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Amphoteric Surface Active Agents with Heterocyclic Ring Based on Industrial Wastes

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SERIES of surface active agents as amphoteric surfactants were prepared by the reaction of N-acyl–2-aminothiazole and/or N-acyl–2-aminopyridine of pure [(decanoic C10 : 0 , dodecanoic C12: 0, tetradecanoic C14 : 0, hexadecanoic C16 : 0, octdecanoic C18 : 0 , octdec 9-enoic C18 : 1, octdec 9, 12-dienoic C18 : 2, mixed fatty acids of Gawafa seed fat and mixed fatty acids of Grape seed oil (GSO)] with 3-chloro 2-hydroxypropane sulfonate and chloroacetic acid to produce amido-sulfobetaine [IVa-i and VI a-i] and amido-betaine [Va-i and VIIa-i] with heterocyclic ring, respectively. The structure of the prepared surface active agents were confirmed by micro-analysis, IR and ^{1}H-NMR spectra. The prepared surface active agents have a double properties, antimicrobial and high emulsification power.

Keywords: Gawafa seed fat (GSF), Grape seed oil (GSO), Amphoteric surfactants antimicrobial and Surface active properties.

The surface active agents derived from natural sources acquired more valuable interest from two points of view; economic (has low price) and environmental pollution (reduced pollution). Our interest was extended to prepare the surface active agents from rubbish sources like fatty acids were extracted from both Mangifera indica[1-2], rice bran oil[3] and Gawafa fat[4] . Since Gawafa seeds have good percentage of saturated fatty acids especially octanoic, dodecanoic, hexadecanoic and octadecanoic acids and small percentage of decanoic and tetradecanoic acids. Also, Grape seed oil has small percentage of saturated fatty acids especially, hexadecanoic and octadecanoic acids and good percentage of unsaturated fatty acids especially linoleic (C18:2) and oleic (C18:1) acids. In general , grape seed oil is very similar to sunflower oil, it is a good all- round oil, high in essentional fatty acid linoleic , but very low in easily oxidized linolenic acid [5] ; it is also, low in saturates. It was interesting to prepare some biologically active simple heterocycles which constitute an important class of organic compounds with diverse biological activities[6-9]. Numerous fatty

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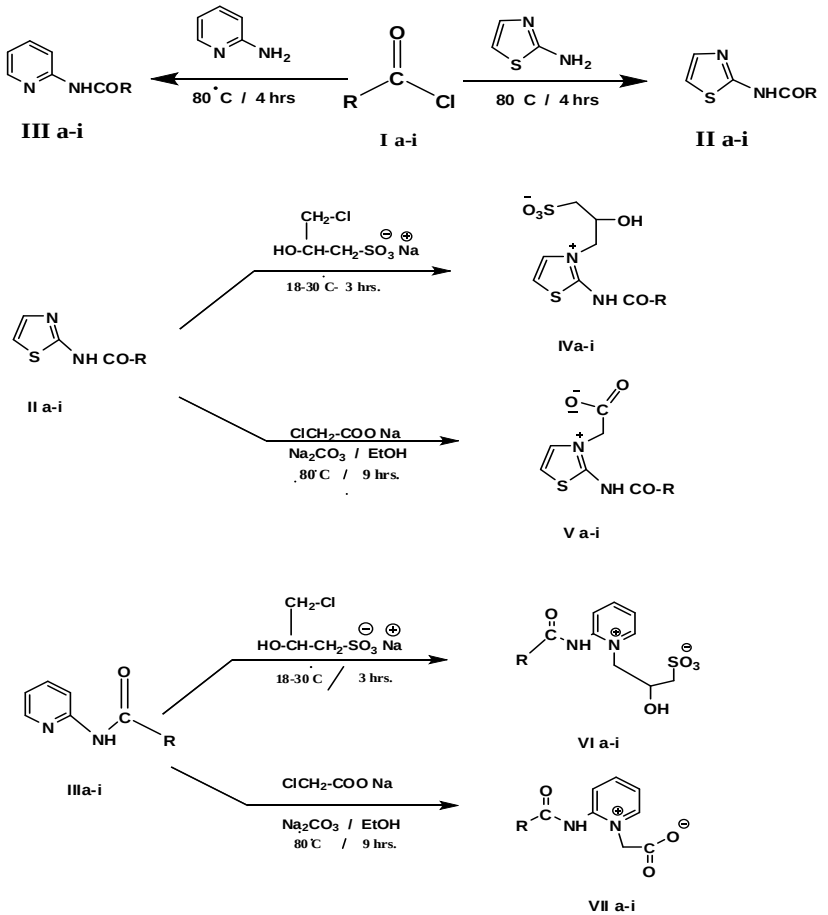
alcohols are now more available in their pure form and inexpensive enough to provide the chemical field with a wealth of reactions in which fatty alcohols are used as raw material in a variety of industrial products like pharmaceuticals [10-11], cosmetics, surfactants, paints,… etc. The amphoteric surface active agents prepared by using 2-hydroxypropane sulfonate (sulfobetaine) offer the most promise as dispersant in the soap based detergents. In the extension of our interest in the preparation and study of the surface properties of surface active agents derived from natural source with heterocyclic ring, we tried to prepare the amidosulfobetaine and amidobetaine amphoteric surface active agents with simple heterocyclic ring from commercial sources (*c.f.* Scheme 1) and study their double properties, antimicrobial and surface active agents properties.



R = ,CH_3-$(CH_2)_8$ - , CH_3-$(CH_2)_{10}$ -,CH_3-$(CH_2)_{12}$ -,CH_3-$(CH_2)_{14}$ - ,CH_3-$(CH_2)_{16}$ - , CH_3-$(CH_2)_7$ CH=CH- $(CH_2)_7$- , CH_3-$(CH_2)_4$ -CH=CH–CH_2CH=CH- $(CH_2)_7$- , mixed alkyl chain of Gawafa fat , mixed alkyl chain of Grape oil. crossponding to a,b, c, d, e, f , g ,h, and i

Scheme 1

Experimental

The IR spectrum was measured by Pye-Unicam SR-1000 infra-red Spectrophotometer as KBr disk or nujl mull and ^{1}H-NMR was done in DMSO and /or $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard [Varian EM-390] Spectrophotometer operating at 260 MHz.

Industrial wastes of Gawafa seeds

Grape seeds, were kindly supplied by El-Nasr Company of canned products, Kaha, and grape seed from Aga juices company Egypt. The oil was extracted from the seeds. The specifications are given in Table 1.

Hydrolysis of crude Gawafa seeds fat and or grape seed oil

The procedure described by El-Sawy *et al.* [12] was followed. The fatty acids mixture was analyzed by G. L. C. and their compositions are given in Table 1

TABLE 1. Fatty acids composition and chemical characteristic of Gawafa fat and Grape oil [12] .

Chemical characteristics	Fatty acid composition Peak area %	
	Gawafa fat	**Grape oil**
Gawafa fat A.V. = 25.5 V. = 11.8 S. V. = 197.8 Unsap =2.03 **Grape Oil:-** A.V. = 3.34 I.V. = 132.8 S. N. = 187.6 Unsap =2.83	**Saturated fatty acids:** Caprylic acid $C_{8:0}$ 12.51 Capric acid $C_{10:0}$ 01.94 Lauric acid $C_{12:0}$ 26.61 Myristic acid $C_{14:0}$ 03.25 Palmitic acid $C_{16:0}$ 20.25 Stearic acid $C_{18:0}$ 31.00 **Unsaturated Fatty acids:** Oleic acid $C_{18:1}$ 04.44	**Saturated fatty acids:** Lauric acid $C_{12:0}$ 00.61 Myristic acid $C_{14:0}$ 00.30 Palmitic acid $C_{16:0}$ 10.23 Stearic acid $C_{18:0}$ 06.42 **Unsaturated Fatty acids:** Palmitoleic acid $C_{16:1}$ 3.10 Oleic acid $C_{18:1}$ 16.21 Linoleic acid $C_{18:2}$ 61.90 Linolenic acid $C_{18:3}$ 1.23

Preparation of acyl chloride

It was prepared as vicous oil from the corresponding acids (decanoic, dodecanoic, tetradecanoic, hexadecanoic, octadecanoic, octadec9-enoic, octadec9,12 dienoic acid, mixed fatty acids of gawafa fat and mixed fatty acids of grape seed oil, respectively according to Youngs *et al.* methods [13] .

Preparation of amido derivatives [6]

N-Acyl–2-aminopyridine and N-acyl–2-aminothiazole derivatives were prepared by condensation of equamolar amounts of the corresponding pure fatty acid chloride of (decanoic C10:0, dodecanoic C12:0, tetradecanoic C14:0, hexadecanoic C16:0, octadecanoic C18:0, 9-ctadecenoic **C**18:1 acids , mixed fatty acids extracted from

Gawafa fat and /or Gape seed oil) with 2-aminothiazole and/or 2-aminopyridine, respectively. The reaction mixture was heated at 80 °C for 4 hr in the presence of catalytic amount of pipridine and dry benzene as solvent. The organic solvent was removed under reduced pressure, and residue was recrystallized from isopropanol. The yield percentage was 84–95 %, the structures of compounds IIa-i, IIIa-i, was confirmed by IR and H^1NMR (*c.f.* Table 2).

Preparation of sodium 1-chloro-2-hydroxy-3-propanesulfonate [6]

Epichlorohydrine (50 g., 0.45 mol) was gradually added to sodium bisulfate (64.7g., 0.621 mol) and sodium sulfate (25.0 g., 0.199 mol) dissolved in 130 ml water. The reaction temperature was maintained between 18–30 °C with aid of a cooling ice bath due to the exothermal reaction. The reaction product precipitated gradually and the pH of the solution remained at 6. After agitation for 2 hr at room temperature, the reaction product was removed by filtration and dried. The yield percentage was 96% and used as crude products in the next steps.

Preparation of amido sulfobetaines (IV, VI). a-l [6]

They are prepared by placing 0.02 mol of sodium 1-chloro-2-hydroxy- 3-propylene sulfonate in 45 ml of water and 0.02 mol of IIa-l or IIIa-l (derivatives) dissolved in 100 ml of ethanol, and refluxed for 3 hr. The reaction mixture was cooled to 50°C, then 0.03 mol of sodium carbonate was added with refluxing for 6 hr. After cooling the product was filtered to remove the residual solid and extracted with 200 ml of petroleum-ether (40–60°C). The remainder (water and alcohol phase) was evaporated to dryness, washed with mixed solvents dichloroethane and acetone (v/v 50%) and dissolved in 75% ethanol. Finally, the pure product was obtained in 55–64 % yield. The structure and purity were identified by TLC, elemental analysis, IR and H^1NMR. (*c.f.* Table 2).

Preparation of amidobetaines (V, VII)a-l [6]

They were prepared by refluxing a solution of 0.016 mol of IIa-i or IIIa-i in 100 ml of absolute ethyl alcohol and 140 ml of aqueous solution containing 40 grams of sodium chloroacetate and 5 grams of sodium bicarbonate in three necked flask with stirring at 80°C for 9 hr. After cooling and removing the solvent to dryness, the reminder was dissolved in distilled water and filtered to remove the insoluble material. The filtrate was evaporated to remove water, dissolved in absolute ethyl alcohol and then filtered to remove inorganic salts (three times). The final products were identified by elemental analysis, IR and ^{1}H-NMR. The yield percentage was (80–90%)(*c. f.* Table 2).

Evaluation method of surface active properties

Surface and interfacial tension measurements

Surface and interfacial tension measurements of the prepared surfactants were made at room temperature (25^{o}C) with a Du Nouy tensiometer (DST 30 Series) using distilled water solution of 0.1% weight concentration[14]. The surface tension of the used distilled water was 73 mN/m and the interfacial tension between medicinal paraffin oil and distilled water was 56.2 mN/m. Surfactant solutions were aged for

1/2 hr before any measurements were made. Three readings were made on each sample to determine any change with time and to obtain an average value [10].

Kraft point was measured as the temperature at which 1 % dispersion solution becomes clear on gradual heating [15].

Wetting time was determined by immersing a sample of cotton fabric in 0.1% aqueous solution of the surfactants [16].

Foaming properties were measured according to Ross and Miles method [17]. The foam production for 0.1 % solution was measured by the foam height initially produced.

Emulsion power: the emulsion was prepared from 10 ml. of 20 m mol aqueous solution of surfactant and 5 ml of paraffin oil at 25°C. The emulsifying property was determined by the ratio between the oil volume separating from the emulsion layer [18].

Stability to hydrolysis: A mixture of 10 m mol surfactant and 10 ml. 0.05 N NaOH were placed in a thermostat at 40°C. The time required for a sample solution to be clouded as a result of hydrolysis shows the stability of surfactant to hydrolysis [19].

Hydrophilic-lipophilic balance (HLB) of a surfactant is a measure of the degree to which it is hydrophilic or lipophilic, determined by calculating values for the different regions of the molecule, as described [20,21].

Biodegradability %: Biodegradation is carried out by bacteria in nature. By enzymatic reactions, a surfactant molecule is ultimately converted into carbon dioxide, water and oxides of the other elements. If the surfactant does not undergo natural biodegradation then it is stable and persists in the environment. For surfactants the rate of biodegradation varies from 1–2 hr for fatty acids, 1–2 days for linear alkyl benzene sulfonates and several months for branched alkyl benzene sulfonates. The rate of biodegradation depends on the surfactant concentration, pH and temperature. The temperature effect is particularly important, since the rate can vary by as much a factor of five between summer and winter in Northern Europe. Two criteria are important when testing for biodegradation: (1) Primary degradation that results in loss of surface activity. (2) Ultimate biodegradation, *i.e.* conversion into carbon dioxide, which can be measured using closed bottle tests. The rate of biodegradation also depends on the surfactant structure. For example, the surfactant must be water soluble. Biodegradability percentage was determined following the method of Eter[22], according to the following equation:

$$D\ \% = \left[\frac{\gamma t - \gamma 0}{\gamma bt - \gamma 0}\right] \times 100$$

where: γt = Surface tension at time t.
$\gamma 0$ = Surface tension at time zero.
γbt = Surface tension of blank at time t, without sample.

Results and Discussion

The preparation of amphoteric surfactants $[IV\text{-}VII]_{a\text{-}i}$ was performed according to the preparation methodology giving suitable yields. Where, the fatty acids converted to the corresponding fatty acid chloride according to Youngs *et al.* method[13]. Then, react with 2-aminothiazole and 2-aminopyridine to afford N-acyl aminothiazole [IIa-i] and 2-N-acyl aminopyridine [IIIa-i], respectively. The IR spectra of the prepared amido-derivatives showed band at cm-1 for (νN-H) , (νC=O of sec. amide). Micro-analysis; Infrared (IR) and Proton Nuclear Magnetic Resonance (1H-NMR) spectra; were carried out to establish the structure of some examples of the prepared amphoteric compounds (Tables 2& 3).

TABLE 2. Micro-analytical data of the synthesized amphoteric sulfobetaine and betaine surfactants containing thiazolium or pyridinium moiety.

Compound number	Mol. Form.	Mol. wt.	Yield %	Microanalysis							
				C%		H%		N%		S%	
				Calc.	Fd.	Calc.	Fd.	Calc.	Fd.	Calc.	Fd.
IVa	$C_{16}H_{28}N_2S_2O_5$	392.14	64	48.96	48.90	7.19	7.10	7.14	7.10	16.34	16.30
IVb	$C_{18}H_{32}N_2S_2O_5$	420.18	62	51.40	51.30	7.67	7.62	6.66	6.60	15.25	15.20
IVc	$C_{20}H_{36}N_2S_2O_5$	448.21	59	53.54	53.30	8.09	8.07	6.24	6.24	14.29	14.30
IVd	$C_{22}H_{40}N_2S_2O_5$	476.24	55	55.43	55.40	8.46	8.45	5.88	5.80	13.45	13.40
IVe	$C_{24}H_{44}N_2S_2O_5$	504.27	64	57.11	57.01	8.79	8.70	5.55	5.50	12.71	12.70
IVf	$C_{24}H_{42}N_2S_2O_5$	502.25	58	57.34	57.30	8.42	8.30	5.57	5.50	12.76	12.70
IVg	$C_{24}H_{40}N_2S_2O_5$	500.24	61	57.57	57.60	8.05	8.00	5.59	5.60	12.81	12.8
IVh	Mixed of GSF	-	62	-	-	-	-	-	-	-	-*
IVi	Mixed of G.O	-	63	-	-	-	-	-	-	-	-*
Va	$C_{15}H_{24}N_2SO_3$	312.15	84	57.66	57.60	7.74	7.70	8.97	8.90	10.26	10.20
Vb	$C_{17}H_{28}N_2SO_3$	340.18	88	59.97	59.90	8.29	8.20	8.23	8.20	9.42	9.42
Vc	$C_{19}H_{32}N_2SO_3$	368.53	80	61.92	61.90	8.75	8.60	7.60	7.60	8.70	8.70
Vd	$C_{21}H_{36}N_2SO_3$	396.25	90	63.60	63.30	9.15	9.20	7.06	7.05	8.09	8.00
Ve	$C_{23}H_{40}N_2SO_3$	424.28	81	65.05	65.00	9.49	9.44	6.60	6.50	7.55	7.60
Vf	$C_{23}H_{38}N_2SO_3$	422.26	83	65.36	65.30	9.06	9.06	6.63	6.60	7.59	7.50
Vg	$C_{23}H_{36}N_2SO_3$	420.24	82	65.68	65.60	8.63	8.60	6.66	6.60	7.63	7.60
VIa	$C_{18}H_{30}N_2SO_5$	386.19	55	55.94	55.80	7.82	7.80	7.25	7.30	8.30	8.20
VIb	$C_{20}H_{34}N_2SO_5$	414.22	61	57.94	57.80	8.27	8.30	6.76	6.70	7.73	7.70
VIc	$C_{22}H_{38}N_2SO_5$	442.25	56	59.70	59.62	8.65	8.70	6.33	6.30	7.24	7.30
VId	$C_{24}H_{30}N_2SO_5$	470.67	59	61.24	61.22	8.99	8.80	5.95	5.90	6.81	6.80
VIe	$C_{24}H_{42}N_2SO_5$	498.31	64	62.62	62.60	9.30	9.20	5.62	5.60	6.43	6.40
VIIc	$C_{21}H_{34}N_2O_3$	362.51	90	69.58	69.50	9.45	9.40	7.73	7.70	-	-
VIId	$C_{23}H_{38}N_2O_3$	390.56	86	70.73	70.70	9.81	9.70	7.17	7.10	-	-
VIIe	$C_{25}H_{42}N_2O_3$	418.61	82	71.73	71.70	10.11	10.00	9.69	9.68	-	-
VIIf	$C_{25}H_{40}N_2O_3$	416.60	85	72.08	72.00	9.68	9.60	6.72	6.72	-	-
VIIg	$C_{25}H_{38}N_2O_3$	414.58	81	72.43	72.40	9.29	9.30	6.76	6.70	-	-

* Mixed compounds.

TABLE 3. Spectral data of some representing examples for amidothiazole and some synthesized amphoteric surfactants.

Compound No.	^{1}HNMR (δ = ppm)	IR (ν / cm^{-1})
II$_b$	δ 0.90 (t, 3H, term.$\underline{CH_3}$); δ 1.0-1.6 (br s.; 18H, $\underline{CH_2}$ chain); δ 2.34 (t, 2H, CH_2-CONH-); δ7.29 (d, 1Ha, one proton attached to sulfur atom in thiazole ring) ; δ7.53(d, 1Hb, the 2$\underline{nd}$ proton beside the nitrogen atom in thiazole ring) and δ 10.8 (s., 1 H for amide proton).	Broad band at 3170- 3240cm^{-1} for(ν_{N-H} of sec. amide), 3020 cm^{-1}(ν_{C-H} aromatic); 2980, 2920 and 2870 cm^{-1} (ν_{C-H} aliphatic); 1670 for ($\nu_{C=O}$ of amide), and 1580, 660cm^{-1} for ($\nu_{C=N,}$ ν_{C-S}) in thiazole ring respectively.
III$_b$	δ 0.88 (t, 3H, term.$\underline{CH_3}$); δ 1.1-1.6 (br s.; 18H, $\underline{CH_2}$ chain); δ 2.34 (t, 2H, $\underline{CH_2}$-CONH-); four types of characteristics protons for pyridinium ring at δ 7.20, 8.02,8.15, and 8.45and δ 10.20 (s., 1H for amide proton).	
IVc	δ 0.88 (t, 3H, term.$\underline{CH_3}$); δ 1.0-1.5 (br s.; 22H, $\underline{CH_2}$ chain); δ 2.36 (t, 2H, CH_2-CONH-);δ 1.64(m, 2H, $\underline{CH_2}$-N +) attached to thiazolium ring; δ 3.2(m.;1H for $\underline{CH}$-OH), δ 3.4-3.7 (m., 2H for -$\underline{CH_2}$-SO_3^- anion); δ 4.6 (s., 1H for hydroxyl group), and characteristics protons for thiazolium ring at δ 7.60(d.2H) ; δ 8.3(d., 1H in the ring) and δ 9.3 ppm (s., 1 H) for amide proton.	Broad band at 3170- 3240cm^{-1} for(ν_{N-H} of sec. amide), 3020 cm^{-1}(ν_{C-H} aromatic); 2980, 2920 and 2870 cm^{-1} (ν_{C-H} aliphatic); 1690 cm^{-1} ($\nu_{C=O}$ of amide); 1620,1570, 690cm^{-1} ($\nu_{C=C}$, $\nu_{C=N,}$ ν_{C-S} in thiazolium ring respectively), sharpe band at 3380 (ν_{OH} of sec. alcohol) , 1210, 1090 cm^{-1} (ν_{C-O}) and characteristics bands at 1270 ,1050 cm^{-1}for (νSO_3^-) respectively.
V$_e$	δ 0.90 (t, 3H, term.$\underline{CH_3}$); δ 1.1-1.6 (br s.; 30H, $\underline{CH_2}$ chain); δ 2.4 (t, 2H, CH_2-CONH-);δ 2.86 (s, 2H, , OOC-$\underline{CH_2}$-N +) attached to thiazolium ring, and characteristics protons for thiazolium ring at δ 7.65(d.2H) ; δ 8.2(d., 1H in the ring) and δ 9.2ppm (s., 1 H) for amide proton.	Broad band at 3170- 3240cm^{-1} for(ν_{N-H} of sec. amide), 3020 cm^{-1}(ν_{C-H} aromatic); 2980, 2920 and 2870 cm^{-1} (ν_{C-H} aliphatic); 1650, 1560cm^{-1} ($\nu_{C=C}$, $\nu_{C=N}$ in pyridinium ring), sharpe band at 3380(ν_{OH} of sec. alcohol) , 1240, 1100 cm^{-1} (ν_{C-O}) and Characteristics band at 1270 ,1050 cm^{-1}for (νSO_3^-) respectively.
VI$_d$	δ 0.87 (t, 3H, term.$\underline{CH_3}$); δ 1.0-1.6 (br s.; 26H, $\underline{CH_2}$ chain); δ 2.34 (t, 2H, $\underline{CH_2}$-CONH-); δ 3,2 (d., 2H for -(HO)-CH-$\underline{CH_2}$-N +), δ 3.1(d., 2H for -$\underline{CH_2}$-SO_3^- anion); δ (s., 1H for hydroxyl group), four types of characteristics protons for pyridinium ring at δ 9.2, 8.50, 9.0 and 9.40 respectively and δ 10.4 ppm (s., 1 H) for amide proton.	
VIIa	δ 0.87 (t, 3H, term.$\underline{CH_3}$); δ 1.0-1.6 (br s.; 14H, $\underline{CH_2}$ chain); δ 2.3 (t, 2H, CH_2-CONH-);δ 2.90 (s, 2H, , OOC-$\underline{CH_2}$-N +) attached to pyridinium ring and four types of characteristics protons for pyridinium ring at δ 7.70, 8.15, 8.50, and 9.05 and δ 9.80 (s., 1H for amide proton).	

Surface properties

Surface and interfacial tensions

The measured values of surface and interfacial tensions of the prepared surfactants are given in Table 4. The surface and interfacial tensions values increased with increasing the hydrophobicity in sulfobetaine and betaine products, respectively [4].

TABLE 4 . Surface properties of synthesized amphoteric containing thiazolium and pyridinium moiety .

Comp.	Surface tension (dyne/cm) 0.1 %	Interfacial tension (dyne/cm) 0.1 %	Kraft point °C 1 %	Wetting time (sec.) 0.1 %	Foam height (mm) 0.1 %	Stability to hydrolysis (Acid) min. : sec.	Stability to hydrolysis (Base) min. : sec.	HLB
IVa	27.6321	7.3540	2	50	180	388 : 00	156 : 23	13.530
IVb	27.9856	8.2354	<0	49	260	396 : 22	159 : 00	12.627
IVc	28.2081	8.42315	<0	48	270	405 : 45	163 : 08	11.837
IVd	29.3684	9.0032	<0	51	280	422 : 32	169 : 38	11.141
IVe	30.2529	9.2370	<0	52	310	435 : 05	170 : 50	10.521
IVf	30.6354	10.3213	<0	56	320	446 : 15	172 : 42	10.564
IVg	30.5236	9.9007	<0	59	330	459 : 33	178 : 50	10.606
IVh	31.3289	9.6573	12	64	360	490 : 30	186 : 31	10.564
IVi	33.2238	10.6564	14	88	320	510 : 15	200 : 22	10.606
Va	29.2584	7.4562	4	60	160	378 : 36	154 : 32	11.868
Vb	29.5698	8.2564	2	65	180	381 : 45	156 : 36	10.887
Vc	30.6498	9.2315	<0	47	240	392 : 00	158 : 00	10.049
Vd	31.7854	9.8976	<0	54	250	413 : 42	163 : 30	9.346
Ve	31.9876	9.0064	6	59	260	416 : 40	166 : 33	8.729
Vf	32.1584	10.4633	5	64	280	432 : 23	169 : 40	8.771
Vg	34.3597	10.9007	3	68	290	446 : 38	176 : 32	8.812
Vh	35.2982	10.6573	17	72	300	480 : 24	183 : 12	8.771
IVi	36.8760	12.7654	15	93	290	590 : 41	199 : 22	8.812
VIa	29.4323	7.0321	5	55	130	388 : 00	156 : 23	13.415
VIb	29.8737	7.9758	3	59	140	396 : 22	159 : 00	12.507
VIc	31.2589	8.2315	<0	49	170	405 : 45	163 : 08	11.714
VId	32.6472	9.1254	<0	56	200	422 : 32	169 : 38	11.072
VIe	33.3526	9.9872	<0	67	210	435 : 05	170 : 50	10.396
VIf	34.6857	10.0214	<0	68	220	446 : 15	172 : 42	10.430
VIg	34.9876	10.8763	<0	70	230	459 : 33	178 : 50	10.472
VIh	35.6422	11.0125	14	79	200	490 : 30	186 : 31	10.430
VIi	37.4322	13.6564	12	110	380	550 : 30	230 : 11	10.472
VIIa	30.3224	9.0321	8	60	120	375 : 36	159 : 55	11.693
VIIb	30.3698	9.6864	6	65	130	386 : 29	160 : 46	11.713
VIIc	31.9876	10.2315	1	47	160	390 : 38	163 : 27	9.883
VIId	32.2620	10.5314	<0	54	180	410 : 24	165 : 07	9.714
VIIe	33.6974	10.0022	<0	59	170	415 : 42	166 : 32	8.559
VIIf	34.6983	11.4664	<0	64	200	418 : 03	178 : 44	8.600
VIIg	35.3597	12.9007	<0	68	180	421 : 59	186 : 39	8.642
VIIh	37.0002	13.6573	9	72	190	469 : 06	191 : 33	8.600
VIIi	38.3256	13.4321	8	95	290	480 : 52	210 : 00	8.642

Error of measurements was
Surface and interfacial tensions = ±0.1 dyne/cm
Kraft point =±1 °C - HLB = ±0.2
Foam height =±2mm
Wetting time= ±1 Sec
Stability to hydrolysis = ±1 min

TABLE 5 . Emulsification power of the synthesized amphoteric surfactants .

Compound No.	t = 0.0 min		t= 5.0 min		t= 10.0 min		t= 20.0 min		t= 30.0 min	
IVa	e	5	e	4.0	e	4.0	e	3.0	e	1.5
	o	0	o	1.0	o	1.0	o	2.0	o	3.5
IVb	e	5	e	4.5	e	4.0	e	3.0	e	1.5
	o	0	o	0.5	o	1.0	o	2.0	o	3.5
IVc	e	5	e	5.0	e	3.5	e	3.5	e	2.0
	o	0	o	0.0	o	1.5	o	1.5	o	3.0
IVd	e	5	e	4.5	e	4.0	e	3.5	e	2.5
	o	0	o	0.5	o	1.0	o	1.5	o	2.5
IVe	e	5	e	4.5	e	4.0	e	3.5	e	3.0
	o	0	o	0.5	o	1.0	o	1.5	o	2.0
IVf	e	5	e	4.0	e	3.5	e	3.0	e	2.5
	o	0	o	1.0	o	1.5	o	2.0	o	2.5
IVg	e	5	e	4.5	e	4.0	e	3.5	e	2.5
	o	0	o	0.5	o	1.0	o	1.5	o	2.5
IVh	e	5	e	5.0	e	4.5	e	4.0	e	3.0
	o	0	o	0.0	o	0.5	o	1.0	o	2.0
IVi	e	5	e	5.0	e	4.5	e	4.0	e	3.5
	o	0	o	0.0	o	0.5	o	1.0	o	1.5
Va	e	5	e	4.0	e	3.0	e	2.5	e	1.0
	o	0	o	1.0	o	2.0	o	2.5	o	4.0
Vb	e	5	e	4.5	e	3.5	e	3.0	e	1.5
	o	0	o	0.5	o	1.5	o	2.0	o	3.5
Vc	e	5	e	4.5	e	4.0	e	3.5	e	2.0
	o	0	o	0.0	o	1.0	o	1.5	o	3.0
Vd	e	5	e	4.5	e	4.0	e	3.5	e	2.0
	o	0	o	0.5	o	1.0	o	1.5	o	3.0
Ve	e	5	e	4.5	e	4.0	e	3.5	e	2.5
	o	0	o	0.5	o	1.0	o	1.5	o	2.5
Vf	e	5	e	4.0	e	3.5	e	3.0	e	2.5
	o	0	o	1.0	o	1.5	o	2.0	o	2.5
Vg	e	5	e	4.5	e	4.0	e	3.5	e	2.0
	o	0	o	0.5	o	1.0	o	1.5	o	3.0
Vh	e	5	e	5.0	e	4.5	e	4.0	e	2.5
	o	0	o	0.0	o	0.5	o	1.0	o	2.5
Vi	e	5	e	5.0	e	4.5	e	4.0	e	3.5
	o	0	o	0.0	o	0.5	o	1.0	o	1.5
VIa	e	5	e	4.0	e	3.5	e	3.0	e	2.0
	o	0	o	1.0	o	1.5	o	2.0	o	3.0
VIb	e	5	e	4.0	e	3.0	e	2.5	e	2.0
	o	0	o	1.0	o	2.0	o	2.5	o	3.0
VIc	e	5	e	4.0	e	3.5	e	3.0	e	2.5
	o	0	o	1.0	o	1.5	o	2.0	o	2.5
VId	e	5	e	4.5	e	4.0	e	3.5	e	2.5
	o	0	o	0.5	o	1.0	o	1.5	o	2.5
VIe	e	5	e	4.5	e	4.0	e	3.5	e	3.0
	o	0	o	0.5	o	1.0	o	1.5	o	2.0
VIf	e	5	e	4.0	e	3.5	e	3.0	e	2.5
	o	0	o	1.0	o	1.5	o	2.0	o	2.5
VIg	e	5	e	4.5	e	4.0	e	3.0	e	3.0
	o	0	o	0.5	o	1.0	o	2.0	o	2.0

TABLE 5 . Cont.

Compound No	t =	0.0 min		t= 5.0 min		t= 10.0 min		t= 20.0 min		t= 30.0 min	
VIh	e	5	e	5.0	e	4.5	e	4.0	e	3.5
	o	0	o	0.0	o	0.5	o	1.0	o	1.5
VIi	e	5	e	5.0	e	4.5	e	4.0	e	3.5
	o	0	o	0.0	o	0.5	o	1.0	o	1.5
VIIa	e	5	e	4.0	e	3.5	e	3.0	e	2.5
	o	0	o	1.0	o	1.5	o	2.0	o	2.5
VIIb	e	5	e	4.0	e	3.0	e	2.5	e	2.0
	o	0	o	1.0	o	2.0	o	2.5	o	3.0
VIIc	e	5	e	4.0	e	3.5	e	3.0	e	2.5
	o	0	o	1.0	o	1.5	o	2.0	o	2.5
VIId	e	5	e	4.5	e	4.0	e	3.0	e	2.5
	o	0	o	0.5	o	1.0	o	2.0	o	2.5
VIIe	e	5	e	4.5	e	4.0	e	3.5	e	3.0
	o	0	o	0.5	o	1.0	o	1.5	o	2.0
VIIf	e	5	e	4.0	e	3.5	e	3.0	e	2.5
	o	0	o	1.0	o	1.5	o	2.0	o	2.5
VIIg	e	5	e	4.5	e	4.0	e	3.0	e	2.5
	o	0	o	0.5	o	1.0	o	2.0	o	2.5
VIIh	e	5	e	5.0	e	3.5	e	4.0	e	3.5
	o	0	o	0.0	o	1.5	o	1.0	o	1.5
VIIi	e	5	e	5.0	e	4.5	e	4.0	e	3.5
	o	0	o	0.0	o	0.5	o	1.0	o	1.5

Kraft Point

The recorded data in Table 4, showed that the surfactants with thiazolium moiety with sulfobetaines of hydrophilic unite satisfy lower values of Kraft point (T_{Kp}). This, might lead to wide uses in industrial applications [4].

Wetting time

The wetting properties of a surfactant is one of its most important surface properties. For example, in laundry cleaning or textile processing, the wetting of surfactants may accelerate the diffusion or penetration of alkali chemicals and dyes into fibers and improve the detergency. From the measured data of the wetting time for the prepared surfactants are illustrated in Table 4. Wetting properties for sulfo-betaines with thiazolium moiety for grape seed oil IV_i recorded good result than other prepared compounds, while the effect of the hydrophobic moiety is negligible [23].

Foaming height

Low-foaming tendency of surfactants is recently considered as an important property in some applications such as dyeing auxiliaries in modern textile dyeing industry. From the data recorded in Table 3 surfactants IV_i,V_i,VI_i and VII_i for mixed fatty derivatives of gawafa fat and grape oil reveal higher foam than all prepared compounds. The relative low-foaming properties of the amphoteric surfactants(amido-betaines) containing pyridinium moiety are recorded for VIIa-g.

Stability to hydrolysis

From the data recorded in Table 4 stability of the synthesized Amphoteric surfactants. It can be seen that all the prepared compound have higher stability in acidic media than in basic medium, this may be due the presence of nitrogen atoms which coordinated with the acid forming more cationic center [24-25] .

Emulsification stability

It was reported that, better emulsifying properties were obtained with derivatives containing pyridinium moiety incorporated with acetate group into their structure [23]. From the data given in Table 5, the prepared compounds exhibit an excellent degree to form emulsions either O/W or W/O for those with high percent of hydrophobicity with pyridinum moiety.

Hydrophilic-lipophilic balance (HLB),

Of a surfactant, one of the most widely used indicators of it suitability for a given application is a measure of a surfactant partitioning tendency between oil and water. Since Griffin first introduced this definition in 1949 [26] . From data recorded in Table 5, HLB values decrease with increase the number of carbon atoms in alkyl chain. On other hand, HLB values for sulfo-thiazolium amphoteric surfactant revealed higher values than other prepared compounds. Also, amphoteric surfactants prepared from grape oil and Juagafa fat given hlb values 8.6-10.6. These values indicate that the synthesized amphoteric surfactants can be used as (W/O (water in oil) emulsifier or oil in water emulsion).

Biodegradability

After use, all surfactants used in laundry detergents, cleaning agents, and dyeing auxiliaries are passed quantitatively into waste water. Because of this fact, the constant input of surfactants into the environment requires a particular ecological characterization of this class of compounds. An excellent review of surfactant biodegradability points out that biodegradability increases with increasing linearity of the hydrophobic group and is reduced, for isomeric materials, by branching in that group and in the presence of aromatic ring [27,28] . Biodegradability is deterred and degradation is slowed as steric hindrance increases [29-30]. Figures 1 and 2 revealed the degradation of the amphoteric surfactants containing the pyridinium moiety(VI_a and VII_a) more than the surfactant containing thiazolium moiety (IV_b and IV_e).

Biological activity

Antimicrobial activity of the prepared compounds was tested via a modification of the cup- plate method [31]. All the prepared surfactants were screened for their bactericidal activities against (*Bacillus sublitis* and *Escherichia coil*) and their antifungal activity against (*Aspergillus niger* and *Candida albicam*). The results are listed in Table 6. It is apparent from that some of the synthesized compounds showed antibacterial activity. However, concerning the activity against Gram positive bacteria compounds IV_b, IV_f, IV_h and IV_i exhibit good activity, where as compounds V_b, VII_d, and VII_i showed moderate activity.

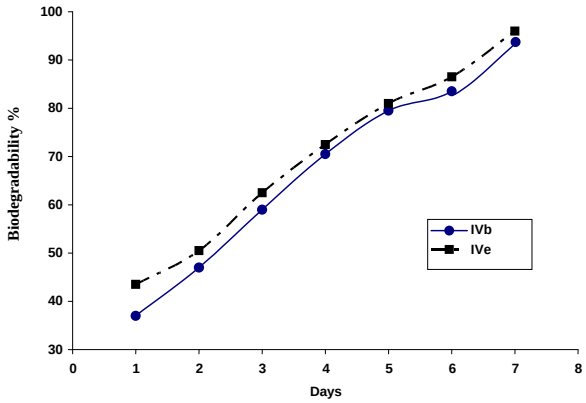


Fig. 1. Biodegradability % of amphoteric surfactant containing thiazolium moiety.

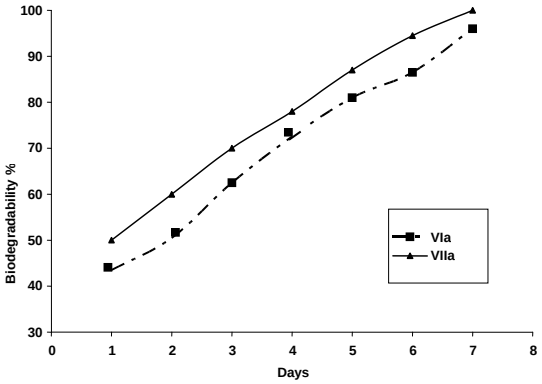


Fig. 2. Biodegradability % of amphoteric surfactant containing pyridinium moiety.

Conclusion

It can be concluded that all prepared amphoteric surfactants exhibited antibacterial and antifungal properties as well as emulsifier properties especially for compound from Grape seed oil and Gawafa fat . Therefore, their potential use in a non edible media such as insecticides or pesticides as well as in the manufacturing of drugs, cosmetics, antibacterial and/or antifungal is recommended.

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TABLE 6. Biological activity of some prepared amphoteric surfactants.

Compound number	Antibacterial		Antifungal	
	Bacillus Subti	Escherichia C	Aspergillus nig	Candida albi
IV_b	++	+	+++	+++
IV_f	+++	++	++	++
IV_h	++	+	++	++
IV_i	+	+	+++	+++
V_f	++	++	+	++
V_h	+	+	-	-
V_i	++	+	-	-
IV_b	++	++	+	+
IV_f	++	++	+	++
VI_b	++	++	+	++
VII_f	++	+	-	-
VII_h	++	+	-	-

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

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مواد ذات نشاط سطحي أمفوتيرية ذات حلقات غير متجانسة من المخلفات الصناعية

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يتناول هذا البحث تشيد بعض المركبات ذات النشاط السطحي الأمفوتيرية والتي تحتوي على حلقة غير متجانسة من الأحماض الدهنية طويلة السلسلة الكربونية وكذلك مخلوط الأحماض المحضر من دهن بذور الجوافة و العنب المحلي).

ويتم هذا علي النحو التالي:-

١. تحضير كلوريد الأحماض الدهنية المشبعة (كابريك ، اللوريك، الميرستيك، البالميتيك ، الستياريك) وغير المشبعة (الأوليك ، اللينوليك) و كذلك مخلوط الأحماض الدهنية لدهن الجوافة و زيت العنب) كلا على حده وذلك بالتفاعل مع كلوريد الثيونيل ثم تفاعل الناتج مع ٢- أمينوثيازوال و ٢-أمينوبريدين على التوالي لتعطي ٢-(ن-أسيل)أمينوثيازول و ٢-(ن-أسيل) أمينو بريدين.

٢. تم تشيد المركبات الأمفوتيرية بتفاعل الناتج مع كلا من ٣- كلورو -٢ - هيدروكسي كبريتات البروبان ، ملح الصوديوم لحامض الخليك لإنتاج أميدوسلفوبيتين، أميدوبيتن.

٣. وقد تم التعرف وإثبات التركيب الكيميائي لتلك المركبات بالتحليل العنصري وبالدراسات الطيفية للأشعة تحت الحمراء والرنين النووي المغناطيسي.

٤. كما تم دراسة الخواص السطحية والتحلل البيولوجي لهذه المركبات ، ووجد أن المركبات الأمفوتيرية الناتجة من مخلوط الأحماض الدهنية المستخلصة من بذور العنب وكذلك بذور الجوافة لهم صفات متواكبة مع المركبات السطحية الناتجة من الأحماض الدهنية التجارية المستخدمة كتقليل التوتر السطحي، والقدرة العالية على الاستحلاب و إنخفاض درجة الكرافت وكذلك المقاومة تجاه البكتيريا والفيروسات وخصوصاً أميدو سلفوبيتين سواء من الأحماض التجارية أو من مخلوط أحماض الدهنية للعنب ويليها المحضر من بذور الجوافة لذلك يمكن التوصية بالاستفادة من هذه المركبات المحضرة من مخلفات البذور النباتية في العديد من الصناعات مثل مبيدات الحشائش وفى مستحضرات التجميل.