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PREPARATION OF SOME SURFACE ACTIVE AGENTS AND DETERMINATION OF ITS PHYSICO CHEMICAL PROPERTIES

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ABSTRACT

Two type of surface active agents anionic and nonionic were prepared from locally raw materials: Fatty acids (lauric and palmitic) reacted with poly ethylene glycol (PEG) 400, 600 in case of nonionic surfactants preparation and fatty acids reacted with potassium hydroxide and calcium oxide in case of anionic surfactants preparation. Locally prepared nonionic surfactants were identified using IR and Massspectroscopy. Physico-chemical properties were assessed such as HLB, critical micelle concentration CMC, free acidity or alkalinity and solubility in different solvents to give prediction of the best use in pesticide formulation. Results obtained indicated that nonionic surfactants PEG 600 ML were miscible in water while, the other nonionic surfactants gave emulsion in water, and showed different solubility in xylene and acetone. On the other hand divalent salts (calcium palmitate and laurate) were insoluble in water or any solvents, therefore it is unsuitable to use in formulation , while, mono valent (potassium laurate and potassium palmitate) were soluble in water. Also the results showed that locally prepared surfactants decreased the surface tension of water , nonionic surfactants PEG 400 ML was the most in decreasing the surface tension followed by PEG 600 ML, on the other hand pt-laurate (ionic surfactant) decreased the surface tension to 29.1 dyne/cm, this finding indicated that these surfactants could be used as wetting and spreading agents. Also the result indicated that laurate esters have HLB 10-12, palmitate esters have HLB 6-8, ionic surfactants (pt-laurate and pt-palmitate) have HLB 12-18 , therefore they were suitable to use as suspending , wetting and spreading agents.

INTRODUCTION

Surface active agent are playing an important role on many fields specially in pesticides in both formulation and optimization of there biological efficiency (Tadros, 1995). Surface active agents are used to reduce the interfacial tension between immiscible liquids or between liquids and solid surfaces. Such surface active agents act as wetting and spreading agents by reducing the surface tension of the spray droplet, so that it spreads on the leaf surface providing more coverage for toxicants by reducing the contact angle of spray drops on the solid surface (El-Sebae 1965).

The main problem which face us that the most surfactants are imported, it is raise the pest control costs. Therefore, efforts should be directed towards preparation of locally surfactants by available and locally materials.

The aim of this research, is preparation ionic and nonionic surfactants by locally and cheap materials and determination their physico-chemical properties.

MATERIALS AND METHODS

1- Materials

All chemicals used in preparation of different nonionic and ionic surfactants were selected as pure grade.

a) Fatty acids

- Lauric acid M.wt = 200.32 produced by Morgan Co. for chemicals Cairo - Egypt.
- Palmitic acid M.wt = 256.42 produced by EL-Gomhoria Co. for chemicals Cairo – Egypt.

b) Poly ethylene glycol (PEG)

- Poly ethylene glycol 600 (PEG-600) M.wt = 590 produced by Morgan Co. for chemicals Cairo – Egypt.
- Poly ethylene glycol 400 (PEG-400) M.wt = 414 produced by EL Gomhoria Co. for chemicals Cairo – Egypt.

c) Other chemicals

- Potassium hydroxide KOH M.wt = 56.11 produced by EL – Naser Co. for chemicals Cairo – Egypt.
- Calcium oxide (dehydrated) CaO M.wt = 56.08 produced by Morgan Co. for chemicals Cairo – Egypt.

A) Preparation methods of nonionic surfactant:-

1- Monofatty acid esters (1a-d).

Nonionic surfactants monofatty esters were prepared according to (Osipow 1964) by heating fatty acid (lauric or palmitic) (0.1 mole) for 30 minute then polyethylene glycol 600 or 400 (0.1 mole) was added drop wisely to heated acid. The temperature then elevated gradually to 350 C° with continuous stirring for 5-6 hrs until all water molecules were evaporated to stop the reversible reaction. The product left to cool to obtain mono fatty acid esters (surfactant) 1a-d.

2) Disfatty acid esters (2a-d).

Nonionic surfactants difatty esters were prepared according to (Osipow, 1964) by heating fatty acid (0.2 mole) for 30 minute then polyethylene glycol (0.1 mole) was added drop wisely to heated acid. The temperature then elevated gradually to 350 C° with continuous stirring for 5-6 hrs until all water molecules were evaporated to stop the reversible reaction. The product left to cool to obtain difatty acid esters (surfactants) 2a-d.

B) Preparation of ionic surfactant (salts of fatty acid).

1- Potassium salt of (lauric and palmitic) acids was prepared by heating (1 mole) of lauric or palmitic acid for 30 minute at 100C° then (1 mole) of KOH dissolved in 5 ml of distillated water was dropped wisely on heated acid with continuous stirring after one hour the product was removed and left for cooling.

2- Calcium salt of (lauric and palmitic acid) was prepared by heating (2 mole) of lauric or palmitic acid for 30 minute at 100 C° then (1 mole) of CaO was added to 5 ml of distillated water and heated until reaching the boiling point of water then the solution was dropped wisely on the heated

acid with continuous stirring for one hour and the product removed for cooling .

C) Identification of the locally prepared surfactant:-

1- Infra Red spectroscopy (IR):

IR was used for the determination of the function groups in the prepared product. IR spectra were recorded (KBr) on a pye - unicom – sp-833 perking Elmer spectrophtometer.

2- Mass spectra (Ms):

Mass spectra was used for the determination of the molecular weight of the prepared products. MS spectra were run on GC mass – QP 1000 EX (SHIMAPZU) Mass spectrometer, micro analytical laboratory, faculty of science, Cairo University.

3- Elemental analysis:

The elemental analysis was done to indicate the percentage of carbon and hydrogen in the products, the analysis was done at the micro analytical laboratory, in Faculty of Science, Cairo University.

D) Determination of physicochemical properties for the locally prepared surfactants:-

1) Solubility:

It was determined by measuring the volume of distilled water, acetone and xylene required for complete solubility or miscibility of 0.5 gram of salts, then % solubility was calculated according to the following equation :

$$\% \text{ solubility} = (0.5/v) \times 100$$

where v is the volume of solvent required for complete solublility (El-Sisi, 1981).

2) Critical Micelle Concentration (CMC):

The value of CMC is the concentration of surfactant at which no more decrease in surface tension could be obtained by raising the surfactant concentration. The method depends on the determination of surface tension (El- Sisi 1985)

Procedure: 2.5 grams of surfactant were added into 250 ML of distilled water and then different concentrations (from 0.1 to 1%) were prepared by diluting the stock solution, the surface tension was measured by DuNoüy Tensiometemer. The value of CMC is the point maximum of surface activity, after which the surfactant tends to coagulate in micelle (Osipow 1964).

3) Hydrophilic – Lipophilic Balance (HLB):

(Greenwaled 1956) stated that the solubility of surfactant in water was considered as an approximate guide to their HLB and their usefulness.

10 grams of surfactant is introduced into 100 ML of distilled water and solubility was observed. HLB values are 1-4 for dispersible surfactants, 3-6 for poor dispersible, 6-8 for milky dispersion after vigorous agitation ,8-10 for stable milky dispersion and 10-13 for translucent to clear dispersion.

4) Free acidity or Alkalinity:

a- Free acidity

It was determined according to guidelines of WHO and FAO (2002) Exactly 10 gram of surfactant was weighed and introduced into 100 ML

distilled water (if surfactant soluble in water) or introduced into 25 ML acetone and 75 ML distilled water (if surfactant immiscible in water). The mixture was titrated immediately with 0.02 NaOH using methyl red as indicator where Blank constant = 0.0098

Acidity as H_2SO_4 = 0.0098 X (a-b)

Where a = volume of 0.02 N NaOH for sample

b = volume of 0.02 N NaOH for Blank

b- Free alkalinity

As mentioned before the mixture was titrated immediately with 0.02 N HCL using methyl red as indicator where Blank constant = 0.008

Alkalinity as NaOH = 0.008 X (c-d)

Where c = volume of 0.02 N HCL for sample

d = volume of 0.02 N HCL for Blank

RESULT AND DISCUSSION

I) Preparation of surfactant:-

a) Nonionic surfactant

1- Monofatty acid esters (1a-d).

Four monofatty acid esters (1a-d) were prepared according to the following chemical equation

$$CH_3(CH_2)_nCOOH + HO(CH_2CH_2O)_mH \xrightarrow[-H_2O]{\Delta} CH_3(CH_2)_nCOO(CH_2CH$$

1- **Poly ethylene glycol 600 mono laurate 1a**
2- **Poly ethylene glycol 600 mono palmitate 1b**
3- **Poly ethylene glycol 400 mono laurate 1c.**
4- **Poly ethylene glycol 400 mono palmitate 1d.**

-The structure of prepared mono ester was confirmed by the following Infra red spectra, Mass Spectra and elemental analysis .

facts: **poly ethylene glycol 600 mono laurate 1a.**

(i) IR spectrum for compound (**1a**) showed absorption bands at 3383 cm^{-1} (γ OH) 2923, 2867 cm^{-1} (γ-CH-alifatic), 1734 cm^{-1} (γ C=O) 1109 cm^{-1}
(γ R-O-R).

(ii) Mass spectrum showed molecular ion peak at m/z = 772

-Poly ethylene glycol 600 mono palmitate 1b.

(i) IR spectrum for compound (**1b**) showed absorption bands at 3349 cm^{-1} (γ OH) 2916, 2870 cm^{-1} (γ-CH-alifatic), 1700 cm^{-1} (γ C=O) 1107 cm^{-1} (γ R-O-R).

(ii) Mass spectrum showed molecular ion peak at m/z = 828.

- Poly ethylene glycol 400 mono laurate 1c.

(i) IR spectrum for compound (**1c**) showed absorption bands at 3376 cm^{-1} (γ OH) 2923, 2858 cm^{-1} (γ-CH-alifatic), 1733 cm^{-1} (γ C=O) 1111 cm^{-1} (γ R-O-R).

(ii) Mass spectrum showed molecular ion peak at m/z = 596

- Poly ethylene glycol 400 mono palmitate 1d.

:i) IR spectrum for compound (**1d**) showed absorption bands at 3359 cm^{-1} (γ OH) 2916, 2871 cm^{-1} (γ-CH-alifatic), 1698 cm^{-1} (γ C=O) 1106 cm^{-1} (γ R-O-R).

(ii) Mass spectrum showed molecular ion peak at m/z = 652

Table (1): Elemental analysis of monofatty acid esters

Compound	Mol for Wt	Yield %	Cal / found	
			% C	% H
1a	$C_{38}H_{76}O_{15}$ 772.98	80	59.04 58.61	9.91 9.51
1b	$C_{42}H_{84}O_{15}$ 829.09	85	60.48 59.81	10.21 9.83
1c	$C_{30}H_{60}O_{11}$ 569.78	80	60.37 59.73	10.13 9.98
1d	$C_{34}H_{68}O_{11}$ 652.88	82	62.25 61.94	10.49 10.11

2) Disfatty acid esters (2a-d).

$$2\,CH_3(CH_2)_nCOOH + HO(CH_2CH_2O)_mH \xrightarrow[-2H_2O]{\Delta} CH_3(CH_2)_nCOO(CH_2CH_2O)_mCO(CH_2)_nCH$$

1- Poly ethylene glycol 600 dilaurate 2a
2- Poly ethylene glycol 600 dipalmitate 2b.
3- Poly ethylene glycol 400 dilaurate 2c
4- Poly ethylene glycol 400 dipalmitate 2d.

- Poly ethylene glycol 600 dilaurate 2a.

- The structure of prepared diester **2a** was confirmed by the following facts:

(i) IR spectrum for compound (**2a**) showed absorption bands at 2923, 2854 cm^{-1} (γ-CH-alifatic), 1735 cm^{-1} (γ C=O) 1111 cm^{-1} (γ R-O-R).

(ii) Mass spectrum showed molecular ion peak at m/z = 954.

- Poly ethylene glycol 600 dipalmitate 2b.

(i) IR spectrum for compound (**2b**) showed absorption bands at 2922, 2868 cm^{-1} (γ-CH-alifatic), 1733 cm^{-1} (γ C=O) 1111 cm^{-1} (γ R-O-R).Ü

Table (2) Elemental analysis of difatty acid esters .

Compound	Mol for Wt	Yield %	Cal / found	
			% C	% H
2a	$C_{50}H_{98}O_{16}$ 955.28	80	62.86 62.23	10.34 10.21
2b	$C_{58}H_{114}O_{16}$ 1067.49	81	65.25 64.86	10.76 10.59
2c	$C_{42}H_{82}O_{12}$ 779.07	85	64.74 64.52	10.60 10.37
2d	$C_{50}H_{98}O_{12}$ 891.28	80	67.37 67.23	11.08 10.95

- Poly ethylene glycol 400 dilaurate 2c.

(i) IR spectrum for compound (**2c**) showed absorption bands at 2924, 2859 cm^{-1} (γ-CH-alifatic), 1734 cm^{-1} (γ C=O) 1112 cm^{-1} (γ R-O-R).

(ii) Mass spectrum showed molecular ion peak at m/z = 778

- Poly ethylene glycol 400 dipalmitate 2d.

(i) IR spectrum for compound (**2d**) showed absorption bands at 2921, 2855 cm^{-1} (γ-CH-alifatic), 1734 cm^{-1} (γ C=O) 1107 cm^{-1} (γ R-O-R).

(ii) Mass spectrum showed molecular ion peak at m/z = 890

II) Determination of physico-chemical properties of locally prepared surfactant.

1- Solubility :-

As shown in table (2) the nonionic surfactant PEG 600 ML (1a) was miscible in water (the common solvent for preparation of soluble formulation and also the diluting agent for pesticides during spraying) while the other nonionic surfactant gave emulsion with water. On the other hand nonionic surfactant showed different solubility in xylene (the common solvent for preparation of emulsifiable concentrate formulation), laurate esters showed high solubility in xylene than palmitate esters, PEG 400 ML (1c) was the most nonionic surfactant in solubility in xylene followed by both PEG 600 ML (1a) and PEG 600 DL (2a).

The same table shows solubility in acetone (the common volatile solvent used in preparation of dry formulation such as wettable powder and dusts) PEG 400 ML (1c) was the most soluble nonionic surfactant in acetone followed by PEG 600 DL (2a) while the palmitate esters were less soluble in acetone than laurate esters.

All prepared ionic surfactant were insoluble in xylene or acetone, potassium laurate and potassium palmitate were soluble in water while their calcium salts were insoluble in water .These results are in agreement with those of (Koich a et al 1969), who stated that divalent salts were less soluble in water than mono valent salts.

From these results it is clear that all nonionic surfactants except PEG600 ML were not suitable to not participate in formulating soluble powder formulation (SP),while only potassium laurate and potassium palmitate were suitable because of their solubility in water.

2- Hydrophilic and Lipophilic Balance (HLB).

Table (3) showed that potassium laurate and potassium palmitate have high HLB value (12-18) as they are completely soluble in water. Nonionic surfactant la,2a,,2c,1c and 2c have HLB, (10-12) where they make translucent to clear dispersion, other nonionic surfactants 1b,2b,1d and 2d have HLB 6-8 as they make milky dispersion in water, indicate that when alkyl chain (Lipophilic part) decrease the HLB value will be increase. Calcium salts of palmitic and lauric acids have 1-3 HLB as they springly soluble in water.

3- Free alkalinity.

From table (3) all nonionic surfactants (esters) have weakly basic nature this may be due to the presence of a lone pair of electrons on oxygen atom in ester bound, also ionic surfactants have basic nature, so it is suitable in case of pesticides which have basic nature or neutral nature to avoid in chemical reaction between the surfactants and pesticides.

Table (2): the solubility or the miscibility of the synthesized ionic and nonionic surfactant.

Surfactants	Water gm/100 water	Xylene gm/100 Xylene	Acetone gm/100 acetone
PEG 600 ML (1a)	Miscible	50 gm	29.4 gm
PEG 600 DL (2a)	Give emulsion	50 gm	33.3 gm
PEG 400 ML (1c)	Give emulsion	62.5 gm	55.5 gm
PEG 400 DL (2c)	Give emulsion	33.3 gm	25 gm
Potassium laurate	2.5 gm	Insoluble	Insoluble
Calcium laurate	Insoluble	Insoluble	Insoluble
PEG 600 MP (1b)	Give emulsion	10 gm	7.1 gm
PEG 600 DP (2b)	Give emulsion	8.3 gm	5.5 gm
PEG 400 MP (1d)	Give emulsion	12.5 gm	6.25 gm
PEG 400 DP (2d)	Give emulsion	7.1 gm	5.5 gm
Potassium palmitate	1.5 by heat	Insoluble	Insoluble
Calcium palmitate	Insoluble	Insoluble	Insoluble

4- Surface tension and critical micelle concentration (CMC).

The data in table (4) indicated that all locally prepared surfactants decrease the surface tension of water and the concentration of the surfactant at which the surface tension could be obtained is called CMC .

- The effect of surfactant structure on CMC value :

a) Effect of the hydrophobic moiety of the surfactant molecule on CMC.

From table (4) surfactants 1c,1a and 1b have CMC values larger than 2c,2a and 2b respectively, these results are in agreement with those of (Tadros, 1995) who postulated that CMC decrease with the increase of alkyl chain length.

Table (3): the free alkalinity, the free acidity and HLB in synthesized ionic and nonionic surfactant:

Surfactants	Free alkalinity As NaOH%	Free acidity As HCL	HLB
1a	0.29	Nil	10-12
2a	0.27	Nil	10-12
1c	0.112	Nil	10-12
2c	0.17	Nil	10-12
Potassium laurate	3.2	Nil	12-18
Calcium laurate	0.33	Nil	1-3
1b	0.112	Nil	6-8
2b	0.16	Nil	6-8
1d	0.104	Nil	6-8
2d	0.112	Nil	6-8
Potassium palmitate	3.2	Nil	12-18
Calcium palmitate	0.3	Nil	1-3

b) Effect of number of ethylene oxide on CMC.

From table (4) , CMC of 1c,2c and 1d are less in the number of ethylene oxide than 1a,2a, and 1b this finding is in agreement with (Rosen 1989) who stated that, the increase of ethylene oxide (EO) content increased water solubility by increasing the hydration ability. However, increased hydration resulted in an increase in the amount of energy required for dehydrating the molecule during its incorporation into micelle. Therefore, increasing EO content increasing the CMC. The same table also shows that at different CMC value, the surfactants showed different value of surface tension which inversely correlated to wetting and spreading ability, 1c showed the lowest value in surface tension followed by 2c,1a and 2a

Table (4): CMC values correlated with surface tension dyne/cm of locally prepared surfactants:

Surfactant	Surface tension (dyne/cm)	CMC%
1a	29.1	0.8
1b	42.75	0.9
1c	27.63	0.7
1d	42.7	0.7
2a	31.09	0.7
2b	44.18	0.7
2c	29.7	0.6
2d	45.6	0.7
Potassium laurate	29.1	0.7
Potassium palmitate	52.6	0.9
Water	72	

As general conclusion , it could be said that all prepared materials were acted as surfactants ,since they reduce surface tension of water therefore, they were suitable to use as wetting , spreading , suspending and emulsifying agents in preparation of suitable formulation .

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تحضير مواد ذات النشاط السطحي وتقدير خواصها الفيزيائية الكيمائية

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تم تحضير نوعان من المركبات ذات النشاط السطحي أيونية ، وغير أيونية من مواد محلية : أحماض دهنية أليفاتية (حمض البالميتك ، حمض لوريك) وكحول البولي إيثلين جليكول ٤٠٠ و ٦٠٠ في حالة المواد ذات النشاط السطحي الغير أيونية و من الأحماض الدهنية و هيدروكسيد البوتاسيوم وأكسيد الكالسيوم لتحضير المواد الأيونية . المواد المحلية المحضرة مواد ذات النشاط سطحي تم إثبات تركيبها الكيميائي عن طريق جهاز الأشعة تحت الحمراء وجهاز طيف الكتلة وتم تقدير خواص هذه المواد المحضرة مثل HLB و CMC والذوبان والقلوية الحرة أو الحامضية الحرة لمعرفة نوع المستحضر المناسب لهم .

دلت النتائج على أن البولى إيثيلين جليكول ٦٠٠ أحادى لورات يذوب فى الماء ولكن بقية المواد الغير أيونية تكون مستحلبات داخل الماء ومن ناحية أخرى هناك إختلاف في مقدار ذوبانها فى الزيلين أو الأسيتون بينما المواد الأيونية لا تذوب فى الزيلين أو الأسيتون ومن ناحية أخرى لا تذوب الأملاح الثنائية (كالسيوم بالميتات الكالسيوم لورات) أما الأملاح الأحادية (البوتاسيوم لورات والبوتاسيوم بالميتات) يذوبوا فى الماء . وأيضا دلت النتائج على أن المواد المحضرة تقلل التوتر السطحي للماء وأكثرها تقليلا هو البولى إيثيلين جليكول ٤٠٠ أحادى لورات يتبعه البولى إيثيلين جليكول ٦٠٠ أحادى لورات وأيضا البوتاسيوم لوارت (مادة ذات نشاط سطحى أيونية) قللت التوتر السطحي إلى٢٩,١ داين/سم وهذا يبين أن هذه المواد تعمل كمواد ناشرة ومبللة . وأيضا دلت النتائج على أن إستيرات اللورات لها HLB من ١٠-١٢ ، وإستيرات البالميتات لها HLB من ٦-٨ (يعملوا كمواد مبللة وناشرة) والمواد الأيونية ذات النشاط السطحي (البوتاسيوم لورات والبوتاسيوم بالميتات) لها HLB من ١٢- ١٨ أما أملاح الكالسيوم فلها HLB من ١-٣ .