RESULTS AND DISCUSSION:

The ***Gawafa fat*** sample obtained by n-hexane extraction was investigated to determine the chemical characteristics and fatty acid compositions.

Chemical characteristics (cf. Table 1):

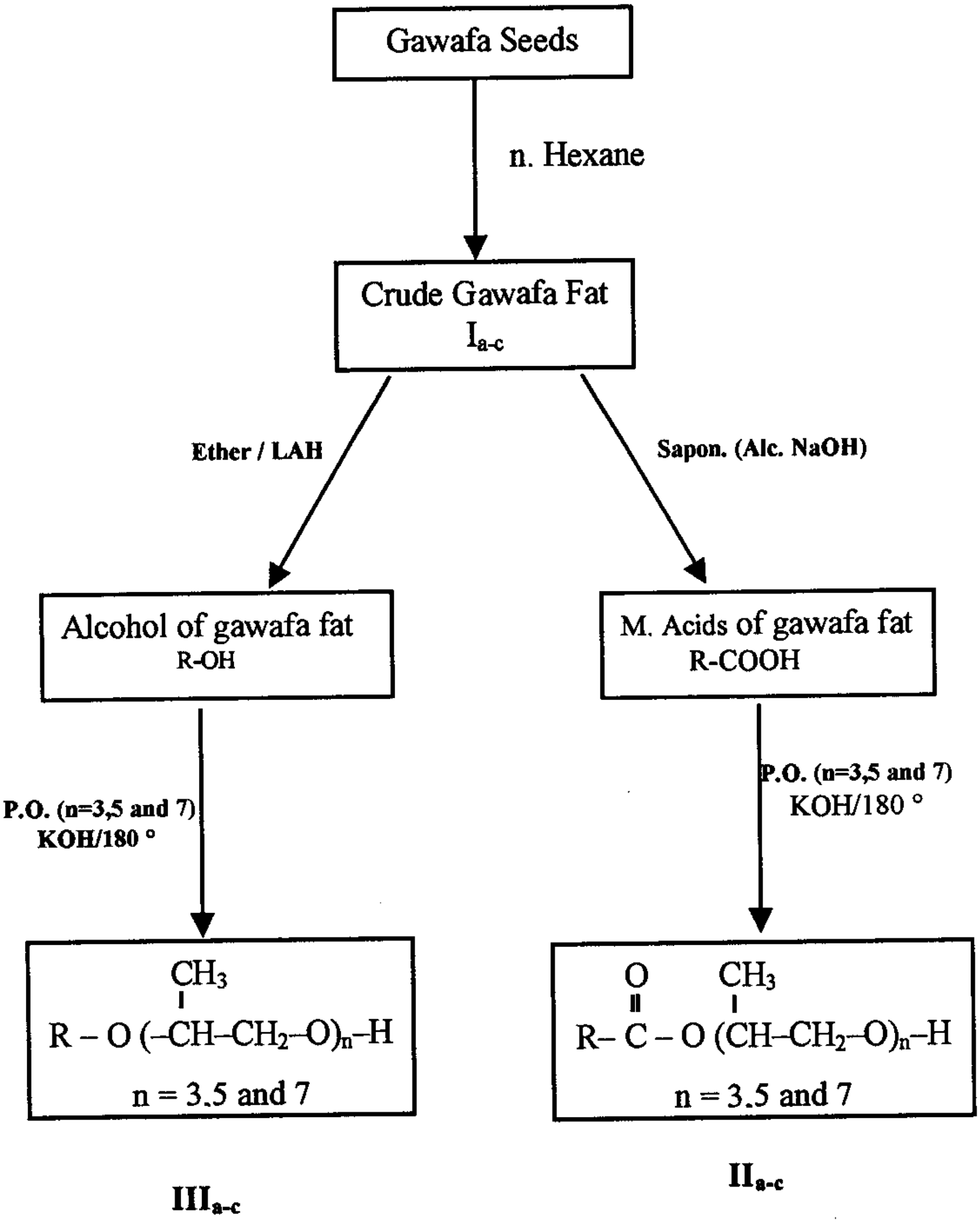
It is shown that, acid value of the solvent extracted oil in the first day of extraction is 25.5. This value increased. after 2 or 3 days to afford 36.5 and 64.5 respectively. The acidic nature of the extracted oil is due to the action of lipase enzyme. Which revealed more activity in nonpolar solvent [1]. On the other hand, saponification value, the unsaturated characters as represented by the iodine value and the Unsaponifiable matter reported values of 197.8, 11.80 and 2.03 respectively.

Fatty acids composition of Gawafa fat.

The fatty acid mixture obtained by **G.L.C** according to **Kush et. al** [100], (cf. Table 1 and fig. 1) . The results indicated that, Gawafa fatty acids are nearly saturated where, the unsaturation is only represented by 4.44 % oleic acid.

Fatty alcohols.

The extent of reduction of fatty esters (metlyl caprate ($C_{10:0}$), laurate ($C_{12:0}$), myristate ($C_{14:0}$), palmitate ($C_{16:0}$), stearate ($C_{18:0}$), oleate ($C_{18:1}$) and fatty acid methyl esters of ***Gawafa fat*** respectively) using LAH.[32] is shown in table 2. The percentage of reduction was calculated on the basis of saponification values, for both esters and their reduced product [33] (cf. Table 2). However, the reduction percent was in all cases over 75 %. The IR spectra of the produced alcohols showed bands of associated hydroxyl groups



Scheme (1)

The surface-active properties of the synthesized surfactants were evaluated from determination of the surface characteristics. Surface and interfacial tension, cloud point, wetting, foam height and emulsification stability were investigated systematically in order to evaluate the possible application of these products in the different industrial fields. Nonionic surfactants were prepared through the reaction of propylene oxide of different molar ratio (n = 3, 5 and 7) with mixed fatty acids and /or fatty alcohols of ***Gawafa fat*** in presence of KOH as catalyst [13], to afford **II_{a-c}** and **III_{a-c}** as nonionic surfactants (cf. Scheme 1).

Surface and interfacial tensions: The surface and interfacial tensions of the prepared oxypropylated fatty acids and/or fatty alcohols (**II_{a-c}, III_{a-c}**) are given in tables 4-5 respectively. Where, oxypropylated fatty alcohols showed lower values than the corresponding fatty acids. On the other hand, the values of surface and interfacial tensions decreased as the number of propylene oxide units increased in the molecule from 3, 5 to 7 respectively [13].

***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 a turbidity on gradual heating . The cloud points of the synthesized surfactants are shown in tables 4 and 5. The cloud point values increased with increasing the propylene oxide units [13].

***Wetting time*::** Nonionic surfactants are among the most powerful wetting agents. The wetting properties of 0.1% solutions in distilled water were measured by the **Draves&Clarkson test** [104]. Tables 4 and 5, showed the times for the prepared oxypropylated fatty acids and or fatty alcohols II_{a-c}, III_{a-c} respectively. Where, III_{a-c} have better wetting properties than II_{a-c}. It is reported that, nonionic surfactants with a low propylene oxide content have been found to be the most efficient wetting promoter [115].

***Emulsion Stability*:** The emulsifying efficiency of a surfactant was related to the polarity of the molecule or the relation between the contribution of the polar hydrophilic head and the nonpolar lipophilic tail. **Griffin** [116] found that, it is possible to define this polarity for nonionic agents in terms of an empirical quantity termed " hydrophile- lipophile balance" or HLB. An arbitrary scale in which the least hydrophilic materials have low HLB number and increasing HLB values corresponding to increasing hydrophilic character representing this. The nature of the emulsifier is inferred from its chemical composition. Linear, long saturated hydrocarbons are strong hydrophobic. Tables 4and 5, showed that, the emulsion stability increases by decreasing the number of propylene oxide [13].

2- Anionic surface active agents:

a)- Alcohol sulfates :

Decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, octadecen9- yl and alcohols obtained from ***Gawafa fat,*** were sulfated using chlorosulfonic acid [40], followed by neutralization using NaOH to afford (**$IV_{a\text{-}g}$**) as anionic surface active agents (cf. Scheme 2). The structure of the prepared compounds was confirmed via elemental analysis (cf. Table 6), IR and ^{1}HNMR. The IR spectra of sodium dodecylsulfate (IV_b), showed bands at 2970, 2930 cm^{-1} for $\nu_{C\text{-}H}$ aliphatic, 1450, 1260 cm^{-1} for $\nu_{C\text{-}O}$ and characteristics bands, for $\nu_{OSO_3\text{-}Na+}$ at 1180, 1090 and 640 cm^{-1} (Fig. 3). On the other hand, the ^{1}H-NMR spectrum of sodium dodecyl sulfate (IV_b) showed the following signals, $\delta = 0.8$ ppm(t., 3H, terminal CH_3), $\delta = 1.0$-1.2 (br.s,20H, CH_2 chain), and $\delta = 3.7$ (t., (2H, CH_2- $\underline{CH_2}$- $OSO_3^-Na^+$) (cf. Fig 4).

b) Sulfation of oxypropylated fatty alcohols:

The sulfation of nonionics may have considerable effect on the properties, of course because changes the oxyalkylated compound from nonionic to anionic surface active agents, and the product is like an ether alcohol sulfate in that, it may have both anionic and nonionic characteristics. Decyl, dodecyl tetradecyl hexadecyl octadecyl octadecen 9-yl and fatty alcohols of ***Gawafa fat,*** were subjected to react with propylene.oxide (molar ratio 1,2 and 3 moles) in presence of KOH at 170 ^{0}C, according to **El-Sawy et. al.**[13], followed by sulfation using chlorosulfonic acid [40], in CCl_4 as solvent. Finally, the products were neutralized with 5 N NaOH to afford sod salt of fatty alcohols ether sulfates $(V\text{-}XI)_{a\text{-}c}$ as anionic surface-active agents (cf. Scheme 2). The structure of the prepared compounds was confirmed via

Surface activity and related properties:

The surface activity and related properties of the prepared sulfated fatty alcohols (**IV**$_{a-g}$) and fatty alcohol ether sulfates (**V-XI**) $_{a-c}$ are given in (Tables 8-10). The ether alcohol sulfates of fatty alcohols have good solubility and detergent properties and are excellent lime soap dispersants, when the degree of oxyalkylation is near one alkyl group [117-119]. Related compounds may be made by the reaction of fatty acids and alcohols with epoxide prior to sulfation . Literature describing the preparation and properties of oxypropylated fatty acids and fatty alcohols and the sulfated products is limited to a few examples [120,121]. It was reported that sulfated oxypropylated compound is more stable than (2-hydroxyethyl) in solution at different pH [122].

Surface and interfacial tension:

The synthesized fatty alcohol sulfate (**IV**$_{a-g}$), showed relatively lower values (37.5- 44.5) dyne/cm for surface tension and (8.0- 15.5) dyne/cm for interfacial tension, the results are given in table 8. It was found that, compound sodium dodecyl sulfate (**IV**$_b$) reported, lower surface and interfacial tension, while surfactants obtained from mixed fatty alcohols prepared from fatty acids of ***Gawafa fat*** (**IV**$_g$) recorded almost the same surface and interfacial tension as those individual commercial unsaturated fatty alcohol (**IV**$_f$). Also, the propenoxylated fatty alcohol sulfates (**V-XI**) $_{a-c}$ indicate lower surface and interfacial tensions as shown in table 9 than all other prepared fatty alcohol sulfate (**IV**$_{a-g}$).

Kraft Point:

Tables 8 and 9, showed that, propenoxylated fatty alcohol sulfates **(V-XI)**$_{a\text{-}c}$ recorded lower values of **T**$_{kp}$ than those of fatty alcohol sulfates **(IV**$_{a\text{-}g}$**)**. These compounds can be used at lower temperatures [47].

Wetting properties:

The ease with which a surface can be wetted by water as other liquids is an important property suitable for many applications. The wetting times for sulfated alcohols **(IV**$_{a\text{-}g}$**)**, showed higher values than those of propenoxylated fatty alcohol sulfate **(V-XI)** $_{a\text{-}c}$,on the other hands, the values of wetting times increase by increasing number of carbon atoms, and decreasing the number of propylene oxide adduct. (cf. Tables 8 and 9)[123].

Emulsification stability:

Studies are still being carried out on the utilization of surfactants in emulsion formation, which is of immense importance to technological development. It was proved that, the emulsifying stability of propenoxylated fatty alcohol sulfate **(V-XI)** $_{a\text{-}c}$ showed comparatively higher values than that, of fatty alcohol sulfates **(IV**$_{a\text{-}g}$**)** (cf. Tables 8 and 9). Also, the emulsion stability increases by increasing number of carbon atom in alkyl chain length and decreases with increasing number of propylene oxide unit through the surfactant moiety[123].

Foam height:

It was reported that, the efficiency of surfactant as a foamier increases with increased alkyl chain length [124]. In general, the foam height for the prepared surfactants **(IV**$_{a\text{-}g}$**)** was higher than that of the propenoxylated fatty alcohol sulfate (V-XI) $_{a-c}$ (cf. Tables 8-9). On the other hand, foam ones;and decreased by increasing propylene oxide unit in surfactant molecule [123].

Stability towards acids and base:

All prepared surfactants were stable in acidic and basic medium but, this stability in acidic medium is higher than in basic medium (cf. Tables 8 and 9). Also, propenoxylated fatty alcohol sulfate showed higher stability towards bases than that, of sulfated fatty alcohols (IV_{a-g}).

Ca^{2+} stability:

From data showed in tables (8 and 9), it is found that, propenoxylated fatty alcohol sulfate (V-XI) $_{a-c}$ showed higher stability to Ca^{2+} than that, of sulfated fatty alcohols (IV_{a-g}), where as the propenoxylated fatty alcohol sulfate tolerates the hard water more than the sulfated fatty alcohols. Ca^{2+} stability increases by increasing the number of propylene oxide unit in surfactant molecule, and decreases on increasing the number of carbon atom in alkyl chain [13].

Critical micelle concentration:

The critical micelle concentration (cmc); of the synthesized surfactant were determined by the surface tension method [111], from data showed in table 10, it can be seen that; the values of cmc decrease with increasing the number of propylene oxide adducts and number of carbon atom in alkyl chain [125].

Hydrophile- Lipophile Balance (HLB)

[illegible]

Where, (HLB), determined according to Dives equation :

$$HLB = [\Sigma(\text{hydrophile}) - \Sigma\,(\text{hydrophobe}) + 7]$$

stretching bands at ν3120 cm^{-1} ν_{C-H} olefinic, and absorption band at 1735 cm^{-1} characteristics for $\nu_{C=O}$ of esters and 1645 cm^{-1} for $\nu_{C=C}$ olefinic (cf. Fig. 9). ^{1}HNMR spectrum of compound (**XIV$_d$**); given, δ = 0.8 (t, 3H, terminal CH_3); δ =1.0- 2.2 (m, 28H, CH_2 chain); δ = 4.3 (d., 2H, CO- O-$\underline{CH_2}$- CH= CH_2), δ =5.4 (d., 2H, CH = $\underline{CH2}$); and δ = 5.9 (m; 1H, OCH_2-$\underline{CH}$= CH_2) (cf. Fig 10).

Mono and dialkyl itaconate esters:

Mono- and diester of itaconic acid were prepared by direct esterification of itaconic acid with fatty alcohols in molar ratio 1:1 and /or 1 : 2 to afford **XV$_{a\text{-}g}$** and **XVI $_{a\text{-}g}$** respectively. The structure was confirmed via its physical properties (cf. tables 14-15), and its spectral data. The IR spectra of mono-decyl itaconic acid ester (**XV$_a$**) revealed the following characteristic bands: broad band at 3500-2600 cm^{-1} ν_{OH} of carboxylic acid; 3130 cm^{-1} ν_{C-H} olefinic protons, 2960, 2870 cm^{-1} ν_{C-H} aliphatic; 1740 cm^{-1} $\nu_{C=O}$ of ester, $\nu_{C=O}$ of acid at 1710 cm^{-1}; 1630 cm^{-1} $\nu_{C=C}$ and 1450, 1260 cm^{-1} for ν_{C-O} (cf. Fig. 11). ^{1}HNMR spectra of dihexadecyl itaconate (**XVI$_d$**), gave the following characteristic peaks: δ = 0.95 ppm (t; 6H, terminal CH_3 in dialkyl chain); δ = 1.2-1.5 ppm (br.s; 56H, CH_2 chain); δ = 3.4 ppm (S., 2H, = C-$\underline{CH_2}$-COOR); δ = 4.05 ppm (t., 2H- CH_2-$\underline{CH_2}$-O-CO-CH_2); δ = 4.2 ppm (t., 2H, C= C-COO-$\underline{CH_2}$) δ = 5.65 ppm (S., ^{1}Hb $\underline{H(a)}$C= C- C) and δ =6.3 ppm (S., 1H, $\underline{Hb}$ H(a)C= C-C) (cf. Fig . 12). IR Spectra of (**XVI$_b$**) (didodecyl itaconate); revealed the following characteristics bands 3120 cm^{-1} ; 2970,2920, 2870 cm^{-1},1745 cm^{-1} $\nu_{C=O}$ of esters,1630 cm^{-1} ν $_{C=C}$ and 1460, 1250 cm^{-1} ν_{C-O} (cf. Fig 13).

Sulfo-fatty esters:

Sulfonated derivatives from the above fatty esters were prepared by the reaction with $NaHSO_3$ in methanol as solvent and in presence of KNO_3 as catalyst [83], to afford **$XVII_{a-g}$**, **$XVIII_{a-g}$**, **XIX_{a-g}** , **XX_{a-g}** **and** **XXI_{a-g}** respectively as anionic surface active agents according to (Scheme 3). The structure of sulfated esters was characterized by their elemental analysis (cf.Tables 16-20) and spectral data. ^{1}HNMR spectrum of compound **(XIX_d)**; showed, δ = 0.75 ppm (t, 3H, terminal CH_3); 1.2- 1.7 (m, 28H, CH_2 chain);δ =2.6- 2.8 ppm (m., 2H, $COOCH_2$- $\underline{CH_2}$- $CH_2\ SO_3^-Na^+$), δ = 4.0 (t., 2H, COO $\underline{CH_2}$); δ = 4.2 (t., 2H, $\underline{CH_2}$-SO_3Na); (cf. Fig. 14). IR spectrum of compounds ($XVII_d$). showed stretching bands at 1725 cm^{-1} for $\nu_{C=O}$ of ester, 1180, 1090 ,640 cm^{-1} ν_{SO_2}, ν_{S-O} in $-SO_3^-Na^+$ groups (cf. Fig 15).

The surface active properties, given in tables (21-25), show that, the products obtained have a pronounced surface activity. The results of emulsification, wetting time, calcium stability, stability to hydrolysis and foaming properties for sulfonated alkyl acrylate and methacrylate **$XVII_{a-g}$** **and** ,**$XVIII_{a-g}$**, reflect the following facts:

1- These types of surfactants were very effective wetting agent in distilled water solution.

2- All the prepared sulfo-esters are stable to hydrolysis in acid media more than in basic, which might indicate that the sulfate group protects the ester linkage through steric hindrance.

Most of the prepared sulfo-esters have good or excellent calcium stability and their stability increases with increasing the number of carbon atoms in alkyl chain of fatty alcohols, also, fatty alcohols of ***Gawafa seed fat***, have excellent ca^{2+} stability.

On the other hand, sulfated allyl alkanoates **XIX_{a-g}** show the following :

1- The products are moderately emulsifying agents as may be seen in table 20, the emulsion stability increased with the molecular weight (M. wt) of the fatty acid moiety in the product.

2- The products were very effective wetting agents in distilled water solution but less than sulfo-alkyl acrylates and methacrylates **$XVII_{a\text{-}g}$ and $XVIII_{a\text{-}g}$** respectively.

3- The products were more stable in acidic media than basic.

4- Foam height is moderate and decreases as the alkyl chain increases.

5- Ca^{2+} stability values show that the esters can be used in very hard water and decreases by increasing the molecular weight of the hydrophobic part in the surfactants under the conditions of constant temperature.

- Disodium salt from, mono alkyl itaconic acid esters, were prepared by neutralization with NaOH till PH =7; to afford **$XX_{a\text{-}g}$**. The physical characteristics were tabulated in (Table 17). The structure as confirmed via IR spectrum of (XXI_d) showed 2970, 2920, 1720,1680, 1460, 1180, 1090, 640 cm^{-1} with discharge of $\nu_{C=C}$ and $\nu_{C\text{-}H}$ olefinic (cf. Fig. 16), on the other hand, ^{1}HNMR spectrum of (**XX_d**) gave, δ = 0.85 ppm (t, 3H, terminal CH_3 in alkyl chain); δ = 1.0-1.4 (br.s., 28H, CH_2 chain); δ = 1.6 (d, 2H, CH_2 – C); δ = 4.0 (t, 2H, CH2- O-C) and δ = 4.2 (d, 2H, O_3S-$\underline{CH_2}$- CH- COO); (cf. Fig. 17).

Tables (24-25) list the surface active properties of sulfated products of mono and dialkyl itaconate (**$XX_{a\text{-}g}$ and $XXI_{a\text{-}g}$**), where, the solubility of disodium salt of mono alkyl sulfo-itaconate (**$XX_{a\text{-}g}$**), was more than mono sodium salt of dialkyl itaconate (**$XXI_{a\text{-}g}$**), their values were expressed as Kraft point, where the solubility decreased with increasing the molecular weight of fatty alcohol, in general, the emulsion stability increased with increasing the number of methylene group in the alkyl chain. On the other hand, dialkyl sulfo itaconate, showed higher values of Kraft point than that of the corresponding mono alkyl sulfo-itaconate (XX_{a-g}). Moreover, dialkyl sulfo-itaconate (XXI_{a-g}),, showed excellent calcium stability than that of disodium salt of mono alkyl sulfo-itaconate(XX_{a-g}) and this stability decreased with increasing the alkyl chain length of fatty alcohols. Also fatty alcohols obtained from ***Gawafa seed fat***, have moderate value of calcium stability, compared to those prepared from the individual fatty alcohols.

Foam height, of disodium salt of sulfo-itaconate ester revealed better foam height values than all prepared sulfo- itaconate esters.

Stability to hydrolysis*:** Stability to hydrolysis in acidic media was more than in basic, for mono sodium salt but this is lower in disodium salt for all prepared sulfo-esters. ***Wetting time: The products of disodium salt were very effective wetting agents in distilled water solution, but less than dialkyl sulfo-itaconate. On the other hand, surface properties of alkylacrylate, and/or alkyl itaconate prepared from ***Gawafa fat,*** were improved by oxypropylation for fatty acids and alcohols of ***Gawafa fat*** before esterification followed by addition of sodium bisulfite (Scheme 4), (cf. Tables 26,27).

Biodegradation (Die- away test in river water):

The results cited in tables (28–34), revealed the fact that, the biodegradability decreased by increasing the number of methylene group in alkyl chain. The sulfated products were more biodegradable than the propenoxylated fatty alcohols. Also, sulfo-alkylacrylate and sulfo-alkylmethacrylate esters have much higher rate of degradation than the sulfo-allyl alkanoates that, gave the lowest rate. Moreover, monosulfo-alkylitaconate esters showed higher biodegradable behavior than dialkyl esters. However, it can be concluded that **Gawafa fat** obtained from industrial wastes can find an economic application as low priced sources in the preparation of surfactants having promising properties to be used in different suitable fields.