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Abstract

Unsaturated fatty N-acyl morpholide and piperidide derivatives were prepared by the reaction of the acid chloride of oleic and linoleic acids as well as the mixed fatty acid chlorides of olive, linseed and castor oils with morpholine and piperidine. The sodium bisulfite and mercapto acetic acid were added to the prepared unsaturated fatty amides to give sulfonated and methylthiocarboxylate morpholide and piperidide derivatives.

These derivatives were characterized using infrared (IR), ^{1}H nuclear magnetic resonance (NMR) and mass spectroscopy (MS), they showed excellent lowering power of surface tension, foaming stability and emulsifying property. On the other hand, these derivatives showed a broad antimicrobial spectra as high as chloramphenicol against all the tested microorganisms. It was found that compounds containing a carboxylate hydrophilic group were less efficient than those with a suflonate group with respect to foaming power, foam stability, emulsification and antimicrobial effect.

Introduction

Surface active agents are amphipathic molecules that consist of a non-polar hydrophobic portion, usually a straight or branched hydrocarbon or fluorocarbon chain containing 8-18 carbon atoms, attached to a polar or ionic portion. The hydrophilic portion can therefore, be nonionic, ionic or zwitterionic, and accompanied by counter ions in the last two cases. The hydrocarbon chain interacts weakly with the water molecules in aqueous environments, whereas the polar or ionic head group interacts strongly with water molecules via dipole or ion-dipole interactions. It is this strong interaction with the water molecules that renders the surfactant soluble in water. However, the cooperative action of dispersion and hydrogen bonding between the water molecules tends to squeeze the hydrocarbon chain out of the water and hence these chains are referred to as hydrophobic. The balance between hydrophobic and hydrophilic parts of the molecule gives these systems their special properties.

Surfactants find application in almost every chemical industry, including detergents, paints, dyestuff, cosmetics, pharmaceutical, agrochemicals, fibers and

plastics. Moreover, surfactants play a major role in the oil industry for example in enhanced and tertiary oil recovery.

Heterocyclic surfactants was found to have good surface active properties, antimicrobial and biodegradability[1].

Laundry detergents were improved with the ability for removing oily impurities contain nonionic surfactants sulfonated fatty alcohols, ethoxylated mercaptants and ethoxylated alkyl-amines[2-7].

In the present work, fatty acyl derivatives are used as intermediates to synthesize the surfactants prepared through the interaction of fatty acid chlorides (oleic & linoleic acids), as well as olive, linseed and castor mixed fatty acids with morpholine and piperidine then the unsaturated fatty acyl compounds were reacted with sodium bisulfite and mercapto acetic acid to give different sulfonated and methyl thiocarboxylate derivatives.

Materials and Methods

Materials

Oleic, linoleic acids as well as sodium bisulfite were supplied from El-Nasr Pharmaceutical Chemicals Co.

Morpholine, piperidine and mercapto acetic acid were purchased from Merck-German.

Castor, olive and linseed oils are from local market. All solvents, used were redistilled just before used**.**

Instruments :

IR spectra were recorded from KBr pellets on a Perkin – Elmer 1430 ratio recording infrared spectrophotometer, Wellesley, MA, USA. ^{1}H-NMR ($CDCl_3$-TMS, δ) were recorded on varian 300 MHz, Mercury-Oxford and a JOEL JNM-PM X90 SI, NMR spectroscopy.

The mass spectra were measured using a model 5988 HB diode-aray spectrometer.

Methods :

i- Preparation of olive, linseed and castor oil mixed fatty acids.

The mixed fatty acids of olive, castor and linseed oils were respectively obtained by saponification of the oil with alcoholic potassium hydroxide. The unsaponifiable matter was removed by extraction with diethylether and the fatty acid solutions were liberated by acidification using hydrochloric acid. The total fatty acids of linseed, olive and castor oils were identified as methyl esters by Gas Chromatography.

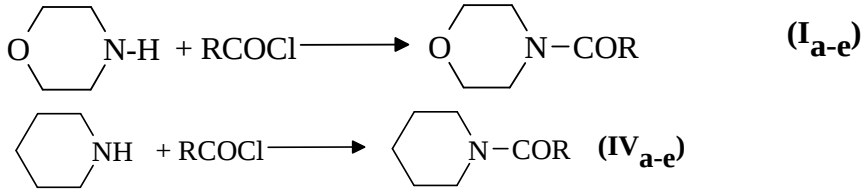
ii- Preparation of fatty acid chloride

The preparation of fatty acid chloride was carried out by treatment of fatty or mixed fatty acids with thionyl chloride according to the procedure described by Weil *et al.*,[8].

$$RCOOH \xrightarrow{SOCl_2} RCOCl$$

iii- Synthesis of N-Acyl Derivatives of Morpholine and Piperidine.

I- Synthesis of N-Acyl Morpholine and piperidine (I_{a-e}, IV_{a-e})



Where R : (a) oleic, (b), linoleic, (c,d,e) olive, linseed and castor mixed fatty acids), respectively.

The preparation of N-oleyl morpholine is described as an example for the preparation of the different N-acyl morpholine and piperidine.

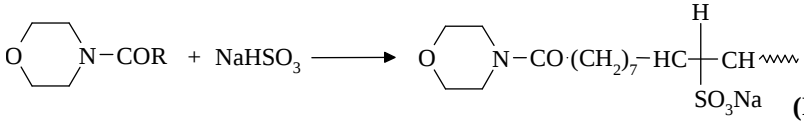
Oleyl chloride (0.023 mol, 7.0 g) was added to morpholine (0.03 mol) or piperidine in a 250 ml flask, equipped with a reflux condenser and a thermometer. The reaction mixture was refluxed gently for about 8hr, and after the reaction was completed, excess morpholine or piperidine was removed under reduced pressure and the product was repeatedly crystallized from a mixture of chloroform: water (2:1/v/v). The structure of the compounds was cheked by IR, ^{1}H–NMR and Mass spectral analysis**.**

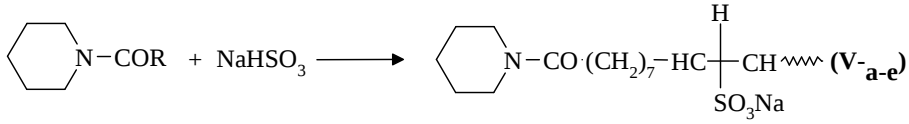
The infrared spectra (cm^{-1})of N-oleyl morpholine showed a strong absorption band at 1732 cm^{-1} for amide group, 1650 cm^{-1} for CH=CH and 2926 cm^{-1} for CH (aliphatic) and proton nuclear magnetic resonance (^{1}HNMR) for N-oleyl morpholide:

^{1}HNMR ppm: δ 0.85 (t, 3H, CH_3), 1.23 (M, 20H, CH_2 Chain), 1.5-1.7 (M, 4H, $\underline{CH_2}\underline{CH_2}$=CH), 1.9-2.1 (M. 2H, $\underline{CH_2}CH_2CO$), 2.2 (t, 2H, $CH_2\underline{CH_2}$ CO), 2.7 (t, 4H, Morph.), 3.5 (t, 4H, Morph) and 5.27-5.40 (M, 2H, CH=CH).

The mass spectrum of compound **(I_a)** showed a molecular ion peak at m/z 351 (4.71%), m/z and the following abundant peak at 212 (3.3%), 226 (2.1%), 239 (1.88%), 128.95 (100%), 139 (2.75%), (2.75%), 86.95 (24.08%).

II- Synthesis of 9(10) Sulfostearamido Morpholine or Piperidine (II_{a-e}, V_{a-e})



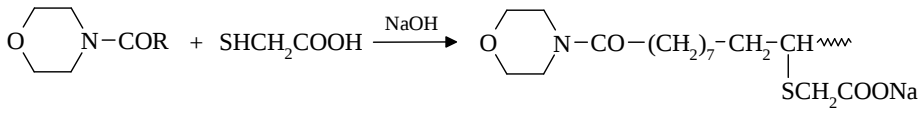


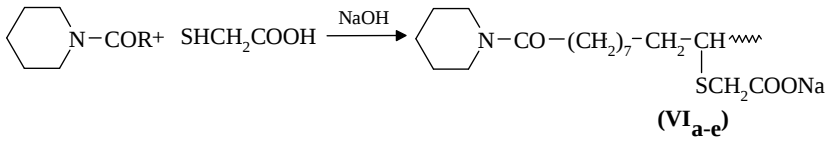
Where R: (a), oleic, (b) linoleic, (c,d,e) olive, linseed and castor mixed fatty acids), respectively.

Sodium bisulfite (1 mole) dissolved in 10 ml water and N-oleyl morpholine or piperidine (1 mole) in 20 ml 95% ethanol were added in a 250 ml flask equipped with a reflux condenser. The mixture was refluxed for 4 hr. on a steam bath, filtered hot by suction and treated with 25 ml of hot 95% ethanol. The solution was cooled in an ice-bath and the precipitated solid was then filtered and vacuum dried. The product was purified by repeated crystallization from ethanol .

The infrared spectra (V_{max} /cm^{-1}) showed the exception absorption band at 1724cm^{-1} for amide, 1222cm^{-1} for O–SO2 group and 2926cm^{-1} for CH aliphatic.

III-Synthesis of 9 (10)-(Carboxymethylthio stearamido Morpholine or piperidine (III_{a-e}, VI_{a-e})





Where R : (a) oleic, (b) linoleic, (c,d,e) olive, linseed and castor mixed fatty acids), respectively.

Mercapto acetic acid (0.28 mole) was added to N-oleyl morpholine or piperidine (0.28 mole) in a 250 flask containing 10 ml chloroform as solvent. The flask was heated while stirring for 4hr at 70˚, then washed with water. The washed solutions

were dried with anhydrous sodium sulfate then the solvent was removed under reduced pressure.

IR spectra of 9(10)carboxymethyl thiostearamido morpholine derivative showed a strong absorption band at 1716cm^{-1} for amide, 2504 cm^{-1} for SH group and 2982 cm^{-1} for CH (aliphatic)

Methods of Evaluation

The surface tension and the behaviour of surfactants at the air water interface was measured using du Nouy ring tensiomter, with platinum-iridium ring. The critical micelle concentration (CmC) was determined from the break point of each surface tension *vs.* Concentration (on log scale) curve. Molecular surface area (A^2), maximum surface excess concentration ($\tau_{max.}$), the efficiency to depress the surface tension (PC_{20}), the effectiveness of interfacial tension reduction (π_{cmc}) at the critical micelle concentration, and the free energy of micellization (ΔG°_{mic})) were calculated[9-14]. Foaming performance of the different synthesized surfactants was evaluated by Ross & Miles test [15,16]. The emulsifying power[17,18] towards different hydrocarbons such as benzene, heptane, hexane and xylene were discussed. The antimicrobial activity of the prepared derivatives against a Gram-positive, Gram negative as well as a fungi was examined[19].

Results and Discussion :

In order to understand the performance and uses of olive, linseed and castor oils, a comparison of the component fatty acids of these oils must be considered.Gas chromatography investigation showed that the total unsaturated fatty acids in linseed, olive and castor, oils are 89.49, 84.13% and 85.30%

The iodine values were dropped after the addition of sulfo and methylthio-carboxylate moieties to the double bonds of unsaturated N-acylamidpmorpholide and piperidide derivatives.

Elemental analysis of compounds ($I_{a,b}$ – $VI_{a,b}$) agreed with the calculated values within limits of experimental error (Table 1).

Table (1): Elemental analysis of compounds (Ia,b – VIa,b)

Compound	C%		H%		N%	
	Calc.	Found	Calc.	Found	Calc.	Found
I_a	75.20	74.80	11.68	10.98	3.99	3.10

I_b	75.64	75.11	11.17	10.55	4.03	3.69
IV_a	79.08	78.78	12.32	11.78	4.01	3.87
IV_b	79.54	79.12	11.82	11.22	4.03	3.91
II_a	58.02	57.81	9.23	8.72	3.07	2.90
II_b	58.28	58.10	8.83	8.22	3.09	2.78
V_a	60.93	60.22	9.71	7.11	3.09	2.92
V_b	61.19	60.88	9.31	9.10	3.10	2.96
III_a	64.86	64.16	10.36	10.21	3.15	3.10
III_b	65.19	64.81	3.95	9.45	3.17	3.02
VI_a	68.03	67.72	10.65	10.05	3.17	2.97
VI_b	68.33	68.21	10.25	9.78	3.18	2.81

Surface tension at the critical micelle concentration (γ_{cmc}), the critical micelle concentration (CmC), maximum surface excess concentration (τ), the minimum surface area/molecule (A_{min}), the standard free energy of micellization (ΔG_{mic}), surface tension efficiency (PC_{20}), CmC/C_{20} ratio and effectiveness (π_{cmc}) of the sulfonated and methyl thiocarboxylate morpholide and piperidide derivatives were summarized in Table (2).

It was noticed that the CmC values of group II_{a-e} ranges from $7.07x10^{-3}$ – $5.62x\ 10^{-4}$ mole/L and ΔG_{mic} were decreased from -21.04 - 12.05 KG/mole.

As shown in Table 2. All the thermodynamic parameters of III_{a-e} series were greater than that of sulfonated derivatives (II_{a-e}) except ΔG_{mic} in general, it could be noticed that piperidide derivatives (V_{a-e}, IV_{a-e}) have smaller ΔG_{mic} than that of morpholide derivatives II_{a-e}, III_{a-e}.

Foaming power of all compounds of this series was tested at different temperatures (25˚C, 40˚C, 60˚C, 80˚C) of 0.1% aqueous solution and the data showed that the foam height increased by increasing temperature and the foam height of oleyl derivatives was greater than those of linoleyl derivatives. Moreover, castor mixed fatty acid derivatives have greater foam height than those of olive mixed fatty acid derivatives due to the presence of hydroxyl group in the former. On the other hand olive and linseed mixed fatty acid derivatives showed foam height almost similar to those obtained from oleic and linoleic acid derivatives.

It was also noticed that foam stability decreased with increasing temperature from 25 to 60˚C for all derivatives of sulfonated N-acyl morpholide except linseed and castor mixed fatty acids and incorporating of a piperidine ring into the hydrophobic alkyl chain resulted some compounds with moderate foam height and foam stability. And it was found that the foam height of castor derivatives was the best at 80˚ (Table 3).

The emulsifying power was tested towards different hydrocarbons such as benzene, heptane, hexane and xylene. It was found that linseed mixed fatty acid

derivatives could produce stable oil-water emulsion (56 h) in xylene so it may be useful in textile processing and dye bathes (Table 4).

The piperidide derivatives showed moderate emulsification power forming fairly stable emulsion towards different hydrocarbons and good emulsifying power was achieved for castor mixed fatty acids towards hexane (60 hr). On the other hand substituted derivatives of linseed mixed fatty acids showed excellent emulsification power with all hydrocarbons used especially with hexane (54 hr).

It was concluded maximum activity for the derivatives was obtained when mercapto acetic acid was added to the internal double bond of unsaturated amides.

A large number of the prepared fatty acid derivatives have been shown to exhibit varying degrees of antimicrobial behaviour. Several of the sulfo and methyl thio carboxylate derivatives of morpholine and piperidine have broad antimicrobial spectra, suggesting that they might have potential utility in biostatic products (Table 5).

Table (2):Surface active properties of 9(10) sulfostearamido and 9(10) carboxymethiostearamido morpholine and piperidine derivative at 5°C.

Surfactants	γ_{CmC} mN/m	CmC mole/L	τ_{max} surface excess (mole,cm^{-2})	Area mole A^2x10^2 cm^{-1}	ΔG_{mic} KJ/mole	C_{20}	PC_{20}	CmC/C_{20}	π_{CmC} mN/m
IIa	25.87	$7.07 x10^{-3}$	1.78	93	-12.05	$5.94 x 10^{-3}$	2.22	1.19	21.75
IIb	28.22	$3.98 x10^{-3}$	2.06	80	13.46-	$2.76 x 10^{-3}$	2.55	1.44	21.83
IIc	25.05	$5.62 x10^{-4}$	1.69	98	18.23-	$3.14 x 10^{-4}$	3.5	1.78	22.00
IId	29.31	$8.91 x10^{-3}$	2.03	81	17.10-	$5.98 x 10^{-4}$	3.22	1.48	21.94
IIe	27.51	$1.77 x10^{-4}$	2.18	76	21.04-	$0.82 x 10^{-4}$	4.08	2.16	24.11
IIIa	27.9	$1.99 x10^{-3}$	1.79	92	-14.82	$3.09 x 10^{-4}$	3.51	6.43	28.16
IIIb	29.0	$8.91 x10^{-4}$	2.03	81	-17.50	$4.89 x 10^{-4}$	3.30	1.55	22.44
IIIc	28.8	$2.50 x10^{-3}$	1.67	99	-14.59	$3.54 x 10^{-4}$	3.10	7.07	27.98
IIId	30.5	$2.23 x10^{-3}$	2.22	74	-14.86	$1.43 x 10^{-3}$	2.84	1.56	22.41
IIIe	29.8	$5.01 x10^{-3}$	2.39	71	-12.90	$3.17 x 10^{-3}$	2.49	1.58	22.58
Va	28.7	$1.77 x10^{-3}$	2.05	80	-15.43	$6.90 x 10^{-4}$	3.16	2.56	24.70
Vb	32.5	$7.07 x10^{-4}$	2.31	71	-17.67	$3.13 x 10^{-4}$	3.50	2.25	24.57
Vc	28.22	$1.25 x10^{-3}$	1.96	84	-16.28	$2.51 x 10^{-4}$	3.59	4.98	27.74
Vd	34.23	$1.12 x10^{-3}$	2.28	72	-16.55	$8.91 x 10^{-5}$	4.05	2.57	34.12
Ve	30.51	$2.82 x10^{-4}$	2.49	66	-19.9	$1.53 x 10^{-4}$	3.81	1.83	23.69
VIa	29.90	$1.12 x10^{-3}$	2.28	72	-16.55	$8.91 x 10^{-5}$	4.05	12.57	34.12
VIb	33.09	$8.91 x10^{-4}$	2.46	67	-17.10	$7.62 x10^{-5}$	4.12	11.69	34.78
VIc	30.50	$2.23 x10^{-3}$	2.21	74	-14.86	$1.43 x 10^{-3}$	2.84	1.56	22.40
VId	36.32	$5.01 x10^{-4}$	2.14	77	-18.51	$3.29 x10^{-4}$	3.45	1.54	22.16
VIe									

32.92	1.17×10^{-4}	2.58	64	-21.30	1.07×10^{-4}	3.97	1.66	23.20

Table (3) Foam Height and foam stability of aqueous solution of 9(10) sulfostearamido carboxymethylthiostearamido of morpholine and piperidine at different temperature

Surfactant	Foam Height (mm)												Foam stability (%)			
	25℃			40 ℃			60 ℃			80 ℃						
	0 min	5 min	10 min	0 min	5 min	10 min	0 min	5 min	10 min	0 min	5 min	10 min	25℃	40℃	60℃	80℃
IIa	90	85	80	95	90	86	100	95	93	105	100	95	11.11	9.40	7.00	9.52
IIb	85	80	75	88	83	80	94	90	88	100	95	90	11.76	9.09	6.38	10.00
IIc	88	83	78	89	85	81	92	90	85	98	92	88	11.36	8.98	7.60	10.20
IId	80	78	75	85	83	80	90	85	80	93	88	83	6.25	5.88	11.11	10.75
IIe	95	88	85	100	90	88	105	98	92	110	105	100	10.52	12.00	12.38	9.09
IIIa	75	70	68	80	73	70	83	80	77	88	84	80	11.11	9.40	7.00	9.52
IIIb	68	65	60	78	75	72	80	77	75	85	80	77	11.76	9.09	6.38	10.00
IIIc	70	68	65	75	70	68	80	77	73	85	80	75	11.36	8.98	7.60	10.20
IIId	65	60	58	73	70	68	78	75	72	80	78	75	6.25	5.88	11.11	10.75
IIIe	80	73	70	83	80	78	85	80	75	90	84	82	10.52	12.00	12.38	9.09
Va	85	83	80	90	88	83	95	92	90	98	96	93	5.88	7.77	5.26	5.10
Vb	80	78	75	85	80	78	90	88	85	95	92	90	6.25	8.23	5.55	5.26
Vc	83	80	78	88	85	80	93	90	88	97	95	92	6.02	9.09	5.38	5.15
Vd	78	75	73	80	78	75	85	83	80	90	88	83	6.41	6.25	5.88	7.77
Ve	88	85	82	93	90	88	95	90	87	100	97	94	6.82	5.37	8.42	6.00
VIa	73	70	67	78	73	70	83	80	78	88	84	80	8.21	10.25	6.02	9.09
VIb	68	66	63	75	72	68	78	75	70	83	80	78	7.35	9.33	10.25	6.02
VIc	70	68	65	76	73	70	80	78	74	85	82	80	7.14	7.89	7.50	5.88
VId	66	64	62	68	66	64	75	73	70	80	77	74	6.06	5.88	6.66	7.50
VIe	75	73	70	80	78	75	85	82	80	90	87	84	6.66	6.25	5.88	6.66

Table (4) : Emulsification of 0.1 aqueous solution of 9(10) sulfostearamido 9(10) carboxy methyl thiostearamido and piperidine derivatives.

	Benzene		***Hepatane***		***Hexane***		***Xylene***	
Surfactants	***hr.***	***min.***	***hr.***	***min.***	***hr.***	***min.***	***hr.***	***min.***
IIa	1.0	10.0	1.0	8.0	1.0	34.0	1.0	54
IIb	1.0	57.0	1.0	52.0	1.0	10.0	2.0	48
IIc	4.0	15.0	2.0	30.0	2.0	50.0	4.0	40
IId	53.0	10.0	54.0	35.0	55.0	10.0	56.0	20
IIe	4.0	10.0	4.0	50.0	5.00	30.0	5.0	55
IIIa	1	7.0	2	20.0	1	15	3	25
IIIb	1	15.0	2	30.0	1	25	3	35.0
IIIc	1	10.0	2	25.0	1	20	3	30
IIId	1	20.0	2	15.0	1	30	3	38
IIIe	1	5.0	2	39	1	10	3	20
Va	1.0	10	1	23	1	27	1	55
Vb	2.0	20	1	55	2	20	2	30
Vc	1.0	35	1	27	1	40	1	50
Vd	5	30	52	10	54	20	55	25
Ve	3	30	5	25	60	10	6	35
VIa	1	20	1	15	2.0	30	2.0	35
VIb	1	30	2.0	25	2.0	35	2.0	40
VIc	1	23	1	20	2.0	40	3.0	43
VId	1	35	1	30	2.0	42	3.0	45

VIe	1	15	1	10	2.0	25	2.0	27

Table (5): Antimicrobial Activity of 10^{-1} mg/ml of 9(10) sulfostearamido 9(10) carboxy methyl thiostearamido and piperidine derivatives.

Surfactants	Bacteria				Fungi	
	Gram + ve		Gram – ve			
	Staphylo-coccus aureus	*Bacillus subtillus*	*Escheric ia coli*	*pseudoma ns aeruginos a*	*Asperg illus niger*	*Aspergil flavus*
IIa	+++	++	+	++	–	+++
IIb	+++	++	+	++	–	+
IIc	++	++	+	++	–	+
IId	+++	+++	+	++	+	++
IIe	+++	++	+	+++	+	+++
IIIa	+++	+++	+++	++++	+++	+++
IIIb	+++	+++	+	++	–	+
IIIc	+++	+++	+++	+++	–	–
IIId	+++	+++	+++	+++	+++	++
IIIe	++++	+++	+++	+++	+++	+++
IVa	+++	+++	+++	+++	+++	++++
IVb	++	++	+	++	+++	++++
IVc	++	++	+	+++	–	–
IVd	+++	++	+	+++	–	–
IVe	+++	+++	+	+++	+	++
Va	+++	+++	+++	++++	–	+
Vb	+++	+++	+	+++	++	+++
Vc	+++	+++	+	+++	–	+
Vd	+++	+++	+++	+++	++++	+++
Ve	+++	+++	+++	+++	+++	++++
References standard	++	+++	++	++	+++	+++
Chloramphenicol was used as a standard antibacterial agent and Grsofluvine was used as a standard antifungal agent						

+ = Inhibition values = 0.1-0.5 cm ; ++ = inhibition values = 0.6-1.4 cm ; +++ = Inhibition values = 1.4-2.5 cm .

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