Synthesis of Some Anionic Surface-Active Agents Containing Hetero-Cyclic Moiety and Study of their Biological Activities

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Abstract: Sodium salt of a-sulphonated fatty acid hydrazide was used as starting material to synthesis some important heterocycles as phthalizine derivatives to produce novel groups of anionic surfactants having a double function, antimicrobial and surface active agents. The structures of these compounds were performed by FTIR and CHN-analysis. The physical properties as (density, pH, concentration color, viscosity and stability to hydrolysis) were determined. The surface active agents were used in (O/W) emulsions depend on value of (HLB) [Hydrophilic-Lipophilic Balance].

Key ward: Anionic surfactants, anionic surfactants hydrazides containing heterocyclic.

Introduction :

An anionic surface-active agent is the reaction product of an organic compound such as high molecular weight acid or alcohol with an inorganic compound such as sodium hydroxide or sulfuric acid, yielding a product wherein the organic part of the molecule or the water-insoluble part of the molecule has a negative charge and the water-soluble part of the molecule wherein the sodium ion has a positive charge. For example soap is an anionic and has the following structure:

$$CH_3(CH2)_{10}COO\text{-}Nat \qquad (1)$$

Also, the reaction product of a long-chain alcohol and sulfuric acid were neutralized with sodium hydroxide has the following structure:

$$CH_3(CH_2)_9OSO_3^-Na^+ \qquad (2)$$

The anionic have the advantage of being high and stable foaming agents; however they have the disadvantage of being (water hardness) or pH changes (1).

The surface-active agent is the principle component of a synthetic detergent but is also assisted in its cleaning agent role by the builders used (sometimes called built detergents) (2). Builders such as the phosphates, metasilicates and carbonates aid in emulsifying soils and suspending dirt in aqueous solutions. The surface-active agents are compounds that have two groups present in the molecule: One being hydrophobic in nature and one being hydrophilic means water-linking and hydrophobic means

water-heating or oil-linking. So when you have a surface-active agent with two groups present, you have a chemical compound that has surface-active properties or the ability to affect the interfacial relationship between two dissimilar substances such as oil and water [3a, 3b]

Biodegradation is a process carried out by bacteria in nature. By a series of enzymatic reactions, a surfactants molecule is ultimately converted in to carbon dioxide, water and oxides of the other elements. For surfactants the rate biodegradation varies from 1-2h for fatty acid, by 1-2 days. In all testing of biodegradation it is important to realize that the rate of degradation depends on factors such as concentration, pH and temperature (4)

The encouraged our to synthesize novel groups of anionic surfactants containg pyridazine, oxadizole, phthalazinone and thiazole derivatives from sodium salt of a sulphonated long chain fatty acids (myristic, palmitic and stearic) hydrazide (Ia -c) is that hopping to these compounds are possessing good surface properties and expected to have biological activities.

Experimental :

IR-spectra were recorded as IIa-c using a FTIR spectrophotometer (8400S SHIMADZU) at Petrochemical Lab. Basrah (the range 4000-200 cm^{21}).

Freezing points osmometer (OSMOMAT 030) was carried out at the College of Education, University of Basrah.

Elemental analyses were carried out at the College of Science, University of Cairo. Giza. Egypt.

pH values were recorded using pH-meter (WTW) at College of Science, University of Basrah.

Density values were recorded using density bottle glass.

Viscosity values were recorded using Viscometer by units (cent-poise).

Melting points values were recorded using Electrothermal (1 9300) made in UK at the College of Education, University of Basrah.

The chemicals are Fatty acid, hydrazine, chloro sulphonic acid, sodium hydroxide, phthalicanhydride, acetic anhydride, acetic acid, dimethylformamide, benzene, methanol, ACOH, ethyl alcohol, acetone, carbon tetra chloride. [Fluka, BDH and North Oil Company / Baiji].

Procedure:

Preparation of fatty acid chloride

Fatty acid chloride was prepared according to a reported procedure [5]

Preparation of fatty acid hydrazides

Acid chloride (0.01mol, 2.46 ml) and hydrazine hydrate (0.01mol, 0.32 ml) were dissolved in 25ml acetone. The mixture was refluxed for 2h. The product is recrystalized from the rest of acid by hot water to obtain hydrazide (6a)

Preparation of sodium salt of a-sulphonated fatty acid hydrazides ($_{Ia-c}$)

A solution of fatty acid hydrazide (0.01mole, 2.5ml) and chloro sulphonic acid (0.01mole, 1.16 ml) in carbon tetra chloride was stirred at room temperature for 2h, then neutralized by (0.1N) of sodium hydroxide. The solid product was filtered and recrystallized by DMF to obtain the product (I a-c) (6a) with (M.P=196°C, 201°C and 216°C) respectively.

Preparation of Oxapyridazinone derivative (II_2)

Equimolar amounts of solution to sodium salt of a-sulphonated fatty acid hydrazides (Ia) and phthalic anhydride in acetic acid were refluxed for (6h) then poured on water. A solid product was precipitated, filtered and recrystalized by ACOH solvent to give phthalizine

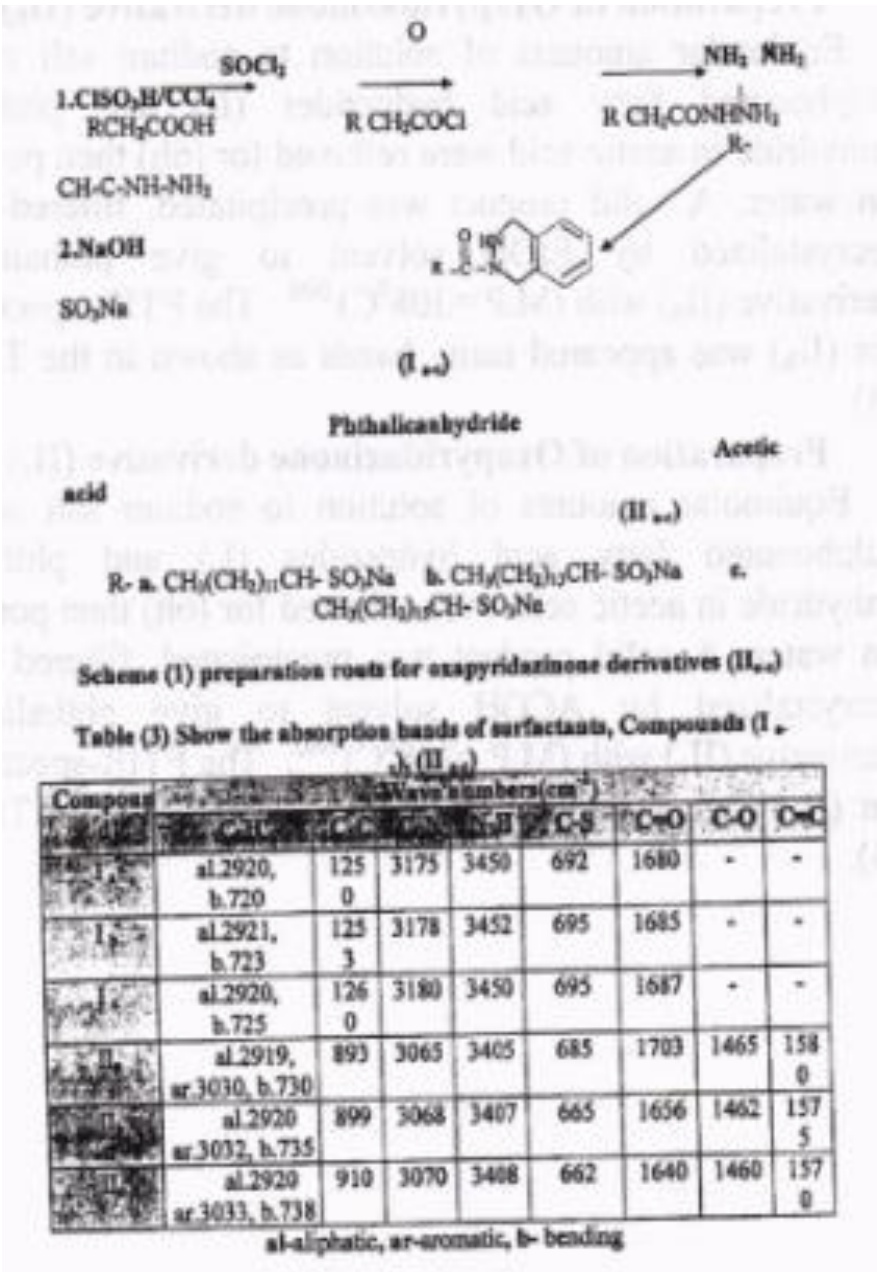
derivative (II) with (M.P=290°C) (6a). The FTIR-spectrum for (II.) was appeared many bands as shown in the Table (3).

Preparation of Oxapyridazinone derivative (II)

Equimolar amounts of solution to sodium salt of a-sulphonated fatty acid hydrazides (Ib) and phthalic anhydride in acetic acid were refluxed for (6h) then poured on water. A solid product was precipitated, filtered and recrystalized by EtOH solvent to give phthalizine derivative (II) with (M.P =308°C) (6a). The FTIR-spectrum for (IIb) was appeared many bands as shown in the Table (3).

Preparation of Oxapyridazinone derivative (II)

Equimolar amounts of solution to sodium salt of a-sulphonated fatty acid hydrazides (Ic) and phthalic anhydride in acetic acid were refluxed for (6h) then poured on water. A solid product was precipitated, filtered and recrystalized by ACOH solvent to give phthalizine derivative (II.) with (M.P=318°C) (6a). The FTIR-spectrum for (II) was appeared many bands as shown in the Table (3).



Scheme (1) preparation routs for oxapyridazinone derivatives (II_{a-c})

Table (3) Show the absorption bands of surfactants, Compounds (I_{a-c}), (II_{a-c})

Compound	Wave numbers (cm^{-1})							
	C-H	C-C	O-H	N-H	C-S	C=O	C-O	C=C
I_a	al.2920, b.720	1250	3175	3450	692	1680	-	-
I_b	al.2921, b.723	1253	3178	3452	695	1685	-	-
I_c	al.2920, b.725	1260	3180	3450	695	1687	-	-
II_a	al.2919, ar.3030, b.730	893	3065	3405	685	1703	1465	1580
II_b	al.2920 ar.3032, b.735	899	3068	3407	665	1656	1462	1575
II_c	al.2920 ar.3033, b.738	910	3070	3408	662	1640	1460	1570

al-aliphatic, ar-aromatic, b- bending

Table (3) Show the absorption bands of surfactants, Compounds (I a-c), (II a-c)
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Ib	al.2921, b.723	1253	3178	3452	695	1685	-	-
Ic	al.2920, b.725	1260	3180	3450	695	1687	-	-
IIa	al.2919, ar.3030, b.730	893	3065	3405	685	1703	1465	1580
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IIc	al.2920 ar.3033, b.738	910	3070	3408	662	1640	1460	1570

Table (5) the activity of the products with the time

Compound	Time (Day)						
	1st	2nd	3rd	4th	5th	6th	7th
IIa	40%	49%	58%	69%	82%	95%	-
IIb	37%	46%	55%	64%	79%	90%	-
IIc	34%	42%	51%	60%	74%	84%	97%

R-a. $CH_3(CH_2)_{11}CH\text{-}SO_3Na$ b. $CH_3(CH_2)_{13}CH\text{-}SO_3Na$

c. $CH_3(CH_2)_{15}CH\text{-}SO_3Na$

Scheme (1) preparation routs for oxapyridazinone

derivatives (II-c)

Synthesis of the solution surfactants

(0.1mole) surfactants were soluble in (100ml) water and ethanol (70:30) to obtain a solution from II. (47.4%), Пь (50.2%) and II. (53%). These solutions were used for dispersing the oil spots in the Iraqi Ports Company with out any negative effect on the water environment and this was a proved by the measurements of biological activity in the laboratories of Petrochemical Company.

Biological activities

The prepared surfactants were test for their bactericidal activities against (Bacillus sublitis and Escherichia coli) and other their antifungal activity against (Aspergillus's Niger and Yeast (Candida albicam). The results obtained indicated that compounds (IIa-c) were relativity more active as bactericide or fungicide agent as shown in Table (1).

Conpound	Bacilhrs sublitls	Escheriehia Coli	AspergWs's NEer	Candilla albbam
IIa	+	+	-	+
IIb	++	+	+	++
IIc	+	++	+	+

Table (1) Biological activity of prepared surfactants, Compounds (II a-c)

+ (positive active), - (negative active)

Procedure:

The Hahn method was used in obtained on disc with diameter (6mm) from filter paper Watman (No.3). The filter paper was electrical treatment in 121°C and (ljaw) for 15min. The prepared surfactants were used as dilute solutions and concentrations (50, 150 and 250ng/disc). The discs were left in room temperature to dry and keep in refrigerator until using.

The Pauen and others were used in determined inhibition zone which was measured by (mm). The Muller-Hinton Agar was prepared and poured in betriedish glass. The four stander bacterial plankton were prepared and moved (4-5) pure colony of bacteria grown on Nutrient Borth and keep in 37°C for (4-6h) until appearing turbid. The area of sterilized cotton containing the Muller-Hinton Agar was abundant in the prepared bacteria plankton in three dimensions to obtain on homogenous grow, after that the betriedishes were moved to incubation in 37°C for (24h) and the measured biological activities through measured the inhibitor zones around all disc in mm (6b)

Results and discussion

The stability of hydrolysis for sodium salt of a-sulphonated fatty acid hydrazides (Ia-c) and oxapyridazinone derivative (II a-c) (10 mmol.) were mixed with (10ml) sodium hydroxide (0.05N) and placed in thermo set at (40°C). The time taken by sample solution to be clouded on a result of hydrolysis shows the stability surfactant to hydrolysis (7). The time of stability surfactant was calculated and shown in Table (2).

Table (2) the physical propcrtie ofthe products (I a-e),(II a-e)

Conpanld	m.wt (g/mol)	Celor	Deliity (g/cm1)
I_a	344	Yellow	١.١٢٥
I_b	372	White Yellow	١.١٤٤
I_c	400	White Yellow	1.148
II_a	474	Brown	1.367
II_b	502	Red Brown	1.395
II_c	530	Red Brown	1.411

Visccity (c.p)	Conc. (mol)	PH	Stability to hydrolysis(h)
1.546	34.4%	8.1	3.7
1.568	37.2%	8.3	4
1.570	40%	8.5	4.3
1.736	47.4%	7.4	6.2
1.762	50.2%	7.6	6.8
1.798	53%	7.8	7

The compounds (Ia-c) were allowed to react with chloroacetic acid in ethyl alcohol, yielding oxapyridazinone derivatives (IIa-c) [65%, 60%, and 60%].

FTIR spectra show (N-H) at 3452-3450 cm^{21}, (C=O) at 1680-1687 cm^{21}, (C-N) at 3180-3174 cm^{21}, (C-H) aliphatic at 2920-2850 cm^{21}, 725-720 cm^{1}, (C-C) at 1260-1248 cm^{21}, and (C-S) at 698-692 cm^{21} for the compounds (I a-c) as explained in Table (3)[8].

While, the compounds of (II a-c) give different bands, (N-H) at 3407-3405 cm^{21}, (C=O) at 1703-1640 cm^{21}, (C-N) at 3070-3065 cm^{21}, (C-H) aliphatic at 2919-2851 cm^{21}, 738-730 cm^{21}, (C-H) aromatic at 3032-3030 cm^{21}, (C-S) at 685-660 cm^{21}, (C-O) at 1465-1460 cm^{21}, (C-C) at 910-893 cm^{21} and (C=C) at 1580-1570 cm^{21} as shown in the Table (3)[8].

Elemental analysis (C, H, N) shows the practical and theoretical values in Table (4).

Table (4) Elemental analysis of the products

Corpound	Practical Value %		
	C	**H**	**N**
IIa	55.25	6.24	5.75
IIb	57.05	6.66	5.23
IIc	58.45	6.82	4.72

Theoretical Value 7٠%		
C	**H**	**N**
55.64	6.56	s.92
57.31	6.93	5.54
58.82	7.36	5.27

The mechanism of the surfactants is used in dispersing oil in water emulsion; The sample which was taken from the Iraqi Ports Company was poured into containers and added the surfactants by spray on the surface. The activity of dispersion was studied with time to know the efficiency of compounds (IIa, IIb, and IIc) on dispersing oil spots. It was noted that the surfactants reduced the surface tension of liquid. In addition to the effect of long chain on dispersion was studied as shown in Table (5)[6b].

Table (5) The activity of the products with the time

Componnd	Time (day)						
	1st	2nd	3rd	4th	5th	6th	7th
II_a	40%	49%	58%	69%	82%	95%	-
II_b	37%	46%	55%	64%	49%	99%	-
II^c	34%	42%	51%	60%	74%	84%	97%

The selection of surfactants depends on hydrophilic-lipophilic balance (HLB), which was calculated by equation (1). The prepared surfactants were used as oil-in-water emulsion (O/W) as shown in Table (6). This value is an induction of the oil or water solubility of the product. The lower (HLB) number is the more water-soluble the product; and in turn, the higher (HLB) number is the more oil-soluble the product[6a, 6b].

$$HLB = 20 * \frac{\text{mole wt.EO} * \text{moles EO}}{\text{mole wt. of adduct}} \quad \ldots\ldots\ldots (1)$$

Value of H LB	Application
0-3	Anti-foaming
4-6	(WO)emulsifuing
7-9	Weuing
8-18	(O/W)emulsiffing
13-15	Detergent
10-18	Solubilizing

The (HLB) was calculated for the prepared surfactants as shown in Table (7).

Table (7) the value of HLB

Corpound	value of H L B
II_a	15.00
II_b	16.50
II_c	17.98

The prepared surfactants were activated toward the bacterial used as shown in Table (8).

Table (8) Inhibitor zones around all discs to the prepared surfactants, Compounds (II_{a-c})

Compound	Bacillus sublitis			Escherichia colis		
	٥٠	١٠٠	١٥٠	٥٠	١٠٠	١٥٠
II_a	-	١,٩	٢,٤	٣,٤	٣,٨	٥
II_b	-	٢,٨	٣,٨	٤,٦	٥,٢	٧,٤
II_c	-	٣		٥	٦,٥	٨

Aspergillus's Niger			Candida albicant		
50	100	150	50	100	150
1.3	2	2.4	1.6	2.3	3
1.9	3.6	3.8	2.3	2.8	3.5
2.3	4	4.7	2.8	3.3	4

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تحضير بعض منشطات السطوح الأنايونية الحاوية على حلقة غير متجانسة ودراسة فعاليتها البايلوجية

د. مهند جواد كاظم

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الخلاصة: تم استخدام مادة ملح الحامض الدهني الحاوي على مجاميع الهايدر لتحضير بعض المركبات الحلقية غير المتجانسة والمتضمنة على الفثاليك انهيدريد في تركيبها باعتبارها منشطات سطوح أنيونية، أذ تمتلك مثل هذه المركبات نوعين من الفعاليات هي كونها مادة منشطة للسطح وكمواد فعالة بايولوجيا. تم استخدام المركبات المحضرة خلال الدراسة بأشعة تحت الحمراء وتحليل العناصر الدقيقة كما هو الحال مع بعض الخصائص الفيزيائية لها مثل (الحامضية، الكثافة اللزوجة، تركيز اللون واستقرارها تجاه التحلل كما اعتبرت هذه المواد من ضمن كواشف مستحلبات النفط في الماء بالاعتماد على قيمة الموازنة بين المجاميع المحبة للماء والمحبة للدهونHLB) .