4. RESULTS AND DISCUSSION

(Part 1)

I.4.1 Separation of aromatic extracts

The results of aromatic extracts separation, as listed in table (3) show that light and medium aromatic extracts, sample contains higher percentage of saturates and lower percentage of resins than those in heavy aromatic extracts sample . This indicates the presence of more contaminates in heavy aromatic extract than in light and medium aromatic extract.

Table (3) separation of aromatic extracts

Hydrocarbon class % wt	LAE	MAE	HAE
Saturates	25.5	19.6	14.7
Mono and di-aromatics	71.1	75.9	79.9
Poly aromatics&resins	1.5	2.5	5.4

I.4.2 Evaluation of the physical and chemical properties of the tested samples:

The physical and chemical properties of the tested samples, which are :

- Local linear alkyl benzene, sample No (1).
- Heavy alkyl benzene, sample No (2).
- light aromatic extract residue, sample No (3).
- Medium aromatic extract residue, sample No (4).
- Heavy aromatic extract residue, sample No (5).
- Blend of (60%HAB+ 40% LAE) sample No (6).
- Blend of (80%HAB+ 20% MAE) sample No (7).
- Blend of (85%HAB+ 15% HAE) sample No (8).

Were listed in table (4).

Evaluation Studying of obtained Results in table 4 are according to the following

- Specific gravity:

The trend of Specific gravity is as follow:

Specific gravity increase

→

Sample (1) Sample (2) Sample (6) Sample (7) Sample (3) Sample (4) sample (8)sample(5)

- Specific gravity of heavy alkyl benzene(HAB) sample (2) is higher than linear alkyl benzene(LAB) sample (1).

- Specific gravity of blend (60% HAB + 40% LAE) sample no (6) is lowers than leaner aromatic extract (LAE) sample no (3).

- Specific gravity of blend (80% HAB + 20% MAE) sample no (7) is lower than (LEA) sample no (3) and (MAE) sample no (4).

- Specific gravity of blend (85% HAB + 15% HAE) sample no (8) is lowers than (HAE) sample no (5).

- Specific gravity of blend (85% HAB + 15% HAE) sample no (8)and(HAE) sample no (5) are much higher than samples no (1, 2,6,7,3and 4) respectively.

This due to presence of bulk group in these samples

Color

- Samples no (1& 2) have the best color.

-Samples no (3, 4 & 5) was dark color.

-Sample no (6) gave moderate color while samples no (7 & 8) gave deep brown color. From results obtained, it was found the percentage of resin or oxygenated compound lower in samples 1 & 2 than sample 6.

Kinematic viscosity

- Sample no. (1) Have lower Kinematic viscosity at 40 ˚ c, CST and 100 ˚c, CST.

-Sample no. (3, 4 & 5) have highest value of Kinematic viscosity at 40 ˚ c, CST and 100 ˚c, CST.

-Sample no. (5) Was not suitable for carrying out the test at 40 ˚ c, CST due to high viscosity.

-Sample no. (2, 6, 7 & 5) have moderate value of Kinematics viscosity at 40 ˚ c, CST and 100 ˚c, CST.

This due to increase of sulphonation group.

Refractive index:-

- Linear alkyl benzene and heavy alkyl benzene, samples (1 & 2) have nearly the same value.

- Heavy aromatic extract sample (5), medium aromatic extract sample (4) , light aromatic extract sample (3), blend of (80% HAB + 20% MAE) sample no (7), and blend (85% HAB + 15%

HAE) sample no (8) these samples have higher refractive index than light aromatic extract and blend (60%HAB + 40%LAE),sample no (6) this may be due to presence of di aromatic extract in these samples.

Sulphonatable content % wt

- The sulphonatable content %wt of Linear alkyl benzene sample (1)(excellent) is the same as heavy alkyl benzene sample (2) and so the sulphonatable content %wt light aromatic extract sample (3) is the same as blend of(80% HAB + 20% MAE) sample no (7) and blend of (60% HAB + 40% LAE) sample no (6) gave very good yield.

- The sulphonatable content %wt of heavy aromatic extract sample (5) and blend (85% HAB + 15% HAE) sample no (8) gave very bad yield.

- The sulphonatable content %wt of heavy aromatic extract sample (5),medium aromatic extract sample (4) and blend (85% HAB + 15% HAE) sample no (8) were gave lower yield this may be due to presence of more contaminates (di aromatics, poly aromatics & resins).

Molecular weights:

- Linear alkyl benzene (LAB) sample (1), heavy alkyl benzene (HAB) sample (2), blend of (60% HAB + 40% LAE) sample no (6) and

Blend of (80% HAB + 20% MAE) sample no (7) have nearly similar Molecular weights.

On the other hand light aromatic extract sample (3) and medium aromatic extract sample (4) have much higher value.

Sulphur and water content:

All the tested samples are free from both sulphur (doctor test) and water.

I.4.3Determination of chemical structures of the tested samples:

I.4.3 Gas chromatography and Mass spectra

The chemical structure of each of (LAB), (HAB), (LAE) and (MAE) were determined by applying GC \ Mass technique, Figures 4, 5, 6& 7 represent their chromatograms respectively, while tables (5), (6), (7) & (8) include the chemical structure of the components exist in each of the them respectively.

Light Alkyl Benzene (LAB) Sample (1), Molecular Structure.

Evaluation study from figure (4) shows that the sample contains eighteen components in different proportions these components were only ones which were traced via applied G.C techniques.

Amass spectrum for each separated component was preceded, to evaluate its fine chemical structure. Table (5) indicates molecular formula, molecular weight of each chemical component in LAB.

Investigation of these results as listed in table (5) and represented in figure (4) indicates the following points: -

1. LAB has eighteen components with different proportions.
2. All components have substitution with branched side chain (C_{11} - C_{13}) at either α, β or both positions to the benzene ring
3. Substituted group were included, $-CH_3$, $-C_2H_5$, $-C_3H_7$, $-C_4H_9$ and $-C_5H_4$.
4. All components gave rise to base peak with m\e 91 except those with α – methyl substituted group which gave a peak with m\e 105.

5. Component number 5, 2-pentyl heptyl benzene (mol.wt.246) represent the highest percentage 22.2 % component has 12 carbon atoms in the side chain.

6. Components 5 -13 have side chain 12 carbon atoms. These 9 components represent about 56 11 % of LAB.

➢ Heavy alkyl benzene (HAB) sample (2) Molecular Structure

Separation of heavy alkyl benzene (HAB) into its chemical components was accomplished by G.C as shown in figure (5) and represented in its chromatogram which shows that this sample contains sixteen components with different proportion.these components were the only ones which traced via applied G.C technique using OV-17colum.

Amass spectrum for each separated component was carried out after gas chromatography separation to detect there sutability for sulphonation.

Investigation of these results as listed in table (6) and represented in figure (5) indicates the following points: -

1- HAB has sixteen components with different proportions.

2- All components have substitution with branched side chain (C_{12} - C_{16}) at either α, β or both positions to the benzene ring

3- Substituted group were included, - CH_3, -C_2H_5, - C_3H_7, - C_4H_9 and – C_5H_{11}.

4- All components gave rise to base peak with m\e 91 except those with α – methyl substituted group which gave a peak with m\e 105.

5- Component number 11 (1-methyl - 2-propyl nonyl benzene) with (mol.wt 260) represent the highest percentage 27.690 % component has 13 carbon atoms in the side chain

6- Components number 7- 12 have side chain 13 carbon atoms. These six components represent about 80.65 % of HAB.

Light aromatic extract (LAE) sample (3) Molecular Structure.)

Separation of light aromatic extract (LAE) sample into its chemical components was accomplished by G.C as shown in figure (6) and represented in its chromatogram which shows that this sample contains seventeen components with different proportion these components were the only ones which traced via applied G.C technique using OV-17colum.

Amass spectrum for each separated component was carried out after gas chromatography separation to detect there sutability for sulphonation.

Investigation of these results as listed in table (7) and represented in figure (6) indicates the following points: -

1- LAE has seventeen components with different proportions.

2- All components have substitution with branched side chain (C_{19} - C_{34}) at either α, β or both positions to the benzene ring

3 - Substituted group were included, - CH_3, - C_4H_9,-OH,-COOH, CL and –NH_2

4- Chlorine is present in components (3-2, 3-3, 3-4) as hydrolysable chlorine, while components (3-1,3-5, 3-8,3-12) contain non-hydrolysable chlorine.

5- Nitrogen is present in components (3-17) only as a primary amino group.

6- Most of the components contain hydroxyl groups in the side chain except (3 - 1) which has a phenol group.

7- The component (3-13), 3-hydroxyoctadecyl phthalic acid represents about 14 % of sample (3) and represent the highest percentage (m.wt.432) this component has 20 carbon atoms in its side chain.

8- All components gave rise to base peak with m\e (40, 43,55,57,73 and 149).

<u>Medium aromatic extract (MAE) sample (4) Molecular Structure</u>-

Separation of light aromatic extract (MAE) sample into its chemical components was accomplished by G.C as shown in figure (7) and represented in its chromatogram which shows that this sample contains seventeen components with different proportion.these components were the only ones which traced via applied G.C technique using OV-17 colum.

Amass spectrum for each separated component was carried out after gas chromatography separation to detect there sutability for sulphonation.

Investigation of these results as listed in table (8) and represented in figure (7) indicates the following points: -

1- MAE has twenty components with different proportions.

2- All components have substitution with branched side chain (C_{20} - C_{31}) at either α, β or both position and p- position to the benzene ring in component (4-3, 4-4, 4-5).

3- Substituted group were included, $-CH_3$, $-C_2H_5$, $-C_3H_7$,- C_4H_9,-OH, - and $-NH_2$

4- Nitrogen is present in components (4-17) only as a primary amino group. This component represents about 6 % of sample (4).

5- Most of the components contain hydroxyl groups in the side chain.

6- The components (4 - 3),(4 - 4)and (4 - 5), which has naphthyl nucleus.

7- The components (4-11), 5,7,12 trihydroxyl nonacosyl benzene, (m.wt.532),represents about 9% of sample (4)which is the highest component percent and contain 29 carbon atom in side chain.

8- All components gave rise to base peak with m\e (57, 82, 91 and 156).

The molecular wights of the 17 component in the light aromatic extract Sample3 are in the range (376-473), while the molecular weight of the twenty components in the medium aromatic extract sample4 are in the range (422-576) except the component (4-1) which has molecular weight 354 with 1.3 %

Light aromatic extract contain some components having chlorine in their structures, while the medium aromatic residue has no chlorine in any of its components

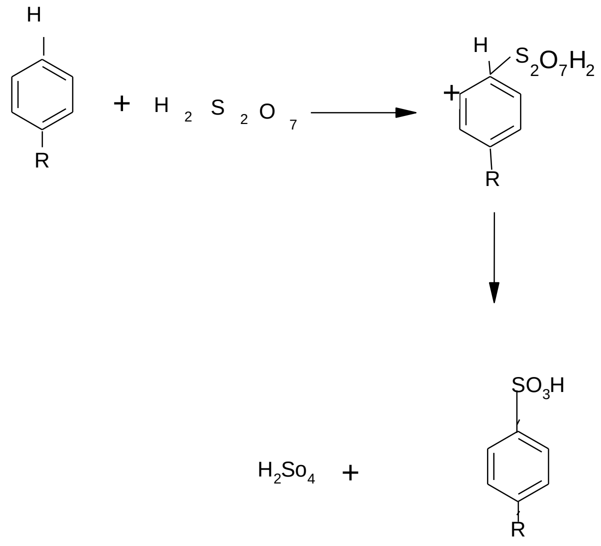
Only one component is each sample (3&4) contain nitrogin as primary amino group.

I.4.4 Sulphonation mechanism of the tested samples

The sulphonation process was applied to the eight samples using concentrated sulphuric acid as sulphonating agent.

Sulphonation with concentrated sulphuric acid was studied by kachurim and sprykov (173){ brand, jarive and horning,chem. Soc,3844 (1959) }.They stated that sulphonation is reversible and the sulphonating species is SO3H.it was suggested that sulphonation with concentrated sulphoric acid proceeds by the following mechanism :

$$3H_2So_4 \rightleftharpoons H_2S_2o_7 + H_3o^+ + HSo_4^-$$



The presence of halogen supstituents in aromatic nucleus (sample 3) decrease the the reactivity towards sulphonation.

It was reported (174,175) that sulphonation of monohalobenzens take place mainly at the para position. The very low o ⁄ p ratio obtained was explained in terms of:

The - I effect of the halogen atom is more effective at the o-position than at p – position at which this effect is nearly diminished.

Supstitution at the o-position is known to be sterically less than at the p- position.

Because of the presence of alcoholic groups in some components of samples (3, 4) (6, 7) sulphation for these samples might occur besides sulphonation. The traditional sulphation process is the interaction of alcohol with sulphoric acid, which is areversible esterfication reaction:

$$ROH + H_2SO_4 \rightarrow ROSO_3H + H_2O$$

The mechanism of the sulphation of alcohols by sulphoric acid in general:

$$H_2SO_4 \rightarrow H_2O^+\text{-}SO_2OH \rightarrow RHO^+\text{-}So_2OH \rightarrow RoSo_2OH$$

Therefore, to decrease the extent of sulphation reaction,n-butyl acetate was added,as a capturing agent,in case of sample (3,4)

which contain alcoholic groups.

I.4.5 Evaluation of sulphonation processes

Evaluation of sulphonation processes were studied to ascertain their suitability in the synthesis of surfactants. The results obtained (cf, table (9) reveal the following

Sulphonation condition for linear alkyl benzene and heavy alkyl benzene sample (1 & 2) are the same and give excellent yields.

Sulphonation process for light aromatic extract sample (3) requires a larger amount of acid and higher temperature than both of linear and heavy alkyl benzene sample (1 & 2) and give good yield.

Sulphonation process for (40 % LAE + 60% HAB) and (20% MAE +80%HAB)

Samples no (6 & 7) requires a larger amount of time and lower temperature than both of sample (1 & 2) and give good yield.

The lower yield of sulphonation production in case of light aromatic extract sample (3), (40 % LAE + 60% HAB)and (20% MAE +80%HAB) sample (6 & 7) than those of linear alkyl benzene and heavy alkyl benzene sample (1 & 2) may be attributed to steric effect. the substitution at the α –c of alkyl side chain, may hinder sulphonation at 0- position to a great extent and may be attributed to the ester formation by sulphation process which may take place, even in the presence of capturing agent (decrease its rate only).

Sulphonation condition for (40 % LAE + 60% HAB)and (20% MAE +80%HAB) sample (6 & 7)are nearly similar and give good yield.

Sulphonation condition for (85 % HAB + 15 % LAE) AND (HAE) sample (8&5)

Are nearly similar and give bad yield.

Sulphonation of (MAE) sample (4) gave moderately yield.

The lowest yield of sulphonation products in case of (MAE) sample (4) even than (LAE) sample (3) may be attributed to the larger number of alcoholic components in sample (4) compared with sample (3) [sample (4) contains nineteen alcoholic components from twenty , sample (3) contains eleven alcoholic components from seventeen] and may be attributed to the ester formation by sulphation process which may tack place, even in the presence the capturing agent (decrease its rate only).

The sulphonation of (LAB) by 98 %(H_2SO_4) at 50-55˚c and digestion time 4 hours

Acid /sample ratio	Yield %
1:1	41.2
1.25:1	80
1.5:1	92
1.7:1	94

-Sulphonation of LAB by 98% H_2SO_4 at 45-55˚c and the time addition of sulphonating agent was (5) minute and Acid /sample ratio (1, 8: 1)

Reaction Temp.,c	Digestion Time,hr	Yield %
45– 50	6	92.3
45- 50	7	93.1
50– 55	8	94.2

The Sulphonation condition trials for heavy alkyl benzene(HAB) sample (2) :

Acid/sample ratio	Reaction Temp.,c	Digestion Time,hr	Yield/100g Sample%
1:1	45-50	2	30.4
1.25:1	45-50	2	50
1.5:1	45-50	2	60.6
1.7:1	45-50	2	65.5
1.8:1	45-50	2	66.2
1:1	45-50	3	35
1.25:1	45-50	3	55.1
1.5:1	45-50	3	62.2
1.7:1	45-50	3	67.5
1.8:1	45-50	3	67.7
1:1	45-50	4	40.7
1.25:1	45-50	4	70.3
1.5:1	45-50	4	77
1.7:1	45-50	4	79.9
1.8:1	45-50	4	79.9
1:1	50-55	2	31.4
1.25:1	50-55	2	63.7
1.5:1	50-55	2	65
1.7:1	50-55	2	71.9
1.8:1	50-55	2	72.9

1:1	50-55	3	33.4
1.25:1	50-55	3	70.5
1.5:1	50-55	3	71.2
1.7:1	50-55	3	82.6
1.8:1	50-55	3	82.8
1:1	50-55	4	51
1:25:1	50-55	4	84.7
1.50:1	50-55	4	90.4
1.7:1	50-55	4	92.0
1.8:1	50-55	4	93.0
1:1	55-60	2	32
1:25:1	55-60	2	73.7
1.50:1	55-60	2	76.8
1.7:1	55-60	2	80.5
1.8:1	55-60	2	81.3
1:1	55-60	3	39.1
1:25:1	55-60	3	76.1
1.50:1	55-60	3	82.5
1.7:1	55-60	3	83.1
1.8:1	55-60	3	83.3
1:1	55-60	4	55
1:25:1	55-60	4	88.8
1.50:1	55-60	4	92.0
1.7:1	55-60	4	93.0
1.8:1	55-60	4	93.0

- Sulphonation conditions of (LAE) sample (3) by H_2SO_4 98%-

Acid/sample ratio	Reaction Temp.ºc	Digestion Time (h)	Yield %wt
1.5:1	50-55	2	55
1.5:1	50-55	3	60
1.6:1	50-55	3	63
1.6:1	50-55	4	70
1.7:1	55-60	4	75
1.7:1	55-60	4	80
1.8:1	55-60	4	80

- Sulphonation condition of(MAE)sample (4) by H_2SO_4 98%-

Acid/sample ratio	Reaction Temp.c	Digestion Time(h)	Yield %wt
1.2:1	50-55	2	6
1.3:1	50-55	2	11
1.4:1	50-55	2	13
1.5:1	60-70	2	7
1.5:1	40-50	2	18
1.6:1	35-40	3	20
1.6:1	35-40	4	35
1.6:1	35-45	6	40
1.6:1	35-45	6	45

- Sulphonation condition of(HAE)sample (5) by H_2SO_4 98%

Acids/sample Ratio	reaction Temp.ºc	Digestion Time(h)	Yield %wt
1.2:1	50-55	2	-
1.2:1	50-55	2	-
1.5:1	50-55	3	5

- Sulphonation condition of(60% HAB+40%LAE)sample(6) by H_2SO_4 98%

Acid/sample ratio	Reaction Temp.c	Digestion Time(h)	Yield %wt
1.2:1	50-55	2	45
1.3:1	50-55	2	50
1.4:1	50-55	2	55
1.5:1	50-55	3	60
1.6:1	55-60	3	65
1.6:1	55-60	4	70
1.6:1	55-60	5	73
1.6:1	35-45	6	76
1.6:1	35-45	6	78
1.6:1	35-45	6	80
1.7:1	35-45	6	85
1.7:1	35-45	6	85

- Sulphonation condition of(80% HAB+20%MAE) sample (7) by H_2SO_4 98%

Acid/sample ratio	Reaction Temp.c	Digestion Time(h)	Yield %wt
1.2:1	50-55	2	45
1.3:1	50-55	2	50
1.4:1	50-55	2	55
1.5:1	50-55	3	60
1.6:1	55-60	3	65
1.6:1	55-60	4	70
1.6:1	45-50	5	73
1.6:1	35-45	6	76
1.6:1	35-45	6	78
1.6:1	35-45	6	80
1.7:1	35-45	6	80
1.7:1	35-45	6	80

- Sulphonation condition of (85% HAB+15%HAE) sample (8) by H_2SO_4 98%

Acids/sample Ratio	reaction temp.c	Digestion Time(h)	Yield %wt
1.2:1	50-55	2	5
1.2:1	50-55	2	7
1.5:1	50-55	3	10
1.5:1	50-55	4	10

Table (9)

Optimum sulphonation conditions by using H_2SO_4 98%

SAMPLE	ACID: SAMPLE RATIO	REACTION TEMP. °C	DIGESTION TIME (H)	YIELD % WT
LAB sample (1)	**1.7 : 1**	**50 - 55**	**4**	**94.0**
HAB sample (2)	**1.8 : 1**	**50 - 60**	**4**	**93.0**
LAE sample (3)	**1.8 : 1**	**55 - 60**	**6**	**80**
MAE sample (4)	**1.6 : 1**	**35 - 45**	**6**	**45**
HAE sample (5)	**1.5 : 1**	**50 - 55**	**3**	**5**
(60%HAB+40%LAE) sample (6)	**1.7 : 1**	**35 - 45**	**6**	**85**
Sample(7) (80%HAB+20%MAE)	**1.7 : 1**	**35 - 45**	**6**	**80**
Sample(8) (85%HAB+15%HAE)	**1.5 : 1**	**50 - 55**	**4**	**10**

Stirring speed, 250-300 rpm

I.4.6 Evaluation of physical and chemical properties of the syntheses sulphonic acid.

Active matter:

- Active matter of (HAE) sulphonic acid and (85%HAB +15%HAE) sulphonic acid gave very low value.

- Active matter of (sample 1), (sample 2) and (sample 6) gave the higher value.

- Active matter of (sample 7 & sample 4) gave moderate value.

Unsulphonated matter

- Unsulphonated matter of (sample 1&sample 2) gave lower value.
- Unsulphonated matter of (sample 3, sample 6 & sample 7) gave moderate value.
- Unsulphonated matter of (sample 4, sample 5 & sample 8) gave higher value.

Free sulphoric acid

- Free sulphoric acid of (sample 5 & sample 8) gave higher value.
- Free sulphoric acid of ((sample 1),(sample 2),(sample 6), (sample 7 & sample 4)gave small nearly similar value.

Kinematic viscosity:

Kinematic viscosity at 25 ˚c and 40 ˚ c of all sample gave nearly the same value without sample(5 & 8) could not give values by this method.

Water content:

-Water content of sample (1&2) gave lower value.

-Water content of samples (3, 4, 6 & 7) gave moderate values and nearly similar.

-Water content of samples (5 & 8) gave higher value.

So we would not use the sample (5 & 8) in prepared the surfactants due to the bad product of them.

Table (10) **Analysis figure of synthized sulphonice acid.**

test	Astm method	LAB sample (1)	HAB sample (2)	LAE sample (3)	MAE (sample 4)	HAE sample (5)	(60%HAB + 40%LAE) sample (6)	80%HAB(+ 20%MAE) sample (7)	(85%HAB + 15%HAE) sample (8)
Active matter % wt	Cetylprednum Bromid D-1681	95	92	70	63	nil	81	77.5	5
Acid value MgKOH/g sample	ASTM-D-1172	210	202	180	170	.....	190	183	…..
Unsulphonated Matter %wt		0.3	0.4	15	17	....	10	12	……
Free sulfuric acid % wt		3.7	3.6	4	6	55	3	5	50
Kinematic viscosity at 40 ˚c	D445	300	353	360	390	....	390	393	…….
Kinematic viscosity at 25 ˚c	D445	855	920	960	980	.....	990	995	…..
Water content% vol.	D95	1.0	4.0	11	14	45	6	5.5	45

I.4.7 Evaluation of physical and chemical properties of the formulated surfactants

Formulated surfactants from the six samples were given the labels 1s, 2 s, 3s, 4s, 6 s and 7 s, respectively.

From the data listed in table (11), we can deduce the following:

Specific gravity

The figure of **specific gravit**y shows the following order:

Specific gravity increase

→

1s 2s 6s 7s 3s 4s.

Specific gravity of prepared surfactants from linear alkyl benzene, heavy alkyl benzene and blend of (60 % HAB + 40 % LAE) samples (1s,2s & 6s) are nearly the same.

Specific gravity of prepared surfactants from (LAE, MAE & 80% HAB +20%LAE) samples (3, 4 & 7) are higher than those samples from all.

Anionic active matter and total active matter of surfactants

Anionic active matter and total active matter of surfactants prepared from linear alkyl benzene, heavy alkyl benzene and blend of (60 % HAB + 40 % LAE) samples (1s,2s & 6s) are nearly the same.

Anionic active matter and total active matter of surfactants prepared from (60% HAB + 40% LAE) & (80% HAB +20% MAE) samples (6 & 7) are lower than (LAB & HAB) samples(1 & 2) this may be due to the presence of bulky group in the position of the side chain components which inhibit sulphonation to some extent at the ortho – position.

Anionic active matter and total active matter of surfactants prepared from (LAE & MAE) samples (3&4) are nearly the same, and much lower than that prepared from linear alkyl benzene (LAB) & (HAB) heavy alkyl benzene sample (1& 2) this may be attributed to the presence of chlorine, and carboxyl groups in the benzene ring of some component of sample (3) which reduced the reactivity of the ring towards sulphonation,

Components (3-1, 3-4, 3-8, 3-12) and (3-13) table (). the presence of bulky groups in the benzene ring of some components of sample (4) may cause certain steric hindrance decreasing the extent of sulphonation, components (4-3, 4-4 and 4-5 (table).

Samples (5 & 8) both of them may be contains bulky groups in the benzene ring of all components this may be cause certain steric hindrance which prevent take place good sulphonation..

Such results are supported by the high percentage of remained inorganic salt in samples analysis.

Kinematic viscosity of surfactants

Kinematic viscosity of surfactants prepared from (HAB) sample (2) is higher than that prepared from (LAB) sample (1)

Kinematic viscosity of surfactants prepared from (LAE), (MAE),(60% HAB + 40% LAE) & (80 HAB + 20 % MAE) are nearly the same and higher than sample (1) LAB & (2) HAB .

Cloud point of surfactants

Cloud point of surfactants prepared from linear alkyl benzene and heavy alkyl benzene gave the best results compared with all samples, while the other four samples gave high values.

Inorganic salt of surfactants prepared from (LAB),(HAB), (60% HAB + 40% LAE) & (80 HAB + 20 % MAE) are nearly the same and lower than (MAE)& (LAE).

Appearance of surfactants

Appearance of surfactants prepared from (LAB) &(HAB) are color less ,surfactant of (60% HAB + 40%LAE) & (80 HAB + 20 % MAE) are clear yellow and the surfactant prepared from (LAE), (MAE) are deep brown.

Table (11)

Physical and chemical properties of formulated surfactants samples

test	Astm method	LAB sample (1)	HAB sample (2)	LAE sample (3)	MAE sample (4)	(60%HAB + 40%LAE) sample (6)	80%HAB(+ 20%MAE) sample (7)
Active matter (anionic) % wt	D-1681	11.8	11.7	7.2	6.3	8.5	9. 5
Total active matter(%wt)	D-820	20.6	20.5	13	14	18	19
Kinematic viscosity at 40 ˚ c	D445	220	255	260	290	290	293
Kinematic viscosity at 25 ˚ c	D445	755	822	860	880	890	895
Specific gravity At 60/60 ˚ f	D-1298	1.0552	1.0557	1.0991	1.0999	1.0558	1.0944
Cloud point ˚ c	D-97	ZERO	-1	25	30	15	16
PH of 0.1%wt	D-1172	7.2	7.5	8.3	8.3	8.7	8.7
In organic salts % wt	D-1568	0.7	1.4	5.2	5.0	1.8	3.0
appearance		colorless	colorless	Brown	Brown	Yellow	Yellow

I.4.8 Evaluation of the formulated surfactants.

I.4.8.1 Detergency power. (176)

Detergency is defined as the" cleaning power". Accordingly a detergent is any agent that cleans. Detergency in both its practical and theoretical aspects is a difficult field for many reasons. In the first place, it is difficult to define detergency or even "Cleanness" quantitatively in terms which are applicable to more than a very limited number of detersive systems. Secondary, it is well recognized that mechanical and geometrical factors are frequently more important than physicochemical factors in determining the cleaning effect. Still another difficulty in systematizing the study of detergency is the high specificity of soil – substrate combination.

The various physical, chemical mechanical and geometrical variables in a detersive system which can influence the resultant cleaning effect had been reviewed and discussed by Schwartz (177).

The phenomenon of solubilization is of interest from the practical as well as the theoretical point of view, and many different aspects of this effect have accordingly been investigated.(178)

For example, the branched- chain naphthenic soaps are less effective than straight -chain soaps of the same molecular weight (179).

Many attempts had been made to relate detergency to the structure of the surfactants, Gray(180) and Ludeman (181) studies a series of o- and p- substituted straight and branched chain p – compounds are considered detergents but the ortho –substituted compounds are more surface active, shown by surface tension lowering.

When the hydrocarbon chain is lengthened greatly, the product becomes less effective due to its decreased solubility.(182)

This occurs also when the aromatic group becomes too large. Likewise, by decreasing the length of alkyl group, solubility increased, detergency falls off, and wetting power increase. Branched chains surfactants improve wetting at the expense of detergency. (183)

Detergency power of the formulated surfactants, samples (1s, 2s). With conc. (0.2 , 0.4 , 0.8 and 1%) in water, are listed in table (12)

The products shows that the detergency power is improved by increasing the surfactant concentration.

The data of table (12) , lead to the following conclusion:

The trend of detergency power shows the following:

Detergency power increase

$$\xrightarrow{\hspace{12cm}}$$

Sample (1) sample (2) sample (6) sample (7) sample (3) sample (4)

Table(12)

Sample no.	Detergency power			
	0.2	0.4	0.8	1.0 w t %
1 s	29.1	44.5	64.7	70.6
2 s	30.2	44.4	63.5	69.7
6 s	47.3	61.0	71.0	80.2
7 s	50.0	70.0	85.0	88.0
3 s	57.0	75.0	87.7	90.1
4 s	62.0	77.5	90.7	92.5

- Surfactants prepared from (LAB) & (HAB) samples (1s& 2s),gave nearly the same values.

- Surfactants prepared from (HAB +LAE) & (HAB +MAE) samples (6&7), Showed good detergency power comparing with (LAB &HAB) sulphonates, Samples (1s&2s).this may be attributed to the high length of its side chain.

- Surfactants prepared from (LAE) & (MAE) samples (3s & 4s), gave excellent values. This may be due to highly long side chain components of samples (3 & 4).

- The detergency power of (HAB + LAE) & (HAB+ MAE) sulphonate, sample (6s& 7s), are in between the detergency power of samples (1s & 2s) from one side and (3s & 4s) from the other side.

I.4.8.2 Wetting power :

Wetting agents are the most common liquid – solid surface active materials.

These consist of water –soluble compounds which are oriented at the surface with polar heads of the molecules in the water phase and nonpolar tails toward the solid. There are other wetting agents, however, such as the collectors used in ore flotation, whose polar groups are more strongly attracted toward the solid than the liquid.

There are the numbers of ways in which wetting agents may alter the characteristics of a liquid –solid system.

In many applications the function of the wetting agent is merely to promote the spreading of a liquid upon a more or less smooth solid surface, so that the latter may be easily coated with a uniform and adherent liquid film.

Wetting agents are often important in their effect upon the ease with which a liquid penetrates a mass of fibers, or other porous structure in which capillarity comes strongly into play.

Table (13) shows the values of the wetting power at concentration 0.2, 0.4, 0.8, and 1 %.in water for the six formulated surfactants. The general feature is the increasing of wetting power with increasing concentration.

Wetting power decrease

Samples (1s &2s)   samples (6s&7s)   sample (3s)   sample (4s)

Table (13)

Sample no.	Time of Wetting			
	0.2%	0.4%	0.8%	1.0 wt %
1s	102	46	6	5
2s	105	35	5	4
6s	395	160	55	36
7s	1080	340	195	140
3s	1100	450	200	155
4s	1200	470	220	160

Wetting powers for surfactants prepared from linear alkyl benzene (LAB) and heavy alkyl benzene (HAB) samples (1s& 2s), have the same excellent values.

Surfactants prepared from (60%HAB +40% LAB) & (80%HAB+ 20% MAE) samples (6s&7s),shows good wetting power compared with samples (1s & 2s),the decreasing of the wetting power may be due to branching at the α –position of the side chains.

Surfactants prepared from light and medium aromatic extracts, samples (3s & 4s),give poor wetting power .this may be attributed to their highly long side-chain components.

I.4.8.3 Emulsification power :

An emulsion is usually defined as a system of two immiscible liquid , one of which is dispersed in the other in the form of small droplets. This definition must be broadened somewhat to include all of the systems which are commonly referred to as emulsions in industrial practice.

The most commonly accepted theory relating to emulsion type was deduced by Bancroft and co –workers (184)and had been confirmed by the work of clowes(185) andothers.

According to this theory, the film of oriented surface active molecules between the tow phases of the emulsion in conceived to be in effect a third phase, possessing separate surface tensions against each of the tow liquids which form the emulsion.

In the case of water – oil emulsion, if the film has a greater affinity for water than for oil, its surface tension will be lower on the water than on the oil side.

The film surface will then tend to curve in such a direction as to reduce the total surface tension, I. e., it will form a curve with the area of low surface tension on the outside and that of high surface tension on the inside, or will tend to enclose globules of oil in water. If the film has a greater affinity for oil than for water, the effect will be reversed, and the tendency will be to form an emulsion of water in oil.

In general, surface active agents which are freely soluble in water but sparingly soluble in oil form emulsions of the oil- in-water type, whereas those more soluble in oil than in water will form emulsion of the water – in -oil type. Emulsification requires at least a C9 straight side chain or greater(168,186) in the case of anionic surfactants.

Values of emulsification powers of the formulated surfactants are listed in table (14),

It is clear that there is a steady increase in the emulsification power with increasing concentration.

The results obtained. Table (14) reveal the following points:

Emulsification powers decrease

$\longrightarrow$

Sample (1s&2s) sample (6s & 7s) sample (4s) sample (3s)

Table(14)

Sample no.	Emulsification power %			
	Concentration % wt			
	0.2	0.4	0.8	1.0 wt %
1s	60	61.7	65.0	66.9
2s	60	61.5	64.8	66.7
6s	48.5	50.2	54.0	56.2
7s	44.2	45.4	48.6	50.0
3s	35.0	36.3	39.7	42.8
4s	40.0	43.0	47.7	49.0

- Surfactants prepared from linear alkyl benzene (LAB) and heavy alkyl benzene (HAB) sample (1s & 2s), give similar emulsification powers.

- Surfactant prepared from (60% HAB + 40% LAE) and (80%HAB +20% MAE) Samples (6s&7s), gives good emulsification power compared with samples (1s&2s).

- surfactant prepared from medium aromatic extract, samples (4s), shows better emulsification power than that prepared from light aromatic extract, (sample 3)

- This may be attributed to the longer side chains components of sample (4) than those of sample (3).

I.4.8.4 Foam volume :

Production of foam by a surfactant solution is a result of its activity at the air – liquid interface. Physical state of adsorbed film (of foam) determines the foam stability.

If that film is of a liquid type the foam collapses rapidly. If it is plastic solid type foam, it is resistant to reputured and it is very stable. Pure liquids are incapable of foaming.(187)

It is difficult to relate foaming effects to other physical or chemical properties of a compound or composition, but many limited correlations had been pointed out.

Gotte (188), for example, showed that in the three series RSO4Na, RSO3 Na, and RCOONa, the minimum concentration necessary to produce foaming is relatively independent of temperature and decreases as the chain length increases. Similar effects for various other compounds and mixtures have been reported(189), but relatively few generalizations can safely be drawn from data of this type. The effect of various electrolytes on the foam stability was studied (190).

It had been noted that solutions of high surface viscosity tend to form voluminous stable foams, whereas low surface viscosity usually, goes with low foam stability (191).

In washing process, foam may serve an indicator that sufficient detergent was added.

It is worthy to mention that not all detergent produce voluminous foam, and recently many types of foamless compounds were found to be very efficient as detergents.

Foaming properties for the formulated surfactants were measured at concentrations 0.2, 0.4, 0.8 & 1% wt. in water and results obtained are listed in table (15). The half life time of the produced foam was taken as a measure for foam stability, which can be considered stable if their half life times exceed 15 minutes

In all cases foam, as expected increases with increasing concentration of surfactants.

The results obtained from table (15) reveal the following points:

A. The order of foam volume is as follows:

Foam volume decrease →

Sample (1s) sample (2s) sample (6s) sample (7s) sample(4s) sample (3s)

Table(15)

Sample no.	Concentration % wt	Foam volume cm³	Foam volume after 15 n. cm³	stability
1s	0.2	70	40	
	0.4	135	70	
	0.8	145	80	Good
	1.0	150	110	
2s	0.2	70	40	
	0.4	80	50	
	0.8	110	55	Moderate
	1.0	120	60	
6s	0.2	60	50	
	0.4	80	70	
	0.8	90	75	High
	1.0	100	85	
7s	0.2	40	15	
	0.4	50	20	
	0.8	70	30	low
	1.0	80	35	
3s	0.2	50	15	
	0.4	60	25	
	0.8	75	35	low
	1.0		40	
4s	0.2	55	20	
	0.4	65	30	
	0.8	80	40	low
	1.0	90	45	

- A remarkable increase of the foam volume with increasing surfactant concentration.

- Surfactants prepared from linear alkyl benzene sample (1) shows a high foam volume than that prepared from heavy alkyl benzene, sample (2s).

- Surfactants prepared from light and medium aromatic extract, samples (3 &4) show lower foam volume which may be due to the highly long of the side chains components of samples (3 & 4).

B. the order of foam stability is as follows:

Foaming stability decrease

→

Sample (6s) sample (7s) sample (1s) sample (2s) sample (3s) sample (4s)

- Surfactant prepared from (60%HAB +40%LAE) & (80%HAB+20%MAE) samples (6s&7s) shows a high foam stability which my be due to branching of the side chain of the components of samples (6s&7s).

- Surfactant prepared from linear alkyl benzene and heavy alkyl benzene give good and moderate foam stability respectively.

- Surfactant prepared from light and medium aromatic extracts give low foam stabilities

Results (part II)

The efficiency of the tested dispersant was 78%.

The crude oil from Suez Gulf dispersed by the sample was found to be low toxic to marine organisms and a highly bio – degradable product according to the attached technical report. Hence, it can be safely used at open sea and dockside equipments.

II.1 Evaluation of effectiveness test of oil dispersant.

II.1 Results and conclusion :

The data obtained from the method mentioned in section above for oil dispersant (OSD) are summarized in the following :

* mean of five response factors at different wave lengths (RFx):

Rf 340 = 0.595 Rf 370 = 0.780 Rf 400 = 1.027

* C mean of replicate test reading at different wavelengths:

C 340 = 8.806 C 370 = 6.24 C 400= 6.408

C mean = (8.806 – 6.24 – 6.408) / 3 = 7.151

* Effectiveness (%) of oil dispersant (EFF D):

Total mass of oil = ν *d = 10 * 0.88 = 8.8

EFFd (%) =(7.151 / 8.8) *100 = 81.3 %

C control = 0.291

EFFc (%) = (0.291/ 8.8) * 100 = 3.3 %

EFF D = EFF d – EFFc = 81.3 -3.3 = 78.0 %

II.2 Evaluation of toxicity and biodegradability test

II.2.A Natural phytoplankton population

II.2.A Results

Table (16): Percentage of chlorophyll-a concentration (μg/1) of the definitive test at each concentration after 96 hours

Concentration (ppm)	Average of chl. A (μg chl. a/1) after 96h	% of reduction compared to control		Contributions to chi^2
		Observed	Expected	
Control	122.07			
5	94.85	22.30	30	0.03
10	63.29	48.16	48	0.98
15	23.79	80.51	68	0.06
20	10.17	91.67	86	0.03
25	0.8.31	93.20	104	-
Total value of chi^2				1.1

Testing the goodness of fit of a probit line:

Since the chlorophyll a concentration tested per concentration is 0.246μg/100ml, the chi^2 value is 1.1 x 2.46 =2.706. The number of concentrations tested and represented was 5, - excluding the control, therefore the number of degrees of freedom is (5 - 2 = 3). Using table of chi^2 for p=0.05, it can be seen that the critical chi^2 with 3 degrees of freedom is 7.82. Since 2.706 < 7,82, the line is a good fit So, the LC50 and its confidence limits can be estimated from this line,

Calculation of the upper and lower confidence limits of the EC50 (median effective concentration) of the definitive toxicity tests by graphical method:

The slop function of the line (S) = $$\frac{\begin{matrix} EC84 + EC50 \\ EC50 \quad EC16 \end{matrix}}{2} = 2.238$$

Calculation f, where: f = antilog $\frac{2.77 \log S}{N} = 1.6648$

N = The total number of replicates tested at concentrations whose expected effects were between 16% and 84% reduction in chlorophyll a concentration = 9.

The upper 95% confidence limits of the 96 hours EC50 = EC50 X f

= 17.15 **ppm**

The median effective concentration after 96 hours = 10.30 **ppm**

The lower 95% confidence limits of the 96 hours EC50 = EC50 / f

= 6.19 **ppm**

PHYTOPLANKTON	
Item	**Concentration (ppm)**
Upper 95% CL of 96h EC50	17.15
Median 96HFC50	10.30
Lower 95% CL of 96h EC50	6.19

II.2. B Shrimp.

II.2.B Results

Table (17): Percentage mortality of shrimps after 48 hours at each concentration of the. definitive test

Concentration (ppm)	**No. of shrimps tested**	**Observed % mortality**	**Expected % mortality**	**Contribution to chi^2**
Control	10	10		
20	10	30	28	0.0002
30	10	50	44	0.0180
40	10	50	58	0.0350
50	10	60	74	0.1000
60	10	100	88	0.1400
1 Total value of chi^2				**0.2932**

Testing the goodness of fit of a probit line:

Since the number of animals tested per concentration is 10, the chi^2 value is 0.2932 x 10 = 2.932, The number of concentrations tested was 5, excluding the control, therefore the number of degrees of freedom is (5 - 2 = 3). Using table of chi^2 for p=0.05, it can be seen that the critical chi^2 with 3 degrees of freedom is 7,82. Since 2.932 < 7.82, the line is a good fit. So, the LC50 and its confidence limits can be estimated from this line.

Calculation of the upper and lower confidence limits of the LC50 of the definitive toxicitv tests by graphical method:

The slop function of the line (S) = $\frac{\begin{matrix} EC84 + EC50 \\ EC50 \quad EC16 \end{matrix}}{2} = 2.2402$

Calculation f, where: f=antilog $\frac{2.77 \log S}{N} = 1.4233$

N= total number of shrimps tested at concentrations whose expected mortalities were between 16% and 84%^ 40.

The upper 95% confidence limits of the 48 hours LC50 = LC50 X f

= 48.39 **ppm**

The median lethal concentration after 48 hours = 34 **ppm**

The lower 95% confidence limits of the 48 hours LC50 = LC50 / f

= 23.89 ppm

SHRIMP	
Item	**Concentration (ppm)**
Upper 95% CL of 48h LC50	48.39
Median 48hLC50	34.00
Lower 95% CL of 48h LC50	23,89

II. 2.C Fishes.

II.2.C Results

Table (18): Percentage mortality of fishes after 96 hours at each concentration of the definitive test

Concentration (ppni)	**No. of fishes tjcsted**	**Observed % mortality**	**Expected % mortality**	**Contribution to chi^2**
Control	10	0		
40	10	10	18	0.0400
50	10	30	31	-
60	10	50	43	0:0200
70	10	60	55	0.0100
80	10	70	67	0.0040
90	10	70	80	0.0600
100	10	90	90	-
Total value of chi^2				**0.134**

Testing the goodness of fit of a probit line:

Since the number of animals tested per concentration is 10, the chi^2 value is 0.134 x 10 = 1.34. The number of concentrations tested was 7, excluding the control, therefore the number of degrees of freedom is (7 -

2 = 5). Using table of chi^2 for p=0.05, it can be seen that the critical chi^2 with 5 degrees of freedom is 11.1. Since 134< 11.1, the line is a good fit. So, the LC50 and its confidence limits can be estimated from this line

<u>Calculation of the upper and lower confidence limits of the LC50 of the definitive toxicity tests by graphical method:</u>

The slop function of the line (S) = $\dfrac{\begin{matrix} EC84 + EC50 \\ EC50 \quad EC16 \end{matrix}}{2}$ =1.5693

Calculation f, where:

$$\text{f} = \text{antilog}\ \frac{2.77 \log S}{N} = 1.1700$$

N = The total number of fishes tested at concentrations whose expected mortalities were between 16% and 84°/o=: 60.

The upper 95% confidence limits of the 96 hours LC50 = LC50 X f

=77.22 **ppm**

The median lethal concentration after 96 hours = **66.00 ppm**

The lower 95% confidence limits of the 96 hours LC50 = LC50 / f

= 56.41 ppm

FISHES	
Item	**Concentration (ppm)**
Upper 95% CL of 96h LC50	77.22
Median 96h LC50	66.00
Lower 95% CL of 96h LC50	56.41

II.3 Evaluation of physical and chemical properties of the formulated surfactants

Specification

Appearance: Pale yellow liquid

Composition: Blend of biodegradable an-ionic, non-ionic surfactants and a hydrocarbon solvent.

Reaction : Neutral, PH = 6.5, can be store safely in mild steel drums.

Specific gravity at 60/60˚f: 1.065 (ASTM D-1298)

Viscosity at 40 ˚c = 101 CST (ASTM D -445)

Viscosity at 25 ˚c = 265 CST (ASTM D-445)

Anionic active matter %wt = 25 % (ASTM D-1681)

Total active matter = 38% (ASTM D-820)

Cloud point ˚c = 10 (ASTM D-97)

Corrosive action: None

Flash point °C: None (ASTM D-93)

Shelf life: Not less than 5 years

Oil Spill Dispersant (OSD)

The crude oil from Suez Gulf dispersed by the sample (OSD) was found to be low toxic to marine organisms and a highly bio – degradable product according to the attached technical report. Hence, it can be safely used at open sea and dockside equipments.

Oil Spill Dispersant (OSD)

- Is a high efficiency, very low toxicity?
- Is it self-biodegradable?
- It has a dual function in that it is suitable for dispersing oil both on the sea or on beaches, rocks, etc; its very low toxicity to marine fauna means that it can be used with safety in shallow waters, estuaries, etc.

Biodegradation of the dispersed oil spill

The maximum degradation rate of the dispersed oil spill was 13.67ppm/day**.**