

# Anionic surface active agents from fatty acid hydrazides containing heterocyclic moiety

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## ÖSSZEFOGLALÁS

a-Szulfonált zsírsav-hidrazidok nátrium sóját használták kiinduló anyagként néhány jelentős heterociklusos vegyület szintéziséhez, így pirazolok, tiazolok, oxadiazolok, benzoxazolok, piridazinok és ftalazinok szintéziséhez, hogy az anionos felületaktív anyagok olyan új csoportját állítsák elő, amelyeknek antimikrobás és egyben felületaktív kettős funkciója van. Ezeknek a vegyületeknek a szerkezetét IR, <sup>1</sup>H NMR és tömegspektrometriás módszerrel vizsgálták. A következő fizikai sajátságokat határozták meg: felületi és határfelületi feszültség, Krafft-pont, habmagasság, nedvesítési idő, emulgáló képesség, kalcium-stabilitás, a hidrolízissel szembeni stabilitás és a kritikus micella-koncentráció (cmc). Meghatározták az antimikrobás hatást és biológiai lebonthatóságot is.

## ABSTRACT

Sodium salt of a-sulphonated fatty acid hydrazide (1) was used as starting material to synthesis some important heterocycles as pyrazoles, thiazoles, oxadiazoles, benzoxazoles, pyridazines, and phthalazines to produce novel groups of anionic surfactants having a double function, antimicrobial and surface active agents. The structure of these compounds was investigated by IR, <sup>1</sup>H NMR and Mass spectra. The physical properties as surface and interfacial tension, Krafft point, foaming height, wetting time, emulsification power, calcium stability, stability to hydrolyses and the critical micelle concentration (cmc) were determined, antimicrobial and biodegradability were also determined.

## ZUSAMMENFASSUNG

Natriumsalz von a-sulfonierten Fettsäurehydraziden wurde als Ausgangsmaterial für die Synthese von einigen wichtigen heterocyclischen Verbindungen wie Pyrazole, Thiazole, Oxadiazole, Benzoxazole, Pyridazine und Phthalazine verwendet. Ziel war die Herstellung einer neuen Gruppe von anionischen oberflächenaktiven Substanzen, die Doppelfunktion, antimikrobielle und oberflächenaktive Funktion aufweisen. Die Struktur dieser Verbindungen wurde mit IR, <sup>1</sup>H NMR und massenspektrometrischer Methoden geprüft. Die folgende physische Eigenschaften wurden bestimmt: Oberflächenspannung, Grenzoberflächenspannung, Krafft-Punkt, Schaumhöhe, Feuchtzeit, Emulgierfähigkeit, Kalkiumstabilität, Stabilität gegen Hydrolyse und kritische Micellenkonzentration (cmc). Die antimikrobielle Wirkung und die biologische Abbaufähigkeit wurden auch bestimmt.

## Introduction

Among anionic surfactants containing an aromatic structure element, the most common group, are alkylbenzene sulfonates accompanied by alkyl-naphthalene sulfonates. In these compounds, hydrophilic sulfonic group is separated from long chain alkyl hydrophobe by single six member benzene or naphthalene rings. The structure analogues to the above ones may be surfactants containing five member heteroaromatic groups. As an example, the derivatives of alkylthiophene or alkylpyrrole having a sulfonic or carboxylic hydrophilic group can be mentioned. Long chain (C<sub>8</sub> to C<sub>18</sub>) 3-n-alkylthiophene, 1-and 3-n alkyl and 3-n-alkanoyl derivatives of pyrrole were obtained as hydrophobic intermediates for synthesis of anionic surfactants containing sulfonic or carboxylic group. In the literature, mainly in patent description, the examples of synthesis of

surface active alkyl benzopyrrole and alkyl benzimidazole sulfonates have been reported [1] The reaction of butyrolactone with primary amines at high temperatures produces N-alkyl substituted pyrrolidones. However, other methods of incorporating the pyrrolidone nucleus also have been investigated. Butyrolactone reacts with diamines, when the diamine is in excess, to afford N-aminoalkyl pyrrolidones, which can be further condensed with fatty acids, anhydrides, acid chlorides, or esters to produce amidoalkyl pyrrolidones. When the fatty acids are in the surfactant range (C<sub>8</sub>–C<sub>16</sub>), highly surface-active compounds are formed [2]. A family of novel monoalkyl glycerol ether surfactants with different hydrophobe lengths (C<sub>9</sub>–C<sub>16</sub>) and tryptophan were synthesized on a laboratory scale and their aqueous surface-active properties are studied [3, 4].

More recently new bis-quaternary pyridinium surfactants were synthesized and characterized. Their surface tension in aqueous media, cmc value, and area per molecule "A" were determined and compared with corresponding monoquaternary-pyridinium bromides which were synthesized and studied [5–7]. It has been well established that various triazoles, oxazoles, benzoxazoles, pyrimidine, pyridazine, pyrazol and thiazoles are of biological interest [8–11]. This encouraged me to synthesize novel groups of anionic surfactants containing pyridazine, oxadiazole, pyrrole, oxadiazine, triazole, phthalazinone and thiazole derivatives from the sodium salt of a-sulphonated long chain fatty acids (myristic, palmitic and stearic) hydrazide (**Ia–c**) hopping to possessing good surface properties and expected to have biological activities.

## Discussion

Thus when compounds (**Ia–c**) were allowed to react with b-benzoyl acrylic acid in n-butanol afforded pyridazine derivatives (**IIa–c**). IR spectra exhibits nC=O at 1701,1625, nC=N at 1615, nC-H aliphatic at (2920–2850) and nC-H aromatic at 3044 cm<sup>-1</sup>.

Similarly, compounds (**Ia–c**) have been reacted with carbon disulphide in presence of potassium hydroxide as catalyst gave oxapyrazole derivatives (**IIIa–c**). IR spectra shows nNH at 3228, nC=N at 1620, nC=S at 1490, nC-H aliphatic at 2920–2850 cm<sup>-1</sup>. The mass spectrum of (**III<sub>a</sub>**) showed molecular ion peak at M<sup>+</sup>+1= 387 and the base peak at 174.

Also, when compounds (**Ia–c**) were allowed to react with chloroacetic acid in ethyl alcohol yielded oxapyridazinone derivatives (**IVa–c**). IR spectra shows nNH at 3437, nC=O at 1654, nC=N at 1618, nCH aliphatic at (2919–

2852)  $\text{cm}^{-1}$ .  $^1\text{H}$ NMR spectrum of (**IVb**) shows signals at  $\delta$ 0.9 (t, 3H, terminal  $\text{CH}_3$ ),  $\delta$ 1.3 (m, 26H,  $\text{CH}_2$  of alkyl chain),  $\delta$ 1.6 (s, 2H,  $\text{CH}_2$  of pyridazine ring),  $\delta$ 2.8 (s, 1H,  $\text{CH-SO}_3\text{Na}$ ) and  $\delta$ 4.1 (s, 1H, NH proton).

Phthalazine derivatives (**Va-c**) were produced by the reaction of compounds (**Ia-c**) with phthalic anhydride in acetic anhydride. IR spectra shows  $\nu_{\text{NH}}$  at 3405,  $\nu_{\text{C=O}}$  at 1703, 1656 and 1640,  $\nu_{\text{CH}}$  aliphatic at (2919–2851),  $\nu_{\text{CH}}$  aromatic at 3032  $\text{cm}^{-1}$ . Mass spectrum of (**V<sub>a</sub>**) shows molecular ion peak  $M^+ + 2 = 476$  and base peak at 147.

When compounds (**Ia-c**) were allowed to react with ethylbenzoyl acetate in ethylalcohol and sodium ethoxide afforded pyrazole derivatives (**VIa-c**). IR spectra shows  $\nu_{\text{C=N}}$  at 1615,  $\nu_{\text{C=O}}$  at 1703,  $\nu_{\text{CH}}$  aliphatic at (2925–2854) and  $\nu_{\text{CH}}$  aromatic at 3020  $\text{cm}^{-1}$ .  $^1\text{H}$ NMR spectrum of (**VI<sub>a</sub>**) shows signals  $\delta$ 0.9 (t, 3H, terminal  $\text{CH}_3$ ),  $\delta$ 1.3 (m, 30H,  $\text{CH}_2$  of alkyl chain),  $\delta$ 5.6 (s, 1H, olefinic CH of the ring),  $\delta$ 1.1 (t, 3H  $\text{CH}_2\text{CH}_3$ ),  $\delta$ 4.1 (q, 2H,  $\text{CH}_2\text{CH}_3$ ), and  $\delta$ 7.2–7.6 (m, 5H, ArH).

On the other hand, when compounds (**Ia-c**) were submitted to react with phenyl isothiocyanate in sodium hydroxide afforded triazole derivatives (**VIIa-c**). IR spectrum shows  $\nu_{\text{C=N}}$  at 1630,  $\nu_{\text{SH}}$  at 2237,  $\nu_{\text{CH}}$  aromatic at 3020 and  $\nu_{\text{C-H}}$  aliphatic at (2920–2850)  $\text{cm}^{-1}$ .

Also, pyrrole derivatives (**VIIIa-c**) were produced from the reaction of compounds (**Ia-c**) with acetyl acetone in glacial acetic acid. IR spectra shows  $\nu_{\text{NH}}$  at 3250,  $\nu_{\text{C=O}}$  at 1680 and  $\nu_{\text{C-H}}$  aliphatic at (2920–2850)  $\text{cm}^{-1}$ .

Treatment of compounds (**Ia-c**) with benzaldehyde lead to formation of Chief base derivatives (**IXa-c**). IR spectra reveals  $\nu_{\text{NH}}$  at 3228,  $\nu_{\text{C=O}}$  at 1670,  $\nu_{\text{C=N}}$  at 1610,  $\nu_{\text{CH}}$  aliphatic at (2921–2852),  $\nu_{\text{CH}}$  aromatic at 3053  $\text{cm}^{-1}$ . The  $^1\text{H}$ NMR spectrum of (**IXa**) shows  $\delta$ 0.9 (t, 3H, for terminal  $\text{CH}_3$ ),  $\delta$ 1.4 (s, 22H, of  $\text{CH}_2$  aliphatic chain),  $\delta$ 6.1 (s, 1H, of  $\text{CH-Ph}$ ),  $\delta$ 7.4–7.7 (m, 5H, ArH),  $\delta$ 2.8 (s, 1H,  $\text{CH-SO}_3\text{Na}$ ) and  $\delta$ 3.6 (s, 1H, NH proton).

Thiazole derivatives (**Xa-c**) were produced by treatment of chief base derivatives (**IXa-c**) with thioglycollic acid in dry benzene. IR spectra shows bands at 3204 for  $\nu_{\text{NH}}$ , at 1678 and 1665 for  $\nu_{\text{C=O}}$ , at (2919–2851) for  $\nu_{\text{CH}}$  aliphatic and at 3099  $\text{cm}^{-1}$  for  $\nu_{\text{CH}}$  aromatic.  $^1\text{H}$ NMR spectrum of (**Xa**) shows signals at  $\delta$ 0.9 (t, 3H, of terminal  $\text{CH}_3$  protons),  $\delta$ 1.2 (s, 30H, of  $\text{CH}_2$  aliphatic protons),  $\delta$ 1.7 (s, 2H,  $\text{CH}_2$  of the ring),  $\delta$ 2.9 (s, 2H,  $\text{CH-Ph}$ ),  $\delta$ 8.7 (s, 1H, NH proton),  $\delta$ 2.7 (s, 1H,  $\text{CHSO}_3\text{Na}$ ) and  $\delta$ 7.3–7.9 (m, 5H, ArH).

Finally, when Chief base derivatives (**IXa-c**) treated with ferric chloride in acetic acid afforded oxadiazole derivatives (**XIa-c**). IR spectra shows  $\nu_{\text{C=N}}$  at 1620,  $\nu_{\text{CH}}$  aliphatic at (2920–2851), and  $\nu_{\text{CH}}$  aromatic at 3047  $\text{cm}^{-1}$ .  $^1\text{H}$ NMR spectrum of (**XI-b**) shows signals at  $\delta$ 0.9 (t, 3H, of terminal  $\text{CH}_3$ ),  $\delta$ 1.2 (s, 26H of  $\text{CH}_2$  aliphatic protons),  $\delta$  7.4–7.8 (m, 5H, ArH) and  $\delta$ 2.8 (s, 1H, of  $\text{CH-SO}_3\text{Na}$ ).

## Surface active properties of anionic surfactants

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

The surface active and related properties of the synthesized compounds including, surface and interfacial tension, Krafft point, wetting time, foaming, emulsification properties, (cmc),  $\text{Ca}^{++}$  stability and stability towards hydrolysis are given in (Table 2). The biodegradability and biological activities were investigated as shown in (Tables 3 and 4).

### Surface and interfacial tension:

The synthesized anionic surfactants with heterocyclic moiety derivatives showed lower values for surface tension and interfacial tension. The results are recorded in (Table 2). It was found that, the lower values of surface and interfacial tension that might be due to the electrostatic repulsion between the ionized molecules. In general, these values are decreases with the decreasing in alkyl chain length [12].

### Krafft point:

The prepared anionic surfactants were measured as the temperature where 1% dispersion becomes clear on gradual heating. All the synthesized surfactants are freely soluble in water at 1 wt % concentration. In general, the Krafft points measurements proved that the higher the molecular weight (i.e. the longer the alkyl chain) the higher the Krafft point. But, this fact may fail due to the presence of retard- ing groups in the same molecule.

### Wetting time:

All the synthesized surfactants are good wetting agent, where wetting time increased as the alkyl chain length increases [12]. The products were thus very effective as wetting agents in distilled water. So, they can find a wide application to play an important role as wetting agents in textile industry.

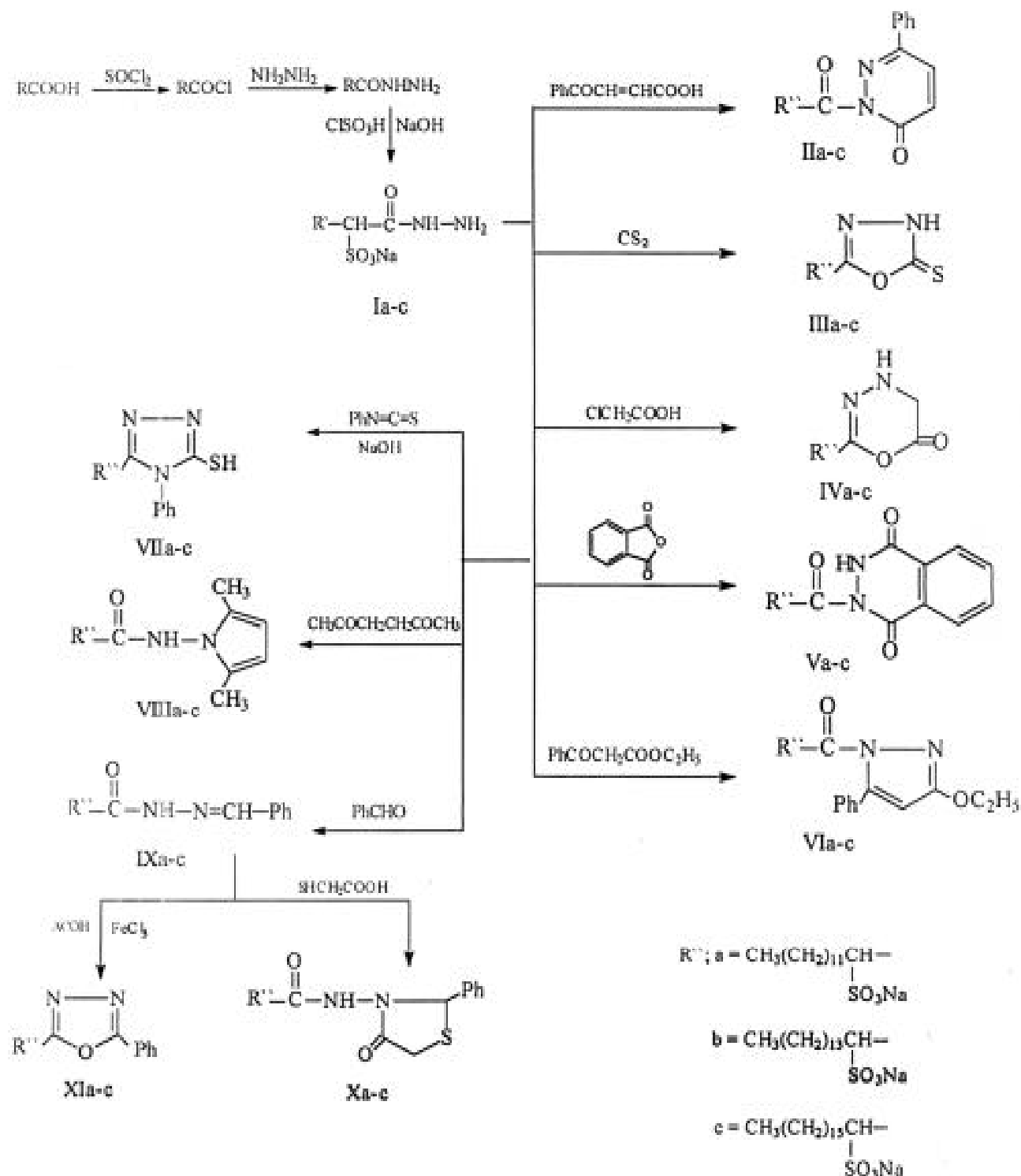
### Foaming height:

It is reported that the efficiency of surfactants as a foamier increases with increasing alkyl chain length [13]. In general, the prepared anionic surfactants with heterocyclic moiety recorded higher values of foaming height.

### Emulsion stability:

The products of anionic surfactants are good emulsifying agents as may be seen in (Table 2). In general, all the prepared compounds possess high emulsion stability, these results, might lead to the application of the surfactants of choice in pesticide and cosmetic formulation [13].

The synthetic route of these groups of anionic surfactant and abbreviations of compounds are shown in the following scheme:



**Ca<sup>++</sup> Stability:**

High calcium stability values show that the prepared surfactants can be used in hard water. The calcium stability decreased with increase in the molecular weight of the surfactant under the conditions of a constant temperature.

**Stability towards hydrolysis:**

In general, the results listed in (Table 2), revealed that, the prepared anionic surfactants are moderately stable in basic medium and the stability increases by increasing the alkyl chain length [14]. Also the results revealed that the compounds (IIa-c), (Va-c) and (VIa-c) possess high values toward alkaline hydrolysis.

Table 1.

Microanalysis of Prepared Surfactants						Analysis data calc./found %			
No.	MF.	M.wt	Solvent	Yield %	Colour	C	H	N	S
I <sub>a</sub>	C <sub>14</sub> H <sub>29</sub> N <sub>2</sub> O <sub>4</sub> S Na	344	EtOH	60	Yellow	48.81	8.42	8.11	9.32
						48.43	8.04	7.60	8.84
I <sub>b</sub>	C <sub>16</sub> H <sub>33</sub> N <sub>2</sub> O <sub>4</sub> S Na	372	MeOH	64	White	51.62	8.83	7.56	8.61
					Yellow	51.21	8.55	7.24	8.33
I <sub>c</sub>	C <sub>18</sub> H <sub>37</sub> N <sub>2</sub> O <sub>4</sub> S Na	400	Benz.	68	White	54.02	9.22	7.05	8.07
					Yellow	53.61	8.73	6.66	7.75
II <sub>a</sub>	C <sub>24</sub> H <sub>33</sub> N <sub>2</sub> O <sub>5</sub> S Na	484	EtOH	65	Yellow	59.52	6.84	5.71	6.61
					Yellow	59.15	6.59	5.37	6.23
II <sub>b</sub>	C <sub>26</sub> H <sub>37</sub> N <sub>2</sub> O <sub>5</sub> S Na	512	ACOH	68	Pale	60.92	7.23	5.41	6.42
					Yellow	60.67	6.82	5.17	5.37
II <sub>c</sub>	C <sub>28</sub> H <sub>41</sub> N <sub>2</sub> O <sub>5</sub> S Na	540	ACOH	70	Pale	62.22	7.61	5.23	5.91
					Yellow	61.73	7.34	4.74	5.45
III <sub>a</sub>	C <sub>15</sub> H <sub>27</sub> N <sub>2</sub> O <sub>4</sub> S <sub>2</sub> Na	386	Benz	75	Brown	46.6	6.99	7.2	16.5
					Brown	46.2	6.67	6.8	16.2
III <sub>b</sub>	C <sub>17</sub> H <sub>31</sub> N <sub>2</sub> O <sub>4</sub> S <sub>2</sub> Na	414	Benz.	78	Red	49.27	7.48	6.76	15.45
					Brown	48.8	7.0	6.3	15.1
III <sub>c</sub>	C <sub>19</sub> H <sub>35</sub> N <sub>2</sub> O <sub>4</sub> S <sub>2</sub> Na	442	MeOH	82	Red	51.51	7.91	6.31	14.44
					Brown	51.23	7.53	6.13	13.95
IV <sub>a</sub>	C <sub>16</sub> H <sub>29</sub> N <sub>2</sub> O <sub>5</sub> S Na	384	Tol.	65	Yellow	50.03	7.53	7.25	8.33
					Yellow	49.16	7.24	6.84	8.02
IV <sub>b</sub>	C <sub>18</sub> H <sub>33</sub> N <sub>2</sub> O <sub>5</sub> S Na	412	Benz.	60	Pale	52.44	8.01	6.71	7.74
					Yellow	52.12	7.62	6.37	7.33
IV <sub>c</sub>	C <sub>20</sub> H <sub>37</sub> N <sub>2</sub> O <sub>5</sub> S Na	440	EtOH	65	Pale	54.52	8.44	6.34	7.24
					Yellow	54.18	7.88	5.73	6.73
V <sub>a</sub>	C <sub>22</sub> H <sub>31</sub> N <sub>2</sub> O <sub>6</sub> S Na	474	ACOH	72	Brown	55.64	6.56	5.92	6.72
					Brown	55.25	6.24	5.75	6.53
V <sub>b</sub>	C <sub>24</sub> H <sub>35</sub> N <sub>2</sub> O <sub>6</sub> S Na	502	EtOH	75	Red	57.31	6.93	5.54	6.33
					Brown	57.05	6.66	5.23	6.08
V <sub>c</sub>	C <sub>26</sub> H <sub>39</sub> N <sub>2</sub> O <sub>6</sub> SNa	530	ACOH	76	Red	58.82	7.36	5.27	6.05
					Brown	58.45	6.82	4.72	5.46
VI <sub>a</sub>	C <sub>21</sub> H <sub>39</sub> N <sub>2</sub> O <sub>6</sub> S Na	470	EtOH	68	Grey	53.62	8.29	5.93	6.83
					Grey	53.41	8.04	5.62	6.54
VI <sub>b</sub>	C <sub>23</sub> H <sub>43</sub> N <sub>2</sub> O <sub>6</sub> S Na	498	Benz.	70	Red	55.44	8.65	5.67	6.42
					Yellow	55.13	8.26	5.52	6.31
VI <sub>c</sub>	C <sub>25</sub> H <sub>47</sub> N <sub>2</sub> O <sub>6</sub> S Na	526	ACOH	70	Brown	57.09	8.95	5.32	6.08
					Brown	56.46	8.69	4.93	5.45
VII <sub>a</sub>	C <sub>21</sub> H <sub>32</sub> N <sub>2</sub> O <sub>3</sub> S Na	471	Benz.	50	Yellow	53.53	6.79	8.92	13.55
					Yellow	53.22	6.53	8.65	13.22
VII <sub>b</sub>	C <sub>23</sub> H <sub>36</sub> N <sub>2</sub> O <sub>3</sub> S Na	499	Benz.	55	Pale	55.32	7.24	8.42	12.83
					Yellow	54.93	6.82	8.13	12.54
VII <sub>c</sub>	C <sub>25</sub> H <sub>40</sub> N <sub>3</sub> O <sub>3</sub> S <sub>2</sub> Na	527	MeOH	62	Pale	56.92	7.59	7.96	12.16
					Yellow	56.65	7.35	7.68	11.84
VIII <sub>a</sub>	C <sub>2</sub> H <sub>35</sub> N <sub>2</sub> O <sub>4</sub> S Na	422	EtOH	58	Brown	56.83	8.29	6.63	7.53
					Brown	56.54	8.05	6.33	7.12
VIII <sub>b</sub>	C <sub>22</sub> H <sub>39</sub> N <sub>2</sub> O <sub>4</sub> S Na	450	ACOH	65	Red	58.36	8.46	6.12	7.14
					Brown	58.25	8.27	5.08	6.37
VIII <sub>c</sub>	C <sub>24</sub> H <sub>43</sub> N <sub>2</sub> O <sub>4</sub> S Na	478	ACOH	60	Red	60.22	8.99	5.83	6.69
					Brown	59.83	8.67	5.53	6.62
IX <sub>a</sub>	C <sub>21</sub> H <sub>33</sub> N <sub>2</sub> O <sub>4</sub> S Na	432	EtOH	65	Yellow	58.33	7.64	6.44	7.46
					Yellow	58.07	7.37	6.17	7.13
IX <sub>b</sub>	C <sub>23</sub> H <sub>37</sub> N <sub>2</sub> O <sub>4</sub> S Na	460	EtOH	62	Yellow	60.08	8.06	6.04	6.96
					Yellow	59.36	7.89	5.66	6.66
IX <sub>c</sub>	C <sub>25</sub> H <sub>41</sub> N <sub>2</sub> O <sub>4</sub> S Na	488	ACOH	65	Yellow	61.43	8.44	5.71	6.54
					Yellow	61.05	8.19	5.33	6.22
X <sub>a</sub>	C <sub>23</sub> H <sub>35</sub> N <sub>2</sub> O <sub>5</sub> S <sub>2</sub> Na	506	EtOH	58	Bill	54.54	6.94	5.51	12.61
					Yellow	54.23	6.62	5.26	12.33
X <sub>b</sub>	C <sub>25</sub> H <sub>39</sub> N <sub>2</sub> O <sub>5</sub> S <sub>2</sub> Na	534	EtOH	50	Pale	56.61	7.34	5.24	11.92
					Yellow	55.83	7.07	4.84	11.63
X <sub>c</sub>	C <sub>27</sub> H <sub>43</sub> N <sub>2</sub> O <sub>5</sub> S <sub>2</sub> Na	562	EtOH	53	Pale	57.62	7.62	4.93	11.36
					Yellow	57.28	7.37	4.57	10.83
XI <sub>a</sub>	C <sub>21</sub> H <sub>31</sub> N <sub>2</sub> O <sub>4</sub> SNa	430	Benz	55	Brown	58.6	7.2	6.5	7.4
					Brown	58.3	6.8	6.2	7.1
XI <sub>b</sub>	C <sub>23</sub> H <sub>35</sub> N <sub>2</sub> O <sub>5</sub> SNa	458	Tol.	58	Brown	60.22	7.64	6.12	6.91
					Brown	59.93	7.37	5.38	6.67
XI <sub>c</sub>	C <sub>25</sub> H <sub>39</sub> N <sub>2</sub> O <sub>4</sub> S Na	486	Tol.	60	Red	61.73	8.02	5.73	6.5
					Brown	6.38	7.74	5.35	6.1

Table 2. Surface properties of the prepared compounds

Comp	Surface tension (dyne/cm) 0.1 ml	Interfacial tension (dyne/cm) 0.1 ml	Krafft Point °C	Wetting Time (sec.)	Emulsion stability (min.)	Foam Height (mm)	CMC cme X 10 <sup>-3</sup>	Ca++ Stability (ppm)	Stability to hydrolysis (min:sec)
Ia	30	7.5	14	65	350	225	9.9	450	385
Ib	32	8.0	16	90	300	220	9.5	380	390
Ic	34	8.5	20	140	260	200	9.1	350	395
IIa	33	8.2	21	90	390	155	6.2	1460	430
IIb	35	8.7	26	120	320	170	5.9	1350	440
IIc	37	9.0	29	156	280	190	5.6	1200	455
IIIa	29	9.5	24	80	340	180	7.1	1240	368
IIIb	32	10.3	26	110	290	200	6.9	1150	375
IIIc	35	11.0	29	135	250	220	6.4	900	384
IVa	31	11.4	18	100	340	185	3.9	1230	345
IVb	33	12.0	21	115	300	200	3.7	1060	349
IVc	35	12.5	24	126	270	230	3.2	850	353
Va	29	6.7	20	85	320	170	7.3	560	407
Vb	31	7.0	23	100	280	190	6.9	500	412
Vc	33	7.5	25	120	240	205	6.7	450	416
VIa	30	8.7	19	90	300	180	5.2	1530	350
VIb	32	9.2	22	105	260	200	4.9	1420	355
VIc	34	10.0	24	115	227	215	4.5	1300	359
VIIa	29	8.5	19	95	330	210	9.2	1260	465
VIIb	31	9.0	21	120	290	220	8.9	1150	469
VIIc	33	9.5	24	134	255	235	8.6	950	472
VIIIa	28	7.0	20	105	320	190	4.0	1360	468
VIIIb	30	7.5	23	115	285	200	3.7	1240	471
VIIIc	32	8.0	25	127	238	205	3.2	1120	175
IXa	32	8.6	19	95	350	180	5.9	1420	350
IXb	34	9.0	22	108	290	200	5.6	1360	353
IXc	36	9.4	26	120	240	210	5.2	1300	358
Xa	31	9.7	17	100	340	199	5.7	643	379
Xb	33	10.2	21	115	280	215	5.3	580	376
Xc	35	10.6	25	130	250	230	4.9	460	372
XIa	30	7.6	21	96	300	200	3.8	1060	398
XIb	32	8.0	24	107	260	210	3.4	910	402
XIc	34	8.5	27	117	220	215	3.0	850	407
XIIa	33	9.0	15	105	310	200	4.9	1230	362
XIIb	35	9.6	18	115	270	215	4.4	1120	359
XIIc	37	10.0	21	128	230	225	4.0	1040	357
XIIIa	34	10.2	21	90	370	190	7.8	1340	477
XIIIb	36	10.5	24	110	290	200	7.5	1290	480
XIIIc	38	11.0	27	125	240	210	7.3	1230	483

**The critical micelle concentrations (cmc):**

The critical micelle concentrations (cmc) of the synthesized surfactants were taken as the concentration at the point of intersection of the two linear portions of  $W^{-1} \log C$ . In general, the values of cmc are inversely proportional to the alkyl chain length [15] and decreased in the order  $C_{14} > C_{16} > C_{18}$  as shown in (Table 2).

**Biodegradability:**

Biodegradation Die-away test in ordinary river water gave satisfactory results (Table 3). All the products had a much higher rate of degradation ranging about 96% degradation during around 5 days.

**Biological activities:**

All the prepared surfactants were tested for their bacterocidal activities against (*Bacillus subtilis* and *Escherichia coli*) and their antifungal activity against (*Aspergillus niger* and *Candida albicans*). The results obtained indicated that compounds (IIIa-c), (VIIa-c) and (Xa-c) were rela-

tively more active as bactericide or fungicide agent than the other compounds (Table 4).

Table 3. Biodegradability of the Prepared Surfactants

Comp	1 <sup>st</sup> day	2 <sup>nd</sup> day	3 <sup>rd</sup> day	4 <sup>th</sup> day	5 <sup>th</sup> day	6 <sup>th</sup> day	7 <sup>th</sup> day
Ia	44	59	71	89	93	—	—
Ib	41	53	65	85	90	95	—
Ic	38	49	61	82	86	92	—
IIa	45	57	66	78	95	—	—
IIb	41	52	61	72	89	96	—
IIc	37	49	57	67	85	90	93
IIIa	41	56	64	79	96	—	—
IIIb	38	51	59	73	93	—	—
IIIc	35	46	55	68	87	92	—
IVa	47	61	73	89	—	—	—
IVb	43	54	67	77	95	—	—
IVc	39	49	62	72	90	96	—
Va	40	49	58	69	82	95	—
Vb	37	46	55	64	79	90	—
Vc	34	42	51	60	74	84	97
VIa	47	55	66	77	89	—	—
VIb	43	51	62	72	86	94	—
VIc	39	50	59	68	80	88	—
VIIa	48	58	68	79	93	—	—
VIIb	45	56	63	74	88	94	—
VIIc	42	50	57	69	83	89	—
VIIIa	48	63	74	86	96	—	—
VIIIb	45	59	68	79	92	—	—
VIIIc	41	52	63	74	89	93	—
IXa	46	59	69	86	95	—	—
IXb	42	54	63	79	90	—	—
IXc	39	48	58	74	86	3	—
Xa	49	66	76	87	94	—	—
Xb	47	57	69	81	89	—	—
Xc	43	52	63	75	85	94	—
XIa	45	56	67	78	89	—	—
XIb	42	52	62	73	85	91	—
XIc	39	48	59	70	82	89	—

**Experimental****Synthesis of fatty acid hydrazides**

Fatty acid hydrazide was prepared from its acid chloride through its reaction with hydrazine hydrate in dry acetone by reflux for 2 hrs, then recrystallization from suitable solvent to obtain the acid hydrazide.

**Synthesis of sodium salt of a-sulphonated fatty acid hydrazides (I).**

A solution of fatty acid hydrazide (0.01 mole) and chlorosulphonic acid (0.01 mole) in carbon tetrachloride was stirring at room temperature about 2hrs, then neutralized by 0.1 N of sodium hydroxide. The solid product was separated and crystallized to obtain the product (Ia-c).

**Reaction of sodium salt of a-sulphonated fatty acid hydrazides (Ia-c) with b-benzoyl acrylic acid. Formation of pyridazine derivatives (II<sub>a-c</sub>)**

A solution of sodium salt of a-sulphonated fatty acid hydrazides (I) (0.01 mole) and b-benzoyl acrylic acid (0.01 mole) in normal butanol (30 ml) was refluxed for 6hrs. The reaction mixture was concentrated. The solid that ob-

Table 4.

Biological activity of prepared surfactants				
Comp	Bacillus subtilis	Escherichia coli	Aspergillus niger	Candida albicans
Ia	+	++	+	+
Ib	++	+	+	++
Ic	+	+	+	+++
IIa	+	+	-	+
IIb	+	+	+	++
IIc	++	++	++	+++
IIIa	+	+	+	++
IIIb	++	++	+	++
IIIc	+++	+	++	+++
IVa	+	-	-	+
IVb	+	+	+	++
IVc	++	+	+	+++
Va	+	+	-	+
Vb	++	+	+	++
Vc	+	++	+	+
VIa	+	+	-	+
VIb	++	++	+	+
VIc	++	+	++	++
VIIa	++	++	+	++
VIIb	++	+	+	++
VIIc	+++	+	++	+++
VIIIa	+	+	+	+
VIIIb	+	++	+	++
VIIIc	++	+	+	+++
IXa	+	+	+	+
IXb	+	+	+	++
IXc	++	++	++	++
Xa	+	+	+	+
Xb	++	+	+	++
Xc	+++	++	++	+++
XIa	+	+	-	+
XIb	+	++	++	++
XIc	++	+	++	+++

tained was crystallized from a proper solvent to give pyridazine derivative (**IIa-c**).

**Reaction of sodium salt of a-sulphonated fatty acid hydrazides (I) with carbon disulphide. Formation of oxapyrazole derivatives (III<sub>a-c</sub>)**

A solution of sodium salt of a-sulphonated fatty acid hydrazides (**I**) (0.01 mole) and carbon disulphide (0.01 mole) with potassium hydroxide (0.01 mole) in ethyl alcohol (30 ml) was refluxed for 4hrs then poured on water and a solid product was obtained. Filtration and recrystallization from a proper solvent to give oxapyrazole derivatives (**IIIa-c**).

**Reaction of sodium salt of a-sulphonated fatty acid hydrazides (I) with chloroacetic acid. Formation of oxapyridazinone derivatives (IV<sub>a-c</sub>)**

A solution of sodium salt of a-sulphonated fatty acid hydrazides (**I**) (0.01 mole) and chloroacetic acid (0.01 mole) in presence of sodium acetate and acetic anhydride was refluxed for 4 hrs then poured on water, a solid product

was obtained. Filtration and recrystallization from suitable solvent to give oxapyridazine derivatives (**IV<sub>a-c</sub>**).

**Reaction of sodium salt of a-sulphonated fatty acid hydrazides (I) with phthalic anhydride. Formation of phthalazine derivatives (V<sub>a-c</sub>)**

A solution of sodium salt of a-sulphonated fatty acid hydrazides (**I**) (0.01 mole) and phthalic anhydride (0.01 mole) in acetic acid was refluxed for 6 hrs, then poured on water, a solid product was precipitated. Filtered and crystallized from a proper solvent to give the product (**V<sub>a-c</sub>**).

**Reaction of sodium salt of a-sulphonated fatty acid hydrazides (I) with ethyl benzoyl acetate. Formation of pyrazole derivatives (VI<sub>a-c</sub>)**

A solution of sodium salt of a-sulphonated fatty acid hydrazides (**I**) (0.01 mole) with ethyl benzoyl acetate (0.01 mole) in ethyl alcohol and sodium ethoxide (0.01 mole) was refluxed for 6 hrs, then poured on water a solid product filtered and crystallized from a suitable solvent to obtain pyrazole derivatives (**VI<sub>a-c</sub>**).

**Reaction of sodium salt of a-sulphonated fatty acid hydrazides (I) with phenyl isothiocyanate. Formation of triazole derivatives (VII<sub>a-c</sub>)**

A solution of sodium salt of a-sulphonated fatty acid hydrazides (**I**) (0.01 mole) and phenyl isothiocyanate (0.01 mole) was refluxed in 10% aq.NaOH (20 ml) for 6hrs. The reaction mixture was then poured on ice-cold water and acidified with acetic acid. The resulting solid was filtered, washed with water, dried and crystallized from a suitable solvent to give the product (**VII<sub>a-c</sub>**).

**Reaction of sodium salt of a-sulphonated fatty acid hydrazides (I) with acetyl acetone. Formation of pyrazole derivatives (VIII<sub>a-c</sub>)**

A solution of sodium salt of a-sulphonated fatty acid hydrazides (**I**) (0.01 mole) and acetyl acetone (0.01 mole) was refluxed in glacial acetic acid (30 ml) at room temperature for 8hrs. The resulting solid was filtered, washed with water and crystallized from a suitable solvent to give (**VIII<sub>a-c</sub>**).

**Reaction of sodium salt of a-sulphonated fatty acid hydrazides (I) with benzaldehyde. Formation of Chief base derivatives (IX<sub>a-c</sub>)**

A solution of sodium salt of a-sulphonated fatty acid hydrazides (**I**) (0.01 mole) with benzaldehyde (0.01 mole) in acetic acid and sodium acetate was refluxed for 3hrs then poured on water. The solid product was filtered and crystallized to obtain the product (**IX<sub>a-c</sub>**).

**Reaction of Chief base (IX<sub>a-c</sub>) with thioglycolic acid. Formation of thiazole derivatives (X<sub>a-c</sub>)**

A solution of chief base (**IX<sub>a-c</sub>**) (0.01 mole) and thioglycolic acid (0.01 mole) in dry benzene (30ml) was refluxed for 6hrs. The mixture was concentrated and crystallized with a proper solvent to give thiazole derivatives (**X<sub>a-c</sub>**).

### Reaction of Chief base ( $IX_{a-c}$ ) with ferric chloride. Formation of oxadiazole derivatives ( $XI_{a-c}$ )

A solution of Chief base ( $IX_{a-c}$ ) (0.01 mole) and ferric chloride (0.01 mole) in acetic acid was stirred for 1 hr and leaved it for 3 days, then poured onto water. A solid product filtered off recrystallized from a suitable solvent to give oxadiazole derivatives ( $XI_{a-c}$ ).

### The surface active properties

Surface and interfacial tension [16], Krafft point [17], wetting time [18], foaming [19] and emulsification properties [20] were determined.

### Critical micelle concentration (cmc)

The critical micelle concentration values for the prepared surfactants were determined by the electrical conductivity method [21].

### Stability to hydrolysis

A mixture of 10 m.mol surfactant and 10 ml 0.05N NaOH were placed in thermostate at 40 °C. The time taken by a sample solution to be clouded on a result of hydrolysis shows the stability of surfactant to hydrolysis [21].

### Ca<sup>++</sup> stability

Calcium stability of compounds was determined by hart method [22].

### Biodegradability

The percentage of biodegradability was measured according to Eter et al. [23].

### Biological activity

Antimicrobial activity of the prepared compounds were tested via a modification of the cup-plate method [24].

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