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Preparation and Evaluation of Novel Water Soluble Nonionic Monoesters with Expected Surface Activity.

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Preparation and evaluation of novel water soluble nonionic monoesters with expected surface activity.

تحضير وتقييم مركبات غير أيونية أحادية الإستر تذوب في الماء متوقع لها نشاط سطحي .

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الملخص العربي:

في هذا البحث تم تحضير خمس سلاسل من مركبات غير أيونية أحادية الإستر متوقع لها نشاطا سطحيا؛ سلسلتين من هذه المركبات ناتجة من إضافة أكسيد البروبيلين (٥،٨،١١،١٤،١٧ جزئ) إلى ٦،١ هكسان جليكول ،ثم تفاعلها مع كلوريدات الأحماض (لاوريل و البالميتويل)، بينما الثلاث سلاسل الأخرى ناتجة من تفاعل جليكولات البولي اثيلين المختلفة (٤٠٠- ١٥٠٠-٢٠٠٠) مع كلوريدات الأحماض (ديكانويل، لاوريل و البالميتويل) ، وقد تم إثبات تركيب هذه المركبات بواسطة طيف الأشعة تحت الحمراء ، والرنين النووي المغناطيسي .وقد تم تقييم الخواص السطحية لهذه المركبات من ناحية التوتر السطحي ، والتوتر السطحي البيني ، والنقطة الحرجة للميسيلات ، وقوة الرغوة ، والقدرة على الاستحلاب ، والقدرة على البلل ، ووجد أن لها خواص سطحية جيدة . وكذلك تم اختبار قابلية هذه المواد على التحلل البيولوجي، ووجد أن معظمها لها قابلية على التحلل السريع مما يجعلها مركبات ذات نشاط سطحي؛ وليست لها مشاكل تلوث بيئية عالية. أيضا تم اختبار ثبات هذه المركبات في الأوساط الحامضية والقاعدية ، وتطبيق هذه المواد في مجال الصباغة على نوعين من الصبغات تذوبان بصعوبة في الماء ، وملاحظ ذوبانية هذه الأصباغ في درجة حرارة الغرفة ، وكذلك قدرتها على التشتت عند ارتفاع درجة حرارة الماء حتى ١٣٠°م .كذلك تم تقييم تأثير البكتيريا و الفطريات على هذه المركبات ، ووجد أن ليس لها تأثير بيولوجي مما يعطي انطباع أن هذه المواد سهلة التحلل فى المصارف المختلفة لنمو البكتيريا والفطريات.

ABSTRACT: A novel five series of monoesters were prepared [two series by reaction of oxypropylated 1, 6 hexane diol with two types of fatty acid chloride (lauroyl and palmitoyl chloride), and three series by the reaction of polyethylene glycol (MWs = 400, 1500, 2000) with three types of fatty acid chloride (decanoyl, lauroyl and palmitoyl chloride)]. The unique structural features of these surfactants were confirmed by spectroscopic tools (IR- ^{1}H NMR). These nonionic monoesters have been found to exhibit excellent surface active properties including surface tension, interfacial tension, critical micelle concentration (CMC), low foaming, emulsion stability, and wetting. Also good biodegradability in river water, stability to hydrolysis in acidic and alkaline media, solubilization and dispersant properties in disperse dye systems were determined and evaluated. The antimicrobial and antifungal properties of these prepared monoesters were measured and evaluated .A comparison studies were done between the chemical structures and surface properties of such compounds.

INTRODUCTION

Surfactants are surface-active compounds that are used as household detergents, for cosmetics, in technical applications and in cleansers. They are amphiphiles that consist of a polar ionic or non-ionic head and a hydrophobic tail [1]. A polymer with surface active properties can be built along three main routs: (i) hydrophobic chains grafted onto a hydrophilic backbone polymer, (ii) hydrophilic chains grafted onto a hydrophobic backbone, and (iii) with alternating hydrophilic and hydrophobic blocks [2-3].

In the past 20 years, polymeric surface active materials have gained enormous popularity in a variety of applications and research fields. The most obvious and best known is stabilization of dispersions [4].
In previous work, we studied the preparation of nonionic polymeric surfactants from dextran a neutral polysaccharide consisting of glucose units. Many studies have been devoted to the chemical modification of dextran for the

attachment of hydrocarbon groups [5-6] .These macromolecular surfactants were applied to the preparation of oil- in –water emulsions, the stability of which has related to the chemical structure of the amphiphilic dextran derivatives [7]. When a surfactant is present in a low concentration in a system, it has the property of adsorbing onto the surface or interfacial properties [8]. Nonionic surfactants find diverse applications both in industry and in the home. Their moderate foaming and good detergency are employed in a variety of ways in leather industry [9]. It is used to accelerate soaking, and liming is improved by the addition of wetting agents [10]. Also nonionic surfactants are used extensively because of their good detergency, easy rinsing and low foaming in cleaning of milk and beer bottles. In the present study we describe the synthesis of such a novel five series nonionic surfactants based on the above concept.

EXPERIMENTAL
Materials

Propylene oxide, 1,6 hexane diol,polyethylene glycol (PEG, MWs=400, 1500, 2000) were obtained from Aldrich (Steinhein, Germany).Fatty acid chloride (decanoyl, lauroyl and palmitoyl chloride), trimethyle amine (TMA) were Merk (Darmstadt) products. Two disperse dyes: [dye I] Dispersol Yellow (Disp. Yellow HG 80) and [dye II] Dispersol Blue (Blue FBL 150) supplied by BASF Co. These disperse dyes have high energy dye (more hydrophobic). All the other chemicals and reagents were of A R grade. The water used was doubly distilled.

Methods
Preparation of oxypropylated 1, 6 hexane diol (oxypropylation process)
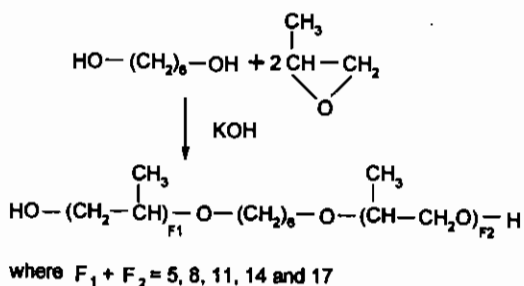
1,6 Hexane diol containing 0.5 per cent KOH was stirred and heated to 160°C while passing a slow steam of nitrogen through the system to flask out oxygen. Nitrogen addition was stopped and propylene oxide was added dropwise with continued stirring and heating under an efficient reflux system. The addition rate was regulated to maintain the temperature
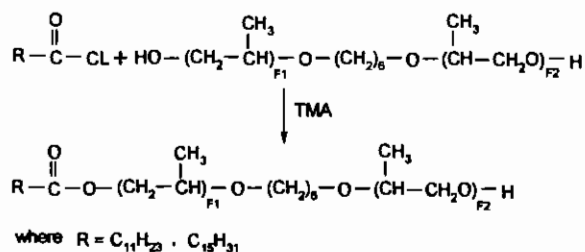
between 160-180°C. The apparatus was then filled with nitrogen, cooled and the reaction vessel was weighted. The difference in weight before and after the end of reaction indicated the amount of propylene oxide consumed in the reaction and from which its number of moles was calculated. The reaction mixture was then dissolved in ethanol (200 ml), n· ·tralized with conc. hydrochloric acid and the product was obtained by distillation of alcohol [11].

Esterfication of 1, 6 hexane diol and poly ethylene glycol with different molecular weights:

1 mole of 1, 6 oxypropylated hexane diol was dissolved in chloroform (25 ml) under stirring, and a drop of trimethyl amine was added as a catalyst. Equal mole amount of fatty acid chloride (palmitoyl or lauroyl chloride) was added dropwise over a period of 3 min at 0-5°C.Continued stirring at this temperature for 24h.Upon completion of the reaction, the solvent was evaporated under vacuum. Also 1 mole of polyethylene glycol was dissolved in chloroform (25ml) under stirring and a drop of trimethyl amine was added as·a catalyst. Equal mole amount of fatty acid chloride (decanoyl, lauroyl or palmitoyl chloride) was added dropwise over a period of 3min at 0-5°C.continued stirring at this temperature for 24h.upon completion of the reaction, the solvent was evaporated under vacuum [12]. The following scheme describes the preparation of the two series of nonionic water soluble monoesters

Step (1)

where $F_1 + F_2$ = 5, 8, 11, 14 and 17

Step (2)

$$R-\overset{\overset{O}{\parallel}}{C}-CL + HO-(CH_2-\overset{\overset{CH_3}{|}}{CH})_{F_1}-O-(CH_2)_6-O-(\overset{\overset{CH_3}{|}}{CH}-CH_2O)_{F_2}-H$$

$$\downarrow TMA$$

$$R-\overset{\overset{O}{\parallel}}{C}-O-(CH_2-\overset{\overset{CH_3}{|}}{CH})_{F_1}-O-(CH_2)_6-O-(\overset{\overset{CH_3}{|}}{CH}-CH_2O)_{F_2}-H$$

where　$R = C_{11}H_{23} \cdot C_{15}H_{31}$

Scheme (1) preparation of two series of water soluble nonionic monoesters IX_1-IX_5 and IIX_1-IIX_5.
Where $F_1+F_2= 5, 8, 11, 14, 17$, and $R=C_{11}H_{23}, R_2=C_{15}H_{31}$

The following scheme describes the preparation of the three series of nonionic water soluble monoesters:-

$$R-\overset{\overset{O}{\parallel}}{C}-Cl + H-(OCH_2-CH_2)_n-OH$$

$$\downarrow TMA$$

$$R-\overset{\overset{O}{\parallel}}{C}-O-(CH_2-CH_2-O)_n-H$$
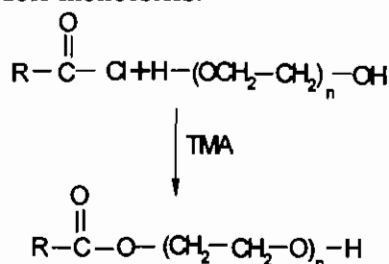
Scheme 2 preparation of three series of water soluble nonionic monoesters IV_1-IV_3, IIV_1-IIV_3 and $IIIV_1-IIIV_3$. Where n= (400, 1500, 2000) and $R = C_9H_{19}, C_{11}H_{23}, C_{15}H_{31}$

Analysis

IR spectra were obtained with Shimadzu (Kyoto, Japan) IR 470 and ^{1}H- NMR spectra were obtained with a Varian USA EM 390 spectrophotometer at 90 MHz with dimethylsulfoxide (DMSO) as a solvent and tetramethylsilane (TMS) as a zero reference.

Measurements

1- **Surface tension** was measured with a DCAT tensiometer using 0.1wt-% solution of surfactant at room temperature 25°C. Also **the interfacial tension** of 0.1 wt-% of surfactant solution was measured using paraffin oil [13].

2- **The CMC** was determined as the concentration at which the surface tension remains practically constant. [14].

3- **Foaming properties** were determined using the Ross-Miles method. [15].

4- **Emulsifying power** was determined according to Takashita et al. [16-17].

5- **Stability to hydrolysis:** A mixture of 10 m.mol surfactant and 10 ml 2N H_2SO_4 or 0.05 N NaOH were placed in thermostat at 40°C. The time it takes for a sample solution to be clouded as a result of hydrolysis shows the stability of surfactant to hydrolysis [11], [18].

6- **Wetting properties** was determined by immersing a sample of cotton fabric (4x4 cm) in 0.1 % aqueous solution of the surfactant at 25°C. The time recorded from the moment the cotton was put into the solution until the moment is started to going down in the wetting time [13], [19].

7- **Cloud point (cp)** was determined by gradually heating 1 % aqueous solution of the prepared surfactant in a controlled temperature bath and recording the temperature at which the clear or nearly clear solutions start to become turbid. The reproducibility of this temperature was checked by cooling the solutions until they become clear again. Each experiment was repeated three times and the average was taken for each surfactant solutions [9], [20].

8- **Dispersant properties** were determined by the following method: A 100 ml solution of 0.1 g of commercial dispersed dye [21-22] and 0.1 g of dispersing agent was adjusted to pH 5.0 by the addition of an appropriate amount of acetic acid. Then, the solution was heated to 130°C by a computer controlled dyeing system for 1h. After this treatment, the solution cooled to 90-95°C and vacuum filtered immediately with a Buchner funnel. The filtrate was diluted with acetone, and the concentration was determined spectrophotometrically. The dispensability was calculated as follows [11], [23].

Dispersibilty (percent) =

$$\frac{\text{dye concentration of filtrate}}{\text{dye concentration of original solution}} \times 100$$

9- **Solubilization** [24] was measured by a usual method that shakes a 50ml. solution containing 40 mg of applied dyes [11],[25]Dispersol Blue (Blue FBL 150) and Dispersol Yellow (Disp. Yellow HG80). The insoluble dyes were removed using a glass filter, and solubilized dyes were extracted from filtrate by toluene and their concentrations determined spectrophotometrically.

10- **Biodegradability %.** Dieawy method using river water samples taken daily, or even more frequently, were filtered through No. 1 **Whatman** filter paper before measuring the surface tension [11],[25] measurements were periodically (each day) on each sample during the degradation test. Biodegradation percent (D) was calculated from the following law.

$$D = \frac{\varphi_t - \varphi_o}{\varphi_{bt} - \varphi_o} \times 100$$

where

φ_t = surface tension at time t

φ_o = Surface tension at time zero (the initial tension)

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

11- **Viscometric measurements** aqueous surfactant solutions were carried-out using Ostwald-type capillary viscometer (0.46 mm diameter) in DMF at $30 \pm 0.05°C$ [26].

12- **Biological activity** The antimicrobial activities of some synthesized compounds were determined in vitro using the hole plate and filter paper disc method [27]

surfactant	F_1+F_2 (n)	Color	Form	Yield %	MW of surfactant	Viscosity η (dL/g)
IX₁	5	Brown	Viscous	85	590	0.120
IX₂	8	Brown	Viscous	82	764	0.135
IX₃	11	Brown	Viscous	89	938	0.240
IX₄	14	Brown	Viscous	87	1112	0.315
IX₄	17	Brown	Viscous	91	1286	0.424
IIX₁	5	Brown	Viscous	81	646	0.215
IIX₂	8	Brown	Viscous	85	820	0.350
IIX₃	11	Brown	Viscous	86	994	0.420
IIX₄	14	Brown	Viscous	91	1168	0.458
IIX₄	17	Brown	Viscous	95	1342	0.522

Table (1) Physical properties of two series of water – soluble nonionic monoesters series IX₁-IX₅ and IIX₁-IIX₅ of oxypropylated diol with lauroyl chloride and palmitoyl chloride respectively

surfactant	Color	Form	Yield %	MW of surfactant	Viscosity η (dL/g)
IV₁	Transpare	Liquid	87	572	0.215
IV₂	White	Solid	92	1672	0.312
IV₃	White	Solid	95	2172	0.400
IIV₁	Transpare	Liquid	91	600	0.320
IIV₂	White	Solid	93	1700	0.414
IIV₃	White	Solid	94	2200	0.510
IIIV₁	Transpare	Liquid	86	656	0.420
IIIV₂	White	Solid	95	1756	0.517
IIIV₃	White	Solid	93	2256	0.620

Table (2) physical properties of three series of water – soluble nonionic monoesters IV₁-IV₃, IIV₁-IIV₃ and IIIV₁-IIIV₃ of polyethylene glycol (MWs=400, 1500, 2000) with decanoyl, lauroyl and palmitoyl chloride respectively.

Results and discussion

Scheme 1 and scheme 2: describe the preparation of the novel five series of water soluble nonionic surfactants. The analytical data and physical properties of these prepared surfactants are shown in tables 1 and 2.

The typical IR spectrum of XI₂ surfactant (Fig.1) displayed broad band at 3400 cm⁻¹(-OH), 2928-2970 cm⁻¹(-CH₂), 1736 cm⁻¹(COO-CH₂), and 1461 cm⁻¹(-CH₃). The compound structure was further supported by the ¹H-MNR spectrum (Fig 2) for XI₂, gave signals at $\delta = 0.8$ ppm (-CH₃), $\delta = 1.2$-1.4 ppm $\delta = 3.3$-3.6 ppm (-CH₂O), and $\delta = 4$-4.3 ppm (COᴖ-CH₂).
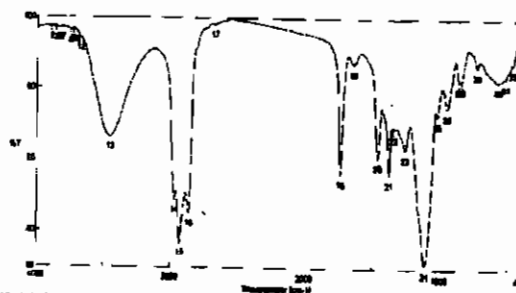

Figure (1) IR- spectrum of IX₂ nonionic monoester, where IX₂ = 8 mol of oxypropylated 1.6 hexane diol with lauroyl chloride.
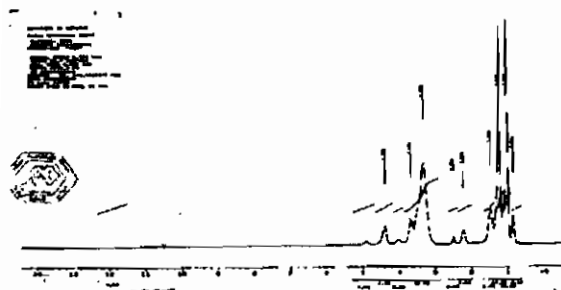
Figure (2) ¹H-NMR spectrum of IX₂ nonionic monoester, where IX₂ = 8 mol of oxypropylated 1.6 hexane diol with lauroyl chlorid

Surface properties

Water-soluble monoesters prepared in this study are observably of an amphipathic structure similar to the structures of traditional surfactants. The saturated aliphatic residues were the hydrophobic portion, and polyoxypropylene chain (non-ionic) was the hydrophilic portion.

Surface tension and interfacial tension

Reduction of surface and interfacial tension is one of the most commonly measured properties of surfactants in solution, since it depends directly on the replacement of molecules of solvent at the interface by molecules of surfactant [3]. The surface tensions of the solutions were reduced by the addition of surfactants because of the amphipathic structure, which caused the concentration of the surfactant molecules at the surface and the reduction of surface tension [8], [28]. Also surfactants that induce low interfacial tensions are important for the preparation of stable emulsions [1], [29].

An increase in the length of polyoxypropylene or polyoxyethylene chains resulted in a clear decrease in surface activity. This phenomenon is due to the increase of hydrophilicity of surfactants. As a result, it decreases the concentration of the surfactants at the surface [30-31]. Inflection points were observed in curves. The concentration at the inflection point corresponds to the critical micelle concentration (CMC) in the case of traditional surfactants [8], [32]. The values found were smaller than the values of traditional surfactants because of the high MWs and large

hydrophobic chains of the water-soluble surfactants. The values increased according to the increase in the length of polyoxypropylene or polyoxyethylene chains (more hydrophilic). The increase in the length of saturated aliphatic alkyl chain led to slight decrease in surface activity [8]. The values of CMC and γ CMC both increased upon increasing the hydrocarbon chain length [13], [15], as shown in tables 3 and 4.

Surfactant	n₁:z	Surface tension (mN/m) 0.1% at 25°C	Interfacial tension (mN/m) 0.1% at 25°C	Cloud point °C	CMC (mol/L)	γ CMC (dyn/cm)	Wetting time	Stability to hydrolysis H⁺ hexane	OH⁻ hexane	HLB
IX₁	5	32	7.5	30	0.00021	35.1	54	00:56:14	00:41:26	9.13
IX₂	8	34	8.5	42	1.0005	38.4	51	01:28:40	00:42:10	12.15
IX₃	11	36	10	45	0.00011	41.2	47	01:50:16	00:43:36	13.60
IX₄	14	38	11	47	1.0025	43.7	43	02:03:16	00:04:07	14.60
IX₅	17	41	12	52	1.0003	45.5	39	03:55:46	00:04:50	15.05
IIX₁	5	36	8	34	1.00002	38.7	57	02:45:16	00:42:15	9.97
IIX₂	8	38	10	37	1.0001	41.2	53	03:44:20	00:43:56	11.31
IIX₃	11	40	12	40	1.00018	43.6	49	05:22:90	00:05:41	12.04
IIX₄	14	42	14	44	1.00032	46.2	46	06:50:30	00:06:50	13.90
IIX₅	17	44	16	47	1.00006	48.2	42	08:10:12	00:07:10	14.69

Table (3) surface properties of two series of water – soluble nonionic monoesters IX₁-IX₅ and IIX₁-IIX₅ of oxypropylated diol with lauroyl chloride and palmitoyl chloride respectively.

Surfactant	Surface tension (mN/m) 0.1% at 25°C	Interfacial tension (mN/m) 0.1% at 25°C	Cloud point °C	CMC (mol/L)	γ CMC (dyn/cm)	Wetting time Sec.	Stability to hydrolysis H⁺ hexane	OH⁻ hexane	HLB
IV₁	39	11	55	0.00014	42.3	50	03:50:10	00:09:10	13.9
IV₂	41	13	58	0.00072	44.8	47	04:16:40	00:10:40	17.94
IV₃	43	15	63	0.00077	46.34	44	06:56:00	00:11:30	18.42
IIV₁	41	13	51	0.00039	42.6	52	04:40:11	00:10:50	13.33
IIV₂	43	15	54	0.00075	45	49	05:55:20	00:12:06	17.65
IIV₃	46	18	58	0.0015	47.85	46	07:10:12	00:14:30	18.18
IIIV₁	44	16	48	0.0013	45.48	55	06:20:10	00:11:40	12.19
IIIV₂	46	19	51	0.0019	47.85	51	07:50:11	00:13:30	17.08
IIIV₃	48	21	54	0.0026	50.39	48	09:10:30	00:15:40	17.73

Table (4) surface properties three series of water – soluble nonionic monoesters IV₁-IV₃, IIV₁-IIV₃ and IIIV₁-IIIV₃ of polyethylene glycol (MWs=400, 1500, 2000) with decanoyl, lauroyl chloride and palmitoyl chloride respectively.,

Foaming properties

The low foaming tendency of surfactants is an important property required in some applications, such as using surfactants as dyeing auxiliaries in modern texti¹ industry.

The low foaming properties of surfactants prepared in the present study are shown in tables 5 and 6. All the compounds exhibited not only low foam production, measured by the height of foam initially produced but also low foaming stability, measured by the height after 3 min [15], [33]. These

low foaming effects are probably due to: (i) the presence of multihydrophilic groups, which caused a considerable increase in the area per molecule and produced less cohesive forces at the surface; (ii) the water soluble surfactants that are believed to coil in the aqueous phase, which decreased the cohesive forces caused by intramolecular and intermolecular bonds [8],[34].

In general the nonionic surfactants form unstable foams, due to the larger surface area per molecules and absence of highly charged films in these foams [35]. In polyoxypropylated or polyoxyethylated nonionics, both foam stability and foam volume reach a maximum at a particular PO and EO chain length and then decrease [36]. This is ascribed to a maximum in intermolecular cohesive forces in the adsorbed film as the PO or EO content increases [3].

Surfactant	F_1+F_2	Foam height(m.m)			
		25°C		85°C	
		Initial	3min	Initial	3min
IX_1	5	56	6	51	zero
IX_2	8	59	9	54	zero
IX_3	11	64	13	58	zero
IX_4	14	68	17	63	zero
IX_6	17	65	15	60	zero
IIX_1	5	60	9	57	zero
IIX_2	8	64	11	61	zero
IIX_3	11	68	15	64	zero
IIX_4	14	72	19	68	zero
IIX_6	17	69	17	65	zero

Table (5) Foaming properties of the two series of water –soluble nonionic monoesters IX_1-IX_5 and IIX_1-IIX_5 of oxypropylated diol with lauroyl chloride and palmitoyl chloride respectively.

Surfactant	Foam height(m.m)			
	25°C		85°C	
	Initial	3min	Initial	3min
IV_1	68	16	64	zero
IV_2	72	19	68	zero
IV_3	70	17	66	zero
IIV_1	71	18	67	zero
IIV_2	75	22	71	zero
IIV_3	72	20	69	zero
$IIIV_1$	73	21	69	zero
$IIIV_2$	77	25	74	zero
$IIIV_3$	75	23	72	zero

Table (6) Foaming properties of the three series of water –soluble nonionic monoesters IV_1-IV_3, IIV_1-IIV_3 and $IIIV_1$-$IIIV_3$ of polyethylene glycol (MWs=400, 1500, 2000) with decanoyl , lauroyl e and palmitoyl chloride respectively.

Wetting properties

Wetting power is another important property of dyeing auxiliaries .In the dyeing process, good wetting power of dyeing auxiliaries may accelerate the diffusion or penetration of dyes into the fibers, as well as improvement with the leveling [37]. It was observed as shown in tables (3, 4) that the increase of the length of aliphatic fatty chain (hydrophobe) led to increase in wetting time [38]. Also all the prepared compounds showed a decrease in wetting time with an increase in the number of propylene oxide or ethylene oxide units in the molecule [39]. This phenomenon, similar to surface tension, is attributed to the enlargement of the hydrophilic portion of surfactant molecule, is resulting in decrease in concentration of surfactant at the liquid surface [37].

Stability to hydrolysis

All the prepared water- soluble nonionic surfactants exhibited good stability, especially in acidic medium, but slightly lower stability in the basic medium, because ester group having long fatty chain resists acidic medium and is easily hydrolyzed in basic medium. The increase of the length of saturated aliphatic fatty chain as shown in tables 3 and 4 leads to increase in stability in both acidic and basic medium [22].

Emulsifying power

Emulsification is one of the most important properties of surfactants. In many textile processes, such as dyeing it is necessary to introduce surfactants into the bath to remove oily impurities from the fibers, In these removal processes, the ability of surfactants to emulsify the oily impurities is important [11]. The emulsifying ability of the prepared surfactants is shown in tables7 and 8, which indicates that all nonionic surfactants exhibit good emulsifying power towards liquid paraffin, kerosene and O-dichlorobenzene. In general the emulsion stability of the prepared surfactants increased by increasing hydrophobic chain

length[13], whereas an increase in the number of repeating units of polypropylene or polyethylene chain length decreased the separation time [31].

Surfactant	F_1+F_2	Separation time hr:min:sec		
		Kerosene	Liquid	O-dichlorobenzene
IX₁	5	00:09:53	00:32:25	00:13:42
IX₂	8	00:08:23	00:31:12	00:12:36
IX₃	11	00:07:42	00:30:24	00:11:28
IX₄	14	00:06:28	00:29:47	00:10:15
IX₅	17	00:04:42	00:27:39	00:09:00
IIX₁	5	00:13:00	00:35:00	00:15:55
IIX₂	8	00:11:24	00:33:12	00:14:20
IIX₃	11	00:09:54	00:31:24	00:12:30
IIX₄	14	00:07:46	00:29:20	00:10:55
IIX₅	17	00:06:31	00:27:12	00.09:59

Table (7) Emulsifying properties of the two series of water – soluble nonionic monoesters IX₁-IX₅ and IIX₁-IIX₅ of oxypropylated diol with lauroyl chloride and palmitoyl chloride respectively..

Surfactant	Separation time hr:min:sec		
	Kerosene	Liquid paraffin	O-dichlorobenzene
IV₁	00:07:10	00:18:54	00:09:00
IV₂	00:06:20	00:17:10	00:08:15
IV₃	00:04:50	00:15:23	00:06:54
IIV₁	00:05:35	00:16:32	00:07:50
IIV₂	00:03:55	00:14:54	00:05:30
IIV₃	00:02:20	00:13:00	00:02:50
IIIV₁	00:03:44	00:14:20	00:05:10
IIIV₂	00:02:10	00:12:54	00:03:20
IIIV₃	00:01:00	00:11:30	00:01:55

Table (8) Emulsifying properties of the three series of water – soluble nonionic monoesters IV₁-IV₃, IIV₁-IIV₃ and IIIV₁-IIIV₃ of polyethylene glycol (MWs=400, 1500,2000) with decanoyl , lauroyl and palmitoyl chloride respectively.

Solubilization

Solubilization is one of the most important properties of surfactants. It may be defined as the spontaneous dissolution of an insoluble substance by reversible interaction with the micelles of surfactants in a solvent to form a thermodynamically stable isotropic solution [34]. In general; solubilization occurred only above the critical micelle concentration (CMC), above this value the amount of the substance solubilized increases with the concentration of surfactants [11].The solubilization of surfactants for two insoluble dyes [21] are shown in figures 3,4,5 and 6 .From these figure a linear relationship was obtained for the solubilization of the dyes with the concentration of surfactants. The solubilization capacity of these surfactants increased

gradually as the number of repeating unit of polyoxypropylene or polyoxyethylene glycol increased. It is believed that the solubilizate of dyes contained amino or carbonyl groups could associate with the polyoxypropylene or polyoxyethylene glycol unit via hydrogen bonds. Also it is found that the solubilization capacity decreases with increasing aliphatic fatty chain length [34].
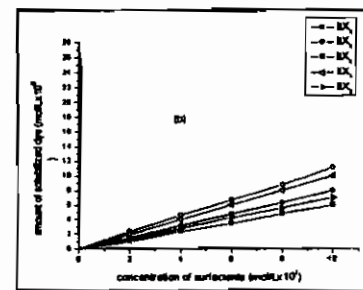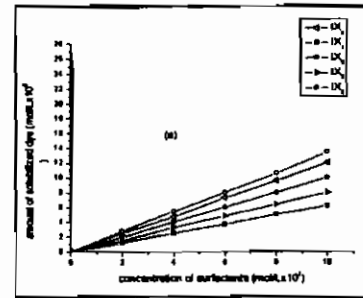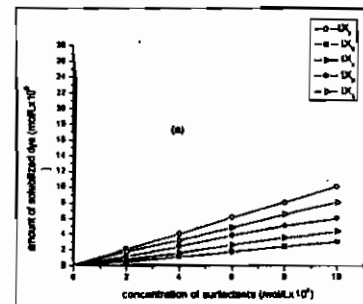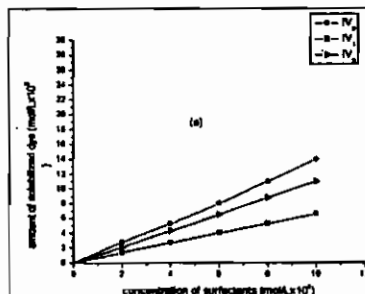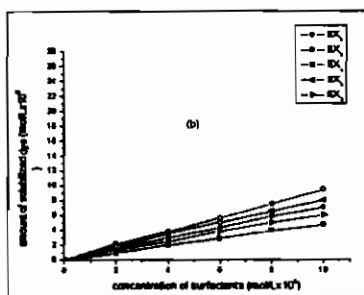

Figure (3) plots of amount of solubilized Dispersol Yellow dye (Disp.Yellow HG80) as function of concentration of the two series of water-soluble nonionic monoesters, where (a) for IX₁-IX₅ and (b) for IIX₁-IIX₅.

Figure(4) plots of amount of solubilized Blue Dye (Blue FBL150) as function of concentration of the two series of water-soluble nonionic monoesterss, where (a) for IX_1-IX_5 and (b) for IIX_1-IIX_5.
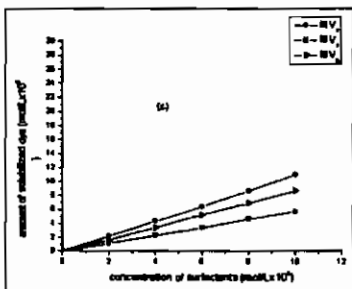

Figure (5) Plots of amount of solubilized Dispersol Yellow dye (Disp.Yellow HG80) as function of concentration of the three series of water-soluble nonionic monoesterss, where (a) for IV_1-IV_3 and (b) for IIV_1-IIV_3 and (c)$IIIV_1$-$IIIV_3$.
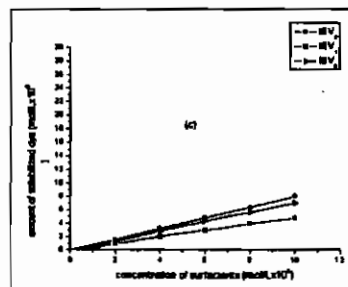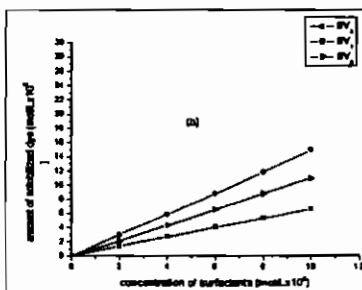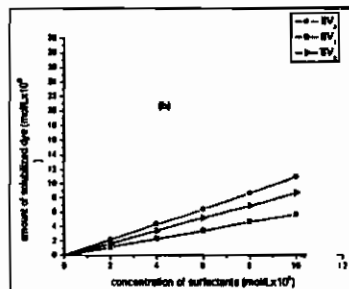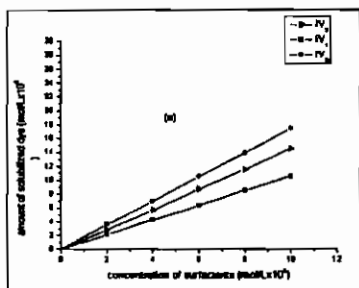

Figure(6) plots of amount of solubilized Blue dye (Blue FBL150) as function of concentration of the three series of water-soluble nonionic monoesters, where (a) for IV_1-IV_3, (b) for IIV_1-IIV_3 and (c) for $IIIV_1$-$IIIV_3$

Dispersant properties (heat stability)

Purified dispersed dyes are hydrophobic and almost insoluble in water [21]. Their low aqueous solubility is attributed to hydrophobic bonding, causing aggregation and precipitation when the concentrations are increased [8]. The formation of such aggregated dye particles is not desirable for dyeing polyester fabrics because the aggregation of the dye particles can cause unleveled or specked dying products and result in a dyeing product with poor value[8],[40]. Generally, some surfactants (i.e. the dispersing agent) are incorporated during production of the final dye power of liquid. Its function is to prevent aggregation and preci ation [41].

However, in some practical dyeing processes, such as the dyeing of polyester fibers at high temperatures, the reaggregation of the dye particles will occur at elevated temperatures when the heat stability of the dispersant system is insufficient to prevent this, an additional dispersing agent with high heat stability may be introduced into the dye bath initially or during the course of dyeing. The water soluble surfactants prepared in this study were evaluated for these cases, and their stability at elevated temperature with two dyes.

These systems [21] are shown in tables 9 and 10. it is clear that in each of the two applied dye systems, the heat stability was improved by the addition of the water-soluble nonionic surfactants. The number of repeating units of polypropylene or polyethylene glycol of these surfactants had only a slight influence on stability. The high heat stability of the water-soluble surfactants was probably caused by their unique structural features: (i) high MW, (ii) the ester linkage of the hydrophobic portion, and (iii) the polyoxypropylene or polyethylene chains of the hydrophilic portion. These structural features favor its adsorption onto the surface of dye crystals. The nonionic portion stabilize the dispersion presumably because of its high hydrated polyoxypropylene or polyoxyethylene chain extending into the solutions in the form of coils that presents an excellent steric barrier to aggregation [42]. In both cases, the hydrophobic groups come into contact with the particle surface, leaving the hydrophilic groups directed toward the aqueous phase and producing solvation protection for dye particles. After elevated temperature, the separation of the novel dispersing agent from dye particles is minimized because of a strong association between the dispersing agent and dye particles, thus resulting in a high stability of these dispersing systems [8].

Surfactant	F_1+F_2	Dispersability %	
		Yellow dye (I)	Blue dye (II)
IX$_1$	5	32.18	21.41
IX$_2$	8	35.40	23.41
IX$_3$	11	38.50	26.30
IX$_4$	14	42.19	28.92
IX$_5$	17	45.95	32.56
IIX$_1$	5	29.22	17.50
IIX$_2$	8	31.91	19.92
IIX$_3$	11	35.72	23.17
IIX$_4$	14	38.12	25.90
IIX$_5$	17	43.92	28.97

Table (9) Dispersant properties of the two series of water–soluble nonionic monoesters IX$_1$-IX$_5$ and IIX$_1$-IIX$_5$ of oxypropylated diol with lauroyl chloride and palmitoyl chloride respectively.

Surfactant	Dispersability %	
	Yellow dye (I)	Blue dye (II)
IV$_1$	42.61	32.56
IV$_2$	43.10	34.71
IV$_3$	47.21	37.20
IIV$_1$	39.71	28.92
IIV$_2$	42.17	31.40
IIV$_3$	45.50	34.12
IIIV$_1$	36.64	32.52
IIIV$_2$	38.18	35.12
IIIV$_3$	42.92	37.97

Table (10) Dispersant properties of the three series of water–soluble nonionic monoesters IV$_1$-IV$_3$, IIV$_1$-IIV$_3$ and IIIV$_1$-IIIV$_3$ of polyethylene glycol (MWs=400, 1500,2000) with capanoyl , lauroyl c and palmitoyl chloride respectively.

Biodegradation

A biodegradation test in ordinary river water [25] gave satisfactory results, as shown in tables 11, 12. All the products had a degradation ranging about 80% during around 6 days. It is suggested that the polyoxypropylene or polyoxyethylene chains become degraded by bacterial or enzyme hydrolysis, the propylene group converted to propylene glycol [43]. The rate of degradation of these compounds depends on the size of molecule; bulky molecule diffuses through the cell membrane, and its degradation is more difficult. This means that the molecule with the least moles of propylene oxide or ethylene oxide is more

degradable than that which contains higher moles of propylene oxide or ethylene oxide [27].

Surfactant	F_1+F_2	1st day	2nd day	3rd day	4th day	5th day	6th day	7th day	8th day
IX₁	5	64	69	77	82	89	93	98	-
IX₂	8	61	66	71	79	85	91	95	-
IX₃	11	57	62	68	75	81	88	91	95
IX₄	14	52	59	65	71	76	84	88	92
IX₅	17	47	54	61	67	73	81	85	89
IIX₁	5	61	65	72	78	86	92	98	-
IIX₂	8	58	61	67	71	82	87	96	-
IIX₃	11	55	58	62	67	78	82	90	95
IIX₄	14	51	55	58	63	74	79	87	93
IIX₅	17	48	51	55	59	68	75	84	91

Table (11) Biodegradability % of the two series of water –soluble nonionic monoesters IX₁-IX₅ and IIX₁-IIX₅ of oxypropylated diol with lauroyl chloride and palmitoyl chloride respectively.

Surfactant	1st day	2nd day	3rd day	4th day	5th day	6th day	7th day	8th day
IV₁	60	66	72	79	86	91	98	-
IV₂	57	62	67	75	81	88	96	-
IV₃	53	57	62	70	77	85	93	95
IIV₁	58	62	69	76	83	89	96	-
IIV₂	55	57	66	72	78	86	94	-
IIV₃	51	54	63	68	73	82	91	94
IIIV₁	55	59	66	72	79	86	93	-
IIIV₂	50	56	63	68	75	83	91	93
IIIV₃	47	52	59	64	71	78	88	90

Table (12) Biodegradability % of the three series of water –soluble nonionic monoesters IV₁-IV₃, IIV₁-IIV₃ and IIIV₁-IIIV₃ of polyethylene glycol (MWs=400, 1500,2000) with decanoyl , lauroyl e and palmitoyl chloride respectively.

Biological activity

From resulting data illustrated in tables13 and 14. It is clear that all species did not exhibit inhibition effect on the growth of the tested organisms, and the bacterial growth was found intensed in the region around the samples. In addition to this, the bacterial species exhibited growth on the samples disc. This means that the tested compounds were degraded and decomposed by the studied bacterial species.

Surfactant	F_1+F_2	Pseudomonas putida	Staphylococcus aureus	Aspergillus niger	Candida albicans
IX₁	5	-	-	-	-
IX₂	8	-	-	-	-
IX₃	11	-	-	-	-
IX₄	14	-	-	-	-
IX₅	17	-	-	-	-
IIX₁	5	-	-	-	-
IIX₂	8	-	-	-	-
IIX₃	11	-	-	-	-
IIX₄	14	-	-	-	-
IIX₅	17	-	-	-	-

Table (13) Biological activity of the two series of water – soluble nonionic monoesters IX₁-IX₅ and IIX₁-IIX₅ of oxypropylated diol with lauroyl chloride and palmitoyl chloride respectively.

Surfactant	Pseudomonas putida	Staphylococcus aureus	Aspergillus niger	Candida albicans
IV₁	-	-	-	-
IV₂	-	-	-	-
IV₃	-	-	-	-
IIV₁	-	-	-	-
IIV₂	-	-	-	-
IIV₃	-	-	-	-
IIIV₁	-	-	-	-
IIIV₂	-	-	-	-
IIIV₃	-	-	-	-

Table (14) Biological activity of the three series of water – soluble nonionic monoesters IV₁-IV₃, IIV₁-IIV₃ and IIIV₁-IIIV₃ of polyethylene glycol (MWs=400, 1500, 2000) with decanoyl, lauroyl and palmitoyl chloride respectively.

Conclusions

Five series of nonionic monoesters , containing hydrophobic and nonionic hydrophilic moieties , two series of them are prepared by reacting oxypropylated 1,6 hexane diol with two types of fatty acid chloride (lauroyl and palmitoyl chloride) and the rest three series are prepared by reacting polyethylene glycol (MWs =400,1500 and 2000) with fatty acid chloride (decanoyl , lauroyl and palmitoyl chloride).These nonionic monoesters exhibit excellent surface active properties including surface tension, interfacial tension, CMC, low foaming, emulsion stability, and wetting, also good biodegradability in river water, stability to hydrolysis in acidic and alkaline medium and increase the penetration of dyes into the fibers of cotton (solubilization and dispersant properties),and have no biological activity.

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