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Synthesis of Anionic Surface Active Agents Containing Heterocyclic Moiety From Long Chain Fatty Alcohols

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1. ABSTRACT

A series of novel groups of anionic surface active agent were synthesized. Synthesis of these surfactants via the reaction of long chain fatty alcohols (octyl, decyl and dodecyl) with maleic anhydride to give monoester. The monoester chloride reacted with amino derivatives of heterocyclic rings followed by addition of NaHSO3 .The surface tension, interfacial tension; Kraft point, emulsifying and wetting power were evaluated. Stability to hydrolysis, biodegradability and biological activities were measured. A comparison studies between the chemical structures and the results were done.

Indexing terms/Keywords

Surfactants, monoester chloride, biodegradability and biological activities

SUBJECT CLASSIFICATION

Organic chemistry - Surfactant chemistry

2. INTRODUCTION

Anionic surfactants are very widely distributed throughout science, technology and everyday life. Examples which at once come to mind are the washing, wetting out of textile materials, the preparation of dispersion and emulsion, the application of agricultural and a wide variety of special uses, the number of which is continually increasing[1].

Among anionic surfactants containing an aromatic structure element are alkyl benzene sulphonate accompanied by alky-naphthalene sulfonates[2-5.] In these compounds, hydrophilic sulfonic group is separated from long chain alkyl hydrophobe by single six member benzene or naphthalene rings. The structure analogues to the above ones may be surfactants containing five member heteroaromatic groups. It has been well established that various thiazole, imidazol, pyrazole, pyridine, pyrimidine and quinoline are of biological interest[6-9]. This encourage us to synthesis a novel groups of anionic surfactants containing those nucleus from long chain fatty alcohols (octyl, decyl, dodecyl alcohols) hopping to possess good surface properties and expected to have biological activities.

3.Experimental procedures

3.1Chemicals

Maleic anhydride, thionyl chloride, octyl alcohol, decyl alcohol, dodecyl alcohol were Merck (Darmstadt) products, 2-amino thiazole, 2- amino imidazol,3-amino pyrazole, 2-amino pyridine,2-amino pyrimidine and 8- amino quinoline were obtained from Aldrich (Steinheim, Germany). All other chemicals (solvents) were of analytical grade. The water used was doubly distilled.

3.2.Synthesis Procedures

3.2.I-synthesis of maleic acid monoester:

It was prepared by refluxing a mixture of maleic anhydride (1.0 mole) with fatty alcohols (1.0 mole) octyl alcohol (a), decyl alcohol (b),dodecyl alcohol (c)in benzene for six hours, in the presence of sulphuric acid as catalyst. After cooling the reaction mixture was distilled with water to ensure removal of unreacted alcohols. Further purification was effected by fractional distillation under vacuum [10].

3.2.II- Synthesis of acyl chloride compounds:

The acyl chloride was formed by refluxing of thionyl chloride with maleic acid monester in water bath at 65 ºC for three hours. After cooling, petroleum ether was added and heated to remove excess of thionyl chloride.[20]

3.2.III- Preparation of anionic compounds:

acyl chloride which was prepared in previous step was reacted with 2- amino thiazole, 2- amino imidazol,3-amino pyrazole, 2-amino pyridine,2-amino pyrimidine and 8- amino quinoline in presence of benzene as solvent for three hours to give the compounds that react with sodium bisulfate to give anionic surfactants (9-14_{a-c}).

3.3 Characterization of the prepared surfactants

The structures of the synthesized compounds were confirmed by infrared (IR) and nuclear magnetic resonance (^{1}H NMR). The qualitative infrared absorption spectra of the synthesized compounds were recorded on a Beckmon 4220 spectrophotometer. The ^{1}HNMR spectra of the compounds under investigation have been recorded in deuterated chloroform ($CDCl_3$) and /or in (DMSO) as a solvent and tetramethyl silane (TMS) as an internal reference with 90 MHz signal and 4.000 gauss magnetic field.

3.4 Properties of the prepared surfactants

3.4.a Surface and interfacial tension

Surface tension and interfacial tension measurements were carried out according to Findlay[11] with a Krüss tensiometer for different concentration of the synthesized surfactants using platinum iridium ring at constant temperature 25°C.Paraffin oil was used for the interfacial tension measurements.

3.4.b Emulsifying power

A 20-ml amount of a different surfactant solution (0.1%) was individually placed in a 100-ml cylinder and then 20 ml of the paraffin oil was added. The cylinder was shaken vigorously for 10 min and then allowed to settle. The time required to separate 18 ml of pure surfactant solution was recorded and the experiment was repeated three times for each surfactant. The average separation time of the three experiments was taken as an indication of the emulsification power of each surfactant [12].

3.4.c Stability to hydrolysis

A mixture of 10 ml. of surfactant and 10ml of 2N sulphuric acid or 0.05 N NaOH were placed in a thermostat at 40°C. The time it takes for a sample solution to be clouded as the result of hydrolysis shows the stability of the surfactant to hydrolysis [13].

3.4.d Wetting properties

It was examind by standard Draves method[14]

3.4.e Kraft point

The temperature at which 1% solution becomes clear on gradual heating gives a convenient measure of aqueous solubility [12].

3.4.f Biodegradability%

Die-awy method using river water samples taken daily, or even more frequently, were filtered through No. 1 **Whatman** filter paper before measuring the surface tension[15] Measurements were periodically (each day) on each sample during the degradation test. Biodegradation percent (D) was calculated from 'the following law.

$$D = \frac{\varphi_t - \varphi_0}{\varphi_{bt} - \varphi_0} \; x\,100$$

where :

φ_t = surface tension at time t

φ_0 = surface tension at time zero (the initial surface tension)

φ_{bt} = surface tension of the blank experiment at time t (i.e without the sample).

4. Result and discussion

The synthetic route of these surfactants was listed in scheme1.The structure of prepared surfactants were confirmed by IR and ^{1}HNMR as shown in table (1).

4.1 Surface active properties and related properties:

The surface active properties and related properties, including surface and interfacial tension, kraft point, foam height, emulsion stability, wetting time and stability to hydrolysis were investigated to evaluate the possible application of these products in different industrial fields. The surface activity and related properties of the synthesized compounds are given in Table (2).

4.2 Surface and interfacial tensions:

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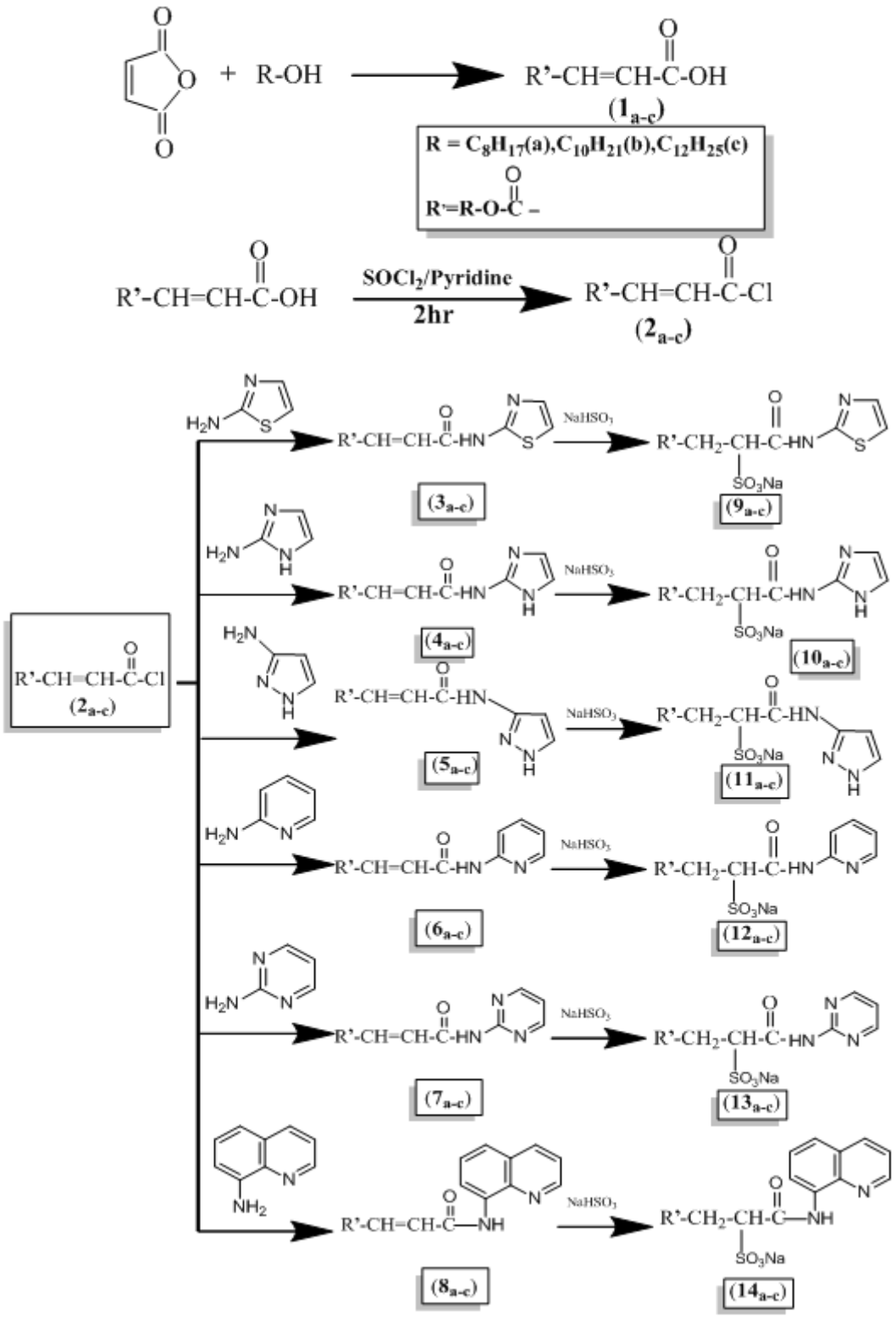
The surface and interfacial tension of the prepared surfactants are given in Table (2). It showed that, the prepared anionic surfactants have good surface properties while they have a strong effect on the value of surface and interfacial tension. This result indicates that these



Scheme (1) synthesis of heterocyclic anionic surfactants

Compounds have a good surface activity. The results show that the surface tension decreases with increasing the alkyl chain length [16].

4.3 Kraft point:

The kraft point for the anionic synthesized surfactants which are freely soluble in water at 1 wt % concentration is ranged between 16 and 13 ℃. While the compounds showed the lowest kraft points that may be attributed to the have the shorter fatty chain length[17].

4.4 Emulsion stability:

The process of emulsification is the dispersion or suspension of fine particles of one liquid in another immiscible liquid. 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 non polar lipophilic tail. From the data recorded in Table (2) the emulsifying properties increased with increasing the alkyl chain length of the fatty acid[12].In fact the results of emulsification have good values which make them used in different industrial applications.

4.5 Wetting time:

The wetting properties of 1.0 % solutions in distilled water were measured. The case with which the surface can be wetted by water as other liquids is an important properity suitable for many applications. Wetting powers obtained for the prepared sulfonamide surfactants are listed in Table (2).These compounds showed a good performance in wetting power. The wetting time slightly increases with increasing the chain length [18].

4.6 Stability to hydrolysis:

All the prepared surfactants showed resistance to hydrolysis, probably because the adjacent sulpho group protects the amide linkage through steric hindrance[13].these results make them stable in acidic and basic medium.From the measuring of the surface properties of the prepared compounds, we can notice that the change in the heterocyclic moiety have a little or no effect on this properties.

4.7 Biodegradability

A biodegradation test in ordinary river water[15] gave good or excellent results table (3). The results of biodegradation reflect the fact that the biodegradability decreases with increasing the length of saturated aliphatic chain, which make the prepared anionic surfactants environmentally favorable.[21]

4.8 Biological activity

Biological activity of the synthesized compounds was reported that amino derivatives have a potential at the pharmacological level, so the antimicrobial activity of some new synthesized compounds was determined in vitro in the Botany Department, Faculty of Science, Benha University, Egypt. With the aim of obtaining specific derivatives that could be potent in medicine, chemistry or agriculture. A variety of species of G-positive bacteria (**Bacillus megathorium**) and G-negative bacteria (**Escherichia coli**) in addition to some fungal plant pathogens (**Mucor Species and Aspergillus flavus**) were used, using a modified Kirby- Bauer disc diffusion method[19].

In every case the minimum inhibitory concentration (MIC, µg/ml) was determined as the lower concentration of the compounds under study, which inhibits bacterial and fungal growth and the results are given in table (4).

It is apparent from the data, that most of the tested compounds have moderate to high activity against micro-ganisms. However, concerning the activity against G-positive bacteria (**Bacillus megathorium**).

Table (1) the IR & ^{1}HNMR spectra of the anionic surfactants

Compound	IR cm^{-1}	^{1}HNMR δ ppm
9_a	(1306 cm^{-1} SO_3),(1690 cm^{-1} C=O of amide), (1738 cm^{-1} C=O of ester),(2940 cm^{-1} C-H aliphatic), (3010 cm^{-1} C-H aromatic)&(2600-3450 cm^{-1} broad NH_2, NH & OH)	0.82(t,term.CH_3),1.2(m,14H of $(CH_2)_7$),2.5(t,CH-SO_3Na) , 2.9(d,CH_2-CH-SO_3Na), 3.75(t,2H,CH_2-O), 4.9 (br.s, 1H,NH-),7.6 (m,2H,aromatic proton)
12_b	(1303 cm^{-1} SO_3),(1692 cm^{-1} C=O of amide), (1735 cm^{-1} C=O of ester),(2920 cm^{-1} C-H aliphatic), (3030 cm^{-1} C-H aromatic)&(2580-3450 cm^{-1} broad NH_2, NH & OH)	0.8(t,term.CH_3),1.1-1.3(m,18H of $(CH_2)_9$),2.4(t,CH-SO_3Na) , 2.9(d,CH_2-CH-SO_3Na), 3.9(t, 2H,CH_2-O),4.9 (br.s, 1H,NH-), 7.3-8.0(m,4H,aromatic proton)
14_c	(1310 cm^{-1} SO_3),(1697 cm^{-1} C=O of amide), (1739 cm^{-1} C=O of ester),(2932 cm^{-1} C-H aliphatic), (3045 cm^{-1} C-H aromatic)&(2600-3460 cm^{-1} broad NH_2, NH & OH)	0.9(t,term.CH_3),1.4(m,22H of $(CH_2)_{11}$),2.5(t,CH-SO_3Na) , 2.9(d,CH_2-CH-SO_3Na), 3.8 (t,2H,CH_2-O), 4.7(br.s,1H, NH-),7.3-8.0(m,6H,aromatic proton)

Table (2) surface properties of the anionic surfactants

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N0.	Structure	Mol. F	Mol. Wt	S.T Dyne/ cm 0.1%	I.T Dyne/ cm 0.1%	K.P 1 wt% ℃	Stability to Hydrolysis min : sec	Wetting power Sec	Emulsification Power min : Sec
9_a		$C_{15}H_{25}O_6N_2S_2Na$	449.5	29	6.5	13	18:40	110	173:13
9_b		$C_{17}H_{29}O_6N_2S_2Na$	477.5	33	8	15	18:45	143	187:10
9_c		$C_{19}H_{33}O_6N_2S_2Na$	505.5	35	9	16.5	19:55	153	190:06
10_a		$C_{15}H_{23}O_6N_3SNa$	396.5	34	8	14	20:30	149	194:17
10_b		$C_{17}H_{27}O_6N_3SNa$	424.5	37	8.5	17	23:34	160	230:16
10_c		$C_{19}H_{31}O_6N_3SNa$	452.5	39	9	19	20:55	189	240:15
11_a		$C_{15}H_{23}O_6N_3SNa$	396.5	36	7	16	19:34	190	235:22
11_b		$C_{17}H_{27}O_6N_3SNa$	424.5	34	8.5	17	22:34	210	254:36
11_c		$C_{19}H_{31}O_6N_3SNa$	452.5	39	10.5	19	24:05	231	266:37
12_a		$C_{17}H_{26}O_6N_2SNa$	409.5	35.5	8.5	13	23:54	210	251:40

12_b		$C_{19}H_{30}O_6N_2SNa$	437.5	36	8.9	16	24:36	234	262:13
12_c		$C_{21}H_{34}O_6N_2SNa$	465.5	39	8.911	18	26:54	255	277:22
13_a		$C_{16}H_{24}O_6N_3SNa$	409.5	34.5	7	17	21:43	195	249:34
13_b		$C_{18}H_{28}O_6N_3SNa$	437.5	39	11	17.5	26:38	260	288:44
13_c		$C_{20}H_{32}O_6N_3SNa$	465.5	42	12.5	19	27:57	276	311:15
14_a		$C_{21}H_{27}O_6N_2SNa$	482.5	33	8	15	29:54	267	245:09
14_b		$C_{23}H_{31}O_6N_2SNa$	510.5	40	12	19	31:34	290	279:50
14_c		$C_{25}H_{35}O_6N_2SNa$	538.5	45	13	20	38:56	333	343:32

Table (3) Biodegradbility percent of prepared anionic surfactants

Surfactant	1st day	2nd day	3rd day	4th day	5th day	6th day	7th day	8th day
9_a	60	64	70	75	83	95	-	-
9_b	57	62	69	73	82	93	-	-
9_c	54	57	63	73	80	86	97	-
10_a	55	59	62	70	75	85	93	-
10_b	51	55	59	64	72	83	88	94

10_c	49	52	55	62	70	82	85	92
11_a	46	58	60	63	70	77	86	93
11_b	45	48	56	68	74	86	91	94
11_c	42	45	57	62	76	83	88	96
12_a	59	62	68	76	81	92	-	-
12_b	55	59	62	73	78	84	93	-
12_c	52	55	58	64	73	82	88	94
13_a	51	55	59	62	71	84	89	-
13_b	49	52	55	61	70	76	84	90
13_c	45	48	53	61	68	72	83	89
14_a	55	58	64	68	78	85	90	-
14_b	50	54	60	66	70	75	83	87
14_c	49	54	54	61	67	72	81	88

Table(4)Antimicrobial activity of the synthesized anionic surfactants

Surfactants	**Bacteria**				**Fungi**			
	E. coli(G^+)		**B. megathorium(G^+)**		**A. flavus**		**Mucor Sp.**	
	A	**MIC**	**A**	**MIC**	**A**	**MIC**	**A**	**MIC**
9_a	+++	300	+	200	++	++	++	200
9_b	+	+	+++	100	++	200	+	++
9_c	+	100	++	100	+	+	++	++

10_a	+	200	++	200	+	++	++	+
10_b	--	100	+	300	+	+	+++	200
10_c	+	200	+	200	+	300	+++	+
11_a	+	100	++	100	+++	+	+	+
11_b	++	200	+	100	+	200	+	++
11_c	+	300	++	200	+	+	+	++
12_a	+	200	++	300	++	200	++	++
12_b	++	200	+	300	++	+	+	++
12_c	+++	100	++	100	+++	+	+	100
13_a	++	+	++	100	+	+++	++	**++**
13_b	++	100	++	100	+	++	++	**200**
13_c	++	+	+++	100	+	100	+	++
14_a	+	200	++	200	+++	+	+++	+++
14_b	++	100	++	100	+	200	+	+
14_c	+	300	+	100	++	100	+++	++

A=Antimicrobial activity of tested compounds, MIC = Minimum inhibitory concentration, - inactive + ≥5mm,slightly active++ ≥7 mm, moderately active +++ ≥10mm, highly active

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