H*	*N*	*S*
18a	$C_{15}H_{28}N_2OS$	284	EtOH	58	White yellow	63.38 63.49	9.85 9.92	9.85 9.95	11.26 11.45
18b	$C_{17}H_{32}N_2OS$	312	MeOH	55	yellow	65.38 65.54	10.25 10.39	8.97 9.16	10.25 10.33
18c	$C_{19}H_{36}N_2OS$	340	EtOH	53	Pale yellow	67.05 67.12	10.58 10.62	8.23 8.45	9.41 9.56
19a	$C_{16}H_{30}N_2O_2$	282	Tol.	55	yellow	68.08 68.16	10.63 10.75	9.92 10.11	
19b	$C_{18}H_{34}N_2O_2$	310	Benz.	53	Red yellow	69.67 69.80	10.92 11.00	9.03 9.22	
19c	$C_{20}H_{38}N_2O_2$	338	EtOH	56	Pale yellow	71.01 71.11	11.24 11.45	8.28 8.45	
20a	$C_{22}H_{32}N_2O_3$	372	EtOH	67	yellow	70.96 71.23	8.60 8.78	6.52 6.72	
20b	$C_{24}H_{36}N_2O_3$	400	AcOH	65	yellow	72.00 72.19	9.01 9.11	7.00 7.18	
20c	$C_{26}H_{40}N_2O_3$	428	AcOH	62	Red yellow	72.89 73.06	9.34 9.51	6.54 6.69	
21a	$C_{25}H_{38}N_2O_2$	398	EtOH	58	White yellow	75.37 75.52	9.54 9.72	7.03 7.22	
21b	$C_{27}H_{42}N_2O_2$	426	Benz.	62	yellow	76.05 76.24	9.85 9.99	6.57 6.75	
21c	$C_{29}H_{46}N_2O_2$	454	Benz.	60	Pale yellow	76.65 76.79	10.13 10.26	6.16 6.32	
22a	$C_{21}H_{38}N_2O_3$	366	MeOH	62	White yellow	68.85 68.99	10.38 11.59	7.65 7.84	
22b	$C_{23}H_{42}N_2O_3$	394	EtOH	65	Yellow	70.05 70.19	10.65 10.79	7.10 7.32	
22c	$C_{25}H_{46}N_2O_3$	422	EtOH	63	Pale yellow	71.09 71.23	10.9 11.15	6.63 6.92	

Table (5): Cont.

No.	M.F.	M.wt	Solvent	Yield %	Color	Analysis data calc./Found %			
						C	*H*	*N*	*S*
23a	$C_{21}H_{34}N_2O$	330	Benz.	62	Brown	76.36 76.52	10.30 10.42	8.48 8.63	
23b	$C_{23}H_{38}N_2O$	358	Tol.	65	Brown	77.09 77.17	10.61 10.83	7.82 7.97	
23c	$C_{25}H_{42}N_2O$	386	EtOH	68	Red brown	77.72 77.83	10.88 11.08	7.25 7.54	
24a	$C_{23}H_{36}N_2O_2S$	404	Benz.	67	yellow	68.31 68.48	8.91 9.08	6.93 7.14	7.92 8.11
24b	$C_{25}H_{40}N_2O_2S$	432	Benz.	63	yellow	69.44 69.68	9.25 9.45	6.48 6.63	7.41 7.53
24c	$C_{27}H_{44}N_2O_2S$	460	Tol.	65	Pale yellow	70.43 70.62	9.56 9.72	9.08 9.23	6.95 7.22
25a	$C_{21}H_{32}N_2O$	328	Benz.	65	brown	76.82 76.99	9.75 9.92	8.53 8.76	
25b	$C_{23}H_{36}N_2O$	356	EtOH	62	Red brown	77.52 77.73	10.11 10.21	7.86 7.95	
25c	$C_{25}H_{40}N_2O$	384	AcOH	60	brown	78.12 78.30	10.41 10.62	7.29 7.35	

Table (6): Surface properties of nonionic surfactants.

Comp.	n	Surface Tension (dyne/cm) 0.1 %	Interfacial Tension (dyne/cm) 0.1 %	Cloud Point °C 1%	Wetting time (sec) 0.1%	Emulsion stability (min.)	Foam height (mm) 1%	cmc x 10^{-3} mole / l
13a	3	30	9.5	79	35	127	118	3.4
	5	32	10.5	95	26	111	126	3.7
	7	34	11.0	>100	20	95	134	3.9
13b	3	31	10.0	70	37	128	126	3.3
	5	33	11.0	90	30	112	135	3.6
	7	36	11.5	95	22	96	150	3.8
13c	3	32	10.5	68	40	130	133	3.2
	5	35	12.0	87	33	115	140	3.4
	7	38	13.5	93	25	98	155	3.6
16a	3	29	7.5	67	43	117	100	3.5
	5	31	9.5	77	34	87	125	4.2
	7	33	10.5	91	27	74	150	4.3
16b	3	30	8.5	63	46	120	105	3.3
	5	32	10.5	72	39	90	128	3.9
	7	35	12.0	88	30	77	146	4.1
16c	3	31	9.5	59	48	125	115	3.1
	5	34	11.0	66	43	92	147	3.7
	7	37	12.5	76	32	79	152	3.9
17a	3	29	9.0	69	46	118	113	3.7
	5	31	10.5	74	36	86	127	3.8
	7	34	11.0	84	27	74	142	4.1
17b	3	31	9.0	64	48	120	115	3.3
	5	34	11.0	79	39	180	130	3.6
	7	37	11.5	88	30	76	146	3.9
17c	3	33	9.5	61	52	123	119	3.1
	5	36	11.5	76	42	90	133	3.5
	7	39	12.0	91	32	70	154	3.8
18a	3	33	8.5	65	41	117	120	4.5
	5	35	9.5	74	33	96	125	4.8
	7	37	10.0	86	28	82	128	5.1
18b	3	34	9.0	62	44	118	120	4.3
	5	37	10.5	70	36	97	127	4.6
	7	39	11.0	92	30	83	130	4.9
18c	3	36	9.5	57	48	120	125	4.1
	5	39	11.0	66	39	99	130	4.4
	7	41	12.5	85	32	85	140	4.7

Table (6): Cont.

Comp.	n	Surface Tension (dyne/cm) 0.1 %	Interfacial Tension (dyne/cm) 0.1 %	Cloud Point °C 1%	Wetting time (sec) 0.1%	Emulsion stability (min.)	Foam height (mm) 1%	cmcx10^{-3} mole / l
19a	3	31	7.5	73	40	105	90	4.1
	5	33	9.0	85	32	81	115	4.3
	7	36	10.0	96	22	59	130	4.6
19b	3	32	8.0	69	43	108	92	3.9
	5	35	10.0	82	34	84	117	4.1
	7	38	11.0	92	26	62	132	4.4
19c	3	34	8.5	66	47	110	95	3.7
	5	37	10.5	79	36	86	120	3.9
	7	39	11.5	89	28	65	140	4.2
20a	3	30	7.0	71	45	125	115	3.7
	5	32	7.5	83	30	88	128	4.0
	7	34	9.0	97	22	76	150	4.2
20b	3	31	7.5	65	47	127	121	3.5
	5	33	8.0	80	33	91	134	3.8
	7	35	9.5	93	25	78	155	3.9
20c	3	32	8.0	63	49	130	126	3.3
	5	35	9.5	78	35	94	143	3.6
	7	37	11.5	91	27	81	160	3.8
23a	3	28	8.5	69	47	83	105	3.7
	5	31	9.5	74	33	73	119	4.0
	7	34	11.0	87	23	64	134	4.3
23b	3	30	8.5	63	49	78	110	3.3
	5	33	10.5	70	36	85	126	3.7
	7	36	12.0	83	25	75	141	4.0
23c	3	31	8.5	58	52	89	116	2.9
	5	35	11.0	64	38	76	130	3.2
	7	38	12.5	80	27	68	153	3.8
24a	3	31	9.0	72	38	81	112	3.8
	5	32	10.0	81	32	68	125	4.2
	7	34	12.0	92	23	57	140	4.6
24b	3	32	9.5	67	41	82	115	3.5
	5	34	10.5	76	35	70	127	3.9
	7	36	11.5	86	27	60	150	4.3
24c	3	34	10.0	61	43	85	120	3.3
	5	36	11.5	69	37	72	130	3.7
	7	38	12.5	84	30	63	155	4.1

Table (7): Biodegradability of the Prepared Surfactants.

No.	n	1st day	2nd day	3rd day	4th day	5th day	6th day	7th day
13a	3	54	67	77	86	93	-	-
	5	49	60	69	81	92	97	-
	7	47	58	64	73	88	94	-
13b	3	52	65	75	84	92	-	-
	5	47	58	66	78	90	-	-
	7	45	54	61	70	85	94	-
13c	3	50	64	73	82	91	-	-
	5	46	57	64	76	87	93	-
	7	43	52	59	68	79	87	94
16a	3	57	65	79	88	93	-	-
	5	54	62		84	91	-	-
	7	51	57	70	75	89	96	-
16b	3	55	64	77	86	92	-	-
	5	51	59	72	81	89	93	-
	7	49	55	66	75	83	95	-
16c	3	54	63	76	84	91	-	-
	5	49	58	69	78	87	92	-
	7	46	53	63	72	80	88	96
17a	3	51	61	70	82	93	-	-
	5	50	59	68	79	88	97	-
	7	47	57	64	75	85	93	-
17b	3	49	59	68	79	90	-	-
	5	48	57	65	75	83	93	-
	7	45	53	61	71	80	89	95
17c	3	48	57	66	78	89	-	-
	5	46	54	62	73	82	93	-
	7	43	51	58	68	78	89	-
18a	3	53	63	72	82	92	-	-
	5	51	59	68	78	89	95	-
	7	48	55	64	76	83	92	-
18b	3	51	61	69	80	89	-	-
	5	48	57	65	75	85	91	-
	7	45	52	62	72	79	89	97
18c	3	49	58	67	78	87	92	-
	5	46	54	62	73	82	89	-
	7	43	79	58	68	77	87	96

Table (7): Cont.

No.	n	1st day	2nd day	3rd day	4th day	5th day	6th day	7th day
19a	3	53	63	72	80	88	96	-
	5	51	61	69	78	87	95	-
	7	49	78	65	7	84	93	-
19b	3	51	61	70	77	86	92	-
	5	49	58	76	75	84	90	-
	7	47	55	62	71	80	89	97
19c	3	50	56	68	75	84	91	-
	5	47	56	64	72	81	89	-
	7	44	53	59	68	77	87	93
20a	3	55	67	78	88	95	-	-
	5	53	63	75	87	93	-	-
	7	51	58	79	81	89	97	-
20b	3	53	65	76	86	92	-	-
	5	51	61	73	85	91	-	-
	7	49	55	67	77	85	95	-
20c	3	53	64	75	86	92	-	-
	5	49	58	70	82	89	-	-
	7	46	53	64	75	83	92	-
23a	3	52	59	67	77	87	-	-
	5	49	57	63	74	85	-	-
	7	47	55	60	72	77	93	-
23b	3	49	57	64	75	84	94	-
	5	47	54	61	72	81	91	-
	7	45	52	58	69	75	89	95
23c	3	47	55	62	74	83	91	-
	5	45	51	58	69	78	88	-
	7	43	48	55	65	72	86	93
24a	3	55	65	78	85	93	-	-
	5	53	63	75	82	87	-	-
	7	50	57	71	78	84	95	-
24b	3	53	63	75	82	91	-	-
	5	51	59	72	79	85	93	-
	7	47	55	67	75	81	88	95
24c	3	52	61	72	80	91	-	-
	5	49	57	68	76	83	92	-
	7	45	52	65	72	79	90	-

Table (8): Antimicrobial activity of nonionic surfactants

Compd.	Bacteria		Fungi	
	Bacillus cercus	*Bacillus circulans*	*Aspergillus's clavatus*	*Penicillum notatum*
13a	-	-	+	+
13b	+	-	+	+
13c	+	+	++	++
14a	-	-	+	+
14b	-	+	+	++
14c	-	+	+	++
15a	-	-	-	+
15b	-	+	+	+
15c	+	+	+	+
16a	+	+	+	+
16b	+	+	+	++
16c	+	+	+	++
17a	+	-	+	+
17b	-	+	+	+
17c	+	+	+	++
18a	-	+	+	++
18b	+	+	+	++
18c	+	+	+	++
19a	+	-	-	+
19b	+	-	+	+
19c	-	-	++	++
20a	+	+	-	+
20b	+	+	-	++
20c	+	+	++	++
21a	-	-	+	+
21b	-	-	+	+
21c	+	+	+	++

Table (8): Cont.

Compd.	Bacteria		Fungi	
	Bacillus cercus	*Bacillus circulans*	*Aspergillus's clavatus*	*Penicillum notatum*
22a	-	-	-	+
22b	+	-	-	+
22c	+	+	+	++
23a	+	+	-	++
23b	+	+	-	++
23c	+	-	-	++
24a	+	+	-	+
24b	++	+	-	++
24c	+	+	+	+++
25a	+	+	-	+
25b	++	+	-	++
25c	+	+	-	++

(+++) Very strong inhibition, (++) strong inhibition, (+) moderate inhibition.

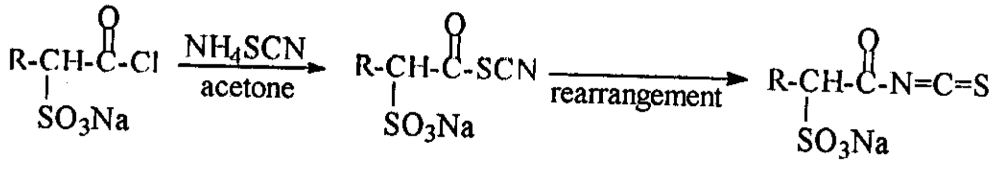
PART (3)

Anionic surfactants containing heterocyclic moiety from α-sulphonated fatty acid isothiocyanate

Among anionic surfactants containing an aromatic structure element are alkyl benzene sulphonate accompanied by alkyl-naphthalene sulfonates [222-225]. In these compounds, hydrophilic sulfonic group is separated from long chain alkyl hydrophobe by single six member benzene or naphthalene rings. The structure analogues to the above ones may be surfactants containing five member heteroaromatic groups. It has been well established that various triazoles, oxazoles, benzoxazoles and thiazoles are of biological interest [203-206]. This encourage us to synthesis a novel groups of anionic surfactants containing those nucleus from sodium salts of α-sulphonated long chain fatty acids (myristic, palmitic and stearic) isothiocyanate by reaction with different nucleophiles as phenyl hydrazine, glycine, anthranilic, o-aminophenol and thioglycollic acid, hopping to possess good surface properties and expected to have biological activities.

Synthesis of α-sulphonated fatty acid isothiocyanate.

The isothiocyanates of sodium salt of α-sulphonated fatty acids (myristic, palmitic and stearic) **(27a-c)** were prepared from its sodium salt of α-sulphonate fatty acid chloride **(26a-c)** (which prepared from the corresponding fatty acid with chlorosulphonic acid in carbon tetrachloride and then reacted with thionyl chloride)[20], through its reaction with ammonium thiocyanate in dry acetone as following:



(26a-c) (27a-c)

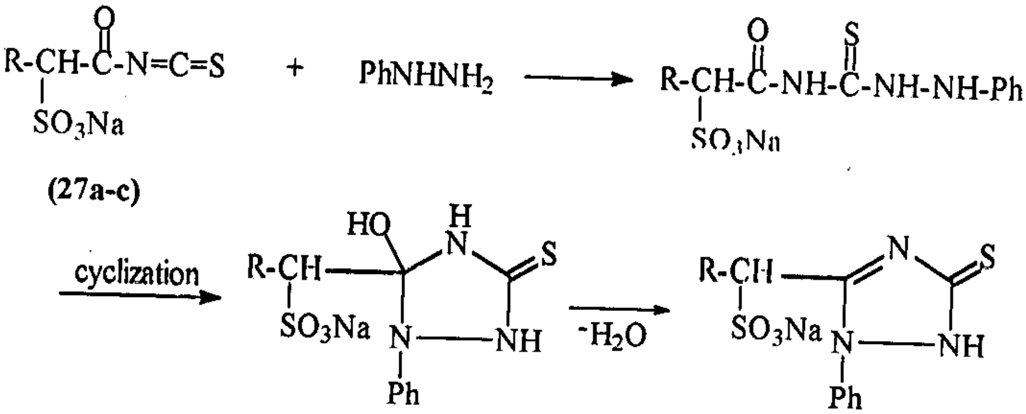
R, a = $C_{12}H_{25}$, b = $C_{14}H_{29}$, c = $C_{16}H_{33}$

The isothiocyanates **(27a-c)** were prepared insitu during the reaction to prevent its decomposition

Synthesis of anionic surfactants containing heterocyclic compounds from α- sulphonated fatty acid isothiocyanate.

1-Synthesis of 1,2,4-triazoline-5-thione derivatives via the reaction of isothiocyanate (27a-c) with phenyl hydrazine.

When the solution of sodium salt of α-sulphonated of fatty acid isothiocyanate **(27a-c)** in acetone was treated with phenyl hydrazine, it gave intemediate, which undergoes cyclization followed by dehydration to give 3 (α-sulphonated alkyl)-2-phenyl-1,2,4-triazolinyl-5-thione **(28a-c)**.



(27a-c) (28a-c)

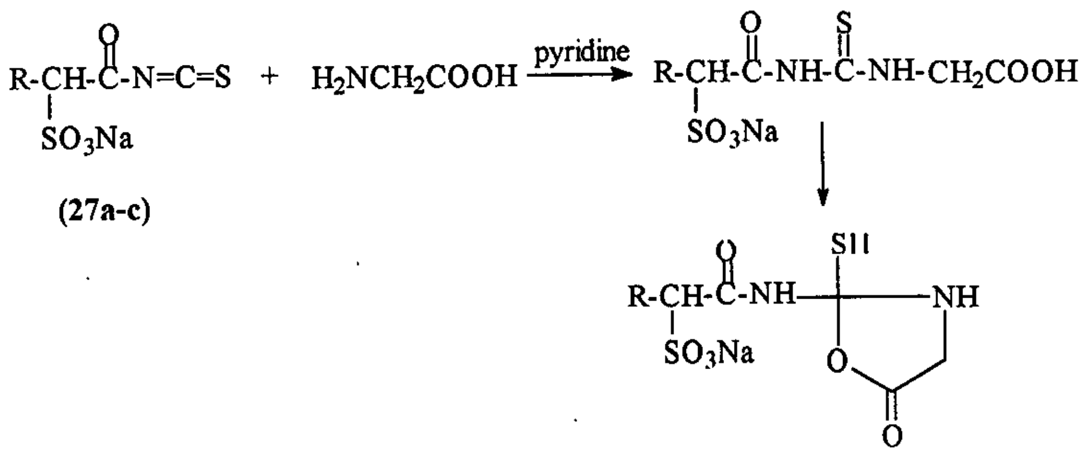
R, a = $C_{12}H_{25}$, b = $C_{14}H_{29}$, c = $C_{16}H_{33}$

IR spectrum of **(28c)** shows, νNH at 3229, νC=N at 1600, νC=S at 1375, νSO_2 at 1180, 689 and νCH's of alkyl chain in region (2920-2850) cm^{-1}.

^{1}HNMR spectrum of **(28c)**, the protons are assigned as follow δ 0.9 (t, 3H, terminal CH_3), δ 1.3 (s, 32H, CH_2 of alkyl chain), δ 2.3 (s, 1H, $CH\text{-}SO_3Na$), δ 7.4-8.2 (m, 5H, ArH) and δ 8.7 (s, 1H, NH). (*cf.* fig. 35).

2-Synthesis of 1,3-oxazolidine-5-one derivatives via the reaction of isothiocyanate (27a-c) with glycine.

Glycine reacts with sodium salt of α-sulphonated of fatty acid isothiocyanate **(27a-c)** in the presence of pyridine as a base to produce thiourea derivatives which cyclized to 2-(sodium salt of α-sulphonated amidoalkyl)-2-thiol-1,3-oxazolidine-5-one **(29a-c)**.



(27a-c)

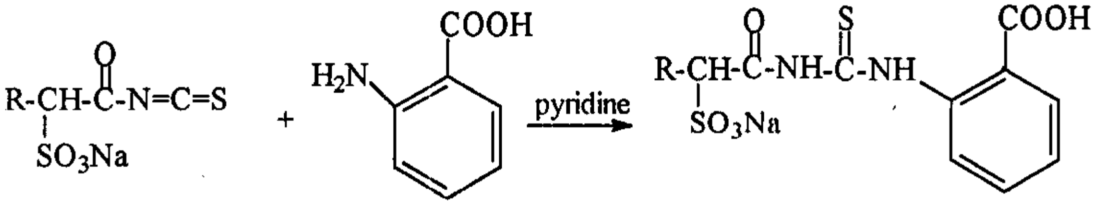
R, a = $C_{12}H_{25}$, b = $C_{14}H_{29}$, c = $C_{16}H_{33}$

(29a-c)

IR spectrum of **(29b)** shows the following bands, νNH's at 3205 and 3319, νSH at 2061, νC=O's at 1647 and 1704, νSO_2 at 1178 and 672 cm^{-1} (*cf.* fig.18).

3- *Synthesis of quinazoline-2-thione -4-one derivatives via the reaction of isothiocyanate (27a-c) with anthranilic acid, followed cyclization.*

Addition of anthranilic acid to sodium salt of α-sulphonated fatty acid isothiocyanate **(27a-c)** leads to the formation of thiourea derivatives **(30a-c)**.



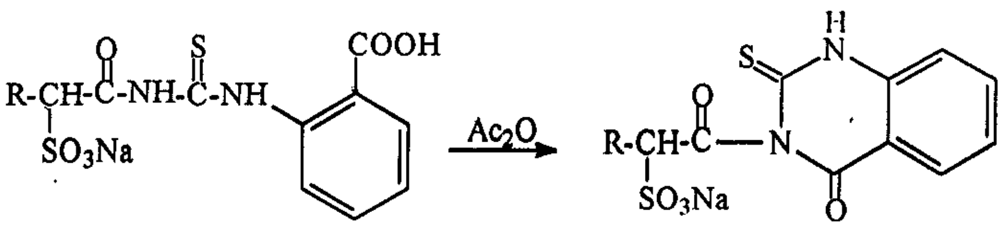
(27a-c) **(30a-c)**

R, a = $C_{12}H_2$, b = $C_{14}H_{29}$, c = $C_{16}H_{33}$

IR spectrum of **(30a)** exhibits, νOH at 3396, νNH's at 3121 and 3195, νC=O of amido at 1650, νC=O of acid at 1702, νC=S at 1379 and νSO_2 at 1077 and 679 cm^{-1}. Also there is a strong band at 2359 $cm^{-1}$for linear structure of the compound.

^{1}HNMR spectrum of **(30c)** shows the signals at δ 0.9 (t, 3H, terminal CH_3), δ 1.2-1.4 (m, 32H, CH_2 of alkyl chain), δ 3.9 (m, 2H, NH protons), δ 9.3 (s, 1H, OH), δ 7.3 (s, 4H, ArH) and δ 2.1 (t, 1H, $CHSO_3Na$) (*cf.* fig.36).

Treating of thiourea derivatives **(30a-c)** with acetic anhydride yielded 1-N (sodium salt of α-sulphonated alkanoyl) 1,3-quinazoline-2-thione -4-one **(31a-c)**.

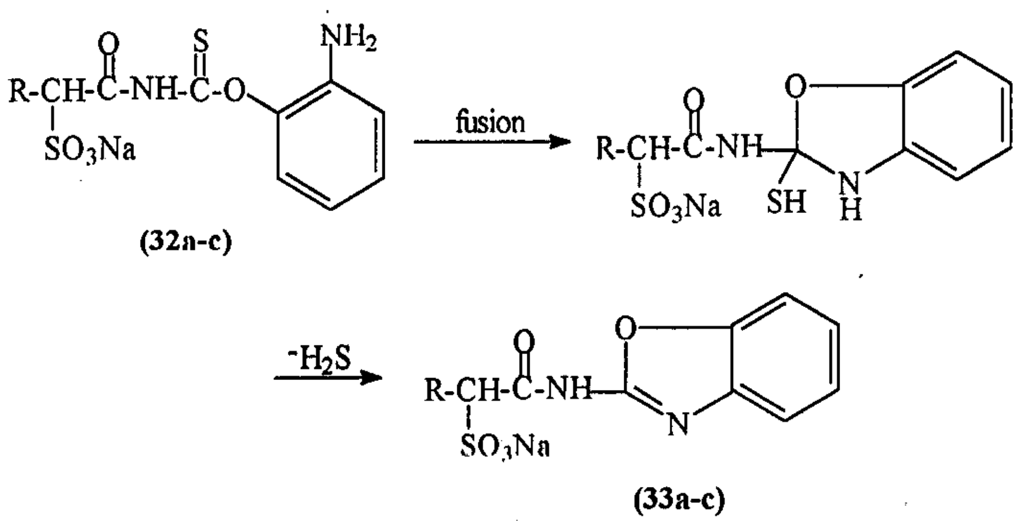


(30a-c) **(31a-c)**

R, a = $C_{12}H_{25}$, b = $C_{14}H_{29}$, c = $C_{16}H_{33}$

[1]HNMR spectrum of **(32c)** shows signals, δ 0.9 (t, 3H, CH_3-C-C), δ (1.2-1.6) (m, 32H, CH_2 of alkyl chain), δ (6.6-7.2) (m, 4H,ArH), δ (7.7-8.5) (a broad s, 1H, NH), δ 2.4 (t, 1H, $CHSO_3Na$). (*cf.* fig. 38).

Cyclization of thiocarbamate derivatives **(32a-c)** by fusion leads to evolution of H_2S gas and formation of 2- (sodium salt of α-sulphonated amidoalkyl)-1,3-benzoxazole **(33a-c)**.



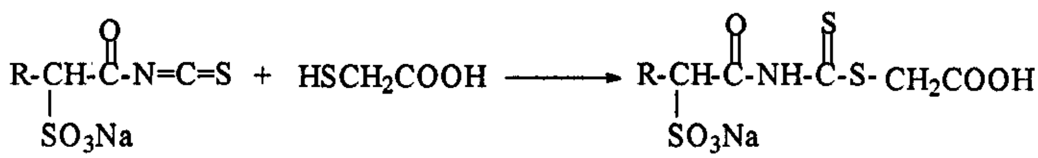
R, a = $C_{12}H_{25}$, b = $C_{14}H_{29}$, c = $C_{16}H_{33}$

IR spectrum of **(33c)** shows the following bands, νNH at 3228, νC=O at 1704, νC=N at 1599, νSO_2 at 1071, 1107 and νCH's aliphatic chain in region (2980-2850) cm^{-1} (*cf.* fig.21).

^{1}HNMR spectrum of **(33c)** shows signals at δ 0.8 (t, 3H, CH_3-C-C), δ 1.2-1.4 (m, 32H, CH_2 alkyl chain), δ 2.1 (t, 1H, $CHSO_3Na$), δ 7.2-7.9 (m, 4H, ArH) and 3.6 (s, 1H, NH) which disappeared by addition of D_2O (*cf.* fig. 39).

5- Synthesis of 1,3-thiazolidine derivatives via the reaction of isothiocyanate (27a-c) with thioglycollic acid, followed by cyclization.

Thioglycollic acid reacts with sodium salt of α-sulphonated of fatty acid isothiocynate **(27a-c)** to produce the adducts **(34a-c)**.



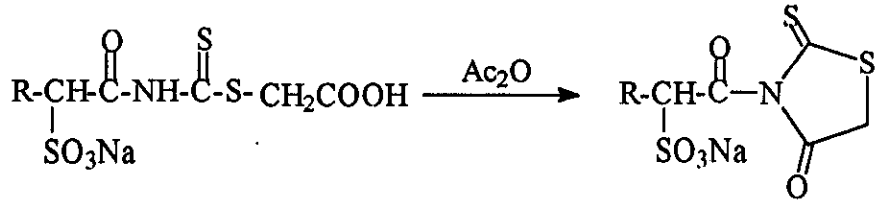
(34a-c)

(27a-c)

R, a = $C_{12}H_{25}$, b = $C_{14}H_{29}$, c = $C_{16}H_{33}$

IR spectrum of **(34c)** exhibits, νNH at 3183, νOH at 3450, νC=O of amid at 1654, νC=O of acid at 1710, νC=S at 1377 and νSO_2 at 1180 and 1268 cm^{-1} (*cf.* fig. 22).

When the products **(34a-c)** were cyclized by acetic anhydride leads to the formation of 3-N (α-sulphonated alkanoyl)-1,3-thiazolidine-2-thione-4-one **(35a-c)**.



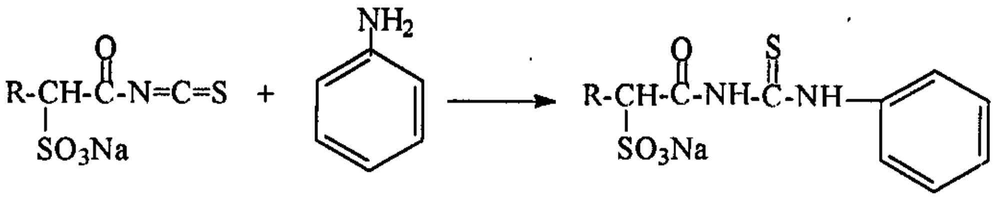
(34a-c) (35a-c)

R, a = $C_{12}H_{25}$, b = $C_{14}H_{29}$, c = $C_{16}H_{33}$

IR spectrum of **(35c)** exhibits, a broad band for νC=O's centerd at 1690, νSO_2, at 969 and νCH's of alkyl chain in region (2920-2850) cm^{-1}.

6-Synthesis of thiourea derivatives via the reaction of isothio-cyanate (27a-c) with aniline.

Sodium salt of α-sulphonated fatty acid isothiocyanate **(27a-c)** reacts with aniline to give thiourea derivatives **(36a-c)** as follow:



(27a-c) (36a-c)

R, a = $C_{12}H_{25}$, b = $C_{14}H_{29}$, c = $C_{16}H_{33}$

IR spectrum of **(36a)** exhibits, two bands at 3146 and 3205 for two νNH's, band at 1652 for νC=O, at 1346 for νC=S and at 1137 and 1221cm^{-1} for νSO_2 (cf. fig. 23).

Surface active properties of anionic surfactants

Anionic surfactants are very widely distributed throughout science, technology, and every day life. Examples which at once come to mind are the washing, wetting out of textile materials, the preparation of dispersions and emulsion, the application of agricultural and a wide variety of special uses, the number of which is continually increasing.

The surface active and related properties of the synthesized compounds including, surface and interfacial tension, Kraft point, wetting time, foaming and emulsification properties are given in (Table 10). Biodegradability and antimicrobial effects were examined and tested in (Table 11,12) respectively.

1- Surface and interfacial tension.

The synthesized anionic surfactants with heterocyclic moiety derivatives showed lower values for surface tension and interfacial tension. The results are recorded in (Table 10). It was found that, the lower values of surface and interfacial tension that may be due to the electrostatic repulsion between the ionized molecule as found by [226] and these values are decreases with the decreasing in alkyl chain length as found by [217].

2- Kraft point.

Kraft point of the prepared anionic surfactants was measured as the temperature where 1% dispersion becomes clear on gradual heating. All the synthesized surfactants are freely soluble in water at 1 wt % concentration and at any temperature. The synthesized anionic surfactants with heterocyclic moiety derivatives showed lower values for Kraft point, this fact may fail due to the presence of retarding groups in the same molecule as found by[226] In general, Kraft points measurements proved that the higher the molecular weight the higher the Kraft point.

3- Wetting time:

All the synthesized surfactants are good wetting agent, where wetting time increased as the alkyl chain length increase as found by[217]. The products were thus very effective as wetting agents in distilled water. So, they can find a wide application to play an important role as wetting agents in textile industry (Table 10).

4- Foaming height:

It is reported that the efficiency of surfactants as a foamer increases with increasing alkyl chain length as found by[218], where the prepared anionic surfactants with heterocyclic moiety recorded higher values of foaming height as found by[237] as recorded in (Table 10).

5- Emulsion stability:

The products of anionic surfactants are good emulsifying agents as may be seen in (Table 10) the emulsion stability increased with the molecular weight of the fatty acid moiety in the product as found by[218].

6- Ca^{++} Stability:

The calcium stability values show that the prepared surfactants can be used in hard water. The calcium stability decreased with an increase in the molecular weight of the hydrophobic part of the surfactant under the conditions of a constant temperature. Concerning the results in (Table 10).

7- Stability towards hydrolysis:

The results listed in (Table 10), revealed that, the prepared anionic surfactants are moderately stable in basic medium and the stability increases by increasing the alkyl chain length as found by[227]. Also, anionic surfactant containing heterocyclic moieties recorded high values toward alkaline hydrolysis as found by [226].

Biodegradability.

The results showed that, the rate of degradation was decreased with increasing the molecular weight or alkyl chain length. This indicated that, the more bulky the molecule was the lower biodegradability of the surfactant as shown in (Table 11).

Biological activity.

The anionic surfactants containing heterocyclic moiety afforded a double function as surface active agents and antimicrobial activities.So, all the prepared surfactants were tested for their bactericidal activities against Eschericia Coli and Bacillus Cereus and their fungicidal activities against Aspergillus Flavus and Penicillium notatum. (Table 12), revealed that the presence of heterocyclic moiety in the prepared anionic surfactant molecule revealed an increase in the biological activity as found by [226].

Table (9): Physical properties of prepared compounds

No.	M.F.	M.wt	Solvent	Yield %	Color	Analysis data calc./ Found %			
						C	*H*	*N*	*S*
28a	$C_{21}H_{32}N_3O_3S_2Na$	461	Benz.	60	yellow	54.66 54.82	6.94 7.21	9.11 9.32	13.88 13.99
28b	$C_{23}H_{36}N_3O_3S_2Na$	489	Tol.	63	Pale yellow	56.44 56.65	7.36 7.45	8.58 8.75	13.08 13.22
28c	$C_{25}H_{40}N_3O_3S_2Na$	517	Benz.	58	Red yellow	58.02 58.61	7.73 7.85	8.12 8.32	12.37 12.55
29a	$C_{17}H_{31}N_2O_6S_2Na$	446	EtOH	55	White yellow	45.74 45.93	6.95 7.23	6.27 6.42	14.34 14.46
29b	$C_{19}H_{35}N_2O_6S_2Na$	474	MeOH	57	yellow	48.10 48.44	7.38 7.55	5.90 6.22	13.50 13.75
29c	$C_{21}H_{39}N_2O_6S_2Na$	502	Benz.	53	Pale yellow	50.19 50.43	7.76 7.92	5.57 5.76	12.74 12.89
30a	$C_{22}H_{33}N_2O_6S_2Na$	508	AcOH	73	yellow	51.96 52.12	6.49 6.72	5.51 5.72	12.59 12.79
30b	$C_{24}H_{37}N_2O_6S_2Na$	536	EtOH	70	Pale yellow	53.73 53.95	6.90 7.22	5.22 5.42	11.94 12.32
30c	$C_{26}H_{41}N_2O_6S_2Na$	564	AcOH	75	Pale yellow	55.31 55.55	7.26 7.35	4.96 5.12	11.34 11.56
31a	$C_{22}H_{31}N_2O_5S_2Na$	490	EtOH	60	Pale yellow	53.87 53.93	6.32 6.45	5.71 5.93	13.06 13.22
31b	$C_{24}H_{35}N_2O_5S_2Na$	518	MeOH	63	Red yellow	55.59 55.83	6.75 6.89	5.40 5.72	12.35 12.45
31c	$C_{26}H_{39}N_2O_5S_2Na$	546	AcOH	66	Red yellow	57.14 57.42	7.14 7.25	5.12 5.33	11.72 11.86
32a	$C_{21}H_{33}N_2O_5S_2Na$	480	Tol.	75	Brown	52.50 52.75	6.87 6.99	5.83 5.99	13.33 13.46
32b	$C_{23}H_{37}N_2O_5S_2Na$	508	Benz.	72	Brown	54.33 54.52	7.28 7.52	5.51 5.83	12.59 12.76
32c	$C_{25}H_{41}N_2O_5S_2Na$	536	Tol.	70	Red brown	55.97 65.22	7.64 7.85	5.22 5.43	11.94 12.22

Table (9): Cont.

No.	M.F.	M.wt	Solvent	Yield %	Color	Analysis data calc./ Found %			
						C	*H*	*N*	*S*
33a	$C_{21}H_{31}N_2O_5SNa$	446	Tol.	65	Brown	56.50 56.83	6.95 7.22	6.27 6.43	7.17 7.25
33b	$C_{23}H_{35}N_2O_5SNa$	474	Benz.	62	Brown	58.22 58.42	7.38 7.54	5.90 6.22	6.75 6.92
33c	$C_{25}H_{39}N_2O_5SNa$	502	Benz.	60	Red brown	59.76 60.92	7.76 7.92	5.57 5.74	6.37 6.54
34a	$C_{17}H_{30}NO_6S_3Na$	463	MeOH	65	Yellow	44.06 44.22	6.47 6.65	3.02 3.22	20.73 20.92
34b	$C_{19}H_{34}NO_6S_3Na$	491	MeOH	63	Pale yellow	46.43 46.55	6.92 7.22	2.85 2.99	19.55 19.72
34c	$C_{21}H_{38}NO_6S_3Na$	519	EtOH	68	Pale yellow	48.55 48.83	7.32 7.52	2.69 2.85	18.49 18.65
35a	$C_{17}H_{28}NO_5S_3Na$	445	EtOH	58	Pale yellow	45.84 45.99	6.29 6.42	3.14 3.35	21.57 21.72
35b	$C_{19}H_{32}NO_5S_3Na$	473	MeOH	62	Pale yellow	48.20 48.35	6.76 6.85	2.95 3.27	20.29 20.45
35c	$C_{21}H_{36}NO_5S_3Na$	501	EtOH	66	Red yellow	50.29 50.72	7.18 7.32	2.79 2.95	19.16 19.41
36a	$C_{21}H_{33}N_2O_4S_2Na$	464	Benz.	70	Yellow	54.31 54.45	7.11 7.25	6.03 6.23	13.79 13.92
36b	$C_{23}H_{37}N_2O_4S_2Na$	492	Tol.	73	Pale yellow	56.09 56.22	7.52 7.73	6.69 6.76	13.00 13.32
36c	$C_{25}H_{41}N_2O_4S_2Na$	520	Tol.	75	Pale yellow	57.69 57.82	7.88 7.95	5.38 5.54	12.30 12.56

Table (10): Surface properties of these compounds.

No.	Surface Tension (dyne/cm) 0.1 %	Interfacial Tension (dyne/cm) 0.1 %	Kraft Point °C 1%	Wetting time (sec.) 0.1%	Emulsion stability (min.)	Foam height (mm) 0.1%	Ca^{++} (ppm)	Stability to hydrolysis Min : Sec
28a	30	7.5	17	65	54	200	450	38 : 15
28b	32	8.0	20	90	61	220	380	39 : 20
28c	34	8.5	25	123	65	225	350	39 : 55
29a	33	8.2	16	90	42	155	1460	44 : 25
29b	35	8.7	19	115	47	170	1350	45 : 12
29c	37	9.0	23	132	55	190	1200	45 : 55
30a	34	9.5	18	80	57	180	1240	37 : 16
30b	37	10.3	22	110	63	200	1150	38 : 31
30c	39	11.0	29	135	68	220	900	38 : 58
31a	33	11.4	16	100	51	185	1230	37 : 10
31b	35	12.0	21	115	56	200	1260	37 : 44
31c	37	12.5	27	126	60	230	850	38 : 03
32a	31	6.7	22	85	63	170	560	43 : 30
32b	33	7.0	25	100	67	190	500	44 : 10
32c	35	7.5	31	120	71	205	450	45 : 05
33a	32	8.7	17	90	61	180	1530	42 : 14
33b	34	9.2	22	105	66	200	1420	43 : 08
33c	36	10.0	26	115	72	215	1300	44 : 16
34a	30	8.5	22	95	57	210	1260	44 : 27
34b	32	9.0	25	120	59	220	1150	45 : 20
34c	34	9.5	28	134	64	235	950	46 : 3
35a	33	7.0	13	105	63	190	1360	43 : 15
35b	36	7.5	19	115	67	200	1240	43 : 59
35c	38	8.0	22	127	72	205	1120	44 : 43
36a	28	8.6	18	95	49	180	1420	39 : 18
36b	30	9.0	22	108	55	200	1360	40 : 02
36c	32	9.4	25	120	59	210	1300	40 : 48

Table (11): Biodegradability of the Prepared Surfactants.

No.	1st day	2nd day	3rd day	4th day	5th day	6th day	7th day
28a	44	52	60	71	84	-	-
28b	41	49	45	65	77	92	-
28c	38	45	51	62	70	84	-
29a	45	55	62	69	78	88	97
29b	41	50	58	66	75	85	-
29c	37	45	54	63	71	83	91
30a	41	51	64	75	90	-	-
30b	38	46	58	72	87	93	-
30c	35	42	53	67	82	90	-
31a	43	50	63	75	92	-	-
31b	39	47	58	71	88	93	-
31c	37	44	54	68	75	89	94
32a	40	49	58	69	82	93	-
32b	37	46	55	64	79	88	97
32c	35	42	51	60	74	86	94
33a	47	55	66	77	89	-	-
33b	43	53	62	72	86	93	-
33c	39	50	58	68	83	89	95
34a	45	56	67	78	90	-	-
34b	42	52	64	75	87	94	-
34c	39	47	59	69	79	89	96
35a	49	58	69	80	93	-	-
35b	45	54	65	77	89	94	-
35c	41	51	61	73	84	90	-
36a	44	53	64	76	89	-	-
36b	41	50	60	71	86	92	-
36c	38	46	55	66	79	89	97

Table(12):Antimicrobial activity of the synthesized anionic surfactants.

Compd	Bacteria		Fungi	
	Bacillus cercus	*Bacillus coli*	*Aspergillus's flavus*	*Penicillum notatum*
28a	+	-	-	+
28b	+	-	+	++
28c	+	+	+	++
29a	++	-	-	+
29b	++	+	-	+
29c	+	+	+	++
30a	+	-	-	++
30b	++	-	-	++
30c	+++	-	+	++
31a	+	-	-	+
31b	++	-	+	+
31c	+	+	++	++
32a	+	-	-	+
32b	+	-	+	++
32c	++	+	++	++
33a	+	-	-	+
33b	+	-	+	+
33c	++	+	+	++
34a	+	-	-	+
34b	++	+	+	++
34c	+++	+	+	+++
35a	+	-	-	++
35b	++	+	-	++
35c	++	+	++	+++
36a	+	-	-	+
36b	+	-	-	++
36c	+	-	+	++

(+++) Very strong inhibition, (++) strong inhibition, (+) moderate inhibition.

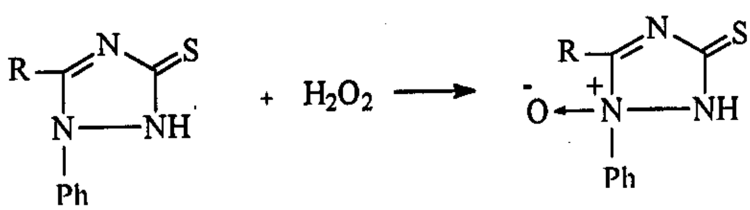
PART (4)

Amphoteric surfactants containing heterocyclic moiety

From the previously synthesized compounds which containing heterocyclic moiety and having a tertiary nitrogen atom, we planned to prepare a further type of surface active agents by treating a tertiary nitrogen atom with hydrogen peroxide or sodium chloroacetate to produce a novel groups of amphoteric surfactants having a double functions antimicrobial and surface active properties, where the amine oxides have excellent foam-stabilizing. They have been used in shampoos and high-duty liquid detergents where they provide detergency, emolliency, and foam-boosting activity [228, 229]. They also perform well in heavy detergent formulations providing good colon detergency. The use of amine oxides in fabric softener formulation has also been reported [230].

Synthesis of amine oxide derivatives.

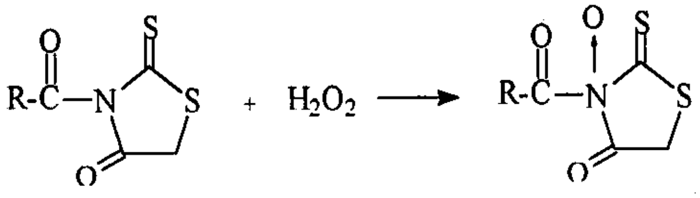
The amine oxides were prepared [104] by oxidation of a tertiary amine with aqueous hydrogen peroxide. So, 3-alkyl-2-phenyl-1,2,4-triazolinyl-5-thione **(4a-c)** were treated with H_2O_2 to produce 3-alkyl-2-phenyl-2-oxid-1,2,4-triazoline-5-thione **(37a-c)**.



(4a-c) **(37a-c)**

R, c = $C_{13}H_{27}$, b = $C_{15}H_{31}$, c = $C_{17}H_{35}$

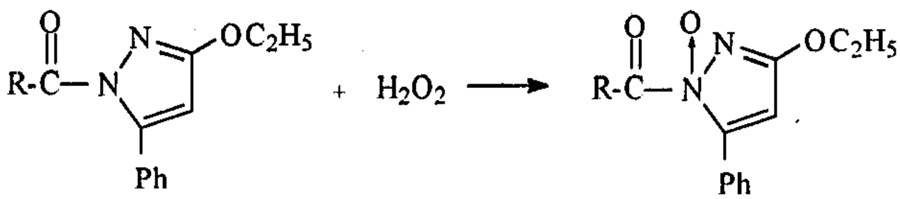
Also, 3-alkanoyl-1,3-thiazolidine-2-thione-4-one **(11a-c)** was used to produce 3-oxide-3-alkanoyl-1,3-thiazohidine-2-thione-4-one **(38a-c)** by oxidation with H_2O_2:



(11a-c) **(38a-c)**

R, c = $C_{13}H_{27}$, b = $C_{15}H_{31}$, c = $C_{17}H_{35}$

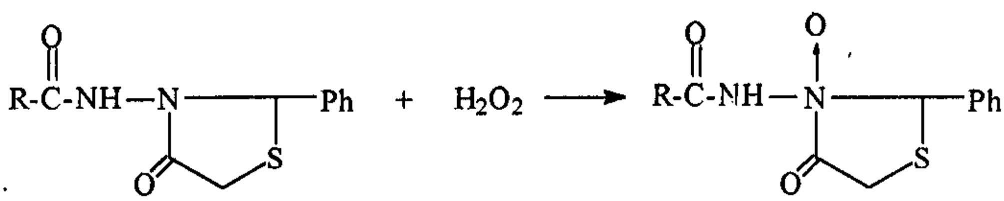
Also,1-N-alkanoyl-3-ethoxy-5-phenyl-1,2-pyrazole **(21a-c)** were used to give 1-N-alkanoyl-N-oxide-3-ethoxy-5-phenyl-1,2-pyrazole **(39a- c)** by oxidation with H_2O_2 as:



(21a-c) **(39a-c)**

R, c = $C_{13}H_{27}$, b = $C_{15}H_{31}$, c = $C_{17}H_{35}$

Finally, 3-N-amidoalkyl-2-phenyl-1,3-thiazole-4-one **(24a-c)** were used to prepare 3-N-amidoalkyl-3-N-oxide-2-phenyl-1,3-thiazole-4-one **(40a-c)** by treating with H_2O_2 as:



(24a-c) **(40a-c)**

R, c = $C_{13}H_{27}$, b = $C_{15}H_{31}$, c = $C_{17}H_{35}$

All synthesized compounds were confirmed by:

IR spectrum of **(38a)** shows band at 1360 cm^{-1} for νN-O, beside the original bands of the compound.

Mass spectrum of **(38b)** shows a molecular ion peak at $M^{+}+1$= 387,3.02% and base peak at m/z = 57,100%. (cf.fig 49.chart 11).

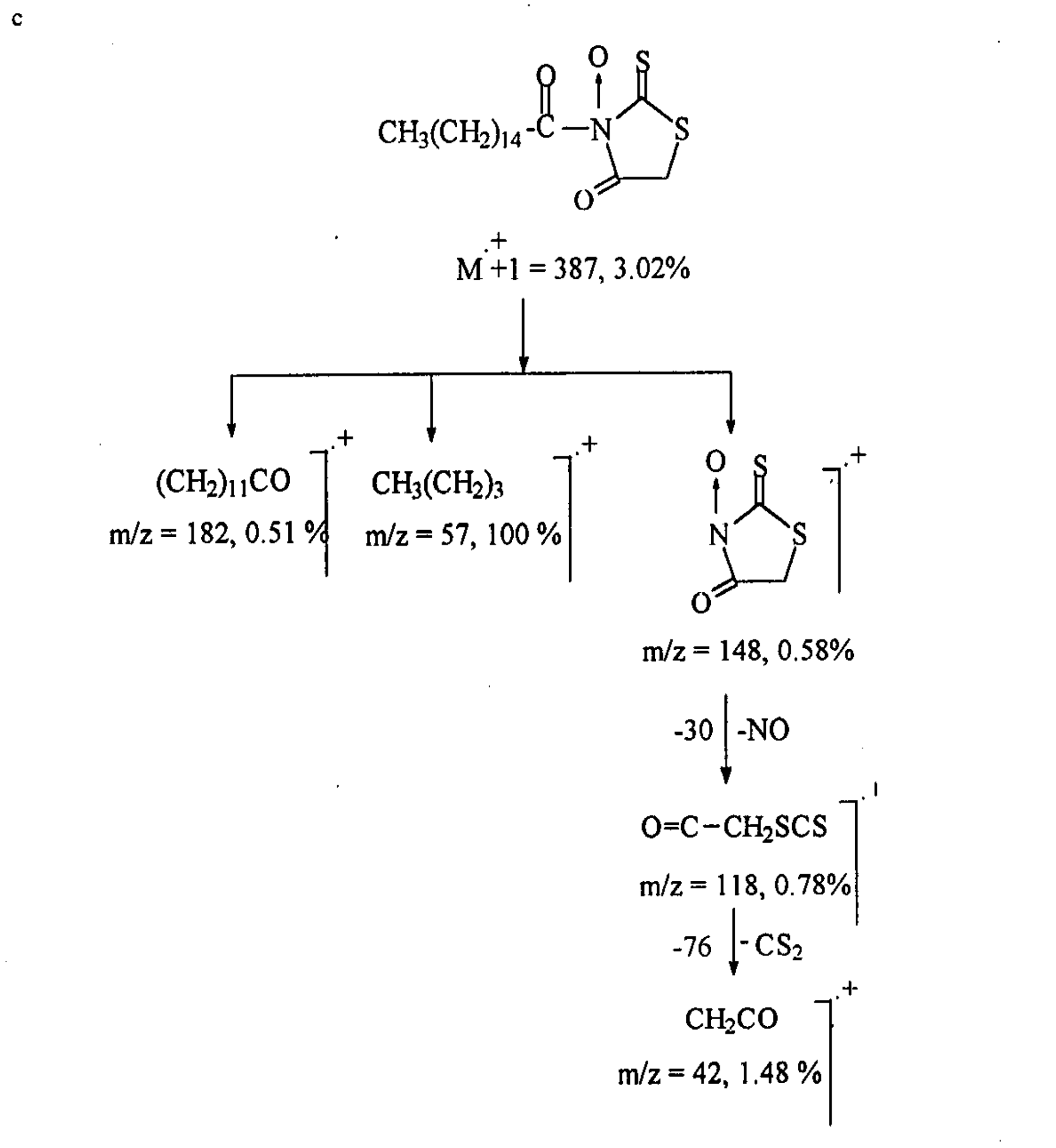


Chart 11

Surface active properties of amphoteric surfactants

The surface active and related properties of the synthesized compounds including, surface and interfacial tension, Kraft point, wetting time, foaming and emulsification properties are given in (Table 14) Biodegradability and biological activity also determined and the results are listed in table (15,16) respectively.

1- Surface and interfacial tension:

In general, surface and interfacial tensions increased with increasing alkyl chain length, where amine oxide surfactants with heterocyclic moiety recorded higher value as found by [132] of surface and interfacial tension as shown in Table (14).

2- Kraft point:

The Kraft points, of individual chain are listed in (table 14). The results indicated that the values of Kraft point increase by increasing the number of hydrophilic group's. All the synthesized amphoteric surfactants are soluble in water and the higher molecular weight is the higher Kraft points measurements as shown in Table (14).

3- Wetting time:

Also, wetting time increased as the alkyl chain length increased. The products were thus very effective as wetting agents in distilled water. So, they confined a wide application to play an important role as wetting agents in textile industry.

4- Foaming height:

Foaming height was reported that the efficiency of surfactants as a foamier increase with increasing alkyl chain length as found by [132]. In general, the prepared amphoteric surfactants from amine oxide recorded higher foam height as shown in Table (14).

5- Emulsion stability:

The prepared amphoteric surfactants afforded higher emulsification stability as found by [102], these results, might lead to the application of the surfactant of choice in pesticide and cosmetic formulation.

6- Stability towards hydrolysis:

Concerning to the stability towards acid and base hydrolysis, all the prepared surfactants have higher stability in acidic than in basic medium The results listed in (Table 14), revealed that, the stability increases by increasing the alkyl chain length. Also, the prepared surfactant containing heterocyclic moieties recorded high values toward stability to hydrolysis as found by [227].

Biodegradation.

The results showed that, the biodegradability decreased with increasing molecular weight or alkyl chain length as shown in Table (15). Also amphoteric surfactants containing heterocyclic moiety afforded a lower biodegradability due to the easy degradation for the heterocyclic moiety as found by [132].

Biological activities

All the prepared surfactants were tested for their bactericidal activities against Bacillus subtless and Bacillus cereus and their fungicidale activities against Aspergillus flavus and Pencillium notatum. Table (16) gives the presence of heterocyclic moiety in the prepared surfactant molecule revealed an increase in the biological activity and a decrease in biodegradability.

Table (13): Physical properties of prepared compounds

No.	M.F.	M.wt	Solvent	Yield %	Color	Analysis data calc./ Found %			
						C	*H*	*N*	*S*
37a	$C_{21}H_{33}N_3OS$	375	Tol.	30	White	67.20 67.51	8.80 8.96	11.20 11.45	8.53 8.72
37b	$C_{23}H_{37}N_3OS$	403	Tol.	35	White yellow	68.48 68.69	9.18 9.27	10.42 10.67	7.94 8.22
37c	$C_{25}H_{41}N_3OS$	431	Benz.	32	White yellow	69.60 69.84	9.51 9.67	9.74 9.92	7.42 7.53
38a	$C_{17}H_{29}NO_3S_2$	359	EtOH	30	Yellow	56.82 56.99	8.07 8.25	3.89 3.95	17.82 17.97
38b	$C_{19}H_{33}NO_3S_2$	387	EtOH	32	Yellow	58.91 59.23	8.52 8.72	3.61 3.82	16.53 16.72
38c	$C_{21}H_{37}NO_3S_2$	415	AcOH	35	Pale yellow	60.72 60.91	8.91 9.12	3.37 3.52	15.42 15.65
39a	$C_{23}H_{36}N_2O_3S$	420	MeOH	30	White yellow	65.71 65.93	8.57 8.74	6.66 6.82	7.61 7.82
39b	$C_{25}H_{40}N_2O_3S$	448	EtOH	35	Yellow	66.96 67.31	8.92 9.13	6.25 6.42	7.14 7.28
39c	$C_{27}H_{44}N_2O_3S$	476	EtOH	37	Yellow	68.06 68.32	9.24 9.35	5.88 5.99	6.72 6.92
40a	$C_{25}H_{40}N_2O_3$	416	Benz.	30	White	72.11 72.36	9.61 9.85	6.73 6.92	
40b	$C_{27}H_{44}N_2O_3$	444	Tol.	32	White	72.97 78.27	9.90 10.22	6.30 6.55	
40c	$C_{29}H_{48}N_2O_3$	472	Tol.	35	White yellow	37.72 37.87	10.16 10.32	5.93 6.11	

Table (14): Surface properties of these compounds.

No.	Surface Tension (dyne/cm) 0.1	Interfacial Tension (dyne/cm) 0.1	kraft Point °C 1%	Wetting time (sec.) 0.1%	Emulsion stability (min.)	Foam height (mm) 1%	Stability to hydrolysis Min : Sec
37a	38	6.2	21	86	55	113	31 : 15
37b	40	6.7	25	95	59	136	32 : 33
37c	41	8.7	29	106	64	145	34 : 16
38a	35	5.7	18	96	51	116	35 : 20
38b	37	7.0	26	101	55	135	36 : 08
38c	39	11.3	34	112	60	165	37 : 36
39a	33	7.5	25	108	71	70	42 : 43
39b	35	8.0	32	112	75	87	44 : 02
39c	37	10.5	37	120	82	112	45 : 13
40a	33	10.0	23	116	63	95	39 : 46
40b	34	11.5	30	122	68	108	40 : 54
40c	36	12.5	35	130	74	117	41 : 32